



Distribution of sedimentary mercury off Svalbard, European Arctic



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HIGHLIGHTS

- Atmospheric Hg signal can be seen in Barents Sea, but it is not clear in fiords.
- Glacier meltwater and rock weathering are important Hg source in the study area.
- Anthropogenic mercury represents minor portion of total concentration in sediments.
- MeHg concentration depends on environmental conditions rather than total Hg.
- Organic carbon content seems to control mercury bioavailability in study area.

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ABSTRACT

The European Arctic, including the Svalbard archipelago, receives mercury loads due to long range atmospheric transport, local contamination, melting of glaciers and as a result of bedrock weathering. Few studies have been devoted to the contamination history and sources of sedimentary mercury in the Svalbard area. This knowledge gap is addressed in this study. Concentrations of total mercury (10–80 ng/g), fractions of mercury differing with affinity to the sediment matrix (88–97% refractory, 3–12% mobile), organic and methyl mercury (100–500 pg/g) were measured in surface and subsurface sediments in the Spitsbergen fjords and in the Barents Sea off Svalbard. The atmospheric mercury signal can be observed in the Barents Sea, while in the Svalbard fjords it is strongly modified by supply of mercury from natural sources that may include weathering of rocks and glaciers melting, all modified by organic matter supply. Sedimentary methyl mercury concentrations seem to be dependent on environmental factors affecting mercury methylation rather than on location of sampling stations.

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1. Introduction

Mercury, is characterized by significant environmental mobility, is accumulated by biota and is toxic to living organisms, including humans (Manahan, 2010). Mercury is in major portion emitted to the atmosphere as gaseous elemental mercury (GEM). Due to its substantial half-life, tropospheric GEM persists long enough to be transported to the high latitudes (Pacyna et al., 2006). There it is readily deposited to the earth's surface during a springtime Atmospheric Mercury Depletion Event (AMDE) (AMAP, 2011). Mercury may be also transported to the Arctic by the North Atlantic Current, and sea ice transport (Phirman et al., 1997; Pavlov et al., 2004). On top of loads from global sources, the Arctic is also supposed to receive contaminants from local sources, e.g. from coal mining activities (Rose et al., 2004; Drevnick et al., 2012).

In the aqueous environment, mercury is easily adsorbed onto sinking suspension and is deposited to bottom sediments. Investigations of lake sediments in the Arctic have proven that up to half of the mercury present in these sediments actually originates from AMDE (Drevnick et al., 2012). It has been postulated that increased scavenging of mercury by suspended organic matter and absorption by plankton contributes to increased concentrations of mercury in surface sediments (Jiang et al., 2011). Investigations of the sediment cores have indicated that the surface concentrations of mercury exceed several times the subsurface ones (Gobeil et al., 1999; Asmund and Nielsen, 2000; Drevnick et al., 2012), a phenomenon attributed to the increased atmospheric transport of mercury to the Arctic.

Total mercury (THg) in surface marine sediments of the Arctic has been continuously measured for several decades. Concentrations of THg in Arctic marine sediments are higher in the high Arctic. For example, concentrations of THg in sediment cores collected from the interior Arctic Ocean, Beaufort Shelf and Greenland coast in the 1980s and 1990s were 10–120, 1–130 and 4–280 ng/g,

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respectively (Asmund and Nielsen, 2000; Kirk et al., 2012), whereas those from Hudson Bay were 8–58 ng/g (Hare et al., 2010). Studies devoted to concentrations of mercury in sediments of the Canadian Arctic and Greenland (Asmund and Nielsen, 2000; Sunderland et al., 2006; Kirk et al., 2012) proved the enrichment factor of mercury in surface sediments was in the range 1.7–2.5. Sedimentary methyl mercury vary from 45 to 1570 pg/g in coastal sites (Sunderland et al., 2006; Fedorov et al., 2010), while concentration in pristine offshore sediments is 72–226 pg/g (Hammerschmidt and Fitzgerald, 2006).

Relatively little attention has been paid to sedimentary mercury in the European Arctic, including Svalbard (AMAP, 2011). The latter location is interesting due to possible local anthropogenic sources of mercury (Drevnick et al., 2012), varying geological bedrock (Pempkowiak et al., 1999), a complex pattern of surface currents carrying both warm and cold water masses into the region (Walczowski, 2013), and recent glaciers melting. Any extensive studies in Svalbard have been devoted to the lacustrine sedimentary mercury (Jiang et al., 2011; Drevnick et al., 2012). Mercury deposition rates in the range 3–10 $\mu\text{g}/\text{m}^2$ annum were reported. The increased concentrations close to a small settlement on the shore of Adventfjord (Isfjord), were attributed to local contamination (Drevnick et al., 2012). Jiang et al. (2011) indicated importance of sedimentation of dead phytoplankton cell remnants, as a mercury deposition mechanism in the Svalbard lake close to Ny-Ålesund.

Sedimentary mercury in Kongsfjord, was studied by Grotti et al. (2013) and Lu et al. (2013). Typical concentrations were found to be in the range 8–63 ng/g d.w., while the background concentration was established to be 9.7 ng/g d.w. Increased concentrations in the surface sediments were attributed to increased atmospheric transport. Holte et al. (1996) postulate mercury concentrations to be at the natural background level in Isfjord. However, the overall distribution of mercury in the surface sediments of Svalbard's fjords is not known, as only Kongsfjord and Isfjord sediments have so far been studied. No reports regarding sedimentary total mercury and methyl-mercury in marine sediments east off Svalbard are available so far.

This study was devoted to establishing the distribution of sedimentary mercury in the Spitsbergen fjords and in the Barents Sea off Svalbard. The different locations were investigated to assess environmental factors (possible local contamination, varying geological setting, hydrological considerations, water depth, sediment texture and organic matter content) which have an influence on Hg distribution. In addition to total mercury, several mercury species were measured including methylmercury, bulk organic mercury and mercury (II) fractions differing with affinity to the sediment matrix.

2. Materials and methods

2.1. Study areas

Marine sediments off Svalbard were the subject of the study. Fjords along the western coast of Spitsbergen, the largest island of the archipelago, and the Barents Sea off the eastern shores of Spitsbergen, were sampled (Fig. 1).

Kongsfjord (Fig. 1) is a glacial fjord located in the northern part of Spitsbergen. The fjord is about 20 km long and its width varies from 4 to 10 km. Sediments are strongly influenced by terrestrial inputs through the melting of five glaciers (Svendsen et al., 2002). Most of the solid material exported by the glacier accumulates on the sea floor within the fjord (Zaborska et al., 2006). The sampling stations (Fig. 1) were chosen to represent glacial runoff influence and distance to the open ocean. Stations K1 and K2,

represent sediments directly impacted by the glacier. Station K5, is close to a little settlement, Ny-Ålesund, that was previously a coal mine (1916–1953) and has recently been inhabited by scientists (100 persons). Station K3 is located at the inter-moraine depression where preferential sediment accumulation occurs.

Isfjord (Fig. 1) is the largest of the Spitsbergen fjords. It has an area of 7309 km². The direct anthropogenic pressure is due to the existence of two large settlements – Longyearbyen and Barentsburg. Both settlements are characterized by coal mining activity, and have coal-fuelled power stations. Sediment samples were collected in one of Isfjord's branches, Adventfjord – in the vicinity of Longyearbyen. Sample I1 was collected close to Longyearbyen, while sample I2 – close to Adventfjord inlet. Adventfjord does not directly receive glacier melting waters but it is supplied by suspension-rich waters that pass a large tidal flat comprising local bedrock weathered material (Zajaczkowski et al., 2004).

Hornsund (Fig. 1) is the most southerly fjord in Spitsbergen and is dominated by cold waters of the Arctic Sørkapp Current. The length of the fjord is some 30 km, the average depth is 90 m. The area of the fjord and the length of the shoreline have been increasing due to the recent glaciers melting (Jania et al., 2005). Hornsund is clearly divided into two basins: the outer basins (with good water exchange with the shelf) and the inner one (separated by moraine thresholds) (e.g., Frankowski and Zioła-Frankowska, 2014). The fjord receives glacier meltwaters from several glaciers. Station H4 is located in the outer fjord, H3 in the transition area between the outer and inner fjords, while stations H1 and H2 are located close to a glacier front. Beach station HB1 represents the inner fjord, HB3 the transition area, while the remaining stations (HB4, 5 and 6) are situated in the outer fjord.

Magdalenefjord (Fig. 1) is 8 km long and up to 5 km wide. It is influenced by the Atlantic West Spitsbergen current. It is a pristine, uninhabited area often visited by tourists' cruisers. Station M1 was situated at the glacier front, while station M2 was located in the outer part of the fjord.

The Barents Sea (Fig. 1) is a continental shelf sea with average depths of 230 m. The Barents Sea floor consists of platform areas, basins and troughs. Coarser sediments are characteristic of shore areas (up to 100–200 m depth). Fine sediments are found along the eastern Svalbard coastline and in troughs. Sampling stations in the Barents Sea were aligned in a N–S transect, starting at latitude 81°16' N (B1) towards 75°39' (B5) (Fig. 1).

2.2. Sample collection

Sediment samples were collected by means of a Gemax corer from r/v "Oceania" (Spitsbergen Fjords) and with a Multi corer from r/v "Jan Mayen" (Barents Sea), in years 2002–2010. Core samples (fjords: H1, H3, K3, I, I2) were cut into 1 cm thick layers of which layers 0–1, 4–5, 8–9 and the 1 cm thick bottom layer were taken for analysis. Two layers of the Barents Sea cores: the topmost 1 cm thick layer and the layer between 18 and 20 cm, considered pre-anthropogenic (Zaborska et al., 2010) were analyzed. Remaining samples represent the 0–3 cm layer of sediments Beach samples were collected with a pre-cleaned polypropylene spatula from low, medium and high water levels. Samples were deep-frozen until analysis on shore.

2.3. Analysis

Prior to analysis, sediment samples were homogenised under a laminar flow hood and aliquots were taken for determinations of moisture, organic carbon and fine-grain fraction contents. Moisture content was used to calculate dry mass of sample as wet sediment was taken for mercury analysis, and all results are reported as mass per dry weight. Fine-grained fraction (<0.067 mm) content

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