Science of the Total Environment 470–471 (2014) 925–933

Contents lists available at ScienceDirect

Science of the Total Environment

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

Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah—Feeding tributary of the Rawal Lake Reservoir, Pakistan

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HIGHLIGHTS

- EF, I_{geo} and MPI were used to determine metal enrichment in sediments of the Kurang stream.
- Cd, Zn, Ni and Mn enrichment was more in sediments.
- Ni and Zn were above ERL values; however, Ni exceeded the ERM values.
- Ni and Zn threats to aquatic ecosystem should not be ignored.

ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form 2 October 2013
Accepted 3 October 2013
Available online 14 November 2013

Editor: Gisela de Aragão Umbuzeiro

Keywords:
Sediments
Multivariate analysis
Enrichment factor
Geo-accumulation index
Heavy metals

ABSTRACT

Heavy metal concentrations in sediments of the Kurang stream: a principal feeding tributary of the Rawal Lake Reservoir were investigated using enrichment factor (EF), geoaccumulation index (I_{geo}) and metal pollution index (MPI) to determine metal accumulation, distribution and its pollution status. Sediment samples were collected from twenty one sites during two year monitoring in pre- and post-monsoon seasons (2007–2008). Heavy metal toxicity risk was assessed using Sediment Quality Guidelines (SQGs), effect range low/effect range median values (ERL/ERM), and threshold effect level/probable effect level (TEL/PEL). Greater mean concentrations of Ni, Mn and Pb were recorded in post-monsoon season whereas metal accumulation pattern in pre-monsoon season followed the order: Zn > Mn > Ni > Cr > Co > Cd > Pb > Cu > Li. Enrichment factor (EF) and geoaccumulation (I_{geo}) values showed that sediments were loaded with Cd, Zn, Ni and Mn. Comparison with uncontaminated background values showed higher concentrations of Cd, Zn and Ni than respective average shale values. Concentrations of Ni and Zn were above ERL values; however, Ni concentration exceeded the ERM values. Sediment contamination was attributed to anthropogenic and natural processes. The results can be used for effective management of fresh water hilly streams of Pakistan.

1. Introduction

Sediment quality is an indicator of water pollution that manifests pollutant variations. Sediment provides a site for biogeochemical cycling and the foundation of the food web (Burton et al., 2001). Sediments have been used as an important tool to assess the health status of aquatic ecosystems (Birch et al., 2001) and are an integral component for functioning of ecological integrity. Sediments act as a sink of organic as well as inorganic pollutants (heavy metals) and provide a history of anthropogenic pollutant input (Santos Bermejo et al., 2003) and environmental changes (Shomar et al., 2005). Heavy metals enter the aquatic ecosystems through point sources such as industrial, municipal and domestic waste water effluents as well as diffuse sources which include surface runoff, erosion, and atmospheric deposition.

Sediment pollution with heavy metals is a worldwide problem (Fernandes et al., 2008; Kucuksezgin et al., 2008) and is considered to be a serious threat to the aquatic ecosystem because of their toxicity, ubiquitous and persistence nature, non-biodegradability and ability to bio-accumulate in food chain (Duman et al., 2007). Sediments serve as the largest pool of metals in aquatic environment. More than 90% of the heavy metal load in the aquatic systems has been found to be associated with suspended particulate matter and sediments (Amin et al., 2009; Zheng et al., 2008). Metals in suspended particulates settle down and pool up in sediments (Kucuksezgin et al., 2008), while the dissolved metals adsorb onto fine particles which may carry them to

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http://dx.doi.org/10.1016/j.scitotenv.2013.10.017

bottom sediments (K.P. Singh et al., 2005). Distribution of heavy metals is influenced by the mineralogical and chemical composition of suspended material, anthropogenic influences, deposition, sorption, enrichment in organism (Jain et al., 2007), and various physico-chemical characteristics (K.P. Singh et al., 2005).

Sediment has widely been studied for anthropogenic impacts on the aquatic environment (Sayadi et al., 2010). Various studies have reported sediment quality assessments, distribution and contamination of heavy metals and quantification of pollution load in sediments of different rivers such as the Po River, Italy (Viganò et al., 2003), the River Gomti, India (V.K. Singh et al., 2005), the Songhua River, China (Lin et al., 2008), and the Shur River (Karbassi et al., 2008) and the Khoshk River (Salati and Moore, 2010) in Iran. However, river sediment contamination has sparsely been investigated in Pakistan in general and no information is available for the Kurang Nallah and its associated streams. The Kurang is a main feeding tributary of the Rawal Lake Reservoir and is the cheapest source of drinking water for the local population. The Kurang has been subjected to heavy metal pollution due to a rapid increase in population and unplanned human settlements in its catchment area, washing activities (human, animal and laundry), recreational activities, poultry waste discharge, dumping of solid waste and direct and/or indirect discharge of untreated domestic effluents. During recent years, annual fish production has been reduced from 450 to 600 tons in the Kurang and Soan Rivers. Therefore, the importance to investigate heavy metal contamination, distribution and possible sources. The present study aimed to (1) determine the accumulation, spatial and temporal distribution trends, and source identification of heavy metals in sediments of the Kurang and its tributaries, (2) quantify the extent of metal pollution using enrichment factor (EF), geoaccumulation indices (I_{geo}) and metal pollution index (MPI), and (3) assess ecological risk of sediments using sediment quality guidelines viz., effect range low/effect range median values (ERL/ERM), and threshold effect level/probable effect level (TEL/PEL).

2. Materials and methods

2.1. Study area

The Kurang is an important watercourse of the Rawalpindi district and is the principal feeding tributary of the Rawal Lake Reservoir, catering for 50% water demand of the fourth largest city (Rawalpindi) of the country. The Kurang makes its origin from numerous natural springs in the Murree Hills and is fed by numerous seasonal and perennial streams. It passes through undulating terrain which is dissected by gullies and ravines, ranging from steep slopes to relatively plain areas. The Kurang is characterized by sluggish flow throughout the year, except during monsoon season when heavy rain fall causes a manifold increase in its runoff. Three important streams join the river along its course: Baroha, Malachh and Shahdara. The mean annual precipitation ranges from 1000 mm to 1500 mm. The bulk of the monsoon precipitation is received during July and August, with monthly averages of 267 mm and 309 mm, respectively. The average monthly maximum and minimum temperature ranges from 16.9 °C to 40.1 °C and from 3.1 °C to 24.7 °C, respectively. The lowest temperature was recorded in the month of January (−4 °C) and the highest was reached in the month of June (48 °C). Relative humidity ranges from 19% to 54% recorded in the month of May and August. Wide seasonal variations in temperature and precipitation characterize the climate as sub-humid. The elevation ranges from 525 to 2181 m. Rocks are composed of red and purple sand stone, limestone, shale, and siltstone. Soils are derived from wind and water laid deposits. Effects of erosion are more pronounced throughout the study area.

2.2. Sediment sampling

Surface pore water sediment samples were collected from twenty one sites along the Kurang River and its feeding tributaries (Fig. 1) during the period of two years on seasonal basis viz., pre-monsoon season (April 2007 and 2008), and post-monsoon season (October 2007 and 2008). Samples that showed no evidence of surface disturbance were retained. The top 2–3 cm was removed, transferred to pre-cleaned polythene bags and sealed. Sediment samples were kept at ~4 °C before laboratory processing. Sediment samples were air dried, crushed, sieved (<2 mm) and stored in pre-washed glass containers at room temperature. Global Positioning System (GPS) was used to locate the sites.

2.3. Determination of metals

For the measurement of total metal concentrations, acid digests of each sediment sample were prepared using USEPA method 3051. Each sediment sample measuring 0.5 g was digested in 10 ml of ultrapure HNO_3 using Microwave Accelerated Reaction System (MARS, CEM®), filtered, and diluted. Total metal concentration of Cr, Mn, Co, Ni, Cu, Cd, Zn, Ca, Mg, Fe, K, Na, Pb, and Li was determined in triplicate in air/acetylene flame using Fast Sequential Atomic Absorption Spectrophotometer (Varian FSAA-240). Results of triplicate analyses revealed good reproducibility of the equipment. Analytical blanks and standard reference material were run in the same way as the samples and heavy metal concentrations were determined using standard solutions prepared in the same acid matrix. Sediment reference material CRM 320 was used (N = 3) to ensure the validation of data and the accuracy and precision of analytical method. The recoveries were 84–105% for all metals regarding their certified/non-certified values, which in general are considered satisfactory. Total heavy metal concentrations were expressed in mg/kg dry sediments.

All the reagents used were of supra quality and of analytical grade. All solutions were prepared using ultra pure water. All plastic, quartz and glassware were soaked in HNO_3 (10%) for at least 24 h and rinsed repeatedly with ultra pure water.

2.4. Measurement of other sediment parameters

Organic matter (OM) was determined by Tyurin's method (Nikolskii, 1964). Sediment pH, electric conductivity (EC) and total dissolve solids (TDS) were determined using a portable pH, EC and TDS millimeter (Milwaukee, model SM 802). Sediment suspension was prepared in 1:9 ratio of sediment to deionized water (10 g soil; 90 ml distilled water). Before the determination of pH, EC, and TDS, the mixture was stirred for sixty seconds at 10 minute intervals for 30 min. The proportion of sand, silt and clay (%) was calculated to determine soil textural class using the Bouycous hydrometer method.

2.5. Quantification of sediment pollution

2.5.1. Enrichment factor (EF)

Normalized enrichment factor is applied (Salati and Moore, 2010) to differentiate metal source originating from anthropogenic and natural means (Selvaraj et al., 2004). This involves normalization of the sediment with respect to reference elements such as Al, and Fe (Acevedo-Figueroa et al., 2006; Amin et al., 2009; Huang and Lin, 2003; Karbassi et al., 2008), Mn, Ti and Sc (Salati and Moore, 2010), and Li and Cs (Pereira et al., 2007). Geochemical normalization has also extensively been used to calculate enrichment and to reduce heavy metal variability caused by grain size and mineralogy of sediments (Zhang and Shan, 2008). Normalized EF of metals in Kurang pore water sediments of each site was calculated using Eq. (1). Manganese (Mn) was used as a reference element to calculate anthropogenic metal enrichments as described by Loska et al. (1997). World average concentration of metals reported for the shale by Turekian and Wedepohl (1961) was used as background values for heavy metals (Cr, Co, Ni, Cu, Cd, Zn, Fe, Pb, and Li). Based on EF values, all the sites were categorized into five main classes (Table 1) (Birch and Olmos, 2008).