Physico-Chemical and Hydraulic Mechanisms of Radionuclide Mobilization in Aquatic Systems

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Abstract. This paper presents main results of joint studies carried out in frame of EC-coordinated ECP-3 Project "Modelling and study of the mechanisms of the transfer of radioactive material from the terrestrial ecosystem to and in water bodies around Chernobyl" in part of geochemical pathways. Physico-chemical models of specific migration processes are developed and recommended for application as sub models for inclusion in the decision support system (JSP-1). Main parameters, determining the behaviour of radionuclides in aquatic ecosystems are identified and methods for their estimation in emergency situations are proposed.

1. Introduction

Following the Chernobyl accident significant quantities of radioactivity were released into the reservoir system on the Dneper river, potentially creating a major radiation hazard to several million people. As a result, in the lower reaches of the Dneper basin between 10-20 % of the dose to man has been calculated to be introduced via water (mainly irrigation). In the city of Kiev the importance of this pathway is much less (a few per cent) but recent studies have shown that, in public perception, water is equal in importance to food as a vector. This is mainly because the Kiev reservoir forms the only direct transport pathway between the reactor and the city. Hence, it is important to understand the processes which are likely to remobilize radioactivity and transport it via aquatic pathways, so that the detailed basis of all decisions can be given to, and accepted by the local population.

Although in Kiev the aquatic pathway is not of major importance, in some country districts the cumulative dose is much higher than average level calculations suggest. This is because some small lakes, which are heavily used by the local population, retain very high levels of radionuclides in the water column. This increases the relative importance of the water pathway for these populations. If effective counter-measures are to be carried out in these local areas it is important to determine the major mechanism in each system which causes high concentrations to be maintained in the water column.

Table 1. Basic characteristics of water bodies under studies in ECP-3

Water body	Location	K^+, mg/l	NH_4^+, mg/l	Sediment type	Deposition type
Kiev reservoir	Ukraine	3 - 4	0.5 - 1	mixed	mixed
Devoke Water	UK	0.4	0.4	organic	condensation
Kozhanovskoe	Russia	10-15	0-5	organic	mixed
Svyatoe	Russia	18-30	15-30	organic	mixed
Glubokoe	Ukraine	10-15	2-12	clay	hot particles

The EC-Coordinated ECP-3 Project "Modelling and study of the mechanisms of the transfer of radioactive material from the terrestrial ecosystem to and in water bodies around Chernobyl" had two main objectives in part of geochemical pathways studies:

1) to identify the fundamental factors controlling radionuclide transport in aquatic systems. To incorporate this understanding into better sub-models of radionuclide behaviour and to extensively test these models before recommending to JSP-1 for inclusion in the decision support system;

2) to identify appropriate methods of study for individual, highly contaminated water bodies in order to understand the processes involved and propose appropriate countermeasures.

Five water bodies, presented in Table 1, were being studied with a view to a) comparing methodologies; b) identifying the main causes of residual high concentrations of radiocesium in the water column and c) verifying models of radiocesium remobilization.

2. Hot particles as a specific feature of the Chernobyl accident

During the explosion and the fire at the fourth unit of the Chernobyl Nuclear Power Plant in April-May 1986 a great amount of dispersed nuclear fuel (fuel hot particles), structural materials, and substances dumped into the reactor and formed in it (condensation hot particles) was released into the atmosphere. The fuel particles were of dense or loose structure and consisted of uranium oxides. Their sizes ranged from hundreds of microns to fractions of a micron. The radionuclide composition of the fuel particles was similar to the fuel make-up in the damaged unit with some depletion of volatile nuclides (^{134,137}Cs, ^{106}Ru etc.). Fuel particles account for more than 90% of the total amount of hot particles. The condensation particles were generally characterized by smaller size and regular form. They can include either a wide spectrum of radionuclides or 1 to 2 radionuclides (for example ^{134,137}Cs; ^{106}Ru; ^{144}Ce + ^{95}Zr; ^{144}Ce + ^{106}Ru etc.).

Release of these fuel and condensation particles into the environment was the main distinguishing feature of the accidental contamination following the Chernobyl accident.

The nuclear weapon testing fallout had more than 90% of ^{90}Sr and ^{137}Cs in water soluble and exchangeable form (i.e., extractable by neutral salt solutions). The fraction of water soluble and exchangeable forms in the Chernobyl fallout was much lower due to the presence of water insoluble hot particles, and depended on the distance from the damaged unit. For example, the fraction of non exchangeable ^{137}Cs in the fallout near Chernobyl was about 75% [1], in the Bryansk region-50-60% and in Cumbria (UK) - about 10% [2]. As a result, the proportion of exchangeable radionuclides in soils in the near zone of the plant during the first years following the accident was much lower than that after the nuclear weapon testing [3]. For this reason, the Chernobyl radionuclides had higher values of distribution coefficient in the "soil-water" system and, hence more slower migration. Wash-off of dissolved ^{90}Sr with surface runoff in the 30-km zone in 1986-1987 was much lower than those obtained at the sites on which ^{90}Sr was applied as a soluble salt [1]. Apart from the differences in the radionuclides speciation in the Chernobyl and nuclear testing fallout, they also differ by the direction of transformation in soil. The mobility of nuclear testing radionuclides decreases with time because of fixation by soil components, while in the near zone of the NPP in the first years following the accident, the predominant process was leaching of radionuclides from hot particles which led to increased migration ability [4].

Thus, the peculiar features of the Chernobyl fallout did not make it possible to use directly the results of the studies of nuclear testing radionuclides and that is why the behavior of hot particles in environment needs in-depth investigation.

3. *Kinetics of radionuclide leaching from hot particles*

The physically based modelling of leaching processes is not easy because of non uniformity of sizes, forms, and chemical nature of particles. Besides, to use the results of such modelling for practical purposes, experimental data are needed about distribution of particles of different composition and sizes over a significant area as well as about characteristics of each type of particles. In view of this, it seems reasonable to use for forecasting integral parameters characterizing the rate of radionuclide leaching in different parts of the contaminated zone. The first order rate constant k_l (leaching) could serve as such a parameter, i.e. $dP/dt = -k_lP$, where P is concentration of radionuclide incorporated in fuel particles, t is time and k_l is a function of surface area of the particle.

As the hot particles dissolved their sizes decrease and the proportion of radionuclides in the particles of worst solubility increase. The first process results in the increase of k_l, and the second in its decrease. The assumption of the balance between the above processes makes it possible to use the first order equations to describe the kinetics of radionuclide leaching from the hot particles. The values k_l may be obtained from data on the transformation of radionuclide forms in soils. The proportion of a radionuclide in fuel particles is assumed to be equal to the fraction of a radionuclide in the non exchangeable form minus that fixed by the soil. In that calculation, it is better to take data on ^{90}Sr which is weakly fixed by soils. The results of calculating of the leaching rate constants are given in Table 2.

The leaching rate constants given in Table 2 agree with the values of k_l calculated from the dissolution rate of fuel particles [5]. The latter constants ranged from 10^{-3} to 10^{-4} day^{-1} for the particles of 50 to 500 μm (1-km zone) and from 10^{-2} to 10^{-3} day^{-1} for the particles of 5 to 50 μm (the region of Chernobyl).

Table 2. Rate constants for ^{90}Sr leaching from the fuel hot particles

Distance from the NPP, km	**Location**	**Rate Constant 10^{-3} day^{-1}**
4 - 10	Flood plain of R. Pripyat	0.15 - 0.87
	Kopachi	0.40 - 0.48
10 - 20	Benevka	1.4 - 1.7
	Chernobyl	1.5
	Korogod	1.0 - 3.6

The calculation and measurements of the proportion of the water soluble and exchangeable forms of ^{90}Sr indicate that at present the amount of radionuclides occurring as a part of the fuel particles is considerable only in the 10-km zone of the NPP, whereas at farther distances, the hot particles have mostly disintegrated.

4. Basic transformation processes of chemical speciations in soil and bottom sediments

The most expedient way to classify radionuclide speciations is to divide them into water soluble, exchangeable, and non exchangeable (fixed) chemical forms in soil [3, 4]. Different chemical forms can be separated by the technique of sequential extraction with solutions of different compositions. The equilibrium between water soluble and exchangeable forms is established quickly and it is reasonable in many cases to consider them as a single mobile form. In terms of chemical forms, fixation of radionuclides is transfer from their mobile form to fixed form. For mathematical description of this process, models were proposed in which fixation was treated as an irreversible process [4, 6]. The data available in literature suggest that at the initial stage of fixation and for processes of relatively short time-scale this assumption is quite warranted. However, the data for long-term transformation of radionuclide chemical forms in soil indicate the existence of a remobilization process opposing to fixation. After ^{137}Cs and ^{90}Sr solutions are applied to soil, the fraction of their exchangeable forms decreases not to zero, as is supposed to happen during irreversible fixation, but to a certain stationary level independent of the amount of radionuclide applied and not changing significantly, at least for several years [7]. With allowance for fixation reversibility and two mechanisms of fixation-selective adsorption and diffusion into the solid phase of soil, transformation of radionuclides chemical forms in soil can be summarized in scheme presented in Figure 1.

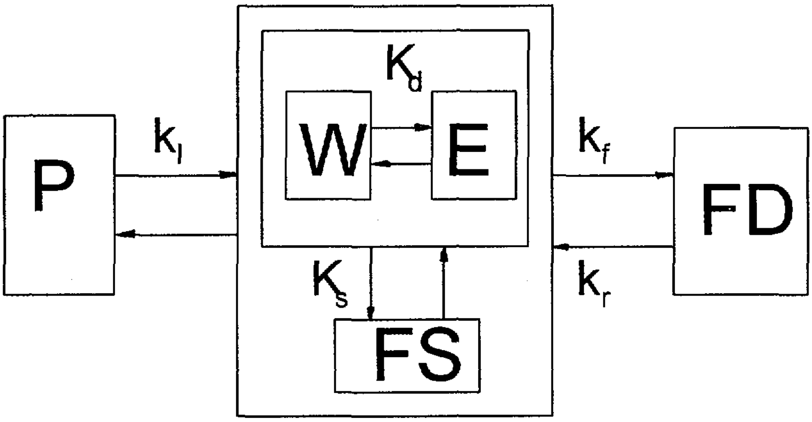

Fig.1 Scheme of Transformation Processes of Chemical Forms in Soil-Water System.
W, E, F are water soluble, exchangeable, mobile and fixed forms, respectively; FS, FD are radionuclides, fixed as a result of selective sorption and diffusion into solid phase respectively; P is radionuclides in fuel particles; k_l, k_f, k_r are first order rate constants of radionuclide leaching from fuel particles, fixation and remobilization respectively; K_d is exchangeable distribution coefficient; K_s is equilibrium constant of selective sorption.

Analytical solution of differential equations corresponding to the scheme of Figure 1 gives following time dependence of mobile radionuclide form after the Chernobyl deposition on soil:

$$m = (1 - K_s)\left[\left(\frac{k_f m_o + k_r - k_l}{k_f + k_r - k_l} - \frac{k_r}{k_f + k_r}\right) e^{-(k_f + k_r)} t + (1 - m_0)\,\frac{K_e - k_r}{k_f + k_r - k_l}\, e^{-k_l t} + \frac{k_r}{k_f + k_r}\right] \quad (1)$$

Where m and m_0 are current and initial fraction of mobile forms in soil, respectively; K_s - equilibrium constant of selective sorption; k_l, k_f, k_r are first order rate constants of radionuclide leaching from fuel particles, fixation and remobilization, respectively.

Experimentally determined transformation parameters of ^{137}Cs for different soil types of 30-km zone are presented in Table 3.

It is expected that fixation rate must be dependent so on the liquid phase chemical composition, for example on the concentration of ammonium in the pore waters of bottom sediments [8]. Experiments have shown that the fixation process proceeds at a faster rate in the interlayers of illite at low levels of competing cations (NH_4 and K), which causes an increase of cesium K_D^{tot} values. Although not enough data have been collected for a statistically significant evaluation, an apparent correspondence of lower contents of exchangeable potassium with higher fractions of fixed ^{137}Cs is observed. Batch experiments carried out with the organic soil (peat bog) from Devoke Water shows this dependence of cesium fixation rate and potassium concentration in solution even for soil aged for a short time (1 hour) (Table 4).

To study in more detail the kinetics of basic ^{137}Cs transformation processes in soils, a long-term laboratory investigation was carried out. It was shown that the interaction of cesium with soils is characterized by three phases with distinctly different time scales: initially rapid uptake (characteristic time about several minutes), relatively slow intermediate uptake (characteristic time about several days) and the third phase with characteristic time about several months. The initial phase is interpreted as the rapid cation-exchange sorption on adsorption sites located on the surface of soil particles, the intermediate phase is a result of cesium redistribution from non-selective to high selective adsorption sites and the third phase seems to be associated with cesium diffusion in mineral particles.

Table 3. Parameters of Chemical Forms Transformation Processes of ^{137}Cs in Typical Soils of 30-km Zone of the Chernobyl NPP

Soil Type	$k_f \cdot 10^2$, day^{-1}	$k_r \cdot 10^3$, day^{-1}	K_s
Sod-podzol, clay	1.1 ± 0.3	2.9±1.1	0.41 ± 0.04
Sod-podzol, sand	1.7 ± 0.2	4.4 ± 0.5	0.54 ± 0.02
Peat bog soil	3.9 ± 0.4	5.2 ± 0.8	0.70 ± 0.02

Table 4 - Fraction of extracted and fixed radiocesium in organic soil (Devoke Water) at different potassium concentrations. Aging time 1 hour.

KCl concentration	Fraction of ^{137}Cs (%)	
M	NH_4Ac-extracted	Fixed
0.01	20.2	40.7
0.025	29.5	31.9
0.05	35.3	22.9
0.1	40.7	17.7

An increase of total distribution coefficients with time is observed. For example, the total distribution coefficient for the soddy-podzolic (mineral) soil MS increases from about 600 $l.kg^{-1}$ after 1 hour to about 20000 $l.kg^{-1}$ after 210 days, implying that the kinetic process is very slow. The time period of ^{137}Cs equilibration in this soil is about one year. In contrast, fixation in the peat soil occured very rapidly so that within two weeks the radiocaesium concentration in the water phase and in the first ammonium extraction were lower than the limit of detection [7].

This implies that, strictly speaking, the total cesium distribution coefficient cannot be used for mathematical modelling of migration processes with characteristic times less than several months. Therefore, it appears that the exchangeable distribution coefficient, which increases slightly during the first few days and then remains constant [7], is a more relevant parameter for modelling short-term (2days - 6 months) transportation processes. It can be calculated as follows:

$$K_d^{ex} = \frac{A_{ex}}{A_W} * \frac{V}{M} \qquad (2)$$

where A_w and A_{ex} represent the radiocaesium activities in the water phase and in the first ammonium acetate extraction respectively, V is avolume of liquid phase and M is a mass of solid phase.

The exchangeable distribution coefficient can also be used to predict radiocaesium K_d^{tot} in bottom sediments and soils under the assumption of pseudo-equilibrium conditions.

5. Prediction of Radionuclide Distribution Between Solid and Liquid phases of Soils and Bottom Sediments

The need for a specific distribution coefficient for modelling particular systems stems from the fact that, on the one hand, this parameter is governing the migration rate of radionuclides in natural water systems, their build-up in fish and vegetation, and, on the other hand, there are no all-purpose K_d values to be used for modelling the behavior of radionuclides in any natural water ecosystem. For example, the quoted K_d values for ^{137}Cs in surface water range over 4 orders of magnitude. Moreover the difference in K_d at the same site for different layers of lake bottom sediment can be as great as two orders of magnitude [8].

The K_d value is also dependent on the time elapsed since after radionuclide contamination of the soil or bottom sediment (ageing effect). Therefore, a reliable prediction of the behaviour of radionuclides is possible only if distribution coefficients for a given soil-water system at a given time are assessed based on the knowledge of mechanisms and kinetics of sorption-desorption processes.

Prediction of the radionuclide distribution in soil-water systems should, generally, be performed in two stages. The first step is prediction of transformation of species and determination of the part of radionuclides in the exchangeable form. The goal of the second step is to make assessment of K_d for the exchangeable form of a radionuclide.

For estimating the distribution coefficient of the exchangeable form of the radionuclide two approaches can be made. Both approaches assume that ^{137}Cs and ^{90}Sr in solution occur in the cationic form and that their exchangeable sorption is described by the equation of the cation exchange. The major difference between them is how non-uniformity of adsorption centres of soils and sediments is accounted for. Under the first approach, external non-homogeneities of adsorption sites are minimized by using a cation-analogue of the radionuclide as a competing cation M which has the closest possible sorption properties [4] to the radionuclide. For determination of required parameters a standard procedure of sequential extractions is used [9,10]. Concentrations of radionuclides and competing cations are determined in a water extraction and the proportion of exchangeable forms in the solid phase is calculated from their concentrations in the acetate extraction. The data obtained are used for calculation of the selectivity coefficient:

$$K_c = \frac{[R]_{ex} * [M]_w}{[R]_w * [M]_{ex}} \qquad (3)$$

$$M = K, NH_4 \; for \; Cs\text{-}137$$
$$M = Ca, Mg \; for \; Sr\text{-}90$$

The calculated selectivity coefficient is then used to predict the distribution coefficient of the exchangeable form of the radionuclide:

$$K_d^{ex} = \frac{K_c \, [M]_{ex}}{[M]_w} \qquad (4)$$

Among the advantages of the procedure is the simplicity of experimental determination of parameters. In addition, parameters can also be assessed from literature data. For example, data concerning the proportion of exchangeable forms of radionuclides and competing cations in soils and sediments determined by the standard method are available for many natural soil-water systems.

The method has been successfully used for predicting distribution of ^{90}Sr and ^{137}Cs in lake bottom sediments and their concentrations in surface runoff [4]. A limitation of the method is that the K_c value can, strictly speaking, depend on the composition of the liquid phase and in those cases when it differs significantly from the composition at which K_c was found, the value should be recalculated. This adds uncertainty to the prediction.

In the approach proposed by A.Cremers and co-workers [11] the non-uniformity of adsorption sites is taken into account through dividing them into selective: frayed edge sites (FES) and regular sites (RES). The distribution coefficient is then calculated as a sum of K_d for FES and RES. Most substrates have radiocesium sorption dominated by the frayed edge sites, highly organic soils being the only relevant exception [12]

The characterization of a system in terms of FES capacity and trace selectivity coefficient K_c (Cs/K) allows predictions of radiocesium distribution coefficients in scenarios for which the FES are homoionically potassium saturated. If the product of the selectivity coefficient K_c (Cs/K) and the capacity of the FES can be treated as a constant defining the radiocesium interception potential (RIP) for the FES, the distribution coefficient for radiocesium can be expressed as:

$$K_d^{FES} = \frac{K_c(Cs/K)[FES]}{m_K} \qquad (5)$$

The radiocesium interception potential $[K_d^{FES}\ m_K]$ can be extended to an ammonium scenario $[K_d^{FES}\ m_{NH4}]$ allowing the measurement of ammonium to potassium selectivity coefficients and an assessment of the relative competitive effect of these cations in the hyper selective sites. Table 5 summarizes the $[K_d^{FES}\ m_K]$ and $[K_d^{FES}\ m_{NH4}]$ values calculated from the mean of the plateau values for a set of soils and sediments. These data are in good agreement with results obtained in other soil and sediment systems [12-17].

The $K_c(NH_4/K)$ which reflects the higher sorption competitivity of ammonium in the FES pool covers a range of 3 to 7. These values provide a rationale for the remobilization of radiocesium from reducing sediments [8,17].

Reasonable predictions of K_d^T values in different ionic scenarios can be made on the basis of eq. (5), taking into account the action of both potassium and ammonium ions. The equation required is:

$$K_d^T = \frac{\left[K_d^{FES} m_K\right]}{K_c(NH_4/K)m_{NH4} + m_K} \qquad (6)$$

where the denominator expresses the total competitive effect of potassium and ammonium ions.

The predicted K_ds values calculated from eq.(6) taking into account $K_d m_K$, $K_c(NH_4/K)$ (Table 5) and potassium and ammonium water composition values are in good agreement with the "in situ" K_ds obtained from the ^{137}Cs contents of sediment and water (column or pore water) [18]. So, the solid/liquid partitioning of radiocesium in field scenarios can reliably be predicted on the basis of sediment laboratory characterizations and water composition. Moreover, it was shown [19] that in situations following a nuclear accident, a first estimate of the radiocesium distribution coefficient in sediments can be deduced solely from the pore water ammonium concentration. This approach, although useful in rationalizing sorption behaviour on the basis of readily measurable properties of the system is, however, of limited interest for the behaviour of radiocesium in the field. The time scale for the model scenario is quite short and the relevance of these characterizations for the long-term behaviour of radiocesium is questionable because of fixation.

Table 5 - Relevant parameters for sediments and soils from different ecosystems.

Sampling places	Sample	Sampling points	CEC meq.100g^{-1}	K_dm_K meq.g^{-1}	K_dm_{NH4} meq.g^{-1}	$K_c(NH_4/K)$
Kiev reservoir, Ukraine	bottom sed.	KRS2(1)*	45-70	4.40	0.67	6.6
		KRS2(2)*		4.67	0.67	7.0
		KRS1(1)*	40-44	1.77	0.36	4.9
		KRS1(2)**		1.63	0.35	4.7
Kiev reser.	suspended matter	6	-	8.64	-	-
Dnieper river		7	-	1.74	-	-
Pripyat river		9	-	0.88	-	-
Kajanovskoe lake, Russia	peat bog soil	807	126	0.24	-	-
Glubokoye lake, Ukraine	bottom sed.	GL3	-	1.04	0.18	5.8
Svjatoye lake, Russia	bottom sed.	1-14cm	37.5	1.03	-	-
		14-28cm	39.5	1.34		
Devoke water, England	bottom sed.	0-2cm	24.3	0.74	0.22	3.4
		2-5cm	16.1	0.60	0.16	3.8
		8-11cm	17.7	0.71	0.21	3.4
		11-15cm	18.0	0.76	0.23	3.3
	peat bog soil	0-5cm	76.7	0.026	-	-
		5-10cm	70.0	0.033	-	-
		10-15cm	75.7	0.019	-	-
		15-20cm	81.5	0.010	-	-
		20-25cm	68.0	0.036	-	-
Chernobyl 10 km zone	alluvial sod soil	201	28.0	0.44	-	-

*- upper layer; **- bottom layer

When considering the long-term behaviour of radiocesium the desorption potential appears to be a key property of the system, particularly when the environmental conditions change (as a result of washout from the water column, or a change in redox conditions in sediments leading to a change in interstitial fluid composition). The behaviour dynamics of radiocesium will be controlled by the potential of the sediment to release the radionuclide, i.e. the size of exchangeable fraction. The virtue of this method is constant values of K_c(FES) for different soils.

It can be concluded that application of both procedures will make it possible to have satisfactory estimates of the distribution coefficient of the exchangeable form of the radionuclide and the choice of method in each particular case should be dictated by the availability of necessary parameters.

6. Study of the effect of organic matter of soils and bottom sediments on the physical-chemical state of radiocesium.

The commonly accepted mechanism of radiocesium fixation is by diffusion into interplanar spaces of clay minerals [20]. It is believed that natural organic matter adsorbs cesium reversibly and non-selectively and clay minerals alone are responsible for cesium fixation, even in soils very rich in organic matter[12]. According to this hypothesis, the correlation between cesium exchangeability and organic matter content would be positive. It was found, however, that the radiocesium exchangeable fraction is very low in some organic soils. The ammonium acetate extractable fraction of Chernobyl ^{137}Cs in the peaty soil from the Kojanovskoe lake watershed was about 2% [8], while the typical value for mineral soils of the same region was 10% [3,4]. Very high radiocesium retention values were also found for peaty soils from the Devoke Water watershed after ^{137}Cs labelling. In these soils, after 3 days aging time, the ammonium chloride extractable fraction was about 2% and it decreased to 0.1% after 2 years.

Qualitative determination of mineral components suggests that the clay mineral content in this soil is very low (below the detection limit). On the basis of these observations, a study has been carried out in order to evaluate how organic matter influences the physico-chemical state of ^{137}Cs in soil and bottom sediments. In this study the standard method of sequential extractions [3,9,10] was used to determine water soluble, exchangeable and acid soluble (HCl 1:1) forms and insoluble residue.

Soil and bottom sediment samples were divided into two groups: for the first group, the samples were analysed without incineration prior to acid extraction. For the second group, the samples were subjected to incineration at 500^0 C, then extracted with ammonium acetate. In this way in the first group of samples, high molecular weight organic matter was preserved during the whole procedure, whereas in the second group of samples the organic matter was removed before the acid extraction. For the bottom sediments no marked difference was noted in radionuclide species determined with and without incineration of the samples. The fraction of ^{137}Cs fixed in the insoluble residue after water, ammonium acetate and acid extractions for these samples is 5 to 20% close to that which is normally detected in soils and bottom sediments. Thus, the organic matter in bottom sediments either does not fix radionuclides, or fixes them in such a way that they are extractable with hydrochloric acid. A similar picture was observed with the sod podzol gley soil.

For the peaty soil the trends are the opposite: the ^{137}Cs fraction in the insoluble residue is 52.8-63.9% of that of the untreated samples and an order of magnitude higher than the fraction of insoluble radionuclide in the burned samples (5.6-8.2%). Similar results were obtained for peaty soil from Devoke Water watershed 2 years after spiking with ^{137}Cs. The ^{137}Cs fraction fixed in the insoluble residue was 16.4% in the burned sample and 59.0% in the unburned. This suggests that 40-50% of ^{137}Cs in these soils is probably fixed by the organic matter and not extracted by concentrated solutions of ammonium acetate and hydrochloric acid. The other possible explanation for these data is a modification of the mineral structure, resulting in an increase in radiocaesium extractability. To check this possibility, two additional experiments were performed. In the first the dependence of the Chernobyl radiocaesium extractability on the temperature pretreament of the samples was studied. The

Table 6 - Exchangeable radiocesium in peaty soil from Kojanovskoe lake catchment as a function of the incineration temperature.

Sample number	Temperature	Lost weight %	Exchangeable ^{137}Cs %
1	room	0	1.2
2	105 ^{0}C	7.7	1.3
3	150 ^{0}C	9.8	1.3
4	200 ^{0}C	74	8.0
5	300 ^{0}C	79	9.5
6	500 ^{0}C	81	11.1

results of this experiment are summarised in Table 6. The data indicate that the main increase in radiocaesium extractability occurs at 200° C when the organic matter starts to burn.

In the second experiment, organic matter from the Kojanovskoe lake peaty soil samples was destroyed by hydrogen peroxide at 60° C over a period of 1 month and radiocesium was extracted from the mineral residue by 1M ammonium acetate solution. Other samples were incinerated at 500°C before ammonium acetate extraction to study how the high temperature treatment alters the extractability of cesium associated with the mineral components of the soil. Table 7 shows the results of these experiments. It can be seen that there is no difference in the radiocaesium exchangeable fraction for the two sample treatments. It seems that caesium released from organic matter was subsequently fixed by mineral components. This process is quite likely because of the wet conditions (H_2O_2 treatment), and high temperature and duration of the experiment. Incineration of the mineral residue at 500° C did not significantly change the caesium extractability. This indicates that this treatment has no effect on sorption properties of the mineral components and therefore the increase of exchangeable caesium content in the original soil is a result of removal of organic matter.

These results can not be explained by any current concept of caesium fixation in soils and bottom sediments. Therefore, the mechanism of radiocaesium interaction with the organic matter of peaty soils calls for further investigation. A probable hypothesis is that radiocaesium fixation by organic matter of peaty soils occurs due to its diffusion into the volume of organic particles. This hypothesis is in good agreement with the result of radiocaesium fixation kinetics by organic and mineral soils [7]. Furthermore, the organic peaty soil from Devoke Water fixed radiocaesium faster than mineral sod podzolic soil from

Table 7 - Exchangeable radiocesium in peaty soil from Kojanovskoe lake catchment as a function of different treatments.

Sample number	Treatment	Lost weight %	Exchangeable ^{137}Cs %
1	H_2O_2	75	2.9
2	H_2O_2+500^{0}C	81	3.4

the Chernobyl area. This phenomenon can be attributed to faster caesium diffusion in amorphous organic particles than in crystalline mineral particles.

7. Radionuclide wash-off with surface run-off from catchment

Surface run-off from catchments is an important source of radionuclides in rivers and lakes in contaminated areas. Normalized wash-off coefficients, defined as the ratio of radionuclide concentration in run-off to surface density of catchment contamination are used to quantify this process [1,4,21,22]. In previous studies [21,22] it was found that ^{137}Cs and Sr-90 concentrations in run-off are independent of plot size and rainfall intensity. This indicates that the radionuclides in the overland flow are in equilibrium with the upper layer of soil and that the rate of attaining sorption-desorption equilibrium is quite high.

The principal mechanism of ^{137}Cs and ^{90}Sr transfer from soil to surface run-off is ion exchange. At ion-exchange equilibrium, the concentrations of identically charged cations are related by the ratio:

$$A_w = A_{ex}B_w/K_c(A\text{-}B)B_{ex} \qquad (7)$$

where A_w, B_w are concentrations of cations A and B in the liquid phase, respectively; A_{ex}, B_{ex} are concentrations of cations A and B in the solid phase,
respectively and $K_c(A\text{-}B)$ is the selectivity coefficient for cation A exchange for cation B.

The concentration of radionuclide, as follows from Eq. (7), is directly proportional to the concentration of competing macro-cations in run-off. Evidence for this is given by simulated rainfall experiments on run-off plots with different cation concentrations in the rainfall water. The cation composition of the run-off is determined by the mineralization of the rainfall water and release of cations from soil solution into run-off. Given free infiltration of rainfall water into the soil, soluble compounds are washed out from the surface layer at the beginning of the rainfall and at some time mineralization of the run-off becomes identical to that of the rainfall. In all experiments in 30-km zone [21,22], this occurred prior to the run-off event. As a result, the equilibrium concentration of radionuclides in the run-off changes only as a result of depletion of exchangeable species in the upper soil layer.

In addition to the cation concentration in run-off, Eq. (7) includes the concentration of exchangeably sorbed cations and radionuclides in the upper soil layer. This can be determined by the standard technique of 1N ammonium acetate extraction [9,10]. However, given non-uniform distribution of radionuclides and macro-cations in soil profile, the result will depend on the depth of the sampled soil layer. One of the ways to solve the problem is using a concept of a complete mixing layer (CML) or in other words, a surface soil layer in which the concentrations of dissolved compounds in soil solution are equal to the run-off concentration. Values of CML in our experiments were determined from the time dependence of ^{90}Sr concentration in run-off in special long-term experiments and were about 5 mm or less at the all plots. According to our data, exchangeably sorbed forms of ^{137}Cs and ^{90}Sr are distributed in the upper soil layer fairly uniformly and the concentration of exchangeable forms of radionuclides and macrocations in the 0-5 mm layer can be used as a measure for their concentration in the CML.

The selectivity coefficients in the "run-off - upper soil layer" system which are required for calculations were obtained from the results of plot experiments

Ca^{2+} and K^+ were used as a competing ions for ^{90}Sr and ^{137}Cs respectively.
The mean value of selectivity coefficient K_c(Sr-Ca) was 2.1±0.9 and K_c(Cs-K) was 20±4.

The values of selectivity coefficients and concentrations of radionuclide exchangeable forms and macrocations in the upper half-centimeter were used to make predictive estimates of the normalized wash-off coefficients of radionuclides in the rainfall run-off from the catchments of the rivers Pripyat and Ilya. The concentration of cations in the runoff was assumed to be identical to that in the rainfall water. The results of this calculations are given in Table 8. Estimated normalized wash-off coefficients are in good agreement with the experimentally measured values.

The approach described for wash-off coefficient estimation was applied to Devoke water catchment. Calculations were carried out using extraction data for the 0-4 cm layer for four soil cores representing the main soil types of the catchment and potassium concentration in rain-water or lake water [23]. Unlike the 30-km zone around Chernobyl, the dominant macrocation in Cumbria rainfall water is sodium. Predicted dissolved radiocesium concentrations ranged from 4-17 mBq/l and 11-54 mBq/l for rain-water and surface water (lake water) respectively. The values based on the potassium concentration in the lake were all within a factor of 2 of the measured lake water radiocesium activity (21±4 mBq/l)

Comparison of Devoke water soil profiles with results for soils in the 30-km zone show that radiocesium from the Chernobyl deposition has been much more mobile in soil and sediments of Devoke water than in 30-km zone. This is unexpected as the soils in the 30-km zone mainly consist of a layer of sand between 0.5 and 2.0 m thick, overlying a podzol. The sands would be expected to have high ^{137}Cs mobilities. However, most of the activity remained near the soil surface. The reason for this apparent inconsistency is that, immediately after the accident, the mobility of ^{137}Cs was governed by the different forms of radiocesium in the deposition. In western Europe (United Kingdom) the deposition was dominated by condensation particles containing at least 85% of the radiocesium in mobile forms [2]. However, in the town of Chernobyl, at the time of the accident, only 26% of the ^{137}Cs was in mobile forms [1].

This fact was exacerbated by at least two other factors:
1) the large difference in annual precipitation: 1840 mm/year for Devoke compared to 550 mm/year around Chernobyl which creates a difference of about a factor of four in run-off coefficients, i.e. 60-70% of the precipitation in the Devoke water catchment is lost through outflowing streams compared to 15-29% in the Chernobyl catchment. Hence much more rain water passes through the surface soil of Devoke water compared to the Chernobyl soils; 2) the very low clay mineral content of upland Cumbrian soils compared to soils in the 30-km zone so that mobile forms represent up to 30% in Cumbria and 5-10% in the 30-km zone causing higher mobility in Cumbrian soils.

Table 8. Predicted and measured normalized radionuclide wash-off coefficients

Location	**Normalized Wash-off Coefficients (10^{-6} mm^{-1})**			
	Predicted		*Measured*	
	Sr-90	**Cs-137**	**Sr-90**	**Cs-137**
Pripyat catchment				
Chernobyl	22±10	1.6±0.8	24±13	2.5±1.2
Kopachi	12±7	-	18±8	-
Ilya catchment				
Staraya Rudnya	34±18	3.7±1.4	36.9±12.2	5.0±2.2
Kliviny				
Rudnya Ilyinetskaya				

As a result ^{137}Cs wash-off coefficients range up to a few percent per annum in the Cumbrian Lake District, whereas coefficients of 0.01-0.1% are found in the 30-km zone [1].

8. Conclusions

The behaviour of radionuclides in aquatic systems is largely dependent on:
- the chemical forms of radionuclides present in atmospheric fallout;
- the rates of transformation processes in soils and bottom sediments;
- environmental parameters, influencing the distribution of exchangeable forms between solid and liquid phases.

The main transformation processes are:
- disintegration of fuel particles, resulting in additional radionuclides passing into the solution;
- fixation of the exchangeable form;
- remobilization, i.e. transfer of the non exchangeable form into exchangeable form.

Transformation of chemical species of radionuclides in soils/sediments can be described by first-order kinetic equations with rate constants determined in field and laboratory experiments.

For predicting vertical and horizontal migration of radionuclides in soils and sediments the values for the following parameters are needed: the proportions of chemical forms in the fallout; the rate constants of transformation processes; adsorption capacities (CEC, FES) and selectivity as a function of depth and cationic composition of the solution in contact with soil or sediments.

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