# Temporal and spatial changes of cadmium in the near-bottom suspended matter of the Pomeranian Bay – Arkona Deep system*

OCEANOLOGIA, 42 (4), 2000.
pp. 483–491.

**KEYWORDS**
Cadmium
Near-bottom suspended matter
Solid speciation
Pomeranian Bay

Andrzej Staniszewski[1]
Ksenia Pazdro[1]
Jacek Bełdowski[1]
Thomas Leipe[2]
Kay-Christian Emeis[2]
Janusz Pempkowiak[1]

[1] Institute of Oceanology,
Polish Academy of Sciences,
Powstańców Warszawy 55, PL–81–712 Sopot, Poland;
e-mail: pempa@iopan.gda.pl

[2] Baltic Sea Research Institute,
Seestrasse 15, 18119 Rostock–Warnemünde, Germany

Manuscript received 17 August 2000, reviewed 29 September 2000, accepted 3 November 2000.

## Abstract

Owing to the high toxicity of cadmium (Cd) towards biota and the considerable quantities of this element entering the environment from anthropogenic sources, interest in its biogeochemistry is increasing. This is also true for the marine environment, which serves as a sink for both natural and anthropogenic Cd loads entering the hydrosphere and the atmosphere. The distribution of Cd in the coastal zone of the marine environment is governed primarily by the flux of

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* The work was carried out as part of the Baltic Sea System Study (BASYS 3a). Results were presented at the 3rd Conference on Trace Metals. Effects on Organisms and Environment. Sopot, 6–8 June 2000.

the so-called fluffy layer suspended matter (FLSM), which spreads across the top of the sea floor as a several-centimetre-thick layer containing highly concentrated suspended matter.

Both total contents and solid speciation of Cd was measured in FLSM collected in the Pomeranian Bay – Arkona Deep system (Western Baltic Proper) in the course of the three-year-long study.

Seasonal changes in the total Cd content (0.5–1.8 $\mu g\ g^{-1}$ dry matter) were attributed to the contribution of organic suspensions originating from algal blooms. The decreasing content of Cd in FLSM offshore is due to the input of Cd-rich suspended matter from the River Odra (Oder), and the decreasing organic matter content in FLSM with increasing depth. The contribution of labile fractions (adsorbed and bound to iron(III) hydroxides) was found to be from 50 to 75% of the total content. In view of the substantial mobility and bioavailability of the fractions, this is a highly alarming feature.

## 1. Introduction

Human activities have caused increasing amounts of heavy metals to be introduced to the environment. Indeed, the quantities of particular metals originating from anthropogenic sources exceed those from the natural ones. One such metal is cadmium (Cd) (Kabata-Pendias & Pendias 1993). Once it has been introduced to the environment, it persists there indefinitely, its concentrations being governed by migration and accumulation processes (Salomons & Förstner 1981). Like other heavy metals, Cd is readily incorporated into the food chain and, owing to its low toxicity threshold, poses a serious threat to human beings (Salomons & Förstner 1981). Contents of Cd in the coastal zone depend on a variety of natural and anthropogenic factors. Separating the most important ones is no mean task, since this zone, especially estuaries, is a biologically, physically and chemically highly dynamic one (Pempkowiak 1997).

In the coastal zone, the most important factor causing Cd to be transported from shallow, highly dynamic river mouths to deeper, less dynamic regions of sedimentation is suspended matter spreading just above the sea bed (Emeis *et al.* in press). Evaluation of the magnitude of this transport requires such factors as the geography of the river mouth, sedimentation rate of suspended matter, resuspension conditions and accumulation by organisms to be taken into consideration.

One of the most important factors influencing Cd concentrations in suspended matter is organic matter. As a result of changes in primary productivity, one should expect seasonal variations in the Cd content of suspended matter both from the bulk water and near-bottom water. Research into the factors affecting Cd migration needs to focus on a well researched system with a clearly defined source of metals (a river mouth) and water masses of known dynamics. The River Odra – Pomeranian Bay – Arkona Deep system fulfils these criteria (Poleszczuk *et al.* 1993, Nauman *et al.* 1996, Pohl *et al.* 1998, Beszczyńska-Möller 1999, Emeis *et al.* in press).

In this paper Cd concentrations in the near-bottom suspended matter (fluffy layer suspended matter – FLSM) of the Pomeranian Bay – Arkona Deep System are discussed. The pattern of concentration was attributed to seasonal and geographic factors.

## 2. Materials and methods

Samples of FLSM were collected by a scuba-diver-operated pump system from the sampling station shown in Fig. 1 on the dates given in Table 1.

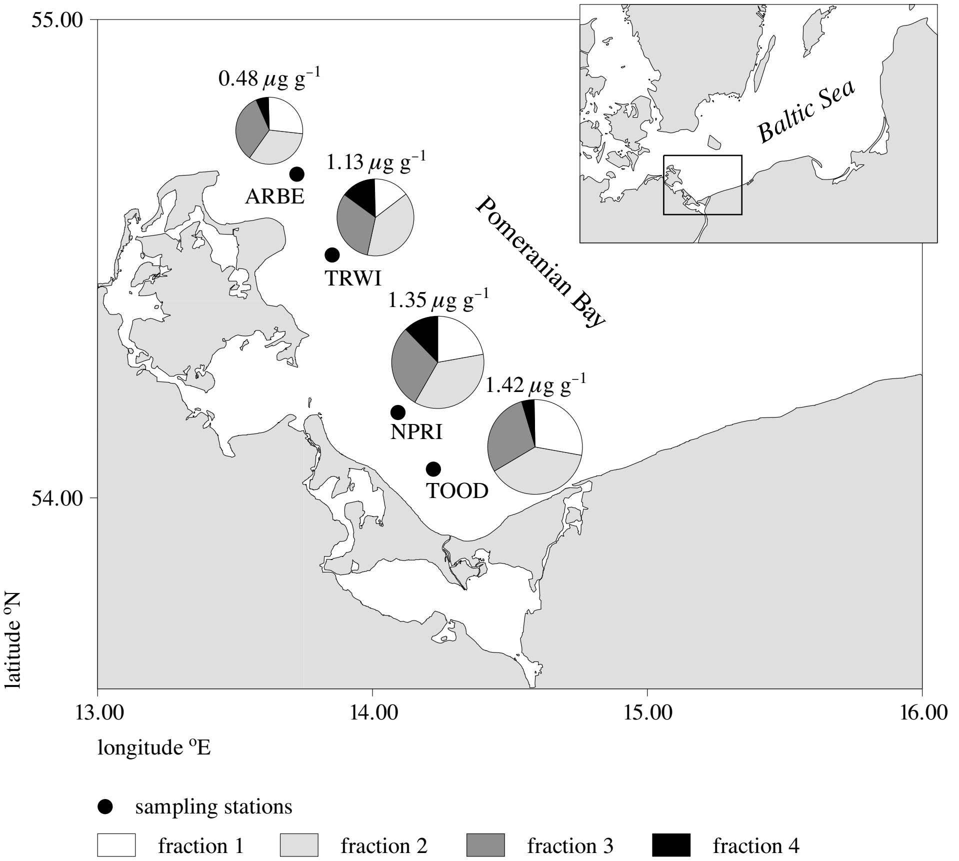

**Fig. 1.** Locations of sampling stations (the diameter of the circle is proportional to the cadmium concentration; the shaded areas of the circle represent the percentage of a given fraction in the total concentration)

**Table 1.** Average cadmium concentrations in fluffy layer suspended matter collected during the cruises

| Sampling date | Average concentration ± SD* [$\mu$g Cd g$^{-1}$] | Lowest concentration [$\mu$g Cd g$^{-1}$] | Highest concentration [$\mu$g Cd g$^{-1}$] |
|---|---|---|---|
| October 1996 | 1.37 ± 0.58 | 0.24 | 1.75 |
| March 1997 | 1.27 ± 0.47 | 0.67 | 1.84 |
| June 1997 | 0.74 ± 0.48 | 0.27 | 1.34 |
| August 1997 | 1.87 ± 0.87 | 0.72 | 2.78 |
| October 1997 | 1.21 ± 0.63 | 0.60 | 2.35 |
| June 1998 | 1.86 ± 0.83 | 1.21 | 2.79 |
| December 1998 | 0.48 ± 0.18 | 0.22 | 0.61 |

* SD – standard deviation.

These samples were transferred to Petri dishes and kept deep-frozen for laboratory analysis. This comprised the following steps: freeze-drying, homogenisation, loss on ignition (a 200 mg subsample was ignited at 450°C for 4 hours), solid speciation of Cd (4-step sequential extraction and digestion of samples).

The sequential extraction of samples was carried out according to the procedure depicted in Fig. 2. Four Cd fractions were measured according to a modified procedure (Pempkowiak *et al.* 1999) originally developed by Salomons & Förstner (1981). The fractions were denoted as fraction 1 – Cd ions adsorbed on suspended matter, fraction 2 – Cd ions bound to hydroxides of iron(III) and manganese(IV), fraction 3 – Cd ions bound to organic matter, and fraction 4 – Cd ions incorporated into the lattice of clay minerals (residual fraction). A subsample of the total mass of 1000 mg dry matter was extracted with the following aqueous solutions (15 cm$^3$ each): A – 0.11 mol dm$^{-3}$ $CH_3COOH$ (fraction 1), B – 0.05 mol dm$^{-3}$ $NH_2OH \cdot HCl$, pH 2.0 (fraction 2), C – 8.8 mol dm$^{-3}$ $H_2O_2$ followed by D – 1.0 mol dm$^{-3}$ $CH_3COONH_4$, pH 2.0 (fraction 3), E – conc. HF:$HNO_3$, 3:1 (fraction 4). Except for B, all solutions were prepared beforehand. Each extraction was carried out at room temperature and mixtures were shaken continuously for 16 hours.

The Cd concentrations in the extracts were measured in an atomic absorption spectrometer model Video 11E (Thermo Jarrel Ash, USA) utilising flame atomisation and background correction. Quality assurance was provided by incorporating into the analysis an ICES/SCOR certified

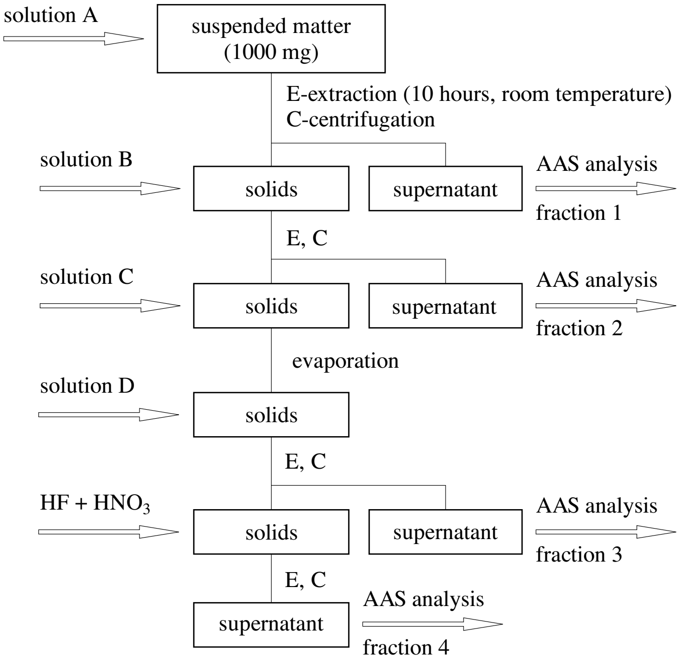

**Fig. 2.** A diagram of the sequential extraction procedure applied in the solid speciation studies

Baltic Sea bottom sediment sample (certified concentration 0.99 ± 0.24 $\mu$g g$^{-1}$, measured concentration 0.97 ± 0.14 $\mu$g g$^{-1}$).

## 3. Results and discussion

The total Cd concentrations in the samples analysed are presented in Figs. 3 and 4. The MANOVA evaluation of results (Cd solid speciation and total contents as dependent variables grouped according to station and season of sampling as independent variables) indicated the distribution of sampling stations (fraction 1 – $p = 0.094$, total content – $p = 0.103$) and the sampling season (percentage contribution of fraction 4 – $p = 0.062$) as independent variables differing statistically at the $p = 0.100$ level. In winter the average concentration (0.5 $\mu$g g$^{-1}$) is much smaller than in summer (1.8 $\mu$g g$^{-1}$). This is best explained by the increase in nutrient cadmium as a result of the element accumulation by algae (Gonzales-Davila 1995, Pohl *et al.* 1998). This explanation is substantiated by the decrease in dissolved Cd caused by algal blooms (Pempkowiak *et al.* 2000).

The average concentrations of Cd in suspended matter samples collected at consecutive stations is presented diagrammatically in Fig. 4. This shows that Cd concentrations decrease with increasing distance from the Odra

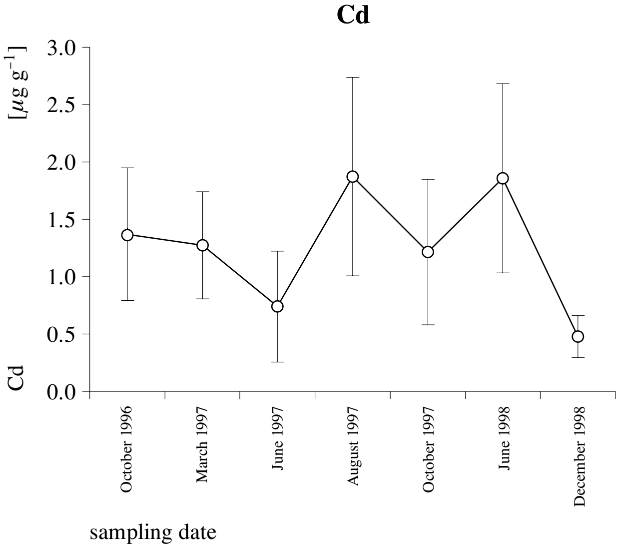

**Fig. 3.** Mean cadmium concentration and standard deviation in fluffy layer samples collected in successive cruises

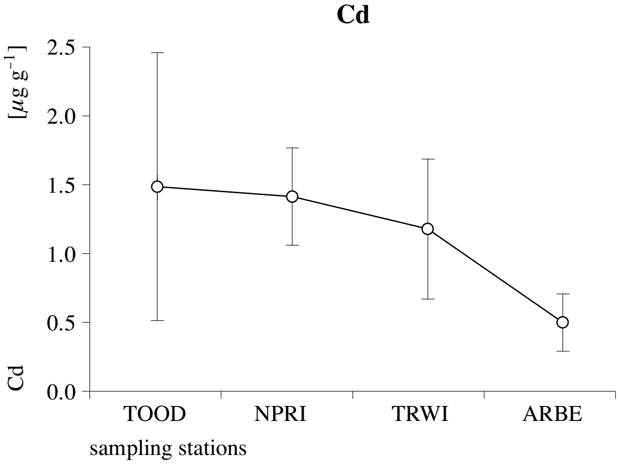

**Fig. 4.** Mean cadmium concentrations in the fluffy layer from successive sampling stations

mouth. This is due to the inflow of Cd-rich suspended matter with the river water, and also to large-scale dilution. Poleszczuk *et al.* (1993) found an average of $2.15 \pm 0.73$ Cd $\mu$g g$^{-1}$ (n = 82) in the suspended matter collected in the Szczecin Lagoon. Suspended matter there can be regarded as the terrestrial end member in the continuous change from fully terrestrial to marine, suspended matter of the investigated system. Another factor contributing to the observed decrease in Cd concentration with distance from the river mouth is the increasing depth of sampling sites there (Table 2); this is responsible for at least the partial degradation of suspended organic matter being deposited on the sea floor.

**Table 2.** Average cadmium concentrations at stations

| Sampling stations* | Depth [m] | Average conc. ± SD** Cd [$\mu$g g$^{-1}$] | Lowest concentration Cd [$\mu$g g$^{-1}$] | Highest concentration Cd [$\mu$g g$^{-1}$] |
|---|---|---|---|---|
| Odas Tonne (TOOD) | 12 | 1.42 ± 0.93 | 0.22 | 2.79 |
| Nordperd Rinne (NPRI) | 17 | 1.35 ± 0.34 | 0.61 | 1.63 |
| Tromper Wiek (TRWI) | 22 | 1.13 ± 0.48 | 0.60 | 1.84 |
| Arkona (ARBE) | 47 | 0.48 ± 0.20 | 0.24 | 0.72 |

*The location of sampling stations is given in Fig. 1.
** SD – standard deviation.

**Table 3.** Average cadmium concentrations in the fractions obtained by sequential extraction

| Sampling stations* | Cadmium concentrations in fractions Cd [$\mu$g g$^{-1}$]** | | | |
|---|---|---|---|---|
| | fraction 1 | fraction 2 | fraction 3 | fraction 4 |
| Odas Tonne (TOOD) | 0.40 | 0.53 | 0.42 | 0.07 |
| Nordperd Rinne (NPRI) | 0.31 | 0.48 | 0.39 | 0.17 |
| Tromper Wiek (TRWI) | 0.31 | 0.36 | 0.39 | 0.07 |
| Arkona (ARBE) | 0.08 | 0.18 | 0.15 | 0.07 |

*The location of sampling stations is given in Fig. 1.
** The percentage contribution of the various fractions is given in Fig. 2.

The concentrations and proportions of Cd in the individual fractions are set out in Fig. 1 and Table 3. A characteristic feature of the Cd distribution among the fractions is the substantial contribution of fraction 1 and fraction 2 to the total concentration of the metal. Both fractions contain labile forms of Cd, believed to be readily bioavailable (Kabata-Pendias & Pendias 1993, Pempkowiak *et al.* 1999). It is worth noting the substantial and rather stable contribution of labile Cd characteristic of all samples ranging, for fraction 1, from 15 to 28%, and for fraction 2, from 32 to 38%. The contribution of residual Cd (fraction 4) ranges from 5 to 15%. This may be due to the variable fine-grain size contents of the samples (Ingri *et al.* 1991, Emeis *et al.* in press). The fine-grain suspended matter contains elevated quantities of heavy metals (Salomons & Förstner 1981).

## 4. Conclusions

The concentration pattern of cadmium in the fluffy layer suspended matter is due both to the geochemical properties of the element and anthropogenic interactions.

The considerable variability in the cadmium concentration is due to the input of organic matter originating during primary productivity. The dependence of Cd concentration on the depth and distance of sampling sites from the river mouth is due to the mineralisation of organic matter deposited on the sea floor and the large-scale dilution of Cd-rich suspended matter brought to the Pomeranian Bay with the Odra river discharge.

## Acknowledgements

The participation of the captain and crew of the r/v 'Prof. Albrecht Penck' are acknowledged.

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