



# Distribution and ecological risk assessment of cadmium in water and sediment in Longjiang River, China: Implication on water quality management after pollution accident

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## HIGHLIGHTS

- Ecological risks (ERs) of cadmium-contaminated water and sediment were assessed.
- ER decreased in water, but increased in sediment after emergent treatments.
- Recovery for water occurred approximately one month later, but two years for sediment.
- ER in sediment after accident decreased during flood period.

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## ABSTRACT

In early January 2012, the Longjiang River was subjected to a serious cadmium (Cd) pollution accident, which led to negatively environmental and social impacts. A series of measures of emergency treatment were subsequently taken to reduce water Cd level. However, little information was available about the change of Cd level in environmental matrices and long-term effect of this pollution accident to aquatic ecosystem. Thus, this study investigated the distribution of Cd in water and sediment of this river for two years since pollution accident, as well as assessed its ecological risk to aquatic ecosystem of Longjiang River. The results showed that it was efficient for taking emergency treatment measures to decrease water Cd concentration to below the threshold value of national drinking water quality standard of China. There was high risk ( $HQ > 1$ ) to aquatic ecosystem in some of reaches between February and July 2012, but low or no risk ( $HQ < 1$ ) between December 2012 to December 2013. Cd concentration in sediment in polluted reaches increased after pollution accident and emergency treatments in 2012, but decreased in 2013. During flood period, the sediment containing high concentration of Cd in Longjiang River was migrated to downstream Liujiang River. Cd content in sediment was reduced to background level after two years of the pollution accident occurrence. The study provides basic information about Cd levels in different media after pollution accident, which is helpful in evaluating the effectiveness of emergency treatments and the variation of ecological risk, as well as in conducting water management and conservation.

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## 1. Introduction

During the process of rapid industrialization, there have been

many heavy metal pollution accidents occurred in the world (Kraus and Wiegand, 2006; Liu et al., 2005; Shinn et al., 2009; Solá et al., 2004; Osán et al., 2007). In China, heavy metal pollution accidents (e.g., cadmium (Cd) pollution in Beijiang in 2005, and in Longjiang in 2012) occurred frequently for the past few years (Xu et al., 2009; Zhang et al., 2013). These pollution accidents not only brought great harm to aquatic organisms (e.g., macrophytes, macrobenthos and fish) living in water and sediment (Audry et al.,

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2004; Burger, 2008; Madejón et al., 2006), but also jeopardized water supply security, as well as further affected food safety and human health by transferring along food chain (Lu et al., 2015). In order to mitigate heavy metal pollutants released from pollution accidents that deleteriously affected environment and organisms, many techniques including coagulation sedimentation, adsorption and catching and flow regulation have been used in heavy metal pollution emergency action (Hashim et al., 2011; Tang et al., 2014; Zhang et al., 2011).

In January 2012, the serious Cd pollution accident occurred in Longjiang River that located in Guangxi Zhuang Autonomous Region, China (Qu et al., 2016a). Cd is recognized as an extremely significant contaminant as its high toxicity and large solubility in water (Hanif et al., 2016). In order to avoid the contamination of Cd to drinking water of millions of dwellers, poly aluminium chloride (PAC) and poly ferric chloride (PFC) in weak alkaline condition were poured into the river as the major measures of emergency pollution treatment to transform ionic Cd in water to hydroxide and carbonate, which further precipitated in the form of flocs mixed with sediment in the river (Zhang et al., 2013). Through the emergency treatments, Cd concentration in water of Liujiang River, which locates in downstream reach of Longjiang River, was below the threshold value of national drinking water quality standard of China, and thus water supply for Liuzhou city was not eventually affected by the pollution accident.

However, the long-term impact of this Cd pollution accident to aquatic ecosystem of Longjiang River was still unknown. In general, chemical composition of surface water and sediment could be affected by numerous natural and anthropogenic factors, which disturbed the balance of pollutants in water and sediments system (Wojtkowska et al., 2016). Specially, the contamination of sediment with heavy metals should be greatly concerned as they acted as a pool of heavy metals and the possible secondary contamination sources (Gati et al., 2016). Sediment-associated heavy metals possessed a potential hazard to the aquatic environment, and may be released to the water column upon disturbance or acidification (Black and Williams, 2001). The disturbance of sediment was relatively weak during the period of emergency treatment for Cd pollution accident in Longjiang River in February 2012 (dry season). However, sediment was frequently affected by flood in Longjiang River from April to September (wet season), thus the sediment that mainly formed during emergency treatments could not be kept on the riverbed, and transported to downstream reach with flood. Previous studies indicated that large amounts of flocs formed by emergency treatments might be dissolved in acid flood and thus further affected water quality again (Liu et al., 2013; Pascaud et al., 2015). Therefore, it was necessary to examine the levels of Cd in water and sediment after pollution accident and emergency treatments in Longjiang River, as well as assess their ecological risks to aquatic organisms during the recovery process of contamination of Cd.

This study, therefore, aimed to (1) evaluate the long-term changes of Cd level in water and sediment of Longjiang river after emergency treatments; (2) examine the levels of Cd in sediment, water and suspended solid during flood period, which were affected by the re-suspension of Cd-contaminated sediment; and (3) assess the potential ecological risks of Cd in water and sediment of Longjiang River and its downstream Liujiang River. The results of this study have imperative implications for emergency treatments, environmental monitoring, ecological risk assessment and water quality management of heavy metals after pollution accident.

## 2. Materials and methods

### 2.1. Study areas

Originating from Sandu county of Guizhou province, Longjiang River is the largest tributary of Liujiang River in the Pearl water system. It stretches for 358 km, including 222 km located in Hechi city of Guangxi Zhuang Autonomous Region. The annual mean precipitation is 1490 mm, 70–90% of which occurs in the flood season from April to September in the region. The sampling sites locate in Longjiang and Liujiang Rivers (Fig. 1), and the brief descriptions of characteristics for these sites are shown in Table S1.

### 2.2. Sampling and Cd analysis

After Cd pollution accident occurring in January 2012 and subsequent emergency treatments that started on January 20 and ended on February 28, 2012, the samples of water and sediment were collected six times at 16 sites between 2012 and 2013 (i.e., February, March, July and December 2012, August and December 2013).

Considering the re-suspension of Cd-contaminated sediment during flood period, samples of water and suspended solid from site 9 and site 12 were additionally collected daily between April and June 2012. And also, two additional samplings of sediment were conducted at sites 5–13 in March and July 2012. Sampling sections were densely set with the distance of about one kilometer for two adjacent sections, and three sediment samples (left, middle and right) were collected in each section.

The pH and water temperature were measured in situ using a multi-parameter water analyzer (YSI-6600V2). Surface water samples were collected and stored in 1000 mL acid-washed polyethylene bottles at 4 °C after the addition of 10 mL 1:1 nitric acid/deionized water (v: v). All water samples were analyzed using atomic absorption spectrometer (AAS, PerkinElmer PE800A). The water samples collected during flood period were filtered using 0.45 µm Whatman filter papers. The filter papers were used to detect Cd in suspended solid with the same analysis method of sediment, with detailed description shown as below. Surface sediments (<5 cm) were collected and kept in ice before being transported to the laboratory analysis. After removal of the fragments and drying at 60 °C until constant weight, the sediment samples were ground with agate mortar and sieved through a 1 mm stainless-steel mesh to obtain a fine homogenous powder. A sample of fine powder (0.5 g) was digested with a concentrated acid mixture of HNO<sub>3</sub>, HF and HClO<sub>4</sub> (Cai et al., 2015). Then they were diluted with distilled water to a volume of 25 mL and analyzed Cd using AAS.

### 2.3. Ecological risk assessment of Cd in water

#### 2.3.1. Data selection

Toxicity data of no observed effect concentration (i.e., NOEC) were extracted from the United States Environmental Protection Agency (US EPA) ECOTOX database (<http://www.epa.gov/ecotox/>) and peer-reviewed literature for nine groups of freshwater organisms, including algae, amphibians, aquatic plants, crustaceans, fish, insects, molluscs, worms and other invertebrates. Only the data of quality of category 2b or above were selected for the analysis. Geometric mean was applied when there were multiple data available for the same species (Wheeler et al., 2002).

#### 2.3.2. Derivation of predicted no effect concentration (PNEC)

The SSD analysis was performed on log-transformed data by use of an SSD generator, which was downloaded from USEPA (<http://>

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