J Radioanal Nucl Chem (2015) 304:21–26
DOI 10.1007/s10967-014-3665-1

Determination of sorption characteristics for artificial radionuclides in the hydrosphere

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Received: 15 September 2014 / Published online: 5 October 2014

Abstract Adsorption onto solid particles plays an important role in the transport of radioactive contaminants in the hydrosphere. Sorption is usually described with a distribution coefficient: a ratio of radioactivity fixed on solid phase and dissolved in water in equilibrium. In this study, we developed, optimised and verified a method that uses a series of batch experiments for determination of the distribution coefficients of radionuclides in sediment–water and suspended solids–water systems. This can be further used for describing radionuclide behaviour in river courses. This work was funded by the Czech Ministry of Interior, as a part of Safety research project.

Keywords Sorption · Artificial radionuclide · Hydrosphere · Sediment · Suspended solids · Distribution coefficient

Introduction

When surface water is polluted, the contaminants are transported together with water; they travel along a river course. During this migration, radionuclides can be fixed onto solids suspended in water, which can settle down after that, or they are sorbed directly onto sediments already deposited on the river bed. These sorption processes influence the migration of radionuclides in the environment and their entrance into food chains.

Sorption is a complex process generally affected by many factors. Primarily, it is the quality of sediments and suspended solids, especially grain size and chemical composition, which can influence the sorption properties significantly. Since it is mainly composed of clay particles, the solid phase in the hydrosphere (sediments and suspended solids) predominantly restrains cations [1, 2] in the pH range common in natural surface water. Moreover, the sorption process is significantly influenced by the sorbed compound properties, especially the size and charge of ions and its chemical species. The latter is dependent on the surrounding environment: pH value, redox conditions or the presence of other substances in the solution [1–3]. In addition, temperature can influence sorption.

Concerning sorption kinetics, it runs rapidly in the beginning, while the slow processes become gradually noticeable later. Equilibrium of the rapid phase is often reached in several hours. However, it can last several weeks till true equilibrium, including the slow processes, is reached. The topics of sorption kinetics and time necessary to reach equilibrium are discussed in several studies [4, 5].

Sorption can be described with the distribution coefficient K_D [6], which expresses the distribution of radionuclide between the water and solid phase in equilibrium state:

$$K_D = \frac{a_e}{c_e}, \tag{1}$$

where K_D is distribution coefficient (l g^{-1}), a_e radionuclide activity sorbed on solid phase in equilibrium (Bq g^{-1}), c_e radionuclide concentration in water in equilibrium (Bq l^{-1}).

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This parameter, which is based on an assumption of linear relationship between the sorbed and dissolved amounts of the radionuclide, is often employed for the sorption description due to its ease of use [3, 5–9]. With the condition that the concentration of the sorbed substance in system is very low, the distribution coefficient can describe the sorption with satisfactory accuracy.

The distribution coefficients are often determined in laboratories using batch tests. However, results of such experiments depend substantially on conditions of the determination; therefore, various data sets can be hardly comparable. Determination of the distribution coefficient is described in documents by the US Environmental Protection Agency (EPA) [10] and ASTM C1733—10 [11]. However, these methods are not specific for determination of sorption parameters in the hydrosphere, but they introduce rather general instructions, not taking into account particularities of river sediments; sorption on suspended solids is not included at all.

In our study, a method for distribution coefficient determination was compiled and tested for artificial radionuclides in sediment-surface water and suspended solids-surface water systems. This paper aims to unify methods for determining the distribution coefficient for radioactive substances in the hydrosphere, so the gained results are not only comparable but also represent the situation in real water environments.

Proposed procedure of determination

Since sorption depends on a number of factors, it is important to respect the natural conditions of the tested site, when conducting the laboratory experiments. In addition, the fundamental requirement is for the test to be easy so that it can be readily used in common radiological laboratories.

The method of distribution coefficient determination for radionuclides in sediments and suspended solids was proposed regarding our former tests, which optimised conditions for the determination, especially solid–liquid ratio, contact time or sample conservation method.

All experiments were conducted under oxic conditions and laboratory temperature.

Method principle

In order to determine the distribution coefficient, the method uses batch tests, when a mixture of solid phase and water with a spike of tested radionuclides is closed into a vessel. This experimental sample is mixed till the sorption equilibrium is reached, and after that, the solid phase is separated from water. Finally, radionuclide amounts in both separated phases are measured and the distribution coefficient is evaluated.

Preparation of test samples

Distribution coefficient determination requires a sample of sediment to be used always with corresponding surface water and sampled in the same site under similar conditions. In the case of suspended solids, it is crucial to collect water samples (containing suspended solids) during a normal state of the river, which means avoiding increased or extremely low flow rates that could influence concentrations of suspended solids or other parameters in the water. If the sediment sample contains coarse particles (for example, stones or plant fragments), they need to be removed. Otherwise, the samples are used without any treatment. Whenever the collected samples are not processed immediately in the laboratory, it is necessary to store them in a refrigerator. If the sediment samples must be stored for a longer period, they can be frozen. Other ways of sample conservation are not recommended, since they can influence sorption properties of the solid phase [12, 13].

To prepare the experimental batch, the wet sediment is placed into vessels in an amount that corresponds to 100 g of dry matter per litre of water. The water, contained in the sediment, is replenished to the required amount with the matching surface water. In the case of suspended solids, the surface water is used for preparing the test sample with its natural suspended solids concentration, without any treatment. That is the reason why it should be as close to the common suspended solids concentration in the site as possible. The volume of the test samples is selected based on the sample amount needed for analysis of the tested radionuclides.

Radionuclides and their spiked activities should be chosen with regard to the purpose of determining the distribution coefficient. Since the sorption behaviour is based on the physical and chemical properties of the studied radionuclide, it is supposed to be the same for all isotopes of one element. Therefore, the concerned radionuclide can be substituted by an alternative isotope of the same element, if it is convenient for the determination. For example, we were concerned in sorption of ^{90}Sr, but we used ^{85}Sr in our experiments. Unlike ^{90}Sr, ^{85}Sr can be detected using gamma-ray spectrometry, which makes its determination much easier. The distribution coefficient, evaluated for ^{85}Sr, can be generalised for any strontium isotope then, including ^{90}Sr.

To determine a particular distribution coefficient we need to prepare an experimental batch of several different radionuclide concentrations added in the same matrix (minimal number is 3, optimal at least 5). Determination of the distribution coefficient using only one activity point is necessary to consider distribution coefficient estimation. Radionuclide solutions added into the test samples should not significantly influence the conditions in the experimental mixture (pH, ion concentrations).

Mixing and separation of phases

After the test samples are prepared, they are mixed using an overhead laboratory shaker. Often, sorption is a very rapid process, so equilibrium is reached within several hours. As the most suitable mixing time, the 24-hour interval was evaluated, which is recommended and frequently used in studies [13, 14]. This interval provides sufficient time for reaching equilibrium in the majority of cases; furthermore, it is convenient due to laboratory working hours. If the mixing time was too long, unfavourable changes in the sediment or water quality would be expectable at laboratory temperature [4, 8].

The next step after the elapsing of the mixing interval is separating the solid and liquid phase. For the system suspended solids–water, the suitable technique is vacuum filtration. On the contrary, when separating sediment from water, the vacuum filtration itself is not sufficient. Therefore, it is necessary to employ centrifugation before the filtration step.

Measurement and evaluation

The radionuclides of interest should be measured in both separated phases—in water and also in sediment or suspended solids. This eliminates sorption of the radionuclides onto the vessel walls or other parts of the apparatus. Based on conducted experiments, sorption on apparatus was proven for some radionuclides in suspended solids–water system. This may be caused by the fact that the concentration of sorbent—solids, suspended in surface water under common, non-flood conditions—is very low. In fact, the suspended solids concentration in surface water was mostly in mg l^{-1}. In the case of sediments, where concentration in the test mixture is 100 g l^{-1}, the sorption of radionuclides on the apparatus is negligible, as it was confirmed experimentally.

The analysis method selection and the measurement conditions depend on the type of tested radionuclides.

If the distribution coefficient estimation was determined based on one concentration point, it could be calculated from measured activities in solid and liquid phases using Eq. (1). Uncertainty of the determined value could be evaluated as a combined uncertainty of radionuclide determination in both phases.

When evaluating the distribution coefficient from a data set, gained from several concentrations in the tested range, the distribution coefficient equals the slope of the regression line that intersects the beginning of the coordinate system, as shown in Figs. 1 and 2. Uncertainty of the distribution coefficient corresponds to the uncertainty of the regression coefficient, evaluated from the linear regression of the experimental data.

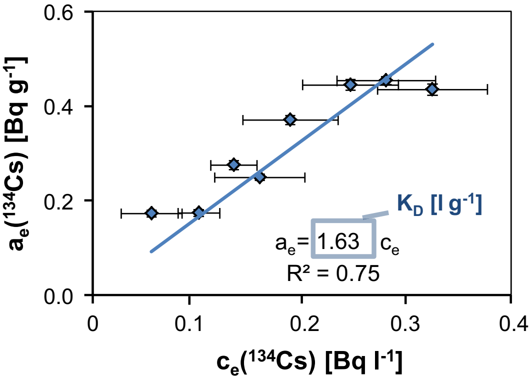

Fig. 1 Evaluation of measured data and determination of the distribution coefficient for ^{134}Cs sorption on sediment from the Vltava Štěchovice profile

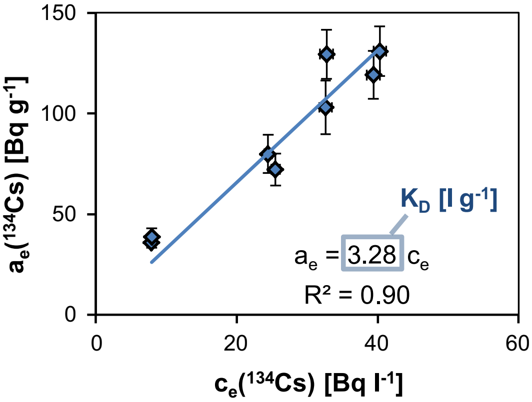

Fig. 2 Evaluation of measured data and determination of the distribution coefficient for ^{134}Cs sorption on suspended solids from the Vltava Štěchovice profile

Method verification

For method verification, samples of sediments and surface water were collected in 13 profiles from the Vltava River in the Czech Republic (see map in Fig. 3) during 2013.

Radionuclides solutions, needed for the distribution coefficient determination, were prepared from materials of certified activities, supplied by the Czech Metrological Institute. The radionuclide analysis was performed using gamma-ray spectroscopy, for which the Canberra-Packard germanium detectors were used. The detectors were calibrated using ^{152}Eu standard (energy calibration) and certified source containing a mixture of artificial radionuclides (efficiency calibration), both provided by the Czech

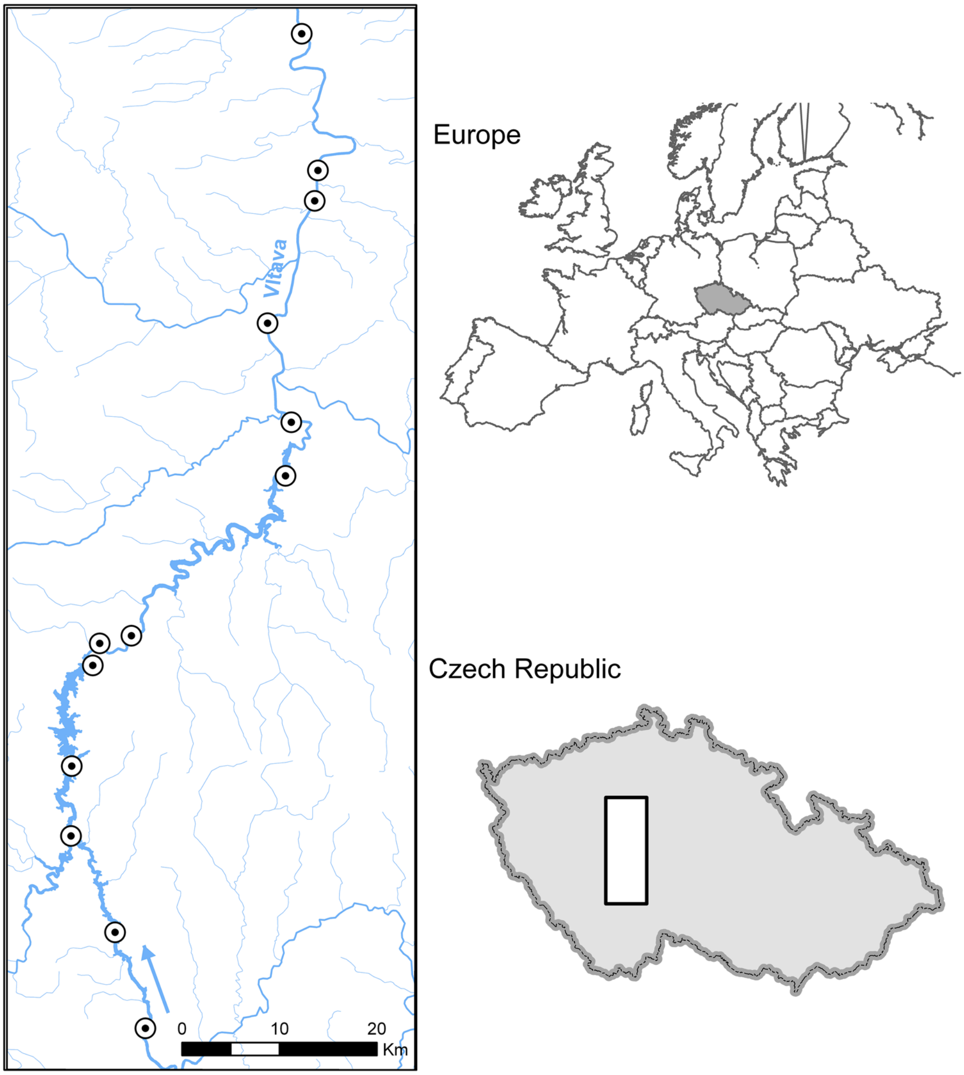

Fig. 3 Map of sites, where samples for the method verification were collected

Metrological Institute. Parameters of the method, used in the laboratory of the T. G. Masaryk Water Research Institute, are stated in Table 1.

The accuracy of the method could not be determined, as no suitable standard was obtainable.

Method range—lower and upper quantification limits—is related to the selected technique of radionuclide analysis and conditions of determination. The lower quantification limit of the distribution coefficient determination depends on the minimal detectable activity of the radionuclide analysis in the solid phase. On the other hand, the upper quantification limit is affected by the minimal detectable activity of the radionuclide analysis in water.

Repeatability of the method was evaluated using two parallel determinations of the same material. Table 2 shows the results of the repeatability determination for the sediment-surface water and suspended solids–water systems. For ^{85}Sr in suspended solids–water system, the repeatability of distribution coefficient determination was not evaluated. As a result of low sorbent concentration and low sorption rate of ^{85}Sr, its activity in the solid phase was below the detection limit of the analysis at conditions of the determination.

Conclusion

In our study, a method of distribution coefficient determination for artificial radionuclides was suggested and verified. This method concerns sediment-surface water and suspended solids-surface water systems, which are key factors influencing the behaviour of radionuclides in the hydrosphere. The determination was designed to be easily conducted in commonly equipped laboratories and to give consistent results. Unifying the method for the determination of these sorption characteristics is necessary for

Table 1 Parameters of method used in the laboratory of the T. G. Masaryk Water Research Institute for method verification

	Sediment–water	Susp. solids–water
Sample conservation	Refrigerating	Fresh, refrigerating
Sediment amount (g)	75	–
Water amount (ml)	750	2,000
Spiked radionuclides [approximate range of activities (Bq l^{-1})]	^{60}Co (1.5–5.0)	^{60}Co (1.0–5.0)
	^{85}Sr (1.5–5.0)	^{85}Sr (1.0–5.0)
	^{131}I (30–100)	^{131}I (20–100)
	^{133}Ba (30–100)	^{133}Ba (20–100)
	^{134}Cs (15–50)	^{134}Cs (10–50)
	^{139}Ce (1.5–5.0)	^{139}Ce (1.0–5.0)
	^{241}Am (1.5–5.0)	^{241}Am (1.0–5.0)
Number of concentration points	4	4
Number of repeating of one concentration point	2	2
Mixing time (h)	24	24
Centrifugation: time (min), speed (min^{-1})	30, 8,000	–
Vacuum filtration: filter porosity (μm)	1.5	0.45
Analytical method	Gamma-ray spectrometry	Gamma-ray spectrometry
Evaluation software	MS Excel	MS Excel

Table 2 Relative repeatability of the method of distribution coefficient determination for the tested radionuclides in sediment–water and suspended solids–water systems

Relative repeatability (%)	Sediment–water	Susp. solids–water
^{60}Co	13.4	4.3
^{85}Sr	9.7	–
^{131}I	21.3	5.1
^{133}Ba	5.3	5.4
^{134}Cs	6.9	4.1
^{139}Ce	18.0	9.8
^{241}Am	20.6	15.4

gaining representative and comparable data, which can be further used for describing the fate of radionuclides in water environment or for modelling their transport along river courses. It is important to remember that the measured distribution coefficients are always specific for the particular substance and system (sediment–water, suspended solids–water). Generalization of determined values can be misleading, just like application of distribution coefficients to another site or substance. Since the sorption can be influenced by many factors, we recommend paying attention to the conditions of the whole determination process from sampling to data evaluation and interpretation. In this manner, determining the distribution coefficients will be reliable.

Acknowledgments This work was prepared with the support of Project VG20122015088 sponsored by the Czech Ministry of Interior.

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