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Potential release of selected trace elements (As, Cd, Cu, Mn, Pb and Zn) from sediments in Cam River-mouth (Vietnam) under influence of pH and oxidation

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HIGHLIGHTS

- ► Release of almost all heavy metals is slower from the oxidized sediment.
- ► Leachability of almost all heavy metals decreases at studied pHs after oxidation.
- ► Change in heavy-metal speciation is consistent with the changed leachability.
- ► Sulfides only play a minor role in retaining heavy metals in the studied sediments.

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ABSTRACT

Since contaminated river-bed sediments in the Cam River-mouth (Vietnam) are regularly dredged and disposed on land, an understanding of the influence of time, pH and oxidation on the leaching behavior of heavy metals (Cd, Cu, Mn, Pb and Zn) and arsenic is necessary for the management of these dredged materials. A 96 h pH_{stat}-leaching test to examine the leaching behavior of elements at pre-set pH values (2, 4, 6, 8 (natural), 9 and 11) and a BCR 3-step extraction to clarify the element fractionation, were performed on a freshly-collected wet suboxic sediment and a dry oxidized sediment. All heavy metals and arsenic display a V-shaped pH-dependent leaching pattern with important releases at pHs 2 and 11. At the investigated pH values, the release of As, Mn, Pb and Zn from the oxidized sediment is slower and lower if compared with the suboxic sediment while the opposite trend is found for Cd and Cu at pHs 2–8. The transfer from the acid-soluble (exchangeable and carbonate-bound) fraction to the reducible (Fe and Mn hydr/oxide-bound) fraction is consistent with the lower leachability of As, Mn and Zn at pHs 2–8 and Pb at pHs 4–8 after oxidation, while the transfer from the oxidizable (organic matter and sulfide-bound) fraction to the reducible fraction relates to the higher leachability of Cd and Cu at pHs 2–8. The lower leachability of all elements at alkaline pHs 9–11 is due to lower leached concentration of organic matter from the oxidized sediment. Sulfides only play a minor role in controlling the leachability of heavy metals and arsenic.

1. Introduction

Cam River is one of the tributaries of the Red River system which plays an important role in socio-economic activities in Northern Vietnam. Over a 20 km length of the Cam River-mouth, the Haiphong Harbor, which is one of the most important harbors for international and national trade in Northern Vietnam, is situated. Moreover, a large industrial zone of Haiphong City is also located along this river-mouth. According to Nguyen and Luu (2004), estimated amounts of 52.6 t of Cu, 20.2 t of Pb, 382 t of Zn, 27.9 t of As and 2.0 t of Cd from Haiphong City are discharged into the Cam River-mouth every year. At present, dredging activities are regularly carried out to maintain the depth for navigation, which as a consequence implies huge amounts of contaminated sediments to be disposed on surrounding paddy fields and landfills. However, a particular strategy for the disposal of dredged sediments requires a comprehensive prediction of its future potential adverse effects. The risks associated with the presence of potentially hazardous elements in dredged sediments are determined by their 'mobile' and 'available' concentrations rather than their total content (Dijkstra et al., 2006; Cappuyns and Swennen, 2008). Therefore, mid- and long-term trends in the mobility of metals under different environmental conditions need to be investigated (Singh et al., 1998; Prica et al., 2010).

With respect to the potential release of heavy metals and arsenic from dredged sediments, changes of redox potential and pH conditions

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are of prime importance. The pH is an important factor controlling the behavior of heavy metals and arsenic in sediments through precipitation/dissolution and adsorption/desorption processes. A change in pH causes an increase or decrease in solubility of sediment-associated heavy metals and arsenic since the strength of metal-binding by organic matter, clay minerals and Al/Fe/Mn hydr/oxides is closely related to pH (Forstner et al., 1994; Tipping et al., 2003). Therefore, the pH_{stat} leaching test (CEN/TS 14429 test) established by the European Committee of Standardization is an important tool in the evaluation of the leachability of elements at different pH values and may be used in the assessment of contaminant release in the long-term perspective. A pH_{stat} test allows assessing how the solubility changes if in situ pH changes occur (Dijkstra et al., 2006; Cappuyns and Swennen, 2008).

Upon on-land disposal, dredged sediments are subjected to oxidation, and the subsequent (bio)chemical reactions affect the mobility of heavy metals and arsenic. Oxidation of organic matter and sulfides occurs as the material comes into contact with atmospheric oxygen, which results in a release of protons. This often causes a decrease in pH, the dissolution of calcium carbonates and other buffering components if present in sediments, which can also release heavy metals and arsenic to porewater (Singh et al., 1998; Cook and Parker, 2003). However, their mobility can be mitigated by the adsorption to or co-precipitation with oxide substrates such as Al, Fe and Mn hydr/oxides (Carroll et al., 2002). Generally, the possible long-term adverse effects are related to the retention capacity for heavy metals and arsenic, which mainly depends on the composition of dredged sediments, to compensate against the oxidation of organic matter and sulfides, the dissolution of carbonates and the acidification of sediments (Singh et al., 1998; Du Laing et al., 2009).

As the oxidation status of the dredged sediments changes, a transfer of elements between different components in the sediments will likely take place (Forstner et al., 1994). In connection with this aspect, a BCR (Community Bureau of Reference) 3-step sequential extraction procedure (Rauret et al., 1999), which is designed to differentiate between the acid-soluble (exchangeable and carbonate-bound), reducible (Fe/Mn hydr/oxide-bound), oxidizable (sulfide and organic matter-bound), and residual (in crystal lattices of primary and secondary minerals) fractions, has been commonly applied. The undisputed advantage of this approach with respect to the estimation of middle- and long-term mobility lies in the fact that redistribution of metals in their (operationally defined) binding phases under changing environmental conditions can be evaluated prior to the actual remobilization of certain elements into the dissolved phase (Forstner et al., 1994). However, some disadvantages are that the metal-binding phases are defined operationally, so real chemical species of metals cannot be clearly determined, and sequential extraction procedures generally possess a low reproducibility.

In many previous studies, an increased mobility of heavy metals and arsenic upon the on-land disposal of dredged sediments was reported (Stigliani et al., 1991; Calmano et al., 1993; Japenga and Salomons, 1993; Tack et al., 1996; Singh et al., 1998; Cook and Parker, 2003; Cappuyns et al., 2006). These authors even considered that the dredged sediments can act as “chemical time bombs” upon on-land disposal. The dredged sediments in rivers were rather anoxic, so heavy metals and arsenic dominated in the oxidizable fraction (mainly sulfide minerals). For these sediments, the dominant transformation of heavy metals and arsenic was from hardly-soluble organic matter and sulfide-bound fraction to easier-soluble exchangeable and carbonate-bound or Fe and Mn hydr/oxide-bound fraction under the effect of oxidation when dredged sediments were exposed to the atmosphere (Calmano et al., 1993; Cook and Parker, 2003).

In the present study, the influence of pH and oxidation on the leaching potential of Cd, Cu, Mn, Pb, Zn and As in river-bed sediments from the Cam River-mouth is investigated. Since the remobilization of these elements is governed by both thermodynamic and kinetic processes, the kinetics of their release in relation to pH and oxidation status is also studied. (Micro)biological reactions are also important, but are, for practical reasons, not the subject of the present paper. In addition, the geochemical distribution and transformation of elements in the sediment under changing redox status are discussed to clarify the association between their leachability with the changes in element fractionation in the sediments.

2. Methodology

2.1. Sampling and sample pretreatment

The sampling campaign was carried out in April 2010. Twenty kilograms of surficial river-bed sediments was collected near Haiphong Harbor (Northern Vietnam) by a stainless-steel trihedral pyramid-shaped 5-liter grab which takes samples of the uppermost 5 cm of the sediment surface. During sampling, precaution was taken to minimize metal contamination from the grab, e.g. the outer part of the sediment sample was removed and only the inner part was further processed. All subsequent materials used for treatment and storage of the samples were non-metallic (plastic or wood). After collection, the freshly-wet sediments were immediately put in tightly-sealed 5-liter plastic containers, and transported to the Vietnam Institute of Geosciences and Mineral Resources. The sediment was homogenized quickly by crumbing and stirring by hand. One aliquot of 10 kg was put in a basin with a height of 10 cm. The basin was perforated with small holes at the walls and bottom to allow water drainage. The basin was then exposed outside to atmospheric conditions for 2 months (May and June 2010) to allow oxidation and ripening. This period was the summer season in Northern Vietnam, in which temperature and rainfall fluctuated between 25–35 °C and 200–300 mm/month respectively, and heavy rains often occurred every three days. Finally, after 2 months of oxidation, the sediment was allowed to dry completely and the dry oxidized sediment was disaggregated and homogenized in an agate mortar, and then put again in a tightly-sealed plastic container. In parallel, another aliquot of 10 kg was put in a tightly-sealed container and placed in the freezer at 4 °C and dark conditions until both types of sediments were brought to the KU Leuven, Belgium for experiments and analyses. The pH and Eh were measured for the fresh and oxidized sediments in a sediment/water suspension (1/2.5) at room temperature (25 ± 1 °C) by using a pH electrode and a glass combination redox electrode consisting of a platinum sensor and a Ag/AgCl reference electrode (Orion, 9778BNWP, Thermo Electron Corp., Beverly, MA, USA), which are connected to a multi-parameter bench meter (MARTINI, Model Mi180, Milwaukee Instrum., Rumania). The pH electrode was calibrated using pH 4 and pH 7 standards and the redox electrode was checked with a 220 mV standard solution (the electrode was used only if the deviation was within ±20 mV). The redox electrode was inserted into the sediment and the absolute redox values were recorded when stable measurements were reached (after about 10 min). Redox data reported in this paper are the relative redox values versus the SHE (standard hydrogen electrode), i.e. after adding 207 mV to the absolute redox values. The measured pH is not significantly different between the fresh (7.62 ± 0.23, $n=3$) and the oxidized (7.78 ± 0.33, $n=3$) sediments while the Eh values indicate a change from a suboxic matrix (104 ± 2 mV, $n=3$) to an oxic matrix (410 ± 8 mV, $n=3$).

2.2. Total-elemental, mineralogical and grain size composition

Total-elemental composition of the sediment was determined by the so-called 4-acid digestion method. One gram of dry sediment was put in a Teflon beaker. After adding 20 ml HNO_{3conc}, the beaker was gently shaken and put on a hot plate at 200 °C until almost dry. Next, 20 ml $HClO_{4conc}$ was added to the beaker (covered with a loose cap) and heated at 240 °C until almost dry. Next, 20 ml HF_{conc}