

Methodology improvement of radiocaesium sorption determinations on bottom sediments from Chernobyl contaminated areas

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Abstract. Characteristics of radiocaesium selective sorption on soils and bottom sediments from Chernobyl contaminated areas, such as, capacity of selective sorption sites (frayed edge sites-[FES] and high affinity sites-[HAS]) and radiocaesium interception potential (RIP) are determined, allowing to predict radiocaesium distribution in the soil-water systems. Experimental methods based on masking of the regular exchange sites (RES) by silver thiourea (AgTU) were carried out. To extent the potential of these methods, the methodology was slightly modified by introduction of additional ammonium extraction of exchangeable radiocaesium after equilibrium time. To obtain [FES] and [HAS] linear form of Langmuir equation was used. Application of linear form of Langmuir equation allows to determine the capacity of selective sorption sites [FES] for organic bottom sediments for which maximum of caesium isotherm does not take place as a result of lattice interlayers collapse. Capacity of high affinity sites [HAS] was determined using Langmuir linearisation of the initial piece of sorption isotherm. In the case of RIP determinations fixation leads to overestimation the value of RIP. The notion of RIP^{ac} (exchangeable RIP-after ammonium acetate extraction) was introduced.

1. INTRODUCTION

Radiocaesium is selectively adsorbed in sediments and soils and the retention in these substrates is essentially controlled by the illite (clay) content. It was reported [1] that sorption sites in illite clay can be divided into surface exchange sites, interlattice positions near the edges of the clay particles (frayed edge sites, FES) and interlattice positions in the interior of the particles. During the same period it was clearly established [2] that cations with low hydration energy such as caesium, potassium and ammonium are thought to induce interlayer dehydration and layer collapse resulting in the fixation of the cation in interlayer positions. Conversely, cations with high hydration energy such as calcium, magnesium, and strontium, produce expanded interlayers and are not fixed. A method based on the use of Ag-thiourea (AgTU) as a masking agent was developed [3]. This complex ion blocks the planar exchange sites, for which it shows significantly higher preference than caesium, and is poorly competitive with caesium in the frayed edge sites. The sorption plateau of the caesium isotherm is identified with the capacity of the FES. It is determined in a suitable high AgTU background concentration and corrected for a small contribution of the planar sites on the basis of the selectivity coefficients $K_c(\text{Cs}/\text{AgTU}) = 0.02$ [4]. However, when this method is used to determine FES of high organic soils and sediments it could happen that the plateau of the isotherm was not reached. An improvement of this methodology was performed in which the application of the Langmuir equation to the caesium isotherm was carried out.

According to some authors [5] the adsorption isotherm with saturation is described by the Langmuir equation:

$$X = \frac{X_m C}{K + C} \quad (1)$$

where X represents the adsorbent concentration in the substrate, C the adsorbent concentration in solution in equilibrium, X_m a maximum surface coverage and K is a constant related to the energy of adsorption.

This equation could be linearised resulting into the following:

$$\frac{1}{X} = \frac{K}{X_m} \left(\frac{1}{C} \right) + \frac{1}{X_m} \quad (2)$$

The FES values can be obtained from the intercept ($1/X_m$) of the dependence inverse concentration of caesium adsorbed ($1/X$) on inverse concentration of caesium in solution ($1/C$). Therefore, the range of isotherm before sorption maximum could be used to obtain FES. Moreover, taking the initial range of the isotherm at low caesium concentrations the capacity of the high affinity sites [HAS] can be determined. The high affinity sites have a very high selectivity to caesium as compared with FES and therefore they will be occupied by caesium in the first run. HAS represented 0.5 to 10% of the FES [6].

In order to predict the radiocaesium distribution in the soil/sediment-water systems it is important to determine the solid-liquid distribution coefficient, K_d . Some authors [3] suggested the use of the radiocaesium interception potential (RIP). The RIP is the product of the FES capacity and the selectivity coefficient of radiocaesium to correspondent competitive ion, usually potassium (RIP_K) or ammonium (RIP_{NH_4}). An improvement of this methodology is proposed which takes into account the caesium fixation during the equilibration time. An additional step of ammonium extraction from the solid after equilibration allows avoiding the overestimation of the value of the exchangeable sorbed caesium.

The objective of this study is to improve the methodology for FES and radiocaesium interception potential (RIP) determinations [3] in a number of organic bottom sediments from Chernobyl contaminated areas.

2. MATERIAL AND METHODS

2.1 Capacity of the FES

Sediment samples (solid/liquid ratio = 0.25g/25ml) were equilibrated (24 hours, end-over-end shaking) by dispersion in an excess of AgTU ($0.015 \text{ mol dm}^{-3}$), centrifuged (30 min., 27000 g) and the supernatant discarded. Radiocaesium sorption isotherms were measured by equilibrating (24 hours, end-over-end shaking) sediment samples with AgTU solutions ($0.015 \text{ mol dm}^{-3}$) containing increasing levels of CsCl (ranging from 10^{-6} to $10^{-4} \text{ mol dm}^{-3}$) ^{134}Cs labelled. Finally, samples were centrifuged and ^{134}Cs activity measured in the liquid phase, by gamma spectrometry, before and after sediment addition. All measurements were carried out in duplicate.

2.2 Radiocaesium interception potential (RIP)

Sediment samples (solid/liquid ratio = 0.25g/25ml) were repeatedly pre-equilibrated (24 hours, end-over-end shaking) with $0.015 \text{ mol dm}^{-3}$ AgTU solutions containing KCl (or NH_4Cl) concentrations ranging from 2×10^{-4} to $10^{-2} \text{ mol dm}^{-3}$. Phase separation was made by centrifugation (30 min., 27000 g). Sediment samples were then equilibrated (24 hours, end-over-end shaking) with the same AgTU-KCl (or NH_4Cl) solutions ^{134}Cs labelled. Afterwards, the samples were centrifuged (30 min., 27000 g) and ^{134}Cs measured on the supernatants after phase separation. For exchangeable radiocaesium determinations, sediment samples were equilibrated (24 hours, end-over-end shaking) with 1 mol dm^{-3} $\text{CH}_3\text{COONH}_4$ and exchangeable ^{134}Cs measured on the supernatants after phase separation (centrifugation 30 min., 27000 g) by gamma spectrometry. All measurements were carried out in duplicate. Distribution coefficient values (K_d and K_d^{ex}) were calculated.

3. RESULTS AND DISCUSSION

3.1 Capacity of the FES

The caesium sorption isotherms obtained are shown in Figure 1. The experimental data have been corrected for a small caesium interception in the regular exchange sites. Such correction is based on the Cs-AgTU selectivity coefficient value (0.02) for the clay planar sites [4]. It is verified that reasonably well-defined plateaus were obtained, except for CL1 (C1) sediment. Any way the FES capacity values were calculated from the mean of the two last points in the curves. The mean values and standard errors (2α) of FES are presented in Table 1. These values range from 2.49 ± 0.44 to 0.87 ± 0.19 meq kg^{-1} .

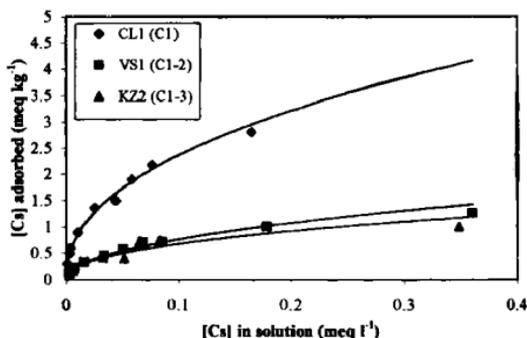


Figure 1: Caesium sorption isotherms in the frayed edge sites of Lakes Constance (CL1 (C1)), Vorsee (VS1 (C1-2)) and Kozhanovskoe (KZ2 (C1-3)) sediments, in the presence of $0.015 \text{ mol dm}^{-3}$ AgTU

Table 1: Results of [FES] determinations using two methods: the isotherm plateau and Langmuir linearisation

Sampling site	Sample references	Isotherm plateau	Langmuir linearisation	
		[FES] meq kg^{-1}	[FES] meq kg^{-1}	[HAS] meq kg^{-1}
Lake Constance	[CL1 (C1)] (0-15 cm)	2.49 ± 0.44	4.31	1.20
Lake Vorsee	[VS1 (C1-2)] (0-20 cm)	1.13 ± 0.18	1.45	0.51
Lake Kozhanovskoe	[KZ2 (C1-3)] (0-15 cm)	0.87 ± 0.19	1.75	0.43

The Langmuir linearisation, i.e., the study of the dependence inverse concentration of caesium adsorbed ($1/X$) on inverse concentration of caesium in solution ($1/C$) originates the conversion of the isotherm into two straight lines: one piece, corresponding to the initial range of the isotherm at low caesium concentrations, which intercept gives the inverse of HAS values; the other one, corresponding to the final range of the isotherm at high caesium concentrations, which intercept gives the inverse of FES values.

The dependence of the inverse concentration of caesium adsorbed versus the inverse concentration of caesium in solution for sediments from Lakes Constance, Vorsee and Kozhanovskoe at low and high range of caesium concentrations are presented in Figure 2a and 2b respectively. The HAS and FES values, in

meq kg⁻¹, obtained from the inverse value of the straight lines intercept are presented in Table 1. It is verified that, in general, FES capacity values are higher than those calculated using the isotherm plateaus. This discrepancy is more pronounced for [CL1(C1)] sediment. This finding is in agreement with what was observed in Figure 1, where isotherm plateau is not well-defined. The [HAS] values obtained seem to be relatively high. This result could be explained by the caesium concentration range used during the experiments, which could not be sufficiently low.

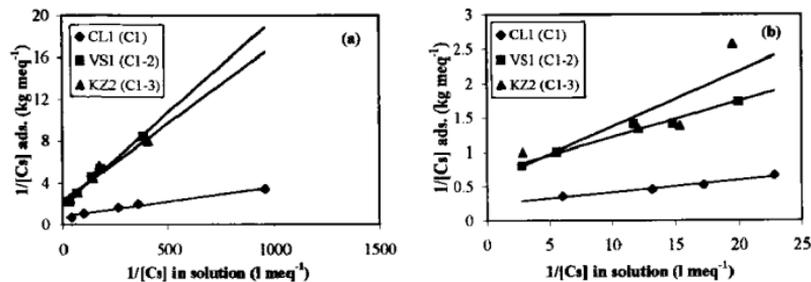


Figure 2: Dependence inverse concentration of caesium adsorbed versus inverse concentration of caesium in solution for Lakes Constance (CL1 (C1)), Vorsee (VS1 (C1-2)) and Kozhanovskoe (KZ2 (C1-3)) sediments; (a) Langmuir linearisation of the initial part of caesium sorption isotherms (at low caesium concentrations); (b) Langmuir linearisation of the final part of caesium sorption isotherms (at high caesium concentrations)

3.2 Radiocaesium interception potential (RIP)

Figure 3 shows the dependence of radiocaesium interception potential in the presence of potassium or ammonium for Lake Constance (a) and Vorsee (b) sediments. It is seen that, in the higher potassium or ammonium concentration range very well defined plateaus ($0.97 < R^2 < 0.99$) were obtained. The numerical data of RIP_K , RIP_K^{ex} , RIP_{NH_4} and $RIP_{NH_4}^{ex}$ corresponding to the mean of plateau values for a set of sediments studied are presented in Table 2. In general, the values obtained in the presence of potassium are higher, by a factor of 3 to 5, than those obtained in the presence of ammonium. This means that the selectivity coefficient ammonium/potassium range from 3 to 5, i.e., ammonium is about four times more competitive in the FES than the potassium ions.

The exchangeable radiocaesium interception potential RIP_K^{ex} and $RIP_{NH_4}^{ex}$ are, in general, two to three times lower than those obtained before the ammonium acetate extraction. This discrepancy is more pronounced in the potassium scenario. An exception, appears for Lake Vorsee [VS1 (C1-2)] sediment in ammonium scenario that presents a similar value for RIP_{NH_4} and $RIP_{NH_4}^{ex}$. In any case, this means that in the radiocaesium interception potential determinations the caesium fixation leads to overestimate the RIP values.

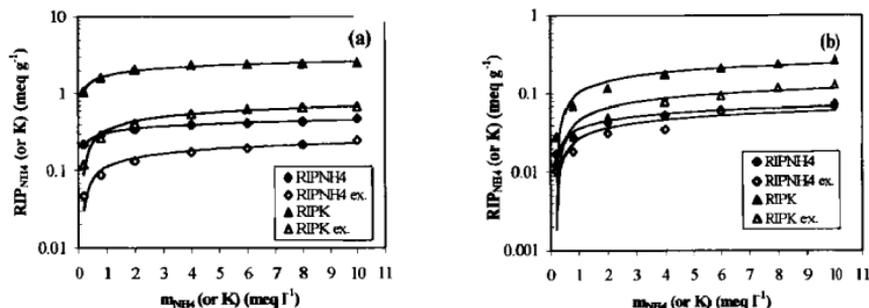


Figure 3: Dependence of radiocaesium interception potential (RIP) in the presence of potassium and ammonium in solution for bottom sediments from Lakes Constance (a) and Vorseck (b), determined using the original method [3] and modified with ammonium acetate extraction (RIP^{ex}) after equilibrium time

Table 2: Radiocaesium interception potential values using the original method [3] (RIP) and modified with ammonium acetate extraction (RIP^{ex}), after equilibrium, in potassium and ammonium scenarios for bottom sediments from Constance, Vorseck, Svyatoye and Kozhanovskoe Lakes

Sampling site	Sample references	RIP _K meq g ⁻¹	RIP _K ^{ex} meq g ⁻¹	RIP _{NH4} meq g ⁻¹	RIP _{NH4} ^{ex} meq g ⁻¹
Lake Constance	[CL1 (C1)] (0-15 cm)	2.52 ± 0.06	0.68 ± 0.02	0.46 ± 0.03	0.23 ± 0.02
Lake Vorseck	[VS1 (C1-2)] (0-20 cm)	0.26 ± 0.02	0.12 ± 0.01	0.068 ± 0.008	0.064 ± 0.006
	[VS2 (C1-2)] (0-20 cm)	0.27 ± 0.02	0.13 ± 0.02	0.087 ± 0.009	0.053 ± 0.001
Lake Svyatoye	[SV2 (C1-3)] (0-15 cm)	0.83 ± 0.01	0.42 ± 0.05	0.23 ± 0.03	0.15 ± 0.01
Lake Kozhanovskoe	[KZ2 (C1-3)] (0-15 cm)	0.39 ± 0.03	0.15 ± 0.01	0.095 ± 0.009	0.043 ± 0.009

4. CONCLUSIONS

Langmuir linearisation of caesium sorption isotherm allows to determine frayed edge sites [FES] and high affinity sites [HAS] of high organic bottom sediments for which well-defined isotherm plateaus were not reached as a result of lattice interlayers collapse.

Introduction of ammonium acetate extraction of exchangeable caesium, after equilibration, improves the accuracy of the radiocaesium interception potential (RIP) measurements and allows avoiding the influence of caesium fixation on results of measurements.

It can be concluded that caesium fixation plays significant role in case of RIP determinations. Values three and two times higher in case of RIP_K and RIP_{NH4} respectively, were found.

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