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Leachability of arsenic and heavy metals from blasted copper slag and contamination of marine sediment and soil in Ninh Hoa district, south central of Vietnam

Tran Thi Thu Dung [a,c,*], Valérie Cappuyns [a,b], Rudy Swennen [a], Elvira Vassilieva [a], Nguyen Ky Phung [d]

[a] Geology, Department of Earth and Environmental Sciences, KU Leuven, Celestijnenlaan 200E, 3001 Heverlee, Belgium
[b] Center for Economics and Corporate Sustainability, Hogeschool-Universiteit Brussel, Warmoesberg 26, 1000 Brussels, Belgium
[c] Faculty of Environment, University of Science, 227 Nguyen Van Cu Street, Ward 4, District 5, Ho Chi Minh City, Viet Nam
[d] Department of Science and Technology, 244 Dien Bien Phu Street, Ward 7, District 3, Ho Chi Minh City, Viet Nam

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ABSTRACT

In recent years, shipping activities developed in Ninh Hoa district (south-central Vietnam), have raised an urgent environmental concern related to the use of copper slag as abrasive material for removing rust from the surface of the ships. This study was conducted to investigate the characteristics of the blasted copper slag (BCS). Enrichment Factors (EF) were used to assess the contamination status of sediments and soils in the surroundings of the BCS dump site. The potential release of As and heavy metals (HMs) from BCS was examined through pH_{stat} and cascade leaching tests in combination with XRD analysis. From the results, As, Cr, Ni, Pb and Zn were characterized as moderate severely enriched to severely enriched while Cu showed extremely severe enrichment in the sediments. Regarding the soil collected at the dump site, it was strongly contaminated with As, Cu and Zn (extremely severe enrichment) whereas Cr, Ni and Pb were ranked as severely enriched. This study also demonstrates that it is important to use local background values of As and HMs in soils and sediments for a correct estimation of the degree of As or HM contamination. The cascade leaching test results from the BCS showed that the concentrations of the regulated HMs leached were lower than the EU limit for non-hazardous waste; except for Cu. Results from pH_{stat} leaching tests at pH 4 with BCS indicated that upon acidification, HM release from the <1 mm fraction is higher compared to the bulk sample. A significant release of Cu from BCS was also observed for both fractions (<1 mm fraction and bulk sample) in pH_{stat} leaching tests. In view of the elevated Cu concentrations found in the slag, the potential recovery of Cu from BCS should be investigated.

1. Introduction

Assessment of heavy metal (HM) contamination is a complex process because of the natural occurrence of HMs in the environment. In general, sediment/soil quality guidelines (SQGs) and some sediment/soil indices such as the geo-accumulation index (Müller, 1969), enrichment factor (Duce et al., 1975), pollution load index (Tomlinson et al., 1980) and marine sediment pollution index (Shin and Lam, 2001) are used to assess the contamination status of sediment/soil. Using SQGs to assess HM contamination in sediment/soil shows some limitations because it does not take into account the background level of HMs and do not include a correction for differences in matrix characteristics (e.g., particle size, organic matter, and mineral composition of the examined soil/sediment). The geo-accumulation index, pollution load index and marine sediment pollution index take into account site specific background concentrations of HMs but do not include a correction for differences in matrix characteristics. The enrichment factor (EF), which uses a normalizer to correct for the differences in particle size and clay mineral content, is widely used in environmental geochemistry to assess the contamination status of HMs in sediment/soil (e.g., Rubio et al., 2000; Woitke et al., 2003; Ho et al., 2012).

The present study was performed in Ninh Hoa, a town located in Khanh Hoa province, south central Vietnam. In recent years, with the development of the shipping industry, there is an urgent environmental concern relating to the use of copper slag as abrasive material for removing rust and marine deposits from ships. A shipyard located at the beach in Ninh Hoa (south of Van Phong bay,

Abbreviations: ANC, acid neutralizing capacity; BCS, blasted copper slag; CLT, cascade leaching test; DL, detection limit; EC, electrical conductivity; EF, enrichment factor; HM, heavy metal; L/S ratio, liquid/solid ratio; SQG, sediment quality guideline.

* Corresponding author at: Faculty of Environment, University of Science, Ho Chi Minh City, Viet Nam. Tel.: +84 8 38353295; fax: +84 8 38304379.
E-mail address: tran_thi_thu_dung@yahoo.com (T.T.T. Dung).

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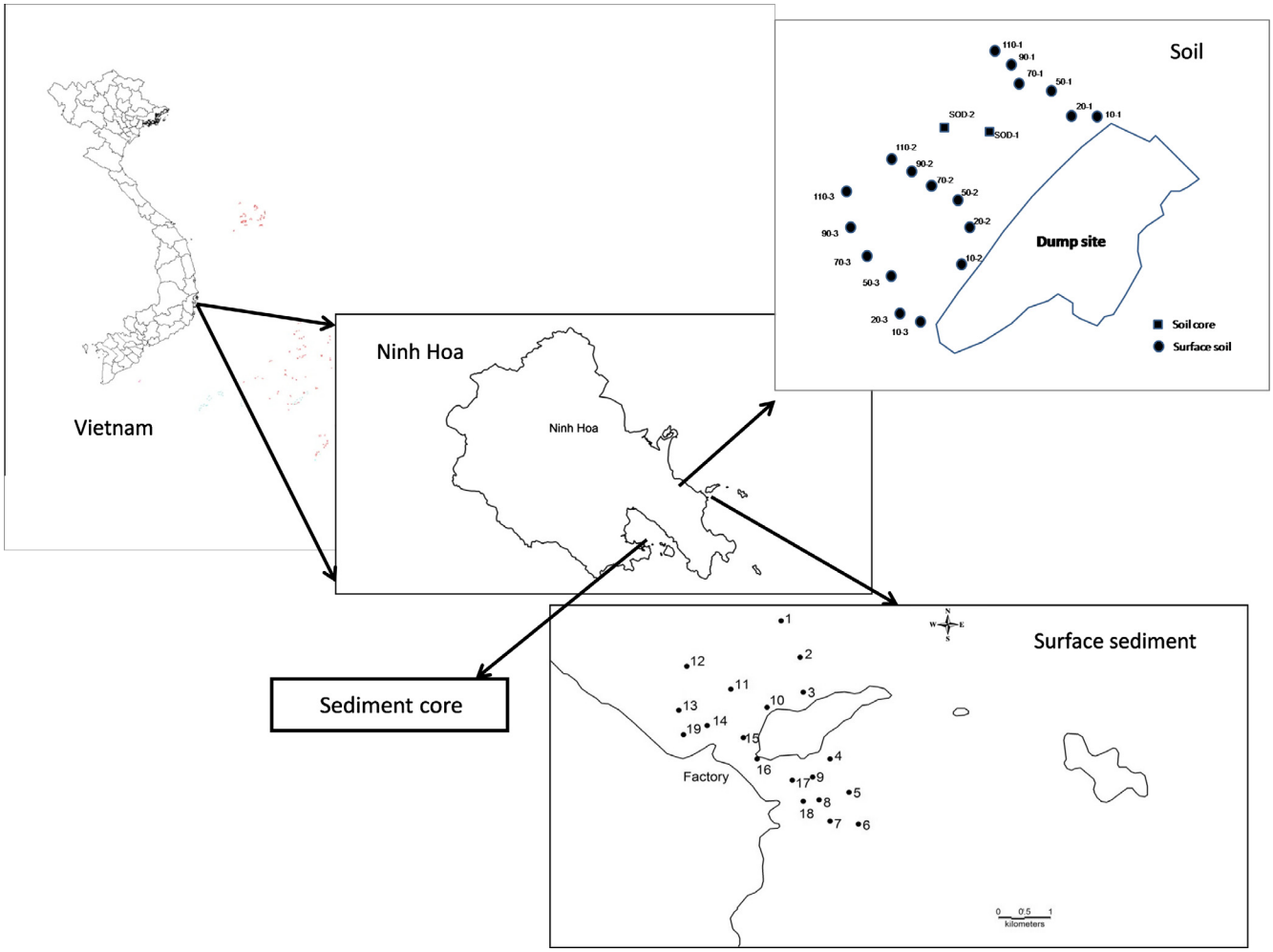

Fig. 1. Location of the sampling sites.

Khanh Hoa province, Fig. 1) has used copper slag as a blasting agent until 2011. Since the year 2000, blasted copper slag (BCS) has been dumped without any treatment in a dump site which is about 3 km from the shipyard. The composition of the BCS and the leachability of As and HMs from BCS has never been studied before, even though it likely is the most important anthropogenic source of HMs in the study area. Moreover, studies on metal contamination in soils and sediments of this area, and in Vietnam in general, are rather limited. Additionally, most of the studies were based on Canadian SQGs and did not take into account the regional background values for HMs (Le, 2003; Nguyen, 2009). Copper slag can be either dumped or recycled as a secondary material (Gorai et al., 2003). Therefore, an environmental study, taking into account the potential release of HMs from BCS, should be carried out in order to provide essential information to select the most "environmentally friendly" management options of these slags: reuse (using BCS without any treatment), recycling (using after some treatment) or controlled disposal. In this work, the actual and long term release of As and HMs from BCS was examined by using a cascade leaching test (NEN 7349). A pH_{stat} leaching test (CEN/TS 14429 test) was carried out to assess As and HM release of BCS under the influence of acidification. Particle size was a variable in the studied BCS (Table 1). To investigate the influence of particle size on the release of As and HMs in BCS, the leaching tests were performed in different particle size fractions (<1 mm and bulk with pH_{stat} leaching test, <1 mm and <125 μm with cascade leaching test). This study also provides a first characterization of As and HM contamination of sediments and soils nearby the BCS dump site.

Although a lot of controversy exists about the use of the term 'heavy metals' (e.g., Batley, 2012; Chapman, 2012), the term 'heavy metals' is used in this study to indicate particularly the elements Cd, Cr, Co, Cu, Ni, Pb and Zn. Arsenic, which is actually a metalloid, will be mentioned separately.

2. Methodology/materials and methods

2.1. Sampling and sample pretreatment

The study area is located in Ninh Hoa, Khanh Hoa province, Vietnam. The geological substrate in this area mainly consists of alternative distribution of Jura–Kreta magmatic rocks, sediments and Quaternary sediments (Nguyen, 2006). Two sampling campaigns were undertaken in December 2010 and in December 2011. Nineteen marine surface sediment samples (approximately 1 kg each) were collected adjacent to the shipyard at 500 m intervals, located near the beach of Ninh Hoa (Fig. 1). The samples were taken from a boat by a grab and the exact coordinates of the sampling locations were recorded by GPS (Garmin – GPS12). Additionally, to infer background concentrations, one sediment core (150 cm in length with a diameter of 7 cm) was collected at a mangrove in an alluvial spit connected to the sea which is located at a distance of 12 km from the shipyard. The geological setting of the cored area is comparable to the study area near the shipyard. After collection, the sediment core was sectioned over 10 cm intervals.

Soil samples were collected at the dump site. At the dump site, surface soil samples were taken approximately 10 m, 20 m, 50 m,