MERCURY POLLUTION OF THE JURAMENTO RIVER WATER SYSTEM (SALTA PROVINCE, ARGENTINA)

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Received June 8, 2004. In final form November 23, 2004

Abstract

Total mercury concentrations, determined by CVAAS on water samples filtered through glass fiber and subjected to oxidative digestion are informed for six rivers and four impoundments of the upper watershed of the Juramento river, in the province of Salta, Argentina. Data correspond to six hydrological years comprising nineteen sampling campaigns. Values are discussed considering water biota protection, and the possible use of these waters to provide drinking water. Probable sources of the high median (0.2-1.0 µg/L) total mercury concentrations are discussed.

Resumen

Se informan las concentraciones totales de mercurio en las aguas de seis ríos y cuatro represas pertenecientes a la alta cuenca del río Juramento en la provincia de Salta, Argentina, determinadas mediante EAAVF sobre muestras filtradas a través de fibra de vidrio y sometidas a digestión oxidante. Los datos corresponden a seis años hidrológicos estudiados a lo largo de diecinueve campañas de muestreo. Los resultados se discuten teniendo en cuenta la protección de la vida acuática y el eventual uso de estas aguas para consumo humano. Se discute el origen probable de las altas concentraciones promedio de mercurio (0,2 - 1,0 µg/L) halladas.

Introduction

Surface waters of the Juramento watershed in Salta Province (Argentina) are being systematically monitored since 1997 by the hydroelectric company Río Juramento S.A. according to the requirements of the Ente Regulador de Servicios Públicos (Public Services Controlling Authority) of Salta. Trace analysis of lead, cadmium, zinc, mercury and boron are carried out in our laboratories. Among the data of the nineteen sampling campaigns, mercury concentrations demand a close scrutiny. The maximum tolerable concentration according to National Law # 24051 [1] of 1 µg/L for drinking water supply, was exceeded in more than 20% at the thirteen sampling points, even at locations without any conspicuous pollution sources of this environmentally highly toxic element. This is particularly dangerous in this semi – arid region where the Juramento river is, by large, the most important water source. As mercury is one of the bioaccumulative heavy metals, its presence in concentrations over the established limit of 0.1 µg/L for water biota preserving [1] could make consumption of fish (mainly silverside, *odontesthes bonariensis*, introduced to the reservoirs for commercial and recreative fishing) dangerous to human health. The magnitude as well as the origin of contamination is considered in this study, so that to assess the possibility of taking protective measures by the controlling authorities.

Global situation

High mercury concentrations have been found at numerous locations around the world, especially in those regions where this metal has been or is mined [2,3], as well as where it has been used as an auxiliary to gold or silver mining [4]. Extensive industrial use of this metal in the past produced important pollution of rivers draining densely populated areas [5], the coincidence of its accumulation in lake sediments with the beginning of the industrial era having been confirmed [6]. Mercury is one of the most toxic metals, interfering seriously with the human central nervous system [7]. In the environment it can be found in its volatile elemental form, as slightly soluble inorganic salts, and as mono- and di-methylated mercury. These last two compounds are the most dangerously toxic forms, because of the ability of living organisms to incorporate them to their metabolism, that leads to the accumulation of mercury in their tissues. Mercury concentration has been found to be accumulated with size and aging, and magnified several times, in fish muscle, proportionally to concentration levels in water [8, 9, 10]. The high volatility of the elemental form of this metal and of its dimethylated compound is the cause of its widespread distribution [5]. In fact, aerial transport is recognized as an important cause of pollution [2, 3, 5].

Description of the area under monitoring.

The thirteen sampling points lay in the area comprised between 24º 48´ - 25º 40´ S and 64º 29´ - 65º 26´ W, covering 5.250 km^2. The climate of the area is semi-arid with annual mean temperature of 17.2ºC, average rainfall of 3 mm/month to 182 mm/month, according to the season, with annual mean (n = 30) of 755 mm. Two rivers conform the big Cabra Corral dam (11.400 ha and 3.130 hm^3) in Lerma Valley, the Arenales with its principal tributaries Arias and Toro – Rosario, and the Guachipas, formed by the confluence of the Calchaquí and Santa María rivers (Figure 1). The Juramento river drains the reservoir leaving the valley through the Peñas Blancas gorge, where a small compensating dike helps regulate the discharge. Some 60 km further on, the reservoir at Miraflores is used to distribute part of its water for irrigation. Its last dam in Salta territory at El Tunal forms a smaller reservoir (320 hm^3), which also receives the Medina river.

Sampling points Rosario, Toro and Medina (and even Arias to some extent) are exposed to urban pollution [11], while those of Toro and Guachipas lie in areas rather distant from any human activity.

Selected general characteristics of the sampling points [12] are listed in Table 1.

Historical discharge values for the rivers [13] show wide fluctuations, as well as their relative magnitude in the rainy season (Table 2), measurements having been suspended at all the hydrological stations of the area.

Experimental

Samples were taken in 5L polyethylene containers, previously washed with analytical reagent nitric acid, rinsed with distilled water and individually sealed in polyethylene bags to avoid contamination during transportation.

Table 1. *Median values of some general characteristics of the rivers and reservoirs at the sampling points.*

	Specific Conductance µS/cm	Suspended Solids mg/L	pH	Dissolved Oxygen %	Temperature ºC	BOD_5 mg O_2/L	COD mg O_2/L
Toro	354	1071	8.4	90	20	5	8
Rosario	256	652	8.2	76	24	35	33
Arias	165	82	8.2	88	24	2	5
Arenales	405	26	7.7	47	22	15	20
Guachipas	1410	365	8.4	80	22	7	11
La Maroma	412	9	8.6	84	22	6	10
El Zapallar	471	119	8.5	79	23	6	14
Cabra Corral Dam	415	3	8.7	88	22	5	12
P. Blancas	470	2	8.1	56	18	3	6
Miraflores	432	11	8.7	97	24	5	8
El Tunal Inlet	564	22	8.6	78	25	9	12
El Tunal Dam	564	10	8.6	95	24	7	10
Medina	676	148	8.4	78	26	7	12

Table 2. Hydrological characteristics of the rivers

River	Mean annual discharge (m^3/s)	Maximum daily Discharge (m^3/s)	Minimum daily discharge (m^3/s)	Hydrological Cycle
Toro	6.5	235	0.9	1929-62
Arias*	7	260	0.5	1945-67
Arenales	24.4	441	5	1941-67
Juramento**	26.5	851	7	1937-67
Calchaquí***	8.5	216	16	1946-54
Medina	3.8	250	0.5	1941-87

**Before its channeling to the aqueduct to the treating facility*
*** Before the Cabra Corral dam was constructed*
**** Main tributary of the Guachipas*

They were delivered to the laboratory in less than three days, filtered through glass fiber filter (Whatman 934-AH or similar) and preserved with $HNO_3/K_2Cr_2O_7$, according to Standard Methods [14]. Just before analysis, duplicate aliquots were digested with hot H_2SO_4, HNO_3, $KMnO_4$ and $K_2S_2O_8$ according to [14], the evolved chlorine was removed in an ultrasonic bath so as to avoid its chemical and spectroscopic interference.

Analysis of mercury was performed by Cold Vapour Atomic Absorption Spectrometry using a GBC AA 904 spectrophotometer equipped with a GBC HG3000 in-line vapour-generating accessory with sodium borohydride as reducing agent.

Typical detection limits were 0.1 – 0.3 µg Hg/L, with an 11 % relative standard deviation between duplicates containing about 1 µg Hg/L (average of 65 samples). Accuracy was controlled by spiking several samples of every digestion batch, with the mean

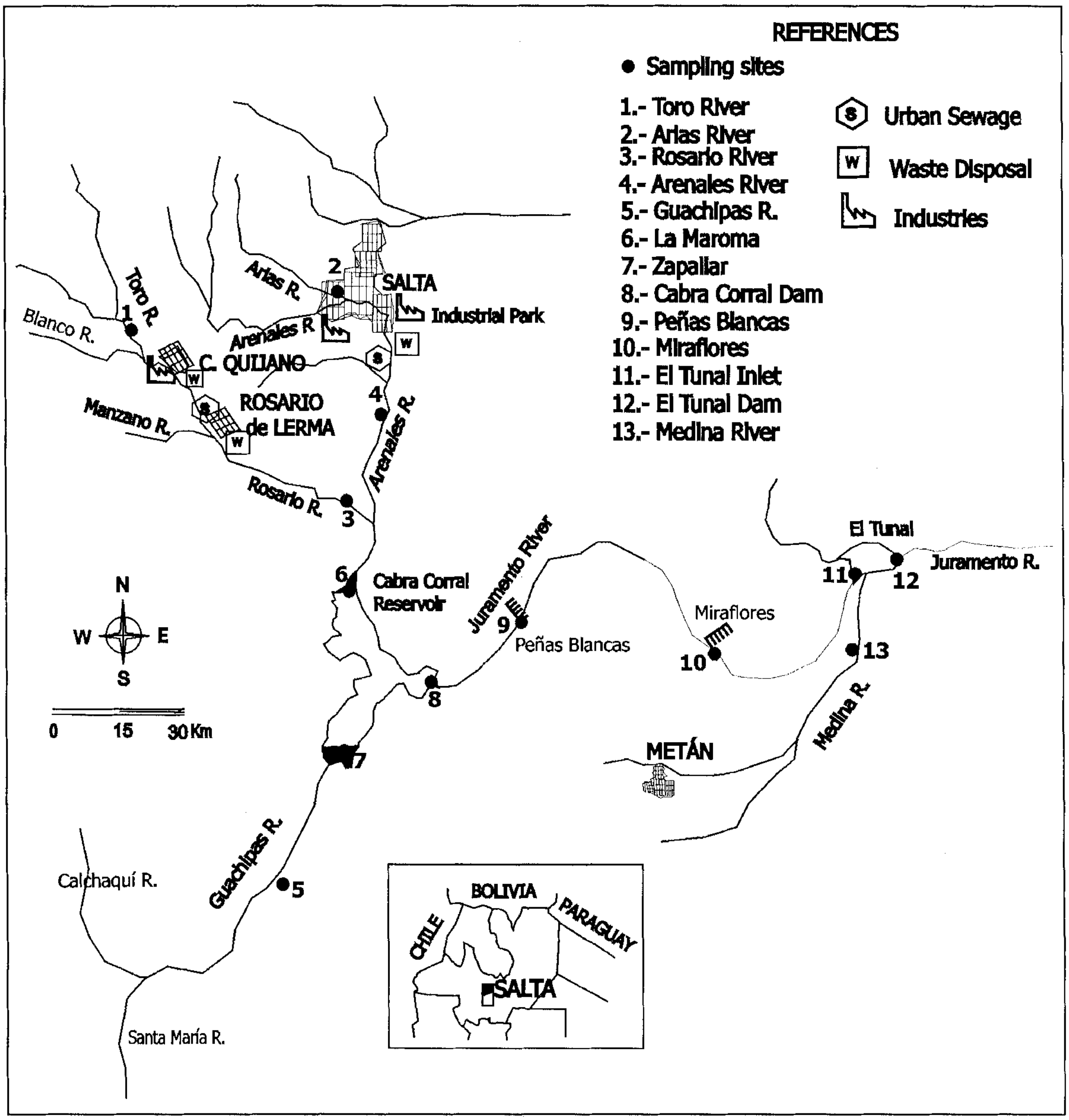

Fig. 1*. Location of sampling points of the Juramento River Water System (Salta, province, Argentina).*

ecovery for spiked samples being 80-120%, as well as by participating in the inter-laboratory exercises organized by INTI (Instituto Nacional de Tecnología Industrial/National Institute of Industrial Technology). Median values, its standard deviation and maxima of mercury concentrations corresponding to nineteen samples collected between 1997 and 2003 for each of the thirteen monitoring points are shown in Table 3.

Table 3. *Statistical parameters of total mercury concentration at the thirteen sampling points based on nineteen data from October 1997 to October 2003*

SAMPLING POINT	Hg CONCENTRATION (μg/L)		
	median	**s (median)**	**maximum**
Toro	0.5	0.72	6.00
Rosario	1.0	1.14	9.50
Arias	0.3	0.42	1.60
Arenales	0.6	0.48	2.60
Guachipas	0.6	0.53	2.60
La Maroma	0.6	0.35	1.50
El Zapallar	0.2	0.35	1.50
Cabra Corral Dam	0.3	0.52	2.00
Cabra Corral (mean)	0.43		
P.Blancas	0.4	0.39	1.60
Miraflores	0.3	0.47	2.00
El Tunal Inlet	0.4	0.37	1.40
El Tunal Dam	0.3	0.35	1.50
El Tunal (mean)	0.40		
Medina	0.8	0.49	2.00

Total concentrations of lead, zinc and cadmium were determined by flame atomic absorption spectrometry after extraction to methyl-isobutylketone with ammonium pyrrolidine-dithiocarbamate at pH 3.5, tamponed with sodium citrate/citric acid buffer. Typical detection limits were 0.01 mg/L for lead, and 1 μg/L for zinc and cadmium. Molecular absorption spectroscopy with Azomethine H as reagent was used to determine boron concentration, detection limit being 0.02 mg/L [15]. This element is a common pollutant in the area being monitored, because Salta is the fourth most important global boron producer [16]. Concentration ranges of these elements are presented in Table 4; cadmium concentrations always fell below its detection limit.

Analysis of standard solutions, as well as blank runs, taken to the sampling sites and later analyzed, assured that contamination during transport as well as losses by adsorption on the sampling vessels was negligible for all trace elements considered. Data were handled according to quality analytical procedures [17].

Discussion

Data processing

Concentrations of trace elements below detection limits were considered as zero for median and mean value calculations, presented in Tables 3 and 4.

Table 4. *Total concentration ranges of some trace pollutants in the rivers and reservoirs at the sampling points (October 1997 to October 2003).*

	B (mg/L)	Zn (μg/L)	Pb (mg/L)
Toro	0.23 – 0.45	<1 - 64	<0.01 – 0.04
Rosario	0.03 – 0.25	<1 - 180	<0.01 – 0.03
Arias	0.01 – 0.12	<1 - 21	<0.01 – 0.03
Arenales	0.11 – 3.42	<1 – 40	<0.01 – 0.04
Guachipas	0.98 – 4.90	<1 - 50	<0.01 – 0.20
La Maroma	0.38 – 0.69	<1 - 70	<0.01 – 0.04
El Zapallar	0.45 – 0.84	<1 - 40	<0.01 – 0.05
Cabra Corral Dam	0.38 – 0.70	<1 - 41	<0.01 – 0.04
P. Blancas	0.49 – 0.75	<1 - 40	<0.01 – 0.04
Miraflores	0.15 – 0.62	<1 - 40	<0.01 – 0.04
El Tunal Inlet	0.50 – 0.66	<1 - 17	<0.01 – 0.05
El Tunal Dam	0.29 – 0.70	<1 - 40	<0.01 – 0.04
Medina	0.10 – 0.43	<1 - 74	<0.01 – 0.08

Correlation graphs were constructed with the 19 sampling data for pairs of sampling points for which mercury concentrations can be expected to be related; Table 5 presents the corresponding linear correlation coefficients, together with their *t* value calculated according to Fisher [18]. When these are higher than the tabulated value of 2, r^2 values can be considered statistically significant at 0.95 confidence level.

Table 5*. Correlation coefficients between Hg concentrations of some of the sampling points and their corresponding t values to be compared with tabulated value t = 2 (P = 0.95)*

	r^2	t
Rosario – La Maroma	0.563	6.9
Peñas Blancas – Miraflores	0.454	3.8
Miraflores – El Tunal (entrance)	0.577	4.8
Medina – El Tunal (mean)	0.490	4.0
Cabra Corral (mean) – Peñas Blancas	0.06	1.0

Magnitude of mercury concentrations

The data are to be considered as total mercury content of water. This means that it includes the concentration of the dissolved mercury, the mercury recovered from the particles not retained by glass fiber filters (which are specially prone to adsorb the different species formed by heavy metal ions in natural aquatic environments), and even organo - metallic mercury.

Recent literature concerning waterborne mercury deals with dissolved mercury, while health authorities generally make reference to total recoverable mercury, considering its bioaccumulative toxic nature [1, 19]. The data presented here can be compared with those obtained by CVAAS analysis without preconcentration, since in order to determine the concentrations of dissolved mercury (ng/L)), some kind of preconcentration is needed plus analysis by atomic fluorescence spectrometry, as recommended [20, 21]. Mean values for mercury concentrations of 1.0 – 1.2 μg/L with maxima of 4.7 – 18.1 μg/L were informed for the Danube river at Budapest, where it collects the effluents of a heavily industrialized region, [22], and of 0.2 to 0.4 μg/L, with maxima of 3.5 μg/L at the Iron Gate reservoir [22]. At Almadén (Spain), near the largest and oldest mercury mine of the world, maximum concentrations of unfiltered samples of the Valdeazogues river ranged from 0.62 to 20.3 μg Hg/L [3]. These concentrations, surprisingly, are of the same order as those found in the Juramento system, where no similar pollution sources occur.

Considered as potential drinking water sources, median concentrations at all sampling sites complied with Law # 24.051, but more than 20 % of the samples had a total mercury concentration equal or higher than the recommended 1 μg/L. Occasionally even the higher limit of 2 μg/L, admitted by the USA EPA [6] was exceeded. For most of the rivers, average values are higher than medians (Table 3), an evidence of infrequent, high values of mercury concentration.

The median total concentrations of mercury in the two more important impoundments, Cabra Corral and El Tunal (Table 3), where silversides are regularly fished, are several times higher than the recommended limit of 0.1 μg/L for water biota preservation [1, 6], so that aquatic life in these reservoirs might be under considerable stress. The relationship between mercury concentrations in fish muscle and that in the water of their habitat is still under investigation, mercury bioconcentration being seasonal and bioavailability depending mainly on the degree of its methylation by bacteria [8, 23], but also on water hardness, alcalinity, pH, calcium concentration and specific conductance, so that these high values by themselves do not measure the magnitude of danger to water biota. The negative correlation reported for mercury concentration in fish muscle and calcium concentration, hardness and alkalinity of the waters, might mean a favourable condition for the Juramento river and its reservoirs, because they are alkaline and moderately hard (120-150 mg $CaCO_3$/L).

Origin of mercury

The frequency distribution of total mercury concentrations in the rivers seem to indicate that 0.1 μg Hg/L could be considered as a background value for the Juramento water system. But much higher concentrations were found with alarming frequency. Maximum values ranged from 2.0 to 9.5 μg Hg/L in the rivers Toro, Guachipas, Arenales, Rosario and Medina.

These figures could be due to pollution in the cases of the Arenales, Rosario and

Medina rivers, all recipients of urban effluents, as well as of agricultural run-offs. The already well demonstrated urban contamination of the Arenales river [11] is evidenced by its pH, dissolved oxygen, BOD_5 and COD medians (Table 1). But median mercury concentration in the Arenales river is not higher than that in the Guachipas river, indicating that there is no important influx of mercury from Salta City. The extremely high mercury concentration found in the sludges of the sewage treatment work (11 µg/g) proves that most of the particles containing the suspended mercury are retained in the settling tanks. The contamination of the Rosario river by partially untreated urban wastewater discharges is confirmed by the very high median BOD_5 and COD values, and the doubling of median mercury concentration at ca. 60 km distance from the sampling site at the Toro river points to a contamination source in the area of the town of Rosario. The contribution of the Rosario river to the mercury content of the Cabra Corral reservoir is evident from the highly significant correlation between mercury concentrations at La Maroma and in the Rosario river (Table 5).

According to the values of the statistical parameters shown in Table 5 correlation coefficients between mercury concentrations at Peñas Blancas and at Miraflores, as well as between those at Miraflores and the inflow of El Tunal reservoir are statistically significant showing that no important amount of mercury is added in this wide, agricultural region, discarding the possibility of significant pollution by agrochemicals. The Medina river has a similarly significant relationship with the average concentration of mercury in the dam of El Tunal showing that this river is partially responsible of its mercury pollution. The absence of correlation between the mean mercury concentrations of the reservoir at Cabra Corral and those at Peñas Blancas is due to the fact that the reservoir water is sampled at a depth of 0.5 m, while the small impoundment at Peñas Blancas receives water from the bottom layer of Cabra Corral, at a depth of 80 m. Stratification of the waters of this reservoir was previously established for boron, [16], and the same situation must hold for mercury, particularly if the high sulphide concentrations at the bottom of the reservoir are considered.

Location of sampling points (Figure 1) provides two sites that can be presumed unpolluted (Toro and Guachipas), as their population density is rather small, there are no heavy metal mining activities, no industrial installations, and agriculture is practiced only on a subsistence level. Yet their median mercury concentrations are high (0.5 and 0.6 µg/L). Airborne contamination is the most probable source of contamination. There are no air quality data to ascertain its existence, but ashes expelled by the sporadic eruptions and fuming of the Lascar volcano, which on the 21^{st} of April 1993 reached even the south of Brasil [24], point to this source. Samples of the ashes collected in the vicinity of sampling points Toro and Medina were analyzed, after being subjected to digestion in diluted *aqua regia*, according to EPA protocol #7471 (1986); their respective mercury content was 0.27 and 0.26 µg/g, significantly higher than the values considered normal for rock forming minerals of less than 0.050 µg/g, and in many cases even less than 0.010 µg/g [25].

The rather high median specific conductance of the Guachipas river indicates its extraordinarily saline nature, due to the numerous geothermal springs flowing into the Calchaquí, its main tributary [26], these could constitute another possible source of mercury for the Guachipas and probably for the Toro river as well.

Conclusions

According to the median values of total mercury concentrations corresponding to nineteen sampling campaigns (Table 3) the upper Juramento water system might be used, in principle, as drinking water source from the river Toro, upstream of Campo Quijano, to the dam at El Tunal, including the Medina river that flows into El Tunal dam. This conclusion is drawn from the fact the average values of mercury fall within the regulation limits. However, the frequent occurrences, fluctuations, of high concentrations of this metal (in 21 to 50 percent of the samples equal or higher than the 1 μg/L limit) makes **unadvisable** their use for human consumption.

Aquatic biota preservation, on the other hand, imposes stricter limits, and the Juramento water system shows median and average values of total mercury concentration several times higher than the 0.1 μg/L recommended by law. This might pose a serious problem for human health, because mercury is accumulated and bioconcentrated specially in the muscle of carnivorous fish, like silverside. Between 1997 and 2003 total mercury concentrations equal or are much higher than the recommended maximum, were found in 53-74% of the water samples of the two big reservoirs at Cabra Corral and El Tunal, where most of silversides are fished.

The real danger to fish life (and the danger posed to human health through fish consumption) will have to be established by biological studies, and the determination of mercury content of fish muscle.

The high mercury concentrations in the unpolluted rivers Toro and Guachipas seem to derive from the ashes of the Lascar volcano dispersed in 1993. The ashes covered a very extensive area, so that it could justify the existence of the abnormally high values of total concentration for this element in the whole Juramento water system under monitoring. But the evident increase of mercury concentration in the Toro after receiving urban effluents shows that in the area of the town of Rosario there is an anthropogenic contribution as well. As there is no way to control the natural background values, a strict quality control of the urban wastewater discharges is needed to diminish the content of this highly toxic heavy metal in the reservoirs.

Aknowledgements

The authors are grateful to the Consejo de Investigación de la Universidad Nacional de Salta for grants received, as well as to the Facultad de Ciencias Exactas of the same University for their sustained support.

References

[1] Decreto 831/93 Reglamentación de la Ley Nacional Nº 24.051 *Boletín Oficial* 03/05/1993 1ª 1ª Sección.

[2] Horvat, M; Covelli, S.; Faganeli, J.; Logar, M.; Mandiĕ, V.; Rajar, R.; Širca, A.; Šagar, D. *The Sci. Tot. Environ.* **1999,** *237/238,* 43.

[3] Berzas Nevado, J.J.; García Bermejo, L.F.; Rodríguez Martín-Doimeadios, R.C. *Eviron. Poll.* **2003,** *122*, 261.
[4] Warwick, J.J.; Taylor, G.E.; Wayne, D.M.; Harness, S.J.; Lyons, W.B. *Understanding The Transport And Fate Of Mercury Within The Carson River System, Nevada,* in: C.R. Cothern, (Ed.), *Trace Substances, Environment and Health*. Lonsdale Press Ltd. London, **1994**, pp. 31–41.
[5] Bailey, R.A.; Clark, H.M.; Ferris, J.P.; Krause, S.; Strong, R.L. *Chemistry of the Environment.* Academic Press, New York, **1978**.
[6] Chapman, D. (Ed.), *Water Quality Assessments*, 2nd ed., E&FN Spon Chapman&Hall, London, **1996**.
[7] Ferguson, J.E., *The Heavy Elements. Chemistry, Environment Impact, and Health Effects*, 2nd ed., Pergamon Press, Oxford, **1991**.
[8] Hanten Jr, R.P.; Neumann, R.M.; Ward, S.M. *Trans. Amer. Fisheries Soc.* **1998,** *127*, 807.
[9] Neumann, R.M.; Ward, S.M. *J. of Freshwater Ecology*, **1999**, *14*, 487.
[10] Kennedy, C.J. *Environ. Poll.* **2003,** *121*, 321.
[11] Musso, H.E. *Impacto Del Municipio De Salta Sobre La Contaminación Del Río Arenales*. Magister Thesis; Universidad Nacional de Tucumán, **2003**.
[12] Hidroeléctrica Río Juramento S.A., *Programa de Monitoreo Cabra Corral – Peñas Blancas – El Tunal*. Informes de tareas desarrolladas, años **1997** al **2003**.
[13] http://www.obraspublicas.gov.ar/hidricos.
[14] Clesceri, L.S.; Greenberg, A.E.; Trussell, R.R. (Eds.), *Métodos Normalizados Para El Análisis De Aguas Potables Y Residuales*, 17th ed., Díaz de Santos S.A., Madrid, **1992**.
[15] Musso,H.; Lomniczi, I. *An. Asoc. Quím. Arg.* **1995,** *83*, 59.
[16] Lomniczi, I.; Musso, H.; Morales, G. *An. Asoc. Quím. Arg.* **1999**, *87*, 181.
[17] Bartram, J.; Ballance, R. (Eds.), *Water Quality Monitoring*, 1st ed., E&FN Spon Chapman & Hall, London, **1996**.
[18] Sánchez de Peña, D., *Fundamentos de Estadística,* 5th ed., Alianza Editorial S.A., España, **1998**.
[19] Bloom, N.S.; Preus, E.; Katon, J.; Hiltner, M. *Anal. Chim. Acta.* **2003,** *479*, 233.
[20] Tavares, G.A.; Ferreira, J.R.; de Carvalho Magalhaes, C.E.; da Silva, N.C.; Tirollo Taddel, M.H. *Roy. Swed. Acad. Sci.* **2003***, 32*, 47.
[21] Molnár, E.; Németh, T. ; Pálmai, O., Problems of Heavy Metals in Hungary –"State-of-the-Art", in: W. Solomons, U. Förstner, P. Mader, (Eds.), *Heavy Metals. Problems and Solutions,* Springer-Verlag, Berlin Heidelberg , **1995**, pp 323-344.
[22] Marjanovic, P.; Miloradov, M.; Cukic, Z., *Heavy Metals in the Danube River in Yugoslavia,* in: W. Solomons, U. Förstner, P. Mader, (Eds.) *Heavy Metals. Problems and Solutions.* Springer-Verlag, Berlin Heidelberg , **1995**, pp. 301-321.
[23] Ward, S.M.; Neumann, R.M., *North Am. Journal Fish. Man..* **1999**, *19*, 89.
[24] http://www.unsa.edu.ar/varias/lascar.
[25] http://www.toxnet.nlm.nih.gov
[26] Lomniczi, I.; Musso, H.; Pereyra, R., *An. Asoc. Quím. Arg.* **1997,** *85*, 283.