

Spatial variability of Arsenic Concentrations in Baltic Sea surface sediments in relation to Sea Dumped Chemical Munitions

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Abstract. Arsenic concentration in marine areas are higher than in terrestrial environment, because most of its compounds are water soluble, and water bodies serve as a sink for this element. Arsenic compounds, though naturally present in the sediments, are considered a threat to the environment, due to possible transformation to its toxic species – As^{3+} and As^{5+} . Natural background concentration of arsenic compounds is highly variable, as it differs both with the type of sediments, presence of ferromanganese nodules, iron sulphides or proximity to sources. In the Baltic Sea, majority of As originates from river runoff, while additional source of arsenic compounds in some areas of the Baltic are arsenic containing chemical warfare agents dumped into the sea after second world war.

Key words: Arsenic, Baltic Sea, Natural background, chemical warfare agents, dumped munitions

Introduction

Arsenic compounds are naturally present in all environmental compartments. As is a component of nearly 200 minerals and its concentration in crust rocks ranges between 0,5 to $2,5\mu\text{g}\cdot\text{g}^{-1}$. Depending on the oxy-redox conditions it occurs in the environment in four oxidation states (As^{3-} , As^0 , As^{3+} , As^{5+}). All arsenic minerals and compounds are soluble but the ability of migrating into the hydrosphere is restricted with binding by clay minerals, iron manganese and aluminium hydroxides, iron sulphides or organic matter.

Specific bacteria, some algae species and fungi present in marine environment have the ability of bounding and methylation of inorganic arsenic. Methylarsonic acid (MMA) and dimethylarsinic acid (DMA) are significantly less toxic. Seafood bioaccumulates mostly the non-toxic arsenobetaine.

Trace elements like arsenic, are considered as harmful for the environment regarding to their function in biochemical processes. As^0 is considered to be nearly harmless metalloid and it is estimated that As^{3+} and As^{5+} may be even hundred times more toxic for organism.

Riverine run-off of As into the Baltic Sea accounts for 200t/year while the total As input is calculated to reach 250t/year. Marine samples of different origin are thought to provide the greatest number of arsenic compounds occurring naturally and are reported to

contain concentrations of As even one order magnitude higher than comparable samples from terrestrial environments (Reimann et al.2009).

In the case of Baltic Sea the additional source of arsenic compounds is undisclosed amount of chemical munition dumped in the sea after the Second World War. After 1945 nearly 30 000 tons of chemical munitions from captured German arsenals was dumped into the Baltic Sea. The amount of arsenic-containing combat agents is approximately one-third of dumped chemical weapon in the Baltic Sea.

Different arsenic compounds are the major components of Chemical Warfare Agents (CWA) such as Clark I, Clark II, Lewisite and Adamsite. Another component of chemical weapons containing arsenic is arsine oil. It is a technical mixture of 50% phenylarsine dichloride, 35% diphenylarsine chloride, 5% of triphenylarsine and 5% arsenic(III) chloride. Despite arsine oils blister properties it was also added to mustard gas due to lowering its freezing point hence it is also plausible to detect evaluated arsenic concentration in areas of mustard gas dumping.

In aqueous environment both Clark I and Clark II rapidly degrade into diphenylarsinous acid which afterwards forms bis(diphenylarsinic) oxide. Its oxidation will lead to diphenylarsinic acid formation. Also adamsite, phenylchloroarsine and trichloroarsine degrade in a similar way with the same hydrolyzed and oxidized

products. However degradation products of arsenic-containing CWA may have similar impact on organisms as their toxicity is equal to their precursors and are persistent in the environment (Missiaen et al.2010). Arsenoorganic compounds decompose later into toxic, inorganic arsenic compounds which are adsorbed to the sediments and suspended matter, desorbed and transported in dissolved form in water column. The whole degradation path results with wide dispersion of arsenic-containing CWA on the 1,5m distance from the leaking container and complete natural degradation of those chemicals is estimated to take even 100 years. Accordingly, occurrence of high arsenic concentrations in some areas in sediment can indicate leakage reflecting the condition of ammunition shells. Those arsenic-containing CWA are able to contaminate in the separate Baltic Deeps Emelyanov, Kravtsov, 2007; Emelyanov et al., 2010; Emelyanov, 2007_{1,2}) areas of bottom sediments due to their low solubility. According to the MERCW investigations evaluated arsenic levels were measured in bottom sediments from much wider area than the primary dumping sites zone.

Study Area

CWA dumpsite in Bornholm area is situated in the east of the isle of Bornholm and is considered to cover area of 8 Nm in diameter from the centre estimated at 55°21'00N, 15°37'02E (HELCOM 2011). Other HELCOM report mentions dumping area stretched between 55°10'N-55°23'N and 15°24'E-15°55'E. Yet as a result of bottom trawling in surrounding areas the deposited ammunition may be replaced, so the threatened area may increase year after year (Khalikov, Savin, 2009). The quantity of munitions dumped in this region is estimated to reach over 11 000 tons in total, and about 31% of that is considered to be arsenic-containing (arsine oil, Clark I, adamsite). Water depth in this area ranges from 75m to 95m.

The Gotland dumpsite is located in the southern part of Gotland Basin and covers area of about 330km² with depths ranging from 70 to 120m. Quantity of chemical munition dumped in this region is estimated for nearly 1000tons (circa 30% of arsenic-containing combat agents). CWA containers are scattered on area twice big as the Bornholm dumpsite. According to the hydrologic conditions (especially scarce bottom currents and stable water stratification) this area is considered to be more suitable for dumping chemical weapon in terms of avoiding human health threat.

Måseskär site is located in eastern part of Skagerrak. In that area depths range from 180m to 230m what gave the opportunity for flooding ships. It is confirmed that at least two ships were sunk and about 1500 tones of toxic agents were dumped in this area. Both Gotland (Emelyanov, 2007₂) and Bornholm (Emelyanov et al., 2010) Deeps bottom are covered with carboniferous mud enriched with organic matter. The mud layer in Bornholm Deep is about 5-6m thick, and in Skagerrak it is about 8m (Emelyanov, 2007₁). The sedimentation rate on Bornholm and Gotland Deeps approximates 1 mm per year. In 60 years after deposition,

the ammunition is covered with mud layer of about 6cm thickness. But the most of shells and bombs sunk in the soft mud and lie at the depth of 0.5-1 m (Missiaen, Feller, 2008).

Results and Discussion

As sedimentological analysis show strong dependence of sediments grain size and metals concentration, fraction of sediments can have an important influence on arsenic enrichment (Emelyanov, Kravtsov, 2007; Emelyanov et al., 2010). The fraction of sediment grains <2µm is one of the major sinks for pollutants introduced into natural waters, mostly because of presence of clay minerals, together with associated coatings of organic material and iron manganese (oxy-)hydroxide precipitation (Garnaga and Stankevicius, 2005). As many metals tend to absorb within fine particle fractions of sediment different fractions of sediment samples are studied – from <2µm to <0,063µm (Emelyanov, Nielsen, 1995). However comparing results of different surveys, Reimann et al. (2009) reported that chosen grain-size fraction of sediment sample should not be a significant factor for the results of arsenic analyses. Sanderson et al.2008 received the highest As concentration (210µg·g⁻¹) in pelitic mud sample – fine grain size. Also Emelyanov et al. (2010) found in Baltic Sea in chemical weapon dumping areas sediments varying from fine-grained sands to pelitic (clayey) mud and aleuro-pelitic mud up to 210 and 277 µg·g⁻¹ As.

Background concentrations of Arsenic in Baltic sediments vary between different basins. While areas under low to moderate anthropogenic influence are characterized with values below 30µg·g⁻¹, some areas with high historical pollution reach up to 210µg·g⁻¹ (Bothnian Bay) (Borg, Jonsson 1996).

Therefore possible impact of dumpsites might be observed only by comparing wide area data and looking for hotspots. In the Gotland Dumpsite, in Lithuanian EEZ significant differences were observed - average value of 9,7µg·g⁻¹ in the dumpsite compared to 2,1µg·g⁻¹ in surrounding locations (Garnaga et al.2006, HELCOM MUNI 2/2011). But in the Litorina muddy strata of the Gotland Deep (in the core Psd 303590) (Emelyanov, 2007₂) reported of 130 µg·g⁻¹ of As. In the eastern part of Gotland Basin and in Gdańsk Basin elevated values of As were observed locally reaching up to 70 µg·g⁻¹ (Emelyanov, Kravtsov, 2007). In the Bornholm dumpsite, differences were observed in Polish EEZ - 29µg·g⁻¹ compared to roughly 15 µg·g⁻¹ in surrounding muddy sands.

Part of Bornholm Basin close to northern border of Polish EEZ is one of the most arsenic contaminated areas of Baltic Sea. It is probably related to the vicinity of chemical munition dumping site and according to normalized As/Fe also to fishing harbors.

Elevated inflow of heavy metals is a result of anthropogenic activity in the Baltic Sea catchment area, nonetheless the type of sedimentary environment also influences its concentrations – regarding to the redox conditions in the sediments the amount of organic matter and pelitic (clayey) fraction contents may vary.

Different sources report that in sediments from the layer between 10 and 15 cm from the bottom surface concentrations of heavy metals are significantly higher than in deeper layers. The input of oxygen rich waters after the stagnation period changes the redox conditions of sediments. Limited exchange of water between Baltic and North Sea and lamination of waters with different temperature and salinity causes long- and short-term periods of oxygen deficiency in some deeper basins but also intermittently in shallow Belts Sea regions (depth <20m). Within anoxic conditions elevated concentrations of Fe(II) and Mn(II) can occur and as a result arsenic concentrations can rise, as it shows strong affinity for those compounds. When oxygen-rich oceanic waters flow appears Fe(II) and Mn(II) are oxidized into Fe(III) and Mn(IV) hydroxides, and complex compounds precipitate on the bottom surface (Emelyanov, et al, 1995). Also diversified mineral composition of bedrock and soils in the catchment area of Baltic Sea can influence natural concentrations of arsenic in marine sediments (for example, glauconite).

Differences in maximum As concentration layer might be also the effect of pollution history, or local sediment accumulation velocity variabilities within the area of Baltic Sea.

In all examined areas elevated arsenic concentrations occur within 15cm depth of sediment cores and remains more or less stable below 20-25cm. This layer can be assumed as pre-industrial geochemical background. Average background values for arsenic range from 5 to 20 $\mu\text{g}\cdot\text{g}^{-1}$. The lowest observed values are reported in Gulf of Riga and western Gotland Basin. In the mud with iron sulphides or manganese nodules in the Gulf of Finland were found up to 150 and 131 $\mu\text{g}\cdot\text{g}^{-1}$ of As correspondingly (Emelyanov, Kravtsov, 2007, p. 804). Abnormal changes in arsenic concentrations in sediment cores from Baltic Sea can be connected to diagenetic processes and in CWA dumping-areas may be with an effect of dumped weapons.

Wide vertical variety of As concentrations in core samples from Bornholm Basin are connected with the differentiation of sediment type, and diagenetic processes in this area. In zones where pycnocline is in contact with sea bottom As concentrations values up to 15 $\mu\text{g}\cdot\text{g}^{-1}$. In sediments deposited below the pycnocline those values reach 24 $\mu\text{g}\cdot\text{g}^{-1}$ in the layer between 4—8cm (Figure 1), but 20cm below the surface As concentrations sometimes exceed 20 $\mu\text{g}\cdot\text{g}^{-1}$ (Emelyanov, Kravtsov, 2007). Yet the anthropogenic influence on its concentrations is certain – in north-eastern part of Bornholm Basin elevated values are found in the layer of 16-18cm deep regardless of the sedimentation environment. In the south part of Gdańsk Basin such trend is not as clear. However in both these regions maximum concentrations occur in the layers 16-54 and 187-226 cm from the bottom surface. Regardless to the area and sedimentation environment a decrease of concentration is observed within surface layers of sediment of 2cm thickness. This can be either a result of decreasing input of arsenic into marine environment, or active exchange between sediments and nearbottom

water. Values of As in surface sediments do not exceed the level of 20 $\mu\text{g}\cdot\text{g}^{-1}$ which is considered as a geochemical background. But in the mud of central part of this Basin (core Psd 303700) we found 14-30 $\mu\text{g}\cdot\text{g}^{-1}$, and in the 6 layers - from 59 to 121 $\mu\text{g}\cdot\text{g}^{-1}$ of As.

Other environmental parameters can influence As concentration in sediments. Strong correlation exists between concentrations of arsenic and iron ($R^2=0,83$). Paka and Spiridonov (2002) claim that elevated arsenic concentration with coexistent decrease of iron and manganese contents might result from occurrence of local source of As. In case of samples with elevated both arsenic and iron or manganese, the possibility of association with chemical munitions is relatively small. Naturally occurring Fe and Mn oxyhydroxides and iron sulphides can actively concentrate trace metals, including arsenic, due to their sorption abilities. Emelyanov (2007) found maximum concentrations of As in samples of mud enriched with authigenic iron sulphides. These minerals are good arsenic concentrators and can contain 270-600 $\mu\text{g}\cdot\text{g}^{-1}$ (Emelyanov 2010, Emelyanov 2007). Arsenic shows no correlation with different microelements nor the pelitic fraction of sediments. It indicates only a weak positive correlation with Mn concentrations ($R=0,22$). In Gotland Deep sediments the maximum values of As were connected with iron sulphides in Ancyclus clay and Litorina mud, and did not result from direct contamination from dumped munitions.

Conclusion

Measuring arsenic concentration in marine sediments and pore water seems to be satisfactory instrument for estimating the amount and threat of CWA in dumping areas. This method is also adequate for screening sediment contamination range on areas beyond the dumping sites.

Moreover further investigations of arsenic concentrations should be carried out including identification of geochemical patterns. Focusing on the surface layers of 5cm thickness may be somehow insufficient for CWA investigations and thicker layer of surface sediments should be analyzed for arsenic. The layer of 10cm from bottom surface is considered to be influenced with mixing processes. As a result pore water enriched with arsenic can migrate in depth... It is also important to provide normalized values of arsenic concentrations including the influence of iron occurring in the sediments and its fraction. Despite As to total Fe correlation their coexistence mechanisms are more complex.

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