

Speciation Gamma-Spectrometry: the Fate of Environmental Radio-Nuclides in Hard-Water Lakes

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A sequential fractionation method for simultaneous and absolute measurement of environmental radio-nuclides, ^{241}Am , ^{210}Pb , ^{226}Ra , ^{137}Cs , ^{40}K and $^{234}\text{Th}/^{238}\text{U}$, by gamma-spectrometry was tested and applied to hard-water lake-sediments. The carbonate, fulvic, humic and mineral insoluble fractions were extracted from the sediments. Correction of self-absorption and geometrical effects, arising from the conditioning of bulk and fractionated sediments, were done using Monte Carlo simulations. This “non-destructive” fractionation procedure allows further analysis of other chemical species in the same fractions thus creating possibilities to study the dynamics of self-cleaning mechanism in lakes. The results demonstrate that the procedure is quantitative and suitable for the determination of environmental key radio-tracers in different fractions. Unlike other fresh-water sediments the major part of the environmental radio-nuclides is associated with “mineral” fractions. This speciation gamma-spectrometry procedure was supplemented by isotope-dilution alpha-spectrometry ^{210}Po (^{210}Pb), for determining the acid-soluble organic fractions in fresh-water lakes. The overall speciation procedure demonstrated that carbonate fractions, extracted from hard-water lake sediments, could be separated either free from, or associated with, fulvic-compounds. This speciation procedure can be applied to other aquatic deposits, however supplementary steps can be added if other data are required.

1. Introduction

Understanding the dynamics of the transfer and accumulation of matter at the earth’s surface is a key issue in global biogeo-chemical cycles. Soils and sediments are expected to be the final repositories of matter in lake-catchment systems, however they still act as dynamic environmental interfaces with the atmosphere and the hydrosphere. Assessing the role of soils and sediments as repositories, and as dynamic interfaces regulating the transfer of matter at critical environmental boundaries, requires using multi-tracer approaches [1–3]. Sequential fractionation and speciation procedures [4–7] are suitable tools for assessing the role of chemical, physical and biological processes on the final fate of matter in aquatic systems. They can provide important information for constructing reliable radio-chronologies, performing quantitative mass-balance studies [9], assessing the environmental behaviour of key tracers/species, and understanding the role of post-depositional processes in delayed-effects [1]. Existing radiochemical fractionation and speciation procedures [4–6, 7] are based on destructive analytical approaches, involving lengthy and complicated chemical separations. Gamma-spectrometry can provide simultaneous information on several key radio-nuclides of relevance for environmental studies [1]. Gamma-spectrometry, by being non-destructive and multi-analytical technique, provides elegant and powerful tool for fractionation and speciation studies. The application of low-level gamma-spectrometry for speciation studies requires developing suitable approaches for absolute and

different properties, sizes, consistence and composition. Selection of appropriate sample-to-detector geometry involves conditioning the fractions in reasonable sizes with suitable matrices as well as choosing the most effective detection-system. In freshwater lakes the production of organic matter, and associated interactions with mineral components having different grain-size, are important mechanisms regulating the accumulation in the sediments. The organic matter of soft-water lakes exists in different forms (fulvic, humic and humate) which vary in their densities, chelation, scavenging and accumulation properties [7]. In hard-water lakes epilimnetic calcite precipitation is strongly influencing the sedimentation process and therefore the accumulation of organic matter, and the preservation of materials, is expected to be different from soft-water lakes. The fractionation experiments presented here illustrates the joint role of calcite precipitation and organic compounds on the final fate of matter in hard-water lakes.

2. Sites and material description

Lake Stechlin, Germany, is one of very few European lakes having well documented records on its geochemical, limnological, ecological and environmental evolution [8]. Earlier studies on this oligotrophic hard-water lake showed that the accumulation of radio-nuclides, except for ^{137}Cs , is enhanced at high organic and low carbonate contents. The high levels of ^{238}U in Lake Stechlin indicate active inputs of other chemical species due to groundwater intrusion [1]. Considerable delay in the accumulation and deposition of mobile radio-nuclides, the so-called “conservative” nuclides such as ^{137}Cs , and to a less extent the bound or “particulate-reactive” ones, including $^{239+240}\text{Pu}$, ^{241}Am and ^{210}Pb , was observed in the lake. This delayed accumulation was explained by re-cycling in the well-oxygenated water-body of Lake Stechlin because of partial mineralisation of the organic matter by the bacterial activity [9]. However, the role of calcite precipitation [10], mineralisation of organic matter and production of soluble metal-complexes, on the self-cleaning mechanism in hard-water lakes is not fully understood. For these reasons speciation experiments were needed to explain: (a) the recycling and delayed accumulation of conservative nuclides; (b) the accumulation of particulate-reactive nuclides; and (c) the balance between biotic-uptake by primary production and a-biotic removal by calcite and mineral deposits. At the beginning of developing this method, two pilot studies were performed on bulk sediments from Lake Stechlin with low (~6%) and high (~50%) carbonates. These experiments were done to modify earlier speciation procedures and indicated that the carbonate and mineral fractions can be potential carriers of various nuclides.

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Suitable and representative sediment layers were, thereafter, selected from a high-resolution core with known chronology, composition, activities and trace-element contents. These samples were used to study the role of sediment composition, i.e. the carbonate, organic and mineral content, on the accumulation of conservative and particulate-reactive nuclides including ^{241}Am , ^{210}Pb , ^{137}Cs , ^{226}Ra , $^{234}\text{Th}/^{238}\text{U}$ and ^{40}K . The samples from the high-resolution core, which consisted of 0.5 cm slices, were combined following their chronological order. Combination of a small number of successive samples gave suitable masses for the speciation procedure.

3. Experimental procedures and coupled environmental-analytical aspects

An earlier fractionation procedure [7], adopted for soft-water lake sediments, was modified and tested before being applied (Fig. 1), 1–3 grams should be suitable to give satisfactory results on most of the radio-nuclides. The sediment samples were freeze dried in order to preserve the original composition and structure of the chemical and physical components. Special attention was, also, given to: (1) differentiate between the carbonate and the fulvic fractions since they are both soluble in dilute acids; and (2) remove the Ca, and other cations, for increasing the extraction yields with the alkali reagents. The initial steps using dilute HCl were thoroughly tested to choose optimum pre-treatment conditions (time, temperature, mechanical stirring, concentration and amount of HCl) for selective extraction of the carbonates and effective removal of cations from the sediments. The extracted fractions (Fig. 1) can be described as follows: (I) Fraction 1 contains the HCl-soluble minerals and decomposition products of the carbonates as well as slight amounts of simple fulvic compounds; (II) Fraction 2 is composed of two parts: the “free” fulvic compounds, sub-fraction (2a), and the “free” humic-matter, sub-fraction (2b); (III) Fraction 3 is composed of insoluble minerals and humic-bound remains including mineral and organic-clay complexes “humates”. This analytical strategy has several advantages: (1) the

separated fractions can be conditioned in different sizes and/or re-analysed by other methods, (2) it has very high separation yields and minimum analytical uncertainties, i.e. the whole procedure becomes quantitative; and (3) it has minimum risks for contamination due to cross-talking and memory-effects. These fractions were conditioned for ultra low-level gamma-spectrometry analysis using a well-Ge and a sandwich planar-Ge system. All samples were sealed against evaporation to preserve their geometry and to avoid damage and contamination of the detectors. Selection of the Ge-detector and choice of the sample-to-detector geometry were based on the most favourable conditions for high detection efficiencies and minimum self-absorption corrections. The self-absorption corrections were performed using validated Monte Carlo simulations where the geometrical parameters, the densities of the bulk samples and their fractions as well as the elemental composition were input parameters [11]. In the fractionation method given here the individual requirements for separating and measuring each of the radio-nuclides have been considered in order to have a coherent multi-analytical procedure. These specific requirements depend on the origin, physical, chemical and environmental properties of the radio-nuclides to be studied [12].

4. Results and discussion

This study showed that the procedure can be performed quantitatively without memory effects that arise from adsorption on glass-ware and cause contamination and cross-talking. The fractions could be reproduced in homogeneous matrices, without bubbles and other imperfections, and conditioned in small tubes. The overall procedure allowed to determine the ratio of various nuclides in the fractions and, thereby, to give some explanations on their temporal behaviour in the environment. Calculation of the individual activity of the fractions involved the use of improved peak-fit-routines especially for small peaks. Monte Carlo self-absorption corrections, at energies below 100 keV, were done using the carbonate, organic and mineral contents as well as the elemental composition of Pb, Cu, Zn, Mn and Fe. Figure 2 shows

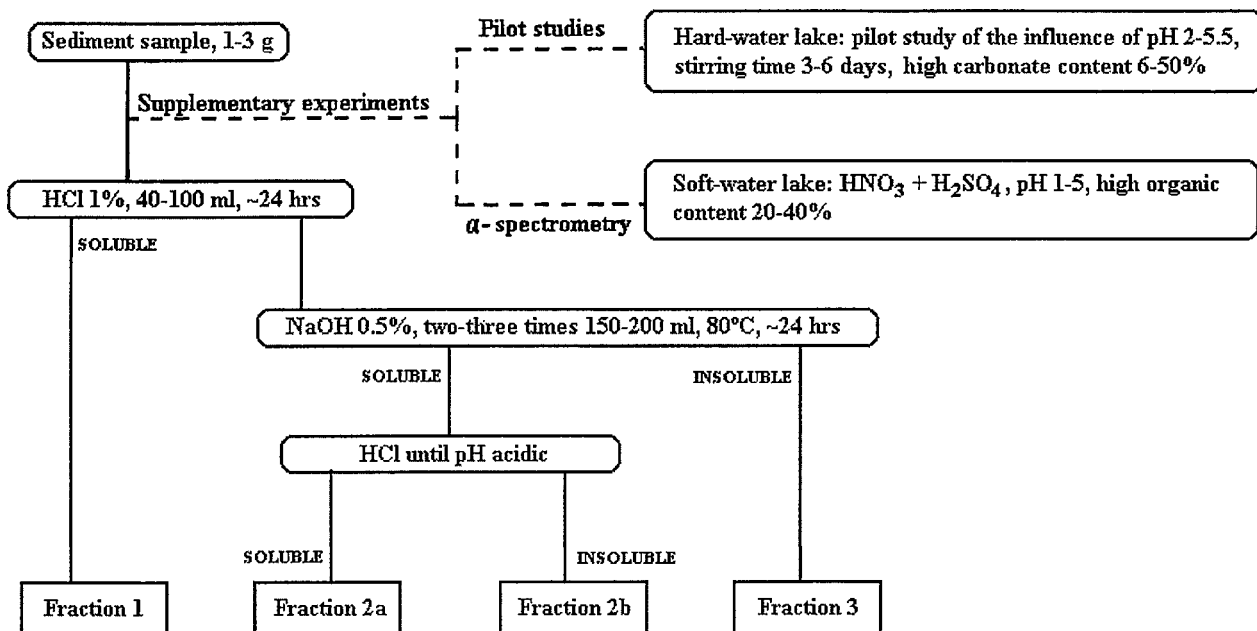


Fig. 1. A summary of the improved chemical procedure utilised to separate the main fractions from the sediments of lake Stechlin.

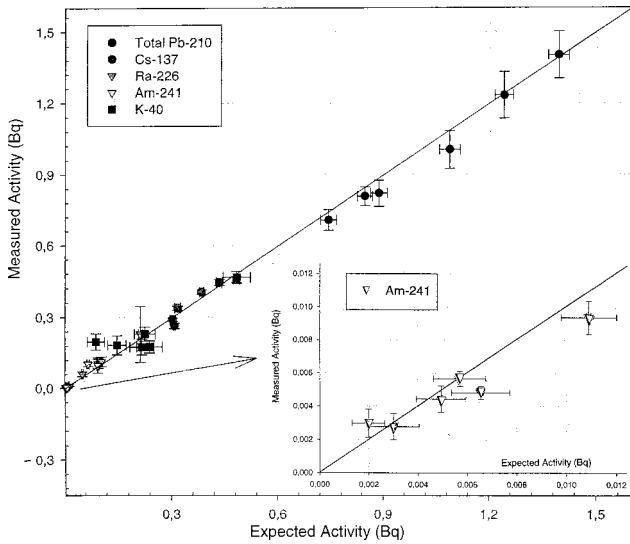


Fig. 2. Comparison of the total activity in the separated fractions with the activities in bulk sediment samples. The data given here has been corrected for self-absorption and geometrical effects. The supplementary figure demonstrates the very low levels of activity measured for Am-241.

the excellent agreement between the sum of the activity in all the fractions and the corresponding activity of the bulk sediments. The importance of the self-absorption corrections are clearly observed for ²¹⁰Pb (46.5 keV) and ²⁴¹Am (59.5 keV) where the original uncorrected data deviated significantly from the straight line. The results of the ²³⁴Th are not given here because of the limited

data. This study shows that environmental gamma spectrometry, by being a non-destructive technique, provides a suitable tool for simultaneous analysis of multi-radiotracers of relevance for holistic studies of the role of fractionation on sedimentation processes in lakes. The speciation, i.e. the distribution in different sediment fractions, of the radio-nuclides is illustrated in Fig. 3. The major part of all the nuclides is, generally, associated with the HCl-soluble mineral compounds, i.e. fraction 1, and/or insoluble mineral complexes, i.e. fraction 3. Only in the case of ²¹⁰Pb a relatively higher percentage, but still limited amounts, exists in “free” organic fulvic compounds thus indicating that ²¹⁰Pb, unlike other radio-nuclides, may reflect the environmental behaviour of free organic fractions. The speciation results, given here, show that the bio-geo-chemical processes influencing the accumulation of elements and compounds in hard-water lakes are completely different as compared to other freshwater bodies [1, 7]. Physical and chemical fractionation mechanisms, occurring in hard-water lakes, are among a web of complex interactions forcing calcite precipitation [13]. Organic (fulvic and humic matter) and inorganic (minerals and trace-elements) species, by being active components in the sedimentation process, can interfere in the calcite precipitation, as imperfections and inhibitors, and modify the course of natural self-cleaning mechanisms. The growth of calcite crystals, for example, can be interrupted by the attachment of fulvic and mineral compounds at the grain boundaries of the poly-crystalline structures, i.e. as imperfections. Small calcite crystals may, also, build surface complexes with fulvic and mineral compounds that can appear as thin amorphous films in large crystal-aggregates. Adsorption of simple molecules

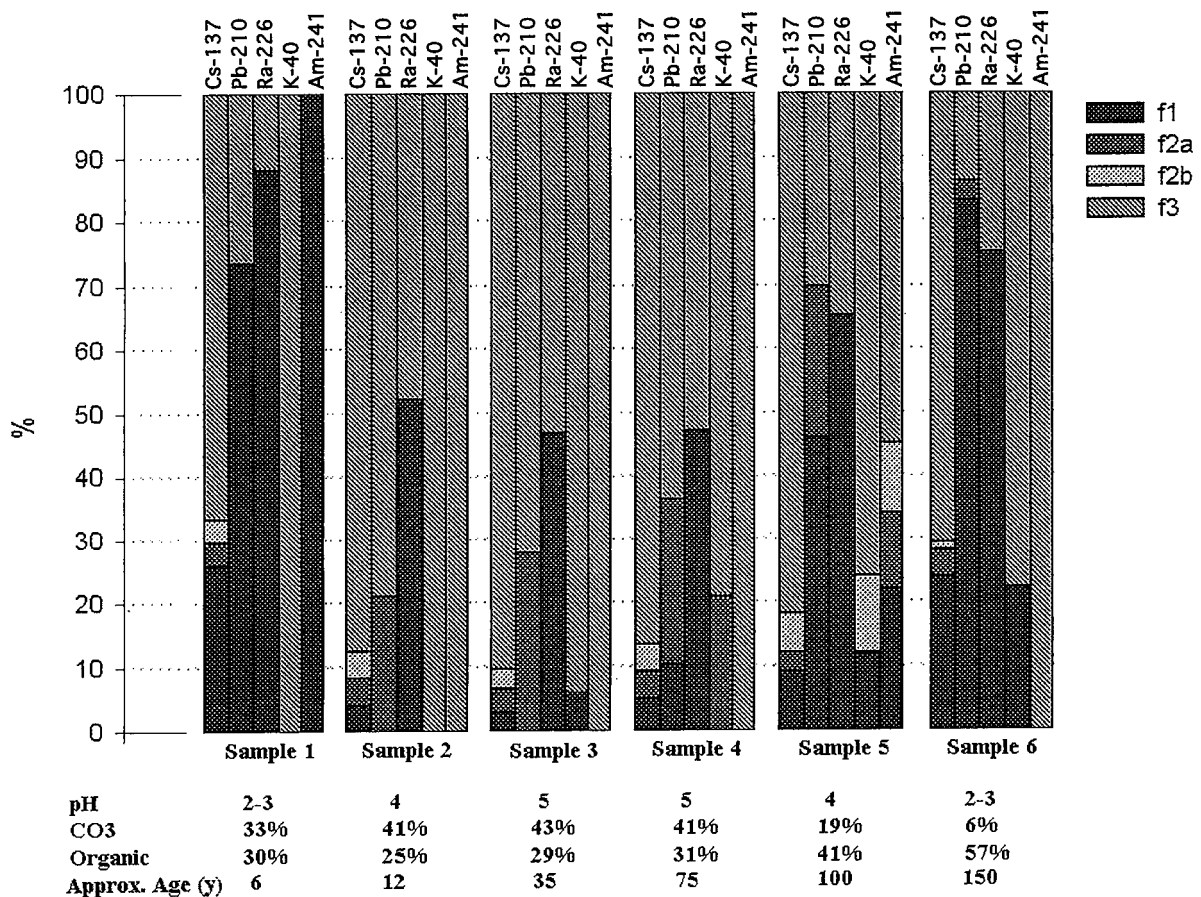


Fig. 3. Activity levels in percentage for the different radio-nuclides in the extracted fractions. The pH of the first HCl extraction step and the specifications of the samples from which the fractions were extracted are given below the figure. Data on Th-234 is commented in the text.

and cations is, also, likely to take place on the surfaces of small crystals and at the intermediate boundaries of the polycrystalline structures [14]. The morphology of pelagic calcite crystals [14] in hard-water lakes depends strongly on many growth parameters [13] such as temperature, rate of super-saturation, concentration of various organic and inorganic inhibitors, etc. The variability in these parameters induces a great diversity not only in crystal forms but, also, in the production of organic-mineral aggregates. The calcite structures of Lake Stechlin can be described as being deformed poly-crystalline aggregates where organic and mineral surface imperfections are very low to be observed by traditional analytical tools [1]. The speciation experiments presented here illustrate how radio-tracers can be used to study the influence of organic and inorganic inhibitors on the growth mechanisms of calcite-aggregates. The data show that the intensive mineralisation by bacterial activity, diagenetic and fermentation processes in upper sediment layers can be difficult to differentiate from the imperfections created during the development of crystalline aggregates in the water column. Trapping and immobilisation of elements by organic matter during primary production is, to some extent, counteracted by mineralisation at deeper depths and during the early stages of accumulation. Organic carbon, sulphur, nitrogen, silica and phosphorus compounds undergo mineralisation that enhances developing mineral-organic complexes as documented in fraction 3. It is, also, interesting to note that calcite precipitation is still effective for the accumulation of elements as can be observed at very low carbonate contents. These arguments demonstrate the importance of calcite precipitation for internal sedimentation mechanisms in hard-water lakes which is, indeed, very different from other freshwater lakes. The decrease in pH in the HCl-dissolution step enhances the soluble mineral fraction 1 which can be partly explained by an increase in soluble fulvic compounds [7]. The speciation of ^{210}Pb in soft-water lake

sediments with similar organic contents, 20–30%, but much lower carbonates (5–15%), is strongly influenced by the behaviour of organic matter. In the sediments of these lakes Fraction 1 is mainly composed of HCl-soluble fulvic compounds [7] and very little amounts, up to 5%, of the ^{210}Pb can be mobilized through the dissolution of “free” fulvic compounds at pH values 2–5.5. Unlike other freshwater lakes, the sediments of Lake Stechlin illustrate the lack of “free” humic compounds with active ion-exchange sites. It seems that “free” fulvic compounds, probably of simple composition, exist in hard-water lake sediments as the only end products of organic matter. This indicates that the remainder of the organic matter must exist in bound forms as surface inhibitors of the calcite grains and/or in complex mineral forms as a result of the intensive mineralization in the lake.

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