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Metal contaminant fluxes across the sediment water interface

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ABSTRACT

To date, most estimates of contaminant fluxes across the sediment/water interface in risk assessments have been done using diffusive flux models. However, the reliability of these is limited as the overall flux from the sediment may have contributions caused by advection and bioturbation. We found through a comparison of modelled fluxes versus measured fluxes, that the methods Benthic Flux Chamber and surface leaching tests in a risk assessment context showed similar magnitude while calculated fluxes deviated at least by a factor of 100 from measured fluxes. This may be explained by the flux contribution in connection with bioturbation. The chamber-measured fluxes of copper were low compared to those of zinc and cobalt, but this is consistent with leaching tests that indicated copper to be more strongly bound. Risk assessments based on total concentrations may be misleading.

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1. Introduction

Sediment pollution is often considered as an end result of unsustainable anthropogenic activity. However, the sediment itself can become a new source of contamination, even after remediation actions have removed the original causes, giving an increased importance to this component for total flux modeling and environmental assessment. In this connection, it is also important to specify, ideally in quantitative terms, the contributing processes of diffusion and advection.

Meteorology is well recognized for its importance for several kinds of processes at the sediment–water interface (Baudo et al., 1990). Changes in light intensity, temperature, or wind (water movements) near the sediment–water interface may result in rapid changes in the concentration and distribution of oxygen in the surface layer of sediments that will influence on the diffusive part of the total contaminant flux from sediments. Increased water turbulence induced by wind may also alter the boundary layers and thus influence on not only the diffusive transport of contaminant but also the flux component caused by the advection. The thickness of the boundary layer will determine not only the distribution of oxygen but also the distribution of microbial processes responsible for the cycling of elements in sediment and thus influences on the flux component caused by bioturbation.

In the Swedish method for risk assessment of sediment, estimates of contaminant transport across the sediment–water interface have so far been done using diffusive flux models. Diffusive flux models are based on concentration gradients between sediment pore water and overlying water or between pore water concentrations at different sediment depths (Eek et al., 2010). However, large uncertainties exist in using diffusive flux models because the overall fluxes (a sum of diffusion, advection and bioturbation) from sediments might be much greater than diffusion alone. Reliability is also limited by the absence of microelectrodes, which do not exist for most contaminants, which makes it difficult/impossible to spatially resolve existing gradients at the sediment–water interface.

In Sweden, Norway and the Netherlands, pore water analyses are used as a basis to quantify the contaminant transport from sediments to the overlying water column by diffusion (Eek et al., 2010). Very few in-situ methods are presently known to quantify the contaminant transport across the sediment–water interface. The interest in the Benthic Flux Chamber (BFC) method in this risk assessment context is that it measures the total contaminant flux (the sum of flux contribution from diffusion, advection and bioturbation mechanisms) from sediments to the overlying water column with very little disturbance of the sediment and the measurements are not affected by currents or bio-film formation (Pakhomova et al., 2007; Eek et al., 2010). However, the method may have minor influences on the actual fluxes if a reduced effect from bioturbation occurs or due to changes in redox or site-specific hydrodynamic properties. These effects are as yet too difficult to measure or to adjust for in the flux models.

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In USA, the BFC method has been used in a risk assessment context for >15 years, mostly in harbours and coastal areas (Hampton and Chadwik, 2000). A project that the US military has conducted showed that the BFC method is well suited to quantify the mobility and bioavailability of metal contaminants in marine sediments (Hampton and Chadwik, 2000). The study showed that the BFC method could be used for heavy metals such as lead, mercury, chromium, zinc, and copper (Hampton and Chadwik, 2000). The method is now certified for these metals by the California Environmental Protection Agency, EPA (Hampton and Chadwik, 2000). The BFC method has not yet been implemented for metals in a risk assessment context in Netherlands, Norway or Sweden (Sweden has no risk assessment guidance for contaminated sediments) even though the BFC method is used in Norway with respect to organic contaminants (Eek et al., 2010).

The BFC method has been used, for instance, in Norwegian studies to assess how efficient different capping materials like active carbon is compared to clay and crushed limestone as a protection against contaminant transport (Cornelissen et al., 2011, 2012). It turned out that measured fluxes in covered areas were less than measured fluxes in reference areas that were not covered.

The BFC method was also used in flux measurements of iron and manganese and was compared to diffusion calculations (Pakhomova et al., 2007). In the study of Pakhomova et al. (2007) measurements with the BFC method resulted in a significant increase in the identified flux of iron and manganese compared to estimated values. Finally nutrient flux has been extensively studied by the BFC method (Tengberg et al., 2003; Thorbergsdóttir et al., 2004; Thorbergsdóttir and Gíslason, 2004; Eek et al., 2010; Viktorsson et al., 2010).

The study presented in this paper was originally initiated as one part of a government mandate recently given to the Swedish Geotechnical Institute to develop approaches that would increase the rate of remediation of contaminated areas in Sweden. A more effective risk assessment and quantification of contaminant fluxes can contribute to this.

The overall aim of the study is to improve the methodology to quantify contaminant fluxes from sediment to the overlying water mass and thus contribute to an improved risk assessment of contaminated sediments. The objectives are to quantify contaminant transport using the in situ BFC methodology and compare these values to diffusion calculations and surface leaching tests. The comparison is made in order to evaluate the usefulness of these methods in a risk assessment context and to make recommendations regarding these specific methods. We also consider the benthic fauna in our study because previous studies in the field have shown that the activity of benthic fauna is widespread in our study area (Göransson et al., 2013).

1.1. Study site

A suitable case study site in Knähakenhamnen (Knähaken harbour) was found through a literature study of sediment analyses in the Helsingborg coastal monitoring program of contaminated sediments (Göransson et al., 2013). Helsingborg is situated by the Kattegat Sea, SW Sweden.

Knähaken harbour is located in the "Industry park of Sweden, IPOS" owned by the Kemira industry group. The chemical industry was started in the area in 1872 by the production of fertilizers and subsequently by the production of sulphuric acid. Copper containing pyrite was used as a raw material for the sulfuric acid and in order to utilize the copper content a copper enrichment plant also was built in 1902. This industry was the reason that the bulk harbour (earlier kopparverkshamnen), nearby the Knähaken harbour study site, was constructed (Fig. 1). Today the Kemira group companies produce sulfuric acid, hydrochloric acid and hydrogen peroxide.

Helsingborg coastal monitoring program of contaminated sediments has been ongoing since 1995. In the monitoring program samples are analysed for metals in sediment from both harbour and industrial areas and also along a gradient from the mouth of the river Råån out into the sea. At the sampling station KED in the Knähaken harbour (Fig. 1) elevated concentrations of Zn, Co and Cu have been detected. The source of pollution has not been localised but may originate not only from a storm water drainage pipe that leads surface water in to the harbour from IPOS but also from large areas of the southern Helsingborg City. A landfill with polluted gypsum is also situated close by the harbour that also may be a source for contaminants in the sediment.

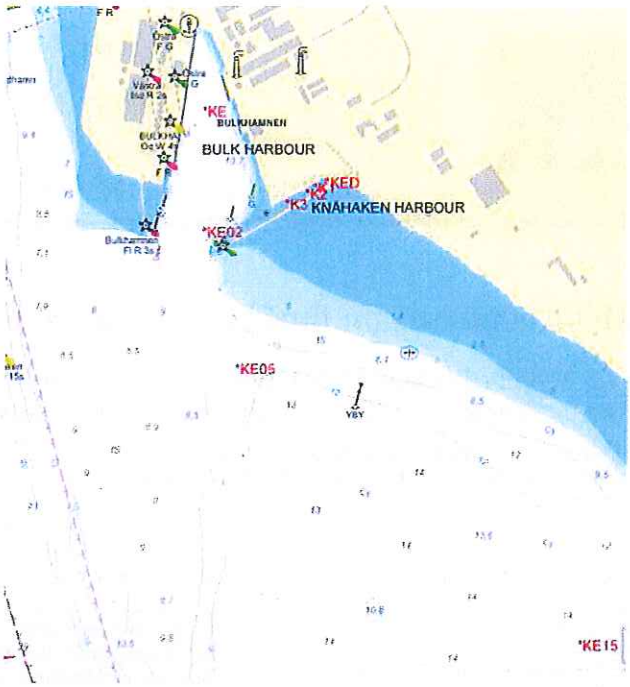

Fig. 1. The figure shows the approximate location of the sampling stations in Knähaken harbour, Helsingborg, Sweden with the sampling site KED innermost in the harbour and closest to the surface water pipe outlet (storm water), sampling stations K1, K2 and K3 are successively further out in the Knähaken harbour.

The high total metal contents found in the sediment samples from KED made it possible to test if contaminant fluxes measured with the benthic flux chamber method, BFC (Hampton and Chadwik, 2000) would differ compared to diffusion calculations based on pore water analysis (Li and Gregory, 1974; Awakura et al., 1989) and surface leaching tests based on sediment samples (NEN 7347).

The sampling campaign of this study in Knähaken harbor was done during the summer and autumn of 2013, complemented by additional BFC measurements in the autumn 2015.

2. Methods

To get a general understanding of the natural hydrographic variability at the study site continuous measurements were made for 28 days (September 2–30, 2013) using two instruments (assigned no. 42 and no. 169) Aanderaa RCM9 multi-sensor instruments (Tengberg et al., 2001, 2003) placed at stations KED and K1 (Fig. 1). Parameters presented here include dissolved oxygen, current speed, temperature and turbidity (particles), which were correlated with precipitation data from the Swedish Meteorological and Hydrological Institute (SMHI), gauging stations *Helsingborg A* and *Lund sol*. Instrument no. 169 was placed close to the storm water drainage pipe in the sampling station KED and instrument no. 42 was placed close to the K2 sample station (Fig. 1).

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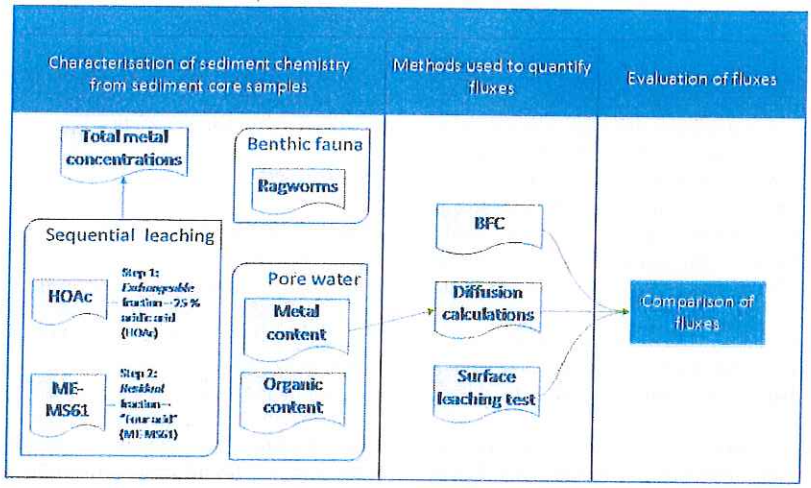

Fig. 2. An overview of the study divided in three different steps: characterization, quantification of fluxes by three different methods and comparison of fluxes. HOAc = leaching by acetic acid, MS-ME61 = leaching by the "Four Acids" method ME-MS61. It is a mixture of several strong acids such as perchloric acid ($HClO_4$), nitric acid (HNO3), hydrofluoric acid (HF) and hydrochloric acid (HCl).

A workflow for the present study is presented in Fig. 2 and contains the following steps:

(1) Sediment characterization.
(2) Quantification of the fluxes using three different methods: a diffusion calculation method, an in situ method (the benthic flux chamber method) and a surface leaching test.
(3) The results are evaluated comparing different element flux.

Since Zn, Co and Cu previously have been detected in elevated concentrations at the site, this study has focused on those three metals.

The geochemical characterization in step (1) was done using ICP measurements of total metal concentration in the sediment, extracted metals using a sequential leaching test (UNEP/IOC/IAEA, 1995) to test leachability, and the metal concentrations in pore water. Total concentration in sediments provides an inventory of the pollutants present in the sediment, but not how strongly they are bounded with mineral particles and organic substances. Sequential leaching thus provides complementary information on how different pollutants are bounded in the sediment, which can often be related to different associations (in minerals, on mineral surfaces or bounded to an organic fraction). These two methods together thus made it possible to evaluate the proportion of the total content that can potentially be spread and become bioavailable.

Sediment pore water was analysed to give information on the actual amount of metals that are available in the pore water and that immediately can be transported out of the sediment. In step (2), three different methods are used in order to quantify the metal transport out of the sediment: a) a diffusion model (Li and Gregory, 1974; Awakura et al., 1989), b) a sediment surface leaching test in the laboratory (NEN 7347), which tries to simulate what happens in reality, and c) an in situ method (BFC) that measures what happens in reality (Thorbergsdóttir and Gíslason, 2004; Thorbergsdóttir et al., 2004). In step (3) the metal fluxes are compared (concentration per surface unit and unit of time) measured and calculated from the three different methods.

2.1. Sediment sampling and characterization

Sediment cores were taken at the sampling stations (Fig. 1) using a Haps-corer (Kanneworff and Nicolaisen, 1973), which is a tube sampler that routinely has been used in the Helsingborg coastal monitoring program for about 20 years (Göransson et al., 2013). When studying the redox profile of earlier cores close to the Knähaken harbour (Helsingborg coastal monitoring program) it was noted that only the uppermost 2–5 cm is oxygenated and that the rest of the sediment is reduced (anoxic). Therefore, sediment subsamples were taken from the sediment core with 5 cm intervals: 0–5 cm, 5–10 cm and 10–15 cm. The choice of 5 cm sections was also necessary to ensure sufficient pore water for pore water analyzes.

2.2. Pore water analysis

Sediment samples from the Haps-corer were homogenized and divided into acid-cleaned centrifuge tubes of 50 ml. Samples were centrifuged at 20,000 *g* (*g*: standard gravity) for about 30 min, then the extruded pore water was decanted and combined into one sample. The material was weighed before centrifugation and after the pore water had been decanted off. A subset of pore water samples was filtered through 0.45 μm cellulose acetate filter and then analyzed for metals and anions. Pore water was also analyzed for TOC (total organic carbon) and TIC (total inorganic carbon) before the pore water had been filtered.

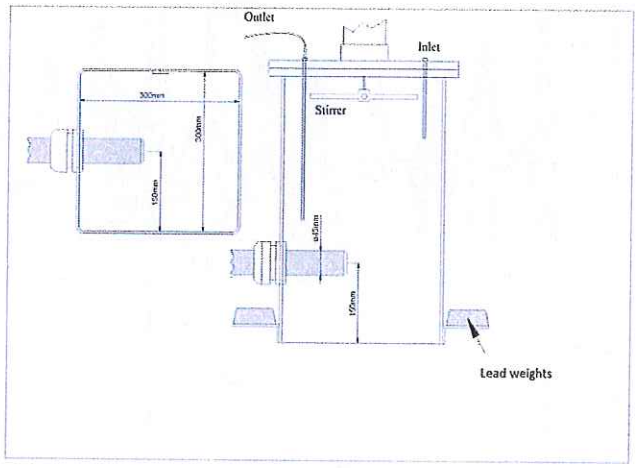

Fig. 3. A schematic drawing of a Benthic flux chamber with a stirrer, lead weights and a probe to measure pH, redox, oxygen and conductivity. The chamber has the dimensions 30 × 30 × 50 cm and is open in the bottom to allow transport of pollutants into it. Samples are taken from the outlet and the inlet is during sampling open to the surrounded sea water to compensate for the lost volume of water.

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2.3. Sequential leaching

The sequential leaching was performed according to UNEP/IOC/IAEA (1995). This method includes an initial leaching step with a 25% acetic acid (fraction 1), followed by a combined leaching step (fraction 2) on the same sediment subsample using the ME-MS61 ("*four acid*") leaching method (ALS Global, 2014). Fraction 1 consists not only of exchangeable metals but also of the less readily exchangeable metals that are organically bound and/or carbonate-bound (Rao et al., 2008). The acetic acid used in this step does thus not affect silicates or iron and manganese minerals (UNEP/IOC/IAEA, 1995). Fraction 2 consists of the more strongly bound metals released with the "*four acids*" method ME-MS61 (ALS Global, 2014). The "*four acids*" method ME-MS61 is a mixture of several strong acids such as perchloric acid ($HClO_4$), nitric acid (HNO_3), hydrofluoric acid (HF) and hydrochloric acid (HCl) (ALS Global, 2014).

These acids release virtually all metals in the sample because the majority of silicates and iron and manganese minerals are dissolved (Rao et al., 2008; ALS Global, 2014).

2.4. Diffusion calculations

In order to estimate the transport of contaminants in the dissolved phase from the sediment the diffusive flux of cobalt and zinc has been calculated by applying Fick's first law:

$$J = -D\,\delta C/\delta x \quad (1)$$

where J = diffusive flux, D = diffusion coefficient and $\delta C/\delta x$ = concentration gradient.

Diffusion coefficients for specific ions, e.g. cobalt (II), are available from the literature (Ullman and Aller, 1982). These coefficients are, when adjusted for temperature and pressure in aqueous solutions, in the range 10^{-5}–10^{-6} $cm^2\ s^{-1}$.

In natural systems, ions and metals are transported to a varying degree bound to organic or inorganic ions or complexes. Coefficients for these complexes are unknown and are therefore difficult to calculate or to estimate. This means that the diffusion coefficients used in these calculations, which have been determined in laboratory experiments

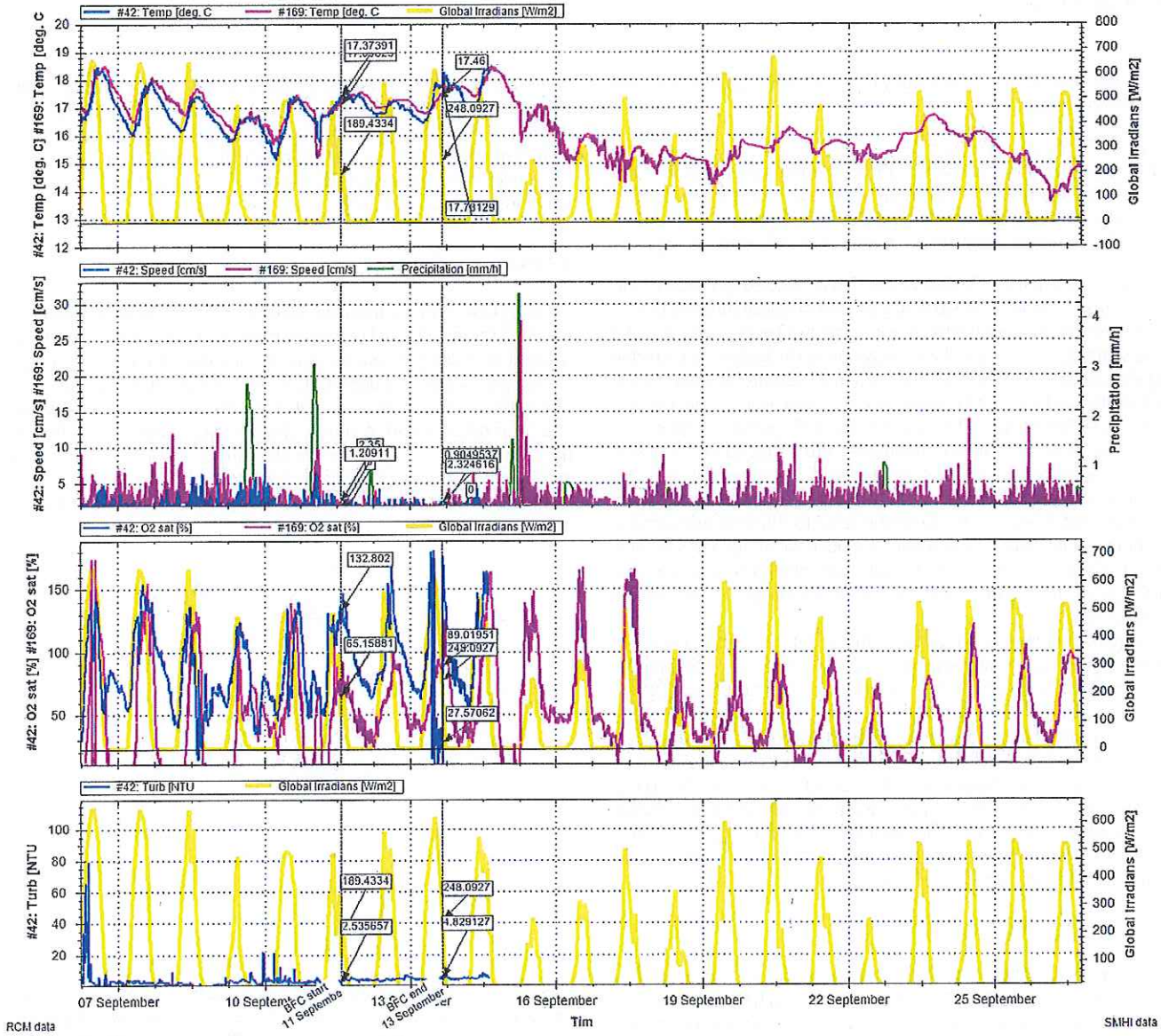

Fig. 4. Sensor data from instrument 42 and 169 for temperature, water discharge (speed), precipitation, irradience, oxygen content and turbidity.

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(Ribeiro et al., 2002) in pure solutions (often at higher concentrations than in the natural environment), will not be entirely relevant in a natural environment. But this modeling is as close as we can currently approximate in a simulation of natural conditions.

In the diffusion calculations a correction must also be introduced to account for the non-linear transport distance due to the sediment porosity structure. A tortuosity of 1.3 and a porosity of 0.7 have therefore been adopted.

2.5. Surface leaching tests

The method SIS-CEN/TS 16637-2 is used for surface leaching tests of inorganic substances from materials with fine particles, such as silt, and where diffusion largely controls the transport of leached substances from the sediment. The material is packed in a cylinder, which is then placed in a larger cylinder of water. A pre-determined amount of water is added and this volume is replaced after fixed time intervals. During surface leaching the sample is leached in the cylinder with water. The water does not flow through the sample, but rather leaching occurs by diffusion from the sample surface. The regular replacement of water above the sediment during the test is to avoid equilibrium conditions that would dampen diffusion. The leachate is analyzed for the ions of interest.

In this study a deviation from the standard-method SIS-CEN/TS 16637-2 was made so that the same polyethylene (PE) pipes used for sampling the sediment later were used as test cylinders. The tube was cut off to two cylinders that were glued to a base plate. This deviation from the standard method provided undisturbed samples with their original layering, structure and composition. Since the pore water analyzes from different sections in the sediment evidenced a clear ion concentration gradient, it was important to test undisturbed samples if possible. Furthermore, this adaption made the SIS-CEN/TS 16637-2 surface leaching more comparable with in situ (natural) conditions and more relevant as a comparison method to the BFC method in this project.

2.6. Benthic flux chamber measurements

Direct sampling of element flux is done with a benthic flux chamber deployed on the sea floor (Fig. 3). It is a closed system except at the sediment–water interface since the chamber is open in the bottom. At given times after the flux chamber (squared 30 × 30 cm, 50 cm overlying water) is deployed on the seafloor, the contaminant transport into the flux chamber and thus the accumulation of contaminants in the chamber water is measured by taking out samples from chamber.

The chamber also has a stirrer for mixing the water-mass (homogenising) and a source of power for the stirrer. As the engine to the stirrer was considered unreliable an alternative water circulation system for mixing of the water mass in the chamber was used. The inlet and the outlet were connected together by the peristaltic pump to create a flow in order to avoid the building of concentration barriers.

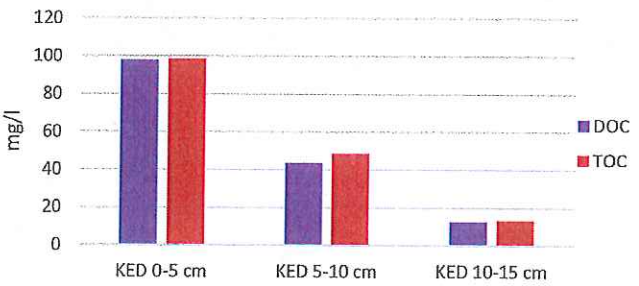

Fig. 5. Organic carbon in sediment pore water, at three depth intervals, sample station KED. The organic carbon content decreases with depth in KED, as in the other analyzed sediment core K1 in Knähaken harbour.

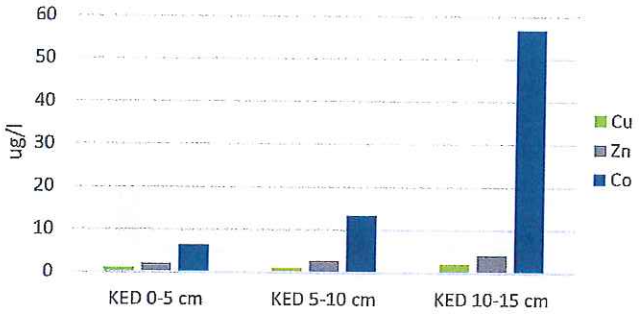

Fig. 6. Metal content in sediment pore water at three depth intervals, sample station KED. The metals Cu, Zn and Co increase with depth in KED, as they do at K1 in Knähaken harbour.

Water samples were pumped to the surface by a peristaltic pump by using a tube that was connected to the outlet (Fig. 3.) The total water volume for all samples together that was taken out from the chamber was less than 1% of the total water volume in the BFC. Corrections for the total sample volume were therefore not considered necessary. The samples were geochemically analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Gas Chromatography–Mass Spectrometry (GC–MS) to determine the different types of contaminants and their concentrations above the sediment per unit area and time.

An entrance to the chamber was also made for a probe containing electrodes for measuring pH, redox, oxygen and electrical conductivity. A frame with lead weights was coupled to the chamber so that it would stand firmly on the sediment to ensure there is no leakage in submerged conditions at the bottom.

2.7. Sampling and analysis of benthic fauna

Benthic fauna was also sampled with the Haps-corer (Kanneworff and Nicolaisen, 1973) at the sampling station: KED = 5 m, K1 = 30 m, K2 = 60 m and K3 = 120 m. Ten replicate samples were taken on each station in a water depth of about 1 m. Samples were sieved through a 1.0 mm sieve and preserved in 96% ethanol before analysis. In the laboratory all specimens were identified to the lowest possible taxon, enumerated and wet weight biomass was determined.

Bioaccumulation of metals was examined in common ragworms *Hediste diversicolor* (Müller, 1776) from the four relatively contaminated stations in the Knähaken harbour and at a distant relatively uncontaminated control site (Skälderviken W, 56° 13,175′N, 12° 46,731′E) with about the same depth and environmental conditions. On each

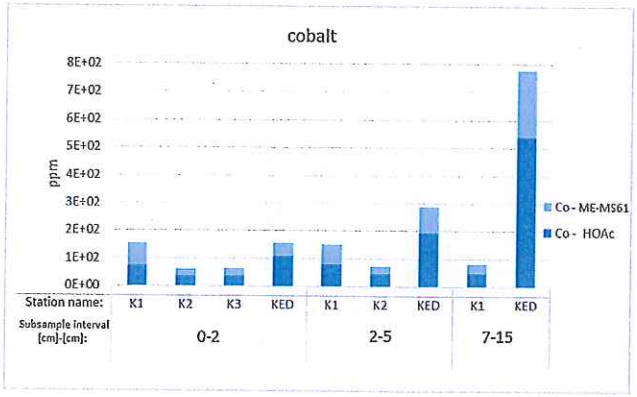

Fig. 7. Sequential leaching of cobalt for each station, grouped by depth intervals. HOAc is acetic acid leaching and MS ME61 is the residual concentration leached with several strong acids such as perchloric acid ($HClO_4$), nitric acid (HNO_3), hydrofluoric acid (HF) and hydrochloric acid (HCl). The combined bar height represents the total leached content.

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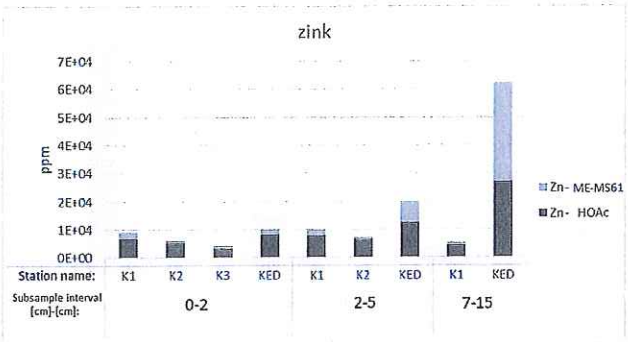

Fig. 8. Sequential leaching of zinc for each station, grouped by depth intervals. HOAc is acetic acid leaching and MS ME61 is the residual concentration leached with several strong acids such as perchloric acid ($HClO_4$), nitric acid (HNO_3), hydrofluoric acid (HF) and hydrochloric acid (HCl). The combined bar height represents the total leached content.

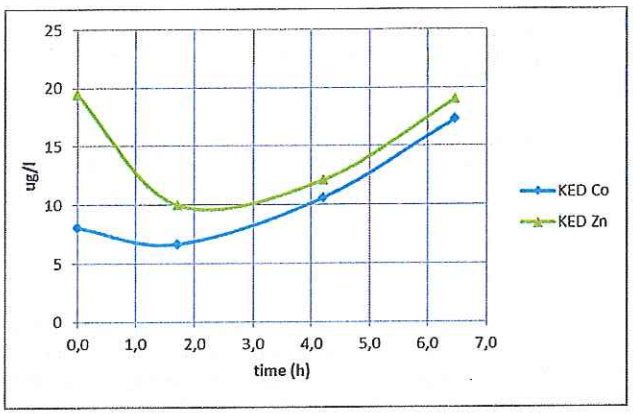

Fig. 10. Changes in concentrations of Co, and Zn with time in the benthic flux chamber during the incubation in the sampling station KED during September 2013.

station 10–17 specimens (2.3–6.7 g) of the polychaete were collected and stored frozen at −20 °C until analysis. Analysis of As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb and Zn was performed according to Swedish standards by Biological Institution, University of Lund. Superficial (0–2 cm) sediment was also sampled at the control site and analyzed for organic content (loss on ignition) and the same metals as in ragworms.

3. Results and discussion

We successfully retrieved the continuously logged data from the Aanderaa RCM9 multi-sensor (no 42 and no 169) as shown in Fig. 4. These data from the autumn of 2013 were plotted with the SMHI meteorological datasets shown in Fig. 4. Water current speeds seem to correlate well with the "*Helsingborg A*" precipitation dataset, which only has three peaks. These peaks can also be seen in the sensor 169 data, but are less clear in the sensor 42 series, which is located further away from the discharge pipe. There are also smaller peaks in the sensor 169 that are not present in the precipitation dataset, which are interpreted chiefly as water current changes induced by the local wind regime. The section between the two black dotted vertical lines marks sampling period for both incubation K1 and KED. Fig. 4 shows that oxygen levels were daily regenerated and that precipitation was intense before and after the BFC field sampling campaign. The elevated precipitation and the discharge as seen before the field campaign (initiated at the 11th of September 2013) are processes in the harbour that will help to dilute any contaminants that stagnant water in the harbour may contain. However, in contrast fresh water also promotes the diffusion gradient, which is a mechanism for contaminant fluxes out of the sediment and which counteracts the dilutive effect of the discharge from the storm water pipe.

There is a distinct positive correlation between periodic variations in oxygen saturation and temperature and the trends in the global irradiance dataset at the meteorological SMHI station "*Lund A*". It is clearly so that during sunny days this shallow site is heated by 1–2 °C, slowing as light intensity decreases toward the end of September. Due to technical difficulties the sonde data, which measured oxygen and temperature inside the BFC chamber, had to be recorded manually. This was done in conjunction with deployment of the chamber and with each following water sample extraction. This data do correspond well with the continuous measurements from sensor 42, and thus the oxygen saturation in the BFC was above 80% during sampling. Temperatures inside the chamber also closely match the corresponding measurements from the sensor 42 dataset. The RCM9 sensor data are useful as it shows the strong correlation between oxygen saturation levels and insolation. This indicates the importance of primary production in the system during day time as well as the high respiration that consumes the oxygen during night time. During the whole campaign, the oxygen saturation at both sensors often exceeded 150% at midday. During the days for water sampling the oxygen levels were generally highest at sensor 42. At sensor 169, all oxygen is frequently consumed during the night declining to 0% saturation. The differences in the data between sensor 42 and 169

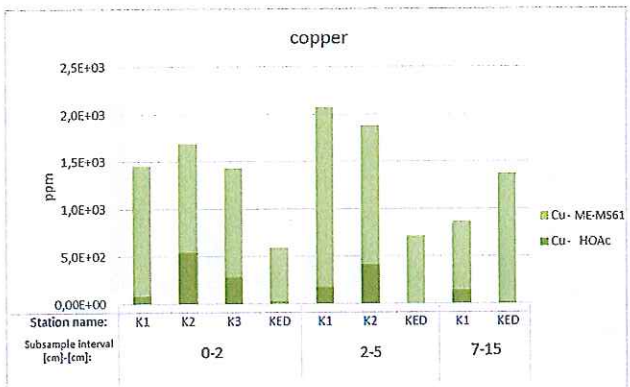

Fig. 9. Sequential leaching of copper for each station, grouped by depth intervals. HOAc is acetic acid leaching and MS ME61 is the residual concentration leached with several strong acids such as perchloric acid ($HClO_4$), nitric acid (HNO_3), hydrofluoric acid (HF) and hydrochloric acid (HCl). The combined bar height represents the total leached content.

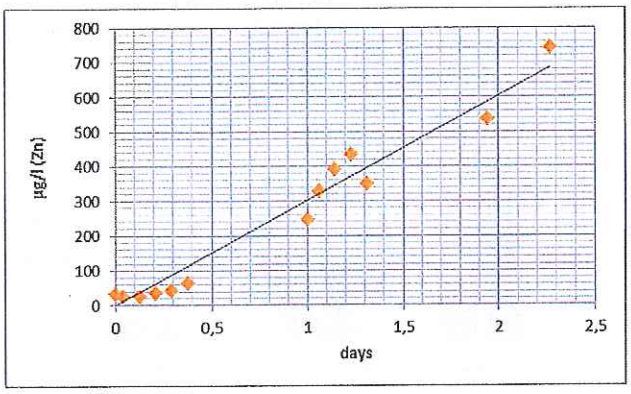

Fig. 11. Incubation in the KED station during September 2015. Changes in Zn concentrations in the flux chamber that shows a linear increasing trend with time.

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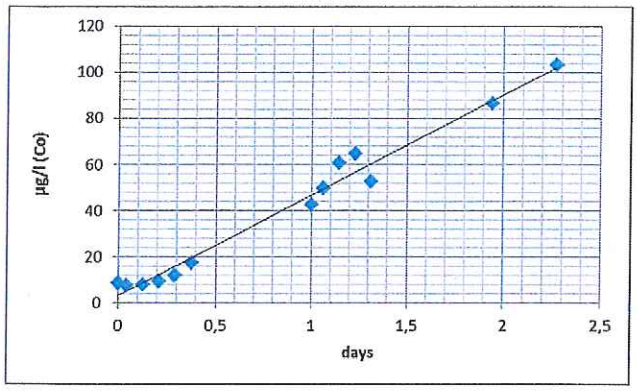

Fig. 12. Incubation in the KED station during September 2015. Changes in Co concentrations in the flux chamber that shows a linear increasing trend with time.

could be explained by the distance from the storm water outlet. Near the outlet there water speeds were often twice as high, as seen in Fig. 4. Higher energy with consequently higher turbidity as well as a more direct influx of nutrients from the outlet could possibly reduce light insolation during the daytime near the outlet and also allow for greater respiration activity during nighttime. This turbulence is consistent with the lack of visibility to the seafloor with less than 2 m depth near the outlet noted in the field.

3.1. Sediment characterization

Our modification of method SIS-CEN/TS 16637–2 to maintain undisturbed sediment layering for surface leaching tests improves the comparison with other methods (see Methods above). This is supported by the results from previous sediment analyses done within the Helsingborg coastal monitoring program (Göransson et al., 2013), where the redox profiles of the sediment in the sampling locations closest to the KED sampling station show that oxygenated conditions prevail in the uppermost 2–5 cm and reduced (anoxic) conditions below that in the rest of the core.

Our results also document that the organic content decreases with depth (Fig. 5) and that metal content increases in the pore water of the deeper samples (Fig. 6).

3.2. Sequential leaching

It is clear from the histograms (Figs. 7–9) that a relatively lower amount of copper, compared with cobalt and zinc, is released in the sequential leaching step with acetic acid (*HOAc*). It was not possible to detect any general trend in terms of fractionation with depth in the sediment between different stations. As shown in Figs. 7–9 copper is usually strongly bound in the sediment, while zinc and cobalt occur as both strongly and loosely bound.

The results highlight the inappropriateness of using total concentrations alone for risk assessment of sediments. A classification based on total concentration can however be used as a screening for hot spots as in the first step (*Trinn.*, 1) in the Norwegian National Guidelines for Risk Assessment of Contaminated Sediments (Klif, 2011). The inappropriateness of basing a risk assessment only on total concentrations is shown by the comparison between total concentrations, pore water analysis, surface leaching tests and the BFC measurements of this study. The study shows that a risk assessment based only on total concentrations would suggest that the risk of spreading copper is greater than the dispersion of cobalt because its total concentration is greater in the sediment. A risk assessment based on total concentrations would thus have been misleading. As can be seen by relative fluxes of these metals derived from the BFC chamber measurements and with surface leaching tests cobalt fluxes dominates over copper and zinc fluxes. Even pore water analyses illustrate the inadequacy of using total concentrations as a basis for a risk assessment, as the cobalt content dominates over both zinc and the copper content in the pore water, contradicting the trend in total concentrations.

3.3. Benthic Flux Chamber measurements

Flux chamber measurements were done in station KED and K1 during 2013 (Fig. 10). After initially relative high concentration of Co and Zn in the first sample of the KED incubation the results showed a gradually increasing trend for both Zn and Co that enabled calculations of fluxes. The incubations and flux chamber measurements in KED and K1 during September 2013 showed that data was too poor to confirm an expected increasing trend in the chamber. In addition problems with the stirring occurred during the incubations of 2013. We thus hoped to confirm the observed trend of 2013 with gradually increasing Zn and Co concentrations in the chamber with additional sampling and measurements in 2015. As expected the incubations in 2015 (Figs. 11–12) confirmed the indication that incubations in 2013 were too short (about 6 h). The longer incubations in 2015 also confirmed the earlier obtained trend with increasing concentrations for both Zn and Co in the chamber (Figs. 11–12) but showed also a similar anomaly with a relatively high initial concentration in the first sample. The reason for a high initial concentration was at first hard to explain from the results of the 2013 incubation. The phenomenon was, however, observed to be method-specific as it is a regular occurring anomaly also for the contaminants Zn and Co in the incubations of 2015. The high initial concentration of the first sample seems to be connected with the deployment of the chamber and may be an effect of resuspension of the sediment (Almroth et al., 2009), resulting in an increased number of mineral particles and organic matter in the water body of the chamber. This suspension process may have temporary allowed desorption of metals from particle surfaces or organic matter, a disturbed equilibrium between solids and solution due to the chamber deployment.

A comparison of contaminant fluxes between BFC measurements, diffusion calculations and surface leaching tests shows that fluxes from BFC measurements and surface leaching tests are similar in magnitude while fluxes estimated by diffusion calculations deviate significantly from the others (Table 1). Diffusive fluxes are much lower than the measured values by the BFC and surface leaching tests, which

Table 1
Comparison of contaminant fluxes between Benthic Flux Chamber (BFC) measurements, diffusion calculations and surface leaching tests.

Sampling location	Flux measured by benthic flux chamber	Calculated flux	Flux measured by surface leaching test in deionized water	Flux measured by surface leaching test in marine water
	(mol/m^2/day)	(mol/m^2/day)	(mol/m^2/day)	(mol/m^2/day)
KED-Zn	$1.5–6.3 \times 10^{-4}$	–	–	–
KED-Co	$3.2–6.0 \times 10^{-4}$		–	–
KED-Cu	–	–	–	–
K1-Zn	2.3×10^{-5}–3.5×10^{-4}	2.1×10^{-7}	3.7×10^{-4}	–
K1-Co	2.7×10^{-5}	2.8×10^{-7}	8.3×10^{-5}	8.03×10^{-5}
K1-Cu	–		7.7×10^{-5}	–

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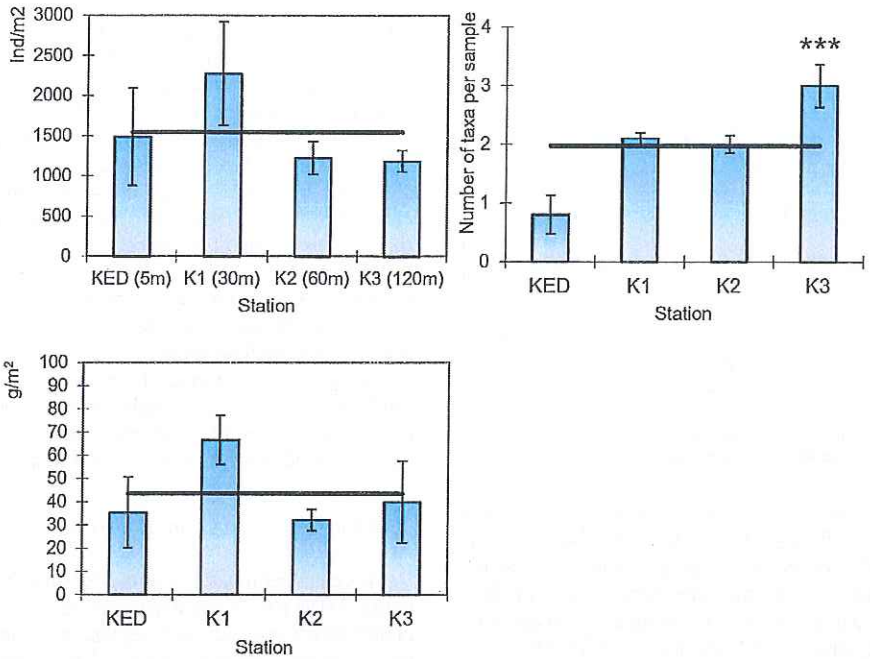

Fig. 13. Abundance (ind/m^2), number of taxa per sample and biomass (g/m^2) at four stations at different distances from an outlet into Knähaken harbour 2013. Mean values and standard deviation. Horizontal line indicates the mean for all stations. *** = $p < 0.001$, ANOVA, Holm–Sidak method.

would mean that only diffusive fluxes highly underestimate the pollutant spreading. Differences between calculated and measured values have also been observed in previous studies. For instance, Pakhomova et al. (2007) made BFC measurements of iron and manganese fluxes, and found that they were significantly greater than calculated fluxes.

It was not possible to avoid redox changes in the sediment when sampling the pore water (that diffusion calculations are based on) since we had to dividing the sediment into centrifuge tubes of 50 ml. Thus, the pore-water speciation may be somewhat different from the one in the original sediment that may have influenced on the pore water chemistry. However, the metals studied are not redox sensitive so redox may in this case only have a minor influence on the solubility of these metals in pore water chemistry (that diffusion calculations was based on).

3.4. Metal concentration in benthic fauna and sediment

Despite large variation within stations there are a significantly greater number of taxa (ANOVA, *Holm–Sidak* method) at the station K3, most distant from the outlet into the Knähaken harbour (Fig. 13) and there is a tendency of a gradual increase. However, there is no such difference when it comes to abundance and biomass.

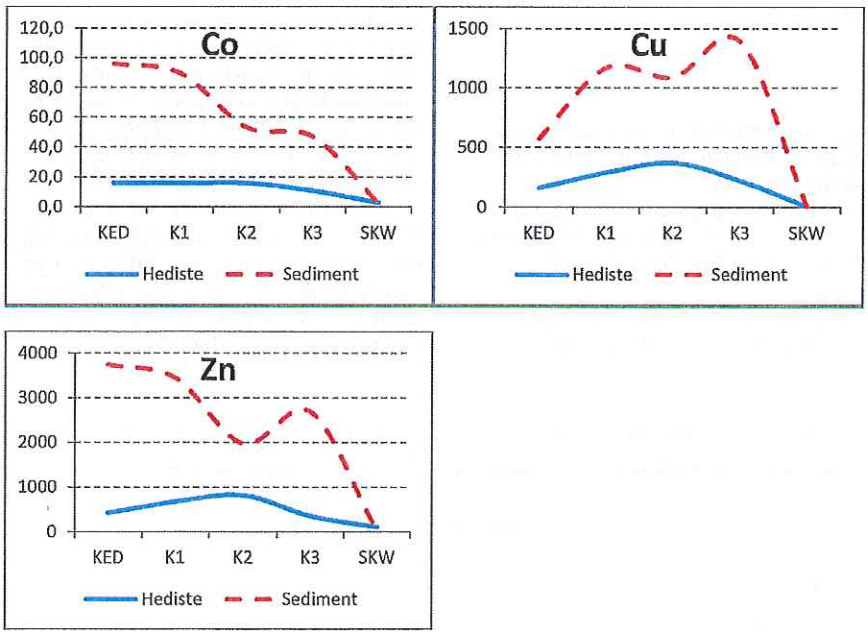

Fig. 14. Concentrations of metals in *Hediste diversicolor* and sediment (mg/kg DW) at four stations in the Knähaken harbour and at a control site (SKW) 2013.

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Concentrations of metals in *H. diversicolor* and in the sediments show generally the same pattern with distance to the outlet in the Knähaken harbour (Fig. 14). The lowest concentration was measured at the very distant control site and highest concentration was measured about 60 m from the outlet into the Knähaken harbour, with the exception of cobalt which shows maximum concentrations adjacent to the outlet. Concentrations of cobalt were also clearly decreasing with distance to the outlet and there is a statistically significant trend in decreasing concentration of cobalt in *H. diversicolor* with distance from the outlet in the Knähaken harbour (linear regression, $r^2 = 0.852$, $p = 0.025$).

Concentration in sediments and *H. diversicolor* reached a peak for most elements at stations K2 and K3, 60–120 m from the outlet into the harbour. There were statistically significant correlations between concentrations in *H. diversicolor* and sediment for cobalt (Pearson correlation, $k = 0.905$, $p = 0.034$) and lead (Pearson correlation, $k = 0.921$, $p = 0.026$).

Concentrations of metals in *H. diversicolor* were generally lower than in sediment from the same station. Differences were clearly greatest in highest concentrations of sediment.

The common ragworm *H. diversicolor* builds Y- or U-shaped burrows in soft sediments which increase the sediment–water interface. When they ventilate their burrows, individuals verticalize oxic zones into the sediment and promote microbial and meiofaunal growth alongside their burrows (Scaps, 2002). Not only this activity, but also feeding and excretion, could also lead to exchange of many substances between sediment and water. The difference between measured fluxes of metals from sediment and calculated diffusion in this study could probably largely depend on bioturbation of *H. diversicolor* in the sediment. This has been shown not only for another polychaete, *Marenzelleria neglecta*, which is also very active in the sediment (Granberg et al., 2008), but also for bivalves and small amphipods (Hedman et al., 2008).

4. Conclusions

When comparing contaminant fluxes measured and modelled with different methods, this study shows that fluxes that are measured with the benthic flux chamber and surface leaching tests are similar in magnitude while modelled fluxes differ from the others. Modelled fluxes deviate at least by a factor of 100 from benthic flux chamber measurements. On the other hand, surface leaching tests give similar results as benthic flux chamber measurements. We suggest that this means that modelled fluxes underestimate contaminant transport from sediments. Some difference between measured fluxes of metals from sediment and calculated diffusion in this study might depend on bioturbation of *H. diversicolor* in the sediment. Statistically significant correlations between Co concentrations in *H. diversicolor* and sediment were also found, but not for Zn and Cu.

Based on the results from this study, modelled fluxes might underestimate the contaminant spreading from the sediment. The total metal analysis compared to the sequential leaching results also indicates that it is not recommended to base a risk assessment only on total concentrations in sediments. Although the total Cu content was high in the sediment, the sequential leaching shows that Cu is mainly strongly bound in the sediment, which also explains why fluxes of Cu from the sediment were low. However, total analysis of metals may be used for screening of contaminants in sediments to get a first opinion as to where hotspots are.

From the results of this study we recommend that the Benthic Flux Chamber be used together with a surface leaching test since the surface leaching test will mainly reflect the diffusive transport and bioturbation component while the Benthic flux chamber will include contributions from diffusion, bioturbation and advection processes. Risk assessment therefore needs to jointly consider these aspects.

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