

Soil Pollution and Soil Protection

F.A.M. de Haan and M.I. Visser-Reyneveld (Editors)

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Preface

It is now widely recognized that an important part of life on earth depends on good quality soil. Unfortunately, throughout the world there are extensive highly industrialized areas where soil quality has deteriorated alarmingly because more chemicals are entering the soil than the soil system can cope with. Unless remedial steps are taken, the resulting accumulation will sooner or later - depending on the soil's buffering capacity - lead to malfunctioning of the soil system, at which point the soil may be considered to be polluted.

Soil protection aims at safeguarding the properties and conditions that ensure that soil functions at least satisfactorily, if not optimally. The soil's functions, however, are diverse, the main examples being plant growth and crop production, the filtering of water and the cycling of elements. The chemical and physical conditions essential for these functions vary enormously, making it extremely difficult to evaluate soil quality quantitatively. It is even more difficult to derive the soil quality standards on which to base effective policy making and legislation on soil protection.

This book provides basic information relating to the evaluation of soil quality, with particular emphasis on the chemical conditions in soil. The main causes and sources of soil pollution and some of the most pronounced effects are described. The chemical, physical and biological interactions of chemicals within the soil system are discussed individually and in various combinations, to clarify the relationships between source and impact. The physical aspects of the transport of contaminants through soils and the problem of soil heterogeneity receive explicit attention. Chemical speciation is dealt with extensively, because it plays a key role in the bioavailability of contaminants which, in turn, is a determinant of the impact of soil pollution.

The impacts of soil pollution on plant growth and on the functioning of the soil ecosystem are also discussed. In addition to these basic topics, the book also covers problems of a more practical nature, such as soil acidification and the use of soil to treat waste. The final chapter describes EU policy on waste treatment systems.

The book has been compiled from lecture handouts prepared for an international PHLO postgraduate course given jointly by Wageningen Agricultural University (The Netherlands) and the Faculties of Agricultural Sciences of the universities of Leuven and Gent (Belgium). Its intended readers are graduates who are professionally involved in soil quality and have to deal with problems of soil protection in the context of education, research, policy making or consultancy.

We would like to give special thanks to Geralda Fonteijn for her sterling help with the typing of the chapters, Jaap Bijkerk for his skilful drawing of the figures and Ernst van Cleef for designing the book's attractive cover.

The editors

Frans A.M. de Haan, Marijke I. Visser-Reyneveld

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1 Soil quality evaluation

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Summary

As compared to the environmental compartments air and water, soil is an extremely complicated system. This is due to a huge variety of soil properties and chemical, physical and biological system conditions. The combination of these makes the development of general rules for quantitative evaluation of soil quality impossible. The large variety of values for the buffering capacity for different soils and different compounds also plays a role in this respect.

Two examples for derivation of effect-oriented soil quality standards are briefly described.

In The Netherlands, a system of reference values was derived, which refers to compound contents in soil reflecting situations of low degree of contamination. For heavy metals, these reference values consist of sliding scales in which the influence of clay content and organic matter content on the metal content is incorporated.

New developments with respect to biological indicators by means of nematodes are briefly discussed.

1.1 General consideration

Of the three environmental compartments air, water and soil, the last gives undoubtedly the most difficulties to assess its quality in a quantitative way. This is mainly due to the fact that soils show a huge variety in composition. This in turn influences the behaviour and effects of compounds in the system in chemical, physical and in biological sense as well.

Soils usually have a much larger buffering capacity than air and water. This property, as schematically indicated in Figure 1.1, can be described as the capacity to allow contents of compounds, once present at optimum level, to increase without actual occurrence of negative effects. Because a number of potentially hazardous compounds are also prerequisites for good soil functioning, these show a positive effect with increasing content at the low concentration level. The area between contents I and II in Figure 1.1 represents the buffering capacity. Actually this buffering capacity is different for all different compounds of interest, and for all different soil properties and varying system conditions occurring in practice. Moreover, these properties and conditions are usually main factors in controlling chemical speciation of a compound under consideration, which in turn plays a major role for its bioavailability, thus influencing its effect.

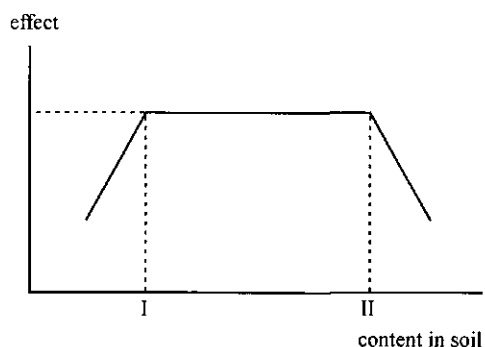


Figure 1.1. Schematic representation of the soil buffering capacity.

However, in order to develop rules and measures for soil protection, quantitative evaluation of soil quality is a prerequisite. During the C.E.C. Conference on 'Scientific basis for soil protection in the European Community' in 1987 (Barth & L'Hermite 1987) agreement was reached that such evaluation should preferably be based on effects that can be expected from the presence and behaviour of pollutants/contaminants in soil. This in turn requires a quantitative risk assessment approach to soil functioning.

Figure 1.2, taken from van Genderen (1987), presents in a schematic way how contaminants may adversely affect humans, plants and animals, including soil organisms. For soil quality evaluation, the following question must be answered: which quantity of a given compound in soil, C_s , is still acceptable in order to protect these three groups of organisms. This question is closely related to risk analysis of health and toxicological considerations. Once the exposure-effect (more strictly dose-effect) relationships are determined, the question is transformed into the assessment of the result of the exposure of the organism of interest.

Sometimes the exposure can be determined in a relatively simple way as in the case of some soil organisms. Usually the concentration (or rather the activity) in the soil solution is of major importance since the exposure dose is the product of the time of exposure and this solution concentration. This means that the relationship between solid phase content and the solution concentration is of prime concern.

Soil chemistry provides a basis to arrive at such relationships for different contaminants and various soil systems. Adsorption and desorption isotherms are the common form of expressing them, and the distribution coefficient, $K_{s,l}$, provides a useful parameter to characterize interactions between the solid and liquid phases of soil.

The concentration in the soil solution is also highly significant with respect to leaching and hence the composition of surface water and groundwater, and the uptake of compounds by plant roots. But these uptake mechanisms are generally fairly complicated (*e.g.* preferential or discriminating uptake) so that the content of the compound in plants, C_p , usually can not simply be derived from transpiration fluxes and solution concentration values.

Whereas the liquid phase concentration generally is the most important, there are a few examples where the exposure, or part of it, is directly governed by the content of the solid phase. These are where the exposure results from ingestion of contaminated soil or dust, as is the case with earthworms (Ma 1983), with grazing animals (Bremner

1981), and with 'pica' and mouthing behaviour (direct soil uptake by children, Brune-kreef 1985). Normally, however, the exposure route is much more complicated, cf. Figure 1.2.

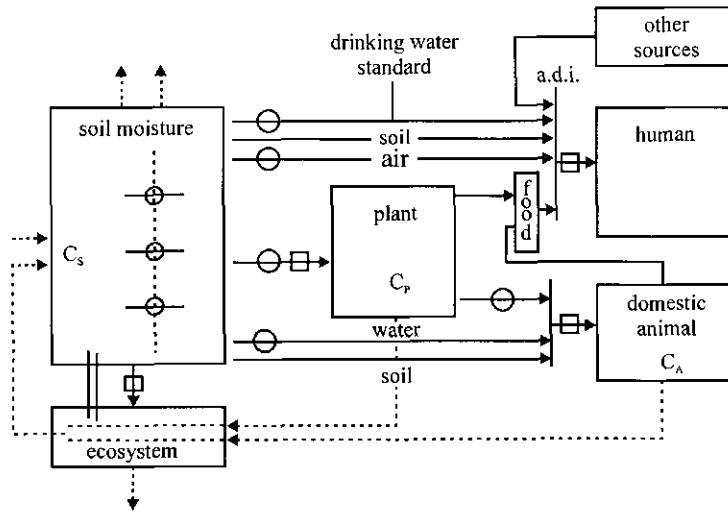


Figure 1.2. Pathways for contaminants from soil to other compartments and groups of organisms. From van Genderen 1987. For most compounds the distribution between solid phase and liquid phase (soil moisture) is of prime concern.

Circles refer to required information about transfer coefficients.

Squares to the same about dose-effect relationships.

The circles in the connecting lines of Figure 1.2 refer to the need for quantitative information about transfer factors of contaminants from the soil to other compartments and organisms indicated. The squares indicate a need for quantitative information about dose-effect relationships in order to estimate the (risk of) effects on humans, animals, plants and the soil ecosystem. The dotted lines back to the soil indicate that part of the contaminants is recycling within the system as for persistent constituents, e.g. heavy metals and slowly degradable organic compounds.

As was stated in a recent report to the C.E.C. on Soil Quality Assessment (de Haan et al. 1989):

ideally, a quantitative evaluation of soil quality requires complete information about all the transfer factors and dose-effect relationships shown in Figure 1.2:

- for all compounds that can cause malfunctioning or disfunctioning of soil;
- for all different soil types and soil properties that are found;
- and for all combinations of the different variables (e.g. pH, redox potential, accompanying compounds) that control compound behaviour in the soil system.

Because this is an impossible task at the present stage of knowledge, a number of limitations and restrictions has to be made in a first approach.

1.2 Soil quality in relation to soil functions

The quality of soil is adversely influenced by contamination (pollution) of the system. The concepts of 'contamination' and 'pollution' of soil are used here in a comparable way as they reflect only a difference in degree of damage to the soil system. Any addition to soil of contaminants, that is of those compounds that may exert adverse effects on soil functioning, can be defined as soil contamination. Because most soils do have a certain buffering capacity, as mentioned earlier, it usually takes some time before the negative effects become apparent. Once this situation occurs the soil can be considered as polluted, which for all practical purposes thus means that malfunctioning (or disfunctioning) of the soil is apparent due to an abundant presence or availability of compounds. Such malfunctioning may refer to one specific function in particular but sometimes also to a combination of different functions.

Some of the most important soil functions are:

- the bearing function, for instance as playground for children and for building of houses;
- the plant growth function; this may as well refer to natural vegetation as the production of crops for animal and human consumption; in relation to crop production not only quantity aspects like yield play a role, but also quality aspects are of concern as health of the consumers can be influenced by plant composition;
- the filtering function of water, groundwater as well as surface water;
- the ecological function of soil, with its contribution to element cycling as an important aspect.

Proper functioning of soil in the above different functions imposes a wide variety of quality criteria. This strongly hampers the introduction of a quality assessment methodology with general applicability and validity.

At first sight the bearing function would probably seem the least demanding, at least once certain physical requirements are met. However, experience of last decades in for instance Love Canal, USA, and Lekkerkerk, The Netherlands, and many other places has learned that also for building of houses some minimal requirements of chemical conditions in the soil are needed; and that a combination of use of the same site for waste disposal and later for urban expansion is not always without problems.

In the panic that arose following the discoveries of somewhat uncautious combinations of soil usages, a strong demand was felt for methods to assess health risks for people living in such polluted areas. And of course it was realized from the very beginning that this would require insight in the quantitative relationships between pollutant exposure of the organism under consideration on the one side and the resulting effects to be expected from this exposure at the other side. However, at the same time it was realized that there are many different pathways of pollutant exposure, of which in case of human beings the most important ones are:

- soil ingestion, especially for young children;
- inhalation of air, containing volatile polluting compounds;
- drinking of water and
- food in the form of plant products and animal products.

If the attention is confined for a moment to the last mentioned pathway it becomes apparent why the evaluation of soil quality in a quantitative way constitutes such a complicated problem. Assume that one can rely on the value of an acceptable daily

intake (ADI) of a certain compound for human beings, and that there is agreement on the allotment of this ADI over different pathways of exposure; then the sequence soil-plant-animal-product-human as shown in Figure 1.2 causes the contribution to human exposure via animal products to be akin to a fourth-order derivative from the soil quality.

This complexity undoubtedly contributed to the fact that the growing general awareness of soil pollution problems caused indeed a certain boom in the development of so-called multimedia exposure models, which unfortunately so far did not surpass the level of qualitative approaches in most cases.

Under the stress of the circumstances following the discoveries of the supposedly severely hazardous situations on built-on waste disposal sites, measures were developed in order to remediate the spot by cleaning up activities or by isolation measures. In this connection in The Netherlands a Soil Cleanup Act was introduced. In order to present some guidelines for estimating the severeness of the situation, so-called A-B-C values were suggested. These were actually meant as signal values with the following meaning:

A-value: background; no problems expected;

B-value: indication of need for further investigation;

C-value: indication of severe pollution and need for action.

Although it was clearly stressed that these values were of a preliminary nature only and should be used carefully, it turned out in practice that they tended to be maintained as rigid, soundly based criteria which supposedly allowed a quantitative risk evaluation of the areas involved. This single-value interpretation of soil quality has led to much commotion (sometimes resembling light degrees of hysteria) and in many cases to damages and economic losses, the necessity of which was at least questionable.

Newly built residential quarters were sometimes completely demolished on the basis of supposed severe health risk or hazards for the environment, even without any quantitative risk assessment.

Despite the problems involved in a scientifically based judgement of situations like above, it must be realized that waste disposal sites are still restricted areas of pollution only. Thus they can more or less be considered as point sources, where control and protection against further environmental damage can be relatively easily performed. This is contrary to the large scale diffuse contamination of soil, which now is also wide-spread. Due to the extended areas involved the possibilities for control and clean-up are then very limited. This forces to protection measures in order to prevent such diffuse contamination and pollution. Main sources for this type of soil degradation are invariably preceding emissions of wastes into air and water, and direct addition of compounds to soil by men.

Sometimes different soil functions may come into conflict with each other. This may for instance be the case when soil is used for crop production, whereas at the same time the groundwater underneath this soil is required for drinking water purposes. So normal nitrogen fertilization of arable land on sandy soils (*e.g.* 200 kg N/ha per yr) results in nitrate leaching to groundwater, under conditions of a precipitation surplus of about 300 mm on annual basis, at a concentration of more than 120 mg NO₃ per liter, thus exceeding the E.C. standard with a factor of roughly 2.5. This clearly indicates that in such cases priorities have to be set with respect to soil functions (or soil uses). A priority given to a certain function, however, obviously will include limitations to other soil uses.

When developing standards for soil quality in relation to soil functions, it might be reasoned that protection of the most susceptible function automatically safeguards all other functions. However, knowledge is insufficient at present even in order to differentiate between degrees of susceptibility. It therefore seems somewhat more realistic to consider a specific soil function as first priority in a certain case, and then try to develop soil quality standards (conditions, requirements) needed to allow this function. Despite this limitation the complexity of the system still leaves enough problems to be solved in soil quality assessment.

A few examples have been described in literature of effect oriented standards for soil quality. Lexmond (1980; 1981) derived a toxicity index with respect to plant growth for copper in soil. The availability of copper for uptake by plant roots appears to be controlled by three main factors, namely the copper content of soil in gram per kg of soil (as measured after extraction with 0.43 molar HNO_3), the organic matter content of soil (expressed as gram organic carbon per kg of soil) and the pH (as measured in a suspension of calciumchloride solution). The two latter factors are of direct importance with respect to copper binding in soil: with increasing organic matter content and increasing pH, copper ions in soil solution are increasingly inactivated. The toxicity index is presented by line 1 in Figure 1.3, together with a number of field data. Values above this line represent the situation where significant damage to soil fertility occurs, resulting in yield depressions of 10% or more. Line 2 in Figure 1.3 refers to a Cu/C ratio of 2. At this value damage to soil fertility as the result of copper availability is unlikely for the pH range which is of interest for agriculture (4.5-7.5).

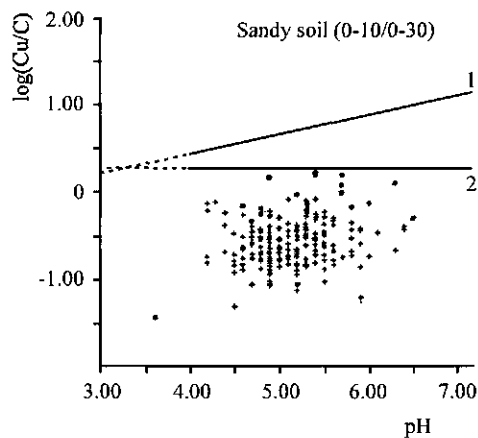


Figure 1.3. Copper toxicity index for maize, grown on sandy soil.

De Haan et al. (1987) derived acceptable Cd contents in soil with respect to leaching of cadmium to groundwater and surface water. For cadmium sorption in the practically relevant concentration range it is found that the Freundlich equation gives a satisfactory description. This equation is given by:

$$q = k \cdot c^n \quad (1)$$

with q = amount adsorbed and c = concentration in solution.

In batch experiments the values k and n were assessed for a number of different soils. In spite of the considerable difficulties with respect to experimental accuracy a number of system parameters that were not sufficiently included in soil type differences, were varied.

These parameters were ionic strength (I_0), solid:solution ratio, electrolyte composition (including the competing heavy metals zinc, lead and copper), pH, etc. As an example of the large differences encountered for one specific soil at varied (Cl^-), I_0 , and (Ca^{2+}), the experimental and fitted isotherms are given in Figure 1.4.

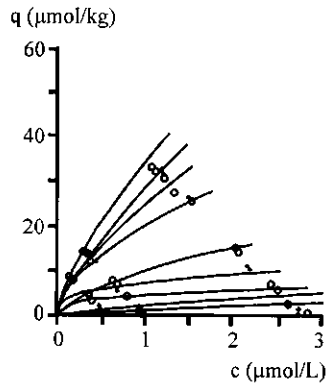


Figure 1.4. Cadmium adsorption (q) as a function of the concentration of cadmium in solution (C), for different values of ionic strength, chloride and calcium concentrations in solution.

The huge influence of these three system parameters on cadmium sorption is clearly demonstrated with the differences in sorption in this figure. This indicates the great care required to assess the adsorption parameters for a particular case as realistic values of the system parameters may differ between, for example agricultural soil water and waste percolation water. Taking into account the major factors controlling cadmium sorption an empirical relation was derived from equation (1):

$$q = k_1 (H^+)^a (Ca^{2+})^b c^n \quad (2)$$

where $a \approx -0.48$ and $b \approx -0.41$ were fairly constant for a wide range of soil types. In order to take into account the effects of ionic strength (I_0) and cadmium chloride complex formation the concentration in equation (2) should be replaced by the Cd^{2+} activity (Chardon 1984). The value of k_1 varied significantly for different conditions even for one soil type. The following relation can be derived to relate sorption to the predominant sorbing phase (organic carbon, oc), and pH:

$$q = k^* oc (H^+)^a c^n \quad (3)$$

with oc as % (w/w) (100 x mass of organic carbon/mass of dry soil) and (H^+) in $mol\ l^{-1}$.

In equation (3), $a \approx -0.48$, and oc varies from 0.8 to 4.0% (w/w). The value found for k^* is on an average 2.37×10^{-5} if q is given in $mol\ kg^{-1}$ and c in $mol\ m^{-3}$. From equations (2) and (3) it is seen that as system parameters may vary in space, this is also the case for concentrations in equilibrium with a designated total cadmium content ρT (on mass basis) given as:

$$\rho T = \rho q + \theta c \quad (4)$$

The definition of acceptable total contents in soil of contaminants should preferably be based on the relation between total content (T) and soil quality. Thus, with equation (4) in combination with equation (1) acceptable total cadmium content in soil may be calculated for different commonly accepted standards for cadmium concentration in ground water and surface water.

In illustration, the following standards are considered (in the units commonly used in this context):

- the Dutch standard for surface water to be used for preparation of drinking water: $1.5\ \mu g\ l^{-1}$;
- the Dutch advisory value for surface water: $2.5\ \mu g\ l^{-1}$;
- the EC standard for drinking water: $5.0\ \mu g\ l^{-1}$;
- the FAO and WHO standards for drinking water: $10.0\ \mu g\ l^{-1}$.

In Table 1.1 the total contents in equilibrium with these concentrations are given for the different k values. A pronounced variation in acceptable total cadmium contents results. The contents given in Table 1.1 may be evaluated with reference to the common total cadmium content found for Dutch agricultural topsoils, which is $T < 0.3\ mg\ kg^{-1}$. A soil with a total content exceeding $1\ mg\ kg^{-1}$ is considered as heavily contaminated.

In both cases it took a number of years of intensive research work in order to collect the data for deriving these standards. It became clear, as should be expected, that the single value approach is useless in case of soil quality evaluation, but that instead sliding scales are required due to varying soil properties and system conditions.

Table 1.1. Acceptable cadmium contents of soil, in mg/kg , for different criteria for the cadmium concentration in soil solution, in $\mu g/l$, for varying values of k ($\mu g^{1-n}\ l^n\ g^{-1}$) and $n = 0.8$.

k	C			
	1.5 $\mu g/l$	2.5 $\mu g/l$	5 $\mu g/l$	10 $\mu g/l$
0.001	0.001	0.002	0.004	0.006
0.01	0.01	0.02	0.04	0.06
0.1	0.1	0.2	0.4	0.4
0.3	0.4	0.6	1.1	1.9
0.5	0.7	1.0	1.8	3.2
0.9	1.2	1.9	3.3	5.7
6	8.3	12.5	21.7	37.9

Because of the unacceptable long time required for standard development for the many compounds of interest, a new approach was followed, namely the development of reference values for soils that can be considered as 'non-polluted' or 'slightly contaminated'. These values have been indicated as 'new Dutch reference values'.

1.3 Reference values for unpolluted soil; heavy metal contents as an example

During the last decade considerable effort has been spent in The Netherlands in order to obtain insight in what levels of heavy metals could be related to good soil quality. Therefore an intensive analysis was made of areas designated as nature reserves, that have been managed as such for a long time (Edelman 1984). 'Good' soil quality should then be interpreted as non-heavily polluted, or almost unpolluted by human activities. It was, of course, realized that a certain degree of contamination by means of deposition from the air is unavoidable for most areas in Europe, and even for probably all areas of the world. This makes it impossible to obtain from present sampling an indication for natural background values, at least for some elements. Cadmium and lead are examples of heavy metals that have been wide-spread by aerial deposition as the result of human activities.

The natural background value depends on the nature of the parent material from which the soil has developed. For The Netherlands this parent material has been brought down from abroad by wind, water or through transport with ice. During transport and deposition a sorting took place according to particle sizes, which meant at the same time a sorting with respect to mineralogical composition. This is of utmost importance for the occurrence of heavy metals. Sand and silt consist of primary minerals which are resistant against weathering, whereas the clay fraction ($< 2 \mu\text{m}$) consists of secondary minerals formed after weathering of less resistant primary minerals. Quartz usually is the most important component of the sand and silt fraction, whereas clay minerals and hydrous oxides constitute the bulk of the clay fraction. The heavy metal content varies between the different minerals. In quartz this content is extremely low. The result is that the heavy metal content of sediments is related to their texture (grain size distribution). These values for natural background contents are fairly well known for different sediments. They may be considered as the natural background because the sediments have been formed and deposited at the time that human influence on heavy metal distribution was still absent. Of course, the original background values have been changed since that time because of soil forming processes and later as the result of human activities, especially when the industrial society became under development.

Therefore, the information gathered by soil sampling of nature reserves, as mentioned before, should preferably be characterized as 'current background values', indicating that they refer to the original values corrected for soil forming processes and air deposition. To give these values the indication 'reference values for good soil quality', as is at present usually done in The Netherlands for policy reasons, is (as a matter of principle) essentially not correct because such an indication would suggest information about desirable metal content and soil functioning. As stated before such information is still lacking. Moreover, it might well be that the contents are below optimum levels for specific soil functions, *e.g.* the crop production function in relation to required levels of those heavy metals which are trace elements for plant growth. Therefore it is preferable to characterize these contents as 'present background values for not abnormally contaminated soils'. Lexmond & Edelman (1987) developed a model which

enables a quantitative description of the influence of clay content and organic matter content of the soil on the occurrence of heavy metals, under consideration of the absence and presence of human influence on the metal contents. These results are summarized in Figure 1.5. For detailed information about the symbols given in Figure 1.5, the reader is referred to the original publication in which the model was derived and discussed.

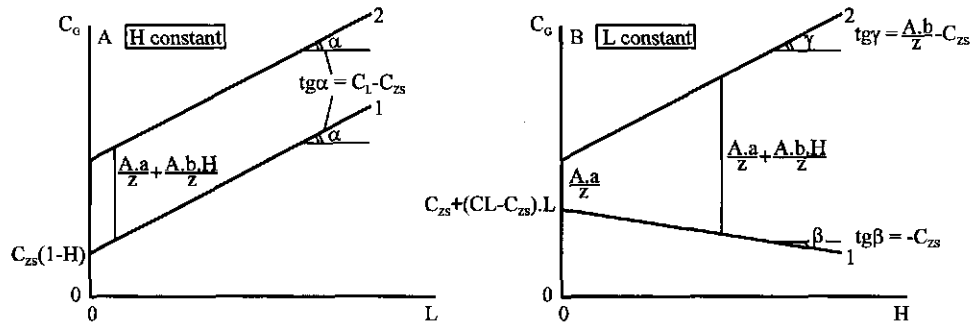


Figure 1.5. The relationship between metal content (C_G) and clay content (L) for constant value of humus content (H) (upper figure), and between metal content and humus content for constant value of clay content (lower part). Lines indicated with 1 and 2 refer to absence and presence, respectively of human influence on metal content. From Lexmond & Edelman 1987.

The symbols in Figure 1.5 have the following meaning:

- C_G : total metal content in soil ($\text{mg} \cdot \text{kg}^{-1}$);
- C_{zs} : metal content of sand and silt fraction ($\text{mg} \cdot \text{kg}^{-1}$);
- C_1 : metal content of clay fraction ($\text{mg} \cdot \text{kg}^{-1}$);
- L : mass clay fraction ($\text{kg} \cdot \text{kg}^{-1}$);
- H : mass humus fraction ($\text{kg} \cdot \text{kg}^{-1}$);
- A : metal load through human activity ($\text{mg} \cdot \text{m}^{-2}$);
- z : depth (m);
- a, b : constants for the relationship between bulk density and humus content.

The value for soil bulk density is decreasing with increasing organic matter content. This means that the same metal deposition leads to a higher increase of content on weight basis for soils with increasing organic matter content.

This model has been used for a profound analysis of the data originally collected by Edelman (1984) in the topsoil (0-10 cm) of nature reserve areas (Lexmond & Edelman 1986; 1987). The results of this analysis are presented here for a few heavy metals in a summarizing manner by means of some figures (cf. Figure 1.6). The figures represent the relationship between the content of the metal indicated (vertical axis, $\text{mg} \cdot \text{kg}^{-1}$) and the clay content of soil (horizontal axis, $\text{g} \cdot \text{kg}^{-1}$).

Points refer to samples with an organic matter content, H , of $< 0.25 \text{ kg} \cdot \text{kg}^{-1}$, whereas open symbols refer to H values $> 0.25 \text{ kg} \cdot \text{kg}^{-1}$. Full-drawn lines represent the relationship meant, whereas the broken lines refer to the upper boundary of the range of element contents normally found in mineral top soils of nature reserve areas.

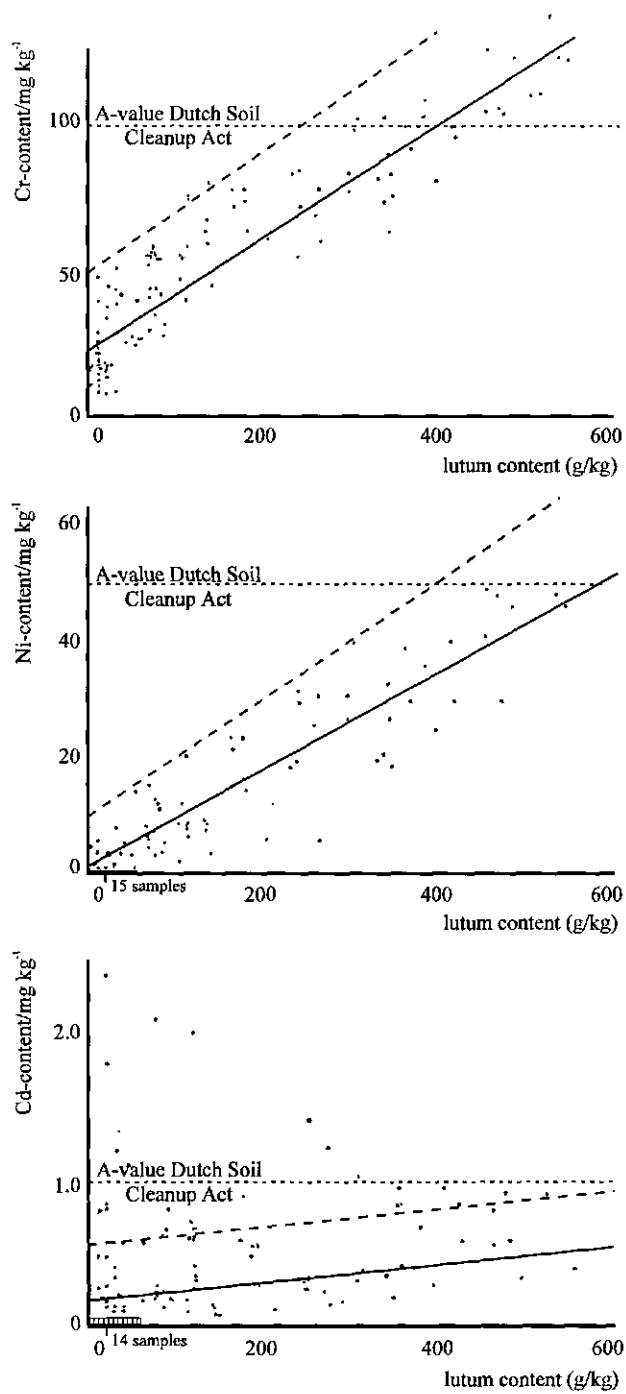


Figure 1.6. Element content in nature reserve soils as related to clay content.

Examples are given for the heavy metals chromium (Cr), nickel (Ni) and cadmium (Cd). In these figures also the original A-values as mentioned in the Dutch Soil Cleanup Act are represented, indicating that these were, for all three elements presented, chosen at the high side.

The Institute of Soil Fertility at Groningen, The Netherlands, has made a comprehensive inventory of heavy metal contents in Dutch arable soils (van Driel & Smilde 1982; Wiersma 1985). These values for topsoil samples (0-20 cm), again as function of the clay content of the soil samples, can now be compared with the data for the nature reserve areas. This comparison is made in Figure 1.7, again for the metals Cr, Ni and Cd. The lines shown in Figure 1.7 refer to the earlier presented upper boundary of the range of element contents found in mineral soils of nature reserve areas.

It is thus shown that for Cr and Ni the situation in arable soils is in fair comparison with that in nature reserve soils. For Cd the arable soils show in a number of cases higher values which undoubtedly must be attributed to the use of phosphate fertilizers. A same comparison for the metals Cu, Hg and Zn would show many more situations where arable soils are higher in content than the nature reserves.

Table 1.2. Reference values for heavy metals, arsenic and fluoride.

compound	SOIL (mg.kg. ⁻¹ dry soil)		GROUNDWATER (μ g.l ⁻¹)
	relationship	standard soil (H=10; L-25)	
Cr	50 + 2L	100	1
Ni	10 + L	35	15
Cu	15 + 0.6 (L+H)	36	15
Zn	50 + 1.5 (2L+H)	140	150
As	15 + 0.4 (L+H)	29	10
Cd	0.4 + 0.007 (L+3H)	0.8	1.5
Hg	0.2 + 0.0017 (2L+H)	0.3	0.05
Pb	50 + L + H	85	15
F	175 + 13L	500	-

The new reference values for heavy metals, arsenic and fluoride in their relationship with organic matter content and clay content of soil is given in Table 1.2. The formulae for calculating the reference values as presented in Table 1.2 have been derived from the inventory data as mentioned before. As an example the values for a so-called standard soil with 25% clay and 10% humus are also presented.

It can not enough be emphasized that the above approach, although it may provide a valuable tool for a first rough evaluation of the degree of soil contamination, is by no means an effect-oriented soil quality assessment. Such assessment should not only consider merely compound presence but also compound behaviour, especially with respect to bioavailability. Although this subject will be given specific attention during this course, a few remarks may be made here.

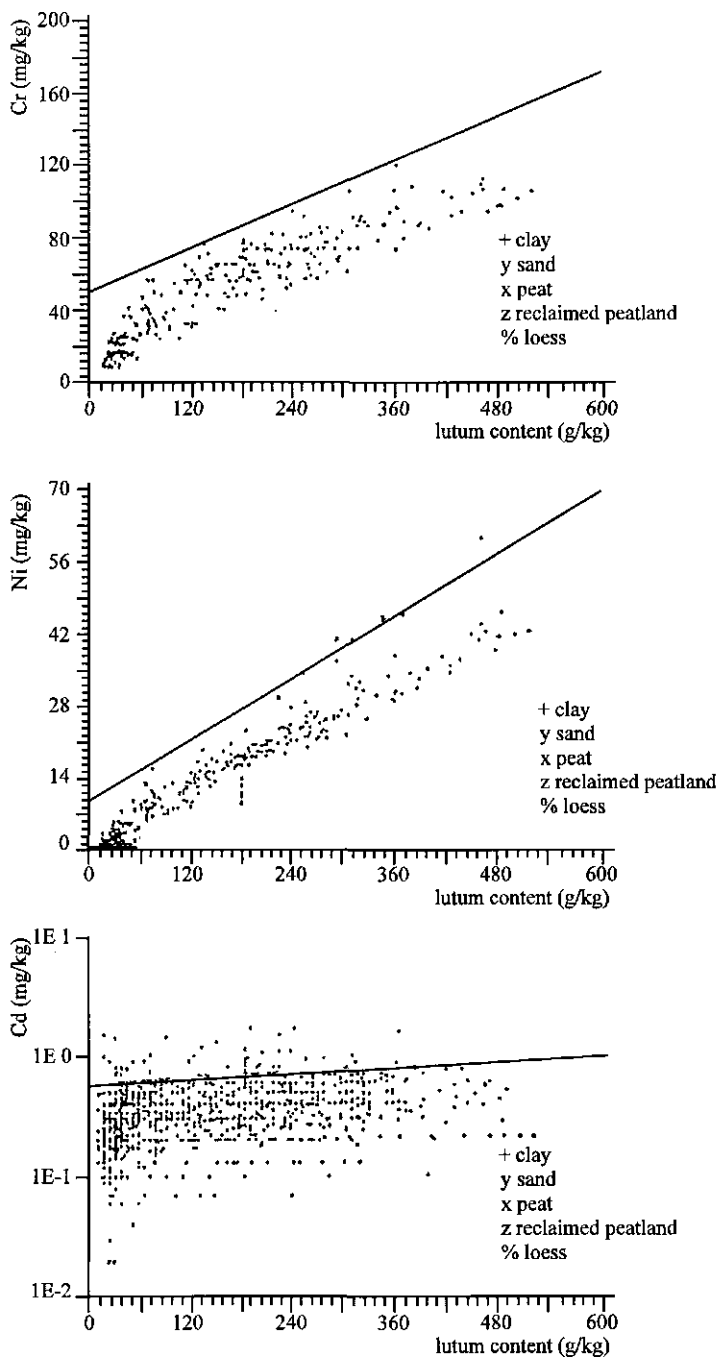


Figure 1.7. Element content in topsoil of arable soils as related to clay content, lines refer to upper boundary in nature reserve soils.

1.4 Some remarks on bioavailability of compounds in soils

The concept of bioavailability is very important with respect to soil quality since it links in principle compound behaviour and the effect of these compounds on organisms. At present these links are not very well established and the word bioavailability sometimes is used more as a buzz word. A precise scientific definition is not simple to derive. Recently, soil chemical aspects of bioavailability have been discussed by van Riemsdijk (1990); some of these aspects are mentioned here.

Bioavailability relates to the availability of a chemical with respect to a specific organism. Bioavailability can only be measured in terms of an effect of a chemical on an organism. This effect is in general a complicated function of the concentration of the specific chemical as present in a certain complex matrix. This matrix may be for instance a certain soil or sediment. The effect that is being measured can be growth, uptake, respiration, degradation, root development, enzymatic activity, etc. When the chemical is of inorganic nature, it is suggested to define bioavailability in terms of the concentration of the inorganic element (Cu, N, P, Al, etc.) whereas for organic pollutants a specific chemical species (*e.g.* HCH) should be used. Bioavailability can thus be described as follows: Bioavailability of an element or organic species as present in a (complex) matrix is related to the possibility to cause an effect (judged positively or negatively) on a specific organism. The bioavailability of an element present in a specific form depends on the type of organism. For blue algae and leguminous plants $N_2(g)$ may be fully available whereas for most plants the bioavailability of nitrogen in the form of $N_2(g)$ is zero. Nitrogen in the form of nitrate may be fully bioavailable. The bioavailability of an element is thus dependent on the form in which it is present. In other words, different chemical species containing the same element may have a completely different bioavailability. The bioavailability is also dependent on the composition of the matrix in which it is embedded. These matrix effects can for instance be caused by competitive effects of other species present in different amounts in various soils, difference in pH, reactive surface etc. The formation of soluble complexes between a metal and organic ligands like humic and fulvic acids may either increase or decrease the bioavailability of this metal. An increase in bioavailability may occur although the metal-organic complex itself is non bioavailable. Enhancement of bioavailability may take place in case the transport of the metal to the organism is limiting the bioavailability. Complexation with dissolved ligands leads to an increased total metal concentration in solution facilitating the transport to the surface of the organism, where it may exert its effect after dissociation into the free metal ion. The organic-metal complex in this case is merely a carrier for transport. A decrease in bioavailability due to metal-organic complex formation may occur when the main effect of the complexation is a decrease in the (available) free metal concentration in solution.

The pH or proton concentration may also strongly affect the bioavailability of an element. The effect of the pH on the bioavailability may strongly depend on the composition of the matrix. In a culture solution, the availability or toxicity as measured by (reduced) growth increases with increasing pH, *i.e.* with decreasing proton concentration (Lexmond 1980). This observation may be explained by the decrease in competition between protons and metal ions at higher pH for surface sites present on the organism (root, cell wall) resulting in a higher affinity of the biosurface for copper leading to increased bioavailability. However, in soils copper toxicity or availability for plants generally leads to a decrease in bioavailability with increasing pH. In the plant-soil system, the copper partitions over the solution phase, the surface of the biota and

the surface of soil colloids. With an increase in pH the preference of copper to bind to the surfaces (both living and dead) will increase because of decreased competition with protons. If the preference for the soil surfaces is increased more strongly than for the surface of the biota, a decrease in bioavailability will be expected as a result of an increase in pH.

Another interesting and complicating aspect of bioavailability is that the organisms may actively influence the bioavailability by changing the chemical composition of their immediate environment which may lead to an increased or decreased bioavailability. An example of a decrease in bioavailability is the excretion of organic ligands by earthworms. The excreted organic ligands bind for instance lead and cadmium rather effectively (Kiewit 1989) thus reducing the bioavailability as measured by the metal uptake of the earthworms from aqueous medium. The above given examples show that for an interpretation of the effect of environmental factors on the bioavailability a rather detailed knowledge is required on the chemical interaction processes. What is needed are generalizable concepts of bioavailability that can be applied to any soil, sediment or aqueous system in order to be able to interpret, predict and model the effect of environmental factors on the bioavailability. The examples given indicate that reaching this goal is a non trivial problem.

1.5 Recent developments in biological soil quality assessment

In addition to physical chemical methods as indication for soil quality, also the biological approach obtained increased attention during recent years. These different approaches may have their own advantages and limitations, but may also be complementary to each other. Ecotoxicological aspects of soil quality is given extensive attention in different parts of this course.

For biological soil quality indication, soil nematodes seem to be promising organisms. There is a large variety of nematodes, which have been very well described and classified. As described by Bongers (1988; 1990) nematodes are almost ideal organisms for laboratory experiments. They can easily be isolated from the soil, there are methods available for automatic counting of the organisms, whereas procedures for automatic identification are well under development now.

At the Department of Nematology of the Wageningen Agricultural University recently a new index has been developed, which can be applied for determination of disturbances within the soil nematodes communities. In cooperation with the British Museum (Natural History) and the University of Milan it is now under study whether this approach may be used Europe-wide for a biological soil qualification system and an ecological soil typology.

The principle of the approach may briefly be described as follows. The composition of the nematodes community is more or less a reflection of soil conditions, with respect to chemical aspects (*e.g.* pollution or contamination) as well as with respect to physical aspects (*e.g.* drought). This may also be indicated as a relationship between nematode community composition and stress conditions in soils.

In this respect the families of nematodes are classified in five different categories, of which the extremes are indicated as Colonists and Ascetics, respectively. The Colonists are considered as more or less opportunistic organisms, which are characterized by a short life cycle, high reproduction and other properties which are related to the ability of filling up so-called ecological vacancies induced by changing soil conditions. The Colonists are the least sensitive for stress conditions. However, after a certain time the

Colonists are replaced by the Ascetics which are very efficient in feeding, have a large competition power and are very sensitive towards disturbances of the system.

The relative presence of Colonists in the nematode community is expressed in a so-called Maturity Index, which can be used as a measure for the degree of disturbance of the soil ecosystem functioning.

This new approach apparently has very promising perspectives and thus deserves further stimulation. Especially the combination of such biological indicators with quantitative description and interpretation of physical-chemical soil conditions may allow an important step forwards into the direction of soil quality assessment.

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2 Soil protection

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2.1 Introduction

Environmental policies concerning air and water quality were already well developed before environmental soil problems gained political attention. Before 1970 the soil was generally considered as an environment with an almost infinite self purifying capacity. One of the reasons for this misunderstanding might have been that effects of poor air and water quality are clearly visible, whereas effects of soil pollution might show up only after an investigation of the soil and groundwater.

Soil problems are quite diverse, and it is now generally felt that an integrated environmental policy for soils is needed. The need for soil protection has been put in an international perspective already in 1972 by the Council of Europe. The Council of Europe is the first political institute created in Europe, in 1949. With 26 Member States it covers more countries than the European Union (EU). As an intergovernmental organization decisions must be approved by all Member States. In their European Soil Charter the general principles of soil protection were laid down. Proposals for international action are presently discussed and are based on the following principles:

- recognition that soil is a common heritage and non renewable resource;
- integration of soil protection into other environmental policies;
- rational use of soil and careful management of soil;
- respect for multifunctionality through harmonization of surface land use;
- the reversibility rule (impact on soil quality by man should be reversible).

It is important to note here that the principles for soil protection are based on 'careful soil management' and reversibility of human impact, and not on a 'back to nature' approach. This underlines the difference between soil protection as an environmental policy, and nature conservancy. A second important point is that these principles anticipate on future landuse, and are in agreement with modern environmental policy objectives like 'sustainable development' (WCED 1987).

Compared to the activities of the Council of Europe, the objectives of the European Unions (EU) environmental policy are less specific. In the Single European Act the environment is considered as a crucial factor in economic development. Soil is not a major policy area in the EU, and soil is not addressed directly in the European legislation. There are however a number of EU directives on waste management and (ground) water quality with beneficial side effects for soil quality:

- the groundwater directive (1979);
- the sewage sludge directive (1986);
- the directives on waste (1975 and 1978);
- the directive on environmental impact assessment (1985);
- the directive on plant protection products (1991).

These directives have to be enforced by legislation at the national level in the Member States. Only a few Member States have legislation that deals with soil protection in general. Mostly soil protection is still based on other laws for instance on agriculture or waste management.

It is beyond the scope of this introduction in soil protection to review for each country the type of laws involved or other legislative aspects. There are however major issues in discussions about soil protection that have to be addressed irrespective of the type of legislation involved:

- general source oriented (preventive) strategies;
- the development and the use of generic guidelines or soil quality criteria;
- the policy objectives for restoration of contaminated land.

These issues will be discussed below. The discussion on the development of soil quality criteria will mainly focus on the procedures that were used in The Netherlands. These methods are fairly general and can be easily modified to meet different policy requirements. Approaches used in other countries are often quite similar.

2.2 Source oriented soil protection

In soil protection policy based on the sustainability principle it will be obvious that human activities that have irreversible effects on the structure and composition of the soil deserve special attention, especially if they endanger any future utilization of the soil by human beings, plant or animals. Therefore much priority must be given to activities that might lead to accumulation of persistent toxic substances in soil and groundwater.

For a large number of sources prevention of soil pollution can be achieved by containment. Emissions to soil and groundwater are prevented by appropriate isolation and control technology. This is the general approach for sources like waste dumps, industrial process plants and petrol stations in most countries. These sources are mostly local and result from activities that do not depend on the input of chemicals in the soil system. Preventive measures are based on concepts like BATNEEC (Best Available Technique Not Entailing Excessive Costs) and only in a few cases on predefined 'acceptable emissions' to the soil. The main discussion in this area of soil protection is about technologies that prevent emissions to occur. Soil scientific and ecological issues are less frequently addressed. In the Dutch soil protection concept this general approach for prevention is labeled the Isolate, Control and Monitoring (ICM) strategy.

For diffuse sources of soil pollution a simple isolate control and monitor strategy will not do. Atmospheric deposition and sedimentation processes in aquatic systems cannot be isolated, and agriculture would be impossible without application of fertilizers. Discussions about preventive strategies are focused on 'acceptable emissions'. Soil scientific and ecological considerations are of prime importance in this field, in contrast to the more technology oriented local source approach. To preserve the quality of the soil, the input of substances into the soil system must balance its natural or agricultural output. Quantitative soil quality criteria are needed here, because if the balance between input and output is reached at higher concentrations of a chemical in the soil, the multifunctionality of the soil might be endangered. These soil quality criteria must be used in conjunction with source oriented measures. In a regulation concerning for instance the application of animal manure on the soil, the maximum dosage of phosphate and nitrogen compounds on the soil has to be related to an acceptable concentra-

tion of these substances in soil and groundwater and the rate at which these substances leave the soil system through the harvesting of crops and the hydrological cycle.

2.3 Soil quality criteria and the assessment of soil pollution

Numerical criteria for the quality of soil and groundwater are important tools in soil protection and cleanup. In the Netherlands two types of soil- and groundwater quality criteria are used: target values and intervention values. If concentrations of polluting substances do not exceed target values the soil is considered to be of good quality. There are no restrictions in land use due to soil pollution. In the preventive approach measures are taken to prevent the exceeding of target values. These values are also the values for a clean soil, the preferential target in cleanup. More information on the use of target values is given by Robberse & Denneman (1993).

Intervention values indicate a level of pollution where soil quality is severely affected, and a cleanup is considered necessary. Target values and intervention values are given in appendix 1.

2.3.1 Derivation of target values

Target values for metals are related to background concentrations in relatively unpolluted rural areas. Background concentrations are related to soil type. As soil types are classified according to the organic matter and clay content of the soil, the relationship between background concentrations and organic matter and clay content can be used to derive soil type dependent target values. Target values were defined as 90-percentiles of concentrations of metals measured in unpolluted agricultural soils and in soils from nature areas. An example of the derivation of the target value for lead is given in Figure 2.1.

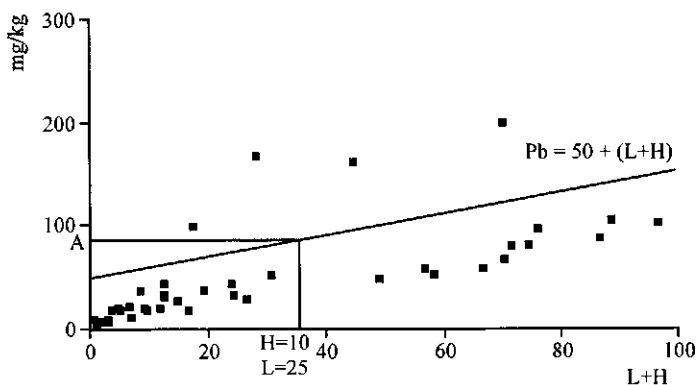


Figure 2.1. Relation between the lead content of the topsoil in nature areas and soil organic matter (H) and clay (L) content (% dry weight of soil). The line representing the target values for various soil types is described by $[Pb] = 50 + (L+H)$. 90% of the data are below this reference line. The formula can be used to compute target values for all soil types. A is the target value (85 mg/kg) for a standard soil (H=10; L=25).

Table 2.1. Formulae relating target values for metals to clay and organic matter content of the soil.

Metal	Formula
chromium	$50+2L$
nickel	$10+L$
copper	$15+0,6(L+H)$
zink	$50+1,5(2L+H)$
cadmium	$0,4+0,007(L+3H)$
mercury	$0,2+0,0017(2L+H)$
lead	$50+L+H$
arsenic	$15+0,4(L+H)$

Formulae for the derivation of target values in relation to clay-(L) and organic matter(H) content of the soil are given in Table 2.1. These formulae are used for soils with an organic matter content between 2% and 30%. Target values for soils outside this range are computed by entering 2 resp. 30 as values for H in the formulae.

Target values for organic contaminants are related to the so-called No Observed Effect Concentrations (NOEC) for soil organisms. Contaminants in the soil at concentrations below NOEC cause no adverse effects on growth, reproduction and survival of a species. Dependent on the availability of toxicological information various methods have been used to derive these values. The preferred method is related to the maximum permissible concentration (MPC) for ecosystems. This level is reached if the NOEC of 5% of the species is exceeded. The basic principles of this method are illustrated in Figure 2.2.

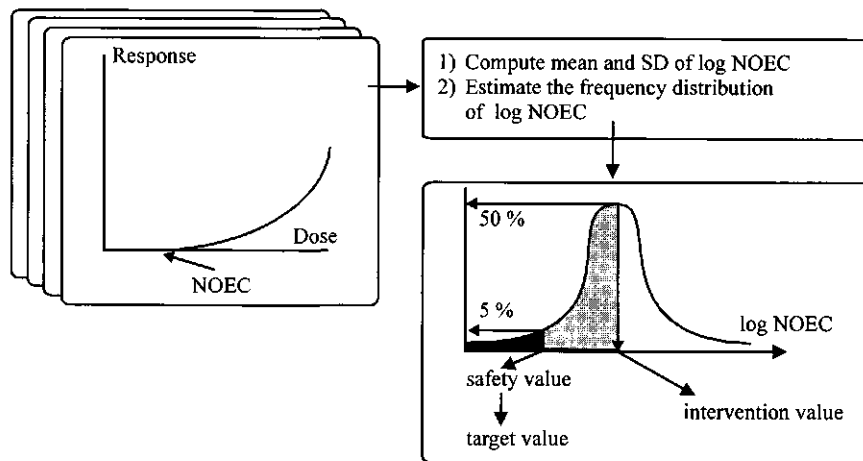


Figure 2.2. Outline of the derivation of risk based ecotoxicological criteria. No Observed Effect Concentrations for different species are used to estimate a frequency distribution of NOEC's on a logarithmic scale. Percentiles (5% and 50%) are used to derive target and intervention values.

Target values for organic substances are derived from MPC levels by dividing MPC by 100, to account for the combined toxicity of the substance and other toxic substances in the environment. At present a discussion is taking place whether this factor 100 should be changed.

For substances where toxicological information on soil organisms is lacking, the target value is estimated by using aquatic toxicity data to derive a target value for water, and computing a value for soil by equilibrium partitioning methods. Values for groundwater are either derived from soil values or values for surface water. In the case that values for groundwater are below detection limits the detection limit is used (VROM 1991).

Target values for organic contaminants in soils are related to the organic matter content of the soil. The relationship is comparable to the relation for metals: a linear relation for soils with an organic matter content between 2% and 30%. Other soils are treated as having either 2 or 30% organic matter.

2.3.2 Derivation of intervention values

Ecotoxicological I-values (Intervention values) are derived directly from the results of ecotoxicological experiments. The average value of the logarithm of NOEC's of different species for a given substance is used or - if lower - the average value of the logarithm of NOEC's for soil microbial processes. So, from an ecological point of view soil clean-up might be needed if the concentration of a chemical substance in the soil is higher than the NOEC of 50% of the species or microbial processes.

Figure 2.3 illustrates the derivation of the ecotoxicological intervention-value for cadmium. If more data were available for the same species or for the same microbial process, the data were pooled by taking the geometric mean. So the basic data for the derivation of I-values pertain to different taxa for species and different microbial processes. Other standards and background levels are given for reference.

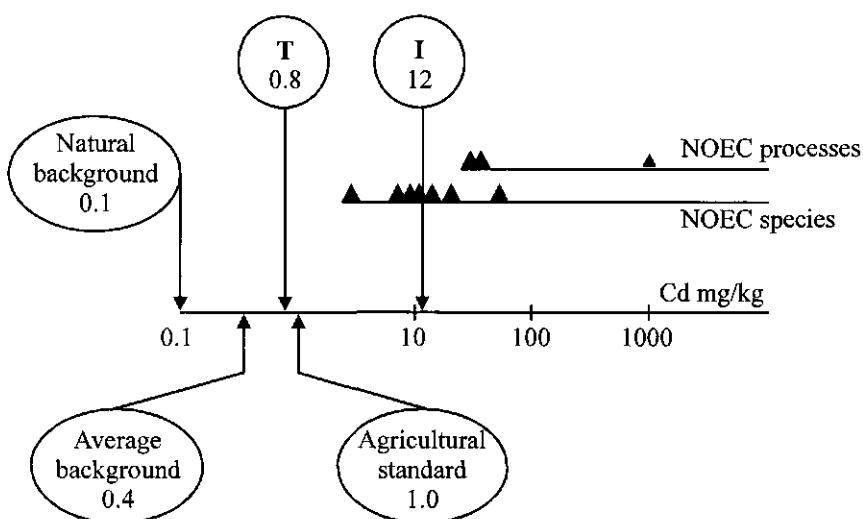


Figure 2.3. Dutch standards for cadmium (mg/kg) for a standard soil (10% organic matter and 25% clay) in relation to background concentrations and ecotoxicological data. T = target value, I = intervention value. Data for the same species and the same microbial processes have been pooled.

In order to derive Intervention-values based on human health a large survey of the toxicological literature was made by Vermeire et al. (1991). Values for Tolerable Daily intake (TDI) were proposed for a large number of soil pollutants, using methods comparable to the derivation of ADI's by WHO. For genotoxic carcinogens the conventional risk level of 10^{-4} death per lifetime (10^{-6} /year) has been used as toxicological limit value.

These toxicological criteria for daily intake had to be related to concentrations of polluting substances in the soil by an exposure model. Human intervention values are based on model computations of potential exposure. These values correspond to a level of soil contamination where daily intake will exceed the TDI if all potential exposure routes are present. Various models for individual exposure routes were combined to yield what is now called the CSOIL model. The model is not very complicated, it merely consists of a large set of formulae and parameters and does not use any advanced mathematical operations (van den Berg 1991; van den Berg & Roels 1991).

One of the important results of the model was that human exposure to soil pollution is to a very large extent (>90% of total exposure) determined by the three exposure routes shown in Figure 2.4:

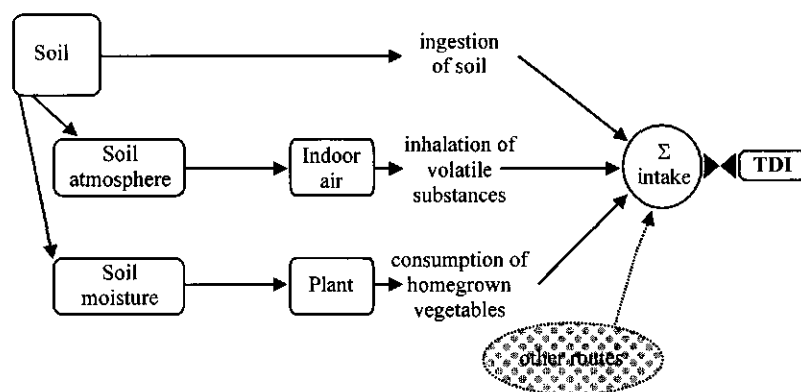


Figure 2.4. Major routes of exposure to soil contamination.

Other routes such as inhalation of soil and dust, dermal contact, consumption of meat and fish, drinking water and bathing and showering were also included in the model. The contribution of these routes to overall exposure is quite small. To yield a single intervention value a choice had to be made between the human value and the ecological value. This single value is needed in the Netherlands for juridical reasons, to provide an unambiguous criterion for sites that fall under the cleanup regulation of the Soil Protection Act. In general the lowest value for each substance is chosen as final intervention value, but there are some exceptions. Sometimes, the lowest value is very unreliable because of the limited amount of (eco)toxicological data that could be used to derive the value. The final decision about values is then made by expert judgment.

After the choice of the integrated intervention value an intervention value for groundwater is computed, assuming equilibrium partitioning between the solid phase of the soil and the water occupying the pore spaces. Because concentrations of polluting substances are usually lower in groundwater due to dilution, the equilibrium value for

water in pore spaces is divided by 10. This is a somewhat arbitrary choice, but it was generally felt that intervention values should be lower than the equilibrium value which can be computed for pore space water based on the intervention values for soil. Finally the intervention values for soil and groundwater are compared with other values used in environmental policy, and intervention values are adjusted to avoid inconsistencies. Intervention values and target values are given in Appendix 2.1. The general procedure for their derivation of intervention values is shown in Figure 2.5. More detailed information is given in van den Berg et al. (1993).

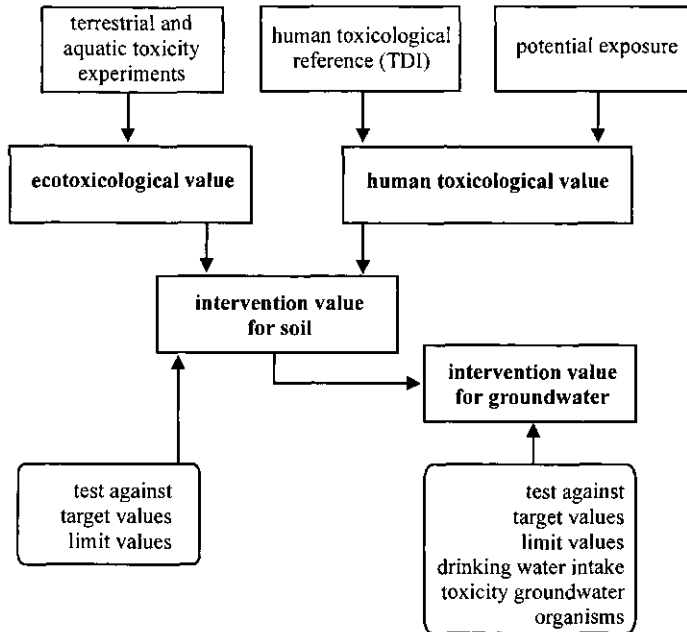


Figure 2.5. General procedure for the derivation of integrated intervention values for soil and groundwater.

2.4 The Dutch system for the assessment of soil pollution

The Dutch system of investigation and decision making is briefly discussed to illustrate the use of generic criteria in decision making. Assessment of soil pollution consists of a number of stages and is based on generic quality criteria for soil and groundwater and site specific conditions. During an assessment the following questions must be answered:

- Is the site seriously polluted?
- Is remediation urgent?
- What is the remediation objective for the site?

2.4.1 Serious pollution

Suspect sites are first subject to a preliminary investigation. The history of the site is studied in order to yield indications about the nature of the polluting substances. If the suspicion is confirmed by the outcome of the 'historical investigation' soil and groundwater are sampled. If contamination of soil and/or groundwater exceeds the average of the target value (T) and the intervention value (I) a further and more extensive investigation must be carried out. In the future the criterion $(T+I)/2$ will be replaced by a statistical criterion which is under development.

If the results of a further investigation indicate contaminant levels above the intervention value the site is registered. The official terminology for a site where intervention values are exceeded is 'serious pollution'. Registration means that authorities are entitled to perform a cleanup on the basis of the Soil protection act. Cleanup of less polluted sites, which might be considered necessary for other reasons, cannot be part of the soil cleanup programme based on the Soil protection act and cannot be financed by this programme.

2.4.2 Urgency of cleanup

Sites where intervention values are exceeded are further assessed as soon as possible to establish the urgency of the cleanup. Urgency depends on actual human risk, ecological impact, and possible dispersion of the contamination.

The decision about the urgency (or priority) of the cleanup is based on site specific considerations, and not on generic soil quality criteria. Urgency will depend on the actual use of the land and the geohydrological situation.

A timetable for remediation of urgent sites will be made in each province or larger city by the provincial or municipal authorities. The most urgent sites have to be remediated within four years. Non urgent sites will remain registered, but are not included in the timetable. Urgency of these sites is reassessed if land use or the geohydrological situation changes.

2.4.3 Cleanup goal

The general goal of a cleanup is the restoration of soil multifunctionality. Target values for clean soil must be reached unless the cleanup:

- will cause environmental problems, or
- is impossible for technical reasons, or
- is too expensive.

Criteria for environmental impact of the cleanup, technical constraints and cost-effectiveness are now being developed to facilitate this decision. If restoration of multifunctionality is not possible because of one of the reasons mentioned above, the site is isolated, controlled and monitored (ICM approach). ICM solutions may involve partial excavations and may be related to current or intended use of the soil, but often involve severe restrictions on land use. Figure 2.6 gives an overview of the decision making process in The Netherlands as described above.

2.4.4 The use of generic criteria in decision making

In a number of countries various approaches have been used to assess the significance of soil contamination and to set cleanup goals. Whether predetermined numerical criteria for critical levels of contaminants in soil, or risk assessment procedures are the optimal tools for decision making (Siegrist 1990) is subject to discussion.

In the decision making process in The Netherlands the use of predetermined numerical criteria (intervention values) is limited to the first stage of the assessment. In later stages decisions are based on site specific investigations and feasibility analyses. The target val-

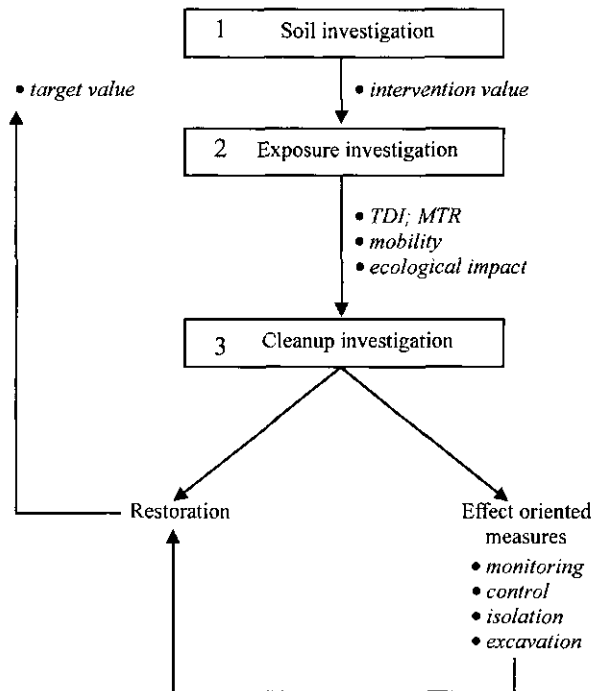


Figure 2.6. Decision making process in The Netherlands: 1) soil investigation to determine if the intervention value is been exceeded; 2) establish the urgency of the cleanup; 3) cleanup investigation to decide on the measures that have to be taken.

ues which are used to describe the cleanup goal for situations where a restoration of soil quality is feasible, are predetermined numerical standards but have no direct influence on the decision about the cleanup goals.

Other countries try to develop a more simple decision making procedure by making extensive use of predetermined soil quality criteria. The Dutch approach has been criticized for being too rigid (intervention values not related to land use) and too complicated (site specific exposure assessment and cleanup feasibility studies). This raised the important questions whether an approach based on predetermined numerical soil quality criteria only could be used for all decisions about contaminated land.

In such an approach decisions are made by comparing concentrations of pollutants in soil and groundwater measured at the site with criteria related to the actual or intended use of the site. If these criteria are exceeded cleanup is necessary. Urgency mainly depends on the amount by which the land use specific standards are exceeded. The cleanup objective is to achieve a situation where the soil quality criteria for the actual or intended land use are no longer exceeded.

The use of land use dependent generic soil quality criteria in every stage of the decision making process may simplify the decisions, but necessarily leads to partial and short term solutions for the contaminated land problem only. If a site is cleaned up for a given land use, future changes in land use may require a second cleanup. Whether the consequences of land use related cleanup for future land use are acceptable is a political choice (see section 2.5). There are however some scientific problems with land use dependent approaches based on soil quality criteria as well. Predetermined numerical criteria have severe limitations if they are used as predictors of actual risks due to exposure to soil pollution in relation to land use. The limitations can be summarized in three categories:

- valid exposure scenario's for the derivation of human health related soil quality criteria;
- constraints on the differentiation of land use dependent soil quality criteria by effects of soil pollution other than human health effects;
- variability and uncertainties in human exposure and effects impose practical limits on the differentiation of criteria with respect to land use.

Valid scenarios for derivation of soil quality criteria based on toxicological limit values such as ADI or TDI assume a lifetime (70 year) exposure. This assumption only holds for exposure to soil pollution in residential areas. In industrial areas for instance people are exposed only during working hours and only part of their lives. The relation between exposure on industrial areas and health risks is not straightforward in this case. Additional assumptions have to be made about 'background' exposure, outside the industrial site after working hours, which might differ due to circumstances which have nothing to do with the pollution at the industrial site. This problem makes the derivation of generic soil quality criteria very difficult for sites without lifetime exposure.

Differences in land use lead to differences in human exposure and differences in health risks. Soil pollution has, however, a number of other adverse effects which do not depend on land use, for instance the contamination of groundwater and surface water. Some ecotoxicological effects might be important as well, even when the site is not used as 'nature'. Adverse effects on soil microbial processes and vegetation are important even in industrial areas and in cities. Biological activity in the soil is needed for the breakdown of polluting substances and the growth of grass and trees. Differentiation of soil quality criteria with respect to land use in relation to human health risks is therefore limited by adverse effects in groundwater and surface water and on biological processes in the soil. Adverse effects other than human health will then determine the maximum value for any land use dependent soil quality criterion.

Risk assessment of contaminated land is plagued by a large number of uncertainties. Due to the heterogeneity of the soil, concentrations of pollutants will vary on a small scale. By consequence estimates of average concentrations in soil and groundwater will not be very precise and may be characterized by a range or a confidence interval. The behavior of a contaminant in soil and uptake by plants are variable as well, and will increase uncertainties about human exposure. Finally, variability in behaviour and physiology of human beings contributes significantly to the uncertainties in an assess-

ment. In actual site specific risk assessment uncertainties are reduced by collecting as much information as possible on the spot. In an approach based on generic soil quality criteria however, site specific information cannot be used. The general assumptions that had to be made in the derivation of criteria of this type will lead to very imprecise statements about health risk of soil pollution. They must be considered as 'order of magnitude' predictions. Conversely land use dependent soil quality criteria must differ by at least a half order of magnitude to be useful in an assessment. It can be doubted whether such large differences are possible in view of other adverse effects on the environment.

Predetermined numerical criteria are much easier to use than site specific modelling and risk assessment methods. Simple testing of measured concentrations in soil and groundwater against predetermined standards is also less expensive than more elaborate risk assessment methods. The arguments presented above however do strongly suggest that an approach based on land use dependent soil quality criteria only might not be feasible. It can be questioned from a scientific point of view whether the decisions based on predetermined generic soil quality criteria alone will be realistic.

A combined approach, using standards to streamline the preliminary stages of an investigation and using site specific exposure and risk assessment to achieve some fine-tuning in later stages of an investigation, may be the most appropriate method for assessment. In fact the approaches used in many countries seem to converge to this combined approach as experience with cleanup of contaminated land increases.

2.5 Policy objectives in soil cleanup

General policies concerning soil protection and restoration are now being developed in a number of countries (Visser 1993). In The Netherlands restoration of contaminated land is considered as a part of soil protection, and the general preventive environmental policy objectives like sustainable landuse or conservation of soil multifunctionality apply to soil restoration as well. The preferred solution for contaminated land problems is therefore a total cleanup. However, if total cleanup of a site leads to excessive costs and technical or environmental problems the decision can be made not to restore the multifunctionality of the soil. This is a site specific decision. A different type of solution is then adopted, which aims at reducing exposure and further contamination of surrounding areas by appropriate isolation measures and control and monitoring strategies. Because exposure depends on land use, this type of solution often depends on the actual use of the soil.

In some other countries, contaminated land is considered from a spatial planning point of view and restoration of contaminated land is - as a general rule - related to the intended use of the land. These differences in policy objectives depend on the way soil pollution problems are perceived and may also be related to economic and geographical factors. The multifunctional position is often considered too idealistic in view of the large number of polluted sites, whereas the advocates of strictly landuse dependent cleanup are criticized for their short-term solutions that will leave a large number of soil problems to future generations. Both policy objectives can result in realistic and reasonable decisions if they are applied with care.

The multifunctional approach emphasizes the long-term impact of soil pollution on the soil environment and stresses the importance of site specific decision making in considering feasible cleanup solutions. The landuse dependent approach emphasizes the direct impact of soil pollution and land use.

If the multifunctional approach takes realistic site specific decisions and if the landuse dependent approach goes beyond restoration of current land use when this can be done with little extra costs, the difference between the two approaches will not be very large from a practical point of view. If 'realistic short term goals' are the strongest selling points in politics, than the landuse dependent approach has the edge over the harder to defend idealistic appeal of the multifunctional position. If 'sustainable development' and 'environmental management' are strong selling points in politics, the multifunctional approach takes the lead, because cleaned sites will not have to remain registered as problems to be solved in future. Moreover, they do not need to be rediscovered when scientific insight into the adverse effects of pollutants change or when land use is changed.

2.6 Concluding remarks

Most countries will agree that the scientific basis for soil protection is important, but the influence of politics in decisions about cleanup or protective measures is also very large. This is especially the case in the field of soil cleanup. From a technical and scientific point of view, the approaches, guidelines, trigger values and decision support systems used in various countries are very different (Visser 1993). However it is generally felt that in practice, if a decision is to be made how to remedy a polluted site, the result will be the same in most cases. There is a number of reasons for this:

- The repertoire of cleanup technologies is rather limited.
- Decisions have to take into account the very large uncertainties in risk assessment and are generally on the safe side, irrespective of some differences in maximum permissible risk levels in various countries.
- For large sites cleanup is very costly, so cleanup will mostly be related to the intended use of the site, or the use of the site is made dependent on the result of the cleanup. The remaining pollution will be contained and controlled if mobile and exposure is likely.
- Small sites will be cleaned up totally. Either because this is the preferred option in policy (Dutch approach) or because it is expedient: registration and control of a small partially decontaminated site is not cost-effective.

The observation that widely different approaches can lead to similar results raises the question whether international harmonisation or standardisation of approaches is worthwhile. Harmonization of soil quality criteria between different countries is very difficult due to differences in natural constitution of soils. Besides, soil quality criteria are not independent scientific entities but tools for managing cleanup operations, so they cannot be uniformed between countries with different political, cultural and socioeconomic background.

Recently the Ad Hoc International Working Group on Contaminated land (Visser 1995) concluded that international efforts should concentrate on cooperation and information exchange in three fields of interest:

- methods for standard setting and risk assessment;
- remediation techniques;
- regulatory design.

Although a complete harmonisation in soil protection at the European level by formulating uniform soil quality standards and uniform regulations is not feasible, much can

be gained by harmonisation of the scientific basis of soil protection and by stimulating the exchange of information and practical experience between countries.

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Appendix 2.1. Target (T-)values and intervention (I-) values. The values in the table are valid for a 'standard' soil (25% clay (<2mm) and 10% organic matter). Intervention values refer to average concentrations of substances in soil over an area of 50 m² and a depth of 0,5 m (25 m³). The relevant volume for groundwater is 100 m³. These spatial scales also apply to deeper layers of the soil.

Substances	Soil (mg/kg)		Groundwater (mg/l)	
	I-values	T-values	I- values	T-values
I. Metals				
arsenic	55	29	60	10
barium	625	200	625	50
cadmium	12	0.8	6	0.4
chromium	380	100	30	1
cobalt	240	20	100	20
copper	190	36	75	15
mercury	10	0.3	0.3	0.05
lead	530	85	75	15
molybdenum	200	10	300	5
nickel	210	35	75	15
zinc	720	140	800	65
II. Inorganic Compounds				
cyanides (free)	20	1	1500	5
cyanides (complex. pH < 5)	650	5	1500	10
cyanides (complex. pH ≥ 5)	50	5	1500	10
thiocyanates	20	-	1500	-
III. Aromatic Compounds				
benzene	1	0.05(d)	30	0.2
ethylbenzene	50	0.05(d)	150	0.2
phenol	40	0.05(d)	2000	0.2
cresol	5	-	200	(d)
toluene	130	0.05(d)	1000	0.2
xylene	25	0.05(d)	70	0.2
catechol	20	-	1250	(d)
resorcinol	10	-	600	-
hydrochinon	10	-	800	-
IV. Polycyclic Aromatic Hydrocarbons				
<i>PAH (sum of 10)</i>	<i>40</i>	<i>I</i>	-	-
naphtalene	-	0.015	70	0.1
anthracene	-	0.05	5	0.02
phenantrene	-	0.045	5	0.02
fluoranthene	-	0.015	1	0.005
benzo(a)anthracene	-	0.02	0.5	0.002
chrysene	-	0.02	0.05	0.002

Appendix 2.1 (continued)

Substances	Soil (mg/kg)		Groundwater (mg/l)	
	I-values	T-values	I-values	T-values
benzo(a)pyrene	-	0.02	0.05	0.001
benzo(ghi)perylene	-	0.02	0.05	0.0002
benzo(k)fluoranthene	-	0.025	0.05	0.001
indeno(1,2,3cd)pyrene	-	0.025	0.05	0.0004
V. Chlorinated Hydrocarbons				
1,2-dichloroethane	4	-	400	0.01(d)
dichloromethane	20	(d)	1000	0.01(d)
tetrachloromethane	1	0.001	10	(d)
tetrachloroethene	4	0.01	40	(d)
trichloromethane	10	0.001	400	(d)
trichloroethene	60	0.001	500	(d)
vinylchloride	0.1	-	0.7	-
<i>Chlorobenzenes (sum)</i>	30	-	-	-
monochlorobenzene	-	(d)	180	0.01(d)
dichlorobenzene	-	0.01	50	0.01(d)
trichlorobenzene	-	0.01	10	0.01(d)
tetrachlorobenzene	-	0.01	2.5	0.01(d)
pentachlorobenzene	-	0.025	1	0.01(d)
hexachlorobenzene	-	0.025	0.5	0.01(d)
<i>Chlorophenols (sum)</i>	10	-	-	-
monochlorophenol	-	0.0025	100	0.25
dichlorophenol	-	0.003	30	0.08
trichlorophenol	-	0.001	10	0.025
tetrachlorophenol	-	0.001	10	0.025
pentachlorophenol	5	0.002	3	0.01
chloronaphtalene	10	-	6	-
<i>PCB's (sum)</i>	1	0.02	0.01	0.01(d)
PCB 28	-	-	-	-
PCB 52	-	-	-	-
PCB 101	-	-	-	-
PCB 118	-	-	-	-
PCB 138	-	-	-	-
PCB 153	-	-	-	-
PCB 180	-	-	-	-
VI. Pesticides				
<i>DDT/DDD/DDE</i>	4	0.0025	0.01	(d)
<i>Sum (of 3 drin's)</i>	4	-	0.1	-
aldrin	-	0.0025	-	(d)
dieldrin	-	0.0005	-	0.00002
endrin	-	0.001	-	(d)

Appendix 2.1 (continued)

Substances	Soil (mg/kg)		Groundwater (mg/l)	
	I-values	T-values	I-values	T-values
<i>HCH-compounds</i>	2	-	1	-
a-HCH	-	0.0025	-	(d)
b-HCH	-	0.001	-	(d)
g-HCH	-	0.00005	-	0.0002
carbaryl	5	-	0.1	0.01(d)
carbofuran	2	-	0.1	0.01(d)
maneb	35	-	0.1	(d)
atrazin	6	0.00005	150	0.0075
VII. Other Compounds				
cyclohexanone	270	0.1	15000	0.5
<i>phthalates (sum)</i>	60	0.1	5	0.5
mineral oil	5000	50	600	50
pyridine	1	0.1	3	0.5
styrene	100	0.1	300	0.5
tetrahydrofuran	0.4	0.1	1	0.5
tetrahydrothiophene	90	0.1	30	0.5
(d) detection limit				

3 Physical concepts of soil pollution

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3.1 Introduction

Large scale degradation of surface, ground- and coastal water due to human activity is taken place in many industrial and developing countries. Surface waters are managed poorly, the interaction between surface and groundwater bodies are often underestimated, leaking liquid and solid disposal sites pose a hazard to surface and groundwater bodies, and the excessive use of agricultural chemicals form a serious treat to the quality of the soil and the underlying aquifers. The migration of inorganic and organic fertilizers, pesticides, or other agrochemicals, is known to pollute the shallow groundwater reserves. For instance as a result of excess manuring, nitrate concentrations, levels in excess of the EC drinking water quality standard of 50 ppm, have been detected in wells throughout Europe. Other solvents and toxic substances from domestic and industrial wastes have been notified to migrate slowly to the groundwater and drinking water supplies.

The solute phase in soils is a mixture of water and substances, very variable in chemical composition. The chemicals species are thereby partially or completely dissolved in the water phase (de Marsily 1986). The conventional view of mass transport in the soil is that of advection moderated by both retardation and attenuation. On the basis of chemical and biological reactions, the uptake by the vegetation and the gaseous losses of the volatile contaminants the presence of the unsaturated zone should in theory generally lead to decreased loadings of contaminants to the groundwater. The unsaturated zone provides a buffer, either preventing or minimizing groundwater contamination from chemicals applied at the ground surface. However, detection of a large number of volatile and nonvolatile contaminants (*e.g.*, pesticides used widely in agriculture and organic contaminants derived from spills or leaks of gasoline and industrial solvents) in both shallow and deep groundwater has raised questions as to the validity of what has been called the 'filter fantasy', *i.e.*, that the unsaturated zone acts as a protective buffer (National Research Council 1990).

An alternative scenario is equally probable. The unsaturated zone might actually serve as a 'source zone' for contamination of groundwater. Pesticides and fertilizers sorbed on mineral and organic constituents of the solid matrix, as well as the residual amounts of gasoline or other organic solvents entrapped within the soil pores, may in fact be released slowly over a long time period, leading to long-term loadings of contaminants into the saturated zone. Thus pump-and-treat methods, may fail because of the long-term 'bleeding' of contaminants from the unsaturated zone overlying the watertable.

It is evident that the role of the unsaturated zone, either as a buffer or as a source, must be carefully evaluated in assessing groundwater contamination and in selecting remedial measures. Coupling of simulation models developed for the unsaturated zone to those for the saturated zone is an essential element of groundwater modelling and is necessary for devising appropriate management/regulatory policies.

The modelling of contaminant behaviour in the unsaturated zone is designed generally to answer the following three questions, listed in order of priority and increasing complexity. First, when might a contaminant arrive at a specified depth? This requires a prediction of the travel time (t_c) for the contaminant to arrive at the specified depth (Z_c) of interest: for example, the bottom of the rootzone, the bottom of the treatment zone at a hazardous waste land treatment (HWLT) facility, or the watertable. Second, how much of the surface applied (or spilled) contaminant might arrive at Z_c ? This requires an estimation of the mass loadings (M_c) of the contaminant beyond the depth Z_c as influenced by retardation resulting from sorption and attenuation as a consequence of various biotic/abiotic transformations during contaminant transport through the unsaturated zone. Finally, it might also be necessary to predict the concentration distribution $[C(z,t)]$ of the contaminant within the unsaturated zone such that the time changes in contaminant concentrations as well as fluxes $[J_c(t)]$ at Z_c may be evaluated in addition to M_c . The spatial and temporal scales at which these questions need to be addressed and the ability to provide the necessary data characterizing the unsaturated zone and the contaminant determine the complexity of the model used and the reliability of the predictions provided by the model(s).

In answering the questions posed above, it is important to understand the coupling between the physical processes of flow and storage, the chemical processes of retention and reaction, and the biological processes of degradation (complete breakdown to nontoxic products) and transformation (partial decomposition that may or may not lead to the production of toxic by-products). It is also necessary to examine the differences in the rates and magnitude of these processes as they occur in the unsaturated zone in contrast to what happens in the saturated zone.

In addition to previous aspects, the boundary condition at the top and bottom of the soil system is characterized by variations in weather conditions, land use, spatial inputs of the chemicals, and variable geo-hydrological conditions. As a consequence of all this, the transfer of solutes in the soil system is a very variable and unsteady process.

Before discussing the processes controlling the transfer of solutes in soils at depth, it is relevant to define what is meant in this context by a solute. Components in the water phase are normally ionized in proportion to the ionic charge of the element. However, dissolved substances can also be present in a chemical form, which can be electrical neutral, or can be aggregated with other molecules and/or ions to form complex substances. Furthermore, it has been observed that salts considered to be insoluble can move in a dissolved state as tracers. In the same way, substances in the form of large molecular aggregates, such as colloids, might be present in, and move with, the liquid phase. All the substances which, in one way or another, form part of the soil fluidum, are known as soil solutes, as long as they do not constitute a mobile phase distinct from the transporting fluid.

Many other substances, such as organic compounds, do not mix with the soil water system. The transport of these compounds can best be described as a multi-phase flow. Processes like volatility (transfer of chemicals to the gaseous phase), immiscibility and hydrophobicity (non mixing of chemicals in the water phase) affect the transport and make the description of the fate and transfer of these compounds rather difficult (Nielsen et al. 1986).

In summary, the processes controlling the fate and transport of chemicals in soils are complex, physical, biological and chemical in nature. Furthermore, contaminant transport is very variable in time and space (Figure 3.1). In the following paragraphs the transport of water and solutes in heterogeneous porous media is discussed briefly. The processes of sorption, degradation, transformation and plant uptake are discussed elsewhere. Although

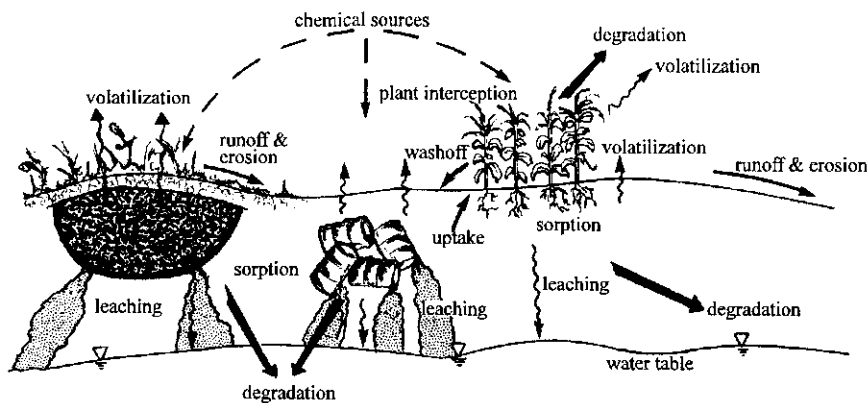


Figure 3.1. Sequential leaching of two sorbed contaminants (1,2) and one non-sorbed contaminant (3) through the rootzone as a result of rainfall above in (a). Note that contaminant 2 is sorbed to a greater extent than contaminant 1 and, as a consequence, is leached to a lesser extent. From National Research Council 1990.

the individual processes take place simultaneously, it is the dynamic, temporal and spatial interaction among the group of processes that determines the ultimate position of a chemical in the soil.

3.2 Conceptualization of the soil system

The transport equations, describing the transfer of a solute in the soil solution, are a function of the way the soil has been conceptualized. In the simplest case, the soil can be conceptualized as a homogeneous, isotherm, rigid, solid matrix with a known pore structure. In addition, the pore geometry is considered to have such dimensions that capillarity can not be neglected. A more complex and realistic transport theory can be developed if heterogeneity of the soil system is recognized. As such, one can assume the soil system to be composed of a number of layers, each having different properties. The porous medium can also contain macropores, in which capillary forces are negligible. Furthermore in shrinking and swelling soils, transport theories should consider the geometry of the soil matrix as time variant. In summary, the transport equations that will be used depend strongly on the way the soil system is conceptualized. In addition, the perception of the soil system depends to a great extent on the scale of study.

At the microscopic scale (scale of the pores), the physical laws governing flow and transport are well known. However, to establish a mathematical algorithm that describes accurately the transport in micropores is an almost impossible task because of the complexity of the pore geometry. As a consequence, far more emphasis has been laid on developing mathematical equations that describe the macroscopic flow and transport. In the macroscopic equations, the state variables (*e.g.* water content, etc.) and material characteristics (*e.g.* porosity, hydraulic conductivity, etc.) are in general defined as averages over a certain volume of soil. This volume is often referred to as a Representative Elementary Volume (REV) (Bear 1972).

Macroscopic equations can be applied at different scales. In this discussion, three

different macroscopic scales are defined, namely: (1) the laboratory, (2) the pedon and (3) the field scale. The considered scales are similar to those given by Dagan (1986) for flow and transport in geological formations (saturated zone). The distinguished scales are not delimited to transport processes for certain scales. Rather, the scale definitions provide a workable frame, allowing to describe in a realistic manner the transport of water and solutes.

The laboratory scale is typical for soil samples, usually soil columns, which are used for measuring soil properties and for studying soil processes. At this scale, which is of the order of 10^{-1} - 1 metre, one-dimensional flow and transport can be considered. In addition, the soil can be treated as a homogeneous medium.

The second scale, called the pedon scale, is related to the thickness of the unsaturated zone, usually 1 - 10^1 metre, with similar size in the horizontal plane. At this scale, soil heterogeneity results in, *e.g.*, short range variation of the permeability, variations of root densities (row/inter-row variations), and the presence of distinct soil layers, tongues and macropores. Due to the spatial variability, flow and transport in the horizontal direction is often significant. Most field monitoring techniques (*e.g.* lysimeters or small field plots equipped with neutron probes, suction samplers, and tensiometers) are adapted to this scale.

The third scale is the field scale. It has the same vertical dimensions as the pedon scale (few metres), but planar dimensions are of the order of magnitude of 10^1 - 10^{3-4} metre. The behaviour of water and chemicals at the field scale can be considered as the average behaviour of the components of a series of pedons. However, one should be aware that at the field scale, an additional component of heterogeneity, in the form of the spatial variation in fertilizer and water application, might be present. For the improvement and optimization of farm management practices, processes should be studied at the field scale.

Until the early 70s, there seemed to be a consensus among soil scientists that field scale water and solute transport could be modelled using the theories developed for describing processes at the laboratory scale. The basic idea behind this consensus was the ultimate belief that the REV, on which parameters representative of the given soil layer are determined, show similar variations to these observed in the field.

As a result of findings from field scale experiments, soil physicists are gradually aware of the existence of considerable lateral variability and heterogeneity of the soil. In addition, as more mechanistic-deterministic models simulating the flow of water and the transport of solutes were tested to field observations, it became clear that most models perform poorly. At present, soil physicists are convinced that one-dimensional models, which fit laboratory experiments relatively well, can no longer be used as a predictive tool for assessing the water and solute transport in the unsaturated zone. Gradually, scientists start realizing that a field reacts differently from a single column.

3.3 Fundamentals of transport processes

Historically, the theory of flow of water and transport of solutes in soils has been derived from laboratory experiments on samples with reduced dimension. Later, the theories were applied and tested on larger scales. In the proceeding discussion of the transport processes the following order of scales will be used: laboratory scale, scale of a pedon and field scale.

3.3.1 Laboratory scale

Due to the shape of the soil samples used in laboratory experiments, transport at the laboratory scale is often assumed to be one-dimensional. In the following paragraphs, the transport theory for one-dimensional flow is discussed. Similar equations, however, can be derived for two- and three-dimensional flows.

Transport of solutes by diffusion

The term diffusion refers to the movement of a solute as a result of Brownian motion. The thermal energy causes the particles to move at random within the phase that contains them. This phase is the soil water solution. To elucidate the concept of Brownian motion, the example of vertical diffusion of solute particles in a cylindric reservoir filled with water (Figure 3.2) is shown.

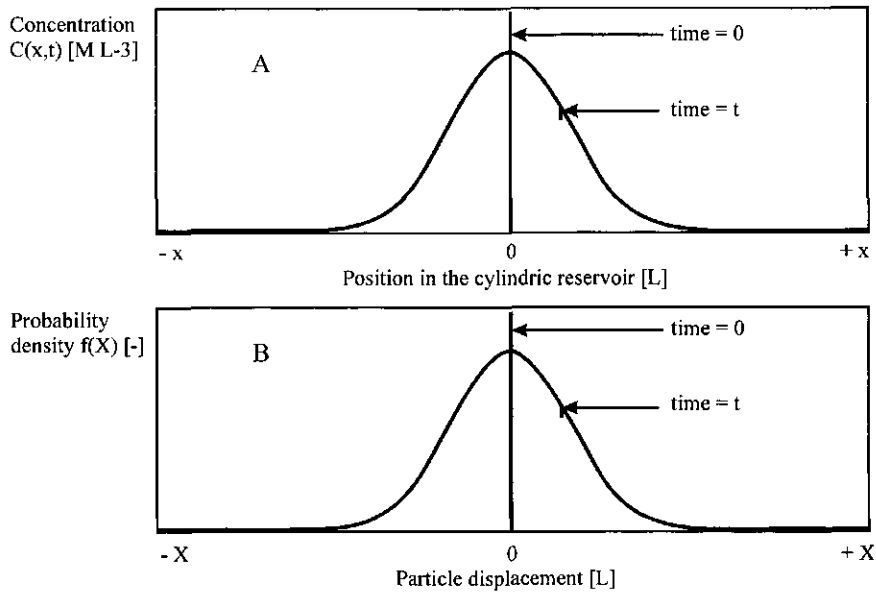


Figure 3.2. Vertical diffusion of solute particles in a reservoir.

Suppose that a fixed amount of solute particles is injected in the middle of the cylindric reservoir ($x = 0$). At the initial time, $t = 0$, a solute spike is positioned at $x = 0$, and due to a series of successive random movements (up and down) of the individual particles, the solute is spread around its initial position. This spreading is enhanced by the fact that more particles can 'jump' away from a position with high concentration than from a position with low concentration. Hence, as a result of purely random movements, we get a net displacement from positions of high concentration to positions of low concentration.

The effect of such random movements can be clarified by considering a simple random walk model in one dimension (Vanmarke 1983). In this concept, a solute molecule is assumed to move randomly on a straight line in steps of unit size Δx [L] over discrete time intervals Δt [T]. The successive movements are statistically independent, and there is an

equal chance of upward or downward movement during each time step. Consequently, the probability that a solute molecule is at position x at time t , $p_x(t)$, can be derived from the probabilities of finding the particle at the two neighbour positions on the line at time $t-\Delta t$:

$$p_x(t) = (1/2)[p_{x+\Delta x}(t-\Delta t)] + (1/2)[p_{x-\Delta x}(t-\Delta t)] \quad (1)$$

By subtracting the term $p_x(t-\Delta t)$ from both sides, one obtains:

$$p_x(t) - p_x(t-\Delta t) = (1/2)[p_{x-\Delta x}(t-\Delta t) - 2p_x(t-\Delta t) + p_{x+\Delta x}(t-\Delta t)] \quad (2)$$

Equation (2) is a difference equation of the first order in time and of the second order in space. In the limit when $\Delta t \rightarrow 0$ and $\Delta x \rightarrow 0$, both the time and space coordinates become continuous:

$$\lim_{\Delta t \rightarrow 0} \{ [p_x(t) - p_x(t-\Delta t)] / \Delta t \} =$$

$$\lim_{\Delta x \rightarrow 0} (\Delta x^2 / 2\Delta t) \{ \Delta x [p_{x+\Delta x}(t-\Delta t) - p_x(t-\Delta t)] - \Delta x [p_x(t-\Delta t) - p_{x-\Delta x}(t-\Delta t)] \} / \Delta x \quad (3)$$

or

$$\delta f(x,t) / \delta t = D_0 [\delta^2 f(x,t) / \delta x^2] \quad (4)$$

where $f(x,t)$ is the probability that a molecule at time t is at position x , and D_0 is equal to $\lim(\Delta x^2 / 2\Delta t)$. Considering equivalency of probabilities and solute concentrations, the classical diffusion equation is obtained:

$$\delta C(x,t) / \delta t = D_0 [\delta^2 C(x,t) / \delta x^2] \quad (5)$$

where C is the resident concentration [$M L^{-3}$], and D_0 [$L^2 T^{-1}$] is called the diffusion coefficient of a solute molecule in a pure liquid.

Defining J_d [$M L^{-2} T^{-1}$] as the (macroscopic) solute flux going through a unit area in the water reservoir and taking into account mass conservation:

$$\delta C / \delta t = - \delta J_d / \delta x \quad (6)$$

Fick's first law is obtained by combining equations (5) and (6):

$$J_d = - D_0 [\delta C / \delta x] \quad (7)$$

The concentration profile $C(x,t)$ shown in Figure 3.2 can be regarded as a probability density function of particle displacements $f(X)$. In this case the variable X is the net displacement of a particle, which at time $t = 0$ was at position $x = 0$. The area under the curve $f(X)$, equals unity. The net displacement of a particle over a time Δt is the sum of a series of independent random displacements (up and down). Due to the central limit theorem, the probability distribution of X , after a sufficiently long time, follows a Gaussian distribution. The distribution has a zero mean, and a variance given by :

$$E[X^2(t)] = 2 D_0 t \quad (8)$$

where E denotes the expected value, and X(t) the net displacement of a particle from t = 0 till t. Hence, the variance of solute displacement is proportional to the time.

In the previous paragraphs, diffusion in a pure water system (e.g. a cylindrical reservoir) was discussed. When solutes move by diffusion in the water phase of soils, the cross sectional area available for diffusion is only a fraction of the total cross sectional area. Due to a restriction in cross sectional area for transport, and the tortuous nature of the pores, the diffusion process in soils results in a slower macroscopic vertical spreading than in a pure water system. For this reason, an effective diffusion coefficient D_e ($< D_0$), which is dependent on the soil water content θ , is used. Fick's law for solutes in soils can be written as:

$$J_{ds} = - D_e (\delta C / \delta x) \quad (9)$$

where J_{ds} is the solute flux in soil due to the diffusion process [$M L^{-2} T^{-1}$].

Transport of solutes by convection (advection)

This is the phenomenon whereby dissolved substances are carried by the moving water. Substances that are carried by the moving water are said to undergo convective, viscous, or mass flow. As a consequence, mass flow of solutes is strongly controlled by the laws determining the transport of water. Traditionally, the empirical law of Darcy, which is similar to Fick's law, is used to describe water transport at the macroscopic scale.

For one-dimensional flow in a soil column, Darcy's law can be written as:

$$J_w = - K(\delta H / \delta x) \quad (10)$$

where J_w is the water flux density [$L^3 L^{-2} T^{-1}$], K the proportionality factor which is called the hydraulic conductivity [$L T^{-1}$], H the hydraulic head [L] and x the depth [L]. The hydraulic head is the sum of the gravitational and matric potential. The former is a function of the position in the gravitational field with regard to a selected reference level, and the latter a function of the binding forces between the water phase and the soil matrix. The matric potential and the soil water content are non-linearly related. The relation is often subjected to hysteresis. The hydraulic conductivity also shows non linearity with the water content and as such with the matric potential. Both relationships, the hydraulic characteristics of a soil, play a key role in the description of the hydraulic status of the soil. A sample of the shape of the basic hydraulic relationships is shown in Figure 3.3. The data were obtained from a laboratory study and a functional relationship was fitted through the data points.

The knowledge of soil water characteristic curves [$\theta(h)$], and soil hydraulic conductivity curves [$K(h)$], is essential for describing water flow and contaminant transport in the unsaturated zone. Because K and θ are both functions of h, K can be stated as a function of θ or h. These relationships have been experimentally measured for a large number of soils, and empirical or theoretically based equations for $\theta(h)$, $K(h)$, and $K(\theta)$ have been derived to predict them. Some of these are listed in Tables 3.1 and 3.2 (National Research Council 1990).

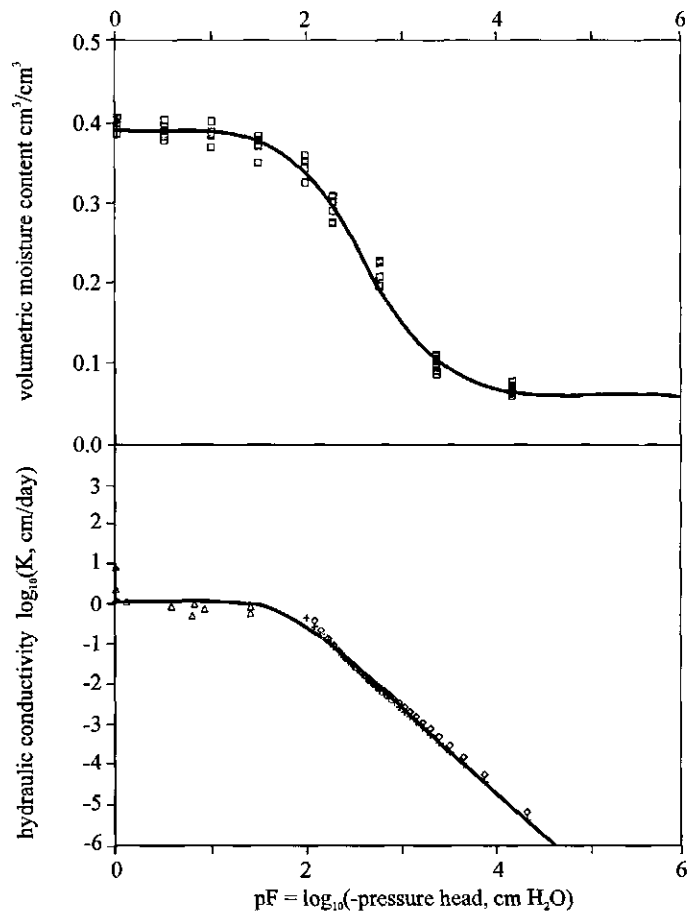


Figure 3.3. Hydraulic properties measured in the Ap horizon of a loamy soil. From Institute for Land and Water Management, K.U. Leuven.

Table 3.1. Some $\theta(h)$ relationships reported in literature. From National Research Council 1990).

Function	Source
$\theta(h) = \theta_r + [a(\theta_s - \theta_r)]/[a + h ^b]$; $h < 0$ $\theta(h) = \theta_s$; $h \geq 0$	Brutsaert 1966
$\theta(h) = \theta_r + [a(\theta_s - \theta_r)]/[a + (\ln h)^b]$; $h < -1$ $\theta(h) = \theta_s$; $h \geq -1$	Haverkamp et al. 1977
$\theta(h) = \theta_r + [\theta_s - \theta_r]/[1 + a(h)^b]^m$; $h < 0$ $\theta(h) = \theta_s$; $h \geq 0$ $m = 1 - 1/b$	van Genuchten 1980
$\theta(h) = \theta_r + [\theta_s - \theta_r][a/ h]^b$; $h < a$ $\theta(h) = \theta_s$; $h \geq 0$	

Note: θ_s is saturated water content, equal to porosity; θ_r is 'residual' water content; h is soil water matric potential; and a , b , and m are constants.

Table 3.2. Some $K(\theta)$ or $K(h)$ relationships reported in the literature. From National Research Council 1990.

Function	Source
$K(h) = a h ^{-b}$	Wind 1955
$K(h) = K_s[\exp(-a h)]$	Gardner 1958
$K(h) = [(h /a)^b + 1]^{-1}$	Gardner 1958
$K(h) = [(h / h_{cr})^b]; h \leq h_{cr} $	Brooks and Corey 1966
$K(h) = K_s; h \geq h_{cr} $	
$K(\theta) = K_s[(\theta - \theta_r)/(\theta_s - \theta_r)]^b; b = 3.5$	Averjanov 1950
$K(h) = \exp\{a h - h_{cr} \}; h_r \leq h \leq h_{cr} $	Rijtema 1965
$K(h) = K_s; h \geq h_{cr} $	
$K(h) = K_i[h / h_i]^b; h < h_i $	
$K(h) = K_s[a/(a + h ^b)]; h < 0; h \geq 0$	Haverkamp et al. 1977
$K(h) = a[\exp(b)(\theta(h))]; \theta < \theta_s$	van Genuchten 1980
$K(\theta) = K_s; \theta = \theta_s$	
$K(h) = K_s[\exp(bh)]; h < 0$	
$K(h) = (K_s); h \geq 0$	
$K(h) = a[(\theta(h))^b]$	

Note: $K(h)$ is hydraulic conductivity at h ; $K(\theta)$ is hydraulic conductivity at θ ; θ is volumetric water content; h is hydraulic potential (and has negative values); K_s is saturated hydraulic conductivity; θ_s is saturated water content; θ_r is 'residual' water content; and a , b , h_{cr} , and h_i are empirical constants by the pore size and shape. Flow in larger pores is faster than in smaller pores and is even faster at the center of the pore than near the periphery. In this way the complexity of the pore system causes mixing of the soil solution along the flow direction, and hence dispersion of the solute. Such mixing, referred to as mechanical dispersion, results in a net flow of solute, proportional to the velocity.

Consider a soil column in which flow is one-dimensional in the vertical direction and where all pore water is mobile. A constant average macroscopic pore velocity in the soil column can be defined as the ratio between the Darcian flux, determined by equation (10), and the volumetric soil water content. Given previous condition, one can calculate the solute flux going through a unit area as:

$$J_{cw} = C J_w = C \theta V \quad (11)$$

where J_{cw} is the convective solute flux density [$M L^{-2} T^{-1}$] imposed by the convective water flow, V the average macroscopic pore velocity [$L^3 L^{-2} T^{-1}$], C the solute concentration [$M L^{-3}$] and J_w the water flux density [$L T^{-1}$].

As a consequence of the soil's porous nature, the actual solute velocity in a pore is not equal to the above defined macroscopic pore water velocity. The actual pore velocity is distributed around the average macroscopic value, in a manner controlled.

Due to the similar effect of mechanical dispersion and chemical diffusion on the mixing of the soil solution, it is often assumed that mechanical dispersion is induced by randomly distributed pore velocities. Following the assumption of randomness, one can describe mechanical dispersion in a similar way as Fick's law (equations (7) and (9)), with the diffusion coefficient D_e or D_0 replaced by a mechanical dispersion coefficient, denoted by D_m .

The total macroscopic convective transport of a solute is usually described by an equation that considers two modes or components of transport: (1) the average flow velocity component (given by equation (11)) and (2) the mechanical dispersion component (Fick's law with D_m). Adding the two components yields the total convective flux, which can be written as:

$$J_{ct} = C J_w - D_m (\delta C / \delta x) \quad (12)$$

where J_{ct} is the total convective solute flux density [$M L^{-2} T^{-1}$]. The assumed similarity between diffusion and mechanical dispersion can be illustrated by means of the example of one-dimensional steady-state water flow in a soil column. Consider, *e.g.*, the displacement of solute particles injected at position $x = 0$ at time $t = 0$ (Figure 3.4a). At time t , the solute spike has moved to position x_1 . Due to local velocity variations in the pores, the solute particles are spread around this position. The foregoing can be described in an alternative way as the probability density function of particle displacements X from time 0 till t (Figure 3.4b). The total displacement X is the result of a series of successive displacements, randomly distributed around the successive mean displacements.

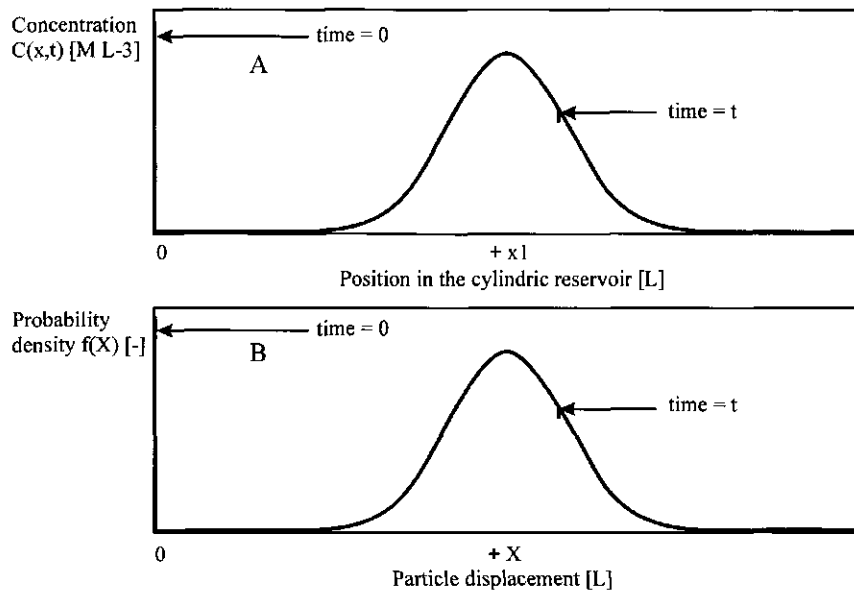


Figure 3.4. Displacement of solute particles in a soil column (a = displacement of solute particles; b = probability density function of particle displacement).

After a sufficiently long time and assuming that the successive small displacements are independent (not auto-correlated in time), the probability density function of X becomes Gaussian (central limit theorem), with a variance expanding proportional with time:

$$E[X^2(t)] = 2 D_m t \quad (13)$$

The underlying concept is thus very similar to the successive random movements of diffusion, induced by Brownian motion.

The proportionality factor D_m is only constant with time (or with the mean travelled distance) if the successive random velocity variations along the pathway are uncorrelated. The following example, with the same steady state water flow and solute injection is used to illustrate the impact of this assumption on solute transport. Consider solute displacements from the initial time to times t and $2t$:

$$\begin{aligned} X_1 &= \text{particle displacement from } t_0 \text{ till } t \\ X_2 &= \text{particle displacement from } t \text{ till } 2t \\ X &= X_1 + X_2 = \text{particle displacement from } t_0 \text{ till } 2t \end{aligned} \quad (14)$$

When the soil column is homogeneous, the same solute dispersion occurs in the time interval $[t_0, t]$ and $[t, 2t]$, hence:

$$\text{var } X_1 = \text{var } X_2 = 2 D_m t \quad (15)$$

If particle displacements, X_1 and X_2 , are uncorrelated [$\text{covar}(X_1, X_2) = 0$], one can write:

$$\text{var } X = \text{var}(X_1 + X_2) = \text{var } X_1 + \text{var } X_2 + 2 \text{covar}(X_1, X_2) = 2 D_m (2t) \quad (16)$$

and, hence, the same Fickian relationship with a constant D applies for displacements over time $2t$. However, if the displacements X_1 and X_2 are positively correlated [$\text{covar}(X_1, X_2) > 0$] due to the fact that the successive velocity variations along the travelled pathway are auto-correlated, the dispersion coefficient will increase with time. The latter often occurs in soils. A solute in a big pore will normally have a high pore velocity during the time interval $[0, t]$. In addition, there is a high probability that the solute particle continues to travel through large pores during the time interval $[t, 2t]$. Hence, it is probable that the velocity remains high, resulting in positively correlated displacements of X_1 and X_2 .

Combined effect of convection and diffusion

By adding the diffusive flux (equation (9)) to the convective flux (equation (12)), one can derive the following relation for the total solute flux:

$$J_t = J_{ds} + J_{ct} = - (D_e + D_m) (\delta C / \delta x) + C J_w \quad (17)$$

At high flow velocities, the dispersion term is usually much higher than the diffusion term. When equation (17) is combined with the continuity equation for solutes (conservation of solute mass), the classical convection dispersion equation is obtained:

$$\delta(C) / \delta t = \delta / \delta x [D^* (\delta C / \delta x)] - \delta(C J_w) / \delta x \quad (18)$$

where t denotes time [T], and D^* [$L^2 T^{-1}$] the apparent diffusion coefficient, which integrates the effect of mechanical dispersion and chemical diffusion. This differential equation is often used to describe the one-dimensional transport of a non-interacting solute.

3.3.2 Pedon scale

It is needless to emphasize that soil physical characteristics measured in the laboratory can differ significantly from those measured in-situ, at the scale of a pedon. In Figure 3.5, for instance, the in-situ measured moisture retention characteristic (MRC) of an Ap horizon is shown together with the average of the MRC measured in the laboratory.

The in-situ measured MRC exhibits a large scatter, and differs statistically from the MRC measured in the laboratory. In addition to the effects of hysteresis and measurement errors, part of the scatter of the in-situ measured MRC is caused by short range variability within the horizon.

Scale effects are even more pronounced at the level of the dispersion coefficient. Typically, dispersion coefficients determined on soil samples underestimate solute dispersion at the pedon scale. To explain this statement, it should be remembered that solute dispersion is caused by variation of pore water velocities as a direct consequence of the heterogeneity of the pore system. At the pedon scale, additional soil variability occurs over distances larger than the sample size. This additional heterogeneity causes extra solute dispersion.

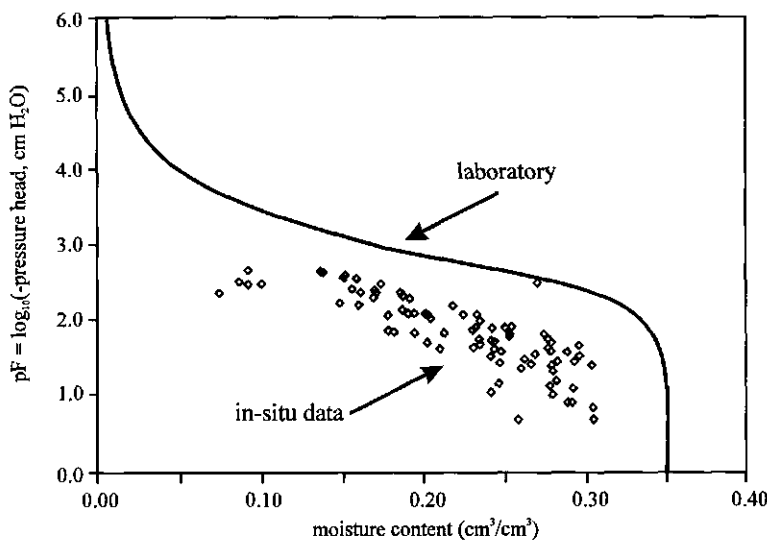


Figure 3.5. Moisture retention characteristic measured in situ (\square) and in the laboratory (-), respectively. From Institute for Land and Water Management, K.U. Leuven.

The presence of macropores complicates the description of transport at the pedon scale even more. Macropores are, *e.g.*, present in well aggregated soils, cracking clay soils, or soils with earthworm holes. The macropore system results in 'by-pass flow', a term used for fast downward flow of water in macropores, which occurs without wetting of the soil matrix. As an example of the influence of macropores on the hydraulic behaviour in soils, the pressure head distribution in a soil column in which an artificial macropore in the

centre of the column has been induced is shown in Figure 3.6. As can be seen from Figure 3.6 the pressure head distribution has a typical two-dimensional nature. The one-dimensional Darcy law is no longer applicable in this soil column. Moreover, the macropore system acts as a system of preferential pathways for the solutes, and hence the concept of 'successive uncorrelated velocity variations' required for the convection-dispersion equation, is no longer valid. Once a solute particle has entered a preferential flow path, it will continuously move downward at a velocity larger than the mean pore velocity.

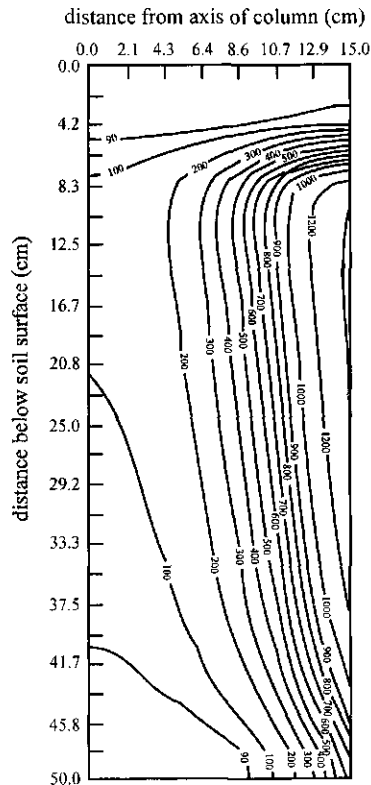


Figure 3.6. Pressure head distribution in a soil column. From Kihupi 1990.

Notwithstanding the obvious scale effects which occur when going from the laboratory to the pedon scale, solute transport processes for management purposes are most often described by combining the 1-D water flow equation, which is based on Darcy's law, (equation (10)) with the 1-D form of the convection-dispersion equation (equation (18)). The typical vertical heterogeneity of the soil profile can easily be taken into account into these 1-D flow and transport models by considering soil layers, to which different soil characteristics are assigned. An illustration of such a model concept is given in Figure 3.7. With this model, the water balance has been simulated for a lysimeter containing a soil monolith from a sandy soil. The simulation was performed using a one-dimensional simulation model (Belmans et al. 1983) which solves the Darcy equation numerically and assumes the existence of three different horizons. The hydraulic parameters for each

horizon were determined independently in the laboratory on samples taken in the close neighbourhood of the lysimeter. Standard techniques were used for the determination of the hydraulic properties on these samples. The figure shows that a 1-D model yields reliable predictions, provided that close attention is paid to the parameterization for the different horizons.

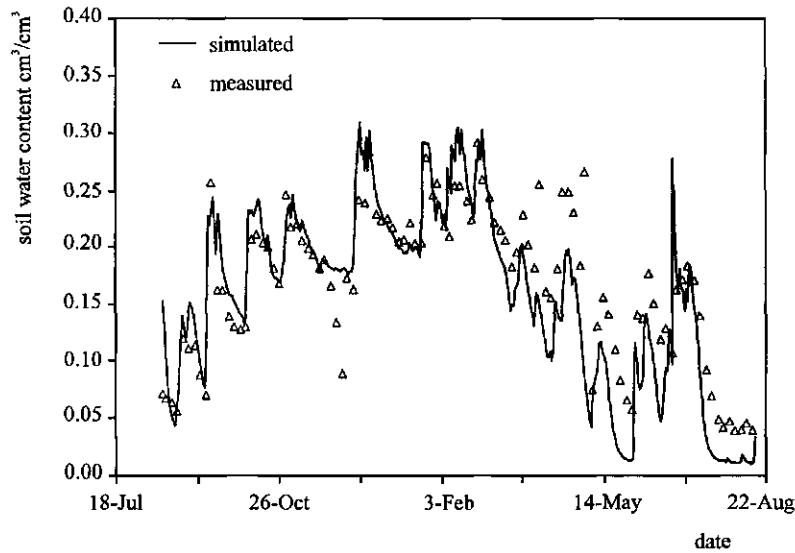


Figure 3.7. Simulated and measured soil water content versus time, for a given depth in a sandy soil. From Institute for Land and Water Management, K.U. Leuven.

To integrate the effect of variability in soil properties, special concepts are often build in the 1-D model. One such typical concept is the two component or two region transport concept (Gaudet 1978; Vanclooster et al. 1992). This concept assumes the existence of an immobile or stagnant soil water phase situated at the intra-aggregate or dead end pores and a mobile soil water region. When describing solute transport in both regions, complete mixing of the solute between both soil water phases is no longer assumed. Rather a solute exchange, controlled by diffusion between both regions, takes place. Transport in a two component medium can be described with the following two equations. For the mobile soil region the following convection-dispersion equation holds:

$$\theta_m [\delta(C_m)/\delta t] + \theta_{im} [\delta C_{im}/\delta t] = \{ \delta/\delta x [D^*(\delta C_m/\delta x)] \} - [\delta(C_m J_w)/\delta x] \quad (19)$$

in which θ_m is the water content [-] which is assumed to be mobile, and C_m [$M L^{-3}$] the concentration amount of a solute in the mobile phase. The exchange between the mobile and the immobile region is integrated in the convection-dispersion equation as a solute sink term (2nd term in equation (19)):

$$\theta_{im} (\delta C_{im}/\delta t) = \alpha (C_m - C_{im}) \quad (20)$$

where θ_{im} [-] is the water content which is excluded for transport, C_{im} [M L⁻³] the concentration of the solute in the stagnant soil region and α is the first order mass transfer coefficient [T⁻¹].

3.3.3 Field scale

Recall that the field scale has the same vertical dimensions as the pedon scale (few metres), but planar dimensions are now of the order of magnitude of 10¹ - 10^{3.4} metre.

Experimental observations (Nielsen et al. 1973; Biggar & Nielsen 1976, Van der Pol et al. 1977; Butters & Jury 1989, among others) suggest that the deterministic equations can no longer be used at this scale without any problem. Findings in groundwater engineering suggest that stochastic theory is more powerful for describing quantitatively transport processes at the field scale.

The increasing interest in stochastic modelling of transport phenomena at the field scale was initiated in early studies (*e.g.* Freeze 1975; Warrick et al. 1977; Russo & Bresler 1981) in which Monte Carlo techniques were used in combination with 1-D models to explore the effect of spatial variable soil properties. In these studies the field is conceptualized as being an ensemble of independent soil columns. In the most simple form, the resident solute concentrations at the position x and time t in each column are assumed to result from a one-dimensional convective flow (local dispersion is neglected). The mean macroscopic pore velocity V [L T⁻¹] differs among the columns and is considered a random variable with probability density function $f(V)$. The ensemble average of solute concentrations for the entire field can be calculated from the equation:

$$\langle C(x,t) \rangle = \int_0^{\infty} C(x,t,V)_{cs} f(V) dV \quad (21)$$

where, $C(x,t,V)_{cs}$ represents the solution of:

$$\delta C / \delta t = - V (\delta C / \delta x) \quad (22)$$

where V is the macroscopic pore velocity, in this case a random variable.

A similar model was developed by Jury (1982) to describe the movement of solute by means of a transfer function. All deterministic transport parameters are abandoned, and the time variable is replaced by the net applied amount of water. The average concentration at depth L after a cumulative net amount of water I has been applied, can be written as:

$$C_L(I) = \int_0^I C_{in}(I-I') f_L(I') dI' \quad (23)$$

The quantity inside the integral is the probability $f_L(I')$ that a solute reaches the depth L between I' and $I' + dI'$, multiplied by the concentration $C_{in}(I - I')$ of the solution applied at the surface at $(I - I')$. If perfect correlation between travel paths at adjacent depths is assumed, the probability density function for transport to other depths $Z > L$ can be calculated from the probability density function for transport to L [perfect correlation implies $f_{2L}(2I) = f_L(I)$].

As an example, Figure 3.8 gives the results from a field study from Butters & Jury (1989). In this figure, measured solute concentration profiles at different depths are compared to model predictions based on two contrasting concepts. The first prediction is based on the convection-dispersion equation which assumes uncorrelated flow. The second prediction is based on the above mentioned transfer function concept which assumes perfectly correlated flow between travel paths at adjacent depths. Both models were calibrated on the concentration profile measured at 0.3 m. The transfer function model, which is actually a stochastic-convective correlated flow model, predicts much better measured solute profiles than the convective-dispersive model. The way flow is conceived is crucial for the correct prediction of the early breakthrough of solutes (*e.g.* pesticides), as can be seen by comparing the tails of the profiles in Figure 3.8.

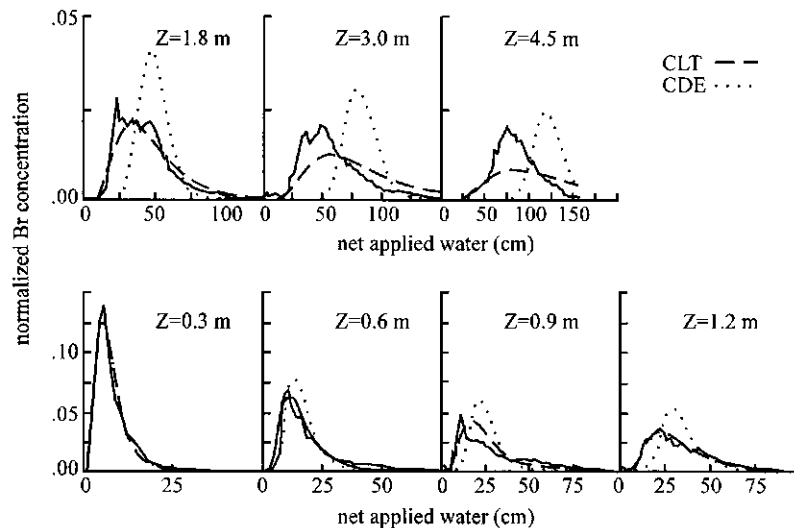


Figure 3.8. Average Br-concentrations from 14 replicates (solid lines) together with predictions from the transfer function model (dashed lines) and the convection-dispersion model (dotted lines). From Butters & Jury 1989.

The poor performance of 1-D models in describing solute transport at field level did encourage researchers to develop stochastic models in which horizontal flow components are no longer ignored. Nowadays, numerical 2-D and 3-D models are used to explore the extent of spatially variable soil properties on predicted transport in different flow domains. Such flow domains are typically composed of blocks having different soil physical properties, which can be spatially related.

Since several parameters are involved when describing transport at field scale, one needs a comprehensive method for describing observed spatial relationships between soil parameters.

In a first and simplified approach the scaling theory can be used to express the variability of soil properties. The scaling theory assumes that the porous medium is conceptualized as scale magnifications of a hypothetical porous medium. Because the particle and void geometry is magnified without reorientation or shape change, a single length parameter, called a scale factor, can characterize the relative magnification of a particular region relative to the reference region. As can be seen in Figure 3.9, the assumption of a similar medium is not always deterministic in explaining the measured variability. New multivariate approaches which use geostatistical techniques and have been developed in the field of mine engineering, seem to offer promising approaches for describing variability at field scale.

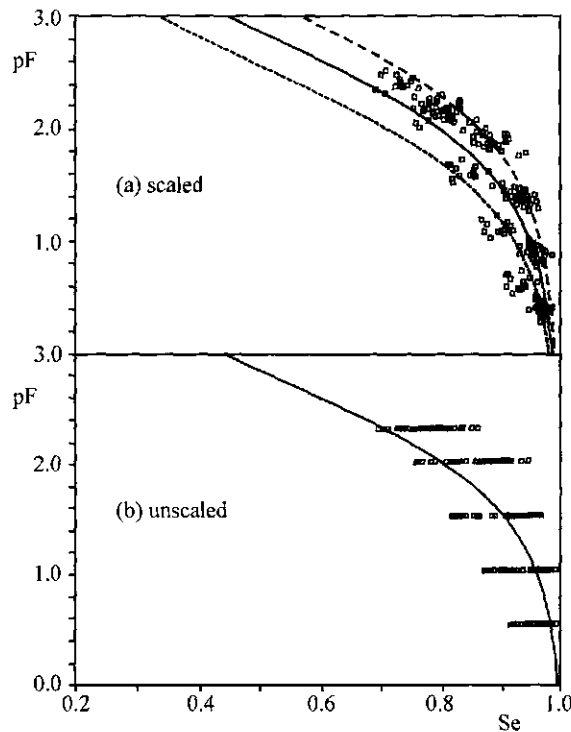


Figure 3.9. Scaled and unscaled hydraulic properties for a loamy field soil. From Diels et al. 1992.

Although the theoretical framework for describing field transport is still in development, deterministic point models, that are adapted or expanded for field purposes, can successfully be used to manage soils. Deterministic point models, such as SWATRE, SWATNIT or WAVE (Belmans et al. 1983; Vereecken et al. 1990; Vanclooster et al. 1994) integrate the current knowledge of the soil-plant processes into a more flexible management tool. Rather, than using the deterministic models for predicting the fate of a solute quantitatively, they can be used in a risk analysis exercise, for ranking different soil types, management scenarios or climatological conditions, according to their vulnerability for being exposed to a certain solute load.

3.4 Integration of different disciplines

It must be pointed out that the transport of adsorbed or reactive chemicals (such as pesticides, heavy metals, radionuclides) which in general pose a far greater risk to the environment than the mobile inert chemicals has not been discussed in this paper. The superposition of spatial variability of adsorption sites, for instance, with spatial variability of water flow rates could have serious implications for chemical transport models. From a mathematical point of view, reacting solutes can easily be treated by considering sink source factors in the above mentioned transport equations. The above discussion, however, reveals that the major limiting factor impeding the development of transport models for reacting solutes on the field scale and regional scale is the lack of coherent data measured at the same scale. Segmented disciplinary research contributes to our lack of theoretical and experimental understanding of the unsaturated zone and precludes the prediction and possible management of the rate of advance of pollutants through it.

3.5 Conclusions

Until the early 70s, there appeared to be a consensus among soil scientists that field scale water and solute transport could be modelled with the theories developed at the laboratory scale. With the publication of some field scale transport experiments, soil physicists were confronted with the high degree of variability and heterogeneity of the soil. Furthermore, they were confronted with the fact that proven transport theories, typically developed for the laboratory scale, performed poorly in field situations. A general applicable transport concept which can be used for the accurate predictions of the fate of a pollutant in the unsaturated zone, is lacking at this moment. Developing new methodologies and measurement techniques to generate the statistical moments for the field parameters, together with the development of computer efficient transport models seem to be the new challenge.

The lack of a general flow model for water and pollutants should not make us feel too pessimistic. The currently available models integrate most of our present knowledge and can be very useful in risk assessment studies and for ranking soil types and management scenarios according to their environmental impact.

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4 Uptake of pollutants by soil organisms

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Summary

Soil organisms tend to take up soil pollutants to a variable degree, depending on a complex of three factors: properties of the soil, characteristics of the chemical, and various organism-related factors. Bioavailability relates to the fraction of a chemical that may potentially be taken up: the actual uptake depends on the physiology of the species. In earthworm studies, it has been demonstrated convincingly that the soil pore water is the major pool from which chemicals are taken up. Soil factors influencing the distribution of a chemical over solid phase and pore water (organic matter, pH, CEC), equally influence the uptake by earthworms.

For heavy metals, uptake patterns have been studied most extensively. Field surveys show that fungi may concentrate metals from soil; through mycorrhiza metals may be transferred to higher plants. Among soil invertebrates, metals are distributed very irregularly. Biomagnification in food chains does not seem to occur; instead, highest concentrations are found in certain taxonomic groups, such as earthworms, isopods, spiders and dipturans. Among the small mammals, Insectivora (mole, shrews) concentrate metals to a high degree, in contrast to Rodentia (voles, mice).

For organic chemicals rather few comparative data are available. Persistent pesticides such as organochlorines are often concentrated in earthworms while PAHs do not seem to cause high residues in soil animals, possibly due to efficient metabolism.

In biomonitoring programmes, levels of pollutants in soil organisms, as well as biomarkers of metabolic effects, may be helpful to indicate changes in soil quality in space and time.

4.1 Introduction

In any healthy soil, a great variety of organisms contribute to the ecological function of the soil. This includes the decomposition of organic matter, the mineralization of nutrients and the formation of humic materials. The organisms vary in size from 1 μm (bacteria) to 10 cm (earthworms). Some of them spend only part of their life-cycle in soil (*e.g.* flies as larvae), while others are bound to the soil more or less permanently (*e.g.* fungivorous mites).

Protection of soil organisms against potential threats is a prerequisite for the maintenance of the ecological function of a soil. In addition, many soil-dwelling organisms serve to feed higher animals such as moles, mice and birds; therefore protecting soil life is also important for life outside the soil.

Contaminants in soil will be taken up to a variable degree by soil organisms. Those organisms carrying high residues will contribute most to the biological dispersal of contaminants. It is of interest to know the critical pathways, as a first step to identify

possible hazardous biological effects of soil pollution.

This contribution aims to indicate some general patterns concerning the distribution of soil contaminants over soil biota. The main emphasis is on biological factors determining the residues, and the possible implications for risk assessment.

4.2 Bioavailability of soil contaminants

The bioavailability of a chemical in soil depends on a complex of factors related to the chemical, the soil and the organism. From the viewpoint of the organism, it suffices to divide the amount present into three fractions:

- (1) the fraction that can be taken up directly;
- (2) the fraction that cannot be taken up directly, but is in kinetic equilibrium with fraction (1), such that, when uptake from fraction (1) does take place, this is replenished from fraction (2);
- (3) the fraction that cannot be taken up at all, even not on the long term.

From the viewpoint of the chemical, one usually discriminates between fractions obtained using various extractants (*e.g.* water, ammonium acetate, hydrogen peroxide, etc.).

It appears to be an impossible task to provide a one-to-one relation between chemical fractionation and biological availability. This is caused by the fact that the uptake and the activity of soil organisms interacts with the speciation of contaminants. For example, earthworms in soil improve aeration, which influences speciation of metals; plants may produce roots exudates that locally increase the bioavailability of metals.

These examples demonstrate that the problem of bioavailability is not to be seen statically, but must be analysed kinetically. The actual uptake of a substance does not only depend on the concentration in the available pool (fraction (1)), but it also depends on the rate constant of the uptake process, that is:

$$a = kVC_a \quad (1)$$

where:

- a = uptake (*e.g.* in $\mu\text{g day}^{-1}$),
- k = rate constant (day^{-1}),
- V = volume of the available pool (*e.g.* in L),
- C_a = concentration in the available pool ($\mu\text{g L}^{-1}$).

Viewed in this perspective, bioavailability is a relative concept: bioavailability increases by a factor of x, when some modulating factor causes the uptake to increase by x, either through an effect on k, or on C_a .

To illustrate the biological component of bioavailability, Table 4.1 provides some data on assimilation of cadmium in four arthropod species (Janssen et al. 1991). Since these organisms take up metals mainly from the food, uptake (a) has been expressed relative to ingestion. The uptake was estimated by fitting a one-compartment linear model to data obtained in experiments where animals were fed contaminated food for 30 days (Figure 4.1).

From the results summarized in Table 4.1 it can be concluded that the uptake efficiency may vary greatly from species to species, even when they are exposed to cadmium in the same chemical form. Moreover, excretion of cadmium is also species-specific, with no

clear relation to assimilation (Table 4.1). A low residue may be the result of a high uptake, combined with a very efficient elimination (*Notiophilus biguttatus*), or it may be the result of a low uptake efficiency, combined with a relatively slow excretion (*Orchesella cincta*). The equilibrium concentrations (Figure 4.1) do not give the right information on species differences in cadmium availability.

Table 4.1. Parameter estimates for cadmium kinetics in four soil arthropods. Data estimated using a one-compartment model as displayed in Figure 4.1. From Janssen et al. 1991.

pecies	Uptake relative to to ingestion (%)	Elimination rate constant (day ⁻¹)
<i>Orchesella cincta</i>	9.4	0.087
<i>Platynothrus peltifer</i>	17.2	0.0013
<i>Notiophilus biguttatus</i>	35.5	0.375
<i>Neobisium muscorum</i>	58.9	0.000

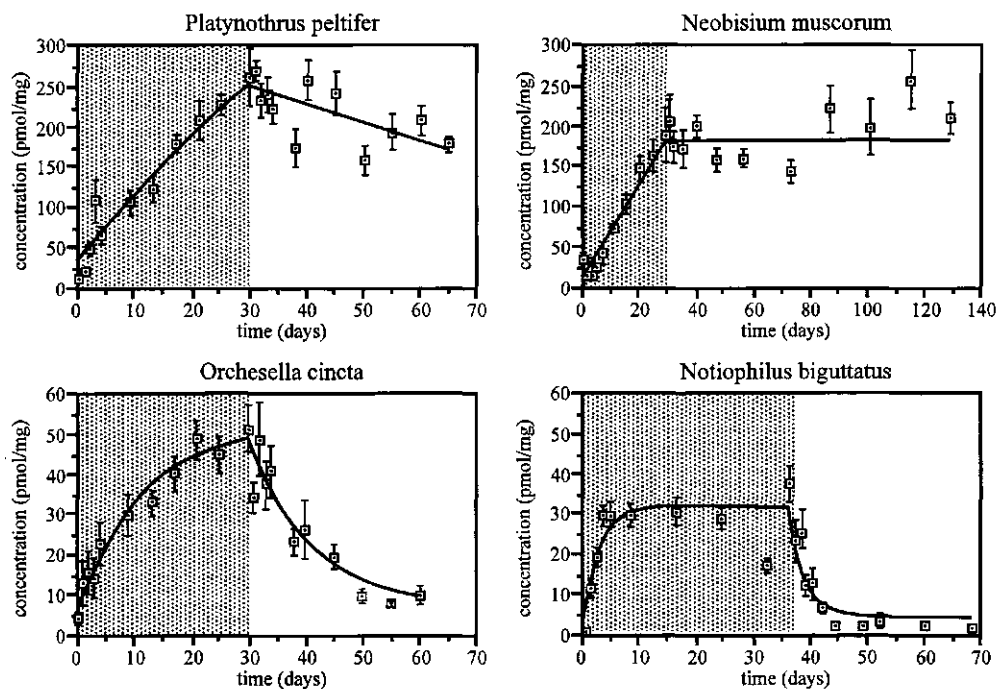


Figure 4.1. Accumulation and elimination of cadmium in four species of soil arthropods. On each time the mean concentration is given, with its standard error (10 replicates). The animals were fed cadmium contaminated food during the unshaded period. For the remaining period, the food did not contain cadmium. The smooth line is a one-compartment model, fitted simultaneously to the data from both the accumulation and the elimination period. From Janssen et al. 1991.

For several soil organisms, it has been shown that the available pool in equation (1) can

be equated with the soil pore water. This holds for both earthworms (van Gestel & Ma 1988) and some springtails such as *Folsomia candida* (Crommentuijn, unpublished). As a consequence, the distribution of a chemical can be viewed as an equilibrium partitioning proces, in a manner similar to the description of bioavailability in sediment sytems (Di Toro et al. 1991):

$$c_{\text{soil}} \rightleftharpoons c_{\text{pore water}} \rightleftharpoons c_{\text{organism}} \quad (2)$$

For organic chemicals with uncharged molecules, the first equilibrium in equation (2) is often summarized using a sorption coefficient K_d , which is a function of the organic matter content of the soil and the hydrophobicity of the chemical (often expressed as its octanol/water partition coefficient). For heavy metals, sorption behaviour is governed by various factors, such as the content and type of clay, organic matter, Fe and Al hydroxides, pH, CEC and redox potential. As a consequence, these factors will also influence the concentration in the organism.

Concentrations in organisms may be expressed relative to concentrations in soil by means of a bioconcentration factor (BCF):

$$\text{BCF} = \frac{c_{\text{organism}}}{c_{\text{soil}}}$$

The BCF will depend on above mentioned soil variables. This was shown clearly in a study by Ma et al. (1983) in which earthworms (*Lumbricus rubellus*) sampled in a gradient around a metal emitting source, were analysed for cadmium, lead, zinc and copper, in relation to various soil variables. Table 4.2 summarizes the data in the form of multiple linear regression equations. The results demonstrate that residues of metals in earthworms not only depend on the metal concentrations in the soil, but moreover increase with decreasing pH (not for Cu), and with decreasing organic matter content (for Pb).

Table 4.2. Multiple linear regression equations for the relation between metals in *Lumbricus rubellus* (y , $\mu\text{g g}^{-1}$), total metal content in soil (x , $\mu\text{g g}^{-1}$), organic matter content (OM, %) and pH. V^2 =percentage of the variance in $\ln y$, explained by regression. From Ma et al. 1983.

Element	Regression equation	V^2
Cd	$\ln y = 5.538 + 0.664 \ln x - 0.404 \text{ pH}$	48
Pb	$\ln y = 4.157 + 1.131 \ln x - 0.176 \text{ OM} - 0.746 \text{ pH}$	67
Zn	$\ln y = 6.791 + 0.343 \ln x - 0.270 \text{ pH}$	43
Cu	$\ln y = 14.88 + 0.344 x$	58

4.3 Uptake of contaminants by soil microflora

Soil contaminants taken up by soil microflora may contribute to two different pathways:

- (1) Many fungi live in close association with the roots of higher plants. In trees, most of these associations take the form of an ectomycorrhiza, while herbs and grasses usually have an endomycorrhiza, either of the vesicular-arbuscular type (VAM), or of the

ericoid type (ECM). Mycorrhizas improve the nutrient supply of the plant, but may also stimulate the uptake of metals, including radioisotopes (Killham & Firestone 1983; Ernst & Van Rooij 1987).

- (2) Fungi and bacteria are ingested by microbivorous invertebrates, such as nematodes, mites and springtails. The feeding activity of these animals may locally reduce the microbial biomass, but it has a generally stimulating effect on organic matter decomposition and nitrogen mineralization (Verhoef & Brussaard 1990).

Concentrations of soil contaminants in soil microflora display a great variability between species. For metals these species differences may amount to a factor of 80 (Ernst 1985). This variation partly relates to specific nutrient requirements of some species. For example in the fruit-bodies of the fly agaric, *Amanita muscaria*, high concentrations of the element vanadium are found. This is explained by the synthesis of a specific vanadium containing compound, amavadin, by these fungi (Bayer & Kneiffel 1972).

To illustrate the above mentioned variation, Table 4.3 lists the concentrations of caesium in the fruit bodies of various species. Radiocaesium was deposited from aerial fall-out following the Chernobyl accident in 1986, was readily accumulated by fungi and was transferred to the budding leaves of the trees, through mycorrhizal associations (Ernst & van Rooij 1987).

Table 4.3. Concentrations of ^{134}Cs + ^{137}Cs in fruit-bodies of various fungi in a forest site influenced by aerial deposition following the Chernobyl accident. From Ernst & van Rooij 1987.

Species	Stalk (Bq kg ⁻¹)	Cap (Bq kg ⁻¹)
Saprophytic fungi		
<i>Macrolepiota procera</i>	20	100
<i>Hygrophoropsis aurantiaca</i>	1075 ± 135	1360 ± 100
Ectomycorrhiza fungi		
<i>Laccaria amethystina</i>	82 ± 10	175 ± 29
<i>Lactarius rufus</i>	834 ± 20	1075 ± 13
<i>Paxillus involutus</i>	1050 3900 ± 600	
<i>Russula emetica</i>	767 ± 85	1225 ± 140
<i>Russula ochroleuc</i>	312 ± 27	375 ± 89
<i>Suillus bocinus</i>	1065 ± 735	1230 ± 424

The accumulation of metals by fungi is also specific to the element. Some elements are usually not concentrated relative to soil (*e.g.* Pb, Ni, Cr), while others are concentrated to a high degree. Maximal BCF-values are 20 for Cu, 38 for Fe, 60 for V, 200 for Au and As, 300 for Cd and Ag, and 550 for Hg (Arnolds et al. 1991). On contaminated soils, many fruit-bodies of fungi contain concentrations high enough to dissuade people from consumption.

4.4 Uptake of contaminants by soil invertebrates

Invertebrates take up contaminants through the food as well as directly through the integument. The second pathway is especially important for those animals with a relatively

permeable skin, such as earthworms (Lumbricidae), potworms (Enchytraeidae) and fly larvae (Diptera).

Animals with a well developed exoskeleton (isopods, beetles) will mostly absorb chemicals from the food, especially for water-soluble (polar) chemicals. For apolar chemicals, such as many pesticides, uptake through the integument is important in many cases. Side-effects of pesticides on soil-dwelling arthropods such as beetles and spiders, are usually mediated by uptake from the substrate through the tarsal segments of the legs (Everts et al. 1991).

The community of soil invertebrates comprises a diverse array of species and therefore offers a good opportunity to identify those factors that may explain why some species do, and others do not contain high concentrations. For cadmium this has been reviewed by Janssen (1991). A classification scheme for soil invertebrates was proposed, in which species were grouped together on the basis of their cadmium content and the kinetics through the body (Table 4.4). An interesting conclusion to be drawn from this review is that cadmium is not always subject to biomagnification. Although some predators contain high levels, other predators contain low levels; among the saprovores, the same range of variation is seen. Thus, some species may be endangered by biomagnification, although the average concentration of cadmium does not increase with the trophic level. As discussed above, the physiology of the species seems to be more important than its trophic status. Table 4.4 suggests that cadmium turnover in soil invertebrates is largely related to taxonomic classification.

Table 4.4. Classification of soil invertebrates according to cadmium turnover. After Janssen 1991. Feeding habits are given as saprotrophic (s), herbivorous (h), omnivorous (o), microbivorous (m), or predatory (p).

Species group	Feeding habit	Residue	Assimilation	Excretion
1. earthworms	s	high	high	low
isopods	s	high	high	low
gastropods	s/h	high	high	low
2. millipedes	s	intermediate	intermediate	?
centipedes	p	low	low	?
3. diplurans	o	high	?	low
4. collembolans	s/m	low	low	high
carabids	p	low	intermediate	very high
ants	o/p	low	?	?
crickets	h	low	low	high
5. pseudoscorpions	p	high	high	low
harvestmen	p	high	intermediate	?
oribatid mites	s/m	intermediate	intermediate	low
gamasid mites	p	high	high	?
spiders	p	high	high	?

Recently, some data have been published on other substances than heavy metals. Polycyclic aromatic hydrocarbons (PAHs) accumulate in forest humus and are taken up by invertebrates such as earthworms and isopods. The residues (normalized to the concentration in soil) are independent of the polarity of the molecule in the case of

earthworms (Figure 4.2). This is in accordance with the pore water hypothesis (Van Gestel & Ma, 1990). For isopods, however, BCF decreases with $\log K_{ow}$, so high molecular weight compounds are retained less, compared to their concentration in soil than low molecular weight compounds. This is an indication for the presence of substance-dependent metabolism of PAH in isopods, but not in earthworms (van Brummelen et al. 1996).

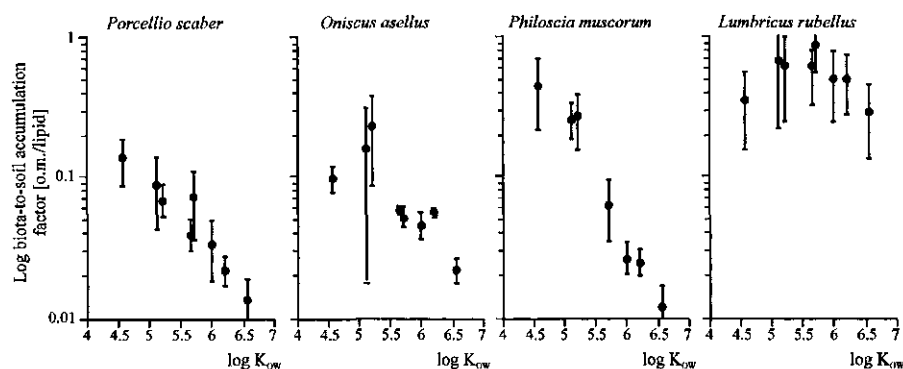


Figure 4.2. Biota-to-soil accumulation factors of PAHs in four invertebrates as a function of the octanol/water partitioning coefficient on double logarithmic scales. Averages and standard deviations are given for the quotient of PAH concentrations in animal tissue on lipid basis and the concentrations in the humus layer of the soil on an organic matter basis. The data are derived from samples taken in a forest close to a blast furnace plant. From van Brummelen et al. 1996. *P. scaber*, *O. asellus* and *P. muscorum* are isopods, *L. rubellus* is an earthworm.

4.5 Uptake of soil contaminants by vertebrates

Vertebrate animals ingest contaminants mainly through the diet and through ingested dust following pruning the fur. Metals are accumulated in the liver and kidneys; lipophilic compounds are concentrated in subcutaneous fat or other fatty tissues.

In contrast to the invertebrate community, there is a clear relation between feeding habit and residue levels among the mammals. The mole, *Talpa europaea*, feeds on animals only, especially on earthworms and insect larvae; the common shrew, *Sorex araneus*, also feeds on earthworms, as well as on beetles, isopods and snails; however the field vole, *Microtus agrestis*, mainly lives on grass stems, fruits and seeds.

As was shown in Table 4.4, earthworms, isopods and snails have a great capacity to concentrate heavy metals from the soil. As a consequence, the carnivorous small mammals (mole, shrews) are exposed to much higher concentrations in their diet compared to herbivorous species (voles). In a contaminated area, concentrations of metals in moles are high enough to cause damage to the kidney, while voles living in the same area hardly run any risk (Table 4.5).

Another aspect determining the exposure of vertebrate animals to soil contamination is the scale of their home range in relation to the contaminated area. When contaminations are restricted to a particular small area, exposure of higher animals, especially birds, may be lower than expected if they also feed outside the contaminated area. For example, the concentrations of DDT in earthworms living in apple and pear orchards are still high due

to the former use of this pesticide. However the levels in wood mice (*Apodemus sylvaticus*) are not so high, due to the fact that this animal integrates the exposure over a large area (Fuchs et al. 1985).

Table 4.5. Cadmium and lead concentrations in liver and kidney of three species of small mammals living in a metal contaminated area. Listed are the geometric mean as well as the highest and the lowest concentrations measured. From Ma 1987 and Ma et al. 1991.

Species	Organ	Cadmium ($\mu\text{g g}^{-1}$)	Lead ($\mu\text{g g}^{-1}$)
Talpa europaea	kidney	180	48
		88 - 149	8 - 438
	liver	152	13
Sorex araneus	kidney	82 - 234	5 - 40
		127	36
	liver	155	3.1
Microtus agrestis	kidney	16 - 541	1.0 - 8.7
		1.8	4.2
	liver	0.48 - 5.4	1.9 - 14
		0.33	1.2
		0.07 - 9.8	0.5 - 4.1

4.6 Monitoring residues and exposure

Concentrations of pollutants in soil only give limited information on potential biological effects. As was argued in section 4.2, bioavailability of chemicals in soil is influenced by a number of factors, which accordingly may influence exposure. Concentrations in soil biota may provide a better insight in possible biological effects. Monitoring programmes have been designed to map spatial and temporal changes in pollutants. This may help environmental policy makers to identify critical areas, and to evaluate the effectiveness of remediation measures.

For soil contamination, there is no extensive tradition in monitoring programmes. Organisms considered to be useful in such programmes are nettles (*Urtica dioica*), earthworms, isopods and shrews (Tolsma et al. 1991). Recently, it has been stressed that residue levels alone may be insufficient to indicate possible negative effects. Therefore, it has been proposed to supplement biomonitoring programmes with so-called biomarkers: biochemical and physiological parameters indicating metabolic changes in response to the toxicant (McCarthy & Shugart 1990). This may include the following:

- (1) Activities of enzymes inhibited by the toxicant. The enzyme d-aminolaevulinic acid dehydratase is specifically inhibited by lead, while the enzyme acetylcholinesterase is inhibited by organophosphate and carbamate pesticides.
- (2) Products of the metabolism. *E.g.* metabolites of benzo(a)pyrene, and DNA adducts are indicative of exposure to PAH.
- (3) Biotransformation activity. This is often measured as a standardized assay (ethoxyresorufin-O-deethylase) for the activity of cytochrome P-450. Increased

biotransformation is indicative of exposure to PAHs and organochlorines (PCBs etc.).

For soil contamination, suitable biomarkers still have to be developed. Biomonitoring programmes have not yet been designed on a large scale.

4.7 Conclusions

Uptake of soil pollution by soil organisms is influenced by several factors. Within the large diversity of soil dwelling species, some critical pathways can be discerned. These include fungi living in association with higher plants (mycorrhiza), saprotrophic invertebrates living on dead organic matter, and some small mammals feeding on invertebrates. Inclusion of animals and plants in monitoring programmes may improve the identification of hazardous sites and temporal trends in soil quality.

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5 Effects of pollutants on soil organisms

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Summary

Damage to the ecological function of a soil is preceded by adverse effects on the organisms carrying out functions. Due to functional redundancy and selection of resistant genotypes, there is however no clear relation between ecological function and species composition of the soil biota.

In laboratory experiments, adverse effects can be studied using a standardized substrate and a range of concentrations, to establish dose-effect relations. Toxicity of chemicals can be expressed as EC50 or NOEC. A variety of test organisms has been employed in soil toxicity tests, but few have been accepted as international standards. The earthworm test using artificial soil is the best developed test available; recently this is supplemented with reproduction toxicity, for earthworms as well as other invertebrates, such as springtails. Microbial tests center on nutrient conversions, enzyme activities, or mutagenicity. In microcosms tests, interactions between different species may be studied.

The results of toxicity tests provide an impression of susceptibilities of soil biota. This may be used to establish soil quality standards; a statistical approach has been formulated in which maximum acceptable concentrations are derived as a percentile of the frequency distribution of NOEC-values.

For degradable chemicals, risk assessment should not only be based on the no-effect-levels, but also on the degradation time and the potential for recovery. The scientific basis for soil ecotoxicological risk assessment systems is however still rather undeveloped.

5.1 Introduction

Adverse effects of soil contaminants are commonly discussed in terms of their implications to soil functions. Every function (*e.g.* carbon mineralization) can however be carried out by more than one organism. Therefore, the soil provides us with a classical example of the ecotoxicological principle of functional redundancy.

Functional redundancy is demonstrated nicely in case-studies on effects of persistent chemicals on soil microflora. Table 5.1 provides a compilation of various soil activity parameters, measured in a gradient study around a brass mill at Gusum, Sweden. It appears that the species composition of the soil fungal community undergoes drastic changes when copper concentrations increase in the gradient; along with these changes, many enzyme activities decrease, although some enzymes show little response. Only at very close distance to the emission source, effects on total litter decomposition become apparent (Table 5.1).

Another example is the well-known insensitivity of carbon dioxide evolution to toxicants, compared to nitrification; the latter process is often the most sensitive criterion related to soil functions. This is attributed to the fact that nitrification is carried out only by a limited

number of bacterial genera (*Nitrosomonas* and *Nitrobacter*), while respiration is carried out by all heterotrophic organisms. Consequently, inhibition of carbon dioxide evolution requires a much more extensive intoxication of the soil community than inhibition of nitrification.

Table 5.1. Overview of biological activity in a pine forest soil surrounding a brass mill at Gusum, Sweden. From Tyler 1974; 1984, and Nordgren et al. 1983.

	10 km from source	Close to source	Units
copper concentration	0.31	157	$\mu\text{mol g}^{-1}$
total mycelial length	3000-4000	500-1500	m g^{-1}
total length FDA-active mycelium	200-500	50-150	m g^{-1}
colony forming units	9.7×10^6	9.7×10^6	CFU g^{-1}
<i>Penicillium</i> (16 species)	30-40	0-10	% of fungal isolates
<i>Oidiodendron</i> (7 species)	30-40	0-5	" " "
<i>Paecilomyces</i> (1 species)	1	5-30	" " "
sterile fungi	5-10	10-30	" " "
soil respiration	0.8	0.1	$\text{mg C g}^{-1} \text{ day}^{-1}$
urease	1.0	0.05	$\text{mg NH}_4\text{-N g}^{-1} \text{ day}^{-1}$
acid phosphatase	7.0	1.0	$\text{mg phenol g}^{-1} \text{ day}^{-1}$
b-glucosidase	0.8	0.8	$\text{mg salignine g}^{-1} \text{ day}^{-1}$
litter decomposition	1.8	0.2	$\text{mg g}^{-1} \text{ day}^{-1}$

Functional redundancy implies an asymmetric relation between ecological structure and ecological function: protection of functions is guaranteed if the ecological structure (species composition, biomass distribution, etc.) is maintained, while on the other hand not every damage to the structure will cause a loss of function. On the basis of this argument, many toxicity tests aim at the performance of single species, or a battery of species selected from a large community. How the effects on these indicator species relate to effects on soil ecological functions is often not very clear.

Another complication relating to structure and function is the development of resistant species populations by the selective action of persistent contaminants, such as heavy metals. The case of metal tolerance in higher plants, such as *Agrostis capillaris*, *Deschampsia cespitosa*, and *Silene cucubalus* has been documented extensively and significant progress has been made in identifying the underlying physiological mechanisms (Verkleij & Schat 1990). For soil microflora, metal tolerance has been demonstrated in a classical study by Jordan & Lechevalier (1975). Especially among actinomycetes, tolerance to zinc in isolates from metal contaminated soils may evolve rather rapidly.

Recently, metal tolerance, in terms of genetic differences between strains stemming from various contaminated soils, has been shown to occur also in soil animals, such as snails (Beeby & Richmond 1987), springtails (Posthuma 1990), and isopods (Donker & Bogert 1991). Genetic variance in populations of the collembolan *Orchesella cincta* was estimated by parent-offspring comparisons, which showed that heritability of tolerance was 33% in a reference population, but did not significantly differ from zero in a tolerant population from a contaminated site (Posthuma et al. 1992). Clearly, metals in soil can exert a selective action when concentrations exceed the no effect level.

The development of adaptation to soil contaminants under natural conditions detracts from the validity of standardized toxicity tests. Moreover, adaptation may entail secondary changes in life-histories, energy budgets and general genetic variance. Any attempt to apply the results of soil toxicity tests for soil protection, must take these factors into account.

This contribution aims to review the various methods, as they are currently employed, to estimate effects of soil pollutants on soil organisms, and to demonstrate how the results of these experiments may be used to establish criteria for soil quality.

5.2 Substrates used in toxicity tests with soil organisms

In toxicity tests with soil organisms described in the literature many different substrates are used. Besides natural and artificial soils, a number of artificial substrates can be identified: quartz sand, silicagel, agar, wet filter paper and water or nutrient solutions. The relevance of these artificial substrates for natural soils is only limited, as it is hard to translate results obtained in such substrates to effect levels in soil. In some tests organisms are not exposed through the substrate they are kept on, but are exposed via the food. It is not certain how results of such tests can be translated to effect levels in soil. For studies on the activity of soil microorganisms, only (freshly sampled) natural soils can be used, as in such studies the effects on the indigenous microflora are determined (Somerville & Greaves 1987).

The great variety of substrates mentioned above indicates that standardization of test substrates is necessary. For reasons of ecological realism, it is essential that exposure in laboratory tests resembles that in the field. The use of real or artificial soils is therefore recommended. As will be demonstrated in this contribution, for reasons of standardization and comparability of tests with different organisms it is advisable to use an artificial soil substrate similar to the one recommended for earthworm toxicity tests (OECD 1984; EEC 1985). This is mixture of quartz-sand (particle size 0.05-0.2 mm, 70%), kaoline clay (20%), and *Sphagnum*-peat (sieved over a 1 mm mesh size sieve, 10%), adjusted to pH 6.0 using calcium carbonate powder.

5.3 Microbial tests

Based on series of workshops held during the seventies and eighties, Somerville & Greaves (1987) formulated a number of recommended tests for assessing the side-effects of pesticides on soil microflora. During the latest workshop in this series, which was held at Basel in 1989, these recommendations were only slightly modified. Basically, for all microbial tests in soil it is essential to use freshly sampled soil containing an active microflora. Prolonged storage and drying of the soil should be avoided. For a proper assessment of the effect of chemicals, at least two different soil types should be used (Somerville & Greaves 1987). Here a short description will be given of a number of tests on microbial processes related to the conversion of nutrients in soil and the activity of certain enzymes.

5.3.1 Soil respiration and mineralization of substrates

The production of CO₂ from small soil samples (100 g) treated with the test chemical is measured continuously or semi-continuously. The tests should run for a minimum of 30 days. Tests may be performed in either unamended soil, or in soil amended with a

substrate. For this purpose mostly 0.5% (w/w) plant or horn meal is used (Somerville & Greaves 1987). The disadvantage of this soil respiration test is that the activity of the total soil microflora is determined. When certain species are affected by the test chemical this will often not be noticed, as other (less sensitive) species may take over the activity of the sensitive ones.

Considering this disadvantage, during the last decade some new test methods have been developed aiming at more specifically determining the effects on (groups of) soil microorganisms. One such new development is the addition of a readily degradable substrate and the determination of the short term respiration rate. Such a test was described by Haanstra & Doelman (1984), using glutamic acid as a substrate. These short-term respiration tests may be combined with a biomass determination, and seem to be more sensitive than the normal respiration tests. Another alternative may be found in the addition of more persistent substrates, such as lignin or cellulose (Ljungdahl & Eriksson 1985). Only a limited number of soil microorganisms is capable of degrading these substrates. When these organisms are affected by the test chemical, no others can take over their activity.

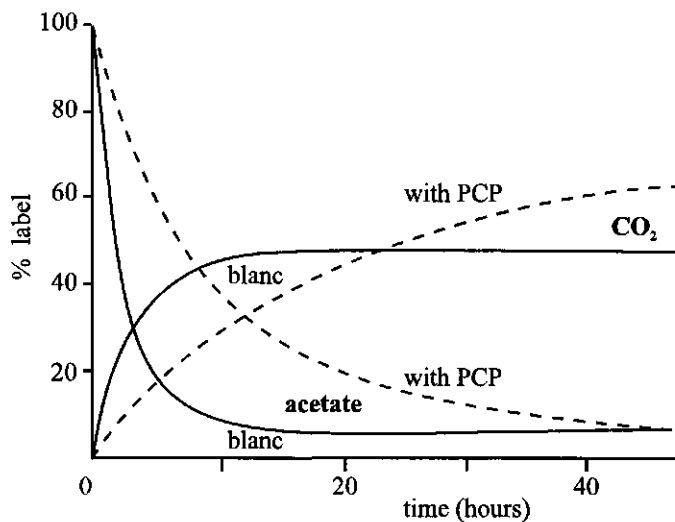


Figure 5.1. The mineralization of acetate at $1 \mu\text{g l}^{-1}$ in a sandy soil at $10 \text{ }^\circ\text{C}$. The mineralization proceeds according to first order kinetics, and is significantly delayed by the addition of pentachlorophenol (PCP). Note that PCP stimulates the release of CO_2 from acetate, which implicates that more substrate is needed for the production of the same amount of biomass. From van Beelen et al. 1990.

The disadvantage of the previously described soil respiration or substrate degradation methods is caused by the fact that less sensitive species of microorganisms may grow on the substrate during the test. This results in a shift among the microflora towards more resistant species, masking the possible elimination of sensitive species. For that reason, van Beelen et al. (1990) developed a test method using the mineralization of low concentrations of ^{14}C -acetate, ^{14}C -chloroform or other labelled substrates. The amount of substrate applied is very low ($1 \mu\text{g l}^{-1}$) to ensure that no growth of the microflora will occur. This amount of substrate is added to a slurry of the test soil prepared by mixing the

homogenized soil with an equal weight of groundwater. The test chemicals are added to the slurry in the desired concentration levels. Samples are incubated at 10 °C. The test duration depends on the capacity of the microflora in the soil sample to mineralize the test substrate, and is chosen depending on the half-life of the acetate mineralization. The acetate mineralization is measured by determining the amount of $^{14}\text{CO}_2$ released from the sample and by determining the amount of ^{14}C remaining in the suspension at the end of the test. Figure 5.1 shows a typical acetate mineralization pattern in a soil sample and the effect of pentachlorophenol.

5.3.2 Ammonification and nitrification

In ammonification tests, the release of inorganic nitrogen from soil organic matter or a substrate (*e.g.* plant material or horn meal) is studied in a way comparable to soil respiration tests. The influence of nitrification, *i.e.* the conversion of ammonia into nitrate, may also be studied in these tests. Ammonification is performed by a wide variety of soil microorganisms, and is therefore relatively insensitive to perturbation. The advantage of nitrification is, that fewer species of microorganisms are involved in this process and that it is considered to be of ecological and agricultural importance. It is therefore recommended to combine these parameters in one test or to run a separate test on nitrification (Somerville & Greaves 1987). Nitrification tests can be performed in soil amended with either $(\text{NH}_4)_2\text{SO}_4$ or with organic substrates such as plant or horn meal. For this purpose an amount of substrate equivalent to ca. 100 mg N kg^{-1} soil is added, and the disappearance of NH_4^+ and the appearance of NO_3^- is monitored. In case the rate of NO_3^- formation does not follow the disappearance rate of the NH_4^+ , the soil should also be checked for the formation of NO_2^- . It is further recommended to check whether the test soil is capable of nitrification, and whether the organic matter amendment is suitable for ammonification and nitrification studies. The duration of the nitrification test depends on the time needed for conversion of the added substrate or to reach an equilibrium between ammonification from soil organic matter and nitrification (Somerville & Greaves 1987).

5.3.3 Urease

At several intervals, small soil samples (6-7 g) are taken and incubated with 5 ml demineralized water and 1.0 ml of a solution containing 60 mM ureum. Incubation is done at 35 °C for 5 h on a shaking water bath. A phenylmercury acetate solution in 2 M KCl is added to the soil samples to stop the urease reaction. After 10 minutes shaking, the soil suspensions are filtered over a filter paper. Filtrates are analysed photometrically at 525 nm for ureum concentrations (NEN 5796 1989).

5.3.4 Dehydrogenase

Soil samples (5-10 g) are incubated with a solution of TTC (2,3,5-triphenyl tetrazolium chloride) in 0.1 M tris buffer solution (pH 7.6) and incubated for 24 hours at 30 or 37 °C. The reduced triphenyl formazan formed is extracted with methanol and quantified by measuring the absorbance at 485 nm (Casida 1964; Thalmann 1968). Dehydrogenase reflects of a broad range of microbial oxidative activities and does not consistently correlate to microbial numbers, CO_2 -evolution or O_2 -consumption. Additionally, dehydrogenase activity may depend upon the nature and concentration of amended C-substrates and alternative electron acceptors (Somerville & Greaves 1987).

5.3.5 Phosphatase

At several intervals, 0.5 g soil samples are taken and incubated with 5 mM p-nitrophenyl-phosphate (p-NPP) for 1 h in a shaker at 20 °C. Phosphatase activity is measured as the amount of p-nitrophenol formed by means of a spectrophotometer (Tabatabai & Bremner 1969). Phosphatase is said to bear little relation with total phosphate availability in soils (Somerville & Greaves 1987). Its relevance for microbial activity in soil may be therefore be questioned.

Somerville & Greaves (1987) stated that soil enzyme activities would be of little value to monitor side effects of pesticides on the microflora. The main reasons for this were:

- the total enzymatic activity of the soil is made up of various fractions and it is extremely difficult to quantify the contribution of each to the catalysis of a particular substrate; furthermore, many enzymes are formed extracellularly, and will still be active also when the microorganisms responsible for their production have been eliminated.
- there is no universally-agreed methodology, and almost any result can be achieved by varying assay conditions (temperature, pH, substrate conditions). Although tests on enzyme activity have been described by many authors, not many data are available to judge the reproducibility of the above described methods.

5.3.6 Mutagenicity tests

Some compounds present in soil as contaminants (e.g. PAHs), are known mutagens and their effects can be assessed by genotoxicity tests developed for drinking water, surface water, and sediments. This may be applicable in industrially contaminated sites, waste disposals, or sewage sludge-amended soils.

The usual approach to assess mutagenicity is to record the number of revertants in a *Salmonella thyphimurium* strain, plated with the test substance on a histidine deficient medium. To include those mutagens that require metabolic activation, a rat liver microsome suspension is added (Ames et al. 1975). In addition to this test, several other procedures have been proposed, which are often more sensitive (van der Gaag 1989).

To apply mutagenicity tests to polluted soils, some way of obtaining an extract has to be applied. This may be crucial for the test results: extractions with solvents such as methanol or dimethylsulfoxide often induce a stronger mutagenic response in the *Salmonella* test, compared to water leachates; this is especially true for superficial soil horizons (Kool et al. 1989; Donnelly et al. 1991).

The ecological relevance of mutagenicity test results for soils is hard to evaluate, as this field of research is still underdeveloped. Mutagenicity is not only detected at contaminated sites, but also in unpolluted soil (Kool et al. 1989; Brown et al. 1985), and often bears no clear relationship with the levels of known chemical mutagens in soil (Donnelly et al. 1991).

5.4 Tests on microfauna and mesofauna

Microfauna and mesofauna are among the most numerous and species-rich groups of soil animals, but their status as test organisms is poor. Yet, many species hold a good promise, as they are often easy to culture and their size allows a small-scale experimental set-up and ease of replication. This review is restricted to saprotrophic species, because of their direct relation to the ecological function of soil.

5.4.1 Protozoans and nematodes

Protozoans and nematodes, like tardigrades, rotifers and copepods, live in the soil pore water and therefore the way to test them is similar to an aquatic toxicity test. Among protozoans the ciliates *Tetrahymena pyriformis*, *Colpoda cucullus*, and *Paramecium aurelia* have been considered (Berhin et al. 1982; Nyberg & Bishop 1983; Janssen, unpublished). Nematode species used are *Coenorhabditis elegans*, *Panagrellus silusiae*, and *Plectus parietinus* (Sturhan 1986; Haight et al. 1982; van Kessel et al. 1989; Kammenga, unpublished). For both groups however, an accepted test procedure is not available.

The problem with these types of tests is not their implementation, but the extrapolation of test results. Usually tests are done in an artificial medium (nutrient solution, agar, etc.), whose composition greatly affects toxicity. If concentrations in test solutions can be equated with pore water concentrations, adsorption data may be used to express the toxicity per unit of soil. However, the validity of this extrapolation still has to be investigated.

The use of small animals with short life-cycles allows higher level toxicological endpoints, such as population increase, species composition, interspecific competition and community succession to be assessed (cf. Niederlehner et al. 1985). Studies like this have not yet been done for the soil environment.

5.4.2 Collembola

Second to earthworms, Collembola is a relatively well investigated group of soil animals. Several species have been used frequently in toxicity experiments: *Onychiurus* spp. (Eijsackers 1978; Bengtsson et al. 1985; Mola et al. 1987), *Folsomia candida* (Thompson & Gore 1972; Tomlin 1977; Iglisch 1986), *Tullbergia granulata* (Subagja & Snider 1981), and *Orchesella cincta* (van Straalen et al. 1989). The first three species are parthenogenetic (thelytokous), while *O. cincta* is sexual, sperm being transferred indirectly through spermatophores deposited on the substrate by the male. Three different exposure systems have been described, that is, through feeding on fungi grown on contaminated agar, through feeding on directly contaminated food, and through residual exposure (treated substrate, e.g. sand, leaves, soil etc.).

When testing Collembola with contaminated fungi, the animals are kept on a plaster of Paris substrate in a Petri dish, while feeding them with a piece of agar, overgrown with hyphae, cut from a malt agar gel on which a fungus (e.g. *Verticillium bulbillosum*) has been inoculated (Bengtsson et al. 1983; 1985). Egg production, growth and survival are recorded regularly throughout a period of several weeks. The advantage of this system is that substances are offered in a natural way, that is, after being taken up and possibly transformed to naturally occurring complexes. On the other hand, concentration levels are difficult to maintain, or to set to certain values, as the fungus will take up chemicals from agar according to mechanisms of its own.

When testing Collembola with directly contaminated food, chemicals are added in water or acetone solution to the food (algae, yeast, ground leaf material) and the solvent is allowed to evaporate, or is just enough to allow for a suitable consistency. The food can be offered as droplets on filter paper discs, while the animals are kept on a plaster or sand substrate. In this manner, concentrations can be manipulated easily, while growth, egg production and survival are monitored over a period of several weeks (van Straalen et al. 1989).

The third system of testing Collembola is to use the artificial soil medium, as developed for the earthworm toxicity test (Jancke 1989; Wohlgemuth et al. 1990; BBA 1990). Ten juvenile collembola (*Folsomia candida*, 10-12 days of age) are placed in a small pot with artificial soil and some dry yeast is provided for food. After a period of 28 days the number of remaining animals, and their offspring is counted, after floating them by pouring an amount of water in each pot. The counting may be facilitated by taking a photograph of the water surface of each pot and projecting this on a screen.

The *Folsomia*-test is very easy to carry out, it requires little attention during the test, and it gives well reproducible results. Another advantage is the use of artificial soil similar to the earthworm test; thus, experimental results can be compared between earthworms and springtails. The only disadvantage of the test is that reproduction cannot be observed directly, and cannot be separated from juvenile mortality and hatching success. The *Folsomia*-test is now in the process of international standardization (BBA 1990).

5.4.3 Oribatid mites

Denneman & van Straalen (1991) described a reproduction toxicity test using the parthenogenetic oribatid mite *Platynothrus peltifer*. This seems to be the only oribatid used so far in soil toxicity experiments, although oribatids comprise hundreds of species and are usually the most numerous group of arthropods in forest soils.

The test with *P. peltifer* uses small plastic pots, with a sand substrate, covered with filter paper, on which drops of contaminated algae are applied. The animals (10 per pot) are transferred to fresh pots every week and the number of eggs laid is counted. The test is very laborious, due to the animals trying to hide their eggs in small crevices; it also a rather lengthy test (9 to 12 weeks) due to the low rate of egg production in this species, and its long life-cycle (1 year), which are remarkable features for such a small animal (\pm 1 mm).

Tests using oribatid mites will not easily lend themselves to standardization and international acceptance. The only reason to mention it here is that in the development of toxicity tests, species like *P. peltifer* tend to be forgotten, although it has been shown that for cadmium, it is the most sensitive soil invertebrate tested thus far, and for both copper and lead, it is more sensitive than springtails (Denneman & van Straalen 1991).

5.5 Earthworm toxicity tests

Earthworms have often been used for soil toxicity experiments. An internationally accepted guideline is available in which the species *Eisenia fetida* is exposed to chemicals mixed homogeneously through an artificially composed medium (70% quartz sand, 20% kaolin clay, 10% *Sphagnum* peat, adjusted to pH 6). The standardized test considers the LC₅₀, determined after a 14 days exposure period (OECD 1984; EEC 1985). This test has now largely replaced earlier methods using silicagel or filter paper as substrates.

The acute earthworm toxicity test has been extended to include an assessment of growth and reproduction (van Gestel et al. 1989). Prior to the test, worms are preincubated for one week in untreated artificial soil. During both the preincubation period and the test proper, ten worms are used per jar, and four jars per treatment level. The worms are fed by supplying a small amount of (untreated) cow dung in a small hole in the middle of the soil. After three weeks, the worms are sorted out of the soil and body weights are determined. The number of cocoons produced is assessed by washing the content of each

jar through 1 and 2 mm sieves placed on top of each other. By incubating cocoons produced for another five weeks in untreated artificial soil, also effects on hatchability (% fertile cocoons, number of juveniles per cocoon) and the total number of offspring per adult worm can be determined. For this purpose, glass petri dishes are used, in which the cocoons are incubated between two layers of artificial soil. After five weeks, the content of the dishes is washed through two 0.5 mm sieves using a shower. The juveniles and cocoons will remain on the sieves and can be washed into a bowl, where the number of fertile, hatched and non-hatched cocoons and of juveniles can be counted. To enable this washing procedure it is advisable to use a small mesh peat (preferable < 0.5 mm ground) to prepare the artificial soil and mix a small amount of cow dung (about 1%) through it, as food source for the juvenile worms. This procedure was shown to be reproducible and highly efficient, recovering on the average 97% of the juveniles (van Gestel et al. 1988).

The method has the advantage that it follows the existing guidelines on acute toxicity testing (OECD 1984; EEC 1984) and uses the same substrate and earthworms species. The method seems to be reproducible, although it has not yet been subjected to a ring test. Van Gestel et al. (1992) demonstrated that there is a negative correlation between earthworm growth and cocoon production. This correlation may affect the way earthworms respond to chemical stress, *i.e.* either by a reduction of cocoon production or a reduced growth. This stresses the need for including both growth and reproduction in a sublethal test.

5.6 Microcosm tests

Since the single species test obviously disregards any ecological interactions between different species, one may question the ecological relevance of these tests. To evaluate effects of chemicals under more natural conditions, model-ecosystems have been designed that capture certain aspects of real ecosystems and are yet simple enough for proper experimentation. For soil, such systems often are called microcosms, or micro-ecosystems.

The microcosm approach allows effects of toxicants to be assessed with two or more organisms being exposed simultaneously and interacting with each other. An important issue for ecotoxicology is the extent to which interactions between species could make a system more sensitive to toxicants than would be expected on the basis of the response of the participating organisms in isolation. For the soil environment, this issue is far from settled, as hardly any studies have been done in this perspective.

Van Wensem et al. (1991) studied the effects of the fungicide triphenyltinhydroxide in micro-ecosystems containing decomposing leaf litter with isopods (*Porcellio scaber*). In these experiments, isopods had a strong effect on the content of soluble ammonium at the end of the experiment: isopods about doubled the ammonium concentration, partly due to excretion, and partly due to possible stimulating effects on the microflora. In systems with isopods, the organotin inhibited ammonification (NOEC = 10 µg g⁻¹), but in systems without isopods, organotin had no significant effect. The addition of isopods in this case made the system a more susceptible tool for demonstrating toxic effects. This response was not expected (the organotin is a fungicide), and would not have been noticed in a single species test using isopods only.

The development of microcosms as ecotoxicological testing tools has not much proceeded beyond the stage of laboratory-specific experimentation. It may be doubted whether micro-ecosystems are likely to contribute significantly to ecotoxicological risk assessment (Smies 1983). Yet, the example given above demonstrates that it may be useful to validate the results from simple tests in more complex systems in some cases, as there are indications that ecological interactions indeed may change the outcome of a test.

5.7 Risk assessment for soil contaminants

Tests methods should not be designed, nor applied, without adjustment to the needs of environmental protection policy. Risk assessment methodologies have been derived to evaluate toxicity data with the aim of deriving maximum acceptable concentrations in soil, or maximum acceptable half-lives of degradable chemicals. For soil, three main approaches can be discerned, to be discussed below.

Although many toxicity data still take the form of LC_{50} 's, recent years have seen a tendency of putting more emphasis on sublethal criteria, especially reproduction. This reflects the growing awareness that population responses to toxicants follow the effects on reproduction quite closely, especially for organisms in the lower trophic levels.

5.7.1 Indicator species

Since international standardization of tests is a very laborious exercise, few accepted tests are available. There is a tendency to use these few tests as 'indicators', that is, to select organisms who combine sensitivity, economic importance and ecological relevance. For soil, the earthworm *Eisenia fetida* could play such a role. The importance of earthworms for maintaining soil fertility is without doubt, and, although *E. fetida* is not a typical soil species, its sensitivity does not differ too much from other earthworms.

Van Gestel (1991) reviewed data on toxicity of various chemicals to earthworms, and concluded that the ratio of LC_{50} 's of *Eisenia* to those of other species varied between 0.07 and 9.2. For chlorobenzenes the difference between *Eisenia* and other species is not greater than 2, while for chlorophenoles and several pesticides it tends to be larger. There seems to be no one species of earthworm that is most sensitive to all chemicals.

When comparing a wider range of species, the above argument is reinforced. Table 5.2 reviews some data on NOEC-values for several chemicals, tested on different species of invertebrates. The most sensitive species (to present knowledge) is different for each chemical. There is no fixed relation between the NOEC of *E. fetida* and the NOEC of the 'most sensitive' species. Sensitivity depends on species-specific receptors for the chemical, as well as on species-specific mechanisms for transformation, detoxification and excretion.

Table 5.2. Comparison between NOEC-values of five substances in soil, for *Eisenia fetida* and other soil invertebrates. From van Straalen 1990.

Chemical	Most sensitive invertebrate tested (to present knowledge)	Ratio of NOEC to NOEC of <i>Eisenia</i>
cadmium	<i>Platynothrus peltifer</i>	14
copper	<i>Arion ater</i>	7
lead	<i>Lumbricus rubellus</i>	4
lindane	<i>Folsomia candida</i>	20
atrazine	<i>Orchesella cincta</i>	12

5.7.2 Sensitivity distributions

When deriving soil quality criteria by extrapolation from data on indicator species, an

application factor should be applied. If a fixed factor would have to be used for all chemicals, Table 5.2 suggests that such a factor should be greater than 20, preferably 100, to protect sensitive species. However for some chemicals such a factor may be unnecessarily large, as the differences between species are not so great (*cf.* lead with cadmium). This calls for an application factor based on the variability of the toxicity data.

Based on Kooijman (1987), van Straalen & Denneman (1989) developed a statistical approach for estimating a benchmark concentration, called HCp, such that:

(1) only a small portion (p%) of soil life is expected to have a NOEC still lower than HCp, and

(2) HCp is lower when there are fewer data (fewer species tested).

Assuming that the NOEC-values of all species in a large community follow a loglogistic distribution, the HCp-value can be estimated as:

$$\text{HCp} = \exp [x_m - k_p s_m d_m] \quad (1)$$

where:

x_m = mean of m NOEC-data, referring to m species tested, transformed to natural logarithms

s_m = standard deviation of the ln (NOEC) data

d_m = a factor depending on the number of species in the data set, given in a table by Kooijman (1987)

k_p = a factor depending on the percentage of unprotected species (p %).

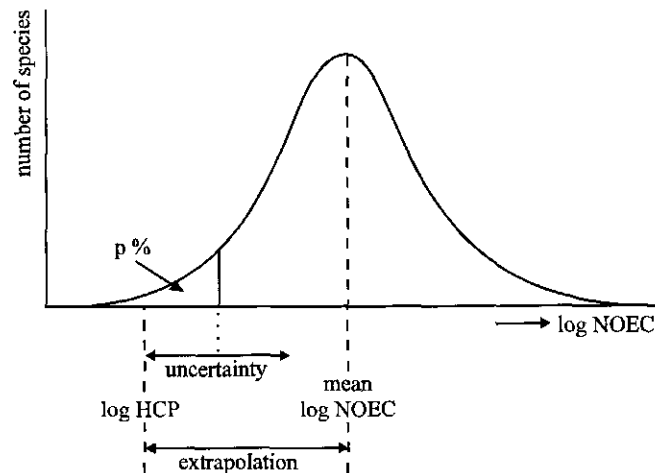


Figure 5.2. Illustration of a model to derive environmental quality criteria as the lower limit of uncertainty margin for the p-percentile of a frequency distribution of NOEC-values.

Figure 5.2 gives an illustration of the model, in which the percentage p has been set to 5%. Recently, the statistical aspects of estimating the uncertainty margin have been reviewed by Aldenberg & Slob (1991) and Wagner & Løkke (1991), and some improvements have been proposed.

Quality criteria derived on the basis of this model often are in the background range (van

Straalen 1990). This means that for almost any chemical, there are a few very sensitive species that are affected when concentrations increase above background.

5.8 Conclusions

Ecotoxicological test methods for soil are relatively underdeveloped. Standardization has been achieved only in a few cases. However, ecotoxicological risk assessment not only calls for better tests, it also requires other criteria (sublethal endpoints), as well as tests on more species. Instead of putting too much effort in standardization, it might also be useful to consider testing other (rare, difficult) species, or to test on sublethal criteria (reproduction). Statistical treatment of toxicity data may help to derive benchmark concentrations of chemicals in soil, and to identify those areas where further test development is needed.

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6 Biotechnological processes for cleaning soils and sediments polluted with organics

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6.1 Introduction

Microorganisms are capable to degrade in normal field soils some 30 tons organic dry matter per ha per year; in subsurface soils and river sediments this potential is about 10 times lower due to oxygen limitation. The principal factors limiting biodegradation are the chemical structure of the organic molecule and its availability. To accelerate soil and sediment clean-up, various technologies are under development; the main axes of progress appear to be the addition of nutrients (*e.g.* the Exxon Valdez clean-up (Atlas 1993)), the activation of microbiota by appropriate cosubstrates (*e.g.* the improved removal of trichloroethylene from aquifers by CH₄-injection (Hopkins et al. 1993)) and the seeding with special microbial potentials (*e.g.* the field application vector used for polychlorinated biphenyls (Lajoie et al. 1993)).

In terms of toxicity of organic polluted soils, it appears that subjecting a soil to a period of intensive microbial activity can reduce the biotoxicity with a factor 5 to 10 and that the measurement of the impact of the aqueous soil leachate by means of a simple bacterial luminescence test gives reliable ecotoxicological information.

This paper deals with organic pollutants in soils and sediments. In soil treatment, a wide range of cleaning techniques can be used. Distinction must be made between *in situ* and *ex situ* treatments. For *ex situ* techniques, the polluted soil is excavated and decontaminated in a reactor. *In situ* treatment is the biological clean-up of contaminated soils on-site without excavation. It is usually applied where contamination is deep in the subsurface or under buildings, roadways, etc.

6.2 Autopurification of the soil ecosystem

The autopurification of the soil is governed by environmental conditions of the ecosystem and the chemical properties of the pollutants.

6.2.1 Soil characteristics

6.2.1.1 Soil biota

In order to have a good understanding of the *biodegradative potential of the soil ecosystem*, one can refer to the following facts about normal aerobic arable soils:

- they contain about 0,5% of organic C; of the total soil C, some 1% is microbial biomass C;
- per ha, a normal soil microbial biomass (approximately 2000 kg wet weight) metabolizes every year some 5-10,000 kg organic matter (rods, crop residues, etc.) to CO₂

(2/3) and own biomass (approximately 1/3);

- as long as the input of fresh organic matter is below 30 tons dry matter per ha per year, relatively rapid conversion without adverse effects on plant growth can be expected.

For subsurface soils and river sediments, the overall influx of oxygen as an electron-acceptor for the microbial biomass is the limiting factor. The overall biodegradation potential is thus of the order of about 1-3 tons organic matter per ha per year.

A significant proportion of the total biodegradative activity, particularly of xenobiotics, involves *cometabolism* (Horvath 1972; Jensen 1963). Cometabolism is a process in which metabolism of a substrate is not accompanied by nutrient assimilation or energy conversion. The substrate being cometabolized is thought to be acted upon by an enzyme having some other physiological role, but the product is not further metabolized by the organism in question. The significance of cometabolism in the degradation of xenobiotics in natural environments has rarely been determined in quantitative terms (Bourquin 1975). Generation of cometabolic products can have several consequences:

- the cometabolic products of one organism may provide a growth substrate for one or more other organisms;
- cometabolic transformations may lead to increased recalcitrance;
- they may be more toxic to microorganisms than the parent chemical.

In most conditions, the necessary microorganisms are sufficiently available in nature. Yet, they might not be present in an optimally organised way (see further).

The kinetics of biodegradation of pollutants in soil systems are usually either zero order or first order. The first case relates to nonspecific altruistic metabolism (cometabolism); the second to normal microbial conversion under substrate limiting conditions. For certain conditions, active growth of the functional species can occur and then second order kinetics are observed (Verstraete & Vanlooche 1975). The modelling of the bioremoval of the pollutant is particularly important to calculate parameters such as the disappearance time (DT-50 or DT-90).

6.2.1.2 Environmental conditions

Temperature

Temperature influences petroleum biodegradation by its effect on the physical nature and chemical composition of the oil, the rate of hydrocarbon metabolism by microorganisms and the composition of the microbial community (Atlas 1981). At low temperatures, the viscosity of the oil increases, the volatilization of toxic short-chain alkanes is reduced, and their water solubility is increased, delaying the onset of biodegradation (Atlas & Bartha 1972). Rates of degradation are generally observed to decrease with decreasing temperature; this is believed to be a result primarily of decreasing rates of enzymatic activity, or the 'Q₁₀' effect. Higher temperatures increase the rate of hydrocarbon metabolism to a maximum, typically in the range of 30 to 40 °C (e.g. phenanthrene: 37 °C), above which the membrane toxicity of hydrocarbons is increased (Bossert & Bartha 1984). The Q₁₀ value can range from 2 to 3.

Water potential

Soil water affects not only the moisture available to organisms but also the soil aeration status, the nature and amount of soluble materials, the osmotic pressure, and the pH of the soil solution. In practice, field capacity is reached at an osmotic pressure of -10 kPa

for sandy soils, -30 kPa for loam and silt loam. Generally, the microbial activity is optimal at about 3/4 of field capacity.

Figures 6.1 and 6.2 illustrate the influence of water potential respectively on the relative rates of CO₂-production and on the relative rates of N-mineralization. Roughly, rates drop to half when the watertable lowers to about 20 m below surface.

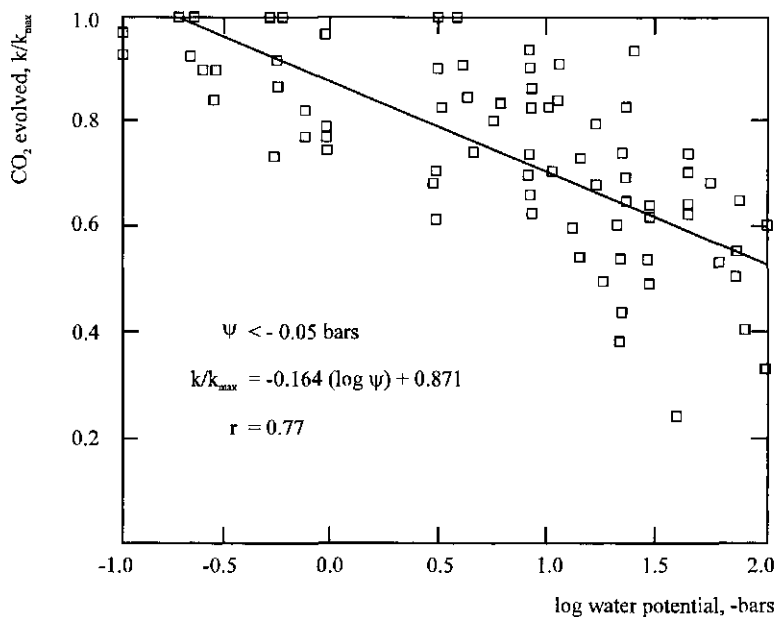


Figure 6.1. Relationship between CO₂ evolved, expressed as a relative rate, and soil-water potential. From Sommers et al. 1981.

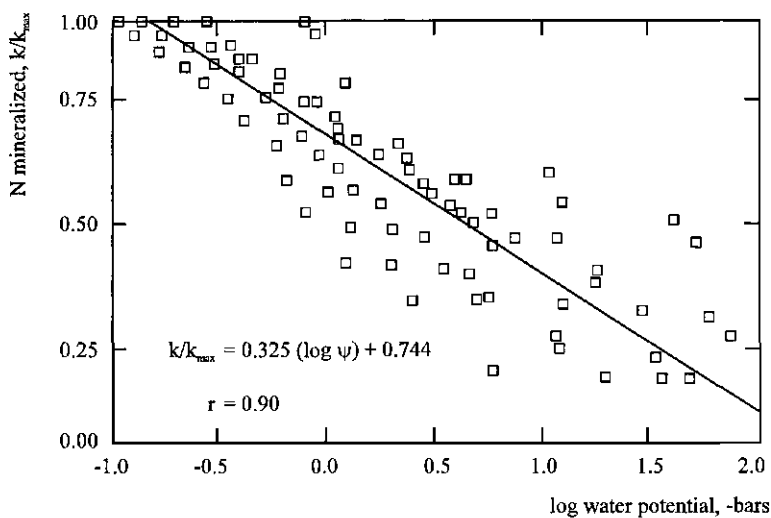


Figure 6.2. Relationship between relative rates of N mineralisation (k/k_{max}) and soil-water potential. From Stanford & Epstein (1974).

Electronacceptor

For electronacceptors, the sequence of use corresponds generally with decreasing orders of the redox potential E_h (Table 6.1).

Table 6.1. View of the redox potential of different electronacceptors. From Thauer et al. 1977; Verstraete 1989.

Electronacceptor	E_h (mV)	Type of microorganism that uses it
$O_2 \rightarrow H_2O$	+ 810	aerobic
$NO_3^- \rightarrow N_2 + H_2O$	+ 430	aerobic
$Fe^{3+} \rightarrow Fe^{2+}$	+ 200	facultative
$R_2-C=O \rightarrow R_2CHOH$	+ 200	facultative
$SO_4^{2-} \rightarrow H_2S + H_2O$	- 250	anaerobic
$CO_2 \rightarrow CH_4 + H_2O$	- 250	anaerobic
$2H^+ + 2e^- \rightarrow H_2$	- 420	anaerobic (pH = 7.0)

Remarkably, certain chlorinated hydrocarbons can be used as electronacceptors. Bosma et al. (1988) and De Bruin et al. (1991) demonstrated that aerobic bacteria, in the absence of oxygen, can use perchloroethylene and reduce it to trichloroethylene.

6.2.2 Properties of pollutants

6.2.2.1 Molecular and physico-chemical aspects

For all compounds formed by nature, there exist microbiological pathways to degrade them to their original mineral components. For most xenobiotic compounds, there are biochemical mechanisms which can alter them, or break them down completely. In Figure 6.3 a list of xenobiotic compounds that can be used as sole carbon source is given. Yet, some chemicals do not resemble at all natural compounds and do not usually induce any microbial activity. They are called *recalcitrant*, persistent or non-biodegradable compounds. This persistence can be due to the structure of the molecule or to the prevailing biotic and abiotic environmental conditions. Pesticides are in general produced via non-enzymatic reactions and their structure may just be too complex for degradation by enzymes of microorganisms. For these compounds, with xenobiotic structure, enzymes may not be present. Yet, enzymes can be induced. A bacterium for instance, capable of using propionate as carbon source and energy source, did not possess the enzyme(s) to degrade 2,2-dichloropropionate. Exposure during 120 days to a mixture of propionate and 2,2-dichloropropionate, led to spontaneous changes which resulted in a metabolic degradation of 2,2-dichloropropionate (Senoir et al. 1976). Figure 6.4 represents some recalcitrant xenobiotic compounds: several halogen substituents on the same or nearby carbon atoms as well as complex structures render molecules poorly accessible to microorganisms.

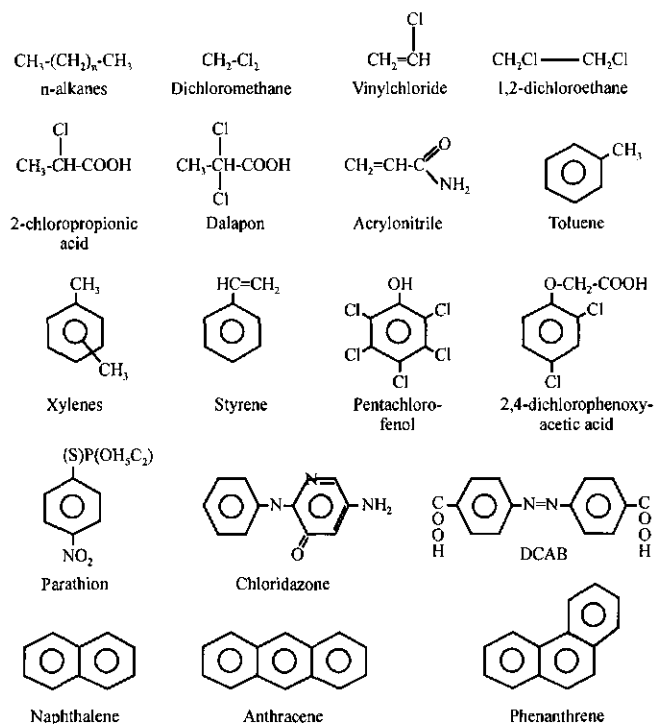


Figure 6.3. Xenobiotic compounds that can be used as sole carbon source. From D. Jansen 1993; personal communication.

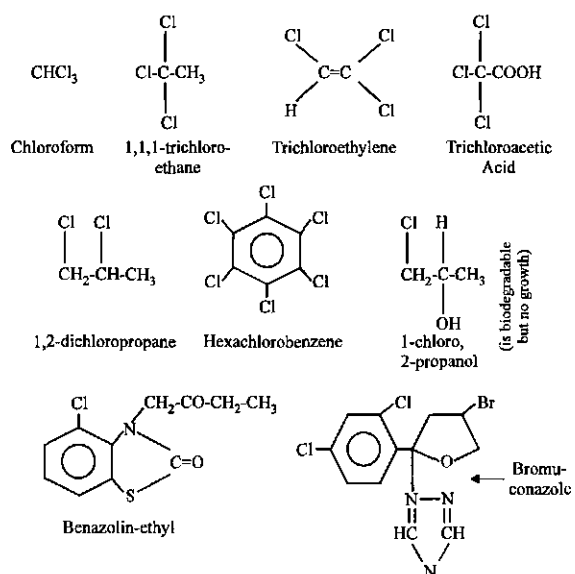


Figure 6.4. Some recalcitrant xenobiotic compounds. Attempts to isolate cultures that aerobically grow on these chemicals have failed so far. These chemicals mineralise some 5 % per year in soils.

Some rules of thumb which can be useful to judge the biodegradability of a chemical compound are given below.

Aliphatic compounds (Alexander 1965; Dias & Alexander 1971):

- short-chain ($< C_8$) and extreme long chain ($> C_{18}$) aliphatic hydrocarbons are not readily biodegraded;
- unsaturated aliphatics are more readily biodegradable than the corresponding saturated hydrocarbons; the more double bonds in the chain, the better the biodegradation;
- the more the chain is branched, the poorer the biodegradation;
- substitution with -OH and -COOH groups is positive; substitution with -Cl, -NO₂ and -SO₃H groups is negative for degradation;
- the more substituents, the stronger the positive or negative effect;
- the closer the substituent towards the active group, the greater the influence.

Aromatic compounds (Alexander & Lustingman 1966):

- substitution of the benzene ring with -OH and -COOH increases the biodegradability;
- substitution of the benzene ring with -Cl, -SO₃H, -NO₂ and -NH₂ inhibits the biodegradability;
- para-isomers are more biodegradable than ortho-isomers and the latter more than the meta-isomers;
- the more ringstructures, the poorer the biodegradation.

6.2.2.2 Bioavailability aspects

Microorganisms act, as far as known, mainly on organics dissolved in the water phase. Hence, only the fraction dissolved in water is 'bioavailable'. The following aspects in that context are of prime importance:

- a) volatilization
- b) solubility
- c) toxicity
- d) sorption-desorption.

a) Volatilization

The volatilization of an organic compound is defined by the *Henry's Law constant* (H_c). Chemicals with high H_c -values are subjected to volatilization, but the same compounds tend to have low vapor pressures and are thus subjected to significant adsorption to soil particles (Mackay et al. 1985).

H_c -values: low : $< 10^{-3}$ Pa.m³/mol (e.g. lindane; $H_c = 7 \cdot 10^{-5}$ Pa.m³/mol)
high: > 1 Pa.m³/mol (e.g. naphthalene; $H_c = 105$ Pa.m³/mol)

Lower polyaromatic hydrocarbons, such as naphthalene, are upon aeration of soils usually stripped out of the soil before microorganisms can consume them.

b) Solubility

The fate and transport of hydrophobic organic pollutants (compounds having a water solubility of less than a few parts per million) in a natural environment is highly dependent upon their sorptive behaviour. The extent of pollutant sorption is influenced by the physical and chemical composition of the sorbent, such as mineral type and organic

carbon content. Beside affecting the physical movement of pollutants, sorption can be involved directly in pollutants degradation via surface-associated chemical processes. The extent of precipitation and sorption phenomena can be significantly minimized by side reactions increasing the solubility of organic pollutants. The following parameters are important:

- a high *water solubility* (WS) infers greater mobility and renders the compound susceptible to increased biodegradation (Stucki & Alexander 1987), but it also increases its chances of having an ecotoxic effect.

WS-values: low: $< 10^{-3}$ g/l (e.g. pyrene; WS = $10^{-3.20}$ g/l); the compound is very apolar
 high: > 1 g/l (e.g. dichlorophenol; WS = 3.80 g/l); the compound is very polar

- the higher the *sorption constant* (K_d), the higher the sorption to the soil matrix, and the lower the availability for the microbiota.

The sorption constant K_d is the partition constant of the Freundlich equation and describes the partitioning of organic compounds between soils/sediments and the water phase.

$$S_{eq} = K_d \cdot C_{eq}^{1/n} \quad (1)$$

with: S_{eq} = concentration on the sorbed material (mg/g)
 C_{eq} = concentration in the aqueous solution (mg/l)
 K_d = sorption constant (is soil specific and correlated to the soil organic matter and/or the soil exchange capacity) (l/g)
 $1/n$ = constant related to the surface sorption capacity of the solid phase

Sorption isotherms of nonionic organic compounds, such as polyaromatic hydrocarbons, are often assumed to be linear (*i.e.*, $n = 1.0$) (Chiou 1989; Hamaker & Thompson 1972; Karickhoff 1984). In this case, K_d is transformed into a linear partition coefficient K_p .

The sorption constants were found to be highly correlated with the organic carbon content of soils/sediments and can be normalized to organic carbon content (OC) by the following equation (Baker et al. 1986; Karickhoff et al. 1979; Means 1980):

$$K_{oc} = K_p/OC \quad (2)$$

with: K_{oc} = sorption constant normalized for organic content
 K_p = linear partition coefficient
 OC = fraction of organic matter (%)

The K_{oc} has shown to be a unique constant for nonpolar compounds which depends on the properties of the compounds being sorbed and on the organic carbon content of the sorbent, but independent of the other sorbent properties (Karickhoff et al. 1979; Means et al. 1980).

K_{oc} -values: low: $< 10^2$ (e.g. benzene; $K_{oc} = 10^{1.90}$) ; the compound is mobile in soil
 high: $> 10^3$ (e.g. phenanthrene; $K_{oc} = 10^{4.36}$) ; the compound is quite well sorbed.

The higher the *octanol/water partition coefficient* (K_{ow} , also known as the P_{ow}), the higher the sorption constants and the higher the half-life ($t_{1/2}$) of the pollutants.

The octanol/water partition coefficient (K_{ow}) describes the ratio of compound concentrations in n-octanol to that in water at equilibrium. It provides a surrogate measure of a compound's tendency to partition between natural organic carbon in soils/sediments and the aqueous phase (water), or between lipid phases of biota and aqueous phases (Mackay & Clark 1991). For biota, the following set of values is used :

K_{ow} -values: low: $< 10^3$ (e.g. benzene; $K_{ow} = 10^{2.13}$) ; chances for biodegradation are good
 high: $> 10^4$ (e.g. chrysene; $K_{ow} = 10^{5.79}$) ; chances for biodegradation are poor

The octanol/water partition coefficient (K_{ow}) (Karickhoff et al. 1979) and the solubility of a hydrophobic organic compound (Chiou et al. 1977) seemed to be good estimators of the sorption constant K_{oc} by the following relationships.

$$\log K_{oc} = \log K_{ow} - 0.210 \quad (r^2 = 0.98)$$

$$\log K_{oc} = - 0.686 \log S + 4.273 \quad (r^2 = 0.94)$$

Wild et al. (1991) found a relationship ($R = 0.88$) between the K_{ow} and the *half-life* ($t_{1/2}$) of the compound in the environment (Figure 6.5). Compounds with a $K_{ow} > 10^6$ (e.g. corone $K_{ow} = 10^{6.1}$) are tightly bound to the organic fraction in soil, which renders them less available for biodegradation, leaching, volatilization and plant uptake.

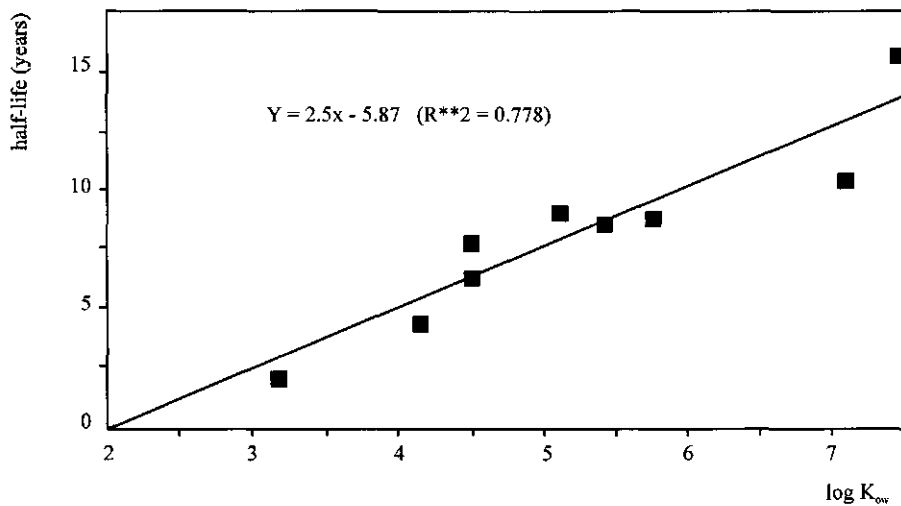


Figure 6.5. Relationship between $\log K_{ow}$ and polyaromatic hydrocarbons (PAHs) half-lives.

These compounds will be very persistent in the environment and have *half-life times of more than 10 years* (Wild et al. 1991). They also possess a high potential for bioaccumulation. Besides the half-life, an analogous parameter, the *disappearance time (DT-50)*, is described in the literature. It is distinguished from the half-life because its definition is not based on degradation kinetics. Atrazine for instance has a DT-50 value of 132 days (Hamaker 1972).

c) Toxicity

One of the problems of the extensive use of organic chemicals is the release of large numbers of various toxic chemicals in the environment. The extremely long life of such chemicals, when present in the soil, greatly amplifies the toxicity and the health risk problems in the area of contamination. This, of course is a reflection of the inability of the native microorganisms to dissimilate such compounds. The following factors are of interest in toxicological research:

- The higher the amount which dissolves in the water phase, the more direct impact the toxicant can have. Weisenfels et al. (1993) studied the toxicity of polyaromatic hydrocarbons (PAH) in soils by examining the effect of the aqueous soil extract on photoluminescent bacteria (Microtox test). The number of times the eluate had to be diluted in order not to affect the bacterial light emission was lower in soils with a high organic matter content and was also lower in soils in which had received an intensive microbiological treatment. Yet, there was no relation what-so-ever with the total amount of PAH present. The results of Microtox test on the water leachate correlated well with fish, daphnia and algae test. The overall message is that subjecting toxic soils to a period of intensive microbial activity can decrease toxicity with a factor of the order 5 to 10 and that it is advisable to make a simple water extract and do a Microtox test, rather than to rely on theoretical principals.

- The higher the octanol/water partition coefficient, the higher potential for bioaccumulation of pollutants, the higher the *bioconcentration factor (BCF)*. Compounds with a low solubility in water usually have an affinity for fatty tissues and thus can be stored and concentrated in tissues with a high lipid content. Such hydrophobic compounds may persist and demonstrate cumulative toxicity to organisms. The toxicity of such compounds can be predicted by the bioconcentration factor (BCF) (Ernst 1988).

BCF-values: potentially toxic if $BCF > 100$ (e.g. naphthalene; $BCF = 100$)

Ernst (1988) found a significant relationship between the bioconcentration factor and the octanol/water partition coefficient for hydrophobic compounds.

$$\log BCF = 0.79 \log K_{ow} - 0.40 \quad (r^2 = 0.96)$$

- The lower the *effective concentration (EC50)* and the *no observed effect concentration (NOEC)*, the higher the potential that a compound is toxic. The EC50 is the concentration of a compound causing a 50 % decrease of a specific activity (e.g. behavioural or physiological) under defined conditions of exposure time (e.g. 24 or 48 h) and test temperature. The NOEC or the no observed effect concentration is the maximum concentration of a test compound that produces no statistically significant harmful effect on

test organisms compared to controls in a specific test.

Values: For pesticides, the following set of values in water is commonly used (personal communication):

$$EC50 < 0.1 \mu\text{g/l} \xrightarrow{1/10} \text{acute NOEC} < 0.01 \mu\text{g/l} \xrightarrow{1/10} \text{chronic NOEC} < 0.001 \mu\text{g/l}$$

d) Sorption-desorption

The distribution of pollutants in the soil is often very irregular. Many compounds are hydrophobic and tend to sorb to soil aggregates (*e.g.* clay minerals and organic matter). It also seems that in time organic pollutants become an integral part of the organic humic matrix. For instance, chloroanilines form covalent bonds with humic acids. In addition, soil pollution with large, irregular particles can take place.

It is generally accepted that the uptake of compounds proceeds via the water phase. Two kinds of behaviour are distinguished: pollutants with Freundlich behaviour and pollutants with slowly-reversible behaviour.

Freundlich equation

The sorption capacity of organic compounds is described in literature by the Freundlich equation. Sorption isotherms of nonionic organic compounds, such as polyaromatic hydrocarbons, are often assumed to be linear (*i.e.*, $n = 1.0$) (Chiou 1989; Hamaker & Thompson 1972; Karickhoff 1984). When determined experimentally, n usually is situated within the range 0.7 to 1.1 for these compounds (Hamaker & Thompson 1972). An example of such a fit with n equal to 1, is presented in Figure 6.6.

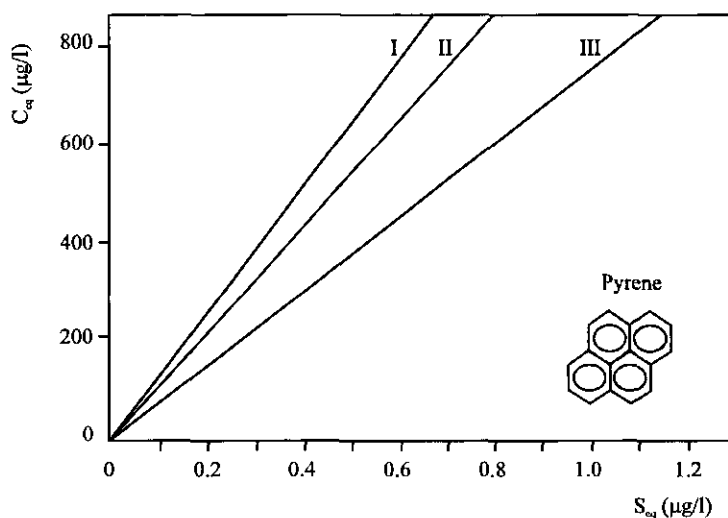


Figure 6.6. Representative sorption isotherms for pyrene in three different soil types with, resp. % clay 31.0 in I; 55.2 in II; 68.6 in III (Means 1980). S_{eq} = concentration of the sorbed material ($\mu\text{g/l}$); C_{eq} = concentration of the aqueous solution ($\mu\text{g/l}$). The more clay, the more sorption.

Slowly-reversible fraction

In practise, it seems that the sorption of many pollutants can not be described by the Freundlich equation. Pignatello & Huang (1991) described the sorption process of atrazine and metalochlor in soils as being composed out of two steps. A *labile fraction* (between 5 and 60% of the total amount) behaved according to the Freundlich equation. Beside this fraction, another fraction of the soil pollutants, the *slowly-reversible fraction* (SRF) was found to be present. This fraction responds very slowly to the aqueous phase. For this fraction, the sorption constants (K_d) are 3 to 42 fold higher than these of the labile fraction. For landfarming this SRF is mineralized at a total rate of 4.5 g hydrocarbons/kg air-dried soil per year in an untreated soil by a temperature of 20 °C, while the labile fraction was mineralized at a total rate of 20 g hydrocarbons/kg air-dried soil per year (Van Eyck et al. 1990).

In general, slowly-reversible sorption is the result from kinetic limitations of the sorption process itself or of diffusion-limited transport of pollutants through soil structures (Brusseau & Rao 1989; Pignatello 1989). Such soil structures may include the interstitial micropores of particle aggregates (*e.g.* clay) or the three dimensional matrix of natural organic matter (Bouchard et al. 1988; Nkedi-Kizza et al. 1989).

Slowly-reversible sorption contributes to the persistence of contaminants by hindering transport and reducing availability to degradative microorganisms (Karickhoff 1980; Pignatello 1989). There is also evidence that slowly desorption reduces the bioavailability of contaminants to higher organisms (Landrum 1989). Actual research concentrates on reducing the SRF by introducing artificial or microbial created *cosorbates* in the soil. Pignatello (1990, unpublished data) showed that the sorption constants of halogenated hydrocarbons were depressed by a factor three in the presence of an excess of a nonpolar cosorbate. McGinley et al. (1989) also observed competitive effects in a soil between hydrophobic organic compounds. However, the conclusion from these studies is that the competitive effects, although possible, are likely to be small when the cosorbates are present at similar concentrations.

6.2.3 Persistent pollutants

Polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), pesticides and explosives have become organic contaminants in soils. The maximum concentration allowed, according to the Dutch A-level, is given in Table 6.2. For these groups of contaminants, considerable information has been gathered about their respective biodegradation pathways and the microorganisms involved. Yet, field data on successful acceleration of biodegradation are thus far scarce.

PAHs

PAHs were produced by nature (*e.g.* forest fires), sediment diagenesis, geological phenomena (*e.g.* volcanos, tar pits, seepage from rock formation) long before man evolved. Thus, they are 'familiar' inputs to the soil ecosystem. However, there is clear evidence that soil PAHs content has increased significantly during the last five decades as a result of industrial or agricultural activities. PAHs are generally formed by pyrolysis or incomplete combustion of organic substances at temperatures between 500-700 °C. They are generally associated with ash particles, tar, smoke and soot. Actually, there is surprisingly little information on the significance of PAHs in relation to soil quality or their persistence and biodegradation, their behaviour in soil-plant

systems and their disappearance from the soil surface layer.

Biodegradation seems to be the key process resulting in PAH losses from soils (Park et al. 1990; Wild et al. 1990). The importance of biodegradation is well established for low molecular weight PAH compounds (\leq 3-ringed PAHs). Anthracene and phenanthrene, for example, can act as sole sources of carbon for microorganisms, while cometabolism of higher molecular weight compounds ($>$ 3-ringed PAHs) has been described (Heitkamp & Cerniglia 1987).

Tabel 6.2. A-values for organic compounds in Dutch soils.

Substance	Reference values at 10 percent organic matter. Amounts of substance allowed per kg dry soil.
<i>a) Halogenated hydrocarbons and choline esterase inhibitors</i>	
endrin; hexachlorocyclohexane	
tetrachloroethane; tetrachloromethane; trichloroethane trichloroethylene; trichloromethane	< 10 μ g
PCB IUPAC numbers 28 and 52	
chloropropene; dichlorobenzene; dichloronitrobenzene; heptachloroepoxide; hexachlorobenzene; hexachlorobutadiene; hexachloroethane; monochloronitrobenzene; tetrachlorobenzene; tetrachloroethylene; trichlorobenzene	
aldrin; dieldrin	< 10 μ g
azinphos-ethyl; azinphos-methyl; chlordane; disulfoton; endosulfan; fenitrothion; parathion(and -methyl); trifluralin; triazophos	
PCB IUPAC numbers 101, 118, 138, 153 and 180	
DDD; DDE; pentachlorophenol	100 μ g
<i>b) Polynuclear aromatic hydrocarbons (PAH)</i>	
chrysene; naphthalene	< 10 μ g
anthracene; benzo(a)pyrene; fluoranthene; phenanthrene	< 100 μ g
benzo(a)anthracene	< 1 mg
benzo(k)fluoranthene; benzo(ghi)perylene; indeno(1,2,3-cd)pyrene;	< 10 mg
<i>c) Mineral oil</i>	
Total	< 50 mg
heptane; octane	< 1 mg

The aerobic biodegradation of lower molecular weight polycyclic aromatic compounds is well understood. The initial step in the degradation is an oxidation reaction (Figure 6.7). Dihydroxylated derivatives are formed by incorporation of molecular oxygen to the aromatic nucleus by a dioxygenase. Further oxidation of the dihydrodiols leads to the formation of catechols that are substrates for other dioxygenases. The latter bring about enzymatic cleavage of the aromatic rings. Cleavage of the catechol can proceed by an ortho cleavage (between two carbon atoms with a hydroxyl group) or by a meta cleavage (between a carbon atom with a hydroxyl group and the adjacent carbon atom without a hydroxyl group).

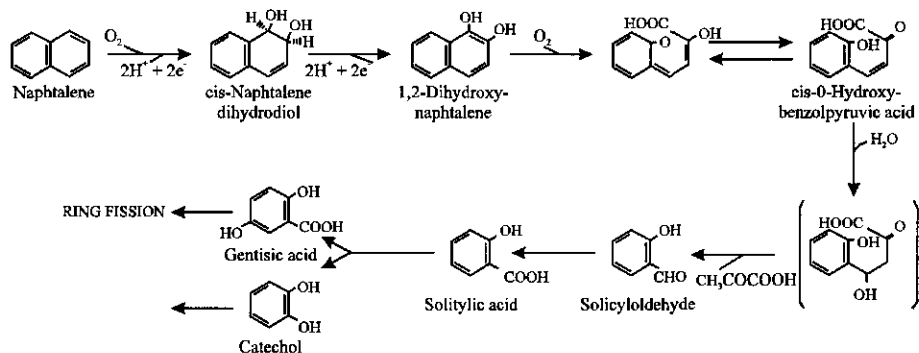


Figure 6.7. The initial reactions of naphthalene biodegradation. From Smith 1990.

Persistence of PAHs in soils varies markedly, and generally increases with increasing molecular weight. The *half-life* ($t_{1/2}$) is assumed to be a good parameter to describe the persistence of PAHs. It can be calculated from the line of best fit of the soil time trend data to the first order equation (Figure 6.5). The greater the number of rings of the PAHs structures, the slower the decline of compound losses with time and thus the greater the half-life. Because the high molecular weight compounds are more recalcitrant, their loss from soil can be followed more accurately. Average half-lives for benzo(ghi)perylene (6 ring PAH) and coronene (7 ring PAH) are about 10 years, while average half-lives for naphthalene (2 ring PAH) and phenanthrene (3 ring PAH) are less than three years.

Because of their high hydrophobicity and low solubility, PAHs occur in the environment mainly attached to particles that decrease their biodegradation. It is known that pure cultures of bacteria can use naphthalene and phenanthrene in the dissolved state only (Wodzinski & Bertolini 1972; Wodzinski & Cole 1974) and therefore the dissolution of solid PAH is a prerequisite for growth. The influence of PAH solubility on the growth of microorganisms was tested by Volkering et al. (1992). They inoculated a *Pseudomonas* strain in batch cultures with equal amounts of naphthalene with different particle diameters and followed the biomass concentration in time. The growth rate of the strain increased with decreasing diameter of substrate particles or increasing available crystal surface area. Thus, the smaller the diameter of the substrate particles, the higher the solubility potential. This can explain the often-observed linear, instead of exponential growth, of bacteria and yeasts on slightly soluble substrates (e.g. McLee &

Davies 1972; Prokop et al. 1971; Stucki & Alexander 1987; Thomas et al. 1986).

Weisenfels et al. (1993) monitored the degradation of so-called soil-borne PAHs in soils of petrochemical sites (gas work sites). They found hardly any degradation over months of time. When they however extracted these soils with toluol in a Soxhlet apparatus, and re-added the PAHs to the soil, they found that in the subsequent month about 2/3 was biodegraded (Figure 6.8). Indeed, the PAHs were made bioavailable, but as time progressed they became again more tightly bound to the humus present in the soil. Indeed humus is considered as a high-molecular, mainly hydrofobic, matrix present in the soil.

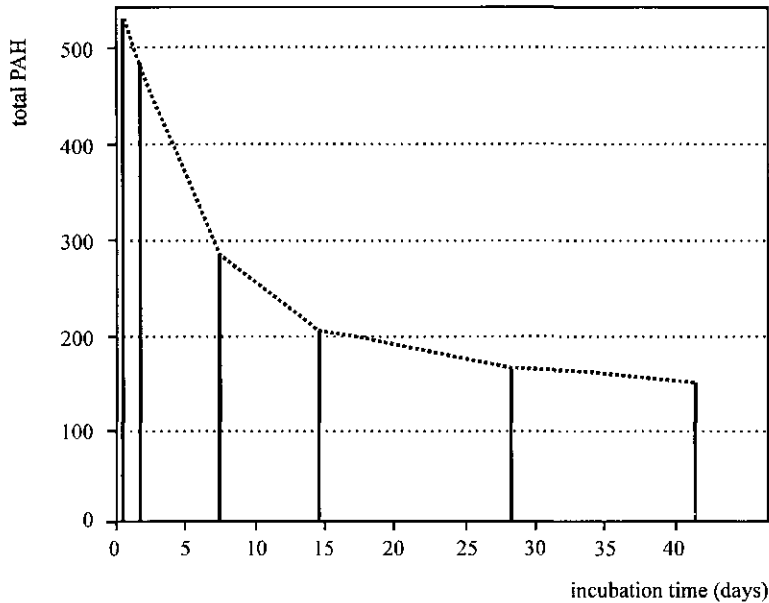


Figure 6.8. Degradation of PAHs in soil after extraction and recontamination of the soil with the extracted PAHs. Note that in the original soil the PAHs were completely inert. From Weisenfels et al. 1993.

Pesticides

Pesticides are chemical agents designed to control a specific pest or a variety of pests detrimental to man, his domesticated animals, cultivated crops, or the flora and fauna which man endeavours to maintain. Modern pest-control research has been concerned with the findings of potent organic compounds to control either a broad or a narrow spectrum of pests, chiefly insects, weeds, and plant pathogens.

The biodegradability of pesticides is of great practical importance since the toxicity of these chemicals is rarely limited to the target organism but often extends to non-target species, including man. Should the chemical be resistant to biodegradation or detoxification, its life in nature may be long, and its concentration could increase with repeated application until levels harmful to non-target organisms are reached. The biodegradation proceeds by hydrolysis of the solvated or adsorbed molecule (*e.g.* organophosphate insecticides) or from microbially and photochemically induced degradation (*e.g.* organochlorine insecticides). Among these alternatives, microbial degradation appears

to be the most common degradation pathway, but its efficiency depends on environmental conditions. Less information is available about the tertiary degradation of pesticides (complete breakdown to inorganic endproducts, *i.e.* CO_2 , NH_4^+ , minerals). Only some rule of thumbs are available. Pesticides with a BOD_5/COD ratio greater than 0.5 are considered as rapidly biodegradable. These pesticides also produce a net CO_2 -production of more than 60% of the theoretically maximum. Pesticides that not apply to these criteria have to be further tested for their biodegradability. This can be done by a C-14 labelled study of minimum one year. Pesticides which have mineralization rates of less than 10% per year, have to be further tested for ecotoxicity; both of the original and all major derivates have hereby to be taken into consideration.

In practice, it seems that the primary degradation of pesticides (altering the identity of the chemical) occurs very fast, but the derivative compounds are considerably more persistent than the parent pesticides. This can be illustrated in the following examples:

- A sulfanylureum is primary degraded very fast to pyridinyl-pyrimidinamines (Figure 6.9), resulting in a half-life of 10-20 days. The pyridinyl-pyrimidinamines however, are very recalcitrant and decrease by aerobic degradation only 5-6% per year.

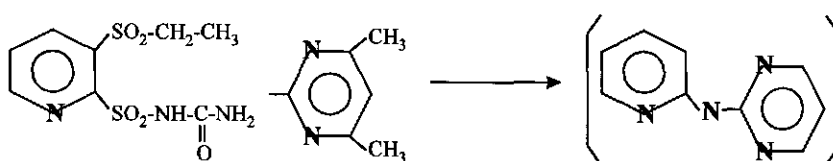


Figure 6.9. Primary degradation of a sulfanylureum pesticide.

- A biphenyl-ether pesticide is hydrolyzed very fast in the soil (Figure 6.10). The residue is strongly adsorbed by the soil organic matter and is tertiary degraded at a rate of a few percent per year. Besides, the residue can be transformed to nitroso and hydroxylamine derivates, which are very toxic, even at low concentrations.

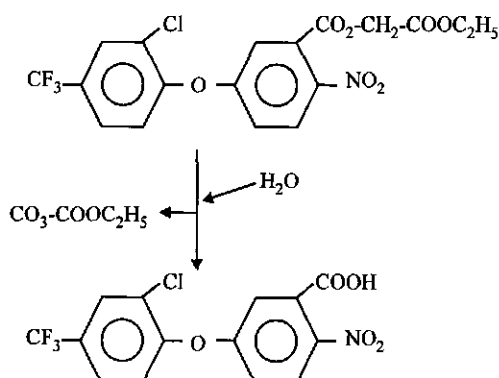


Figure 6.10. Primary degradation of a biphenyl-ether pesticide.

Explosives

The compound TNT (2,4,6-trinitrotoluene) is the predominant conventional explosive used by military forces (Williams et al. 1988). Unfortunately, past practices for the disposal of TNT-containing wastes generated during the production of TNT and military activities which use TNT have led to soil, sediment and water contamination. This is of concern because exposure to TNT is known to cause pancytopenia, a disorder of the blood-forming tissues characterised by a pronounced decrease in the number of leukocytes, erythrocytes, and reticulocytes in humans and other mammals (Harris & Kellermeyer 1970). Also, TNT is toxic to fathead minnows and bluegills at concentration 2 to 3 $\mu\text{g/ml}$ (Hudock & Gring 1970).

Recent studies have shown that the wood-rotting fungus, *Phanerochaete chrysosporium*, possesses remarkable biodegradative properties (Arjmand & Sandermann 1985; Bumpus 1989; Hammel et al. 1986). This fungus is one of the few microorganisms able to degrade lignin. *Phanerochaete chrysosporium* is also able to degrade a wide variety of pollutants such as DDT {1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane}, lindane (1,2,3,4,5,6-hexachlorocyclohexane), chloroanilines and polychlorinated biphenyls and also TNT (Fernando et al. 1990).

Recent studies about remediation of explosives have been done by Williams & Myler (1990) by composting the contaminated soil in an aerated static pile (see section 6.3.3.2). The degradation proceeded according to first order kinetics with a DT-50 of ca 20 days.

6.2.4 Kinetics

6.2.4.1 Chemical

The speed of reaction is dependent on the activation of the molecules, alone or in group, by collision:

$$v = -\frac{dC}{dt} = k \cdot C^n \quad \text{or} \quad v = \frac{dy}{dt} = k(C_0 - y)^n$$

After integration this results in:

$$C = C_0^{1-n} + (n-1)k \cdot t \quad \text{and} \quad y = C_0 - \{C_0^{1-n} + (n-1)k \cdot t\}^{1/1-n}$$

with: C = concentration of substrate at moment t (g/l)

n = exponent

k = rate constant (1/day)

y = amount of substrate converted (g/l)

C₀ = initial amount of substrate available (g/l)

Quite important in this context are the following parameters (for n = 1)

$$\text{DT-50} = \frac{C_0^{1-n} \{(0.5)^{1-n} - 1\}}{(n-1) k}$$

i.e. the time necessary for removal of 50% of the initial amount of substrate; and

$$DT-90 = \frac{C_0^{1-n} \{(0.1)^{1-n} - 1\}}{(n-1) k}$$

i.e. the time necessary for removal of 90% of the initial amount of substrate.

Note that DT-50 and DT-90 are dependent of C_0 when n is different from 1.

For first order reaction, one often refers to the half-life of a chemical ($t_{1/2}$; is independent of C).

6.2.4.2 Biological

The general model is based on two principles.

Growth occurs according to the Monod principle:

$$\frac{dS}{dt} = \frac{q_{max} \cdot X \cdot S}{K_s + S}$$

with: X = biomass (g DW/l)

DW = dry weight

S = soluble substrate (g/l)

q_{max} = maximum amount of substrate removed per unit biomass and per unit time (g bCOD/g DW.d)

K_s = substrate affinity (g/l)

Biomass increase is directly related to substrate removal:

$$X = X_0 + Y (S_0 - S)$$

with: Y = cell yield coefficient

X_0 = biomass at zero time (g DW/l)

S_0 = soluble substrate at zero time (g/l)

Substitution of the Monod equation in the latter equation and integration gives:

$$- \frac{1}{q_{max}} \left(- \left(\frac{K_s}{X_0 + Y \cdot S_0} + \frac{1}{Y} \right) \ln (X_0 + Y \cdot S_0 - Y \cdot S) + \left(\frac{K_s}{X_0 + Y \cdot S_0} \right) \ln \left(\frac{S \cdot X_0}{S_0} \right) + \frac{1}{Y} \ln X_0 \right) = t$$

6.3 Technical aspects

There exists a variety of physicochemical techniques for the cleanup of contaminated soil and groundwater. These include excavation followed by incineration or chemical treatment, in situ vapour-phase stripping of volatiles and the extraction of contaminated water for treatment with activated charcoal, resins or chemical agents. A view of the application possibilities of the different cleaning techniques is given in Table 6.3. All these processes may be effective if correctly applied and operated, but they may prove expensive if large-scale excavation or long-term treatment is necessary. Furthermore,

certain approaches may not result in total decontamination. As result there is growing interest in the use of microbial biodegradation activity for the treatment of contaminated soil and ground water, either alone or in collaboration with one of the physicochemical techniques. The aim of microbially-based clean-up methods is to provide optimum environmental conditions either in situ or by means of bioreactors, so that biodegradation can proceed at the maximum sustainable rate.

Table 6.3. View of the different clean-up possibilities and the application possibilities for different pollutants. From Spruijtenburg 1992.

Technique	Pollutants					
	Aliphatics Aromatics	PAHs	Chlorinated hydrocarbons volatile	Chlorinated hydrocarbons not volatile	Heavy metals	cyanides
steamstripping	+	-	+	-	-	-
evaporation (300 °C)	+	+/-	+/-	-	+/-	+/-
evaporation (700 °C)	+	+/-	+	+/-	-	+
burning (> 700°C)	+	+	+/-	+/-	-	+
extraction	+	+/-	+	+	+	+
flotation	+	+/-	+	+	+	+
biological	+	+/-	+/-	+/-	-	-

+ : positive result; - : negative result.

6.3.1 Enhancement of biodegradation

The biodegradation of pollutants can be enhanced by providing good environmental conditions for the microbial soil community. According to De Borger et al. (1978), biodegradation rates in contaminated soils can be enhanced by the following factors :

C/N/P balance

When soils are polluted with hydrocarbons, its nutritional balance and particularly C/N/P-ratio is completely disturbed.

To optimise the C/N/P balance to 100/10/1, inorganic nitrogen (NH_4NO_3) fertilizers, and inorganic (KH_2PO_4) or organic (glycerolphosphate, triethylphosphate) phosphate fertilizers can be used. De Borger et al. (1978) found, that in the presence of this fertilizers, the rate of hydrocarbon breakdown increases with a factor of about 2. Similar results have been reported by Atlas & Bartha (1973) and Jobson et al. (1974). The effect of nutrients added in varying quantities on the biodegradation of crude oil in soil is given in Figure 6.11. The amount of nutrients was based on a layer thickness of 25 cm.

Bioremediation has been successfully applied as biotechnological approach for the treatment of the 1989 Alaskan oil spill in Prince William Sound, Alaska, by the Exxon Valdez. A fivefold increase in rates of oil biodegradation was measured after the application of three types of nutrient supplementation: a water-soluble (N/P:23/2 garden fertilizer formulation), a slow release (isobutylenediurea and Customblen) and an oleophilic (Inopol EAP 22) fertilizer (Atlas 1993).

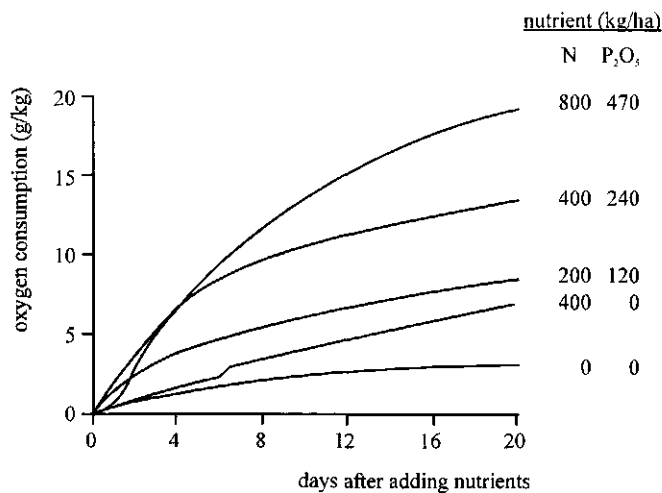


Figure 6.11. Effect of nutrients added in varying quantities on the biodegradation in soil. The cumulative oxygen consumption of soil polluted with crude oil as function of time is given. From Harmsen 1992.

pH

The soil pH is important, because at low pH-values fungi are favored, while at high pH-values actinomycetes grow better. Fusey et al. (1975) and De Borger et al. (1978) found that at neutral pH, bacteria as well as actinomycetes and fungi can be active and increase the rate of biodegradation with a factor 1.5 to 2, compared to a pH of 4.2 and 9.0. Dibble & Bartha (1979) found that in a naturally acidic soil the highest rate of oily sludge biodegradation was achieved when its pH was augmented to 7.8 by addition of CaCO₃.

Temperature

Soil temperature has a major influence on the rate of oil biodegradation. Temperatures, and particularly temperature fluctuations, largely influence microbial degradation in soils. Vanlooche et al. (1975) reported hydrocarbon degradation between -2 and 72 °C. Data by Dibble & Bartha (1979), Jensen (1975) and Kincannon (1972) all indicated that a maximum oil biodegradation in soils occurs between 20 and 30 °C. Biodegradation becomes insignificant under 5 °C and at 13 °C it is only about half the rate observed between 20 and 30 °C. For rapid microbial clean-up, the soil temperature should be kept above 15 °C. Generally, in the range 10-40 °C, a Q₁₀-factor of 2 to 3 is applicable.

Soil moisture content

Soil water affects not only the moisture available to organisms but also the soil aeration status, the nature and amount of soluble materials, the osmotic pressure, and the pH of the soil solution. The moisture content may therefore influence the availability of the compound and thus the rate of biodegradation. This is demonstrated in Figure 6.12, in which the effect of moisture content on the biodegradation rate of α -hexa-chlorocyclohexane (HCH) in soil at different temperatures is given (Bachmann 1987). The aerobic

biodegradation of organics in soil is greatest when the moisture content is 50 to 70% of the soil water holding capacity (Dibble & Bartha 1979). On a percent weight basis, the favorable moisture content may vary from 10-30% of the soil weight depending on the soil texture. Extremely wet soils decrease biodegradation by limiting oxygen availability.

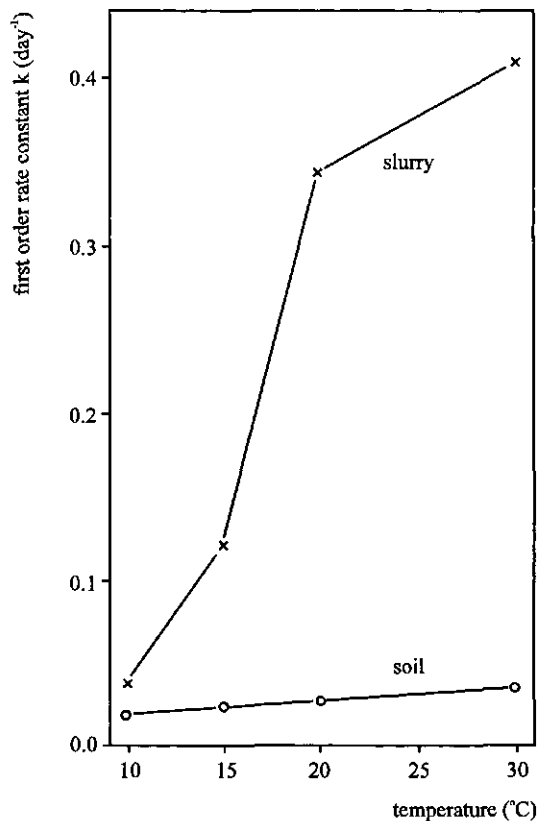


Figure 6.12. Effect of moisture content at different temperatures on the first-order rate of α -HCH mineralization in soil (slurry: 100 g/l, dry weight; soil: 20% moisture, w/w).

Cosubstrates

For soils and river sediments contaminated with mixtures of low molecular weight hydrocarbons adding fertilizers and ensuring an adequate supply of oxygen is mostly all that is needed to stimulate the degradation of the pollutants. For some pollutants the degradation can be stimulated by adding cosubstrates. Effective cometabolic transformations of chlorinated aliphatic hydrocarbons such as trichloroethylene by bacterial oxygenase systems have been demonstrated by aerobic microorganisms growing on methane, ethylene, propane, toluene, phenol, cresol, ammonia and isopropene (Hopkins et al. 1993).

Aeration (oxygen), alternative electronacceptors

Because the initiation of the hydrocarbon degradation is based on the insertion of molecular oxygen, aeration is very important. In soils, aeration of the upper soil layers, can be improved by ploughing, discing and air injection. The absence of oxygen in the soil is often limiting the biodegradation. When hydrocarbons migrate into the subsoil, microbial degradation will deplete the oxygen in that zone and create anoxic circumstances. In these cases, alternative electronacceptors (SO_4^{2-} , NO_3^- , NO_2^- , Fe- and Mn-oxides) can enhance the biodegradation if the organisms have the appropriate enzyme systems.

Surfactants

One of the major problems in hydrocarbon metabolization is to make the hydrophobic carbon source accessible to the microbial cell. The high insolubility of alkanes can be enhanced by the use of surfactants and biosurfactants. During growth, hydrocarbon utilizing microorganisms often produce very effective and efficient biosurfactants, which create emulsions to increase the interfacial area between the pollutants and the aqueous phase. (Bio)surfactants reduce the surface tension and form a microemulsion of the displaced pollutants (oil) and the miscible phase. Mueller et al. (1990) reported a complete biodegradation of fluoranthene (PAH) by pure cultures of *Pseudomonas paucimobilis*. This was partially attributed to the use of Tween 80 as surfactant in the medium, that increased the bioavailability of the substrate. The effect of detergents on the residual concentration (400 mg oil/ kg dry soil) was studied on soil from a landfarming experiment, polluted with gas oil (Nieveen & Verheijen 1988; unpublished data). The results are given in Table 6.4.

Table 6.4. Effect of detergents (0, 0,2 and 2,0 g/l) on the solubility of a residual fraction oil in soil. One liter of detergent solution has been shaken with 250 g of soil.

Detergent (g/l)	Mineral oil in water (mg/l)		
	0	0.2	2
serqua 710	0.4	0.5	4.3
dobanol 91-5	0.4	1.4	11.1
dobanol 91-6	0.4	1.6	39.4
dobanol 91-8	0.4	1.2	15.1

The solubility of the residual concentration of the remaining gas oil in soil had been increased by detergents. The highest solubility was obtained with Dobanol 91-6.

Inocula

In recent years, a lot of discussion has been raised about 'bioremediation' of soils and sediments. One generally focusses on the addition of specific microorganisms. A few generalizing remarks can be made in this respect. Only for very special pollutants under special conditions, it appears necessary to inoc-ulate with specific organisms. Cases where effective stimulation due to inoculation have been reported are :

- degradation of the pesticide kelthane (DDT-analogue) in soil by a lab-strain of *Pseudomonas aeruginosa* (Golovleva et al. 1982);
- degradation of 2,4,5 T in soil by inoculation with a strain of *Pseudomonas cepacia* (Catterjee et al. 1982);
- degradation of chlorobenzenes in soil suspensions by inoculation with lab-adapted *Pseudomonas* sp. (van der Meer et al. 1987);
- degradation of PCBs by inoculation with natural occurring *Pseudomonas paucimobilis* cloned with a broad substrate specificity PCB-degradative plasmid and a special detergent as carbon source for that *Pseudomonas* (the so-called field application vector concept) (Lajoie et al. 1993).

These cases refer to lab-scale experiments; no cases at field scale are known to us. The bottleneck appears to be the introduction of the strains in the environment; indeed the autochthonous species tend to rapidly eliminate the newly introduced strains. Therefore, focus is at present on the following approaches:

- introduction of capable strains, in association with a consortium of cooperative strains, preferably after partial or full elimination of the existing microbiota;
- introduction of genes (or plasmids) which are subsequently taken up and used by the natural soil microbiota;
- introduction of specific substrate analogues (and or genes) in order to 'assist the breeding' of well adapted species and species associations.

All of these approaches are currently under intensive development.

6.3.2 In situ treatment

In situ treatment involves the controlled management and manipulation of microbial processes in the whole of the soil profile. This requires an understanding of the microbial processes needed to degrade the pollutants and of the soil's physical and chemical environmental effects on the microbial processes. In situ bioremediation of pollutants is gaining interest because of several reasons. It is a less expensive technique as excavation and transport costs are avoided. Furthermore, the contaminants are degraded to harmless inorganic products and no toxic wastes should remain after biological clean-up. In situ systems often utilize aerobic processes and involve the addition of oxygen, nutrients and specific microorganisms, to the subsurface area of contamination. The in situ techniques can be divided in:

- pump and treat
- steam stripping
- air stripping
- electroreclamation.

The technique that should be used depends on the physical properties of the pollutants, the initial concentration of the pollutants, the required final concentration and the physico-chemical characteristics of the soil.

The technique with most full scale experiences is that of pump and treat. This in situ (bio)remediation process consists usually of the recovery of the contaminated groundwater and its consequent treatment in a surface (bio)reactor, followed by reinjection upstream of the contaminated area. Before injection, nutrients and oxygen can be mixed with the water to enhance the subsurface active microbiota. The technique is shown in Fig-

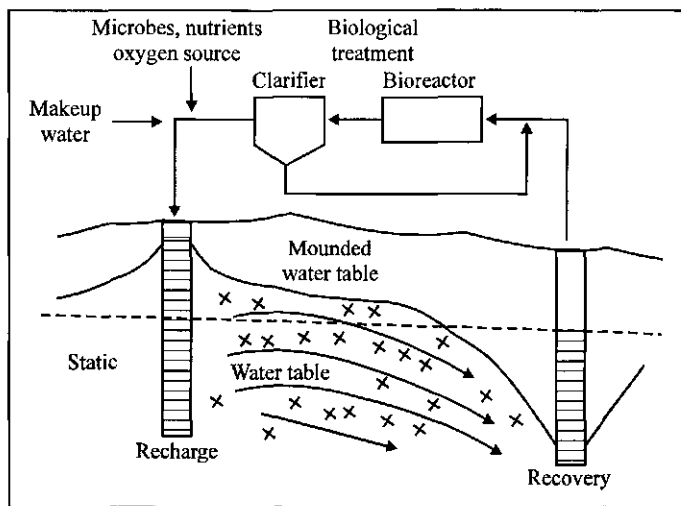


Figure 6.13. *In situ* bioreclamation using recharge wells or trenches. From Bourquin 1989.

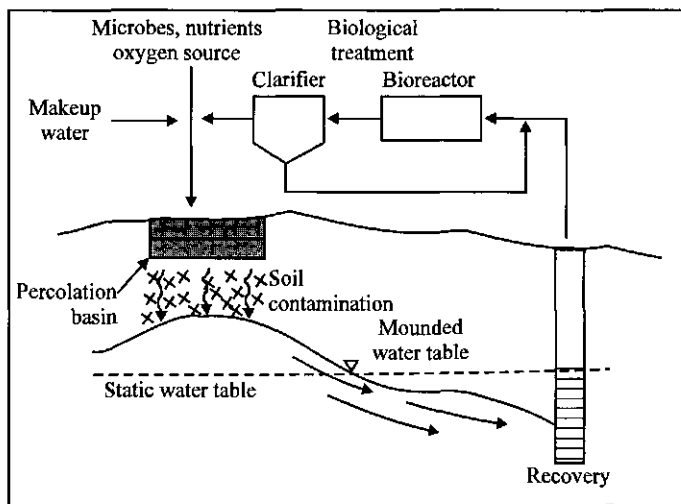


Figure 6.14. *In situ* bioreclamation using infiltration technique. From Bourquin 1989.

Figure 6.13. The soil should have a moderate hydraulic permeability ($K > 1$ m/d). Biological degradation of subsurface contaminants can be accomplished through delivery of an oxygenated nutrient solution to the zone of contamination. Contaminated soils above the water table can be treated by artificially raising the ground water table. Water is cycled through the subsurface using a series of recovery and recharge trenches or wells (Figure 6.13). Water may be oxygenated by sparging with air or pure oxygen or by adding hydrogen peroxide. The supplemented recharge water, which may be delivered through wells or trenches, enhances the biodegradation of hydrocarbons. The system

can be 'cycled' by reversing the role of the recharge and discharge wells to the target zones, if contamination exists above the existing water table (Figure 6.14). A significant problem that may be encountered with this extraction processes is that many organic compounds may strongly sorb to soil and will be difficult to remove (Morgan & Watkinson 1989). Mobilisation of contaminants by percolation with detergents may cause soil pore blockage due to precipitation; furthermore, the detergents will themselves require biodegradation (Lee et al. 1987).

Microbial clean-up by enhancement of anaerobic degradative activity in situ has received less study. A trial under laboratory conditions using a sandy clay soil containing trichloroethane demonstrated that continuous supply with inorganic nutrients and ethanol resulted in the selection of a methanogenic community capable of complete degradation of the contaminant (Boyer et al. 1987). Under field conditions, soil flooding has been shown to enhance degradation of a variety of compounds including DDT {1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane} (Castro & Yoshida 1974), 2,4-D (2,4-dichlorophenoxyacetic acid)(Yoshida & Castro 1975) and the pesticide toxaphene (Mirsatari et al. 1987). The use of induced denitrifying conditions to enhance anaerobic degradation of halogenated organics has not been reported. However there is a report of nitrate-supplementation resulting in enhanced degradation of mineral oil contamination in an aquifer (Gottfreund et al. 1985).

Recent information about the in situ extraction technique had been reported by the firm Ecova, Italy. The firm is operating three in situ systems to remediate petroleum-contaminated soils and groundwaters:

- In the largest bioremediation project, nearly 1 million m³ of total petroleum hydrocarbons (TPH)-contaminated groundwater and 50,000 m³ of soil are being treated using in situ bioremediation. Initial concentrations of TPH average 2,660 ppm. This concentration is being reduced to 200 ppm TPH in soil and 15 ppm in groundwater in 3 years.
- In south California, a major refinery has contaminated soils with diesel and heavy hydrocarbons. Approximately 30,000 m³ of soil is treated using an in situ extraction treatment system. The total TPH concentration is in the order of 100,000 ppm and the clean-up level is 10,000 ppm. The treatment time is in the order of 20 years.
- An other in situ project is the biodegradation of trichloroethylene (TCE) in subsurface soils and in groundwater in California. The process uses aerobic degradation principles for the introduction of nutrients, oxygen and naturally occurring bacteria into the subsurface. It is based on the enrichment of specific TCE-degrading bacteria and the introduction of these bacteria into the contaminant plume. The amount TCE decreased in the groundwater from 3,000 ppb to less than 100 ppb in only seven days. A further decline to a mean value of 78 ppb was observed over the next 10 days.

The Exxon Valdez spill clean-up is an excellent example of the treatment for the clean-up of oil pollutants from shorelines. The application of three fertilizers (see section 6.3.1; C/N/P balans) to field test plots stimulated the biodegradation so that the surfaces of the oil-blackened rocks on the shoreline turned white and were essentially oil-free within 10 days after treatment. A fivefold increase in rates of oil biodegradation typically followed after fertilizer application.

6.3.3 Ex situ treatment

6.3.3.1 Landfarming

The most widely applied biological treatment method is landfarming (Maag 1990). In this 'low-tech' treatment method, excavated polluted soils are mixed with microorganisms and evenly spread out on the so-called landfarm (Figure 6.15). Farming techniques, such as fertilizing (optimal C/N/P = 100/10/1) and plowing are used to stimulate the microbial activity in the soil. In landfarming, the organic pollutant is aerobically converted to carbon dioxide, water and biomass. Different soil types can be treated; clay and silty soils are difficult to handle due to the presence of large agglomerates. Landfarming can also be used as an in situ technique.

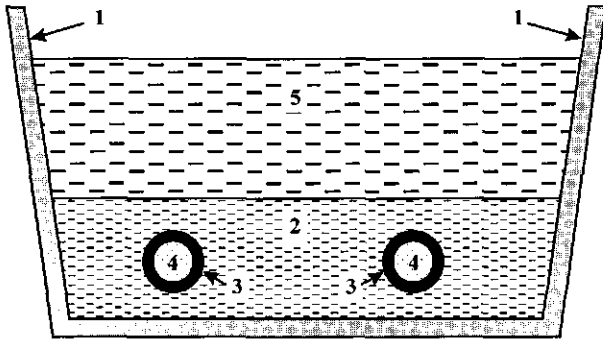


Figure 6.15. Schematic view of a landfarm. From Hoeks 1985. With: 1. plastic sheet; 2. 40 cm course sand; 3. gravel layer around drain; 4. drain to collect leachate; 5. 40 cm polluted soil.

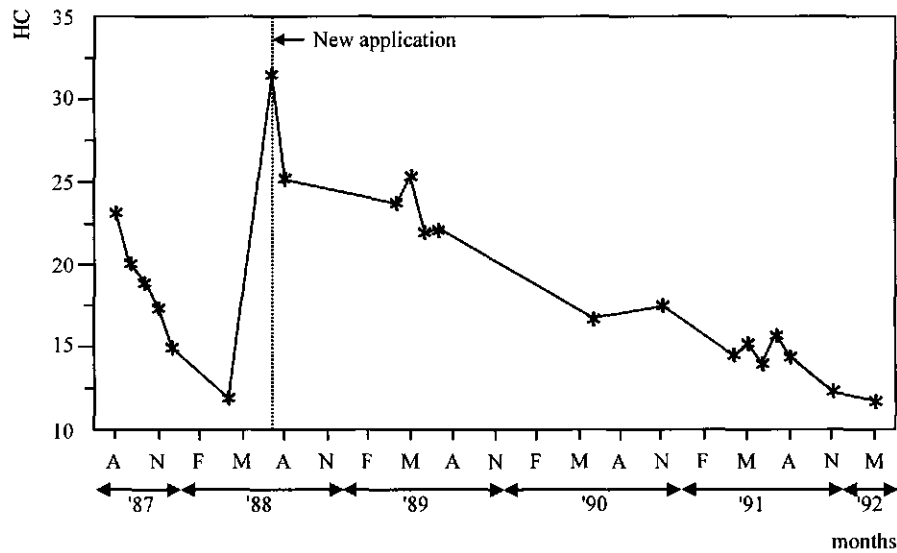


Figure 6.16. Average HC concentrations (g/kg dry weight) at the test area from August '87 till March '92.

Costs: ca. 50 ECU/ton soil treated
 Problems: - takes 2 to 20 years
 - large areas of land required
 - sensitive to changes in environmental conditions
 Advantage: - biological soil decontamination

Landfarming experiments had been done by Genouw et al. (1993) on Texaco loam soil, polluted with 23.1 g oil/kg dry soil (Figure 6.16). Monthly tillage of the contaminated soil to a depth of 30 cm was applied to maintain good soil structure, adequate oxygen supply and homogeneous distribution of the pollutants. Nutrients were added to obtain a C/N/P balance in the range of 100/10/1.

Within a period of 9 months, the oil was degraded to a residual concentration of 11.8 g/kg dry soil at an overall degradation rate of 15 g/kg dry soil per year. The degradation showed first order reaction kinetics. The best fit was obtained for the following equation ($R^2 = 0.973$, $df = 4$, $P < 0.01$).

$$\ln Y = 3.260 - 0.083 X$$

with : Y = amount of HC extracted (g/kg dry soil)
 X = time (months)

The second supply of 1 350 m³ oil sludge increased the HC concentration to 31.4 g/kg dry soil. After 11 months, the HC were degraded to a concentration of 23.6 g/kg dry soil, which is equivalent to a degradation rate of 8.5 g/kg dry soil per year. In the subsequent 29 months, the HC concentration decreased slowly to 14.3 g/kg dry soil. The microbial activity decreased from about 60 to 5 mg CO₂-C/kg dry soil per day over this period (results not shown). The residual HC fraction was further mineralized at an overall degradation rate of 3.8 g/kg dry soil per year. After approximately five years of landfarming, a concentration of 11.6 g/kg dry soil was reached. The HC degradation pattern during the second period also showed first order reaction kinetics. The best fit was obtained for the following equation ($R^2 = 0.953$, $df = 15$, $P < 0.01$).

$$\ln Y = 3,385 - 0.0195 X$$

According to this equation, another 17 and 25 years of landfarming will be necessary to reach a residual HC concentration of 500 mg (Dutch B-value) and 50 mg (Dutch A-value) of hydrocarbons, respectively. Landfarming experiments by Hoeks et al. (1988) on a soil contaminated with 15 g crude oil/kg dry soil also indicated a labile fraction of 10 g oil/kg dry soil and a slowly-reversible fraction of 5 g oil/kg dry soil.

On site, the migration of oil, nitrate and phosphate to the ground water was negligible. The oil remained in the subsurface at a depth of 25-30 cm. This was also the working depth of the cultivator. Similar results were obtained by Hoeks et al. (1988).

Experiments with three different crops (fodder vetch, couch-grass and Italian rye-grass) to detect potential phytotoxic side-effects showed the decreased growth of fodder vetch and couch-grass, but did not affect the growth of Italian rye-grass. Acute toxicity tests with rodtox, streptox and microtox, on the landfarm leachate, manifested no toxicity for these test organisms.

6.3.3.2 Composting technique

Composting is a modification of the solid-phase treatment, in which the system is operating at a higher temperature due to increased biological activity. Excavated polluted soils are mixed with compost or peat to improve soil structure (porosity), and with microorganisms to stimulate the biodegradation. The soil mixture is placed in rows (windrow-system), static piles or in bioreactors and as by landfarming stimulated by controlling the following environmental conditions:

- Temperature: thermophilic: 65-75 °C (Beltsville system). The microbiota is very restricted.
- mesophilic: 40-45 °C (Rutgers system). The microbiota is diverse, fungi participate intensively.
- Moisture content (40-60%): if too low: add water or sludge; if too high: add straw, bark,...
- pH (6,5): control generally not necessary.
- Minerals (C/N/P = 100/3/1): control by addition of N-P materials (manure, urea,...) and C-rich materials (paper, bark).
- Oxygen demand (1,2 m³ air/kg organic matter.day).

Measures have to be taken to avoid air, soil and groundwater pollution.

Costs : ca. 25 - 75 ECU/ton soil treated

Problem : requires months to years

Advantages: . elevated temperatures increase the reaction rate and solubility;
. the opportunity for cometabolism is enhanced due to the range of alternative substrates present and the high level of metabolic activity;
. the change of the physical/chemical conditions within the microenvironments of a composting mass results in a diversity of microbial communities and metabolic activity, thereby increasing the number and type of microorganisms to which a contaminant is exposed.

This technology is appropriate for highly contaminated soils, poorly textured and structured soils, and in areas where temperature is critical to the sustained treatment process. Two methods are widely used for commercial-scale composting, *i.e.* the windrow system, in which composting is controlled by periodic turning of the material, and aerated static piles, in which air is introduced at controlled rates.

Windrow

Successful large scale work on microbiological decontamination of pollutant contaminated soils in windrow systems is reported by Valo & Salkinoja-Salonen (1984). They described the composting of 70 m³ of heavily chlorophenol contaminated soil (400-500 mg chlorophenols/kg fresh soil), collected around the dipping basin of a sawmill. The soil consisted of gravel and sand with little organic matter (< 2% on wet weight), and was mixed with 35 m³ of softwood bark, 3 m³ of ash and nutrients. The soil was buffered to a pH near to neutral. It was assumed that the bark protected chlorophenol (CP)-degraders against toxicity of chlorophenol (Apajalahti & Salkinoja-Salonen 1984); that it provided organic matter (temperature maintenance of the compost); that it may have

served as a source of CP degrading microorganisms (Salkinoja-Salonen et al. 1983) and that it promoted aeration in the compost. In June 1984, the mixture was piled into windrows, 50 m³ each, and into two 1.5 m³ pilotcomposts with an initial concentration of chlorophenols of 200-300 mg/kg dry windrow soil. A mixed culture of laboratory-grown chlorophenol degrading bacteria was added to one of the 1,5 m³ pilot composts (10⁵ bacteria/g of compost). Figure 6.17 shows the disappearance rate of chlorophenols outdoor after 500 days of composting (Valo & Salkinoja-Salonen 1986).

In the two 50 m³ windrows and the pilot composts, the concentration of chlorophenols decreased fast to 30 mg/kg in four summer months, then it slowed down and after the second summer of composting the concentration in the composts was 15 mg/kg. The first two months of composting were most effective with a half-life time for chlorophenols of 25-50 days. The temperature of the compost was about 5-15 °C above the ambient temperature; the highest temperatures were measured close to the surface, 32°C in midsummer and 15 °C in October. Also in the center of the windrows, the temperature was more than 5 °C above the ambient air. In the winter, the surface of all windrows was frozen. The contaminated soil was found to contain CP-degrading microbes, 5 x 10⁶ cfu/g of dry windrow material.

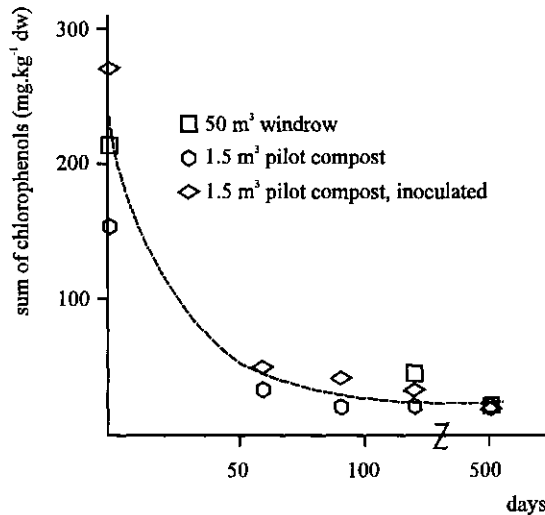


Figure 6.17. Disappearance of chlorophenols under field conditions after 500 days of composting.

Laboratory experiments with samples from the windrow compost showed that chlorophenols were truly degraded and that loss of chlorophenols by evaporation was less than 1.5% under the prevailing circumstances. Laboratory experiments also showed that degradation of chlorophenols (120 mg/kg) was accelerated (0.25 mg/kg dry weight per day) when sterilized contaminated soil was inoculated with *Rhodococcus chlorophenolicus* or naturally occurring microbes of the field composts.

Static pile

Williams & Myler (1990) described a static pile composting treatment for remediating soils and sediments contaminated with explosives like TNT, RDX, HMX and tetryl. The mixture to be composted was prepared using manure and straw, alfalfa, horse

feed, and contaminated sediment (Table 6.5).

Table 6.5. Material balance of the mixture composted

Material	Percent (%)	
	Volume	Mass
sediment	3	24
alfalfa	38	10
straw/manure	47	25
horse feed	12	41

Temperature and oxygen in the compost pile were controlled using a drainage tubing placed in a wood chip base and connected to an explosion-proof radial-blade blower. The blower was used to blow air through the compost pile. Both mesophilic and thermophilic temperatures were investigated to determine if the higher microbial diversity (and assumed metabolic diversity) present under mesophilic conditions would result in a greater overall contaminant destruction than that observed at thermophilic temperatures. Thermophilic temperatures were assumed to result in higher rates of transformation mediated by a more narrow range of microorganisms. The mixture was placed in a static pile of ca 3 m wide and 2 m high and covered with ca 30 cm woodchips as an insulator (Figure 6.18).

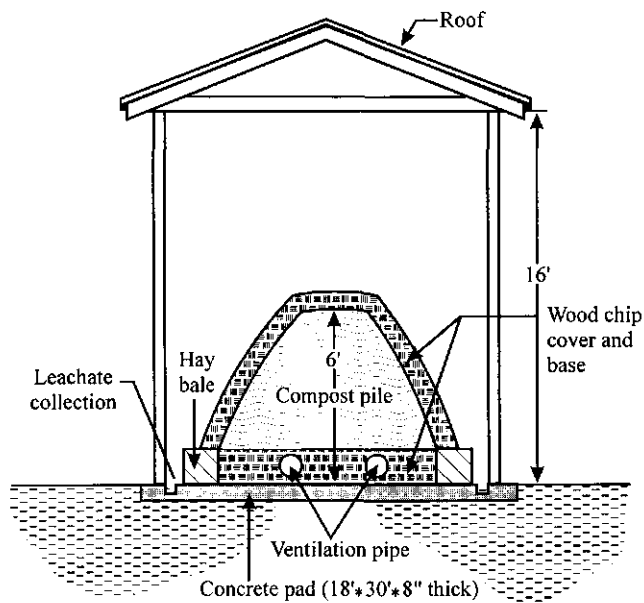


Figure 6.18. Schematic view of a static pile.

Degradation of TNT, RDX and HMX proceeded according to first order kinetics. Half-life-times were 11.9 days for TNT, 17.3 for RDX and 22.8 days for HMX under thermophilic conditions. Under mesophilic conditions, the values were respectively 21.9; 30.1 and 42.0 days. The appearance of the compost changed considerably during composting. Initially, it had a highly fibrous appearance, a rough structure, and it had the smell of the manure and feed compounds. After 100 days of composting, the compost had become more soil-like and less fibrous in appearance. At the end of composting, the compost had both the appearance and smell of loamy soil. The treatment costs per ton soil are in the order of 75 ECU.

6.3.3.3 Bioreactors

In this technique, excavated polluted soil is treated in a reactor under optimal conditions and in most cases by means of an adapted population of microorganisms.

Costs : ca. 125 ECU/ton

Problem : complex technology

- Advantages:
- . process management and control is possible
 - . specific cultures or inocula can be added easily
 - . increased contact between microorganisms and contaminants
 - . decreased acclimatisation times
 - . faster biodegradation rates.

Case study: DITS (Dual Injected Turbulent Separation)-reactor (Kleijntjes 1991)

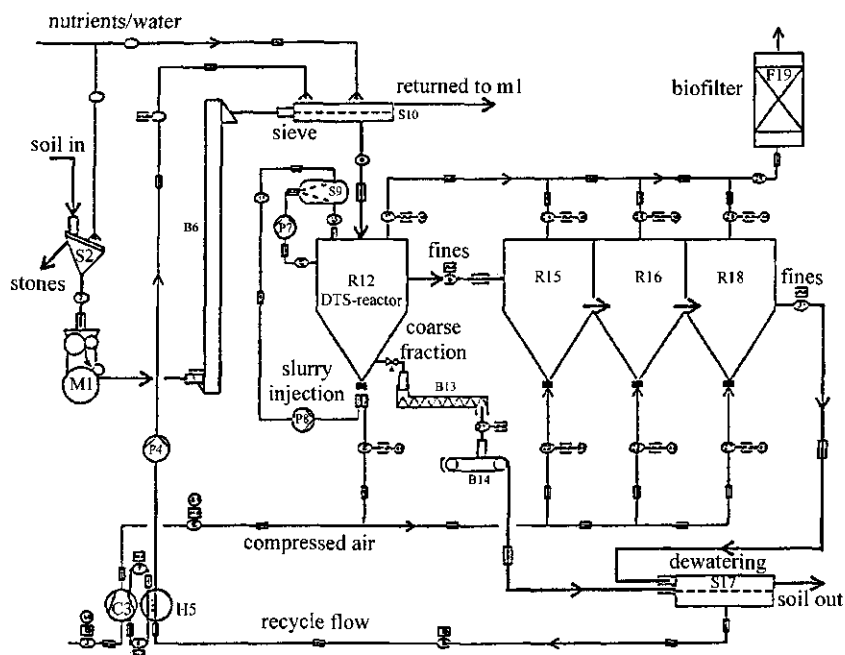


Figure 6.19. Reactor design and flowsheet of the DITS-reactor. From Kleijntjes 1991.

In the first cylindrical tank (DITS reactor, R12; height (H)/ diameter (D) $\approx 2/3$), with a conical bottom (so-called Pachuca tank), the coarse soil fraction is fluidized in the bottom zone by means of an upward injected slurry flow, while fine soil particles are kept in turbulent suspension in the aerated bulk compartment. From the bottom of the first reactor, the coarse fraction is withdrawn and passed directly to a dewatering section (S17). The fine material, containing most adsorbed pollutants (Assink 1988), is given a further treatment in a cascade of air agitated bioreactors (R15-R18).

Assuming this first order desorption process to be rate-limiting in the decontamination, it can be calculated that in order to reach the Dutch A-level (0.05 g/kg soil dry weight) for the oil spill of 3.0 g/kg soil dry weight, a solid residence time of about 30 days is required.

The overall degradation rate varied from 0.2 to 2 g oil/kg soil per day. These conversion rates obtained by the DITS process are about *100-200 times higher* than those obtained in landfarming (Bonnier 1980).

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7 Use of microorganisms in soil sanitation

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Summary

The persistence of xenobiotic compounds at numerous locations in nature has raised questions about the potential of microorganisms to degrade these pollutants.

In laboratory experiments has been demonstrated that many of these compounds can be degraded by microorganisms. Specific conditions and special microorganisms are often required and the degradation may vary from mineralization to only a limited change in the structure of the molecule. The long persistence in nature of in principle biodegradable compounds suggests that other factors than the interactions between a microorganism and a xenobiotic molecule play a role. In fact, nature, degree and rate of biodegradation are determined by several factors.

One has to do with the xenobiotic compound. Both intrinsic properties like complexity of structure, presence of halogen substituents and physical characteristics determine whether the compound can be degraded.

A second factor are 'environmental' conditions. Redox conditions determine the prevailing microbial species and thus the type of biodegradation reactions. Temperature, concentration and availability are influencing the rate with which a compound is transformed.

7.1 Introduction

The presence of organic compounds is essential for the survival of many microorganisms. Via *metabolic* reactions they are capable to convert an organic molecule into inorganic constituents like CO_2 , NO_3^- , SO_4^{2-} and PO_4^{3-} (mineralization). Growth and proliferation of the microorganisms is then a result of the use of the released energy and of the incorporation of a portion of the carbon into biomass. In addition to metabolic reactions, *co-metabolic* reactions may take place. In these reactions, in which only a small alteration of the molecular structure occurs (transformation), neither the energy nor the carbon of the molecule are used by the microorganisms. Co-metabolism of an organic molecule only takes place if in addition other molecules are used for biosynthetic purposes.

In the twentieth century many organic compounds, which have been produced by chemical synthesis for industrial or agricultural purposes (sometimes called *xenobiotics*) have entered the environment. Some of these organic compounds are similar to natural ones, but many are quite different and may never have existed in natural environments. As a consequence, microorganisms may have difficulties to degrade the latter ones. All xenobiotic compounds, of which many are toxic, will eventually show up in the soil. Here they are exposed to enzymatic and non-enzymatic reactions.

Non-enzymatic reactions in the soil can cause only minor changes in the chemical

structure of a compound, while major changes (leading to degradation) have to occur through biological reactions. This paper will deal with a number of aspects which are of influence on the nature and rate with which these xenobiotic compounds can be transformed by microorganisms in soil systems.

7.2 Biodegradation

For the ultimate disappearance of xenobiotic compounds in soil and groundwater, they have to undergo biodegradation and not only biotransformation. Although for many xenobiotic compounds has been found that they can indeed be degraded by microorganisms to harmless inorganic end products, many have also been found just to undergo transformations.

Several bacteria have been isolated which can use di- and trichlorobenzenes as only carbon and energy source under aerobic conditions (Schraa et al. 1986, van der Meer et al. 1987, Haigler et al. 1988), with only inorganic compounds as end products. In the absence of molecular oxygen, at low redox conditions, these chlorinated benzenes have been found to undergo reductive dechlorination (Bosma et al. 1988). Monochlorobenzene was formed as a stable end product and additional transformations under these conditions have not yet been witnessed. In general, we can say that highly chlorinated compounds need anaerobic conditions for the transformation to lower chlorinated compounds, before under aerobic conditions mineralization will occur.

Co-metabolism has also been observed with xenobiotic compounds. Trichloroethylene (TCE) is transformed by methanotrophic bacteria in one reaction step into an epoxide. The enzyme methane monooxygenase is, because of its low specificity, responsible for the reaction. The bacteria do not seem to have any benefit from this one reaction.

If a compound is stable to degradation it is often referred to as being persistent or recalcitrant. This persistence can be due to the structure of the molecule or to the prevailing environmental conditions. Pesticides are in general produced via non-enzymatic reactions and their structure may be just too complex for degradation by the enzymes of microorganisms. Atrazine and bentazon are examples of pesticides, which are notorious soil and groundwater pollutants and which have a 'complex' structure (Figure 7.1).

Environmental conditions include physical conditions (*e.g.* temperature and availability of the compound), chemical conditions (pH, redox potential, concentration of the compound, type of electronacceptor, essential growth factors, etc.) and biological conditions (presence of the desired microorganisms). An initial persistent compound may

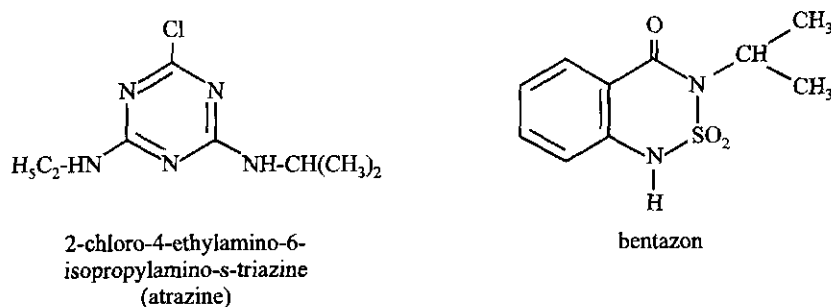


Figure 7.1. Pesticides which seem to be persistent because of their structure.

undergo biodegradation by varying a specific environmental parameter. Tetrachloroethene (PCE), a widespread groundwater contaminant, is persistent in the presence of molecular oxygen, but under anaerobic conditions a complete dechlorination to ethene may take place. In Table 7.1 examples are given of the biodegradation of a number of problematic compounds under aerobic and anaerobic conditions.

In the following paragraphs several factors that determine nature, degree and rate of biodegradation of xenobiotic compounds in soil and groundwater will be discussed. These factors are: structure of the compound, availability in the presence of soil particles, aerobic/anaerobic conditions, concentration of the compound, temperature and water content.

Table 7.1. Examples of what is known about biodegradation under aerobic and anaerobic conditions.

Classes of compounds	Biodegradation*	
	aerobically	anaerobically
Chlorobenzenes		
pentachlorobenzene	-	+ (L)
hexachlorobenzene	-	+ (L)
Chlorophenols		
3,4-dichlorophenol	+ (L)	+ (L)
2,3,5-trichlorophenol	+ (L)	+ (L)
2,3,4,5-tetrachlorophenol	+ (L)	+ (L)
pentachlorophenol	+ (L,F)	+ (L,F)
Chloroanilines		
2-chloroaniline	+ (L)	-
3,4-dichloroaniline	-	-
2,4,5-trichloroaniline	-	-
Polychlorinated biphenyls (PCBs)		
PCB 28	+ (L)	-
PCB 52	+ (L)	?
PCB 138	-	?
Polycyclic aromatic hydrocarbons		
fluoranthene	+ (L)	-
benzo(a)pyrene	+/- (L,V)	-
benzo(ghi)perylene	?	-
Dioxins and furans		
as TCDD equivalents	+ (L)	?

* Biodegradation observed in laboratory- (L) or fieldstudies (F).

7.3 Structure of the xenobiotic compound

Degradation of a xenobiotic compound via existing metabolic routes in microorganisms may take place when the structure of the molecule is identical or shows a strong resemblance to molecules which are normally used for cell synthesis. An inhibition can often be witnessed when the molecule has specific substituents (*e.g.* halogen atoms and methyl groups). The rate of degradation is then mainly determined by the kind and number of substituents and the location in the molecule (Table 7.2).

Table 7.2. Relative conversion rates of different chlorinated benzoates by *Alcaligenes eutrophus* B9. From Knackmuss 1975.

Substrate	Product (dihydro-dihydroxybenzoate, DHB)	Rate of oxidation of substituted benzoates
benzoate	DHB	1000
2-chlorobenzoate	----	0
2-methylbenzoate	----	0
3-chlorobenzoate	3-chloro-DHB 5-chloro-DHB	50 100
3-methylbenzoate	3-methyl-DHB 5-methyl-DHB	31 215
3,5-dichlorobenzoate	3,5-dichloro-DHB	2
3,5-dimethylbenzoate	3,5-dimethyl-DHB	2
4-chlorobenzoate	4-chloro-DHB	1
3,4-dichlorobenzoate	4,5-dichloro-DHB	1
4-methylbenzoate	4-methyl-DHB	4

For compounds with a 'new' structure, enzymes may not be present. A bacterium, capable of using propionate as carbon and energy source, did not possess the enzyme(s) to degrade 2,2-dichloropropionate. Exposure during 120 days to a mixture of propionate and 2,2-dichloropropionate, led to spontaneous genetic changes which resulted in a metabolic degradation of 2,2-dichloropropionate (Senior et al. 1976).

Molecule size is another aspect of the importance of the structure of a compound which is determining the rate of degradation. The influence of the molecule size on the

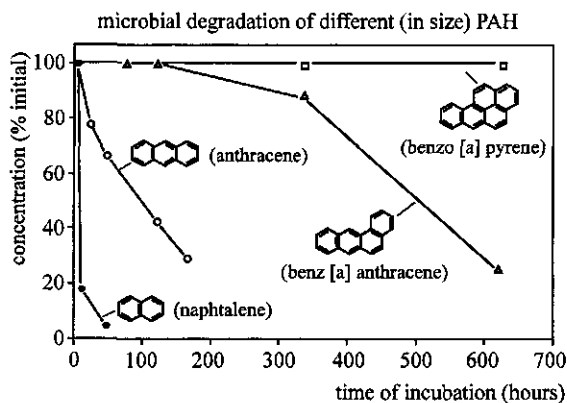


Figure 7.2. Microbial degradation of several polycyclic aromatic compounds.

rate of biodegradation of a number of polycyclic aromatic compounds is shown in Figure 7.2.

An increase in number of aromatic rings leads to a lower degradation rate. Although the simultaneous decrease in solubility has an effect, uptake by the microbial cell and positioning in the active centre of the oxygenase enzyme will be hindered by the increase in molecule size.

7.4 Availability

The distribution of pollutants in the soil is often very irregular. Many compounds are hydrophobic and tend to adsorb to soil aggregates (*e.g.* clay minerals and organic matter). It also seems that in time organic pollutants become an integral part of the organic matrix. Of chloroanilines it is known that they can form covalent bonds with humic acids ('bound residues'). In addition, soil pollution with large, irregular particles can take place. Examples are tar globules during oil spills and the formation of calcareous aggregates in a soil in which hexachlorocyclohexane (HCH) wastes were disposed of in the presence of large quantities of lime.

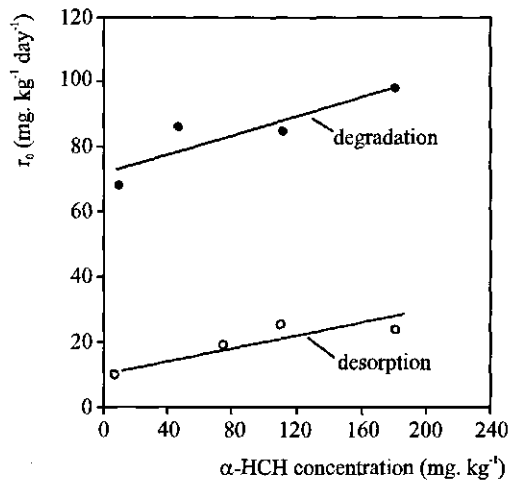


Figure 7.3. Comparison of maximum desorption and biodegradation rates of α -HCH.

It is generally accepted that the uptake of compounds by bacteria proceeds via the waterphase. This was for instance demonstrated by Ogram et al. (1985) for the uptake of 2,4-dichlorophenoxyacetic acid from soil. In a study by Rijnaarts et al. (1990) it was found that within certain limits the degradation rate of α -HCH under aerobic conditions was limited by mass transport in and desorption from soil aggregates and not by the activity of the degrading microorganisms. These results are visualized in Figure 7.3, in which a comparison has been made between the maximum desorption and biodegradation rates of α -HCH at different HCH concentrations in a soil slurry.

7.5 Environmental factors

In addition to the above mentioned availability, other important environmental factors which determine whether biodegradation takes place and what the rate of degradation is are: redox condition, concentration of the xenobiotic compound, presence of nutrients, moisture content, pH and temperature. Degradation only takes place if, and that is partly dependent on the xenobiotic compound, for each factor certain conditions are met.

7.5.1 Redox condition

The presence of a specific electronacceptor determines both the sort of microbial population as the possibility to degradation. The mineralization of a hypothetical chlorinated compound with four different electron acceptors is given in simple reactions in Figure 7.4.

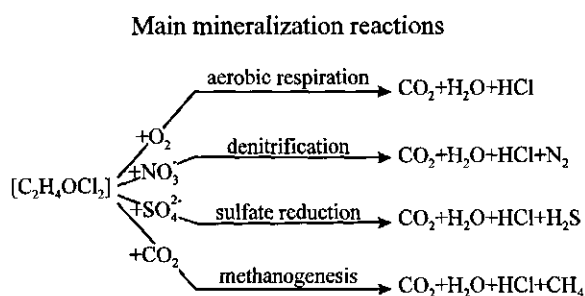


Figure 7.4. Mineralization of a chlorinated compound with four different electronacceptors.

Molecular oxygen is somewhat different from the other electron acceptors, because it does not only function as an acceptor but also as a reactant in oxidation reactions of *e.g.* aromatic compounds (oxygenases).

Some compounds require aerobic conditions for biodegradation (monochlorobenzene), while others are degraded under strict anaerobic conditions (tetrachloroethylene, hexachlorobenzene). In a study by Bachmann et al. (1988a) it was shown that α -HCH could be degraded under both aerobic and methanogenic conditions, while it was persistent in the presence of nitrate and sulfate as electron acceptor (Figure 7.5). There were two big differences between the aerobic and the methanogenic bio-degradation. Under aerobic conditions the degradation was much faster, while also complete mineralization occurred. Under methanogenic conditions several toxic intermediates accumulated (*e.g.* monochlorobenzene).

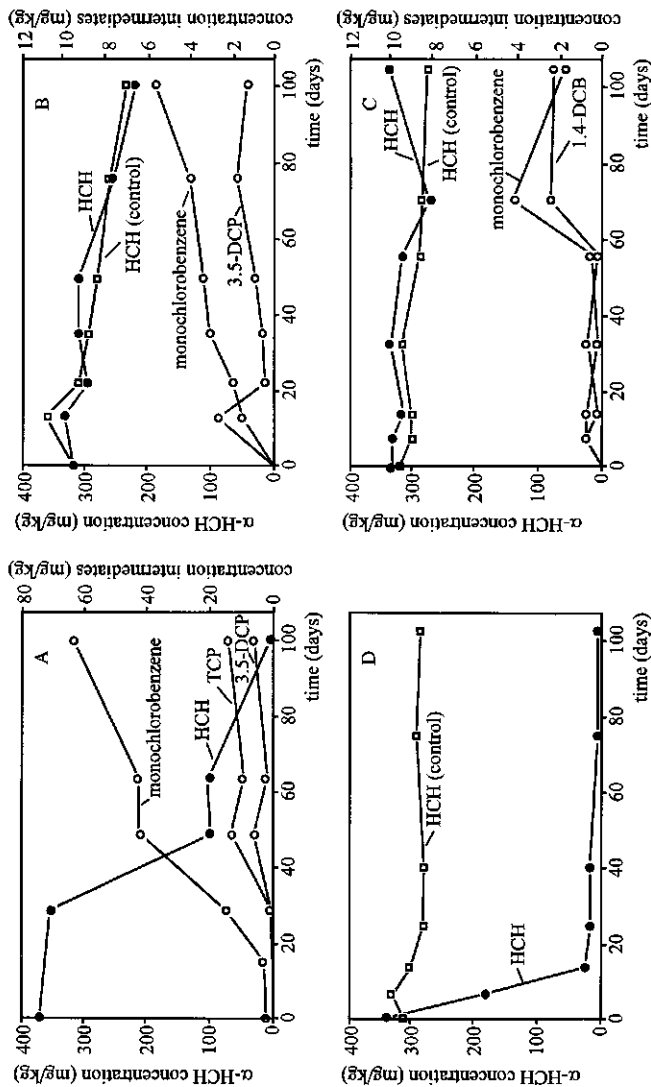


Figure 7.5. Biodegradation of α -HCH in soil slurries under different redox conditions (methanogenic [A], sulfate reducing [B], denitrifying [C] and aerobic [D]).

7.5.2 Concentration

The rate of biodegradation of a xenobiotic compound can in general be described by first order kinetics. This is valid as long as a) the microorganisms use the compound as a carbon and energy source, and b) the availability does not become a limiting factor. Biodegradation may be hampered at high and low substrate concentrations.

At high concentrations the compound can become toxic for the microorganisms (Figure 7.6). A *Corynebacterium* sp., isolated from river Rhine sediment and capable of mineralizing *o*-xylene at a concentration of 80 mg/l, was unable to degrade it at double the concentration (Schraa et al. 1987). At low concentrations, often in the $\mu\text{g/l}$ - ng/l range, there may not be enough energy and carbon available for growth or maintenance. Rest concentrations have been observed for several xenobiotic compounds in soil and groundwater. Initially it was assumed that microorganisms were not able to degrade these compounds at these low concentrations ('threshold concentration'). Recent experiments do suggest that this inability is not a characteristic of the microorganisms, but is caused by not yet fully understood interactions between the microorganisms, the xenobiotic compound and the soil structure.

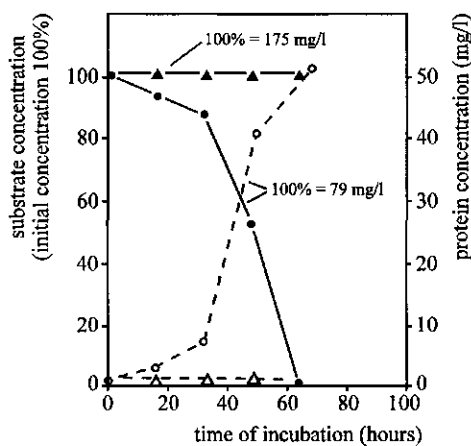


Figure 7.6. Degradation of *o*-xylene by *Corynebacterium* sp. at two different concentrations.

7.5.3 Temperature

This factor influences just as the presence of nutrients (especially nitrogen and phosphorus), moisture content and pH, the general metabolic activities of microorganisms. Within a certain temperature range the optimum activity of soil microorganisms is more or less constant, but outside this range drastic decreases occur. This effect can be seen in Figure 7.7, in which the biodegradation rate of α -HCH as a function of the temperature is given (Bachmann et al. 1988b).

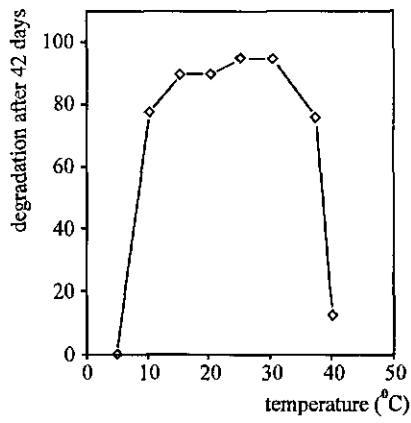


Figure 7.7. Effect of temperature on the aerobic biodegradation of α -HCH in soil.

7.5.4 Water content

Water content is one of the most important factors affecting the growth of microorganisms in natural environments. On one hand there is the water availability for microorganisms, which is determined by the presence of solid substances and surfaces and by the solutes in the water. On the other hand water serves in soil as a transport medium to make nutrients and xenobiotic compounds more accessible to the microorganisms.

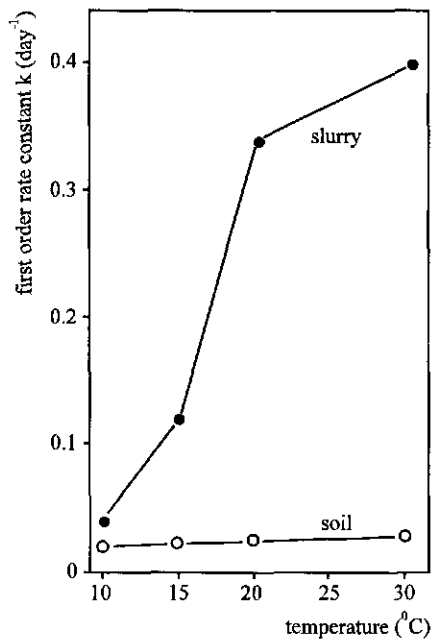


Figure 7.8. Effect of water content at different temperatures on the first-order rate of α -HCH mineralization in soil (slurry: 100 g/l, dry weight; soil: 20% moisture, w/w).

The water content may therefore influence the availability of the compound and thus the rate of biodegradation. This is demonstrated in Figure 7.8, in which the effect of water content on the biodegradation rate of α -HCH in soil at different temperatures is given (Bachmann 1987).

7.6 Concluding remarks

Laboratory experiments have demonstrated that many organic compounds that are responsible for soil and groundwater pollution, like (halogenated) solvents, polycyclic aromatic compounds and several pesticides, can be degraded by microorganisms. The fact that these organisms have often been isolated from polluted sites, also demonstrates the potential of *in situ* degradation. Several factors, among which availability and environmental conditions, determine the rate and degree of degradation.

In addition, for some compounds the structure may be so complex that microorganisms capable of degrading them do not naturally occur.

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8 Precipitation - dissolution reactions

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8.1 Introduction

Many elements that occur naturally in the soil, as well as compounds that are of importance with respect to pollution, can occur in the soil system as a three dimensional precipitate. Other possibilities are the occurrence as an adsorbed species at the interface between soil particles and the soil solution or they may be present 'dissolved' in the soil solution phase. In Table 8.1 some examples are given for a few elements with respect to the solid phases in which these elements may occur in the soil. It will be clear that in this table only a very small fraction of the various possibilities are listed.

Table 8.1. Elements and solid phases in which these element may be incorporated.

Element	Solid phase (mineral)
Na	feldspar
K	feldspar
Cd	$\text{CdCO}_3(\text{s})$, $\text{CdS}(\text{s})$
Fe	$\text{Fe}(\text{OH})_3(\text{s})$, $\text{FeCO}_3(\text{s})$, $\text{FeS}(\text{s})$, $\text{FeS}_2(\text{s})$
Pb	$\text{Pb}_3(\text{PO}_4)_2(\text{s})$, $\text{PbSO}_4(\text{s})$
Ca	$\text{CaCO}_3(\text{s})$, calciumoxalate

Also sparingly soluble organic compounds can be present in solid organic precipitates. As an example may be mentioned the polyaromatic hydrocarbons most of which are very insoluble in an aqueous medium. Often one is interested in the activity (concentration) of an element, or the activity of a certain dissolved complex or species that contains this element in the soil solution. The activity in the solution phase may be determined completely by the occurrence of one or more solid phases. The resulting activity may be the result of equilibrium processes, the result of slow formation of compounds, or the result of very slow dissolution kinetics of compounds present in the system. With respect to the behaviour of some pollutants in the soil system these processes may be of great importance. For instance, the solution concentration of cadmium in calcareous soils may be determined by $\text{CdCO}_3(\text{s})$, whereas the solution concentration of heavy metals under reduced conditions may be governed by equilibrium with metalsulfide precipitates, which have a very low solubility.

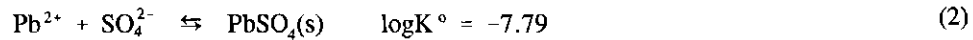
8.2 Equilibrium

An important characteristic of a *pure* solid phase is that the chemical activity of such a solid phase equals one. This implies that the equilibrium composition of the system is independent of the amount of the solid phase present, as long as it is present.

A solid phase can be formed when the change of the Gibbs free energy of the reaction of formation, ΔG_r , is smaller than zero. In case ΔG_r equals zero, there is equilibrium and if its value is positive than dissolution has to take place until equilibrium is reached provided the solid phase is still present in the system. If the solid phase is not present in the system and if the calculated ΔG_r value is positive, then it means that this phase can not be formed from this solution phase. The ΔG_r can be calculated as follows:

$$\Delta G_r = RT \ln Q/K^\circ \quad (1)$$

where R is the gas constant, T the absolute temperature, Q the ion activity product of the reaction and K° the equilibrium constant of the reaction. As an example the formation reaction of lead sulphate is given:



The ion activity product Q of this reaction equals:

$$Q = \frac{(\text{PbSO}_4(\text{s}))}{(\text{Pb}^{2+})(\text{SO}_4^{2-})} = \frac{1}{(\text{Pb}^{2+})(\text{SO}_4^{2-})} \quad (3)$$

The formulation of the ion activity product equals the formulation for the equilibrium constant, in case of equation (2) this is:

$$K^\circ = \frac{1}{(\text{Pb}^{2+})(\text{SO}_4^{2-})} \quad (4)$$

The difference between Q and K° is that Q may have any value which depends on the composition of the system, whereas K° is a constant. In case $Q = K^\circ$ it follows from equation (1) that $\Delta G_r = 0$ meaning equilibrium conditions.

In practice often the saturation index is used to test whether a system is undersaturated, at equilibrium, or supersaturated with respect to a solid phase. The saturation index, SI, can be expressed as:

$$\text{SI} = \log(Q_{\text{SP}}/K_{\text{SP}}) \quad (5)$$

Where K_{SP} is the solubility product of the solid phase and Q_{SP} is the ionactivity product of the solid phase written as a dissolution reaction. For the same example it follows that Q_{SP} equals:

$$Q_{\text{SP}} = (\text{Pb}^{2+})(\text{SO}_4^{2-}) \quad (6)$$

and

$$K_{\text{SP}} = \frac{1}{K^\circ}$$

It follows that Q_{SP} :

$$Q_{SP}/K_{SP} = (Q/K^0)^{-1} \quad (7)$$

This has as result that $SI > 0$ indicates that the system is supersaturated with respect to the solid phase and $SI < 0$ indicates that it is undersaturated.

An important restriction in case of chemical equilibrium calculations is that the system should not be 'overdetermined' (more independent equations than unknowns). An example of an 'overdetermined' system is when two different $Al(OH)_3(s)$ minerals are present at the same time, for example gibbsite and amorphous $Al(OH)_3(s)$. The reaction equations for the formation reaction are identical, the only difference is the value of the equilibrium constant which is different because the structure of the solid phase is different. At complete equilibrium it is impossible that two solid phases with the same formulation of the ion activity product but with different equilibrium constants can coexist. This can very easily be illustrated using the given example:



$$\log K_{am}^0 = -9.66 \quad \log K_{gibb}^0 = -8.04$$

$$\rightarrow (Al^{3+}) = (K^0)^{-1} (H^+)^3 \quad (9)$$

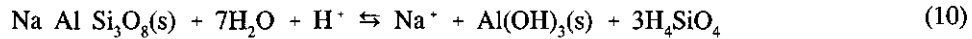
Equation (9) implies that the value of (Al^{3+}) at a certain pH depends on the type of $Al(OH)_3(s)$ being present. If both would be present at the same time then equation (9) predicts that at a certain pH the solution should have two different values of (Al^{3+}) , which is impossible in a homogeneous solution phase. Application of equation (9) with the appropriate $\log K$ values given at equation (8) shows that equilibrium with amorphous $Al(OH)_3$ will give at a certain pH value a higher Al^{3+} concentration than equilibrium with gibbsite. The higher Al^{3+} concentration means super saturation with respect to the gibbsite and amorphous $Al(OH)_3$ will be transformed to a less soluble form (gibbsite). At complete equilibrium all amorphous $Al(OH)_3(s)$ should have been dissolved and only gibbsite can be present. However, the solution phase can be in equilibrium with amorphous $Al(OH)_3(s)$ during a very long time, provided that the rate of dissolution of amorphous $Al(OH)_3(s)$ is much larger than the rate of formation of gibbsite and that the latter in absolute terms is also characterised by a very low rate of formation. Such a transition period can last very long (years), and during this transition period the composition of the soil solution is in equilibrium with the more soluble phase, although also the more stable phase may be present. For equilibrium calculations one can thus use the $\log K^0$ value of amorphous $Al(OH)_3(s)$ in such a case. Such a situation is called partial equilibrium.

Chemical equilibrium calculations of even very complex systems can at present be performed relatively easily from a computational point of view using computer programs to calculate chemical speciation. In practice however, it is much more complicated because one needs to have insight in the chemical kinetics. Especially in relation to equilibria involving solid phases the kinetics are often rather slow and of a complex nature.

The book of Lindsay (1979) is an illustration of many solid phase equilibria that are of relevance for the soil system. This book is based upon the idea that the activity in solution of various species is fully determined by equilibrium between the solution phase and one or more solid phases. In practical situations kinetics may be important and/or adsorption phenomena instead of equilibrium with solid phases.

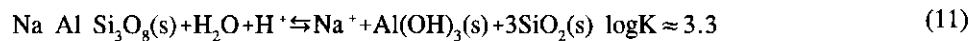
8.3 Some aspects of kinetics of dissolution and precipitation

Several reactions involving formation or dissolution of solid phases that are of environmental concern are characterised by slow kinetics. For a quantitative description it is necessary to deal with the kinetics of the processes next to equilibrium aspects. Primary minerals in the soil or aquifer system like various feldspar minerals (aluminium silicates) are rather soluble at pH values below pH 7. However, of many feldspars the rate of dissolution is very low. These primary minerals play an important role with respect to the buffermechanism of the soil or subsoil with respect to protons. They are also important as a source of cations like K^+ , Ca^{2+} and Mg^{2+} . The following reaction equation describes the solubility relationship for the sodium feldspar, albite:



This equation describes the incongruent dissolution of the sodium feldspar. It is called incongruent dissolution because part of the ions present in the mineral do not dissolve but are retained in the form of a secondary mineral, in this case $Al(OH)_3(s)$. During the process of soil formation, as we will see later, the reaction of equation (10) is often not in equilibrium but goes to the right. The result of the dissolution process is that a proton is replaced by a cation, here the sodium ion. Weathering of other feldspars results in replacement of protons for other cations like K^+ and Ca^{2+} . The aluminium ion is not released into the soil solution during weathering if the pH is above five, because the solubility of $Al(OH)_3(s)$ is very low. Apart from formation of $Al(OH)_3(s)$ also secondary aluminium silicate clay minerals may be formed as a result of the weathering process.

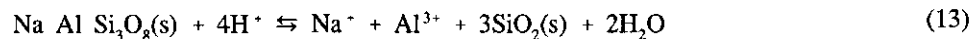
Equation (10) can be written in a slightly different form if we realise that in the soil always quartz or other silicon oxides are present. The concentration of H_4SiO_4 can in principle not become higher than the solubility of $SiO_2(s)$. This leads to the following equation:



Realising that the activity of the pure phases can be set to one, it follows that:

$$[Na^+] = (H^+)10^{3.3} \quad (12)$$

If the pH equals 3.3, which is a realistic value in acid forest soils, the sodium concentration at equilibrium according to equation (12) should be one mole per liter. The actual concentration in an acid forest soil may be around 0.3 mmol/l. Conclusion, there is no equilibrium. The same reasoning can also be done as follows, at 0.3 mmol/l for $[Na^+]$, according to equation (12) the pH should be 6.8 at equilibrium. In other words if there would be equilibrium the forest soil would probably not be very acid! In practice, there is no equilibrium, the soil solution is undersaturated with respect to feldspar and there is a continuous driving force for dissolution ($\Delta G_r < 0$) of feldspars. The continuous weathering of feldspar has led to a built up of $Al(OH)_3(s)$ in the soil. With a lowering of the pH below five the solubility of $Al(OH)_3(s)$ starts to increase strongly and the dissolution reaction can now be written as:



The main process that is now responsible for the consumption of protons is the release of aluminium ions. The aluminium ions will mainly be the result of dissolution of $Al(OH)_3(s)$

already present in the soil, because the dissolution kinetics of $\text{Al}(\text{OH})_3(\text{s})$ are faster than that of most feldspars. The increase in Al^{3+} leads to a release of Mg^{2+} of the exchange complex that may be leached to the groundwater. The high ratio of ($\text{Al}^{3+}/\text{Mg}^{2+}$) that results and the increased concentrations of heavy metal ions lead to a deterioration of the soil quality which may result in a deterioration of the quality of the forest and even lead to forest die back.

A semi-empirical equation that is sometimes used to describe the dissolution kinetics of minerals is:

$$R = \text{mol-mineral}/(\text{time}\cdot\text{unit-soil}) = k^* \left(1 - \frac{Q}{K^o}\right) \quad (14)$$

The parameter b is an empirical constant, K^o is the chemical equilibrium constant of the dissolution reaction, $10^{3.3}$ in case of equation (11), Q is the reaction quotient of the same reaction and k^* is a rate constant that includes the surface area of the dissolving mineral per unit soil. Equation (14) leads to $R = 0$ when $Q = K^o$, in other words the net weathering rate is zero when there is equilibrium. When there is a strong undersaturation, $Q \ll K^o$, there is a positive dissolution rate which under these conditions simply equals:

$$R = k^* \quad (15)$$

Equation (15) predicts a constant dissolution rate for large undersaturation. However, the rate may still depend on the pH of the solution. For this reason an asterix is used as a superscript for the rate constant.

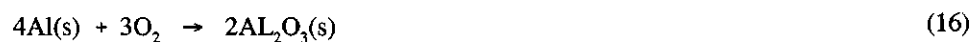
The dissolution rate for a potassium feldspar may be in the order of $50 \mu\text{mol}$ silica per m^2 feldspar per year. Small particles will therefore contribute much more to the dissolution rate than larger particles. However, feldspars are normally found in the larger size fraction of the soil mineral phase and that is another reason why the effective weathering rate of feldspar in the field is rather low.

A more detailed mechanistic approach may yield insight in the factors that influence the value of k^* . As an example of such an approach reference is made to Hiemstra & van Riemsdijk (1990) and references cited in that paper.

8.4 Diffusion - precipitation kinetics

The formation of a solid phase may be a relatively fast reaction when all the components forming the new solid phase are initially present in the solution phase. The initial precipitate being formed may be a rather disordered, amorphous, mineral phase which may be very slowly converted into a more stable crystalline solid phase.

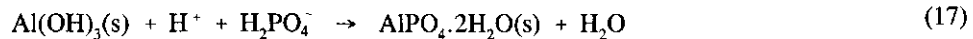
Another situation occurs when one of the constituents of the new solid phase to be formed is initially present in another solid phase. In that case reaction rates are often rather low. An example is a sheet of aluminum metal in the presence of air. The oxygen content of the air is approximately constant and under these conditions the chemically stable situation is that all aluminum metal should be converted into aluminumoxide or aluminumhydroxide:



What happens in practice is that O_2 molecules first adsorb on the surface of the aluminum

metal, the aluminum atoms at the interface between metal and air are converted into aluminum(hydr)oxide and this newly formed phase remains attached to the underlying metal. The reaction can now only proceed when the oxygen diffuses through this thin coating of aluminum(hydr)oxide to reach the underlying aluminum metal. The thicker the coating becomes the slower the conversion rate will become. If the coating has a rather high resistance against diffusion (not very porous) and if the coating sticks to the underlying material it is said that a protective coating is being formed that practically stops further conversion of the underlying material.

A similar situation may occur in soils. Iron and aluminum(hydr)oxides are very insoluble for $\text{pH} > 5.2$. This means that only an extremely low concentration of aluminum and iron ions is present in the soil solution phase under these conditions. When phosphate is added to the soil *e.g.* in the form of liquid manure (pig slurry etc.) or as commercial fertilizer the situation may become such that the system is supersaturated with respect to the formation of aluminum phosphate. The following reaction now should take place:



Reaction (17) states that an aluminum phosphate phase is being formed at the expense of $\text{Al(OH)}_3(\text{s})$. When the pH and the phosphate concentration in solution are kept constant, a constant supersaturation or driving force will exist for the formation of the aluminum phosphate phase. Such an experiment can be performed in the laboratory. The result of such an experiment is that initially phosphate reacts quite rapidly and then the reaction rate becomes lower and lower the further the reaction proceeds. Even after a year reaction time only a small fraction of the original $\text{Al(OH)}_3(\text{s})$ is converted into aluminum phosphate although the equilibrium condition for such an experiment would be a complete conversion.

This is thus typically a process where kinetics are very important. The reaction rate is most probably diffusion controlled. The process is schematically depicted in Figure 8.1. The diffusion rate depends on:

- the thickness of the coating, δ , which is a function of the amount that has been sorbed in the coating, S
- the reactive surface area, A , which may be a function of S
- effective diffusion constant, D , of the chemical species through the coating
- shape of the particle.

The size of the particles also plays a very important role. Small particles have a high surface area per unit mass of solid, the degree of conversion of the particles into the new phase will for certain conditions be strongly dependent on the initial particle size.

Very small particles can be completely converted into the new phase whereas very big particles are hardly converted at all. A very nice example of the effect of particle size on this type of kinetics is the oxidation of iron, in the presence of air. For larger particles the process of conversion of iron metal into iron(hydr)oxide is rather slow, but very tiny particles known as pyrophoric iron (pyros = fire) will react very vigorously, it will 'burn' when it comes into contact with air (remember the experiment at the end of the lecture).

In the engineering literature the diffusion precipitation model is also known as the unreacted shrinking core model. In the model it is assumed that a relatively sharp (moving) boundary will develop between the coating that is formed at the expense of the original particle and the not yet converted original particle. In Figure 8.2 the movement of phosphate into ferrihydrite particles is shown. The white dots represent phosphate and the

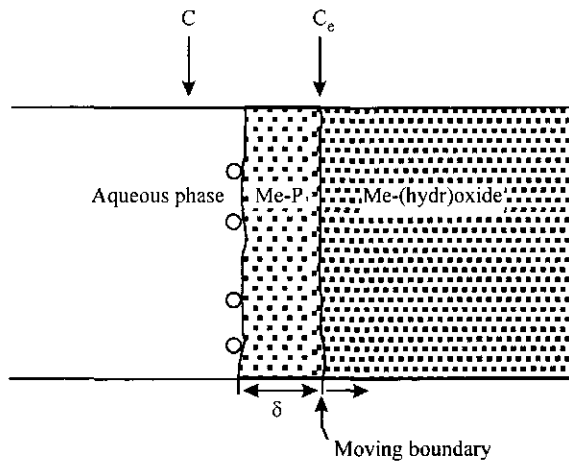


Figure 8.1. Schematic representation of the diffusion precipitation process. C represents the phosphate concentration in solution, and c_e the concentration at the interface between the two solid phases; c_e may represent the concentration when there is equilibrium between the two phases. The open circles represent adsorbed phosphate.

Migration of PO_4 in ferrihydrite

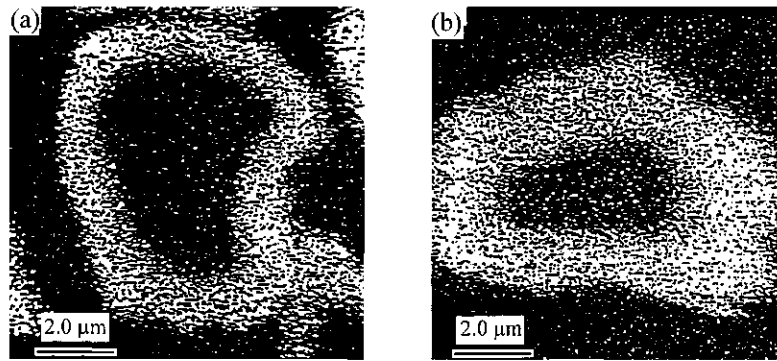


Figure 8.2. The distribution of phosphate in ferrihydrite particles. (a) Ferrihydrite particle reacted with phosphate for 1h. (b) Ferrihydrite particle reacted with phosphate for 1d.

black innercore is the part of the particle which the phosphate has not yet reached. By comparing the result for one hour (Figure 8.2a) and one day (Figure 8.2b) it can be seen that the phosphate front moves into the particle and that the boundary is indeed rather sharp. In this case the particles are highly porous and it is questionable whether a real coating is being formed or that it is more a diffusion process plus adsorption on the walls of the pores.

The reaction rate for unreacted shrinking core (USC) model can be described as:

$$\frac{\partial S}{\partial t} = f(S,L)(c-c_e) \quad (18)$$

The term $f(S,L)$ means that it is a function of the amount sorbed in the coating, S , and the shape and size of the particle, L . Only for a very well defined particle the expression for $f(S,L)$ can be substituted in equation (18) and it can be solved. For a soil a whole collection of different reactive particles may exist. For each reactive particle that reacts according to a USC process equation (18) applies.

We can integrate equation (18) according to:

$$\int f(S,L)^{-1} dS = \int (c-c_e)dt = \text{Int.} \quad (19)$$

The term $f(c-c_e)dt$ can be calculated if the solution concentration is measured as a function of time and if a value for c_e is assumed. The value of this integral should be equal to $f(S,L)^{-1}dS$. For a particle with a given shape and size there is a unique relationship between the measurable value of Int. and the amount reacted in the coating formation process S . The relationship itself can only be predicted in case the particle size and shape and the effective diffusion constant are known.

The integral defined in equation (19) is an 'exposure integral', which is also known in the field of toxicology. What equation (19) tells us is that a given value of the exposure integral for a certain particle corresponds with one value of S . One and the same value of the exposure integral can be obtained for quite different circumstances. A low concentration during a long reaction time may yield the same integral value as a higher concentration during a short reaction time, the model says that in both cases the 'exposure' is the same and that also the amount reacted should be the same. The same arguments also apply for any mixture of particles with different particle sizes and shapes. It is thus expected that the model might be applicable to a soil.

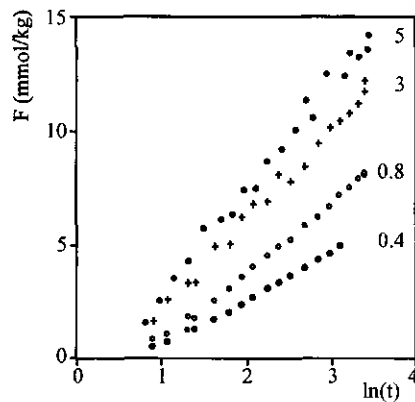


Figure 8.3. Phosphate sorption to a sandy soil (F , in mmol/kg) as a function of the natural logarithm of reaction time (t in hours) where the phosphate concentration is kept constant during the reaction. In the figure four different experiments are represented, the difference being the phosphate concentration in solution (0.4, 0.8, 3 and 5 mmol/L phosphate).

In Figure 8.3 the total phosphate sorption, denoted by F , as a function of time on a logarithmic scale is plotted as measured for four different phosphate concentrations in solution ranging from 0.4 mmol/L - 5 mmol/L. During an experiment the solution concentration is kept constant. On a logarithmic scale almost straight lines result, meaning that the rate decreases exponentially with the progression of the reaction.

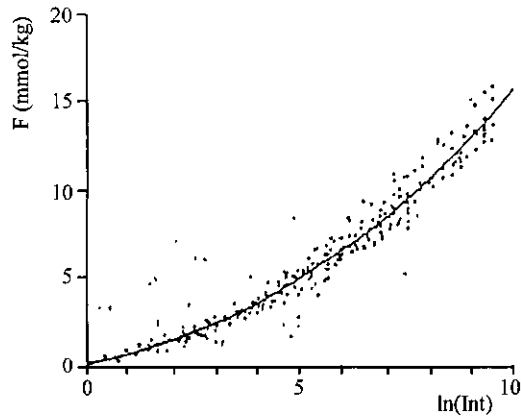


Figure 8.4. Phosphate sorption measured at a whole series of constant phosphate concentrations (see Figure 8.3) represented as a function of the natural logarithm of the calculated 'exposure' integral. The line represents a polynomial that was fitted through the data prints.

In Figure 8.4 data originating from a whole series of experiments similar to those of Figure 8.3 are now plotted as a function of the natural logarithm of the exposure integral. The theory states that all points with the same exposure should coalesce into one point. Since the total sorption of course increases with the exposure a line should result. The course of this line is not predicted from theory, apart from the fact that the slope of the line should be ≥ 0 .

The drawn line is a polynomial that is fitted through the points. It is clear that the points do not correspond exactly to the theory since deviation from the line in vertical direction do exist. These deviations may be partly due to experimental error in the measurement and partly due to the fact that the suggested model is not perfect. Once the relationship between F and the exposure integral is established for a soil this relationship (the polynomials) can be used to make independent predictions.

In Figure 8.5 an experiment is performed where at $t = 0$ phosphate is added to a soil/water mixture with a certain solid solution ratio. The concentration is measured as a function of time (open circles). The solid line is predicted based on the polynomial of Figure 8.4. The agreement between the prediction and the measurements is very good. In Figures 8.3-8.5 a logarithmic scale is used not because of principal reasons but because in this way rather small values and relatively large values can be represented more clearly in one figure.

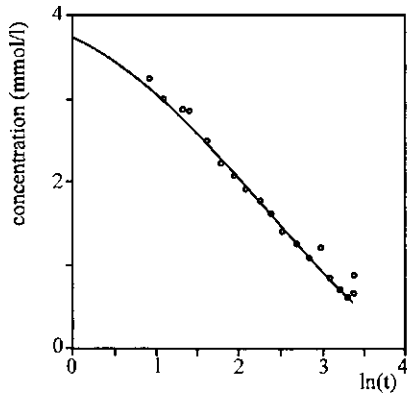


Figure 8.5. The concentration in the solution phase during reaction of phosphate with a sandy soil as a function of (the natural logarithm of) the reaction time ($t = \text{hr}$). The concentration decreases as a consequence of the proceeding sorption process. The circles represent measurements, the line is an independent prediction based on the application of the diffusion/precipitation model (or USC model) using the earlier obtained relationship between sorption and the exposure integral (see Figure 8.4).

8.5 References

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9 Basic principles of chemical speciation calculations

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Summary

The distribution of components over the different forms ('species') in which they are present in different soil phases (speciation) can be calculated by solving mass balance equations. Soil phases include different species (complexes) in the water phase, gases in the gas phase, minerals, organic liquids (NAPL) and adsorbed components (surface species) in the solid phase. An overview of a system description is usually presented in the form of a so-called 'table of species'. Adsorption- and desorption processes are described by means of either the Langmuir- or the Freundlich sorption model. This chapter includes a few simple examples of speciation calculations.

9.1 Introduction

Chemical speciation comprises the distribution of chemical compounds over the different forms in which they are present in different phases of a soil-water system. In other words, it concerns both their distribution over different phases in a soil-water system (the solid-, water- and gas phases, and possibly also the biota phase) and the different forms in which they are present in these phases. Furthermore, the situation in a state of chemical equilibrium is considered, rather than how equilibrium is attained or how long it will take to attain equilibrium. With regard to speciation, the following text discusses only ionic compounds, although it also applies to organic chemicals.

Speciation calculations are used for determining the chemical equilibrium composition of soil-water systems, *i.e.* the total amounts or concentrations of the various species present in the system. In such calculations, physico-chemical processes such as complexation, hydrolysis, precipitation, dissolution, volatilization, oxidation, reduction, adsorption and desorption need to be considered. As far as the biota phase is involved, bioaccumulation or uptake by organisms should also be taken into account. However, there are no simple partition models for ionic compounds with regard to the biota phase and therefore uptake is often described as if it concerns adsorption onto cell walls (Plette et al. 1996).

Compounds may be present in the form of various species, such as:

- *in the water phase:*

free ions	: H^+ , Cd^{2+} , OH^- , Cl^- , PO_4^{3-} , Al^{3+}
complexes (ion pairs)	: $CdCl^+$, $AlOH^{2+}$, $H_2PO_4^-$, chelates (EDTA)
metal-DOC complexes	: Cu-DOC (DOC = Dissolved Organic Carbon)

- *in the solid phase:*
 - minerals or solids : CdS(s) , $\text{CdCO}_3\text{(s)}$, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O(s)}$, $\text{Fe(OH)}_3\text{(s)}$
 - organic liquids : Benzeen, Toluene, Tri, Per, oil, PAH, Tar
 - adsorbed to soil particles : Various sorption models:
 - (surface species)
 - Langmuir, Freundlich, Ion Exchange
 - Variable charge models, heterogeneity models
- *in the gas phase:*
 - gases : $\text{NH}_3\text{(g)}$, $\text{CO}_2\text{(g)}$, $\text{H}_2\text{S(g)}$, HCN(g)
- *in the biota phase* : accumulated in organisms; no simple partition models are available, except models for organic chemicals.

It is often necessary to do speciation calculations, because there is a lack of proper analytical methods for the direct identification and determination of species concentrations. In most cases, only the total amounts of compounds can be determined by analytical methods, not the amounts of their specific forms (*e.g.* only the total amount of Cd can be determined, not the concentration of Cd^{2+}). Important exceptions are proton activity (pH) and redox potential (relative electron activity), which can easily be measured, whereas it is very difficult to estimate their total amounts in soil-water systems.

To give an example, speciation calculations need to be done in the case of risk assessments, as these require detailed information on the identities and concentrations of prevailing species because of differences in toxicity and/or behaviour in the soil-water system.

In other words, speciation calculations can supplement data which have been obtained by means of available analytical methods (*e.g.* total amounts of compounds). The remaining text explains how such calculations are done and what data they require. A few simple examples are included. For more information on the concerned systematic method for solving chemical equilibria, refer to the workbook 'Chemical Equilibria in Soil, Water, Sediment; Part B' (Keizer & van Riemsdijk 1992).

9.2 Arithmetic method

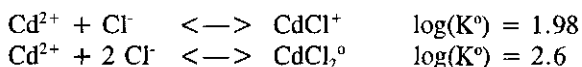
The first step of the systematic method for solving chemical equilibria consists of defining the system which contains all the relevant components. These components could be considered the 'building blocks' or 'basic entities' of the system. Many different species may be present; they are the reaction products of the components which react with each other. Components themselves are also considered species.

The equilibrium constant or formation constant (K°) of an equilibrium reaction is defined as the species activity divided by the product of the component activities. For diluted solutions with very low salt concentrations, the activities of the components are equal to their concentrations.

Example of a system description:

Components : Cd^{2+} and Cl^-
Species : Cd^{2+} , Cl^- , CdCl^+ and CdCl_2°

Equilibrium reactions:



$$\begin{aligned} (\text{CdCl}^+) &= (\text{Cd}^{2+}) \cdot (\text{Cl}^-) \cdot 10^{1.98} & : \text{ activity of species CdCl}^+ \\ (\text{CdCl}_2^0) &= (\text{Cd}^{2+}) \cdot (\text{Cl}^-)^2 \cdot 10^{2.6} & : \text{ activity of species CdCl}_2^0 \end{aligned}$$

Commonly, free cations and free anions are considered components of systems (*e.g.* H^+ , Cd^{2+} , PO_4^{3-} , Al^{3+} , Cl^-).

A chemical equilibrium problem is solved by calculating the distribution of the components over all species present in the system. This requires knowledge of the concentrations or activities (*e.g.* pH) and/or the total amounts of the components (*e.g.* Cd(t)). The total amount of a component, distributed over several species, may be expressed in terms of the mass balance of that component.

Example of mass balance equations for the Cd-Cl system:

$$\begin{aligned} \text{Cd}(t) &= [\text{Cd}^{2+}] + [\text{CdCl}^+] + [\text{CdCl}_2^0]: \text{ total amount of Cd} \\ \text{Cl}(t) &= [\text{Cl}^-] + [\text{CdCl}^+] + 2 [\text{CdCl}_2^0]: \text{ total amount of Cl} \end{aligned}$$

In this text () is used for the activities of species or components, and [] for their concentrations.

If mass balances are used, the calculations need to be done in terms of concentrations, and all species need to be expressed in terms of components and formation constants. However, such constants are normally defined in terms of activities. Therefore, activities need to be converted to concentrations. For such conversions, activity coefficients are used, as follows:

$$a_i = f_i \cdot c_i \tag{1}$$

a_i : the activity of species i (mol/l)
 c_i : the concentration of species i (mol/l)
 f_i : the activity coefficient of species i

The activity coefficients can be readily calculated using the following Davies equation:

$$\log(f_i) = -0.51Z_i^2 \left(\frac{\sqrt{U}}{1+\sqrt{U}} - 0.2U \right) \tag{2}$$

Z_i : the valence of species i
 U : ionic strength (mol/l)

The above formula can be used for calculating the activity coefficient for a given ionic strength, provided the latter does not exceed a value of approximately 0.5. In the case

of higher values, the Davies equation needs to be adapted. The ionic strength is calculated using the following formula:

$$U = 0.5 \sum_{i=1}^n (C_i Z_i^2) \quad (3)$$

n : the total number of species

This problem can be solved only by iteration. In many practical situations, a reasonably accurate estimate of the ionic strength can be made on the basis of known component concentrations and/or total amounts present in solution, and therefore this iteration procedure need not be applied.

Example: Estimate U on the basis of the total amounts of the components present in a solution containing 0.02 mol/l CdCl₂:

$$U = 0.5 (0.02 * 4 + 0.04 * 1) = 0.06 \text{ mol/l}$$

For values of f_i for ions with abs(z) = 1, 2, 3 and 4 for different values of U (0 - 0.5 mol/l), see Figure 9.1.

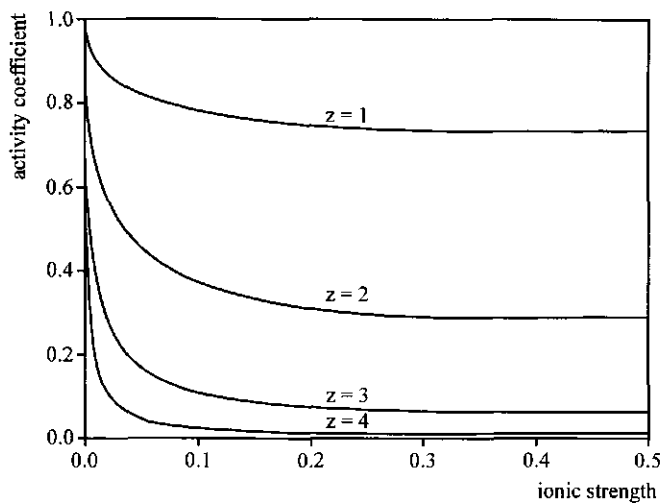
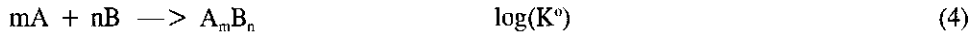


Figure 9.1. Activity coefficient versus ionic strength for z = 1, 2, 3 and 4.

In solving chemical equilibria, the following systematic approach is usually taken: Calculate the activity coefficients on the basis of an estimated ionic strength, and convert the equilibrium constants regarding the basic set of equilibrium reactions to 'concentration constants'. Thus, the 'concentration constants' apply to the given ionic strength.

For example, consider the formation of species A_mB_n from components A and B:



K° is the formation constant for this reaction and is expressed in terms of activities ($U = 0$):

K^c is the formation constant expressed in terms of concentrations ($U = C$).

$$K^\circ = \frac{(\text{A}_m\text{B}_n)}{(\text{A})^m \cdot (\text{B})^n} \quad (5)$$

K° is converted to K^c as follows:

$$K^\circ = \frac{(\text{A})^m \cdot (\text{B})^n}{(\text{A}_m\text{B}_n)} = \frac{(f_A)^m \cdot (f_B)^n [\text{A}]^m \cdot [\text{B}]^n}{f_{\text{A}_m\text{B}_n} [\text{A}_m\text{B}_n]} = K^c \cdot \frac{(f_A)^m \cdot (f_B)^n}{f_{\text{A}_m\text{B}_n}} \quad (6)$$

f_A : the activity coefficient of component A

f_B : the activity coefficient of component B

$f_{\text{A}_m\text{B}_n}$: the activity coefficient of species A_mB_n

In order to solve the equilibrium problem - the distribution of A and B over the species A, B and A_mB_n - the mass balances of the components A and B need to be expressed in terms of component concentrations, as follows:

$$\text{A}(t) = [\text{A}] + m \cdot [\text{A}_m\text{B}_n] \quad (7)$$

$$\text{B}(t) = [\text{B}] + n \cdot [\text{A}_m\text{B}_n] \quad (8)$$

The concentration of species A_mB_n is equal to:

$$[\text{A}_m\text{B}_n] = [\text{A}]^m \cdot [\text{B}]^n \cdot K^c \quad \text{Thus:}$$

$$\text{A}(t) = [\text{A}] + m \cdot [\text{A}]^m \cdot [\text{B}]^n \cdot K^c \quad (9)$$

$$\text{B}(t) = [\text{B}] + n \cdot [\text{A}]^m \cdot [\text{B}]^n \cdot K^c \quad (10)$$

If $\text{A}(t)$, $\text{B}(t)$ and K^c are known, these two equations can be solved, because then only two unknown variables ($[\text{A}]$ and $[\text{B}]$) are left. For solving such equations, usually a numerical solution method needs to be used (*e.g.* the Newton-Raphson method). Furthermore, for starting calculations, the component concentrations in the state of equilibrium ($[\text{A}]$ and $[\text{B}]$) need to be estimated.

In the case of practical applications, it is necessary to know what components and species are relevant to the system concerned, and to have reliable $\log(K^\circ)$ values at one's disposal. Data on what species may be present and their $\log(K^\circ)$ values can be found in handbooks on stability constants (*e.g.* Sillen & Martell 1971; Smith & Martell 1976), soil chemistry (*e.g.* Lindsay 1979) and water chemistry (*e.g.* Stumm & Morgan 1981). These constants can also be found in the databases of many computer programs (*e.g.* MINEQL (Westall et al. 1976), GEOCHEM (Sposito & Mattigod 1980) and ECOSAT (Keizer & van Riemsdijk 1994)). For an overview see Loeppert et al. (1995).

9.3 Table of species

The classic method for describing the various mass balances of components, in which species concentrations are expressed in terms of component concentrations and K^c values (equations (9) and (10)), often leads to long, confusing equations, especially if they include the numerical values of the various formation constants.

A convenient alternative is a so-called 'table of species'. In a condensed form, such a table gives an almost complete overview of the system concerned. The structure of such a table is illustrated in Table 9.1, using the above example concerning a system with components A and B and species A, B and A_mB_n :

Table 9.1. Table of species.

Components	A	B	log (K)
species			
A	1	0	0
B	0	1	0
A_mB_n	m	n	log K^c
Total	A(t)	B(t)	

All species present in the system are listed in the column on the far left-hand side. Their charges are not indicated, however, so as to keep the table orderly. The selected components are given in the upper row of the table, as is $\log(K)$. The numbers in the columns below the components indicate how often these components are present in the species concerned (the stoichiometric coefficient). The $\log(K)$ column gives the $\log(K^c)$ values for the species concerned. For components, these values equal 0. The row at the bottom gives the total amounts for the components (mol/l).

The species concentration (mol/l), expressed in the concentrations of the components, may be derived directly from the table as:

Read the table horizontally:

$$[A] = [A]^1 \cdot [B]^0 \cdot 10^0 \quad \text{or} \quad \log[A] = 1 \cdot \log[A] + 0 \cdot \log[B] + 0 \quad (11)$$

$$[B] = [A]^0 \cdot [B]^1 \cdot 10^0 \quad \text{or} \quad \log[B] = 0 \cdot \log[A] + 1 \cdot \log[B] + 0 \quad (12)$$

$$[A_mB_n] = [A]^m \cdot [B]^n \cdot K^c \quad \text{or} \quad \log[A_mB_n] = m \cdot \log[A] + n \cdot \log[B] + \log(K^c) \quad (13)$$

The expression for the mass balance for a certain component may also be derived directly from the table, as it is equal to the sum of the products of the numbers (stoichiometric coefficients) in the component column and the concentrations of the accompanying species, as follows :

Read the table vertically:

$$A(t) = 1 \cdot [A] + 0 \cdot [B] + m \cdot [A_mB_n] \quad (14)$$

$$B(t) = 0 \cdot [A] + 1 \cdot [B] + n \cdot [A_mB_n] \quad (15)$$

This table of species contains all information necessary for doing the calculations, namely:

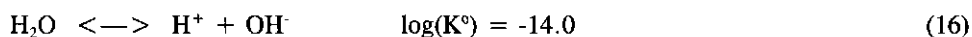
- the components and species present
- the $\log K^c$ values for the species
- the total amounts of the components.

The ionic strength needs to be known (if it has not already been calculated), as well as the charges of the components (for calculating the activity coefficients) and the estimates of the component concentrations (for starting the iteration process).

Particular attention should be paid to the values of $\log K^c$. Sometimes, there is confusion over which value is correct, for example, in the case of minerals for which the solubility values are unknown. Sometimes, even the correct values are unknown, *e.g.* in the case of metal-DOC complexes (DOC = Dissolved Organic Matter) or surface species (parameters of a sorption model).

9.4 H₂O dissociation equilibrium

Up until now, the solvent water (H₂O) has not explicitly been taken into account, although it is an essential part of the systems in which we are interested. Even more important is the fact that H₂O participates in many equilibrium reactions, such as the dissociation of H₃PO₄ and the formation of hydrolysis products. This means that the dissociation equilibrium of H₂O also belongs to the basic set of equations describing the system. Its equation is as follows:



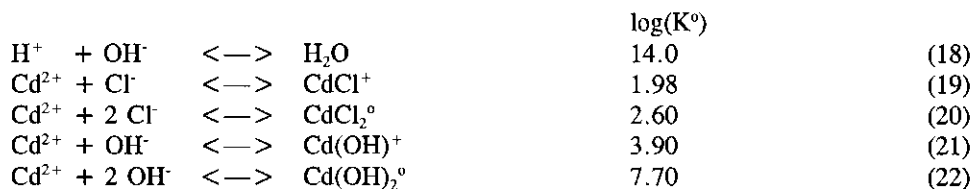
As the activity of water in many diluted solutions is practically equal to 1, the expression for the ion product of water can be simplified as indicated in equation (17).

$$K^\circ = \frac{(\text{H}^+)(\text{OH}^-)}{(\text{H}_2\text{O})} \approx (\text{H}^+)(\text{OH}^-) = 10^{-14.0} \quad (17)$$

The mass balances for the components H⁺ and OH⁻ (H(t) and OH(t)) now include the concentration of water ([H₂O]) as a term. It is equal to 1000/18 = 55.56 mol/l at 25 °C. The H₂O phase now appears in a separate part of the table of species, designated by 'phases' (see Table 9.2). The log(K) column now contains the dissociation constant instead of the formation constant. Horizontally, the table now includes an expression for the ion product of water (equation (17)) instead of the concentration of water. Vertically, the total amounts of the components are still expressed, including the components present in H₂O. The same procedure can be applied to minerals. In this, the solubility constant (K_s) is placed in the log(K) column (see section 9.6).

The complexation of Cd²⁺ with Cl⁻ and OH⁻ is given here as an example. Assume that 0.02 mol/l CdCl₂ and 0.01 mol/l HCl have been dissolved in water. For convenience, U is assumed to be equal to 0 ($\log(K^c) = \log(K^\circ)$).

The following equilibrium reactions are relevant:



The table of species belonging to this system is represented in Table 9.2.

Mass balance equations :

$$\text{Cd(t)} = [\text{Cd}^{2+}] + [\text{CdCl}^+] + [\text{CdCl}_2^{\circ}] + [\text{Cd(OH)}^+] + [\text{Cd(OH)}_2^{\circ}] = 0.02 \text{ mol/l} \quad (23)$$

$$\text{Cl(t)} = [\text{Cl}^-] + [\text{CdCl}^+] + 2 [\text{CdCl}_2^{\circ}] = 0.05 \text{ mol/l} \quad (24)$$

$$\text{H(t)} = [\text{H}^+] + [\text{H}_2\text{O}] = 0.01 + 55.56 = 55.57 \text{ mol/l} \quad (25)$$

$$\text{OH(t)} = [\text{OH}^-] + [\text{H}_2\text{O}] + [\text{Cd(OH)}^+] + 2 [\text{Cd(OH)}_2^{\circ}] = 55.56 \text{ mol/l} \quad (26)$$

Table 9.2. Table of species: 0.02 mol/l CdCl₂ + 0.01 mol/l HCl; U = 0.

Components	Cd	Cl	H	OH	log(K)
Species					
Cd	1	0	0	0	0
Cl	0	1	0	0	0
H	0	0	1	0	0
OH	0	0	0	1	0
CdCl	1	1	0	0	1.98
CdCl ₂	1	2	0	0	2.6
CdOH	1	0	0	1	3.9
Cd(OH) ₂	1	0	0	2	7.7
Phases					
H ₂ O	0	0	1	1	-14.0
Total	Cd(t)	Cl(t)	H(t)	OH(t)	
	0.02	0.05	55.57	55.56	

[H₂O] appears in the mass balances for H and OH. *In both cases*, this term is multiplied by one, because H₂O is composed of a combination of one H⁺ unit and one OH⁻ unit.

The concentration of a species may be expressed as a product of component concentrations and K^c values. However, this does not apply to the water phase. For diluted systems, the concentration of water is practically constant. In such a case, the activity coefficient of water is unity. This approximation may be used for most environmental systems.

Because the activity coefficient of water is unity, it is possible to eliminate one of the components (H⁺ or OH⁻) from the set by expressing one in terms of the other. Here, the component OH⁻ is eliminated. The set of mass balance equations can now be reduced by one in order to calculate the concentrations of the remaining components. In

other words, the system loses one degree of freedom. This reduction of the number of mass balance equations is done in such a way that the concentration of water (which is not unity!) is eliminated from the set of equations. This is possible by combining the mass balances of H^+ and OH^- as follows:

$$H(t) - OH(t) = [H^+] - [OH^-] - [Cd(OH)^+] - 2 [Cd(OH)_2^0] = 0.01 \text{ mol/l} \quad (27)$$

$$\text{or with : } [OH^-] = [H^+]^{-1} \cdot 10^{-14.0} \quad (28)$$

$$H(t) - OH(t) = [H^+] - [H^+]^{-1} \cdot 10^{-14.0} - [Cd^{2+}] \cdot [H^+]^{-1} \cdot 10^{-10.1} - 2[Cd^{2+}] \cdot [H^+]^{-2} \cdot 10^{-20.3} \quad (29)$$

The last equation shows that the coefficients in the H^+ column of the table of species (Table 9.2) have been changed by subtracting the coefficient in the OH^- column from the one in the H^+ column. The $\log(K^\circ)$ values have been adjusted by adding -14.0 times the coefficient in the OH^- column. The value of $H(t) - OH(t)$ is equal to the total amount of component H^+ minus the total amount of component OH^- (mol/l). The result of this operation is shown in Table 9.3.

In contrast to ordinary mass balances, $H(t) - OH(t)$ may have negative values or be equal to 0, because it is a linear combination of two ordinary mass balances.

Table 9.3. Table of species. 0.02 mol/l $CdCl_2$ + 0.01 mol/l HCl ; $U = 0$. Reduction based on the H_2O dissociation equilibrium.

Components	Cd	Cl	H	$\log(K)$
Species				
Cd	1	0	0	0
Cl	0	1	0	0
H	0	0	1	0
OH	0	0	-1	-14.0
$CdCl$	1	1	0	1.98
$CdCl_2$	1	2	0	2.6
$CdOH$	1	0	-1	-10.1
$Cd(OH)_2$	1	0	-2	-20.3
<hr/>				
Total	Cd(t)	Cl(t)	H(t) - OH(t)	
	0.02	0.05	0.01	

If precipitates (pure solid phases or minerals) are formed, a situation arises which is completely analogous to the one encountered in the case of reduction with the H_2O dissociation equilibrium (see section 9.6).

9.5 Constant component concentrations or activities

If the concentration or activity of a component is known, that is, if it has a constant value (e.g. pH), the set of mass balance equations can be further reduced. In the table of species, the column of the component with known concentration (if the activity is

known, it should be converted to concentration) is then omitted, and the log(K) column is adjusted.

In many practical situations, the pH has a constant, known (measured) value. The total amount of H(t) - OH(t) is then not relevant to the solution of the chemical equilibrium problem.

Consider, for example, the dissociation of H₃PO₄. The relevant equilibrium reactions are as follows:



The table of species for this system is presented in Table 9.4. It is assumed that U = 0, H(t) - OH(t) = 0.02 mol/l and PO₄(t) = 0.01 mol/l.

Table 9.4. Table of species. Reduction based on the H₂O dissociation equilibrium; U = 0.

Components	H	PO ₄	log(K)
Species			
H	1	0	0
OH	-1	0	-14.0
PO ₄	0	1	0
HPO ₄	1	1	12.35
H ₂ PO ₄	2	1	19.55
H ₃ PO ₄	3	1	21.70
Total	H(t) - OH(t) 0.02	PO ₄ (t) 0.01	

From Table 9.4, it can be deduced that:

$$[\text{H}_3\text{PO}_4^0] = [\text{H}^+]^3 \cdot [\text{PO}_4^{3-}] \cdot 10^{21.70}$$

Replace, for example, [H⁺] by 10⁻⁶, i.e. pH = 6 (U = 0). This results in the following:

$$[\text{H}_3\text{PO}_4^0] = [\text{PO}_4^{3-}] \cdot 10^{21.70} \cdot 10^{-18} = [\text{PO}_4^{3-}] \cdot 10^{3.70}$$

Thus, the log(K) column should be adjusted by adding the product of the coefficient of the 'known' component column and the logarithm of the actual component concentration to the original log(K) value. In Table 9.5, this situation is elaborated upon for the given example with a concentration of H⁺ which is assumed to be known.

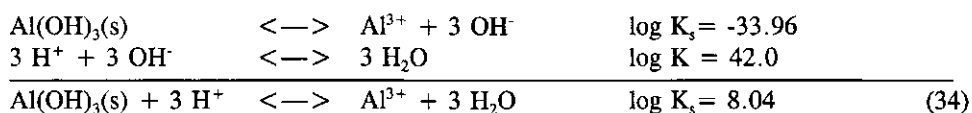
Table 9.5. Table of species. Reduction based on the H₂O dissociation equilibrium; known value for [H⁺]; U = 0.

Components	PO ₄	log(K)
Species		
H	0	0 + log(H)
OH	0	-14.0 - log(H)
PO ₄	1	0
HPO ₄	1	12.35 + log(H)
H ₂ PO ₄	1	19.55 + 2 log(H)
H ₃ PO ₄	1	21.70 + 3 log(H)
Total	PO ₄ (t) 0.01	

The species H⁺ and OH⁻ may be omitted from the table, because their values are known or can be calculated directly (the coefficient in the PO₄ column equals 0).

9.6 Equilibria with minerals

It is typical of minerals that their quantities do not affect the equilibrium composition of the solution of the system in which they are present. In other words, the activity of pure minerals is equal to 1 (compare this situation with that of the water phase in section 9.4). Based on the equilibrium reaction, the solubility constant K_s of minerals may be defined as follows (the equilibrium reaction for gibbsite is given as an example):



$$K_s = (\text{Al}^{3+}) \cdot (\text{H}^+)^{-3} = 10^{8.04} \quad (35)$$

The product (Al³⁺) · (H⁺)⁻³ is called the ion activity product (IAP).

Equation (35) may be written as follows:

$$\log [\text{Al}^{3+}] = 8.04 - 3 \text{pH} \quad (36)$$

This simple relation can be plotted in a so-called 'solubility diagram' (Figure 9.2).

At equilibrium, the ion activity product (IAP) equals K_s. If IAP > K_s, the solution is supersaturated with respect to gibbsite, and the mineral will be formed (precipitation). If IAP < K_s, the solution is undersaturated with respect to gibbsite, and the gibbsite present will dissolve until either IAP equals K_s, or all gibbsite has dissolved (see Figure 9.2).

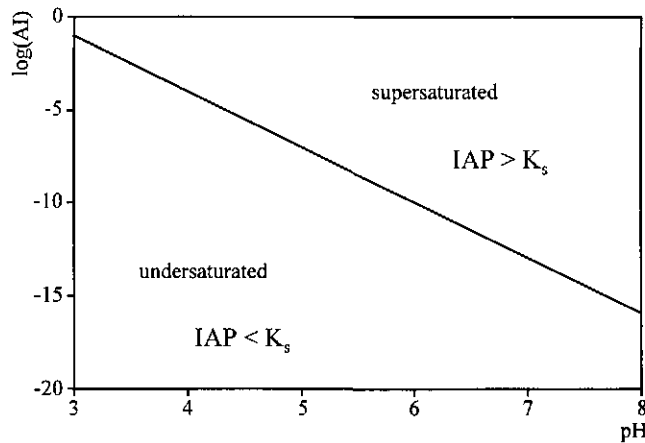


Figure 9.2. The solubility diagram for gibbsite, in which $\log(\text{Al}^{3+})$ is plotted against pH.

The calculation of chemical equilibria may be complicated as a result of slow reaction rates, especially if solid phases are involved. Reaction rates for species in solution are generally rather high, so that the calculated equilibrium composition for a system without solid phases, gas phase or surface sorption sites is normally reached within seconds.

One mineral is usually converted very slowly into another (dissolution and precipitation of minerals). In fact, sometimes the conversion rate is so low that the system may be described on the basis of a partial equilibrium. Similar problems may arise in the case of adsorption and desorption processes, although higher conversion rates are involved in this.

Handbooks on stability constants sometimes give many different $\log(K_s^0)$ values for relationships which are basically the same, e.g. for the solubility product of $\text{Al}(\text{OH})_3(\text{s})$: $(\text{Al}^{3+}) \cdot (\text{OH}^-)^3$, or for $\text{Fe}(\text{OH})_3(\text{s})$: $(\text{Fe}^{3+}) \cdot (\text{OH}^-)^3$. For the relevant equilibrium reactions and $\log(K_s^0)$ values, refer to Table 9.6.

Table 9.6. Equilibrium reactions and $\log(K_s^0)$ values for $\text{Al}(\text{OH})_3(\text{s})$ and $\text{Fe}(\text{OH})_3(\text{s})$.

Nr.	Mineral	Reaction		$\log(K_s^0)$
1	amorphous $\text{Al}(\text{OH})_3$	$\text{Al}(\text{OH})_3(\text{s})$	$\longleftrightarrow \text{Al}^{3+} + 3 \text{OH}^-$	-32.34
2	boehmite	$\text{Al}(\text{OH})_3(\text{s})$	$\longleftrightarrow \text{Al}^{3+} + 3 \text{OH}^-$	-33.87
3	bayerite	$\text{Al}(\text{OH})_3(\text{s})$	$\longleftrightarrow \text{Al}^{3+} + 3 \text{OH}^-$	-33.49
4	gibbsite	$\text{Al}(\text{OH})_3(\text{s})$	$\longleftrightarrow \text{Al}^{3+} + 3 \text{OH}^-$	-33.96
5	amorphous $\text{Fe}(\text{OH})_3$	$\text{Fe}(\text{OH})_3(\text{s})$	$\longleftrightarrow \text{Fe}^{3+} + 3 \text{OH}^-$	-38.46
6	hematite	$0.5\alpha\text{-FeOOH}(\text{s}) + 1.5 \text{H}_2\text{O}$	$\longleftrightarrow \text{Fe}^{3+} + 3 \text{OH}^-$	-41.91
7	goethite	$\alpha\text{-Fe}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}$	$\longleftrightarrow \text{Fe}^{3+} + 3 \text{OH}^-$	-42.02

The reason that these values are different is that the minerals concerned have a slightly different crystal lattice. It will be obvious that the composition of a solution in equilibrium with $\text{Al}(\text{OH})_3(\text{s})$ can correspond to only one of the four above-mentioned solubility relations. At complete equilibrium, the system will in principle be characterised by the most stable mineral.

Any mixture of amorphous $\text{Al}(\text{OH})_3(\text{s})$, boehmite and bayerite in contact with water will finally convert to gibbsite. The reactions involved are extremely slow. A conversion may be disregarded, if its reaction rate is low compared to the time scale of interest. The conversion of amorphous $\text{Al}(\text{OH})_3(\text{s})$ into gibbsite will in general take months, or even years. The equilibrium composition of the system containing water and amorphous $\text{Al}(\text{OH})_3(\text{s})$ can thus be predicted using equation (1) of Table 9.6, as long as the equilibrium between dissolved aluminium species and amorphous $\text{Al}(\text{OH})_3(\text{s})$ is established relatively quickly.

9.7 Adsorption and desorption equilibria

The behaviour of compounds in soil-water systems is often strongly influenced by adsorption and desorption processes. The most important reactive surfaces are located on clay minerals, metal (hydr)oxides and organic matter.

For the description of the relationship between a dissolved substance and its adsorbed form, various model equations may be used, such as the Langmuir equation, the Freundlich equation, various ion-exchange equations, and (electrostatic) models which take into account the (variable) charge of the reactive surfaces and the charge of the sorbing substance (species).

The systematic method for solving chemical equilibria presented in the previous sections may also be applied to these sorption models. By considering the amount of a component adsorbed on the solid-phase as a species 'dissolved' in the soil solution, it is possible to treat adsorption and desorption equilibria in the same way that chemical equilibria for species in the water phase are treated.

Equations describing adsorption or desorption processes, or describing ion exchange reactions, should be changed in such a way that they become comparable to 'normal' chemical equilibrium equations. Therefore, they need to be expressed in terms of the components of the system, and characterized by an equilibrium constant. This is elaborated upon below for two adsorption/desorption models (Langmuir and Freundlich). Regarding ion-exchange, an approach can be taken which is similar to the Langmuir model (Keizer & van Riemsdijk 1992).

9.7.1 Langmuir model

The Langmuir model may be represented by:

$[Q_i]$: the concentration of the adsorbed component i in mol/kg

$$[Q_i] = \frac{K_i \cdot Q(t) \cdot [i]}{(1 + K_i \cdot [i])} \quad (37)$$

$[i]$: concentration of component i (mol/l)

$Q(t)$: the total amount of surface sites available for adsorption (mol/kg)

K_i : the Langmuir sorption constant for component i (l/mol)

with $Q(t) = [Q] + [Q_i]$

$[Q]$: the concentration of surface sites still available for adsorption (mol/kg)

After substituting $Q(t)$ in (37), the Langmuir model may be formulated as:

$$[Q_i] = K_i \cdot [Q] \cdot [i] \quad (38)$$

This equation is comparable to the equation for the concentration of dissolved species expressed in terms of component concentrations and formation constants. If the surface sites available for adsorption (Q) are considered a component and the adsorbed amount of component i is considered a species (Q_i), this type of adsorption/desorption equilibrium can be treated as a normal chemical equilibrium. $Q(t)$ equals the mass balance for component Q .

The concentrations of Q , Q_i and $Q(t)$ (expressed in mol/kg) need to be converted into concentrations expressed in mol/l using either the soil solution ratio (kg/l), or the soil moisture content (l/kg). This is necessary in order to calculate the mass balance of the adsorbing component.

If several components compete for the same sorption sites, different K_i values for the various adsorbed components may be assumed to exist (multicomponent Langmuir model). The parameter values K_i and $Q(t)$ can be derived from measurement data of adsorption or desorption experiments, or can be estimated by applying linear regression analyses to the linearized Langmuir equation, as follows:

$$\frac{[i]}{[Q_i]} = \frac{1}{K_i \cdot Q(t)} + \frac{[i]}{Q(t)} \quad (39)$$

Table 9.7. Table of species. Cd sorption from a $CdCl_2$ solution according to the Langmuir model. $U = 0$. The species are similar to those in Table 9.3. Reduction based on the H_2O dissociation equilibrium.

Components	Cd	Cl	H	Q	log(K)
Species					
Cd	1	0	0	0	0
Cl	0	1	0	0	0
H	0	0	1	0	0
OH	0	0	-1	0	-14
Q	0	0	0	1	0
CdCl	1	1	0	0	1.98
CdCl ₂	1	2	0	0	2.6
CdOH	1	0	-1	0	-10.1
Cd(OH) ₂	1	0	-2	0	-20.3
Q _{cd}	1	0	0	1	log(K _{cd})
Total	Cd(t)	Cl(t)	H(t)-OH(t)	Q(t)	

The values found for K_i and $Q(t)$ apply only to the specific experimental conditions used. Important variables are, for instance: ionic strength, temperature, pH, soil type, other competing components, and soil/solution ratio.

The speciation is illustrated in Table 9.7 in the form of the table of species for cadmium adsorption from a CdCl_2 solution (see Table 9.3).

In soil systems, the value of $H(t) - OH(t)$ is usually unknown. Therefore, pH should be measured and used as an input variable in order to eliminate the H^+ column in the table of species (see also section 9.5).

9.7.2 Freundlich model

The Freundlich sorption model is very similar to a 'normal' chemical equilibrium equation, as follows:

$$[Q_i] = K_i [i]^n \quad (40)$$

Q_i : the concentration of the adsorbed component i in mol/kg

$[i]$: the concentration of component i (mol/l)

K_i : the Freundlich sorption constant for component i ($l^n \cdot \text{kg}^{-1} \cdot \text{mol}^{1-n}$)

n : model parameter

The adsorbed amount of component i may be considered a 'dissolved' species. No extra components need to be introduced. The concentration of Q_i (expressed in mol/kg) needs to be converted into concentration expressed in mol/l, using either the soil solution ratio (kg/l), or the soil moisture content (l/kg), in order to make it possible to calculate the mass balance.

The values for the model parameters K_i and n can be obtained using the linearized Freundlich equation, which is formulated as follows:

$$\log([Q_i]) = \log(K_i) + n \log([i]) \quad (41)$$

The values can be estimated on the basis of measurement data of adsorption or desorption experiments using linear regression analyses. The values found for K_i and n apply only to the specific experimental conditions used. Important variables are, for instance: ionic strength, temperature, pH, soil type, other competing components, and soil/solution ratio.

Because the value of n is usually not equal to 1 (except in the case of a linear adsorption model), it is difficult to calculate the mass balance for component i . The species Q_i has been formed by adsorption of 1 mol of i per mol of Q_i , and not by adsorption of n mol of i per mol of Q_i . This means that in calculating the species concentration of Q_i , the actual value of n needs to be used, but in calculating the total amount of component i (mass balance), n should be equal to 1. To do this with a computer program, the calculation procedure needs to be slightly adapted (as is done in the ECOSAT computer program).

Many adsorption and desorption processes (especially those of heavy metals) are pH dependent and can be described by a pH-dependent Freundlich model, according to the following formula:

$$[Q_i] = K_r [H]^m [i]^n \quad (42)$$

In this case, information about the effect of adsorption or desorption of component *i* on the mass balance $H(t) - OH(t)$ is also necessary. Even without adsorption or desorption processes, the value of $H(t) - OH(t)$ is usually unknown in soil systems. Therefore, the pH-dependent Freundlich model can only be applied to known (measured at equilibrium) pH values (see also section 9.5). In most soils, pH will be buffered to a constant value upon metal adsorption or desorption.

The above is illustrated in the form of the table of species for Cd adsorption from a $CdCl_2$ solution in Table 9.8.

Table 9.8. Table of species. Cd sorption from a $CdCl_2$ solution according to the pH-dependent Freundlich model. $U = 0$. The species are similar to those in Table 9.3. Reduction based on H_2O dissociation equilibrium.

Components	Cd	Cl	H	log(K)
Species				
Cd	1	0	0	0
Cl	0	1	0	0
H	0	0	1	0
OH	0	0	-1	-14
$CdCl$	1	1	0	1.98
$CdCl_2$	1	2	0	2.6
$CdOH$	1	0	-1	-10.1
$Cd(OH)_2$	1	0	-2	-20.3
Q_{Cd}	n^*	0	m	$\log(K_{Cd})$
Total	Cd(t)	Cl(t)	H(t) - OH(t)	

* read horizontally : $n = n$; $m = m$
 read vertically : $n = 1$; $m = 0$

This table can be reduced further, using the known pH value (see section 9.5).

9.8 References

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10 Adsorption and desorption reactions I: basic principles and simplified models

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10.1 Introduction

The mobility and the bioavailability of species in the 'soil', be it a terrestrial soil, a submerged soil or aquifer, is strongly dependent on the distribution of this species over the solid phase and the solution phase of the 'soil' system.

This distribution may be governed by various different chemical processes and is dependent on a series of environmental conditions and also dependent on the particular solid phase composition of the soil sample that is studied. With environmental conditions mainly the composition of the solution phase is meant, *i.e.* the pH, the redox status and the concentration of other species that may affect the distribution of the species of interest. Other species may interact with the species of interest by means of competition for the same adsorption sites or by formation of complexes with the species of interest that have a different affinity for the solid phase than the uncomplexed species.

Chemical processes that may affect the distribution of chemicals over the solution phase and the solid phase are:

- complexation in solution
- specific adsorption (soil organic matter, metal(hydr)oxides, clay)
- ion exchange (clay)
- (co) precipitation/dissolution
- solid solution formation.

Almost all these processes are dependent on the composition of a particular soil. This means that for the same composition of the solution phase the distribution over the solid phase and the solution phase may vary widely dependent on the composition of the solid phase. On the other hand, for the same solid phase composition but for different solution conditions also enormous differences in the distribution of a chemical over the solution and the solid phase can be obtained.

Also the dependency of different chemical interaction processes on the solution conditions (*e.g.* pH) may be quite different. Ideally, one should be able to interpret the behaviour of a chemical in a soil system based upon detailed knowledge of the various interaction processes. However, fundamental knowledge with respect to specific adsorption processes is still limited. Moreover, even when all the fundamental details of the various interaction processes would be known for individual reactions, application to a soil system is still not easy.

In order to be able to apply the more fundamental models, one should be able to assess the content of reactive surface sites of the various reactive surfaces of clays, metal (hydr)oxides and humic and fulvic type materials present in a particular soil. This in itself

is not an easy task. Also, since various processes may operate simultaneously, one should be able to calculate the distribution taking into account the possibility of all known chemical reactions.

Another complicating factor is that the kinetics of some processes may be so slow that complete equilibrium is not obtained within a reasonable time span. This further complicates the measurement and the interpretation of the behaviour of chemicals in the soil system. In this chapter we will neglect kinetic complications and mainly focus on relatively simple adsorption equations and discuss how these adsorption equations can be incorporated into chemical speciation programs.

10.2 Monocomponent Langmuir model

The Langmuir adsorption model can be derived in various ways. The idea is that there are adsorption sites that may react with a species present in the solution phase to form an adsorbed species, whereas the surface sites that have not reacted are considered to be 'free' sites. The affinity of a (surface) site for an adsorbing species is characterized by an affinity constant. Furthermore it is assumed that all adsorption sites are equal. The binding may be written as:



where S represents a free site, A represents the adsorbing species forming the occupied site SA and K_{SA} is the affinity constant for this reaction.

This reaction equation is similar to reactions occurring only in the solution phase like the reaction between acetate and a proton, forming acetic acid:



The dissociated acetate molecules can be regarded as the free sites that can 'adsorb' a proton. The affinity constant K_{HAc} can be defined as:

$$K_{HAc} = \frac{(HAc)}{(Ac^-)(H^+)} \quad (3)$$

where the brackets denote activities. With the help of activity coefficients γ_i , the equation can be expressed in terms of concentrations that can be measured (mole/l) denoted by $[\]$:

$$K_{HAc} = \frac{[HAc]\gamma_{HAc}}{[Ac^-]\gamma_{Ac^-}[H^+]\gamma_{H^+}} \quad (4)$$

In dilute solutions the values of γ_i are approximately one and the activity correction can be neglected. The constant K_{SA} can be defined similarly as:

$$K_{SA} \equiv \frac{(SA)}{(S)(A)} \quad (5)$$

The essential difference between equations (3) and (5) is that (SA) and (S) are activities of surface species, whereas all activities in equation (3) refer to dissolved species. Equation (5) can be written in terms of in principle measurable concentrations and activity

coefficients as follows:

$$K_{SA} = \frac{\{SA\} f_{SA}}{\{S\}f_s[A]f_A} \quad (6)$$

The curly brackets are used to denote surface concentrations which can be expressed in mole per square metre of reactive surface. Note that the actual units into which the surface concentrations are expressed do not affect the value of the equilibrium constant K_{SA} , because the units of the surface species cancel. One may thus use other units like mole fraction or mole per kg adsorbent etc. It is customary to assume that the ratio of the activity coefficients of the surface species equals one. In other words one can in practice often neglect the activity coefficients of the surface species in equations of the type of equation (6). The activity coefficient for the adsorbing species is in case of adsorption of a charged species to variable charged surfaces, like soil organic matter or metal(hydr)oxides, of a more complex nature than the activity coefficient of the proton in equation (4). This is caused by the presence of a rather strong electric field that surrounds (variable) charge interfaces which affects the concentration of charged adsorbing species near the binding sites. The concentration near the binding sites can be approximated by the concentration in the solution multiplied with a Boltzman accumulation factor. This Boltzman factor can be seen as a type of activity coefficient correction.

In case of adsorption to variable charged interfaces like soil organic matter or metal(hydr)oxides the activity coefficient f_A includes the Boltzman factor of the adsorbing ion. The expression for f_A in equation (6) may thus be set equal to:

$$f_A = f_{A,solution} \exp(-Z_A F \Psi / RT) \quad (7)$$

where $f_{A,solution}$ is the usual solution phase activity coefficient and the second term on the right hand side of equation (7) equals the Boltzmann factor. z_A is the charge of the adsorbing ion (including sign), F is the Faraday constant, R the gas constant, T the absolute temperature and Ψ is the electric potential of the surface. The Boltzman factor can thus be seen as an extra activity coefficient that accounts for the effect of the electric field around a particle. Since we are dealing at present with simplified adsorption equations we will neglect all sorts of activity corrections and set them all equal to one.

In order to arrive at a Langmuir type adsorption equation we have to realize that in case only one species is adsorbing to the surface the total site concentration $\{S_t\}$ equals:

$$\{S_t\} = \{SA\} + \{S\} \quad (8)$$

By combining equation (8) with equation (6), $\{S\}$ can be eliminated and after rearrangement and taking all activity coefficients equal to one, it follows that:

$$\{SA\} = \frac{\{S_t\} K_{SA} [A]}{1 + K_{SA} [A]} \quad (9)$$

Equation (9) equals the Langmuir adsorption equation, where S_t equals the adsorption maximum, and $\{SA\}$ the amount adsorbed of species A.

Dividing both sides of equation (9) by $\{S_t\}$ leads to the expression for the fraction of the adsorption sites covered by A, θ_A being equal to:

$$\theta_A = \frac{K_{SA}[A]}{1 + K_{SA}[A]} \quad (10)$$

Because of the similarity between Langmuir adsorption and reactions between species in the solution phase it is very easy to combine in a standard chemical speciation model, reactions in the solution phase with adsorption of the Langmuir type. Central in the formulation of a chemical equilibrium problem is the table of species where all possible species are listed and expressed in terms of component concentrations and logK values. For acetic acid in water Table 10.1 of species equals:

Table 10.1. Speciation table for acetic acid.

Components	Ac	H	log (K)
Species			
H	0	1	0
OH	0	-1	-14.0
Ac	1	0	0
HAc	1	1	4.76
Total	Ac(t)	H(t) - OH (t)	

Reading the table in horizontal direction, it is a short hand notation for the expression of all chemical species in the systems expressed in terms of a chosen set of independent components and logK values, where the coefficients in a row are the exponents to which the components have to be raised. For example:

$$[\text{OH}] = [\text{Ac}]^0[\text{H}]^{-1} 10^{-14} = [\text{H}]^{-1} 10^{-14} \quad (11)$$

$$[\text{H Ac}] = [\text{Ac}]^1[\text{H}]^1 10^{4.76} \quad (12)$$

For each component a mass balance can be formulated. The table of species is also a short hand notation for the mass balances. Each column represents a mass balance. The coefficients in a column are the coefficients of the various species in the particular mass balance. For all species containing the component Ac the first column in Table 10.1 represents the mass balance of Ac(t) and can be read as:

$$\text{Ac}(t) = 0[\text{H}] + 0[\text{OH}] + 1[\text{HAc}] + 1[\text{Ac}] = [\text{Ac}] + [\text{HAc}] \quad (13)$$

The chemical problem can now be expressed as two equations (the two mass balances) with two unknowns (the component concentrations) provided that the value of Ac(t) and H(t) - OH(t) is known. Such a problem can be solved mathematically for instance using a computer program that is aimed at solving a set of chemical equilibria. Let us now consider the table of species in case of Langmuir adsorption (Table 10.2). As components we may choose the unoccupied site, S and A. This leads to the following table of species.

Table 10.2. Speciation table for sorption of A to a surface site S.

Components	S	A	log(K)
Species			
S	1	0	0
A	0	1	0
SA	1	1	log(K)
Total	S(t)	A(t)	

It follows from Table 10.2 that in the mass balance A(t) both a surface species and a dissolved species occur in one and the same mass balance. This means that both types of species should be expressed in the same units. Because the choice of the units of the surface species does not affect the value of the affinity constant and since all other equilibria taking place in the solution phase are expressed in moles per liter, it is most practical to use moles per liter solution for both mass balances. The value of S(t) should thus be specified in moles per liter. The result of the calculation is then that the concentration of all surface species are expressed also in moles per liter. The solid solution ratio expressed as kg/l or m²/l can be used to convert the concentration of the surface species into the desired units.

As stated before it is now also possible to combine chemical reactions in solution with surface adsorption reactions. Let us assume that Cd²⁺ adsorbs specifically to the soil surface and that the affinity of cadmium chloride complexes for the reactive surface sites in the soil is so low that they effectively can be neglected as adsorbing species. The formation of cadmium/chloride complexes nevertheless has an effect on the cadmium adsorption, although the complexes themselves are considered not to adsorb, because the concentration of [Cd²⁺] is lowered due to the formation of complexes with chloride. If the adsorption can be described with a Langmuir adsorption equation and if competition with other cations is neglected the table of species for this system can be formulated as:

Table 10.3. Speciation of CdCl₂ in the presence of a surface site S.

Components	S	Cd	Cl	log (k)
Species				
S	1	0	0	0
SCd	1	1	0	log K _{SCd}
Cd	0	1	0	0
CdCl	0	1	1	1.98
CdCl ₂	0	1	2	2.60
Total	S(t)	Cd(t)	Cl(t)	

Using Table 10.3 the effect of a certain total chloride concentration on the cadmium

adsorption can easily be calculated.

Often competition between species for the same adsorption sites is of importance. In such a situation an equation like equation (5) still holds but no longer equations (9) and (10). Let us first consider the equivalent problem in solution chemistry using again the acetate as an example. Acetate may not only react with a proton but it may also form a complex with for instance Cd^{2+} . This reaction can be formulated as:



This reaction can easily be incorporated in an extended version of the table of species as given in Table 10.1, by adding two extra species, Cd^{2+} and CdAc^+ and one extra mass balance for Cd(t).

Using such a table of species, it may be calculated how much of the total acetate is present as Ac^- , HAc or CdAc^+ for particular values of the various mass balances.

In fact competition for adsorption sites in the Langmuir approach works exactly in the same way. In the example for cadmium adsorption it is realistic to assume that calcium competes in a soil system for the same adsorption sites. Because of the analogy with the reactions in solutions, it is clear that this competition can easily be incorporated, for instance by extending Table 10.3, by introducing two new species, Ca and SCa , and a mass balance for calcium. The question remains how equations (9) and (10) change in case of competitive adsorption. By using in essence the same method as for the non competitive case it can easily be shown that for the situation of calcium and cadmium competition the expression for θ_{Cd} now equals:

$$\theta_{\text{Cd}} = \frac{K_{\text{SCd}}[\text{Cd}^{2+}]}{1 + K_{\text{SCd}}[\text{Cd}^{2+}] + K_{\text{SCa}}[\text{Ca}^{2+}]} \quad (15)$$

and for θ_{Ca} equals:

$$\theta_{\text{Ca}} = \frac{K_{\text{SCa}}[\text{Ca}^{2+}]}{1 + K_{\text{SCd}}[\text{Cd}^{2+}] + K_{\text{SCa}}[\text{Ca}^{2+}]} \quad (16)$$

Equations (15) and (16) can easily be formulated in a more general form. In case of competition between n adsorbing species the expression for θ_i equals:

$$\theta_i = \frac{K_{\text{Si}}[\text{C}_i]}{1 + \sum_{i=1}^{i=n} K_{\text{Si}}[\text{C}_i]} \quad (17)$$

where i indicates an adsorbing species.

The difference between Langmuir type expressions and the table of species approach is that in order to obtain the Langmuir type expression the concentration of free surface sites is eliminated, whereas in the table of species it remains as an unknown. The advantage of the table of species approach is that it allows for calculation of complex systems with standard chemical equilibrium programs. The advantage of the Langmuir type expression is that it is easier to get insight in the qualitative behaviour of the system. For practical purposes both numerical calculations and insight in the expected behaviour of the system

are important. For instance when $[Ca^{2+}] \gg [Cd^{2+}]$ and $[Ca^{2+}]$ is approximately constant equation (15) reduces to a linear adsorption isotherm for cadmium adsorption when in addition $K_{SCa}[Ca^{2+}] \gg 1$:

$$\theta_{Cd} \approx \frac{K_{SCd}}{K_{SCa}[Ca^{2+}]} [Cd^{2+}] \quad (18a)$$

$$\theta_{cd} \approx K [Cd^{2+}] \quad (18b)$$

with $K' = K_{SCd}/(K_{SCa} [Ca^{2+}])$.

Equation (18b) may be written in terms of the concentration of surface species by multiplying both sides of equation (18b) with $S(t)$.

$$\{SCd\} \approx S(t)K [Cd^{2+}] \quad (18c)$$

$$\{SCd\} = K^* [Cd^{2+}] \quad (18d)$$

with $K^* = S(t) K'$.

In fact equation (18d) is the expression for a linear adsorption isotherm. This derivation shows that the proportionality constant K^* is a mixed constant that consists of the affinity constants K_{SCd} and K_{SCa} , the calcium concentration in solution and the adsorption maximum $S(t)$, expressed in the same units as S_{Cd} .

The proportionality constant K^* may for instance be obtained from a single experiment aimed at measuring cadmium adsorption to a soil in a calcium chloride background for low cadmium concentrations. The analysis given above shows that it is expected that the value of K^* obtained depends on the 'environmental' conditions, *i.e.* the concentration of calcium chloride used. The analysis also shows that the proportionality constant is not expected to be the same for different soils. The dependency on soil type arises because the adsorption maximum $S(t)$ is dependent on the available reactive surface in the soil which is a function of the composition of the soil. If the organic matter would be mainly responsible for the observed behaviour then it is to be expected that the value of K^* , when measured at the same concentration of calcium chloride in different soils, is a function of the organic matter content of the soil. Furthermore, if little is known on the exact adsorption mechanism and if a linear isotherm is measured, it is also impossible to derive an affinity constant and an adsorption maximum from these data.

10.3 Freundlich adsorption model

Another simple adsorption model that is often used when little is known about the adsorption mechanisms is the Freundlich adsorption model. The concentration of an adsorbed species $\{SA\}$ is in the Freundlich model given by:

$$\{SA\} = K_{SA}^F (A)^m \quad m \leq 1 \quad (19)$$

where $\{SA\}$ represents the amount adsorbed of species A expressed per unit amount of

adsorbent, K_{SA}^F is the Freundlich constant and m is another constant. When m in equation (19) equals 1 a linear adsorption isotherm results. Only when m equals one the value of the exponent is equal to the number of units of A per unit of SA. In case of the usual species in chemical equilibria the exponent always reflects the number of moles of the components that are involved in the 'construction' of a species. Note also that in the Freundlich model there is no need for a surface species S as a component.

The derivation of a linear isotherm from the Langmuir model discussed before, suggests that the total concentration of adsorption sites, *i.e.* the adsorption maximum is probably incorporated in the Freundlich constant.

This has as result that the units of the Freundlich constant are a function of the units into which {SA} is expressed. This in contrast with the Langmuir affinity constant. The dimension of the Freundlich constant is furthermore dependent on the value of m .

Incorporation of the Freundlich model into a standard chemical speciation code is less straightforward than it is for the Langmuir model. Since SA and A appear in the same mass balance and since it is logical to express the concentration of A in mole/l, SA should also be expressed in moles per liter. This means that always a conversion factor is necessary.

$$[SA](\text{mole/l}) = \gamma K_{SA}^F [A]^m \quad (19a)$$

When the value of K_{SA}^F corresponds with the amount adsorbed in moles per kg adsorbent, the value of γ equals the Solid Solution Ratio (SSR), in kg/l.

The table of species that is equivalent to Table 10.2 is given in Table 10.4.

Table 10.4. Speciation table for Freundlich adsorption.

Components	A	logK
Species		
SA	$m, 1$	$\log K_{SA}^F = \log y$
A	1	0
Total	A(t)	

Instead of one, now two coefficients appear for the adsorbed species in the column of the adsorbing component. The coefficient m should be used when the table is used to express the surface species in terms of the component concentration and the $\log K$ value (horizontal direction) and the value of one should be used as a coefficient in the mass balance (vertical direction) since there is always one mole of component A present per mole of SA.

A disadvantage of the Freundlich model is that the effect of species that compete for the same adsorption sites is not included in the model. With respect to the effect of the pH on metal ion adsorption in soils the following pH dependent Freundlich type equation often gives a good description of metal ion adsorption data:

$$\{SMe\} = K_{SMc}^F (Me)^m (H^+)^{\alpha} \quad (20)$$

One of the most difficult problems in soil systems and chemical speciation models is to use the proton concentration as a component in the model, this is to say to use the pH as an output of the model calculation based upon the combined proton-hydroxyl mass balance. This is so because so many different reactions are involved in the (combined) proton balance of a soil, that at present it is hardly possible to use the pH as an 'output' parameter of a mechanistically oriented speciation calculation of a soil. A more empirical approach would be to measure an acid/base titration curve of a soil and use an empirical proton adsorption equation to account for proton buffering processes occurring in the soil system.

This whole problem can be circumvented when the adsorption data are collected at various constant pH values and the pH is used as an input parameter in the speciation model. This means that the effect of the pH on the system is incorporated in the 'adjusted' logK values and the proton is not treated as an unknown component concentration. Equation (20) can be used to calculate a K^F that is valid for a particular pH. The calculation then reduces to the problem specified in Table 10.4.

10.4 Heterogeneous adsorption equations

In order to get a better understanding of the Freundlich model it is useful to consider the effect of chemical heterogeneity on the adsorption. One may consider a mixture of different site types, where each site type behaves like a Langmuir type adsorption (see equations (9) and (10), but each site type is characterized by a different value of the affinity constant).

The total adsorption is the weighted sum of the contribution of the individual site types if it is assumed that the different site types behave fully independently. The weighting factor is simply the fraction of the total concentration of sites that is of a particular type. The total adsorption can thus be represented by:

$$\{SA\}_t = \sum_{i=1}^{i=n} f_i \{S_i\} \frac{K_{SA,i}[A]}{1 + K_{SA,i}[A]} \quad (21)$$

where f_i indicates the fraction of the total number of sites that is of type i , $\{S_i\}$ is the total site concentration of the mixture of different site types and $K_{SA,i}$ is the affinity constant of site type i for species A .

For a soil system the number of different site types and their respective affinity constants are often unknown. If the various parameters would be known it is in principle of course no problem to include all these different surface species in a speciation model. This can be done by introducing as many different surface components as it is assumed that there are site types.

Another approach is to assume that the heterogeneity can be characterized by a continuous distribution of affinity constants. In this case the total sorption is obtained by integration over the whole distribution:

$$\{SA\}_t = \{S_t\} \int f(\log K) \theta \, d \log K \quad (22)$$

where $f(\log K)$ is the normalized distribution function of all logK values and θ is described by the Langmuir expression (equation (10)). For a few specific types of distribution

functions equation (22) results in analytical expressions for the adsorption equation. A rather well known equation that results when a semi-Gaussian distribution equation is used is the Langmuir-Freundlich equation:

$$\{SA\}_i = \{S\} \frac{(\tilde{K}[A])^m}{1 + (\tilde{K}[A])^m} \quad 0 < m \leq 1 \quad (23)$$

The parameter \tilde{K} corresponds to the position of the peak of the affinity distribution on the $\log K$ axis. It is in fact the weighted average affinity constant of the heterogeneous mixture. The parameter m characterizes the width of the distribution. The smaller the value of m the wider the distribution function and the larger the heterogeneity. For $m=1$ equation (23) equals the homogeneous Langmuir equation. Equation (23) may be used to describe the acid/base characteristics of humic and fulvic acids, or other natural organic matter, when the electrostatic effects are included via a Boltzmann factor and when for the species A the proton is taken. To complete such a model one needs a double layer model in order to be able to calculate the potential that is part of the Boltzmann term. For humic and fulvic acids it can be shown that either a spherical or a cylindrical double layer model can be used. In doing so, one assumes that the mixture of organic molecules can be represented by one type of equivalent particles with average dimensions that is characterized by a certain chemical heterogeneity. The radius of the 'particles' in case of a spherical geometry is for fulvic acids around 0.6-0.9 nm. The specific surface area of these 'particles' may be estimated to be several thousand square metre per gram organic material.

For small values of $[A]$ the denominator in equation (23) approaches one and equation (23) reduces to:

$$\{SA\}_i = \{S\}(\tilde{K})^m [A]^m \quad (24)$$

or:

$$\{SA\}_i = K_{SA}^F [A]^m \quad (25)$$

In this way it is shown that the Freundlich equation can be derived from the assumption of a particular type of heterogeneity and that it may apply for relatively low values of $[A]$. In this derivation of the Freundlich model it follows that:

$$K_{SA}^F = \{S\} (\tilde{K})^m \quad (26)$$

This shows that, as suggested before, the Freundlich constant is proportional with the total site concentration or the adsorption maximum and that its units are dependent on the units in which the surface site concentration is expressed (mole/kg, mole/m² etc.) and that the units are dependent on the value of m . For a soil system it is not so easy to establish the relevant adsorption maximum. However, the adsorption maximum is expected to vary considerably between various soils because the solid phase composition of soils may differ considerably. If for a certain range of soil types and a range of concentrations in solution it is assumed that mainly one type of soil component is of relevance for the adsorption reaction, the empirical Freundlich equation can further be adapted to take into account the variability between different soils. For instance in case of cadmium and copper adsorption

it is often assumed that mainly the soil organic matter content is responsible for the metal ion adsorption. In that case it may be assumed that the parameter K_{SMc} in equation (20) is proportional to the organic matter content of the soil and this leads to:

$$\{SMe\} = f_{org} K_{SMc} (H^+)^{\alpha} (Me)^m \quad (27)$$

Where K_{SMc} is still not an affinity constant in the same sense as it is in the Langmuir model. Moreover the value of K_{SMc} in equation (27) is of course different from the value of K_{SMc}^F in equation (20). Equation (27) is still a Freundlich type model where the Freundlich parameter has become a function of the pH of the (soil) solution and a function of the organic matter content of the soil:

$$K_{SMc}^F = f_{org} (H^+)^{\alpha} K_{SMc} \quad (28)$$

This model approach has been tested for various soils and cadmium adsorption. The value of K_{SCd} , has been estimated to be 0.35 ± 0.25 , α is in the range -0.5 to -0.6 whereas m is in the range 0.75 to 0.9. The value of K_{SCd} given corresponds with $\{SCd\}$ expressed in mole per kg sorbent (soil) and f_{org} expressed in gram organic carbon per gram soil (de Haan et al. 1987).

The semi-empirical pH dependent Freundlich equation can be interpreted in terms of an exchange reaction between protons and metal ions for a heterogeneous system, where the exchange reaction is written as:



with

$$\{S\} = \{SH_b\} + \{SMe\}$$

and

$$\theta_{Me} = \frac{\{SMe\}}{\{S\}} \quad (30)$$

This leads to the expression for a specific site type of:

$$\theta_{Me} = \frac{K_{ex}(Me)/(H)^b}{1 + K_{ex}(Me)/(H)^b} \quad (31)$$

When equation (31) is used to represent θ in equation (22) and when it is assumed that the distribution of $\log K_{ex}$ is characterized by a semi-Gaussian distribution function, the result of the integration equals:

$$\{SMe\}_t = \{S\} \frac{[\bar{K}_{ex}(Me)/(H)^b]^m}{1 + [\bar{K}_{ex}(Me)/(H)^b]^m} \quad (32)$$

Equation (32) can be simplified for the condition that $[K_{ex}(Me)/(H)^b]^m \ll 1$ to: Comparison of equations (27) and (33) shows that:

$$\{SMe_i\} = \{S_i\} \tilde{K}_{ex}^m (Me)^m (H)^{mb} \quad (33)$$

$$\alpha = -mb, m = m \text{ and } f_{org} K_{SMe} = \{S_i\} (K_{ex})^m.$$

The heterogeneous adsorption of equation (23) can not be solved with a standard speciation program. However, it is possible to include this type of adsorption model into a speciation program by adjusting the program. Under certain assumptions also analytical heterogeneous adsorption equations can be derived in case of competitive adsorption.

An advantage of equation (23) is that the complexity of the heterogeneity can be introduced by only one extra parameter compared to a homogeneous adsorption model. Moreover, the constant K has the same dimension as the Langmuir affinity constant and its dimension is not affected by the value of m .

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11 Adsorption and desorption II: comparison of models for adsorption, solid solution and surface precipitation¹

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11.1 Introduction

The composition of the soil solution is generally strongly influenced by the nature and the composition of solid phases present in the soil system. Interaction between the soil solution and the solid phases may occur through processes like ion exchange, adsorption/desorption, precipitation/dissolution and diffusion. A mixture of different, often ionic, species interacts with a mixture of different sorbents.

For a particular practical problem one would often like to understand and predict, or quantitatively describe, the effect the addition or removal of a certain amount of matter has on the system. Such an effect may vary as a function of time and as a function of the activity of other species in the system. In soil fertility, for instance, one would like to know how the concentration of a certain macro- or micro-nutrient is affected by a certain application rate (and/or rate of uptake) of nutrients and how this effect depends on soil characteristics. A similar situation arises if one wants to describe the effect of a certain soil pollutant on plant growth or on plant uptake. The transport of a dissolved species through the soil is also affected by the interaction with the solid phase.

These interaction processes are thus of importance with respect to the modelling of leaching of species to surface or groundwater. Because of the many variables that influence the interaction of a chemical with soil, it is no wonder that we are at the moment still far removed from a detailed quantitative understanding of the interaction processes that govern the soil solution composition. Even for relatively 'pure' model systems, like a well characterized crystalline metal oxide in contact with an electrolyte solution, a variety of conceptually different models may be used to describe measurements equally well. Even for such model systems, distinguishing between phenomena like adsorption, formation of surface coating, or formation of solid solutions is quite difficult in practice (Sposito 1986) due to the often gradual transition between these processes.

First the processes mentioned will be discussed in general terms. In Figure 11.1A a species adsorbed on the surface of a non-porous adsorbent is shown. Such a situation is characterized by relatively fast kinetics (seconds to minutes) and by a unique relationship between the amount of species adsorbed per unit adsorbent and the concentration of this species in solution at constant temperature and at constant solution composition (apart from the species of interest). This relationship is the adsorption isotherm. For

¹ This chapter has been published in: G.H. Bolt, M.F. de Boodt, M.H.B. Hayes & M.B. McBride (Eds), *Interactions at the Soil Colloid - Soil Solution Interface*. 1991. Kluwer Academic Publishers, Dordrecht. p. 241-256.

this situation, adsorption will be reversible. The desorption reaction is thus governed by the same functional relationship ('adsorption isotherm') as the adsorption reaction.

In Figure 11.1B the situation for a porous sorbent is shown. The adsorbing species can enter some of the pores. The adsorption kinetics may be much different from the situation in Figure 11.1A. Adsorption on the outer surface will still be quite rapid, whereas slow diffusion may control the reaction rate of the binding to the inner surfaces. To determine the equilibrium situation is thus more difficult than the situation in Figure 11.1A. Apart from kinetic differences, the adsorption isotherm may change as a function of the porosity because the chemical environment of the adsorption sites in the pores may be quite different from the ones at the outer surface. Desorption out of the small pores is expected to be a very slow process. This may cause apparent hysteresis upon desorption.

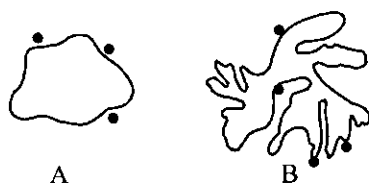


Figure 11.1. Schematic drawing of a species adsorbed on a non-porous solid (A) and on a porous solid (B).

Sposito (1986) defines absorption as diffusion of an aqueous species into a solid phase. This definition is confusing, since apart from diffusion, adsorption on the walls of the pores may take place.

Apart from the equilibrium isotherm, quantitative insight into the kinetics of adsorption and desorption may also be required in practice (for example, to describe plant uptake and leaching), especially in the case of porous sorbents.

In Figure 11.2A the situation is depicted where the original solid surface is coated with a new solid phase. The constituent ions of this coating may also adsorb on the outer surface of the surface coating. One should distinguish here between a coating that has been formed at the expense of the underlying solid, *e.g.* formation of $\text{Al}_2\text{O}_3(\text{s})$ on the surface of metallic aluminum exposed to oxygen, and a coating that leaves the original underlying solid intact, *e.g.* formation of $\text{Fe}_2\text{O}_3(\text{s})$ on $\text{SiO}_2(\text{s})$. It will be clear that in both cases there is a gradual transition from adsorption on the original surface into formation of a two- or three-dimensional surface coating. The kinetics of such pro-



Figure 11.2. (A) A solution species has reacted with the surface of the original solid (hatched part) to form a coating (dotted part) of a new phase (shrinking core), the species is also adsorbed on the coating. (B) A solution species has completely converted the original solid to form a solid solution. Adsorption of species (● and ▲) that are constituents of the solid solutions takes also place.

cesses may be of great practical concern. Full equilibrium is often not obtained. In Figure 11.2B a complete solid solution between two solid phases is shown. Starting with one homogeneous solid a complete homogeneous solid solution will seldom be obtained at field or laboratory temperature and time scales of weeks (Bohn & Bohn 1986). The establishment of the reaction kinetics and the degree of reversibility for such systems are also of relevance.

In order to be able to judge what type of model is best suited to a certain application, it is of interest to compare some of the models that have been devised to describe the processes depicted in the Figures 11.1 and 11.2. In this contribution we discuss four different electrochemical models that can be used to describe adsorption of phosphate on iron oxide as a function of solution phosphate concentration and pH. Precipitation, formation of coatings and solid-solutions are discussed in relation to the reaction of phosphate with metal oxides. Lastly, the surface precipitation model as formulated by Farley et al. (1985) is discussed.

11.2 Modelling phosphate adsorption on metal-oxides

For a more general discussion on electrochemical adsorption models we refer to Bolt & van Riemsdijk (1982) (Chapter 2), Schindler & Stumm (1982) (Chapter 4) and limit the present discussion to the application of electrochemical models for describing the phosphate adsorption on iron-oxide. The underlying basis of all these models is a set of reaction equations that formulate the formation of surface species. The sum of the individual surface coverages of different types of surface species equals the total site density of the surface. By expressing all formation reactions in terms of a chosen reference surface species, the adsorption density of the other surface species can be expressed as a function of the concentration of species in solution at the plane of adsorption and the affinity constants (see equations (1) to (4)). For a metal oxide it is normally assumed that the following surface sites at least are present: SO^- , SOH^0 and SOH_2^+ . When SO^- is chosen as the reference site, the following reactions can be formulated:



Using equation (1), equation (2a) can be expressed in terms of SO^- .



Using the mass balance for the surface sites, the reference site can be eliminated, leading to:

$$\Theta_{\text{SOH}^0} = \frac{K_{\text{H1}} C_{\text{H}}}{1 + K_{\text{H1}} C_{\text{H}} + K_{\text{H1}} K_{\text{H2}} (C_{\text{H}})^2} \quad (3a)$$

$$\Theta_{\text{SOH}_2^+} = \frac{K_{\text{H1}} K_{\text{H2}} (C_{\text{H}})^2}{1 + K_{\text{H1}} C_{\text{H}} + K_{\text{H1}} K_{\text{H2}} (C_{\text{H}})^2} \quad (3b)$$

$$\Theta_{\text{SO}^-} = 1 - \Theta_{\text{SOH}} - \Theta_{\text{SOH}_2^+} \quad (3c)$$

where Θ_i is the relative surface coverage of a given surface site type i and C_H is the concentration (activity) of protons at the plane of adsorption. The concentration of C_H is related to the concentration of H^+ in the bulk of the solution, $C_{\text{H},b}$ using:

$$C_H = C_{\text{H},b} \exp(-F\Psi / RT) \quad (4)$$

where Ψ is the potential at the plane of adsorption, F is the Faraday constant, R the Boltzman constant, and T absolute temperature (K). At least three research groups (Bowden et al. 1980; Sigg & Stumm 1981; Goldberg & Sposito 1984) have extended equations (1) to (3) to modelling phosphate adsorption on iron oxide. The various approaches differ with respect to the number and nature of phosphate surface species presumed to be at the surface, the location of the adsorbed phosphate ions (plane of adsorption with respect to the surface) and the method used to calculate the surface potential.

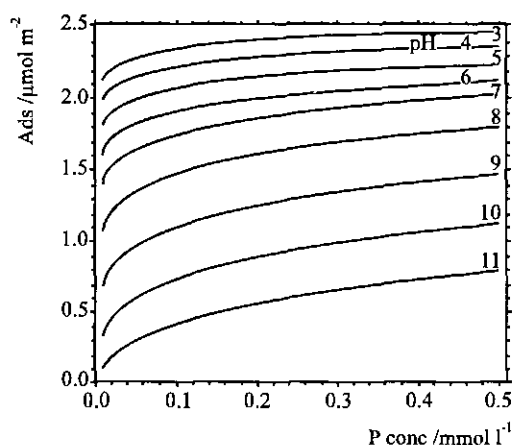


Figure 11.3. Adsorption isotherms for phosphate on goethite at different pH values. Goldberg & Sposito (1984) have used essentially the same model as Sigg & Stumm (1981), the only difference being that they did not consider the bi-dentate phosphate surface species. Therefore apart from constants that can be obtained from acid/base titration curves (K_{H_1} , K_{H_2} , an electrical capacitance and a total surface site density), they introduced three affinity constants, which are estimated by fitting the electrochemical model to the data.

The most elaborate model in terms of the number of surface species is the work of Sigg & Stumm (1981), which considers three mono-dentate phosphate surface species and two bi-dentate species. All surface species are considered to be formed by ligand exchange of a surface oxygen (which is coordinated to an underlying metal atom) with an oxygen of a phosphate species. By introducing five adjustable affinity constants they are able to describe the phosphate adsorption as a function of pH on goethite. In Figure 11.3 a set of phosphate adsorption isotherms at different pH values is given.

In the work of Bowden (1973) and Bowden et al. (1980), only one surface phosphate

species is considered. It is positioned some distance from the "SOH-plane" and the surface phosphate has its own adsorption maximum independent from the SO^- , SOH and SOH_2^+ sites. In the Bowden model the last three sites are actually referred to as Γ_{OH} , 'empty', and Γ_H effectively. Although the terminology is different, the result is equivalent to equations (1) to (3) ($\Gamma_H = N_s \theta_{SOH_2}$, where N_s is the total surface site density).

Phosphate adsorption as formulated by Bowden is not in accord with a ligand exchange mechanism. Although only one phosphate surface species is considered, three adjustable parameters (one affinity constant, one extra adsorption maximum, and one extra electric capacitance value) are introduced in order to extend the basic metal oxide model to include pH dependent phosphate adsorption.

All three models (Sigg & Stumm 1981; Goldberg & Sposito 1984; Bowden et al. 1980) may be used satisfactorily to describe phosphate adsorption as a function of pH. A possibility to discriminate between the different approaches may be the ratio of hydroxyl desorbed (or protons adsorbed) to phosphate adsorbed at constant pH. It is relatively simple to obtain this information, while it can also be calculated using the different model approaches. A physically realistic model should be able to model both the adsorption and the 'exchange'. Spectroscopic information may be used to establish the real nature of the phosphate adsorbed on the surface.

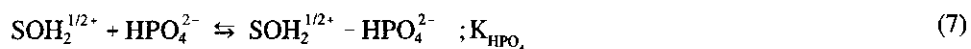
Recently it has been shown with the so-called 'one-pK' model that the basic charging (acid-base titration) behaviour of a metal oxide can be described using only one affinity constant instead of two (Bolt & van Riemsdijk 1982; van Riemsdijk et al. 1986; van Riemsdijk et al. 1987; Bolt & van Riemsdijk 1986; Westall 1987). A detailed description of proton binding to (hydr-)oxide surfaces is given by Hiemstra et al. (1989). In addition to this acid/base titration behaviour, the model has also been used to describe metal ion adsorption on metal oxides as a function of pH (van Riemsdijk et al. 1987). Here we will show that this approach can also be extended to model adsorption of phosphate. The basic charging equation of the one-pK model is:



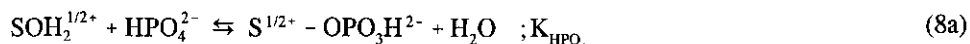
The model is tested for phosphate adsorption using data as published by Bowden et al. (1980). These measurements were obtained with potassium chloride as background electrolyte. Bowden et al. (1980) also considered specific adsorption of potassium and chloride, with a higher affinity constant for potassium than for chloride. In our modelling, we considered specific adsorption of potassium:



The adsorbed potassium is located at the *d*-plane (*i.e.* the plane where the diffuse layer begins). Phosphate adsorption is facilitated by introducing one adsorbed phosphate species, also located at the *d*-plane:



Equation (7) is indistinguishable from a ligand exchange mechanism, which would be described by:



It can be seen (Figure 11.4) that the one-pK model can be extended to get a good description of phosphate adsorption on goethite. Only one phosphate specific adjustable parameter is necessary to obtain these results. However, it may be noted that this good result is not possible when potassium is treated as an indifferent ion (at least not for the total surface site density assumed here). The specific adsorption of potassium influences the calculated phosphate adsorption, especially at high pH values. In fact, phosphate adsorption at high pH is much more sensitive to the exact value of the affinity constant for potassium than is the acid/base titration curve in a background electrolyte of potassium chloride. This means that, based on the phosphate measurements, the value of $\log K_K$ was adjusted in such a way that a good description of the charging behaviour in the absence of phosphate is retained. The constants used to derive Figure 11.4 are given in Table 11.1.

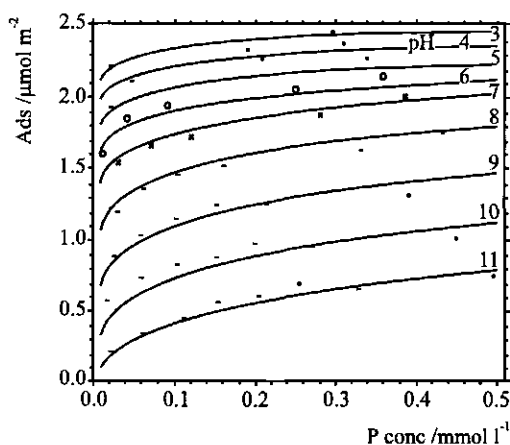


Figure 11.4. The curves are calculated adsorption isotherms using the one-pK basic Stern model (see Table 11.1). The experimental data are for phosphate adsorption on goethite. From Bowden et al. 1980.

Table 11.1. Constants used for the calculation of curves in Figure 11.4 using the one-pK basic Stern model. C = Stern layer capacitance.

$\log K_H$	= 8.5	(see equation (5))
$\log K_K$	= -0.5	(see equation (6))
$\log K_{\text{HPO}_4}$	= 6.65	(see equation (7))
N_s	= 6.5 sites nm^{-2}	
C	= 2 Farad m^{-2}	

Thus, it has been shown that electrochemical adsorption models may be quite successful in describing phosphate adsorption over a wide range of conditions using a limited

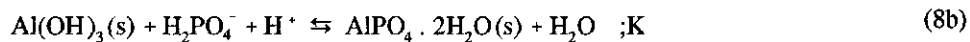
amount of phosphate specific adsorption parameters (1 to 5, depending on the specific model). These models are in principle very well suited to model competitive adsorption of mixed anion systems for metal oxide surfaces, such as phosphate/silicate (Sigg 1979; Bolt & van Riemsdijk 1982) or phosphate/citrate.

If one is interested in describing phosphate adsorption in the field, a different approach is probably more appropriate. It can be seen from Figures 11.3 and 11.4 that the difference in adsorption behaviour between pH 4 and 6 is only minor. In noncalcareous agricultural soils, the pH will generally be in the range 4.5-6.5. The phosphate adsorption behaviour may thus be approached by using only one average isotherm for this pH range. This average isotherm can be described by a simple Langmuir equation resulting in one apparent affinity constant and one apparent adsorption maximum. The available reactive metal oxide surface area in the soil may differ considerably from place to place in the field. This variation directly influences the value of the apparent phosphate adsorption maximum (mol/kg soil). As a first approximation, one might assume the type of reactive surface to be relatively constant in the soil, leading to the introduction of only one (apparent) phosphate affinity constant. If one has established the frequency distribution (relative occurrence) of the apparent adsorption maximum, one can calculate the distribution of the phosphate activity in the soil profile as a function of phosphate input using stochastic models (van der Zee & van Riemsdijk 1986b).

For a complete model description one also has to consider the possibility of the formation of phosphate precipitates. An example of a (deterministic) dynamic model of phosphate reaction considering both adsorption and precipitation in acid sandy soil is given by van der Zee & van Riemsdijk (1986a).

11.3 Precipitation

Apart from ion adsorption at the solid-solution interface, precipitation phenomena may also occur. Precipitation may take place from solution by the formation of separate three-dimensional crystals. This form of precipitation will not be discussed here. Another possibility is the situation where at least one of the constituents of the newly formed phase is in a relatively insoluble solid phase and the other constituents are present in the solution phase. This situation occurs for instance when a phosphate containing solution is brought into contact with $\text{Al}(\text{OH})_3(\text{s})$ or $\text{Fe}_2\text{O}_3(\text{s})$. Formation of metal phosphate may take place (apart from adsorption) when the system is supersaturated with respect to the metal phosphate, *i.e.*, when the change of free energy of the reaction, ΔG_r , is negative. Consider, for instance, the following reaction:



When the pH and phosphate concentration of a solution of NaH_2PO_4 in contact with $\text{Al}(\text{OH})_3(\text{s})$ are kept constant such that ΔG_r of equation (8b) is negative, the degree of supersaturation is also constant. The thermodynamic equilibrium for such a system would be reached when all the $\text{Al}(\text{OH})_3(\text{s})$ is completely converted into $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$. Experiments performed under conditions described above have shown that overall equilibrium (complete conversion) is not reached even for a considerable degree of supersaturation and a reaction time of one month (van Riemsdijk & Lyklema 1980a, 1980b). Similar experiments with acid sandy soils lead to the same conclusion (van

Riemsdijk et al. 1984). The reaction mechanism, that is in accord with a whole series of different observations for the experiments cited, is the formation of a coating of metal phosphate at the expense of the underlying metal hydroxide. A diffusion-precipitation model has been developed that can model the reaction kinetics of such a process as a function of the phosphate concentration in solution (at constant pH) and the degree of conversion of the metal hydroxide (van Riemsdijk et al. 1984a, 1984b).

11.4 Solid solution

An other precipitation phenomenon is the formation of solid solutions. A solid solution is a stable solid mixture of two or more solids. The ionic activity product, IAP, of one of the (solid) constituents at equilibrium is no longer a constant (which would be the case for a pure solid phase) but is a function of its concentration in the solid mixture phases, according to:

$$(\text{IAP})_i = g_i X_i K_i^{\text{SP}} \quad (9)$$

where g_i is the activity coefficient of solid i in the solid solution, X_i is the mole fraction of solid i and K_i^{SP} is the solubility product of the pure mineral i . A solid solution is ideal when $g_i = 1$. From equation (9) it follows that the IAP of a constituent that is present as a minor component in a solid solution (at equilibrium) may be much smaller than the solubility product of the pure mineral, whereas the IAP of the major constituent is only slightly different from K^{SP} . The solid solution theory is an equilibrium theory. At equilibrium the solid solution phase should thus be homogeneous. It will also be very difficult to prove that a solid solution has been formed. The rate of formation of a homogeneous solid solution, starting with one homogeneous solid phase and a supersaturated solution is in general extremely slow. In recent soils literature (Bohn 1981; Bohn & Bohn 1986; Miller et al. 1986), it has been proposed that measurements that are currently interpreted in terms of adsorption models, should preferably be interpreted in terms of solid solution theory. The idea behind this approach is that the solid mixing is confined to the surface, leading to a sort of two-dimensional solid solution in equilibrium with the solution phase. The mixing rate with the bulk of the solid phase is thus assumed negligible. Experiments of phosphate with gibbsite at constant supersaturation (van Riemsdijk & Lyklema 1980a, 1980b) show that this last assumption is not always correct. Although the reaction rate is slow, it has been shown without doubt that the reaction may proceed beyond the amount that can be accommodated at the gibbsite surface. Small metal hydroxide particles may even be converted completely into metal phosphate in a relatively short reaction period (van Riemsdijk et al. 1977). In the case of phosphate sorption measurements as shown in Figure 11.4 for goethite, it is almost certain that the reaction is confined to the surface. In the following discussion, the solid solution approach to describe adsorption data will be demonstrated for phosphate adsorption on goethite.

The fraction of iron phosphate in the solid solution is denoted by X . Because the sum of the fractions of iron phosphate and iron oxide in this case equals one, it follows that the fraction of iron oxide in the solid solution equals $1 - X$. The solubility products of pure goethite and iron phosphate are defined as follows:

$$K_{\text{Fe}_2\text{O}_3}^{\text{SP}} = (\text{Fe}^{3+}) (\text{H}^+)^{-3} \quad (10)$$

$$K_{\text{FePO}_4}^{\text{SP}} = (\text{Fe}^{3+}) (\text{PO}_4^{3-}) \quad (11)$$

The activity of PO_4^{3-} is a function of the total phosphate concentration in solution, P_t , according to:

$$(\text{PO}_4^{3-}) = \gamma P_t \quad (12)$$

where γ is a function of the dissociation constants of phosphoric acid, the pH and the ionic strength. Using equation (9), the activity of iron in equilibrium with the solid solution is:

$$(\text{Fe}^{3+}) = g_{\text{Fe}_2\text{O}_3} (1-X) (\text{H}^+)^3 K_{\text{Fe}_2\text{O}_3}^{\text{SP}} \quad (13)$$

The activity product of iron phosphate (using equations (9), (12) and (13)) equals:

$$\gamma P_t g_{\text{Fe}_2\text{O}_3} (1-X) (\text{H}^+)^3 K_{\text{Fe}_2\text{O}_3}^{\text{SP}} = g_{\text{FePO}_4} X K_{\text{FePO}_4}^{\text{SP}} \quad (14)$$

Rearrangement of equation (14) leads to:

$$\frac{X}{1-X} = g_{\text{Fe}_2\text{O}_3} (g_{\text{FePO}_4})^{-1} \{ K_{\text{Fe}_2\text{O}_3}^{\text{SP}} (K_{\text{FePO}_4}^{\text{SP}})^{-1} \gamma (\text{H}^+)^3 \} P_t \quad (15)$$

The term within curly brackets (= K^*) is a constant for a given pH. For adsorption, it seems reasonable to equate with the fraction of surface sites that is occupied with phosphate. When the total surface site density is denoted by N_s (mol/m²), the phosphate adsorption density, Γ_p , thus equals:

$$\Gamma_p = X N_s \quad (16)$$

Combining equations (15) and (16) results in:

$$\Gamma_p = \frac{N_s g^* K^* P_t}{1 + g^* K^* P_t} \quad (17)$$

where $g^* = g_{\text{Fe}_2\text{O}_3}/g_{\text{FePO}_4}$. Equation (17) has the form of a simple Langmuir equation, where K^* is a pH-dependent parameter. When the surface coverage with phosphate is low, which is the case at high pH for a wide range of P_t (see Figure 11.3), X will be $\ll 1$. In that case equation (16) can be approximated by:

$$\Gamma_p = N_s g^* K^* P_t \quad (17a)$$

In the case of an ideal solid solution ($g^* = 1$) equation (17a) predicts a linear isotherm. The experimental results (Figure 11.4) show a very strong non-linearity of the phosphate adsorption at high pH, where $X \ll 1$. When the adsorption is interpreted in terms of solid solution theory it thus means that g^* is a function of Γ_p and probably also of the pH. So in order to apply solid solution theory successfully one needs a simple relationship from which g^* can be calculated with as few adjustable parameters as possible. Even when this would be possible, there are still severe limitations to this approach when compared with sophisticated adsorption models. Effects of the ionic strength on the adsorption can be

modelled relatively simply using electrochemical adsorption models, as well as the acid/base titration curves of metal oxides in the absence of phosphate. With the one-pK electrochemical model, phosphate adsorption as a function of pH can be described (see Figure 11.4) by introducing only one adjustable affinity parameter. How all this can be done in a straightforward manner using the solid solution approach is unclear. However, in a qualitative sense, the solid solution approach can be useful. For example, it directly predicts the relative preference of a metal oxide for different anions. This can be derived by comparing the parameter K^* of equation (17) for different anions and a given metal oxide. K^* follows directly from solubility products, dissociation constants and the pH. A similar approach is possible for adsorption of metal ions.

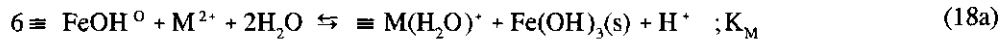
Sigg & Stumm (1981), on the other hand, correlate the relative preference of a metal oxide surface for dissolved anions with the stability constants for the formation of the iron-anion complex in the solution phase.

11.5 Solid solution plus electrochemical adsorption of cations

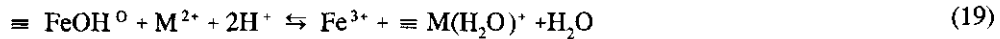
Farley et al. (1985) developed a 'surface precipitation' model that combines the concepts of electrochemical adsorption with solid solution formation. An ion that has reacted with the solid is either considered adsorbed at the interface between the solid and the aqueous phase, or present in a solid solution. The electrochemical model they use is the two-pK constant capacitance model, where all adsorbed species are positioned in the same plane. For such a type of model, adsorption of a bivalent metal on iron hydroxide may be represented as:



In the surface precipitation model this formulation is slightly altered. A surface iron species on which a bivalent metal adsorbs is considered to be no longer in contact with the aqueous phase. This 'buried' iron species is now part of the interior of the solid where it forms a solid solution of $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{M}(\text{OH})_2(\text{s})$. The adsorption equation (18) in the case of the surface precipitation model is reformulated as:



where $\equiv \text{M}(\text{H}_2\text{O})^+$ represents a hydrated bivalent metal adsorbed on the surface of the iron hydroxide. The activity of $\text{Fe}(\text{OH})_3(\text{s})$ equals one in the absence of a solid solution, in this case equation (18a) is equivalent to equation (18). By combining equation (18a) with the solubility equation of iron hydroxide it can be seen that the proposed adsorption mechanism is equal to an exchange between a surface iron and a bivalent metal ion:



It may be noted that equations (18a) and (19) are not properly balanced in terms of the number of oxygen and hydrogen atoms. This is caused by the schematic notation of the surface metal species, which does not show the full coordination structure of the surface metal species.

In Figure 11.5 a schematic drawing of the surface of the iron hydroxide particle is given. The hatched area represents the interior of the solid that consists of a solid solution of $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{M}(\text{OH})_2(\text{s})$. In this surface precipitation model it is assumed that the

solid solution shows ideal behaviour. This means that $g_i = 1$ and that the activity of the metal hydroxide (IAP/K^{SP}) is equal to its mole fraction. In order to be able to apply this model successfully to experimental data Farley et al. (1985) have to assume that only a small fraction (ca. 2%) of the total number of iron surface sites is available for adsorption (exchange) of bivalent metal ion. This causes a relatively low adsorption maximum for the bivalent metal, forcing the sorption in excess of this adsorption maximum to be considered as present in the solid solution. For a given set of input data, the activities of (H^+), (Fe^{3+}) and (M^{2+}) in solution, the concentration of adsorbed bivalent metal and the mole fractions in the solid solution can be calculated using this surface precipitation model. The model has eight parameters, seven of which are treated as adjustable parameters. Three adjustable parameters are specific for the sorption of bivalent metal ions; the others are determined from acid/base titration experiments. The parameters are: the site density of surface sites that are *not* available for adsorption for adsorption of bivalent metal, N_{S1} ; the site density of surface sites that can (in addition to proton association and dissociation) also adsorb bivalent metal ions, N_{S2} ; the solubility product of pure iron hydroxide, $K^{SP}_{Fe(OH)_3}$; the solubility product for the bivalent metal hydroxide, $K^{SP}_{M(OH)_2}$; an affinity parameter for adsorption of bivalent metal, K_M ; two proton affinity constants K_{H1} and K_{H2} ; and an electrical capacitance, C . The value of $K^{SP}_{Fe(OH)_3}$ is taken from literature. The speciation of bivalent metal calculated with the model is not very sensitive to the exact values of $K^{SP}_{Fe(OH)_3}$. The three fitting parameters that facilitate description of bivalent metal adsorption, according to Farley et al. (1985), are N_{S2} , $K^{SP}_{M(OH)_2}$ and K_M . The results obtained for the solubility products of zinc and copper are within the range of values found in literature, for lead and cadmium the solubility products obtained by fitting are ten to one hundred times lower than the lowest value reported by Sillen & Martell (1964).

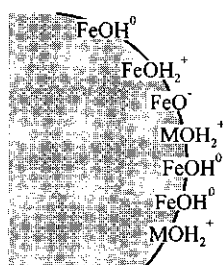


Figure 11.5. A schematic drawing of surface precipitation in the model of Farley et al. (1985).

The surface precipitation model is able to describe sorption of bivalent metal ions as a function of pH over a wide range of metal concentration. However, when the restriction on the availability of surface sites for bivalent metal adsorption is not made, it is also possible to model the adsorption of bivalent metal ions on metal oxides without the concept of solid solution. Sorption of cadmium on hematite as a function of pH has been described quite well using the one-pK electrochemical adsorption model with only one extra adjustable affinity parameter (van Riemsdijk et al. 1987). These data covered a wide range of concentrations, with emphasis on the higher concentration range. At these relatively high M^{2+} concentrations (up to $10^{-2}M$) the contribution of solid solution would be expected to be most significant, but the data could be described by considering only electrochemical adsorption. More research will be needed to establish the relevance of

solid solution. Apart from equilibrium models, equal emphasis should be given to kinetic behaviour (Dzombak & Morel 1986), the reversibility of the reaction and competition of ions in mixed electrolyte solutions.

11.6 Concluding remarks

The relationships between the amount of solute associated with the solid phase as a function of solution composition can be described using a whole range of different models. If one is merely interested in a mathematical description of such a relationship for a limited range of solution composition (*e.g.* adsorption of a cation or anion on a metal oxide at constant pH and ionic strength), any simple relationship (*e.g.* Langmuir, Freundlich) that can adequately fit the data is appropriate.

Mechanistic models that take into account the electrical repulsion or attraction of ions on charged interfaces have the advantage that they can be applied successfully over a much wider range of solution composition. Especially when the effects of pH or ion competition in multi-solute systems are of interest, these electrochemical models may yield good results. However, it is not possible to define a unique electrochemical adsorption model based on a limited set of data. At least four different electrochemical models can be used to describe phosphate adsorption as a function of pH and phosphate concentration. The models differ (among others) in the number of phosphate surface species that are invoked, and in the assumed structure of the interface between solid and solution. The often made objection to these models is that the number of adjustable parameters in these models is excessive. That this is not necessarily true is shown by applying the relatively simple one-pK model to phosphate adsorption.

Another conceptual approach to model ion adsorption is the two-dimensional solid solution on the surface of a sorbent. This concept has certain advantages, because it may predict the relative preference of a certain sorbent for different ions based on solubility products. However, the solid solution approach does not take explicitly into account the effect of a variable surface potential on the adsorption. This effect is incorporated into the solid-phase activity coefficients.

At this moment the electrochemical adsorption models are, in our opinion, the best choice to model adsorption over a wide range of solution conditions. Sorption is not always restricted to the outer surface of the sorbent; this is the case when a surface precipitate or solid solution is formed, or in general when diffusion takes place into a porous solid. In these cases the reaction kinetics are relatively slow, and it is often necessary to have a quantitative description of the reaction rate. In such cases, hysteresis is often observed between the adsorption and desorption reaction.

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12 Behaviour and fate of organic contaminants in soil and groundwater

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Summary

Soil reaction processes of organic contaminants presenting a threat to soil and groundwater are reviewed. Attention is given to mobility of organic liquids, volatilization, sorption, partition to dissolved organic carbon (DOC), cosolvency effects, transformation and formation of intermediates in soil. Quantification and modelling of these processes are discussed.

The influence of soil properties *e.g.* redox potential, pH, and organic carbon content are being emphasized. Examples of intermediate formation are presented. Conclusions are drawn about the potential threat of compound groups for top soil and groundwater, in either diffuse or local soil immission. One conclusion is that in local immissions little protection is to be expected from the top soil with respect to degradation, sorptive binding and removal by volatilization.

12.1 Introduction

Since the seventies the industrialized world is aware of many thousands of cases of pollution of soil and groundwater with organic compounds (Assink & van den Brink 1986; Wolf et al. 1988). In many cases the risks for human health are evident; risks for ecosystems are far more difficult to estimate and less well defined. Some common cases in the countries of Western Europe and the US are the widespread observations around 1980 of volatile chlorinated hydrocarbons in drinking water wells, the observations of polycyclic and monocyclic aromatic hydrocarbons and phenolic compounds under hundreds of abandoned coal gas factories and the presence of dioxins in topsoil around waste incineration plants.

Organic contaminants reach soil and groundwater along various routes. The immission route is one factor that determines the risk. Diffuse immissions occur on a regional scale in relatively low but continuous fluxes. Examples are atmospheric deposition, drift of dust, pesticide application and river bank infiltration. In diffuse immissions the threat to *e.g.* groundwater is not necessarily present. Soil passage may eliminate compounds.

In local immissions, *e.g.* from abandoned factory terrains, waste dump sites and calamity sites, where fluxes and concentrations are extremely high, there usually is direct risk to the groundwater. Future diffuse soil immissions are hard to control and to limit. Future local soil immissions are easier to regulate and to control.

Other factors that determine the risks of immissions are:

- the biological effects of the compounds and their intermediate compounds

- the mobility of the compounds and intermediates in soils
- the persistence of the compounds and intermediates.

This syllabus will deal with processes in soil and groundwater that are specific for organic contaminants, *i.e.*:

- transport of an organic liquid
- volatilization
- sorption
- transformation and formation of intermediates.

In a given soil/groundwater system and immission regime these processes determine the fate and risks of compounds.

Organic contaminants can be grouped according to similarity in chemical structure (Table 12.1). In Table 12.1 only the well known organic soil contaminants are listed. The total number of organic contaminants that form a threat to soil and groundwater will be much larger. Unknown are particularly the more polar compounds, for which detection techniques are still insufficient.

As pesticide structures are very diverse we will mainly focus on non-pesticide organics in this review.

Table 12.1. Major groups of organic soil contaminants and some representative compounds.

Group	Representative compounds
monocyclic aromatics	benzene toluene o,m,p-xylene
volatile halogenated aliphatics	methylene chloride trichloroethene (TRI) tetrachloroethene (PER)
halogenated aromatics	1,4-dichlorobenzene hexachlorobenzene (HCB)
substituted phenols	2,4,5-trichlorophenol pentachlorophenol (PCP)
polycyclic aromatic hydrocarbons (PAH)	naphthalene benzo(a)pyrene
aliphatic hydrocarbons	n-octane n-heptadecane
mineral oil	
low-volatile chlorinated hydrocarbons	hexachlorocyclohexane (HCH)-isomers DDT polychlorinated biphenyls (PCB's) tetrachloro-dibenzo-p-dioxines(TCDD's)

12.2 Processes

12.2.1 Mobility of an organic liquid

By local immissions, *e.g.* by calamities, where organic compounds infiltrate into the soil as organic liquids, the pore content of the soil consists of two or three phases, *i.e.* water, organic liquid and (in the unsaturated zone) air. Both liquids will move by potential gradients as described by Darcy's law. In saturated soil the density (δ) and dynamic viscosity (η) of the liquid and the pore geometry of the soil determine the hydraulic conductivity of the liquid in the soil (k_h):

$$k_h = k_i (\delta/\eta) \quad (1)$$

with: k_i = intrinsic conductivity of the soil (m^3/s^2), k_h in (m/s), δ in (kg/m^3) and η in (Pa.s).

Table 12.2. Indicative physico-chemical properties of a selection of organic soil contaminants, collected from various sources.

Compound	Solubility in water (25 °C) (mg/l)	Vapour pressure (20 °C) (Pa)	Liquid density (20 °C) (kg/l)	Henry constant (-)	Log K_{ow}
Chloroform	8200	25598	1.49	0.17	1.97
Trichloroethene	1100*	9866	1.46	0.52	2.29
Tetrachloroethene	140	2533	1.62	1.32	2.88
1,1,1-trichloroethane	720	16532	1.32	1.35	2.17
1,4-dichlorobenzene	145	7.99	-	0.04	3.38
Hexachlorobenzene	6×10^{-3}	1.3×10^{-3}	-	0.03	6.06
Benzene	1800	13332**	0.87	0.25	2.13*
Toluene	535	3866	0.87	0.29	2.69
3-monochlorophenol	26000	13.33	-	3×10^{-5}	2.50
2,4,5-trichlorophenol	1200*	-	-	-	3.88
Pentachlorophenol	14*	1.33×10^{-2}	-	1×10^{-4}	5.05
Naphthalene	32	12.00**	-	0.02	3.30
Benzo(a)pyrene	4×10^{-3}	8×10^{-7} **	-	2×10^{-5}	6.06
N-octane	0.66	1867	0.70	142	4.00
N-heptadecane	5×10^{-3}	13×10^{-5}	0.78	3×10^{-3}	8.50
α -HCH	1.5	3.4×10^{-3}	-	27×10^{-5}	3.81
β -HCH	0.2	3.8×10^{-5}	-	2×10^{-5}	3.72
Γ -HCH	7.3	1.25×10^{-3}	-	2×10^{-5}	3.85
DDT	3×10^{-3}	2.7×10^{-3} **	-	1×10^{-3}	6.19
2,4,5,2',4',5'-PCB	1×10^{-3}	?	-	0.93***	6.90
2,3,7,8-TCDD	2×10^{-3}	?	-	-	3.52
Fuel oil	-	-	0.95	-	-
Gasoline	150-300	-	0.72-0.78	-	-

* at 20 °C, ** at 25 °C, *** from Anderson & Parker (1990), - = not liquid at normal soil temperature and ? = unknown.

Table 12.2 gives the density of some organic liquids. Thus gasoline, aromatic hydrocarbons and most chlorinated hydrocarbons (*e.g.* trichloroethene with $\gamma = 0.58$ mPa.s) have a larger mobility in saturated soil than water. Diesel and fuel oil are less mobile than water.

An organic liquid of density larger than water sinks below the groundwater table down to a layer sufficiently impervious to this liquid. Schwille (1985) demonstrates this for tetrachloroethene. Table 12.2 shows this to happen to all chlorinated aliphatics listed. Due to their lower density than water oil, gasoline and monocyclic aromatics will float on the water table. Spreading is dependent on the surface tension of the compounds with air and with water (Adamson 1990).

Infiltration of an organic liquid in dry soil is determined by its surface tension with air and its contact angle with the pore wall. Assuming contact angles to be near zero, the volatile chlorinated hydrocarbons with surface tensions around 20-30 mN/m infiltrate faster in dry soil than water does.

Transport models for multiphase flow and infiltration in soil and groundwater are rarely applied in practice. For reviews and applications see Dracos (1987) and Feenstra (1990) for groundwater systems and Cary *et al.* (1989) for unsaturated soil.

Part of the (components of) the organic liquid will slowly dissolve in the adjacent water and a part will volatilize into the soil air. Transformations will be considerably more rapid in the water phase than in the bulk organic phase. For risk assessment and remedial treatment it is essential to know the rate of dissolution of a component from an organic liquid body into groundwater. This rate is described as a first order process. The rate constant is linearly proportional to the activity coefficient ratio for the component in the organic liquid and water respectively. In addition the rate constant is linearly proportional to the groundwater flow rate (Mackay *et al.* 1991).

12.2.2 Volatilization

The rate of removal of organic compounds by volatilization from soil and groundwater is determined by (a) their escape tendency from water phase to gas phase and (b) their diffusion coefficient in the gas phase of the unsaturated zone.

Gas diffusion coefficients can be estimated with *e.g.* the Millington-Quirk model (Anderson & Parker 1990), where pore geometry and moisture content are of dominating importance. The escape tendency from the water phase is determined by the equilibrium concentration ratio of the compound in pore air and pore water. This ratio is given by Henry's law constant (H). In dimensionless form:

$$H = \frac{0.12 PM}{TS} \quad (2)$$

with: P = saturated vapour pressure of the pure organic liquid (Pa)

M = molecular weight

T = temperature (K)

S = solubility in water (g/m³)

Table 12.2 lists the parameters P, S and H for a number of compounds. H was calculated with equation (2). Although for many compounds the vapour pressure is very low, volatilization may still be of importance due to their low water solubility. For these

compounds the Henry constant calculated with equation (2) may have large inaccuracy. Park et al. (1990) observed in unsaturated soils that volatilization accounted for approximately 30 and 20% loss of naphthalene and 1-methyl naphthalene respectively, whereas for twelve other PAH (polycyclic aromatic hydrocarbons) volatilization appeared negligible. It should be emphasized that the parameters listed are for pure water. Presence of co-solutes may severely modify them.

A vapour transport model for organic compounds in soil in which these parameters are applied is that by Jury et al. (1983). Anderson & Parker (1990) applied this model to test the sensitivity of volatilization of PCB's for H. They found that H influences the volatilization rate in dry soil through the effective diffusion coefficient.

At the moisture and temperature regimes in northwestern Europe, particularly in autumn and winter, gas diffusion in the unsaturated soil is relatively small. At these conditions disappearance of volatile chlorinated alkanes and alkenes from soil to the atmosphere is slow when the compounds are at a slight depth below soil surface (de Greef et al. 1986). The risk of groundwater contamination by immission of these compounds in the unsaturated zone is therefore large. As a removal mechanism volatilization of organic compounds from the groundwater zone to the atmosphere is of little importance. This is supported by the many cases of groundwater contamination by volatile aliphatics, which have been present in groundwater for tens of years. The liquid diffusion in the saturated zone is a slow process and the gas diffusion distance in the unsaturated zone is large.

12.2.3 Processes in the pore solution

Most organic compounds known to be environmentally hazardous are hydrophobic (Tables 12.1 and 12.2), *i.e.* well soluble in non-polar solvents and poorly soluble in water. This is expressed by a high octanol/water partition coefficient (K_{ow}). More hydrophilic compounds, like alcohols, phenol, cresols and carboxylic acids are more mobile and more biodegradable in soils and less bio-accumulating. This discussion will be limited to hydrophobic organic compounds.

12.2.3.1 Equilibrium sorption on the solid phase

By adsorption a compound dissolved in pore water is partitioned over the solid and liquid phases. In convective and diffusive transport of a solute in pore water the front or the peak of the solution is retarded by adsorption. To quantify adsorption for practical purposes usually equilibrium partitioning is assumed. Equilibrium is described by an adsorption isotherm, determined in the laboratory in contact times of two days or less. For organic compounds in soil the Freundlich isotherm appears applicable:

$$Q = k c^{1/n} \quad (3)$$

with: Q = adsorption per unit mass of solid (mg/kg), c = equilibrium concentration in the pore solution (mg/dm³), k = adsorption coefficient (dimension dependent on $1/n$) and $1/n$ = dimensionless constant, normally $\ll 1$.

In the concentration range of environmental concern linearity of the isotherm is often assumed, *i.e.*:

$$Q = k_p c \quad (4)$$

with: k_p = the partition coefficient (dm^3/kg).

The experiments by Chiou et al. (1979) with volatile chlorinated aliphatics and aromatics gave confidence to this assumption. Linearity would point at real partitioning between bulk phases. In later work by e.g. Friesel et al. (1984), Verheul et al. (1986) and Ball & Roberts (1991a) non-linearity was observed for the same compounds within the concentration range of $1000 \mu\text{g}/\text{dm}^3$. The former two report $1/n$ -values between 0.8 and 1.16. For chlorophenols Lagas et al. (1986) observed non-linearity at concentrations $> 0.5 \mu\text{M}$ with $1/n$ between 0.8 and 0.96.

Equation (4) may be acceptable for a first screening in practice, but at high concentrations it can lead to overestimation of adsorbed quantities.

Whereas more polar compounds, e.g. 1,4-dioxane, urea, ethanol and phenol, also adsorb significantly on mineral soil components like montmorillonite and Fe oxides (Zhang et al. 1990; McBride & Kung 1991), strictly hydrophobic compounds adsorb practically only on the organic fraction of the soil. For these compounds a significant correlation is generally found between k_p and the organic carbon content (f_{oc}) of the soil. A normalized partition coefficient is defined by:

$$k_{oc} = k_p / f_{oc} \quad (5)$$

For non-proton-dissociating hydrophobic compounds (Tables 12.1 and 12.2, except for the substituted phenols) several authors report empirically observed linear relationships between $\log k_{oc}$ and $\log K_{ow}$ (for references see Table 12.3):

$$k_{oc} = A K_{ow}^B \quad (6)$$

The applicability of linear free energy relationships may explain these observations. Similar relationships between k_{oc} and S (solubility in water) are reported in the literature. Validity of equation (6) points at partitioning between bulk solid and liquid phases. Although it is suggested that this would be a unique relationship, many values for A and B are reported in literature, differing per compound group and type of adsorbent studied (Table 12.3).

A critical examination of the applicability of this hydrophobic sorption theory was carried out by Mingelgrin & Gerstl (1983).

The composition and structure of organic matter varies between soil types due to differences in origin. Grathwohl (1990) demonstrates that this strongly influences the sorption affinity for hydrophobic organic compounds. He finds a decrease in sorption with increasing proportions of oxygen-containing functional groups in natural organic substances. Thus young organic matter has a sorption of more than an order of magnitude lower than fossil organic matter. Therefore k_{oc} may not be as unique a property of a compound as is suggested by the above theory.

Polycyclic aromatic hydrocarbons (PAH), PCB's, DDT, HCB, HCH-isomers and dioxins show particularly strong adsorption in soils, confirmed by their K_{ow} values (Table 12.2). Very low mobility and bioavailability may be expected for these compounds.

For proton-dissociating hydrophobic compounds, i.e. amines, carboxylic acids and substituted phenols, the hydrophobic sorption theory holds for the undissociated species

so that pH of the pore solution and pK_a (the acid dissociation constant) of the compound have to be taken into account. For the chlorophenols pK_a varies between 9.37 for 3-chlorophenol and 4.74 for pentachlorophenol, depending on the degree of chlorination and the molecular structure. At neutral or higher soil pH, e.g. in calcareous soils, pentachlorophenol is present only as phenolate anion.

Table 12.3. Equations of the type $\log k_{oc} = B \log K_{ow} + \log A$ from various references.

Ref.	B	Log A	Sorbates	Sorbents
1	0.524	0.618	pesticides	soils
2	1.00	-0.21	PAH	sediments
3	1.029	-0.18	pesticides	soils
4	0.989	-0.346	PAH	sediments/soils
5	0.72	0.49	halogenated aliphatics and aromatics	sediments/soils
6	0.937	-0.006	chloro-s-triazines and dinitroanilines	sediments
7	0.904	-0.54	aromatics, PCB's and chlorobenzenes	soils
8	0.909	0.088	34 different compounds	soils
9	0.87	-0.06	pesticides	soils
10	0.992	-0.213	volatile chlorinated aliphatics and aromatics	soils

1 = Briggs 1973

2 = Karickhoff et al. 1979

3 = Rao & Davidson 1982

4 = Karickhoff 1981

5 = Schwarzenbach & Westall 1981

6 = Brown & Flag 1981

7 = Chiou et al. 1983

8 = Hasset et al. 1983

9 = Mingelgrin & Gerstl 1983

10 = Verheul et al. 1986

For chlorophenols Schellenberg et al. (1984) introduced a correction factor into equation (6), assuming that only the non-dissociated fraction (f_{nd}) is adsorbed:

$$k_{oc} = A f_{nd} K_{ow}^B \quad (7)$$

$$\text{with: } f_{nd} = 1/(1 + 10^{pH-pK_a}) \quad (8)$$

The role of pK_a and pH in the sorption of 2,4,5-trichlorophenol is demonstrated in Figure 12.1. Experimental values of A and B for chlorophenols are presented by Schellenberg et al. (1984) and Lagas et al. (1986).

Lee et al. (1990) observed that adsorption of the phenolate ion is positive in soils and increases with ionic strength, suggesting that the formation of neutral ion pairs with cations is involved. McBride & Kung (1991) demonstrated the adsorption of substituted phenols on Fe oxides. They found evidence for adsorption by ligand exchange in addition to physical sorption.

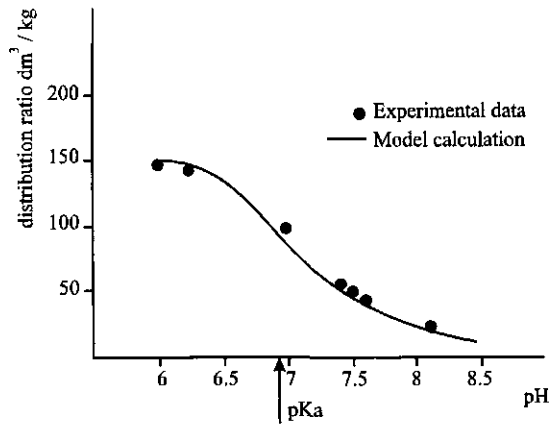


Figure 12.1. Predicted and experimentally determined overall distribution ratio's for 2,4,5-trichlorophenol. From Schellenberg et al. 1984.

The retardation factor (R) for the velocity of a front or a pulse of contaminant solution with respect to the moving solvent water is calculated by equation (9) or (10). R also stands for the fraction of the total contaminant content in the soil that is present in the pore solution.

For non-linear Freundlich isotherms:

$$R = 1 + (\beta/\Theta)(1/n) k c^{(1/n)-1} \quad (9)$$

For linear isotherms:

$$R = 1 + (\beta/\Theta) k_p \quad (10)$$

with: β = bulk density of the soil (kg/dm^3) and Θ = volumetric moisture content of the soil (-).

12.2.3.2 Non-equilibrium in the sorption process

The assumption of (reversible) adsorption equilibrium during transport in soil, implied in the use of the retardation factor, is not always correct. Neither is this assumption always correct in batch adsorption experiments. This is a weakness in the empirical relationships reported in Table 12.3.

Schwarzenbach & Westall (1981) and Friesel et al. (1984) report rapid and reversible equilibrium for volatile chlorinated alkanes and alkenes and chlorobenzenes within the duration of their batch experiments. Karickhoff & Morris (1985) on the other hand demonstrate for both adsorption and desorption of hexa- and pentachlorobenzene that it takes weeks to months before equilibrium is attained. Similar observations were made by Pignatello (1990a,b) for halogenated alkanes and alkenes.

Ball & Roberts (1991a,b) need contact times of tens to hundreds of days to reach adsorption equilibrium for tetrachloroethene and 1,2,4,5-tetrachlorobenzene on aquifer sand. They doubt whether equilibrium was attained in the experiments from which the empirical relationships were derived. The authors of all these articles and others (Brusseau et al. 1991) conclude that the kinetics of sorption is determined by diffusion in the organic matrix of the soil.

Poor reversibility of sorption of hydrophobic contaminants is manifested by the observations of non-extractably bound residues in soil, often reported for pesticides. In laboratory studies of one week contact time Scheunert (1987) observed bound residues of chlorobenzenes, some PCB's and chlorophenols of respectively < 9%, <7.5% and <60%. Knowledge on the fate of bound residues in soil in the long run is poor. A review is given by Bollag & Loll (1983).

12.2.3.3 Interaction with dissolved organic carbon

The pore solution of soils and aquifers usually contains dissolved organic matter (DOC) consisting of large molecules. For groundwater a few mg/dm³ DOC is typical, but the concentration may reach a few hundred mg/dm³ in groundwater near a waste dump site (Kan & Tomson 1990). In soil horizons concentrations generally are higher, depending on the content and age of the solid organic matter present and on the vegetation.

Hydrophobic organic contaminants in the water phase not only bind to solid organic matter but also to DOC. Therefore the presence of DOC will enhance the apparent solubility of contaminants and reduce the apparent partition coefficient of the soil. It will thus facilitate the movement of the contaminant. For very insoluble contaminants ignoring the effect of DOC may result in an error in the transport velocity of several orders of magnitude. The hydrophobic sorption model presented therefore has to be corrected for this influence. This was done by different authors (Enfield et al. 1989; Pankow & McKenzie 1991; Magee et al. 1991). For non-dissociating hydrophobics Kan & Tomson (1990) presented the correction to equation (3) as follows:

$$Q = k C^{1/n} / (1 + K_{\text{DOC}} \text{DOC})^{1/n} \quad (11)$$

with: C = the total contaminant concentration in solution (mg/dm³), DOC = concentration DOC in (kg/dm³) and K_{DOC} = DOC/water partition coefficient of the contaminant (dm³/kg), *i.e.*:

$$K_{\text{DOC}} = \frac{\text{mg bound compound/kg DOC}}{\text{mg free compound /dm}^3 \text{ water}}$$

For linear adsorption isotherms the retardation factor now becomes:

$$R = 1 + (\beta/\theta) k_p / (1 + K_{\text{DOC}} \text{DOC}) \quad (12)$$

The authors assume that for the partitioning of compounds to DOC the same proportionality holds as in equation (6). Using this equation for partitioning to both solid organic matter and DOC, it is derived from equation (12) that for either highly hydrophobic compounds (large K_{ow}) or high concentration of DOC in water, a relatively negligible fraction of the compound will be free in the water, so that:

$$R = 1 + (\beta/\theta) (f_{oc}/\text{DOC}) \quad (13)$$

Equation (13) suggests that for all compounds with a K_{ow} larger than a certain value the average velocity will be independent of the kind of compound. This value is calculated from:

$$A K_{ow}^B \text{ DOC} \gg 1 \quad (14)$$

Figure 12.2 shows a plot by Kan & Tomson of equation (12) with equation (6) substituted, using the parameters A and B from Karickhoff et al. (1979).

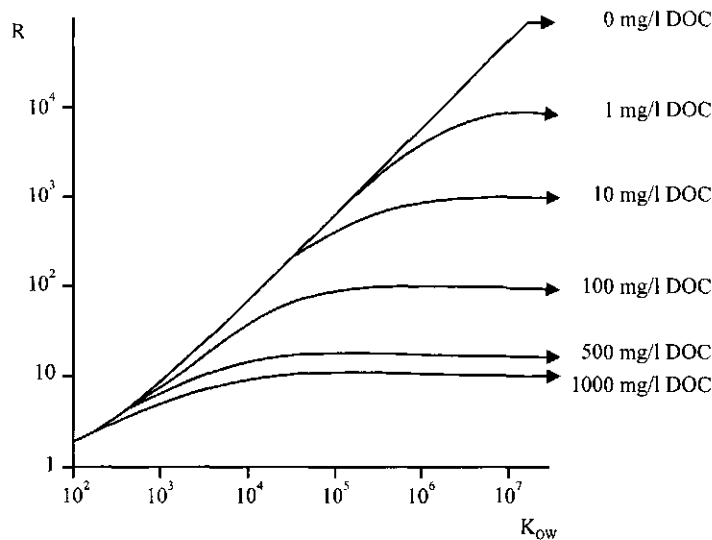


Figure 12.2. Plot of the relative retardation factor vs the octanol/water partition coefficient at DOC concentrations from 0 to 1000 mg/l. The curves were drawn using equation (12) and (6), and $OC = 0.0027$, $\beta = 1.572$ and $\theta = 0.4$. From Kan & Tomson 1990.

Although we will not elaborate on it, one should realise that DOC in turn may become adsorbed to soil materials (Jardine et al. 1989).

12.2.3.4 Interaction with organic cosolvents and cosolutes

Mixtures of solvents (water and organic solvents) and solutes may exist in soil and groundwater, particularly at local pollution sites. The above described sorption models need to be modified to account for the presence of cosolvents and cosolutes (Rao et al. 1990; Brusseau et al. 1991).

For sorption of organic solutes from binary mixed solvents Rao et al. (1985) presented a log-linear cosolvency model, relating the equilibrium sorption constant to the volume fraction of cosolvent:

$$\log k_{pb} = \log k_p - \sigma f_c \quad (15)$$

with: k_{pb} = the equilibrium sorption coefficient in the binary solvent, f_c = the volume fraction of the cosolvent and σ = the cosolvency power of the cosolvent for the particular solute.

The cosolvency power is approached by:

$$\sigma = \log (S_c/S) \quad (16)$$

with: S_c = the solubility of the solute in the cosolvent.

The reduction of sorption by the presence of cosolvents predicted by this model is very dependent on the polarity and the miscibility of the cosolvent with water, as demonstrated by Rao et al. (1990). In laboratory experiments these authors found that non-polar cosolvents and cosolutes, *e.g.* toluene, p-xylene and trichloroethene, do not significantly influence sorption of hydrophobic organics by soils, as opposed to polar cosolvents, *e.g.* nitrobenzene and o-cresol, which significantly decreased sorption.

Brusseau et. al. (1991) ascribe an additional influence of cosolvents on sorption of hydrophobic solutes. From experiments they infer that the rate of sorption is increased by the presence of a cosolvent. They explain this by increased diffusive permeability of the soil organic matter by its swelling in the presence of a solvent of reduced polarity. If significant on field scale, this might have important consequences for soil clean-up techniques based on desorption.

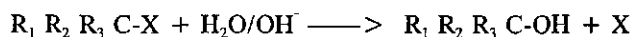
A complete picture of effects of cosolutes and cosolvents on sorption does not yet exist as can be inferred from Brusseau (1991), who found enhanced sorption of hydrophobic solutes by the presence of tetrachloroethylene as cosolute in low organic carbon aquifer material.

12.2.3.5 Transformation

In soils organic compounds are subjected to transformation processes of both biological and chemical nature. In relevant biological processes enzymes play a catalizing role. Alexander (1981) states that non-enzymatic reactions seldom lead to changes in chemical structure of importance. Microorganisms are present not only in soils but also in groundwater, even at great depth (Wilson & McNabb 1983). To assess the role of transformation one needs to know:

- the route of transformation, *i.e.* the intermediates formed and the order of their formation
- the kinetics of transformation steps
- the dependence of kinetic parameters on environmental factors.

Of the *chemical processes* in soils (oxidation, reduction, hydrolysis, nucleophilic substitution processes) chemical hydrolysis is probably the most important. An example is the hydrolysis of halogenated aliphatics:



X = Cl, Br, I.

Hydrolysis is observed to be a first order process, with a half life highly dependent on temperature. Hydrolysis generally leads to more hydrophilic intermediates, more mobile than the parent compound. For most halogenated alkanes, alkenes, aromatic hydrocarbons and phenols chemical hydrolysis in soil is of low importance. Half life times of a year, for methyl chloride, to hundreds of years (3500 years for chloroform) were reported. An exemption are some singular bromoalkanes, *e.g.* methyl bromide with half life of some 20 days.

Analogous to chemical hydrolysis some hydrophobic compounds can be subject to substitutions with CN^- and HS^- . In anaerobic groundwater, at sulphate reducing conditions, Schwarzenbach et al.(1985) observed the formation of dialkylsulphides from alkylbromides. These persistent compounds are very toxic.

In *biological transformations* hydrolysis, oxidation, reduction, dehalogenation, etc. are catalyzed by enzymes. Figure 12.3 gives examples of biological oxidation and reduction reactions (see also Alexander 1985). The reaction rate of biotransformation in soil is often observed to follow Monod kinetics (Howard & Banerjee 1984):

$$\frac{dC}{dt} = \frac{-k_1 g C}{K_m + C} \quad (17)$$

with: g = enzyme concentration (mg/dm^3), $k_1 g$ = maximum transformation rate, ($\text{mg} \cdot \text{dm}^{-3} \cdot \text{d}^{-1}$), K_m = the concentration where the transformation rate equals half the maximum value (mg/dm^3) and t = time (d).

At low concentrations equation (17) reduces to a first order rate model. At high concentrations it reduces to a zero order model.

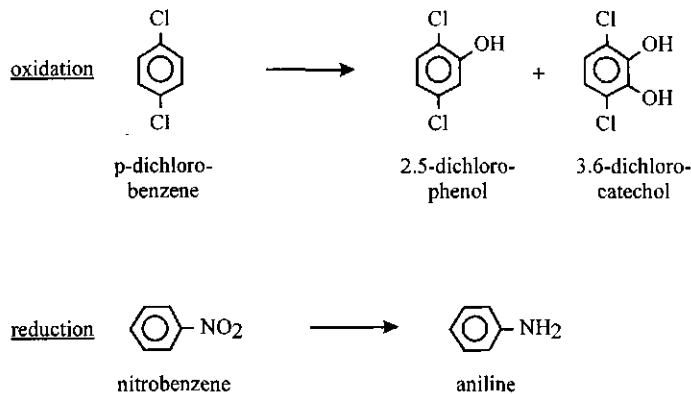


Figure 12.3. Biological oxidation and reduction reactions.

The intrinsic biodegradability of a compound is determined by its molecular structure: at higher degree of chlorination a lower degradation rate; branched molecules are less degradable than non-branched. In addition transformation is strongly influenced by environmental factors *i.e.*:

- moisture content
- redox potential
- organic carbon content
- other carbon and/or energy sources
- temperature
- pH
- nutrient concentrations.

By adsorption on solid matter contaminants are protected against microbial attack. Thus they will be more persistent in soils of higher organic carbon content, as was confirmed by Aronstein et al. (1991) who used surfactants to desorb PAH and stimulate biodegradation.

The effect of redox potential on transformation was studied in the laboratory by Bouwer & McCarty (1983a,b), Bouwer & Wright (1986), Klecka et al. (1990), Cobb & Bouwer (1991) and many others. These authors found no degradation of halogenated aliphatics at aerobic conditions. At methanogenic conditions Bouwer & McCarty observed more than 90 % removal within two days, after an acclimation period of < 10 weeks, using acetate as a primary carbon source. At denitrifying and sulphate reducing conditions only some compounds (*i.e.* carbontetrachloride and bromoform) were degraded. Klecka et al. observed immediate biodegradation of 1,1,1-trichloroethane in samples from an aquifer both at methanogenic and sulphate reducing conditions. They did not observe degradation at aerobic and denitrifying conditions. Part of the transformation route is by biological, reductive dehalogenation. According to Cline & Viste (1985) reductive dehalogenation occurs below a redox potential of 0.35 V in the presence of a primary carbon source. Intermediates found by Klecka et al. were 1,1-dichloroethane and chloroethane; in addition they found 1,1-dichloroethene as an abiotic transformation product.

For chloroanilines biological reductive dehalogenation in polluted aquifers was observed when methanogenic but not sulphate reducing conditions prevail (Kuhn & Sufliita 1989).

On the other hand chlorobenzenes (Bouwer & McCarty 1983; Loch et al. 1986), ethylbenzene, and naphthalene appear to be only degradable at aerobic conditions. In aerobic bank infiltration water Schwarzenbach et al. (1983) observed a very rapid removal of alkyl- and chlorobenzenes and naphthalene. Benzene at low concentrations is degraded in aerobic soils.

For low concentrations of Γ -HCH at aerobic conditions half life values were found between 100 and more than 1000 days, whereas at anaerobic conditions they ranged between 10 and 175 days. Kampe (1980) reported the same order of magnitude for α -HCH and estimated a half life of 8 years for β -HCH.

Chlorophenols and phenol seem to degrade fairly rapidly in soils. Smith & Novak (1987) observed complete transformation of these compounds within 2-4 months, at concentrations up to 2000 mg/dm³. Others found degradation limited to aerobic conditions.

The very persistent PCB's are adsorbed very strongly in soils, which enhances their persistence. Persistence increases with degree of chlorination of the PCB (Scheunert 1987). For dioxins, both in the laboratory and in the field, half life values were at least one year.

Wilson & Mc Nabb (1983) reviewed the state of the research on biodegradation till then. In Table 12.4 their expectations about transformation in groundwater is summarized.

Addition of the nutrients N, P and K caused an increased mineralization of toluene in contaminated groundwater near a chemical waste disposal site (Armstrong et al. 1991). The authors suggest that the subsurface microflora in the contaminated region had adapted to degrade toluene.

Table 12.4. Expected biotransformation of selected organic contaminants in groundwater. From Wilson & McNabb 1983.

Class of Compounds	Aerobic Water Concentration of Pollutant, $\mu\text{g/l}$		Anaerobic Water
	> 100	< 10	
Halogenated Aliphatic Hydrocarbons			
Trichloroethylene	none	none	possible*
Tetrachloroethylene	none	none	possible*
1,1,1-Trichloroethane	none	none	possible*
Carbon Tetrachloride	none	none	possible*
Chloroform	none	none	possible*
Methylene Chloride	possible	improbable	possible
1,2-Dichloroethane	possible	improbable	possible
Brominated methanes	improbable	improbable	probable
Chlorobenzenes			
Chlorobenzene	probable	possible	none
1,2-Dichlorobenzene	probable	possible	none
1,4-Dichlorobenzene	probable	possible	none
1,3-Dichlorobenzene	improbable	improbable	none
Alkylbenzenes			
Benzene	probable	possible	none
Toluene	probable	possible	none
Dimethylbenzenes	probable	possible	none
Styrene	probable	possible	none
Phenol and Alkyl Phenols	probable	probable	probable**
Chlorophenols	probable	possible	possible
Aliphatic Hydrocarbons	probable	possible	none
Polynuclear Aromatic Hydrocarbons			
Two and three rings	possible	possible	none
Four and more rings	improbable	improbable	none

* Possible, probably incomplete

** Probable, at high concentration.

As was touched on before most transformation processes do not directly lead to complete mineralization of the compound. Large numbers of intermediates can be formed. Worth mentioning is the formation by sequential reductive dehalogenation of the very toxic, carcinogenic and persistent vinyl chloride via the formation of 1,2-dichloroethene from tri- and tetrachloroethene. Barrio-Lage et al. (1990) derived a half

life value for vinyl chloride in soil and water microcosms under anaerobic conditions of 57 years. For metabolites of some other compound groups we refer to the work by Scheunert (1987). This author concludes that of many compounds metabolites are formed which are more polar than the parent compound and therefore more mobile.

12.3 Conclusions

To estimate concentrations of contaminants and biological exposure in soil and groundwater, data about immission quantities and routes are required as input in distribution models in which the processes discussed are integrated. From the above process descriptions we will attempt to draw rough conclusions about the expected distribution for the mentioned groups of compounds. The conclusions are well supported by field observations in groundwater in many western countries (Loch et al. 1989). We will distinguish between diffuse and local immissions at the soil surface.

In *diffuse immissions* the following risks are expected:

Volatile halogenated aliphatics leach to the groundwater, where they will disperse. Particularly in aerobic groundwater they are very persistent.

PAH and low-volatile chlorinated hydrocarbons are persistently present in topsoils containing some organic matter, and may accumulate there. Leaching of these compounds will be extremely slow, unless preferential flow paths are present, but they will ultimately reach the groundwater because of their persistence.

Of the other compound groups risks may be small because of their relatively high aerobic degradability. Exceptions, like HCB, should not be overlooked.

In *local immissions* it is not justified to expect much protection by transformation and adsorption. This is because at the high loads toxic effects on micro organisms, multi-phase transport, facilitated transport by cosolvency, and supersaturation of the soils' sorptive capacity may be expected. In local immission risk of breakthrough in the groundwater is high for all groups of compounds. Organic liquids of monocyclic aromatics and mineral oil will spread on the water table and slowly dissolve from there. Biodegradation of the dissolved fraction in aerobic groundwater will lead to slow removal.

Organic liquids of volatile halogenated aliphatics will sink below the water table by density effects. Deep in the aquifer they then are a long lasting source of compounds slowly dissolving in the groundwater. The degree of aerobicity in the aquifer determines the degradability of these solutes.

For neither immission route is volatilization a removal process that provides sufficient protection for soil and groundwater. Most data and models are derived from laboratory experiments. Because of the large influence of soil composition one has to be careful with extrapolations to the field situation.

In the above conclusions intermediate compounds were hardly taken into account. Much attention for intermediates behaviour is required in future research.

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13 Introduction to soil chemical aspects of bioavailability

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13.1 Introduction; general definition of bioavailability

The main purpose of this chapter series is to give insight in the relation between soil chemical processes and bioavailability.

The concept of bioavailability probably originates from the field of soil fertility where the study of the availability of fertilizers for plant growth is a classical problem. More recently the notion of bioavailability has become of importance for research areas like Soil Ecology, Soil Quality, Soil Pollution, Water Quality and Ecotoxicology. With respect to the biota also a wide variety of organisms is subject of study in relation to bioavailability e.g. plants, algae, fish, microbes, earth worms, etc.

Bioavailability relates to the availability of a chemical with respect to a specific organism. The bioavailability is normally measured in terms of an effect that is dependent on the concentration of a specific chemical. This effect can be growth, uptake, respiration, degradation, root development, etc. We can describe bioavailability as follows:

Bioavailability of an element (Cu, N, P, Al, etc.) or organic species (e.g. HCH) as present in a (complex) matrix is related to the possibility to cause an effect (judged positively or negatively) on a specific organism.

As an example we can use the element nitrogen. Nitrogen is abundantly present in the air and also in the gaseous phase of the soil. However, the bioavailability (uptake, growth) of nitrogen present in the form of $N_2(g)$ is for most plants zero. Still, blue algae and leguminous plants can use $N_2(g)$, the latter through the intermediate of nitrogen fixing bacteria present in root modules (symbiosis). This leads to the following conclusion:

The bioavailability of an element present in a specific form depends on the type of organism.

A main topic in the relation between the total content of an element in a system and effects of this element on biota present in that system, is speciation. Speciation can be defined as the distribution of the total content of the element over all possible chemical forms (species) either in the solid, the liquid or the biotic phase of the system under study. In a soil system, this distribution is influenced by a great number of processes like adsorption, complexation and precipitation, which on their turn depend on the element properties, soil properties, and environmental conditions like pH, salt level, redox potential.

Nitrogen as NO_3^- in a culture solution is fully available for plants, uptake may proceed until all nitrate has been consumed. Nitrogen as present in organic molecules is not available:

The bioavailability of an element is dependent on the form in which it is present, or in other words: different species, containing the same element, may have a completely different bioavailability for the same organism.

The $N_2(g)$ and $NaNO_3$ case of non bioavailability can be compared with the Tantalus torment. Tantalus is a person in the Greek mythology who was convicted by the Gods to undergo three torments. He had to stay in a pond with the water close to his lips and with plenty of fruits hanging over the water (Figure 13.1). When he wanted to drink, the water level would lower as fast as he tried to reach it. Similarly as he wanted to pick the fruits, the wind would blow them out of reach. Although water and food were present in sufficient quantities, they were not available to him so he had to suffer from extreme thirst and hunger. The third torment was a big stone hanging above his head that could fall down any moment. The first two torments symbolize limited bioavailability, there may be enough of a certain element present in the immediate surrounding, but it is not available.

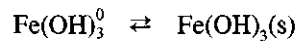
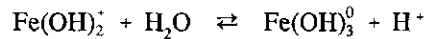
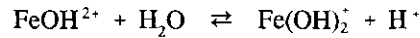
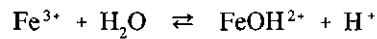


Figure 13.1. The Tantalus torment, severe hunger and thirst in the presence of enough food and water as a metaphor for the concept of bioavailability.

In the next two paragraphs, some general considerations concerning bioavailability are illustrated. Both the impact of the solution chemistry, the formation of complexes with organic and inorganic ligands, and the impact of sorption to the soil solid phase will be discussed.

13.2 Availability of iron in culture media

Iron is also essential for growth of most organisms. If we add iron to a culture medium in the form of the soluble salt FeCl_3 we observe a very low availability for plant uptake. The FeCl_3 will dissociate to Fe^{3+} and 3Cl^- in water. The following reactions can now take place:



or:



At constant pH, the solution buffers the solution at a constant total dissolved iron concentration. The total dissolved iron is equal to:

$$\text{Fe}_{\text{soluble}}(\text{t}) = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe(OH)}_2^+] + [\text{Fe(OH)}_3^0]$$

Because the solubility of ironhydroxide is extremely low, almost all the iron that is added will be present as $\text{Fe(OH)}_3(\text{s})$. The concentration of dissolved iron species is extremely low.

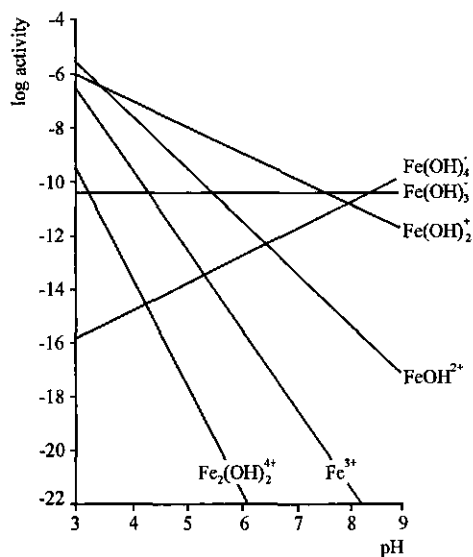


Figure 13.2. The hydrolysis of Fe(III) in equilibrium with soil-Fe.

The logarithm of the activity (= concentration in diluted solution) of the various dissolved iron species in equilibrium with $\text{Fe}(\text{OH})_3$ as it may occur in soil is graphically represented as a function of pH in Figure 13.2.

The interaction between the iron in the matrix and the plant or microorganism is via soluble iron. It may be stressed that it is *not* the fact that iron is mainly present in the form of a precipitate *as such* that causes the limited bioavailability because the ironhydroxide can replenish the iron removed from the solution by dissolution, indicating that *potentially* all the iron is available. So, why is it that apparently the iron is hardly bioavailable? In principle there may be two different explanations:

Dissolution kinetics may cause reduced bioavailability, or:

Buffering of an in itself available species may occur at such low concentrations that reduced bioavailability is the result.

In *this* case the last explanation is the most likely explanation. The solution concentration is so low that the rate of uptake of iron along with the evaporated water is not at all sufficient to satisfy the demand. Another rate limiting process might be diffusion to the plant root (or to the surface of the microorganism). The rate of this process is a function of the concentration gradient that develops in the vicinity of the root or cel surface. A simple rate equation is:

$$R = AD \frac{(c_{\text{sol}} - c_{\text{org}})}{d} \approx k * c_{\text{sol}}$$

When R is the rate of uptake (mol/s), A is the area of the organism, D the diffusion coefficient, d the distance over which the concentration gradient develops, c_{sol} the concentration at the solution side of the gradient and c_{org} the concentration at the organism side of the concentration gradient (see Figure 13.3). If A, D, d are constant and if $c_{\text{org}} \ll c_{\text{sol}}$ then the rate R is proportional with the concentration in solution. In case of the iron example the soluble concentration is so low that the maximum uptake rate that can be sustained by diffusion is in fact lower than the required uptake rate for an optimal effect.

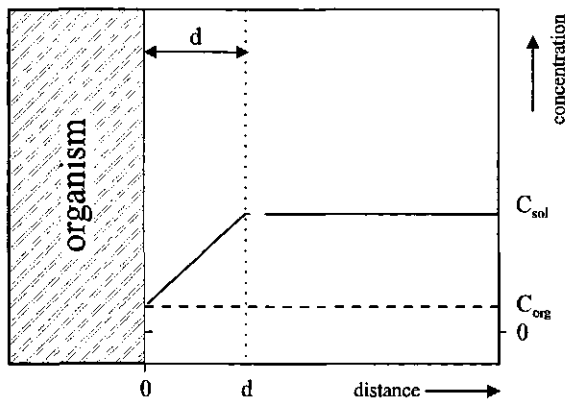
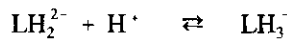
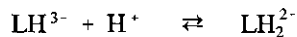


Figure 13.3. Schematic representation of the concentration gradient over a diffusion layer with thickness d. The concentration near the surface of the organism is kept low by uptake (or by degradation in case of bacterial decomposition).

The transport process is in this case the cause of a strongly reduced bioavailability. The bioavailability of an element thus may be low because the concentration in solution of an available species is too low for efficient uptake. Formation of soluble complexes may increase the total concentration of an element in solution. As complex formers one may think in terms of small organic ions like acetate, citrate and EDTA or in terms of natural organic macromolecules like fulvic acids. All complex formers mentioned are naturally occurring, except EDTA, which stands for Ethylene Diamine Tetra Acetic acid. EDTA is used in culture solutions to increase the total concentration of dissolved iron. EDTA is a four-protic acid. The fully dissociated ligand is often symbolically represented by L^{4-} . Using this notation the following reactions represent the interaction between L^{4-} , protons and Fe^{3+} :



The total concentration of soluble iron is now composed of the soluble iron (hydroxy) species plus the iron-EDTA species:

$$Fe_{\text{soluble}}(t) = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^+] + [Fe(OH)_3^0] + [FeHL^0] + [FeL^{-}]$$

We may now compare the situation of $Fe(OH)_3(s)$ in equilibrium with a solution of a certain pH with $Fe(OH)_3(s)$ in equilibrium with a solution that contains EDTA, or another ligand that forms strong (dissolved) complexes with iron at the same pH.

In both situations the concentration of dissolved iron (hydroxy) species is exactly equal. The only difference is that, in the case with the complex former, the total dissolved iron concentration is increased since the additional species containing complexed iron are absent in the first case. The iron complexes itself are *not* bioavailable. However, they contribute to the transport of iron to the organism where the complex may dissociate to deliver the iron in its available form. The iron complex can thus be seen as a transport vehicle that is able to deliver, after dissociation, the iron in bioavailable form. This leads to the following conclusion:

In case of transport limitation, the increase of the total concentration in solution of an element due to the formation of soluble complexes that are itself non bioavailable may increase the bioavailability of this element.

However, complex formation does not necessarily lead to increased bioavailability. For instance, for the element copper, Cu^{2+} is bioavailable and an essential element for growth of most organisms. Algae are very sensitive with respect to copper. If the (Cu^{2+}) is too high, copper will become toxic. Because of the high sensitivity this may already occur at very low concentration levels of Cu^{2+} . Adding a ligand that may form strong complexes

with copper such as dissolved natural organic matter will lower the concentration of free Cu^{2+} since it is in general *not* buffered by a pure solid phase. This has as consequence that the introduction of dissolved ligands may lead to:

Complex formation of an element with e.g. dissolved natural organic matter may reduce the bioavailability of an element.

Also for copper in principle, transport may in some cases be limiting bioavailability in soils. In this case formation of soluble complexes may lead to increased bioavailability, similarly as discussed for iron.

13.3 Impact of the presence of soil on copper availability for maize

The bioavailability of a chemical species is dependent on the composition of the matrix (e.g. fresh water, salt water, sediment, soil types) in which it is embedded.

As stated earlier, the bioavailability of an element depends also on the matrix in which it is embedded. When Cu^{2+} is present in a culture solution it is found that the toxicity of Cu^{2+} for plants *increases* with increasing pH, *i.e.* with decreasing proton concentration in the medium.

Another observation is that the copper toxicity for plants growing on a soil *decreases* when the pH is increased at one and the same total amount of copper present per unit amount of soil.

The pH, or proton concentration, may strongly affect the bioavailability of an element. The effect of the pH on the bioavailability may depend on the matrix.

One may assume a close relationship between the amount that can be bound by an organism, and the amount of metal that potentially causes an effect. Thus, in the case of the culture solution, the effect of the pH on copper toxicity may be explained by the effect of competition between protons and metal ions for surface sites present on the organism (See Figure 13.4).

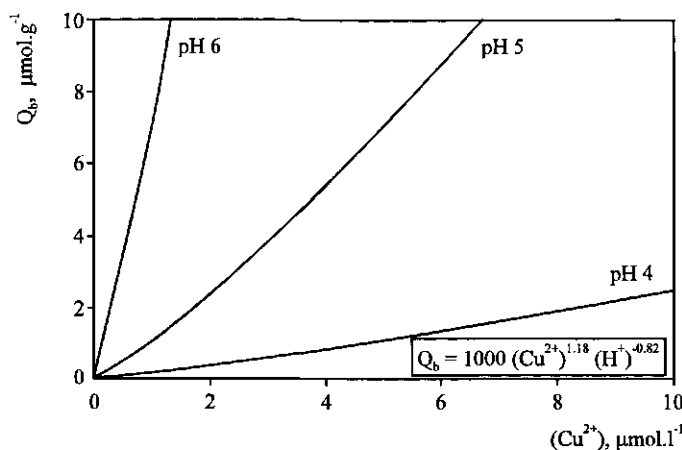


Figure 13.4. Copper binding to maize root cell walls.

But how can we explain the different effect of pH on the copper toxicity when soil is present? In the case of soil biota plus soil, the copper may adsorb on the reactive surfaces of the soil solid phase (*e.g.* organic matter) or on the surface of the biota. The exposure to the metal is expected to take place via the solution, so exposure to organisms that have a more complex uptake route (*e.g.*, uptake of soil) will not be discussed here. Thus, interaction between a soil organism and metal ions present in soil can be easily understood by considering the organism to be an additional reactive soil component, with its own (pH and other environmental-factor dependent) binding characteristics.

According to this concept, the copper ions will be partitioned over the solution phase, the surface of the biota and the surface of the soil. This is schematically represented in the diagram of Figure 13.5.

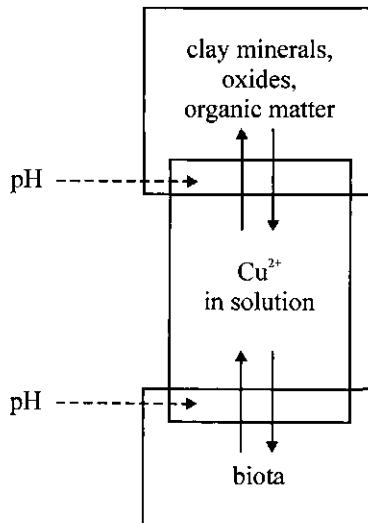


Figure 13.5. Sorption of the metal ion by the organism is the result of competition for that metal ion by all reactive components (including the organism) present in the system.

For reactive elements like copper, the amount in solution will be very small compared to the amount adsorbed. The majority of the copper ions will be in the adsorbed state. If there is equilibrium between solution and solid phase, decrease of the solution concentration will lead to desorption. Nederlof & van Riemsdijk (1995) calculated the distribution of copper over the abiotic and biotic components in a sandy soil, assuming an organic matter content of 1.6%, a waterfilled porosity of 0.3, and an amount of 0.4 g biota per kg soil. Indeed, under these conditions, more than 99% of the total copper is bound to the soil solid phase.

The contribution of copper bound to biota and the free metal ions present in solution to the total metal content of the soil can be neglected. This implicates that for practical purposes the amount of copper bound to the abiotic, solid soil components is equal to the total amount of copper present in the soil:

$$(\text{Cu})_t = Q_s$$

and that the free copper ion concentration is fully determined by the sorption equilibrium with the soil solid phase.

The relationship between the amount adsorbed to the soil (Q_s , the subscript s is related to soil), and the concentration in solution, which is called the adsorption isotherm, can be given by a simple (pH dependent) Freundlich equation:

$$Q_s = K_s (Cu^{2+})^a (H^+)^b$$

Similarly, copper ion binding by the maize plant roots (Q_b , the subscript b is related to biota) can be described:

$$Q_b = K_b (Cu^{2+})^a (H^+)^b$$

In these two equations, the value of the constant K and the exponents a and b depend on the characteristics of the reactive surfaces of respectively the soil and the biotum.

Binding of copper ions from solution to the soil is increased at higher pH (see Figure 13.6). Thus, at a constant total copper content of the soil, an increase of the soil pH will lead to a reduction of the concentration free copper in soil solution. As already is shown in Figure 13.4, sorption to the maize roots also depends on the concentration of copper ions in solution and the pH.

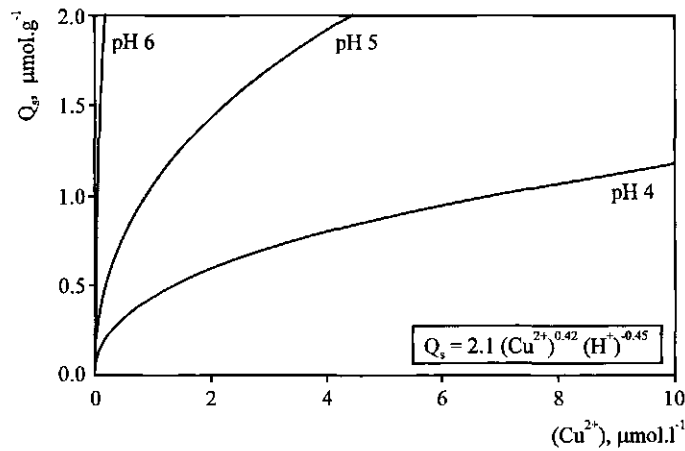


Figure 13.6. Copper binding to a sandy soil.

In a soil system, the increased pH will increase the affinity for copper of both the root cell walls and the soil. Due to the increased copper binding to soil, the concentration free copper ions in solution is reduced. Thus, on the one hand the copper binding to the root increases with increasing pH, on the other hand the reduced copper ion concentration will lead to a lower amount of copper sorbed by the root. Therefore, it is difficult to predict the final effect of a changing soil pH for the copper sorption to the maize root. However, by combining the three equations given above, binding to biota can be expressed as a function of total copper in soil ((Cu_t)) and pH:

$$Q_b = K_b K_s^{-a_b/a_s} (\text{Cu})_i^{a_b/a_s} (\text{H}^+)^{b_b - b_s a_b/a_s}$$

Thus enabling the calculation of the sorption to maize root cell walls in the given soil system. The derivation of these latter equations is described in more detail in Nederlof & van Riemsdijk (1995), and in Nederlof et al. (1993).

The results of the model calculations are shown in Figure 13.7. With increasing pH in soil less copper is bound to the maize root cell walls. This is in full agreement with the observed differences of the influence of pH on copper toxicity in solution or in soil environment.

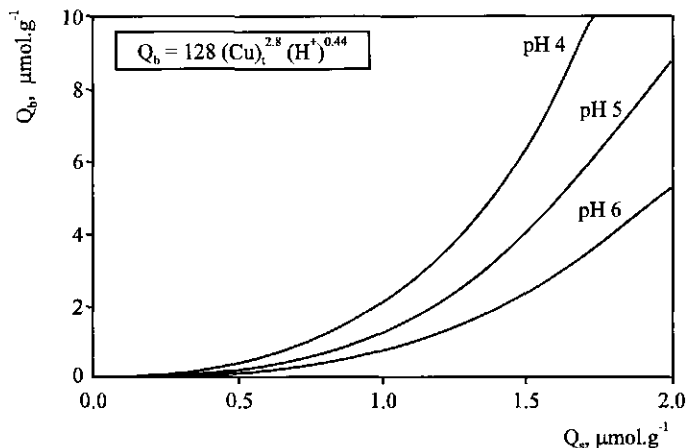


Figure 13.7. Predicted copper binding to maize root cell walls if the maize were grown on soil.

In case exposure only takes place via the free metal ions in the soil solution, the speciation approach may be a valuable tool in predicting quantitatively the metal sorption to biota present in a complex system, and to predict the relative change in availability due to environmental changes. As for the effects for biota, this approach will enable at least a qualitative statement on the impact of changing environmental conditions. A more detailed discussion on this concept is given by Nederlof & van Riemsdijk (1995) and Plette et al. (1996).

To understand, predict, model, the effect of environmental factors on the bioavailability a detailed knowledge on chemical interaction processes is required.

An aspect not yet discussed that may be important in studying bioavailability is the fact that:

Organisms may actively influence the bioavailability by changing the chemical composition of their immediate environment. This may lead to increased or decreased bioavailability.

E.g., some plants have the ability to decrease the pH of the rhizosphere by means of excretion of organic acids. This will lead to increased availability of phosphate as present in rock phosphate (basic calcium phosphate precipitates). In this case the organism

influences its surroundings to increase the bioavailability which is favourable for the organism. Another example is earthworms. Earthworms may also excrete organic substances. These substances can bind copper ions very strongly, leading to a reduction of the concentration of free copper. In cases of copper toxicity for the earthworms, this influence leads to a decreased bioavailability (effect toxicity) which is beneficial for the organism.

In conclusion of this introductory chapter it might be stated that:

To obtain generalizable concepts of bioavailability and to be able to apply these concepts to any soil, sediment or aqueous system, fundamental mechanisms should be understood both qualitatively and quantitatively.

13.4 References

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14 The application of chemical speciation calculations

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Summary

Chemical speciation calculations are done in order to evaluate the complexation behaviour of components in solutions, to predict the behaviour of components in soil-water systems (their distribution over soil phases), and to determine solubility relationships regarding components in the 'solid phase' of the soil (*e.g.* solubility products for minerals, or parameters for sorption models). In such calculations, it is assumed that chemical equilibrium exists during the period of interest. This text discusses several examples of: complexation behaviour (Cd-Cl, Al-OH, cyanides, metal-DOC), the prediction of the behaviour of components in soils (Cd in harbour sludge, cyanide in contaminated soils, heavy metal extraction with chelates), the determination of solubility products (iron oxide and Prussian blue), and the determination of the parameters of a sorption model (pH-dependent Freundlich model). Speciation calculations are briefly discussed in relation to dynamic processes, such as the transport of components (multi-component transport).

14.1 Introduction

For determining the chemical equilibrium composition of a soil-water system, speciation calculations are applied in addition to carrying out chemical analysis. As already discussed (Chapter 9), analytical methods often yield only total amounts of components, rather than species concentrations, except for H^+ (pH) and e^- (Eh). For risk assessments, often detailed information on concentrations is needed, even if the concentrations of the species present in the system concerned are extremely low. This information is also needed in order to describe the behaviour of compounds in a soil-water system.

Speciation calculations yield the total amounts and concentrations or activities of components and species present in the different phases of a soil-water system. Next, it is possible to calculate the distribution of a component over the different species present. For systems that are completely known (*i.e.* all the components and species as well as their formation constants are known), this may be sufficient, but speciation calculations can also be applied when predicting the chemical equilibrium composition in situations or under conditions which are expected to be present at other places, or at a later time.

However, important data necessary in order to describe a certain system is often missing. Such data can be found by means of additional analysis or experiments, as well as by speciation calculations. Well-known examples are the determination of the solubility products of minerals, the estimation of the parameters of sorption models

(*e.g.* Freundlich or Langmuir), and the determination of the formation constants of specific complexes. In all such cases, the calculated activities of the components are used for estimating the unknown parameters.

Thus, chemical speciation calculations are applied in order to:

- evaluate the complexation behaviour of components in solution;
- predict the behaviour of components (their distribution over soil phases);
- determine the solubility relationships concerning minerals or adsorbed components.

In such calculations, chemical equilibrium is assumed to exist. Although this often is not the case, speciation calculations may still be carried out. For example, in the case of minerals, partial equilibrium may be assumed (see Chapter 9). In the case of faster dynamic processes, speciation can be calculated over different time intervals. Examples of such processes are: the dissolution or precipitation of minerals, the uptake of compounds by organisms, and the transport of components through soil. In such cases, speciation calculations concern (are part of) the dynamic process involved in the behaviour of compounds in the soil-water system.

In the remainder of this text, examples are given of these types of speciation applications. Chemical speciation is calculated using the ECOSAT computer program (Keizer & van Riemsdijk 1994).

14.2 The evaluation of complexation behaviour

For calculating the distribution of a component over the different species present, the species concentrations are divided by the total amount of that component (calculation of fraction or percentage). By way of such calculations, the most important forms of the component can be established. This may be interesting in view of differences in toxicity or mobility among the species concerned. It is assumed here that the $\log(K^\circ)$ values for all relevant species (complexes or ion pairs) are known.

14.2.1 The complexation of cadmium with chlorides

In solutions containing chlorides (*e.g.* seawater, CaCl_2 extracts), heavy metals, such as Cd, Pb, Hg and Zn, tend to form chloride complexes (Hahne & Kroontje 1973; Lindsay 1979). Such complexes are often less toxic and considerably more mobile in soil due to a more negative charge.

In order to illustrate this, the formation of cadmium chloride complexes is calculated for a simple system which contains only the components Cd^{2+} and Cl^- . The total amounts chosen are: 10^{-5} mol/l for $\text{Cd}(t)$, and the following range of values for $\text{Cl}(t)$: 0.001 mol/l - 0.1 mol/l. The ionic strength (I) is kept constant at a value of 0.1 mol/l. The species present are shown in Table 14.1, which is the table of species for this system.

The calculated % distribution of $\text{Cd}(t)$ over all five cadmium species is represented in Figure 14.1. It shows that, even at low chloride concentrations, the complexation of cadmium with chlorides is very significant.

Table 14.1. Table of species for the Cd-Cl system. $U = 0.1$. The $\log(K^\circ)$ values were taken from Lindsay (1979).

Components	Cd	Cl	$\log(K)$
Species			
Cd	1	0	0
Cl	0	1	0
CdCl	1	1	1.98
CdCl ₂	1	2	2.6
CdCl ₃	1	3	2.4
CdCl ₄	1	4	1.7
Total	10^{-5}	0.001 - 0.1	

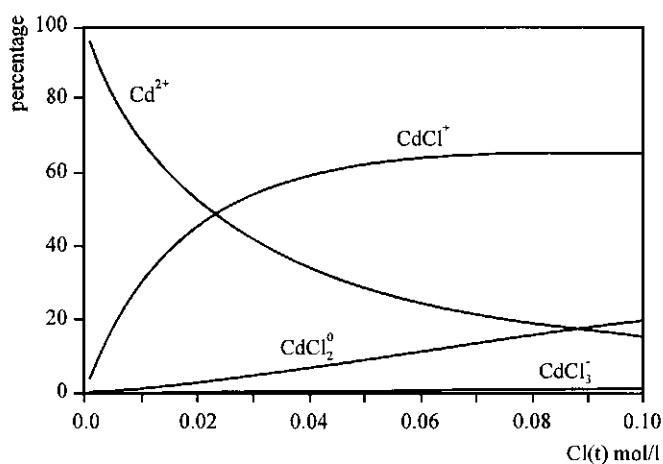


Figure 14.1. The percentage distribution of Cd(t) in solution over different Cd-Cl species as a function of the total chloride concentration. $Cd(t) = 10^{-5}$ mol/l, $U = 0.1$ mol/l.

14.2.2 Aluminium hydrolysis

Many cations form hydrolysis products when dissolved in water, especially at higher pH levels (Hahne & Kroontje 1973; Lindsay 1979). This is a very important phenomenon, because hydrolysis either reduces the activity of free cations, or increases the total amounts of components in solution. In the case of most heavy metals, hydrolysis starts at pH levels of around 6 to 7. However, in the case of mercury (Hg^{2+}) and aluminium (Al^{3+}) it starts at much lower values, namely at pH levels of around 3 to 4. In order to illustrate this, the speciation calculation results for Al hydrolysis are given.

System description:

Aluminium is dissolved in water ($Al(t) = 10^{-6}$ mol/l), the ionic strength is set at 0.01 mol/l, and the pH ranges between 3 and 9. The species present are listed in Table 14.2, which is the table of species for this system.

Table 14.2. The table of species for the Al-OH system. $U = 0.01$. $\text{pH} = 3 - 9$. The $\text{Log}(K^0)$ values were taken from Lindsay (1979).

Components	Al	H	$\log(K)$
Species			
Al	1	0	0
H	0	1	0
OH	0	-1	-14.0
AlOH	1	-1	-5.02
Al(OH) ₂	1	-2	-9.3
Al(OH) ₃	1	-3	-14.99
Al(OH) ₄	1	-4	-23.33
Al ₂ (OH) ₂	2	-2	-7.69
Total	10 ⁻⁶	?	

This table can be reduced with the known activity coefficient of H^+ (see section 9.5 in 'Basic Principles of Chemical Speciation Calculations').

The calculated distribution of Al(t) over the different hydroxyl complexes is depicted in Figure 14.2. It shows that at pH levels above approximately 5, only a small part of the Al is present in its free, non-complexed form. As this is its most reactive form regarding sorption onto soil particles, equilibrium reactions with Al hydroxides, and for example the formation of Al-DOC complexes, it demonstrates that pH strongly affects the behaviour of Al in soil-water systems. Considering this complexation behaviour, higher Al(t) values in solution can be expected.

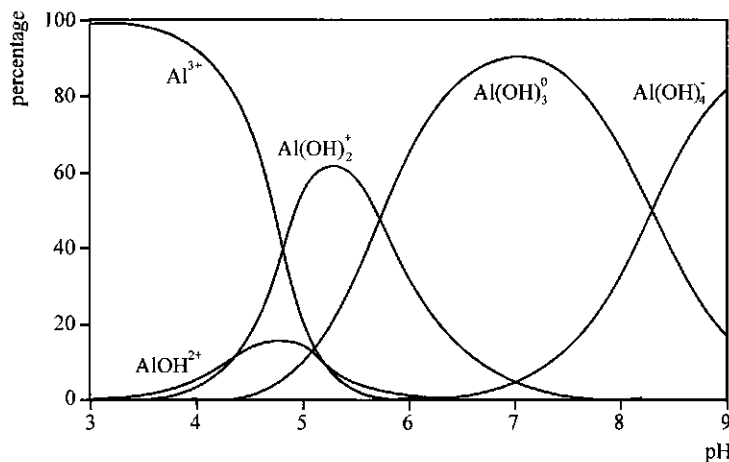


Figure 14.2. The % distribution of Al(t) in solution over different hydrolysis species as a function of pH. $\text{Al}(t) = 10^{-6} \text{ mol/l}$, $U = 0.01 \text{ mol/l}$.

14.2.3 Cyanide speciation in solution

In the case of soils contaminated with cyanide, it is important to determine which form of cyanide predominates in the water phase. The cyanide species CN^- , $\text{HCN}(\text{aq})$ and $\text{HCN}(\text{g})$ are very toxic, whereas iron cyanide complexes ($\text{Fe}(\text{CN})_6$) are barely toxic.

Cyanide contamination (*e.g.* at former gas-works sites) often exists in the form of iron cyanide complexes and iron cyanide minerals. These substances have also formed in soils after contamination with high concentrations of $\text{HCN}(\text{aq})$ or CN^- , at places where iron hydroxide was present and the pH was sufficiently high. Dissolved $\text{Fe}(\text{CN})_6$ can form complexes with Ca^{2+} , K^+ and H^+ . For all the equilibrium reactions which are relevant to a cyanide soil-water system, see Table 14.3. Because iron is present in the form of Fe^{3+} , iron hydroxide can form at high pH values.

Table 14.3. The chemical equilibrium reactions and formation constants ($\log K^\circ$) used for calculating cyanide speciation.

Reaction			$\log K^\circ$
$\text{H}^+ + \text{CN}^-$	\longleftrightarrow	$\text{HCN}_{(\text{aq})}$	9.2
$\text{H}^+ + \text{CN}^-$	\longleftrightarrow	$\text{HCN}_{(\text{g})}$	6.8
$\text{Fe}^{3+} + 6 \text{CN}^-$	\longleftrightarrow	$\text{Fe}(\text{CN})_6^{3-}$	43.9
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{Ca}^{2+}$	\longleftrightarrow	$\text{CaFe}(\text{CN})_6^-$	46.5
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{K}^+$	\longleftrightarrow	$\text{KFe}(\text{CN})_6^{2-}$	45.4
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^-$	\longleftrightarrow	$\text{Fe}(\text{CN})_6^{4-}$	49.9
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + \text{H}^+$	\longleftrightarrow	$\text{HFe}(\text{CN})_6^{3-}$	54.3
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + 2 \text{H}^+$	\longleftrightarrow	$\text{H}_2\text{Fe}(\text{CN})_6^{2-}$	56.7
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + \text{Ca}^{2+}$	\longleftrightarrow	$\text{CaFe}(\text{CN})_6^{2-}$	54.0
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + 2 \text{Ca}^{2+}$	\longleftrightarrow	$\text{Ca}_2\text{Fe}(\text{CN})_6^0$	55.3
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + \text{Ca}^{2+} + \text{H}^+$	\longleftrightarrow	$\text{CaHFe}(\text{CN})_6^-$	57.0
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + \text{K}^+$	\longleftrightarrow	$\text{KFe}(\text{CN})_6^{3-}$	52.4
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + 2 \text{K}^+$	\longleftrightarrow	$\text{K}_2\text{Fe}(\text{CN})_6^{2-}$	53.3
$\text{Fe}^{3+} + 6 \text{CN}^- + \text{e}^- + \text{K}^+ + \text{H}^+$	\longleftrightarrow	$\text{KHFe}(\text{CN})_6^{2-}$	55.7
$\text{Fe}^{3+} + \text{e}^-$	\longleftrightarrow	Fe^{2+}	13.0
$\text{Fe}(\text{OH})_3(\text{s}) + 3 \text{H}^+$	\longleftrightarrow	$\text{Fe}^{3+} + 3 \text{H}_2\text{O}$	2.7

Speciation calculations for the system described above, with the components CN^- , Fe^{3+} , H^+ , e^- , Ca^{2+} , K^+ and other species as mentioned in Table 14.3, can be done only if the activities or total amounts of all components are known. In the case of a soil-water system, acceptable values for $\text{Ca}(\text{t})$ and $\text{K}(\text{t})$ may be chosen (*e.g.* 5 mM and 1 mM respectively). Furthermore, it is assumed that the activity of Fe^{3+} is controlled by equilibrium with solid $\text{Fe}(\text{OH})_3$. The values chosen for $\text{CN}(\text{t})$, pH and pe should be relevant to contaminated soil-water systems.

The results of these calculations are presented in Figure 14.3, which shows the areas of predominance (> 50 %) of free cyanide ($\text{HCN}_{(\text{aq})} + \text{CN}^-$) and $\text{Fe}(\text{CN})_6$ complexes ($\text{Fe}(\text{CN})_6(\text{t})$). It demonstrates that the distribution of cyanide over toxic and non-toxic forms depends on the total amount of cyanide present as well as on the pH and redox potential. $\text{Fe}(\text{CN})_6$ complexes are stable only at high pH values, low pe and high $\text{CN}(\text{t})$. Thus, under normal soil conditions, all the cyanide is expected to be present in its toxic, free form.

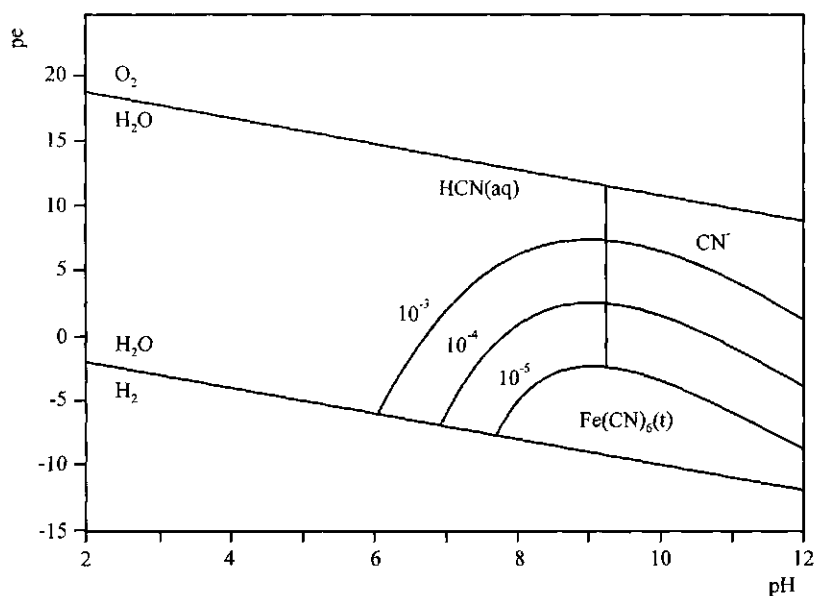


Figure 14.3. The predominance of cyanide species in solution as a function of pH, pe and total cyanide concentration ($CN(t) = 10^{-3}, 10^{-4}$ and 10^{-5} M) at equilibrium with solid $Fe(OH)_3$, as calculated using the equations listed in Table 14.3. In the area indicated by ' $Fe(CN)_6$ ', cyanide is predominantly present in the form of one or more of its complexed species, while in the remaining area it is predominantly present in its free forms. $Ca(t) = 5$ mM, $K(t) = 1$ mM, ionic strength = 0.01 M.

However, this predicted result was not found in groundwater samples. Chemical analysis revealed that all the cyanide in these samples was present mainly in the form of $Fe(CN)_6$ complexes (Meeussen et al. 1992a). A possible explanation is that the assumption of chemical equilibrium does not apply in this case. The cyanide speciation was found to be very sensitive to light. Daylight may considerably promote the decomposition of $Fe(CN)_6$ complexes (all the $Fe(CN)_6$ was decomposed within 4 days; the initial decomposition rate was 8% per hour). In soil solutions and groundwater, however, such decomposition does not occur, due to lack of light. Under dark conditions, $Fe(CN)_6$ is obviously the stable form of cyanide. Therefore, water samples should be kept in the dark, when concentrations of free cyanide need to be determined.

14.2.4 Metal-DOC complexation

Heavy metals may form complexes with dissolved organic matter (DOC, humic acids, or fulvic acids). Depending on the type of metal, type of DOC and environmental conditions, up to approx. 99% of the total amount of a heavy metal in a soil solution may be complexed with DOC. However, this applies only to metals which form strong complexes, such as Cu and Pb. In the case of such metals as Cd and Zn, a much lower percentage of their total amount in solution will become complexed (up to approximate-

ly 50%).

For calculating the distribution of a metal over the different species present in a solution, the formation constants of the metal-DOC complexes and their stoichiometry need to be known. Regarding the formation of complexes with dissolved natural organic ligands, so far only empirical models and some experimental data are available (Sposito 1986; Buffle 1988).

A more recent approach is based on the combined treatment of the heterogeneous nature of reactive groups and the variable charge effects of the binding of ions to polyelectrolytes (de Wit et al. 1991).

It is difficult to find reliable data on the stoichiometry of complexes formed and metal-DOC formation constants for the following reasons:

- The composition and characteristics of DOC depend heavily on its origin due to chemical heterogeneity.
- The complexation characteristics of DOC depend on the existing conditions, such as pH, ionic strength, the cation composition of the solution, etc., *i.e.* variable charge effects.
- Conditional formation constants are often determined only for specific DOC (*e.g.* water extracts from sewage sludge or humic acid) and specific environmental conditions (*e.g.* pH and ionic strength).
- The binding of metals to DOC is affected by the variable charge and chemical heterogeneity of polyelectrolytes. Therefore, such binding should be described using a variable charge model and a distribution function for the affinity constants (de Wit et al. 1991; Benedetti et al. 1996).

Thus, using one of those conditional $\log(K)$ values which are now and then determined, can easily lead to inaccurate results. However, such values are suitable for a qualitative description of the binding of metals to DOC for which the $\log(K)$ values were determined (Baham & Sposito 1986, Dudley et al. 1987).

14.3 The prediction of the behaviour of components

Speciation calculations can be applied for predicting the effects of changing soil conditions (*e.g.* pH, redox potential, ionic strength, temperature, the total amount of components) on the concentrations of components in different soil phases. Next, the results can be used for describing the behaviour of components in comparable soil-water systems. This applies in the first place to speciation calculations concerning dynamic processes (*e.g.* the transport of components through soil).

14.3.1 Cadmium in harbour sludge

For assessing the potential risks of heavy metals in harbour sludge, the mobility of cadmium was investigated in relation to the conditions present in such sludge. Harbour sludge consists of sand, clay, (hydr)oxides, carbonates and organic matter, often contains high amounts of heavy metals, has a high pH, and is initially aerobic (high redox potential).

As a result of the oxidation of organic matter by micro-organisms, the sludge will

gradually become anaerobic (a process which takes years). Due to the presence of sulphates in the salty water or sludge, metal sulphides are formed (reduction of SO_4^{2-}). Consequently, the mobility of the heavy metals will decrease considerably.

Cadmium may be present in the soil solution either in the form of free Cd^{2+} or complexed with either chloride (-Cl), sulphate ($-\text{SO}_4$), carbonate ($-\text{CO}_3$), or sulphide (-HS). In the solid phase, cadmium may be either adsorbed onto soil particles, or present as a mineral (e.g. $\text{CdCO}_3(\text{s})$ or $\text{CdS}(\text{s})$). Iron in the form of $\text{Fe}(\text{OH})_3(\text{s})$ will dissolve, and precipitate as iron sulphide (e.g. $\text{FeS}_2(\text{s})$ pyrite) after reduction of the sulphate.

System description :

Components	: Cd^{2+} , Cl ⁻ , H ⁺ , CO_3^{2-} , SO_4^{2-} , e ⁻ , OH ⁻ , Fe^{3+}
Species	: components + Cd-Cl, Cd-OH, Cd- CO_3 , Cd- SO_4 , Cd-HS, H- CO_3 , H- SO_4 , H-HS, Fe-OH complexes
Surface species	: Q_{Cd} (pH-dependent Freundlich sorption model)
Minerals	: $\text{CdCO}_3(\text{s})$, $\text{CdS}(\text{s})$, $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{FeS}_2(\text{s})$
SSR	: 5 kg/l (soil/solution ratio)
Cd(t)	: 0.5 mmol/l = 11.24 mg/kg
$\text{SO}_4(\text{t})$: 10^{-4} mol/l and 10^{-3} mol/l
Cl(t)	: 0.1 mol/l
P- CO_2	: 3×10^{-3} bar (constant partial gas pressure)
pH	: 8
pe	: 8 (aerobic) and -5 (anaerobic)
Ionic strength	: 0.1 mol/l

$$Q_{\text{Cd}} = K \cdot (\text{H}^+)^m \cdot (\text{Cd}^{2+})^n$$

where: $\log(K) = -3$, $m = -0.5$ and $n = 0.8$

Table 14.4 shows the results of the calculations expressed in the % distribution of Cd(t) over the soil phases and the Cd(t) concentration in solution. In the aerobic situation, Cd is present partly in adsorbed form and partly as $\text{CdCO}_3(\text{s})$. The Cd(t) concentration in solution is rather high, due to the formation of sulphate-, chloride- and carbonate complexes. As far as the anaerobic situation is concerned, if enough sulphide is available, all cadmium will be present in the $\text{CdS}(\text{s})$ form, and therefore the Cd(t) concentrations in solution will be very low. Most of the dissolved cadmium will be complexed with HS. The total Cd concentration in solution depends additionally on the total amounts of iron and sulphate available, as well as on the type of iron-sulphide mineral formed.

Table 14.4. The calculated distribution and concentrations of cadmium in harbour sludge in the case of an aerobic environment, as well as an anaerobic one, with different sulphate concentrations.

system	Cd(t) mol/l	% dissolved	% adsorbed	% $\text{CdCO}_3(\text{s})$	% CdS
aerobic	2.27E-7	0.1	14.01	85.9	0
anaerobic					
$\text{SO}_4(\text{t}) = 1\text{E-}4$	2.26E-7	0.05	14.0	65.95	20.0
$\text{SO}_4(\text{t}) = 1\text{E-}3$	2.10E-13	0.0	0.0	0.0	100

14.3.2 Cyanide in contaminated soils

The behaviour of cyanide in soils is governed by the interaction between dissolved iron-cyanide complexes ($\text{Fe}(\text{CN})_6$) and the 'solid phase' of the soil. This interaction determines the distribution of cyanide over the solid- and water phases and thus controls its concentrations in groundwater and its transport rates. Although $\text{Fe}(\text{CN})_6$ complexes are unstable under normal soil conditions, in the dark their decomposition rates are so low that free cyanide will not be present in measurable quantities (Meeussen et al. 1992a). Contamination in the form of free cyanides may be the only exception to this rule.

Possible ways of interaction between iron cyanide and the 'solid phase' of the soil are adsorption and precipitation. In the case of precipitation, the concentrations of cyanide in solution are not related to the total cyanide content of the soil, contrary to the case with adsorbed cyanide. For contaminated acid soils from former gas-works sites, it was proven that cyanide was present in the form of an iron-cyanide mineral (Meeussen et al. 1990).

The composition and solubility product of the mineral present determine how the concentration of dissolved cyanide depends on such parameters as pH, redox potential, ionic strength, $\text{Ca}(t)$, etc. Considering the blue colour of contaminated soils, it is very likely that Prussian blue ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$, a precipitate of Fe^{3+} and $\text{Fe}(\text{CN})_6^{4-}$), is the mineral controlling the concentration of cyanide in solution. The solubility product of this mineral equals $10^{-84.5}$ (Meeussen et al. 1992b). In soils, the activity of Fe^{3+} is controlled by an iron hydroxide (*e.g.* amorphous $\text{Fe}(\text{OH})_3(s)$).

Solubility relationships:

Reaction	$\log(K_s^0)$
$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(s) \rightleftharpoons 4 \text{Fe}^{3+} + 3 e^- + 3 \text{Fe}(\text{CN})_6^{3-}$	-84.5
$4 \text{Fe}^{3+} + 12 \text{H}_2\text{O} \rightleftharpoons 12 \text{H}^+ + 4 \text{Fe}(\text{OH})_3(s)$	4.16
PB + 12 $\text{H}_2\text{O} \rightleftharpoons 12 \text{H}^+ + 4 \text{Fe}(\text{OH})_3(s) + 3 \text{Fe}(\text{CN})_6^{3-} + 3 e^-$	-70.36

Based on the solubility relation representing the dissolution of Prussian blue (PB) and subsequent formation of amorphous iron hydroxide, the solubility of complexed cyanide can be calculated as a function of pH (Figure 14.4). This speciation calculation is based on both the above-mentioned solubility relationships and the formation of different $\text{Fe}(\text{CN})_6$ species ($\text{Fe}(\text{CN})_6$ does not decompose here). In Table 14.3, the component CN^- was replaced by $\text{Fe}(\text{CN})_6^{3-}$ (third equation). It was assumed that $\text{Fe}(t)$, $\text{Fe}(\text{CN})_6(t)$ and $e(t)$ are determined by the total amount of Prussian blue present. $\text{Ca}(t) = 10 \text{ mM}$, $\text{K}(t) = 1 \text{ mM}$, $U = 0.03 \text{ mol/l}$.

The above results show that the solubility of this mineral depends heavily on pH. In soils with pH levels above approximately 6, the solubility of Prussian blue is very high. Furthermore, in this pH range adsorption does not play a major role. Therefore, cyanide will be very mobile. As indicated in Figure 14.4, the total concentrations of cyanide in soil extracts at high pH values ($\text{pH} > 6$) are not at equilibrium with Prussian blue, contrary to soil extracts at low pH levels. Such concentrations are limited by the total amount of cyanide present in the soil samples taken, and probably also by the slow dissolution kinetics of Prussian blue present. The slow dissolution kinetics of spilled Prussian blue might also explain the presence of this mineral in such soils, as

at these pH values this mineral is very soluble. An other explanation for the behaviour at high pH might be the presence of an other cyanide mineral with a much lower solubility *e.g.* $\text{Mn}_2\text{Fe}(\text{CN})_6$ (Keizer et al. 1995).

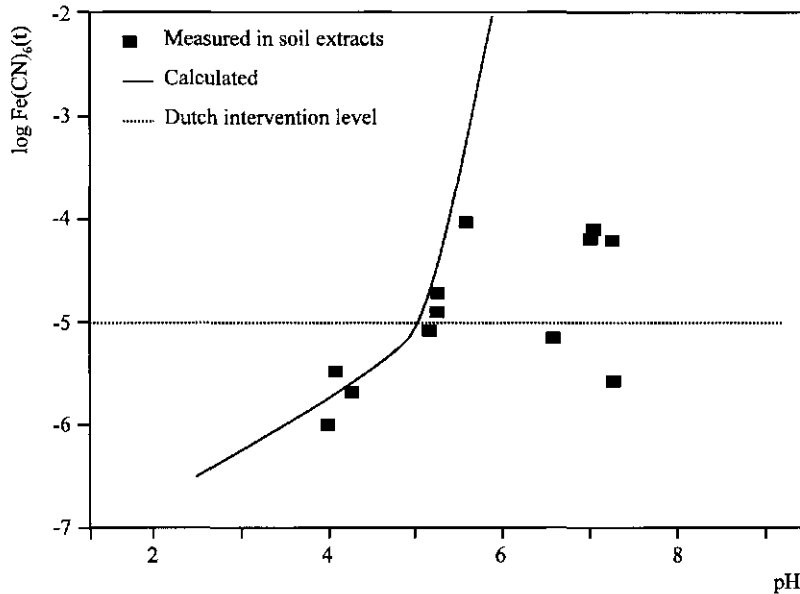


Figure 14.4. The total cyanide concentration ($\log(\text{Fe}(\text{CN})_6(t))$) as a function of pH at equilibrium with Prussian blue (calculated) and as measured in CaCl_2 extracts of contaminated soils.

14.3.3 Chelate extraction of heavy metals

Chelates such as EDTA, DTPA and NTA are well-known for their ability to either keep heavy metals in solution, or to bring them into solution. They may be used for extracting soils in order to assess the availability to plants of heavy metals, as well as for extracting heavy metals from contaminated soils, so as to clean them up. When the solubility relationships for all metals which form complexes with the chelate concerned are known, speciation calculations can be done, and the results be applied for optimising extraction conditions (pH, chelate type, concentration, etc.).

As an example, the extraction of copper from a contaminated soil using the chelates EDTA and NTA is predicted at different pH values (Figure 14.5). It is assumed that only H^+ , Cu^{2+} , Al^{3+} , Fe^{3+} and Ca^{2+} form complexes with these chelates.

System description:

Components: H^+ , Cu^{2+} , Al^{3+} , Fe^{3+} , Ca^{2+} , and either EDTA^{4-} or NTA^{3-}

species: components + complexes with OH and either EDTA or NTA

$U = 0.015$

$(\text{Ca}^{2+}) = 0.01 \text{ mol/l}$

pH = 4 - 7

Chelate concentration : 1 mM

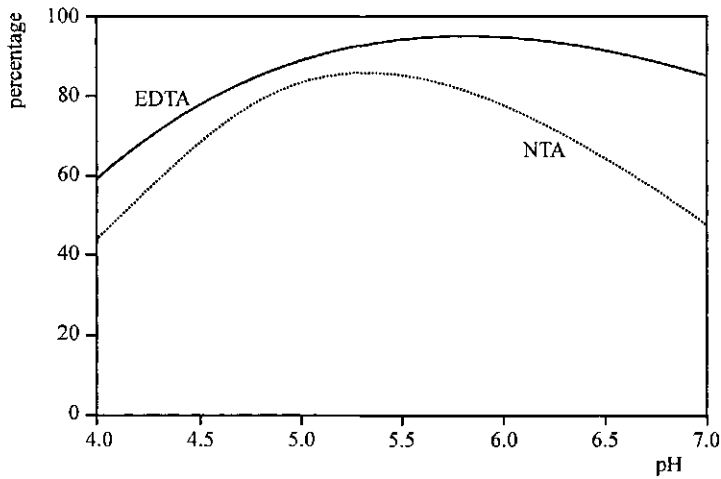


Figure 14.5. The amount of Cu expressed as a percentage of the initial Cu content in the soil, extracted by either EDTA or NTA, as a function of pH.

Cu desorption according to a pH-dependent Freundlich model (Figure 14.9):

$$Q_{Cu} = 10^{-3} \cdot (H^+)^{-0.5} \cdot (Cu^{2+})^{0.4}$$

soil solution ratio: 0.25 kg/l

initial Cu content: 100 mg/kg

minerals: Al(OH)₃ (gibbsite) and FeOOH (goethite).

Figure 14.5 shows that EDTA is much more capable than NTA of extracting copper, and that the greatest extraction occurs at approx. pH 5.5. A disadvantage of using chelates as EDTA and NTA is that strong complexes are formed with metals such as Al, Fe and Ca, which are always present in soils. Also other heavy metals, such as Zn,

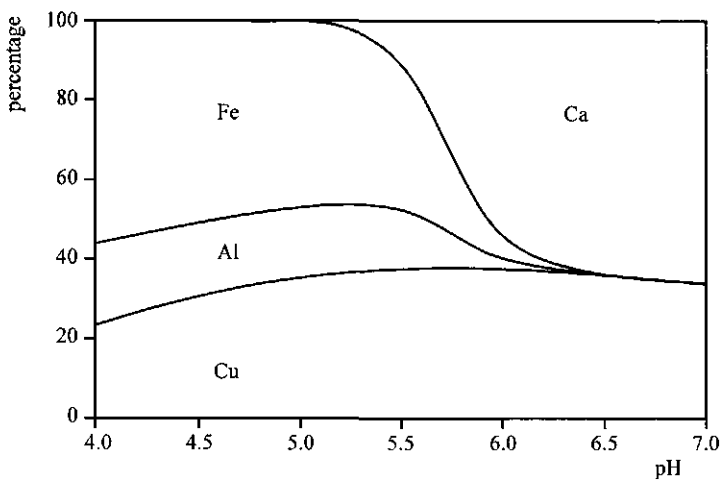


Figure 14.6. Percentage distribution of EDTA(t) in solution over Cu, Ca, Al and Fe as a function of pH.

Pb, Cd and Mn, may form complexes, if they are present and their solubility is high enough. A large part of the EDTA in solution will be complexed with these metals, depending on the pH and their solubility in the soil (Figure 14.6). Thus, speciation calculations can provide more insight into the efficiency of certain chelates in extracting heavy metals from soils. Based on the relevant solubility relationships, it is easy to predict the extraction behaviour of different chelates with various soil conditions.

14.3.4 Multi-component transport

The mobility of metals in soils is of interest in relation to groundwater contamination, risk assessment, and soil remediation. Such mobility depends on the interaction between the metals and the solid phase, which may be the result of adsorption/desorption- as well as precipitation/dissolution phenomena. Due to the strong influence exerted by the formation of complexes with dissolved inorganic and organic compounds, and the competition of different species for sorption sites, it is very difficult to describe speciation in relation to component transport.

In practice, people are often interested in the effects of chemical interactions on soil- and groundwater quality. The multi-component transport behaviour involved can be described by combining an equilibrium-chemistry code (speciation program) with a transport algorithm (Jennings et al. 1982; van Riemsdijk & van der Zee 1989).

Obviously, reliable results can be obtained only if speciation is correctly modelled. This implies that there is a need for appropriate models which describe the complex interactions between components and the 'solid phase' of the soil. In the case at hand, also the kinetic aspects of the relevant physico-chemical processes are important (slow dissolution/precipitation, and slow adsorption/desorption). Reference is made to the work of Brusseau et al. (1989).

14.4 Determination of the solubility product of minerals

It is often unknown which minerals are present in soils or which solubility product should be used. For minerals with a pH-dependent solubility, the solubility relationship can be found rather easily, by plotting the $\log(\text{metal activity})$ against the pH (solubility diagram; Figure 14.7). Such minerals are, for example, all hydroxides and carbonates ($\text{Fe}(\text{OH})_3(\text{s})$, $\text{Al}(\text{OH})_3(\text{s})$, $\text{CdCO}_3(\text{s})$).

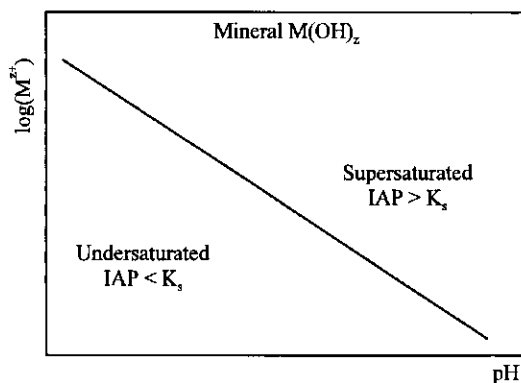


Figure 14.7. The solubility diagram for a metal hydroxide. $\text{IAP} = (M^{2+})(\text{OH}^-)^2$.

Before this solubility relationship can be determined, the concentrations in solution, at different pH values, of the components present in the mineral must be determined. However, this often leads to highly erroneous results, because usually only the total amounts of the metals can be determined, and not the 'free metal' activity (*e.g.* Fe(t) and Fe^{3+}) respectively). Moreover, the total concentrations of the components in solution are often below the detection limits of the available analytical methods.

In order to improve such analytical data, the total concentrations of the metals in solution can be increased by adding chelates (*e.g.* EDTA or NTA). The distribution of the component over the species in solution, and the component activity can then be calculated as follows:

The mass balance for metal M:

$$M(t) = [M^{z+}] + [M\text{-inorganic}] + [M\text{-chelate}]$$

- M(t) : the total amount of metal M (mol/l)
 $[M^{z+}]$: the free-metal concentration (mol/l)
[M-inorganic] : the concentration of all inorganic metal complexes (*e.g.* M-OH)
[M-chelate] : the concentration of all metal-chelate complexes (*e.g.* M-EDTA)

If all $\log(K^{\circ})$ values for the species present are known, and the total component amounts in solution have been measured, then, the component activity can be calculated. Such component activities are used for the determination of the regression line in the solubility diagram (Figure 14.7), in which $\log(M^{z+})$ is plotted against pH, and for calculating the ion activity product ($\text{IAP} = (M^{z+})(\text{OH}^{-})^z$). At equilibrium, the solubility product equals IAP (see also 'Basic Principles of Chemical Speciation Calculations').

Because chelates such as EDTA or DTPA form complexes with many of the metals normally present in soils (*e.g.* Fe, Al, Zn, Cu, Mn, Ca, Mg), all such metals must be taken into account, insofar as they will significantly contribute to the mass balance of the chelate concerned (see also section 14.3.3). Furthermore, the total amount of the chelate needs to be measured, because its value in solution may have become lower, due to sorption onto soil particles.

If the presence of DOC is not taken into account, serious errors may result, as soil solutions and extracts always contain some DOC. Therefore, the mass balance of metal M must be extended as follows, so as to include the concentrations of the metal-DOC complexes ([M-DOC]):

$$M(t) = [M^{z+}] + [M\text{-inorganic}] + [M\text{-chelate}] + [M\text{-DOC}]$$

There is a possibility that such M-DOC complexes contribute significantly to M(t). If so, there is a major problem, because $\log(K^{\circ})$ values for M-DOC complexes are often unknown (see section 14.2.4). If not, they may be disregarded.

An example of the above is the determination of the solubility product of iron hydroxide in soils (Norvell & Lindsay 1982). The equilibrium between soil Fe and chelated Fe (Fe-EDTA) was established by either varying the fraction of EDTA associated with Fe, or slightly altering the pH of the soil. Corrections were made in order to account for the differential sorption of various EDTA chelate species onto the soils. After measuring Fe(t), EDTA(t), Ca(t) and pH in the equilibrium solution, the activity

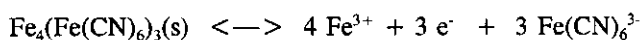
of Fe^{3+} and the $(\text{Fe}^{3+})(\text{OH}^-)^3$ ion activity product were calculated. Unfortunately, the total amounts of other metals were not measured, and the formation of M-DOC complexes, too, was disregarded.

Calculated component activities may also be used for checking whether equilibrium exists with a specific mineral; namely, by plotting the metal activity found in the metal's solubility diagram. This was done for cadmium in soils, with DTPA as chelate (Workman & Lindsay 1990). Unfortunately, the total amounts of other metals were not measured, and the formation of M-DOC complexes, too, was disregarded.

14.4.1 The solubility product of Prussian blue

Determination of the solubility product of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ (Prussian blue) is discussed here in more detail. It was found that this mineral controls $\text{Fe}(\text{CN})_6$ concentrations in the soil solution and groundwater at former gas-works sites (Meeussen et al. 1990). The solubility product was estimated by means of experiments in which Prussian blue was precipitated from solutions containing $\text{Fe}(\text{CN})_6$, some Ca and K, and iron chelated with either EGTA, or HEDTA, or NTA, or citrate (Meeussen et al. 1992b). No other metals or metal-DOC complexes were present.

Precipitation/dissolution reaction:



The added chelate prevents iron from precipitating as iron hydroxide (such precipitation usually occurs at high pH values in soils). Because the exact value of the solubility coefficient of the iron hydroxide formed is unknown, the Fe^{3+} activity cannot be calculated accurately in such a case. Therefore, it was necessary to add a chelate with a

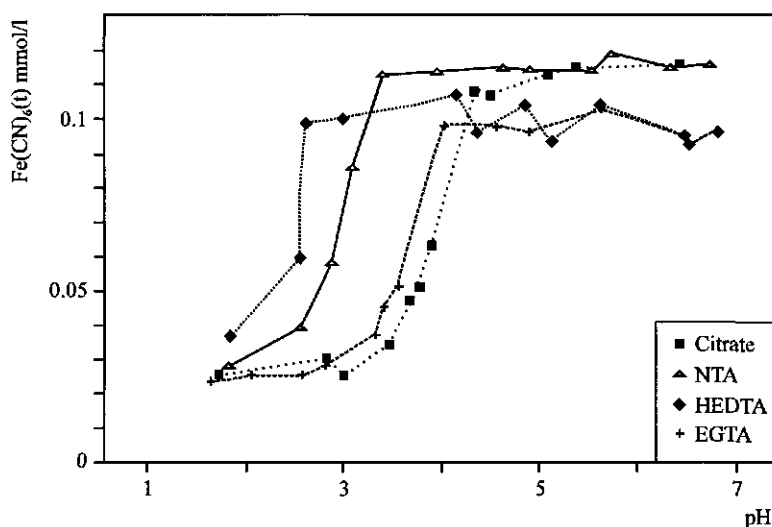


Figure 14.8. The remaining total concentrations of complexed cyanide at different pH values in solutions containing 1 mM of complexing agent (citrate, EGTA, HEDTA, NTA), approx. 0.1 mM of Fe^{3+} , and approx. 0.1 mM of $\text{Fe}(\text{CN})_6^{4-}$.

high affinity for iron. If $\text{Fe}(\text{CN})_6^{3-}$ has a higher affinity for iron than the chelate, and the ion activity product for Prussian blue is larger than its solubility product, iron cyanide will precipitate. Otherwise both cyanide and iron will remain in solution. Due to competition of protons with Fe^{3+} , the stability of chelate-iron complexes is pH-dependent. This implies that below a certain pH, Prussian blue will precipitate. The pH at which this occurs depends on the affinity of iron for the chelate used (Figure 14.8).

The ion activity product (IAP), which is equal to the solubility product K_s at equilibrium, can be formulated as:

$$\text{IAP} = (\text{Fe}^{3+})^4 \cdot (\text{Fe}(\text{CN})_6^{3-})^3 \cdot (\text{e}^-)^3$$

The solubility product of Prussian blue can be estimated by calculating the activities of Fe^{3+} , $\text{Fe}(\text{CN})_6^{3-}$ and e^- in solutions in which there is equilibrium with precipitated Prussian blue. All solutions were analyzed for $\text{Fe}(\text{t})$, $\text{Fe}(\text{CN})_6(\text{t})$, Eh, and pH. In the speciation calculations, $\text{Fe}(\text{t}^*)$ ($= \text{Fe}(\text{t}) - \text{Fe}(\text{CN})_6(\text{t})$) was used for calculating the total amount of iron not associated with cyanide; (e^-) was calculated from the measured redox potential ($\text{pe} = 16.95 \text{ Eh}$); $\text{Ca}(\text{t})$, $\text{K}(\text{t})$ and $\text{chelate}(\text{t})$ were assumed to be equal to the added amount. For the $\text{Fe}(\text{CN})_6$ species present in this system, see Table 14.3.

Applying four different chelates with different affinities for iron makes it possible to do such calculations at different pH values. The most reliable data are obtained in situations where the $\text{Fe}(\text{CN})_6$ concentration has decreased because of precipitation, but where measurable amounts of iron are still present. The values obtained with the different chelates and at different pH values were found to pretty much agree (see also section 14.3.2).

14.5 The determination of sorption model parameters

The adsorption or desorption of heavy metals can be described by means of semi-empirical sorption models, such as the (multi-component) Langmuir model and the (pH-dependent) Freundlich model. More sophisticated models take variable charge and chemical heterogeneity into account (variable charge or surface complexation models).

These semi-empirical models can be used only if the existing environmental conditions agree to those at which the model parameters have been determined. This means that parameters describing a multi-component (competitive) adsorption/desorption reaction must be determined experimentally for a particular soil, once an appropriate sorption model has been chosen. In the case of a multi-component interaction, this implies extensive experimental work, especially when there are many species competing for the adsorption sites (*e.g.* H^+ , Ca^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Al^{3+}). In addition to such competing cations, ionic strength will affect the parameter values.

Before model parameters can be derived from experimental data, the activity of the sorbing component must be calculated from the measured total amount. Some practical problems in determining the activity of metal M are:

- The measured $\text{M}(\text{t})$ is usually not equal to $[\text{M}^{z+}]$, due to the formation of inorganic and organic metal complexes:

$$\text{M}(\text{t}) = [\text{M}^{z+}] + [\text{M-inorganic}] + [\text{M-DOC}]$$

The contribution of $[\text{M-DOC}]$ may not be disregarded in this case, especially not when dealing with metals (such as Fe, Al, Cu and Pb) which form stable complexes

with dissolved organic matter (see also section 14.2.4).

- In soil-water extracts and soil solutions, $M(t)$ often drops to below the detection limits of the available analytical methods.
- Many heavy metals are strongly bound to the 'solid phase' of the soil. Under such conditions, it is very difficult to determine the model parameters of a desorption isotherm by extracting the soil with either water or a salt solution (e.g. 0.01 M $\text{Ca}(\text{NO}_3)_2$). Due to chemical hysteresis, it is often impossible to use adsorption isotherms for describing desorption. It is much easier to determine adsorption isotherms by adding different amounts of the metal concerned to the soil suspension, and then measuring equilibrium concentrations.

Adding a chelate (e.g. EDTA, DTPA or NTA) which forms stable metal complexes (M-chelate) may be of great help in avoiding and solving the problems mentioned above. The mass balance for metal M then equals:

$$M(t) = [M^{z+}] + [M\text{-inorganic}] + [M\text{-DOC}] + [M\text{-chelate}]$$

- The total amount of metal M in solution will increase due to complexation with the chelate. This may lead to a more accurate analysis of $M(t)$.
- $[M\text{-DOC}]$ may be disregarded compared to $[M\text{-chelate}]$.
- Considerably more metal will desorb from the 'solid phase' of the soil. This is especially useful in the case of such metals as Cu and Pb. By varying the chelate-soil ratio and the pH, the values of different points on the desorption isotherm can be obtained.
- $\text{Log}(K^o)$ values for metal-chelate complexes are well-known. By applying speciation calculations in which such values are used, it is possible to calculate the 'free metal' concentration or activity.

The accuracy of the calculated activity may be affected by either the accumulation of errors in the mass-balance values of all the metals competing for the chelate (see also section 14.3.3), or by significant adsorption of the chelate itself. The latter can be overcome by measuring the concentration of dissolved chelate directly.

If the free-metal activity at equilibrium with the adsorbed amount of metal is known, the model parameters can be estimated based on the experimentally-derived data set. In using the Langmuir model and the pH-dependent Freundlich model, simple linear-regression analysis can be applied (see Chapter 9).

14.5.1 The pH-dependent Freundlich sorption model

The pH-dependent Freundlich model may be formulated as:

$$Q_M = K_M \cdot (H^+)^m \cdot (M^{z+})^n$$

where:

- (M^{z+}) : the activity of component M with valence $z+$ (mol/l)
- Q_M : the adsorbed amount of component M ([surface species] in mol/kg)
- (H^+) : the activity of component H^+ (mol/l)
- K_M, m, n : the parameters of the Freundlich sorption model

In Figure 14.9, the isotherms for two different pH values are plotted. For determining the model parameters, it is enough to collect experimental data for several combinations of Q_M , (M^{z+}) and pH. This is done by extracting the contaminated soil with a salt solution containing different amounts of chelate (e.g. EDTA). The soil pH can be varied by adding different amounts of either acid or base. As soon as there is equilibrium, the pH, chelate(t) and $M(t)$ in solution are measured. The total initial amount of the metal in the soil needs to be measured as well.

After extraction, Q_M and (M^{z+}) are calculated from the measured total amounts. After linearization, the parameters in this equation are estimated using multiple linear-regression analysis.

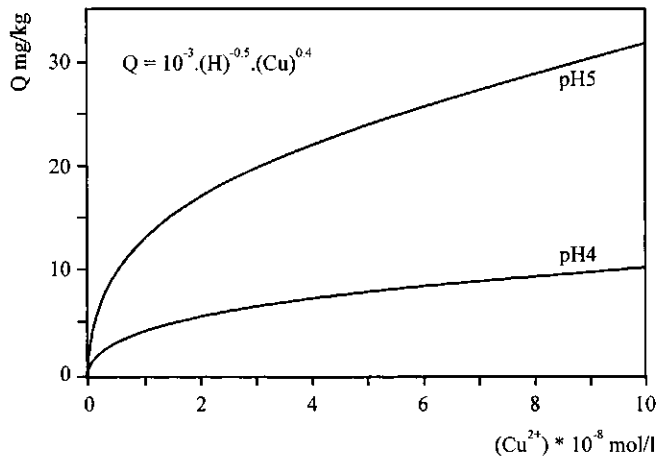


Figure 14.9. The pH-dependent Freundlich model for Cu in a sandy soil.

The application of semi-empirical models, such as the pH-dependent Freundlich equation, is limited to those conditions at which the model parameters have been determined. As there are no practical relevant alternatives at this moment, we are forced to use them. However, we should be aware of their limitations.

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15 Soil protection in relation to soil vulnerability

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15.1 Introduction

Soil vulnerability is difficult to define, because the question has to be answered: 'vulnerable to what?'. Environmental legislation in different countries emphasizes the multifunctionality of the soil system, including at least the agronomic, ecological and carrier function. Vulnerability provides a measure for the ease by which activities of man can adversely affect these functions. For example, a soil with a low adsorptive capacity and with a high groundwater-table can retain only low quantities of phosphates which are applied to the soil as part of fertilization practices. Leaching of phosphates to the groundwater is bound to occur rapidly, and the soil system may be considered to be vulnerable to the adverse effects of fertilization. Soil protection would imply restriction of the rate of fertilization to, preferably, a level which corresponds to the quantity taken up by the plant. This may, however, not be feasible in the short run because of political and economic reasons. Then, limits have to be defined for yearly fertilization rates which will, for a specified period, not result in complete saturation of the phosphate sorption capacity of the soil volume between the surface and the highest groundwater level. Such rates will be characteristically different for different soils.

This arbitrary example serves only to illustrate the principles involved and also shows the importance to link soil protection measures directly to the assumed vulnerability. In doing so, many questions arise again:

1. Is the problem a serious one and are countermeasures really necessary?
2. What are critical levels of the pollutant which should not be exceeded?
3. Are the underlying physical, chemical and biological processes adequately understood to allow scientifically acceptable characterization?

For the example of phosphate fertilization we may conclude that phosphate pollution of groundwater is unfavorable as it adversely affects groundwater quality and may lead to eutrophication of surface waters when the polluted groundwater flows into surface-water bodies. As to critical levels of phosphates in ground- and surface water, there have been many studies which have not resulted in a unified set of critical phosphate contents in water. This may be explained by the complex character of natural ecosystems with irregular weather patterns, and unpredictable dilution processes and flow patterns of groundwater. In terms of knowledge of the underlying basic processes, a scientist will never be of the opinion that available knowledge is adequate. With regard to phosphates, much remains to be learned about basic adsorption and desorption processes. Still, some empirical relationships have been developed that relate phosphate adsorption to iron and aluminium contents in the soil. These allow at least some semi-quantitative evaluations.

In contrast to phosphates, other chemicals, such as biocides, organic pollutants and heavy metals may present direct health hazards both when they occur in soil or when leached to groundwater. But also for these compounds the same basic questions have to be answered that were briefly analysed for phosphates.

So far, attention was confined to soil vulnerability following additions of chemical compounds to the soil system. In practice, these are likely to be of most practical significance. However, use of soil in mechanised farming systems can strongly affect physical properties which, in turn, govern solute and air dynamics. When discussing vulnerability, physical aspects need attention as well.

Finally, we should recognize that any discussion of soil protection in relation to soil vulnerability is basically a flawed one because such a discussion implicitly assumes that less protection is needed for soils that are less vulnerable. Returning to our example of phosphate fertilization, we implicitly assume that a deep soil with no water table and a high adsorptive capacity needs less protection as compared with the shallow soil discussed earlier. In fact, less protection implies that more phosphates can be 'stored' in the soil and that, therefore, higher rates of fertilization would be acceptable. Once the relatively high phosphate adsorption capacity of a soil is saturated, however, it is likely that desorption will occur later, possibly followed by pollution of groundwater. Using soil as a 'sink' is tricky, because the 'sink' is not protected and isolated as water continually percolates through the soil. Again, what is said about phosphate can be said with more concern about various other chemical compounds: the 'chemical time-bomb' is a modern expression for this major environmental concern.

Pollution of water and air are directly visible and can be smelled or tasted. Soil pollution is invisible and leads to effects sometimes only after many, many years. The only real solution to the problem is, of course, to avoid application of potentially polluting substances to any soil and to apply nutrients only to a level which can be effectively utilized by crops. After years of neglect, society is still catching up to face up to this challenge. As we reach for these lofty goals which are bound to take many years to be realized, we have to struggle to restrict the damage as much as possible for the near future. This, then, is the context within which we will discuss soil protection in relation to soil vulnerability.

15.2 Vulnerability maps

Soil surveys have been made in many countries and their interpretation has traditionally been focused on agronomic issues. More recently soil maps have also been used to express relative vulnerabilities of soils in a given area of land (Breeuwsmas et al. 1986). Three examples for different sandy soils in the south of the Netherlands, shown in Figure 15.1, express: (1) The accumulated cation exchange capacity (CEC) in soil from the surface to the groundwater, separated in terms of the average highest and lowest level during the seasons. (2) The phosphate sorption capacity, calculated as in (1), and (3) The average travel time, calculated as in (1) for a flux of 7 mm/day, considering the hydraulic properties of the different soils. Higher values for the three parameters considered here imply a higher buffering capacity of the soil system and, therefore, a lower probability for groundwater pollution. Characteristic differences obtained between the different soil types and maps, such as these, can be helpful to select areas of land with relatively low vulnerabilities.

One major problem occurs when preparing vulnerability maps. Data are needed for CEC, phosphate adsorption capacity and hydraulic soil characteristics. Such data are gen-

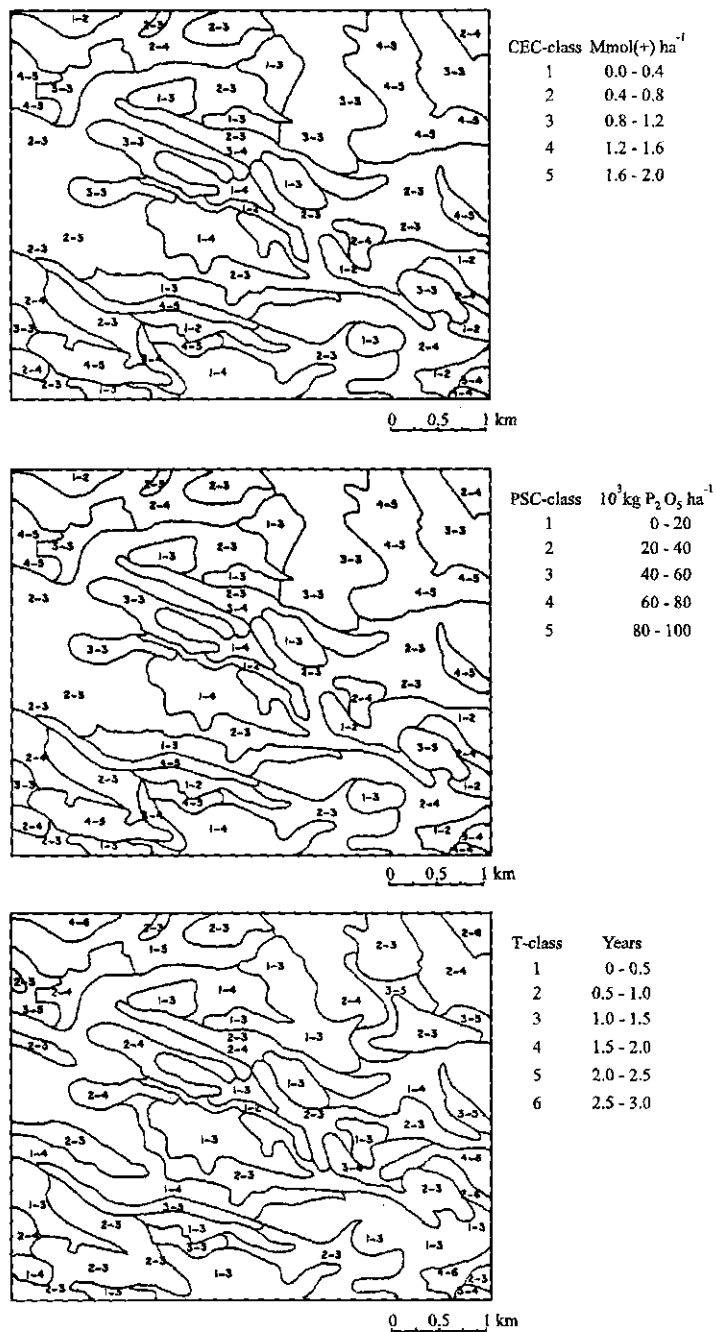


Figure 15.1. Vulnerability map of a sandy area in The Netherlands, with emphasis on CEC, Phosphate Sorption Capacity and Travel times in soil between the surface and the average highest and lowest water table level. (Two class numbers on the map). From Breeuwsma et al. 1986.

erally not available. Use is therefore made of so-called pedotransferfunctions which relate available soil data in soil survey reports to data needed to realize modern applications of soil maps, as discussed here. For CEC a relationship has been developed with % organic matter and % clay, which are both reported in the context of soil surveys, as follows:

$$\text{CEC} = 1.5 \times \% \text{ organic matter} + 0.5 \times \% \text{ clay} \quad (1)$$

For phosphate sorption capacity the following relation is used:

$$\text{PSC} = 0.4 (\text{Al-ox} + \text{Fe-ox}) \quad (2)$$

Where Al-ox and Fe-ox are the extractable aluminum and iron, respectively, using oxalate acid. The Al and Fe contents of soil are known for major soil types in the context of pedological studies. Their determination is relatively simple. Hydraulic characteristics, needed to estimate travel times, are related to soil textural classes.

Pedotransferfunctions are very useful to increase the value of existing soil information which is often in a form that cannot be used directly. Their use is crucial because measurement of all important environmental soil characteristics in all soils would be prohibitively expensive and would take too much time.

Pedotransferfunctions can be incorporated into Geographic Information Systems (GIS) which contain soil maps of different scales and associated data from the different soil units being distinguished which, as a consequence, are geo-referenced. Such databases can be used to make scenario calculations for land use planning purposes. An example for the maize crop is shown in Figure 15.2 indicating the total area of phosphate saturated soils in The Netherlands for different fertilization scenario's.

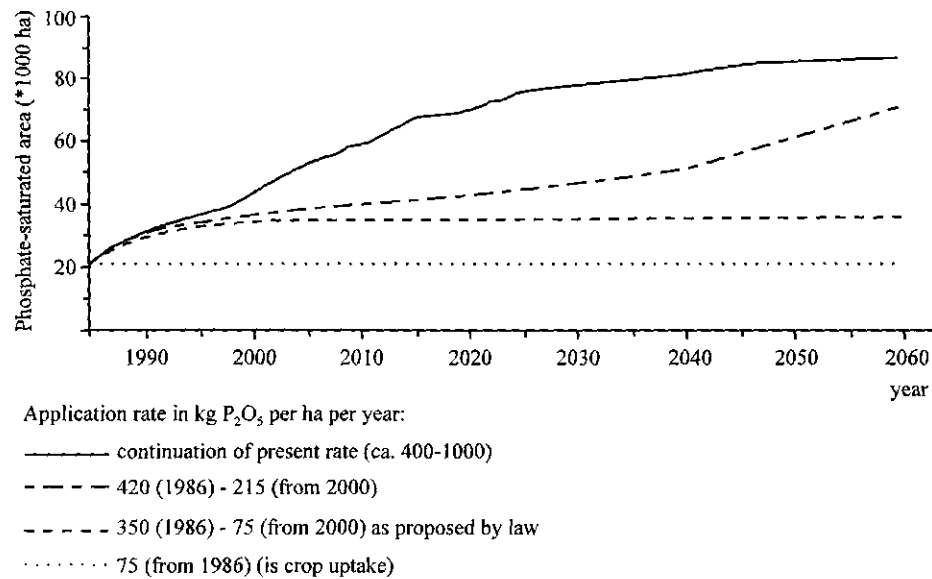


Figure 15.2. Predictions of the total area with phosphate saturated soils in The Netherlands as a function of four future use-scenario's.

The example demonstrates that the estimated saturated area in 1986 (20,000 ha) will not increase in size if fertilization does not exceed crop uptake (75 kg/ha yr). Different rates of reduction lead to different saturated areas in time. If current practices don't change the area will increase more than four times. This type of scenario analysis, using a GIS is useful for planning purposes. The different adsorption capacities reflect relative vulnerabilities and scenario's reflect the effect of different protection measures.

15.3 Sampling: how to get representative data for areas of land?

The examples, described above, implicitly assume that soils within the different delineated areas of the soil map are homogeneous because calculations are made for one 'representative' soil profile for each mapping unit. In reality, soils are quite heterogeneous in the field even though differences between different mapping units are usually larger than differences within units. This heterogeneity is an important aspect of vulnerability because differences in properties within mapping units imply that, for example, breakthrough of a pollutant can locally occur more rapidly than would be expected judging by average values. Two procedures can be followed when expressing heterogeneity within mapping units:

1. Populations of data are described rather than average values only, and these are derived from separate measurements within each mapping unit. Stochastic expressions for these populations allow statements such as: 'the probability that a certain value will be exceeded is 80% etc...'
2. Use of geostatistics which expresses differences among multiple measurements as a function of distances between individual observations. An essential element for geostatistical analysis is the variogram which expresses the variance as a function of distances between observation points. This variogram can be used for interpolation techniques, such as kriging, which allow predictions of values for unsampled locations together with an estimate of the error of the prediction. So, again: rather than produce an average value, a location-specific value is predicted together with its variance (*e.g.* Stein et al. 1991). Figure 15.4 shows two variograms based on field measurements of the Cd content of surface soil in two areas where Zn production resulted in soil pollution of surrounding areas. (Figure 15.3.) The variogram for area 1 shows a variance of 0.33 for distances between points of less than 25 m. The variance rises linearly to 0.45 at a distance of 350 m. The variance for area 2 is significantly lower and rises from 0.075 to 0.15. Such variograms can be used to determine distances between observation points (sampling densities) as a function of the variance expressed by the variogram. More sampling points in a given area do not necessarily result in increased precision of estimates, as this depends on the shape of the semi-variogram. This aspect is specifically illustrated for the two study areas in Figure 15.5 where distance between sampling points is shown as a function of precision. Precision in area 2 is higher at the same boring density than the one in area 1 as a result of the different variograms.

Selection of a desired degree of precision can thus be translated in a corresponding observation density. This approach has been successfully applied to cut costs up to 40%, since standard sampling schemes often require too many observations. The case study illustrates a need to make well documented observations which are defined in terms of location. A minimal number of observations, to be estimated by analysing the variogram, can thus be used to obtain estimates for new points or areas of land by using interpolation. In this way, variation within mapping units of the soil map and its

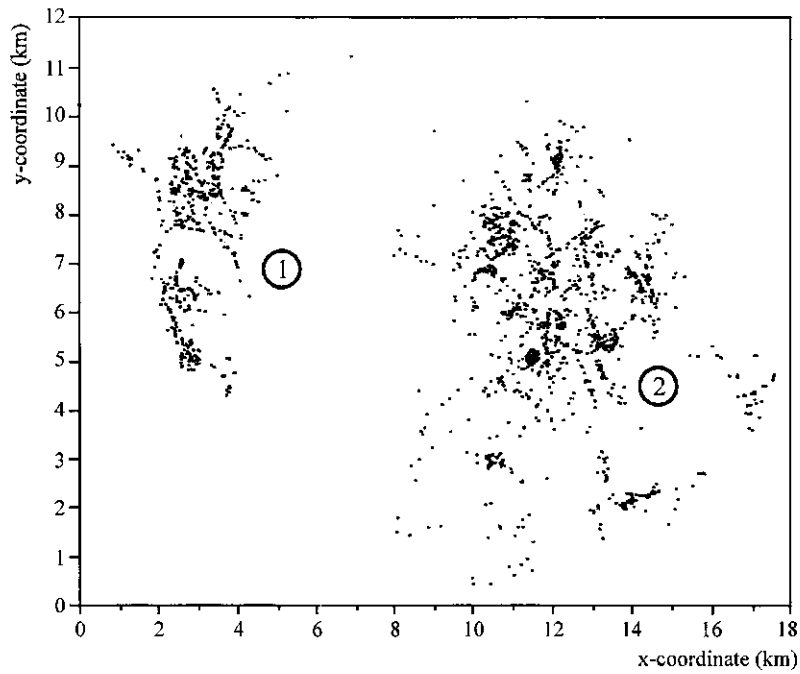


Figure 15.3. Sampling locations for Cd in topsoils of two sandy areas in The Netherlands - 590 samples were taken in area 1 and 1430 samples in area 2.

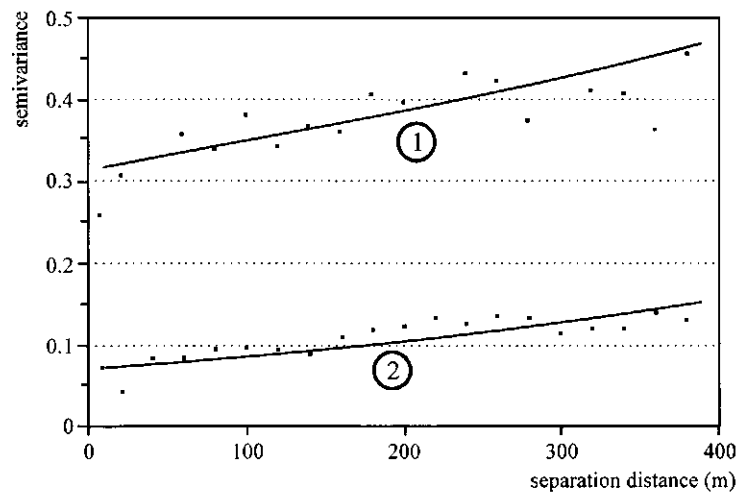


Figure 15.4. Two semivariograms for Cd contents of the topsoil in two sandy areas in The Netherlands.

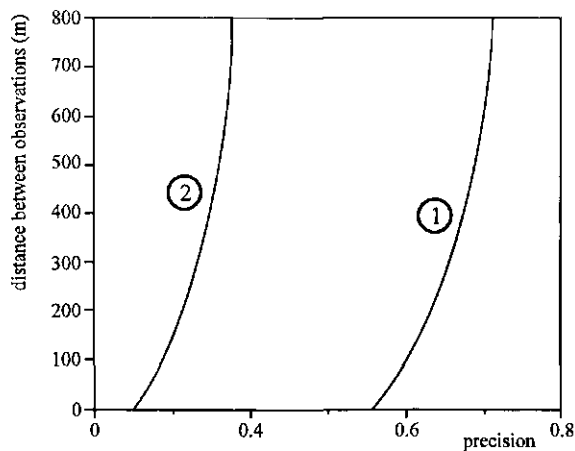


Figure 15.5. Distance between observations as a function of the precision of kriging predictions, defined in terms of standard deviation of the prediction error.

effects on vulnerability can be well expressed at the lowest possible cost. Also, protection measures can be fine-tuned to local differences within areas of land. A practical example of this is being developed in the USA, where 'Farming by soil' receives currently much emphasis in agricultural research. The procedure implies area specific fertilization and application of biocides as a function of different soil conditions within fields. Computer techniques are used to achieve this. By fine-tuning application of fertilizers and biocides on the basis of a variability analysis, economic advantages are achieved for the farmer as his costs are cut, while environmental objectives are served by avoiding local overdosage of chemicals and the associated pollution.

15.4 Expressions in terms of probabilities

The above examples considered effects of variability in space on soil vulnerability, by focusing on properties of mapping units of the soil map and their internal variability to be characterized by (geo)statistics. In practice, conditions are even more complicated because of variability in time. Soil behaviour is to a large extent determined by weather conditions. To illustrate this point we will discuss a case study on the effects of soil compaction on the agricultural quality of a sandy loam soil in The Netherlands. (Bouma & Hack ten Broeke 1992).

These soils are vulnerable to compaction by agricultural machinery and soil protection measures should preferably be based on a quantitative analysis of the physical processes in both compacted and non compacted soils.

This was done by applying the SWANY simulation model for solute movement and crop growth. Calculations were made for a period of thirty years for a sandy loam soil with a porous structure as found under permanent grassland and for a similar, but compacted soil with a plowpan. Hydraulic conductivities and moisture retention curves were needed for major horizons in both soils to run the model. Measurements were made in sixfold in each type to obtain an expression for spatial variability (see Figure 15.6, which shows the observed range).

Runs made for a period of thirty years were expressed in terms of probability of occur-

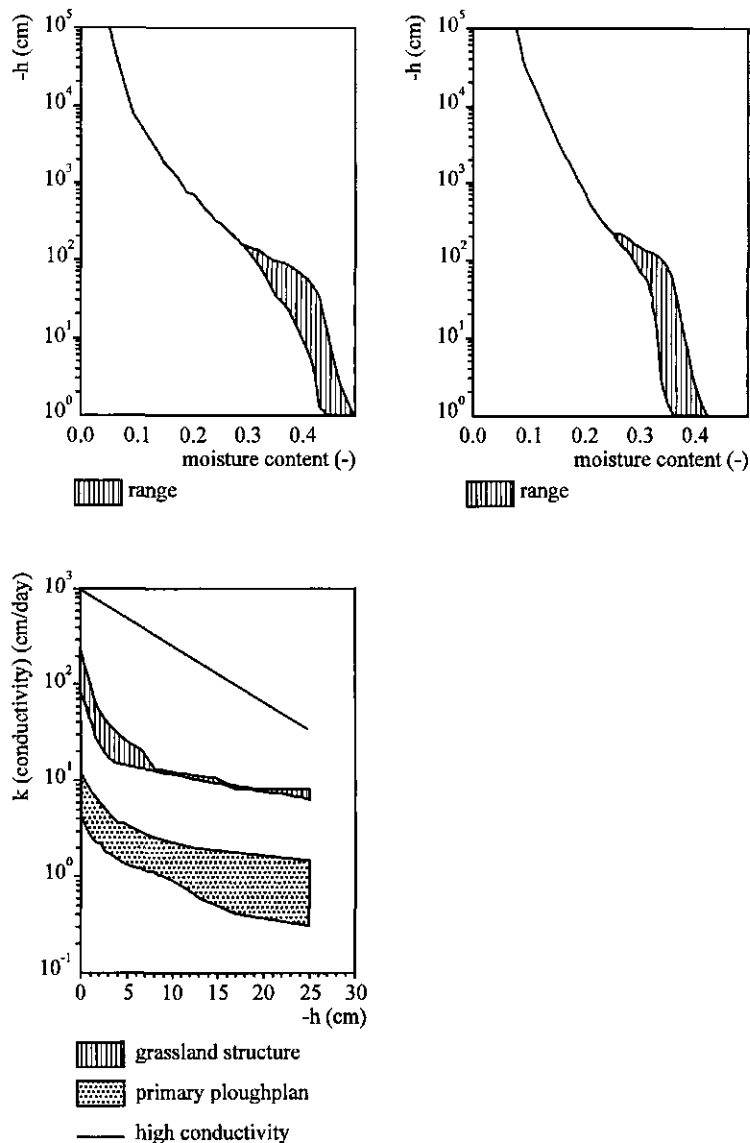


Figure 15.6. Basic hydraulic characteristics and their variability for a Dutch sandy loam soil with two types of soil structure: a loose structure under grassland and a compacted structure under arable land.

occurrence. Figure 15.7 shows, as an example, the probability that the air content in surface soil will be higher than 10%. Field measurements have indicated that this and higher contents of air are associated with adequate aeration by diffusion, allowing good root development and activity. The simulation model has calculated the water content in the soil for every day of the 30 year period. Total porosity is known from the moisture retention curve, so the air content can easily be estimated. For every day of the year we have therefore 30 values of air contents, some below and some above 10% by

volume. Thus, probabilities can be calculated which express both variability in space and in time. We see higher probabilities from May to August in the soil with the grassland structure, but lower values in the winter period from November to February. (Figure 15.6). Ranges of values, which express spatial variability, are higher in the grassland soil. For example, the probability that the air content on April 1 is higher than 10%, ranges from 15% to 48% in the grassland soil, and from 40% to 43% in the compacted soil. Depending on the objectives of a study, the user can choose whatever values he considers to be most relevant. Similar expressions can be obtained for *e.g.* crop yields, trafficability, nitrate or pesticide leaching and other land qualities that are of practical interest. A recent study on pesticide leaching, which included probabilistic expressions, was presented by Petach et al. (1991). Finke (1993) presented a study in which the nitrate content in percolation soil water was calculated with a simulation model as a function of different application schemes for animal manure.

The concept of expressing soil properties, as discussed, in terms of probabilities of occurrence rather than in terms of average values, represents a proper reflection of conditions in nature. In fact, it would be realistic to also express critical contents of chemical compounds in soil and water in such terms.

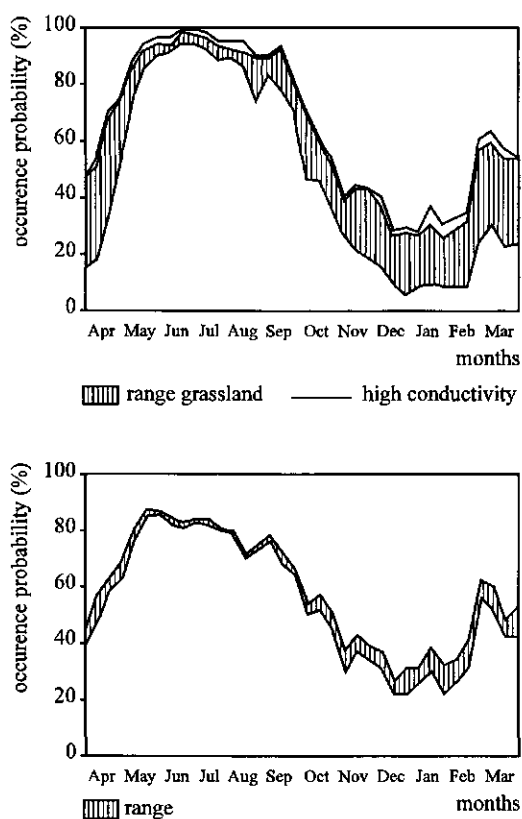


Figure 15.7. Probabilities for adequate aeration of the root zone in a sandy loam soil with two types of structure. Figures are based on simulations for a 30-year period, and reflect variability of the basic soil hydraulic parameters.

Finally, we followed here a combination of a deterministic-mechanistic approach of calculating water and air contents in the soil. Next, values obtained were expressed stochastically. This combination of techniques has proved to be attractive for practical application.

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16 Effects acid atmospheric deposition on soil and groundwater

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16.1 Introduction

'Acid atmospheric deposition' refers to wet and dry deposition of acid and potentially acid substances from the atmosphere on the earth's surface. These substances include strong mineral acids dissolved in rain water ('acid rain' sensu stricto), as well as such acids dissolved in aerosols and mist, and gases that can be turned into strong mineral acids after deposition. 'Acid rain' is only a fraction (often between 0.3 and 0.7) of total acid deposition, although the term is often used to indicate all of acid deposition.

Locally, burning of sulfur-rich coal and roasting of sulfidic ores has for centuries been recognized as a problem for the health of people as well as trees. The strong increase in the use of fossil fuel after World War II, and the dilution of the polluting gases by the erection of higher smoke stacks, transformed the problems from local to regional and continental scales. Acid atmospheric deposition became recognized as a problem in relation to acidification of lakes and streams in Scandinavia and Northeastern America in the early seventies (Likens & Bormann 1974). Decline in numbers of salmonid fish were soon found to be associated with low pH and high levels of dissolved aluminium (Schofield & Trofner 1980). Although some argued that acidification in relation to changes in land use was more important (Rosenqvist 1979), it is now generally recognized that high acidity in precipitation, mainly due to industrial emissions of SO₂, was the main cause of water acidification and fish decline. Dramatic improvements of surface water quality by decreasing ambient atmospheric acid loads have been demonstrated in small watersheds in southern Norway where precipitation was intercepted by transparent roofs, and replaced by pre-industrial precipitation (Wright et al. 1988). Ulrich et al. (1979) were among the first to call attention to acidification of forest soils from acid atmospheric deposition and its potentially harmful effects on forest ecosystems. The first comprehensive effort to inventory acid rain problems in tropical countries was provided by Rohde & Herrera (1988).

In addition to sulfuric acid from SO₂ (released during burning of sulfur-rich fossil fuel), nitric acid from NO_x (formed during internal combustion) and from NH₃ (from intensive cattle production) were recognized as increasingly important contributors to acid deposition in the 1980's.

Elevated atmospheric deposition of nitrogen affects ecosystems not only by acidification, but also by eutrophication. This is one of the reasons why the causal relations between acid deposition and the growth and vitality of plants are extremely complex. It is now generally recognized that acid deposition strongly affects (1) the chemistry of sensitive soils, surface - and groundwaters, and (2) aquatic life in acidified waters. But apart from local tree decline in heavily impacted forests, and from widely observed

eutrophication of forests, negative effects of acid deposition on the growth of higher plants have rarely been established unambiguously.

In this text, the following aspects will be treated:

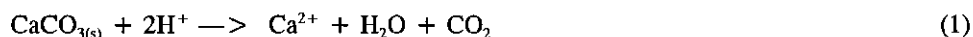
- the nature of soil acidification
- the nature of acid deposition
- the sources of soil acidification
- effects of acid deposition on soils and ground water
- predicting effects of continuing and decreasing acid deposition
- estimating critical loads of acid deposition for soils and ground waters.

Whereas the principles discussed here are generally valid, most examples given refer to the situation in The Netherlands.

16.2 The nature of soil acidification

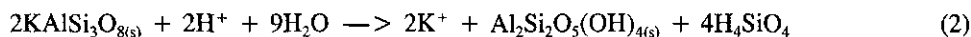
We will illustrate the process of soil acidification by discussing a hypothetical experiment involving adding free protons (H^+) to a soil. As will be shown later, such protons can come from natural processes ('natural soil acidification') or from acid deposition driven by air pollution ('anthropogenic soil acidification'). The range of H^+ addition normally varies from 0.05 to 20 $kmol_c^1$ of H^+ per ha of land surface per year. Most or practically all of the H^+ ions added to the soil normally undergo some reaction with different solid phases present in the soil. By the reaction, such H^+ buffering phases are either consumed or lose their capacity to consume H^+ . Two important characteristics of each phase that consumes H^+ are the kinetics of the reaction and the amount of that phase present in the soil. Reactions can be considered 'rapid' if the consumption of H^+ per unit time exceeds the rate of addition of H^+ . The buffer capacity can be considered very small if it is equivalent to only a few to several tens of years of H^+ added to the soil. It can be considered very large if it is equivalent to thousands of years of H^+ addition.

An example of a rapid reaction is the dissolution of calcium carbonate:



Due to this reaction, protons are removed from solution and replaced by Ca^{2+} , while solid calcium carbonate dissolves. If one or more of the reaction products are removed, *e.g.* by leaching of the Ca^{2+} , the process has become irreversible, and the buffer capacity of the soil has been lowered. The buffer capacity due to calcium carbonate varies from nil in non-calcareous soils, to very large in calcareous soils. By its rapid neutralization of H^+ , $CaCO_3$ maintains the pH of the soil above 6.5 as long as it is present. In non-calcareous soils, which usually have a pH below 6.5, dissolution or transformation of aluminum silicates can be important in neutralizing H^+ . The reaction of aluminum silicates with H^+ is a much slower process than the dissolution of $CaCO_3$. However, because aluminum silicates are a major constituent of most soils, the buffer capacity involved is often large. An example is K-feldspar, which can be transformed to kaolinite as follows:

¹ mol_c refers to moles unit charge, obtained by multiplying molar concentration by ionic charge.



Cation exchange can also buffer H^+ if the pH falls below 6.5. It involves replacement of cations adsorbed to clay and to organic matter by H^+ . Buffering of H^+ by aluminum hydroxide is important in strongly acid soils:



The reverse reaction, whereby Al hydroxide is formed from dissolved Al^{3+} and water under the formation of H^+ , can take *e.g.* when percolating dissolved Al^{3+} moves into a subsoil with a relatively high pH.

To predict the course of soil acidification, it is important to know the buffer *capacity* of the phases undergoing rapid reactions with H^+ , while the buffering *rate* needs to be known for phases that buffer slowly (Table 16.1).

Table 16.1. Capacity, rate and pH range of important H^+ buffering processes in typical Dutch forest soils. From de Vries & Kros 1989.

Buffer mechanism	pH range	Buffer capacity kmol _c /ha.cm	Buffer rate kmol _c /ha.a
Carbonate weathering	> 6.5	26 per % CaCO_3^*	high
Silicate weathering	< 6.5	45-70	0.1-1
Cation exchange	4.0-6.5	1.95 per % organic matter*; 0.65 per % clay*	high
Al-hydroxide weathering	< 4.0	5-45	high

* Expressed as mass fraction.

Figure 16.1 shows how the pH might change upon addition of H^+ to a soil containing all buffering components listed in Table 16.1.

As long as the soil is still calcareous, its pH will hardly change, and will be maintained between 7 and 8. After all CaCO_3 has been consumed by H^+ , buffering by silicates will take over. The pH will now decrease because the rate of addition of H^+ exceeds the rate of removal of H^+ . Cation exchange can take place simultaneously with the weathering of silicates. At $\text{pH} > 7$ the cation exchange complex is fully saturated with K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . By the time the pH has dropped to about 4, these cations have been replaced almost wholly by H^+ and Al^{3+} . The fraction of the complex occupied by mono- and divalent metal ions is called 'base saturation'. The term 'base' refers to the fact that K^+ , Na^+ , Ca^{2+} , and Mg^{2+} are derived from easily soluble hydroxides, or strong bases. Finally, continued addition of strong acid will lead to dissolution of aluminum hydroxide according to reaction (3). The exact relationship

between the pH and the amount of H^+ added depends not only on the composition of the soil, but also on the rate of H^+ addition. When a certain amount of strong mineral acid is supplied much more rapidly than it can be neutralized by *e.g.* silicate minerals (cf Table 16.1), the final pH will be lower than when that same quantity of acid is supplied at a slower rate (Figure 16.1).

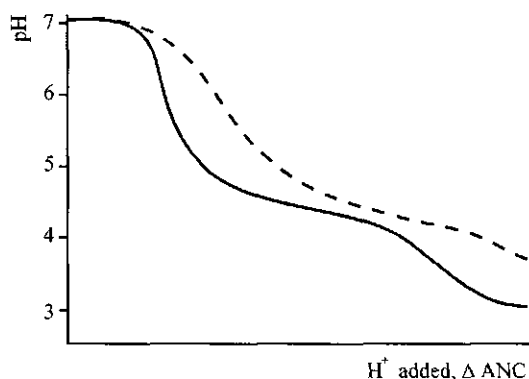


Figure 16.1. Hypothetical titration curve of a calcareous clay soil upon slow (broken line) or quick (solid line) acidification.

The hypothetical experiment illustrated in Figure 16.1 resembles soil acidification of an initially calcareous soil. Hundreds or thousands of years of natural soil acidification might be needed to reach a soil pH of about 4. In case of elevated atmospheric inputs of acids resulting from air pollution, less time would be needed to reach the same total acid addition, while the final pH would be lower.

The titration curve in Figure 16.1 could be obtained by adding strong mineral acid to a soil in a closed container. However, soil acidification in the field usually involves removal of reaction products by vertical percolation. A prerequisite for percolation is that, counted over a year, rain plus snowfall exceeds evapotranspiration. In The Netherlands and Belgium, precipitation excess is in the order of 100 to 300 mm, largely depending on the vegetation cover. Removal of the cations released during soil acidification (see equations 1-3) by leaching, moreover, requires the presence of mobile anions. These are in fact derived from the acids involved in soil acidification: SO_4^{2-} (derived from H_2SO_4), NO_3^- (derived from HNO_3), HCO_3^- (derived from H_2CO_3), and organic anions (derived from organic acids).

While the reader will by now have an intuitive grasp of the concept of soil acidification, we still lack a definition of the process. One commonly used definition emphasizes the changes taking place in the soil solution:

Soil acidification is a decrease in the pH of the soil solution (or of an aqueous extract of the soil).

A second definition emphasizes changes in the solid phases of the soil:

Soil acidification is a decrease in the acid neutralizing capacity (ANC) of the soil².

The two definitions differ in that the first one refers to changes along the vertical axis of Figure 16.1, while the second definition refers to the horizontal axis. So, according to the first definition, no soil acidification occurs when a calcareous soil is losing CaCO_3 , while the same process would be termed soil acidification according to the second definition. The decrease in pH emphasized in the first definition measures the change in actual acid intensity, a factor of great ecological significance. The decrease in buffering capacity is of no direct ecological significance (plants do not 'see' how much acid neutralizing capacity is still present), but its quantification is useful when accounting the fate of acid added to a soil.

16.3 The sources of soil acidification

Input of strong acids from the atmosphere due to anthropogenic acid deposition is an obvious source of soil acidification. So is natural strong acid deposition *e.g.* of S compounds derived from volcanic activity. As indicated above, however, atmospheric acid deposition is relatively unimportant under natural conditions. The major sources of H^+ in natural soil acidification are:

- weak acids such as CO_2 or organic acids
- higher uptake of cations than of (strong-acid) anions by plants
- strong mineral acids (especially HNO_3) produced as end products of oxidative decomposition of organic N.

The weak acids can acidify the soil (according to definition #2) only if the dissociated anions are leached from the soil together with the cations mobilized by the H^+ produced during dissociation. This requires annual net percolation of water through the soil. The strong mineral acids can acidify the soil only if the N and S involved are not taken up again by plants or microorganisms, *i.e.* if the nutrient cycle involving those nutrients is leaky. Finally, excess uptake of cations by plants can lead to permanent soil acidification only if the plant material containing the cations is removed, *e.g.* by harvesting of forest products.

The role of weak natural acids, of plant uptake, and of nitrogen compounds in somewhat greater detail will be discussed.

16.3.1 Weak acids

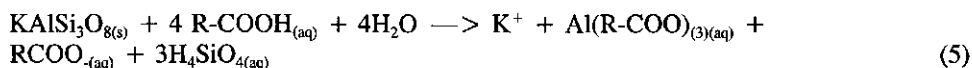
In calcareous soils, CO_2 derived from root respiration and decomposition of dead plant material, is the dominant acidifying agent. It dissociates into HCO_3^- and H^+ , dissolving CaCO_3 as follows:

² the ANC can be defined as the sum of (the quantitative important) base components minus that of (prevalent) strong acid components present in soil minerals and at the exchange complex:
 $\text{ANC} = 6\text{Al}_2\text{O} + 2\text{CaO} + 2\text{MgO} + 2\text{K}_2\text{O} + 2\text{Na}_2\text{O} - 2\text{SO}_3 - 2\text{P}_2\text{O}_5$ (4), expressed in moles of these components per volume (or land surface area) of soil. All soil minerals of quantitative importance, plus the exchangeable cations, can be thought of as being made up of these components plus the components SiO_2 , Fe_2O_3 , CO_2 and H_2O . The latter four can be considered as inert, *i.e.* they do not consume or produce protons when titrating a soil with acid down to a pH of 3, and they are therefore not included in the ANC.



As a result calcium and bicarbonate ions can be leached from the soil. The decrease in ANC as a result of this process in Dutch calcareous soils is in the order of 10 to 20 kmol/ha.a. Dissociation of CO₂ is important only at pH above 5. It can, therefore, not cause soil pH values much below 5, and can play no role in strongly acid soils.

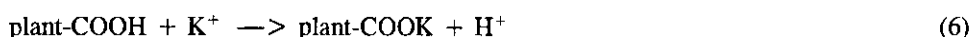
Many simple aliphatic and phenolic organic acids produced in the course of decomposition of plant remains and soil organic matter do not only deprotonate, but may also form complexes with metal ions such as Al. A hypothetical example is the dissolution of K-feldspar:



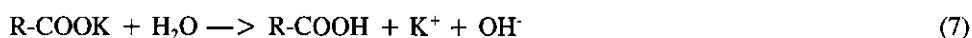
Organic acids may be (partly) decomposed by microbes. This will cause precipitation of Al (as hydroxide or solid Al-organic complex), leading to the formation of so-called podzolic soils (soils characterized by dark illuvial soil horizons of organic compounds and Al). However, most of the mono- and divalent cations will continue to be leached. The decrease in ANC resulting from organic acids is usually in the order of 0.1 to 0.5 kmol/ha.a. (de Vries & Breeuwsma 1986). Many organic acids are stronger than carbonic acids, and may eventually cause soil pH values in the order of 3.5 to 4.

16.3.2 Plant uptake

Plants usually take up more cations than anions, and balance the positive excess charge by exuding protons at their root surface. This is illustrated by uptake of K⁺:



Upon death and decay of the plant, the process is reversed:



so that no net soil acidification takes place. The accumulation over many centuries of cation nutrients in a steady state pool of living biomass, *e.g.* in an undisturbed primary forest, involves a relatively small soil acidification (in the order of 50 to 100 kmol/ha). By removing these accumulated cations, *e.g.* by harvesting wood and crops, the soil acidification becomes permanent. Rates of soil acidification resulting from litter raking in forests (a widespread practice to 'collect' fertility before the advent of fertilizers) was in the order of 0.5 kmol/ha.yr. Removal of trees and crop residues increases soil acidification by values in the order of resp. 1 and 3 kmol/ha.yr.

16.3.3 Acidification from N compounds

In terrestrial ecosystems, the bulk of N is normally bound in soil organic matter. As long as this N remains tied up in the organic matter, or stays in the nutrient cycle, no net acidification will take place. However, mineralization of organic N to NH₄⁺, followed by oxidation of NH₄⁺ to nitric acid (normally under the influence of autotrophic microbes: nitrification), and by leaching of nitrate, causes strong soil acidification.

fication:



This source of acidification may be important when mineralization of soil organic matter is stimulated, while at the same time the uptake of N by the vegetation is decreased, *e.g.* during deforestation or drainage of wetlands.

16.3.4 Acid deposition

As discussed before, the main sources of anthropogenic soil acidification are (1) sulfuric acid from SO_2 produced by burning of sulfur-rich fossil fuel, and (2) nitric acid produced from NO_x formed in internal combustion engines and from NH_3 emitted from animal excreta in intensive animal production. The sulfur and nitrogen gases can be transported through the atmosphere over distances in the order of 10^0 to 10^3 km before they are deposited again on the earth's surface. Deposited N and S are either still in gaseous form, or as dissolved or aerosolic acids or salts, after transformation of SO_2 and NO_x to sulfuric and nitric acids. NH_3 readily reacts with these acids to form dissolved or aerosolic ammonium sulfate. With rain and snow the dissolved reaction products can be added directly to the soil. However, dry deposition of gases and aerosols, in particular on vegetation surfaces is quantitatively more important than wet deposition, in particular relatively close to the source (*i.e.* within 10^0 to 10^2 km).

If all of the sulfur and nitrogen originating from SO_2 , NO_x , and NH_3 , deposited on a certain area of land, would be transformed to sulfuric and nitric acid and would be available for leaching of cations, acidification is maximal, and the so-called potential acid deposition (PAD) is realized:

$$\text{PAD} = D_{\text{SO}_2} + D_{\text{NO}_x} + D_{\text{NH}_3} \quad (9)$$

In equation (9) D_x stands for total (wet + dry) deposition of compound X in $\text{mol} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$. Usually this potential acid deposition is not fully realized because part of the deposition, especially the N compounds, are assimilated into the living biomass, and stored in soil organic matter. In case of acidification by atmospheric ammonium sulfate we can distinguish three cases:

- The ammonium sulfate is leached without being taken up by plants, or being nitrified. ANC does not change, so there is no soil acidification.
- All ammonium is taken up by the plant. H_2SO_4 is left behind, and the ANC decreases by 2 mol per mol of $(\text{NH}_4)_2\text{SO}_4$ deposited. This decrease in ANC can be attributed to the SO_2 from which the sulfate originated.
- All ammonium is nitrified and the NO_3^- formed is leached (equation 9). The ANC decreases by 4 moles per mole of ammonium sulfate. Half of the acidification can be attributed to SO_2 , half to NH_3 .

Table 16.2 shows calculated values for the deposition of the various components for 'average' land cover and forest for various years and regions in The Netherlands. Table 16.2 illustrates (1) the effect of forest in increasing deposition of SO_2 and NH_3 , (2) the link between proximity of refineries and high SO_2 deposition (in the province of South Holland), and between intensive bio industry and high NH_3 deposition (in North Lim-

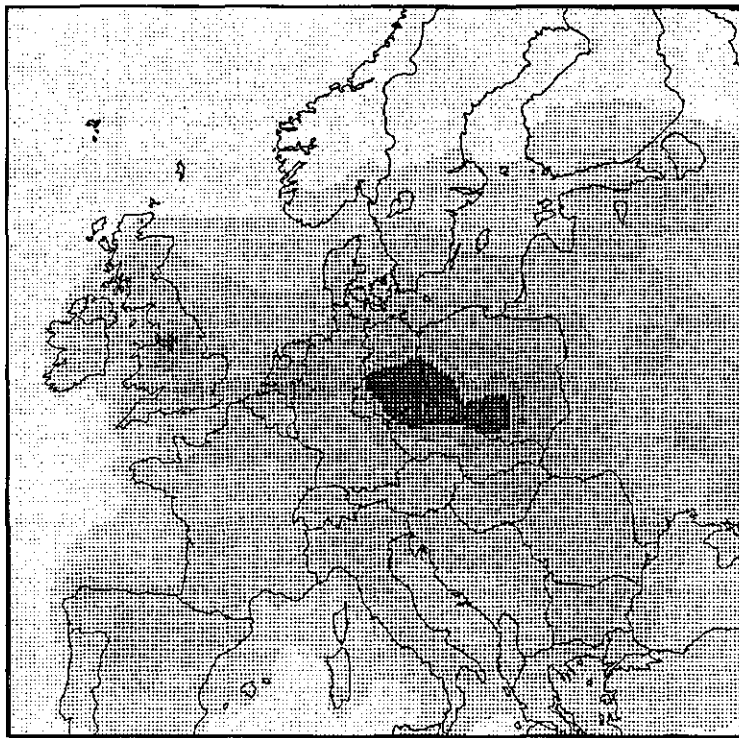
burg), and (3) the effect of a predominance of relatively clean maritime air on total deposition (in North Holland). The lowering in the mean PAD for the whole country from 6700 mol/ha.a in 1980 to 4700 mol₂/ha.a in 1989 was mainly due to decreased SO₂ emissions.

Table 16.2. Deposition fluxes of acidifying substances in 1980 and 1989 in The Netherlands (means for the whole country, for forest within the country and for three provinces). From Erisman & Heij 1991.

Area/Province	Year	SO ₂	NO _y	NH ₃	Potential Acid Deposition*		
					dry	wet	total
					mol ₂ ha ⁻¹ a ⁻¹		
Netherlands (mean)	1980	3140	1690	2500	5000	1700	6700
Netherlands (mean)	1989	1340	1550	2190	3300	1700	4700
Netherlands (forest)	1989	1500	1300	2530	4000	1400	5300
North Holland	1989	1060	1120	1170	2100	1200	3300
South Holland	1989	2000	1310	1410	3100	1300	4400
North Limburg	1989	1580	1190	4110	4900	1900	6800

* PAD has been corrected for deposition of bases and is therefore lower than the sum of SO₂, NO_y and NH₃.

PAD values in the central industrialized part of Europe are of the same magnitude as those in The Netherlands, but the contribution of SO₂ is generally higher and that of NH₃ is normally lower than in The Netherlands (Figure 16.2). In southern Scandinavia and northeastern USA, where the effects of acid deposition (on lakes and fish) were noticed first, PAD is generally less, in the order of 1000 to 2000 mol/ha.a, and is mainly due to SO₂. Natural background levels of PAD are probably about 300 mol/ha.a. (Galloway et al. 1984).



riivm



Figure 16.2. Potential deposition in Europe in 1988 ($\text{mol}_e \text{ha}^{-1} \text{a}^{-1}$). From Erisman & Heij 1991.

16.4 Effects of acid deposition on soils and groundwater

16.4.1 Forest and heath land versus agricultural land

Natural and anthropogenic atmospheric acidification take place regardless of the type of land use. However, apart from rarely serious direct damage by NH_3 and SO_2 on plant leaves, atmospheric acidification on arable land is of little concern. First, most agricultural land is limed regularly to undo the effects of natural acidification and of crop removal (see section 16.3.2). The extra costs of liming to undo acidification due to atmospheric deposition (50 kg of CaCO_3 per kmol of acid deposition) for the individual farmer are usually small. Second, forest soils are usually poorer (*i.e.* lower in bases and in weatherable minerals) than most agricultural soils, and are therefore more sensitive to acidification by strong mineral acids. Thirdly, dry deposition is generally higher on trees than on lower vegetations, increasing the acid deposition on forests relative to that on agricultural land. Deposition on forests is increased most strongly along forest edges. This is an important factor in a country such as The Netherlands with its patchwork of woodlands.

For the reasons listed above most of the following discussion is related to soil acidification on forests and heath lands.

16.4.2 Measurements of soil acidification

Comparison of ANC values of weathered topsoil compared to unweathered subsoil in soil profiles in homogeneous parent material (*e.g.* eolian sediments or hard rock) can provide an estimate of the accumulated soil acidification since the beginning of soil formation. If the age of the soil is known, the mean annual rate of soil acidification (Δ ANC) can be calculated. If the soils are relatively old, *e.g.* in the order of 10^4 years, the Δ ANC can be attributed wholly to natural soil acidification. For non-calcareous Dutch forest soils, the mean annual Δ ANC ranged from 0.02 to 0.6 kmol_c/ha.a (de Vries & Breeuwsma 1986).

Recent soil acidification can be quantified in two ways. The first method involves a comparison of soil samples taken from the same site at different times. There are two problems with this approach. First, the amounts of base cations removed annually during soil acidification are small relative to the amounts present in the solid plus adsorbed form. Second, spatial variability at short distances may be appreciable. To be able to detect changes from analyses of soils samples, therefore, the sampling interval needs to be long, *i.e.* usually in the order of decades. Comparison of soil samples taken decades ago and taken again in the 1970's and 1980's from the same sites in the FRG (Ulrich et al. 1980; Butzke 1981), Austria (Glatzel & Kazda 1985) and in South Sweden (Tamm & Hallbaecken 1988; Falkengren-Grerup et al. 1987) show indeed that soil pH and base saturation have decreased dramatically throughout the root zone of most forest soils. The most comprehensive study is that by Tamm & Hallbaecken (1988). They accounted for the effect of stand age on soil pH, and showed a strong pH increase in the South, but little change in pH in soils of Northern Sweden, where acid atmospheric deposition is only a fraction of that in the South. Such studies cannot prove that acid deposition is the cause of the observed soil acidification. However, because the acidification is in the same order as that expected from the general level of acid atmospheric deposition on the basis of simulation models (see section 16.6), there can be little doubt about the cause.

The second method, based on an input-output budget, provides a direct link with atmospheric deposition. By measuring or estimating annual inputs of all major inorganic compounds in atmospheric deposition, and outputs by drainage and removal of harvested wood, the rate of soil acidification can be quantified on an annual basis. A great disadvantage is the large number of samples and measurements required to obtain such a budget. Table 16.3 gives an input-output budget for a Scots pine stand in The Netherlands. The ionic fluxes were obtained by (1) estimating monthly water input and drainage fluxes, (2) multiplying those fluxes with measured monthly ionic concentrations in the soil solution, and (3) summing up monthly values to annual values.

The results of Table 16.3 are characteristic for actual soil acidification in Dutch forest soils. Input and output of SO_4^{2-} are fairly similar, indicating near-equilibrium between dissolved sulfate and the sorption sites for sulfate in the soil after many years of high deposition of sulfate. The high throughfall input of NH_4^+ reflects the high deposition of ammonia, mainly in dry form, on the forest canopy. Only a small part of the ammonium is leached, the remainder being stored in the system (soil plus vegetation) and/or nitrified to HNO_3 . Nitrate output far exceeds nitrate input, which must be attributed indeed to nitrification of ammonium. The strong soil acidification associated with this

process (equation (9) is reflected by the dissolution and leaching of Al^{3+} .

The soil acidification resulting from atmospheric deposition (ΔANC_{DEP}) can be calculated from:

$$\Delta ANC_{DEP} = \Delta H^+ + \Delta NH_4^+ - \Delta NO_3^- - \Delta SO_4^{2-} - \Delta Cl^- \quad (10)$$

whereby each term on the righthand side refers to the difference between input and output flux, expressed in $mol_c/ha.a$.

The average soil acidification from atmospheric deposition equals $4.9 \text{ kmol}_c/ha.a$. (cf. Table 16.3), 30 % of which can be attributed to nitrification of incoming ammonium. The contribution of 'natural' soil acidification is much less: tree growth at Tongbersven decreases ANC annually by $0.5 \text{ kmol}_c/ha.a$ and dissociation of organic acids by $0.2 \text{ kmol}_c/ha.a$. The complete hydrogen ion budget (van Breemen et al. 1984) for the site is given in Table 16.4.

Table 16.3. Hydrochemical input-output budget for a Scots pine stand, Tongbersven, The Netherlands. Input refers to water collected below the tree canopy (throughfall water), output is drainage water below the root zone, at 57 cm depth. The results are mean annual values for the period 1983-1987. From Mulder et al. 1989.

	water	H^+	A^-	K^+	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}
	cm	$kmol_c \text{ ha}^{-1} \text{ a}^{-1}$										
input	80	-2	-	0.1	1.1	0.3	0.3	0.0	3.7	1.2	0.6	3.2
output	24	0.2	0.2	0.1	0.8	0.2	0.3	5.3	0.7	1.2	2.1	4.4
balance	56	-4	-2	0.0	0.3	0.1	0.0	-5.3	3.0	0.0	-1.5	-8

A^- refers to organic anions.

Table 16.4. H^+ budget of the Tongbersven Scots pine stand, The Netherlands. Mean annual data ($kmol_c/ha.a$) for 1983-1987.

H^+ sources	H^+ sinks		
atmospheric deposition	4.9	weathering of Al	5.3
net cation uptake by trees	0.5	weathering of bases	0.1
organic acid dissociation	0.2	leaching of H^+	5.4
totals	5.6		5.8

The results of Table 16.4 are typical of forest soils in Central and Western Europe. Together with the low rates of natural soil acidification, they attest to the overwhelming dominance of present-day acid atmospheric deposition over natural acidification in (non-calcareous) forest soils.

16.4.3 Ecological and health effects of soil acidification

Although experiments under controlled conditions show that high soil acidity affects many plants through toxic effects of high concentrations of dissolved Al^{3+} on roots (Cronan et al. 1989), it is extremely difficult to unambiguously demonstrate such effects in acidified soils in the field. The same is true for the effects of disturbed nutrient supply (as evinced *e.g.* by Al/Ca , NH_4/Mg and NH_4/K ratios in the soil solution or in aqueous soil extracts) on nutrient uptake and vitality of plant species (see *e.g.* Roelofs et al. 1985). Nevertheless, frequent negative correlations between such ratios and the health of trees or the condition of the fine-root system provide sufficient circumstantial evidence to point to soil acidification as an important factor involved in the forest decline symptoms observed in many parts of Europe since the early 1980's. More direct links have been established between anthropogenic atmospheric deposition and (1) the decline of many mycorrhizal fungi (incl. *Cantharellus*), and (2) the increase in nitrophytic plants in forests and heathlands, including the accelerated transformation of heathlands to grasslands (Heij et al. 1991).

Another environmental effect is that on the ground water composition. The most recent, upper strata of aquifers under forests in The Netherlands have strongly elevated concentrations of NO_3^- , sometimes associated with low pH and high Al. Nitrate concentrations in excess of drinking water standards (> 25 or > 50 mg NO_3^- per liter) are now commonplace under forests and can be linked directly to the high rates of drainage of nitrate from the overlying soils (Heij & Schneider 1991).

16.5 Predicting effects of acid atmospheric deposition

16.5.1 Diagnosis and prognosis

Sound environmental policy is based on a good characterization of present environmental conditions (diagnosis), and on an adequate evaluation of changes in those conditions in the future (prognosis). The future conditions depend, of course, on developments in economy and technology, and associated energy trends, as well as in environmental measures. Both in diagnosis and prognosis of effects of atmospheric deposition on soils and ecosystems simulation models are frequently used. The effects of deposition and other environmental boundary conditions (*e.g.* initial soil properties, climate, type of vegetation) on soil properties can be evaluated by dynamic or by static models. Static, or equilibrium, models predict the steady state situation that may be reached after an indeterminate period of time of a given atmospheric deposition input. Dynamic models calculate the change in soil properties as a function of time, with or without changes in atmospheric deposition.

Static models only consider simplified soil and vegetation processes, without adsorption and ion exchange.

Static models are particularly useful for the derivation of critical loads of N and S. The dynamic models are more complex and are often used for scenario-analysis on a countrywide- or continental scale. Figure 16.3 illustrates the processes and their relationships involved in the more complex dynamic multi-(soil)layer model RESAM (de Vries & Kros 1989). The use of RESAM for prognosis is illustrated in Figure 16.4. The simulations refer to changes in pH and the Al/Ca molar ratio in the soil solution of an acid brown forest soil under Douglas fir. Continued acid deposition (scenarios 2 and 3) causes a further decrease in pH, as expected. Decreased deposition (scenario 4) leads

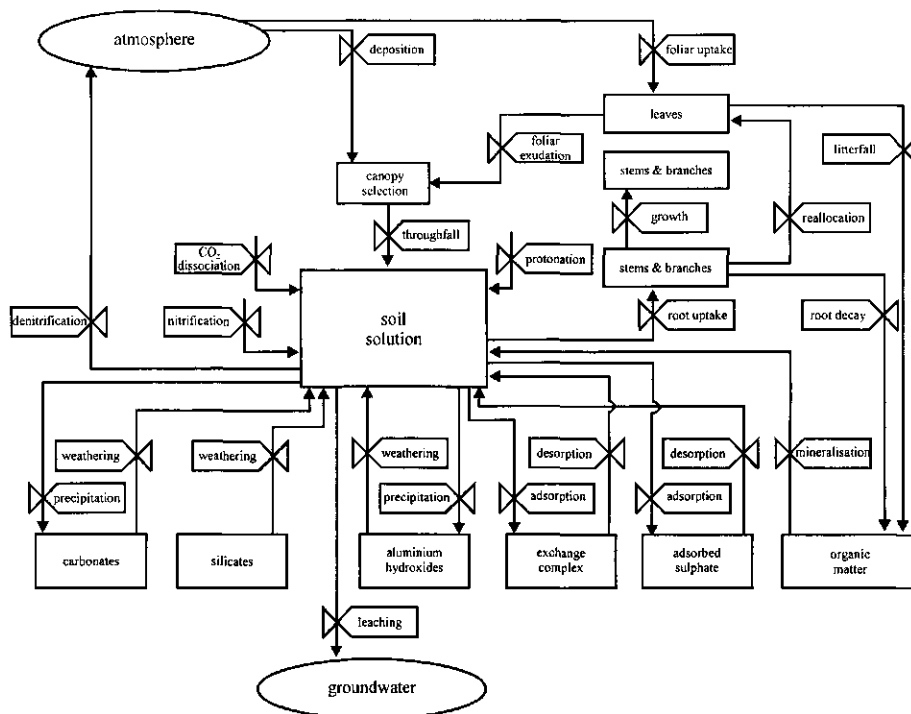


Figure 16.3. Relation diagram of the RESAM model. From de Vries & Kros 1991.

to a (temporary) increase in pH, and decreasing dissolved Al, leading to decreased Al/Ca ratios, also according to intuitive expectation. Quite surprising, however, is that Al/Ca ratios decrease too with strong soil acidification following deposition scenarios 2 and 3. Normally, the elevated solubility of Al³⁺ with decreasing pH will lead to higher, not lower Al/Ca ratios. The lower Al/Ca ratios are caused by decreasing contents of solid Al phases (mainly organically bound Al), available for buffering of strong acids (Mulder et al. 1989). Results from a nation-wide application of RESAM for The Netherlands (de Vries et al. 1991; Table 16.5) show how a number of chemical soil solution indicators are expected to change with time if total deposition would decrease from 4.4 kmol_c/ha.yr in 1990 to 0.7 kmol_c/ha.yr in 2050.

Dynamic models are often used also for analysing hydrochemical monitoring data obtained from intensively studied field sites. Figure 16.5 shows results from a similar dynamic model (WATERSTOF) to evaluate long-term monitoring data on the composition of the soil solution in strongly acidified soils under spruce in Solling, Germany (Wesselink et al in prep.). Model and monitoring data illustrate (1) the pronounced seasonality of sulfate concentrations in the surface soil, and (2) the increase of sulfate concentrations from low to more or less constant high values after saturation of the sulfate sorption capacity of the soil between 1974 and 1979.

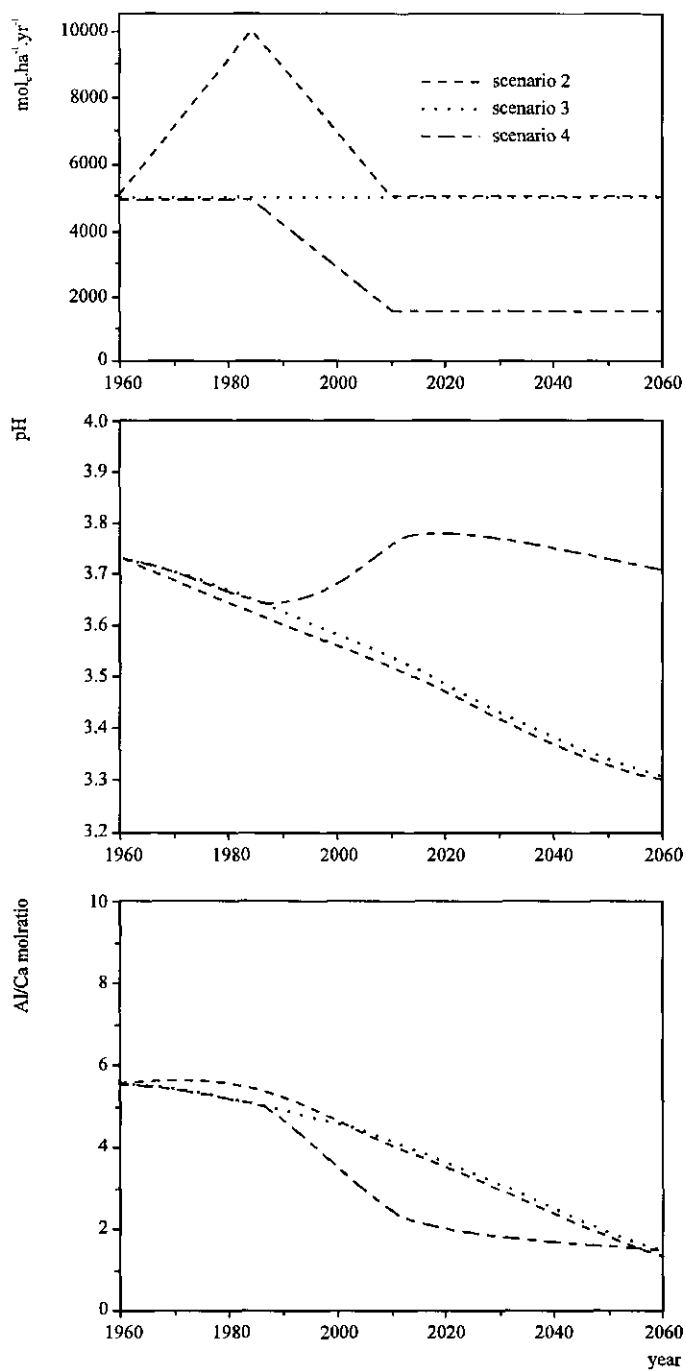


Figure 16.4. Changes in deposition with time for three scenarios (a) and the effect on pH (b) and Al/Ca ratio (c) in the topsoil of a leptic podzol. From de Vries & Kros 1989.

Table 16.5. Predicted median values for chemical indicators in soil solution in the surface soil (surf.) and subsoil (subs.) under Douglas (D), Scots Pine (P) and Oak (O), following a drastic decrease in atmospheric deposition. Model results using RESAM. From de Vries et al. 1991.

Chemical indicator	Unit	Soil depth	1990			2010			2050		
			D	P	O	D	P	O	D	P	O
pH		surf.	3.6	3.6	3.8	3.9	3.9	4.2	4.4	4.4	4.5
		subs.	3.7	3.8	3.8	3.9	4.0	4.0	4.1	4.2	4.4
Al	mol _e /m ³	surf.	0.8	0.6	0.3	0.2	0.1	0.1	0.0	0.0	0.0
		subs.	1.7	1.3	0.8	0.6	0.4	0.3	0.1	0.1	0.1
Al/Ca	mol/mol	surf.	3.7	3.1	1.5	1.2	1.0	0.4	0.2	0.2	0.1
NH ₄ /K	mol/mol	surf.	2.6	2.8	2.4	2.9	3.1	2.6	1.9	2.1	1.7
NO ₃	mol/m ³	subs.	1.1	0.7	0.5	0.4	0.2	0.2	0.1	0.1	0.0

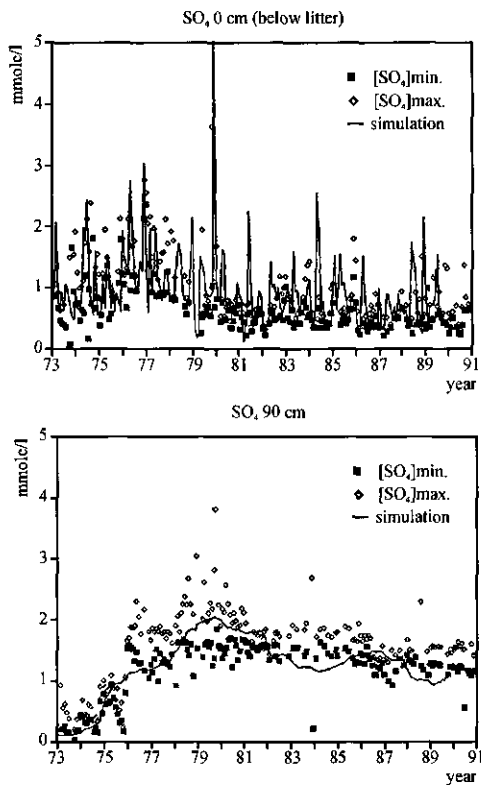


Figure 16.5. Measured (symbols) and simulated (lines) concentrations of dissolved sulfate just below the forest floor and at 90 cm depth in an acid brown forest soil under Norway Spruce in Solling, Germany, between 1973 and 1988. From Wesselink et al. in preparation.

16.5.2 Estimating critical loads

A critical load has been defined as 'A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson & Grenfelt 1988). For determining critical loads of atmospheric deposition the exposure is usually set equal to the annual atmospheric input of potential acidity (PAD) or of total nitrogen. The sensitive element may be a stand of a particular tree species, some other plant or animal species, or it may be the groundwater composition with its suitability for drinking water in mind.

The first step in setting a critical load is to specify threshold values for the most critical chemical properties of *e.g.* the soil solution, that should not be exceeded so as to prevent significant harmful effects. Table 16.6 shows the threshold values for such properties for forest soils and for ground water, as used in The Netherlands (de Vries 1991). These threshold values are usually based on results of toxicological studies under controlled laboratory or greenhouse conditions, or of epidemiological research.

Table 16.6. Threshold values proposed for chemical indicators that define critical loads for forest soils and for groundwater in The Netherlands.

Chemical indicator	Unit	Forests soil	Groundwater
Al	mol _c m ⁻³	0.2	0.02
Al/Ca	mol/mol	1	irrelevant
pH		4.0	6.0
Alkalinity	mol m ⁻³	-0.3	0.14
NO ₃	mol m ⁻³	0.10	0.8
NH ₄ /K	mol/mol	5	irrelevant

$$\text{Alkalinity} = [\text{HCO}_3] + \text{organic anions} - [\text{H}^+] - [\text{Al}^{3+}]$$

Long-term (static) mass balance models are used to derive critical deposition levels, because it is a safe steady state situation that should be aimed at. Every critical threshold value may lead to another critical load. Table 16.7 shows the estimated critical loads for nitrogen and total potential acidity on coniferous and deciduous trees on non-calcareous sandy soils under Dutch conditions (de Vries & Kros 1991).

One of the most simple static models involved here is the critical load of nitrogen deposition to prevent excessive nitrate in ground water. It is based on the equation

$$\text{CL} (N_{\text{dl}}) = N_{\text{gu}} + N_{\text{de}} + N_{\text{im}} (\text{crit}) + \text{NO}_{3,\text{le}}(\text{crit}) \quad (11)$$

in which CL stands for critical load, 'N_{dl}' for total (wet plus dry) atmospheric deposition of N, 'gu' stands for growth uptake by trees, 'de' for denitrification, 'im' for immobilisation of N in soil organic matter, and 'le' for leaching to the ground water. The suffix 'crit' refers to a possible threshold value in the N budget. NO_{3,le}(crit) depends on the selected critical element or function of the ecosystem. If protection of groundwater for use as drinking water is aimed at, its value can be calculated by multi-

Table 16.7. Mean critical loads (mol_c/ha.a) for nitrogen and total acid on non-calcareous forest soils in The Netherlands.

Critical element	Type of forest	
	Deciduous	Coniferous
Critical load for total acid		
root damage (Al/Ca)	1100-1400	1400-1700
depletion of soil Al	1200	1500
excessive Al in ground water	500	300

Critical element	Type of forest	
	Deciduous	Coniferous
Critical load for nitrogen		
frost damage/diseases	1500-3000	
disturbed nutrition	800-1250	
excessive nitrate in ground water	900-1500	1700-2900

plying the excess precipitation over evapotranspiration by the threshold value, *e.g.* 25 mg/l of nitrate in drinking water. $N_{in}(crit)$ is the critical rate for N immobilisation to prevent C/N ratios in soil organic matter from dropping to values that may cause N saturation.

Provided that sufficient spatial information is available, critical loads can be presented by means of maps depicting the percentage of a certain area (usually a grid cell) where a certain critical load is exceeded. This provides additional information useful for making policy decisions. An example is shown in Figure 16.6 (de Vries et al. 1992).

16.5.3 Uncertainty in model calculations

Even though the models discussed here have been partly validated using monitoring data (see *e.g.* Figure 16.5), the uncertainties can be large due to uncertainties in model input data, model structure, and critical chemical values.

The model itself introduces further uncertainties due to (1) simplifications inherent in modelling, (2) incompleteness of the model (*e.g.* N fixation, denitrification and complex hydrological processes, such as bypass flow, are not normally included), (3) uncertainties about values for model parameters, and (4) spatial and temporal variability under field conditions. Uncertainties about the critical chemical values are partly due to a large variation in critical values for different species.

Figure 16.7 gives the outcome of a Monte Carlo uncertainty analysis of the change in molar NH_4/K ration in the soil solution of an acid forest soil in response to a decreasing atmospheric N input. In the analysis, 75 of the 200 parameter used in RESAM were varied, using 250 Monte Carlo runs. Uncertainties were similar for the Al/Ca ratio, but appreciably less for pH and dissolved NO_3 .

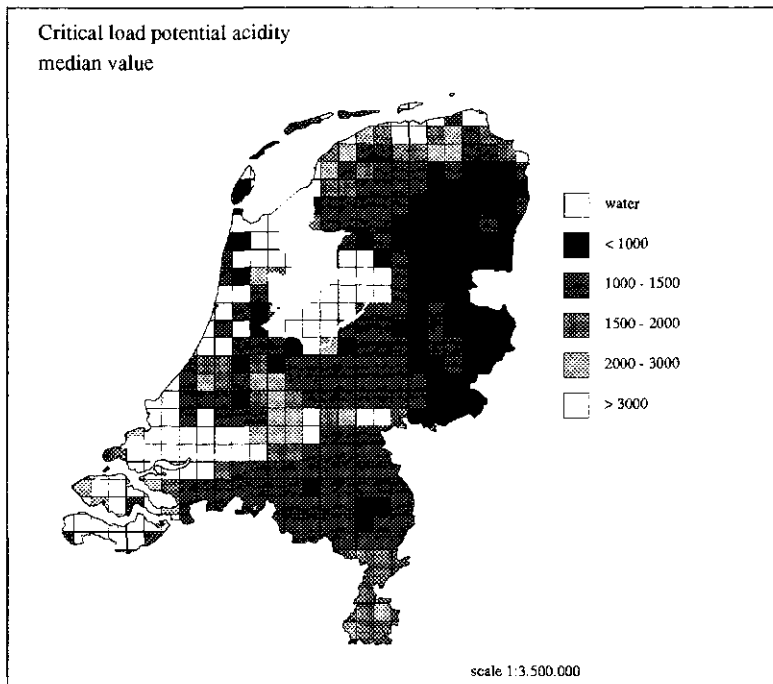
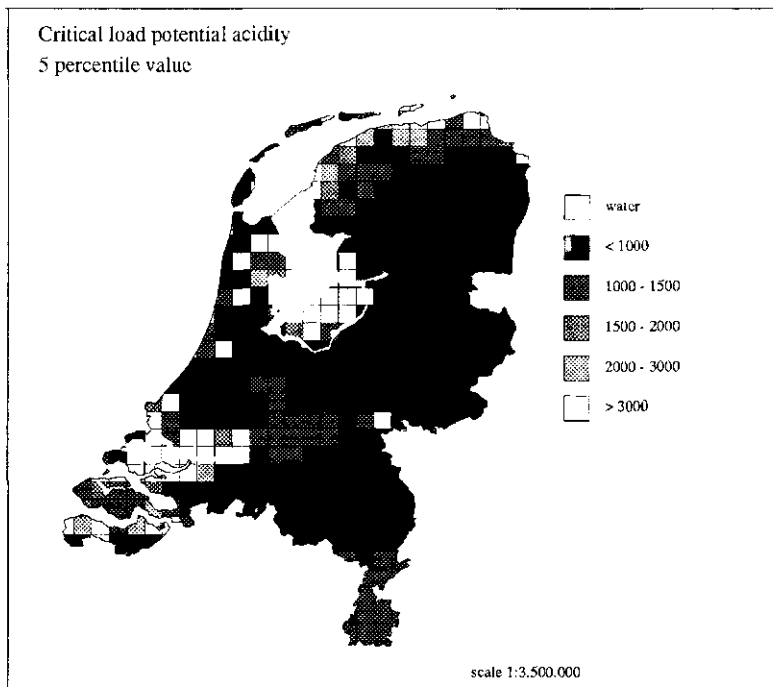


Figure 16.6. Five and fifty percent values of critical loads for acid N deposition (mol/ha.a) in The Netherlands for forest soils in 10*10 km grid cells.

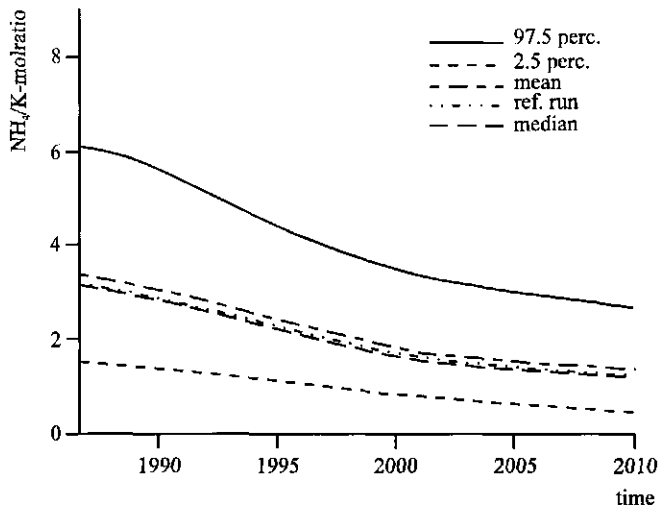


Figure 16.7. Uncertainty range in of the temporal development of the molar NH_4/K ratio in the surface soil of an acid forest soils in response to decreased N input. From de Vries & Kros 1991.

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17 Soil-plant relationship in contaminated soils

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17.1 Introduction

Soil contamination generally refers to an increased concentration of natural or man-made chemicals in the soil profile as a result of human activities. Its effect on the plant will depend on:

- the total amount present in the soil
- the proportion of the total that is accessible to the plant roots
- the ability of the plants to transfer the metals across the soil-root interface.

The total amount of any mineral compound in the soil is derived in the first place from natural sources but may be increased by man's industrial or agricultural activities.

It is not always easy to distinguish between the chemical forms of elements derived from rocks by natural processes of pedological weathering and the forms arising from environmental pollution.

Plants do not only take up nutrient elements and molecules necessary for their normal development but also other compounds that are present in the growth medium in a so-called available form. The accessibility of any element to plants in a given soil is determined by its chemical form and its location within the soil. The most readily available elements are those present in the soil solution in the ionic state or as soluble complexes, the least available are those firmly bound within the structure of solids, for instance, within the crystal lattice of primary rock minerals. Between these extremes the most important pool of available material is associated with charged sites on surfaces of the soils exchange complex. The equilibria between soluble, exchangeable and other solid forms have extensively been discussed in other lectures. Uptake directly is related to these solid-liquid interactions.

The soil-root interface is not a passive inert sieve. The root surface is an active boundary with characteristics varying with plant species and dependent on the particular element. Moreover the soil environment, immediately adjacent to the roots can be strongly influenced by root exudates (Merckx et al. 1986) so that apart from biochemical processes of transfer across cell walls within the roots, chemical processes of dissolution, chelation and precipitation outside the root also occur. Microbial activity in the rhizosphere is an additional factor that must be taken into account. Sometimes accumulation of element like Fe, Al or Cu on plant roots may occur without any measurable transfer to above-ground tissues.

17.2 Root uptake

Root uptake of elements (ions) means translocation from the soil solution into the cell cytoplasm. Therefore ions have to be transported through the cell wall and the plasma-membrane. For most higher plants the cell wall has a complex microfibrillic structure of

cellulose and pectine and is permeable for air, water and soluble compounds. The permeability of the plasmalemma is more selective; this membrane consists of a lipid bilayer in which globular proteins are embedded. As well hydrophobic as hydrophilic spots are locally present. Proteins may form hydrophilic channels through the membrane allowing transport of water and anorganic ions.

Although ion uptake by plants seems to be metabolically controlled, unwanted elements are taken up and accumulated.

Two main theories allow a better understanding of the uptake mechanisms.

17.2.1 Carrier theory

Carriers are plant-made (specific?) molecules that after activation by phosphorylation may form a carrier-ion-complex with ions diffused through the cell wall. This complex may migrate from the outside of the plantmembrane towards a phosphatase localized at the innerside of the membrane. Here the carrier-ion-complex is splitted and the ion is released into the cytoplasm. Activity of the carrier may be regenerated by a carrier-ATP-kinase and the newly phosphorylated carrier may diffuse again to the outside of the membrane to start a new uptake process. Thus essential nutrients are taken up. When the carriers are missing specificity also unwanted ions in this way actively may be taken up.

17.2.2 Electrical chemical potential gradient theory

The main driving force for micro-element uptake by plants is the electrical chemical potential gradient of each absorbable ion species that exists across the plasma membrane of root cells. This gradient is composed of two components:

- the activity gradient of each ion
- the plasma membrane electrical potential gradient (Kochian 1991). Root cells of many plant species have plasma membrane potentials ranging from -120 to -180 mV, creating an electrical gradient across the membrane that largely drives cation uptake. Additionally the activity of metal cations in the cytoplasm must be maintained at low levels in order for cells to avoid harmful redox reactions that can result from the presence of free ionic forms of these chemically reactive metals. This very large negative membrane potentials coupled to the very low intracellular activity of (noxious) metals result in a very large driving force for metal uptake. This mechanism is not selective for different ions; selectivity may be improved by the presence of ion channels allowing 'facilitated diffusion'.

Calcium-ion-channels have been identified in plasma membranes of higher plant cells (Spalding et al. 1992). However it is reasonable to suggest that Ca^{2+} channels may be plasma membrane passageways for other divalent cations, such as Fe^{2+} , Mg^{2+} , Ba^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+} .

17.3 Translocation in the plant

Once taken up ions may be translocated to different parts of the plant. Very little is known however, about the processes controlling long-distance translocation of metals in plant sap.

Solubility in water here plays a dominant role. The presence of chelating ligands such as citric acid, amino acids, sugars and phenols is most important in the control of cation translocation.

Nicotianamine, a non-protein amino acid, seems to play a central role in metal-binding and transport of divalent cations (Scholz et al. 1988) but also poly(γ -glutamyl-cysteinyl)-n-glycine peptides have high binding capacities for metal ions and have been studied intensively because of their association with heavy metal tolerance mechanisms in higher plant cells (Steffens 1990).

However, numerous other factors such as pH, the oxidation-reduction state, competing cations, hydrolysis, polymerization and the formation of insoluble salts (e.g. phosphate, oxalate etc.) may govern metal mobility within plant tissues.

Translocation of Fe, Zn, Cu, Cd and Ni occurs mainly as complexed forms, while Mn and Mg might be found as cations in the vascular system. Lead seems to be strongly immobilized in the root cell wall as lead-pyrophosphate.

The distribution and accumulation patterns of various elements vary considerably according to the element, the kind of plant and the growth season. A relative common phenomenon however is the accumulation and immobilization of trace metals in roots especially when their supply is abundant.

The complex nature of uptake and translocation of ions clearly is shown in the results of an experiment conducted in our laboratory. Cucumber and maize seedlings were grown for four weeks under controlled conditions in an equilibrated nutrient solution. After two weeks the Cu-concentration in the nutrient solution was increased from 0.08 mg/l to 2 mg/l using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Cu-EDTA (Cu-ethylene-diamine-tetra-acetic acid) or Cu-TETREN (Cu-tetra-ethylene-penta-amine); to the control treatment no additional Cu was added. It may be assumed that at the pH of the nutrient solution the respective Cu-forms added mainly were Cu^{++} , Cu-EDTA²⁻ and Cu-TETREN²⁺. The nutrient solution was replaced daily to minimise effects of species transformations eventually caused by pH or rhizobial exudates. Plants were harvested after another two weeks. Above-ground parts and roots were analysed separately. The results summarised in Table 17.1 clearly show that uptake and translocation of the same element strongly depend on the chemical form added and that the behaviour of both plant species is completely different. CopperII from CuSO_4 and Cu-TETREN, both cationic, are taken up to a greater extent than Cu-EDTA, the anionic form.

This behaviour is similar for both plant species but more pronounced for cucumber. According to Cottenie & Camerlynck (1980) monocot plants (maize) show a lower metal uptake than dicots (cucumber); this phenomenon may be related to the amount of negatively charged binding sites on the root membrane surface, known as the root cation exchange capacity that is lower for monocots than for dicots as stated by Crooke (1964). The translocation of Cu also is strongly affected by the chemical form Cu is applied. When the ratio root-Cu/shoot-Cu is used as an indicator for translocation, it is seen that for cucumber the ratios are 2.2, 88.9, 9.6 and 2.4 for the control, CuSO_4 , Cu-EDTA and Cu-TETREN respectively, suggesting that upon enhanced supply Cu^{++} is immobilized in the root, some 9 and 37 times more than Cu-EDTA and Cu-TETREN respectively. In the case of maize, Cu-EDTA seems to be stronger immobilized in the root than Cu^{++} and Cu-TETREN. Uptake and accumulation of Cu-TETREN show some particular aspects. Cucumber shoots grown on the nutrient solutions containing Cu-TETREN have a Cu-concentration higher than 500 $\mu\text{g/g}$ without any negative yield effect. When CuSO_4 is applied yield depression starts when the Cu content in the plant exceeds 30 $\mu\text{g/g}$. It might be suggested that Cu-TETREN, being a very stable complex

(log K = 24.3) is taken up and translocated in the plant as such, it is not recognized by the plant as Cu. The plants own chelating agents apparently are not able to release Cu from the TETREN complex and the metabolism is not disturbed. On the contrary, when the Cu⁺⁺-activity in the nutrient solution increases translocation to the shoot is directly blocked and immobilization in the roots occurs; in the experimental situation this is linked to an important growth reduction.

Table 17.1. Yield and concentration of Cu in shoots and roots of cucumber and maize grown in nutrient solutions.

Species treatment (mg Cu/l)	Shoots		Roots	
	Fresh weight/ culture vessel (g)	Cu(dry weight basis) (μ g/g)	Fresh weight/ culture vessel (g)	Cu (dry weight basis) (μ g/g)
Cucumber				
Control (0.08 mg/l)	49.3	10.9	19.7	24.4
CuSO ₄ (2 mg/l)	12.0	57.2	7.3	5086
Cu-EDTA (2 mg/l)	54.5	25.6	25.2	247
Cu-TETREN (2 mg/l)	50.5	505	19.9	1195
Maize				
Control (0.08 mg/l)	21.8	8.5	9.8	14.0
CuSO ₄ (2 mg/l)	22.5	34.1	9.2	221
Cu-EDTA (2 mg/l)	25.3	12.0	12.8	218
Cu-TETREN (2 mg/l)	32.1	45.0	13.5	407

17.4 Accumulation and toxicity

The total sum of cations in plant tissues is only slightly influenced by variations of individual cation availability, however an extreme increase in the supply of one cation species may decrease the uptake of other cations due to competition for the active absorption sites on the root surface.

Accumulation of any element in the plant tissue finally will cause metabolic disorders resulting in growth depression. Beckett & Davis (1977) have defined the upper critical concentration of an element in the plant as the concentration at which yield is first

reduced. Figure 17.1 is illustrating the estimation of the critical foliar concentration for Zn using ryegrass as indicator plant.

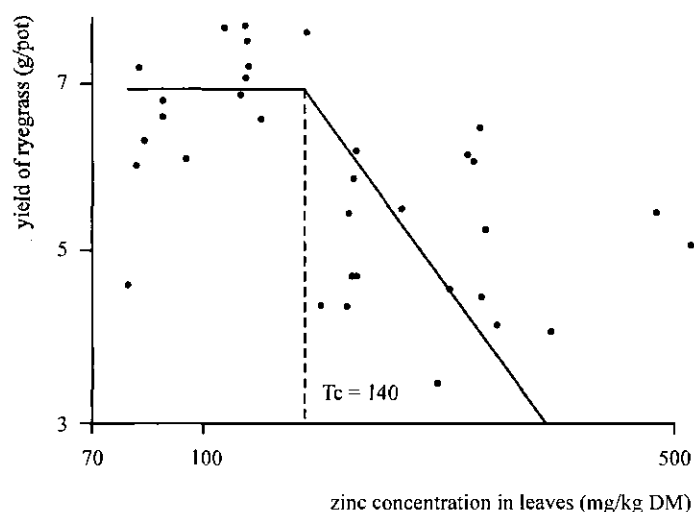


Figure 17.1. Estimation of the upper critical concentration (T_c) of Zn in ryegrass. From Davis & Carlton-Smith (1984).

For any element and plant species this critical level (T_c) may be estimated. If phytotoxic effects of potentially harmful elements were only dependent on critical concentrations in the plant tissues T_c should be a very practical tool. However, Verloo et al. (1985) clearly demonstrated that this level also is influenced by soil characteristics as CEC, pH, organic matter etc. affecting the chemical form and thus, uptake, translocation and phytotoxicity of the elements. For maize T_c for Zn was 225, 600 and 95 $\mu\text{g/g}$ when plants were grown on a sandy soil pH H_2O 4.55, a sandy loam soil pH H_2O 6.05 and a heavy clay soil pH H_2O 8.10 respectively. According to Smilde (1981) critical leaf concentrations were lower for metals applied in combination than for single metals. Kabata-Pendias & Pendias (1985) reported that in spite of the diversity in toxic levels, it can be stated that the most toxic metals for higher plant are Hg, Cu, Ni, Pb, Co, Cd and probably Ag, Be and Sn; it was added that the toxic concentrations of these elements in plants are very difficult to establish.

Some plants are known to accumulate elements and to survive on soils that are even strongly contaminated, they are tolerant. There is no mechanism of tolerance in a simple sense but it results from a series of several metabolic processes such as:

- selective uptake of ions
- decreased permeability of membranes
- immobilization of ions in roots, foliage or seeds and removal of metabolic reactions
- alteration in metabolic patterns
- adaptation of a physiological metal in an enzyme to toxic metal replacement
- release of excess ions through leaching from foliage or leaf shedding.

Clysters et al. (1991) demonstrated that net photosynthesis of bean seedlings de-creased after assimilation of toxic amounts of zinc by the roots. This effect was related to replacement of essential Mn^{2+} by Zn^{2+} in the water splitting enzyme of the thylakoid membrane inhibited photosynthetic electron transport and partial substitution of Mg^{2+} by Zn^{2+} in the ternary ribulose 1.5 biphosphate carboxylase - CO_2 - metal $^{2+}$ complex. These authors also stated that in plants treated with toxic amounts of Cu and Zn membrane activity was affected by lipid peroxidation.

It seems that the occurrence of natural or anthropogenic sites of high toxic metal concentrations has acted as a powerful selective factor to plants. While most species have been unable to tolerate the physiological and biochemical stresses imposed, a few have responded with the evolution of metal tolerant populations. *Viola calaminaria*, the field violet, is growing well on soil with levels in excess of 1% Zn.

Metal tolerance appears to be genetically controlled in a Mendelian manner, though the specific mechanisms involved may be several and additive.

17.5 Influence of soil factors

All factors that may affect the concentration and chemical form of ions in the soil solution finally will influence plant availability and uptake. Most important are: total soil content, pH, clay mineralogy and content, organic matter and redox potential. With respect to metals and inorganic ions actually an extended literature is available (Merian 1991; Kabata-Pendias 1985; Adriano 1986). Indirectly the effects of organic compounds are evaluated through their interactions with metals.

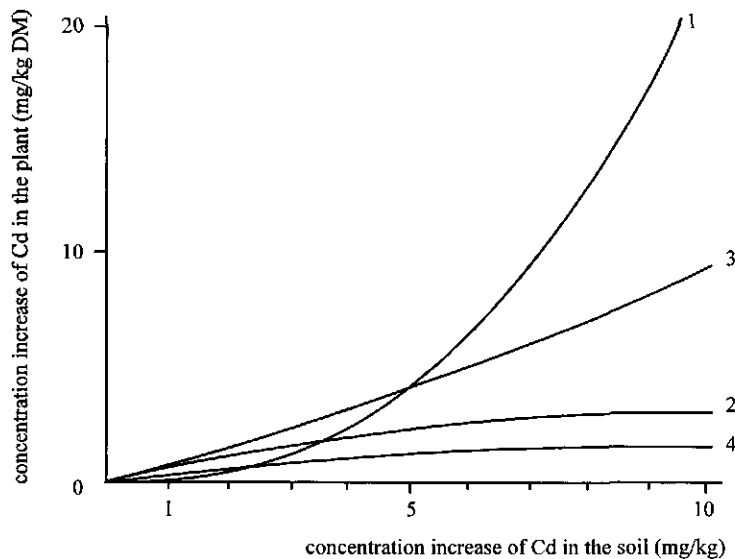


Figure 17.2. Uptake of Cd by ryegrass from a sandy soil contaminated with $CdSO_4$ (1) or sewage sludge (2) and a heavy clay soil contaminated with $CdSO_4$ (3) or sewage sludge (4). From Verloo 1992.

Increasing the total content of any element in the soil will result in an increased plant uptake. In Figure 17.2 the concentration increase of Cd in ryegrass is plotted as a function of the concentration increase in a sandy soil and a heavy clay polder soil. Cadmium has been added as CdSO₄ and a Cd-rich sewage sludge. The different uptake patterns of ryegrass grown on the strongly polluted soils can completely be explained by the higher pH and sorption capacity (CEC) of the clay soil, however at lower contamination levels more Cd was taken up from the heavy clay. Eeckhout (1991) clearly demonstrated that this rather exceptional behaviour was due to formation of cadmium chloride complexes in the polder soil.

The differences observed between CdSO₄ and Cd applied in sewage sludge may not only be explained by species characteristics but are also related to increased sorption capacity and organic matter content of the soil induced by sewage sludge application. Thus, total contents in soils are only meaningful when the relations with plant uptake, as given in Figure 17.2, are known.

The estimation of upper critical concentrations of pollutants in plants (see Figure 17.1) also has led to the estimation of the corresponding upper critical concentrations in the soil. Additional valuable information is obtained from the estimation of the transfer-coefficient T being the slope of the uptake curves. The values of T, given in Table 17.2, have been calculated as:

$$T = \frac{\text{sum of concentration increases in the plant}}{\text{sum of concentration increases in the soil}}$$

Table 17.2. Transfercoefficients for some plants and elements. From (1) De Haan et al. (1985) - (2) personal data.

Plant	Transfercoefficients					Ref
	Cd	Cu	Ni	Pb	Zn	
oats (green crop)	1.54	0.05	0.69	0.02	1.18	(1)
oats (straw)	0.53	0.01	0.19	0.02	1.79	(1)
oats (grain)	0.09	0.02	0.49	0.002	0.35	(1)
maize (green crop)	1.05	0.07	0.07	-	0.63	(2)
spinach	5.22	0.51	0.54	-	2.04	(2)
radish (green)	5.20	0.68	0.74	-	1.74	(2)
radish (tuber)	0.66	0.13	0.10	-	0.42	(2)

Remarkable differences between elements and plant parts and species are demonstrated.

Soil factors also effect the transfercoefficients. Using data published by De Haan et al. (1985), and Verloo et al. (1987) it can be summarised that on an average the transfercoefficient decrease per unit CEC increase (meq. 100 g⁻¹) in the soil may be estimated at 0.002, 0.0005, 0.0156, 0.0001 and 0.010 for Cd, Cu, Ni, Pb and Zn respectively. Per unit pH decrease of the soil the corresponding transfercoefficient increase is estimated to vary between 0.68-4.95, 0.06-0.18, 0.74-1.31 and 3.40-3.80 for Cd, Cu, Ni and Zn respectively, the lower limits corresponding to monocot plants, the high ones to dicots.

From these data it can be concluded that in practice the accumulation of elements like Cd and Zn is mainly controlled by the soil pH, influences of CEC are negligible. For Cu and Ni interactions with CEC and eventually other soil characteristics may be more pronounced.

The use of predictive models for the accumulation of contaminants by plants (Browne et al. 1984) is not yet very successful.

Combined efforts of soil chemists able to model species and concentrations of pollutants in any soil system, and plant physiologists able to model transfer, uptake, translocation and toxicity towards any, plant are urgently needed. Soil-plant relationships in contaminated soils still have a promising future.

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18 Soil as a waste management system

Restraints imposed by persistent constituents

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Summary

Soil can be considered as an extremely reactive biofilter in which processes of physical, chemical and biological nature take place. These processes may occur separately or in a combined way, simultaneously or subsequently. As such the soil system may offer an excellent opportunity for disposal and natural treatment of wastes, sometimes combined with efficient reuse of constituents present in the waste materials, for example in agricultural or horticultural crop production.

One of the main problems with wastes is brought forward by their composition. Even if they contain reusable constituents only, like in the case of potato starch wastewater, these usually do not prevail at optimum relative concentrations for fertilization purposes. If then application rates are adjusted to the constituent at minimum level, additional fertilization with for instance artificial fertilizers may allow optimal recycling of the waste without adverse environmental effects.

However, examples of such wastes are scarce. In most cases there is an imbalance of constituents in the wastes, especially if these contain compounds which cause potential hazards. Examples in this respect are persistent constituents like heavy metals or certain organic chemicals. Repeated application to soil of wastes containing such persistent hazardous compounds may introduce the build-up of a chemical time-bomb.

The same is true for phosphate. Repeated excessive application of this major plant nutrient element as compared to plant uptake occurs in areas with an animal manure excess problem. This causes saturation of the P-binding capacity of soil, which eventually will lead to phosphate leaching at unacceptable concentrations to groundwater and surface water. Once the leaching process starts, it will continue for very long time periods (decades).

Some important aspects of reactions in soil of major plant nutrients (N, P, K) from wastes are briefly discussed. Main attention is given to persistent constituents which impose limitations to waste usage in order to prevent pollution of soil, groundwater and surface water.

18.1 Introduction

Present society, especially in industrialized countries, produces huge amounts of waste products of all different types. In many cases soil is involved in the storage, disposal or reuse of these wastes. Sometimes the waste is of such a nature that only storage on or in soil can be considered, for example the inorganic part of household waste and car

wrecks. Many waste materials, however, do contain constituents which may be reused after application to soil. This contribution is confined to these types of wastes.

They include for example domestic waste water, waste water resulting from specific agricultural industries like canneries and potato starch processing, different types of compost, sewage sludge, and animal slurries. Because of the enormous expansion of animal husbandry in specific areas, animal manure is considered there sometimes more as a waste than as fertilizer.

It has been known for long that soil has the potential to 'treat' wastes in such a way that valuable constituents may be utilized at the same time, especially by means of plant growth and crop production. The oldest example, of course, is the use of 'night soil'. Far before the large scale introduction of treatment of domestic sewage water in waste water treatment plants, it was common practice in many communities to make use of so-called sewage farms. Here the soil in use for agricultural production (mainly as pasture) was regularly flooded with raw sewage water. By sampling and analyzing the resulting groundwater and drainage water it could be concluded that removal rates of constituents from the sewage water were extremely high. Depending on the type of soil it was found that phosphate removal was even higher than in tertiary treatment plants (more than 98%, Beek & de Haan 1974). The soils involved were high in aluminum- and iron-(hydr)oxides. Of course it must be realized that those compounds which are not taken up by the crop or leached to the groundwater will accumulate in the soil and thus in the end may lead to soil saturation problems in such systems. Even domestic sewage water has the problem of containing not only organic matter and the plant nutrients N, P, and K, but also heavy metals are present. Moreover, disease germs can be spread in this way. Therefore cattle grazing on sewage farms had yearly to be vaccinated against splenic fever. This type of disadvantage, and especially the large surface area involved, caused that most sewage farms have been abandoned at present. The remainder from sewage water treatment in wastewater treatment plants, in the form of sewage sludge, still causes problems with respect to soil quality, when applied to land. This is obvious because these sludges contain potentially hazardous compounds in enriched concentrations as compared to the sewage water.

Specific wastewaters contain merely constituents of vegetables or agricultural products as in the case of cannery wastewater and potato starch wastewater. These wastes are in principle very suitable for reuse as fertilizers in crop production, as is for example shown by Campbell Soup Company in Texas, USA, and Scholtens Potato Starch Industry in Emlichheim, Germany. However, also here several disadvantages are involved as compared to the use of artificial fertilizers. In the first place one has to take into account the working coefficient of nitrogen. This working coefficient reflects the efficiency of a nutrient present in waste as compared to the use of the same nutrient in the form of artificial fertilizer. Because this working coefficient may vary considerably depending on climatic conditions during the growth of the crop, an important uncertainty results about the fertilization level. These coefficients always play a great part with the use of organic wastes for fertilization purposes, especially for nitrogen. For the other major plant nutrients, phosphorus and potassium, they are usually around 0.8-1.0, thus reflecting a more or less comparable efficiency as for artificial fertilizers. The latter, however, are available with different relative contents of N, P, K, thus enabling fairly precise adjustment of fertilizer application to soil fertility requirements. In wastewaters the relative contents of N, P and K are entirely dependent on the nature and composition of the products where the waste is derived from. Sometimes this composition is strongly deviating from fertilization requirements. In these cases the

wastewater application rates should be based on the nutrient element which is at minimum level, with additional use of artificial fertilizer. But this is usually not done because of the extra costs and labour involved. In practice therefore wastewater application rates are usually taken so large that overdosing with certain nutrients results, which may induce various adverse environmental effects.

This imbalance of elements in most waste products constitutes the major problem with respect to their reuse. When this is true for the major elements N, P, K, it is even more so for elements or constituents like heavy metals, which are required for plant growth at relatively low level only. Sometimes these metals are abundant in wastes at any content because they are not necessary (and even hazardous) for proper soil functioning, as in the case of cadmium. The same may hold for persistent organic chemicals. It are especially such constituents which pose severe limitations on the reuse of wastes by application to soil because of their threat to soil quality. The wastes involved are for instance sewage sludges, certain types of compost, and so-called 'black soil' (an artificial mixture of wastes with peat and other soil material).

In the sequel some aspects of chemical reactions in soil of the major plant nutrient elements are first briefly discussed, especially in the light of possible adverse consequences for environmental quality. Then some attention is given to restricted use of wastes because of their undesirable composition.

18.2 Nitrogen reactions in soil

Main reactions of nitrogen in soil after application of waste (water) are schematically presented in Figure 18.1, taken from Lance (1972). A recent review on nitrogen reactions in forest soils was given by Johnson (1992) which also presents a complete analysis of the complexity of nitrogen behaviour in soil. The main difference between forest and agricultural land is that nitrogen uptake by trees is relatively small as compared to agricultural crops. On the other hand loads are usually also small in forest as compared to agricultural production.

Figure 18.1 departs from the effluent of a secondary sewage water treatment (Flushing Meadows Project near Phoenix, Arizona), but comparable reaction mechanisms will apply when use is made of completely different waste materials like *e.g.* potato starch processing wastewater (de Haan et al. 1973), manure (Klausner et al. 1971), septic tank effluents (Walker et al. 1973), or generally any nitrogen source which does contain the nitrogen predominantly in the ammonium form. Taking the above picture as a guideline, the different reactions can best be discussed by tracing the various inorganic nitrogen compounds involved.

Under alkaline conditions part of the NH_4^+ entering the soil may revert to NH_3 , and losses of N due to volatilization of NH_3 may then become substantial, as is extensively described in the contribution of van Breemen to this course about acidification of soil.

In order to prevent NH_3 volatilization after application of animal slurries to soil, an official regulation has been introduced in The Netherlands, which prescribes the practical way of application of the slurry. The slurry must either be injected into the soil or be worked in, *e.g.* by ploughing, directly after application. Deminishing NH_3 volatilization of course results in higher efficiency of nitrogen use, and hence larger problems with respect to possible nitrogen leaching. At present experiments are performed for acidification of the slurries by means of nitric acid addition. Although this may indeed prevent NH_3 volatilization, on the other hand the amount of nitrogen is then considerably enlarged which seems somewhat unlogical for areas where already a

great nitrogen surplus exists because of intensive animal husbandry. Acidification of the slurry requires renewed adjustment of the application rate of plant nutrient requirements. For situations where injection or working in of the slurry is impossible (peat soils) or undesirable (areas with pasture birds colonies) the new method may have some perspective.

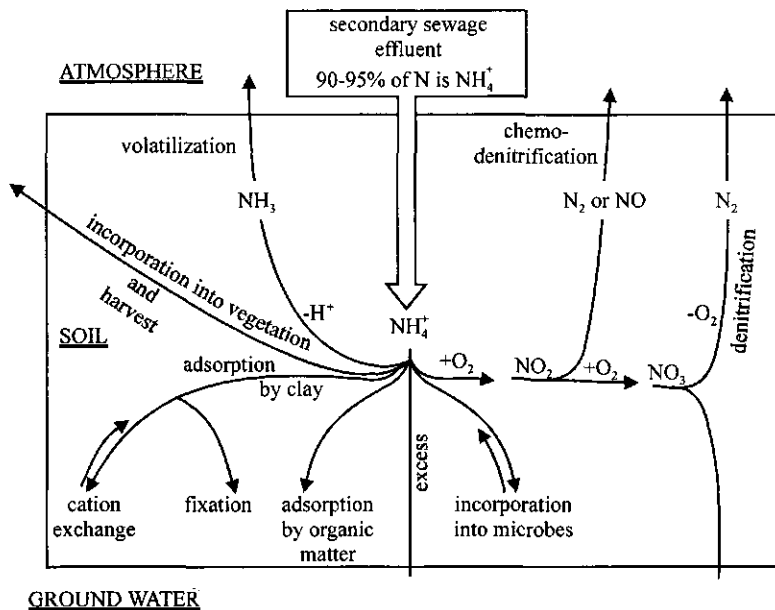


Figure 18.1. Transformations of nitrogen in soil, departing from a NH_4^+ -source.

A number of plant species may use ammonium as a primary source of nitrogen and hence part of the amount applied may leave the system this way. The remaining ammonium will now be displaced through soil subject to several types of adsorption and fixation processes, namely regular cation exchange, intra-lattice fixation much alike K-fixation as is described later, and direct chemical incorporation into some humus intermediates. Finally ammonium may become incorporated into microbial tissue, thus re-entering living organisms, and again be subjected to mineralization upon a decrease of the size of the microbial population.

Ammonium not intercepted through one of the above mentioned mechanisms may leach to deeper soil layers and eventually reach the groundwater. It may, however, also undergo nitrification if the specific requirements for this reaction are met.

The main conditions for nitrification are:

- sufficient amounts of nitrifying micro-organisms;
- sufficient supply of free oxygen;
- presence of suitable energy sources;
- satisfactory conditions with respect to moisture and temperature levels.

The nitrification process itself consists of a number of different steps in which intermediate compounds are formed. Formation of several of these NO_x compounds is undesirable as they may, after volatilization, contribute to destruction of the ozon layer.

Nitrate ions formed by nitrification or added as such to the soil are highly mobile in most soils because they are not significantly adsorbed onto the soil solid phase. They are thus leached down with the carrier stream (the retardation factor equals zero), unless they are intercepted by plant roots and taken up as nutrient ions. Nitrate leaching may result in undesirable quality of groundwater to be used for drinking water purposes because of giving use to methaemoglobinemia ('blue baby disease'). Therefore nitrate drinking water standards are set by the WHO at 50 mg NO_3 per liter; the EC has lowered this value to 25 mg NO_3 per liter.

Figure 18.2, resulting from groundwater analysis in an area with large manure surpluses, shows that here these standards can not be met anymore. It must be feared that the increase of nitrate contents, as measured over the past decades, will still continue, even if any further nitrogen application to soil would be terminated from now on, because of excessive manure applications in the past.

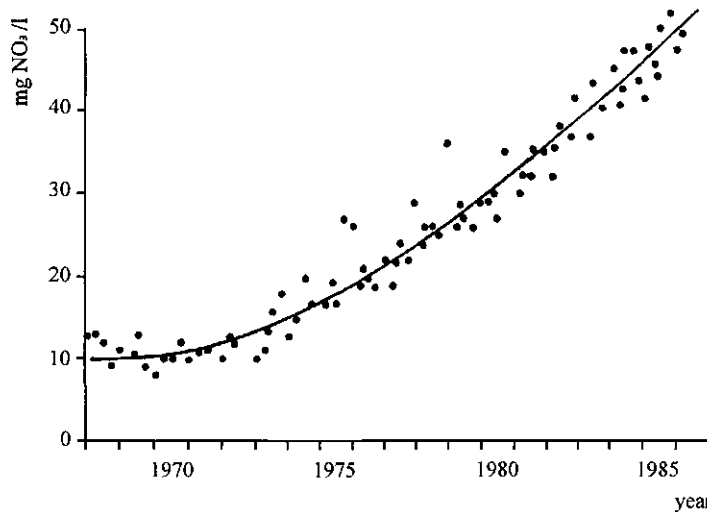


Figure 18.2. Nitrate content in deep groundwater, as a function of time, in an area of intensive animal husbandry.

The only way of removal of nitrogen from the system, once present as nitrate, is given by the microbial process of denitrification. In contrast to nitrification this process requires reducing conditions, plus again an energy source. Accordingly these processes, if occurring both in one system, will occur in a sequence in time and/or in space. As furthermore denitrification, leading to the formation of gaseous N_2 , acts only on nitrate ions, nitrification must precede denitrification if nitrogen enters the soil as ammonium. In a global sense, denitrification constitutes the closing link in the nitrogen cycle, since only in this way nitrogen returns to its ultimate source, namely N_2 of the earth's atmosphere.

Summarizing the situation with respect to the management of excess of nitrogen compounds entering locally the soil as in many waste management systems, it may be concluded that undesirable environmental effects are to be expected primarily from NH_3 volatilization, and from excesses of nitrate ions leaving the topsoil and reaching groundwater or open water. Although the soil is capable of retaining temporarily increased levels of nitrogen, this is of no avail on the long run as such retention implies a labile storage in organic nitrogen forms. In practice such storage will eventually lead to a new steady state at an increased intensity level where the larger input is accompanied by an increased output of the mineralization and leaching processes, exerting an undesirable impact on the environment. Only if the increase of the input is balanced by a removal via harvested crops or by increased denitrification will it be possible to maintain the output via leaching water at an acceptable level.

18.3 Phosphate reactions in soil

In most wastes P prevails in the form of inorganic phosphates. This is also the case with animal manures, where roughly 80% is found in inorganic form (Gerritse 1976). Soils usually have a very large bonding capacity for phosphate. For detailed information about the reaction mechanisms involved the reader is referred to the contribution of van Riemsdijk and van der Zee to this course, and the extensive literature reviews presented there. The attention will be restricted here to the practical effects of this phosphate bonding in case of waste application to soil, and the environmental consequences of phosphate saturation of soil systems.

Phosphate in soil is largely immobile, being either adsorbed or precipitated, while a small fraction may move with leaching water at concentrations which are generally not larger than about 10^{-5} molar. Reports on phosphate distributions with depths thus invariably indicate an accumulation in the topsoil layer. This was even the case in systems of very high phosphate applications as on sewage farms (Beek & de Haan 1974). Figure 18.3 shows the course of the P content with depth, expressed as mg P_2O_5 per 100 g of dry soil, on a sewage farm, which is in normal agricultural use as grassland for pasture. The fields are, already for more than 60 years, flooded on rotation basis with raw domestic sewage water at a rate of about 350-400 mm each month.

The dotted line in Figure 18.3 represents the situation on non-flooded soil. To this purpose soil profiles were sampled on the forest land soils that surround the farm and from which the sewage farm has been reclaimed. The difference between both situations refers to a total amount of 15,700 kg P_2O_5 per hectare; 90% of this total phosphate storage is obtained in the upper 40 cm and even 65% in the 20 top layer (which is regularly ploughed). One hundred percent efficiency in phosphate removal from the water would lead to a so-called block-front in the proceeding of P-saturation of the soil. Some dispersion always occurs because of heterogeneity of the soil system.

This soil property of effectively bonding of phosphate ions has thus been applied in practice for removal of phosphate from wastewater. At the same time it is the reason that excessive supply of phosphate in manure slurries in certain areas has not led so far to large-scale leaching of phosphate from soil, which would damage surface water bodies by eutrophication. On long term, however, any significant overdose as compared to plant uptake will inevitably induce complete saturation of the bonding capacity. Again of course, the time scale involved is depending on the magnitude of the remaining bonding capacity on the one side and of the overdose on the other.

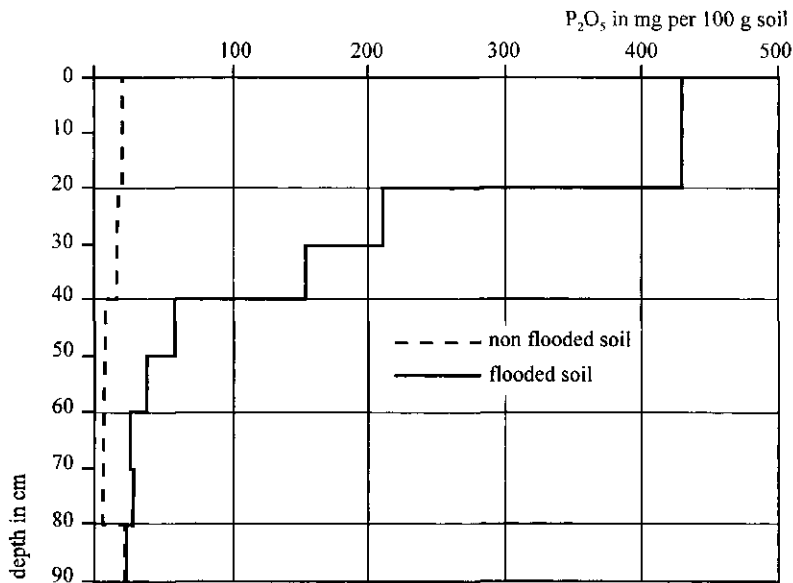


Figure 18.3. Phosphate distribution with depth on a sewage farm as compared to the non-treated soil.

Behaviour of phosphate in soil thus received considerable attention in research programmes. Initially mainly with respect to plant nutrition and soil fertility aspects presently also in relation to possible environmental damage. Main soil compounds responsible for phosphate bonding are organic matter, clay minerals and (hydr)oxides of Al and Fe. Beek & van Riemsdijk (1979) gave an extensive review on phosphate bonding in soil. A model which satisfactorily describes the bonding mechanism in sandy soils was developed by van Riemsdijk et al. (1984) and van der Zee & van Riemsdijk (1986; 1987). A formula of general validity for homogeneous soil describing the transport of the phosphate saturation front in soil was presented by Lexmond et al. (1982). As long as the shape of the saturation front in penetrating the soil does not alter, the rate of movement of this saturation front may be described with the following simple relationship between the proceeding saturation, phosphate load and bonding capacity:

$$y = \frac{(A - U)}{B \cdot S} \cdot 141 \quad (1)$$

in which

y = velocity of saturation front, in $\text{cm} \cdot \text{yr}^{-1}$

A = phosphate supply to soil, in $\text{kg P}_2\text{O}_5 \text{ ha}^{-1} \cdot \text{yr}^{-1}$

U = uptake and removal by crop, in $\text{kg P}_2\text{O}_5 \text{ ha}^{-1} \cdot \text{y}^{-1}$

B = dry bulk density of soil, in $\text{kg} \cdot \text{m}^{-3}$

S = remaining phosphate sorption capacity, in $\text{mmol P} \cdot \text{kg}^{-1}$.

The value of S thus constitutes a crucial point. It may be determined by the use of sophisticated techniques as developed by van Riemsdijk et al. (1986). Fortunately it can also be reasonably well approached by analytical techniques which are more easily accessible. As shown by Lexmond et al. (1982) and van der Zee (1987) for many soils a good correlation exists between the total amount of P that can be bound and the amount of reactive Fe and Al as determined by oxalate extraction. However, it is the presently remaining bonding capacity, S, that counts. S thus is the main parameter for vulnerability of soil for phosphate leaching. The relationship of equation (1) has graphically been visualized in Figure 18.4.

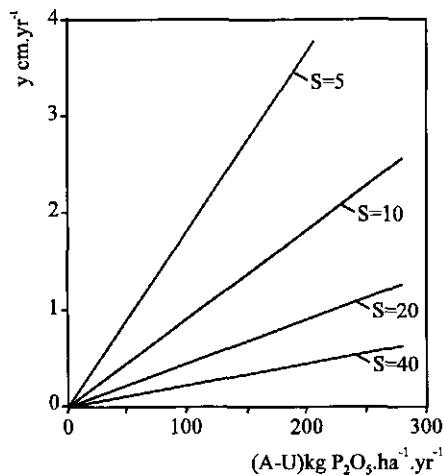


Figure 18.4. Velocity of phosphate saturation front in soil as a function of net P addition, for a number of values of remaining phosphate bonding capacity; soil bulk density = 1500 kg.m⁻³.

Table 18.1. P removal from soil, in kg P₂O₅ ha⁻¹.yr⁻¹, for a number of crops at assumed dry matter production corresponding to good yield.

Crop	Dry matter production kg.ha ⁻¹	P removal kg P ₂ O ₅ ha ⁻¹
wheat	9,000	57
rye	7,200	32
corn (grain)	4,700	32
silage corn	12,500	82
potatoes	9,200	55
sugar beets	19,600	102
hay	4,000	32

The value of U is related to the type of crop and to crop yield. In Table 18.1 some examples are presented. On pasture farms P removal is usually very low because animal products like meat and milk are the only ways of discharge there.

The value of A (P supply with fertilizer) is strongly dependent on the fertility status of soil with respect to phosphate, which again is inversely related to the remaining bonding of P in soil. There is not much sense in giving average data for this supply as can be calculated from P fertilizer consumption in the different EC member states and agricultural areas involved. Agricultural soils with extremely low capacity for phosphate bonding will probably first induce the P leaching problem. Probability for saturation of soil with P by the use of mineral fertilizers is low when the official fertilization recommendation of extension services are followed. Then the supply is adjusted on the basis of P availability according to soil sample analysis. The availability will automatically increase with proceeding saturation of the bonding capacity, and when saturation is reached, the recommended supply should not exceed P removal by crop. There are several reasons in practice, however, for deviations from these official recommendations. One would be non-regular soil sampling and analysis, and supply on the basis of farmers' experience. Another one would be the use of *e.g.* 'Starting' doses of mineral P in silage corn, even when the P fertility status of soil is very high. As compared to mineral P, however, P overdosing as the result of manure surpluses seems far more important since in that case values of (A-U) may easily amount to several hundreds of $\text{kg P}_2\text{O}_5 \text{ ha}^{-1} \cdot \text{yr}^{-1}$.

The approach presented above also allows a risk evaluation for P leaching. Figure 18.5, taken from Van Riemsdijk et al. (1983) presents an example.

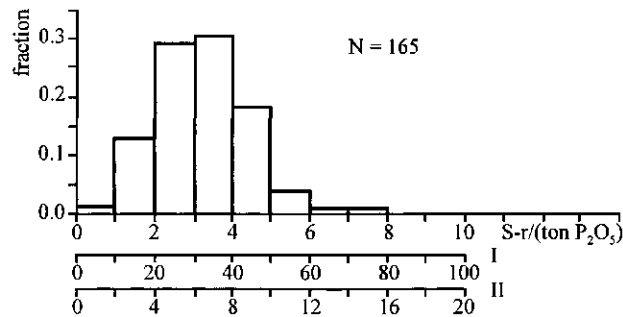


Figure 18.5. Frequency distribution of remaining P sorption capacity for topsoil of 165 different parcels in a certain region in the Netherlands. Axes I and II refer to time of saturation (years) for P supply rates of 160 and 560 $\text{kg P}_2\text{O}_5 \text{ ha}^{-1} \cdot \text{yr}^{-1}$.

Here the frequency distribution for the value of the remaining P sorption capacity, expressed in metric $\text{ton P}_2\text{O}_5 \text{ ha}^{-1}$, has been given for the top layer of 165 agricultural parcels in a certain region in The Netherlands. By translating the capacity axis for given supply rates (160 and 560 $\text{kg P}_2\text{O}_5 \text{ ha}^{-1} \cdot \text{yr}^{-1}$, in this case), a transformation is obtained to the number of years it will last before this layer will be saturated with P.

Saturation of soil profiles should be avoided because the combined effect of desorption and continued supply will harm surface water quality. These effects are most severe with animal manures, because of the high P concentration involved. In that case the phosphate concentration in the leachate exceeds the eutrophication standard with a factor of about thousand indicating that 1 m^2 of saturated soil may ruin the water quality of 1000 surrounding m^2 .

It is therefore that in the Dutch General Administrative Order (GAO) on manure application special attention is given to the phosphate saturation problem.

In order to prevent soils from phosphate leaching, the decree on use of animal manure applies standards based on the phosphate content of the manure. A differentiation was made between application rates for grassland, silage corn and arable land. The final goal is set at an application rate which balances the uptake of phosphate by crops, which is on the average 70 kg P₂O₅ per hectare per year. This is in accordance with the principle that addition of substances to soil should not exceed the (acceptable) removal by crops and by leaching. Because of the excessive availability of manures, this goal can be reached only after a certain time period, during which the application rates are stepwise decreased. Table 18.2 gives the application rates for the various soil uses and different phases. An exception clause was introduced for those soils which are to be considered as phosphate saturated. Here, the final rate was made applicable from the moment of effectuation of the GAO. Assessment of (the degree of) phosphate saturation of soil can be obtained by means of soil analysis according to the 'Protocol phosphate-saturated soils' (van der Zee et al. 1990). The above phosphate regulations are equally applicable to all materials covered by the decree on use of other organic fertilizers, and hence to the different types of compost.

Table 18.2. Application rates for animal manure, expressed as kg P₂O₅ ha/yr.

Period	Grassland	Silage Corn	Arable land
1-5-'87/1-1-'911	250	350	125
1-1-'91/1-1-'95	200	250	125
1-1-'95	175	175	125
2000	final rate	final rate	final rate

In all cases where soil is used as a waste management system the problem of P-saturation in relation to soil heterogeneity should be given special consideration. The heterogeneity aspects refer to the local variations in P bonding capacity of the soil (expressed as oxalate extractable iron and aluminum) and to the present degree of saturation. This heterogeneity, in combination with the large risk of phosphate leaching, makes it inappropriate that calculations are performed on the basis of average values. An extensive study in this area by van der Zee (1987) has shown how use can be made of stochastic approaches.

18.4 Potassium reactions in soil

The last major plant nutrient element, namely potassium, occurs in soil as a monovalent cation, and hence its behaviour is relatively easy to describe as compared to nitrogen and phosphorus. For equilibrium conditions, the relative occupation of the cation exchange complex of soil with K⁺ can be arrived at by using standard equations of Kerr and Gapon. Cation exchange induces retardation of transport, which can be expressed by a retardation factor, to be derived from exchange isotherms (Bolt & Bruggenwert 1976).

Another situation arises when so-called fixation occurs, which may be found for K^+ , and NH_4^+ as well, in clay minerals of the illitic type. Clay minerals with 'hexagonal' holes between the O-atoms (belonging to the 2:1 clay mineral types) show some preference for specific cations (K, NH_4 , Rb, Cs) which in dehydrated form 'fitt well' in these holes. The result is a somewhat higher selectivity coefficient for these ions as compared to other monovalent cations, for example Na.

Illites belong to the mica types of minerals. They have the ability to 'lock in' considerable amounts of K-ions in the hexagonal holes, which may several times exceed the cation exchange capacity of the exterior sites of the clay particles. Intensification of agricultural use of many alluvial soils, consisting of illitic type minerals, faces the problem of K-fixation resulting in too low availability of this nutrient for plant growth. Because of the competition for fixation between NH_4 and K, this may be remedied in part by simultaneous fertilization of potassium and nitrogen in the form of NH_4 .

In case of complete fixation, the retardation of the ions in soil become infinity and hence the mobility zero. However, for other conditions the transport of K in soil can be described by the normally applied theory of translocation of solute compounds in porous, adsorbing media.

One of the problems with too high availability of K in pasture is the occurrence of grass tetany with cattle. Extra addition of Mg to the diet may remedy this.

As known so far, no negative results occur from high K levels in groundwater to be used for drinking water purposes. Nevertheless a K standard for groundwater has been introduced within the EC, at 40 mg K per liter. This may lead to problems with groundwater quality in the near future in certain areas where K leaching results in higher values. The above is an example of a situation where 'officially' an environmental problem will be introduced as the result of application of a standard without sufficient scientific background.

18.5 Limitations in waste management by occurrence of heavy metals

As mentioned before many waste products applied to soil show a severe imbalance between major plant nutrient elements and heavy metals. One of the most pronounced examples is pig slurry, which, although in itself not a waste, is sometimes brought onto soil in excessive amounts. In the past these slurries were rich in Cu because of copper addition to the pig feed in order to improve the feed conversion rate. An official EC regulation has lowered the copper addition to about one quarter of the original value, which has considerably improved the situation. Nevertheless the imbalance as mentioned still exists and thus large pig manure application will lead to enhanced damage to soil fertility. The same holds for waste products like sewage sludges and compost.

In the following, the attention will be focussed on the approach as followed in The Netherlands in the framework of the Soil Protection Act, introduced on January 1, 1987. Because this act is a skeleton law, implementation is achieved by G.A.O.'s and Decrees on use of specific materials on soil. From these, compost is taken here as an example. Although the sequel thus is limited to the Dutch case with respect to compost, the approach is of general validity for other situations and other waste materials. First of all quality criteria of different types of compost with respect to heavy metal content have been set, as shown in Table 18.3, together with maximum application rates, presented in Table 18.4.

Table 18.3. Maximum values of some major heavy metal contents (mg/kg dry matter) in the different compost qualities as distinguished in the Dutch compost decree. A minimum organic matter content of 20% on dry matter basis is required for all composts.

Metal	Compost quality			
	Compost A ¹⁾	Compost B ²⁾	Clean compost C ³⁾	Very clean compost
Cd	2	1	1	0.7
Cr	200	50	70	50
Cu	300	60	90	25
Hg	2	0.3	0.7	0.2
Ni	50	20	20	10
Pb	200	100	120	65
Zn	900	200	280	75
As	25	15	15	5

1) until 1-1-1995.

2) as from 1-1-1995.

3) until 1-1-1995.

Table 18.4. Maximum application rates (in metric tons of dry matter per hectare) of different types of compost for different soil uses.

Soil use	Compost (until 1-1-'95)	Clean compost (until 1-1-'95)	Compost (as from 1-1-'95)
grassland	1.5/y or 3/2 y or 6/4	3/y or 6/2 y	1.5/y or 3/2 y or 6/4 y
arable land and silage corn	3/y or 6/2 y or 12/4 y	6/y or 12/2 y	3/y or 6/2 y or 12/4 y
other soil use	6/y	12/y	6/y

These data may now be evaluated against the background of sustainable soil use.

One of the aims of soil protection regulations should be to ensure that agriculture is environmentally sustainable. This means that no adverse short- or long-term effects on soil, ground water, or crop quality may occur. Among others in the context of compost use, this implies constraints with regard to the balance of contaminants present in compost.

When a ploughed layer is considered the balance for a particular contaminant (*e.g.* heavy metal) reads:

$$\frac{dT}{dt} = \frac{dI}{dt} - \frac{dJ}{dt} - \frac{dP}{dt} \quad (2)$$

where *t* is time in years, *T* is the accumulated amount in the ploughed layer, *I* is the annual input of contaminant, *J* is the annually leached quantity into groundwater, and *P*

is the annual plant uptake. Hence as well as the other terms have the dimension (mass/[area.depth.year]) where depth typically stands for ploughing layer thickness. When the input rate (dI/dt) exceeds the removal by leaching and plant uptake (and harvesting), accumulation in soil occurs. When the input and removal rates balance each other, no accumulation occurs and the content in soil (T) is in steady state. For a more or less constant input rate (due to atmospheric deposition and contamination of fertilizer with heavy metals) it usually takes a long time to raise T from negligible values to the level of soil quality standards (van der Zee et al. 1990).

The complication in evaluating (2) is that the accumulation (*e.g.* by adsorption), leaching rate, and plant uptake all depend on the concentration in solution, c . Hence, to resolve (2), the functions that express the relationships between T , I , J , P and c are needed. Whereas often the functions $J(c)$ and $P(c)$ may be linear (Boekhold & van der Zee 1991), the function $T(c)$ is usually non-linear for heavy metals (Lexmond 1980; Christensen 1981; De Haan et al. 1987). This implies that except for special cases, (2) has to be calculated numerically. However, mostly the mentioned functions are inadequately known. Therefore it is usually impossible to calculate with sufficient accuracy whether a particular constant input rate leads first to exceeded crop quality, ground water quality, or soil quality standards, and at what time this will occur. For illustration, an example where such an assessment is feasible (for cadmium) is shown in Figure 18.6 (Boekhold & van der Zee 1991). Because this work is readily available details given in that reference are omitted here.

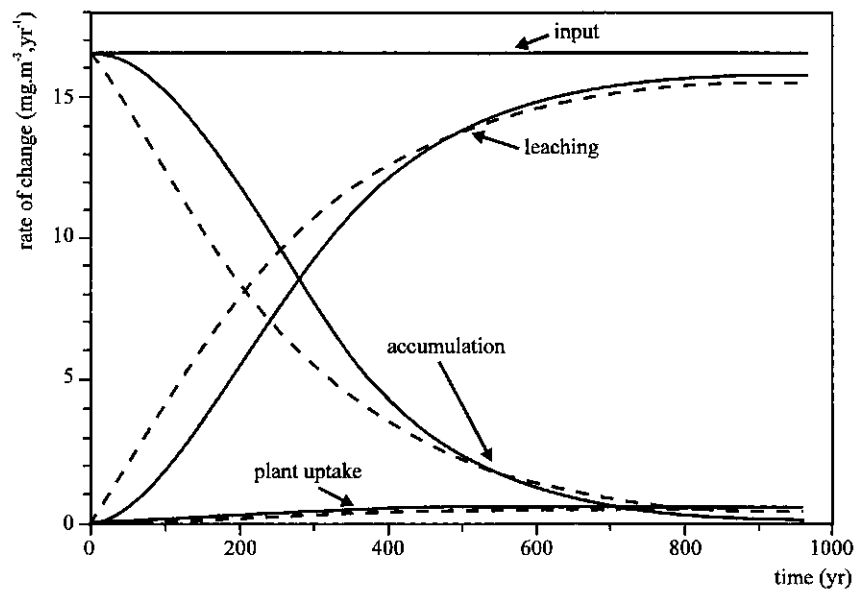


Figure 18.6. Cadmium balance as a function of time for a sandy soil and uptake by barley. Solid lines: analytical solution; dashed lines: numerical solution of the balance equation. From Boekhold & van der Zee 1991.

As an alternative the definition of sustainability may be reconsidered. It implies that even at steady state the balance should be in agreement with existing crop, soil, and ground water quality standards. Hence, a particular currently accepted application rate of compost and fertilizer and diffuse atmospheric heavy metal deposition may not give rise to exceeded standards in the future. At least for crop and ground water quality this situation can be more easily evaluated, as will be shown later.

For illustration of this approach, first the acceptable removal is quantified. Because available Dutch ground water quality standards are maximum permissible levels, the choice was made to take the 'stand-still' (no increasing contamination) principle for ground water as the point of departure for acceptable leaching rates. Therefore, concentrations may not increase beyond mean values currently measured in ground water (Ferdinandus et al. 1989). Multiplication of these concentrations with the net precipitation ($0.25 \text{ m}^3/\text{m}^2 \text{ year}$) yields the acceptable leaching losses of Table 18.5. The dimension is ($\text{mg}/\text{m}^2 \text{ year}$) because it was assumed that no accumulation occurs between the ploughed layer and 1 m depth (otherwise it should be ($\text{mg}/\text{m}^3 \text{ year}$)).

Table 18.5. Calculated acceptable removal of heavy metals by leaching and by harvesting different crops.

Removal by	Acceptable removal in $\text{mg}/\text{m}^2 \text{ year}$			
	Cd	Cu	Pb	Zn
Leaching	0.1	1.3	1.3	7.5
crop-harvest for				
(i) human consumption	0.03 - 0.25	3.6 - 11.0	0.1 - 0.5	36.0 - 110
(ii) animal fodder	0.15 - 0.75	3.6 - 13.5	7.0 - 31.0	36.0 - 135
vegetables*	0.43 - 0.85	3.7 - 7.5	1.7 - 4.5	37.0 - 75.0
Total (range)	0.13 - 0.95	4.9 - 14.8	1.4 - 32.3	43.5 - 143

* Relatively large values because of more harvests per year.

The acceptable removal in harvested plant material depends on the mean yield and acceptable tissue concentrations. Omitting details given elsewhere (Ferdinandus 1989), several vegetable rotation schemes and crops used for human consumption and for animal fodder were considered. Either quality standards (Pb, Cd) or the lowest tissue concentrations, where observed phyto-toxicity (Cu, Zn) was observed (MacNicol & Becket 1985), were used. Although, in view of differences in yields and acceptable concentrations, this gives only an average picture it serves for illustration. The results are given in Table 18.5. Observe, that for natural reserves the only removal is by leaching.

With regard to the input rates, it is necessary for an urbanized country like The Netherlands to take diffuse atmospheric deposition into consideration. Average data are provided in Table 18.6. To calculate the contribution of heavy metals due to compost and fertilizer applications, the fertilizer scenario needs to be known. With approximately 1.2% N, 0.6% P_2O_5 , and 1% K_2O (percentage by mass dry matter) in vegetable, fruit and garden waste compost, it is obvious that the nutrient requirements can not be

Table 18.6. Heavy metal loads via atmospheric deposition, fertilizer and compost applications.

Source	Scenario ^{*)}	Mean load in mg/m ² year			
		Cd	Cu	Pb	Zn
- Atm. Deposition	-	0.2	3.2	13.0	20.0
- Agriculture					
(i) Fertilizer	-	0.55	1.7	4.7	15.5
(ii) Compost + Fert.	1	0.59	10.0	15.9	36.4
	2	0.66	18.8	33	65
	3	0.88	36.6	62	124

^{*)} see text.

met by compost application rates of 1.5-6 metric tons per year. Therefore it is assumed that the maximum permitted application rate of compost is combined with additional fertilizer applications. In Table 18.6 the resulting applications of heavy metals are given. In the calculations it was assumed that 1.5, 3 or 6 metric tons of compost were applied (scenarios 1, 2 and 3, respectively) per year per hectare. Furthermore, when this appeared necessary an additional fertilizer application was given to meet the demands for N, P₂O₅ and K₂O, assuming nitrogen was given as calcium ammonium nitrate which requires 0.46 kg CaO/kg N-fertilizer to neutralize its acidifying effect. The latter compound and the fertilizers also lead to heavy metal contamination as may be inferred from the case where no compost was applied. The crop requirements were assumed to be 140 kg N, 65 kg P₂O₅, and 84 kg K₂O (all per hectare per year) for agriculture. Usually, contamination by compost additions was the more important one. For vegetable-horticulture no calculations were provided in view of the wide variation in nutrients needed (2-4 times as much N, P₂O₅, and K₂O) and the large differences between crops in the ratios N: P: K. On average, the extra contribution of fertilizer to the heavy metal loads in horticulture equals 1.1 mg Cd/m² year and for Cu, Pb and Zn, 1.7, 6.5, and 30.0 mg/m² year, respectively, compared with the cases (i) and (ii-3) in Table 18.6.

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At this stage it is possible to compare the results of Tables 18.5 and 18.6. It is clear that the currently tolerated use of compost leads to positive balances for most scenarios

of Table 18.6. Consequently, it may be concluded that application rates of compost as indicated in Table 18.3, using a tolerated composition of compost as given in Table 18.1 column B, is not sustainable. Accumulation in soil, increased leaching rates, unacceptable product quality or a combination of these phenomena must be anticipated at the long term.

For a consistent set of environmental regulations of all compartments (atmosphere, soil, ground- and surface water) constraints should be set, *e.g.* for compost use, on the contaminant that is the first to lead to problems. With regard to fertilizer use, the concept of 'discrepancy factor' may be introduced to facilitate the analysis which contaminant is most abundant (Scholtens & van der Zee 1991). The discrepancy factor F_d for essential elements (nutrients) may be defined as the ratio of application rate R_a over the removal rate R_r ,

$$F_d = \frac{R_a}{R_r} \quad (3)$$

where the removal rate should be taken equal to the uptake that is in agreement with a good product quality and the acceptable leaching. When F_d exceeds unity an excessive amount is applied. For a particular yield and optimal crop composition, F_d can be calculated. Because F_d for phosphorus applied with animal manure to soil exceeded the F_d -numbers for nitrogen and potassium, Dutch manure regulations were based on the phosphorus-balance of soil. As defined by (3), F_d exceeds unity (and is in fact infinitely large) for all non-essential elements, because the highest quality product would contain zero contaminants.

To make the F_d -concept more general and also useful for non-essential elements, R_r in (3) may be redefined as the uptake rate in agreement with acceptable product quality. Theoretically, the F_d -concept may be used to assess which of the considered heavy metals leads to environmental problems first.

As an illustration of the presented concept, R_r is calculated as the total rates given in Table 18.5 (using the lowest values of these ranges as those reflect standards for human consumption best). The application (or input) rate is obtained by summing the atmospheric deposition with those compost scenarios that may be acceptable (*i.e.*, Table 18.6 (ii)-1 and (ii)-2). The discrepancy factors are given in Table 18.7, and reveal that is F_d largest for Pb.

Table 18.7. Discrepancy factors F_d for two different cases of compost and fertilizer applications.

Scenario	Cd	Cu	Pb	Zn
1	6.0	2.7	20.6	1.3
2	6.6	4.5	32.9	2.0

This suggests that the greatest problems will be encountered for this element. It does not, though, imply that the problems for Pb are manifest earlier than for other heavy metals, because it is not clear whether for example leaching of Pb and the other metals

occurs at the same time. It does imply, that for the given scenarios the compost applications should be restricted based on Pb. If this is done, no problems are expected for the other elements. Approximately, the acceptable compost application rate of 1.5 metric tons/ha yr as given in Table 18.4 should be reduced by a factor twenty based on the discrepancy factor of Pb.

It needs to be mentioned that the given estimates should be applied after taking into consideration that:

1. even if no compost is applied, the required use of fertilizer may lead to F_d -factors exceeding unity, where another heavy metal may become limiting;
2. soil quality as such has not been considered, *i.e.*, adverse affects on the soil ecosystem were not accounted for;
3. depending on the relative importance of plant uptake and leaching, and the atmospheric deposition rate (which is difficult to influence), the F_d -factors for different elements may have to be significantly different to yield a conclusive strategy.

In conclusion of the above it may be stated that:

- Results of balance calculations for heavy metals, using average values, turn out to be discouraging for compost use.
- In part this may be due to the chosen sharp criterium: should production for human consumption be feasible everywhere?
- In part this is also due to diffuse (atmospheric) contamination. It seems obvious to reduce Pb-emissions. (Currently the standard of 200 mg/kg is not met). Atmospheric emissions are apparently not taken into account in the compost regulations.
- Spatial variability of diverse contamination fluxes was not taken into account: in urban areas Pb-fluxes may significantly exceed the average, in rural areas the opposite may be true. Nevertheless, the calculations provide a warning that current compost regulations may even violate the concept of sustainability on average.
- In particular care should be taken with regard to allotment-gardens because:
 - . very clean compost is not that much different in quality;
 - . the application rates may be large;
 - . due to their location in urban areas, the atmospheric deposition may be relatively large;
 - . exposure to poor quality crops is systematically large due to consistent consumption by the same producers.

The general conclusion when considering soil as a waste management system, unfortunately, must be that, although many wastes do contain valuable constituents, their use is severely restricted from a soil protection point of view.

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19 Community policy on contaminated land

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19.1 Introduction

It is only in relative recent times - within the last 10 years or so - that the Community and its Member States have become concerned about the problem of contaminated land. Environmental policies originally (in the early 1970s) adopted a curative and sectoral approach, aimed at solving particular problems relating to air, water, waste, etc. The results were frequently insufficient to rectify the situations concerned. At the most, this approach could limit the damage, but could not prevent it. I am not saying that it was not good at all but it took account only of serious cases of point source contamination, aiming to deal with emergency cases such as the Seveso disaster and the pollution of the Rhine in 1986.

Emergency measures can, indeed, deal with individual problems as they occur, but the economic and social costs are high, and the quality of the treatment used frequently suffers. This is why a number of Member States have developed their own policies for tackling the problem.

In some Member States there was, and to some extent still is, a considerable lack of systematic awareness of the scale of the problem, either in the individual countries or in the Community as a whole. Such awareness is an absolute prerequisite if we are to draw up a policy for dealing with the problem of contaminated land on the basis of swift action to tackle the existing problems and preventive measures to ensure that such problems do not recur in future.

Contaminated land policy in the European Community is aimed primarily at dealing with pollution arising from disused industrial sites and from waste tips. These are long-term problems which severely handicap the development of the areas concerned and are a serious threat to groundwater resources.

19.2 Definition and types of contamination

19.2.1 Definitions

There exists no generally accepted definition for contaminated land in the European Communities. Some Member States have defined it in the following ways:

Denmark: Land which presents a threat to groundwater resources or to the health of local residents (Danish National Agency for Environmental Protection, 1985);

Germany: Land that presents a potential direct or indirect threat to the health and the welfare of humans and economically natural resources, such as livestock,

crops and groundwater resources (Federal Ministry of Research and Technology, 1981);

United Kingdom: 'Contaminated land' is any land that appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under land, that

- a) significant harm, or
- b) pollution or is likely to be, caused.

'Harm' means harm to the health of living organisms or other interference with the ecological systems of which they form part, and, in the case of man, includes harm to his property;

The Netherlands: Land where substances are present in the soil in concentrations higher than those in which they would normally be expected to occur and where they pose a serious threat to public health and the environment (Ministry of Housing, Physical Planning and Environment, 1983).

For the purposes of European Community Policy as expressed in current Directives, 'contaminated land' means any land which has been contaminated by the deposit existence of any type of waste upon it or by industrial activity. In view of these different definitions we have organized a general study on the various types of contaminated land, and our first task is to give them a standard definition.

19.2.2 Types of soil contamination

Generally speaking, two types of soil contamination can be distinguished:

Diffuse contamination:

Pollution of a large area by particular source. Such pollution includes:

- air pollution ('acid rain'), associated with emissions of sulphur dioxide, nitrogen oxides, etc. by industry, domestic fuels, traffic, etc.;
- the prolonged and excessive use of fertilizers, pesticides, herbicides and sewage sludge in agriculture. (Note that this use of chemicals is the result of the CAP).

Point source contamination:

Geographically restricted local pollution by accidental, incidental or deliberate human activity. Such pollution arises from the following industrial activities:

- transport of chemicals;
- storage of raw materials;
- production processes;
- storage of products (leakage, spillage);
- disused production plants and former industrial sites.

Point source contamination also arise from the following waste disposal facilities:

- municipal landfills;
- hazardous waste landfills;
- co-disposal landfills;
- abandoned waste disposal sites.

It is this second type of soil contamination with which Community policy is chiefly concerned, at least at the level of the unit which deals with waste management policy. Another unit deals with emissions from industrial installations and products.

19.3 Regulatory action by the European communities regarding soil contamination

Soil contamination has not received major attention and has not been a priority issue for Community environment policy until very recently.

In the Community approach to regulating the problem, two stages can be distinguished: an initial stage, until 1986, during which the prevention of soil contamination was considered only in the general context of environmental legislation and a second stage, after 1986, the year in which the first legislation specifically dealing with soil was adopted. Since that year, other legislative measures to protect soil have been introduced, and soil protection has become an integral part of Community environmental policy.

19.3.1 The Treaty of Rome, the Single European Act, and the Maastricht Treaty

Independently of the foregoing, the general objectives and principles of the Treaty of Rome as amended by the Single European Act (1987, Article 130r) equally apply to soil protection policy. These principles are also taken up in the Treaty of Maastricht signed by the Ministers of Foreign Affairs of the 12 Member States in February 1992, ratified by the 12 Member States and in application from 1 November 1993.

Article 130r of the Maastricht Treaty states that:

- "1. Action by the Community relating to the environment shall have the following objectives:
 - (i) the preservation, the protection and the improvement of the quality of the environment;
 - (ii) the protection of human health.
2. It is based on the principles that preventive action should be taken, that environmental damage should as a priority be rectified at source, and that the polluter should pay. Environmental protection requirements shall be a component of the Community's other policies.
3. In preparing its action relating to the environment, the Community shall take account of:
 - (i) available scientific and technical data;
 - (ii) environmental conditions in the various regions of the Community;
 - (iii) the potential benefits and costs of action or of lack of action;
 - (iv) the economic and social development of the Community as a whole and the balanced development of its regions.
4. Within their respective spheres of competence, the Community and the Member States shall cooperate with third countries and with the relevant international organizations. The arrangements for Community cooperation may be the subject of agreements between the Community and the third parties concerned, which shall be negotiated and concluded in accordance with Article 228.
The previous paragraph shall be without prejudice to Member States' competence to negotiate in international bodies and to conclude international agreements."

Soil protection should be tackled via a 'multi-media approach', since soil forms part of various ecosystems and dealing with the problems of soil pollution should not cause problems in other environmental sectors (water, air).

Taking into account the fact that the soil is linked with the atmosphere, hydrosphere, biosphere and lithosphere, a number of EC Directives apply in one way or another to soil conservation, but the only one which relates directly to soil and defines limit values for pollutants is the Directive on sewage sludge in agriculture (86/278/EEC). However, there is also a proposal for a Directive on waste disposal which deals with the problem of restoring the land after the disposal site is closed.

Before addressing that subject I would like to gather together a number of articles from Community Directives which have some relevance to soil protection.

19.3.2 Council Directives

19.3.2.1 Council Directive of 15 July 1975 on waste (75/442/EEC) (OJ L 194, 25.7.1975), as amended by Directive 91/156/EEC

Article 4

"Member States shall take the necessary measures to ensure that waste is disposed of without endangering human health and without harming the environment, and in particular: without risk to water, air, soil and plants and animals". The new Directive adds: "Member States shall also take the necessary measures to prohibit the abandonment, dumping or uncontrolled disposal of waste".

19.3.2.2 Council Directive of 20 March 1978 on toxic and dangerous waste (78/319/EEC) (OJ L 84, 31.3.78)

This Directive has been repealed by Directive 91/689/EEC on hazardous waste. This new Directive refers directly to the framework Directive on waste. The sentence relating to the requirement that the hazardous waste present on a site be recorded and identified has been retained in what has become Article 2 of the new Directive. The fact that the more recently adopted Directive considerably enlarges the definition of hazardous waste also indirectly alters the conditions covering the landfill disposal of such waste.

19.3.2.3 Council Directive of 16 June 1975 on the disposal of waste oils (75/439/EEC) (OJ L 194, 25.7.1975)

Article 4

"Member States shall take the necessary measures to ensure the prohibition of:

- a) any discharge of waste oils into inland surface water, groundwater, territorial sea water and drainage systems;
- b) any deposit and/or discharge of waste oils harmful to the soil and any uncontrolled discharges of residues resulting from the processing of waste oils".

19.3.2.4 Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances (OJ L 20, 21.1.1980)

This Directive, in its aim to prevent the pollution of groundwater by certain families and groups of substances (Annex I: List I and II of families and groups of substances), is implicitly related to the prevention of soil pollution, given the intimate relationship between soil and groundwater. In the Articles of the Directive it is stipulated that Member States must take the necessary steps to prevent or limit the introduction into groundwater of the substances listed in I or II, for which purpose they must:

- a) prohibit all direct discharge of substances included in list I;
- b) subject to an environmental impact study all direct discharges of substances in list II;
- c) subject to an environmental impact study any disposal of these substances (list I and II) which might lead to their indirect discharge into groundwater;
- d) take the appropriate measures to prevent any indirect discharge of the substances referred to in the two lists.

When disposal of the substances listed might lead to their indirect discharge, the measures to be taken include specifying the place and method of disposal being used.

19.3.2.5 Council Directive of 27 June 1985 on the assessment of the effects of certain public and private projects on the environment (85/337/EEC) (OJ L 275, 5.7.1985)

Article 3

"The environmental impact assessment will identify, describe and assess in an appropriate manner, in the light of each individual case and in accordance with Articles 4 to 11, the direct and indirect effects of a project on the following:

- human beings, fauna and flora;
- soil, water, air, climate and the landscape;
- the interaction between the factors mentioned in the first and second indent;
- material assets and the cultural heritage".

19.3.2.6 Council Directive (86/278/EEC) of 12 June 1986 on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture (OJ L 181, 4.7.1986)

This Directive marks a turning point in the Community's policy in soil contamination, though its scope is restricted to preventing the accumulation of heavy metals in soil fertilized with sewage sludge. The purpose of this Directive is to regulate the use of sewage sludge in agriculture in such a way as to prevent harmful effects on soil, vegetation, animals and people, thereby encouraging the correct use of such sewage sludge. The Annexes to the Directive set limit values for concentrations of heavy metals in soil to which sludge is applied, the concentration of heavy metals in sludge and the maximum annual quantities of such heavy metals which may safely be introduced into soil intended for agriculture. Member States must take specific steps to ensure that the accumulation of heavy metals in the soil does not exceed the limit values laid down. If these are exceeded, Member States must ban the use of sewage sludge in agriculture.

19.3.3 The significance of the fourth Environmental Action Programme (1987-1992) for soil protection (OJ C 328, 7.12.1987)

The first three Environmental Action Programmes concentrated on pollution problems affecting specific environmental media (air, water, soil), so that - as stated in the introduction - the approach to pollution control has been of a 'sectoral' nature.

"One inevitable consequence of the sectoral approach to pollution is that, as standards are tightened in one area, so the pressure may increase in another area".

The global approach of the Fourth Action Programme changed the Community's environmental strategy to a multi-media and multi-sectoral pollution control policy. As the soil is a very complex biosystem, and as there are many different types of soils and pollutants, the comprehensive approach to soil protection will aim:

- to encourage coordination between policies to ensure that soil protection is more effectively taken into account in particular in the Community's agricultural and regional development policies;
- to reduce the damage caused by agriculture to the ecological infrastructure by proposing measures (within the context of the reform of the Common Agricultural Policy) to encourage less intensive livestock production systems, to reduce the use of agricultural chemicals and to ensure the proper management of agricultural waste (especially from intensive livestock units);
- to prevent soil erosion and the rapid run-off of water (including the identification and mapping of rapidly erodable soils throughout the Community);
- to identify and clean up polluted waste disposal sites; to encourage the recovery and re-use of contaminated land (*e.g.* old industrial sites, derelict mining land etc.) and to reduce the hazard to soil from current waste disposal practices;
- to encourage the development of innovative soil protection techniques and the transfer of relevant know-how.
- and, in the 5th Action Programme, to develop the subsidiarity by principle and the co-responsibility.

The Fifth Programme, adopted in February 1992, also emphasizes these aims but adds what I consider to be the most important method for achieving this approach, namely public awareness, information and training measures. These are more important than even legislation in achieving the policy's objectives.

19.3.4 Community Strategy for Waste Management (SEC 89, 934 final, 18.9.1989)

Adopted by the Commission on 13 September 1989, this document lays down five guidelines on which to develop the Community's waste management policy:

- prevention;
- recycling and re-use;
- optimization of final disposal;
- regulation of waste transport;
- remedial action.

The implementation of these guidelines will make a decisive contribution to reducing the pressure of pollution on soils in the Community and will help correct some of the problems inherited from the past.

The prevention or minimization of waste production and the promotion of recycling and re-use should together help reduce the need for waste disposal sites and facilities. Furthermore, the stated objective of considering landfill as the last resort in waste management and the requirement to use every possible method of treating waste prior to disposal so as to reduce its volume or potential harmfulness will help achieve the same objective of reducing damage to the soil from waste disposal.

19.3.5 This Commission Communication led to a reply from the Council in the form of the Resolution on waste policy (OJ C 122, 18.5.1990)

This document, basically the endorsement by the Council of the Commission's Strategy for Waste Management, insists on the need to reduce the quantity and toxicity of waste to landfill via the appropriate pre-treatment methods and, with a view to the long-term prevention of soil contamination by landfills, calls for post-closure supervision of the these facilities.

19.3.6 New Directives or proposals for new Directives

The Directive on batteries and accumulators containing dangerous substances, adopted in 1991, is one example of legislation which will help reduce soil pollution: it sets limits to the heavy metal content of batteries, provides for their separate collection and special treatment and, finally, for their landfill disposal with other wastes. A proposal for a Directive on the landfill of wastes is also on the table at the moment. If adopted, it will define the different classes of landfill, the general and specific requirements to be met by such facilities, the types of waste to be accepted, waste acceptance procedures and the procedures for operation, closure and after-care of a landfill. Existing landfill sites will have to bring their standards up to those required by the Directive. Insurance and financial guarantee provisions and the creation of a waste management fund are among the innovations introduced by the proposed Directive, in order to cover the expenses arising from the operations needed to prevent or remedy the environmental damage caused by waste disposal.

The main purpose of this Directive is to introduce rules for protecting the soil-groundwater system from possible damage due to the landfill of waste. With regard to Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, its scope might be extended to the use of sludge in forestry, with the definition of *ad hoc* standards for this use. In the same context, quality standards might be set for compost. Finally, the proposal for a Directive on civil liability for damage and injury to the environment caused by waste will act as a deterrent for thoughtless waste disposal and will help encourage producers and holders of waste to take preventive measures to avoid damaging the environment.

19.4 Community action on soil contamination

19.4.1 Studies and reports

Five major studies have so far been ordered and/or financed by the Commission to analyze the extent of soil contamination in the Member States. The most comprehensive (and recent) one is entitled 'Survey of E.U. Member States: Contaminated Land: Definitions, Registers and Priorities of Action' by AEA Technology, 1994.

It presents for the, then, 12 Member States of the E.U. the institutional and legal framework, definitions, registers, priorities of action and financial and liability aspects of rehabilitation of contaminated lands and presents recommendations for remediation strategy.

It is completed by a Technology Catalogue.

19.4.2 Actions

In December 1994, the German Federal Ministry for Environment convened a meeting of representatives of each Ministry of the Member States called 'Common Forum on contaminated land in the E.U.'. The objective is to exchange information and to cooperate in the matter. A second meeting was held in Maastricht in November 1995, and a third one is scheduled in Stockholm in September 1996. The Commission took part in that work.

One of the results of the forum is the launching of a COST action in March 1996. COST is a programme of DG XII of the Commission (Cooperation in the field of Scientific and Technical Research) which aims at organising meetings of researchers from the 15 Member States, with the view to exchange information and experience.

The objectives of the COST programme on contaminated lands, called CARACAS (Concerned Action on Risk Assessment for Contaminated Sites) are:

- to identify, compile, assess and review all relevant RTD projects and scientific approaches for risk assessment developed in the Member States of the European Union;
- to propose scientific priorities for future programmes and projects of the European Commission and the E.U. Member States;
- to elaborate guidelines and recommendations for assessing risks of contaminated sites.

This approach will probably give better results than whatever legislation in a matter in which the subsidiarity principle has to be applied.

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