



# Spatial distribution, environmental assessment and source identification of metals content in surface sediments of freshwater reservoir, Pakistan



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## ARTICLE INFO

### Article history:

Received 26 June 2015

Accepted 6 February 2016

Editorial handling - H. Guo

### Keywords:

Metal

Risk assessment

Contamination

Pollution load index

Multivariate analysis

Pakistan

## ABSTRACT

Surface sediments were collected from different sites of a freshwater reservoir, Pakistan, and analyzed for eight metals (Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn) using flame atomic absorption spectrometry. The estimated metals levels were found higher than other reported studies. The environmental indices including geoaccumulation index, enrichment factor and contamination factor identified Cd, Co, Pb and Zn as the priority pollutants of concern. Chromium, Cu and Mn were also found to be enriched in some areas. The pollution load index ( $\geq 1$ ) indicated progressive deterioration of the sediments quality. Principal component and cluster analyses revealed that Cd, Co, Pb and Zn were mainly originated from agricultural activities, domestic wastes, road runoffs and recreational activities. Chromium, Cu, Fe and Mn were mainly derived from natural sources though Cr, Cu and Mn were partially contributed by human inputs. Based on spatial distribution, inlet and middle sites of the reservoir were found more contaminated. This study would drive urgent attention to develop preventive actions and remediation processes for aquatic system protection and future restoration of the reservoir.

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## 1. Introduction

Heavy metal pollution in aquatic ecosystems has got sizeable consideration owing to their toxicity, persistence and biological buildup (Varol, 2011; Jiang et al., 2012; Li et al., 2013). Concentrations of heavy metals in sediments are affected by both geogenic and anthropogenic factors (Lalah et al., 2008). Natural factors include benthic agitation, flow changes, rocks weathering and natural erosion etc., while anthropogenic factors include sewage discharge, industrial wastewater discharge, atmospheric deposition, agricultural runoff and fertilizer leaching etc. (Romic and Romic, 2003; Tang et al., 2010; Choi et al., 2012; Srebotnjak et al., 2012; Rodriguez-Martin et al., 2013; Su et al., 2013; Islam et al., 2014). In aquatic environment, heavy metals exhibit high attraction for particular matter and will hence accumulate in sediments (Sundaray et al., 2011). Once absorbed and accumulated on sediments, though, chemical and biological processes may permit heavy metals to be desorbed from surface sediments as a result of which they are discharged into the water column (Li and Davis,

2008; Dong et al., 2012; Cheng et al., 2013). Sediments, afterward, can act as a sink and potential secondary source of contaminants in aquatic environment (Caeiro et al., 2005; Segura et al., 2006; Yu et al., 2008; Bai et al., 2011). Therefore, the research on heavy metals in surface sediments provides significant insights into the metal pollution and associated risks in order to protect corresponding aquatic ecosystem.

The objectives of this study were to (1) assess the concentration and spatial distributions of selected metals (Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn) in surface sediments from Simly Lake, Pakistan, (2) determine the potential environmental risk employing enrichment factor (EF), geo-accumulation index ( $I_{geo}$ ), contamination factor (CF) and pollution load index (PLI), and (3) identify the natural and/or anthropogenic sources of these metals using statistical techniques such as, principal component analysis (PCA) and cluster analysis (CA). It is further anticipated that this study would provide a geochemical data related to the spatial distribution and contamination of the metals in the freshwater reservoir which would help to provide essential information to support environmental control actions for the anthropogenic pollutants in the natural ecosystem.

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Fig. 1. Location map of the study area.

## 2. Materials and methods

### 2.1. Study area

Simly Lake (longitude: 73°20' E and latitude: 33°43' N) is a freshwater source for the residents of Islamabad, the capital city of Pakistan (Fig. 1). It is an 80 m high, earthen embankment reservoir on the Soan river, near Bhara Kahu town, 30 km east of Islamabad. It was constructed in 1983 and is spread over an area of 28,750 acres. The water stored in this lake is fed by the melting snow and natural springs from Murree hills and other surrounding areas. It is a popular picnic spot because of its scenic location. This lake provides recreation facilities like boating, sailing, fishing and water skiing. Untreated domestic wastewater effluents, agricultural and road runoffs, and pollutants released during recreational activities are among the major metal contamination sources in this lake.

### 2.2. Sample collection and storage

A total of 50 composite surface sediments (0–15 cm, top layer) were collected from Simly Lake, Pakistan in June 2013. Each composite sample was composed of 3–5 subsamples from an area of about 20 m<sup>2</sup>. The sediments samples were collected in pre-cleaned Zip-locked polythene bags by using a sediments snapper (Ø5 cm). The collected samples were placed in an ice-cooler and transported to the laboratory immediately. Then the samples were dried, grounded, homogenized, sieved through a 2 mm nylon mesh after removing stones or other debris, sealed in pre-cleaned polythene bags and stored in a refrigerator until further processing (Kannan et al., 2008; Nemati et al., 2011; Saleem et al., 2013).

### 2.3. Reagents and glassware

All reagents used were of analytical grade (certified purity >99.9%) procured from E. Merck, Germany or BDH, UK. Double distilled water was used for the preparation of all solutions. Metal standard solutions used for the calibration were prepared by diluting the stock solutions (1000 mg/L) of each metal. All glassware used was cleaned by soaking in dilute acid (20% HNO<sub>3</sub>, v/v) for at least 24 h, followed by repeated rinsing with double distilled water (Diaz-de Alba et al., 2011). Finally the glassware was dried in an electric oven maintained at 80 °C for about eight hours prior to use.

### 2.4. Chemical analyses and quality control

The pH was measured with a multimeter (Bench Meter, Martini Instrument Mi 180) in a 1:2 sediment:water suspension (Radojevic and Bashkin, 1999). For the measurement of pseudo-total metal levels, an aliquot of 1–2 g dried sediments was digested in a microwave oven using a freshly prepared acid mixture (9 mL HNO<sub>3</sub> and 3 mL HCl) (USEPA, 2007). After microwave digestion, the sample solutions were filtered (0.45 μm, pore size) and stored at 4 °C in a refrigerator until further analysis. A reagent blank was also prepared containing same amounts of the reagents without sediment sample along with each batch of samples.

The samples were then analyzed for Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn by flame atomic absorption spectrometry. Calibration line method was followed for quantification of the selected metals and the samples were appropriately diluted whenever required (Radojevic and Bashkin, 1999; Iqbal and Shah, 2011). All measurements were made in triplicate and the results were shown as the mean. Instrument settings were as recommended in the manufacturer's manual, with wavelengths (nm) of 228.8 (Cd), 240.7 (Co), 357.9 (Cr), 324.8 (Cu), 248.3 (Fe), 279.5 (Mn), 217.0 (Pb) and 213.9 (Zn). For quality assurance and quality control, the precision and accuracy of the chemical methods were ensured by analyzing the standard material (SRM 2709) and reagents blanks, with each batch of samples. The percentage recoveries of the metals in the standard reference material samples ranged from 93 to 104%. Some sediment samples were also analyzed for cross comparison at an independent laboratory and a maximum of ±2.5% difference was found in the two results.

### 2.5. Environmental risk assessment

Metal contamination in the sediments was assessed using geo-accumulation index ( $I_{geo}$ ), enrichment factor (EF), contamination factor (CF) and pollution load index (PLI).  $I_{geo}$ , CF and EF are the most common methods to assess the ecological risk by a single element, whereas PLI evaluates the environmental risk posed by multiple elements (Caeiro et al., 2005; Li et al., 2012; Zhao et al., 2012; Cheng et al., 2013; Hou et al., 2013; Wang et al., 2014a).

#### 2.5.1. Geo-accumulation index ( $I_{geo}$ )

The  $I_{geo}$  enables the assessment of contamination by comparing the current and pre-industrial concentrations of the metals

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