Ecotoxicology and Environmental Safety 141 (2017) 75–84

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Multi-phase distribution and comprehensive ecological risk assessment of heavy metal pollutants in a river affected by acid mine drainage

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ARTICLE INFO

Keywords:
Heavy metals
Multi-phase distribution
Fraction analysis
Experts scoring
Comprehensive ecological risk index

ABSTRACT

To date, there is a lack of a comprehensive research on heavy metals detection and ecological risk assessment in river water, sediments, pore water (PW) and suspended solids (SS). Here, the concentrations of heavy metals, including Cu, Zn, Mn, Cd, Pb and As, and their distribution between the four phases was studied. Samples for analysis were taken from twelve sites of the Hengshi River, Guangdong Province, China, during the rainy and dry seasons. A new comprehensive ecological risk index (CERI) based on considering metal contents, pollution indices, toxicity coefficients and water categories is offered for prediction of potential risk on aquatic organisms. The results of comprehensive analysis showed that the highest concentrations of Cu, Zn and Mn of 6.42, 87.17 and 98.74 mg/L, respectively, in PW were comparable with those in water, while concentrations of Cd, Pb and As of 609.5, 2757 and 96.38 μg/L, respectively, were 2–5 times higher. The sum of the exchangeable and carbonate fractions of target metals in sediments followed the order of Cd > Mn > Zn > Pb > Cu > As. The distribution of heavy metals in phases followed the order of sediment > SS > water > PW, having the sum content in water and PW lower than 2% of total. The elevated ecological risk for a single metal and the phase were 34,585 for Cd and 1160 for water, respectively, implied Cd as a priority pollutant in the considered area. According to the CERI, the maximum risk value of 769.3 was smaller than 1160 in water, but higher than those in other phases. Out of considering the water categories and contribution coefficients, the CERI was proved to be more reliable for assessing the pollution of rivers with heavy metals. These results imply that the CERI has a potential of adequate assessment of multi-phase composite metals pollution.

1. Introduction

An increased industrial production and urbanization is responsible for increasing concentration of environmental pollutants, such as heavy metals and toxic organic compounds. Heavy metals mainly come from the discharges produced by anthropogenic activities, including minerals mining and processing, disposal of municipal sewage, agricultural and domestic run-offs and transport (Guerra-Garcia and Garcia-Goméz, 2005; Ouyang et al., 2006). Significant quantities of heavy metals are discharged to aquatic environment and accumulate in sediments, which may directly pollute the water in rivers, resulting in sublethal or lethal effect on local fish populations and accumulating in crops through irrigation (Cai et al., 2015; Paulino et al., 2014). The heavy metals accumulated in sediments may be released to water through sediment resuspension, desorption, reduction or oxidation reactions, and the degradation of organic tissues (Dong et al., 2012; Zhao et al., 2013). Such processes increase the concentration of dissolved metals threatening ecosystems and human health.

Heavy metals entering the river water react with organic polymers or clay minerals, forming complexes or chelates, ultimately settling and accumulating in sediments (Fu et al., 2014; Suthar et al., 2009; Zhang et al., 2015). They also inevitably occur in pore water (PW) and suspended solids (SS). Heavy metals in water are easily transmitted and accumulated in animal organisms entering the food chains (Zhuang et al., 2009a, 2009b). Overall, heavy metals in watershed are mainly distributed in four phases, water, sediments, PW and SS, participating in continuous dynamic migration and transmission processes. They undergo a series of physical, chemical and biological transformations, causing a risk to water biotic population.

Quality indices are widely used to assess the status of pollution of aquatic media and sediments with metals. Table S1 shows the major assessment indices for heavy metals pollution globally. These indices

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http://dx.doi.org/10.1016/j.ecoenv.2017.03.009
Received 24 July 2016; Received in revised form 14 December 2016; Accepted 7 March 2017

have been developed approaching from the total contents, fraction contents, toxicity coefficients and sediment quality guideline values. They are applied to the assessment of the state of pollution with metals as an aggregative measure, being seemingly a suitable tool for environmental management (Abrahim and Parker, 2008; Müller, 1969; Håkanson, 1980; Jain, 2004; Long et al., 2006; Loska and Wiechula, 2003; Pejman et al., 2015; Saeedi and Jamshidi-Zanjani, 2015). However, the overwhelming majority of researchers detected and evaluated the toxicity of heavy metals in a single phase only, mainly focusing at the contents in water and sediments (Fu et al., 2014; Islam et al., 2015; Kadhum et al., 2015). Zhang et al. (2015) initiated a research on heavy metals detection in aquatic media, biological tissues and sediments of Songhua River, and proposed a comprehensive ecological risk assessment model to select priority pollutants. This study, however, was of a preliminary character, and the description of model was incomplete. The research phases were not comprehensive, and the biological phase should be the receptor of ecological risk. To date, the authors failed to find reports containing comprehensive analysis of heavy metals pollution in river water, sediments, PW and SS. The last two positions are important since rivers affected by acid mine drainage (AMD) exhibit high heavy metal concentrations detected in PW and SS (Arora et al., 2015; Singhal et al., 2006), making these phases essential for river pollution proper assessment and effective restoration. The development of comprehensive ecological risk assessment index for composite heavy metals pollution is an objective of this study.

The study of the total contents of heavy metals (Cu, Zn, Mn, Cd, Pb, As) distributed in all four phases, water, sediments, PW and SS of the Hengshi River (affected by AMD from the Dabaoshan mine in Guangdong Province, China) was undertaken. In addition, the fraction contents in surface sediments were determined. The comprehensive ecological risk index (CERI) was developed considering pollution indices combined with toxicity coefficients and water categories to be used in assessment of potential effect on aquatic organisms. A comparative analysis between the CERI results and the ecological risk values of metals in a single phase was conducted to determine the reliability of the proposed index and the pollution degree of the target river.

2. Materials and methods

2.1. Geography and characteristics of the site of research

The Dabaoshan Mine (24°34′28″N, 113°43′42″E) is a poly-metallic sulfide meso-hypothermal deposit, located at the boundary between Qujiang and Wengyuan counties of Guangdong Province, China. The area is situated in a subtropical humid monsoon climate, the local annual average rainfall is about 1800 mm and the temperature about 20 °C (Li et al., 2009; Zhuang et al., 2009a, 2009b). Since 1970s, large-scale surface mining of iron ore has been in operation together with smaller scale underground mining of copper containing chalcopyrite, zinc containing sphalerite and lead containing galena ores (Chen et al., 2007). The large-scale mining stopped in 2011, leaving large amounts of untreated mining wastes and tailings exposed to the environment. These materials spread downstream with surface erosion, rain-runoff and wind action, generating AMD and the environmentally significant metals release (Liao et al., 2016).

To intercept the floodwater and retain the mud at the mining waste stockpiles in mountains, a dam wall was constructed across the valley to form a reservoir to trap sediments in the mud-retaining impoundment (MRI) (Lin et al., 2007; Zhao et al., 2012). The water in the MRI has characteristic for AMD low pH and red color due to high concentrations of sulfuric acid and ferric ions (Fig. 1). The MRI was rapidly filled up with sediments from the upper catchment due to severe soil erosion, exhausting the capacity of the reservoir. As a result, the AMD was continuously overflowing downstream for years at the starting point of the Hengshi River used as an irrigation source for local agriculture (Zhao et al., 2012). The Hengshi River, joined with a few tributaries, Lengshui River, Fanshui River and Taiping River, flows into the Wengjiang River and, further, the Beijiang River (Fig. 1). Due to the AMD, the upstream of the Hengshi River is filled with yellowish red (orange ochre) precipitates, forming a yellow stream channel. The Shangba village, located about 13.5 km downstream from the MRI, is internationally known as a cancer village, the inhabitants of which use the polluted river water for irrigation. However, there is still a paucity of detailed data on heavy metal distribution, phase allocation relation and comprehensive ecological risk assessment of the Hengshi River.

2.2. Sampling and pre-treatment

Sampling from Hengshi River was carried out in August 2013, the rainy season, and January 2014, dry season. The water and sediment samples collected from each sampling site consisted of 4–5 composite samples, and were taken at the depth of 1–20 cm. The locations of sampling sites were determined using a portable Global Positioning System (GPS) navigator. The sampling sites were classified into two groups based on hydrodynamic and geological conditions, S1 to S12 were collected from the main stream, affected by AMD, while K1 to K4 taken from the places located at the tributaries and considered as reference samples (Fig. 1). The widths, depths and flow velocities of the Hengshi River were also measured at each sampling site, the detailed description is given in Table S2.

Water samples for the analysis of heavy metals concentration were filtered through 0.45 µm cellulose filters *in situ*. Analytically grade pure HNO_3 was added to samples to keep pH below 2.0 for preservation. The samples were stored in high-density polyethylene bottles and stored in an icebox during transportation. At each sampling site, 1 L mixed water samples were collected for obtaining non-filterable SS. These samples were stored in glass bottles and were filtered using 0.45 µm membrane filters upon arriving to the laboratory. The filtrate was discarded, the filters with SS were collected and dried in an oven at 60 °C, and analyzed identically to the samples of sediments.

About 2 kg of rainy mixed sediment samples at each sampling site were collected and stored in dark bottles. About a half of the sample was used for the analysis of the metals contents, the other half was used for the PW extraction for analysis using a centrifuge. The sediment samples were freeze dried, the pebbles and plant fragments were removed using a 2 mm sieve, the samples were grinded, screened through a 0.15 µm sieve and stored in glass jars at 4 °C. The prepared sediment samples in amount of 0.20g were mixed with 6.5 mL of HNO_3 and 2.6 mL HF (5:2) in the digestion autoclave and digested for 30 min in the microwave oven (MARSX-press, CEM). The digestion solution was placed to an evaporation dish and the excess acid was removed by heating at the electric hot plate. The dry solid samples were dissolved in 50 mL of water and filtered through 0.45 µm membrane filters for the metals analysis (Liao et al., 2016). The chemical fractions of the heavy metals in surface sediments were determined using the classical 5-step Tessier sequential extraction procedure (Tessier et al., 1979).

2.3. Analytical methods and quality assurance

According to the results of previous studies in this area, selected Cu, Zn, Mn, Cd, As, Pb as target metals (Lin et al., 2007; Zhao et al., 2012). The concentrations of heavy metals were determined using the atomic absorption method with a variety of detectors attributable to the nature and the content of selected metals. Specific methods for the metals were described by Liao et al. (2016). The results of triplicate analyses revealed a good reproducibility.

Appropriate quality assurance procedures were carried out and precautions were taken to ensure reliability of the results. The analytical data quality was guaranteed implementing the laboratory quality assurance and quality control methods, including the using of