

A MATHEMATICAL MODEL TO PREDICT NICKEL CONCENTRATION IN KARAJ RIVER SEDIMENTS

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ABSTRACT

The contamination of surface waters through human activities has been intensified over the past years as population density has increased. Nickel is a metallic element and fuel combustion, nickel mining, refining waste, sewage sludge, and incineration are the major sources of nickel propagation. Nickel from various industrial wastewaters and other sources finally are disposed into water bodies. In this work, Karaj river was considered from 50° to 50° 14' longitudes and 35° 45' to 35° 58' latitudes and the presence of nickel was also assessed in this area. Sixteen stations were randomly selected and sediment samples were collected in polyethylene containers. Some water quality parameters such as pH, temperature, dissolved oxygen, electrical conductivity, were determined by direct on-site measurements. To measure COD, 16 water samples were collected in dark bottles and transferred to laboratory spatial parameters such as slope and distance from start point were also calculated by ARCGIS 9.2. The relation between Ni concentration with spatial parameters and water quality parameters were obtained by multivariate analysis. Results showed that there was a significant relation between Ni concentration in sediments and distance from start point and electrical conductivity.

Key words: Karaj river, pollution, nickel, sediment, mathematical model

INTRODUCTION

The contamination of surface waters through human activities has been increased over the past years as population density has increased. To fully understand the anthropogenic impact on an ecosystem, long-term data from chemical, physical and biological indicators are needed. To many people, heavy metal pollution is a problem associated with areas of intensive industry. Metals, such as nickel and cadmium, are also found in road runoff and exhaust. Metals strongly associated with the surface of particles, their transport and deposition in estuarine and coastal systems are often closely related to the transport and deposition of fine-grained sediments (Olsen *et al.*, 1982; Dzombak and Morel, 1987; Davis and Hem, 1989;

Scheidigger *et al.*, 1997; Bertsch and Seaman, 1999). In the absence of significant changes in sediment texture, trace metal accumulation rates in sediment cores can reflect variations in metal inputs in a given system over long periods of time. A large amount of the total elemental constitution of most sediments is in a residual fraction as part of the natural minerals that make up the sediment particles. These residual elements are not bioaccessible; the remaining elements in sediments are adsorbed to or complexed with various sediment components and may be bioaccessible. In oxidized sediments, cations may be adsorbed to clay particles, iron, manganese and aluminum oxide coatings on clay particles, or dissolved and particulate organic matter. As the concentration of oxygen in sediment decreases, usually because of

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microbial degradation of organic matter, oxide coatings begin to dissolve, releasing adsorbed cations. In oxygen-deficient sediments, many cations react with sulfide produced by bacteria and fungi to form insoluble sulfides. Many chemical species may be released from absorbed or complexed phases into sediment pore water in ionic, bioavailable forms following changes in oxidation/reduction potential. Microbial degradation of organic matter may also release adsorbed species to pore water (Apostoli *et al.*, 2006).

Many contain heavy metals Environmental Protection Agency (USEPA) estimated that there are 550 million used mobile phones sitting in United states. homes, waiting to go into landfills. The vast majority of these phones contain nickel-cadmium batteries and the problem increases by 50 million more cellular phones each year (Farr, 2004). Estimates made by Schmidt and Andren indicated that fuel combustion, nickel mining, refining waste, sewage sludge and incineration are the major source of nickel propagation (Schmidt and Andren, 1980). Nickel from various industrial processes and other sources finally reach wastewater (Hertel *et al.*, 1991).

In rivers, nickel is transported mainly as a precipitated coating on particles and in association with organic matter; in lakes, the ionic form and the association with organic matter are predominant (Snodgras, 1980). Nickel may be deposited in the sediment by such processes as precipitation, complexation and adsorption on clay particles and via uptake by biota. Because of microbial activity or changes in physical and chemical parameters including pH, ionic strength and particle concentration, sorption processes may be reversed (Di Toro *et al.*, 1986) leading to release of nickel from the sediment. Aquatic plants are also known to take up and accumulate nickel (Jenkins, 1980 a). As algae are at the lower end of many food chains, this fact needs special consideration. The highest nickel levels found in aquatic algae and spermatophytes in contaminated areas were 150.9mg/kg dry weight or 690mg/kg wet/kg wet weight, respectively, exceeding normal levels by more than 10 times (Jenkins, 1980a).

The aims of the present work were to (1) investigate the presence of Ni (II) in Karaj river and (2) present the mathematical model for predicting Ni (II) concentration in Karaj river sediments.

MATERIALS AND METHODS

Description of the area under study

Karaj river in this study is considered from 50° to 50° 14' longitudes and 35° 45' to 35° 58' latitudes. The study area is located in the lower part of Amir Kabir dam with 844.98km² watershed and is not an industrial area. Investigations have shown that villages are main sources of pollution in this river that discharge their waste into the river. Heavy metal pollution in this area can be related to previous emissions from pollution sources.

Spatial characteristics

The spatial characteristics such as slope and distance from start point were derived from digital map layers and aerial or satellite images by ARC GIS 9.2 software (Table 1). GIS (Geographic Information System) provides a consistent method for watershed and stream network delineation using Digital Elevation Models (DEM) of land-surface terrain (Xinhao, 1998).

Table 1: Geographic coordinates and spatial characteristics in each sampling point in karaj river

Station.No	Longitude (degree)	Latitude (degree)	Slope (degree)	Distance (m)
1	51.05813	35.93466	2	0
2	51.05594	35.92653	2	1280
3	51.04743	35.91719	28	2400
4	51.04992	35.87208	15	8000
5	51.05782	35.86229	15	9300
6	51.04562	35.83398	2	13400
7	51.02951	35.82848	2	15000
8	51.01942	35.82087	2	16500
9	51.01083	35.81108	2	17700
10	51.00330	35.79790	2	19000
11	51.01076	35.79030	6	20200
12	51.00925	35.78590	2	21000
13	51.01565	35.77933	2	23000
14	51.02070	35.77011	2	24400
15	51.03344	35.75449	2	25500
16	51.03681	35.74201	2	27000

Environmental analysis

Some parameters including temperature (T), electrical conductivity (EC), pH, dissolved oxygen (DO) made by direct on-site measurements. Sixteen water samples were also collected in dark polyethylene containers and transferred to chemical laboratory for measuring COD.

Collection and treatment of samples

Sampling was performed on May 2007; 16 stations were selected randomly for sampling in Karaj river. Geographic coordinates of sampling points were determined by GPS (Global Positioning System).

Sampling points are shown in Fig.1.

For this study 16 surface sediment samples were collected with a grab. The samples were removed from the superficial layer with a polyethylene spoon to avoid contamination, and stored in polyethylene bottles, previously cleaned with 10% nitric acid for 24h and rinsed with distilled water. Sediments were dried at room temperature and then ground and sieved through a 0.710mm sieve to 30mL of an acidic solvent involving 1:3 mixtures of HNO₃ and HCl and heated by a water bath for 20min at 70°C 80°C moderately. The samples were agitated on shaker for 30min and then filtrated. To obtain a calibration graph 4 standard solutions were prepared in 2, 4, 5, 8mg/L with nitrate nickel (II)

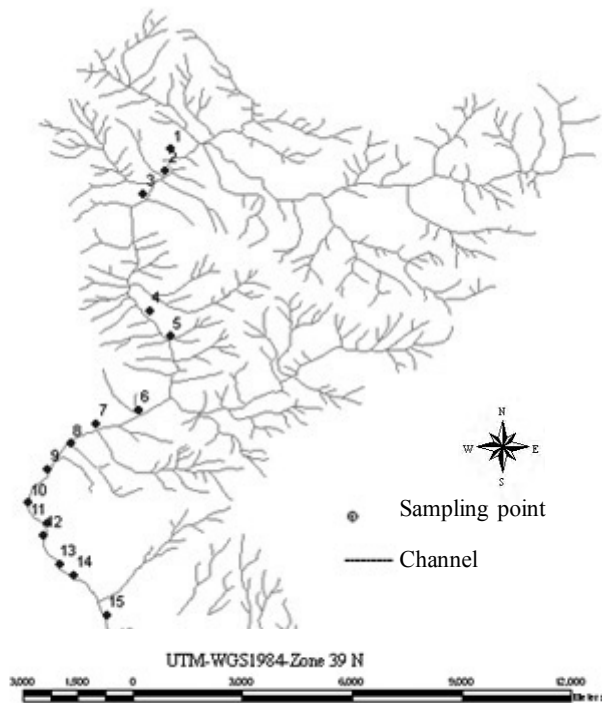


Fig 1: sampling points in karaj river sediments

in deionised water. The standard solution absorbances and the concentration of Ni (II) in solvent phase were measured by flame Atomic Absorption Spectrophotometer (AAS, GBC-932 plus) in 232nm wavelength. Measurements, however, were triplicated.

Statistical analysis

The Ni concentration was reported as mg/g of sediment; hence the relation between Ni (II) concentration and measured parameters were acquired by multivariate regression analysis.

ANOVA Analysis was used for assessing the significance of predictive model; both statistical methods were applied using SPSS V.15.

RESULTS

All results acquired of water quality parameter measurements are presented in (Table 2).

The multivariate regression was used to obtain a linear equation for estimating of nickel concentration. Equation 1 shows a correlation between Ni concentrations in sediment with two measured parameters.

$$C_{(Ni)} \text{ (mg/g in sediment)} = 148.050 + 1.188(\text{DISTANCE}) - 0.715(\text{EC}) \quad (1)$$

(R² = 0.708)

This model was statistically rigorous at the %99 of confidence level since p values for independent variable were all less than 0.01. This model shows that nearly %71 variability in Ni (II) concentration could be described by EC and distance. Results obtained from ANOVA analysis showed as P value for predictive model is significant (P<0.01).

Incorporating the other measured parameters did not improve the model fitness.

Table 2: Water quality parameters measured in Karaj river

Factors	mean±SD	Range
T (°C)	15.31±2.12	11.50-17.50
pH	6.72±0.06	6.60-6.80
DO (mg/L)	7.96±0.47	7.30-8.90
EC (µs/cm)	200.78±9.36	189.50-217.00
COD (mg/L)	23.60±2.22	8.80-140.00

Table 3: Mean and standard deviation for nickel concentration in three measurements in Karaj river Sediments

Ni (mg/g sediment)	Mean±SD
First measurement	0.022±0.007
Second measurement	0.023±0.007
Third measurement	0.022±0.006

DISCUSSION

As the model reveals, nickel concentration is strongly correlated with distance. It can be interpreted that with increasing distance, the number of point source and non-point source pollution are increasing; therefore, large quantity of waste containing Ni is deposited. EC is important for fitness of model, but has negative coefficient. It means that, the increasing of EC gives rise to decreasing of Ni concentration in sediment. These suspended ions were increased EC of water. As

water pH was acidic, hence most Ni enters the water body resulting to the reverse ratio with EC. In this study static data with no temporal components were used. However, with the evolution of temporal GISs recording spatio-temporal analysis, some results can be provided to better evaluate the existing situation and predict the future trend. Some parameters which have not been considered at this stage of the research could affect the result as well. For example the geological setting is significant as it has influenced the morphology of the region. In addition, understanding these geological and geomorphologic systems provides the necessary framework to study the impact of human intervention in the catchments (Pred and Cox, 2002). Many studies show the effectiveness of multivariate analysis for extracting mathematical model to prediction. For instance the relation between chromium sorption with soil properties has been assessed (Salmasi, 2007).

Other study considers the mathematical relationship between concentration of Chlorophyll a and seven environmental factors, i.e. Lake water temperature, Secci-depth (SD), pH, DO, COD, total nitrogen (TN), total phosphorus (TP) in Qiandaohu Lake. Stepwise linear regression used in this paper. The results showed that SD, TP and pH were the most significant factors affecting Chlorophyll a concentration (Jiao Yan *et al.*, 2004). As the region of Karaj is not industrialised and has low population, the occurrence of metals is likely to be natural and the metal distribution is primarily controlled by natural processes. In this respect, the main objective of the current study of metal distribution and concentration is to establish a baseline of comparison for future environmental investigation to locate such sites and assess local processes.

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