

# Dissolved and suspended forms of caesium-137 in marine and riverine environments of the southern Baltic ecosystem

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**Abstract** Dissolved and particulate activities of caesium-137 are presented for the coastal and open southern Baltic Sea waters, fluvial waters (the Vistula and Świna rivers) and lagoon waters (the Vistula Lagoon) during 1996–1999 and compared to those collected before the Chernobyl accident.  $^{137}\text{Cs}$  was measured in the Baltic Sea waters at different depths as well as 0.2–0.3 m above the sea bed. In a layer of the Gdańsk Bay waters (the Gdańsk Deep location), extending from the surface down to 1–2 meters above the sea bed, the caesium-137 concentrations ranged between 57 and 66  $\text{Bq m}^{-3}$  in 1999, whereas in the layer situated 0.2–0.3 m above the sea bed its concentration increased up to 87  $\text{Bq m}^{-3}$ . This phenomenon was also observed in 1994 and 1998. The concentrations of caesium-137 in riverine suspended particulate matter (r SPM) are lower than in the marine SMP (m SMP) and its activity attains respectively 36 and 222  $\text{Bq kg}^{-1}$  based on dry weight. The proportion of caesium-137 in the suspended form in the Baltic Sea waters does not exceed 2 per cent, while in the fluvial suspended form it is as high as 55 per cent.

**Key words** Baltic waters • dissolved form • fluvial waters • radiocaesium • suspended form

## Introduction

Recent pollution level with caesium-137 in the Baltic Sea is dominated by atmospheric fallout, fluvial run-off and influx of oceanic waters from the North Sea. In addition, the North Sea waters are polluted with radioactive wastes released from nuclear fuel reprocessing plants in Sellafield (the United Kingdom) and La Hague (France) [4, 7]. The Chernobyl accident on April 26th, 1986 added to the atmosphere large amounts of radionuclides including the long-lived caesium-137. As much as 85 per cent of caesium-137 deposited in the Baltic Sea is of the Chernobyl origin. It is a predominant radionuclide responsible for the actual radioactive pollution level in the Baltic Sea waters [12].

Within the framework of the Helsinki Convention, the Baltic Sea waters have been monitored every year from the surface down to 1–2 meters above the sea bed for the contents of artificial radionuclides including caesium-137. However, this survey did not discriminate between dissolved and suspended forms of caesium-137 in the sea water and did not account for such water regions as lagoons and rivers feeding the southern Baltic Sea.

Hence the objective of this work was to estimate the contribution of the suspended and dissolved forms of caesium-137 in the Baltic Sea waters, river water and lagoon water and to determine its concentrations in water layers adjacent to the bottom (0.2–0.3 m above the sea floor). Further, its concentrations in the Baltic Sea waters before and after the Chernobyl accident have been compared.

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Received: 10 September 2001, Accepted: 12 March 2002

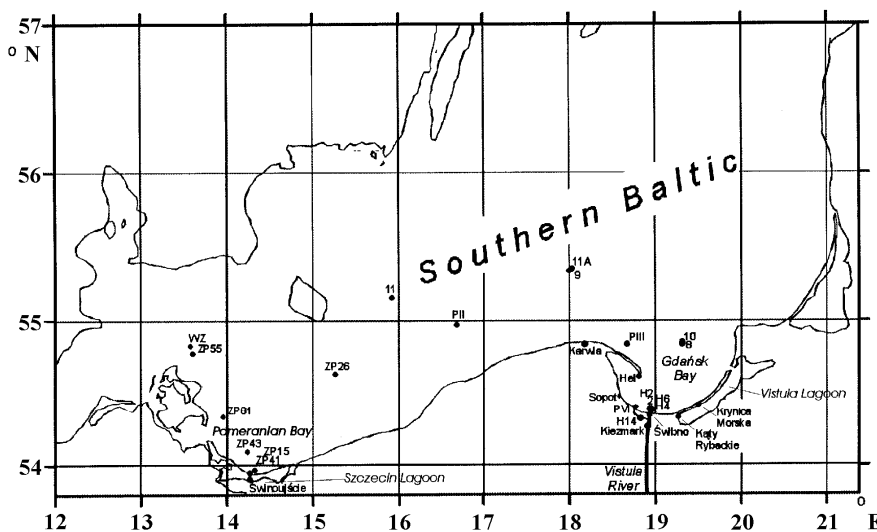


Fig. 1. Sampling stations in the southern Baltic Sea in 1996–1999.

## Materials and methods

Samples were collected during the cruises continued from 1996 through 1999 (Fig. 1). Water samples taken during 1996–1998 were filtered through Sartorius membrane filters (pore size 0.45  $\mu\text{m}$ ), while those sampled in 1999 were filtered through Whatman GF/F glass microfibre filters. The filters together with suspended matter were dried at 60°C, kept in a desiccator for 1 h and weighed. The filtrate was acidified to pH 1–2 and a 10 mg of a natural carrier of caesium was added. After equilibration (for approx. 20 min), 1.2 g of ammonium phospho(V)dodecamolybdate(VI) (AMP) was added and the content was stirred for 20 min. After 24 h the liquid was decanted and the precipitate was chromatographed on a Bio-Rex 40 ion-exchange resin [1]. Following separation of accompanying ions ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$ ), caesium was eluted with 3 M hydrochloric acid.

The caesium-containing solution was then evaporated to dryness, digested and dissolved in dilute hydrochloric acid. From this solution caesium was precipitated as chloroplatinate, its yield was determined gravimetrically [1] and the  $\beta$ -radiation was counted in an apparatus housing a low-background Geiger-Müller multiscouter (Risø, Denmark).

The suspended matter collected on the Sartorius and GF/F filters was transferred to Teflon evaporating dishes, 10 mg of the natural carrier of caesium was added and the sus-

pension was extracted twice with a hot 8 M nitric acid solution. The non-dissolved fraction was treated with 40% hydrofluoric acid in the presence of a fresh amount of the natural caesium carrier. The solvents from both fractions were evaporated, the residue was dissolved in dilute hydrochloric acid and radiocaesium was analyzed using standard radiochemical procedures [1] and beta counting. The accuracy of the method was assessed by replicate determinations of the certified reference material SD-N-1 (IAEA, Vienna), which had a certified concentration of  $^{137}\text{Cs}$  of 13.32  $\text{Bq kg}^{-1}$ . Six analyses of the standard gave a mean value of the  $^{137}\text{Cs}$  concentration of  $13.0 \pm 0.8 \text{ Bq kg}^{-1}$ .

## Results and discussion

The results are summarized in Tables 1–6. They show the dissolved and suspended caesium-137 concentrations in many water types, including coastal and open sea waters, fluvial waters (the Vistula, Dead Vistula and Świna rivers) and the lagoon waters (the Vistula Lagoon). To date, no reports on pollution of the Vistula Lagoon waters with caesium-137 have been available.

The caesium-137 activities in the Baltic Sea measured from the surface down to 1–2 m above the sea bed tend to decrease with time. For instance, in the Gdańsk Bay (the Gdańsk Deep location) its concentrations in 1998 ranged

Area/Station	Date of sampling	Coordinates	Sampling depth (m)	Salinity (PSU)	$^{137}\text{Cs}$ ( $\text{Bq m}^{-3} \pm 1\sigma^*$ )
Vistula river Mikoszewo Kieźmark	8.09.1996	54°20.4' 18°56.5' 54°15.5' 18°56.5'	0	0.47	1.6 $\pm$ 0.1
Vistula river Świnno	8.09.1996	54°20.4' 18°56.1'	0	0.50	1.5 $\pm$ 0.1
Vistula Lagoon Kąty Rybackie	8.09.1996	54°20.2' 19°13.6'	0	2.19	3.6 $\pm$ 0.1
Southern Baltic					
Karwia	5.10.1996	54°50.0' 18°11.2'	0	7.22	41 $\pm$ 1
Hel	16.05.1996	54°36.1' 18°49.0'	0	NM	86 $\pm$ 1
Sopot	21.02.1996	54°26.5' 18°34.2'	0	6.55	68 $\pm$ 1
Sopot	30.05.1996	54°26.5' 18°34.2'	0	NM	76 $\pm$ 1
Krynica Morska	10.05.1996	54°20.3' 19°27.0'	0	4.15	86 $\pm$ 1

Table 1. Activity concentrations of caesium-137 in the filtered surface sea water samples taken from the southern Baltic Sea and Vistula river in 1996.

NM – not measured.

\* – the error represents counting error only.

Area/Station	Depth (m)	Date of sampling	Coordinates	Sampling depth (m)	Salinity (PSU)	<sup>137</sup> Cs (Bq m <sup>-3</sup> ±1σ)
Świna river Świnoujście	10	10.08.1997	53°54.1' 14°16.2'	0	0.23	4.5±0.1
Pomeranian Bay (coast)						
ZP41	10	13.08.1997	53°56.6' 14°16.7'	0	3.45	31±1
ZP15	10	10.08.1997	53°57.6' 14°19.6'	0	4.85	48±1
ZP43	13	13.08.1997	54°05.3' 14°15.3'	0	6.03	60±1
Pomeranian Bay (open)						
ZP61	17	12.08.1997	54°19.2' 13°57.6'	0	4.46	83±1
WZ	47	12.08.1997	54°49.1' 13°34.8'	0	7.36	81±1
ZP26	61	11.08.1997	54°37.7' 15°16.0'	0	7.45	65±1
ZP55	47	12.08.1997	54°46.0' 13°36.8'	0	6.76	67±1
Southern Baltic						
PII	18	17.08.1997	54°58.0' 16°42.0'	0	NM	49±1
PIII	41	17.08.1997	54°50.0' 18°40.0'	0	6.37	73±1
Vistula river mouth						
PVI	17	18.08.1997	54°23.5' 18°48.0'	0	4.04	34±1

**Table 2.** Activity concentrations of caesium-137 in the filtered surface sea water samples taken from the southern Baltic Sea and Świna river in 1997.

NM – not measured.

from 55 to 76 Bq m<sup>-3</sup> (67±8 (SD) Bq m<sup>-3</sup> on average), whereas in 1999 they ranged from 57 to 66 Bq m<sup>-3</sup> (61±3 (SD) Bq m<sup>-3</sup> on average) (cf. Tables 3 and 4).

The Vistula waters are considerably less polluted with caesium-137 than the Baltic Sea waters (the Gdańsk Bay location), respective concentrations in 1999 being 0.8 and 61 Bq m<sup>-3</sup> (Table 4). The <sup>137</sup>Cs levels in Vistula waters declined rapidly from 25.8 Bq m<sup>-3</sup> in 1989 to 1.5 Bq m<sup>-3</sup> in 1995 [10, 11].

In seven Japanese rivers flowing far off industrial and municipal centres, the total <sup>137</sup>Cs levels during 1985–1987 were also low ranging between 0.063 and 1.89 Bq m<sup>-3</sup> [3].

Again, the waters of the Świna river, connecting the Pomeranian Bay with the Szczecin Lagoon are more polluted than the Vistula waters on account of the so-called backwater of sea waters, and the caesium-137 concentration in them is as high as 4.5 Bq m<sup>-3</sup> (Table 2). Similar <sup>137</sup>Cs levels (4.9–8.8 Bq m<sup>-3</sup>) were recorded in the 0–11 m column of the Szczecin Lagoon waters [12].

The caesium-137 activity in the Vistula Lagoon linked with the Baltic Sea through the Pilawa Straits attains a level of 3.6 Bq m<sup>-3</sup>, being one order of magnitude lower than that in the Baltic Sea waters (Table 1). The cleaning processes of caesium-137 occurring in the Baltic Sea

Area/Station	Depth (m)	Date of sampling	Coordinates	Sampling depth (m)	Salinity (PSU)	<sup>137</sup> Cs (Bq m <sup>-3</sup> ±1σ)
Dead Vistula river H14	6.1	10.09.1998	54°20.6' 18°49.4'	0	4.78	19±1
Vistula river+Vistula river mouth						
H4	3.7	10.09.1998	54°21.9' 18°57.0'	0		
H6	8.6	10.09.1998	54°21.9' 18°57.4'	0	0.52	1.3±0.1
Gdańsk Bay						
2	14.5	8.09.1998	54°22.6' 18°56.6'	0	NM	58±1
				13	NM	78±1
H2	14.5	10.09.1998	54°22.5' 18°57.9'	0	3.88	78±1
Southern Baltic						
8	109	9.09.1998	54°50.0' 19°19.5'	0	6.94	73±1
				30	6.89	76±1
				60	7.34	70±1
				75	9.48	72±1
				90	11.23	62±1
				107	11.77	55±1
				108	11.99	62±1
				108.5	11.99	62±1
				108.8	11.99	87±1
9	78	10.09.1998	55°20.0' 18°00.3'	0	7.04	75±1
				30	6.91	78±1
				50	7.17	81±1
				70	10.42	62±1
				73	11.85	61±1
				74	12.41	54±1
				75	12.51	53±1
				77.8	12.51	62±1
11	91.5	10.09.1998	55°09.1' 15°55.1'	91.3	NM	52±1

**Table 3.** Activity concentrations of caesium-137 in the filtered sea water samples taken from the southern Baltic Sea and Vistula river in 1998.

NM – not measured.

Area/Station	Depth (m)	Date of sampling	Coordinates	Sampling depth (m)	Salinity (PSU)	$^{137}\text{Cs}$ ( $\text{Bq m}^{-3} \pm 1\sigma$ )
Southern Baltic 10	112	20.05.1999	54°49.9' 19°19.6'	0	6.62	60±1
				30	7.15	66±1
				60	7.22	63±1
				75	8.93	66±1
				90	10.95	60±1
				110	11.58	61±1
				110.5	11.84	57±1
				111.0	11.84	59±1
				111.8	11.84	87±1
				11A	80.4	23.05.1999
Vistula river Kiezmark	0	10.10.1999	54°15.47' 18°56.5'	0	0.53	0.8±0.1

**Table 4.** Activity concentrations of caesium-137 in the filtered sea water samples taken from the southern Baltic Sea and Vistula river in 1999.

waters proceed slowly and they still show a several times higher levels of the radionuclide, relative to the period before the Chernobyl accident (cf. Tables 1–4 and 7) which took place 15 years ago, in spite of the fact that total exchange of the Baltic Sea waters occurs during 30 years.

The contribution of suspended forms of caesium-137 in the Baltic Sea waters is low, not exceeding 2 per cent. On the other hand, in the fluvial run-off its contribution is relatively high, attaining 55 per cent (Table 6). There is also a massive impact of the suspended form of  $^{137}\text{Cs}$  on the transport of the radionuclide in both the Japanese rivers (from 10 to 35 per cent) [3] and in the estuarine waters of the Weser river (Germany) [8].

Concentrations of caesium-137 in the fluvial suspended matter are distinctly lower than those in marine suspensions (Table 6) owing to the differences in the physicochemical and biological composition of the suspensions and in physico-

chemical differences between the fluvial and sea waters which affect the sorption of caesium-137 on the particles.

Also the enrichment factors (EF) of caesium-137 in the fluvial suspension/fluvial water system differ markedly from those of the marine suspension/Baltic Sea water system. They are much higher for the fluvial system (suspension/water amounting to  $123 \times 10^3$ , whereas with the marine system (suspension/water) they attain a value of merely  $4 \times 10^3$  (Table 6).

It has been found that the Baltic Sea waters overlying the sea bed (0.2 to 0.3 m above the bed) contain more caesium-137 than those in the layer extending from the surface down to 1–2 meters above the sea bed, attaining  $87 \text{ Bq m}^{-3}$  (Tables 3 and 4). When taking the samples, the oxic/anoxic status of the sediment was not measured, but it is well known that the Gdańsk Deep (Stations 8 and 10) have the status of anoxic sediment [13] and precautions were taken to minimize the loss of sample integrity.

Sampling site	Year of sampling	Volume of water ( $\text{dm}^3$ )	SPM (g)	$^{137}\text{Cs}$		SPM ( $\text{mg dm}^{-3}$ )
				( $\text{Bq m}^{-3} \pm 1\sigma$ )	( $\text{Bq kg}^{-1} \pm 1\sigma \text{ d.w.}$ )	
Vistula river Mikoszewo	1996	34.9	2.3408	0.7±0.1	10±1	67.1
Kiezmark	1996	pooled sample				
Świbno	1996	pooled sample				
Vistula river Kiezmark	1999	40.5	1.1406	1.0±0.1	36±1	28.2
Vistula river÷Vistula river mouth H4-H6	1998	86.0	0.2597	0.5±0.1	161±4	3.0
		pooled sample				
Świna river Świnoujście	1997	120.5	2.6683	0.7±0.1	30±1	22.1
Pomeranian Bay ZP61	1997	26.2	0.1480	1.3±0.1	211±5	5.6
WZ	1997	pooled sample				
Southern Baltic Sea 8	1998	66.3	0.7419	1.7±0.1	151±1	11.2
9	1998					
Sopot	1996					
Krynica Morska	1996					
Karwia	1996					
Southern Baltic Sea 10	1999	40.5	0.774	0.4±0.1	222±8	1.9
		pooled sample				

**Table 5.** Activity concentrations of caesium-137 in suspended particulate matter (SPM).

Sampling site	Year of sampling	Dissolved form (Bq m <sup>-3</sup> )	<sup>137</sup> Cs in suspended form			*EF
			(Bq m <sup>-3</sup> )	(%)	(Bq kg <sup>-1</sup> d.w.)	
Vistula river Mikoszewo	1996					
Kieźmark	1996	1.6	0.7	30	10	6000
Świbno	1996					
Vistula river Kieźmark	1999	0.8	1	55	36	45000
Vistula river+Vistula river mouth H4-H6	1998	1.3	0.5	27	161	123×10 <sup>3</sup>
Świna river Świnoujście	1997	4.5	0.7	13	30	7000
Pomeranian Bay ZP61	1997					
WZ	1997	82	1.3	1.6	211	3000
Southern Baltic Sea 8	1998					
9	1998					
Sopot	1996	67	1.7	2	151	2000
Krynica Morska	1996					
Karwia	1996					
Southern Baltic Sea 10	1999	61	0.4	0.6	222	4000

**Table 6.** Enrichment factor (EF), between sedimenting material and water, and percentage of suspended forms of caesium-137 (southern Baltic Sea, Vistula river, Świna river).

\*EF (enrichment factor) = concentration of the nuclide in suspended matter (mBq kg<sup>-1</sup> dry matter) divided by concentration of the nuclide in the water body (mBq dm<sup>-3</sup>).

Losses of radiocaesium could have taken place from the pore water to fresh iron oxide coating formed from the oxidation of Fe(II). An iron oxide film formed on the walls of some containers during storage, was removed, digested in nitric acid and counted. It was found that the iron oxide films ( $n=3$ ) contained less than 60 mBq of <sup>137</sup>Cs, negligible compared to about 45 Bq in the bulk sediment. Furthermore, the pore waters were filtered prior to the pre-concentration thereby removing most of the remnant particulate material. Thus, while losses of dissolved <sup>137</sup>Cs in pore waters cannot be entirely excluded, the values reported here represent lower limits [6]. Moreover, there is evidence in the literature that iron and manganese oxides are poor adsorbents of caesium-137 [6]. This phenomenon can be explained in terms of desorption processes of caesium-137 concentrated in bottom deposits rather than in terms of waters penetrating from the North Sea, which during recent

**Table 7.** Mean activity concentrations of caesium-137 and caesium-134 in the southern Baltic water during 1984–1998 (mBq dm<sup>-3</sup>) [4<sup>\*</sup>, 12].

	Year	<sup>137</sup> Cs	<sup>134</sup> Cs
Before the Chernobyl accident	1984	13.3 <sup>*</sup>	ND
	1985	12.6	ND
After the accident	1986	86	45
	1987	61	24
	1988	92	19
	1989	100	16
	1990	96	15
	1991	101	10
	1992	96	6
	1993	93	4
	1994	87	<2
	1995	79	<2
	1996	95	<2
1997	78	<2	
1998	67	<2	

ND – not detected.

years has been less polluted with caesium-137 than the Baltic Sea waters (Table 8).

Recognition of the nature of desorption processes of caesium-137 proceeding in the Baltic Sea needs more complex studies and merits attention as the final link of migration of caesium-137 in the Baltic Sea ecosystem are bottom deposits.

## Conclusions

- In the fluvial transport of caesium-137, the suspended form predominates constituting up to 55 per cent of the transported radionuclide;
- in the Baltic Sea waters, the contribution of the suspended form of caesium-137 is considerably lower than that in the fluvial water and does not exceed 2 per cent;
- concentrations of caesium-137 in the fluvial suspended matter are distinctly lower than those in marine suspensions;
- enrichment factors of caesium-137 in the fluvial suspension/fluvial water system are higher than for the marine suspension/Baltic Sea water system;
- caesium-137 activity gradient has developed at the sea water/bottom interface at Gdańsk Deep as a result of backward diffusion from soft sediments;

**Table 8.** Surface caesium-137 activity concentration (on 01-01-1990) in various ocean areas [9].

FAO region	Typical value <sup>137</sup> Cs (Bq m <sup>-3</sup> )
Baltic Sea	125
Black Sea	52
Irish Sea	55
Adriatic Sea	5.4
North Sea	12
Barents Sea	10

– concentrations of the dissolved form of caesium-137 in the Baltic Sea waters are still elevated relative to those recorded before the Chernobyl accident and actually place the Baltic Sea among the most polluted water areas in the World Ocean.

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