# **Sedimentation rates and dating of bottom sediments in the Southern Baltic Sea region**

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**Abstract.** Sedimentation rates and dating of bottom sediments were estimated in two sampling stations of the Gulf of Gdańsk and in four stations in the open sea area. Estimations were based on vertical distributions of <sup>210</sup>Pb, <sup>137</sup>Cs and <sup>239,240</sup>Pu activity concentrations in sediment core samples taken in 1998–2007. Two dating models based on changes of activity concentrations of <sup>210</sup>Pb<sub>unsup</sub> were used: 1) CF:CS (Constant Flux Constant Sedimentation rate-model) and 2) CRS (Constant Rate of Supply-model). <sup>137</sup>Cs and <sup>239,240</sup>Pu were applied as time markers. <sup>137</sup>Cs originates mostly from the Chernobyl accident in 1986, whereas <sup>239,240</sup>Pu comes from the global fallout in 1963. The validation of the <sup>210</sup>Pb methods was performed by activity peak of <sup>137</sup>Cs and <sup>239,240</sup>Pu. Sediment accumulation rate (g·cm<sup>-2</sup>·y<sup>-1</sup>) was constant along sediment core. Annually accumulated layer, (mm·y<sup>-1</sup>) decreased with sediment depth in all the locations. In the Gulf of Gdańsk sedimentation rate in the upper layer was about 3.6 mm·y–1, and it decreased in the deeper layers to about 1.1 mm·y–1. Sedimentation rates in the open sea area were lower than in the gulf region and the lowest was observed in the Bornholm Deep, being about 0.95 mm·y<sup>-1</sup> in the upper layer and 0.35 mm·y<sup>-1</sup> in the deeper layer. The growth of a 5 cm thick layer took 27–37 years in the Gulf of Gdańsk, and 61–105 years in the open sea area. It is suggested that the mean values obtained from the models would give a most reliable estimation of the sedimentation rates.

**Key words:** sedimentation rate • <sup>210</sup>Pb • <sup>137</sup>Cs • <sup>239,240</sup>Pu • Southern Baltic • bottom sediment

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# **Introduction**

Bottom sediments are formed from organic and inorganic particles which settle from water body of aquatic reservoirs. Sedimentation process causes a continuous increase of the sediment, with a sedimentation rate characteristic of a given location. However, in the long period of time sedimentation rate may vary considerably. The uneven distribution of various sediments reveals the dynamic nature of the sedimentation processes in the Baltic Sea. The central region of the Southern Baltic is characterised by accumulation of fine-grained, soft silty and muddy sediments [5]. Contaminants from water are adsorbed on the settled particles and bottom sediments. Particles reach the seafloor by vertical transport and by near-bottom lateral transport [3]. Accumulated radionuclides are more or less permanently fixed to the bottom sediments depending on their properties and sediment qualities. Horizontal and vertical distributions of artificial radionuclides in the bottom sediments show contamination sources and their variability in time [5].

The sediment accumulation rate is the main parameter in contamination studies in the aquatic environment, and 210Pb is widely applied as a tracer in the deposition history of bottom sediments, their dating and estimation of sedimentation rates. The main source of 210Pb  $(T_{1/2} = 22.3 \text{ years})$  in the environment is the direct dry and wet deposition from atmosphere. Most of 210Pb derives from the decay of gaseous<sup>222</sup>Rn introduced into the atmosphere from the earth's crust. In addition, 210Pb was introduced to atmosphere during nuclear explosions in the reaction <sup>208</sup>Pb (2n, $\gamma$ )<sup>210</sup>Pb [8].

Small content of <sup>210</sup>Pb is also introduced from phosphoric fertilizers reach in 226Ra [6] and, as a result, of conventional coal power plants and petrol combustion [7]. Part of 210Pb in bottom sediments also results from the decay of 226Ra present in the sediment.

Dating methods, which are based on activity concentrations of 210Pb, can be applied for the last 100–150 years [1, 2, 10]. The 210Pb methods need an independent validation. The chronology of changes in the environment is validated by the distribution of other isotopes along the bottom sediment profiles. Validation for the last 30–40 years is made via fallout records of artificial radionuclides, like 137Cs, 239,240Pu or 241Am which exist in the environment since the first weapon tests.

The purpose of this study was to determine sedimentation rate in the Basin of Gdańsk (two locations in the Gulf of Gdańsk and two in the open sea area) and in the Bornholm Basin (two locations). For determination of sedimentation rates the 210Pb method was used. The results obtained were validated by applying activity peaks of 137Cs and 239,240Pu.

# **Materials and methods**

# Sampling

Bottom sediment core samples were collected in 1998–2007 from various regions of southern part of the Baltic Sea. Sampling cruises into the Baltic Sea with research vessel "Baltica" were organised by the Institute of Meteorology and Water Management once a year from June to August. At each sampling station, five or six core samples were taken with the gravity corer of the Niemisto type of inner diameter 55 mm. Core samples were sectioned into sub-samples: 1 cm slices from 0 to 5 cm and 2 cm slices from 5 to 19 cm depth. Sub-samples from each sampling station were combined and frozen immediately after sampling. In the Laboratory unfrozen samples were weighed before and after drying. The location (latitude and longitude), depth of sampling stations and coring date are presented in Table 1.

#### Analytical methods

The <sup>210</sup>Pb and <sup>137</sup>Cs activity concentrations were determined by gamma spectrometry from the gamma emission at 46.52 and 661.66 keV, respectively [1]. The gamma spectrometer consisted of a high purity germanium detector with an energy resolution of 1.8 keV for  ${}^{60}Co$  (1332 keV) and with a relative efficiency of 33%. The detector was placed inside a lead shield with walls 10 cm thick which were lined with a 2 mm layer of copper. Till year 2001, the detector was connected to a multichannel analyser Canberra, Series 90. Since the year 2002 it was connected to Canberra MULTIPORT II MCA with GENIE-2000. Lower limit of detection (LLD) of  $^{210}Pb$  and  $^{137}Cs$  for counting time 170,000 s was 0.13 Bq/sample and 0.025 Bq/sample, respectively.

Plutonium was separated by ion exchange, followed by the electrodeposition onto stainless steel disks. 242Pu was used as an internal tracer for counting alpha activity and chemical recovery [14]. Activity of plutonium was measured by alpha spectrometry using a PIPS detector with an efficiency of 32% placed in a vacuum chamber. LLD for counting time of 164,000 s was 0.2 mBq/sample.

Concentration of 226Ra was determined radiochemically using the emanation method (measurement of <sup>222</sup>Rn and its daughters in the Lucas-type scintillation chambers) preceded by separation of radium [13]. LLD with the counting time 21,600 s was equal to 0.73 mBq/sample.

The reliablity of the applied methods was checked in the determinations of radionuclides in reference materials (IAEA-300, IAEA-326, IAEA-327, IAEA-375) and in the Proficiency Test organized by the IAEA in 2002. Analytical results for  $^{137}Cs$ ,  $^{210}Pb$ ,  $^{239,240}Pu$  and  $^{226}Ra$  are presented in Table 2. Calculated u-test values indicate that our results do not differ significantly from the IAEA values at the probability greater than 0.1. Calculated precision was on average  $7.1\%$  for  $137Cs$ ,  $18.9\%$ for <sup>210</sup>Pb, 9.30% for <sup>239,240</sup>Pu and 19.2% for one sample of 226Ra. The above data show that the applied methods fulfil the IAEA criteria of accuracy and precision.

### Models

The vertical distribution of naturally occurring 210Pb has been used for the sediment dating and estimation of sediment accumulation rate. The total activity concentrations of  $^{210}Pb$  ( $^{210}Pb_{\text{tot}}$ ) in the bottom sediments consist of <sup>210</sup>Pb unsupported (<sup>210</sup>Pb<sub>unsup</sub>), originated from atmosphere, and <sup>210</sup>Pb supported (<sup>210</sup>Pb<sub>sup</sub>) formed as a result of radioactive decay of 226Ra in the sediment. In

**Table 1.** Sampling stations, location and year of sampling



	Radionuclide	Unit	Recommended value	Activities measured in this work
IAEA-300 – Sediment	$^{137}Cs$	$Bq \cdot kg^{-1}$	1066.6	$1055 \pm 37.8$
	$^{210}Pb$	$Bq \cdot kg^{-1}$	$364 \pm 57$	$370 \pm 7.44$
	239,240Pu	$Bq \cdot kg^{-1}$	3.55	$3.20 \pm 0.40$
$IAEA-326 - Soil$	137Cs	$Bq$ · $kg^{-1}$	$137.5 \pm 19.0$	$129 \pm 3.1$
	$^{210}Pb$	$Bq \cdot kg^{-1}$	$53.3 \pm 10.6$	$51.0 \pm 1.52$
	$^{226}Ra$	$Bq \cdot kg^{-1}$	$32.6 \pm 6.2$	$33.8 \pm 0.81$
$IAEA-327 - Soil$	137Cs	$Bq \cdot kg^{-1}$	$24.9 \pm 1.8$	$26.2 \pm 0.66$
	$^{210}Pb$	$Bq \cdot kg^{-1}$	$58.8 \pm 12.1$	$58.0 \pm 1.61$
	$^{239,240}Pu$	$Bq \cdot kg^{-1}$	$0.58 \pm 0.06$	$0.46 \pm 0.05$
$IAEA-375 - Soil$	137Cs	$Bq$ · $kg^{-1}$	5280	$5281 \pm 57$
	$^{226}Ra$	$Bq \cdot kg^{-1}$	20.0	$20.5 \pm 1.42$
	$239,240$ P <sub>11</sub>	$Bq \cdot kg^{-1}$	0.30	$0.297 \pm 0.032$
Proficiency Test, spiked matrix	239,240Pu $239,240$ P <sub>11</sub> 239,240Pu 239,240Pu $^{137}Cs$ ${}^{137}Cs$	Bq Bq Bq $Bq \cdot g^{-1}$ $Bq \cdot kg^{-1}$ $Bq \cdot kg^{-1}$	$0.077 \pm 0.0016$ $0.077 \pm 0.0016$ $0.077 \pm 0.0016$ $0.244 \pm 0.0049$ $34.9 \pm 1.0$ $21,200 \pm 320$	$0.080 \pm 0.0057$ $0.081 \pm 0.0069$ $0.077 \pm 0.0058$ $0.241 \pm 0.0175$ $32.57 \pm 0.74$ $22,279 \pm 563$

**Table 2.** Radionuclide concentrations in reference materials and spiked matrix

the dating models, activity concentrations of  $^{210}Pb_{unsup}$ in particular layers of the bottom sediments was used. Two dating models based on changes of activity concentrations of 210Pb were used: 1) CF:CS (Constant Flux Constant Sedimentation rate-model) and 2) CRS (Constant Rate of Supply-model) [2, 12].

The validation of the above methods was performed by the activity peak of 137Cs or 239,240Pu.Caesium-137 in the Baltic Sea originates mostly from the fallout of the Chernobyl accident in 1986, whereas plutonium originates from the weapon tests, giving the maximum global fallout in 1963[4, 9]. In calculations it was accepted that the sedimentation rate has been constant between the year 1986 or 1963 and the sampling year.

# **Results and discussion**

Activity concentrations of 210Pb strongly differed in the subregions. In the upper layer 0–1 cm of the sediments, activity concentrations of total 210Pb decreased from about  $430$  Bq·kg<sup>-1</sup> in the Gulf of Gdańsk to about 60 Bq·kg<sup>-1</sup> in the Bornholm Basin. Unsupported  $2^{10}Pb$ decreased from 400 to 20 Bq·kg–1, respectively. Also differed the smallest depths in the bottom sediment where the activity concentrations of total <sup>210</sup>Pb were the same as the concentration of 226Ra. The smallest depth was 12–16 cm in the Gulf of Gdańsk, 5–8 cm in the Gdańsk Deep, and 3–5 cm in the Bornholm Basin. Figure 1 shows the vertical distribution of activity concentrations of the total 210Pb and unsupported 210Pb at chosen stations and years in the Gulf of Gdańsk, the Gdańsk Deep and the Bornholm Basin.

Table 3 presents the sediment accumulation rates (SAR), annual accumulation layer (AAL), and total <sup>137</sup>Cs activity estimated at six stations from 27 sediment cores. SAR and AAL were estimated with the CF:CS model. The highest SAR values were observed at the P110 sampling station (Gulf of Gdańsk), whereas the lowest were in P5 (Bornholm Deep). SAR and  $^{137}Cs$ <sub>tot</sub> varied in the sampling years. The smallest differences between SAR values (456–613 g·m<sup>-2</sup>·y<sup>-1</sup>) were found at P110. The largest differences occurred at station P1, where SAR ranged from 151 to 685 g·m<sup>-2</sup>·y<sup>-1</sup>. Similar observations were reported by Mattila *et al*. [9] in the Gulf of Finland and the Baltic Proper. According to their explanation, these variations result from the heterogeneity of soft sediment deposits. At Eastern Gotland spatial variability of SAR were 10.5–527  $g·m<sup>-2</sup>·y<sup>-1</sup>$  with an average value of  $129 \pm 112$  [3].

The highest total <sup>137</sup>Cs activities occurred at station P110 in the Gulf of Gdańsk (average 4722 Bq·m<sup>-2</sup>). At other stations in the region of the Gdańsk Basin these activities were lower (average from 2034 Bq·m–2 at P116



**Fig. 1.** Vertical distribution of  $^{210}Pb_{unsup}$  and  $^{210}Pb_{tot}$  in bottom sediments in the Gulf of Gdańsk (P110/2002), in the Gdańsk Deep (P1/2003) and in the Bornholm Basin (P39/2003).



**Table 3.** Sediment accumulation rate (SAR) and annual accumulation layer (AAL) estimated with CF:CS model, and total  $^{137}Cs$  activity ( $^{137}Cs$ <sub>tot</sub>)

 $\alpha$ <sup>a</sup> Value  $\pm$  standard uncertainty.  $<sup>b</sup>$  Mean  $\pm$  standard error of the mean.</sup>

to 3441 Bq·m<sup>-2</sup> at P140). Significantly lower were the  $137Cs$  activities in the Bornholm Basin: 1400 Bq·m<sup>-2</sup> at P5 and 1552 Bq·m–2 at P39.

Correlation coefficients (*r*) between the SAR and total 137Cs activity were high, particulary for the stations P116, P1, P140, and P5, being 0.97, 1.00, 0.98 and 1.00, respectively. For the calculation of *r* numbers of samples in particular locations were: 5 in P116, 5 in P1, 4 in P140, and 3 in P5. High correlations indicate that the estimation of SAR is correct. The same was earlier concluded by Mattila *et al*. [9].

The AAL values for the layer 0–10 cm ranged from  $0.52$  mm·y<sup>-1</sup> in core taken in 2006 from the Bornholm Deep to  $3.90$  mm·y<sup>-1</sup> in core taken in 1999 from the Gdańsk Deep (Table 3). The above values are in good agreement with the values reported earlier by Niemisto [10] for the Baltic Proper  $(0.5-2.0 \text{ mm·y}^{-1})$  and Pempkowiak [11] for the Southern Baltic (0.15–2.26 mm·y<sup>-1</sup>).

Average values of annually accumulated layers (mm·y–1) in consecutive layers at each station are presented in Fig. 2 to Fig. 6. In all locations the AAL decrease with depth of the sediment. The highest values were found in the Gulf of Gdańsk (Fig. 2); they decreased from about 3.6 mm·y<sup>-1</sup> in the upper layer to about 1.1 mm·y<sup>-1</sup> in the deepest layer. The lowest AAL values were found in the Bornholm Deep (Fig. 6) – from 0.95 mm·y<sup>-1</sup> in the upper layer to 0.35 mm·y<sup>-1</sup> at the depth of 12 cm. In the Bornholm Basin (Fig. 5) the AAL values were about two times higher than those at P5 – 1.98 mm·y<sup>-1</sup> and they decreased to 0.89 mm·y<sup>-1</sup> in the depth of 12 cm. Decrease of AAL values in deep layers is associated with increasing sediment density. In the Gulf of Gdańsk at P110 and P116 the density of sediments varied between the upper and deepest layer by a factor of about 3 and 4, respectively. Similar factor was found for the Gdańsk Deep (P1), whereas in the



**Fig. 2.** Average annual accumulation layers at P110 and at P116 stations in the Gulf of Gdańsk.

open see the differences were smaller, being about 2. AAL values changed inversely with density. This means that the deeper layer of the sediments were more compressed than the upper ones.

In the Gulf of Gdańsk SAR and AAL are higher than those in the open sea. This can be explained by the close distance (about 15 km of the P110 station and about 30 km of the P116 station) from the mouth



**Fig. 3.** Average annual accumulation layers at P1 station in the Gdańsk Deep.



**Fig. 4.** Average annual accumulation layers at P140 station in the Gdańsk Basin.



**Fig. 5.** Average annual accumulation layers at P39 station in the Bornholm Basin.

of the Vistula river which transports large amounts of organic and inorganic particles causing an increase of the sedimentation.

In Table 4 there are presented the average AAL and SAR estimated by means of two 210Pb models and by the 239,240Pu and 137Cs models. The latter artificial isotopes are used as time markers for validation of the  $210Pb$ models. However, the validation was possible only for four locations, situated in the Basin of Gdańsk. In the Bornholm Basin the patterns of the <sup>239,240</sup>Pu and <sup>137</sup>Cs distribution profiles were broad and their peaks were not clear enough to be used as reliable time markers. In Table 4 there is also given the age of the 5 cm layers of sediments.

AAL estimation by means of the CF:CS model was performed for the 5 cm and 10 cm layers in all locations, while estimation by the CRS model for the 5 cm and 10 cm layers was made only for P110 and P116. At the other locations, such calculation was limited to 5 cm layer. The peak of 137Cs was always observed in the 5 cm layer, whereas the peak of  $239,240$ Pu was usually observed at the depth of 7–9 cm.

Table 4 shows that the results obtained with the models used can differ by up to 60 percent. Typically, values of AAL obtained with the CRS,  $^{239,240}$ Pu and  $^{137}Cs$ models are by 20% to 30% lower than those obtained with the CF:CS model. SAR estimated by <sup>239,240</sup>Pu were about 40% lower or about 50% higher than those esti-



**Fig. 6.** Average annual accumulation layers at P5 station in the Bornholm Deep.



 $\overline{r}$ 



mated by the CF:CS model. Usually, the <sup>137</sup>Cs models gave lower values of SAR in comparison to the CF:CS model. This indicates that most reliable would be the values of the mean from different models.

Dating of the bottom sediments were estimated applying the CRS model. The rate of growth of the sediments strongly differs in the locations studied (Table 4). The fasters growth occurred in the Gulf of Gdańsk, where the growth of 5 cm layer takes 27–37 years. Evidently, it is associated with the close distance to the mouth of the Vistula river, which transports organic and inorganic material. The 5 cm depth layers in P1 and P140 grow for 69 and 71 years. In the Bornholm Basin, the process of growing takes 61 years in the sampling station P39, and about 105 years in P5.

# **Conclusions**

Activity concentrations of 210Pb differed in the studied locations of sampling stations, being the highest in the Gulf of Gdańsk and the lowest in the Bornholm Basin. Sedimentation rates (SAR and AAL) calculated from the vertical distribution of unsupported 210Pb differ in subregions. In the Gulf of Gdańsk they are higher than those in the open sea what can result from the transport of organic and inorganic particles with the Vistula river water.

AAL and SAR estimated by the means of the CF:CS model were on average about 20% higher than those from the CRS model. This small difference indicates that both the models are comparable. Validation of the models based on unsupported <sup>210</sup>Pb using of <sup>239,240</sup>Pu and  $137Cs$  time markers confirm reliability of the estimated SAR and AAL values. It is suggested that the mean value from all the applied models should be taken for the estimation of dating and of sedimentation rate.

The results of this study indicate that the process of the formation of bottom sediments in the open sea is much slower than that in the gulf areas. In the Gulf of Gdańsk the 5 cm layers of the sediments were formed during 27 to 37 years, while in the open sea it took from 61 to 105 years.

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