BIOGEOCHEMISTRY OF URANIUM IN THE SOUTHERN BALTIC ECOSYSTEM

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Abstract

The determination of uranium isotopes in different components of the Southern Baltic (sediments, soil, birds, river) is presented and discussed in this paper. The Baltic Sea is one of the most polluted water regions in the world. On the basis of the studies was found that the most important process of uranium geochemical migration in the Southern Baltic Sea ecosystem is the sedimentation of suspended material and the vertical diffusion from sediments into the bottom water. Considerable amounts of uranium isotopes are introduced into the Baltic waters together with annual inflows of saline and well-aerated waters from the North Sea. Also very high uranium concentrations are the result of weathering and erosional processes of the rocks (e.g. Sudetic rocks) which contain elevated natural concentrations of this radionuclide. Considerable amounts of uranium isotopes are introduced into the Baltic waters together with annual inflows from the Vistula and Oder rivers, also from saline and well-aerated waters from the North Sea. The results of many our studies confirm the significant role of human activities and phosphogypsum stockpile in Wiślinka as a source of these isotopes in southern Baltic.

Key words: uranium isotopes, the Southern Baltic, sediments, surface and bottom water, Baltic organisms, marine birds, phosphogypsum stockpile

INTRODUCTION

Uranium is a silvery-white metallic chemical element in the actinide series of the periodic table, with atomic number 92. The 1789 discovery of uranium in the mineral pitchblend is credited to Martin Heinrich Klaproth, who named the new element after the planet Uranus. Eugène-Melchior Péligot was the first person to isolate the metallic uranium and its radioactive properties were discovered in 1896 by Antoine Becquerel. Uranium is a radioactive and toxic metal, and it is a hazardous environmental pollutant. It is relatively highly toxic to humans, both chemically and
radiologically (its progeny are highly radioactive isotopes). Natural uranium consists of three alpha radioactive isotopes: 99.2745% of $^{238}$U, 0.7200% of $^{235}$U, and 0.0054% of $^{234}$U (Niesmiejanow 1975, Browne and Firestone 1986, Bou-Rabee et al. 1995, Sam et al. 1999, Bagatti et al. 2003, Meirath et al. 2003). $^{238}$U and its decay products are the important sources of exposure of man to radioactivity. Uranium metal has three allotropic forms: α (orthorombic), stable up to 667.7°C, β (tetragonal), stable from 667.7 to 774.8°C and γ (body-centered-cubic) from 774.8°C to melting point – this is the most malleable and ductile state. Uranium occurs naturally in the earth in the form of chemical compounds in an amount of 2.4 ppm. You can find it in rocks, soil, water, plants, animals, and even in the human body. Uranium is accumulated in granites and sedimentary rocks by geological process. The most common uranium-containing minerals are: uraninite (UO$_2$/UO$_3$) (a complex uranium oxide), autunite Ca(UO$_2$)$_2$(PO$_4$)$_2$·10-12H$_2$O (a hydrated calcium uranium phosphate), brannerite UTi$_2$O$_6$ (a uranium calcium cerium iron oxide) and carnotite K$_2$(UO$_2$)$_2$(VO$_4$)$_2$·1-3H$_2$O (a hydrated potassium uranium vanadate) (Brzyska 1987, Szymański 1996, Szabó Nagy et al. 2009). Natural uranium contains too little of the isotope $^{235}$U, to be used as fissile material and requires a series of actions for increasing the content of this isotope in a process called enrichment. As a result of this processing enriched uranium (containing more than 3% of the isotope $^{235}$U) and depleted uranium waste called (containing less than 0.7% of the isotope $^{235}$U) are obtained. Uranium is also used to produce nuclear weapons, in radiation therapy (in medicine), for the manufacture of luminescent paints, ceramics, photography, for the manufacture of dyes, it is also important scientifically and it has a very limited collectors’ values (due to radioactive properties) (Edwards 1999, Priest 2001, Zarkadas et al. 2001).

Uranium isotopes $^{234}$U and $^{238}$U are not present in radioactive equilibrium in the natural environment, which indicates that their activities are not equal. Especially in the aquatic environment deviations from the equilibrium are large. The average values of the activity ratio between $^{234}$U and $^{238}$U are in the range from 0.51 to 9.02 for groundwater, from 1.11 to 5.14 for salt water, from 1.00 to 2.14 for river water, from 0.80 to 1.00 for suspension river, 1.14 for oceanic water and 1.17 for Baltic water (Ku et al. 1977, Barr et al. 1979, Szefler 1987a, Skwarzec 1995). In rocks, soils and sediments uranium isotopes $^{234}$U and $^{238}$U are in relative equilibrium (from 0.84 to 1.19 for oceanic basalts, from 0.70 to 1.16 for phosphorite concretions, from 0.83 to 1.28 for oceanic sediments and from 0.98 to 1.04 for Baltic sediments) (Szefler 1987b, c, Skwarzec 1995). There are several reasons for the radioactivity disequilibrium: radioactive decay energy, related to the secretion of α particles with atoms nuclei, causes a “kickback” to the newly created isotopes for distance $10^{-7}$-$10^{-6}$ cm from sites in the crystal lattice occupied by atoms of the isotope $^{238}$U output. Consequently, the $^{234}$U atoms are less related to the structure of minerals than the $^{238}$U atoms, and easier to diffuse to the surface of mineral grains and the cracks. In the oxidizing environment of the surface layer of minerals containing uranium from the water, $^{235}$U atoms are more easily leached into solution, yielding the oxidizing process to uranium (VI) faster than $^{238}$U atoms. Hence the isotope $^{234}$U shows greater mobility in the surface area. The differences in geochemical behavior between $^{234}$U and $^{238}$U isotopes mark in a surface environments, where the waters are more enriched in


$^{234}\text{U}$ in relation to $^{238}\text{U}$, while in the rocks inverse relationship are observed (Fleischer and Raabe 1978).

The principal source of uranium in the natural environment is the atmospheric precipitation of terrigenic material, soil resuspension, rock weathering, as well as river waters and fertilizers. Moreover, the concentration of uranium in the natural environment is increased by human activity including industry, fossil fuel combustion, phosphate fertilizers in agriculture, and domestic and industrial sewage. On the other hand large amounts of uranium contents are produced by the modern industry: metallurgy, oil refinery, nuclear industry, nuclear weapon tests, the use of uranium ammunition, the manufacture and processing of fuel rods, ore mining, as well as phosphogypsum waste heaps (Polanński and Smulikowski 1969, Sam and Holm 1995, Skwarzec 1995, 2002, Bolivar et al. 1996, Martinez-Aguirre and Garcia-León 1997, Martinez-Aguirre et al. 1997, Sam et al. 1999, Vrecjak and Benedik 2002, Skwarzec et al. 2010c, Boryło et al. 2009, 2012, Boryło and Skwarzec 2011, Andreou et al. 2012, Wang et al. 2012). The main contamination sources in the Baltic Sea waters are precipitation, river run-off and inflow from the North Sea, but a potential risk is nuclear power plants (e.g. Sweden, Finland, Russia) (Skwarzec 2011). Red Book, officially titled “Uranium 2007: Resources, production and demand” (2008), includes an estimate of identified uranium reserves – the production costs can be less than $130 per kilogram – at 5.5 million tonnes, which is much higher than the number 4.7 million tons given in 2005. Red Book says that undiscovered uranium resources (identified on the basis of the geological characteristics of already identified resources) are 10.5 million tonnes. Compared to estimates from 2005, included in the previous report, this represents an increase of 0.5 million tonnes. It is caused by the discovery of new reserves of uranium and re-checking the resources already identified, following the increase in the price of uranium. According to the Red Book, nuclear power in the world will grow from 372 GWe in 2007 to 509-663 GWe in 2030. “This expansion will lead to an increase in annual demand for uranium at 94,000-122,000 tonnes for reactors in use today”, shall develop (PAA 2008).

The aim of this work was estimation of the most important source of uranium isotopes in the southern Baltic ecosystem. It is well known that the drainage basins of the Vistula, Oder and Pomeranian rivers, wet and dry atmospheric fallout, particles of weathered rocks and intense human activities (mainly farming) are the sources of uranium.

**MATERIALS AND METHODS**

The analytical environmental samples include: sediment, organisms and surface water samples collected between 1997-2004 from the southern Baltic Sea, as well as phosphogypsum and surface water samples from area around the phosphogypsum stockpile in Wiślinka.

The analytical procedure of uranium determination of uranium isotopes ($^{234}\text{U}$, $^{238}\text{U}$) in analyzed samples was based on co-precipitation of water samples and mineralization in concentrated acids HNO$_3$, HCl and HF, and separation on the anion exchange resins (Skwarzec 1995, 1997, 2009, Boryło 2013). The activities of $^{234}\text{U}$ and $^{238}\text{U}$
were measured using an alpha spectrometer (Alpha Analyst S470). The results of $^{234}$U and $^{238}$U concentrations in analyzed samples are given with standard deviation (SD) calculated for a 95% confidence interval ($\pm 2\sigma$). The concentrations of uranium isotopes in the IAEA-300, IAEA-367, IAEA-312 and IAEA-375 samples were consistent with the reference values reported by the IAEA. The accuracy of the analytical method and measure of precision was estimated to be below 2.4% and 3% respectively.

RESULTS AND DISCUSSION

*Uranium in waters and sediments of the Southern Baltic*

The uranium content in the analyzed water samples and sediments of the Southern Baltic were differentiated (Table 1). In marine environment uranium exists principally as U(VI) and U(IV), where uranium (IV) compounds are weakly dissolved and in reduction areas the growth of stable form of uranium (IV) can be expected (Bonatti et al. 1971). In neutral or little alkaline waters uranium (VI) exists predominantly in the dissolved carbonate anions $[\text{UO}_2(\text{CO}_3)_3]^+$ and $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ (Sackett et al. 1973). This autogenic uranium in seawater should be accumulated in marine organisms. The uranium concentration in the Southern Baltic surface waters ranges between 0.68 and 0.85 $\mu$g·dm$^{-3}$ and correlates with salinity. The mean values of the activity ratio $^{234}$U/$^{238}$U in ocean water are estimated at 1.14, while in the Baltic water 1.17 (Skwarzec 1995, 2011). The relatively small differences of uranium concentration were observed in the sediments collected in Gdańsk and Puck Bay (3.16-4.12 mg·kg$^{-1}$ d.wt. and 3.16-4.12 mg·kg$^{-1}$ d.wt. relatively). Comparable values of uranium concentrations were measured in the sediments of the Gdańsk and the Bornholm Deep (0.56-4.36 and 0.54-3.77 mg·kg$^{-1}$ d.wt. respectively). The highest values were reported in the sediments taken from the Słupsk Bank and the Słupsk Narrow (0.66-7.11 mg·kg$^{-1}$ d.wt.), while the smallest in the Bornholm Deep (Skwarzec et al. 2002), what is probably connected with the information about the geological structure of the seabed. The processes occurring around the coastline are valuable, too. The highest concentration of uranium in the Słupsk Narrow is associated with the presence of nodules – the mineral aggregate formed by the gradual accumulation of minerals around an object in the rock. In the Słupsk Narrow basin there dominate iron-manganese, discoid-shaped ring of brown colour concretions and ellipsoid-shaped band of brown colour. Most are scattered on the bottom or partially buried in sediment and they are the result of crystallization of oxides of manganese, iron, nickel, cobalt and copper around a hard object (e.g. shells) in well-oxygenated waters. Concretions resting on the sediment surface react with seawater and their shells are enriched in iron and cobalt. The shells of buried nodules – which react both with water and sediment – are enhanced by manganese and copper (Depowski et al. 1998, Sobota et al. 2004, Jiang et al. 2005). The mechanism of uranium densification in the nodules is associated with its hydrogenic nature in concretions, which is precipitated from seawater with the participation of iron and manganese hydroxides, as well as with volcanogenic hypothesis and with the fact that uranium exists in sea
### Table 1
Average uranium concentration and values of the activity $^{234}$U/$^{238}$U ratio in environmental samples (n = 5), (n – number of individuals)

<table>
<thead>
<tr>
<th>Component</th>
<th>Total uranium concentration</th>
<th>The values of the $^{234}$U/$^{238}$U activity ratio</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>sediments, Baltic and birds [mg·kg$^{-1}$]; Baltic water [µg·dm$^{-3}$]; river water [mg·m$^{-3}$]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baltic waters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface water</td>
<td>3.69-6.11</td>
<td>1.12-1.14</td>
<td>Skwarzec et al. 2002</td>
</tr>
<tr>
<td>bottom water</td>
<td>1.81-3.81</td>
<td>1.16-1.34</td>
<td></td>
</tr>
<tr>
<td>interstitial water</td>
<td>21.9-31.4</td>
<td>1.17-1.18</td>
<td></td>
</tr>
<tr>
<td>Baltic sediments</td>
<td>0.54-7.11</td>
<td>0.48-1.27</td>
<td>Skwarzec et al. 2002</td>
</tr>
<tr>
<td>Baltic organisms</td>
<td>9.14·10$^{-4}$-0.45</td>
<td>1.04-1.39</td>
<td>Skwarzec et al. 2004, 2006</td>
</tr>
<tr>
<td>phytoplankton</td>
<td>0.45</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>phytobenthos</td>
<td>0.29</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>zooplankton</td>
<td>0.11</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>zoobenthos:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Crustacea</em></td>
<td>0.12</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>clames (<em>Bivalvia</em>)</td>
<td>0.07</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>fish:</td>
<td>4.08·10$^{-3}$</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>digestive system</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>muscles</td>
<td>9.14·10$^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baltic birds</td>
<td>2.33-18.08</td>
<td>0.75-1.12</td>
<td>Boryło et al. 2010</td>
</tr>
<tr>
<td>Rivers water</td>
<td>0.16-5.57</td>
<td>1.00-1.94</td>
<td>Skwarzec et al. 2010a, b</td>
</tr>
<tr>
<td>Area around the phosphogypsum stockpile in Wiślinka (northern Poland)</td>
<td>0.05-900</td>
<td>1.00-1.10</td>
<td>Boryło et al. 2009</td>
</tr>
<tr>
<td>Martwa Wisła River</td>
<td>0.81-1.00</td>
<td>1.10-1.20</td>
<td>Boryło et al. 2009</td>
</tr>
</tbody>
</table>

Water as a negatively charged carbonate complex $[\text{UO}_2(\text{CO}_3)_3]^4-$, which precipitates in the biogenic way or is absorbed onto the surface of the loams. A similar situation is also observed in the sediment of the Słupsk Bank, where there were found small concentrations of uranium (which are not due to different geological sediments and gravel), especially poor in uranium, but the reservoir is an important source of uranium due to the possibility of the formation of iron-manganese nodules there. In the case of the Bornholm and the Gdańsk deeps sediments uranium concentration is related to the dominant presence in the area of clays, silts, loams and sands (Uścinowicz and Zachowicz 1991, 1992, 1994). Into the bottom sediments in the Gdańsk Deep reservoir flow river waters, which contain not only uranium from the weathering of rock, but also anthropogenic uranium associated with human activity, carried
out mainly in agriculture and mining in the catchment area of the Vistula. The higher uranium contents in sediments and the high values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ in this basin are associated with the presence of uranium from the phosphate fertilizers in cultivated fields and uranium contained in the salty waters of mines. At the bottom of the Puck Bay there are deposits of potassium-magnesium salts. In the 70’s of the twentieth century, there were ideas to cut off the part of the Puck Bay with a dam in order to start an opencast exploitation of these deposits. Uranium in sediments of the Southern Baltic Sea is mainly terrigenic origin, while the share of the autogenic component is negligible. This fact is consistent with the uranium content in the suspended and dissolved forms of bottom waters. Approximately 10-13% of the total uranium content in bottom water is connected with suspension, where its concentration ranges from 2.20 to 4.95 mg·kg$^{-1}$ d.wt. (Skwarzec et al. 2002). The results of uranium content in the suspension are higher than the value of its concentration in the surface layers of bottom sediments, which indicates that it is one of the main sources of uranium in sediments. The concentration of uranium in sediments increases with depth of the sediment core, indicating the vertical diffusion processes of uranium from sediments to the bottom water through the interstitial water, and diagenetic changes occurring in the sediment material. The interstitial water plays a very important role in the uranium migration because it penetrates the superficial layers of sediments and increases values of the activity ratio $^{234}\text{U}/^{238}\text{U}$, as well as causes leaching of uranium from the sediment into the sea water. The specific effect of the interstitial water is made clear in the sediments from the Słupsk Bank, where the activity ratio of $^{234}\text{U}/^{238}\text{U}$ ranged from 0.48 to 0.98. The values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ in the other analyzed sediments of the Southern Baltic are in the range between 0.83 and 1.28 and are close to the values of the Baltic sediments (0.98-1.04) (Skwarzec et al. 2002). The results of activity ratio $^{234}\text{U}/^{238}\text{U}$ values in the bottom sediments of the Słupsk Bank are close to the values of the activity ratio in the nodules (0.78-1.36 in nodules and 0.70-1.16 in phosphoric nodules). The increase of the activity ratio in the upper layers of sediments is associated with the effect of terrigenic material falling, on the other hand, this layer is under significant influence of sea water, which causes a clear increase in the activity ratio $^{234}\text{U}/^{238}\text{U}$ in the surface layer of sediment as compared with segments lying below the sediment layer. Uranium nuclides ($^{234}\text{U}$ and $^{238}\text{U}$) in the sediments of the Gdańsk Basin, the Słupsk Narrow and the Bornholm Deep are in relative equilibrium because the values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ ranged from 0.92 to 1.06 (Skwarzec et al. 2002). The small differences of the uranium content of the Southern Baltic Sea bottom waters were observed. The uranium concentrations varied between 1.81 and 3.81 µg·dm$^{-3}$, while the values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ are comparable for all the analyzed basins and range from 1.16 to 1.19 in the Bornholm Deep, 1.18 in the Gdańsk Deep, and 1.19 for the Słupsk Narrow (Skwarzec et al. 2002) and are typical for groundwater, where the values of this activity ratio are between 0.51 and 9.02. The obtained results of activity ratio values in the bottom water samples are therefore comparable to the value characteristic of the Baltic waters. Small changes of uranium concentrations were observed in surface waters of the Southern Baltic Sea, too (3.69-6.11 µg·dm$^{-3}$) (Skwarzec et al. 2002). The lowest concentration of uranium in water of the Słupsk Narrow is associated with the absence of significant flow to this basin of river wa-
ters, which increased the size of the uranium in the sea. Also the Słupsk Narrow is distant from the interaction of waters of the Baltic and the North seas, therefore the share of water with a higher uranium content decreases here. Slightly higher concentration of uranium was observed in the surface water of the Bornholm Deep, where there are salty waters from the North Sea and the Oder River waters from the Pomeranian Bay. The highest concentrations of uranium were measured in surface waters of the Gdańsk Deep (Table 1), which, like the bottom waters, is associated with heavy rains in 1998. Water flowing into the Gdańsk Bay mainly from the Vistula River, introduced a significant part of nutrient salts, which contain big amounts of anthropogenic uranium. Thus, the concentration of uranium in surface waters is determined by the proportion in which the waters of the Baltic Sea and river waters are mixed. The analysis of sediment samples, surface and bottom waters of the Southern Baltic Sea shows a special role the fresh waters play, because after the flood in 1997 in all the analyzed samples, the concentration of uranium and values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ were higher (1.34 for the bottom waters and 1.27 for sediments). The concentration of uranium in interstitial water samples from the Southern Baltic ranged from 21.9 µg·dm$^{-3}$ to 31.4 µg·dm$^{-3}$ (Skwarzec et al. 2002) and is almost ten times higher than the values of uranium concentration in the bottom water samples. The values of the activity ratio in the analyzed samples of interstitial water from the Southern Baltic ranged from 1.17 to 1.18 and are consistent with the value recorded for the Baltic waters. This does not mean that the uranium contained here is of hydrogenic origin, because its concentration in the interstitial water is significantly higher than in the bottom water. Activation of uranium to the interstitial water is possible due to the processes taking place in diagenetic sediment material, due to the release of adsorbed uranium by organic matter.

**Uranium in Baltic organisms**

The distribution of radionuclides, including uranium, in aquatic organisms is a very difficult process. This is mainly due to the great diversity of many species of aquatic organisms which are involved in a complicated series of aquatic food chain. In addition, higher organisms, as opposed to lower, due to the possession of various organs, have a more uneven accumulation of radionuclides. Knowledge of the uranium content in the tissues of marine organisms and in the surrounding water allows to assess the degree of its accumulation in biota. This value is referred to as the coefficient of concentration of the element. Baltic organisms are characterized by very low affinity for uranium, in contrast to the polonium and plutonium. The source of uranium in the Baltic plants and animals is the sea water (Table 1). The values of the bioconcentration factor (BCF) in the Baltic organisms ranged from 0.4 in the muscle of fish to 120 or 130 in clams (Bivalvia) and crustaceans respectively (Skwarzec et al. 2012). The concentration of $^{238}\text{U}$ in the analyzed Baltic organisms ranged from 0.0112 Bq·kg$^{-1}$ d.wt. (9.14×10$^{-4}$ mg·kg$^{-1}$ d.wt. total uranium) in the muscle of fish to 5.5 Bq·kg$^{-1}$ d.wt. in phytoplankton (0.45 mg·kg$^{-1}$ d.wt. total uranium) (Table 1; Skwarzec et al. 2006). The $^{238}\text{U}$ concentration in Baltic zoobenthos ranged from 0.3 to 1.5 Bq·kg$^{-1}$ d.wt., and the observed differences can be the result of the eating habits of the tested organisms. The values of uranium concentrations in
phytoplankton organisms (0.45 mg⋅kg\(^{-1}\) d.wt.) are about 4 times higher than zooplankton organisms, where the concentration of this radionuclide was estimated at 0.11 mg⋅kg\(^{-1}\) d.wt., which indicates that uranium is easier and more eagerly accumulated by the phytoplankton. The values of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) in the representatives of the phytoplankton and zooplankton from the Southern Baltic (from 1.13 to 1.16) are very similar to the values in ocean water and Baltic water (1.14 and 1.17 respectively) (Skwarzec et al. 2004). Uranium concentrations in zoobenthos organisms ranged from 0.07 mg⋅kg\(^{-1}\) d.wt. and 0.12 mg⋅kg\(^{-1}\) d.wt. while the values of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) ranged from 1.04 to 1.39. The lowest concentrations of uranium were estimated for fish from the Baltic (9.14⋅10\(^{-4}\)-0.05 mg⋅kg\(^{-1}\) d.wt.), while the values of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) were similar to other Baltic organisms (1.10-1.13). The average value of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) in the analyzed Baltic organisms is 1.15 and is close to the value, which characterizes the Baltic seawater (1.18 and 1.17, respectively). This fact proves that the main source of uranium in the Baltic organisms is sea water (Skwarzec et al. 2004, 2006). The relative radioactive equilibrium is observed in the sediments of the Southern Baltic, where the values activity ratio \(^{234}\text{U}/^{238}\text{U}\) is close to 1 (from 0.92 to 0.97, except for the sediments collected after the flood in 1997). In the waters of the Southern Baltic the values of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) ranged from 1.18 to 1.20 (Skwarzec et al. 2004, 2006, 2012).

**Uranium in marine birds**

Structure and physiology of birds is constantly changing during the successive phases of growth, as well as under the influence of several physico-chemical factors in the environment. The accumulation of uranium in their bodies is related primarily to the content of elements in the diet, the concentration of radionuclides in the environment in which birds live. Seabirds are typical animals, which live both in water and on land, and to their body penetrate both radionuclides from the marine waters and from the air. Uranium isotopes were determined in the marine birds from the Polish area of the Southern Baltic Sea among species permanently residing at the Southern Baltic (razorbill *Alca torda*, great cormorant *Phalacrocorax carbo*, eurasian coot *Fulica atra*), species of wintering birds (tufted duck *Aythya fuligula*, common eider *Somateria mollissima*, long-tailed duck *Clangula hyemalis*, velvet scoter *Melanitta fusca*) and species of migrating birds (black guillemot *Cepphus grylle*, red-throated diver *Gavia stellata*, common guillemot *Uria aalge*). The analyzed material consisted of dead sea birds which were found on the beach or were caught by fishermen in nets while fishing. The sea birds are an important link in the migration of uranium in the trophic chain of the marine ecosystem. The uranium concentration is very irregularly distributed in organs and tissues of marine birds (Table 1). The value of uranium concentration is low, as in marine organisms, but higher than in fish and depends on the content of this element in the food and the environment in which they live. In sea birds, spending much of their life on the open waters uranium concentrations were lower, the higher were in coastal birds. The largest uranium concentrations are characteristic for carnivorous and herbivorous species, the smallest for species eating fish. The values of uranium concentration
in whole organism are within the limits from 2.33 mg·kg\(^{-1}\) w.wt. in \(A.\) tarda to 18.08 mg·kg\(^{-1}\) w.wt. in \(A.\) fuligula. The highest uranium concentrations were observed in rest of viscera (from 3.94 mg·kg\(^{-1}\) w.wt. for \(A.\) tarda to 75.23 mg·kg\(^{-1}\) w.wt. for \(A.\) fuligula) and feathers (from 6.26 mg·kg\(^{-1}\) w.wt. for \(F.\) atra to 23.97 mg·kg\(^{-1}\) w.wt. in \(P.\) carbo), while the smallest in muscles (from 0.21 mg·kg\(^{-1}\) w.wt. in \(A.\) tarda to 11.77 mg·kg\(^{-1}\) w.wt. for \(C.\) grylle). The concentration of uranium in organs and tissues of seabirds decreases in the series: rest of viscera > feathers > skin > liver > skeleton > muscles. A size of uranium concentration in marine birds is associated with moulting effect. It was found that as a result of this process, the birds are losing a large part of radionuclides contained in their bodies. After moulting process the concentrations of uranium isotopes \(^{234}\text{U}\) and \(^{238}\text{U}\) in marine birds tissues and organs were much less in comparison with other species. The sea birds before moulting are characterized by significantly higher concentrations of uranium. Some radionuclides contained in the feathers are built into their structure and come from the bird body, and some is adsorbed on their surface from the atmosphere and is applied to them with uropygial gland during their maintenance. Research on the origin of uranium in feathers showed that approximately 37% of its content is embedded in the body during growth, and more than 67% is adsorbed on the surface and comes mainly from the air. Also, the isotopic composition of radionuclides adsorbed on feathers shows contamination of the environment in which they reside. In the case of migratory birds, the isotopic composition analysis of radionuclides in the feathers can be used to track their migration routes. The feathers of marine birds accumulate significant amounts of radionuclides in aquatic and terrestrial environment (depending on species), due to the periodic changes of plumage. The values of ratio \(^{234}\text{U}/^{238}\text{U}\) in marine birds are between 0.90 and 1.23, but the average values of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) oscillate around 1.00 and are in the range from 0.75 in common guillemot to 1.12 in common eider. The obtained results are slightly lower than for marine organisms inhabiting the southern part of the Baltic Sea. The values of the activity ratio \(^{234}\text{U}/^{238}\text{U}\) in organs and tissues of the analyzed sea birds are in a very wide range from 0.35 in the muscles of black guillemot to 1.25 in the skeleton of red-throated diver, which shows the different behavior of uranium isotopes in organs and tissues of seabirds. The values of the activity ratio \(^{235}\text{U}/^{238}\text{U}\) in the analyzed organs and tissues of marine birds ranged from 0.032 in skeleton of common eider to 0.050 in feathers of great cormorant (the majority of research does not take into account the value of this ratio due to the low \(^{235}\text{U}\) determination). The values of uranium participation factor (PF) suggest that the uranium in the links: seabird → fish is accumulated (PF > 2), but in the trophic links seabirds → crustaceans and bivalves PF values are much smaller than 1.00 (Boryło et al. 2010).

**The inflow of uranium from catchment areas of the Vistula and Oder rivers**

Among the many sources of radioactive isotopes, which constitute direct or indirect threat for the rivers and the Baltic Sea as the most important are fallout, coal mines and sewage discharged from nuclear power plants. Analyzed concentrations of uranium isotopes \(^{234}\text{U}\) and \(^{238}\text{U}\) were very diverse. Higher uranium concentrations were found in the basin of the Vistula and Oder rivers in the spring and the autumn,
while the smallest in the summer. The values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ in rivers water ranged from 1.22 to 1.40 (the average 1.31) (Skwarzec 1995, 2002). Uranium isotopes $^{234}\text{U}$ and $^{238}\text{U}$ are not in radioactive equilibrium in the Vistula and Oder rivers water samples and values of this proportion are between 1.00 and 2.14 (Table 1). The greatest values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ along the main stream of the Vistula and Oder rivers were observed in the summer in Kraków (1.94) and Głogów (1.84) respectively, the lowest in the winter in Malbork (1.05) and Gozdowice (1.20) (respectively). Among the Vistula and Oder tributaries the largest value of the activity ratio $^{234}\text{U}/^{238}\text{U}$ was recorded in the waters of the Bzura (1.61) and the Bystrzyca (1.61), the smallest in the Bug with the Narew (1.02) and the Noteć (1.03),

Table 2

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Drainage basin of the Vistula</th>
<th>Drainage basin of the Oder</th>
<th>Pomeranian rivers</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}\text{U}$ [GBq]</td>
<td>276.80</td>
<td>126.29</td>
<td>8.24</td>
<td>411.33</td>
</tr>
<tr>
<td>$^{238}\text{U}$ [GBq]</td>
<td>230.60</td>
<td>100.80</td>
<td>7.36</td>
<td>338.76</td>
</tr>
<tr>
<td>U total [t]</td>
<td>18.80</td>
<td>8.19</td>
<td>0.60</td>
<td>27.59</td>
</tr>
</tbody>
</table>

Fig. 1. The annual flow of $^{234}\text{U}$ and $^{238}\text{U}$ isotopes from the drainage basins of the Vistula, the Oder and the Pomeranian rivers into the Baltic Sea
respectively (Skwarzec et al. 2010a, b). In the Vistula and Oder rivers, with the increase of salinity, the values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ decreases. Runoff values of uranium isotopes are the largest in the area of the estuary. The highest concentrations of uranium were measured in the spring and the autumn, which is associated with the use of phosphate fertilizers in agriculture, increased underground and surface runoff of snowmelt water, the discharge of saline mine waters from the Upper Silesian Industrial Region and the Lower Silesian Coal Basin, increased deposition of dry atmospheric fallout in the winter period – the burning of coal, oil and gas and increased soil erosion and leaching of substances from the soil by infiltrating water and transporting uranium with the material of the river. In the summer and the winter, these processes are much less severe. During the year the highest values of surface runoff of $^{238}\text{U}$ flow from the Vistula and Oder rivers drainage area were observed in Kiezmak and Widuchowa (222.8 GBq·year$^{-1}$ and 107.0 GBq·year$^{-1}$), the smallest in Kraków and Chałupki (7.0 GBq·year$^{-1}$ and 5.0 GBq·year$^{-1}$). Among the Vistula and Oder rivers tributaries the highest surface runoff of $^{238}\text{U}$ was noticed for the Bug with Narew and the Warta (81.2 GBq·year$^{-1}$ and 27 GBq·year$^{-1}$, respectively), the lowest for the Brda and the Mała Panew (3.1 GBq·year$^{-1}$ and 0.27 GBq·year$^{-1}$). The highest annual surface runoff of $^{238}\text{U}$ from the Vistula and Oder rivers tributaries was observed for the Dunajec, the San and the Bystrzyca (2330 kBq·year$^{-1}$·km$^{-2}$, 1590 kBq·year$^{-1}$·km$^{-2}$ and 5244 kBq·year$^{-1}$·km$^{-2}$), the lowest for the Narew and the Mała Panew (430 kBq·year$^{-1}$·km$^{-2}$ and 126 kBq·year$^{-1}$·km$^{-2}$). Total annual flow of uranium from the Vistula and Oder rivers drainages to the Baltic Sea was calculated as 18.8 ton·year$^{-1}$ and 8.2 ton·year$^{-1}$, respectively (Table 2, Fig. 1).

The higher values of the concentration of uranium and activity ratio $^{234}\text{U}/^{238}\text{U}$ were calculated for the mountain Polish rivers in contrast to the plain Polish rivers. A particularly high concentration of uranium and surface flow of uranium several times larger than in the other tributaries were observed in the Bystrzyca. It is the typical mountain river and therefore a higher concentration of uranium in river water is mainly a result of higher concentrations of this element in the parent’s rocks. The tributary of the Bystrzyca basin is in the Karkonosze, which are built mainly from gneiss, pink and red granite, where the uranium concentration reaches about 20 g/ton and slate with lots of crystalline dolomite and marble. In aquatic environment uranium is mobile in oxidizing conditions and is leached from the rocks to surface waters. The source of $^{238}\text{U}$ in the Bystrzyca is not only the leaching of uranium, but also the presence of this nuclide in the salty waters of the mine (the Lower Silesian Coal Basin). The value of the activity ratio $^{234}\text{U}/^{238}\text{U}$ in salty water ranged from 1.11 to 5.14. The values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ in the Bystrzyca are also close to the values, which are in mining drilling (1.55). The large values of the analyzed activity ratio are caused by human activities in the basin, mainly in agriculture (using phosphate fertilizers) and mining (mine water discharge into the river) as well as the presence of uranium ores in these areas. In Poland uranium ore was mined in five places: Kowary, Kletno, Radoniów and Kopaniec in the Sudetes, and Rudki around Nowa Słupia in the Świętokrzyskie Mountains. The largest and longest running (from 1954 to 1973) of operating uranium mines in Poland was “Wolność” mine in Kowary, where the fluorite used as a flux was mined from 1958. Since 1973
in Poland uranium has not been produced. The data of the amounts of the mined uranium are not precise and ambiguous. According to some sources there was mined about 650 tons, according to other sources 850 tons (Rejman 1996).

Along the Pomeranian rivers, the largest uranium concentrations were observed in the Rega, the lowest in the Słupia. The values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ ranged from 1.06 to 1.15. Annual runoffs on the uranium radionuclides from the Pomeranian rivers were: 15.6 GBq $^{234}\text{U}$ and $^{238}\text{U}$ (8.24 GBq for $^{234}\text{U}$ and 7.36 GBq for $^{238}\text{U}$). The drainage basins of the Vistula, the Oder and the Pomeranian rivers are main sources of uranium in the Southern Baltic Sea. Every year about 750 GBq of $^{234+238}\text{U}$ flow from these rivers to the Southern Baltic (Skwarzec et al. 2010b) (Table 2, Fig. 1).

The influence of the phosphogypsum stockpile in Wiślinka on the contamination of the Southern Baltic ecosystem

According to the ordinance of the Polish Ministry of Environmental Protection the phosphogypsum is not a hazardous waste but it is treated as production waste, preparation of turnover and using phosphoric chemicals (Skwarzec et al. 2010, Boryło et al. 2012). According to the decision of voivodeship national council (GW-II-0531/115/67) in Gdańsk, the phosphogypsum waste heap came into existence on 10$^{th}$ March 1966, but its construction started on 27$^{th}$ December 1967. The phosphate rocks contain a lot of natural radionuclides, especially forms of uranium and thorium decay series. The radionuclides of uranium ($^{234}\text{U}, ^{235}\text{U}, ^{238}\text{U}$), thorium ($^{232}\text{Th}$) and existing in the equilibrium with them radionuclides of radium ($^{226}\text{Ra}, ^{228}\text{Ra}$), polonium ($^{210}\text{Po}$) and lead ($^{210}\text{Pb}$) almost always exist in sedimentary phosphoric rocks. Generally uranium ($^{234}\text{U}, ^{238}\text{U}$), radium ($^{226}\text{Ra}$), polonium ($^{210}\text{Po}$) and lead ($^{210}\text{Pb}$) radionuclides belong to the most radiotoxic, dangerous alpha emitters. Phosphoric acid, the material for the production of phosphate fertilizers is obtained in a wet process by reaction of the phosphatic rocks with sulphuric acid. In this process the uranium is associated with the phosphoric acid fraction, while the $^{210}\text{Po}$ and $^{210}\text{Pb}$ are bound to the phosphogypsum fraction (Baxter 1996, Hull and Burnett 1996). The concentration of uranium in surface water samples collected near Wiślinka ranged widely between 0.05 µg·dm$^{-3}$ and 430 µg·dm$^{-3}$ (Table 1, Fig. 1). In phosphogypsum samples uranium concentration varied between 4.03 mg·kg$^{-1}$ d.wt. in samples collected in 1997 and 0.65 mg·kg$^{-1}$ d.wt. in samples taken in 2007 (Boryło et al. 2009). The largest uranium concentration in analyzed water samples taken in the vicinity of the phosphogypsum waste heap indicates that uranium is lixiviated from phosphogypsum waste dump to retention reservoir and pumping station. The lower uranium concentration in surface water samples taken from the Martwa Wisła River shows that the migration and distribution of uranium radionuclides from the phosphogypsum waste heap to the Martwa Wisła River are rather slow. We observed that the values of the activity ratio $^{234}\text{U}/^{238}\text{U}$ in the water with immediate surroundings of waste heap were close to 1 and ranged between 1.00 and 1.10, while in surface river water from the Martwa Wisła River were higher than one (1.10-1.20) (Boryło et al. 2009). The values of the activity ratio in waters of retention reservoir are typical for soil and rock samples. The maximum uranium concentration in the
analyzed water samples, about one hundred times higher than it was observed in the pumping station, was found in retention reservoir (430 µg·dm⁻³ for total uranium in surface water and 900 µg·dm⁻³ in bottom water). The \(^{234}\text{U}/^{238}\text{U}\) activity ratio is approximately one in the phosphogypsum samples, and was estimated at 0.90 and 0.97. The analysis of values of activity ratio \(^{234}\text{U}/^{238}\text{U}\) in water samples from the Martwa Wisła River indicated that uranium is eluted from phosphogypsum waste and via river system is transported to the Bay of Gdańsk. The values of the activity ratio in the various analyzed components of marine environment are presented on Figure 2.

**CONCLUSION**

The area of the Southern Baltic is characterised by high industrial and farming activities, contributing to the annual run-off from the Vistula and Oder rivers. Moreover, phosphatic fertilizers and phosphogypsum contain considerable amounts of uranium. The contents of uranium in the sediments of the southern Baltic decrease with the sediment depth, which suggests its diffusion from bottom sediments to the bottom water through pore waters and diagenetic transformations in the sedimentary material. The content of uranium in the sediments of the Southern Baltic is a result of its penetration into the sediments profile and its flow with pore (e.g. Słupsk Bank). In others regions of the Southern Baltic uranium isotopes are in a relative
equilibrium, which is reflected by the activity ratio $^{234}\text{U}/^{238}\text{U}$ ranging between 0.99 and 1.10. The most important sources of uranium in waters of the Southern Baltic are erosion of rock materials, leaching, wet and dry atmospheric fallout as well as human activities carried out in the mining and agriculture.

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Migrację uranu zapoczątkowują procesy wietrzenia skał oraz erozja gleb. Uran wprowadzany jest do wody morskiej w różnorodnych postaciach geochemicznych, zawiesiny minerałów wietrzeniowych oraz w formie wolnych jonów U\(^{6+}\). Ważną rolę w migracji uranu w środowisku odgrywa również proces dyfuzji z osadów dennych, w których stwierdzono niższe stężenia uranu przy powierzchni niż w warstwach głębszych. Najważniejszym procesem geochemicznej migracji uranu w ekosystemie Południowego Bałtyku jest sedimentacja materiału lądowego i zawiesiny wód lądowych oraz pionowa dyfuzja z osadów do wody przydennnej za pośrednictwem wody porowej oraz zmian diagenetycznych zachodzących w osadach. Organizmy bałtyckie charakteryzują bardzo małe powinowactwo do uranu. Źródłem uranu w bałtyckich organizmach roślinnych i zwierzęcych jest woda morska, nie zaś osad denný, o czym świadczą wartości ilorazu aktywności \(^{234}\text{U}/^{238}\text{U}\), które w tych organizmach wynoszą około 1,15 i są porównywalne do wartości charakteryzującej wodę morską i bałtycką (odpowiednio 1,18 i 1,17). Wszystką równowagę promieniotwórczą obserwuje się natomiast w osadach dennych Południowego Bałtyku, gdzie wartości stosunku aktywności są zbliżone do 1 (od 0,92 do 0,97, z wyjątkiem osadów dennych zebranych po powodzi w 1997 roku). W wodach przydennych i powierzchniowych Południowego Bałtyku wartości stosunku aktywności \(^{234}\text{U}/^{238}\text{U}\) mieszczą się na natomiaść w przedziale od 1,18 do 1,20, co oznacza, że izotopy \(^{234}\text{U}\) i \(^{238}\text{U}\) nie występują w równowadze promieniotwórczej. Niższe wartości stosunku aktywności \(^{234}\text{U}/^{238}\text{U}\) są natomiast charakterystyczne dla ptaków morskich (0,75-1,12). Stężenie uranu w ich narządach i tkankach maleje w szeregu: pozostałe trzewia > pióra > skóra > wątroba > szkielet > mięśnie. Bardzo istotnym zjawiskiem mającym wpływ na wielkość stężenia badanych radionuklidów w organizmach ptaków morskich jest pierzenie, w wyniku którego ptaki tracą znaczną część zawartych w nich radionuklidów. Część radionuklidów zawartych w piórach jest wbudowana w ich strukturę i pochodzi z organizmu ptaka, a część jest zaabsorbowana na ich powierzchni z atmosfery oraz nanoszona jest na nie wraz z wydzieliną gruczołu kuprowego podczas ich konserwacji. Badania pochodzenia uranu w piórajach wykazały, że około 37% jego zawartości jest wbudowywane w nie z organizmu w czasie wzrostu, a ponad 67% jest zaabsorbowane na ich powierzchni i pochodzi głównie z powietrza.

Wisła oraz Odra wraz z dopływami, jak też rzeki przemysłowe (Rega, Parsęta i Słupia), są ważnymi źródłami spływu uranu do Morza Bałtyckiego. Powierzchnia zlewni Wisły, Odry oraz Obry stanowi około 99% powierzchni Polski, zatem szacuje się, że z całego obszaru Polski wpływ tych rzekami około 750 GBq izotopów uranu \(^{234}\text{U}\) i \(^{238}\text{U}\). Wśród wielu innych źródeł izotopów promieniotwórczych, które stanowią pośrednie lub bezpośrednie zagrożenie skażenie dla rzek i ekosystemu Południowego Bałtyku, za najważniejsze uznaje się kopalnie węgla kamiennego (np. Górnośląski Okręg Przemysłowy i Dolnośląskie Zagłębie Węgla) oraz działalność człowieka związaną z przemysłem metalurgicznym i jądrowym, spalaniem paliw kopalnych, stosowaniem nawozów fosforowych w rolnictwie, rafineriami rudy naftowej, testami i próbami broni nuklearnej, produkcją i przetwarzaniem prętów paliwowych, górnickich oraz hałd.