



## Revisiting the biogeochemistry of arsenic in the Baltic Sea: Impact of anthropogenic activity



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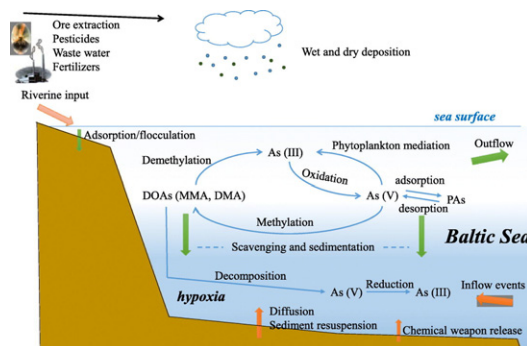
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### HIGHLIGHTS

- Biogeochemical cycling of arsenic in the Baltic Sea, a famous hypoxic zone, was studied.
- TDIA concentrations in 2011 showed no significant difference with 1981, and remain at “natural” level.
- Upward redox boundary indicated by elevated As(III) concentrations in the deep water reflected the deterioration of water environment, and potentially damage to the ecosystem in the Baltic Sea.

### GRAPHICAL ABSTRACT



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### ABSTRACT

With the increase in anthropogenic environmental disruption, the behavior of arsenic in the Baltic Sea has received more scientific attention because of its complex forms and toxicity, and was re-visited to determine if there have been measurable changes recently. A cruise was conducted in 10–19 May 2011 to investigate the species and distribution of total dissolved inorganic arsenic (TDIAs:  $[\text{TDIAs}] = [\text{As(V)}] + [\text{As(III)}]$ ) revealing links between the hydrographic dynamics and biological/chemical reactions in the Baltic Sea. In addition, long-term (2002–2010) time-series investigations of particulate arsenic in the Gotland Basin were also conducted in February every year for monitoring purposes. The behavior of TDIA was non-conservative due to the removal and regeneration processes occurring in the Baltic Sea. Biological scavenging plays a dominant role as sink for TDIA, with removal amount of  $3.1 \pm 1.6$  nmol/L above the pycnocline of the Baltic Sea. Significant regeneration of TDIA was observed below the pycnocline of the Baltic Sea, which was closely related to hypoxia. The decomposition of organic arsenic and release from the sediment by desorption of As-bearing Fe and Mn oxides were thought to be two major sources for TDIA regeneration. The median concentration of TDIA (8.4 nmol/L) was much lower than in most marginal seas and oceans, including the near-bottom water around a chemical weapon dumpsite (13.9 nmol/L). The hypoxia in the deep water contributed to the increase in As(III) concentrations based on the relationship between As(III)/TDIA ratio and apparent oxygen utilization. If the difference of As(III) profiles (1981 and 2011) actually represents a long-term increase in As(III) concentrations and a shoaling of the As(III) chemocline, these factors could enhance the toxic effects and extend the residence time of arsenic and, hence, potentially have negative impacts on fisheries and ecosystem health in the Baltic Sea.

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## 1. Introduction

Arsenic (As) is of great concern in the terrestrial as well as aquatic environments because of its high toxicity. It ranks first on the list of hazardous substances (Kim and Nriagu, 2000; Hu and Cai, 2009), though it is only the 20th most abundant element in the Earth's crust (1.8 mg/kg, Cao et al., 1994; Lide, 1996). High concentrations of arsenic will be extremely harmful to human health by affecting cell respiration, enzyme action, breaking chromosomes, and increasing the risk of cancer as it is absorbed (Matschullat, 2000; Hu and Cai, 2009). The geochemical cycle of As in the natural marine environment is complex due to the existence of different oxidation states (+5, +3, 0, -3) and its complicated chemical properties. Inorganic species of arsenic are known to be highly toxic to microbial and phytoplankton species. Arsenate (As(V),  $\text{AsO}_4^{3-}$ ) is stable in oxic water and arsenite (As(III),  $\text{AsO}_3^{3-}$ ) is most toxic and can be generated by phytoplankton production, bacterial dissimilatory reduction, or photochemical reaction (Neff, 1997; Oremland et al., 2000). In most hypoxic zones, the percentage contribution of As(III) reduced from As(V) can be >80% of total As(III) in the near-bottom water, such as Baltic Sea (Andreae and Froelich, 1984), Black Sea (Cutter, 1991), and Changjiang Estuary (Li et al., 2014). Organic species [e.g., monomethylarsenic (MA) and dimethylarsine (DMA)] can be produced through phytoplankton detoxification, microbial action, or bioaccumulation and release (Andreae and Klumpp, 1979; Sanders and Riedel, 1993; Millward et al., 1997; Hasegawa et al., 2001), and can be converted into inorganic species through the decomposition process (Hanaoka et al., 1993; Dani, 2010a). In general, most dissolved arsenic occurs in inorganic forms in natural waters, with the ratio of organic arsenic to total dissolved arsenic typically <20% (Cutter et al., 2001; Li et al., 2014).

Arsenic in the aquatic environment is usually derived from natural sources such as volcanism, weathering, and wildland fires; and anthropogenic sources such as mining, smelting, burning of fossil fuels, wood preservation, agriculture (herbicides, pesticides, fungicides, and fertilizers), and chemical weapons etc. (NRC, 1977; Cullen and Reimer, 1989; Nriagu, 1994). Arsenic from these natural and anthropogenic sources is mainly transported into the marine environment through riverine input and atmospheric deposition. The arsenic content in riverine and estuarine waters are more variable as a result of varying bedrock lithology and river inputs, but are usually low, at typically <2  $\mu\text{g/L}$  for river water and 4  $\mu\text{g/L}$  for estuarine waters under natural conditions (Smedley and Kinniburgh, 2002). There are approximately 57,000 tons of arsenic discharge into the ocean by riverine input every year, which accounted for >50% of the total input flux of arsenic (Matschullat, 2000). In addition, atmospheric deposition flux of arsenic was estimated to be 6200 tons/yr, accounting for ~10% of the total riverine input to the oceans (Matschullat, 2000). However, this ratio will significantly increase to 30% and even more in the open ocean or some marginal seas which are beyond the direct influence of rivers (Cutter and Cutter, 1995; Ren et al., 2007; Li et al., 2017).

Evidence shows that the anthropogenic sources have largely surpassed the natural sources as the principal source of arsenic input into the biosphere (Dani, 2010b). Dani (2010a) reported the effects of long-term exposure to even low environmental arsenic on age-related cognitive decline in European countries. Loring et al. (1995) found extremely high levels of arsenic in the sediments of the fjord Guba Chernaya on the southwestern coast of Novaya Zemlya, which could be explained by deposition of As-rich radioactive particulate material dispersed by underwater nuclear explosions. Chemical warfare agents (CWAs) have been disposed of in various ways over the past decades following the disarmament of Germany after the World War II. Approximately 11,000 tons of CWAs have been dumped in the Baltic Sea east of the island Bornholm since 1950s (HELCOM, 1994). This has caused concerns over potential human and environmental health risks around the dumpsite (Sanderson et al., 2009). Arsenic-containing CWAs (of which 2033 tons were dumped) are made up of 50% phenyldichloroarsine,

35% Clark I, 5% trichloroarsine and 5% triphenylarsine, and 5% unidentified carrier co-solvent (Sanderson et al., 2008). The extent of corrosion of the CWAs shells resting on the seabed and in the sediment for approximately 70 years and subsequent release of the toxic arsenic compounds raise environmental and human health concerns among neighbouring Baltic countries.

Here we present the results of total dissolved inorganic arsenic (TDIAs,  $[\text{As(V)}] + [\text{As(III)}]$ ) and As(III) in the Baltic Sea and also time-series of particulate arsenic (PAs) in the Gotland Basin, using data originally collected for monitoring purposes from 2002 to 2010. We compare the TDIAs concentration in May 2011 with the results of Andreae and Froelich (1984) and assess whether there have been measurable changes of arsenic concentrations in recent years in the Baltic Sea. In addition, the possible effects of redox processes on the biogeochemical cycling of arsenic have also been taken into account, including the transformation of arsenic species, the regeneration of arsenic in the deep water, and hence the change of toxicity. The study was designed to help us better understand the current status of arsenic in this special anoxic environment, and consequent effects on the fisheries, the ecosystem, and human health in the Baltic Sea.

## 2. Materials and methods

### 2.1. Study area

The Baltic Sea is a semi-enclosed brackish water body located in Northern Europe, with an area of 412,560 km<sup>2</sup>, an average depth of 52 m and maximum depth of 459 m (Rheinheimer, 1995). It is structured into a series of basins separated by sills, including the Bothnian Bay, the Bothnian Sea, the Gulfs of Finland and Riga and the Baltic Proper (Siegel et al., 2009; Fu, 2013). Water balance is affected by freshwater input from rivers and by precipitation and evaporation as well as exchange with the North Sea via the Skagerrak; however, the shallow, narrow Belt Sea permits only a slow and limited water exchange between the Baltic Sea and the North Sea (Lehmann et al., 2004). The estuarine circulation and positive water balance resulted in a permanent stratification of water masses in the Baltic Proper (Grasshoff and Voipio, 1981). The salinities of the upper layer of brackish water and deep waters are about 7–8 psu and 11–13 psu, respectively. A permanent pycnocline is formed between these water masses, at depths varying between c. 30 m in the Arkona Basin, c. 60 m in the Bornholm Basin, and c. 80 m in the Gotland Basin, which impedes the vertical mixing of the water column and ventilation to the bottom (Matthäus and Schinke, 1999; Zillén et al., 2008).

The average residence time of the water in the Baltic Sea is >30 years, which promotes stagnation in the deeper basins and the accumulation of pollutants (Omstedt and Hansson, 2006). Large hypoxic areas (defined as <2 mg/L DO) have been described in the Baltic deep water since the 1950s, and the conditions of oxygen depletion have deteriorated over the last century (Savchuk, 2010). Oxygenation of deep waters usually occurs by occasional oxygenated salt water intrusions from the North Sea (Yakushev et al., 2011). The inflows in summer 2002, winter 2003 and summer 2003 terminated the stagnation period in the Baltic deep water which lasted since 1995 (Lehmann et al., 2004). A baroclinic inflow in summer, followed by small barotropic inflows in 2007 and 2009 were observed in the central Baltic deep-water (Neumann et al., 2017). Alternations of oxic and anoxic conditions in the deep waters affect the redox conditions and, thus, the species composition and distribution of arsenic in the water column.

### 2.2. Sample locations and sampling

In order to access the systematic information on the current status of arsenic in the Baltic Sea, we were invited by Dr. Christa Pohl of Leibniz Institute for Baltic Sea Research Warnemünde (IOW) to participate in a regular monitoring cruise conducted from 10 to 19 May 2011 aboard

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