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AN EVALUATION OF THE CHEMICAL- AND PHYSICO CHEMICAL PROCESSES POSSIBLY CONTROLLING THE MIGRATION BEHAVIOUR OF IODINE IN THE TERRESTRIAL ENVIRONMENT.

by

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Jesper V. Christiansen and Lars Carlsen

Abstract

The report gives an overview of the environmental cycle of iodine, especially focussing on the possible reactions being responsible for the retention of iodine in the terrestrial environment.

During the last two decades evidence for the presence of iodine in soil as organically bound has been presented. The major part of inorganic iodine in the terrestrial environment will, under physical and chemical conditions normally prevailing, exist as iodide. No evidence for a direct reaction between iodide and organic material has been presented, whereas strong support for the engagement of microbial activity in the formation of organic iodine compounds in soil has been obtained. Incorporation of iodine in humic substances as a result of enzymatic catalysis, involving an enzyme of the peroxidase group appears reasonable. It is concluded that microbiological activity involving extracellular enzymes most probably is resonsible for the possible retention of iodine in the terrestrial environment. It is suggested that these reactions in detail should be studied experimentally.

CONTENTS

1. IODINE IN THE ENVIRONMENT

Iodine is one of the less abundant elements in the environment. With an average concentration in the lithosphere of 0.3 ppm iodine appears as number 46 among the more common elements. Thus, iodine does not belong to the 32 elements that constitute 96.6% of the lithosphere (Chilean Iodine Educational Bureau, 1956). Nevertheless iodine appears as one of the essential elements for mammals, including humans, a fact which was recognized several decades ago. Due to the widely prevalent desease goitre, which is caused by iodine deficiency, major efforts were devoted to studies of the distribution, concentrations and environmental cycle of iodine. In recent years the long-lived radioactive iodine isotope, ^{129}I ($t_{1/2} = 1.56 \times 10^7$ years) has received considerable attention as a byproduct of nuclear energy production. ^{129}I released to the environment, e.g. by nuclear accidents may be accumulated in the thyroid gland by incorporation in the thyroid hormone, causing damaging internal radiation doses.

It is generally believed that an enzyme of the peroxidase group, thyroid peroxidase, is responsible for the iodination of the aminoacid tyrosine in thyroglubulin in the presence of hydrogen peroxide and iodide in the thyroid gland.
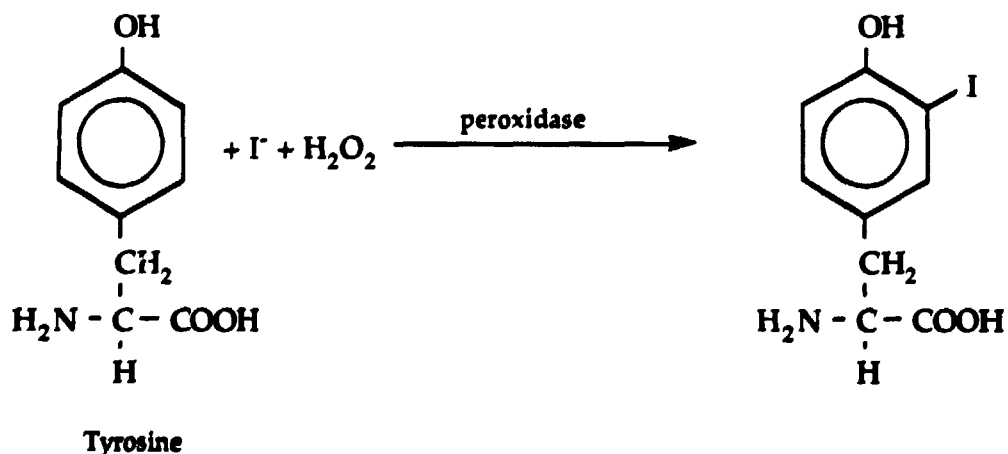
Tyrosine

Analoguously it has been shown that the iodination of tyrosine and histidine *in vitro* are catalyzed by different peroxidases (Morrison and Schonbaum, 1976).

$$CH_2CH(NH_2)COOH$$

NH

N
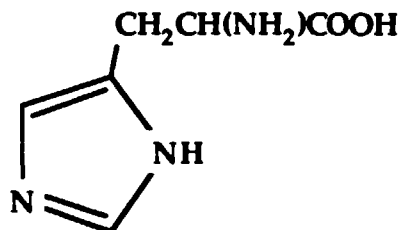
Histidine

Apart from the iodination of the tyrosine, iodine apparently does not participate in the metabolism of higher animals or plants (Whitehead, 1984).

1.1. Iodine Concentrations in the Environment

Typical concentrations of iodine in different parts of the environment has recently been reviewed by Whitehead (1984), the data being summarized in Table 1. Also recent reviews by Coughtrey et al. (1983,1985) and Bowen (1979) should be consulted.

Table 1. Typical Iodine Concentrations in the Environment

Igneous rocks	0.08-0.50	mg/kg
Sedimentary rocks	0.2-10.0	mg/kg
Marine Sediments	3-400	mg/kg
Soils	0.5-20	mg/kg
Coal	1-15	mg/kg
Higher plants	0.05-0.5	mg/kg
Marine algae	90-2500	mg/kg

table 1 cont...

Mammalian tissues	0.05-0.5	mg/kg[a]
Marine fish	0.5-6	mg/kg[b]
Sweetwater fish	0.06-0.2	mg/kg
Seawater	45-60	μg/L
Rainwater	0.5-5.0	μg/L
River-and Lake water	0.5-20	μg/L
Atmosphere	10-20	ng/m^3

[a] excluding thyroids
[b] including shellfish (soft tissue)

1.1.1. Rocks and Soils

In 1956 the Chilean Iodine Educational Bureau (CIEB) collected available data and compared the iodine content in source-rocks and the correspondingly derived soils (CIEB, 1956).

Table 2 Iodine Concentrations (μg/kg) in Source Rocks and correspondingly derived Soils

	Parent Material	Derived Soil
Igneous Rocks (all)	521	9.338
Basic	495	10.172
Intermediate	523	8.342
Acid	542	6.105
Sedimentary Rocks (all)	1.545	3.850
Limestone rocks	1.179	4.506
Sandstone rocks	1.743	3.647
Shales and Argillites	2.180	2.221
Metamorphic Rocks (all)	1.612	5.312

Apparently sedimentary rocks contain iodine in significantly higher concentrations than found in igneous rocks (Table 2), which probably can be explained by an accumulation of iodine during the sedimentation process, originating from the source rock as well as from, e.g., biological activity. Additionally, it can be noted (Table 2) that the iodine concentration increases by a factor of ca. 20 from igneous rocks to soils, whereas the increase amounts to a factor of only 1-4 from sediments to soils.

CIEB (1956) suggested that the explanation for these variations to some extent may be due to the porous structure of the sediments, which may cause an enhanced leaching. However, it should be noted that this explanation is in contradiction with the fact that the transformation of igneous rocks to soils of necessity must involve intermediary structures of sedimentary character. Thus, the actual nature of the iodine-containing materials as well as the conditions of the igneous rock to soil transformation most probably play a dominant role; the eventual explanation, however, is still lacking.

Attempts to correlate the iodine content in soils with single components of the latter, indicate a connection between iodine content and the content of organic matter as well as between iodine content and the content of the so-called sesquioxides, i.e. Fe_2O_3 and Al_2O_3 (Whitehead, 1973a).

Typically soils exhibiting high organic content appear to constitute an increased iodine concentration. Hence, Whitehead (1979) reported iodine levels up to 100 ppm for certain peaty soils. However, no clear-cut picture is developed, which by some authors has been explained by a hypothesis stating that the major amount of iodine in soils originates from the atmosphere and that the environmental iodine-cycle is rather slow. Thus, "young" soils, i.e. soils developed after the last ice age have not yet obtained iodine concentrations as high as the "older" soils, despite a potentially more favourable composition (CIEB, 1956; Goldsmith, 1958).

It has been suggested that iodine concentrations in soils could be related to the distance from the sea, *i.e.* the iodine should predominantly be supplied as a consequence of precipitation with rainwater (McClendon, 1939; Karelina, 1961). This hypothesis has, however, been rejected by Cohen (1985), who stated that the iodine concentrations for sedimentary rocks, which constitute 80% of the earth's crust, reported by Bowen (1979) merely account for the concentrations found in soils. Furthermore, Cohen (1985) questioned a long-distance transport of iodide, *e.g.*, as adsorbed to particulate matter. However, apparently he disregards the fact that the major transport of iodine from the sea to the atmosphere most probably takes place in the gaseous state as methyl iodide (CH_3I) (Rasmussen et al., 1982), and due to a relatively slow transformations in the atmosphere of CH_3I to iodide and iodate (*vide infra*) the overall residence time of iodine in the atmosphere will probably be enhanced, whereby a more pronounced distribution appears possible. The average residence time of iodine in the atmosphere has been reported by Kocher (1981) to be approx. 15 days.

A further support for the rejection of the sea-to-soil transport hypothesis is found in the fact that iodine concentrations in rivers typically are higher than in rainwater, probably as a result of leaching. However, in this context it is necessary to take into account evaporation from the soil surface as well as from sweet-water areas in order to be able to compare the concentrations directly. Since iodine concentrations in soils on the average are two orders of magnitude higher than those found in rivers and lakes, we suggest that iodine concentrations in rivers should be compared to those in pore-water in order eventually to evaluate the possible accumulation of iodine in soils as a result of iodine participation with rainwater.

Model calculations and the yearly amounts of iodine transported may be rather uncertain. Since the iodine concentrations in soils apparently reflect the operation of a variety of mechanisms, it is somewhat difficult to draw any final conclusions. However, it seems that the sea-to-soil transport

mechanism, as suggested by Goldsmith (1958), does not necessarily play any dominant role.

1.1.2. Sweet Waters (Rivers, Lakes)

Whitehead (1984) reported iodine concentrations in rivers and lakes in the range of approx. 0.5-20 ppb. In general, these concentrations are lower than those found in sea-water; probably as a result of a relative low evaporation compared to draining. In periods of stagnation, iodine appears to be accumulated in bottom-water and bottom-sediments, apparently due to adsorption of iodide ions to suspended particles of iron-, aluminium-, and manganese hydroxides, subsequently precipitating. Due to the oxygen deficient conditions, reductive changes of the metal hydroxides may cause release of iodide, which, hence, will be accumulated in the bottom-water and -sediments (Sugavara et al., 1958).

A possible accumulation of iodine in sweet-water animals or -plants, analogously to what can be observed in marine organisms is apparently not reported.

1.1.3. Sea

Typical concentrations of iodine in the marine environment amount to 45-50 ppb (Whitehead 1984). The apparently enhanced iodine concentrations relative to those found in sweet-water environments are explained by a supply of iodine-containing material from the earth's crust, both dissolved as well as undissolved and the subsequent accumulation caused by the evaporation of water from the sea surface. However, the accumulation factor for iodine appears to be lower than that for chlorine, which may be explained by the operation of an active "pump" that releases iodine from the sea. The average residence time of iodine in the sea appears to be 1.1 year in contrast to ca. 100 years for chlorine (Bowen, 1979). The iodine-to-chlorine ratio in the

sea is significantly smaller than found in the atmosphere, which may be taken as a support of an active transport of iodine from the sea (*vide supra*). Marine organisms as algae and fish accumulate iodine, which may be an important transfer path to humans. In marine sediments iodine concentrations of 3-400 ppm have been reported, which appears to be significantly higher than for sweet-water sediments, the latter typically exhibiting *ca.* 6 ppm (Brehler and Fuge, 1974; Mun and Bazilerich, 1963).

It should be noted that in sea-water iodate (IO_3^-) appears as the thermodynamically more stable iodine species. The apparent enhanced content of iodide in the upper layers can most probably be ascribed to the operation of living organisms, as Tsonogai and Sase (1969) have demonstrated that certain organisms enzymatically (nitrate-reductase) are able to reduce iodate to iodide.

1.1.4. Atmosphere

The concentration of iodine in the atmosphere appears to be in the range of 10-20 ng/m^3 (Whitehead, 1984), predominantly originating from the sea in the form of methyliodide (CH_3I) released by marine algae (Rasmussen et al., 1982). Direct evaporation of elemental iodine (I_2) is assumed to be of minor importance only. Aerosolizing of seawater with subsequent adsorption of dissolved iodide/iodate to suspended particles in the air has been mentioned as a possible source (Whitehead, 1984). However, this mechanism also is assumed to be considerably less important in comparison to the methyl iodide path (Whitehead, 1984). Rasmussen et al. (1982) reported the flow of iodine in the form of methyl iodide from the sea to be 1.2×10^9 kg/year.

In rainwater iodine is generally found as a mixture of iodide (55%) and iodate (45%) (Jones, 1981), suggesting the methyl iodide is transformed into these species. Whitehead (1984) mentions photochemical reactions as well as reactions involving ozone as possible explanations.

It has been calculated (Whitehead, 1984) that the combustion of fossil fuel contributes to atmospheric iodine by 4×10^5 kg/year, which appears to be less than 0.1% of the amount of iodine which yearly is exchanged between the atmosphere and the earth surface incl. the sea.

Radioiodine, e.g. ^{129}I may be introduced to the environment owing to nuclear operations, mainly reprocessing and disposal of nuclear waste. In addition ^{129}I is formed as a decay product from $^{235/238}U$. McKay et al. (1982) calculated that the yearly production of ^{129}I in the EC-countries (European Community) in 1988 would amount 340-550 kg/year, and that the total production in these countries will reach 12.2×10^3 kg in the year 2000. It is to be noted that under normal operations the release of ^{129}I from nuclear facilities is kept to a minimum except when major accidents occur which eject large amounts of ^{129}I into the atmosphere. Obviously the radiological aspect rather than the physical amount of this isotope is of major concern.

1.1.5. Plants

In the case of higher plants, iodine concentrations in the range of 50-500 ppm are generally found. Whitehead (1979) reported an average of 16 ppm iodine in lichen. A slight tendency of decreasing concentrations with increasing distance from the sea was noted, the significance of which has been discussed by Cohen (1985) (vide supra). It is in this connection important to note that lichen accumulate trace elements through direct uptake from the air. This is also to a certain extent true for other plants, where especially the stomata apparently play a dominant role.

1.1.6. Animals

Iodine appears essential for certain corals, fungi and vertebrates. In mammals the major part of iodine is located in the thyroid gland, in human beings it is approx. 18 out of 20 mg *i.e.* 90% (Bowen, 1979), which as mentioned previously appears to be of paramount importance in relation to the radiological aspects of ^{129}I.

2. THE ENVIRONMENTAL CYCLE OF IODINE

In the course of time several attempts to describe the global environmental cycle of iodine have appeared. In 1981 Kocher proposed a model dealing with different compartments and the mutual yearly transport, whereas a model by Whitehead (1984) takes its starting point in the different mechanisms involved in the iodine-cycle. In outline no discrepancy between the two models seems to exist, obviously owing to the fact that both models basically are founded on the same sources. A later revision of the Kocher model (White and Smith, 1984) was limited to two aspects, an adjustment of the values for the transport between the single compartment and subdivision of the "soil compartment" into a solid- and a liquid part. This subdivision obviously gives a more detailed picture of the actual phenomena influencing the transport of iodine in the environment. In Fig. 1 the models proposed by Whitehead (1984) and Kocher (1981)/White and Smith (1984) are combined and further extended with some mechanistic considerations.
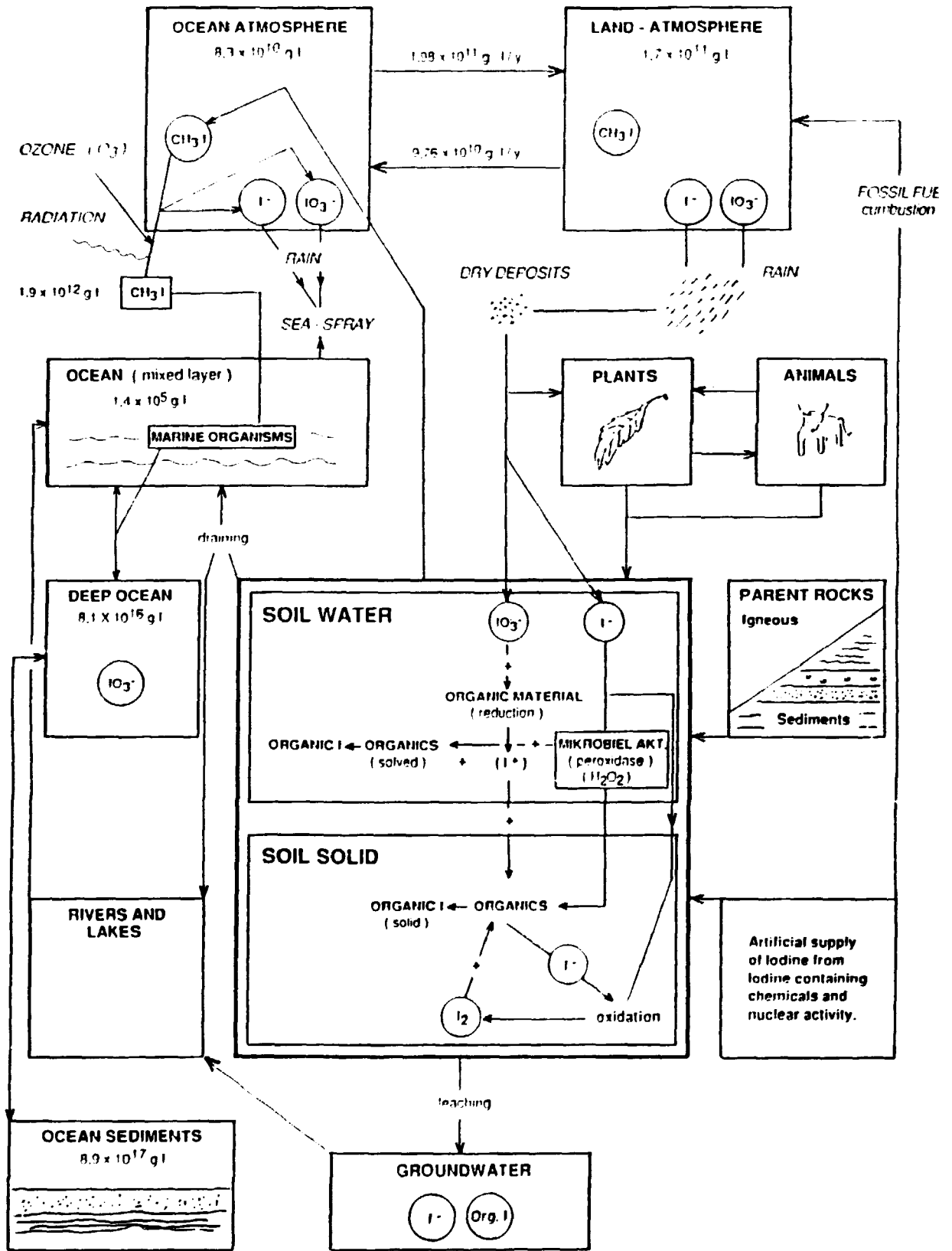
Figure 1. Environmental Cycle of Iodine

3. SORPTION/DESORPTION OF IODINE IN SOIL

In the terrestrial environment iodine will predominantly exist as iodide, as visualized in the stability diagram (Fig. 2) based upon the data given by Bowen (1979). The dotted area corresponds to conditions to be found in groundwater (Jensen, 1982).
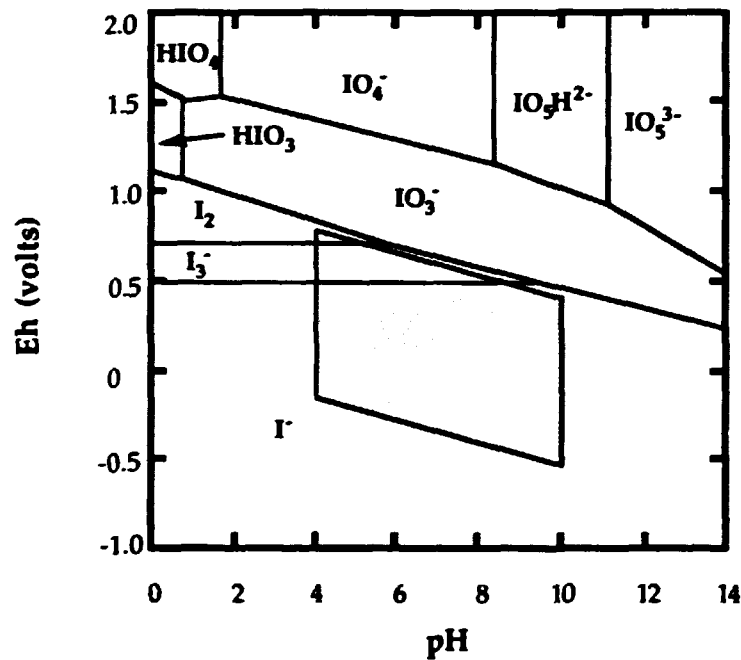
Figure 2. Speciation of Iodine in Water as Function of pH and Eh

The possible retention of iodine in soil can be regarded as the combined effect of sorption- and desorption processes. The adsorption of iodine to different soil components has been demonstrated to operate to some extent, e.g. the adsorption to sesquioxides (Al_2O_3 and Fe_2O_3) and to organic material (Whitehead, 1974a). Furthermore, it has been noted that certain clay minerals are able to sorb iodine (Whitehead, 1974a; Vinogradov, 1959).

The sorption ability of the different soil components towards iodine appears to be more or less pH-dependent. In addition it is important to note that the iodine sorption apparently depends on the contact time. Hence, it must be concluded that the sorption of iodine in soil at least to some extent, is kinetically controlled. Finally, it should be mentioned that the actual nature of the iodine, *i.e.* elemental iodine, iodide, iodate etc., obviously is of major importance (*vide infra*).

It was noted by Whitehead (1973a) that a 0.05 M EDTA solution leached more iodine from a soil sample than 0.42 M acetic acid. It was argued that the explanation was to be found in the association of I⁻ with to polyvalent metal ions. Thus the complexation of the metal ions, which is significantly more effective using EDTA than acetic acid as ligand, released iodide to the liquid phase.

Only few reports have appeared on the possible influence of single factors on the retention of iodine in soil. A major part of the available material in this context is apparently the result of Whitehead's work (1973a,b; 1974a,b; 1975, 1978, 1979). A potentially important factor, the microbiological activity has, however, been neglected by Whitehead, but has been discussed by Raja and Babcock (1961), Behrens (1982, 1985, 1986) and Börs (1984). In the following, the possible significance of the single factors in determining the retention properties of iodine in soils shall be discussed.

3.1. Clay Minerals and Sesquioxides (Al_2O_3, Fe_2O_3)

Clay minerals exhibit anion exchange capacity to some minor extent, as the edges, due to discontinuities in the XY-plane, are positively changed. Anions are sorbed to these positions and may, especially at higher pH-values be exchanged by hydroxide ions (Gast, 1977).

The adsorption of iodide to a series of clay minerals has been investigated. Whitehead (1974a) concluded that iodide, in concentrations of 7.88×10^{-7} and 3.15×10^{-6} M was not sorbed to kaolinite or montmorillonite. On the other hand, Raja and Babcock (1961) found that minor amounts of iodide could be adsorbed to kaolinite, montmorillonite and bentonite. The presence of dissolved calcium salts decreased the sorption ability of the two latter clay types.

Whitehead (1981) investigated the ability of different soil constituents to reduce the loss of iodine (supplied as iodide) to the air. It was concluded that montmorillonite/sand and kaolinite/sand reduce the loss to 44 and 76%, respectively, compared to pure sand (100%). Apparently, the two clay minerals appear more effective in reducing iodine loss to the air than to the interstitial water. In both cases montmorillonite appears as the more effective clay mineral (pH < 7). Finally, it can be mentioned that Vinogradov (1959) reported illite as the more effective clay type. However, it can most probably be concluded that clay minerals are considered to be of lesser importance as soil constituents in the sense of an iodide- sorbing property.

It is interesting to note that the above-described effects, i.e. release of iodine to water and air possibly could be a result of the actual redox conditions in the clay. Thus, Torstenfelt (1986) studied the diffusion of iodide in bentonite, concluding the presence of two different species exhibiting diffusion coefficients equal to 2.6×10^{-12} and 2.4×10^{-13} m^2/s for water and air, respectively. It was concluded that the results were consistent with a simultaneous existence of I^- and HIO in the clay.

Sesquioxides, Al_2O_3 and Fe_2O_3, have been reported to influence the retention of iodine in soil (Whitehead, 1973a,b; 1974a,b). Thus, a positive correlation between iodine content and the content of sesquioxides in 23 English soils could be established. Furthermore, it was demonstrated that freshly precipitated Fe_2O_3 and Al_2O_3 could adsorb iodide. A pronounced

effect on the sorbing ability of the sesquioxides towards iodide as a function of pH was noted. The sorbing ability decreases with increasing pH. Thus, Fe_2O_3 and Al_2O_3 do not sorb iodide at pH-values above ca. 7 and 8, respectively.

In a review on anion-adsorption, Parfitt (1978) concluded that similarities in mechanisms for sorption of different anions apparently exist. Protonation of M-OH groups on the mineral surface leads to positively charged sites and, hence, attraction and sorption of anions. Maximum anion adsorption takes place at rather low pH-values, close to the pK_a-value for the acid $M-OH_2^+$. Parfitt (1978) suggests that the sorption of halides at low pH takes place due to electrostatic attraction as

$$M-OH_2^+ + I^- \longrightarrow M-OH_2^+-I^-$$

A wide variety of anions appears to be more subjected to adsorption than the halides. Thus, in the eventual competition for the relatively small number of sites available, it seems likely that iodide will not be sorbed to any major extent. This might, on the other hand, suggest that the significant sorption of iodide to Fe_2O_3 and Al_2O_3 reported by Whitehead (1974a) is a result of the absence of concurrent anions in these experiments.

Finally, it can be mentioned that drying, as long as organic matter is absent, influences the sorption process only slightly. Hence, it can be concluded that the mineral components of soil most probably will play any predominant role (Benes, 1985) only in the case of rather extreme conditions, where electrostatically controlled reaction mechanisms are dominant.
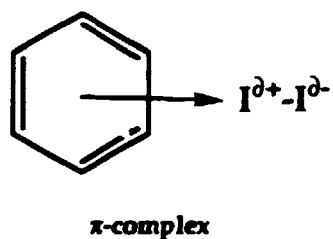
3.2. Organic Matter

It seems that organic matter in the form of soil component exhibits the paramount influence on the retention of iodine. Thus, Whitehead (1973a,b) noted a reasonable correlation between iodine content and that of organic matter in different soils. However, Benes (1985) emphasized that the "quality" of the organic matter would be of importance in relation to the retention properties, as a podzol with the highest organic content (4.9%) of 5 soils studied, exhibited the lowest tendency towards iodine retention. These results agree with a study of Whitehead (1974b) that discloses the effect of composting. An increased ability towards iodine retention was observed for crushed plant material < 24-week-compost < soil. The eventual state of organic matter in soil are humic substances such as humic- and fulvic acids. These substances exhibit a rather complicated polymeric nature. Based on a large number of analytical data, Schnitzer (1979) formulated a "model humic acid" containing aliphatic- phenolic- and benzene carboxylic groups in amounts corresponding to 24.0, 20.3, and 32.0%, respectively. In addition, it has been reported that humic substances typically contain thiol groups (Choudry, 1981).
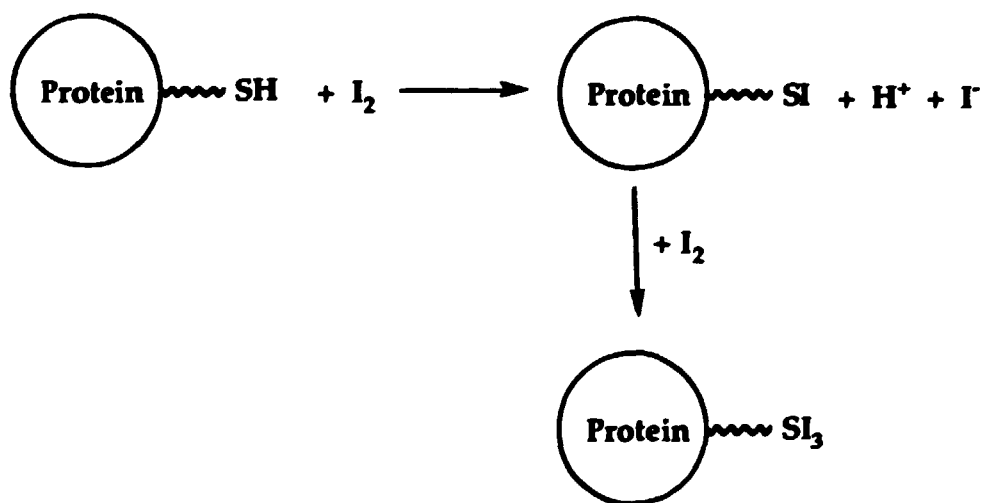
Iodination reactions involving structures typical for humic substances have been reported. Thus, Fawcett and Kirkwood (1953) found that elemental iodine (I_2) reacted directly with polyphenols, leading to iodine-substituted species.
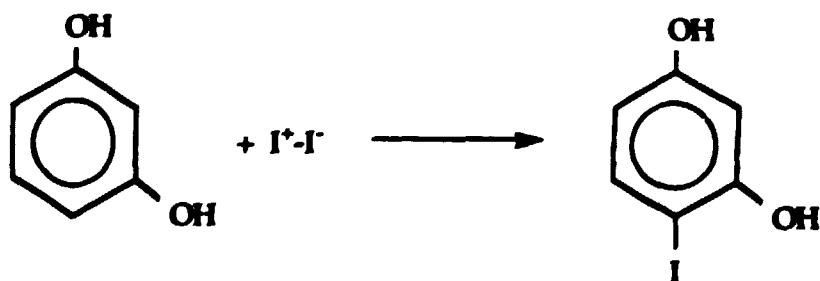
The formation of π-complexes between elemental iodine and aromatic structures has been reported by Allinger et al. (1976)

$$\text{(benzene ring)} \longrightarrow I^{\partial+}-I^{\partial-}$$

π-complex

Finally, it can be mentioned that mercapto groups in proteins react with elemental iodine, possibly in excess-leading structures containing -SI and -SI$_3$ moieties (Jirovsek and Pritchard, 1971).

$$\text{Protein} \sim\sim \text{SH} + I_2 \longrightarrow \text{Protein} \sim\sim \text{SI} + H^+ + I^-$$

$$+ I_2$$

$$\text{Protein} \sim\sim \text{SI}_3$$

Hence, it must be concluded that the organic matter in soil may be expected *a priori* to take part in a variety of reactions involving iodine and hereby possibly participate in the retention of iodine in the terrestrial environment.

3.3. Microbiological Activity

Only few reports have appeared on the possible influence of microbiological activity in the reactions of iodine in the environment. Nevertheless, based on our introductory remarks, it appears plausible that enzymatically catalyzed reactions would be of importance.

Behrens (1982) found that the radio-iodide supplied to different types of surface-water and pore-water was transformed into non-iodide to a significant extent, as only approx. 20% remained as iodide. It was found that the reaction apparently was independent of light energy present, and radiochemical reactions could be excluded also. However, it was demonstrated that the reaction could be suppressed if the water samples were heated to boiling before adding iodide. On the other hand, the iodide-transforming ability could easily be reestablished by grafting the samples with non-sterile water or even house-dust. These results certainly strongly suggest that the transformation of iodide in these systems does involve microbiological activity.

A further confirmation of the suggestion that microbiological activity plays a dominant role in the possible retention of iodine in soil was obtained through simple batch-type experiments (Behrens, 1982). It was demonstrated by these experiments that the transformation rate of iodide significantly decreased with increasing depth of origin of the sample, and that batch-type-derived K_d-values were found of up to three orders of magnitude higher for non-sterile than for sterile samples.

Water samples filtered through a 0.2 µm membrane still exhibited the ability to transform iodide; this ability, however, decreases as a function of exposure to light. In addition, the effect of the filtrate was reduced as a function of heat. Based on these results, it was concluded that the transformation was controlled by extracellular enzymes, which could be denaturated by light and

heat. It was also concluded that microorganisms, either through secretion or decay, would supply additional enzymes (Behrens, 1982).

In his study Behrens (1982) also noted that addition of glucose or hydrogen peroxide increased the rate of transformation, which suggested the possible involvement of the enzyme glucoseoxidase, through production of H_2O_2, in combination with an enzyme of the peroxidase group, e.g. lactoperoxidase, which is known to use hydrogen peroxide in its reactions.

The iodine-containing species produced was established by chromatography and electrophorese to exhibit molecular weights in the range of 500-10,000, which could suggest protein character. However, Behrens (1985,1986) suggested that these species are the results of iodine incorporation in substances of humic nature.

It is surprising that the assumed incorporation of iodine in organic structures seems to be reversible, as the percentage of iodide in surface water apparently is reestablished a few days after removing the free iodide (Behrens, 1982).

Some sorption experiments with iodate were carried out; however, only minor sorption was noted, which could not be inferred to be a result of microbiological activity. On the other hand, it appears that microbiological activity is involved in the reduction of iodate to iodide; subsequently, of course, the iodide produced may take part in the above mentioned enzymatically induced iodination reactions of organic structures. Finally, it was demonstrated that the transformation of iodide takes place only in the presence of oxygen, whereas anaerobic conditions lead to the release of iodide to the liquid phase (Behrens, 1982). In view of the apparent predominant role played by microbiological activity in determining the distribution coefficients, K_D, and, hence, the sorption processes of iodide in general, it is strongly suggested that previous results should be reevaluated.

In addition, it is strongly emphasized that in studies of alternative sorption mechanisms, sterile samples should be applied.

The enzyme lactoperoxidase belongs to the group of enzymes, which by Behrens (1982) has been suggested as being responsible for transforming iodide in the geosphere. It has been proved in a series of studies that lactoperoxidase in the presence of hydrogen peroxide can promote the iodination of tyrosine as well as the tyrosine derivatives (cf. e.g. Morrison and Bayse, 1970). As e.g. humic acids contain major amounts of phenolic groups (Schnitzer, 1979), it seems obvious that a mechanism involving enzymatic iodination of these organic structures is present.

In an early work by Raja and Babcock (1961), results that indicate the operation of microorganisms in the retention of iodide in soil were reported. However, the proposal was rejected, since treatment with 80% ethanol apparently did not influence the retention ability. Alternatively, it might be an explanation that the extracellular enzyme suggested by Behrens (1982) as being responsible for the iodine-fixation, is not denaturated by 80% ethanol. This assumption is strongly supported by the more or less unchanged catalytic effect of lactoperoxidase that is apparent at least after a short-period-treatment with an 80% ethanolic solution (Christiansen and Carlsen, unpublished).

Column-type experiments by Behrens (1985, 1986) demonstrated the possible retention of iodine in top soil layers. A 20-cm soil column was passed through with water for 10 days at a rate of 10 ml/cm^2 day. On the third day radioiodide was added and after the expiration of the 10-day period the iodine concentrations were determined as a function of depth (cf. Table 3).

Table 3. Radioiodine Distribution Through a 200 mm Soil Column After
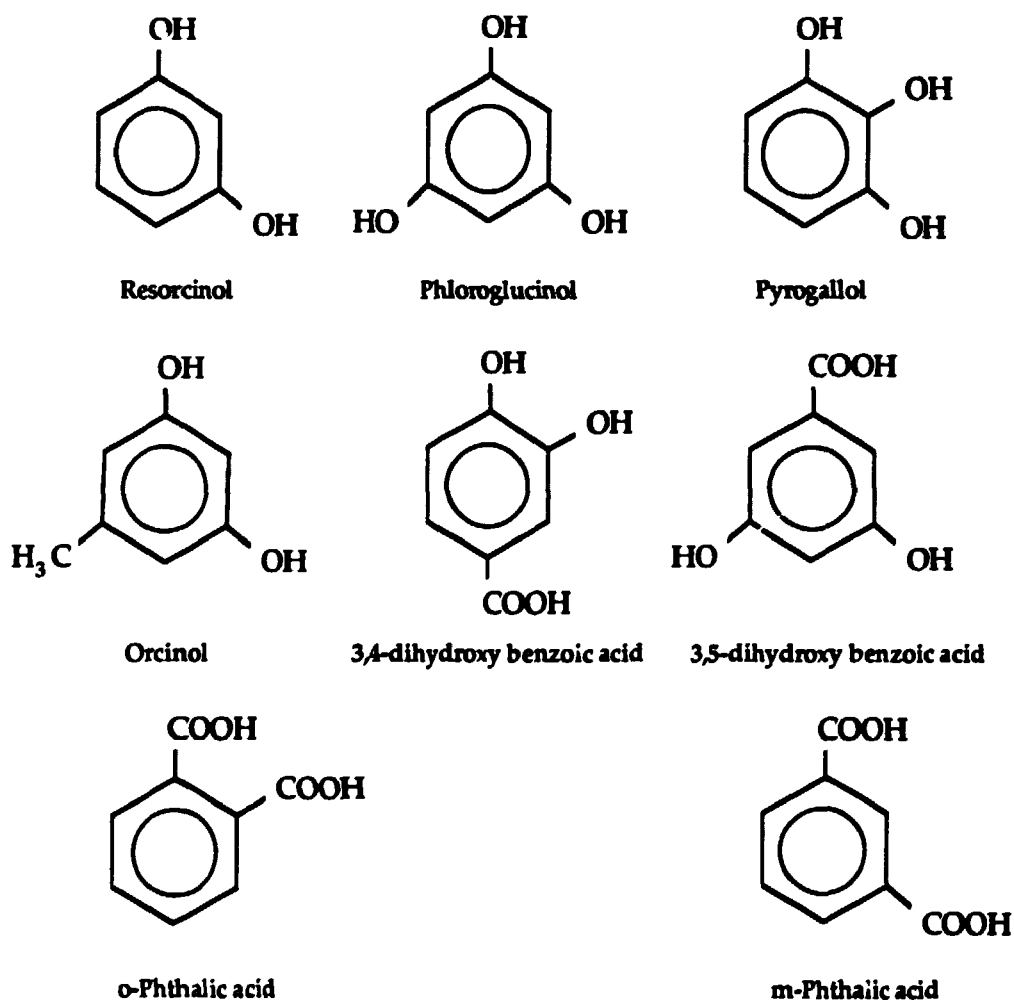7 Days of Water Percolation under Water Unsaturated Conditions.

Depth of Layer (mm)	Fraction of total injected radioiodine
0 - 5	77.75
5 - 10	18.60
10 - 15	1.78
15 - 20	0.69
20 - 25	0.32
25 - 30	0.19
30 - 35	0.12
35 - 40	0.09
40 - 45	0.06
45 - 50	0.05
50 -100	0.18
100-200	0.04

Obviously 96% of the added iodide can be found again in the upper 10 mm of the column, suggesting the operation of a rather efficient retention mechanism. In this context, it is important to note that analogous experiments carried out under anaerobic conditions or after applying autoclavated column material revealed, practically speaking, no retention of the applied iodide. Behrens concluded that under normal top-soil conditions 99.9% of the added iodide will bind to solid organic material, whereas the remaining 0.1% will be present in solution. The soluble iodine fraction constitutes of 20% iodide and 80% organically bound iodine (Behrens, 1985, 1986).

These experiments appear as further support for the operation of an enzymatically controlled iodination of soil organic matter as the predominant retention mechanism for externally supplied iodide. However, iodide released to the soil during mineral degradation can, to a certain extent, also be expected to be found as organically bound.

The possible involvement of extracellular enzymes in the iodination reactions of phenolic compound has been studied in a few cases. These studies seem to justify enzymatic engagement in the fixation of iodine to the organic fraction of soil.

Cooksey et al. (1985) reported on a series of possible decomposition products of humic acid for antithyroid effect in rats.

OH

OH

OH

Resorcinol

Phloroglucinol

Pyrogallol

OH

OH

COOH

H₃C

OH

Orcinol

3,4-dihydroxy benzoic acid

3,5-dihydroxy benzoic acid

COOH

COOH

o-Phthalic acid

m-Phthalic acid

It was observed that a major effect could be noted in the cases of resorcinol, phloroglucinol, orcinol and 3,5-dihydroxy benzoic acid. A common feature for these compounds is the *meta*-positioned hydroxy groups. Unfortunately,

no attempt to detect possible iodinated derivatives of these species was carried out. However, it seems plausible that aromatic structures like those described above may inhibit the thyroid metabolism by competitive inhibition, i.e. these compounds are more readily iodinated than tyrosine. It is suggested that the possible retention of iodine in soil will be due to analogous reactions as those being responsible for iodine incorporation in the thyroid hormone.

As mentioned previously, Behrens (1982) suggested the involvement of a peroxidase in the iodination of humic material. Taking the above into consideration this suggestion seems to be supported by the following facts:

1) Tyrosine is iodinated by peroxidase ortho to the OH-group in the presence of hydrogen peroxide (Morrison and Bayse, 1970).

2) After treatment with resorcinol, mono-iodinated resorcinol could be detected in thin slices of rat thyroid gland (Fawcett and Kirkwood, 1953).

3) Lactoperoxidase apparently is able to induce iodination reactions in organic compounds (Benenson and Mersel, 1978).

It has e.g. been demonstrated by Benes (1985) that the equilibrium between dissolved iodide and the sorbed iodine species typically is relatively slow. This does not contradict the assumption of an extracellular process, where only rather low concentrations of enzyme and hydrogen peroxide can be expected. Thus, the iodination reaction must be regarded as a result of a series of bimolecular reactions.

In agreement with this, Morrison and Bayse (1970) observed a direct proportionality between the rate of iodination and enzyme concentration. Finally, it can be mentioned that the iodination of tyrosine appears more efficient at pH 5 than at pH 7 (Morrison and Bayes, 1970), which also may have some relevance to the equilibrium reaction in the soil-ground water system.

In a very recent paper, François (1987) studied the fixation of iodine in marine sediments, the actual iodine species under investigation being iodate (IO_3^-). The fact that he observed fixation of iodide to the organic fraction, *i.e.* humic material, was rationalized in terms of a reduction of iodate by humic acid to "an electropositive iodine species", followed by electrophilic substitution:

$$IO_3^- + \text{Humic Acid} \longrightarrow \text{"}I^{+n}\text{"}$$
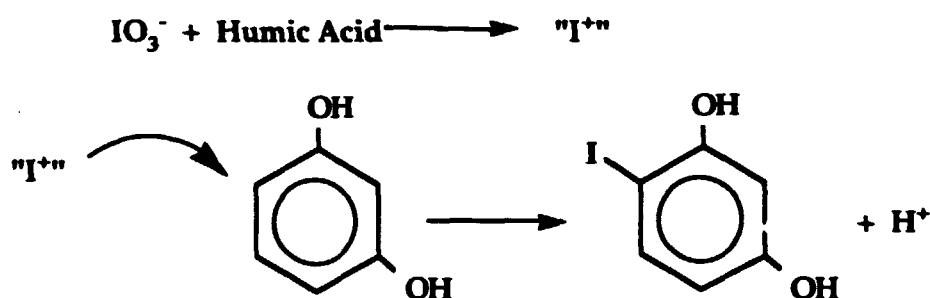
It is furthermore interesting to note that if resorcinol was added to samples of marine sediments, mono-, di-, as well as triiodinated resorcinol could subsequently be detected, which must be regarded as strongly supportive for the above hypothesis.

It has been demonstrated that if iodine was present as iodide in aqueous solutions of phenolic compounds in concentrations which make an oxidation into elemental iodine, either provoked by the action of atmospheric oxygen or possibly by the addition of hydrogen peroxide, this would lead to the formation of iodine substituted phenols (Christiansen and Carlsen, unpublished). On the other hard, for low iodide concentrations, *e.g.* around 10^{-4} molar, neither equal concentrations of hydrogen peroxide, nor atmospheric oxygen will be able to produce a major transformation into elemental iodine within a short period of time; it is unambigous that the addition of catalytic amounts of lactoperoxidase promote the iodination reaction (Christiansen and Carlsen, unpublished). In an aqueous solution of phenol, iodide and hydrogen peroxide, all in 10^{-4} molar concentrations,

addition a lactoperoxidase will, within 5 min, result in a transformation of appr. 55% of the phenol into iodinated derivatives. Nearly 90% of the iodine can be found organically bound. The reaction products are 2-iodophenol, 4-iodophenol, 2,6-diiodophenol, 2,4-diiodophenol and 2,4,6-triiodophenol.

As a final support for the importance of microorganisms in the transformation of iodine in soils by reactions as outlined above, it is emphasized that both hydrogen peroxide as well as extracellular peroxidases are found in soil. Behrens (1986) reported that hydrogen peroxide is produced in the groundwater system owing to microbiological activity, and Bartha and Bordeleau (1969) reported on investigations demonstrating peroxidase activity in soil. They concluded, based on a technique developed during the study of the activity of extracellular peroxidases in soil that significant amounts of these species are present.

3.4. Distribution Coefficients

Distribution coefficients at large may give some preliminary suggestions as to the behaviour of trace elements in the environment. However, these results must be taken with great caution.

Wildung et al. (1974) determined K_D-values for iodide in a variety of soils by applying a batch-type technique. Furthermore, the soils were characterized by their content of silt, clay and organic matter. A positive correlation ($r^2 = 0.47$) between the iodide K_D-values and the silt content was established. This might be caused by the dependence of the surface coating with amorphous iron and aluminium on the grain size.

Based on the percentage of silt, clay and organic matter and the K_D-values obtained, the following multiple regression equations were derived for iodide and methyliodide (Wildung et al. , 1974):

$$K_D \text{ (iodide)} = 0.33 \text{ silt} + 0.09 \text{ organic } (r^2 = 0.71)$$

$$K_D \text{ (methyliodide)} = 0.027 \text{ clay} + 0.10 \text{ organic } (r^2 = 0.96)$$

Sheppard et al. (1984) applied these equations to calculate K_D-values for a series of soils with a composition close to those studied by Wildung et al. (1974) (vide supra). Application of the equation for iodide K_D-values in the range of 5-20 ml/g were found, which should be compared to experimental results by Benes (1985), who determined values of 3.8 to 6.3 ml/g. It must, however, be emphasized that no information concerning equilibration time was given. Thus, the possible time dependence for an eventual conclusion concerning the existence/lack of equilibration, can be evaluated.

Sheppard et al. (1987) found that K_D-values for iodide decreased 3 to 4 orders of magnitude within the range of 0-60 cm of the upper B-horizon. These results appear to be in good agreement with those previously reported by Behrens (1982) (vide supra). However, in spite of the equality of data obtained in batch-type experiments and lysimeter experiments Sheppard et al. (1987) concluded that the eventual significance of K_D-values is rather limited. Hence, model calculations based on such values will, accordingly be highly defective.

A wide variety of factors may influence the actual values for distribution coefficients. Based on his linear-component model, Kocher (1981) concluded that the observed K_D-values for iodine, reported throughout the literature in general must be too low. The explanation for this should be the time dependence of the retention mechanisms, i.e. the very slow establishment of equilibrium.

4. CONCLUSION

Based on the results discussed above we conclude that most probably the degree of retention observed for externally supplied iodine, in the form of iodide, in soil/ground water system will be dependent on the following factors:

- *the presence of oxygen, i.e. oxidizing conditions*
- *microbiological activity, i.e. the presence/production of peroxidases as well as production of hydrogen peroxide*
- *the quality as well as quantity of organic material in the actual soil/sediment,*
- *the contact time between dissolved iodide and the organic matter*
- *pH of the liquid phase.*

The reaction between elemental iodine and phenolic compounds takes place without engaging peroxidase. However, under conditions normally prevailing, the concentrations of iodide as well as of the oxidizing species will be so low that this reaction can be left out of consideration. Even if minor amounts of peroxidase are present, the enzymatically provoked reaction will totally dominate the picture.

It should, however, be emphasized that the eventual answer concerning the possible operation of an enzymatically induced iodination of humic material is still missing. The studies by Behrens (1982,1985,1986) supplementary to studies in this laboratory are, nevertheless, strongly indicative. Hence, we must conclude that enzymatically controlled iodination of organic matter, predominantly humic material, must be regarded as the most important geochemical sink for iodine in the terrestrial environment. Only in media without any content of an organic nature other mechanisms, as *e.g.* anion exchange, come into play and may, hence, control the migration behaviour.

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Abstract (Max. 2000 char.)
The report gives an overview of the environmental cycle of iodine,
especially focusing on the possible reactions being responsible
for the retention of iodine in the terrestrial environment. During
the last two decades evidence for the presence of iodine in soil
as organically bound has been presented. The major part of in-
organic iodine in the terrestrial environment will, under physical
and chemical conditions normally prevailing, exist as iodide. No
evidence for a direct reaction between iodide and organic material
has been presented, whereas strong support for the engagement of
microbial activity in the formation of organic iodine compounds in
soil has been obtained. Incorporation of iodine in humic substances
as a result of enzymatic catalysis, involving an enzyme of the
peroxidase group appears reasonable. It is concluded that micro-
biological activity involving extracellular enzymes most probably
is responsible for the possible retention of iodine in the terre-
strial environment. It is suggested that these reactions in detail
should be studied experimentally.