

DETERMINATION OF HEAVY METALS CALCIUM (CA), CHLORINE (CL) IONS AS SALT OF THE WATER BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY IN THE TAJAN WATER WAY RIVER, IRAN

ABSTRACT

Purpose: Increasing salt of water is a world-wide problem, heavy metals belonging to the most important materials. The progress of industries has led to increased emission of pollutants and salt of water into ecosystems. Tajan is one of navigable river in the North of Iran. Along the Tajan agricultural industries units such as piping, steel, paint making, paper mill, fish cultivation, abbotiors, electroplating industries drain their waste water into the river. In this study, the concentrations of Calcium(CA), Chlorine(CL) ions as salt of the water in the Tajan river have been determined

Methods: Samples were collected from 5 stations along the river, in autumn and winter 2004. Heavy metal concentrations were measured by graphite furnace atomic absorption spectrometry.

Results: The minimal and maximal concentrations of these metals in autumn were 58.3–75.4, 44.3–209ppm, for Ca, Cl respectively. The minimal and maximal concentrations of these metals in winter were 58.1–73.9, 55.6–117.25 ppm for Ca, Cl respectively.

Conclusion: The results show that the salt of the water has increased along the river, down to the estuary at the Caspian Sea.

Keywords: Caspian Sea, Tajan river, Heavy metal, Calcium, Chlorine

INTRODUCTION

Industrialisation leads to to increase of salt of water into ecosystems . Calcium(CA), Chlorine(CL) ions are discharged into rivers and lakes and leaches into the soil and ground water, or is emitted into air as particulate matter(1-3). Heavy metals are critical in this regard because of their easy uptake into the food chain and because of bioaccumulation processes(4-6).

Tajan is one of navigable river in, and many industries such as metal, petrochemical and oil industries are located along its banks. Tajan river provides the water supply for these industries and is the source of drinking water for cities such as Sari, Dodangheh and Meayandrood. Its fish is one of the main sources of protein for human nutrition in the region, therefore presence of heavy metals in Tajan river pose a risk for food contamination(7).

In this study, concentrations of heavy metals have been determined at 5 different sampling stations upstream and downstream of important industrial areas along the river during two seasons, autumn and winter 2004.

Materials and methods

Concentrations of heavy metals in the river were measured. First, essential information about morphology and hydrology of river was obtained and the sources of pollution identified. According to this information, 5 sampling stations were chosen along the river (Figure 1 and Table 1). In selecting these stations the following criteria were considered: slope of the riverbank, route of the river, location of industries and their waste outlets, and accessibility for sampling(7-9).



Figure 1. Map of Tajan river.

Table 1. Water sampling stations along the Tajan river

Station Number	Name of Station	Location
S1	Dam(Dam of martyr Rajai)	Reference Station
S2	Road	15 km Road Dam - Sari
S3	railway	District Railway
S4	Bridge	Tajan Bridge
S5	End station	Entrance Tajan river to Caspian sea

Water samples were collected during November 2004 and February 2005. At each station nine water samples were collected using 1-l polyethylene acid-washed containers(10).The containers were rinsed with 5% nitric acid and distilled water and were washed with river water before sampling. Samples were acidified with 1–2 ml of concentrated nitric acid ($\text{pH}<2$). The samples were transported to the laboratory according to standard protocols. Before analysis, samples taken at the same water depth from one station were pooled. Analysis was carried out by graphite furnace atomic absorption spectrometry (SHIMADSO AA680). Samples were quantified by using standard solutions of the stock solution of soluble salts of the respective metal(11, 12). Bi distilled water was used for dilution of the samples.

Calcium(CA), Chlorine(CL) ions concentrations of selected stations were compared with concentrations found at locations further downstream (see Table 2 and Table 3 for station pairs). For comparison of the pollution in autumn versus winter five sites were selected (Figure 2&3). The statistical analysis was done using the Student's *t*-test or ANOVA, followed by Tukey test.

Results

Autumn conditions

The mean concentrations of Calcium at each of the five stations were significantly different from the respective downstream station of the station pairs ($P<0.001$), with the exception of station number S3 (Table 2). Also, the mean concentration of Chlorine at each station was significantly different from the respective downstream station of paired stations ($P<0.05$; Table 2).

Table 2. Comparison of Ca and Cl concentration at five selected sampling stations in autumn 2004

Station	S1 ^a	S2	S3	S4	S5 ^b
Ca (ppm)	75±0.4	58±0.6	69.3±3.1	73.8±0.5	75.4±1.3
Cl(ppm)	131.6±0.2	66.2±1.7	44±0.4	63.9±1.5	209±1.1

Data are presented as means±S.E.M. of three experiments, ^aupstream and ^bdownstream station of the two paired stations. * $P<0.05$, ** $P<0.01$, *** $P<0.001$, significantly different from other station. See Fig. 1 for geographical location and regional industry of stations

Winter conditions

The mean concentrations of Calcium in each of the five stations were significantly different from the respective downstream station of paired stations ($P<0.01$) with the exception of station numbers S4 (Table 3). The mean concentrations of Chlorine in each station were significantly different from the compared downstream stations ($P<0.001$.)

Table 3. Comparison of Ca and Cl concentration at five selected sampling stations in winter 2004

Station	S1 ^a	S2	S3	S4	S5 ^b
Ca (ppm)	68.1±0.7	62.5±1.2	68.4±1.8	73.9±0.9	58.1±1.04
Cl(ppm)	58.5±0.9	65.8±0.9	55.6±1.0	57±0.6	117±1.3

Data are presented as means±S.E.M. of three experiments, ^aupstream and ^bdownstream station of the two paired stations. * $P<0.05$, ** $P<0.01$, *** $P<0.001$, significantly different from the other station. See Fig. 1 for geographical location and regional industry of stations.

Seasonal comparison of heavy metal (Ca, Cl) concentrations in autumn and winter 2004

Figure 2 demonstrates that at all sampling stations the mean concentrations of heavy metal of Calcium in winter were significantly. Also, the mean concentrations of Chlorine in winter were significantly and consistently lower than in autumn (Figure 3).

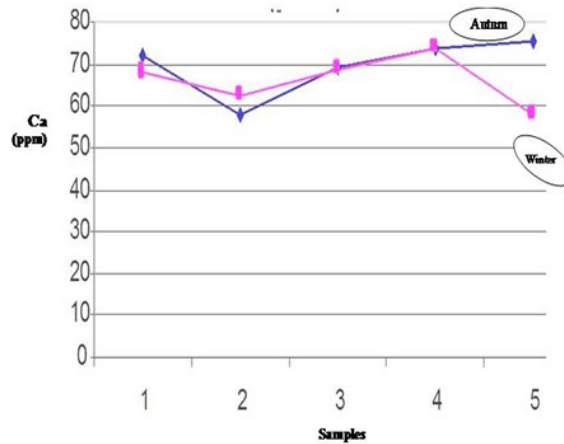


Figure 2. Seasonal comparison of heavy metal (Ca) concentrations at five stations along the Tajan river in autumn and winter 2004

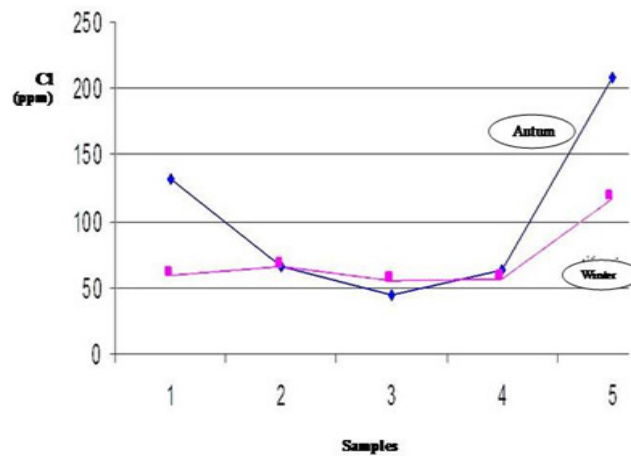


Figure 3. Seasonal comparison of heavy metal (Cl) concentrations at five stations along the Tajan river in autumn and winter 2004

DISCUSSION

Many environmental problems have been generated by humans and their activities. The main sources of salt of water of the Tajan river are urban, agricultural and industrial wastewaters. Industrial wastewaters and sewage of metropolitan centres, small electroplating workshops, repair shops, hospitals and medical and scientific laboratories, as well as surface runoff of cities are main sources of such urban wastewaters (13). The major sources of pollution and salt of water in agricultural wastewater are fertilisers containing heavy metals such as Cd, Pb, Ca, Cr, Zn, Cu, Cl and Ni. Fungicides and algacides used in fish farming are other sources of pollutants, mainly consisting of copper compounds (14, 15). The Mazandaran province in Iran was chosen for this study because this is one of the most important agricultural centres of Iran. There are different kinds of industries in this province, such as power plants, pipe, steel, paper, and paint production plants, as well as food, beverage, and dairy industries. From these sources heavy metals (Cu, Fe, Cd, Pb, Zn, Cr, and Ni) (16, 17) and may leach into the waters (Table 2&3).

In this study heavy metal concentrations were determined at five stations along the river. Comparisons among sampling sites (upstream stations were paired with stations further downstream). The upstream station numbers S1 (Dam), with the lowest concentrations of heavy metals, were considered as 'reference stations'. The results revealed higher concentrations of all two heavy metals (Ca, and Cl) at downstream stations station numbers S5 (End station) compared to upstream stations (Dam), and all concentrations of lead were higher in autumn than in winter. Also and all concentrations of cadmium were higher in winter than in autumn

Several sources for the increased metal concentrations appear likely. Chemical fertilisers containing Ni and Pb are used in agricultural industries of the regions around Tajan. Fungicides are used in fish farming in order to prevent epidemic diseases such as fin erosion. Fungicides and algacides are used in the paper industry for pulp making, in order to protect papers from mould development; these preparations contain copper compounds. Cu, Cr, and Pb compounds are used as pigments in the painting industry and as anti-fouling agents in marine paints(18). The wastewater of these industries is discharged to Tajan river directly, without any remediation; only a simple physical screening is being performed(Figure 2).

Figure 3 shows that the mean concentrations of Calcium in winter are higher than in autumn. This may be due to several reasons. The highest rainfalls in these regions occur in January and February. The turbulence of the water stream in winter is higher, because the seasonal floods lead to disturbances in the river base. Suspension of sediments into the water body may increase the metal concentration in the water. In addition, heavy rain falls lead to farm draining. Large amounts of pesticides containing metal compounds are brought via surface runoff from the farms to the river, contributing highly to the agricultural pollution(19).

In essence, our investigations of pollution of the Tajan river provide a typical example of environmental problems in a country like Iran.

Acknowledgements

This research was partially supported by a grant from the research council of Mazandaran University of Medical Sciences, Iran

References

1. Abernathy AR, Larson GL. and Mathews RC. Heavy metals in the surficial sediments of Fontana Lake, North Carolina. *Water Res* 1984; 18: 351–354.
2. Bourn W S. Ecological and physiological studies on certain aquatic angiosperms. *Contr. Boyce Thompson Inst* 1932;4: 425.
3. Lane TW, Morel FM. A biological function for cadmium in marine diatoms. Harbhajan Singh. *Mycoremediation: Fungal Bioremediation* 2004; 509.
4. Beijer K, Jernelöv A. Sources, transport and transformation of metals in the environment. In: Friberg, L., Nordberg, G.F., Vouk, V.B. (Eds.), *Handbook on the Toxicology of Metals*. Elsevier, Amsterdam 1986; 68–84.
5. John H. Duffus ""Heavy metals" a meaningless term? (IUPAC Technical Report)" *Pure and Applied Chemistry* 2002; 74: 793–807.
6. Harnly JM. Multielement atomic absorption with a continuum source, *Anal. Chem* 1986; 58: 933A-943A.
7. Jafarzadeh N, Morovaty K. 1996. Detection and determination of heavy metals in Karoon river: first report. Ahwaz Medical Sciences University and EPA of Khoozestan, Ahwaz 1996; 112–124.
8. Walsh A. The application of atomic absorption spectra to chemical analysis, *Spectrochim. Acta* 1955; 7: 108–117.
9. L,vov BV. Fifty years of atomic absorption spectrometry; *J. Anal. Chem* 2005; 60: 382–392.
10. Csuros M. *Environmental Sampling and Analysis for Technicians*. Lewis Publ., Boca Raton, FL 1994; 3–43.

11. Krajca, JM. Water Sampling. Horwood, Chichester 1989; 52–96.
12. Gutekunst B. Development of a method for the detection of heavy metal discharges into the sewer system. Final Report. Govt. Rep. Announcements & Index (GRA&I) 1988; 15: 81–90.
13. Babich H and Stotsky G. . Nickel toxicity to fungi: influence of environmental factors. Ecotoxicol. Environ. Saf 1982; 6: 577–589.
14. Spence, DF. and Green RW. Effects of nickel on seven species of fresh water algae. Environ. Pollut 1981; 25: 241–247.
15. Feick G R, Home A and Yeaple D. Release of mercury from contaminated freshwater sediments by the runoff of road deicing salt. Science 1972; 175: 1142 .
16. Vernet JP. Environmental contamination. In: A Selection of Papers Presented at the fifth International Conference on Environmental Contamination, Morges, Switzerland, 29 September–1 October 1992. Elsevier, Amsterdam 1993; 212–256.
17. Ramelow GJ Biven SL, Zhang Y, Beck J, Young JC, Callahan JD and Marcon, MF. The identification of point sources of heavy metals in industrially impacted water way by periphyton and surface sediment monitoring. *Water Air Soil Pollut* 1992. **65**: 157–190.
18. Teeter J W. Effects of sodium chloride on the sago pondweed. J. Wildl. Mgmt 1965; 29: 838..
19. Rauret G, Rubiv R, Sacher JF and Casassas E. Determination and speciation of copper and lead in sediment of a Mediterranean river. Water Res 1988; 22: 449–455.

¹Mohammad Karami*, Pouneh Ebrahimi, ³Samaneh Mortazavi -moghadam

¹ Associate Professor, Department of Toxicology-Pharmacology and Pharmaceutical Sciences Research Center, School of Pharmacy, Mazandaran University of Medical Sciences, Sari (Iran).

Department of Chemistry, Faculty of Basic Sciences, Golestan University, Gorgan, Iran,

³ Department of Toxicopharmacology , School of Pharmacy, Mazandaran University of Medical Sciences, Sari, Iran,