CHEMICAL ASPECTS OF SOIL QUALITY

W. H. Van Riemsdijk

Department of Soil Science and Plant Nutrition
Agricultural University, Wageningen

Table of Contents

1 RELATIONSHIP SOIL CHEMISTRY - SOIL FUNCTIONS

The relationship between soil chemistry and the respective soil functions as to be considered in the forthcoming EC research program will first be discussed briefly.

1.1 Soil Chemistry in Relation to the Filtering Function of Soil

Groundwater and surface water pollution may result from soil pollution. The risk depends on the persistency and the mobility of the pollutant and the mobility in the aqueous phase of the soil, subsoil or the aquifer depends strongly on its interaction with the solid matrix. Measuring, understanding and modelling the interaction of dissolved species with the soil solid matrix or with soil components is one of the central themes of soil chemistry. This branch of science is thus of direct relevance for the study of the relationship between soil quality evaluation and the filtering function.

1.2 Soil Chemistry in Relation to Crop Production

A major problem in the study of the relationship between soil quality and crop production and quality is to determine the **availability** of a pollutant. In general, there is no direct relationship between total amount of an element in the soil and the amount taken up by a plant growing in this soil. Uptake of pollutants may negatively influence the quality of consumable products. Often, with respect to toxicity of an element there is no direct relationship with the total amount in the soil. The toxicity may influence crop yields. The phytotoxicity of copper after any concentration is strongly dependent on the pH of the soil solution (Lexmond,1980). The pH affects both the distribution of the metal over the soil solution and the solid matrix as well as the distribution trough the soil solution and the plant root. One of the important chemical factors that may affect the availability or toxicity of an element is its distribution between different chemical forms (e.g. free ions, inorganic and organic complexes, various adsorbed species etc.). (De Haan and Van Riemsdijk, 1986; De Haan et al., 1987). As an obvious example, aluminium present in minerals like montmorillonite is almost completely unavailable and non-toxic, whereas dissolved Al^{3+} may be very toxic. Attempts to relate Al-toxicity to the total Al content of soils leads to erroneous results. Thus for a 'proper' definition of soil quality in relation to crop growth, it is necessary to be able to assess, understand and ideally to predict the forms in which a pollutant may be present in the soil system as a function of variables such as: pH, salt concentration, soil type, its concentration and temperature.

1.3 Soil Chemistry in Relation to Soil Ecosystems

Soil organisms such as earth worms, and soil microorganisms, interact with the soil environment amongst other factors through (ad)sorption of pollutants present in the soil solution on to the surface of the organism. This means that as with the factors discussed in the previous section, it is necessary to asses, understand and to predict the forms in which a pollutant may be present as a function of environmental variables. In addition to the interaction between the solution composition and the solid matrix the laws that determine the interaction between the composition of the soil solution and the surface of the organisms are required. **Cooperation between soil or surface chemists with soil biologists is necessary to obtain real progress in this field.** The work of Goncalves et al., (1987) is an example of an attempt to measure and interpret the interaction of metal ions with the surface of microbes using physical chemical methods and models.

2 SOIL CHEMISTRY IN RELATION TO SOIL QUALITY STANDARDS

Ideally a soil quality standard should be based on the risk that a given pollution concentration in given circumstances has no negative effects on the soil functions already listed. The composition of the soil solution often plays an important role and is strongly dependent on many (chemical) environmental factors.

A soil quality standard can be established directly or indirectly. An upper tolerable limit for the pollutant content in groundwater or in an edible product may be used to derive a maximum tolerable limit for a given soil. In order to be able to do this for water quality or product quality much fundamental physical, chemical and biological knowledge, that is often lacking, is required. Present knowledge indicates that such an indirectly derived soil quality standard will vary with soil type. For a proper risk assessment it is necessary to incorporate the variability of physical and chemical parameters in the field into the risk assessment model (De Haan et al., 1987; Van der Zee et al., 1987b; Van der Zee et al., 1988a,b)

3 SOIL CHEMICAL KNOWLEDGE THAT SHOULD IDEALLY BE AVAILABLE

In order to be able to interpret the effect of pollution on various soil functions and thus to be able to define soil quality, the bio-availability of a pollutant and its concentration in the soil solution as a function of the pollution load for any soil has to be determerd. **For these purposes the distribution of a chemical over all its possible forms has to be predicted in a relatively detailed and quantitative manner.** Present knowledge is too limited, to do this given the complexity of the problem that has to be solved. In the following paragraphs the state of the art in to this area is critically reviewed, with the emphasis on the most recent literature.

4 THE CHEMICAL HETEROGENEITY OF SOIL AND ITS EFFECTS ON SOIL CHEMISTRY AND SPECIATION

4.1 General Introduction

Soil is as a complex mixture of inorganic and organic constituents. The inorganic fraction may contain silica (SiO_2); metal (hydr)oxides of iron, aluminium, manganese and titanium; clay minerals like illite, montmorillonite, kaolinite; calcium carbonate and primary minerals like feldspars. The Soil Organic Matter, SOM, fraction of the soil is often split operationally in to a humic acid, fulvic acid and humine fractions (Schnitzer and Kahn,1972). The inorganic fraction often consists partly of crystalline relatively pure minerals and partly of more amorphous not very clearly defined solid phases. The composition of this highly complex matrix obviously differs considerably with soil type. A clay soil has a relatively high fraction of clay minerals, in contrast to sandy or peaty soils which have a relatively low fraction. However, even within one soil type, and even within one field, the composition varies.

The interaction of a chemical with the soil matrix may be controlled by surface chemical phenomena like specific adsorption or ion exchange and/or by the formation of solid phases containing the chemical (Van Riemsdijk and Van der Zee, 1989b). Which type of process is dominant not only depends on the chemical or soil type, but also on the environmental conditions prevailing in the soil solution such as pH and redox potential. For instance, adsorption of cadmium on the reactive surfaces of the soil is dominant under oxidized conditions with $pH<7$, whereas precipitation as cadmium carbonate is dominant for oxidized conditions and $pH>7$ (Brümmer,1981) and precipitation as cadmium sulfide is dominant under reducing conditions.

Because of the complexity of the soil matrix, it is difficult to define the nature and extent of the reactive surfaces present in a soil sample. A multitude of different reactive surfaces exist, each possessing a multitude of different types of reactive groups. The affinity of the various reactive sites for a specific chemical may vary considerably. The distribution of a chemical over the solution and the solid matrix is a function of the composition of the solid matrix. A simple example will illustrate this. If a "soil" consisted of only pure quartz grains, the available reactive surface would be very small and hardly any adsorption will occur but adding a few percent of iron oxide or SOM, both being characterised by a high surface area per unit mass, may lead to a considerable adsorption.

4.2 Analysis of Surface Heterogeneity and Heterogeneous Adsorption Models

The chemical heterogeneity of a reactive surface influences the adsorption behaviour of a chemical. The (intrinsic) chemical heterogeneity is characterised by the distribution of sites, with respect to their affinities for a chemical, over the total number of sites. Such a distribution is called the affinity distribution. This can be determined by analyzing the adsorption isotherm. Various mathematical techniques are available for this purpose (Nederlof et al.,1988; Nederlof et al.,1989; Sacher and Morrison, 1979; Vos and Koopal, 1985). Complications are the variable charge character of certain reactive surfaces, the number and accuracy of the data which affect the analysis and the effect of other ions competing for the same sorption sites. Another problem is that often only a part, "window", of the isotherm can be measured. For special types of affinity distributions, the general isotherm is a simple mathematical function (Jaroniec, 1983; Sips, 1948; Sips, 1950; Toth et al., 1974; Van Riemsdijk et al., 1986, 1987a). If it is assumed that the affinity distributions for various adsorbing species have a similar shape, competitive multi component analogues of the mono component heterogeneous adsorption equation can be derived (Jaroniec, 1983; Van Riemsdijk et al., 1986, 1987a). The advantage of these heterogeneous adsorption equations is that only one extra parameter is added to these describing the homogeneous conditions. This extra parameter characterizes the width of the distribution function: the wider the affinity distribution, the more heterogeneous is the reactive surface. This type of equations can also be used to describe ion exchange (Sposito, 1980).

4.3 Effects of Competition and Complexation

The distribution of an element over the solution and the soil solid phase(s) is not only a function of the composition of the solid matrix, but also of the solution composition. For instance adsorption of metals is strongly dependent on the pH of the solution (Chardon, 1984; De Haan and Van Riemsdijk, 1986; De Haan et al., 1987; Van der Zee et al., 1988b). Apart from the pH, the adsorption may be influenced by the presence of other species that compete for the same sorption sites. An example is the influence of the zinc and calcium concentration on the cadmium adsorption in soils (Christensen,1987 ; Chardon, 1984). Because soil is often polluted with a mixture of metals, competition may in such cases considerably reduce the adsorption of the weakly adsorbing metals such as cadmium compared with pollution by only one metal. This causes enhanced mobility and bioavailability (Schmitt and Sticher, 1986). The combination of competitive adsorption and transport in the soil may even lead temporarily to concentrations in the soil solution that are higher than the input concentration (Schmitt and Sticher, 1986)!

Formation of soluble complexes may also greatly affect the interaction with the solid phase. The formation of complexes with inorganic ligands, e.g. $CdCl^+$, and organic ligands, e.g. complexes of metals with organic ligands like citrate, often reduce (Chardon, 1984) the amount adsorbed for a given total solution metal concentration, because the affinity of the metal complexes for the surface sites may be appreciably lower than that of the free metal ion. The work of Schmitt and Sticher (1986) clearly shows that cadmium adsorption may be considerably reduced in the presence of other metal ions, leading to a much higher mobility in practice than is anticipated from laboratory experiments that neglect effects of competition and complex formation.

In fig. 1, the large variation in metal adsorption that may occur for one and the same soil as a function of different solution compositions is illustrated for cadmium. In this case the ionic strength, the chloride concentration and the calcium concentration are the variables influencing the shape of the cadmium isotherm.

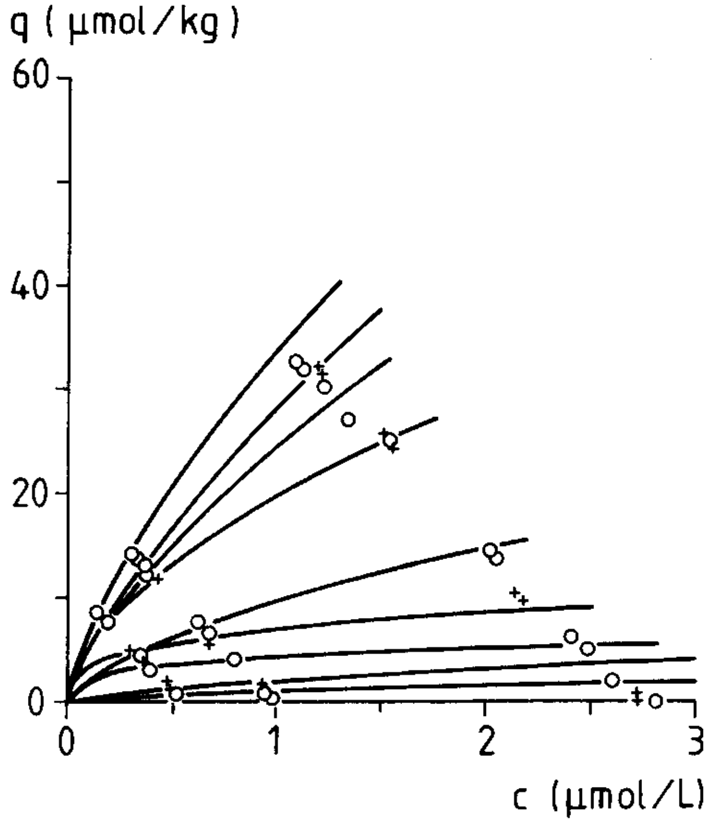

Figure 1 Cadmium sorption on one soil, q, as a function of the cadmium concentration in solution, c, for different values of ionic strength, chloride and calcium concentrations in solution.

4.4 Critical Evaluation of Existent (Chemical) Methodologies Dealing with the Complexity of Soil Systems

The preceding arguments show that natural variation in both the solution composition and the composition of the solid matrix may lead to a very large variation in the distribution behaviour of one and the same chemical in different locations. It is thus far from simple to obtain information that has general validity, which for the purposes of a European policy on soil quality is required. Several approaches can be found in the soil chemical literature that are attempt to obtain this type of information.

One approach is to discriminate the total content of a chemical over various operationally defined fractions in the solid phase. This solid phase 'speciation' is obtained by employing sequential extraction procedures. For metal speciation in sediments the following fractions are "defined" by sequential extraction (Chao, 1972; Förstner et al., 1979; Salomons and Förstner, 1984; Tessier et al., 1979; Unger and Allen, 1988);

1) exchangeable metals plus metals associated with calcium carbonate;
2) metals presented in easily reduced phases, mainly metals associated with manganese oxides and partly also associated with amorphous iron oxides;
3) metals associated with amorphous and poorly crystalline iron oxides;
4) metals associated with organic matter or present as metal sulphides, and
5) a residual fraction

Sequential extraction with different extraction agents by definition leads to different metal fractions. Whether the fractions obtained do indeed represent the various pools is questionable. Gruebel et al. (1988) tested a sequential extraction procedure for arsenic and selenium using well characterized minerals. Their work shows that the various phases may not always be identified correctly.

Identifying operationally defined fractions in itself does not lead to the possibility of predicting the interaction between a chemical and different soils, sediments and aquifer materials. One step in that direction is the work of Unger and Allen (1988) who combined the measurement of the partitioning of a metal over the solution phase and the sediment with a sequential extraction procedure. In this way they were able to 'speciate' the amount (ad)sorbed as a function of the loading of the sediment with the metal. They estimated a binding capacity and an average equilibrium 'constant' for each of the five fractions that were discriminated in this study. How this binding capacity is related to soil or sediment type was not part of their study.

The relation between soil characteristics and the observed overall interaction behaviour of a chemical can be studied by measuring the partitioning of a chemical over solution and solid phase for a whole range of different soils and sediments (McLaren et al., 1986; Gerritse et al., 1982). Although the methodology in itself is promising, there are some serious problems that may explain why the results published so far are often disappointing. The first is that the soil characteristics measured are poorly (operationally) defined and are not necessarily good estimators for the various types of reactive surfaces present.

The second, very important, problem is that the chemical composition of the aqueous phase from which the adsorption is studied generally varies with the different soils. Although the same electrolyte may be added to all soils, the resulting aqueous medium is **not** the same. An obvious and very important factor is the pH of the aqueous phase which is buffered by the soil particles, resulting in different pH values of the electrolyte solutions. Since the pH influences most chemical interactions in soil, the result of such a study is sometimes that the pH is **the** soil characteristic responsible for differences in behaviour between various soils (Gerritse, 1982). This suggests that different soils when brought to the same pH should show the same adsorption behaviour. This is obviously not true. Another example of unintentional differences in the resulting composition of the aqueous phase is the presence of a variable amount of competitor species. Studying cadmium adsorption for a range of soils will in general lead to a release of a variable amount of zinc ions, the resulting cadmium adsorption is not only a function of the various reactive surfaces being present and the resulting pH, but also depends on the degree of competition with zinc ions (Christensen, 1987).

The third problem is that soils as sampled may already contain a varying amount adsorbed of the species of interest. To be able to make a good comparison between the different soils, the desorption behaviour of the species of interest should be studied. Studying desorption is often extremely difficult, especially that of high affinity adsorption, i.e. a steep ad(de)sorption isotherm. Recently a promising new methodology for studying phosphate desorption has been developed (Van der Zee et al., 1987a).

Another approach in trying to obtaining results of a more general validity for a wide range of soils is to study the interaction of a chemical with various soil components as a means to interpret the difference in behaviour between various soils or sediments. An example is the work of McLaren et al.,(1986) who studied the adsorption of cobalt with different soil components and also with different soils. At present, this procedure is also not successful mainly for two reasons. The first is that the fundamental knowledge about the physico chemical interaction mechanisms between species and the various soil components is at present not well enough established. McLaren et al.,(1986) used empirical equations to describe the measured interaction with soil components. The measurements with the soil components were done for a very limited range of solution conditions, at one pH only, and the empirical model used does not allow for estimating the interaction behaviour for other solution conditions than those of the measurements. The adsorption measurements with the different soils were done with one electrolyte solution resulting in different pH values for the different soils studied. Comparison between these adsorption measurements and those of soil components based on one pH measurement is bound to fail.

The second important difficulty is to establish the content and nature of the various reactive surfaces present in a soil sample.

For the development of general applicable soil chemical knowledge that can be used to interpret the bio-availablity, toxicity and mobility of pollutants, it is essential to have insight into the fundamental physical chemical interaction of species with soil components. In the next section the state of the art with respect to modeling of adsorption of ions on soil components is reviewed.

5 REVIEW OF STATE OF THE ART OF ADSORPTION MODELS FOR SOIL COMPONENTS

5.1 Adsorption Models for Clay Minerals

Clay minerals, such as illite and montmorillonite, are 'platy' crystals that exhibit a constant negative surface charge on the plate sides of the minerals, leading to positive adsorption of cations and negative adsorption of anions. The adsorption capacity of the constant charge faces is called the Cation Exchange Capacity, CEC. The theory of cation exchange is well established (Bolt, 1982; Sposito, 1981). In practice semi-empirical exchange equations are often used to describe cation exchange. Examples are the Gapon, the Vanselow, and the Gaines Thomas equations. Another possibility is to apply the earlier mentioned analytical heterogeneous adsorption models (see 4.2) to ion exchange (Sposito, 1980). The exchange can also be predicted based on diffuse double layer theory. Recently, a new semi-theoretical approach to cation exchange has been presented (Bruggenwert et al., 1987). The cation exchange on clay minerals is an important process for description of the interaction of cations in solution with the soil solid phase that are present in considerable concentration, like Na^+, K^+, Ca^{2+}, and under strongly acid conditions also Al^{3+}.

For adsorption of species that occur in trace quantities, i.e. most pollutants, the edge faces of clay minerals may dominate the interaction behaviour. The surface of these edges resembles those of metal oxides, leading to variable charge characteristics. A complication is that the electric field emanating from the constant charge surface may influence the charge on the edge faces of the clay mineral (Secor and Radke, 1985). This effect and the influence it has on the interaction of cations and anions on the edge faces of clay minerals has hardly been investigated so far. Another interesting aspect is the interaction of clays with aluminium hydroxide polymers. This combination seems to be very reactive for the specific adsorption of heavy metal ions (Keizer and Bruggenwert, 1989) .

5.2 Adsorption Models for Metal Oxides

Metal (hydr)oxides of iron, aluminium, manganese and titanium are important reactive surfaces in soils, aquifers and sediments with respect to interaction with positively charged species like H^+, Al^{3+}, Cd^{2+}, Zn^{2+}, Pb^{2+} and Cu^{2+} and with negatively charged species like phosphate, arsenate, sulphate, selenite, borate and fluoride. Organic species may also adsorb on metal oxides (Kummert and Stumm, 1980). The adsorption of species on oxides is strongly dependent on the pH; this is caused principally by the variable pH dependent surface charge and potential of metal (hydr)oxides.

5.2.1 Relationship between surface charge (potential) and pH

Metal oxides are amphoteric surfaces which may be either positively or negatively charged depending on the pH of the system. The pH at which the metal(hydr)oxide is uncharged is called the point of zero charge, pzc. The pzc of metal (hydr)oxides differs considerably, ranging from 2 for silica to around 10 for some iron oxides. The primary surface charge, in the absence of specific adsorptions of ions other than H^+, depends on the pH and on the electrolyte concentration or ionic strength. The most widely used model to interpret the variable charge characteristics is the so called two pK model (Davis et al., 1978; Davis and Leckie, 1978; Schindler et al., 1976; Sigg and Stumm, 1981; Westall and Hohl, 1980; Zachara et al., 1987). In this model it is assumed that there is only one type of reactive group present on the surface of a metal (hydr)oxide that may react with protons according to the following two reactions,

$$SO^- + H_s^+ \rightleftarrows SOH^0 \qquad ;K_{H1}$$

$$SOH^0 + H_s^+ \rightleftarrows SOH_2^+ \qquad ;K_{H2}$$

where SO^-, SOH^0, SOH^{2+} represent three **different surface species** belonging to **one and the same reactive surface oxygen group**, and H^+_s is the proton concentration near the plane of adsorption which is related to the concentration in solution, $[H^+]$, via,

$$[H_s^+] = [H^+]\exp(-F\psi_0/RT)$$

where ψ_0 is the surface potential. In order to be able to model the variable charge characteristics, an additional expression is required that relates the surface charge and the surface potential. This relationship is provided by assuming a specific double layer model. In the 'oxide' literature different approaches can be found. Sometimes only a diffuse Gouy Chapman double layer is assumed (Healy and White, 1978), or it is assumed that the ratio between surface charge and potential is constant leading to the so called constant capacitance model (Kummert and Stumm, 1980; Schindler et al., 1976; Sigg and Stumm , 1981), or a combination of a Stern layer with a Gouy Chapman double layer often indicated as the Basic Stern model is used (Hiemstra et al., 1987, 1989a, 1989b; Van Riemsdijk et al., 1986; Van Riemsdijk et al., 1987a,b; Westall and Hohl, 1980), or a model where three planes near the surface plus a diffuse double layer model is used which is called the triple layer model (Benjamin and Leckie, 1981, Davis et al., 1978; Davis and Leckie, 1978). The basic charging reactions in all these approaches are equal, they only differ in the relation(s) used to relate the surface charge and the surface potential. A disadvantage of the constant capacitance model is that it cannot be used to describe the charging at variable salt level, since the 'constant' capacitance is in practice a function of the salt concentration. A disadvantage of the triple layer model, as used in the literature is that, in addition to the reactions with protons, pair formation with simple electrolyte ions such as sodium and chloride has also to be included in the model, and this increases the number of adjustable parameters. These variable charge, variable potential, models have been successfully used to describe surface charge-pH curves as a function of salt level for various metal (hydr) oxides. The model parameters, the two proton affinity constants and the Stern layer capacitance are treated as adjustable parameters. The proton affinity constants may differ considerably for various metal (hydr)oxides.

An alternative to the two pK model is the one pK model (Hiemstra et al., 1987, 1989a, 1989b; Van Riemsdijk et al., 1986, 1987a, 1987b); this assumes that the basic charging reaction can be described with the following reaction,

$$SOH^{1/2-} + H^+_s \rightleftarrows SOH_2^{1/2+} \qquad ; K_H$$

The surface charge is dependent on the ratio between the two different species belonging to the same surface group. It follows from this model that log K_H equals the pzc of the metal (hydr)oxide. The advantage of the one pK model is its extreme simplicity, the fact that it has one parameter less than the two pK model and that the proton affinity constant follows directly from the pzc. This one pK model gives as good a description of the available data as the two pK model for most metal oxides with the exception of silica.

Both the one and the two pK model approach assume the presence of only one type of reactive group. However, it is well known from infrared analysis that different types of surface oxygen groups are present on metal (hydr)oxides (Jones and Hockey, 1971; Lewis and Farmer, 1986; Parfitt et al., 1975). Surface oxygen may be singly, doubly or triply coordinated to an underlying metal ion. It is to be expected that the reactivity of these oxygen groups towards proton adsorption differ considerably. Recently a new model, the MUSIC (MUlti SIte Complexation) model, has been developed that takes these three different types of surface groups into account (Hiemstra et al., 1989a,b). Each type of surface group may react with two protons. The affinity constants for the proton adsorption reactions for the various groups of a range of different metal (hydr)oxides are **predicted** by the new model, leading to the possibility of **predicting** the variable charge behaviour of metal oxides. It predicts that the difference between the log K values for two consecutive proton adsorption reactions for one type of surface group is very large (around 14 log K units). The one and two pK models are special cases of this more general new model. The predictions are in good agreement with existing experimental data (Hiemstra et al., 1989b). It follows from the model that different crystal planes of the same metal (hydr)oxide may exhibit a quite different charging behaviour, due to a different composition with respect to the various types of reactive surface groups. This may have important implications for the specific adsorption of species other than protons on metal hydr(oxides). For gibbsite ($Al(OH)_3$) it predicts that the dominant crystal plane (001) is **uncharged** for pH values below ten, whereas a negative surface charge develops for pH values higher than ten. In the normal pH range only the edge faces will develop a (positive) surface charge. These predictions are also in accordance with experimental information (Hiemstra et al., 1989b). Specific adsorption of anions on gibbsite thus probably only occurs on the edge faces. This explains the different shape of the charging curve for silica compared with other oxides.

5.2.2 Specific adsorption of species other than protons

The modelling of specific adsorption of cations and anions based on the classical one and two pK metal oxide models is obtained by assuming the presence of one or more types of surface complexes for the specific adsorbing species, leading to the introduction of one or more extra adjustable parameters. Phosphate adsorption on iron oxides has been modelled in at least four different ways (Bowden et al., 1980; Sigg and Stumm, 1981; Goldberg and Sposito, 1984; Van Riemsdijk and Van der Zee, 1989b). All approaches lead to a reasonable description of the phosphate adsorption as a function of pH and phosphate concentration. The number of different phosphate species, and thus also the number of extra parameters, ranges from one (Van Riemsdijk and Van Der Zee, 1989b) to five (Sigg and Stumm, 1981). To descripe the adsorption of cadmium on iron oxides different approaches, all based on variable charge models, have been adopted (Van Riemsdijk et al., 1987a; Fokkink, 1987). Spectroscopic methods (Motschi, 1987) may be helpful in identifying the exact nature of the surface complex. If clear evidence of the nature of the surface complexes is available, then the formation constants of these complexes can be calculated using variable charge models and experimental information on the adsorption of each of the species.

Although sometimes more than one type of surface complex is invoked to describe the adsorption of a certain element, normally the basic assumption is only the presence of one type of reactive group (that may form various surface complexes) since the modelling is based on the classical one or two pK model. It has been suggested in the literature (Benjamin and Leckie, 1981) that adsorption of metal ions on oxides can only be modelled satisfactorily when the surface is considered to be heterogeneous.

Anyhow, it is to be expected that as with protons, the affinity for other species reacting with the different types of surface groups (singly, doubly, triply coordinated) may vary considerably. An extra complication is the presence of various crystal planes and, in soils, the presence of different metal oxides. Although recently insight in to the variable charge characteristics of oxides has increased considerably, the present state of the art of modelling of specific adsorption of species other than protons is far from satisfactory.

5.3 Adsorption Models for Soil Organic Matter

Soil organic matter is considered to be a very important reactive component of many soils, both for ion adsorption and for adsorption of organic pollutants. Ion adsorption is discussed first.

5.3.1 Ion adsorption models for soil organic matter

Soil organic matter, SOM, is chemically very heterogeneous because of the presence of various types of functional groups, e.g. alcoholic, phenolic, carboxylic OH groups and to a minor extent also reactive nitrogen and sulphur containing groups. Their affinity for protons and metal ions differs considerably. The reactivity of a certain group, e.g. a phenolic -OH group, is also a function of the other in its neighbourhood. Soil organic matter exhibits variable charge characteristics as discussed for metal oxides. The primary surface charge and potential is determined by the proton concentration in solution and the ionic strength. Specific adsorption of ions other than H^+ have a secondary influence on the surface charge. A difference with the metal oxides is that SOM is mainly negatively charged, the more so the higher the pH, whereas metal oxides may be either positively or negatively charged depending on the pH. The variable charge characteristics of SOM and the competition of protons and metal ions for the same sorption sites cause that metal ion adsorption on SOM is pH dependent.

The description of metal ion adsorption on SOM at present is mainly done by assuming a set of hypothetical ligands. Apparent binding constants that apply to one pH and ionic strength are determined by fitting, very limited experimental data, to a very simplistic model. Recently a review on this of approach has been presented (Sposito, 1986). An obvious disadvantage of such a procedure is that the number of hypothetical ligands that has to be chosen to describe the data is arbitrary. The apparent affinity constants obtained depends strongly on the number of ligands presumed (Dzombak et al., 1986a,b). Moreover, if binding of several metal ions are studied independently, at the same pH, the result for a mixture of metals is not predicted correctly (Hering and Morel, 1988). A somewhat different approach is to use a mixture of simple organic ligands and to use stability constants as given in literature for the chosen ligands. It thus assumes that the behaviour of a macro-molecule may be mimicked by using a mixture of monomers. That this is not realistic can simply be shown by comparing the behaviour of a simple poly-electrolyte with only one structural unit and the corresponding monomer. The difference between the two is that the dissociation of the (identical) groups becomes increasingly more difficult with progressing dissociation, i.e. with increasing pH, because of the build up of the electric field around the macro-molecule. The effective or apparent proton affinity 'constant' becomes larger than the intrinsic proton affinity constant for the macro-molecule, whereas, for the monomer, the effective affinity constant is not affected by the pH. This may explain why the results of this ligand mixture approach are disappointing (Baham and Sposito, 1986;).

Recently, the results of a few attempts have been presented which try to combine the variable charge characteristics with the intrinsic chemical heterogeneity into one adsorption model (Ephraim et al., 1986; Ephraim and Marinsky, 1986; Tipping et al., 1988). However, in neither attempt, were the authors able to determine the chemical heterogeneity independently and the variable charge characteristics from experimental information. *A priori* simplifying assumptions had to be made about the nature of the chemical heterogeneity.

The results of Tipping et al. (1988) seem especially encouraging. The model developed, based on experiments with purified organic matter, was reasobably successful in correlating data collected from different surface waters. The research was mainly aimed at describing the binding of aluminium to organic matter in acid organic soils (Tipping and Hurley, 1988).

Very recently, a methodology has been proposed which makes it possible to estimate independently the intrinsic affinity distribution and the double layer model, both of which are required to describe are variable charge characteristics of SOM (De Wit et al., 1988; Nederlof et al., 1988). Preliminary results obtained by application of this approach to sets of data available in literature, for fulvic and humic acids, are promising (De Wit et al., 1989).

For transport of those pollutants in soil and aquifers that may adsorb onto SOM, it is very important to know under what conditions which part of the SOM may be present in the soil solution. The presence of pollutants in the soil solution adsorbed onto dissolved soil organic matter may enhance the mobility of these pollutants. The 'solubility' of SOM depends amongst other things on the size of the molecules. Fulvic acids are smaller and more soluble than the larger humic acids. The surface charge is also an important factor in the solubility, a high surface charge seems to promote the solubility (Tipping et al., 1988). Cross linking of soil organic molecules may be promoted by specifically adsorbed metal ions, leading to the formation of larger aggregates, which are less soluble. The chemical nature of dissolved organic matter may be a function of the soil type and the vegetation growing on the soil (Aris and Ziechmann, 1988).

5.3.2 Adsorption of hydrophobic organic pollutants

Hydrophobic organic pollutants may adsorb on to SOM. The behaviour of these pollutants depends on their water solubility, volatility, viscosity, melting point, and the octanol water distribution coefficient, K_{ow}.

Jury and co-workers (Jury et al., 1983; Jury et al., 1984a,b,c; Jury et al., 1987) have developed assessment models aimed at assessing the relative pollution hazard of organic chemicals. They do this by calculating the persistence and the mobility, both in the gas phase and the solution phase, of various chemicals for specified conditions for a few soil types. Most parameters required for their model can be simply estimated from basic chemical properties. The soil water distribution coefficient is estimated from the octanol water distribution coefficient and the soil organic matter content. The water air distribution coefficient, the Henry constant, if not available as such can be estimated from the solubility of the chemical and its saturated vapour pressure. The microbial degradation is calculated by assuming first order decay. The content of an organic chemical in the soil at a certain depth may decrease due to, degradation, volatilization to the atmosphere, or due to leaching to deeper soil layers. Jury et al. (Jury et al., 1983; Jury et al., 1984a,b,c; Jury et al., 1987) specially emphasize the volatile organic chemicals. These substances can spread rapidly through the soil to the ground water by means of transportation through the gas phase of the soil, as they may leave the soil by volatilization.

Various empirical models have been used to relate the K_{ow} to the distribution coefficient that is applicable for the distribution over the solution phase and the SOM, the K_{oc} (Karickhoff et al., 1979; Chiou et al., 1983). There is evidence that the type of organic matter (e.g. $A_{horizon}$ or $B_{horizon}$) may influence the value of the K_{oc}.

The soil water distribution coefficient is also dependent on the type of organic molecule being adsorbed. Recently a model has been presented from which the soil water distribution coefficient can be calculated from the chemical structure of the adsorbing molecule (Sabljic, 1987). The model is applicable to nonionic organic chemicals.

For specific organic chemicals and soil types, other sorbents than SOM may be of importance, e.g. clay minerals and metal oxides.

Ionizable hydrophobic chemicals have a pH dependent charge. This in combination with the variable charge characteristics of SOM produces a strongly pH dependent distribution coefficient (Schellenberg et al., 1984; Westall, 1987). Adsorption of permanently charged hydrophobic compounds is also pH dependent, because of the pH dependent surface charge of the sorbent (SOM or metal oxide) (Westall, 1987)

6 CHEMICAL KINETICS

Sometimes chemical kinetics determine the behaviour of chemicals in soils. For instance the production of base cations by weathering of primary minerals in soil is completely determined by chemical kinetics and not by a rapidly dissolving which would allow the use of chemical equilibrium models. The dissolution kinetics of primary minerals and metal oxides is considered to be a surface controlled phenomenon. The magnitude of the pH dependent variable surface charge is an important variable in the description of the surface controlled 'dissolution' rate (Hiemstra and Van Riemsdijk, 1989; Stumm and Furrer, 1987). Hiemstra and Van Riemsdijk (1989) developed the MAC (Multi Activated Complex) model. With it, they were able to predict the pH and salt dependency of the dissolution rate of quartz using only one adjustable parameter. The 'dissolution' kinetics are also influenced by the formation of surface complexes with organic and inorganic ligands (Stumm and Furrer, 1987).

Sorption of pollutants may also be a relatively slow process. For a proper interpretation of the short term, as well as the long term, effects of a chemical has on the ecosystem, it is essential to be aware of and to be able to quantify the kinetics of the interaction processes. Slow sorption processes may be due to diffusion into microporous soil particles (Willet et al., 1988), due to the formation of a surface coating through which the reactant has to diffuse (Van Riemsdijk and Lyklema, 1980), or to a slow rearrangement of adsorbed molecules in a more stable, less active, configuration. A theoretical model has been developed that is applicable for a mixture of reactive particles that may differ in size, shape and porosity and which can be used for interpolation and extrapolation of many slow diffusion controlled reactions in soil (Van Riemsdijk et al., 1984; Van der Zee et al., 1989; Van der Zee and Van Riemsdijk, 1989). Examples can be found in the literature for slow sorption kinetics of anions such as phosphate (Van Riemsdijk et al., 1984), as well as for heavy metals (McLaren et al., 1986). In the last study it is not so much the slow kinetics that are emphasized but more the decrease of the reversibility of the reaction with increasing reaction time; this might be caused by rearrangement of adsorbed species to more strongly bound positions.

7 SOIL CHEMISTRY AND TRANSPORT

Available soil chemical knowledge, put in to the appropriate algorithms can be combined with soil water transport models. With such computer programs, the transport of chemicals in the soil can be calculated. In essence, there are two different methods of combining the two areas of research (Van Riemsdijk and Van der Zee, 1989a). The simplest and the most useful method is to treat the soil chemistry as a subroutine of the water transport program. However, doing this creates extra numerical dispersion. This 'mathematical' effect can be corrected by using an iteration technique (Cederberg et al., 1985; Herzer and Kinzelbach, 1989).

8 AREAS FOR SOIL CHEMICAL RESEARCH

8.1 General

In order to be able to interpret and define soil quality in a sensible way, one has to be able to deal with the variable composition of the soil solution and the soil solid phase. This variability strongly affects the distribution of a chemical over various species both in the solution phase and the solid phase. Knowledge of this distribution and the factors that affect it are of relevance to the interpretation of all soil functions considered in relation to soil quality. In the long run, only a fundamental approach will enable satisfactory progress in this area. Moreover a multi-disciplinary approach or for some problems even an interdisciplinary approach may be required. **Co-operation between the more fundamental oriented disciplines like soil chemistry, soil physics, and soil (micro)biology with the more effect oriented disciplines that deal with soil functioning is of utmost importance.**

It is thus recommended that joint research proposals should at least cover more than one discipline. Within such a group at least one "**reference**" soil should be used by the different disciplines as a means to exchange information.

8.2 Reactive Surfaces

Fundamental knowledge about the interaction of pollutants with reactive surfaces present in soil, like metal oxides, clay and soil organic matter is extremely important for a proper interpretation of soil quality.

8.2.1 Metal oxides

So far fundamental research of adsorption of chemicals on to metal oxides has been limited to relatively simple systems. Heavy metal ion adsorption is often studied with one metal ion, e.g. cadmium, in a 1:1 electrolyte, e.g. a potassium nitrate solution, as a function of pH under nitrogen atmosphere. To obtain insight in to the binding mechanisms such an approach is perfectly logical and justifiable. However in order to be able to apply knowledge about the surface chemistry of metal oxides to soil systems, more representative conditions of the soil system should be studied and they should incorporate the effect of competition between metal ions and the effect of relevant anions on the metal ion adsorption on metal oxides.

The theory of metal ion adsorption on metal oxides should also be further developed. Ideally such a theory leads to the possibility of *a priori* predictions of the intrinsic affinity constants for the interaction of various metal ions with the various surface groups of a series of relevant metal oxides. Such a theory has recently been developed for proton adsorption on metal oxides (Hiemstra et al., 1989a,b).

8.2.2 Clay

The ion exchange process has historically been emphasized in research on interaction of ions with clay. However, trace metals are present in the soil solution in minor quantities compared to the major cations like Ca^{2+}, K^+ and Na^+. Adsorption and interpretation of trace metals in the presence of common cations in concentrations relevant for the soil has not had much attention. Possible competition between metals is similarly as for metal oxides an important issue. Specific adsorption of metal ions on clay at low concentrations is probably quite different from normal ion exchange.

8.2.3 Soil organic matter

Only very recently has progress has been made in applying physical chemical models to the binding of ions to soil organic matter. Since soil organic matter is believed to be one of the most important reactive surfaces, this area needs much more attention.

The functional groups present on soil organic matter supposedly resemble those present on roots of plants or on the surface of soil microorganisms. Partitioning of metals over the soil solution and the surface of the soil organic matter, or partitioning over soil solution and the surface of plant roots or of bacteria may thus be described with similar interaction models.

Transport of chemicals adsorbed on to dissolved organic matter may often dominate the transport of slightly soluble chemicals. This process may strongly influence the mobility and the bioavailability of such chemicals. It is thus important to establish quantitatively the factors that influence the solubility of soil organic matter. This is an extremely important, but also extremely difficult area of research, because of the many factors that influence the solubility of soil organic matter.

Adsorption of organic matter on to metal oxides and clay may influence the adsorption properties of the system in such a way that the combined effect does not equal the sum of the individual parts. Theoretical and experimental work in this area of research is of importance.

8.3 Whole Soil

8.3.1 Desorption

Development of new techniques to study desorption of metals already present in the soil is of great practical importance. Such techniques may help to evaluate the potential risk of soil pollution.

8.3.2 Characterization of soil surfaces

In order to be able to compare results obtained from different soils, it is necessary to establish the differences in (surface) composition between them. For this purpose, techniques that can establish the quantity and type of reactive surfaces in soils, directly or indirectly, are needed.

8.3.3 Interaction of metals for a range of soils and a range of solution conditions

In order to be able to apply knowledge of the surface chemistry of soil components to soil systems, it is necessary to have a large data set for the interaction of chemicals (e.g. metals) with soils of different composition. The interaction should be measured for each soil for a wide range of well characterized solution conditions. The soils should be characterized as well as possible for each type and quantity of reactive surfaces present. Such a data set would give the opportunity of testing how far existing or newly developed physical chemical models describe the variability of the data set. The challenge is to describe the variability with as few adjustable parameters as possible. Once such a procedure is successful, the validated models could be used to estimate the speciation for any given soil by measuring only the relevant soil characteristics. Such a tool could be very useful in helping to establish criteria for soil quality. It could also be useful in helping to interpret results of effect-oriented soil research.

8.3.4 Hydrophobic organic pollutants

The chemistry of uncharged hydrophobic chemicals in soils seems to be rather well established. An important lacking piece of information is the possibility of transport with dissolved organic matter. Thus issue has been discussed in section 5.3.

Another possible area for research is how the pH and salt level affect the distribution of ionic and ionizable organic pollutants over the solution and the solid phase of the soil. This subject can also only be studied satisfatorily in combination with research on the charging behaviour of soil organic matter. This is necessary becuase it is the interaction of the variably charged soil organic matter and the charged organic pollutant that causes the pH and salt dependency of the distribution coefficient. Thus in order to make progress in this area of research, a thorough understanding of the physical chemical behaviour of soil organic matter is required. At present that knowledge is very limited.

9 PRIORITIES OF RESEARCH FOR SOIL CHEMICAL ASPECTS OF SOIL QUALITY

- Since soil organic matter influences the behaviour of many pollutants in soil, and because knowledge of soil organic matter is at present very limited, research in to soil organic matter (as described in paragraph 8.2.3) is the first priority.
- Second is the research area 'whole soil', (paragraphs 8.3.1-8.3.3). Within this area the collection of the data set (8.3.3) has the highest priority, followed by the development of techniques for the characterization of soil surfaces (8.3.2).
- Third is research on metal oxides (8.2.1).
- Fourth are the hydrophobic organic pollutants. This lower priority results from the fact that knowledge of the uncharged hydrophobic pollutants, is already considerable, but knowledge of the physical chemical behaviour of soil organic matter needs to be improved.

10 BIBLIOGRAPHY

Aris, J. and Ziechmann, W. (1988) Interactions of organic matter and alluminum ions in acid forest soil solutions: metal complexation, flocculation, and precipitation. **Soil Science 145,** 437-447

Baham, J. and Sposito, G. (1986) Proton and metal complexation by water-soluble ligands extracted from anaerobically digested sewage sludge. **J. Environ. Qual. 15,** 239-244

Benjamin, M.M. and Leckie, J.O. (1981) Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. **J. Colloid Interface Sci. 79,** 209-221

Bolt, G.H. (1982) **Soil Chemistry B. Physico-chemical models**, 2nd ed. Elsevier, Amsterdam 479 pp.

Bowden, J.W., Nagarajah, S., Barrow, N.J., Posner, A.M. and Quirk, J.P. (1980) Describing the adsorption of phosphate, citrate and selenite on a variable charge mineral surface. **Aust. J. Soil Res. 18,** 49-60

Bruggenwert, M.G.M., Keizer, P. and Koorevaar, P. (1987) Adsorption of aluminium ions by montmorillonite: influence of aluminium speciation. **Neth. J. Agric. Sci. 35,** 259-269

Brümmer, G. (1981) Adsorption und desorption oder ausfällung und auflösung als lösungskonzentration bestimmendes vorgänge in Böden. **Mitteilgn. Dtsch. Bodenkundl. Gesellsch. 30,** 7-18

Cederberg, G.H., Street, R.L. and Leckie, J.O. (1985) A groundwater mass transport and equilibrium chemistry model for multi-component systems. **Water Resources Res. 21,** 1095-1104

Chao, L.L. (1972) Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. **Soil Sci. Soc. Am. Proc. 36,** 764-768

Chardon, W. (1984) **Mobility of cadmium in soils. (In Dutch)** Serie Bodembescherming No 36. Staatsuitgeverij, 's-Gravenhage, 200 pp.

Chiou, C.T., Porter, P.E. and Schmedding, D.W. (1983) Partition equilibria of nonionic organic compounds between soil organic matter and water. **Environ. Sci. Technol. 17,** 227-231

Christensen, T.H. (1987) Cadmium soil sorption at low concentrations: VI. A model for zinc competition. **Water Air and Soil Pollution 34,** 305-314

Davis, J.A., James, R.O. and Leckie J.O. (1978) Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. **J. Colloid Interface Sci. 63,** 480-499

Davis, J.A. and Leckie J.O. (1978) Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhdroxide and adsorption of metal ions. **J. Colloid Interface Sci. 67,** 90-107

De Haan, F.A.M. and Van Riemsdijk, W.H. (1986) Behaviour of inorganic contaminants in soil. In: J.W.Assink and W.J. van den Brink (Eds.), **Contaminated soil.** Martinus Nijhoff,Dordrecht, p. 19-32.

De Haan, F.A.M., Van der Zee, S.E.A.T.M and Van Riemsdijk, W.H. (1987) The role of soil chemistry and soil physics in protecting soil quality: variability of sorption and transport of cadmium as an example. **Neth.J.Agric.Sci. 35,** 347-359.

De Wit, J.C.M., Van Riemsdijk, W.H. and Koopal, L.K. (1988) Heavy metal ion binding on homogeneous and heterogeneous colloids. In: M.Astruc and J.N.Lester (Eds.) **Heavy metals in the hydrological cycle.** Selper Ltd, London, p. 369-376.

De Wit, J.C.M., Van Riemsdijk, W.H. and Koopal, L.K. (1989) Proton and metal ion binding on humic substances. In: (Eds.) **Metals speciation, separation and recovery.** Lewis Publishing company (in press)

Dzombak, D.A., Fish, W. and Morel, F.M.M. (1986a) Metal-humate interactions. I. Discrete ligand and continuous distribution models. **Environ. Sci. Technol. 20,** 669-675.

Dzombak, D.A., Fish, W. and Morel, F.M.M. (1986b) Metal-humate interactions II. Application and comparison of models. **Environ. Sci. Technol. 20,** 676-683.

Ephraim, J., Alegret, S., Mathuthu, A., Bicking, M., Malcom, R.L. and Marinsky, J.A. (1986) A unified physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids). II. Influence of polyelectrolyte properties and functional group heterogeneity on the protonation equilibria of fulvic acid. **Environ. Sci. Technol. 20,** 354-366

Ephraim, J. and Marinsky, J.A. (1986) A unified physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids). III. Influence of polyelectrolyte properties and functional group heterogeneity on the copper ion binding equilibria in an Armadale **Environ. Sci. Technol. 20,** 367-376

Fokkink, L.G.J. (1987) **Ion adsorption on oxides.** Ph. D. thesis, Agricultural University, Wageningen, 127 pp.

Förstner, U., Calmano, W., Conradt, K., Jaksch, H., Schimkus, C. and Schoer, J. (1979) Chemical speciation of heavy metals in solid waste materials (sewage sludge, minig wastes, dredged materials, polluted sediments) by sequential extraction. **Proc. Conf. Heavy metals in the Environment**, Amsterdam, 698-704

Gerritse, R.G., Vriesema, R., Dalenburg, J.W. and De Roos, H.P. (1982) Effect of sewage sludge on trace element mobility in soils. **J. Environ. Qual. 11,** 359-364

Goldberg, S. and Sposito, G. (1984) A chemical model for phosphate adsorption by soils; I. Reference oxide minerals. **Soil Sci. Soc. Am. J. 48,** 772-778

Goncalves, M.d.L.S., Sigg, L.M., Reutlinger, M. and Stumm, W. (1987) Metal ion binding by biological surfaces; voltametric assessment in presence of bacteria. **Sci. Tot. Environ. 60,** 105-119

Gruebel, K.A., Davis, J.A. and Leckie, J.O. (1988) The feasibility of using sequential extraction techniques for arsenic and selenium in soils and sediments. **Soil Sci. Soc. Am. J. 52,** 390-397

Healy, T.W. and White, C.R. (1978) Ionizable surface group models of aqueous interfaces. **Adv. Colloid Interface Sci. 9,** 309-345.

Hering, J.G. and Morell, F.M.M. (1988) Humic acid complexation of calcium and copper. **Environ. Sci. Technol. 22,** 1243-1237

Herzer, J. and Kizelbach, W. (1989) Coupling of transport and chemical processes in numerical transport models. **Geoderma** (in press)

Hiemstra, T., Van Riemsdijk, W.H and Bruggenwert, M.G.M. (1987) Proton adsorption mechanism at the gibbsite and aluminium oxide solid/solution interface. **Neth. J. Agric. Sci. 35,** 281-294.

Hiemstra, T., Van Riemsdijk, W.H. and Bolt, G.H. (1989) Multisite proton adsorption modelling at the solid/solution interface of (hydr)oxides: A new approach. I. Model description and evaluation of of intrinsic reaction constants. **J. Colloid Interface Sci.** (in press)

Hiemstra, T., De Wit, J.C.M. and Van Riemsdijk, W.H. (1989) Multisite proton adsorption modelling at the solid/solution interface of (hydr)oxides: A new approach. II. Application to various important (hydr)oxides. **J. Colloid Interface Sci.** (in press)

Hiemstra, T. and Van Riemsdijk, W.H. (1989) Multi activated-complex dissolution of metal(hydr)oxides: a thermodynamic approach applied to quartz. **J. Colloid Interface Sci.** (submitted)

Jaroniec, M. (1983) Physical adsorption on heterogeneous surfaces. **Adv. Colloid Interface Sci. 18,** 149-225.

Jones, P. and Hockey, J.A. (1971) Infra-red studies of rutile surfaces, part 2- hydroxylation, hydration and structure of rutile surfaces. **Trans. Faraday Soc. 67,** 2679-2685

Jury, W.A., Spencer, W.F. and Farmer, W.J. (1983) Behavaior assessment model for trace organics in soil. I. Model description. **J. Environ. Qual. 12,** 558-564

Jury, W.A., Farmer, W.J. and Spencer, W.F. (1984a) Behavaior assessment model for trace organics in soil. II. Chemical classification parameter sensitivity. **J. Environ. Qual. 13,** 467-572

Jury, W.A., Spencer, W.F. and Farmer, W.J. (1984b) Behavaior assessment model for trace organics in soil. III. Application of screening model. **J. Environ. Qual. 13,** 573-579

Jury, W.A., Spencer, W.F. and Farmer, W.J. (1984c) Behavaior assessment model for trace organics in soil. IV. Review of experimental evidence. **J. Environ. Qual. 13,** 580-586

Jury, W.A., Focht, D.D. and Farmer, W.J. (1987) Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradetion. **J. Environ. Qual. 16,** 422-428

Keizer, P. and Bruggenwert, M.G.M. (1989) Adsorption of heavy metals by clay-aluminiumhydroxide-complexes. In G.H.Bolt (Ed.) **Interactions at the soil colloid - soil solution interface.** (in press).

Koopal, L.K., Van Riemsdijk, W.H. and Roffey, M.G. (1987) Surface ionization and complexation models: A comparison of methods for determining model parameters. **J. Colloid Interface Sci. 118,** 117-136.

Kummert, R. and Stumm, W. (1980) Surface complexation of organic acids on hydrous γ-Al_2O_3. **J. Colloid Interface Sci. 75,** 373-385

Karickhoff, S.W., Brown, D.S. and Scott, T.A. (1979) Sorption of hydrophobic pollutants on natural sediments. **Water Res. 13,** 241-248

Lexmond, Th.M. (1980) The effect of soil pH on copper toxicity to forage maize grown under field conditions. **Neth. J. Agric. Sci. 28,** 164-183

Lewis, D.G. and Farmer, V.C. (1986) Infrared adsorption of surface hydroxyl groups and lattice vibrations an lepidocrocite (γ-FeOOH) and boehmite (γ-AlOOH). **Clay Minerals 21,** 93-100

Marinsky, J.A. and Ephraim, J. (1986) A unified physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids). I. Anlysis of the influence of polyelectrolyte properties on protonation equilibria an ionic media: Fundamental concepts. **Environ. Sci. Technol. 20,** 349-353

McLaren, R.G., Lawson, D.M. and Swift, R.S. (1986) Sorption and desorption of cobalt by soils and soil components. **J. Soil Sci. 37,** 413-426

Motschi, H. (1987) Aspects of the molecular structure in surface complexes; spectroscopic investigations. in: W.Stumm (Ed.) **Aquatic surface chemistry.** Wiley, New York, p. 197-219

Nederlof, M.M., Van Riemsdijk, W.H. and Koopal, L.K. (1988) Methods to determine affinity distributions for metal ion binding in heterogeneous systems. *In:* M.Astruc and J.N.Lester (Eds.) **Heavy metals in the hydrological cycle.** Selper Ltd, London, p. 361-368.

Nederlof, M.M., Van Riemsdijk, W.H. and Koopal, L.K. (1989) Determination of adsorption affinity distributions: a comparison of various methods related to local isotherm approximations. **J. Colloid Interface Sci.** (submitted)

Parfitt, L.R., Atkinson, R.J. and Smart, R.St.C. (1975) The mechanism of phosphate fixation by iron oxides. **Soil Sci. Soc. Amer. Proc. 39,** 837-841

Sabljic, A. (1987) On the prediction of soil sorption coefficients of organic pollutants from molecular structure: Application of molecular topology model. **Environ. Sci. Technol. 21,** 358-366

Sacher, R.S. and Morrison, I.D. (1979) An improved CAEDMON program for the adsorption isotherms of heterogeneous substrates. **J. Colloid Interface Sci. 70,** 153-166.

Salomons, W. and Förstner, U. (1984) **Metals in the hydrocycle.** Springer Verlag, Berlin, 344 pp

Schellenberg, K., Leuenberger, C. and Schwarzenbach, R.P. (1984) Sorption of chlorinated phenols by natural sediments and aquifer materials. **Environ. Sci. Technol. 18,** 652-657

Schindler, P.W., Fürst, B., Dick, R and Wolf, P.U. (1976) Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+}, Cu^{2+}, Pd^{2+} and Cd^{2+}. **J. Colloid Interface Sci. 55,** 469-475

Schmitt, H.W. and Sticher, H. (1986) Long term trend analysis of heavy metal content and translocation in soils. **Geoderma 38,** 195-207

Schnitzer, M. and Kahn, S.U. (1972) **Humic substaces in the environment.** Dekker, New York

Schwarzenbach, R.P. and Westall, J. (1981) Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. **Environ. Sci. Technol. 17,** 472-479

Secor, R.B. and Radke, C.J. (1985) Spillover of the diffuse double layer on montmorillonite particles. **J. Colloid Interface Sci. 103,** 237-244

Sigg, L.M. and Stumm, W. (1981) The interaction of anions and weak acids with hydrous goethite (α-FeOOH) surface. **Colloids and Surfaces 2,** 101-117

Sips, R. (1948) On the structure of a catalyst surface. **J. Chem. Phys. 16,** 490-495.

Sips, R. (1950) On the structure of a catalyst surface II. **J. Chem. Phys. 18,** 1024-1026.

Sposito, G. (1980) Derivation of the Freundlich equation for ion exchange in soils. **Soil Sci. Soc. Amer. J. 44,** 652-654

Sposito, G. (1981) **The thermodynamics of soil solutions.** Oxford Clarendon Press, 223 pp.

Sposito, G. (1986) Sorption of trace metals by humic materials in soils and natural waters. **CRC Critical Reviews in Environ. Control 16,** 193-229.

Stumm, W. and Furrer, G. (1987) The dissolution of oxides and aluminum silicates; examples of surface-coordination controlled kinetics. In: W.Stumm (Ed.) **Aquatic surface chemistry.** Wiley, New York, p. 197-219

Tessier, A., Campbell, P.G.C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. **Anal. Chem. 51,** 844-851

Tipping, E., Backes, C.A., and Hurley, M.A. (1988) The complexation of protons and aluminium and calcium by aquatic humic substances: a model incorporating bindig-site heterogeneity and macro-ionic effects. **Water Res. 22,** 597-611

Tipping, E. and Hurley, M.A. (1988) A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. **J. Soil Sci. 39,** 505-519

Toth, J., Rudzinsky, W., Waksmundzki, A., Jaroniec, M. and Solokowski, S. (1974) Adsorption of gases on heterogeneous solid surfaces: The energy distribution corresponding to a new equation for monolayer adsorption. **Acta Chim. Hung. 82,** 11-21.

Unger, M.T. and Allen, H.E. (1988) Distribution model of metal binding to natural sediments. In : M. Astruc and J.N. Lester (Eds.) **Heavy metals in the hydrological cycle.** Selper Ltd., London p. 481-488

Van der Zee, S.E.A.T.M., Fokkink, L.G.J. and Van Riemsdijk, W.H. (1987a) A new technique for assesment of reversibly adsorbed phosphate. **Soil Sci. Soc. Am. J. 51,** 599-604.

Van der Zee, S.E.A.T.M., Van Riemsdijk, W.H., Lexmond, Th.M. and De Haan, F.A.M. (1987b) Vulnerability in relation to physico-chemical compound behaviour and spatially variable soil properties. In: W. van Duijvenboden and H.G.van Waegeningh (Eds.) **Vulnerability of soil and groundwater to pollutants.** TNO, The Hague, p. 515-526.

Van der Zee, S.E.A.T.M., Nederlof, M.M., Van Riemsdijk, W.H. and De Haan, F.A.M. (1988a) Spatial variability of phosphate adsorption parameters. **J. Environ. Qual. 17,** 682-688

Van der Zee, S.E.A.T.M., Van Riemsdijk, W.H. and De Haan, F.A.M. (1988b) Transport of heavy metals and phosphate in heterogeneous soils. In: K.Wolf, W.J. van den Brink and F.J. Colon (Eds.) **Contaminated Soil '88.** Kluwer Academic Publishers, Dordrecht, p. 23-32.

Van der Zee, S.E.A.T.M., Van Riemsdijk, W.H. and Van Grinsven, J.J.M. (1989) Extrapolation and interpolation by time-scaling in systems with diffusion controlled kinetics and first order reaction rates. **Neth.J.Agric.Sci.** (in press)

Van der Zee, S.E.A.T.M. and Van Riemsdijk, W.H. (1989) Model for the reaction kinetics of phosphate with oxides and soil. In G.H.Bolt (Ed.), **Interactions at the soil colloid - soil solution interface.** (in press).

Van Riemsdijk, W.H. and Lyklema, J. (1980) The reaction of phosphate with aluminum hydroxide in relation with phosphate bonding in soils. **Colloids and Surfaces 1,** 33-44

Van Riemsdijk, W.H., Boumans, L.J.M. and De Haan, F.A.M. (1984) Phosphate sorption by soils. I. A diffusion-precipitation model for the reaction of phosphate with metal-oxides in soil. **Soil Sci. Soc. Am. J. 48,** 537-540.

Van Riemsdijk, W.H., Bolt, G.H., Koopal, L.K. and Blaakmeer, J. (1986) Electrolyte adsorption on heterogeneous surfaces: Adsorption models. **J. Colloid Interface Sci. 109,** 219-228.

Van Riemsdijk, W.H., De Wit, J.C.M., Koopal, L.K. and Bolt, G.H. (1987a) Metal ion adsorption on heterogeneous surfaces. Adsorption models. **J. Colloid Interface Sci. 116,** 511-522.

Van Riemsdijk, W.H., Koopal, L.K. and De Wit, J.C.M. (1987b) Heterogeneity and electrolyte adsorption:Intrinsic and electrostatic effects. **Neth.J.Agric.Sci. 35,** 241-257.

Van Riemsdijk, W.H. and Van der Zee, S.E.A.T.M (1989a) Multi component transport modelling of enhanced metal leaching using synthetic ligands. **Geoderma** (in press)

Van Riemsdijk, W.H. and Van der Zee, S.E.A.T.M (1989b) Comparison of models for adsorption, solid solution and surface precipitation. In: G.H.Bolt (Ed.), **Interactions at the soil colloid - soil solution interface.** (in press).

Vos, C.H. and Koopal, L.K. (1985) Surface heterogeneity analysis by gas adsorption ; improved calculation of the adsorption energy distribution using an algorithm named CAESAR. **J. Colloid Interface Sci. 105,** 183-196.

Westall, J. and Hohl, H. (1980) A comparison of electrostatic models for the oxide/solution interface. **Adv. Colloid Interface Science 12,** 265-294

Westall, J. (1987) Adsorption mechanisms in aquatic surface chemistry. In: W.Stumm (Ed.) **Aquatic surface chemistry.** Wiley, New York, p. 3-32

Willet, I.R., Chartres, C.J. and Naguyen, T.T. (1988) Migration of phosphate into aggregated particles of ferrihydrite. **J. Soil Sci. 39,** 275-282

Zachara, J.M., Girvin, D.C., Schmidt, L. and Resch, C.T. (1987) Chromate adsorption on amorphous iron oxyhdroxide in the presence of major groundwater ions. **Environ. Sci. Technol. 21**, 589-594