Less metal fluxes than expected from fibrous marine sediments

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Abstract

Deposits of fibrous sediment, which include fiberbanks and fiber-rich sediments, are known to exist on the Swedish seafloor adjacent to coastaly located former pulp and paper industries. These deposits contain concentrations of hazardous substances that exceed national background levels and contravene national environmental quality objectives (EQOs). In this study of metal fluxes from fibrous sediments using benthic flux chamber measurements (BFC) in situ we obtained detected fluxes of Co, Mo, Ni and Zn, but no fluxes of Pb, Hg and Cr. The absence of fluxes of some of the analyzed metals indicates particle bound transport of Pb, Cr and Hg from fiberbanks even though Hg might become methylated under anoxic conditions and, in that case, may enter the food chain. We found less metal fluxes than expected and thus emphasize the importance of in-situ flux measurements as a compliment to sediment metal concentrations within risk assessments of contaminated sediments.

1. Introduction

The forest industry is prominent in Sweden and plays an important role in the national economy. Various sub-industries exist in the forest industry, such as pulp and paper, sawn timber, wood (chip) board and refined wood-based fuels. Among sub-industries, the Swedish pulp and paper industry is the largest in Europe and fourth largest in the world, after USA, Brazil and Canada (Suhr et al., 2015; FAO, 2018, Apler et al., 2019).

The Swedish paper and pulp industry expanded most during the early-mid 20th century and until regulated environmental legislation was enforced in 1969 waste from the industry, including process waters, was released untreated into lakes and coastal waters. Urged by the environmental legislation external treatment systems were installed at all pulp and paper mills (SFS 1969:387: Norrström, 2015). However, large deposits of fibrous waste that accumulated prior to legislation have been identified by marine geological surveys (Apler et al., 2014; Norrlin et al., 2016). Surveys of coasts and lakes in northern Sweden established that fiber affected sediments cover at least approximately 29 km² and of these relatively thick deposits cover an area of about 2.6 km² (Apler et al., 2014; Norrlin et al., 2016). Apler et al. (2019) differentiate between (i) fiberbanks, which are relatively thick deposits of fibrous residues and wood ships often found close to the industrial source and (ii) fiber-rich sediments, which are a mixture of fibrous residues and natural sediment that exist in river beds or marine accumulation areas. Fiberbanks are characterised by elevated organic carbon (cellulose) content, low bulk density, and levels of metals and persistent organic pollutants that are frequently classified as high compared to national background values (Apler et al., 2019). We emphasize that fiberbanks are thought to derive from earlier than 1969, when the waste discharge from the pulp and paper industry was unregulated.

These sediments of anthropogenic origin are contaminated by persistent organic pollutants and metals (Elert et al., 1992; Drott et al., 2007; Skyllberg et al., 2007; Regnell et al., 2014; Wiederhold et al., 2015; Zhu et al., 2018; Apler et al., 2019). There is growing concern that contaminants in fiberbanks have dispersed, and can continue to disperse to areas where they can bioaccumulate and biomagnify. For example, contaminants from Swedish fiberbanks have tentatively been connected to a regional decline in the reproductive ability of the sea eagle (Haliaeetus albicilla) (Bignert and Helander, 2015; Hellström, 2015; Swedish EPA, 2008). However, limited research has been conducted into the mechanisms and dispersal pathways of contaminants from fibrous sediments (Apler et al., 2019).

One characteristic of fiberbank deposits is their high gas content (e.g. methane and carbon dioxide), reflected by the scattered hydroacoustic signature of fiberbank, as a consequence of the microbial decomposition of organic matter and the production of an anaerobic...
environment. Fiberbanks can, therefore, be considered as so-called “dead zones” (Diaz and Rosenberg, 2008) because of the anaerobic environment and the absence of benthic macrofauna. Today it is thus difficult for stakeholders or local decision makers to plan ecosystem services, bathing facilities or harbor constructions in areas where fiberbanks are located as long as the fiberbanks remain on seafloor without any remediation action.

Metals found in fiberbanks are linked to emissions from pulp and paper mills and from the various processes in the manufacture. Mercury (Hg) is the only metal that was intentionally used in the manufacturing process and elevated concentrations of it has often been found in fibrous sediments (Apler et al., 2019). Hg was used in the manufacturing of pulp and paper as a catalyst in the chlor-alkali process, which produced chlorine gas for bleaching (Lindqvist et al., 1991; Wiederhold et al., 2015) as a slimeicide to prevent fouling in process tubes (Lindqvist et al., 1991; Wiederhold et al., 2015) and to protect pulp fibers from microbiological degradation (Skyllberg et al., 2007). However, wastewaters from pulp and paper industries also contained other metals and metalloids, such as lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) (Monte et al., 2009; Apler et al., 2019). Kraft pulp residue sludges (e.g. green liquor sludge), contain different amounts of metals such as barium (Ba), Cr, Cd, Cu, Pb, Ni and Zn (Monte et al., 2009; Suhr et al., 2015; Svrek and Smith, 2003).

The nowadays outdated sulfite cooking process may also have contributed to emissions of metals such as Fe, Cu, As, Zn, Ni, and Co, which are found in pyrite ash, a mineral by-product of the production of sulfuric acid that was used in the sulfite cooking process (Tugrul et al., 2003).

In an earlier study of metal contents in fiberbanks at Väja and Sandviken, and in fiber-rich sediments at Väja at the estuary of Ångermanälven (Apler et al., 2019) some metals were found to be above national background levels for marine and brackish sediments. Cd was i.e. found to deviate largely from national background values in the Väja fiberbank deposit and in the Väja fiber-rich sediment, while both Cr and Pb differs widely from the national background values in the Sandviken fiberbank (Apler et al., 2019).

Acute toxicity depends on bioavailability, which is a measure of the concentration of free metal ions in solution (Harrison, 2001). Metal speciation in sediments and their sorption capacity are controlled by different factors such as the content of total organic carbon (TOC), clay and sulfur (S) in the sediment. It has e.g. been reported that TOC can have an influence on metal speciation of e.g. Cd, Hg and Pb as these toxic metals become stronger bonded by organic carbon (Hammerschmidt and Fitzgerald, 2004; Chakraborty et al., 2012; Chakraborty et al., 2014). The toxicity and bioavailability of Hg are also more dependent on its speciation than on its total concentration in sediments (Chakraborty et al., 2014; Chakraborty et al., 2015).

In this context, fibrous sediments are of environmental concern because they contain a larger proportion of organic material (OM) than natural clayey sediments in accumulation areas of the Gulf of Bothnia. However, besides decreasing bioavailability due to bonding to organic matter, non-residual/dynamic complexes of Hg such as methylmercury (CH₃Hg⁺) will increase its biological impact.

So far, a limited amount of research (Frogner-Kockum et al., 2016; Apler et al., 2019) has been conducted within the field of possible mechanisms and dispersal pathways of contaminants from minerogenic and fibrous sediments to the aquatic system, the rates of contaminant transport and the threat they may pose to the environment. Contaminants in the pores of the studied fiberbanks are to a very low degree bioavailable as free ions (Apler et al., 2019) which is due to calculated adsorption coefficients in Apler et al. (2019) mostly associated with particulate matter. Contaminants can furthermore most likely both be adsorbed to the organic material (e.g. cellulose) or to clay particles in the fiberbank (and in fiber-rich sediments). Thus, it is considered as important to analyse the transport of free ions (fluxes) out of the fiberbank deposit compared to total levels of contaminants in fiberbanks in order to establish and make it evident that there are indeed only some metals that are spread as free ions from the fiberbanks.

In Sweden, no guidance for risk assessment of sediments presently exist. However, in earlier Swedish strategies for risk assessments of sediments estimates of contaminant transport of free ions across the sediment-water interface are based on diffusive calculations (Swedish EPA, 2007). In the Norwegian guidance for risk assessment pore water analyses are used to quantify the dispersion of contaminants from sediments to the overlying water column (Eek et al., 2010). Such quantification relies on diffusive models based on Fick’s law. However, significant uncertainties stem from using diffusive flux models because the real flux is a sum of diffusion, advection and bioturbation and therefore might be much greater than diffusive flux alone. Diffusion is a continual process, while advection processes occur more stochastically, depending on the location and characteristics of the individual fiberbanks.

In a pioneering work by Frogner-Kockum et al. (2016) flux measurements with a benthic flux chamber (BFC) were used for the first time to determine in-situ metal fluxes from contaminated sediments in a risk assessment context. Earlier BFC studies exist, but the emphasis in those has been on sediment-water exchange of trace metals, outside the context of risk assessment (e.g. Hall, 1984; Hall et al., 1984; Sundby et al., 1986; Westerlund et al., 1989; Pakhomova et al., 2007). The most extensive use of the BFC method has however been to determine sediment-water exchange of nutrients (e.g. Tengberg et al., 2003; Viktorsson et al., 2013).

This study contributes to an initiative to expedite remediation of contaminated fibrous sediments, specifically to develop methods that may be useful in site characterization and environmental risk assessment. Results are presented of a relatively new in-situ method for studies of fluxes of metals of environmental concern. The main aim was to test a benthic lander system (BFC) in bottom waters for the determination of metal fluxes of environmental concern originating from fiberbank deposits, fiber-rich sediments and reference gyttja clays. Another aim was to compare the BFC measured metal fluxes with that of model predicted fluxes, and to compare the BFC measured metal fluxes with the total content of metals in these three different sediment types. This study was part of a larger project (TREASURE – Targeting emerging contaminated sediments along the uplifting northern Baltic coast of Sweden for remediation), which had the overall aim to develop new methods to assess the risk of dispersal of contaminants from fibrous sediments.

1.1. Study site

The two studied fiberbank sites were selected as parts of the TREASURE project and are situated in a brackish fjord-like estuary of Ångermanälven river in north-eastern Sweden (Fig. 1). The non-tidal estuary is one of the largest in the area and it is a sub basin of the Bothnian Sea. The basin stretches approximately 50 km from the inner bay to the shore of the Gulf of Bothnia’s coast. The aforementioned study sites, called Väja and Sandviken, are located in the westernmost part of the Ångermanälven River estuary, in the intermediate river basin between the shallower distal slope at the river mouth in the north and the sill located halfway into the estuary. The fiberbank (FB) deposits are located on the steep shore line whereas the fiber-rich (FR) sediments exist more widely over the river basin. Figs. 1 and 2 shows the estimated distribution of fiberbank deposits and fiber-rich sediments for the two study sites. The Figs. 1 and 2 also show the locations for the BFC in-situ measurements, and the reference station M0062. For a more detailed description of the sampling sites, see Figs. 1 and 2 and Apler et al. (2019).
2. Methods

2.1. Sediment sampling and analysis

2.1.1. Sediment and pore water sampling

Methods for sediment sampling and pore water extraction are described in detail in Apler et al. (2019) and in Appendix 1. Sediment samples were collected at three sites within the Sandviken fiberbank ($n = 3$) and at two sites in the Väja fiberbank ($n = 2$). The fiber-rich sites and reference station were represented with one sample each (Table 1).

The fiber-rich and the gyttja clay sediments were sampled using a GEMAX corer (described by Niemistö, 1974) and the surface sediments (0–4 cm) were recovered. The unconsolidated sediments in the Väja fiberbank were sampled using a box corer (L 30 x W 30 x H 50 cm) where bulk samples (0–30 cm) were taken out. The fiberbank in Sandviken was sampled with an Orange peel bucket sampler (OPB) due to the rough texture of the deposit. Bulk samples (0–40 cm) were taken out from Sandviken fiberbank.

2.1.2. Analyses of metals, TOC and DOC

Metal analysis in sediment and pore water are not retrieved exactly from the same sampling point as the samples from the benthic flux chambers and hence, they are considered “mean” concentrations of the whole fiberbank. Porewater extraction was carried out by centrifuging the sediment samples approximately two weeks after fieldwork. Methods for analyses of sediment and pore water concentrations of metals, TOC and dissolved organic carbon (DOC) are described in detail in Apler et al. (2019) and in Appendix 1.

Water samples from the BFC were analyzed for As, Cd, Co, Cr, Cu, Mo, Ni, Pb, S and Zn in the same manner as described in Apler et al. (2019) and in Appendix 1. The laboratory analyses of metals were done by ALS Scandinavia AB in Luleå, Sweden, by using ICP-SFMS and ICP-AES after partial with 1/1 HNO$_3$/water in closed Teflon vessels. Mercury was analyzed using atomic fluorescence spectrometry (AFS) after digestion.

TOC and DOC contents of water samples were measured at ALS Czech Republic by IR detection. Sediment TOC was determined at the Swedish University of Agricultural Sciences (laboratory of the Department of Soil and Environment) by elemental analysis. To differentiate between inorganic (carbonates) and organic carbon a sample was first combusted at 550 °C to remove the organic fraction.

2.2. Benthic lander deployments and metal flux measurements

Field work was carried out August 9–15, 2015, using the Geological Survey of Sweden’s vessel S/V Ocean surveyor. During the field work, two benthic landers constructed by Gothenburg University (see Tengberg et al., 2003, for a full technical description) were used to make autonomous incubations and collect water samples to measure dissolved metal concentrations over time. The type of lander is an autonomous modular vehicle capable of operation in marine waters to a depth of < 1000 m and it consists of two parts, an inner and an outer frame that are both made of titanium. The outer frame serves mainly as a carrier platform for the syntactic foam buoyancy package, the ballast and the acoustic release system for the ballast release. The inner frame (Fig. 3), which was used without the outer frame in this project, is a versatile system that carries two experimental modules (the small lander) and four experimental modules (the big lander). The modules can easily be exchanged if necessary. The middle of the inner frame holds two pressure cases that contain one “pre-programmed” controller with batteries and one data logger with batteries. The controller runs all the mechanical operations such as the water sample collection by the syringes, sediments sampling (only in the big lander), variation in stirring speed, etc. A more thorough description of the BFC method used for flux measurements of trace elements was presented by Almroth et al. (2009).

In this project, four squared incubation chambers modules were used in the Big Lander and two in the Small Lander. The Big Lander and the Small Lander were used to make replicates at all sites, up to 6 chamber incubations in total (Table 1). Each chamber, which has a horizontal surface area of 400 cm$^2$, was equipped with 10 syringes which automatically collected water samples at pre-programmed time intervals from the bottom water inside the chambers. All chambers were equipped with a horizontal stirrer placed centrally at the top of the chamber.
Optical oxygen sensors (oxygen optodes model 3830 or 3835, the Big and the Small Lander, respectively) measured dissolved oxygen concentration inside each chamber during the incubations. Chamber turbidity was measured by optical turbidity sensors (model 3612A) measured inside each chamber, salinity by inductive conductivity/temperature sensor (model 3919A). All sensors were from Aanderaa Data Instruments (Norway). In addition, we measured oxygen, temperature and salinity outside Small Lander’s chambers. Data from all sensors were recorded at 1-min interval.

After each deployment, chamber oxygen, salinity and turbidity data were downloaded and checked immediately to assess incubation quality. Based on the sensor data analysis and on performance of chamber water sampling mechanics, 3 chambers were selected for sampling metals, and the rest for sampling dissolved inorganic carbon (DIC).

Metal fluxes at five sites in total, two fiberbank sites (named FBV and FBS, Fig. 2) and two fiber-rich sediment sites (named FRV and Sed—S, Fig. 2) and at one reference site M0062 (Table 1). Measurements were done with the two landers simultaneously (a big and a small lander) at each site. The unconsolidated nature of the fiberbank in Väja required test deployments to assess the best way to deploy the landers, which, was done with the help of several added trawl balls to prevent the landers from sinking too deep into the sediment. Chamber fluxes of oxygen were measured, and chamber oxygen data was then used to indicate how long each incubation needed to be.

2.3. Chamber flux calculations

Dissolved metals and DIC were sampled from the incubation chambers at five pre-determined points in time. Linear regression of
concentration versus time was used to calculate the slope ($\Delta C/\Delta t$) with the validity tested using F-statistics at $P = .1$. Use of linear regression for calculating the flux assumes that a flux rate does not change over time or concentration, which are common designs of chamber flux experiments.

Data point outliers per chamber were rejected according to the following rationale: the starting point as due to the effect of the injection for chamber volume determination, which could have been a possible source of contamination; the final point as conditions in the chamber could have changed during the incubation, which would affect metal flux rates; or one point during the experiment, due to analytical error.

Based on the slopes, individual chamber fluxes ($F_{\text{CHAMBER}}$) (mmol m$^{-2}$ day$^{-1}$) were calculated according to the formula:

$$F_{\text{CHAMBER}} = H \times \Delta C/\Delta t$$

where $H$ is the height of the chamber and $\Delta C/\Delta t$ is the slope of linear regression of concentration ($C$) change in chamber water with time ($t$). The in-situ chamber height $H$ was calculated based on chamber salinity measurements and MilliQ water injection of known volume:

$$H = \frac{V_{\text{inj}} \times S_{\text{al1}}/(S_{\text{al1}} - S_{\text{al2}})}{A_{\text{CHAMBER}}}$$

where $V_{\text{inj}}$ is the known injection volume (typically 55–60 mL of MilliQ water was injected), $S_{\text{al1}}$ and $S_{\text{al2}}$ is salinity inside the chamber before and after injection, and $A_{\text{CHAMBER}}$ is the area of incubated sediment (chamber area, 400 cm$^2$).

### 2.4. Diffusive flux calculations

Diffusive fluxes ($F_{\text{PW}}$) were calculated based on the gradient between the porewater and the bottom water from the incubation chamber according to:

$$F_{\text{PW}} = \frac{q_{\text{SED}} (C_{\text{PW}} - C_{\text{BW}})}{S_{\text{eddepth}}}$$

where $q_{\text{SED}}$ is the sediment diffusion coefficient, $C_{\text{PW}}$ is the porewater concentration, $C_{\text{BW}}$ is the concentration of the metal in the bottom water (chamber water sample at time point 1, average for 3 chambers is used), and $S_{\text{eddepth}}$ is the porewater sampling depth related to the surface of sediment.

### 3. Results

#### 3.1. Benthic flux chamber measurements

**3.1.1. In situ chamber measurements**

In situ measurements of Oxygen, DIC, Salinity and temperature are important they provide information about leakage during incubations, reactivity, organic carbon content and of the redox conditions.

Oxygen and DIC fluxes (Table 2) are more specifically indicators of benthic microbial activity and degradation of organic material (OM) in sediment. Three types of sediment respiration patterns were observed: 1) very strong oxygen consumption at Väja (in both fiberbank and fiber-rich sediment); 2) moderate consumption at Sandviken fiber deposit and 3) low consumption at the reference site M0062 and at Sandviken sediment (Sed–S). This classification is supported by the measured DIC flux rates.

At Väja (both the fiberbank and fiber-rich sediment) higher oxygen

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**Table 1**

Lander stations, coordinates (SWEREF 99TM), water depths and solute sampling scheme. Metal and DIC sampling was made from the Big Lander (chambers 1,2,3,4) and/or the Small Lander (chambers A and B). Abbreviations: DIC = Dissolved inorganic carbon, FBV = Fiberbank Väja = FRV = Fiber rich-sediment Väja, FBS = Fiberbank Sandviken, Sed-S = Sediment Sandviken, b = big lander, s = small lander.

| Site     | Coordinates | Depth (m) | Incubation time (h) | Metals, chamber | DIC, chamber |
|----------|-------------|-----------|---------------------|-----------------|--------------|
| FBV-test-b | X 637920,59  Y 6985870,30 | ~17 | 9 | NA | NA |
| FBV-test-s | X 637905,22  Y 6985811,05 | ~14 | 11 | | |
| FBV-b    | X 637940,00  Y 6985865,00 | ~18 | 8.5 | 1,2,4 | 3,A |
| FBV-s    | X 637872,00  Y 6985880,00 | ~17 | 8.5 | | |
| FRV-b    | X 637965,15  Y 6985945,11 | ~34 | 16.5 | 2,4,8 | A |
| FRV-s    | X 637985,62  Y 6985976,09 | ~36 | 16.5 | | |
| FBV-b    | X 640046,82  Y 6983630,40 | ~14 | 12.5 | 1,3,4 | A |
| FBV-s    | X 640033,06  Y 6983645,22 | ~14 | 12.5 | | |
| SedS-b   | X 641003,0   Y 6983748,32 | ~24 | 30.5 | 2,3,4 | A,B |
| SedS-s   | X 641008,31  Y 6983733,59 | ~27 | 30.5 | | |
| M0062-b  | X 641730,73  Y 6983740,39 | ~67 | 8.5 | 2,3,4 | N.A. |
| M0062-s  | X 641706,00  Y 6983738,00 | ~68 | 8.5 | | |

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Fig. 3. The lander is built up by separate benthic flux chamber modules as shown to the left by the arrow. The Big Lander used has four modules (as in figure to the left) while the Small Lander has two modules. The Big Lander chambers can capture and bring the incubated sediment back on deck for visual inspection and sampling. The photo in the middle shows the Big Lander being lifted up after a deployment onboard S/V Ocean Surveyor assisted by Mikhail Kononets and Paul Frogner-Kockum. A magnified detail to the right shows Big Lander chamber 1 with incubated water sediment (the blue frame) and a rack with sampling syringes which is a part of chamber water sampling system (the white frame). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
fluxes were always associated with higher oxygen consumption rates: oxygen measurements showed concentrations between 80 and 200 μM and oxygen consumption rates between 27.6 and 58.4 mmol m⁻² day⁻¹. These results indicate that oxygen consumption is limited by availability of oxygen, i.e. diffusive transport of oxygen into the sediment limits oxygen consumption rate. Chamber DIC measurements at Väja showed strong release of DIC, 145-221 mmol m⁻² day⁻¹. High DIC to oxygen flux ratio indicates strong contribution of anaerobic processes to the total organic matter degradation rate. Also, when the landers were back on deck, gas bubbles were observed in the incubated sediment and the first sampling syringe was filled with gas. This was probably an indication of methane release due to anaerobic respiration processes, although the gas was not analyzed. Very high oxygen and DIC fluxes, and presence of gas bubbles in sediment indicate extremely strong microbial activity at the site Väja. At Sandviken, the fiberbank showed relatively high oxygen consumption. DIC flux estimates were not possible because the DIC data were not good enough to calculate a statistically valid ΔC/Δt slope, but the possible flux range indicated by the DIC data was 40 to 120 mmol m⁻² day⁻¹ (data not shown). Compared to Väja, oxygen flux measurements showed lower consumption at higher dissolved oxygen concentration. In any case, the oxygen consumption rate of around 20 mmol m⁻² day⁻¹ in the Väja fiberbank is significantly higher than the Sandviken fiberbank, fiber rich sediment from Väja, Sandviken sediment (Sed—S) and the reference site M0062. Sandviken sediment (Sed—S) and the reference site M0062 showed similarly low oxygen consumption rates of around 4 mmol m⁻² day⁻¹. The DIC flux of 10 mmol m⁻² day⁻¹ exceeds the oxygen flux by a factor of 2.5 which indicates the importance of anaerobic OM degradation processes. DIC was not sampled at the reference site M0062 because the duration of the deployment was considered to be too short to reliably estimate DIC fluxes (8.5 h compared to 30.5 h at Sandviken sediment, Sed—S).

3.1.2. Analysis of incubated water

Metal analyses of incubated water from deployed benthic landers showed that As, Hg, Pb and Cd were below the detection limit for all chamber samples. Cu and Cr were detected in some samples, but the number of data points was insufficient to evaluate by a linear regression. Some valid sample values for Mo and Ni and for Co showed an increased trend for the release with time that made it possible to calculate fluxes based on these elements (Table 3). Considering measured fluxes, the Mo flux from the Väja fiberbank was 0.5 μmol/m²/day, whereas a flux of 0.42 μmol/m²/day was obtained at the Sandviken fiberbank (Table 3; Fig. 4a and b), and a flux of 0.7 μmol m⁻² day⁻¹ was obtained in the Väja fiber rich sediment (FRV). 0.5 (± 2). The predicted flux of Mo from Väja fiberbank based on Eq. (3) was much lower, 0.1 μmol/m²/day. Fluxes for Ni were in the range from 2.9 μmol m⁻² day⁻¹ at Sandviken’s fiberbank compared to 6.8 at the Väja fiberbank (Table 3; Fig. 5a and b), whereas predicted fluxes were at least one order of magnitude lower and in the range 0.03–0.5 μmol m⁻² day⁻¹. Ni fluxes at fiberbank deposits at Väja, 6.8 μmol m⁻² day⁻¹, may also be compared to the about three times lower flux value in Väja fiber rich sediment (FRV), 2.2 μmol m⁻² day⁻¹. This measured flux value may furthermore be compared to a predicted flux for Ni in Väja fiber rich sediments (FRV) that was at least two orders of magnitude lower, 0.0014 μmol m⁻² day⁻¹ (Table 3; Fig. 5c).

The Co flux from fiberbank deposit at Väja, 3.0 μmol m⁻² day⁻¹, may also be compared to Co fluxes in fiber-rich sediments at Väja 1.2 μmol m⁻² day⁻¹ (Fig. 6) and Sandviken sediments (Sed-S), 0.7 μmol m⁻² day⁻¹ that is about three times lower. The predicted Co flux in fiber-rich sediment at Väja was however at least two orders of magnitude lower, 0.01 μmol m⁻² day⁻¹ than the measured value.

Results of chamber flux measurements are presented in the Table 3 and the measured concentrations for the elements with valid fluxes are presented as plots in Appendix 1.

4. Discussion

4.1. Metal fluxes from anoxic sediments

A study of metal levels in fibrous sediments (Apler et al., 2019; Table 2) reveal that the levels of Cd in fiberbank deposit and fiber-rich sediment, in the Väja area (see Fig. 1 for location), largely deviate from background concentrations (class 4, Table 4). In Sandviken, only the fiberbank deposit seems to be affected by metal pollution, and it is Cd and Hg levels that largely deviate from the national background whereas Cr and Pb show a very large deviation (class 5, Table 4).

The sampling stations located further out from the fiberbank deposits (i.e., fiber-rich sediment, gyttja clays in Sandviken and the reference station M0062) contain metals in concentrations that resemble or moderately deviate from the national background (Table 4). When comparing metal concentrations measured outside of the fiberbanks of Sandviken and Väja, they are in the same order of magnitude as the offshore monitoring station (SE-2) located outside the Ångermanälven estuary (see Fig. 1 for location) which is considered unaffected by land-based point sources of pollution (Apler and Joseffson, 2016).

Given the high organic content of fiberbanks, we expect pore waters in fiberbanks (and fiber-rich sediment) to be anoxic. Hence, except for maybe the few uppermost centimetres in fiberbanks we can expect metal species in porewater to occur in a reduced state. However, we only obtained fluxes for Co, Mo, Ni and Zn and could compare these fluxes with model predictions and to the metal content in fiberbanks.

Model predictions were based on the top 4 cm sediment at Sandviken, while they were based on the top 40 cm sediment at Väja, which might make a comparison between measured and evaluated fluxes at Väja less reliable.

Concerning measured fluxes, no fluxes of Pb, Hg and Cr were detected even though Pb, Hg and Cr occurs in relatively high concentrations in fiberbanks compared to national background levels. Thus, in
Table 3
Chamber metal flux data (F in table) in the two fiberbank deposits, the fiber-rich sediments and the reference site. ND = not detected, measured concentrations were below detection limit. As, Hg, Pb and Cd were below the detection limit for all chamber water samples. Cr and Co were measured in some samples, but there were not enough data to calculate fluxes. IF = metal concentrations were measured, but flux (the ΔC/Δt slope) was not statistically valid. Flux ± Standard deviation (where applicable). Fpw = Diffusive fluxes calculated.

| Type of sample | Fiberbank | Reference sediment | Fiber sediment |
|----------------|-----------|--------------------|---------------|
|                | Väja (FBV) | Sandviken (FBS) | M0062 | Väja Fiber rich sediment (FRV) | Sandviken (Sed-S) |
| Co μmol m⁻² day⁻¹ | F = 3.0 (n = 1) IF (n = 2) Fpw = ND | ND | ND | F = 1.2 ± 1.2 (n = 3) Fpw = 0.1 | NA |
| Mo μmol m⁻² day⁻¹ | F = 0.5 ± 0.2 (n = 2) IF (n = 2) Fpw = 0.02 | 1.0 (n = 1) IF (n = 2) Fpw = 0.13 | IF (n = 3) | IF (n = 3) | F = 0.7 ± 0.2 (n = 2) |
| Ni μmol m⁻² day⁻¹ | F = 6.8 ± 2.5 (n = 3) IF (n = 3) Fpw = 0.5 | IF (n = 3) | Fpw = 0.08 | IF (n = 3) | 0.7 ± 2.3 (n = 2) |
| Zn μmol m⁻² day⁻¹ | ND (n = 2) IF (n = 3) Fpw = NA | IF (n = 1) | 17.0 (n = 1) | ND (n = 1) IF (n = 1) Fpw = NA | F = 14.2 ± 12.0 (n = 2) |

Fig. 4. a. Results from the incubation at Väja fiberbank deposit. The concentration change in the chambers with time is shown for Mo for chambers one and two. The fluxes are calculated from the slope of the linear regression line. b. Results from the incubation at the Sandviken fiberbank deposit. The concentration change in the chamber with time is shown for Mo for chamber 3. The flux is calculated from the slope of the linear regression line.

Contrast to a high initial total content of Pb, Hg and Cr in fiberbanks flux data obtained from fiberbank deposits and fiber rich sediments shows that Pb, Hg, As and Cd, concentrations were below limit of quantification (LOQ) and that the number of data points for Cu and Cr were insufficient for fluxes to be reliably determined. However, the sediment concentrations of metals used for estimation of fluxes are reflecting means in the FB sediments and near-by values for the fiber-rich and clayey stations which could affect the outcome of the estimations.

The most unexpected difference between flux measurements and sediment analysis is however a lack of Cr fluxes from the fiberbank in Sandviken. Cr occurs mainly in concentrations that deviates largely from national background levels (class 5, Table 4) in all three triplicate sediment samples of the Sandviken fiberbank. Apler et al. (2019) showed that Cr was present in Väja’s pore water whose sediment Cr content had a more moderate deviation from national background levels (Table 4). A lack of Cr concentrations in incubated water samples from Sandviken sediment was thus not expected but may possibly be due to the low solubility of Cr(III) which is usually dominating over Cr (VI) in anoxic environments (Rifkin et al., 2004).

The lack of Pb fluxes was also a contradiction to what might be expected. Pb was namely found in elevated concentration (class 5, Table 4) in one of the triplicate samples from Sandvikens fiberbank and in moderate levels (over national background) in the other two samples (class 3). It is, therefore, fully possible that an absence of soluble Pb concentrations in BFC incubations partly reflect fluxes from sediments that had a moderate deviation from national background, but it may also have other explanations. Below the redox cline of Baltic Sea, soluble concentrations Pb (and of Cd, and Cu) normally decrease whereas soluble Co (Co²⁺) usually increase (Borg and Jonsson, 1996; Dyrrsen and Kremling, 1990). The absence of Pb ions (and of Cd) during incubations on reduced sediments is thus either due to the precipitation of insoluble sulphides of these elements in the pore water or formation of metal sulphide complex at reduced conditions, but may also be due to adsorption of these elements to solid phases in fiberbanks. The measurable fluxes of Co, Mo, Ni, V and Zn may be explained by the higher solubility associated with these elements whereas solubility of Pb is lower in the presence of sulfur that thus also may explain the lack of fluxes of this metal (Ditoro et al., 1996; Dyrrsen and Kremling, 1990).

A comparison of measured fluxes between the two fiberbank deposits, Väja and Sandviken (FBV and FBS) in this study, shows that fluxes of Mo and Ni are in the same order of magnitude at both sites which strengthens the reliability of each individual measurement. Also, the fluxes of Mo and Ni in fiber-rich sediment (FRV) are in the same order of magnitude as the ones measured from fiberbanks.

A study of pore and bottom water metal concentrations by Apler et al. (2019) on the same fiberbank material also supports the hypothesis that some metals in the two fiberbank deposits are strongly adsorbed to organic matter (OM). Results from a porewater characterization by Apler et al. (2019) shows that dissolved Hg and Cd were not quantifiable and that As, Cu, Pb and Zn were below LOQ. These findings are supported by some studies (Hammerschmidt and
showing that TOC strongly bonds Cd, Hg and Pb in sediments. Chakraborty et al. (2015) suggest that marine OM probably has a higher affinity for Hg than terrestrial OM. On the other hand, a lack of quantifiable levels of Hg (and Cd) in pore water and negligible fluxes from the sediment may however partly also be explained by low initial sediment concentrations of Hg (and Cd) compared to other analyzed metals.

Furthermore, estimated sediment-water distribution coefficients ($K_{D}$) for metals (Apler et al., 2019) shows on a high sorption for Pb to the solid phase in Sandvikens fiberbank and on a high sorption for Cr to the solid phase of the Väja fiberbanks. It may thus be a reasonable explanation of the low fluxes of Pb and Cr from fiberbanks of this study. The Pb sorption to solid phases was also found to be higher than for other metals at all sites where it was quantifiable (Apler et al., 2019).
a lack of quantifiable Hg levels in porewaters has also been explained by an observed formation of methyl Hg (Me-Hg). However, it has furthermore been reported that Hg may form the insoluble metacinnabar (HgS) in the presence of S at anoxic conditions.

In normal cases, an introduction of oxygenated waters into aquatic basins will involve the formation of oxyhydroxides of metals that will be re-released to the water column. However, in-situ BFC measurements of fiberbanks shows that this kind of sediments are very reactive. Especially the fiberbank and fiber rich sediment of Väja (FBV and FRV) was very reactive and Sandvikens fiberbank (FBS) was reactive to a moderate degree and this reactivity is due to the high rate of organic matter decomposition that consumes all oxygen, and subsequent anaerobic respiration with methane production. Thus, except for some of the uppermost centimetres this type of organic rich sediment probably will bind the metals in a reduced state.

Out from the results of this study it may thus be suggested that Pb, Hg and Cr are transported particle bound from eroding fiberbanks out to the fiber rich sediment. As an alternative to this pathway for Hg, another study (Wiener et al., 2003) has shown that Me-Hg may be formed at the conditions (anaerobic) prevailing in fiberbanks.

Wiener et al., (2003) suggest that Hg may be transported out of anaerobic sediments like Me-Hg via bacteria and then further through plankton, invertebrates to vegetative fish and predatory fish. In any case, this means that Pb and Cr preferably may be associated with dispersion processes by e.g. re-suspension during sediment erosion (and more seldom by landslides) rather than from diffusion or from bio-uptake in the local environment. Less fluxes with respect to toxic metals than probably may be expected were thus found at the incubations on fiberbanks and fiber rich sediments, and significant differences between observed metal fluxes and model predictions. We thus demonstrate that it is appropriate for risk assessment of contaminated sediments, such as fiberbanks to complement metal concentration data in fiberbanks with in situ flux measurements.

4.2. Metal flux approaches in a risk assessment context

We have shown here that diffusion model-based metal flux predictions, which are constrained solely by pore water concentrations, are 1 to 2 orders of magnitude lower compared to metal fluxes measured in situ. This difference between measured and predicted fluxes was generally prevailing for most comparisons (Table 3). The contradiction between in situ measured and predicted fluxes in this study thus appears to be a rule rather than an exception and differences of a similar magnitude between measured and predicted fluxes from minerogenic sediments have also been observed earlier by Frogren-Kockum et al. (2016). Based on the results from this and earlier studies, model predicted fluxes can underestimate true fluxes, and risk assessment based solely on predicted fluxes may be unrealistic.

5. Conclusions

In this study, we detected benthic fluxes of Co, Mo, Ni and Zn. In contrast to relatively high concentrations in fiberbanks compared to national background levels of Pb, Hg and Cr, benthic flux chamber measurements obtained at both fiberbank deposits and fiber rich sediments showed that Pb, Hg, As and Cd concentrations were below limit of quantification (LOQ) and that the number of data points for Cu and Cr were insufficient for fluxes to be reliably determined. The non-detectable fluxes of Pb and Cr may be explained by some of these metals likely being strongly adsorbed to the solid phases of the fiberbank deposits. The absence of quantifiable Hg concentrations in porewaters may on the other hand likely be explained by formation of Me-Hg in sediments at anoxic conditions.

It may thus be concluded that Co, Mo, Ni and Zn are transported in solution by diffusion and Pb and Cr are transported particle bound from fiberbanks. This conclusion means that only some metals (like Pb and Cr) are associated with re-suspension processes during erosion (including landslides) rather than from diffusion or from bio-uptake in the local environment.

Consequently, there is a large contradiction between total metal contents in fiberbanks and their observed fluxes. Significant differences between measured metal fluxes and model predictions based in diffusion were also found. This study thus demonstrates that it is appropriate to complement total metal content of fiberbanks with in situ benthic flux chamber measurements in the risk assessment of contaminated sediments. This approach creates a better understanding of metal dispersion and its impact on aquatic ecosystems.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2019.110750.

CRediT authorship contribution statement

Paul Frogren-Kockum: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Funding acquisition, Methodology, Writing - original draft, Writing - review & editing.
Mikhail Kononets: Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing - original draft, Writing - review & editing. Anna Apler: Formal analysis, Investigation, Resources, Visualization, Writing - original draft, Writing - review & editing. Per O.J. Hall: Methodology, Resources, Formal analysis, Conceptualization, Supervision, Validation, Writing - review & editing.
Ian Snowball: Investigation, Project administration, Supervision, Funding acquisition, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study is part of the TREASURE project, funded by The Swedish Research Council FORMAS (grant no. 214-2014-63) and co-funded by the Swedish Geological Survey (grant no. 362-1493/2013), the Swedish Geotechnical Institute, Uppsala University, Stockholm University, Lund University and the Center for Marine Environmental Sciences (MARUM) at Bremen University. We thank the head of the SGU department of Marine Environment and Planning (Lovisa Zillen-Snowball), the crew on S/V Ocean Surveyor, all participants in the TREASURE project, and Jim Hedfors at SGU for providing the bathymetric maps.

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