

ESTABLISHMENT OF EQUILIBRIUM BETWEEN RADIOIODINE AND SOIL

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The radioiodine retention effectiveness and its retention rates in different soils were determined. The effects of various factors on the retention dynamics preceding the equilibrium establishment, particularly the role of organic soil substances, have been followed.

The radionuclide ^{129}I becomes a permanent contaminant of the environment and this contamination acquires a global character. Its worldwide amount increases annually by about 11 TBq and in the year 2 000 it should reach 1.5 PBq (ref.¹). Due to these facts this radionuclide is being monitored and the parameters characterizing the dynamics of its abundance in important components of the environment are being evaluated, both qualitatively and quantitatively. The behaviour of ^{129}I in soils² is considered to be very important, among others also due to the fact that iodine washed out from the atmosphere by the rain water is transferred from 60–90% into the soil³ and the experimental results of ^{129}I vertical distribution indicate its long retention in the upper, agriculturally exploited soil horizon⁴.

The equilibrium establishment rate of radioiodine in the soil belongs to the most important parameters. It is influenced not only by the process of contamination, by the origin and form of radioiodine⁵, but also by the chemical composition of the soil⁶. The studies published so far dealt only with the state after the true thermodynamic equilibrium was achieved⁶. In this paper the attention was focused on the problems of the retention kinetics of radioiodine in soils in the period preceding the equilibrium establishment.

EXPERIMENTAL

The experiments were carried out with five basic types of Czechoslovak soils; in all cases the samples were taken from the top soil. Sampling localities and some important physical and chemical data about these soils were published elsewhere⁷. For the short-term model experiments of the retention kinetics determination (up to 20 days) the radionuclide ^{131}I and for the long-term experiments the radionuclide ^{125}I were used, both in the form of iodide.

The soil suspension was shaken in closed glass centrifugation probes in a horizontal shaker, the phases were separated by centrifugation. After different times t of the contact of radioiodine

with the soil (using cycles of 7 hours of intense shaking followed by 17 hours of rest) the distribution of the radionuclide between the solid and liquid phases was determined radiometrically and the acidity of the liquid phase was measured. The ratio of the weight of the soil sample m to the volume V of the liquid phase was kept constant during the experiments, $m/V = 0.1 \text{ g ml}^{-1}$. From the distribution of the radionuclide activity between the solid and liquid phases the values of the relative retention y were determined (y is the ratio of the radionuclide retained by the soil to its total amount in the system) and after the establishment of a constant distribution of the radionuclide between phases the distribution constants K_D were calculated (K_D is the amount of the radionuclide retained by 1 g of the soil divided by the remaining amount in 1 ml of the solution). The radioiodine retention rate τ is in this study defined by the reciprocal value of the time necessary for the establishment of the steady distribution of the radionuclide between the soil and the solution and the latent retention time t_1 is then given by the time of the contact of the solution with the soil until the radionuclide retention in the solid phase separated by centrifugation starts to be detectable (the retention detectability is defined as $3\sqrt{N_{bg}}$, where N_{bg} is the count rate of the background).

The content of the humus substances x_h in soils was determined by thermogravimetry, the oxidizable carbon content c_{ox} was determined after oxidation with the chromic acid in the presence of sulphuric acid by the titration of the nonconsumed acid by the solution of Mohr salt using an apparatus for the dead-stop titration. The participation of various chemical forms of radioiodine in the aqueous phase was determined by TLC with a silica gel adsorbent.

RESULTS AND DISCUSSION

Both the organic and mineral soil components participate on the radioiodine retention in soils. Both these components of the solid soil phase initiate different processes and participate on different retention mechanisms.

The dynamics of the radioiodine retention by soils is much slower than that of the equilibrium establishment of other radionuclides, particularly of the nuclides having a cationic character. Fig. 1 presents the comparison of the retention kinetics dependences for $^{90}\text{Sr}^{2+}$, $^{137}\text{Cs}^+$, and $^{125,131}\text{I}^-$ in chernozem and in the acid brown soil from a neutral aqueous solution. The establishment of the equilibrium distribution between the soil and the solution takes tens of minutes for radiostrontium, hours for radiocesium, and tens of days for radioiodine. Moreover, in the case of radioiodine only a quasiequilibrium state is established as it follows from the facts given below. Different courses of the radiostrontium, radiocesium, and radioiodine retention processes are due to different retention mechanisms. The retention of radiostrontium and radiocesium is governed by the mineral soil component while predominantly the organic soil component is responsible for the radioiodine retention (particulatly in the natural conditions).

Table I presents the content of humus and oxidizable carbon in the soil samples under study and Fig. 2 gives the thermogravimetric curves of two soil samples chosen so that they differ significantly by the total content of the organic components and very substantially by the saturation of the sorption complex. The data on the oxidizable carbon in humus and the different shapes of thermogravimetric curves bear

out the qualitatively different composition of the organic substances in individual soils.

For the interaction of radioiodine with the soil not only the amount but also the quality of organic substances in humus are decisive. The results of the fractionation of the heterogeneous, polydisperse mixture of the isolated iodine-humus soil com-

TABLE I
Content of organic substances (x_h) and of the oxidizable carbon (c_{ox}) in soils

Soil	x_h , %	c_{ox} , %
Chernozem	3.4	1.69
Brown soil	3.2	1.04
Brown acid soil	3.85	1.94
Podzolic soil	4.9	2.04
Illimerized soil	3.7	1.27

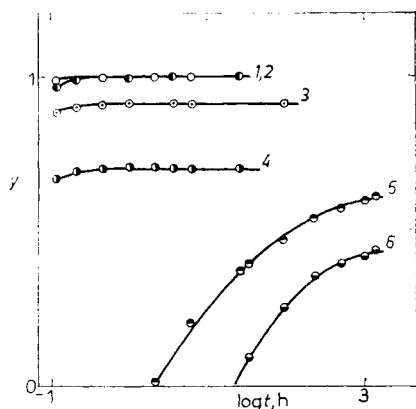


FIG. 1

Differences in the establishment of equilibrium concentrations of radiostrontium (Sr^{2+}), radiocesium (Cs^+) and radioiodine (I^-) in the system soil-water. Curve 1 ^{137}Cs , chernozem; 2 ^{137}Cs , brown acid soil; 3 ^{90}Sr , chernozem; 4 ^{90}Sr , brown acid soil; 5 $^{125,131}I$, chernozem; 6 $^{125,131}I$, brown acid soil

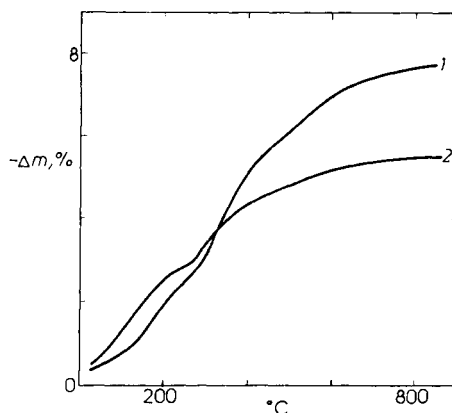


FIG. 2

The weight decrease $-\Delta m$ of soils during thermogravimetry. Curve 1 podzolic soil; 2 chernozem

pounds achieved by the gel filtration on Sephadex G-50 and G-70 and by the disc electrophoresis in the polyacrylamide gel indicate⁶ that in the direct contact of radioiodine with the soil its interaction with certain molecular fractions of the organic substances proceeds preferentially, particularly the interaction with the compounds with high content of carbon and with a relatively high condensation degree of molecules. Moreover, the incorporation of iodine into different organic compounds proceeds by completely different rates and the iodine bond strength in these compounds changes with time.

The differences in the radioiodine retention from the aqueous solutions in soils are demonstrated in Fig. 3. Only parts of these dependences are given, characterizing the process preceding the equilibrium establishment. The following interaction conditions were studied: the effect of the medium acidity and the radioiodine retention by soil samples from which all the organic substances were removed by calcination. It is evident that the retention rate depends very strongly on pH, for the given soil it increases with the decrease of the aqueous phase pH value. It was found that it is not connected with the equilibrium pH value establishment in the system; the retention rate is much slower. For instance, the equilibrium pH value in brown soil was reached with 1 min in $0.05 \text{ mol.l}^{-1}\text{-HCl}$, within 60 min in water, and within 2 min in $0.05 \text{ mol.l}^{-1} \text{ NaOH}$ while the respective equilibrium retention times were 2 hours in the first medium, 85 days in the second one, and in the case of $0.05 \text{ mol.l}^{-1}\text{-NaOH}$ 85 days of contact were not sufficient for a detectable radionuclide retention. It was also observed that the retention is slowed down by the presence of the ^{127}I isotopic carrier. The experiments with thermally treated soil samples (*i.e.*, with samples without organic substances) show that the mineral component of the solid soil phase is the decisive factor in the retention process under extreme conditions under which the electrostatic mechanism of retention takes place.

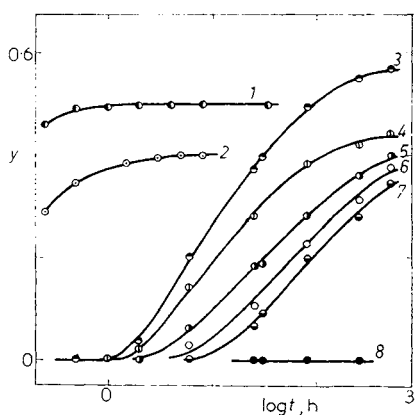


FIG. 3

The retention dynamics of radioiodine in different types of Czechoslovak soils from the aqueous solutions. Curve 1 brown soil, $0.5 \text{ mol.l}^{-1}\text{-HCl}$; 2 brown soil, annealed, $0.5 \text{ mol.l}^{-1}\text{-HCl}$; 3 chernozem, H_2O ; 4 illimerized soil, H_2O ; 5 brown soil, H_2O ; 6 brown acid soil, H_2O ; 7 podzolic soil, H_2O ; 8 brown soil, $0.05 \text{ mol.l}^{-1}\text{-NaOH}$

The experiments carried out with neutral aqueous solutions allows us to draw certain conclusions about the radioiodine retention under natural conditions. From our experiments it follows that the organic compounds contained in the soil humus influence not only the rate of the equilibrium concentration establishment but also the amount of the retained radionuclide. Table II presents the effectivenesses, rates, and periods of latent retention of radioiodine for all 5 soils under study. The fact that the podzolic soil exhibits the lowest values of effectiveness and retention rate from all soils under study (in spite of the highest content of humus in this soil) demonstrates that the quality of humus is the decisive factor for the retention, particularly the presence of organic substances with a higher number of active centers in the molecule. Such compounds are evidently most abundant in the chernozem as it follows from the data given in Table II. The number of active centers can be quantitatively characterized, *e.g.*, by the experimentally determined ratio of the iodine content to the content of carbon in the molecules.

Among the components with a high number of active centers belong also the organic soil substances soluble in water, high values have been found also for the fulvic acid fractions. During the radioiodine retention and during the establishment of the equilibrium distribution between the radionuclide and the natural iodine in soils the radionuclide interacts first with the soil organic substances extracted into the solution. This is demonstrated on the $y-t$ curves (Fig. 3) where in the initial stages $y = 0$. Using TL chromatography it could be proved that already in this latent phase of retention a great part of the initial radioiodine is bound to the organic soil substances present in the solution. Only afterwards the activity of the radionuclide in the centrifugate starts to increase. This is due to the lower interaction rates with insoluble organic substances and also due to the transformation of the iodo-organic compounds.

TABLE II

Certain physico-chemical parameters of the radioiodine retention in the system soil-water

Soil	K_d , ml g ⁻¹	τ , 10 ⁴ , h ⁻¹	t_1 , h
Chernozem	6.3	6.5	1.2
Brown soil	5.6	4.9	2.1
Brown acid soil	4.3	6.0	3.2
Podzolic soil	3.8	1.2	6.0
Illimerized soil	4.7	7.6	1.7

Because the bond strength of iodine in various organic compounds changes with time⁶ and the transformation of iodoorganic compounds is not yet completed, the observed steady distribution of radioiodine between the soil and solution must be considered only as a quasiequilibrium. For the reasons mentioned above, the establishment of the true thermodynamic equilibrium is necessarily a very lengthy process.

Certain results published recently⁸ indicate that the interaction of radioiodine with the soil is also influenced by the microorganisms present in the soil. In the interpretation of our results these processes were not taken into account.

REFERENCES

1. Handl J., Kühn W.: *Atomkernenergie* 29, 232 (1977).
2. Saas A., Grauby A.: *Health Phys.* 31, 21 (1976).
3. Tikhomirov F. A., Ryzhova I. M.: *Atomnaya Energiya* 51, 44 (1981).
4. Anderson T. J.: Report DP-1526/1978.
5. Saas A.: *Radioprotection* 11, 205 (1976).
6. Kasparov S. V.: *Avtoreferat dissertatsii*. MGU, Moscow 1980.
7. Beneš J., Frána J.: *Agrochémia* 21, 16 (1981).
8. Bors J., Martens R., Kühn K.: *Atomkernenergie/Kerntechnik* 44, 87 (1984).

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