

Radium-226 in water and sediments of the southern Baltic Sea*

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Radium
Sea-water
Sediments

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Abstract

Distribution of radium-226 in the southern Baltic was investigated. Surface and near-bottom sea-water samples as well as sediment samples were collected at 22 stations in July 1981. Radium-226 was determined by the emanation method. The average radium-226 activity in the southern Baltic waters was $1.8 \text{ mBq} \cdot \text{dm}^{-3}$ ($0.5 \cdot 10^{-13} \text{ g} \cdot \text{dm}^{-3}$); activity in sediments was more differentiated and ranged from 3.6 to $47 \text{ mBq} \cdot \text{g}^{-1}$ of dry matter (1 to $13 \cdot 10^{-13} \text{ g} \cdot \text{g}^{-1}$), depending on the kind of sediment. A highly significant positive correlation between salinity and radium content, both in bottom waters and in sediments was found.

1. Introduction

Radium in the marine environment was the subject of a number of publications, but still there is a need for information on the marine biogeochemistry of this element. The papers have dealt mainly with ^{226}Ra , the isotope of the longest half-life. Besides, the majority of the studies was performed in the ocean environment and not in the sea environment (GEOSECS Program, 1973–1979; Kowalewska, 1984). As far as the Baltic is concerned, only scarce information about ^{226}Ra distribution is available (Koczy, Tomic, Hecht, 1957).

This work presents the results of analysis of ^{226}Ra content in water and sediment samples collected in the southern Baltic. During the cruise the *in situ* measurements of salinity, temperature and oxygen content were carried out simultaneously with the sample collection.

The sediment analysis included also determination of organic carbon, iron, manganese, barium and opaline-silica, macro- and microscopic description as well as grain-size analysis of the samples.

* The investigations were carried out under the research programme MR.I.15, coordinated by the Institute of Oceanology of the Polish Academy of Sciences.

2. Experimental

2.1. Sampling

Samples were collected in July 1981 during the cruise of r/v 'Profesor Siedlecki' (location of sampling stations—see map in Fig. 1).

20 dm³ surface and near-bottom (~2 m above bottom) water samples were collected in acid-rinsed and then equilibrated with sea-water polyethylene containers.

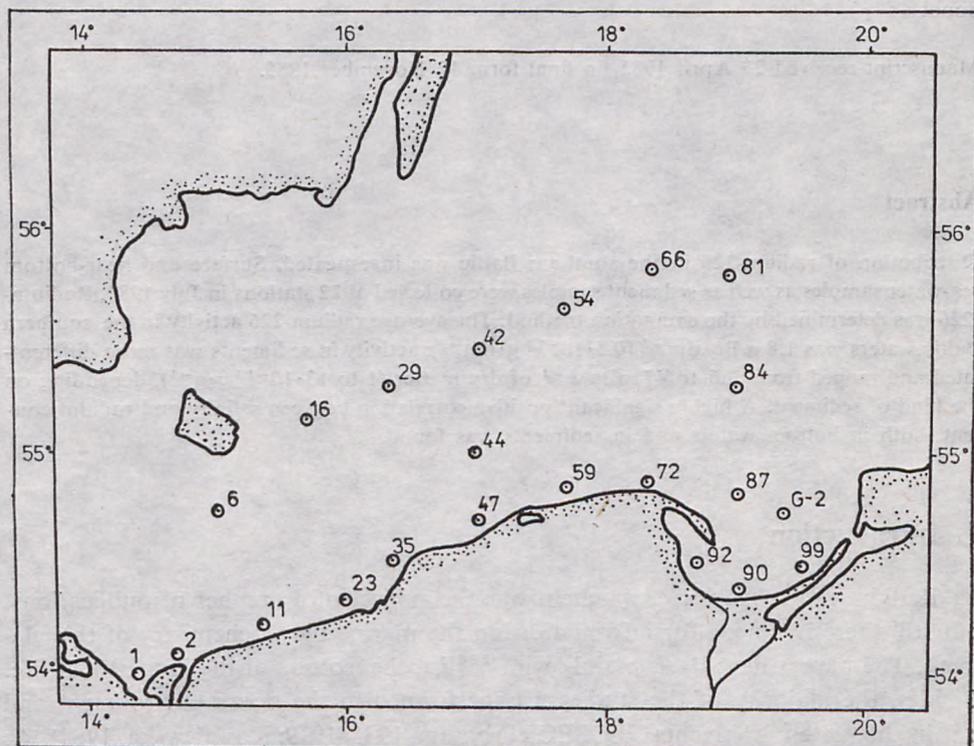


Fig. 1. Location of sampling stations

Water was filtered aboard within twelve hours since sampling, through a Whatman GF/C glass-fibre filter which, as it had been tested, did not contain or sorb from a sea-water sample measurable amounts of radium. The filtered samples were acidified to pH=2 with concentrated HNO₃ and stored in polyethylene containers until further analysis.

Sediment samples were collected from the top 5 cm layer of the material, taken by a grab sampler, in polyethylene bottles and stored at 4°C.

2.2. Apparatus

^{226}Ra activity was determined by the emanation method, using the apparatus constructed in the Institute of Oceanology (scheme—see Fig. 2). Glass bubblers and scintillation cells were similar to those used in the Central Laboratory for Radiological Protection.

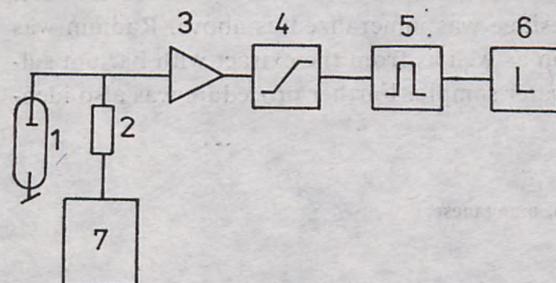


Fig. 2. Scheme of measuring apparatus

1—photomultiplier, 2—resistance, 3—amplifier, 4—discriminator and modulation, 5—system start-stop, 6—counter, 7—high voltage generator

Atomic absorption spectrometry measurements were carried out using an instrumental laboratory spectrometer, Type 151.

A Sartorius balance Type 4610 was used for the grain-size analysis of sediments.

2.3. Procedures

2.3.1. ^{226}Ra determination in water

Radium from water samples was isolated by coprecipitation with aluminium phosphate, with an addition of Pb (II) carrier (Koide, Bruland, 1975). The gelatinous precipitate was dissolved in concentrated HNO_3 and radium was reprecipitated with barium sulphate. Next, barium sulphate was dissolved in the hot alkaline (0.1 M) solution of EDTA disodium salt to the final volume of 25 cm^3 . The yield of radium precipitation was determined in every sample by atomic absorption spectrometry measurement of Pb (II) and Ba carrier recovery, first in the acid HNO_3 solution, second one in the alkaline EDTA solution. Then the sample was transferred into a bubbler and de-emanated with argon. The tightly closed bubbler was stored for at least ten days. After this time ^{226}Ra formed in the bubbler was de-emanated with argon into the scintillation cell and activity of the sample was determined.

The mean analytical error of the method was $\pm 10\%$.

2.3.2. Ra-226 determination in sediments

A sediment sample (1+4 g) dried at 110°C and homogenized in the agate mortar was mineralized in the platinum crucible with the use of concentrated acids (3·10 ml 40% HF, after each portion 1 cm³ HClO₄, heated to the white fumes, at the end 3·1 cm³ HClO₄). The final product of mineralization was dissolved in 2 cm³ of concentrated HCl and diluted with redistilled water to 100 cm³. Four sediment samples were extracted before mineralization with 8 M HNO₃ on a water bath for 8 hours. After separation of the extract, the residue was mineralized as above. Radium was precipitated from the obtained solution as well as from the extract with barium sulphate, similarly as in the case of sea-water sample. Further procedure was also identical.

2.3.3. Determination of organic carbon, iron, manganese, barium, and opaline-silica (in sediments)

Organic carbon was determined by the chromic acid titration method (Goudette *et al.*, 1974). The error of the method is estimated at ±3% (Forstner, Wittman, 1981).

To determine the iron, manganese, and barium level the samples were mineralized according to the same procedure as in radium analysis. Then, the obtained solution was tested by atomic absorption spectrometry method.

The determination of opaline-silica was as follows: a sample (0.2–0.4 g) dried at 110°C was gently heated with the addition of 25 cm³ of water and 4 cm³ of 5% potassium persulphate alkaline solution, in a platinum crucible on a sand bath. Silicate was determined by the standard spectrophotometric method (Grasshoff, 1976) based on formation of the yellow silicomolybdic acid, reduced to the blue complex with ascorbic acid.

2.3.4. Grain-size analysis

An organic matter in a wet sediment sample was destroyed by an addition of H₂O₂. After total destruction of the organic matter, the sample was dried at 60°C. The dried sediment sample was washed with distilled water through a sieve of 0.063 mm. The fraction of grain size smaller than 0.063 mm was dried again at the same temperature and 0.5 g of the sediment was taken for sedimental analysis using a sedimentation balance.

3. Results and discussion

The results of water analysis are given in Table 1. The concentration level of radium in surface waters was rather constant, lower concentrations were only the Odra and the Vistula estuaries. This might be caused by the lower concentration near in river than in sea-water (Grzybowska *et al.*, 1983), *eg* stations 1 and 90. The

Table 1. Ra-226 content in water samples

Station	Depth of sample collection [m]	²²⁶ Ra	
		mBq·dm ⁻³	·10 ⁻¹³ g·dm ⁻³
1	0	1.2	0.35
	9	1.3	0.35
2	0	1.1	0.30
	10	1.3	0.37
6	0	1.9	0.52
	54	1.9	0.53
11	0	1.9	0.52
	13	1.9	0.53
16	0	2.2	0.60
	93	4.5	1.24
23	0	1.9	0.52
	13	1.7	0.48
29	0	1.6	0.45
	64	2.2	0.60
35	0	1.5	0.41
	15	2.0	0.55
42	0	2.1	0.58
	37	2.3	0.62
44	0	1.9	0.52
	58	2.0	0.55
47	0	1.7	0.46
	17	2.0	0.54
54	0	1.5	0.42
	54	1.7	0.47
59	0	1.8	0.49
	15	1.9	0.52
66	0	1.5	0.41
	92	2.2	0.60
72	0	1.5	0.43
	17	1.9	0.52
81	0	2.0	0.56
	90	2.0	0.55
84	0	2.0	0.54
	83	2.0	0.55
87	0	1.9	0.51
	100	2.3	0.62
90	0	1.5	0.40
	19	1.9	0.53
92	0	1.2	0.34
	12	1.9	0.53
99	0	1.5	0.42
	60	2.3	0.62
G-2	0	1.7	0.47
	107	2.8	0.77

Table 2. Supplementary data for a sea-water analysis

Station	Salinity [%]		Temperature [°C]		Oxygen content [% of saturation]		Plankton* [g·m ⁻²]
	surface water	bottom water	surface water	bottom water	surface water	bottom water	
1	6.953	7.401	17.47	14.95	105.86	35.58	—
2	7.517	7.598	15.81	14.85	90.07	81.16	5.65
6	7.813	9.321	16.55	3.43	110.95	59.01	3.45
11	7.877	8.014	13.22	10.57	96.64	87.51	0.33
16	7.835	15.621	16.53	5.86	112.45	1.26	0.0
23	7.762	8.018	15.66	8.87	107.43	78.03	0.10
29	7.853	13.146	15.59	5.37	109.14	14.26	0.0
35	7.773	7.773	15.12	15.11	102.18	101.84	0.0
42	7.785	7.938	14.86	5.53	106.36	79.31	0.0
44	7.976	8.223	15.25	3.27	109.20	79.08	0.0
47	7.822	7.814	16.28	16.25	102.34	101.66	3.47
54	7.722	7.950	14.93	4.38	105.69	78.10	0.0
59	7.784	7.792	16.98	16.58	103.72	96.36	0.0
66	7.793	10.862	15.27	4.62	108.59	9.94	0.0
72	7.865	7.856	16.26	16.04	100.86	99.21	0.0
81	7.772	10.491	14.57	4.37	104.76	11.39	0.0
84	7.797	10.359	15.14	4.30	108.00	12.76	0.0
87	7.589	11.631	15.74	5.04	107.13	3.97	0.06
90	4.931	7.552	17.57	14.60	113.98	59.65	0.0
92	7.338	7.368	16.97	16.25	117.50	95.69	0.30
99	7.153	7.147	17.06	3.67	115.08	73.45	0.75
G-2	7.702	11.693	15.64	5.10	108.70	1.68	0.0

* Plankton determined in surface water, includes phytoplankton: *Bacilliarophyta* and *Radiolaria* (Borysiak, Ringer, 1982).

Table 3. Ra-226 content in sediment samples

Sta- tion	Ra-226		Sta- tion	Ra-226	
	mBq·g ⁻¹ · 10 ⁻¹³ g·g ⁻¹ of dry matter	of dry matter		mBq·g ⁻¹ · 10 ⁻¹³ g·g ⁻¹ of dry matter	of dry matter
1	3.8	1.06	54	17.1	4.72
2	5.1	1.40	59	5.1	1.41
6	17.4	4.79	66	44.9	12.37
11	5.0	1.39	72	3.1	0.86
16	46.5	12.82	84	11.5	3.18
23	11.3	3.12	87	36.8	10.16
29	31.8	8.76	90	13.5	3.71
35	7.6	2.09	92	6.8	1.88
42	5.1	1.42	99	31.0	8.56
44	13.4	3.70	G-2	30.2	8.34
47	4.5	1.24			

Table 4. Characteristics of sediment samples

Station	Macroscopic description of material taken by sampler	Microscopically determined predominant grain size fraction*	% C _{org}
1	fine sand, top layer-mud	sand	—
2	sand + black mud	silty sand	—
6	black ooze + sand	silty sand	0.63
11	fine sand	sand	—
16	grey-bluish mud	clay	4.48
23	sand + gravel	sand/gravel	—
29	red clay, sand, gravel, concretions	clay	0.40
35	fine sand, gravel, stones	silty sand	—
42	fine sand	sand	—
44	sand, top layer-grey mud	silt	0.77
47	fine sand	sand	—
54	sand, gravel, clay, concretions	sand/gravel	0.34
59	fine sand + detritus	sand/silt	0.10
66	top layer — black ooze, bottom — clay, H ₂ S	silt/silty sand	0.80
77	sand of various grain size	sand	—
84	mud	silt	1.14
87	black mud, H ₂ S	silt/clay	4.86
90	black-olive green mud + sand	silty sand	1.01
92	sand + mud	sand/silt	—
99	black-grey mud	clay	3.67
G-2	top layer — black mud, bottom — clay	clay	5.19

* sand — > 63 μ m; silt — 2–63 μ m; clay — < 2 μ m

Table 5. Grain-size analysis of sediment samples

Station	Weight % of fraction						
	0.063	0.031	0.016	0.01	0.008	0.004	< 0.004
6	62.19	20.36	4.74	2.15	1.46	2.48	6.62
16	4.40	9.70	3.49	4.87	3.63	15.06	58.85
66	46.75	11.34	5.06	3.83	2.26	6.84	23.92
90	76.88	6.51	2.78	0.92	0.94	1.75	10.22
99	1.10	13.75	13.10	8.11	4.65	9.94	49.35
G-2	1.64	4.03	2.21	3.64	3.84	10.48	74.16

additional cause of this decrease might be the absorption of radium by plankton species occurring in the area. As shows Table 2, phytoplankton species of the classes *Bacilliarophyta* and *Radiolaria* occurred mainly just near the Odra estuary as well as in the Gulf of Gdańsk (stations 2, 92, 99) and the fact of fixation of radium by the hard parts of plankton is well known in literature (Bishop *et al.*, 1977). At some stations the concentration of ²²⁶Ra in bottom waters was distinctly greater than the surface concentration, *eg* near the Bornholm Deep (station 16), in the Gulf Gdańsk (stations G-2, 87, 99). The difference was also visible in the values of mean concentration, which was lower in surface water (1.7 mBq·dm⁻³) than in bottom

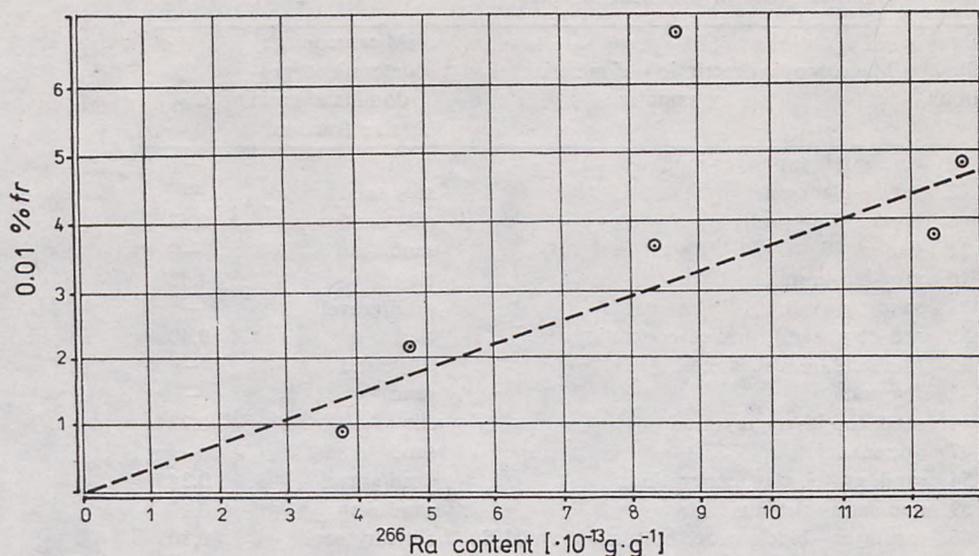


Fig. 3. Grain-size analysis; Ra-226 in sediments *vs* % of 0.01 mm fraction content

waters ($2.2 \text{ mBq} \cdot \text{dm}^{-3}$). The respective values for off-shore waters were greater (1.8 and $2.4 \text{ mBq} \cdot \text{dm}^{-3}$) than for near-shore waters (1.5 and $1.8 \text{ mBq} \cdot \text{dm}^{-3}$).

The radium concentration in sediments (Table 3) was more differentiated than that in water and depended on the kind of sediment. Table 4 shows the general characteristics of the type of sediment, *ie* macroscopic and organic carbon determination.

Table 6. Ra-226 content in the extracted sediment samples

Station	Sample*	Ra-226 [$\cdot 10^{-13} \text{ g} \cdot \text{g}^{-1}$]	$\frac{\text{Ra}(1)}{\text{Ra}(2)} \cdot 100\%*$
59	1	0.22	18
	2	1.19	
66	1	3.02	32
	2	9.35	
90	1	0.94	34
	2	2.77	
99	1	2.19	34
	2	6.37	

* 1—extracted with 8 M HNO_3 ; 2—mineralized residue

Only pure sandy sediments were not the subject of organic carbon analysis. Besides, six samples of sediments were taken for the grain-size analysis with the use of sedimentation balance (Table 5).

As it had been expected, the sandy sediments contained much less radium than the muddy ones. Radium content in sands was at almost constant level of $5 \text{ mBq} \cdot \text{g}^{-1}$ of dry matter. The samples containing considerable admixture of other than quartz

mineral grains or concretions had higher radium content, *eg* sediments from the stations 23 and 35, but probably the finer fractions are responsible for radium fixation, as it was found that the higher per cent of the fine grains the higher ^{226}Ra content; this relation, however, was not strong. The most visible is the correlation with the weight per cent of 0.01 mm fraction (Fig. 3). The amount of radium which

Table 7. Iron, manganese, barium and opaline-silica contents in sediment samples

Station	Fe [% wt]	Mn [% wt]	Ba [mg·g ⁻¹]	Si [mg·g ⁻¹]
6	1.6	0.019	0.7	2.8
16	4.7	0.098	0.6	10.9
23	0.8	0.021	0.4	—
29	3.6	0.092	1.5	3.3
44	1.3	0.019	0.4	4.6
54	0.9	0.027	0.7	3.7
59	0.5	0.023	0.4	0.5
66	3.1	0.044	0.6	3.3
84	2.2	0.027	0.3	9.0
87	4.1	0.045	0.5	22.4
90	1.3	0.018	0.5	3.8
99	3.7	0.032	0.8	9.9
G-2	5.2	0.079	0.7	15.1

Table 8. Correlation of Ra-226 concentration in sediments with salinity, temperature and content of other elements

Correlation of ^{226}Ra in sediments with		Correlation coefficient (<i>r</i>)	Significance level (<i>P</i>)
Of bottom water	salinity [%]	0.83	0.001
	t [°C]	-0.65	0.01
	O ₂ [%]	-0.77	0.001
	% Fe	0.84	0.005
	% Mn	0.73	0.025
	% C _{org}	0.62	≤ 0.1
	Si	0.47	< 0.1
	% C _{org} , Si	0.66	< 0.1

could be extracted by 8 M HNO₃, *ie* the amount proportional to the adsorbed radium quantity was lower for the sandy sediment than for the muddy sediments (Table 6).

The chemical analysis for iron, manganese and barium content, *ie* the elements which geochemistry is known to correlate with geochemistry of radium, was carried out for all the sediments containing considerable fine-grain fractions (Table 7). In these samples opaline-silica was also determined to examine the extent of radium removal by diatoms from sea-water to sediments.

To check whether there was a relationship between the radium concentration in sediments and all the determined quantities, the data were subjected to the linear correlation analysis. Table 8 presents these cases in which the correlation was pro-

bable. It was highly possible that there was correlation between the iron and radium contents ($r=0.83$ at the 0.001 significance level), more probable than with the manganese content. Correlation with organic carbon and silica was not so evident. There was no observable correlation with barium content.

For comparison with the present results the concentrations of ^{226}Ra determined for the northwest Atlantic (Broecker *et al.*, 1976) and the Baltic waters (Koczy *et al.*, 1957) are given in Table 9. In the water samples collected in 1953 at five stations, ^{226}Ra concentration was of the same order of magnitude as the values obtained in the present study. Koczy *et al.* found the surface concentrations lower than the near-bottom ones (with the exception of the Gotland Deep). The authors attributed this increase of activity with depth to that the source of ^{226}Ra for Baltic water was

Table 9. Literature data—Ra-226 concentration in sea-water

Sea	Depth	Ra-226 [$\cdot 10^{-13}$ $\text{g} \cdot \text{dm}^{-3}$]
Northwest Atlantic Ocean*	Surface Waters	0.4
	Bottom waters	0.8
Baltic Sea**:		
N 59°46, E 19°47	5 m	0.12
	100 m	0.46
N 59°24, E 21°36	5 m	0.52
	Landsort Deep	0.20
Gotland Deep	45 m	0.20
	445 m	0.47
Hälsingborg	40 m	0.60
	220 m	0.28
Hälsingborg	5 m	0.12
	27 m	0.45

* After Broecker, 1976;

** after Koczy *et al.*, 1957

Table 10. Correlation analyses of the data for water samples

Correlation of	Correlation coefficient (r)	Significance level (P)
^{226}Ra in		
surface water		
with: salinity [%]	0.39	<0.1
t[°C]	-0.42	<0.1
diatoms	-0.50	0.1
^{226}Ra in		
bottom water		
with: salinity [%]	0.79	0.001
t[°C]	-0.36	<0.1
O ₂ [%]	-0.47	0.1
Ra-226 sed.	0.68	0.025

^{230}Th from sediments. Such interpretation of the observed vertical concentration gradient was next generally accepted in the marine geochemistry of radium.

In the present work the correlation coefficient between the radium concentration in bottom waters and in sediments was 0.68 at the 0.025 significance level (Table 10). It suggested a relationship between these two quantities. However, more probable was a correlation between salinity and radium content both in bottom waters and in sediments (Tables 8, 10). The correlation coefficients were 0.79 and 0.83, respectively, both significant at the 0.001 level.

The above correlation with salinity suggests that, apart from the other sources, the water exchange between the North Sea and the Baltic had a decisive influence on ^{226}Ra concentration level in the Baltic waters. It also seems that radium is precipitated from water to sediments mainly with iron compounds.

No correlation was found between salinity of surface waters and the radium concentration.

4. Conclusions

(i) The average activity of ^{226}Ra in the southern Baltic waters was $1.8 \text{ mBq} \cdot \text{dm}^{-3}$ ($0.5 \cdot 10^{-13} \text{ g} \cdot \text{dm}^{-3}$); ^{226}Ra activity in sediments was more differentiated and ranged from 3.6 to $47 \text{ mBq} \cdot \text{g}^{-1}$ (1 to $13 \cdot 10^{-13} \text{ g} \cdot \text{g}^{-1}$) of dry matter, depending on the kind of sediment.

(ii) ^{226}Ra content in surface waters was uniform (about $1.7 \text{ mBq} \cdot \text{dm}^{-3} = 0.46 \cdot 10^{-13} \text{ g} \cdot \text{dm}^{-3}$) and lower than in bottom waters ($2.2 \text{ mBq} \cdot \text{dm}^{-3} = 0.60 \cdot 10^{-13} \text{ g} \cdot \text{dm}^{-3}$).

(iii) There was a highly significant positive correlation between salinity and radium content, both in bottom waters and in sediments, so one may conclude that the water exchange between the North Sea and the Baltic had a decisive influence on ^{226}Ra concentration in the Baltic waters.

(iv) A highly significant positive correlation between iron and radium contents in sediment samples indicated that radium was precipitated from sea-water to sediments mainly with iron compounds.

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