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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.

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.

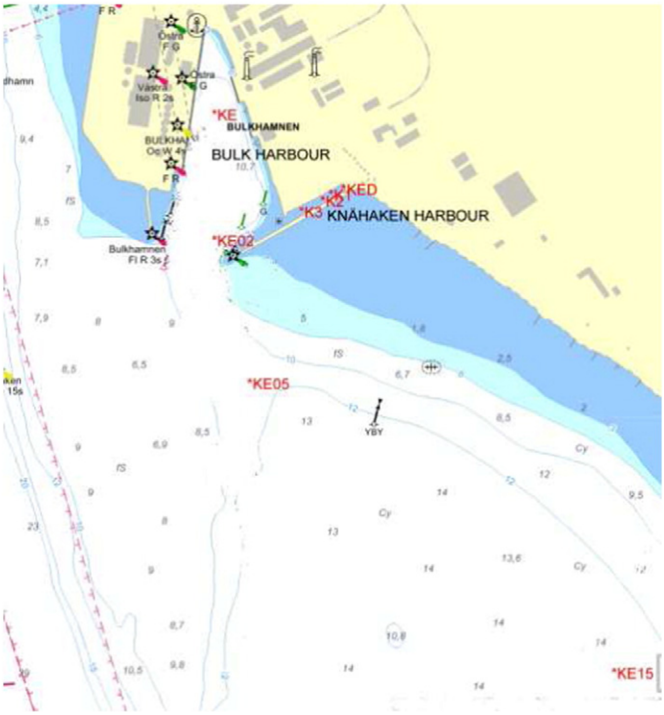

Fig. 1. The figure shows the approximate location of the sampling stations in Knähaken harbour, Helsingborg, Sweden with the sampling site KED innermost in the harbour and closest to the surface water pipe outlet (storm water), sampling stations K1, K2 and K3 are successively further out in the Knähaken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

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.

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).