

Total reflection X ray fluorescence in environmental and geochemical studies: unveiling solute provenance in streams during a rain episode

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Rural population uses water for irrigation, animal watering and for their own consumption, therefore water contamination is a major concern and a priority for its inhabitants. Unveiling the presence and source of contaminants can help to understand the dynamic of pollutants and therefore define management politics to address the issue. One way to elucidate the origin of contaminants in surface water is by studying rain episodes, relating water discharge with changes in solute concentration. Total Reflection x-ray Fluorescence (TXRF) was used as the main analytical technique. The study was based on the analysis of samples originating from a Pampean stream (Buenos Aires, Argentina). Solutes (As, P, Ca, Fe, K, Zn, Br) were monitored before, during and after a storm event. During the monitoring it was observed that As was diluted at the beginning of the episode and concentration increased slowly after the rain ceased. The pattern of As is consistent with Ca, K and Fe behavior, revealing a groundwater source. Instead, P concentration increased in the early hours, it was diluted later and finally increased. This behavior indicates that the source of this analyte is superficial and sub superficial water, implying a runoff origin. The simultaneous determination of these analytes by TXRF allowed comparing solute behavior under the same episode, allowing reveal their provenance. Copyright © 2016 John Wiley & Sons, Ltd.

Introduction

In rural zones, the main source of water for crop irrigation, animal watering and domestic purposes, is groundwater, complemented with the contribution of surface water. Water contamination is, thus, a major concern and a priority for rural inhabitants. Identifying the source of contaminants can help to understand the dynamic of pollutants transport and therefore support the design of corrective/mitigation strategies to address the issue.

The study of rain episodes is a way to elucidate the origin of solutes in stream waters^[1]. Stream water composition is influenced by runoff, land use, edaphology, climate, geomorphology, topography and the activity of the organisms. Solute source in streams can be natural or anthropogenic. The main contamination pathway into surface waters is through soil-associated contaminants following erosion, but also, surface direct flow during storms, contributes to lateral input into small streams^[2].

The aim of this research was to unveil solute source in streams during a storm event. Total reflection X ray fluorescence (TXRF) was chosen among other analytical techniques due to its multielemental information, easy quantification, minimum generated wastes and small amount of required sample^[3]. The multielemental information is an advantage for investigating water quality in not yet explored environments.

The present study can be applied to any stream, regardless of its location and the topography of the region. In order to carry out this study, La Chozza stream, a low order Pampean stream belonging to the Reconquista river basin, was selected.

From a local point of view, this research is important because La Chozza stream is in the Pampean region, a vast area of Argentina that covers over 50 million hectares. This region is densely populated and is of fundamental importance to man for its high livestock and crop yield^[4]. Both of these activities profit from groundwater and Pampean streams to increase their productivity. Nevertheless, in many of these places water quality is still unknown, as well as the source of contaminants.

Most Pampean streams originate in small depressions and their primary water source is groundwater. The bed is usually hard, homogeneous and the presence of stones is scarce. Due to the gentle slope of the region, water flows slowly.

Recently, arsenic was found in superficial waters^[5]. Arsenic most frequent oxidation states are +3 and +5. Arsenite (+3) is highly toxic due to its mobility and toxicity compared to arsenate (+5) which is

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easily adsorbed. However, in this environment, the most frequent chemical species is $+5$ its speciation can occur by biotransformation by microorganisms^[6,7].

Another present element in Pampean streams is phosphorus^[8], one of the major biogeochemical elements in the earth's crust. In nature, phosphate is the most frequent species of P^[9]. It is known that P can come through bedrock leaching but also, increased soil fertilization in the region may be an artificial source of this element^[10]. Excessive phosphate fertilization can reach stream water by runoff, causing algal proliferation and eutrophication^[11].

Investigations on the source of As and P in Pampean streams are scarce. In the case of As, most of the investigations lead to a natural origin of this solute in groundwater. According to the literature, volcanic origin of the sediments cause As presence in groundwater^[12], but no studies have been performed to investigate its origin in superficial waters.

In the case of P, Chornomaz *et al.*^[13] found an increase of P in surface waters due to sewage inputs after rains. Also, because of the increment in agricultural use of the land and the fact that riparian vegetation is mostly pastures, high levels of runoff are expected^[14,15]. Nevertheless, Amuchástegui *et al.*^[10] found high levels of this nutrient in Pampean streams but did not find a correlation between land use and P in the dry season, indicating that a natural source of this nutrient is also present.

During rain episodes, stream recharge changes in proportion and relevance due to the contribution of different sources: groundwater, soil and runoff^[16–18]. The study of discharge (Q) and solute concentration's (C) changes during these episodes is a way to elucidate the origin of solutes in surface waters^[1]. The relationship between Q and C follows cyclic trajectories that are referred to as hysteresis because the way they increase and decrease are different and it has been studied by several authors^[19–21]. This hysteresis occurs because the variation in concentration is not merely the product of dilution but also the product of endmembers mixing, that is, the mixing of the different components of discharge^[22]. Depending on the solute properties and the basin characteristics, different C–Q hysteresis loops can be obtained. These loops are used to determine in which source the solute predominates, unveiling its origin.

In this study, we considered that the patterns of the C–Q hysteresis could be explained using a mass balance mixing model with three solute sources: groundwater, runoff and soil water, as Evans and Davies^[1] proposed. According to this model, six types of C–Q hysteresis loops could be described with their own rotational pattern, curvature and trend.

Experimental

Sampling area

La Choza stream (34°42,182'S, 59°04,717'O) was selected as study site because it is a rural stream with little influence of urban or industrial wastes. This stream is located in Buenos Aires province and is part of the Pampean region (Fig. 1). This region is characterized by temperate humid climate, with annual mean rainfalls ranging 700 mm to 1200 mm^[23]. Maximum and minimum rainfall occurs in March and in June respectively. La Choza stream is 30 km long and drains an area of approximately 440 km², being one of the major contributors to the Reconquista river. The area is part of a floodplain, the soils of the basin are poorly drained, with low permeability and the bed is made of a complex of undifferentiated alkaline, saline and hydromorphic soils. The sampling site was located 31 m over the sea level, and 8 km from its headings. At that location, La Choza is a second order stream, according to Strahler's classification^[24]. In this area, 55% of the land is devoted to cattle farming and 45% to agriculture^[4]. Surrounding fields present soybean, wheat or corn crops, which are often amended with P fertilizers.

Monitoring and sampling

In this study, a rain episode occurred during autumn 2014 was monitored. The study consisted in monitoring the variation of stream water parameters as well as solute concentrations before, during and after the rain event, until discharge returned to its initial value. The frequency of the monitoring was daily before the storm, increasing during the event.

In each monitoring, hydrological parameters of the stream (width, depth, water velocity) were measured as described in

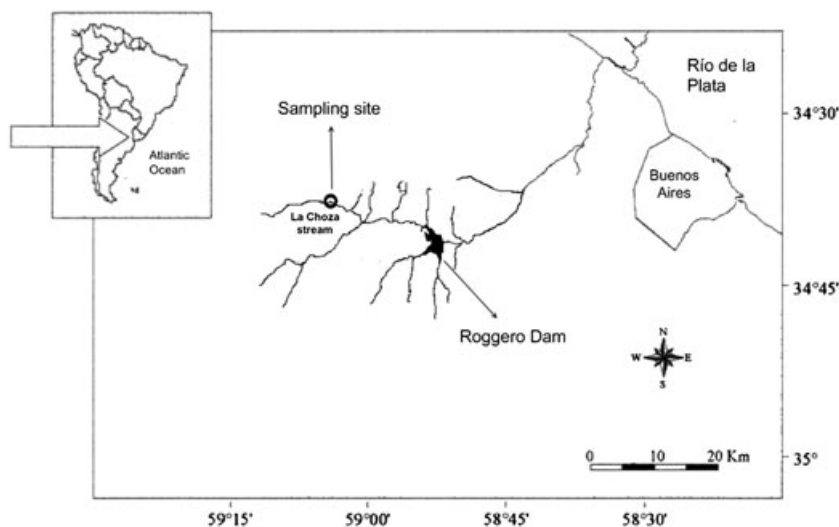


Figure 1. Location of the studied site in Buenos Aires province, Argentina.

Elosegi & Sabater^[25]. Also, physical and chemical parameters (temperature, pH, conductivity, dissolved oxygen and oxygen saturation) were measured *in situ* with a probe (HACH; Germany). Discharge (Q) was calculated by the area–velocity method following the procedure described by Gordon, McMahon, Finlayson, Gippel, & Nathan^[24]. Rainfall was measured with a pluviometer in the vicinities of the stream.

Simultaneously, water samples were collected in order to investigate As and P source, as well as other companion elements. Samples were taken in triplicate using 15-ml falcons previously cleaned by washing with pure water added with a few milliliters of nitric acid and refrigerated at 4 °C. In order to determine dissolved species concentration, samples were filtered through a 0.45- μm cellulose acetate filters (MUNKTELL®) and then acidified with 10% v/v Suprapur nitric acid (J. T. Baker®) in order to preserve the analytes in solution. In all cases, samples were analyzed directly without preconcentration. In order to evaluate the dynamic of As transport and its bioavailability in the stream, adsorbed as well as dissolved fractions were determined. For total As determination, samples were acidified before filtration, allowing desorption of this analyte from the suspended particles. To study the statistical differences between the levels of total and dissolved As, two-way-ANOVA was performed, using time and the dissolved/adsorbed As as factors. Samples for soluble reactive phosphorus (SRP) were filtered but not acidified.

Analytical determinations

For quantitative TXRF determinations, 10 μl of 100 mg l^{-1} cobalt used as internal standard was added to 1 ml of each sample to be analyzed. An aliquot of 10 μl of this solution was placed on an acid-cleaned siliconized quartz reflector and evaporated under an infrared light until dryness. The analyte concentrations (C) were then calculated through a calibration curve and the total procedure was validated using the NIST 1643f—Trace Elements in Water standard reference material. Quantitative determinations were carried out by obtaining multielemental calibration curves (using five aqueous standards in 2% HNO_3) and analyzing the samples as described before, following the literature^[3]. Calibration curves were checked every 10 samples and corrected if necessary. Confidence limits of interpolated value data were calculated by the software employed.

In the case of P, bioavailability of this element was considered relevant. Therefore, SRP was determined colorimetrically following Carvalho, Koe, and Tavares^[26].

Instrumentation

TXRF analysis was carried out using a system composed by an X-ray spectrometer, a tube excitation system, a total reflection module and spectrum acquisition and quantitation software. The X-ray spectrometer consisted of an 80 mm^2 Si(Li) detector with 166 eV FWHM for 5.9 keV and 0.008-mm-thick Be window, an Ortec 672 fast spectroscopy amplifier and a ADC Nucleus PCA2. This system included pile-up rejection and live time correction. A Mo anode fine focus X-ray tube was used. The excitation conditions were 40 kV and 30 mA in all cases. The total reflection module designed at the Atominsitute, Vienna was employed. Spectra were analyzed using the AXIL program.

SRP was colorimetrically determined measuring the absorbance of the molybdate-blue complex at 875 nm using an UV–Visible spectrophotometer (Hitachi U2001 UV Vis Spectrophotometer).

Validation of the method

In order to provide reliable results, analytical determinations followed validation parameters according to ISO/IEC 17025^[27].

Accuracy of the procedure was tested by analyzing one certified reference material: NIST SRM 1643f “trace elements in water”. The measured values were the means of three independent determinations and the standard deviations were calculated for a 95% confidence level. With the aim to compare quantitative deviations, As determinations were performed in an atomic absorption spectrometer with hydride generation (AA-HG, Analyst 200, Perkin Elmer) with a previous reduction using 5% (w/w) KI and 5% (w/w) Ascorbic Acid. Uncertainty in measurement with TXRF, considering sampling preparation and instrumentation was of 15% for 20 $\mu\text{g l}^{-1}$ and the same was considered for AA-HG. Phosphorus and Bromide validation was conducted using the 89886 Multielement Anion Standard Solution, certified reference material (Sigma Aldrich, 10.0 $\text{mg kg}^{-1} \pm 0.2\%$ F^- , Cl^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} each anion). Adequate dilutions were performed in order to avoid significant concentration differences between reference material and samples

Detection limits

For TXRF analyses, detection limits were calculated as three times the square root of standard deviation of the background as close as possible to the maximum signal. The detection limit (DL) was extrapolated according to Eqn (1), which assumes a 1000-s lifetime:

$$DL = \left[\frac{3\sqrt{l_b t}}{l_i t} \right] C_i \quad (1)$$

where l_b is the background intensity, l_i is the net intensity (counts s^{-1}), C_i is the element concentration ($\mu\text{g l}^{-1}$) and t (s) is the measuring time^[28]. Peak and background were evaluated by means of the QXAS Software.

The DL for phosphate was calculated as $3 \times \text{blank SD}/(\text{slope of calibration curve})$ ^[29]. At the absorbance maximum, the DL was 3.8 $\mu\text{g l}^{-1}$.

Hydrological and hysteresis descriptors

In order to describe this hydrological process, a hydrograph was constructed plotting the discharge (Q) *versus* time. Several descriptors were selected to define the event: The relative magnitude of the discharge change (Q); the relative duration in which the discharge reaches its maximum value ($D_{Q_{\text{max}}}$); the time in which the discharge returns to its initial value (D_{Q_i}) and the slope (k , $\text{m}^3 \cdot \text{s}^{-1} \cdot \text{day}^{-1}$) of the recession limb, which was obtained by fitting the data to an exponential decay curve, representing the recovery time of the stream. Equations for these descriptors can be found in Table 1.

Concentration (C) *versus* Q graphs were performed in order to infer the behavior and source of each studied analyte. The rotational pattern, curvature and trend of the hysteresis loops were analyzed. In each case, the initial concentration (C_i), the maximum concentration (C_{max}) and the concentration when the discharge reaches its maximum value (C_{peak}) were used to calculate the relative solute concentration changes (C ,^[21] Table 1). Negative C values indicate C–Q hystereses which follow a negative trend with respect to the discharge (i.e. solute dilution). Positive C values indicate the opposite case (i.e. solute flushing).

Table 1. Hydrological and hysteresis descriptors calculated to describe the storm event with their equations. Q_{max} is the maximum discharge during the event. Q_i is the initial discharge. t_{peak} is the time when the discharge reaches its maximum value. T_{total} is the total duration of the storm event. C_{peak} is the concentration of the analyte when the discharge reaches its maximum value. C_i is the initial concentration of the analyte. C_{max} is the maximum concentration of the analyte

Descriptors	Symbol	Equation
Hydrological		
Relative magnitude of the discharge change (%)	Q	$\Delta Q = \frac{Q_{max} - Q_i}{Q_i} * 100$
Relative time in which the discharge reaches its maximum value (%)	D_{Qmax}	$D_{Qmax} = \frac{t_{peak}}{t_{total}} * 100$
Relative time in which the discharge returns to its initial value (%)	D_{Qf}	$D_{Qf} = \frac{t_{total} - t_{peak}}{t_{total}} * 100$
Hysteresis		
Relative solute concentration changes(%)	ΔC	$\Delta C = \frac{C_{peak} - C_i}{C_{max}} * 100$

Results

Storm event characterization

The physical and chemical parameters of the stream measured during the storm event are shown in Table 2. Changes in water temperature are consistent with diurnal variations and season. It can be observed that pH values were slightly basic during the whole event, reaching values closer to neutrality when runoff and soil water were predominant. Also, dissolved oxygen was adequate for aquatic life. Electrical conductivity was high, due to high levels of bicarbonates and other electrolytes typical of Pampean streams [8,30]. A significant correlation between As levels and conductivity was also observed. This is evidenced by a Pearson's coefficient of correlation of 0.5 with $p = 0.0002$ for a 95% confidence level (Fig. 2).

The magnitude of the precipitation was 51 mm approximately, distributed primarily in three days, increasing the discharge 300 times above the initial. The hydrograph curve (Fig. 3) was asymmetrical. The delay between the peak discharge and the beginning of the rainfall was approximately two days (52 hours) and the high discharge due to rainfall episode lasted 5 days. Changes in discharge are due to variation in width, depth and water velocity. The latter is the only component that remains altered during the whole period. Furthermore, water velocity does not return to initial levels after the 14th day of monitoring.

Table 3 shows the hydrological descriptors calculated as shown in Table 1. The relative magnitude of the discharge change (Q) was high. Run-off, groundwater and soil water arrived at the river reaching the peak discharge when 28% of the period had lapsed.

Table 2. Minimum, maximum, mean values and standard deviation (SD) of physical and chemical parameters of the stream water measured during the event ($n = 20$). T° is temperature, COND is electrical conductivity ($\mu S cm^{-1}$), DO is dissolved oxygen ($mg l^{-1}$) and %Sat is oxygen saturation

	T°	pH	COND	DO	%Sat
Min	16.3	7.3	145.0	4.3	50.9
Max	30.9	8.3	1418.0	7.5	77.8
Mean ($n = 20$)	22.4	7.7	414.1	5.6	63.6
SD	4.3	0.2	388.4	0.9	7.9

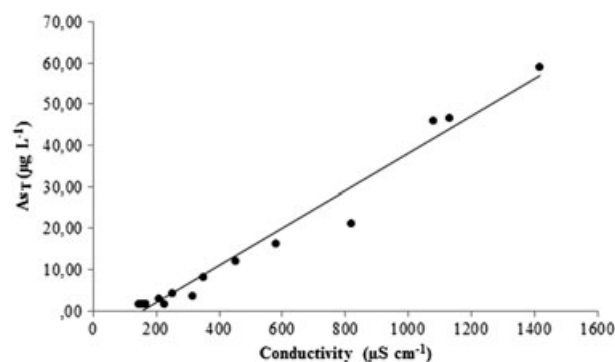


Figure 2. Total arsenic versus conductivity. The line represents the linear correlation.

Instead, the falling limb shows that water continued discharging into the river after the peak had passed, but in a moderate way (Table 3), as the k value of the logistic regression shows ($p < 0.0001$, $R^2 = 0.988$). The maximum and minimum values of daily discharge differed by a factor of 2 during the days subsequent to the peak discharge.

Solute dynamics

Dissolved As concentration did not differ significantly from total As ($p = 0.79$) during the flood event. Arsenic was rapidly diluted at the beginning of the rain episode and concentration increased slowly after the rain ceased. Arsenic concentration returned to its initial levels 5 days after the rain stopped. Instead, SRP concentration increased in the early hours, it was diluted later and finally increased, slowly returning to its initial levels 5 days after the rain stopped. Moreover, concentrations of Ca, Fe, K, Zn and Br were detected by TXRF and were explored as candidate tracers of groundwater [31,32].

In our study, it can be seen that some of the solutes showed hysteresis. C describes the relative changes in solute concentration and hysteresis trend, as it was defined before (Table 4). As, Br, Ca, Fe, K show a negative C value indicating that C/Q hysteresis had a negative trend with respect to the discharge (i.e. solute dilution). SRP and Zn show positive values indicating the opposite case (i.e. solute flushing). It must be noted that for Zn, C value is close to 0, implying that Zn shows little hysteresis.

Figure 4 shows hysteresis plots. According to this figure K and Zn's C/Q response is linear and hysteresis is not observed. For the other solutes the rotational pattern is clockwise, and the curvature is concave. In the case of Ca, Fe, As and Br, the trend is negative, and for SRP, the trend is positive.

Validation of the method

The accuracy tests showed a variation of less than 10% between the certified value and the measured value (Table 5), which was good enough to guarantee the analytical results. Also, samples determined by AA-HG were in good agreement with TXRF results. Uncertainty in measurement with TXRF, considering sampling preparation and instrumentation was of 15% for $20 \mu g l^{-1}$ and the same was applicable for AA-HG. Under these considerations, results coming from both techniques were comparable.

Figure 5 shows two typical spectra of collected samples obtained before and during the storm event. It can be noticed that, previous

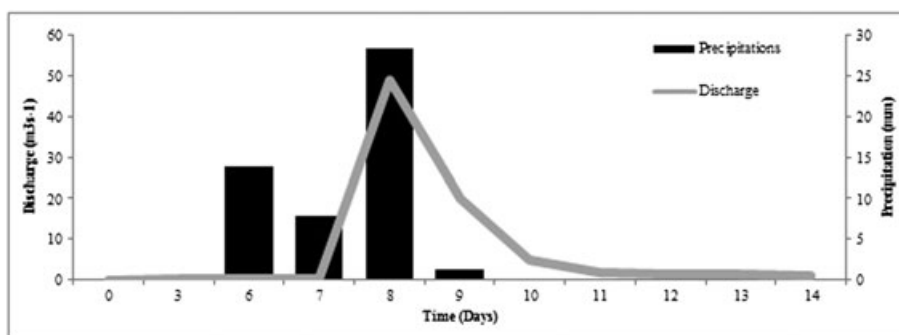


Figure 3. Flood hydrograph. Plot of the variation of average daily discharge (left axis, grey line) and precipitations with respect to time (right axis, black columns).

to the event, most of the elements are concentrated and during the event the only one present is P.

Discussion

Storm event

The rain episode was analyzed as a single pulse. When the storm event occurred, an abrupt rising limb was observed, reflected in the D_{Qmax} . This may be due to the high intensity of the storm and the relatively low tree riparian vegetation which usually retains water. Elosegi et al. [33] observed that the intensity of the rainfall influences the amount of runoff that arrives to the stream. At equal amount of precipitations, an intense storm produces more runoff than a prolonged drizzle, as larger drops seal the surface pores of the soil, reducing infiltration.

Considering that the study site has very gentle slope; water tends to be retained, although increasing retention time. The slow return of discharge to its initial value (D_{Qf}) may be due to the many transient storage zones gradually draining. Furthermore, the lowering of phreatic levels must occur in order to facilitate drainage of the stream [34].

It can be observed that pH values were slightly basic during the whole event, reaching values closer to neutrality when runoff and soil water were predominant. This is consistent with other pH

values reported for Pampean streams [8,35,36]. Rain water contributes with the dilution of the stream and, as a consequence of that, pH decreases during high flow and returns to its initial value after the event. Also, dissolved oxygen was never below 4 mg l^{-1} , which is the lowest limit accepted for the protection of aquatic life [37].

The relative magnitude of the discharge change (Q) was high compared to other lowland streams [38], but is in agreement with changes observed in nearby streams [39]. On the other hand, these magnitudes are high compared to mountain rivers with pronounced slopes [18].

In addition, Q remarks that these lands are very floodable. This matter must be taken into account for planning the expansion of the urban territory. Usually this is not contemplated in the area, leading to natural catastrophes.

Solute dynamics

This study provided new information on the distribution of As and P as well as the unveiling their source in stream water.

Arsenic expected levels for lotic environments of uncontaminated water are 0.13 to $2.1 \mu\text{g l}^{-1}$ [40–42]. Levels found in La Choza stream far exceed this threshold. These concentrations are lower than those found in literature for groundwater of the Pampa [43] but are similar to those found in surface waters in other regions, such as polluted rivers in Europe (4.5 to 45 mg l^{-1} , [42]). In turn, they are within the range of concentrations reported for other surface water bodies influenced by the presence of As in groundwater (7 – 114 mg l^{-1} in Córdoba, Argentina, [44] 190 – $21\,800 \text{ mg l}^{-1}$ in northern Chile, [45]). The hysteresis diagrams for As show a similar pattern to C3 shown by Evans and Davies [1]. This pattern has a clockwise rotational direction, a concave curvature and a negative trend, which corresponds to a solute that comes mostly from groundwater, because during the event is diluted with rainwater

Table 3. Hydrological and hysteresis descriptors calculated to describe the storm event. A minimum and maximum value is given in the physical descriptors. Q is the discharge. Q is the relative magnitude of the discharge change (%). D_{qmax} is the relative time in which the discharge reaches its maximum value (%), D_{Qf} is the Relative time in which the discharge returns to its initial value (%) and k is the slope of the falling limb ($\text{m}^3 \cdot \text{s}^{-1} \cdot \text{day}^{-1}$)

Hydrological descriptors		
Width (m)	<i>min</i>	5.2
	<i>max</i>	23.8
Depth (m)	<i>min</i>	0.3
	<i>max</i>	2.7
Water velocity (m s^{-1})	<i>min</i>	0.14
	<i>max</i>	1.03
Q ($\text{m}^3 \text{s}^{-1}$)	<i>min</i>	0.12
	<i>max</i>	66.19
Q		55,056
D_{qmax} (%)		28
D_{Qf} (%)		72
k ($\text{m}^3 \cdot \text{s}^{-1} \cdot \text{day}^{-1}$)		12.99

Table 4. Solute behavior during storm event. Maximum and minimum solute concentrations and Relative solute concentration changes (%) during the storm event

Solutes	max ($\mu\text{g l}^{-1}$)	min ($\mu\text{g l}^{-1}$)	C (%)
As	59	2	-97
Br	160	20	-69
Ca	5450	730	-68
Fe	2860	1020	-20
K	2670	1340	-27
SRP	520	180	19
Zn	450	60	2

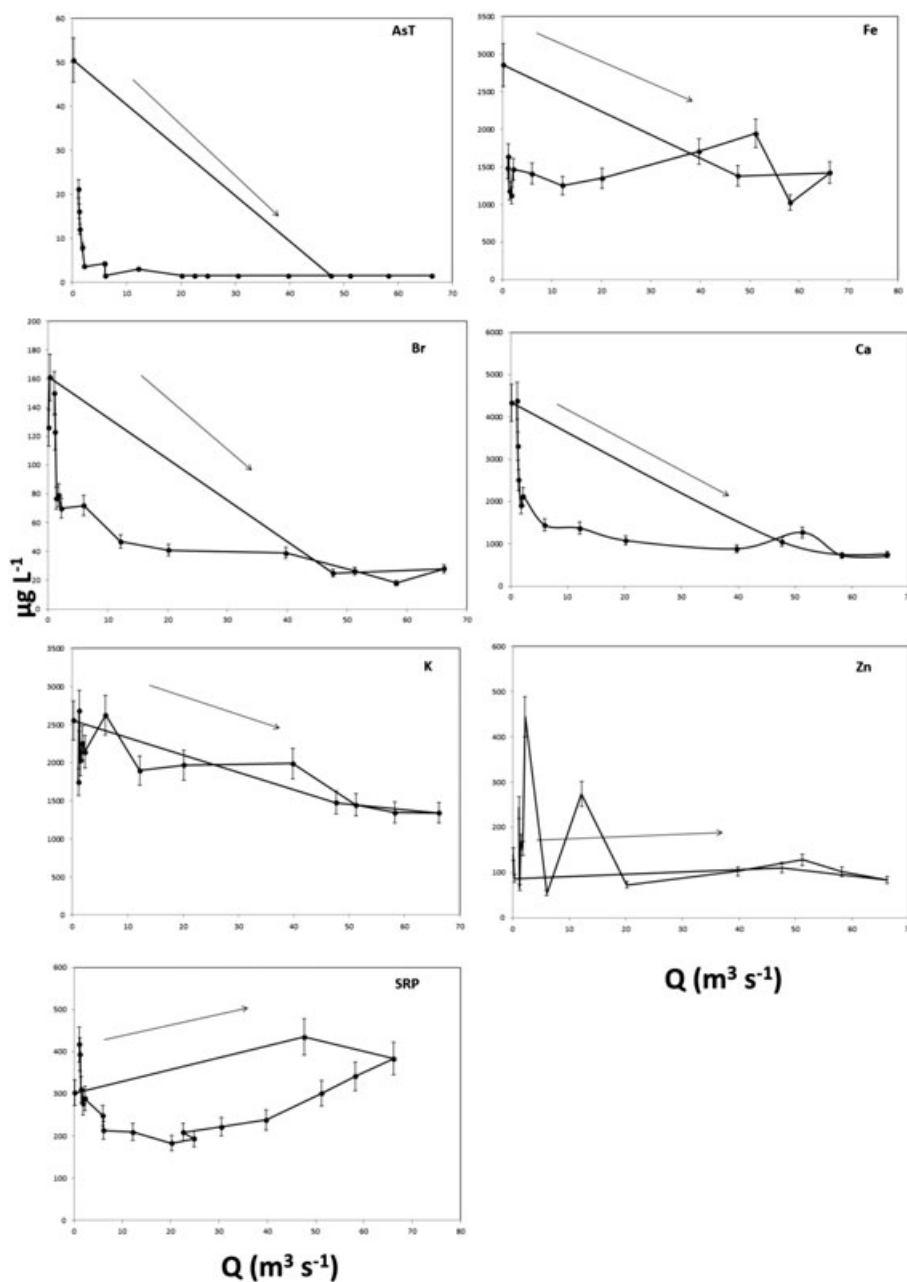


Figure 4. C/Q hysteresis loops created plotting each solute concentration *versus* discharge during the episode. Each plot shows the behavior of one of the solutes. AsT is Total.

Table 5. Limits of detection (L.O.D.) and reported and measured element concentration for standard reference material (NIST 1643f and Sigma Aldrich 89886 when indicated by *). SD is standard deviation

Element	Concentration ($\mu\text{g l}^{-1}$)				
	Certified	SD	Measured	SD	L.O.D.
As	57.42	0.38	55	6	2
Br (*)	10 000	20	9532	950	3
Ca	29 430	330	29 020	2961	5
Fe	93.44	0.78	100	10	5
K	1932.6	9.4	1892	180	10
P (*n)	3260	7	3205	317	10
Zn	74.4	1.7	82	7	1

and returns to its original level when the input of groundwater returns to be predominant.

The correlation between As and the conductivity is due to the fact that both have a common provenance. One possible explanation is that one of the predominant inputs to stream water comes from rainfall, so the degree of mineralization of these waters is low. However, groundwater is the result of prolonged contact between rainwater and minerals from the bedrock where chemical and physical processes such as dissolution, adsorption-desorption and concentration occur. This explains why electrical conductivity is closely associated with the composition of the rock which is in contact with water. A relationship can be established between the conductivity of the surface water and groundwater, so that the conductivity works as a natural groundwater tracer^[46]. Therefore, when groundwater is the predominant source of the stream,

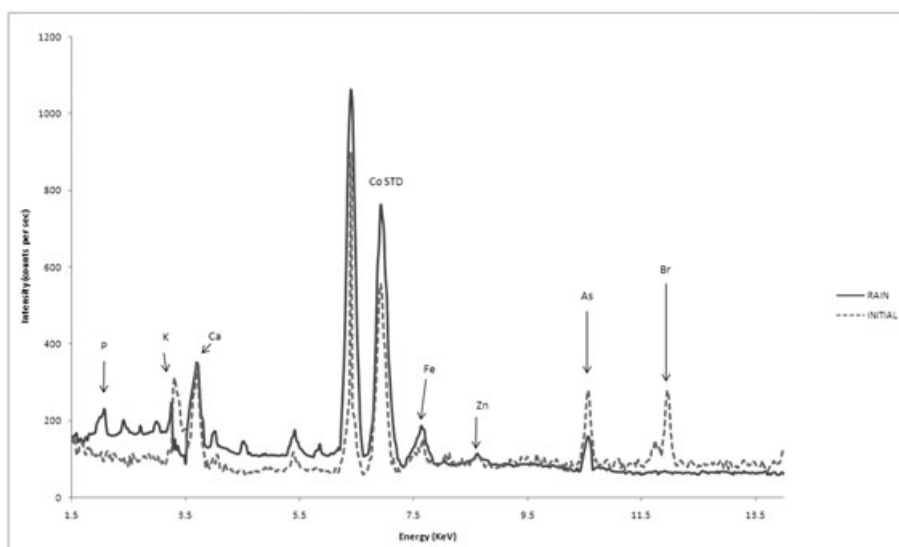


Figure 5. TXRF spectra corresponding to the moment of the peak discharge (filled line) and to the initial discharge (dashed line).

this is reflected in an increased conductivity and, at the same time, the concentration of As.

Arsenic results show that, during the episode, no significant differences between dissolved and total As levels were found. This implies that suspended particulate material did not adsorb significant amounts of As and that its transport through the lotic system is in dissolved form, being available for uptake by organisms.

With regard to P, concentrations found were elevated, in line with our expectations. It is known that P is present in the surface waters of the Pampas at high levels^[8,47,48], exceeding the characteristic threshold for eutrophic environments^[49]. The hysteresis diagram for SRP has a different pattern than As. For this solute, the diagram is similar to C2 shown by Evans and Davies (1998). C2 diagram shows a clockwise rotational direction, a concave curvature and a positive trend, indicating that the solute comes mostly from runoff. This can be explained considering that the study zone is an agricultural area in which phosphate is applied fertilizer^[4,48], creating diffuse sources of pollution in the stream^[50]. Given the criteria of Evans and Davis^[1] we can conclude that the input of P in stream water depends on rain events. Although this analysis is frequently used to describe P dynamics, it must be noted that P is not a conservative solute because it can be consumed by aquatic organisms. Nevertheless, the amount of biomass present in the stream can be a negligible influence on the drastic changes observed during the flood event^[51].

Rainfall regulates As concentration in the stream as its levels decrease when rainfall occurs. In turn, rainfall regulates exposure to As, that can generate toxicity to organisms that are part of the stream ecosystem^[52]. Moreover, rainfall increases P levels in the stream, which is an important factor for generating eutrophic conditions^[53].

The determination of these analytes in the same sample allowed comparing their behavior under the same discharge, allowing revealing their origin.

With regard to other studied solutes, all of them showed a C3 pattern according to Evans and Davies^[1], except for Zn, which did not show hysteresis in the C/Q plot. In this case, this element dilutes during the event. The levels of Zn exceeded the allowed values for aquatic life protection and cattle drinking according to Argentinian regulations. Likewise, similar values were reported for

other Pampean streams^[5]. It is known that Zn can cause acute toxicity when concentrations are as low as $90 \mu\text{g l}^{-1}$ but water hardness has a protective effect over aquatic organisms^[54].

According to^[55] solutes can be separated in major, secondary or minor dissolved constituents of groundwater. Ca is a major constituent, K and Fe are secondary constituents and Zn and Br are minor constituents of groundwater. This concurs with our observations of element occurrence.

The TXRF technique is well suited for studying rain episodes providing adequate detection limits for this purpose. No sample preparation is required which is a benefit to prevent possible contamination by other processes and is less time consuming. The use of an internal standard is required for quantification purposes correcting for any variation in sample deposition on the reflector's surface which could produce random errors. This technique competes successfully with other analytical techniques due to its excellent sensitivity for trace elements and multielemental information.

Unveiling the source of contaminants can help to understand the dynamic of pollutants and therefore define management politics to address the issue. Knowing that P entrance to these streams is runoff dependent, fertilizer application should be as far from rains as possible and buffer zones to retain P are highly recommended.

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