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Carbon and Pu isotopes in Baltic Sea sediments

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ABSTRACT

Distributions of ^{137}Cs, $^{239,240}Pu$, $\Delta^{14}C$ and $\delta^{13}C$ measured in sediments indicated low ^{137}Cs and $^{239,240}Pu$ activities in the Curonian Lagoon and higher levels in the open Baltic Sea. Depleted $\delta^{13}C_{TOC}$ values were found in the Curonian Lagoon as compared with the open Baltic Sea, while the most depleted $\Delta^{14}C_{TOC}$ values were found in the Gotland Deep. The global fallout Pu dominated in the deeper zones of the Baltic Sea, while higher $^{240}Pu/^{239}Pu$ atom ratios were characteristic of the coastal regions.

1. Introduction

European seas including the Baltic Sea have been contaminated by radionuclides due to global fallout from atmospheric nuclear weapons tests, the Chernobyl and other nuclear accidents as well as transport of radionuclides with the river water inflow from contaminated areas (HELCOM, 1995; Livingston and Povinec, 2002). Radiocarbon and stable carbon isotopes have been widely used to trace the origin and fate of organic carbon (OC) in the environment (Alling et al., 2008; Kim et al., 2011). They were applied to identify sources of OC in the marine environment (Chanton et al., 2012; Vonk et al., 2012). Microbial communities responsible for biodegradation of organic contaminants of different origins can produce specific biomarkers (White et al., 1997). Releases of specific microbiologically-derived lipids into the environment with characteristic carbon isotopic composition (unusual for the given region) can serve as indicators of contamination of the marine environment.

In spite of low concentrations, radioactive and stable isotopes can be used to trace various pollutants in the environment. Application of isotopes in tracer studies requires precise isotopic analysis, accurate determination of their concentrations and estimation of their sources. This can be achieved by modern high-sensitive analytical methods based on mass spectrometry (e.g., accelerator mass spectrometry (AMS), inductively coupled plasma mass spectrometry (ICPMS)), and on radiometric techniques (Povinec et al., 2008).

The aim of this study was to determine activity concentrations and the isotope ratios of stable and radioactive isotopes in bottom sediments of the Curonian Lagoon and the Baltic Sea in order to estimate their possible application in tracer studies, specifically oriented on the search for isotope signals from dumped chemical weapons in the Gotland Deep of the Baltic Sea.

2. Experimental

The location of sampling stations in the Baltic Sea is presented in Fig. 1. Bottom sediment samples were collected during different sampling campaigns in 2011 – 2014, with the exception of the station R7 where sampling was carried out in 2010–2012. The bottom sediments in the Baltic Sea were collected using a Van Veen grab sampler, while the Bottom Sampler acc. Ekman-Birge with an effective grasping area of 225 cm^2 and the weight of 3.5 kg was used for the bottom sediment sampling in the Curonian Lagoon.

The sediment samples were acidified with HCl to remove carbonates, dried at 60 °C overnight, then weighed and placed into tin cups. The content and isotopic ratios of carbon in the samples were measured using a Thermo Scientific Delta V Advantage mass spectrometer

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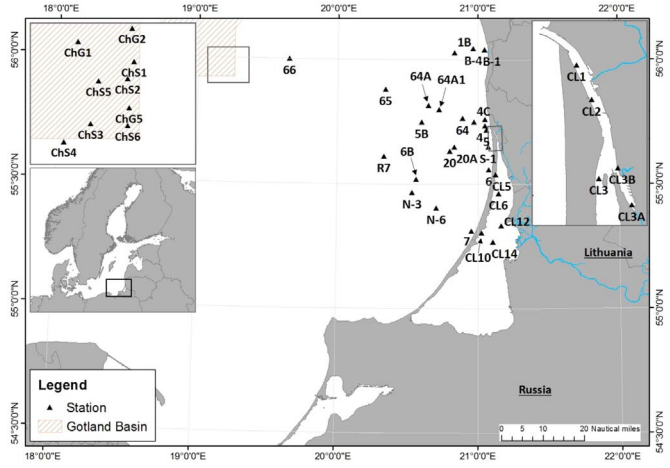

Fig. 1. Sampling locations in the Baltic Sea and the Curonian Lagoon.

(coupled to a Flash EA 1112 elemental analyzer) at the Center for Physical Sciences and Technology of the State Research Institute (SRI) in Vilnius (Lithuania). Measurements of $\Delta^{14}C_{TOC}$ in sediments and in different classes of organic substances were carried out using a 1.0 MV HVE Tandetron AMS facility in the Department of Geosciences of the National Taiwan University. All samples were pretreated free of carbonate. The counting uncertainty of ^{14}C for the OXII standard is generally < 0.3% (1σ) and the standard deviation of $\Delta^{14}C_{TOC}$ for repeated OXII standard measurement is about 1‰ (1σ).

Plutonium from sediments was first separated by the TOPO/cyclohexane extraction and then purified using UTEVA, TRU and TEVA resins (100–150 μm). The applied radioanalytical procedures are described in detail by Lujanienė (2013). The ^{242}Pu source was used as a yield tracer during the separation procedure. The Pu isotope ratios were determined either by Inductively Coupled Plasma Mass Spectrometry (ICP–MS, ELEMENT-2) or by the AMS at the University of Naples. The precision of Pu measurements was better than ± 4% (at 1σ level), and the detection limit was 5 mBq/kg. Accuracy and precision of the analyses were tested using reference materials IAEA-135, NIST SRM No 4350B and 4357 as well as information from an intercomparison exercises organized by the Riso National Laboratory (Denmark), and proficiency tests organized by National Physical Laboratory (UK).

The ^{137}Cs activities were measured non-destructively with an intrinsic germanium detector (resolution 1.9 keV/1.33 Mev and efficiency 42%). Calibration sources were prepared from the AMERSHAM (UK) reference solutions. The measurement accuracy was tested in intercomparison runs, organized by the Riso National Laboratory.

3. Results and discussion

3.1. Distribution of ^{137}Cs and $^{239,240}Pu$ in Curonian Lagoon and Baltic Sea sediments

Measurements performed in 2011–2014 showed wide variations of activity concentrations of ^{137}Cs and $^{239,240}Pu$ in bottom sediments of the Lithuanian waters of the Baltic Sea. Average data on distribution of ^{137}Cs and $^{239,240}Pu$ activities in bottom sediments are presented in Fig. 2. Average ^{137}Cs activity concentrations varied from 7.6 ± 0.5 Bq/kg to 200 ± 10 Bq/kg with the mean value of 30.4 ± 2.2 Bq/kg in the Baltic Sea, while in the Curonian Lagoon activities ranged from 1.24 ± 0.07 Bq/kg to 10.4 ± 0.5 Bq/kg with the mean value of 15.0 ± 0.9 Bq/kg. The lowest value was found in the bottom sediments at the sampling station CL12 in the Curonian Lagoon, while the highest value was detected in the Baltic Sea at the station R7. Station R7 is located in the accumulation zone at the Nemunas River crease. Our previous studies indicated wide variations (60–500 Bq/kg) in ^{137}Cs activity concentrations (including the presence of "hot" particles) in this region (Lujanienė et al., 2014). The minimal (in 2010–2012) concentration of 75 ± 4 Bq/kg was used for mapping the ^{137}Cs distribution in the area due to a huge difference in the activity concentration as compared with other stations. Average $^{239,240}Pu$ activity concentrations ranged from 0.030 ± 0.002 Bq/kg to 3.03 ± 0.19 Bq/kg with the mean value of 0.44 ± 0.03 Bq/kg in the Baltic Sea, whereas in the Curonian Lagoon Pu activities varied from 0.040 ± 0.003 Bq/kg to 1.35 ± 0.09 Bq/kg (mean value of 0.26 ± 0.02 Bq/kg). The lowest and highest values were measured in the surface sediments of the Baltic Sea at the stations 1B and R7, respectively. The $^{137}Cs/^{239,240}Pu$ activity ratio varied from 10 to 1010 (with average value of 350 ± 20) and it was slightly lower as compared to our previous study (Lujanienė et al., 2014) where the $^{137}Cs/^{239,240}Pu$ ratio was found to be from 30 to 1130 (with average value of 390 ± 30). The highest value was found at the station 4 in the Baltic Sea and the lowest values – in the Gotland Deep at the stations ChG5. The observed variations of the $^{137}Cs/^{239,240}Pu$ ratio in bottom sediments resulted from mixing of sediments due to the shallow average depth of the Baltic Sea, and the wave-induced resuspension occurring in large areas of the sea. The average $^{137}Cs/^{239,240}Pu$ ratio (with decay corrected to the Chernobyl accident) values are presented in Fig. 3.

Plutonium isotope ratios have been frequently used to determine sources of radioactive contamination (Livingston and Povinec, 2002). The most important Pu source in the Baltic Sea is global fallout with well-known characteristic activity ratios ($^{238}Pu/^{239,240}Pu$ ~ 0.03, $^{137}Cs/^{239,240}Pu$ ~ 30 (the decay corrected value to the Chernobyl accident is ~ 54), and the atom ratios ($^{240}Pu/^{239}Pu$ ~ 0.18) (UNSCEAR, 1982, Bunzl and Kracke, 1988). The observed $^{137}Cs/^{239,240}Pu$ ratios (> 54) indicate an impact of the Chernobyl accident on ^{137}Cs levels in the sediments.

Another important signature for Europe is the $^{238}Pu/^{239,240}Pu$ activity ratio (~ 0.45) and the $^{240}Pu/^{239}Pu$ atom ratio (~0.40), which represent the typical Pu isotope ratios affected by the Chernobyl accident (Livingston and Povinec, 2002). The observed ranges of the $^{238}Pu/^{239,240}Pu$ ratio from 0.018 to 0.3 (mean 0.092) in bottom sediment samples indicated a presence of small amount of Chernobyl-derived plutonium in the region as the global fallout ratio is 0.03. The higher $^{238}Pu/^{239,240}Pu$ ratios were detected at the coastal sampling stations (e.g., 4) of the Baltic Sea, at the sampling stations of the Curonian Lagoon (e.g., CL10), and at the sampling station in the Baltic Sea where bottom sediments originated from the Curonian Lagoon (e.g. 20 A), as well as at sampling stations located at the wash of the Neman River (e.g., R7). At the open sea sampling stations (e.g., N-6, 64, 64A1and ChS2), the $^{238}Pu/^{239,240}Pu$ ratios were rather low, if any contribution of the Chernobyl-derived plutonium was present. Higher activities were found in the deep regions of the Baltic Sea, which were consistent with the bottom sediment mineralogy (Remeikaitė-Nikienė et al., 2012). It is very well known that the highest concentrations of metals and radionuclide activities occur in fine-grained organic-rich sediments (HELCOM, 2010). The concentrations of radionuclides in the finest sediment fractions can be generally many times greater than in coarse grained-fractions (Lujanienė et al., 2006). Shallow water areas are dominated by sand and coarse sediments with a low content of organic matter, whereas clay sediments with a high content of organic matter occur in deeper water areas (Leivuori, 1998; Lujanienė et al., 2010, 2013).

3.2. Distribution of $\delta^{13}C$ and $\Delta^{14}C$ in Curonian Lagoon and Baltic Sea sediments

The observed radionuclide activities in the bottom sediments well correlated with the total organic carbon (TOC) and clay mineral content (Lujaniene et al., 2014). The TOC and $\delta^{13}C$ were measured in bottom sediment samples collected in the Baltic Sea and the Curonian Lagoon in 2012–2014. The data on the $\delta^{13}C$ distribution (Fig. 4) showed that higher values of $\delta^{13}C$ were mainly measured at the sampling station