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Rev.	Revisionsst. Datum	verant. Stelle	Gegenzeichn. Name	rev. Seite	Kat. *)	Erläuterung der Revision

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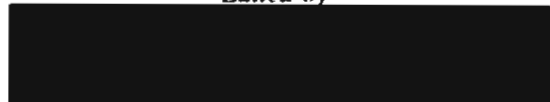
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SPECIATION OF FISSION AND ACTIVATION PRODUCTS IN THE ENVIRONMENT

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SPECIATION OF RADIOIODINE IN AQUATIC AND TERRESTRIAL SYSTEMS
UNDER THE INFLUENCE OF BIOGEOCHEMICAL PROCESSES

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ABSTRACT

In aerated surface and soil water iodide undergoes chemical reactions which bind the iodine on dissolved organic compounds. The reactions seem to be instigated by microbial activity. In detail they appear as an iodination of organics effected by extracellular enzymes. The reactions tend to reach equilibria determining the distribution of iodine on different species. In soil/water systems iodine is bound on undissolved organics in the same manner. Humic substances seem to play a considerable role in binding the converted iodine. Iodate is not formed under these oxidizing reactions. It is found to be reduced and thus involved in the above processes. Under reducing conditions no conversion of iodide occurs; rather a retransformation of organically bound iodine to iodide was found in anaerobic systems.

1 INTRODUCTION

The behaviour and the fate of radionuclides in the environment is basically connected with their chemical state on the one hand and with the chemical conditions of the systems on the other. Thus a thorough understanding of chemical processes in environmental systems and resulting speciation of radionuclides is indispensable for the discussion of their behaviour, e.g. in radioecological respect.

This report deals with investigations on the chemical conversion of radioiodine which was added in the form of I^- or IO_3^- to samples of surface fresh water or to soil/water systems. In aerated systems usually transformation of I^- in other chemical forms (except IO_3^-) and strong fixation of the radioiodine by soils was observed while IO_3^- seemed to be included in the processes after an evident reduction to I^- . In contrast to that under strictly anaerobic conditions, I^- proved to be stable.

In the course of the investigations, inorganic reactions including isotope exchange and photochemical or radiochemical conversion were excluded as a cause for the observed reactions. Rather, the evidence showed

that microbial activity should be responsible for this behaviour of radioiodine in environmental systems. The following observations among others allow for this conclusion:

- The ability of samples of surface fresh water or soil water to convert I^- is lost if the samples are preheated to boiling before the addition of radioiodide. Fixation of radioiodine, added in the form of I^- , by soils, does not occur if the material is autoclaved prior to the experiment. These observations can be seen in the context of inactivation of microbial activity by heat.
- In some samples of deep groundwater normally being inactive to convert I^- , after initial periods of inactivity, up to several weeks or sometimes months, a beginning of iodide conversion was observed. Similarly, iodide conversion in autoclaved surface water could be instigated by incubation with small amounts of untreated surface water, soil or even with normal house dust. These findings indicate that the observed conversion of I^- can be linked to the growth and interaction of microorganisms in the respective water samples.

In the following, a selection of experimental results is given to characterize the conditions of the reactions as well as the speciation of iodine in the systems in question.

2 EXPERIMENTS

2.1 Methods

The distinction between I^- and other radioactive iodine compounds which formed in surface and soil water, was made by coprecipitation of the I^- with AgCl, maintaining an excess of Cl^- over Ag^+ . Under this condition considerable amounts of other iodine compounds than I^- remained in the filtrates¹. Separation and characterisation of other iodine species in solutions was achieved by thin layer chromatography², continuous electrophoresis (method by Hannig³) and size exclusion chromatography. The sorption behaviour of radioiodine in soil/water systems was investigated in batch shaking tests and in soil column tests.

2.2 Observation of iodide conversion in surface and soil water

When radioiodide is added to surface or soil water a fraction of it becomes non-precipitable with AgCl. After some time equilibria are attained (Figure 1, a) in which generally 15-25% of the iodine remains as I^- or at least in a form which behaves like I^- in the precipitation reaction and in

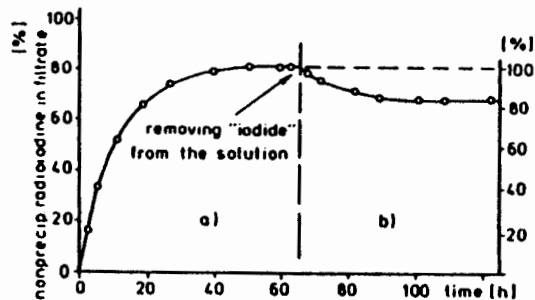


FIGURE 1 Formation of non-precipitable iodine compounds from I^- in river water (a); re-establishment of equilibrium after removal of I^- from the solution (b). Added iodine concentration: 10^{-8} M.

all other tests applied. Transformation of I^- proceeds at the highest observed rates if its concentration is on the order of 10^{-8} M, which is also the concentration of naturally occurring iodine in fresh water (0.5-2 ppb). When the concentration of I^- added is higher by one or several orders of magnitude, the reaction rate is lower, however the same equilibrium state is attained (Figure 2). It seems worth noting that, in contrast to the differing reaction rates at different iodine concentration levels the turnover rates of the formation of non-precipitable iodine are all about the same value, indicating a certain capacity of the system for the transformation of I^- . The existence of an equilibrium is shown by removing the I^- fraction from the solution (Figure 1, b); after some time the same state of equilibrium between I^- and converted iodine as before is re-established, indicating the release of I^- out of the converted forms of iodine.

2.3 Effects of water sterilization by filtration and of heating the sterile filtrates

Surface and soil water that were filtered through a $0.2 \mu m$ membrane filter showed the same ability of iodide conversion as the untreated samples, sometimes with a moderate reduction of the conversion rates. Storing the filtrates in darkness for several months resulted in a slight reduction of the iodide converting ability merely, which decreased drastically when the samples were exposed to intensive light. When the filtrates were heated for some minutes at elevated temperatures before adding the radioiodide, the activity of the filtrates to convert I^- decreased with increasing temperatures (Figure 3).

These experiments indicate that the substances causing the iodide conversion can occur in the aqueous solutions independently from microorganisms. This fact can be explained with the iodide conversion by extracellular enzymes which can be destroyed or denaturated by light or by heat.

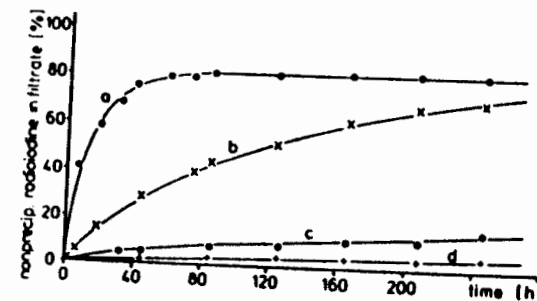


FIGURE 2 Formation of non-precipitable iodine compounds from I^- in river water. Iodine concentrations: a) carrier-free; b) 10^{-7} M; c) 10^{-6} M; d) 10^{-5} M.

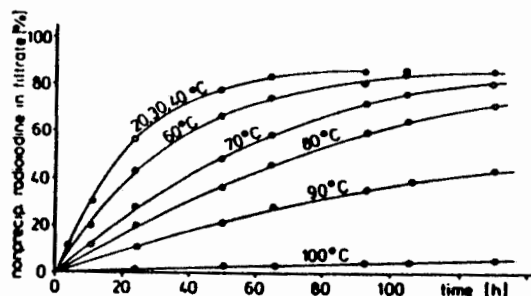


FIGURE 3 Formation of non-precipitable iodine compounds in sterile filtrated river water that has been heated for 2 minutes to the temperatures given in the figure. Added iodine concentration: 10^{-8} M.

2.4 Redox behaviour of the converted iodine

Addition of sulphite to samples of surface or soil water caused a partial retransformation of converted iodine to I^- . As soon as the sulphite disappears from the solution by selfoxidation, the same equilibrium as before will be re-established. Exclusion of air oxygen, e.g. by flushing the water samples with nitrogen gas caused stability of the added I^- which however was converted in the described way after reoxygenation of the samples. Further information on the redox behaviour was obtained from soil/water batch and column tests (cf. 2.6, 2.7).

2.5 Chromatography and electrophoresis

Thin layer chromatography under simultaneous electrophoretic separation of surface and soil water yielded, beside some unconverted I^- , several anionic radioiodine containing spots which could not be related to known species if iodine³. Continuous electrophoretic separations showed the converted iodine to occur in a broad band of anions with different electrophoretic mobilities, lower than that of I^- .

Size exclusion chromatograms of surface and soil water containing converted radioiodine were run under simultaneous detection of radioactivity and UV-absorbance (254 nm) in the column effluents. Good correlations were obtained between absorbance peaks (representing organic substances) and radioactivity peaks, indicating that the radioiodine was associated with organic substances (Figure 4). Peaks a) and b) can be attributed to humic substances with molecular weights in the range of 1000 to 10 000.

2.6 Soil/water batch tests

Batch shaking tests were run with a variety of soils and aqueous solutions, using mostly a solid to liquid ratio of 0.25 g/ml. Radioiodine that was added as I^- was generally sorbed by soil materials at relatively fast rates. Simultaneously in the batch solutions a fraction of the radioiodine was converted in the manner described above. After the phase of rapid sorption,

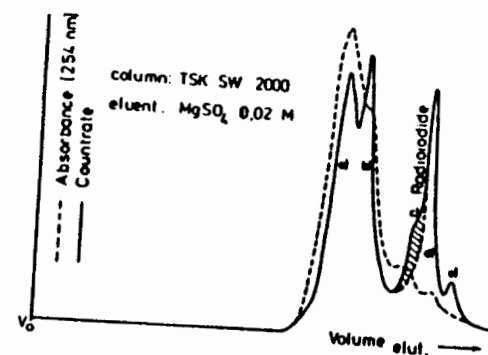


FIGURE 4 Size exclusion chromatography of iodine compounds that have been formed from radioactive I^- in soil water; the hatched area corresponds to I^- in equilibrium with the other iodine compounds.

another phase with a lower rate of sorption follows (Figure 5, curve a) in which a decrease of the converted radioiodine in the solution together with a further decrease of iodide concentration can be observed. Thus finally a good deal of the previously dissolved converted radioiodine is also sorbed by the soils.

Relatively high K_D -values of radioiodine, ranging from several hundred to more than a thousand, were found in batch equilibria with organic soils. In contrast to the experiments with untreated soils, no conversion of I^- in the batch solutions and no corresponding sorption of radioiodine occurred in batches with autoclaved soils.

Under anaerobic conditions, generated by oxygen exclusion at the beginning or during the experiments, in batch tests a drastic release of iodine out of the converted and sorbed forms under batch-formation of I^- was observed (Figure 5, curves b₁ and b₂). A relation of iodine release to nitrate reduction in anaerobic batches was found (Figure 5, curves c₁ and c₂).

2.7 Soil column tests

In soil column tests, under water saturated as well as unsaturated conditions, generally strong fixation of radioiodine which was applied as I^- occurred (example in Table I). Obviously, chemical conversions of I^- as described in the preceding chapters, will be responsible for that. In contrast, in columns with autoclaved soils, no sorption of radioiodine was observed, leaving the columns in unconverted form as I^- and thus indicating the influence of speciation on sorption and migration processes.

IO_3^- and iodine bound by organics as obtained in transformation of I^- in surface or soil water, showed lower rates of sorption by soils than iodine in the form of I^- did, suggesting involvement of further reactions like reduction of IO_3^- or deiodination of organics in the sorption process.

3 DISCUSSION

The experiments demonstrate that in aquatic and terrestrial environments speciation of iodine should be related to microbial activity. Looked at it more closely, the direct action of microorganisms seems to play a minor role. As can be derived from the processes in the aqueous phase, the

reactions appear as an oxidative transformation of iodine into organic bonds, mediated by extracellular enzyme systems. Enzymic iodination processes are well known to occur in biological systems and they are also applied in vitro for production of organic iodine compounds. Such iodinating

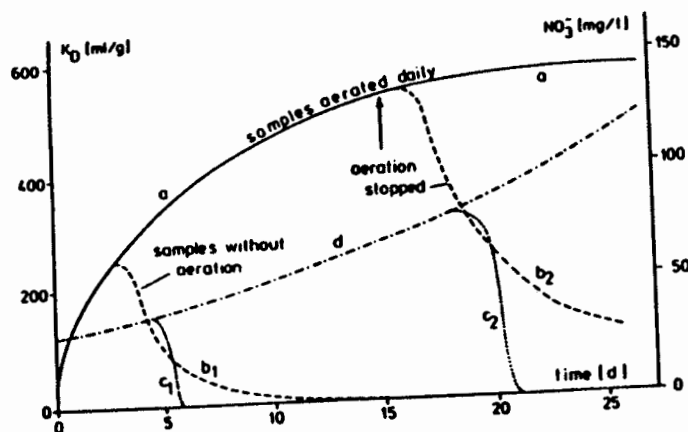


FIGURE 5 Iodine distribution coefficients (K_D) in soil/water batch. a) aerated samples; b₁) non-aerated samples; b₂) aeration stopped after 15 days; d, c₁, c₂) NO_3^- concentrations in samples corresp. to a, b₁, b₂.

TABLE I Distribution of radioiodine in a soil column after 7 days of water percolation under water unsaturated condition; injection of radioiodide into the column inlet on the 3rd day of a 10 days run.
Column length: 200 mm Flow rate: 10 ml/cm²·d
Soil type: brown earth

Depth of layer mm	Fraction of total inj. 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

enzyme systems consist of peroxidases and components generating H_2O_2 , e.g. as a by-product in the oxidation of glucose with help of glucose oxidase. All these prerequisites exist in the environmental systems in question.

The iodination processes appear to be reversible to a large extent. This is suggested by the release of I^- from the organic fractions under anaerobic and other reducing conditions. So far, the actual distribution of iodine among different chemical forms in environmental systems is given by an equilibrium of processes binding iodine in organic materials as well as releasing it continuously. Thus with time, newly introduced radioiodine can mix with the stable resident iodine in the systems.

As a result of the above processes speciation of iodine in surface fresh water and water/soil systems shows I^- as the only inorganic component beside a variety of organic iodine compounds. In the water phase generally about 15-20% of the iodine is found as I^- . In organic soils more than 99.9% of total iodine is associated with undissolved, obviously organic matter, based on iodine distribution coefficients of several hundreds ml/g, while the fraction of dissolved iodine is made up of I^- and organic iodine compounds according to the above ratio (Figure 6). The organic compounds that bind iodine in the conversion processes are not yet fully identified. However, humic substances seem to play a considerable role in binding the converted iodine.

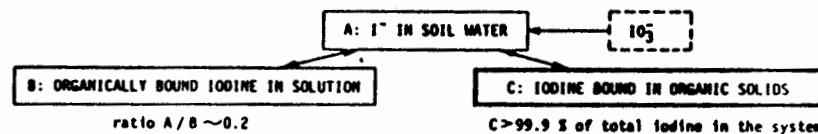


FIGURE 6 Schematic of iodine distribution in soil/water systems.

These considerations are in agreement with most of the results of many investigations on the behaviour of iodine in environments reported thus far. Bonding of iodine to organic material has become evident during the last decades in studies on sorption of iodine by soil through the work of Raja⁴, Wildung⁵, Whitehead⁶⁻⁸, Saas^{9,10}, Szabó¹¹, Prokhorov¹², Tikhomirov¹³ and others. Reduction of IO_3^- in soils was shown in several studies^{7,11,12}. Tikhomirov¹³ analysed the distribution of organically bound radioiodine in soils with respect to different types of organics showing humic and fulvic acids as the dominant acceptors. Radioecological observations of a decreasing bioavailability of radioiodine newly introduced into soils made by Saas⁹ and Schüttelkopf¹⁴ coincide with the proposed mechanism of a gradual mixing of the radioiodine with the stable iodine content of the soils.

Finally, the above processes and resulting speciation of radioiodine may also be of importance concerning its migration in soils. Complete mixing of added radioiodine and existing stable iodine is a requirement for the effectiveness of a dynamic compartment model¹⁵, suggesting fallout iodine residence times in surface soils of several thousands of years. Residence times on the same order can also be derived from batch distribution coefficients for radioiodine in soils measured in our experiments ranging from several hundreds to more than a thousand ml/g.

4 ACKNOWLEDGMENT

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DISCUSSION

BONOTTO:

Does autoclaving affect the organic substances present in water and their capability of binding iodine?

BEHRENS:

Of course autoclaving means a heavy stress to organic materials present in water and soil and will "denature" them to some extent so that a change but no abolition of iodine uptake will result. The full disappearance of iodine binding by organics will thus more reflect full inactivation of microbial and correlated activity.

IODINE-125 AND IODINE-131 IN THE THAMES VALLEY AND OTHER AREAS

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ABSTRACT

Part of the Iodine-125 and Iodine-131 waste from hospitals and research centres is discarded down drains and passes through sewage and water reclamation works into the river system. Relatively high concentrations of radioiodine occur in outfalls that discharge into the river Thames, lower levels are found in the mainstream river and less still in the reservoirs and tap water supplies abstracted from the river. The pathway from waste to drinking water could account for the low levels of Iodine-125 found in the thyroid glands of some farm animals and human beings in the Thames valley.

1 INTRODUCTION

Whilst monitoring the ^{129}I ($T_{1/2} = 1.6 \times 10^7$ yr) content of thyroid glands from farm animals at varying distances from nuclear-fuel reprocessing plants it was noticed that low levels of radioiodine were present in some animals far distant from nuclear installations and radionuclide production sources. In particular it was found that thyroids from control sheep housed at the Central Veterinary Laboratories (C.V.L.), Weybridge, Surrey, contained similar activities to those grazing around Windscale, Cumbria, 300 miles to the north of Weybridge. The shorter half-life of the Weybridge samples eventually identified the radioiodine present as ^{125}I ($T_{1/2} = 60$ d) which, like ^{129}I , emits photons close to 30 keV.

The possibility of self-contamination of specimens was carefully investigated and ultimately eliminated. The origin and environmental pathways of such ^{125}I , and also ^{131}I , found in the Thames valley and elsewhere is the subject of this paper.