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Anthropogenic plutonium radioisotopes in the ecosystem components of Sevastopol Bay (the Black Sea)

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Abstract. Modern levels (2010-2020) of $^{239+240}$Pu activity concentration in Sevastopol Bay (Black Sea) surface waters, 0-5 cm layer of bottom sediments and hydrobionts were determined by multistage radiochemical technique. The $^{239+240}$Pu activity concentrations in Sevastopol Bay surface water were on relatively low level: 1.08±0.09 – 1.54±0.17 mBq·m^{-3}. The maximum value of $^{239+240}$Pu activity concentration in the bottom sediments surface layer was observed in Sevastopol Bay mouth (993±90 mBq·kg^{-1}) and it decreased with distance from the bay entrance to its tail end down to the minimum value – 276±53 mBq·kg^{-1}. Based on these results as well as on published data the $^{239+240}$Pu deposition density distribution in the bay boxes and their inventory in 0-5 cm layer of bottom sediments were estimated in every boxes. Total $^{239+240}$Pu inventory in the bottom sediments surface layer was estimated at 121 MBq, with the highest deposition density value determined in the mouth part of the bay. Among studied hydrobiont species the highest $^{239+240}$Pu content was determined for mollusks (for their shells) *Mytilus galloprovincialis* (Lamarck, 1819) while the lowest – for fish *Scorpaena porcus* (Linnaeus, 1758). Accumulation ability of studied ecosystem components of Sevastopol Bay against $^{239+240}$Pu was characterized by evaluating concentration factors (C_f). It was shown that the bottom sediments of the bay were the main depot for plutonium anthropogenic radionucludes (C_f ($^{239+240}$Pu) = n·10^5). The C_f ($^{239+240}$Pu) were from two to three orders of magnitude lower for the hydrobionts of the bay: n·10^3 for brown algae and mollusks and n·10^2 for green algae and fish.

1. Introduction

The Black Sea is one of the most polluted inland seas, being affected with pollutants of different origin including anthropogenic radionuclides [1]. In the second half of the 20-th century the Black Sea has received the input of different artificial radionuclides, including plutonium. The main sources of the Black Sea radioactive contamination were atmospheric global fallout after the nuclear weapon tests and the accident on Chernobyl nuclear power plant (ChNPP) [1, 2].

Most of atmospheric fallout originated from the 1960's when the majority of high-yield nuclear devices were tested [3]. The Black Sea located exactly in the 40-50º N latitude band where the maximum global fallout was observed [4]. The density of 239+240Pu input to the surface of the Black

Sea reached 81 Bq·m-2 and the total inventory of 239+240Pu in the Black Sea related directly to the atmospheric global fallout was estimated at 35 TBq [4, 5].

After the ChNPP accident (1986) the Black Sea received radioactive contamination from the atmospheric fallout as well as from rivers runoff: Dnieper, Dniester, Danube and Bug rivers [6]. The total inventory of 239+240Pu in the Black Sea related to the Chernobyl fallout was estimated at 4.6 TBq [5].

Secondary radioactive contamination of the Black Sea ecosystems was considered earlier due to increased runoff from the Dnieper and Danube rivers in 1995-1999 and possible role of radioisotopes remobilization from the bottom sediments as well in 2010-2013 [7]. The last event was the result of the discharge that began in 2010 when contaminated waters from the ChNPP cooler pond were drained into the Pripyat River and then they migrated along the Dnieper River to the Black Sea. After 2010 in the Black Sea areas, an increase of activity concentration of the Chernobyl radioisotopes was noted [7]. This fact was confirmed with higher activity ratio of 238Pu/239+240Pu in 2013 in upper layer of bottom sediments in the Black Sea north-western part near the Dnieper-Bug estuary [8]. The fact should be noticed that nowadays 9 countries have 54 nuclear power units in operation in the Black Sea drainage basin, and all of them could be considered as potential source of radioactive contamination [9].

So, it is an important task to identify processes of 239+240Pu radioecological behavior in the Black Sea, especially for coastal ecosystems which are insufficiently studied in this aspect. Sevastopol Bay is the largest on the Crimean Peninsula southwestern coast and it is widely used in economic and recreation spheres. At the same time various species of aquatic organisms live in the Sevastopol Bay ecosystem, many of which are widely used as a seafood. In sea area near the entrance to the bay and in mouth part of the bay there are aquaculture farms for the cultivation of bivalve mollusks, in particular Mytilus galloprovincialis (Lamarck, 1819) [10].

The aim of this paper was to assess the modern (2010-2020) levels of 239+240Pu activity concentration in Sevastopol Bay ecosystem components: water, bottom sediments and biota (fish, mollusks and algae), as well as to estimate the 239+240Pu deposition density distribution in the bay boxes and their inventory in boxes, moreover total inventory in the whole bay in the surface (0-5 cm) bottom sediments and concentration factors (Cf) for bottom sediments and various biota species against plutonium.

2. Methods

Sampling was carried out in 2010-2020 in Sevastopol Bay (Figure 1) with four boxes being distinguished according to their different hydrological and hydrochemical regimes and pollution degree [11]. Surface (0-5 cm) layer of bottom sediments was sampled at stations 1-8 by 58 mm i.d. acrylic tube equipped with vacuum lock [12]. Sampling of surface water (1 m3) was performed in four boxes of the bay at stations 2, 5, 6, 8 and in the open sea area abeam the entrance to the bay (st. 1) by using radial flow pump with plastic scoop wheel equipped with plastic tubing excluding contact of water with metal parts. Samples of fish Spicara maena (Linnaeus, 1758) and Scorpaena porcus (Linnaeus, 1758), shells of bivalve mollusks Mytilus galloprovincialis (Lamarck, 1819), brown algae Cystoseira barbata (C. Agardh, 1820) and green algae Cladophora laetevirens (Kützing, 1843) were taken to assess the level of 239+240Pu accumulation by hydrobionts.

Plutonium radioisotopes were determined by multistage radiochemical technique [13, 14]. Sediments were dried at 60 ºC and homogenized, than aliquot for analysis (20 g) was taken and ashed in the muffle furnace. Seawater samples were concentrated with two consequent sorption techniques: three-stage co-precipitation with MnO2 and two-stage co-precipitation with Fe(OH)3. This allowed concentrating of isotopes to be determined, reducing the samples volume from 1000 l down to 100-150 ml. Samples of biota were dried at 60 ºC, ashed in the muffle furnace, homogenized and then the aliquot (10-20 g) of ashed residue was taken for analysis.

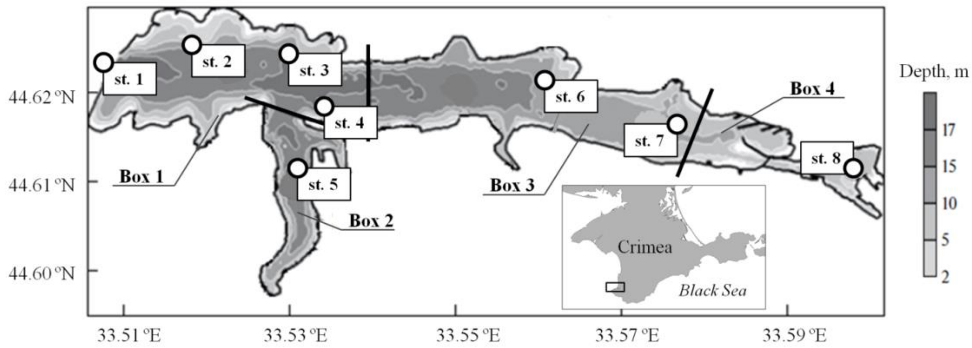

Figure 1. Map of Sevastopol Bay with sampling stations (black lines – borders of the boxes).

The ashed samples of bottom sediments and hydrobionts were subjected to double leaching in a mixture of HNO_3 and H_2O_2 in a bain-marie and then, along with concentrated water samples, to double ion-exchange purification using anion-exchange resin. The resulting eluated samples containing purified plutonium were electroplated on stainless steel disks thus preparing counting sources for alpha-spectrometry.

To control the radiochemical yield, 10 mBq of 242Pu to each sample were added. All counting samples were measured using semiconductor alpha-spectrometric complex ORTEC OCTETE (USA) with semiconductor detectors. The 239+240Pu activity concentration was calculated using the value of 242Pu added as internal standard and volume or weight of each sample aliquot according to [13]. The uncertainties of 239+240Pu activity concentrations included 1σ counting errors of net counts of each radionuclide and its chemical yield tracer combined with uncertainties of tracer addition and weighting procedure. The 239+240Pu activity concentration was presented in mBq·m-3 for surface water, in mBq·kg-1 dry weight for bottom sediments and in mBq·kg-1 wet weight for hydrobionts.

The assessment of the 239+240Pu deposition density (P, Bq·m-2) and 239+240Pu inventory (Z, Bq) in the 0-5 cm layer of the Sevastopol Bay bottom sediments was carried out based on the bay morphometric characteristics [11, 15], as well as the values of sedimentation rates (SR, mm·year-1) and mass accumulation rates (MAR, g·m-2·year-1) according to data for box 1 [16] and data for boxes 2-4 [15].

3. Results

The 239+240Pu activity concentration was determined in the bottom sediments of Sevastopol bay for all four boxes on stations 2-8 and at the station 1 – outside the bay, abeam the bay entrance. The obtained data on the 239+240Pu activity concentration distribution in the 0-5 cm surface layer of bottom sediments on eight stations is presented on Figure 2 [12].

Nowadays data on surface seawater have been received for the middle part of the bay (st. 6), for the bay mouth (st. 2) and for the open sea area (st. 1). The 239+240Pu content in the Sevastopol Bay surface water was on relatively low level (Table 1).

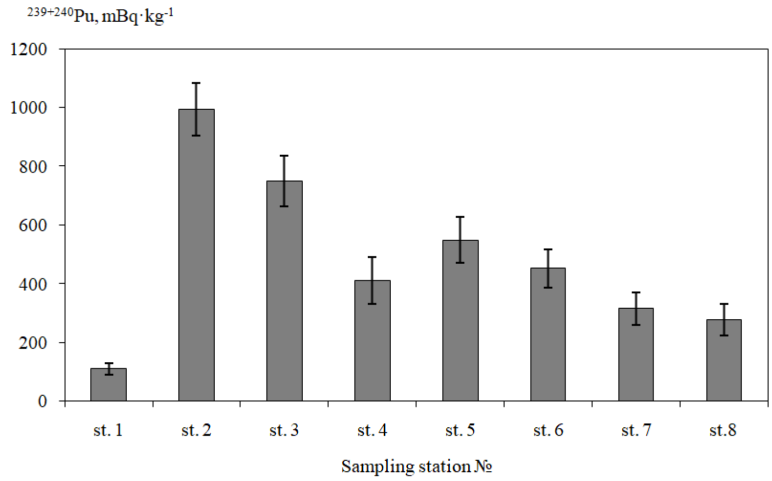

Figure 2. The $^{239+240}Pu$ activity concentration distribution in the 0-5 cm surface layer of bottom sediments in the studied sea areas.

Table 1. The $^{239+240}Pu$ activity concentration in the surface seawater of the investigated sea areas.

Number of sampling station	Data of sampling	$^{239+240}Pu \pm 1\sigma$, mBq·m^{-3}
1	08.04.2019	1.10±0.21
2	30.05.2019	1.54±0.17
6	13.06.2019	1.08±0.09

To determine the levels of plutonium radioisotopes in hydrobionts, a multicellular perennial algae – C. barbata, an annual algae – C. laetevirens, in a bivalve filter-feeder mollusk – M. galloprovicialis and two fish species (S. porcus – a demersal fish leading a sedentary lifestyle and S. maena – a free-swimming fish living in coastal waters) were selected. The results of 239+240Pu activity concentration determination in the Sevastopol bay hydrobionts are shown on Figure 3.

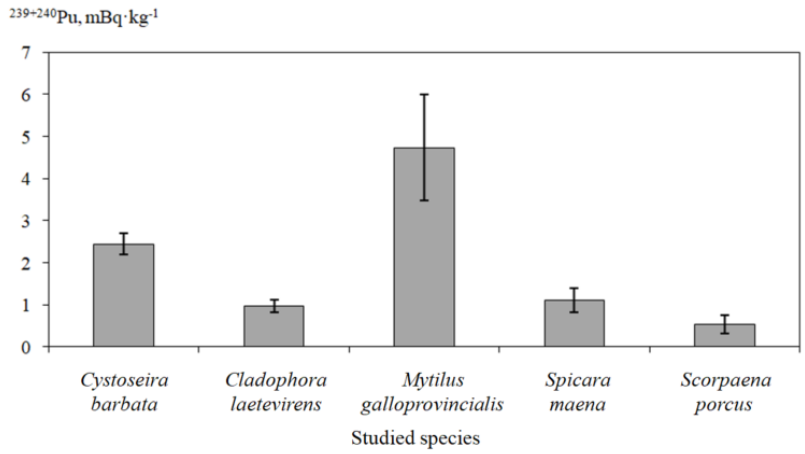

Figure 3. The $^{239+240}Pu$ activity concentration in studied species of the Sevastopol Bay hydrobionts.

4. Discussion

Generally, the character of plutonium radioisotopes behavior is influenced by its physic-chemical properties and a variety of biogeochemical processes in the marine environment, e.g. solubilisation, complexation, colloid formation, sorption on suspended matter [17]. The plutonium oxidation state also has a significant effect on its mobility and biogeochemical behavior in marine ecosystems, as well as Eh and pH of water environment [18]. It was shown that plutonium radioisotopes demonstrate pedotropic character of behavior in the Black Sea, i.e. they are easily scavenged by downward flux of suspended matter and eliminated from the water column to the bottom sediments [5].

The results of our study showed that at all sampling stations the $^{239+240}$Pu activity concentration in the Sevastopol Bay surface water was almost the same within the statistical uncertainties of the obtained values (Table 1). The temporal trends of $^{239+240}$Pu activity concentrations in surface water for the deep-sea basin of the Black Sea showed its exponential decrease in post-Chernobyl period from 13.5±3.0 (1986) to 0.48±0.3 (2013) mBq·m^{-3} [5]. However, for the Sevastopol Bay surface waters the values of plutonium activity concentration were higher. This fact is probably can be explained by the higher concentration of suspended matter in the investigated coastal area. Plutonium may also be remobilized from the bottom sediments of the bay due to their roiling as a result of active navigation and secondary radioactive contamination after 2010 with sea water from the Black Sea north-western part.

The maximum values of $^{239+240}$Pu activity concentrations in the bottom sediments surface layer (fig. 2) were observed in the Sevastopol Bay mouth (st. 2) and they decreased with distance from the bay mouth (from st. 2 to st. 8). At the same time, the lowest $^{239+240}$Pu activity concentration in the bottom sediments was found for the open sea part of the studied area (st. 1). It should be noted that the bottom sediments in the bay are mainly composed of silts, while outside the bay – they are mostly sands. Earlier it was shown that silt bottom sediments in the Black Sea coastal areas had the higher accumulation ability with respect to $^{239+240}$Pu than sandy bottom sediments [5].

Based on the plutonium activity concentrations data in the surface layer of the Sevastopol Bay bottom sediments, an assessment of the $^{239+240}$Pu deposition density distribution and their inventories in 0-5 cm layer of the sediments in every boxes and total inventory in the whole bay was carried out (Figure 1, 4). The highest value of plutonium deposition density was noted for box 1, while for the open sea area it was minimal (Figure 4A). Probably, this fact is caused by different granulometric composition of bottom sediments. In addition to this, the construction of breakwaters at the Sevastopol Bay mouth, completed in 1986, was likely to have led to mass accumulation rate increase in this area of the bay. In turn, this could have led to the accelerated deposition of plutonium, being pedotropic element, to the bottom sediments of the bay mouth. The value of $^{239+240}$Pu inventory in the 0-5 cm layer of bottom sediments in the box 1 was 71.8 MBq (Figure 4B).

The lowest value of $^{239+240}$Pu inventory was determined in the box 4 – 3.4 MBq (Figure 4B). Apparently, this was caused by the fact that the Chernaya River flowed into this part of the bay, bringing a large amount of coarse sedimentary material, bounding plutonium to a much lesser extent. Also, this box is the smallest in area, which causes a low $^{239+240}$Pu inventory value compared to the box 3 (32.4 MBq), although the $^{239+240}$Pu deposition density values in them are close (Figure 4).

Box 2 is relatively isolated from big part of the bay and small in area but its bottom sediments are mainly represented by silts which must cause higher $^{239+240}$Pu deposition density values and lower values of $^{239+240}$Pu inventory (13.4 MBq) compared to box 3. The total $^{239+240}$Pu inventory in the 0-5 cm sediment layer of the entire Sevastopol Bay was 121 MBq (Figure 4).

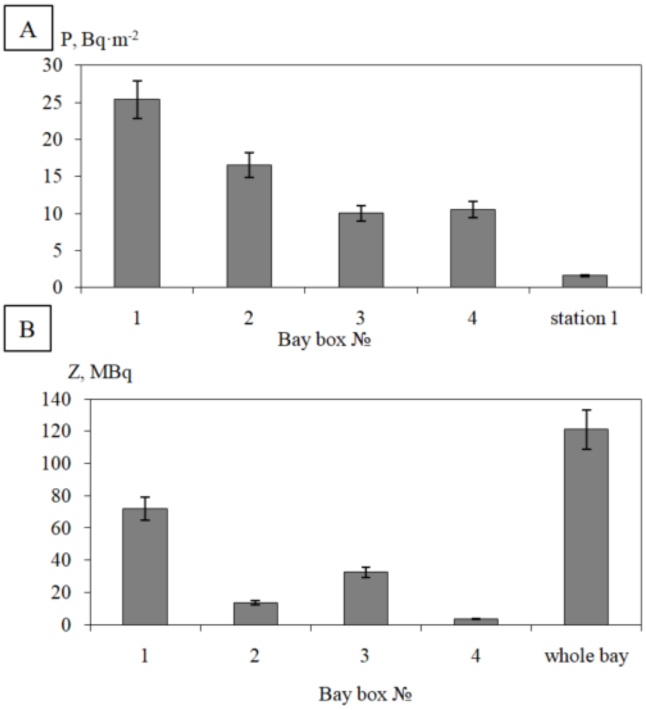

Figure 4. The 239+240Pu deposition density distribution (A) and 239+240Pu inventory (B) in the 0-5 cm layer of the bottom sediments in Sevastopol Bay and st. 1.

The current levels of 239+240Pu activity concentrations in the Sevastopol Bay hydrobionts are relatively low (Figure 3). However, the modern data about plutonium activity concentrations in the seawater, bottom sediments and hydrobionts of Sevastopol Bay make allowed the 239+240Pu concentration factors calculating for the studied species and bottom sediments (Figure 5).

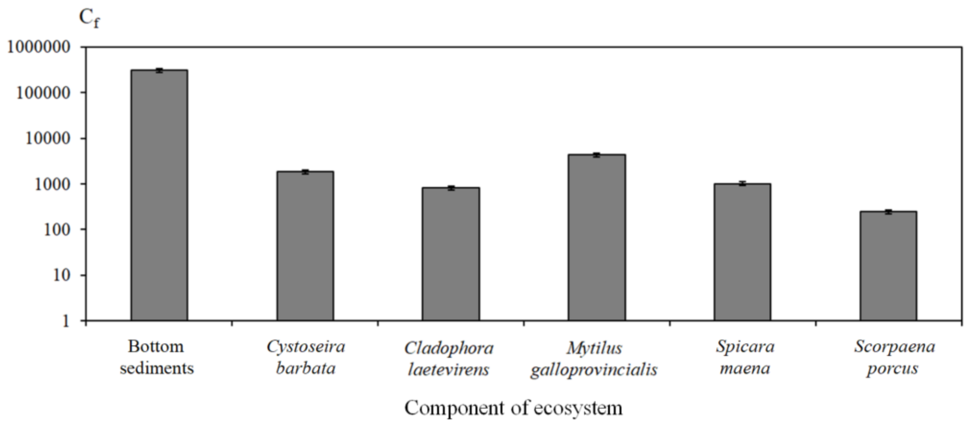

Figure 5. The $^{239+240}$Pu concentration factors for bottom sediments and studied hydrobionts species of Sevastopol Bay.

The highest values of 239+240Pu concentration factors were determined for bottom sediments – n·105. This confirms the fact that bottom sediments play the leading role in plutonium redistribution in the Black Sea coastal ecosystems. The 239+240Pu concentration factors were from two to three orders of magnitude lower for representatives of the Sevastopol Bay marine biota. Wherein, fish, which are most often consumed by humans for food among studied species, have the least accumulation ability against anthropogenic plutonium radioisotopes. Among all studied hydrobionts, the highest values of

239+240Pu concentration factors were in perennial multicellular brown alga genus Cystoseira. This alga contains a large amount of substances that absorb heavy metals well. In particular, it contains about 20-30% of the dry weight of alginates, which can serve as a sorbent for radioisotopes of plutonium and determine the high accumulation ability of algae in relation to plutonium as a heavy metal [19].

5. Conclusions

The modern (2010-2020) levels of 239+240Pu activity concentration in the Sevastopol Bay ecosystem components were determined. The 239+240Pu deposition density distribution and inventory values in the surface (0-5 cm) bottom sediments in Sevastopol Bay were estimated. The 239+240Pu concentration factors for bottom sediments and studied hydrobiont species of Sevastopol Bay as a quantitative parameter of their accumulation ability were obtained.

The highest levels of 239+240Pu activity concentration among the studied ecosystem components were observed in bottom sediments. The highest 239+240Pu deposition density and inventory values in the surface layer of bottom sediments were determined in the Sevastopol Bay mouth area (box 1). The total 239+240Pu inventory in the upper 0-5 cm sediment layer of the entire bay was estimated at 121 MBq.

It was shown that bottom sediments have the highest 239+240Pu concentration factors (n·105). This fact confirms pedotropic type of plutonium behavior in the Black Sea coastal areas, i.e. the bottom sediments are the main depot for this anthropogenic radionuclides in Sevastopol Bay.

Among the studied hydrobionts 239+240Pu concentration factors decreased in the range: brown algae and mollusks (n·103) – green algae and fish (n·102).

Therefore, among the components of the bay ecosystem, the greatest influence on the redistribution of plutonium radioisotopes in the bay can be exerted by silt bottom sediments and thickets of perennial multicellular brown alga genus Cystoseira and mussel shells.

Acknowledgements

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