IMPACT OF EUTROPHICATION AND CLIMATE CHANGE ON Cd AND OTHER TRACE METAL DYNAMIC IN THE GULF OF RIGA, BALTIC SEA

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The ability of Cd and other trace metals to be incorporated in living phytoplankton cells has been widely used to explain its dynamic in marine ecosystem. However, the discrepancy between results from water column studies and those from studies in sediments remain unexplained. This strongly suggests a need for study with a more interconnected approach in identification of the main governing factors of trace element dynamics. Therefore, we conducted this study, which linked sedimentary records of trace elements with particular emphasis on Cd with available supporting information from sediments and water column. The concentrations of Cu, Mn, Cd and Cr in sediments of the Gulf of Riga exhibited significant ($P < 0.01$) positive relationships, while concentrations of Al and Ni had significant ($P < 0.01$ and $P < 0.05$, respectively) negative correlation with concentrations of TC. Concentrations of Zn, Pb and Fe in sediments did not exhibit significant correlation with concentrations of total carbon (TC). The vertical profiles of concentrations of several elements indicated that their accumulation patterns in sediments have changed substantially over time in respect to that of TC. The magnitude of change varied substantially from retaining positive correlation but changing element ratio value, in case of Cd, to complete shift from positive correlation to negative, in case of Zn and Cu.

Key words: Gulf of Riga, trace metals in sediments.

INTRODUCTION

Over the past decades, worldwide as well as in the Baltic Sea, trace metals, such as Zn, Cd, Mn, Cu have been extensively studied in the marine environment, both as limiting nutrients (Sunda and Huntsman, 1998; Muller *et al.*, 2003; Leblanc *et al.*, 2005) and as toxicants (Schneider and Pohl, 1996; Leivuori and Vallius, 1998; Dippner and Pohl, 2004). During most of these studies, Cd has received specific attention, since although Cd usually is considered to be non-essential for biological processes or even toxic to marine organisms, it has the ability to become incorporated in living cells by specialised membrane proteins (Lee *et al.*, 1995; Sunda and Huntsman, 1998), where it can become incorporated in some enzymes, for example substituting Zn (Morel *et al.*, 1994; Cullen *et al.*, 1999). It has been shown that under Zn, Mn and Fe limitation conditions phytoplankton growth can be stimulated by Cd (Lee and Morel, 1995; Sunda and Huntsman 2000; Xu and Morel 2013), thereby boosting Cd uptake by phytoplankton. At the same time, it has been noted that under non-limiting concentrations the uptake of Cd by phytoplankton is proportional to its concentration in water (Connell and Sanders, 1999) and it has been even suggested that Cd as well as Cu and Zn uptake by phytoplankton can be controlled by non-metabolic process

(Miao *et al.*, 2005). Thus, although there is still ongoing discussion on factors controlling Cd levels in phytoplankton, it is widely accepted that its behavior is nutrient like. Therefore, the temporal or spatial depletion of dissolved Cd concentrations (Bruland *et al.*, 1978; Schneider and Pohl, 1996), or a significant increase in particular Cd concentrations in surface waters (Poikane *et al.*, 2005, is usually attributed to Cd uptake by phytoplankton. In addition to that, Cd is known to remain in dissolved phase under oxic conditions (Pohl *et al.*, 1998; Pohl and Hennings, 1999), thus excluding deposition to sediment surface, while adsorbed at the surface of mineral particles in well-oxygenated marine basins, such as the Gulf of Riga. Furthermore, sediment records of Cd in some sub-basins of the Baltic Sea (Leivuori *et al.*, 2000) indicate that the Cd deposition rate has increased similarly to that of carbon over the last 50 to 100 years. However, evidence from the recent seasonal sediment trap study by Leivuori and Vallius (1998) indicates that Cd concentration is not correlated with carbon concentration in the settling phase.

This controversial observation led us to hypothesise that the Cd deposition rate in the Baltic Sea has been affected by changes in phytoplankton species composition, as evidenced by paleoecological studies (Olli *et al.*, 2007). In or-

Fig. 1. The Gulf of Riga with location of sampling station marked by x. Inserted map in lower left corner shows the location of the gulf within the Baltic Sea.

der to test the hypothesis in this publication we determined trace metal concentrations in sediments sampled in the Gulf of Riga at locations with good coverage of supporting monitoring data.

MATERIALS AND METHODS

A site with 43 m depth (Fig. 1) located (57°18'N; 23°51'E) in the Gulf of Riga, which had good coverage of monitoring data, was chosen for this study. The average sediment accumulation rate ($0.04 \text{ g cm}^{-2} \text{ yr}^{-1}$ of dry matter) for this area was estimated by ^{210}Pb dating method. For our study we used a 25-cm deep sediment core sampled in April 2003 using a modified Kajak type gravity corer (Blomqvist and Abrahamsson, 1985) equipped with an acrylic liner (8 cm in diameter). The core was sliced in 1 cm intervals, freeze-dried and stored at the Latvian Institute of Aquatic Ecology. Total carbon (TC) and total nitrogen (TN) in sediments were determined by high temperature combustion (Elemental Analyzer Vario EL III), BSi was extracted with 1% Na_2CO_3 and determined by the molybdenum blue method (DeMaster, 1981). Samples for trace metal analysis were digested according to a modified total wet digestion method described by Hovind and Skei (1992) in a PTFE vessel with a mixture of sub-boiled nitric acid and suprapure hydrofluoric acid at 96°C in a water bath for 2 h. Dissolved samples were evaporated to wet salts and cooled; then 2 cm^3 suprapure 30% (w/w) hydrogen peroxide was added and vessels were heated to $50 \pm 5^\circ\text{C}$ for a sufficiently long time for

only wet salts to remain. After cooling, the samples were transferred and diluted with 10% (w/w) sub-boiled nitric acid solution into volumetric flasks. Al, Fe, Mn and Zn in all samples were determined by flame-AAS (Varian Spectra AA 880). Cd, Cu, Ni, Pb and Cr were determined by graphite furnace AAS (Varian Spectra AA 880Z) with Zeeman background correction. Precision for determination of Al, Fe and Mn was 5%, for Zn – 10%, for Cd, Ni and Pb – 15%, and for Cu and Cr – 20%. For quality control of trace metal measurements, sediment test material QTM063MS supplied for the QUASIMEME Laboratory Performance Studies was used as reference material.

Accumulation rates of elements ($\text{g m}^{-2} \text{ yr}^{-1}$) were calculated from their concentrations in sediments and estimated average accumulation rate of sediments.

Supporting information and data from the water column (phytoplankton species composition and abundance) was obtained from the Latvian marine monitoring programme (Latvian Institute of Aquatic Ecology) and (particulate trace element concentrations in water columns and trace element concentration in the nepheloid layer) from a published research project (Poikane *et al.*, 2005).

Linear correlation between variables was tested by using Pearson correlation approach. The slope was estimated by applying simple linear regression calculations.

RESULTS

The concentration range of measured elements in the sediment were 2.7–5.5% TC, 0.33–0.65% TN, 2.2–6.5% BSi, $0.22\text{--}1.37 \text{ mg kg}^{-1} \text{ dw}$ Cd, $931\text{--}3764 \text{ mg kg}^{-1} \text{ dw}$ Mn, $40\text{--}51 \text{ mg kg}^{-1} \text{ dw}$ Ni, $80\text{--}100 \text{ mg kg}^{-1} \text{ dw}$ Cr, 4.6–5.8 % Fe, $34\text{--}61 \text{ mg kg}^{-1} \text{ dw}$ Pb, $26\text{--}37 \text{ mg kg}^{-1} \text{ dw}$ Cu and $111\text{--}326 \text{ mg kg}^{-1} \text{ dw}$ Zn.

TC, BSi, Mn, Cd (Fig. 2) and TN concentrations significantly ($P < 0.01$) increased from deeper sediment layers to

Fig. 2. Vertical profiles of Mn, Cd, TC and BSi in the sediments.

wards the surface. In the top 6–10 cm, corresponding to about 1960, a gradual concentration increase of TC (slope = 0.02; $R^2 = 0.8$) changed to more rapid increase (slope = 0.3; $R^2 = 0.99$) in recent sediments. Similarly, Zn, Cu, and Cr also showed increasing concentration, but which did not change in rate of increase. The concentrations of Al and Ni decreased towards the sediment surface, while Fe and Pb concentrations did not show trends.

As could be expected, the concentrations of nutrients (TN and BSi), as well as most nutrient-like elements (Cu, Mn, Cr and Cd), were significantly ($P < 0.01$) positively correlated with TC and significantly ($P < 0.01$) negatively correlated with Al (Table 1). Fe and Zn, which are also usually considered to be elements used by phytoplankton, did not exhibit significant correlation with TC (Table 1). At the

same time, accumulation rates of Cu and Cr were positively correlated with both accumulation rates of TC and Al (Table 2), indicating that Cu and Cr is deposited to the sea floor by particles of both abiotic and biotic origin. No such correlation was observed between accumulation rates of Cd and Al.

The increase of average accumulation rates in the periods prior to the 1960s, compared to the most recent period, was by 80% for TC, TN and Mn, 100% for BSi and 70% for Cd. Cu (20%) and Zn and Cr (10%) exhibited a much lower increase in accumulation rates, while the accumulation rates of Al, Fe and Ni did not exhibit any detectable change. Consequently, substantial differences between ratios of accumulation rates of TC, Cu, Cr and Zn prior to and after the 1960s were observed. For example, the Cu accumulation

Table 1

PEARSON CORRELATION COEFFICIENTS BETWEEN ELEMENT CONCENTRATIONS MEASURED IN A SEDIMENT CORE, $n = 30$

	Zn	Cu	Mn	Al	Cd	Cr	Ni	Pb	Fe	C	N	BSi
Zn	1											
Cu	0.347*	1										
Mn	0.139	0.597**	1									
Al	- 0.020	- 0.348*	- 0.369*	1								
Cd	0.332*	0.902**	0.599**	- 0.480**	1							
Cr	0.300	0.720**	0.494**	- 0.088	0.550**	1						
Ni	0.329*	- 0.008	- 0.229	0.590**	- 0.078	0.143	1					
Pb	0.582**	0.334*	0.129	0.063	0.198	0.478**	0.188	1				
Fe	0.452**	0.164	0.059	0.251	0.177	0.157	0.636**	0.409*	1			
TC	0.063	0.660**	0.644**	- 0.707**	0.677**	0.510**	- 0.385*	- 0.033	- 0.203	1		
TN	0.036	0.633**	0.631**	- 0.716**	0.658**	0.487**	- 0.394*	- 0.063	- 0.223	0.998**	1	
BSi	0.113	0.586**	0.551**	- 0.748**	0.631**	0.460**	- 0.415*	0.063	- 0.116	0.951**	0.951**	1

* $P \leq 0.05$.

** $P \leq 0.01$.

Table 2

PEARSON CORRELATION COEFFICIENTS BETWEEN ELEMENT ACCUMULATION RATES IN SEDIMENTS

	C	B-Si	Cd	Zn	Al	Cu	Cr	Fe	Ni	N
B-Si	0.96***	1								
Cd	0.73***	0.67***	1							
Zn	0.57**	0.51**	0.69***	1						
Al	0.28	0.138	0.2	0.56**	1					
Cu	0.80***	0.69***	0.81***	0.85***	0.66***	1				
Cr	0.72***	0.61***	0.58***	0.77***	0.80***	0.92***	1			
Fe	0.48**	0.4	0.43*	0.73***	0.83***	0.76***	0.83***	1		
Ni	0.46*	0.34	0.37	0.65***	0.91***	0.77***	0.86***	0.93***	1	
N	1.00***	0.96***	0.72***	0.55**	0.27	0.79***	0.72***	0.47**	0.46*	1
Mn	0.67***	0.61***	0.60***	0.41*	0.17	0.55**	0.49**	0.32	0.21	0.67***

* $P \leq 0,050$

** $P \leq 0,010$

*** $P \leq 0.001$

Fig. 3. Cu and TC accumulation rate in sediments. Circles represent the time period prior to the 1960s, squares after.

rates demonstrated a very tight correlation with accumulation rates of TC up to 1960s (Fig. 3). Thereafter, the correlation remained positive, but was weaker. Furthermore, accumulation rates of Zn did not exhibit any significant correlation with accumulation rates of TC when the whole sediment core was considered. However, when the sediment core was divided in periods prior to and after the 1960s, clear correlation between accumulation rates of Zn and TC was observed (Fig. 4). The accumulation rates of Cd (Fig. 5) and Mn exhibited close correlation with accumulation rates of TC, excepting in the top 4–5 cm sediments.

DISCUSSION

There are very few reliable measurements of trace element concentrations in Baltic Sea water (Schneider and Pohl, 1996; Dippner and Pohl, 2004). However, according to the collected data, the concentration levels observed in the water column are much higher than those considered to be limiting for phytoplankton growth (Lee and Morel, 1995). Therefore, we can assume that in the Baltic Sea enhanced uptake of Cd by phytoplankton under Zn, Fe or Mn limiting conditions is not plausible and it can be assumed that Cd and possibly other trace element uptake is proportional to trace element concentrations in water, as shown by Connell and Sanders (1999) and Miao *et al.* (2005). The factors controlling this process are still poorly described. Furthermore, it has been shown that phytoplankton capacity to uptake trace elements varies depending on the species (Sunda and Huntsman, 1998; Ho *et al.*, 2003). Smetacek (1980) and numerous later investigations have shown that major deposition of particulate material to sediment surface occurs after spring bloom. The spring bloom species composition and its changes have been of particular interest when analyzing accumulation patterns of elements. Trace element uptake experiments (Sunda and Huntsman, 1998; Ho *et al.*, 2003) showed that both major spring phytoplankton bloom

Fig. 4. Zn and TC accumulation rate in sediments. Circles represent the time period prior to the 1960s, squares after.

Fig. 5. Cd and TC accumulation rate in sediments. Circles represent time period prior to 1989, squares after.

forming groups, diatoms and dinoflagellates, readily assimilate Cd and other nutrient-like trace elements. Therefore, we can assume that observations of our study, as well as those of earlier investigations (Poikane, 2008) showing positive correlation between nutrient-like trace element and carbon concentrations in sediments of the Gulf of Riga, reflect deposition of trace elements along with deposition of phytoplankton cells. However, this assumption cannot explain the shift in ratio between trace element and TC accumulation rates observed in our study, and therefore, we have to assume that other factors are controlling accumulation rates of trace elements.

The ratio BSi (%) : TC (%) ratio was relatively stable up to 1960s (0.96), then changed to 0.86 (1960s to 1980s) and then to 1.17 resulting in a 20 % increase of BSi : TC concentration ratio by 1980s. Since diatoms generally have a significantly lower content of trace elements than other

phytoplankton groups (Ho *et al.*, 2003) it seems likely that diatom-dominated bloom sedimentation would result in lower surface sediment enrichment by trace elements than dinoflagellate-dominated blooms. This is in agreement with results of sediment trap studies by Leivuori and Vallius (1998), which showed that the majority of annually deposited phytoplankton material was of diatom origin with low content of trace elements and the annual deposition of trace elements was not controlled by spring bloom deposition. Furthermore, relatively high concentrations of particulate Cd with no significant concentration increase for other trace elements have been observed in surface waters of the Gulf of Riga (Poikane *et al.*, 2005) during a dinoflagellate (77 %, mostly *Peridiniella catenata*) dominated phytoplankton spring bloom in 2001 (Latvian Institute of Aquatic Ecology). This confirms that the observed increase of Cd concentration in sediments is controlled by dinoflagellate deposition. Therefore, the decrease in Cd concentration in sediments in proportion to TC, observed in the 1980, can be explained by shifts in relative proportions of material originating from diatom and dinoflagellate cells in favour of diatoms. The exact reason for this shift is still unclear, since monitoring is not regular and sufficiently frequent fully reflect spring bloom species composition monitoring. Possibly, substantial increase in nutrient loading to the sea occurred (Stålnacke *et al.*, 1999) resulting in increased phytoplankton biomass, which might have caused changes in the diatom/dinoflagellate ratio during spring blooms. However, this cannot be supported by actual phytoplankton data. Furthermore, such change would be more gradual. Therefore, the abrupt shift concept proposed by Möllman *et al.* (2008) seems more likely to explain the abrupt change in the accumulation pattern of Cd. As it has been shown by Möllman *et al.* (2008), the effect of climate resulted in shift of spring zooplankton biomass (ICES 2007), e.g., significant increase of biomass of the copepods *Acartia* spp. and *Eurytemora affinis*, in spring observed since 1985 (Diekmann and Möllmann, 2010). Since dinoflagellates usually form the second stage of the spring phytoplankton bloom then they would be more affected by earlier development of a zooplankton population than diatoms, and thus relative to diatom cell density, less dinoflagellate cells will be deposited on sediment surface due to increased grazing pressure. This is supported also by seasonal data on phytoplankton cell composition in the nepheloid layer during 2001 (Jurgensone, unpublished), which showed that more than 90% of identifiable cells in this layer were *Thalassiosira baltica*, even though the spring bloom was dominated by dinoflagellates.

Mn demonstrated an accumulation pattern similar to TC, and as observed also for Cd, there was a lower accumulation rate in the uppermost 2–5 cm. This might represent a specific case explained by its mobility under reduced conditions (Gobeil *et al.*, 1997; Kuzyk *et al.*, 2011). There have been no direct measurements of redox condition that would allow to describe its long term dynamics in Gulf of Riga sediments. However, during the late 1980s–1990s, the overlying water layer above sediments experienced a severe ox-

Fig. 6. Ni (circles) and Cr (squares) concentration correlation with chlorophyll a ($R^2 = 0.7$ and 0.8 , respectively) in nepheloid layer from April to October 2002.

xygen deficit, which certainly influenced redox conditions of the surface sediments of the Gulf of Riga. Therefore, we can assume that during that period Mn was extensively released from sediments due to unfavourable redox conditions. With reestablishment of favourable redox conditions, re-adsorption of Mn on would have been promoted.

The shift in accumulation patterns of Zn, Cu and Cr that occurred in the 1960s cannot be explained by increased zooplankton grazing pressure. The very slight (10–20%) increase in accumulation rates as well as significant ($P < 0.001$) correlation of accumulation rates of these elements and Al might suggest that the material containing these elements, which is deposited on the sediment surface, has abiotic origin. However, earlier investigations (e.g. Sunda and Huntsman 1998; Ho *et al.*, 2003) indicate that phytoplankton cells assimilate these elements, and this was shown also in our study by a positive correlation with TC. Furthermore, significant positive chlorophyll a correlation with Ni ($R^2 = 0.7$) and Cr ($R^2 = 0.8$) (Fig. 5) in the nepheloid layer sampled during April – October 2002 (data from Poikane *et al.*, 2005) strongly suggested that these elements were most likely incorporated in the bloom forming species *Chaetoceros wighamii* cells and were deposited along with them. Therefore, we suggest that in the case of Zn, Cu, and Cr, and to some extent also Ni, the major source for accumulation in sediments has abiotic material, while material of biotic origin, including detritus (Leivuori and Vallius, 1998), has secondary importance.

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EITROFIKĀCIJAS UN KLIMATA MAIŅAS IETEKME UZ Cd UN CITU METĀLU ELEMENTU PĒDU DINAMIKU BALTIJAS JŪRAS RĪGAS LĪCĪ

Fitoplanktona spēja iesaistīt Cd šūnā ir plaši izmantota lai skaidrotu Cd dinamiku jūras ekosistēmās. Tai pašā laikā ir novērotas analīžu rezultātu atšķirības ūdenī un sedimentos, kuras līdz šim nav izskaidrotas. Tas nosaka nepieciešamību veikt pētījumu, kurā tiktu sasaistīti galvenie pēdu elementu dinamiku kontrolējošie faktori. Šajā pētījumā tika saistīts pēdu elementu vertikālais sadalījums sedimentos ar pieejamo atbalstošo informāciju no sedimentiem un ūdens kolonnā, īpašu uzmanību pievēršot Cd. Rīgas līča sedimentos novērotās Cu, Mn, Cd un Cr koncentrācijas uzrāda nozīmīgu ($P < 0.01$) pozitīvu korelāciju ar TC (kopējais ogleklis). Tai pašā laikā Al un Ni uzrāda nozīmīgu ($P < 0.01$) negatīvu korelāciju ar TC. Savukārt Zn, Pb un Fe koncentrācijas sedimentos neuzrāda nozīmīgu korelāciju ar TC. Vairāki no apskatītajiem elementiem skaidri parādīja, ka laika gaitā ir būtiski mainījušies to akumulācijas režīmi attiecībā pret TC akumulācijas režīmu. Izmaiņu lielums ir atšķirīgs atšķirīgiem elementiem.