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Arsenic in the health of ecosystems: spatial distribution in water, sediment and aquatic biota of Pampean streams

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Abstract A survey of arsenic and phosphorus in Pampean streams of Buenos Aires province was performed. Nitrates and ammonia were also determined. Stream water was sampled as well as stream sediment and filamentous algae. Results show that 32 streams exceeded the arsenic recommended guidelines for human consumption of 10 μg L^{-1} and six exceeded recommended values for aquatic organisms' protection of 50 μg L^{-1}. The average concentration found was 36.54 μg L^{-1} and areas with more concentration of As are located in the southern region of the province, in streams that are tributaries of the Atlantic Ocean. Other regions with high As concentration are the Matanza River tributaries and the Arrecifes River tributaries. No differences of As concentration was found between stream sediments. Also, no seasonal pattern of As concentration was observed in one stream sampled during a year, but a positive correlation between As and the conductivity (p = 0.0002) and pH (p = 0.01) of the streams was found. Also, As bioaccumulation was detected for all the algae sampled, but no correlation between As accumulated and As in the stream water was found. Ammonia levels exceeded recommended guidelines for human consumption in the Argentinean law in 30 streams. The characterization performed in this study provides relevant information on the distribution of arsenic and its origin and mobility.

Keywords Arsenic · Phosphorus · Bioaccumulation · Pampean streams · Buenos Aires · Argentina

Introduction

Arsenic (As) is a toxic element of great concern because of its large-scale contamination in many areas of the world. Tens of millions of people in countries such as India, Bangladesh, and Argentina suffer from arsenicosis (as poisoning) by consuming As-contaminated groundwater (Smedley and Kinniburgh 2002). In Argentina, this disease is called HACRE (in spanish, acronym for Hidroarsenicismo Regional Endémico). The concentrations of As are in many cases significantly higher than 10 μg L^{-1}, which is stipulated by the World Health

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Organization (WHO 1984) safety limit of As in drinking water (Smedley and Kinniburgh 2002).

The Pampean region comprises an area of over 70 Mha, covering part of Argentina, Brazil, and Uruguay. Currently, this region is of fundamental importance to man for its high crop and livestock yield. Because of these uses, the agricultural region of the Pampas consumes about 600 mm per year of water (Viglizzo and Jobbágy 2006).

Water resources in the region are abundant, because the rainfall is between 700 and 1200 mm annually (Matteucci 2012). Groundwater aquifers in the Pampas are usually oxidant with high salinity and hardness, and arsenic is widely found (Auge 2014). It is believed that the presence of As in groundwater is determined by the nature and origin of the soil (Raychowdhury et al. 2013; Smedley et al. 2005). In addition, groundwater can incorporate As to the surface water (Anawar et al. 2003; Fendorf et al. 2010; Peters et al. 2006), because when heavy rainfall occurs, phreatic levels rise and streams are recharged with both water and solute coming from it (Elosegi et al. 2009). Therefore, the presence of As in streams is expected in areas with As enriched groundwater (Rodríguez Castro et al. 2016).

The presence of As in surface waters has a major impact on aquatic organisms (Rahman et al. 2012). Often, water characterization does not reflect the true risk of exposure and uptake by these organisms (Coste et al. 2002; Guasch et al. 2012). Also, there is a variety of factors that influence the bioavailability and stability of As. For proper characterization of the effects of pollution on the ecosystem, it is important to understand As dynamics in the natural environment. Therefore, measuring As bioaccumulation allows inference of the biological quality of an ecosystem (Lagadic and Caquet 1998). Bioaccumulation of contaminants by primary producers like algae is also important to understand its impact on the food web (Sabater et al. 2007) and to study trophic transfer and biomagnification at higher levels (Guasch et al. 2012).

Bioaccumulation and toxic effects of As to the organisms are affected by a variety of factors that influence both its bioavailability and stability. The presence of phosphorus influences As bioaccumulation in primary producers (Planas and Healey 1978). This nutrient is essential for organisms and several studies show that As uptake by cells, both prokaryotic and eukaryotic, is linked to intracellular and environmental P levels (Harold and Baarda 1966; Wang et al. 2013). Also, due to chemical similarity between arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}), both the most common forms in surface waters, uptake of As occurs through P transporters (Villa-bellosta and Sorribas 2010). In Buenos Aires, a few studies have monitored As bioaccumulation in fish (Avigliano et al. 2015; Rosso et al. 2013; Schenone et al. 2014) and sediments (Schenone et al. 2007), but there is no information on As bioaccumulation by algae. Besides, there are no studies that measure simultaneously As levels in different matrices, giving an integral view of As fate in the ecosystem. Also, the study of temporal variations in As concentration can help elucidate the dynamic of this metalloid.

The aim of this study was to explore As levels in different matrices of the north eastern Pampean streams of Buenos Aires, in order to describe spatial and temporal patterns, as well as the impact of this solute in the base of the aquatic food web. For this purpose, we determined As in stream water, sediments and its bioaccumulation in filamentous algae, relating it to other chemical and physical parameters.

Materials and methods

Study site

Most of the Buenos Aires streams originate in small depressions and are fed by groundwater. They usually have low flows due to the gentle slope of the region. The predominant bed is usually hard and homogeneous with fine sediments, mainly clay and silt. According to Frenguelli (1956), river systems are divided into four hydrological regions. One corresponds to the tributaries of the Salado River, located in the North center of Buenos Aires. The second is the system of Vallimanca stream, which begins near Ventania Mountain ranges and extends to the Northeast. The third system is comprised of the tributaries of the Paraná and Rio de la Plata rivers, extending from the middle to the East, in the Northern region of the province. The fourth system is formed by the tributaries of the Atlantic Ocean and occupies the Southern and Eastern region of the province.

Spatial characterization

In order to perform a spatial characterization of As concentration in Pampean streams, As levels were measured in the streams. Fifty-eight sites located in 40 streams were sampled in autumn (Fig. 1). Sampled streams belong to Matanza, Reconquista, Paraná de las Palmas, Arrecifes, Luján, de la Cruz, and Areco basins (third system defined by Frenguelli). Tributary streams of the Río de la Plata (belonging to the third region) and of the Atlantic coast (fourth region) were also sampled.

Physical and chemical parameters (pH, temperature, conductivity, dissolved oxygen, and oxygen saturation percentage) were measured in situ using a probe (HACH LANGE GmbH, Germany). Water samples were taken for Total As, P (as soluble reactive phosphorus, SRP), nitrate, and ammonia determinations. Filamentous algae samples were collected if present. The collected water samples were filtered with glass fiber filters GF/F (Munktell ®) and placed in plastic vials kept in a freezer at −20 °C.

SRP was determined following Carvalho et al. (1998). Ammonium (N-NH_4) was analyzed with the indophenol blue method following APHA (2005). Nitrates were measured by reaction with sulfanilamide, with a previous cadmium reduction in the case of nitrates (APHA 2005).

Water samples for As determination were acidified with 10% *v*/*v* Suprapur nitric acid (J.T. Baker®) in order to preserve the analytes in solution. Total As was determined using an atomic absorption spectrophotometer with hydride generation (AA-HG, Analyst 200, Perkin Elmer) with a previous reduction using 5% (*w*/*w*) KI and 5% (*w*/*w*) ascorbic acid.

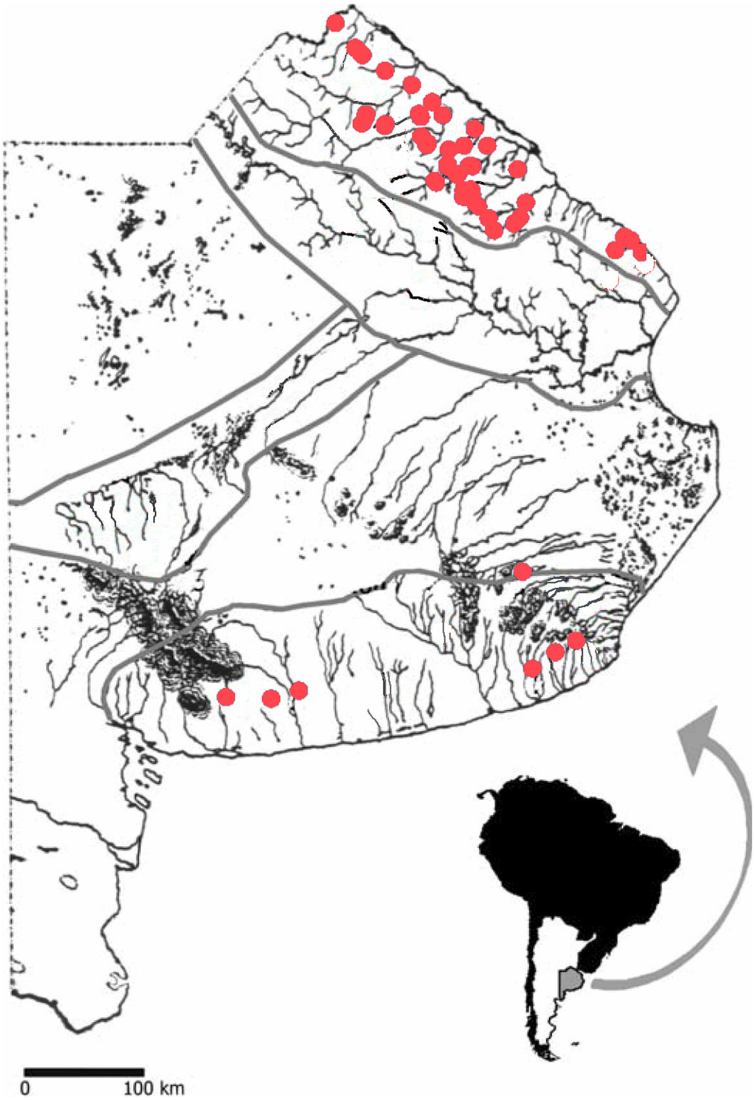


Fig. 1 Map of Buenos Aires province (Argentina) with sampling sites. Fluvial systems proposed by Frenguelli (1956) are shown. (1) Salado river and its tributaries; (2) Vallimanca stream; (3) tributaries of the Paraná and Río de la Plata rivers; and (4) tributaries of the Atlantic Ocean

Filamentous algae samples were observed under an optical microscope Nikon Optiphot with immersion objectives and identified to genus. Then, biomass was dried in an oven at 60 °C until constant weight was achieved. This weight was considered as the dry weight (DW) of the sample. Digestion of the dry biomass was performed to measure the content of As by means of ultrasonic acid extraction (Alvarez et al. 2003; De la Calle et al. 2013). For this purpose, the dry biomass was ground in an Agatha mortar. Then 50 mg were weighed in an eppendorf tube (1.5 mL volume). One milliliter of a cobalt solution (Accu Trace, NIST, New Haven, USA) as internal standard (10 mg L^{-1}) and analytical grade nitric acid (Riedel de Haen, Merk, Germany) 10% *v/v* was added to the sample in the eppendorf tube. The samples were digested for 30 min in an ultrasonic bath. Ten microliters of the digested sample were placed on an acid-cleaned quartz reflector and evaporated on a heating plate until dryness. Arsenic and P were measured in a Picofox S2 X-ray fluorescence spectrometer with total reflection geometry (TXRF). The spectra were collected during 250 s of live counting time and analyzed by software Spectra. The concentration of As and P in 1 g dry weight of the algae was then calculated.

In order to determine sediment composition, sediments of seven streams were collected with a core and placed in a plastic flask. Once in the lab samples were dried at 50–60 °C in a room specially conditioned for this purpose. To allow drying of the whole content, the sample was extended on a table covered with a polyethylene film. Samples were manually ground using an agate mortar to break down aggregates, and subdivided by using five steps quartering; a portion of 500 g was taken and ground again using tungsten carbide mortars in a Shatter box mill. This sub-sample was sieved through a nylon sieve of 60 μm. A portion of 10 g was weighted and as powder was introduced in the energy dispersive X-ray fluorescence (EDXRF) spectrometer. Measurements were performed in a HORIBA XGT7200 spectrometer using a Rhodium X-ray tube operated at 50 kV.

Data analysis

The As/P ratio of each stream and the intracellular As/P ratio of the filamentous algae was calculated. The As bioconcentration factor (BCF) was defined as the concentration of As in the dry biomass (μg g^{-1}) divided by the concentration of As in the stream (mg L^{-1}). Finally, correlations between physical and chemical variables were sought by calculating the Pearson coefficient in each case using the Infostat software ®. For this correlation, data from urban streams were not considered.

To perform a contour map for As in Buenos Aires, the obtained results were gathered together with other coming from bibliography (Rosso et al. 2011) in one database. The contour map was made using the Surfer 8 software with the Kriging gridding method. This method allowed elaborating isoconcentration curves of As, to analyze the distribution at the streams of the Buenos Aires province.

Temporal characterization.

After spatial characterization, in order to perform a temporal characterization of As concentration in Pampean streams, La Choza stream (34°42,182′S, 59°04,717′O) was chosen as reference. This second order stream has typical characteristics of Pampean streams and is one of the three tributaries of the Reconquista river. It has a length of 30 km and drains an area of 440 km^2. The selected site is 31 m above the sea level and is located 8 km down from its head. Meteorological data from the site were provided by the Center for Research Teaching and Extension in Agricultural Production (CIDEPA, Luján, Buenos Aires) and seasonal mean precipitation was calculated.

Water samples were collected at the stream monthly during 1 year. Physical and chemical parameters as well as sample collection, storage, and As and P determination were performed as explained previously.

Correlations between As and physical and chemical parameters, as well as As/P ratio were studied by calculating the Pearson correlation coefficient. To test whether there were significant differences in total As concentration among seasons, one-way ANOVA with four levels (the four seasons) was performed.

Results

Spatial characterization

Physical and chemical parameters are shown in Table 1. The survey of 40 lotic courses in the province of Buenos Aires showed that these are highly oxygenated streams with slightly alkaline pH and high conductivities.

Table 1 Mean, median, standard deviation (SD), minimum (MIN), and maximum (MAX) value found for the physical and chemical parameters of the sampled streams

	DO (mg L^{-1})	%Sat	pH	COND (µS cm^{-1})	TEMP	SRP (mg L^{-1})	NO_3^- (mg L^{-1})	NH_4^+ (µg L^{-1})	As (µg L^{-1})
MEAN	10.94	104.10	8.32	1338.39	13.64	0.27	5.9	344.7	36.54
SD	3.37	35.73	0.29	701.35	2.60	0.36	3.1	404.5	21.72
MEDIAN	10.90	99.40	8.33	1127	13.95	0.16	5.5	203.0	31.33
MIN	1.86	17.30	7.85	338	7.80	0.00	1.4	0.0	5.00
MAX	19.30	198.00	9.07	4040	19.30	1.77	14.0	1668.4	125.30
N	50	45	56	57	57	57	50	50	57

DO dissolved oxygen, *%SAT* percentage of oxygen saturation in water, *COND* conductivity (µScm^{-1}), *TEMP* temperature (°C), *SRP* soluble reactive phosphorus (mgL^{-1}), NO_3^- nitrates (mg L^{-1}), NH_4^+ ammonia (µg L^{-1}), *As* dissolved arsenic (µg L^{-1})

In the case of arsenic, 32 streams exceeded the recommended guidelines for human consumption suggested by the WHO (10 µg L^{-1}) and six exceeded recommended values for aquatic organism protection (50 µg L^{-1}). The average concentration found was 36.54 µg L^{-1}, with a maximum of 125.3 µg L^{-1} (Table 1). According to the isoconcentration curves generated with the software Surfer, reflecting the levels of As in the lotic courses of Buenos Aires (Fig. 2) areas with more concentration of As are located in the southern region of the province. These streams are tributaries of the Atlantic Ocean. Other regions with high As concentration are the Matanza River tributaries and the Arrecifes River tributaries.

Furthermore, levels of SRP found in streams are high, with an average of 0.27 mg L^{-1} (Table 1). These values greatly exceed the threshold of 0.075 mg L^{-1} that classifies streams as eutrophic (Dodds et al. 1998). The region of higher levels of phosphorous is located at the northeast. In the case of ammonia, 30 streams exceeded the guide level recommended for human consumption in the Argentinean Law (Law 24.051, Decree 831/1993 Annex 2).

A positive and highly significant correlation between the concentration of As and conductivity of streams was found ($p = 0.001$, Fig. 3, Pearson's $R = 0.63$). Furthermore, another positive and significant correlation between As and pH ($p = 0.002$, Fig. 4, Pearson's $R = 0.41$) was found.

The content of As in filamentous algae was analyzed. In most of the cases, the genus found was *Spirogyra* and in all cases, there was bioaccumulation. Other represented genera were *Cladophora* and *Oedogonium*. Arsenic levels found in the dry biomass are shown in Table 2. The correlation between these values and the levels of As in the stream was not significant ($p = 0.38$), although correlation between As in the stream and bioconcentration factor ($p < 0.02$, Pearson's $R = -0.56$) was found.

Elemental scanning of the sediment of seven streams is shown in Table 3. The most represented elements are Si, Fe, Ca, and Al. As content represents less than 0.02% of sediment mass and no differences between As content between streams is observed. In the case of P, there is more heterogeneity between streams, being more abundant in Las Flores and Arroyo Grande streams.

Temporal characterization

Mean precipitations were 103 mm for summer, 67.5 mm for autumn, 90.5 mm for winter and 206.3 mm for spring. Temporal variation of As concentration in La Choza Stream do not show seasonal patterns according to the ANOVA analysis ($p = 0.055$, Fig. 5). All measurements ranged from 5 to 46 µgAs L^{-1}, and the average was 23.3 µgAs L^{-1}. Arsenic concentration was positively correlated with the conductivity (Pearson's $R = 0.85$; $p = 0.03$).

Discussion

The characterization performed in this study provides relevant information on the distribution of arsenic in surface waters. Arsenic expected levels for pristine streams range from 0.13 to 2.1 µg L^{-1} (Andreae et al. 1983; Froelich et al. 1985; Seyler and Martin 1991). The levels found in Buenos Aires streams far exceed this

Fig. 2 Map of the Buenos Aires province with As concentration curves from streams sampled and studied in De la Calle et al. (2013) ($n = 89$). To the right, the reference card shows a color code for As concentrations (µg L^{-1}). In the lower section, a scale of distances (in Km) is shown

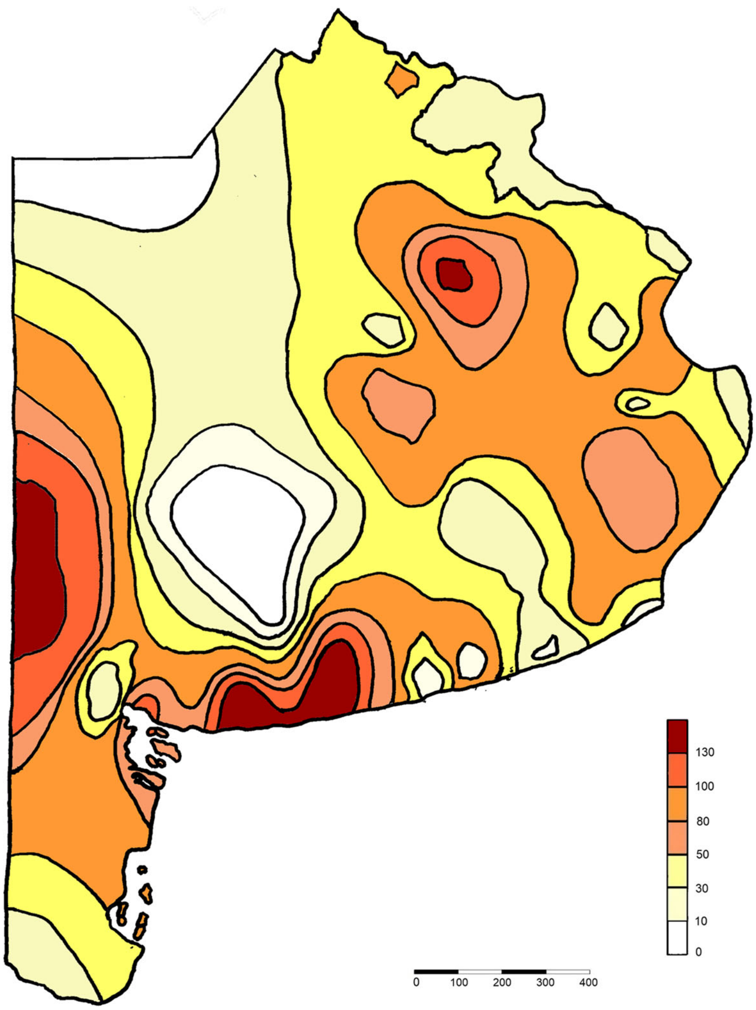


Fig. 3 Arsenic vs. conductivity in streams sampled. The line shows the linear correlation

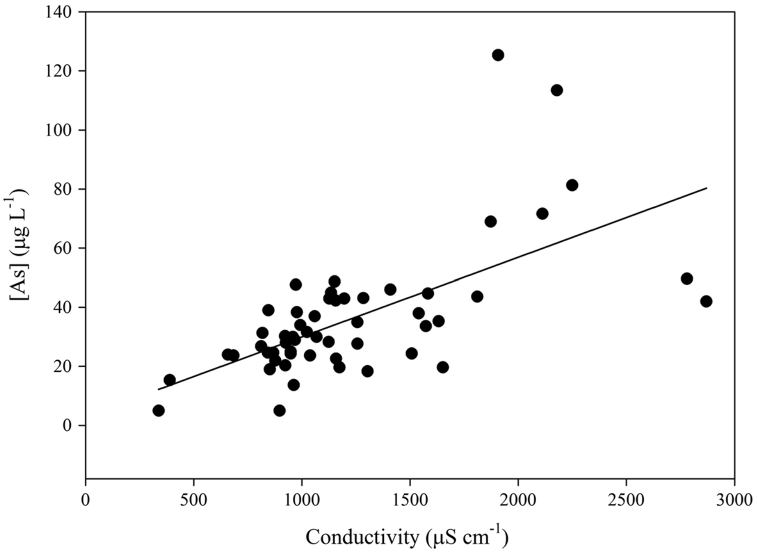
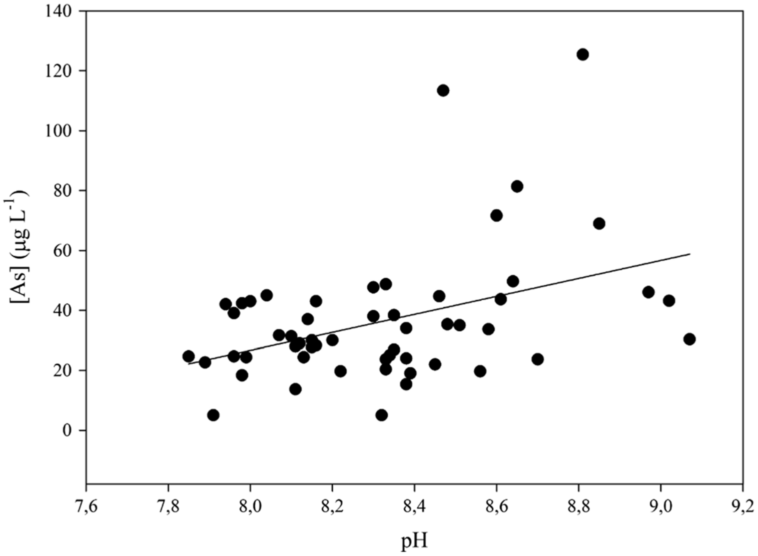


Fig. 4 Arsenic vs. pH in streams sampled. The line shows the linear correlation



threshold. Besides, As levels are similar to those found in surface waters in other regions of the world, such as polluted rivers from Europe (4.5–45 µg L^{-1} (Seyler and Martin 1991)). These concentrations are lower than those found in literature for groundwater from the Pampean region (Aloupi et al. 2009; Bundschuh et al. 2004; Farias et al. 2003; Fiorentino et al. 2009; Rosso et al. 2013) which is estimated to have origin in the quaternary volcanic sediments (Aloupi et al. 2009; Raychowdhury et al. 2013), but they are within the range of concentrations reported for other surface waters influenced by the presence of As in groundwater (7–114 µg L^{-1} in Córdoba, Argentina (Lerda and Prosperi 1996) and 190–21,800 µg L^{-1} in northern Chile (Cáceres et al. 1992)).

Also, As the original material constituting the Pampean loess is responsible for arsenic levels in groundwater, it also may have influenced surface water, due to the source of the water in these streams. This effect is generally observed in surface waters with higher content of dissolved salts. Stream conductivity is intimately associated with the composition of the bedrock which is in contact with groundwater. Thus, surface water conductivity can work as a natural tracer of groundwater solutes (Wieland et al. 2004). Although correlations are not enough evidence of causality, both conductivity and pH measured presented a wide range, and can cover a large spectrum of situations, which gives an empirical explanation to the correlation. Thus, the strong positive correlation between As and conductivity suggests that both come from the same source, aligning with the hypothesis of a groundwater origin of As. Previous studies using conductivity and measuring solute changes during a storm event support that As provenance is groundwater (Rodríguez Castro et al. 2016). As arsenic in surface water depends on the contribution of groundwater, the absence of a seasonal pattern of As concentration is expectable, since As levels may be more related to recent rain episodes than to the lapsing season.

Differences in spatial distribution of As may evidence an heterogeneous sediment deposition of the original volcanic materials but also anthropic effect of transference of groundwater to superficial waters (Giorgi 2016).

Arsenic concentration in streams is due to the groundwater component of the total discharge. As other factors such as runoff contribute to stream discharge, arsenic concentration in surface water is lower than that observed in groundwater. pH can also reflect the presence of certain solutes coming from groundwater, although this parameter is highly modified by the metabolism of producers. Correlations between conductivity and pH with As levels in surface water was not observed by Rosso et al. (2011). This could be because the areas sampled by this group did not show such a wide range of variability, preventing this reflection. Analyzing As levels found in this study together with the one performed by Rosso et al. (2011), it can be seen that the northern region has lower As levels than the southern region. Areas of higher As concentration are the Salado

Table 2 Total As and P bioaccumulation in the dry weight (DW) of filamentous algae collected in Buenos Aires streams. Streams are ordered by basin and each stream presents its latitude and longitude. Also As/P ratio of the algae as well as in the stream are shown. As and soluble reactive phosphorus (SRP) levels in the stream are presented in μg L^{-1}. Below, mean, standard deviation, minimum and maximum are shown. Mean, standard deviation (SD), minimum (MIN) and maximum (MAX) of the streams samples are also added

Stream	Lat S	Long W	As (μg gDW^{-1})	P (μg g DW^{-1})	As/P	μgSRP L^{-1} stream	μgAs L^{-1} stream	As/P stream	BCF	Predominant genera
Contador	34° 6′55.13″S	60° 3′2.87″O	9.48	1939.70	0.005	205	45	0.22	211	*Spirogyra sp.*
Gómez	34°13′40.04″S	59°29′58.41″O	8.82	838.90	0.011	181	22	0.12	401	*Spirogyra sp.*
Horqueta	34° 7′32.78″S	59°50′13.45″O	33.92	5161.20	0.007	147	37	0.25	917	*Batrachospermum sp.*
Vagues 1	34°17′33.11″S	59°27′1.17″O	5.70	1329.76	0.004	134	38	0.28	149	*Spirogyra sp.*
Vagues 2	34°16′45.49″S	59°26′27.49″O	12.66	2507.74	0.005	245	19	0.08	666	*Spirogyra sp.*
Vagues 2	34°16′45.49″S	59°26′27.49″O	7.90	2760.02	0.003	245	19	0.08	416	*Cladophora sp.*
Nutrias	34°42′7.44″S	59°6′39.37″O	8.84	1329.50	0.007	158	13	0.09	647	*Spirogyra sp.*
Durazno	34°45′27.63″S	58°59′38.58″O	12.34	1648.94	0.007	8	43	5.10	283	NA
La Choza 1	34°41′8.43″S	59° 1′40.76″O	3.20	3737.32	0.001	115	29	0.25	110	NA
La Choza 2	34°42′10.51″S	59° 4′42.69″O	25.10	5492.14	0.005	83	38	0.46	661	Species 1
La Choza 2	34°42′10.51″S	59° 4′42.69″O	20.46	2411.20	0.008	83	38	0.46	538	Species 2
Oro	34°35′22.13″S	59°21′49.81″O	19.72	3832.28	0.005	91	43	0.47	438	NA
Las Flores	34°27′29.97″S	59° 3′15.84″O	9.70	1791.36	0.005	312	24	0.08	404	*Cladophora sp.*
Juan Blanco	35° 8′28.19″S	57°26′18.79″O	11.22	4845.74	0.002	267	5	0.02	2244	NA
Mostazas	34°46′33.74″S	58°58′13.55″O	30.20	2635.34	0.011	89	18	0.20	1647	NA
De la Cruz 1	34°19′48.96″S	59°14′39.92″O	2.92	4170.84	0.001	113	24	0.22	120	*Cladophora sp.*
De la Cruz 2	34°26′45.07″S	59°15′17.86″O	10.96	1348.26	0.008	252	25	0.10	459	*Oedogonium sp.*
MEAN			13.71	2810.60	0.006	161	28.4	0.50	606.49	
SD			2.20	355.91	332.4	35.9	20.1	2.85	558.87	
MIN			2.920	838.90	0.001	8	5.0	0.02	110	
MAX			33.92	5492.14	0.011	312	45.0	5.10	2244	

NA not available, *BCF* bioconcentration factor

Table 3 Elemental scanning of the sediment from seven streams of Buenos Aires province performed with energy dispersive X-ray fluorescence (EDXRF) spectrometer. Results are expressed as percentage of mass of the element

Stream	Mg	Al	Si	P	S	K	Ca	Ti	V	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr
Las Flores	Bdl	9.66	53.93	0.49	0.29	3.65	12.96	1.73	bdl	0.93	15.71	bdl	0.03	0.03	0.01	0.06	0.22
El Pescado	2.27	6.73	33.29	Bdl	0.6	2.37	38.67	1.31	0.06	0.36	13.79	bdl	bdl	0.02	0.01	0.04	0.24
La Carolina	Bdl	7.93	60.47	Bdl	1.36	3.97	8.29	1.51	0.03	0.33	15.53	0.01	bdl	0.04	0.02	0.06	0.26
Arroyo Grande	1.61	9.54	58.19	0.5	0.55	4.32	8.59	1.9	0.11	0.23	13.97	bdl	bdl	0.18	0.01	0.02	0.1
Indio Rico	1.51	Bdl	55.03	0.19	2.06	4.56	12.1	2.12	0.13	0.37	21.19	0.03	0.03	0.07	bdl	0.08	0.4
El Moro	1.7	11.18	54.56	0.18	0.28	4.19	6.6	1.92	0.05	0.23	18.45	bdl	bdl	0.04	0.01	0.07	0.27
Los Gauchos	Bdl	9.57	51.01	0.25	0.94	3.54	15.69	1.52	0.11	0.36	15.42	bdl	bdl	bdl	0.02	bdl	0.4

Bdl bellow detection limits

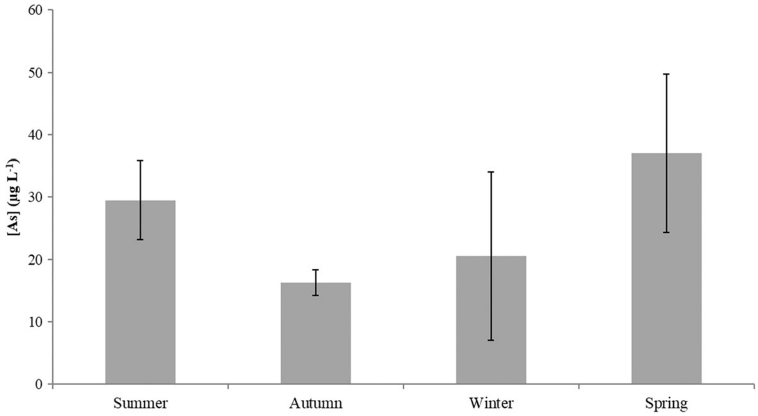
basin and the southern coastal area of the province. This means that the streams with more conductivity (i.e., dissolved solids) have probably more As concentration.

Concerning phosphorus, concentrations found were elevated. Previous studies have shown that P is present in surface waters of the Pampean region at high levels (Feijoó and Lombardo 2007; Neschuk et al. 2005; O'Farrell et al. 2002). Nevertheless, the presence of As was then unknown and this fact may have led to an overestimation of P due to As interference in the colorimetric technique commonly used for the determination of soluble reactive phosphorus (APHA 2005). Some of the streams sampled may have been wrongly assigned as eutrophic water bodies' giving a set of mistaken attributes to their communities. For this reason, it is important to perform new surveys on P levels of these lotic courses, using the protocol suggested by Carvalho et al. (1998).

Observing the distribution of As and P, it can be noticed that the distribution of these solutes does not follow the same pattern. The southern region has a greater As influence and the presence of P is reduced. This may represent a threat to communities belonging to these streams, since the presence of P has an attenuating effect on As toxicity (Blanck et al. 1988; Rodríguez Castro et al. 2014; Wang et al. 2013). Besides, previous studies performed by our group suggest that the provenance of P solute is the runoff (Rodríguez Castro et al. 2016). This is expectable considering that the study area has a high proportion of agricultural use of the land in which P is applied as fertilizer to soils (Neschuk et al. 2005; Viglizzo and Jobbágy 2006, Feijoó et al. 2011), creating diffuse sources of pollution in the streams (Jarvie et al. 2010). Even though P and As distribution follow different patterns, sediment P concentration in some of the streams sampled suggests that P source can also be natural.

Filamentous algae were found in many of the sampled streams. In most cases, algae found belonged to the Chlorophyta division. Arsenic content in the dry biomass was found in all samples, indicating that the metalloid is available for its uptake

Fig. 5 Average As concentration of each season of the year ($n = 3$). Bars show standard deviation



and that there is an accumulation by these organisms. Exposure and bioaccumulation of a contaminant are the first phases for assessing the impact of a compound in the environment (Rand 1995). The need for further studies to evaluate its effect on these and other organisms is compelling. Concentration found in the biomass is relatively low, considering that Pell et al. (2013) found levels from 182 to 1110 μg gDW^{-1} in the filamentous green algae *Cladophora sp*. in northern Chile. The difference between the bioaccumulation levels may reflect the different As concentrations in the environment, because surface waters in this Chilean region were in the range of 700–1200 μg L^{-1}, 30 times higher than those found in Buenos Aires streams. In turn, the bioconcentration factors are very similar in the two studies. The correlation between total As and total P in filamentous algae may be due to differences in maturity of the sample. To harvest algal biomass without taking into consideration the stage of growth and exposure history of the algae to solutes in the surrounding environment can lead to lack of correlation between bioaccumulation and water concentration of As and P (Serra et al. 2009). Comparison between bioaccumulation of filamentous algae and fish from the same area (Rosso et al. 2013) shows that algae levels are usually higher. The maximum concentration found in ten species of fish from Pampean streams was 4 μgAs gDW^{-1}, like the minimum value found in this study, in algae for the stream De La Cruz. This indicates that in systems like Pampean streams, biomagnification is not observed. This is consistent with observations in other river systems (Rahman et al. 2012). Despite this, there is an uptake of As by producers in Pampean streams of Buenos Aires and it is likely that exposure to this metalloid may have a harmful effect. Also, detoxification paths or tolerance mechanisms can be metabolically expensive, impacting the ecosystem function. As said before, rainfall determines As concentration in the stream because it has a groundwater origin and when it rains, a dilution of the metalloid occurs. This relation was not observed in La Choza stream, between seasonal mean precipitations and As temporal variation, maybe due to the short duration of the dilution. Furthermore, this modulates As bioavailability for uptake by organisms, which can bioaccumulate it. Apart from regulating As concentration in the stream, rain can drag biomass rooted to the bed (Vilches and Giorgi 2010). If it is assumed that P and As play a complementary role competing for uptake into the algae, it can be expected that As effects on them depend not only on the As levels in water but also on P concentration.

However, bioaccumulation can occur in all types of environments although this is a complex phenomenon to study because of the different age of organisms sampled, their detoxification mechanisms, and their exposure history.

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