# Effect of dissolved oxygen and nutrient levels on heavy metal contents and fractions in river surface sediments

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## HIGHLIGHTS

- Aerobic environment and high nutrient levels promoted the adsorption of Pb, Zn and Fe in sediments.
- Anoxic environment decreased the potential bioavailability risk of Pb, Zn, Ni, Cu, Mo and Fe. Anoxic environment reduced the percentage of potentially mobile fraction of Pb, Zn, Cu and Fe.
- DO and nutrient level had no influence on the total content of Ni.

## GRAPHICAL ABSTRACT
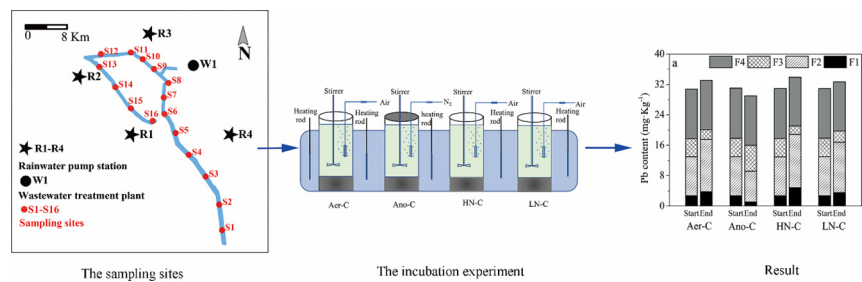


## ARTICLE INFO

## ABSTRACT

In aquatic systems worldwide, heavy metal pollution has been increasing alongside rapidly growing anthropogenic activities, and most heavy metals are stored in sediments. Overlying water conditions may influence whether sediments act as heavy metal sinks or sources. In this study, we investigated the effects of the dissolved oxygen (DO) and nutrient levels of overlying water on the total contents and fractions of Pb, Zn, Ni, Cu, Mo, and Fe in river surface sediments. Sediments and overlying water were collected from a tributary of the Hai River in Tianjin, China, and then incubated for 61 days under laboratory conditions. The chemical speciation of heavy metals was determined following the modified Community Bureau of Reference (BCR) three-step sequential extraction procedure. The results showed that Pb, Zn, and Fe were released from the sediments in an anoxic environment and adsorbed from the overlying water in an aerobic environment. High nutrient levels facilitated the adsorption of Pb, Zn, and Cu, and Fe in the sediments, while the total content of Mo was higher under low nutrient level conditions. The DO and nutrient levels appeared to have no influence on the total content of Ni. According to the risk assessment code classification (RAC), anoxic conditions decrease the potential bioavailability risks of Pb, Zn, Ni, Cu, Mo, and Fe. Anoxic conditions can also reduce the percentage of the potentially mobile fractions of Pb, Zn, Cu, and Fe. The low nutrient level contributed, to some extent, to reducing the potential bioavailability risk of Pb, but increasing the risk of Cu. The high nutrient level increased the potentially mobile fractions of Pb, Zn, Cu, and Fe. The information obtained in this study improves our scientific understanding of the effects of overlying water conditions on the total heavy metal contents and fractions.

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## 1. Introduction

Heavy metals are natural constituents of the Earth's crust, and small amounts of several metals are required for plant and animal growth (Nagajyoti et al., 2010). However, alongside rapid economic

development, heavy metal pollution has been increasing worldwide and has received global attention owing to the environmental toxicity, abundance, and persistence of metals (Fu et al., 2014; Gashi et al., 2016; Jiang et al., 2017; Rosado et al., 2016; Yang et al., 2014). Heavy metal pollution originates from natural and anthropogenic sources; the natural sources include rock weathering and soil erosion, and the anthropogenic sources include domestic sewage, industrial wastewater, mining wastewater, agricultural fertilizer leachate, and coal burning (Alvarez-Vazquez et al., 2017; Davis and Birch, 2010; Pan and Wang, 2012; Skordas et al., 2014; Yuan et al., 2009). With rapid urbanization and industrialization over the past several decades, human activities have become the main sources of heavy metals in the environment (Islam et al., 2015).

When metals enter water bodies, they can be harmful to aquatic ecosystems through a range of biochemical and physiological processes and can accumulate in sediments, approximately 85% of heavy metals accumulate in surface sediments (Bosch et al., 2016; Nagajyoti et al., 2010; Zhang et al., 2016a). In the sediments, metals bind to various components in various ways, including occlusion in amorphous materials, absorption onto the surface of Fe–Mn oxy-hydroxides, complexion with organic matter, and incorporation into metal sulfides (Gendron et al., 1986; Huerta-Diaz and Morse, 1992; Huerta-Diaz et al., 1998; Peng et al., 2009; Zhang et al., 2014; Zhang et al., 2016b). To a large degree, different metal forms exhibit different mobilities, chemical interactions, biological availabilities, and toxicities (Hooda, 2010; Tessier et al., 1979; Xu et al., 2017). Therefore, measuring total metals may not be enough to provide sufficient information regarding the transformations and transfers of heavy metals in aquatic environments (Morelli and Gasparon, 2014; Singh et al., 2005). In this study, the various fractions of metals were obtained following the Community Bureau of Reference (BCR) sequential extraction procedure, which enables the detection of exchangeable (soluble species, species with cation exchange sites, and carbonate-bound species), reducible (Fe–Mn oxy-hydroxide-bound), oxidizable (organic matter-bound and sulfide-bound), and residual (mineral matrix-bound) forms of metals (Mossop and Davidson, 2003; Rauret et al., 1999). The risk assessment code (RAC) was introduced to assess the availability and mobility of heavy metals in sediments (Ke et al., 2017; Perin et al., 1985). RAC is based on the different metal fractions in sediments, and the strength of the bonding between heavy metals and other components in sediment is used to determine the bioavailability of the metal and the risk it poses to an aquatic environment (Morelli and Gasparon, 2014; Yang et al., 2014). The potentially mobile fraction was considered to be the sum of the first three steps from the BCR sequential extraction procedure to the total metal content, i.e., the exchangeable, reducible, and oxidizable fractions (Delgado et al., 2011; Pérez et al., 2008).

Changes in overlying water conditions may influence whether sediments act as heavy metal sinks or sources. Metal adsorption and precipitation are enhanced in alkaline environments, while, in acidic environments, $H^+$ can weaken metal associations and hinder the retention of metals by sediments (Atkinson et al., 2007; Li et al., 2013; Najafi and Jalali, 2016). During a 40-day laboratory incubation experiment, Banks et al. (2012) observed the release of Fe and Mn from sediments as hypoxia developed. However, Li et al. (2013) found that higher dissolved oxygen (DO) concentrations in overlying water better facilitated the release of the Zn, Cu, Cr, and Pb than lower DO concentrations. Through multivariate techniques, Fu et al. (2014) found that the ammonia nitrogen, total nitrogen, orthophosphate, total phosphate, and permanganate index in water were related to metal sedimentation in the Jialu River. In Lake Chaohu, significantly positive correlations were observed between nutrient and metal contents (Zhang et al., 2007). The presence of salinity and humic acid was found to accelerate the dissolution of CuS, but inhibited the dissolution of ZnS and PbS (Chou et al., 2018). Microbes could affect the changes in metal speciation, toxicity and mobility (Gadd, 2010). Sulfur-reducing bacteria was particularly important in reductive precipitation of $Cr^{6+}$, $Tc^{7+}$ and $Pb^{2+}$, and could share physiological properties of both sulfate- and metal-reducing groups of bacteria to use $Cr^{7+}$, $U^{6+}$, $Mn^{4+}$ and $Fe^{3+}$ as sole electron acceptors (Du Laing et al., 2009; Lloyd and Renshaw, 2005; Tebo and Obraztsova, 1998). Moreover, it was seen that temperature, salinity, ionic strength, and organic matter significantly influenced the release of heavy metals from sediments (Atkinson et al., 2007; Butler, 2009; Li et al., 2013; Zhang et al., 2014). Although with many important knowledges gained from various studies, the collective effects of dissolved oxygen and nutrient level on heavy metal contents and fractions have not been well characterized. In addition, the incubation experiments help to demonstrate a causative link between dissolve oxygen and nutrient level in overlying water and heavy metal fractions in sediments that has previously not been explored.

The objectives of this study were: (1) to ascertain naturally occurring patterns of overlying water conditions relative to heavy metal contents in sediment from a tributary of the Hai river, (2) to experimentally investigate the effect of manipulating dissolved oxygen and nutrient level of overlying water on the speciation of heavy metals in sediments, (3) to determine changes in heavy metal bioavailability and potentially mobile fraction due to overlying water conditions. The information derived from this study can provide a baseline for predicting relative changes in the total metal contents, fractions, and availability with changes in environmental factors, and then be used to implement appropriate methods of environmental management in other polluted catchments worldwide.

## 2. Materials and methods

### 2.1. Research area

Surface sediments and overlying water were collected from Yuanjia River, a typical tributary of the Hai River (39.136° N, 117.397°E) in Tianjin, China. The length of the river is 65 km, and the surface area of basin is 300 km$^2$. This area has been undergoing rapid and intense industrialization and urbanization over the past two decades. The land along the river is used as industrial, residential, transport, and agricultural land. The main soil types are brown, cinnamon, moist soil and the river sediment is dominated by clay and silt. This river receives a large input of nutrients from wastewater discharged from activated sludge treatment and runoff from the rainwater pump stations (Fig. 1). Its shallowness (1.0 m) and slow flow velocity (close to zero) increase the risk of eutrophication. The mean annual precipitation in the study area is 600 mm, which mostly occurs from July to September, and the mean annual air temperature is 14 °C (Data from Tianjin Meteorological Bureau).

### 2.2. Field sampling

Samples were collected from 16 locations (S1–S16) over 2 km in September 2016 to conduct a basin-scale field investigation (Fig. 1). Surface sediment samples (to a depth of 10 cm) were collected using a Peterson grab sampler (ETC-200, China), and the overlying water samples (20 cm above the sediment's surface) were collected using a plexiglass water sampler (Jc-800, China). At each site, two sediment samples and two overlying water samples were collected. All sediment samples were stored in polyethylene bags, and the overlying water samples were stored in polyethylene bottles. The samples were sent to the laboratory shortly after collection for analysis. The water temperature, pH, and DO concentrations were measured in the field using a HACH HQ30D probe. The redox potential (ORP) was also measured in-situ using a Thermo Scientific Orion 310P-02A meter with an Orion 96–98 probe. The measurement of temperature, pH, DO, and ORP were performed twice.

One representative site (S6) was selected for further incubation experiments. Sixteen replicate sediment cores (50 cm × 15 cm diameter) were collected from S6 (sampling region 100 m × 10 m) using a