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Contents continued on back cover

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Geographic Distribution of Arsenic and Trace Metals in Lotic Ecosystems of the Pampa Plain, Argentina

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Abstract In this paper, the geographic distribution of arsenic and other trace elements in surface waters of 39 lotic ecosystems of central Argentina was evaluated. Manganese and arsenic were the most conspicuous elements, being present in 82% and 59% of the sampled ecosystems of this region, respectively. As concentration averaged 113.69 μg L^{-1} varying between 55 and 198 μg L^{-1}, other trace elements were hardly detected or not detected at all. It was remarkable the absence of detectable concentrations of anthropogenically derived metals as lead (Pb) and cadmium (Cd).

Keywords Arsenic · Trace metals · Lotic ecosystems · Argentina

The presence of trace metals in groundwaters is largely determined by the nature and origin of soils. Groundwaters, in turn, may be responsible for an important load of these elements to the surface environments. Numerous articles worldwide have addressed the quality of groundwaters regarding content of trace metals, with particular emphasis in arsenic (Anawar et al. 2003; Peters et al. 2006; Fendorf et al. 2010, among others). Similarly, arsenic and other trace metals have been documented as significant water-quality problems in the Pampa Plain, particularly in aquifers from Córdoba, Santa Fe and Buenos Aires Provinces (Nicolli et al. 1989; Smedley et al. 2002; Paoloni et al. 2005, 2009). Comparatively, regional studies covering large areas of surface drainages are less common (Young and Blevins 1981; Baig et al. 2010; Li and Zhang 2010). This is an inconvenient gap since ultimately, the presence of trace metals in surface waters may represent a risk for humans, livestock and the aquatic biota. An appropriate knowledge on the level of contamination of surface waters is particularly important from a conservation and health viewpoint. The aim of the present paper was to evaluate the geographic distribution of arsenic and other trace elements occurrence in surface waters of lotic ecosystems of central Argentina.

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Materials and Methods

The Pampa Plain is a vast region located in central Argentina. It is characterized by gentle slopes where most of the land is devoted to agricultural practices. Hydrography is dominated by a large number of shallow lakes and low order rivers and streams (Frenguelli 1956). The Pampa Plain is mostly drained by the Salado-Vallimanca system. The others basins of the region are dominated by streams heading at two mountain systems and running throughout the lowland plains before reaching the Atlantic Ocean.

For this study 39 different lotic ecosystems, encompassing streams, rivers and channels were surveyed. A total of four trips during the first week of September were necessary to sample all ecosystems covering an area of more than 120,000 km^2 (Fig. 1). The simultaneous regional sampling scheme was aimed to minimize bias resulting from delayed side effects of meteorological processes. This is particularly important, since it has been already shown that storm events may affect trace metal transport from land to water ecosystems (Lawson and Mason 2001).

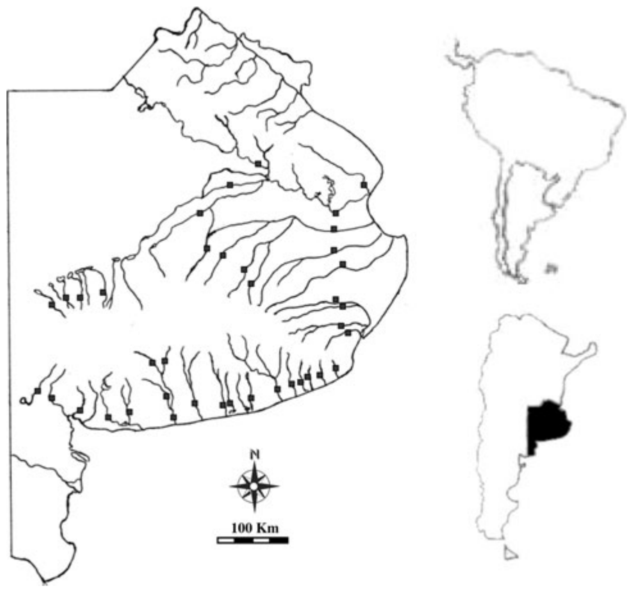

Fig. 1 Locations of sampling sites along 39 lotic ecosystems in the Pampa Plain

At each sampling site, water conductivity ($\mu S\ cm^{-1}$) and pH were measured. Surface water samples for dissolved metal determination were collected manually at 0.5 m depth with 0.5 L polyethylene-tereftalate bottles. Samples were taken by triplicate. Samples were immediately transported to the laboratory and filtered through acid treated Whatman GF/F glass fiber filters (0.45 mm) with vacuum. A sub-sample of 100 ml filtered water was acidified to pH < 2. These samples were stored in darkness at 4°C up to the analytical treatment. Collection, preservation, preparation, pretreatment and analyses of water samples were conducted according to APHA (1995). Heavy metals and trace elements were determined by ICP-OES using a Perkin Good Elmer 2000 DV. The use of last generation facilities like ICP-OES, allow to detect concentrations at $\mu g\ L^{-1}$ level (Farías et al. 2003). Reference materials with trazability certificate (Perkin-Elmer) were used for calibration. Metal contents in water were expressed in $\mu g\ L^{-1}$ (or ppb). The ICP-OES detection limits for the elements analysed were for As: 10 $\mu g\ L^{-1}$, Cd: 4 $\mu g\ L^{-1}$, Cr: 5 $\mu g\ L^{-1}$, Cu: 5 $\mu g\ L^{-1}$, Mn: 2 $\mu g\ L^{-1}$, Ni: 6 $\mu g\ L^{-1}$, Pb: 12 $\mu g\ L^{-1}$ and Zn: 15 $\mu g\ L^{-1}$. Pearson-product moment correlation analysis was performed in order to evaluate relationships between trace metals, pH and water conductivity.

Results and Discussion

Trace metals were not detected in 3 sites (Quequén Grande, Cura Malal Grande and Las Brusquitas) (Table 1). In 13 sites Mn was the only detectable trace metal. In the Quequén Salado, Sauce Grande and Grande rivers only As was detected. At least two of the analysed trace metals were above the limit of detection in the remaining 20 sites. Manganese was the most conspicuous element in lotic ecosystems of this region, being detected in 82% of the sampled ecosystems (Table 1). Mn concentration ranged between 3 and 113 $\mu g\ L^{-1}$, averaging 26.09 $\mu g\ L^{-1}$. Arsenic was detected in 59% of the sampled sites (Table 1), with concentrations ranging between 55 and 198 $\mu g\ L^{-1}$, averaging 113.69 $\mu g\ L^{-1}$. Arsenic concentrations were above the World Health Organization (WHO) and United State Environmental Protection Agency (USEPA) guidelines for drinking water (10 $\mu g\ L^{-1}$ As).

Sampled ecosystems were characterized by alkaline waters (pH always above 8) with high conductivities (Table 1). Correlation analysis showed that pH and water conductivity were not related with As and Mn. On the other hand, As and Mn were not interrelated. Nevertheless, the higher As concentrations (over 120 $\mu g\ L^{-1}$) only occurred in waters with low Mn concentration (Fig. 2). Whilst As and Mn were conspicuously found in surface drainages of the Pampa Plain, other elements were hardly detected or not detected at all. Cadmiun, Ni, Pb and Zn were below the limit of detection in all samples. Chromium and Cu were detected only in two ecosystems (Table 1).

The Chaco-Pampa Plain is one of the largest regions in the world (*ca.* one million km^2) with the presence of As in groundwater (Smedley and Kinniburg 2002). Therefore, it is quite probable that our results reflect the relationship between groundwater and surface water in the study area. Indeed, aquifers from drainages located in the southern Pampas are highly contaminated with As (Paoloni et al. 2005, 2009). Arsenic concentrations determined in this study are below the values measured in groundwaters of northern Pampa Plain (Farías et al. 2003), La Pampa (Smedley et al. 2002) and some locations of Córdoba (Pérez Carrera and Fernández Cirelli 2004) which may reach concentrations as high as 590, 4,900 and 4,500 $\mu g\ L^{-1}$, respectively.

Some studies have found that the dissolved As in groundwaters shows a positive correlation with pH (Smedley et al. 2002). The high pHs are thought to be the dominant control on As mobilisation. At high pH, arsenate sorption onto Fe oxides (but also Mn oxides) is weakest (Dzombak and Morel 1990). In this study, a significant relationship between pH and the As concentration was not found. Smedley et al. (2002) also found that arsenic showed no correlation with Fe, Mn or Al, although the few samples with high concentrations of these elements had relatively low As concentrations. Similarly, surface waters of Pampa lotic ecosystems with high concentrations of Mn displayed average to low concentrations of As (Fig. 2).

Table 1 Location (latitude and longitude) trace metal concentrations (μg L^{-1}), pH and water conductivity (Cond. in μS cm^{-1}) in sampled ecosystems

Site	Lat. S	Long. W	Cond.	pH	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Chapaleofu	37°12.358	59°21.509	719	8.45	<10	<4	<5	<5	7	<6	<12	<15
de los Huesos	37°04.875	59°32.333	690	8.67	78	<4	<5	6	<2	<6	<12	<15
Azul	36°45.147	59°51.243	927	8.46	76	<4	<5	<5	7	<6	<12	<15
Tapalque	36°16.052	59°58.667	908	10.33	106	<4	<5	<5	24	<6	<12	<15
Las Flores	35°51.086	59°50.242	952	9.51	<10	<4	<5	<5	111	<6	<12	<15
Vallimanca	35°27.612	59°34.548	7,180	9.81	98	<4	<5	<5	113	<6	<12	<15
Salado	35°21.375	59°19.796	4,000	9.47	158	<4	<5	<5	5	<6	<12	<15
Salado	35°57.64	57°51.155	7,510	9.29	<10	<4	<5	<5	22	<6	<12	<15
Vivorata	37°44.100	57°38.873	1,096	8.91	73	<4	<5	<5	29	<6	<12	<15
Grande	37°31.462	57°42.449	1,004	9.23	101	<4	<5	<5	<2	<6	<12	<15
Chico	37°15.574	57°46.947	720	9.38	91	<4	<5	<5	14	<6	<12	<15
CANAL 5	37°12.967	57°47.685	771	9.26	106	<4	<5	<5	13	<6	<12	<15
CANAL 2	36°45.153	57°48.145	851	9.78	99	<4	<5	<5	75	<6	<12	<15
CANAL 1	36°30.227	57°43.334	1,270	10.56	<10	<4	<5	<5	23	<6	<12	<15
CANAL 9	36°16.798	57°42.247	689	9.48	103	<4	<5	<5	3	<6	<12	<15
Sanborombom	35°42.576	57°21.480	606	8.18	87	<4	<5	<5	83	<6	<12	<15
El Pescado	38°17.817	58°14.758	885	8.71	100	<4	7	<5	3	<6	<12	<15
Malacara	38°20.833	58°22.140	1,129	8.94	<10	<4	<5	<5	28	<6	<12	<15
El Moro	38°25.685	58°27.685	1,091	9.1	<10	<4	<5	<5	11	<6	<12	<15
Quequen Grande	38°33.636	58°43.064	1,160	8.34	<10	<4	<5	<5	<2	<6	<12	<15
Mendoza	38°33.229	59°18.925	1,496	9.02	114	<4	<5	<5	5	<6	<12	<15
Cortaderas	38°38.266	59°34.605	2,365	9.36	<10	<4	<5	<5	6	<6	<12	<15
Cristiano Muerto	38°40.022	59°41.497	1,303	9.11	<10	<4	<5	<5	6	<6	<12	<15
Claromeco	38°42.169	60°10.126	1,919	9.02	124	<4	<5	16	6	<6	<12	<15
Indio Rico	38°36.182	60°38.840	1,669	9.22	134	<4	<5	<5	29	<6	<12	<15
de las Mostazas	38°45.703	61°20.537	2,190	8.96	181	<4	<5	<5	30	<6	<12	<15
Naposta Gde	38°46.228	62°14.024	1,594	8.89	130	<4	<5	<5	10	<6	<12	<15
Sauce Chico	38°29.824	62°38.779	969	8.97	<10	<4	<5	<5	8	<6	<12	<15
Chasico	38°23.635	62 50.63	3,270	9.11	198	<4	10	<5	9	<6	<12	<15
Pique	37°12.575	62°38.997	733	8.58	123	<4	<5	<5	6	<6	<12	<15
Guamini	37°10.77	60°26.06	749	8.62	<10	<4	<5	<5	45	<6	<12	<15
Cura Malal Gde	37°14.51	62°08.067	483	8.83	<10	<4	<5	<5	<2	<6	<12	<15
Sauce Corto	37°36.062	61°51.895	484	8.6	<10	<4	<5	<5	11	<6	<12	<15
Pillahuinco Gde	38°14.1836	60°46.4404	625	10.3	<10	<4	<5	<5	7	<6	<12	<15
Arr. Quequen	38°15.102	60°44.490	486	8.84	94	<4	<5	<5	73	<6	<12	<15
La Carolina	38°20.195	60°59.417	1,245	9.41	<10	<4	<5	<5	13	<6	<12	<15
Las Brusquitas	38°14.564	57°46.708	1,192	8.84	<10	<4	<5	<5	<2	<6	<12	<15
Sauce Grande	38°45.5060	61°42.3995	1,550	8.01	55	<4	<5	<5	<2	<6	<12	<15
Quequen Salado	38°36.1634	60°36.3547	5,100	9.19	186	<4	<5	<5	<2	<6	<12	<15

The environmental state of many lotic ecosystems in the Pampa Plain, Argentina, regarding the concentration of several potentially hazardous elements, was mapped. It was remarkable the absence of detectable concentrations of anthropogenically derived metals as Pb and Cd. Conversely, natural pollution of surface water by As seemed to be a regional problem. These results have strong implications for planning management and conservation strategies. Subsequent investigations should focus in detail on those lotic ecosystems where the highest arsenic concentrations were observed in order to understand the geochemistry of the aquifers and the characteristics of the arsenic source minerals. On the other hand, as arsenic is usually highly and positively correlated with another

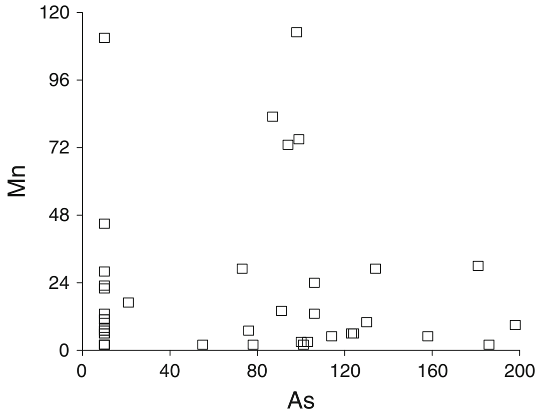

Fig. 2 Relationship between concentration of Mn (μg L^{-1}) and As (μg L^{-1}) in lotic ecosystems of the Pampa Plain

problematic element for human health, as fluoride (F), further investigations about this element are also advised. Indeed, fluoride contamination of aquifers in a vast region of southern Pampa Plain was already identified (Paoloni et al. 2007). The same trend must be expected for vanadium (V), whose origin is the same as for As and there is a good correlation between both of them (Heredia and Fernández Cirelli 2009). In solution, F and V are likely to occur dominantly as fluoride and vanadate species which, like As, are preferentially mobilised at high pH (Smedley et al. 2002).Therefore, due to the high pH that characterizes the surface waters of Pampa Plain, all these elements may be found in solution.

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References

Anawar HM, Akaib J, Komakic K, Teraod H, Yoshiokae T, Ishizukaf T, Safiullahg S, Kato K (2003) Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. J Geochem Explor 77:109–131

APHA (American Public Health Association) (1995) Standard methods for examination of water and wastewater, 19th edn. American Public Health Association, Washington

Baig JA, Kazi TG, Shah AQ, Kandhro GA, Afridi HI, Arain MB, Jamali MK, Jalbani N (2010) Speciation and evaluation of arsenic in surface water and groundwater samples: a multivariate case study. Ecotox Environ Safe 73:914–923

Dzombak DA, Morel FMM (1990) Surface complexation modeling: hydrous ferric oxide. Wiley, New York

Farías SS, Casa VA, Vázquez C, Ferpozzi L, Pucci GN, Cohen IM (2003) Natural contamination with arsenic and other trace elements in ground waters of Argentine Pampean Plain. Sci Total Environ 309:187–199

Fendorf S, Michael HA, van Geen A (2010) Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. Science 328:1123–1127

Frenguelli J (1956) Rasgos generales de la hidrografía de la Provincia de Buenos Aires. LEMIT Serie II: 1–19

Heredia OS, Fernández Cirelli A (2009) Trace elements distribution in soil, pore water and groundwater in Buenos Aires, Argentina. Geoderma 149:409–414

Lawson N, Mason R (2001) Concentration of mercury, methylmercury, cadmium, lead, arsenic, and selenium in the rain and stream water of two contrasting watersheds in western Maryland. Wat Res Vol 35(17):4039–4052

Li S, Zhang Q (2010) Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. J Hazard M 181:1051–1058

Nicolli HB, Suriano JM, Gómez Peral MA, Ferpozzi LH, Baleani OH (1989) Groundwater contamination with arsenic and other trace-elements in an area of the Pampa, province of Córdoba, Argentina. Environ Geol Water Sci 14:3–16

Paoloni JD, Sequeira ME, Fiorentino CE (2005) Mapping of arsenic content and distribution in groundwater in the Southeast Pampa Argentina. J Environ Health 67(8):50–53

Paoloni JD, Fiorentino CE, Sequeira ME (2007) Fluoride contamination of aquifers in the southeast subhumid pampa, Argentina. Environ Toxicol 18:317–320

Paoloni JD, Sequeira ME, Espósito ME, Fiorentino CE, Blanco MC (2009) Arsenic in water resources of the Southern Pampa Plains, Argentina. J Environ Pub Health. doi:10.1155/2009/216470

Pérez Carrera A, Fernández Cirelli A (2004) Niveles de arsénico y flúor en agua de bebida animal en establecimientos de producción lechera (Pcia. de Córdoba, Argentina). Investigación Veterinaria 6(1):51–59

Peters SC, Blum JD, Karagas MR, Chamberlain CP, Sjostrom DJ (2006) Sources and exposure of the New Hampshire population to arsenic in public and private drinking water supplies. Chem Geol 228:72–84

Smedley P, Kinniburg D (2002) A review of the source, behaviour and distribution of arsenic in natural waters. Appl Geochem 17:517–568

Smedley PL, Nicolli HB, Macdonald DMJ, Barros AJ, Tullio JO (2002) Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Appl Geochem 17:259–284

Young GJ, Blevins RD (1981) Heavy metal concentrations in the Holston River Basin (Tennessee). Arch Environm Contam Toxicol 10:541–560