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## Geochemical Assessment of Some Heavy Metal Levels in Neka River Sediments-Neka City, Iran

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**Abstract:** The Neka River watershed covers a large portion of Mazandaran province, Iran and is centrally important to both recreational and other activities in the region. In order to assess current water quality conditions distribution of three heavy metals were determined in river sediments at four sampling stations in the watershed. Cu, Cr and Fe concentrations were determined using flame atomic absorption spectrometry. Standard operating procedures for the analysis of metals were used. Metal concentrations in sediments ranged from 6.35 to 13.56 for Cu, 17.66 to 209.7 Cr and 1.5 to 23.4 for Fe mg g<sup>-1</sup> dry weight sediment. The results showed higher concentrations of Cu, Cr and Fe in the test samples compared to that in the control. Significant difference in level of Cu, Cr and Fe was seen between test and control groups ( $p < 0.05$  for Cu and Fe ;  $p < 0.001$  for Cr). This study can be an alarm to researchers for more study about pollution of sediments in Mazandaran and finding proper methods for reducing and removing.

**Key words:** Heavy metals, sediments, Neka River, geochemical assessment, Iran

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### INTRODUCTION

Environmental contamination from heavy metals is of concern because they exhibit behaviour consistent with those of persistent toxic chemicals. Unlike many organic Contaminants that lose toxicity with biodegradation, metals can not be degraded further and their toxic effects can be long lasting (Clark, 1992). And whilst their concentrations in biota can increase through bioaccumulation, heavy metals are also known to have toxic effects at very low concentrations (Guhathakurta and Kaviraj, 2000). Sediments play a useful role in the assessment of heavy metal contamination (Guhathakurta and Kaviraj, 2000; Lee *et al.*, 2000). This is because in unperturbed environments, heavy metals are preferentially transferred from the dissolved to the particulate phase and as a result metal concentrations in sediments are generally much higher than in the overlying water and therefore more easily detected. The advantage of using sediments then is that the analytical problems associated with the detection of low but significant amounts of metals in water do not have to be addressed. Also, continuous monitoring of water is not necessary as sediment concentrations indicate contamination loads over longer periods of time (Lee *et al.*, 2000).

Heavy metals occur in the environment both as a result of natural processes and as pollutants from human activities. Contamination of the watery environment by

metals has risen in recent years due to the global population increase and industrial development (Guhathakurta and Kaviraj, 2000).

The River burden of heavy metals and different kinds of pollution is now a serious environmental concern and public interest regarding this issue has been increasing (Lee *et al.*, 2000). Research efforts have focused primarily on salt marshes, estuaries and coastal environments since these highly productive and sensitive areas are often directly and most seriously affected and exposed to this problem because of their proximity to sources of pollution (Miramand *et al.*, 2001; Ni *et al.*, 2000). Nevertheless, in recent years effluent discharges have been reduced considerably and the main concern has therefore, shifted from the impact of direct loading to possible effects of contaminants in the sediment caused by these discharges (Ruiz and Saiz-Salinas, 2000).

Metals tend to accumulate in sediments from where they may be released, moving up through the food chain (Bellucci *et al.*, 2002; Bertolotto *et al.*, 2003). Little is known about the bioavailability of sediment associated contaminants to marine organisms. However it is becoming increasingly important to understand metal accumulation within food webs, because once these heavy metals reach man, they may produce chronic and acute ailments. Regarding these aspects, various estuarine and coastal species have been studied with respect to their differing abilities to concentrate certain

metals and the effects that metal exposure can produce on them (McCready *et al.*, 2000).

Neka River originates from Shah-Koh mountain and enters the sea through Neka city. After flowing through the pass of Shamshir Bor, it flows into the Caspian Sea in the vicinity of Nowzar Abad. At first the course that this river flows is a mountainous one, with beautiful valleys covered with forests. On the condition that access is gained to the fringes of this river, recreational grounds or areas near Yanehsar can be accounted as attractive regions. It is one of the important and nourishing rivers. Its length is about 180 km with a basin area of about 3000 km<sup>2</sup>. It is a permanent river with an annual average flow of 148.2 million m<sup>3</sup>.

In contrast too many cases in Europe where pollutants from industrial regions are discharged into rivers and brought to the estuaries via fluvial action, in the Tajan. Most pollutants are discharged from agricultural activities and some local industries.

This study deals with concentrations of Cu, Cr and Fe that were extracted from the stream sediments located along a stream system in a populated region of Neka River. Stream sediments were used because heavy metal concentrations selectively integrate in geochemical phases in sediments.

## MATERIALS AND METHODS

**Choice of sediment size and sample collection:** Higher heavy metal concentrations are generally found on smaller grains of sediment because of the higher surface area to grain-size ratio. Therefore, the smaller the grain size, the higher the metal concentration accumulation. The project used sediment samples sieved PE-mesh of 63 Am to restrict the grain size for more accurate results.

Four stream sediment samples were collected in four sites of the Neka River (N1-N4) two of these samples were taken upstream (N1 and N2) as controls and others (N3 and N4) from downstream as test. At each sample site, the samples were wet sieved and the sediments between the mesh sizes of PE-mesh of 63 Am were saved for chemical analysis. At each sample site, a GPS instrument was used to save the location of the sample site as a way point in the instrument.

Sampling was carried out in August 2004 at 4 stations. Three samples were collected along transects at 500, 700 and 1000 m from the shoreline at each location. A Van Veen grab was used; whose penetration was typically 10-20 cm. We selected for analysis only the topmost sediment (2 cm) that was carefully removed with a plastic spoon and transferred to plastic vessels. Samples were stored at -18°C before analysis.

**Chemical extraction methods:** All steps carried out by method of Ruiz and Saiz-Salinas (2000). Analyses were done at the Environmental Quality Laboratory of Mazandaran Environmental Agency of Iran. The superficial two centimetres of the corer sediments that passed through a PE-mesh of 63 Am were dried at 85°C to constant weight, prior to homogenization by an agate mortar and pestle. In order to avoid interference of organic matter in the results and convert the metals to their free form, applying method no. 3051 of the EPA, duplicates of subsamples (0.5-1 g) were mixed with 10 mL concentrated nitric acid and digested by microwave (CEM, MDS 2100) in a closed fluorocarbon vessel. Quantification was by ASS (Shimadzu AA-680) with graphite furnace atomization (Shimadzu GFA-4B) or flame atomisation, depending on the concentration of the element analysed. Hg content was quantified by the cold vapour technique according to the method established by the US Environment Protection Agency and American Public Health Association guidelines. Quality control included procedural blanks; measurement of standards obtained from the National Institute of Standards and Technology and spiked samples.

Cu, Cr and Fe concentrations were determined using flame atomic absorption spectrometry. Standard operating procedures for the analysis of metals were used. A reference material for marine sediments (BCSS-1) which is certified for total metal content was analysed for total metals and the reliability of the instrumental technique was verified.

## RESULTS AND DISCUSSION

The results of the concentrations of the heavy metals in the geochemical phases of the stream sediment samples are given in Table 1.

For Cu, there was significantly different among sites: one group downstream (site N3) had the maximum level and one group in upstream (site N1) showed the minimum ( $p < 0.05$ ). For Cr, there were significant differences among test and control sites but no different among control sites or test. Fe pollution has a difference from other metals. This is correlated with urbanization and density of population. The concentration is higher in the upstream

Table 1: Heavy metal concentrations ( $\mu\text{g g}^{-1}$ ) in the sediments at the four sites analyzed: N1-N4 from Neka River (mean value±standard deviation)

Sampling site	Cu	Cr	Fe
N1 (Control)	6.35±0.35	19.33±0.66	88.42±0.61*
N2 (Control)	7.34±0.52	17.66±0.46	102.43±0.55*
N3 (Test)	13.56±0.53*	30.44±0.78**	41.33±0.23
N4 (Test)	13.35±0.35*	29.65±0.66**	44.29±0.44

\* Significant difference at  $p < 0.05$ , \*\* Significant difference at  $p < 0.001$

Table 2: Metal concentrations in sediments ( $\mu\text{g g}^{-1}$ ) material (Guhathakurta and Kaviraj, 2000; Lee *et al.*, 2000)

Metal	Cu	Cr	Fe
Experimental value	13.45±2.5	30.04±4.33	42.81±3.3
Certified value	18.5±2.7	22.7±3.4	35.55±2.3

area and could be associated with the localization industrial plants (iron-steel plants, oil transfer docks and other industrial plants). Considering the results in Table 1, it seems that the Cu and Cr contamination levels in sediments are lower than those found in sediments in different studies and the Fe Contamination is higher. Therefore, the concentration of Cu and Cr for each sample of each site was compared with the Guhathakurta and Kaviraj (2000). No sample analysed had values exceeding the set limits (lead  $100 \mu\text{g g}^{-1}$ ); In general, all these concentrations are considered to be of no concern for public health. But nothing is known specifically on toxicological effects of low levels of others heavy metals such as Cd, Pb in sediments particularly in combination with other contaminants (Piccolo *et al.*, 2000; Anonymous, 1999; McCready *et al.*, 2000; Nes and Oug, 1997; Notar *et al.*, 2001; Prahel *et al.*, 1994).

According to Table 2 Cu, Cr and Fe concentrations in sediments at studied sites are not higher than ones proposed in the certified reference material (Guhathakurta and Kaviraj, 2000; Lee *et al.*, 2000). Although this study was not concerned with assessing the impact of contamination on the area's living resources, the low concentrations detected and the low apparent spread of contamination to areas further afield could be causing harmful effects. Efforts towards site remediation must include a thorough assessment of waste management practices of industries located upstream of the estuary.

It is assumed, therefore based on our data, that the current concentrations of pollutants in the Tajan River should not pose a serious threat to the Public health and that chemical contamination should not be a limiting factor. Taking into account pH levels at each sample site and also collecting more samples of the study area could improve this study.

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