CAPÍTULO 17

CHEMICAL ELEMENTS IN SUPERFICIAL SEDIMENTS OF FIVE RESERVOIRS IN THE CATALONIA AND ARAGON REGIONS (SPAIN): IS THERE AN ANTHROPOGENIC CONTRIBUTION?

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ABSTRACT

Evaluation was made of the sediments of five Spanish reservoirs, four in the Catalonia region (the Sau, Susqueda, Foix, and Santa Fe reservoirs), and one in the Aragon region (the Barasona reservoir). The sediments were collected in 2011. At the Barasona, Sau, and Foix reservoirs, the sediments were obtained at three sites, one in the upper region of the reservoir, at the entrance of the main river, one in the zone near the dam, and another in the central region, between the river and dam regions. At the Santa Fe and Susqueda reservoirs, the sediments were obtained only near the dam. The superficial sediment was sampled with a 400 cm^2 Lenz type dredge. In the laboratory, the sediment samples were dried at 60 $^{\circ}$C and ground in a glass mortar. The concentrations of different chemical species were determined by X-ray fluorescence and by a microwave digestion procedure (using Teflon bottles with HCl and HNO$_3$). Measurements were made of the following species: Al$_2$O$_3$, P$_2$O$_5$, K$_2$O, CaO, SiO$_2$, TiO$_2$, MnO, Fe$_2$O$_3$, MgO, Na$_2$O, Ag, As, Ba, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, Hf, I, La, Mo, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Te, Th, Tl, U, V, W, Y, Yb, Zn, and Zr. The data revealed intra- and inter-reservoir spatial heterogeneity, with the Sau, Susqueda, and Foix reservoirs generally showing higher concentrations than the Santa Fe and Barasona reservoirs, which could be attributed to anthropogenic contributions.

1 INTRODUCTION

From an ecological point of view, reservoirs are transitional systems between rivers and lakes, but not only in the sense that they are transformations of rivers to lakes (MARCÉ, 2007), because the river continues to exert a great influence on them. According to Kimmel et al. (1990), three theoretical areas can be observed in reservoirs: riverine, transitional, and lacustrine areas. In order to understand their structure, dynamics, and functional complexity, reservoirs must therefore be studied taking into account this spatial horizontal component. Reservoirs have specific characteristics that depend on the watershed and on anthropic uses of the system (TUNDISI, 1985). Their morphometric features and position in the watershed enable them to act as accumulators of information about processes that occur in the hydrographic basin, affecting biological communities and reflected in changes in phytoplankton and zooplankton populations (TUNDISI, op. cit.). Besides the allochthonous influence, the nature of a reservoir is also influenced by factors including residence time, morphometry, and depth. Reservoirs provide records of past and present events in the drainage basin, while the dynamics, structure, and functioning of these aquatic ecosystems are, in part, influenced by external factors (HENRY, 1990).

Emissions of metals and other contaminants from agriculture and industry, amongst other sources, can affect water bodies directly due to discharge in wastewater, or indirectly following release to the atmosphere or soil, and subsequent transfer to aquatic systems (NRIAGU, 1989; FOSTER; CHARLESWORTH, 1996; YABE; OLIVEIRA, 1998; LOKESHWARI; HANDRAPPA, 2007; GALÁN; ROMERO, 2008). High contaminant concentrations can compromise the quality of water and sediment, affecting the future use of reservoirs, reinforcing the need for constant monitoring to evaluate the concentrations of metals and other species. Potential contaminants can have geogenic or anthropic origins (GALÁN; ROMERO, 2008; NRIAGU, 1989). The former include the bedrock from which the soil was formed, volcanic activity, or mineralization leachate, while emissions from human activities increase total inputs of certain species, such as metals, above the inputs associated with weathering processes in the watershed.

According to Schropp et al. (1990), study of the metal concentrations in the sediment provides temporally integrated contamination information, which can be more useful than the evaluation of concentrations in the water column alone. The metal concentrations found in the sediment are often higher than found in water, which can reduce problems related to contamination during analyses. Measurement of concentrations in reservoir sediments can therefore be a valuable tool for the evaluation of environmental contamination by metals, reflecting the types of land use and activities in catchments areas. From the point of view of monitoring, it can help in identifying suitable locations for measurements, such as near local sources of anthropogenic contamination (COAKLEY et al., 1993; DELVALLS et al., 2004; LOKESHWARI; CHANDRAPPA, 2007; RODRÍGUEZ-OBESO et al., 2007; XUE et al., 2007). Determination of concentrations of species in the sediment that can be attributed to anthropogenic contamination can be achieved by chemical extraction, analysis of the sediment fraction <63 μm, or by normalization employing conservative elements.

The chemical extraction commonly used in sediment characterization studies is not considered appropriate for assessment of the fraction of metals originating from anthropogenic contamination. When the metal is derived from an anthropogenic source, it can be released and quantified after treatment of the sediment with acid, followed by the use of a reducing agent (LUOMA; RAINBOW, 2008). The natural background metal content, present in the crystalline structure of sediments (usually silicates), is not attacked by this procedure, so the metals present in the matrix are not quantified, enabling discrimination of the fraction due to anthropogenic contamination. However, Luoma; Rainbow (op. cit.) suggest that this approach may be liable to error, because gradual migration of metals can occur from the surface to the nucleus of the particle. Use of a surface extraction process is therefore unable to evaluate all the anthropic metal content, some of which remains trapped in the matrix.

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In the absence of anthropogenic contamination, adsorbed metals are continuously renewed by micro scale cycling, especially at the complex interface of reducing sediments. Thus, the oxides of uncontaminated sediments may contain substantial concentrations of adsorbed metals that are released at low pH. Another possibility is to analyze the concentrations of metals present in the sediment fraction <63 μm, which possesses the greatest quantity of active sites for adsorption of metals (LUOMA; RAINBOW, 2008).

Another way of evaluating relative abundance is to normalize the concentration values using a conservative element (such as Al) that is determined in the same sample and whose abundance is considered to be similar in most geochemical environments (COAKLEY et al., 1993; COAKLEY; POULTON, 1993; SHARMA et al., 1999; ARMSTRONG et al., 2005; LUOMA; RAINBOW, op. cit.; GALÁN; ROMERO, 2008). The use of conservative elements eliminates possible physical and chemical interferences. For example, the raw concentration (mg metal / kg dry sediment) can differ depending on the particle size and type (such as clay or sand). Metals are often found at higher concentrations in sediments composed of smaller particles, due to the presence of more binding sites, while sandy sediments possess fewer active sites. Hence, a high sediment metal concentration may not always be due to anthropogenic contamination, because the characteristics of the sediment may differ between and within reservoirs. Normalization enables a better comparison of concentrations within a reservoir, as well as between different reservoirs.

The aim of this study was to assess possible contamination of the sediments of five reservoirs located in northeastern Spain (in the Autonomous Communities of Catalonia and Aragon), with emphasis on metals and some of the essential micronutrients and macronutrients. It was expected that the reservoirs located in more industrialized and populated regions would exhibit greater anthropogenic contributions to the concentrations of these species in the surface sediment.

2 STUDY AREA

Sediment samples were collected from five reservoirs: the Sau, Susqueda, Santa Fe, and Foix reservoirs in the Autonomous Community of Catalonia, and the Barasona reservoir in the Autonomous Community of Aragon (Figure 1).

Figure 1: Detail of the study region showing the locations of the Foix, Sau, Susqueda, and Santa Fe reservoirs, in the Catalonia region, and the Barasona reservoir in the Aragon region, Spain. Source: Google Earth v. 7.1.2.2041.

Most of the river basins in the Mediterranean region of Spain, including the Ter River, have been affected by anthropogenic activities for centuries, with their waters used for domestic, agricultural, and industrial water supplies, as well as power generation, waste disposal, and recreation (SABATER et al., 1992). In the 1950s, two large reservoirs were constructed in the

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middle stretch of the Ter River, namely the Sau and Susqueda reservoirs. Since then, extensive industrial development and unplanned growth of urban centers has resulted in large sewage inputs to the river. Activities including intensive farming, urban development, and industry depend on its waters. At present, the Ter only remains undisturbed in some of its first and second order tributaries (SABATER et al., op. cit.). The Ter River drains about 3,010 km^2 of the northern part of Catalonia. It rises at 2,400 m above sea level in the Pyrenees and flows 208 km down to the Mediterranean Sea. During its course, it receives the inputs of many tributaries. In the upper reaches, the largest of these is the Freser River (a fourth order tributary). The upper Ter and Freser basins receive many small streams feeding from the Pyrenees. In its central stretch, the Ter receives small second to third order streams originating from middle-mountain basins. The Ter headwaters and some of the tributaries in the middle stretch flow over granites and slates, while a few tributaries drain areas that are rich in gypsum (SABATER et al., op. cit.).

The Susqueda and Sau reservoirs are used for water storage, while the El Pasteral, a small reservoir located after Susqueda, is used for water regulation. After El Pasteral, a canal conveys water to the city of Barcelona. For ensure water quality (or minimize eutrophization) several measures were applied (ARMENGOL et al., 2009):

1) Wastewater purification: All outputs from point sources in the upper basin of the Ter River are passed through biological treatment plants equipped with tertiary treatment. Implementation of this system, which was completed in 1998, consisted of two phases, the first to remove phosphorus and the second to reduce inputs of nitrogen. Since then, nutrient inputs to the reservoir have decreased to the levels measured in 1964.

2) Depuration: Encouragement of internal physical, chemical, and biological processes that might decrease the movement of organic matter and nutrients, and limit their entry into the reservoir (ARMENGOL et al., 1999, *apud* ARMENGOL et al., 2009).

3) Hydraulic management: The aim is to increase the thermal stability of the water column and select the best quality water for extraction from each reservoir. This involves the manipulation of water depth, with water proceeding from the Sau reservoir to an intermediate layer in the Susqueda reservoir. This process enables improvement of water quality in the intermediate layer by the injection of water with higher oxygen content (ARMENGOL et al., op. cit.).

The Sau reservoir, at 41º 58' 4.28" N and 2º 24' 46.32" E, has a total length of 18 km and maximum depth of 75 m, although the lacustrine zone is only 3,600 m long, with a maximum width of 1,300 m. Its maximum height is 426 meters above sea level, and the deepest bottom is located at 365 m above sea level (BECKER et al., 2010; ORDÓÑEZ, 2010). The Sau is considered eutrophic and monomictic, and this canyon-shaped reservoir supplies drinking water to Barcelona (FEIJOÓ et al., 2008).

The Susqueda reservoir is situated 350 m above sea level in a zone of mineralized waters. It has a maximum volume of 233 hm^3 and a maximum depth of 129 m. It is a mesoeutrophic reservoir with continuous hypoxia in the bottom waters and occasional anoxia (PALAU et al., 2010).

The Sau, Susqueda, and El Pasteral reservoirs have a combined capacity of 0.402 km^3 and average water residence times of 117, 143, and 1.7 days, respectively (SABATER et al., 1992).

Even in the case of the Sau reservoir, which is the entry point for water from the river, and whose water presents lower temperature and higher quality, it is essential to ensure good water quality in the hypolimnion (MARCÉ et al., 2006).

The Foix reservoir (41º 15' 21" N, 1º 38' 53" E, 61 m above sea level) receives water from the river of the same name (MARCÉ et al., 2000). The dam was constructed in 1928 in order to provide water to different cities and farmland, but its water is no longer used for human consumption, due to its poor quality. The main morphometric characteristics of the Foix reservoir are a catchment area of 3.12x10^6 m^2, surface area of 7.2x10^5 m^2, maximum volume of 5.9x10^6 m^3, maximum depth of 11 m, and average depth of 7 m. The Foix reservoir is considered hot monomictic and hypereutrophic, and below a depth of 6 meters the dissolved oxygen (DO) concentration never exceeds 7 mg/L and the water can be anoxic during some periods. At the surface, mainly due to phytoplankton primary

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productivity, DO levels can reach 20 mg/L. The electrical conductivity varies from 900 to 1700 µS/cm, with high levels of nitrite and orthophosphate (exceeding 70 µM in the metalimnion in summer), although dissolved nutrients show marked seasonal patterns and depth profiles (MARCÉ et al., op. cit.). The reservoir dynamics are strongly influenced by the long water residence time, which varies from 230 to 800 days (MARCÉ; ARMENGOL, 2005). The region has low rainfall of 500-550 mm/year (CUSTODIO et al., 1993). The zooplankton community of the Foix is dominated by rotifers and microcrustaceans, mostly heleoplanktonic, representing about 50% of the taxa observed, with marked spatial heterogeneity, especially when comparing the fauna of the upper part, near the river, with that of the deepest region, close to the dam (MARCÉ; ARMENGOL, op. cit.; MARCÉ et al., 2005).

The Santa Fe reservoir is located at an altitude of 1,102 m, on the Gualba River in the Tordera basin of the Montseny Natural Park (a Biosphere Reserve designated by UNESCO). The reservoir has a surface area of 6 ha, capacity of 1 hm^3, and surface area of 4,500 m^2. The water has electrical conductivity of 38 μS/cm and 100 μg chlorophyll/m^2 (average values integrated for a water column of 8 m) (CAROL et al., 2006; CAPUTO, 2010; NAVARRO et al., 2010; MAGRAMA, 2014). According to Carlson's Trophic State Index (TSI), this reservoir can be considered mesoeutrophic, with advanced trophic state unrelated to human activities, attributed to the surrounding dense cover of deciduous trees (GENERALITAT DE CATALUNYA, 2005).

The Barasona reservoir is located in a depression in the south of the Esera River basin. It has an area of 692 ha, maximum depth of 60 m, average depth of 16.5 m, volume of 92x10^6 m^3, and installed power generation capacity of 26 MW (INFRAECO, 2006). The depression consists of relatively soft tertiary material that gives rise to a monotonous series of conglomerates, sandstones, and clays. The reservoir is one of the oldest in Spain, completed in 1932, and its depth was increased in 1972 (INFRAECO, op. cit.; VALERO-GARCÉS et al., 1997). It was built to regulate the flow of the Esera River, but its waters are also used for public supply, irrigation, and recreational activities. The Barasona is a typical monomictic reservoir. In summer, the thermocline is located at 7 m depth and the photic zone varies between 2.6 and 5.4 m. The average residence time is approximately 1.2 months, with a maximum of 3-4 months in February. The Barasona reservoir is considered mesotrophic (INFRAECO, op. cit.; ALATORRE, 2010). It has lost much of its water storage capacity due to high inputs and accumulation of sediment, although water flushing was conducted in 1995, 1996, and 1997 (ARMENGOL, 1998; YBARS, 1998).

3 MATERIALS AND METHODS

3.1 SAMPLING DESIGN AND FIELD PROCEDURES

The chemical species determined in this work included heavy metals with atomic weights greater than that of iron, essential trace elements such as As, Co, Cr , Cu, Fe, Mn, Mo, Se, V, and Zn, non-essential heavy metals (Cd, Hg, Ni, Pb, Sb, Sn, and Ti), other essential micronutrients (I and Si), and nutrients (Ca, Cl, Mg, K, Na, and S) (GALÁN; ROMERO, 2008).

The sediments were collected on 25th October 2011 at the Santa Fe and Foix reservoirs, on 15th November 2011 at the Susqueda reservoir, on 16th November 2011 at the Sau reservoir, and on 18th July 2011 at the Barasona reservoir. The collection sites are described in Table 1 and are illustrated in Figures 1, 2, and 3. At the Barasona, Sau, and Foix reservoirs, the sediments were obtained at three locations, one (denoted *river*) in the upper region of the reservoir, at the entrance of the main river, one (denoted *dam*) in the zone near the dam, and one (denoted *center*) in the middle region of the reservoir, between the river and the dam. At the Barasona reservoir, a sample (denoted *arm*) was also collected in the lateral arm, near the dam. At the Santa Fe and Susqueda reservoirs, the sediments (denoted *dam*) were obtained at a single point near the dam. Collections were made using a 400 cm^2 Lenz type dredge (Figures 4 and 5b). A single sample was taken in each region (Figure 2). The depth from 0-2 cm was separated, and the remaining sediment portion was partitioned into two parts, representing an intermediate fraction and one from the bottom of the

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dredge (Figure 4). These different depth fractions were denoted A (0-2 cm portion), B (intermediate portion), and C (deepest portion) (Figure 4c). In the case of the samples from the Susqueda reservoir, only fractions A and B were analyzed. The data are presented as the means for the different fractions.

For each depth (Figure 5), two pots, previously washed with dilute nitric acid (10% v/v), were filled to the top with sediment, closed to avoid interaction of the collected sediment with atmospheric oxygen, and kept in a cool and dark bag.

Table 1: Geographical coordinates of the sampling points at each reservoir. Source: Instituto Geológico y Minero de España - http://www.igme.es/infoigme/visor/

Reservoir	Code*	Sampling station			
		Arm	River (R)*	Center (C)*	Dam (D)*
Barasona	BS	42°7'35"N 0°20'20"E	42°10'44"N 0°20'11"E	42°10'14"N 0°20'8"E	42°7'52"N 0°19'19"E
Foix	F		41°15'32"N °37'59"E	41°15'23"N 1°38'25"E	41°15'20"N 1°38'57"E
Sau	Sau		41°58'49"N 2°19'47"E	41°59'44"N 2°18'37"E	41°58'16"N 2°23'39"E
Santa Fe	SF				41°46'6"N 2°28'13"E
Susqueda	Sus				41°58'45"N 2°31'12"E

* Code used in the statistical analyses, Figures, and Tables.
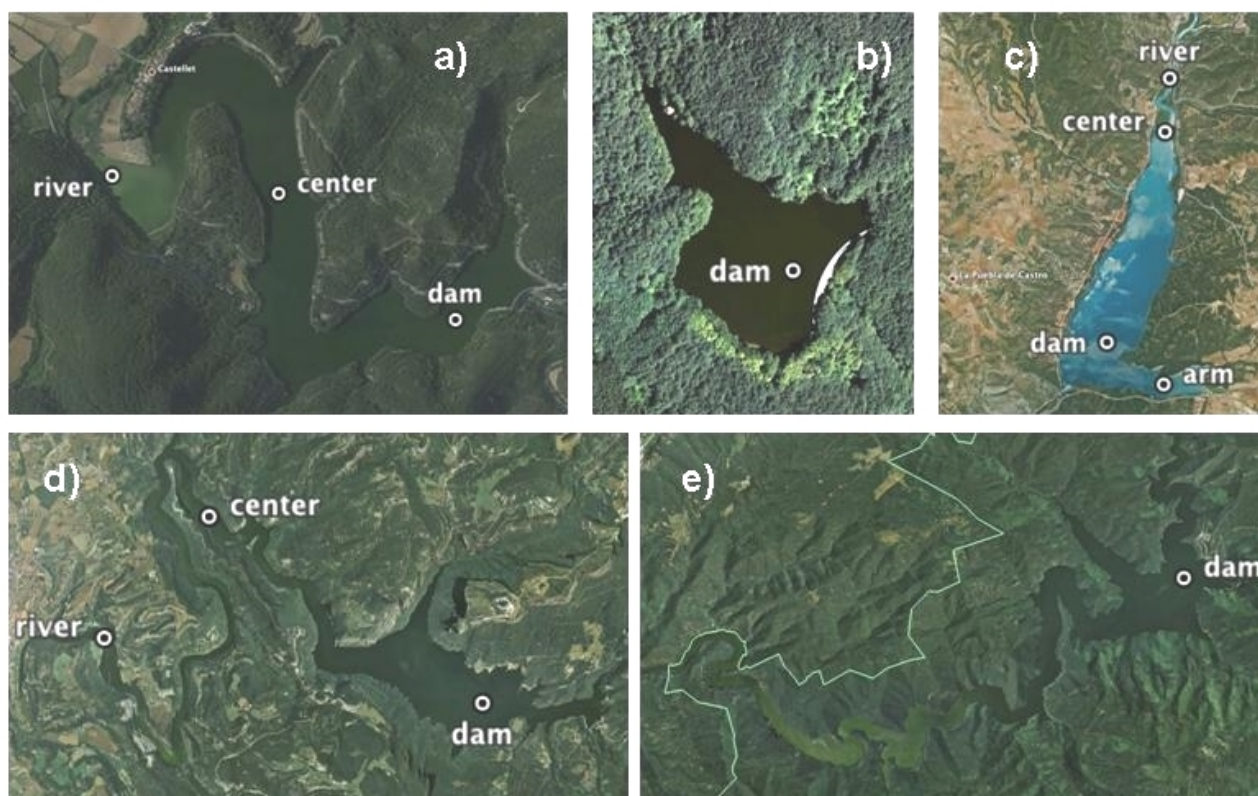
Figure 2: Location of sampling stations (◎) at the Foix (a), Santa Fe (b), Barasona (c), Sau (d), and Susqueda (e) reservoirs. Source: Google Earth v. 5.2.1.1588.

3.2 LABORATORY PROCEDURES

In the laboratory, the sediment samples were kept in a refrigerator until processing, which was performed within three days after collection. The sediments were first dried at 60 °C (LEMES et al., 2003), then triturated in a glass mortar (Figure 6) and placed in Ziploc bags. Samples from Santa Fe (dam) and Sau (center, fraction A), which contained substantial amounts of organic material, were previously sieved to a 2 mm mesh size, dried, triturated, and calcined (for 4 hours at 450 °C) in order to eliminate the organic matter.

a)

b)

Foix

c)

d)

Santa Fe

e)

f)

Susqueda

g)

h)

Sau

Figure 3: General views of the reservoirs studied. Foix reservoir near the dam (a) and at the entrance of the main river (b); Santa Fe reservoir, at the entrance of the main river (c) and at the dam (d); Susqueda reservoir, near the dam (e and f); Sau reservoir, at the river (g) and in the dam area (h). The photographs were taken on 25/10/11 (a, b, c, d), 15/11/11 (e and f), and 16/11/11 (g and h).

a)   b)   c)
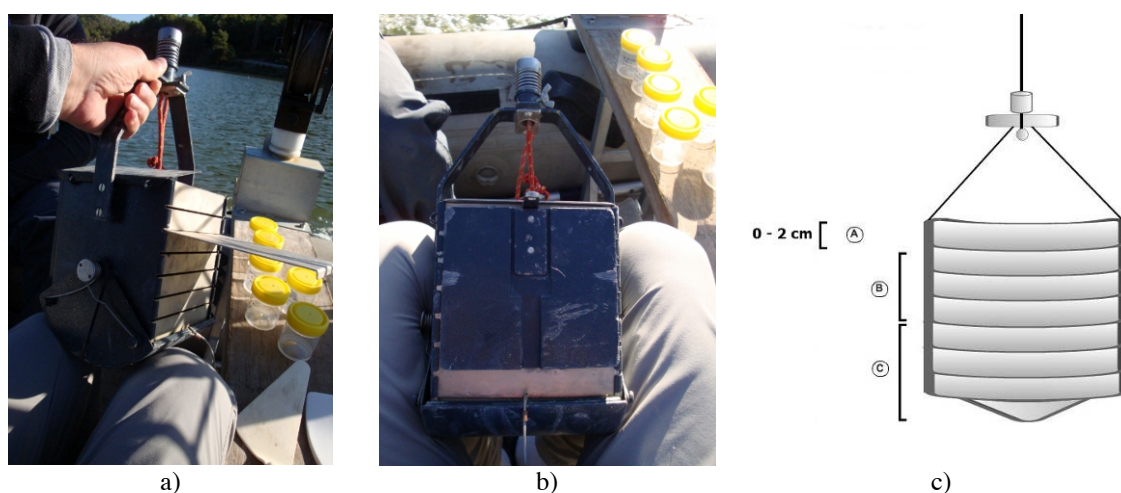
Figure 4: Dredge with (a) one side open, showing the window with openings for the passage of the cutting blade, and (b) closed for collecting the sediment. Three layers were separated (c), from 0 to 2 cm of depth (portion Ⓐ), intermediate (Ⓑ), and deepest (Ⓒ). The codes used in the statistical analysis (A, B, and C) represent portions Ⓐ, Ⓑ, and Ⓒ, respectively.

a)   b)

c)   d)
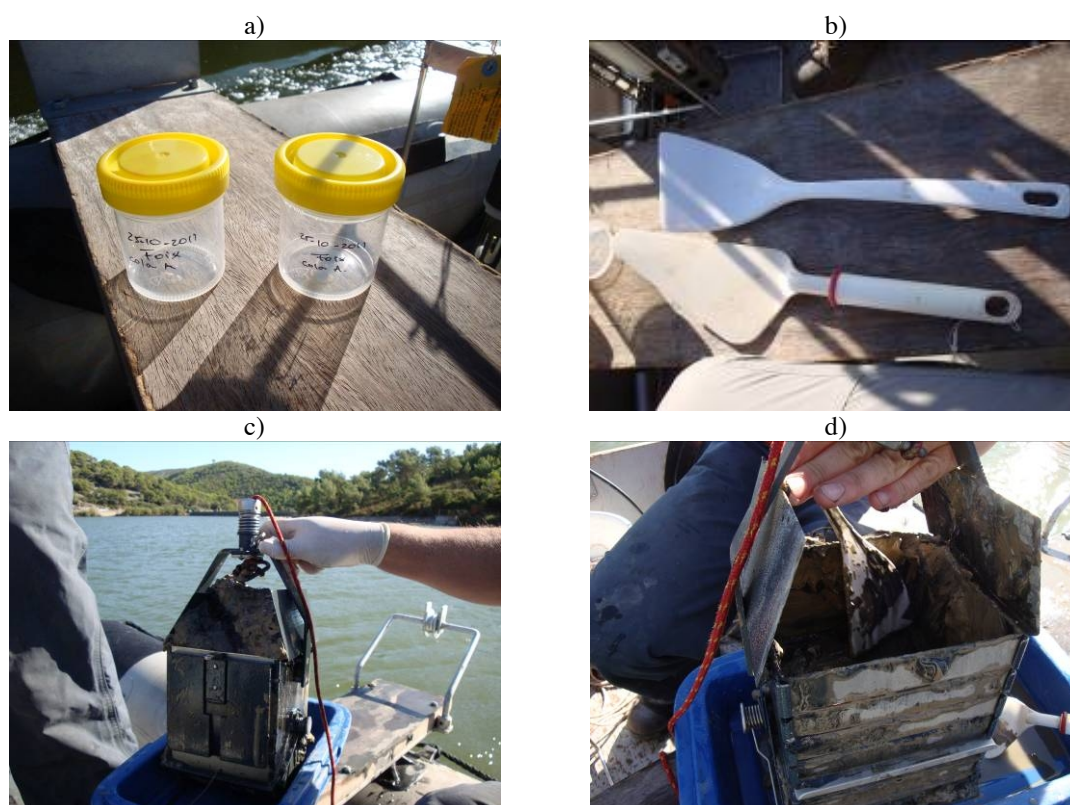
Figure 5: Bottles used to store the collected sediments (a), instruments used to remove the sediments (b), discharge of the collected sediment (c), and removal of the sample (d).

The concentrations of the elements were determined by X-ray fluorescence (XRF). The dried and ground sediments were processed by two procedures, as described by LÓPEZ et al. (2006) and adopted in the X-ray Fluorescence Laboratory of Barcelona University. To determine the contents of Al_2O_3, P_2O_5, K_2O, CaO, SiO_2, TiO_2, MnO, Fe_2O_3, MgO, and Na_2O, the sediment samples were diluted 20-fold by addition of lithium tetraborate (Alfa Aesar) (Figure 7) and melted at 1120 $^{\circ}$C in a radio frequency induction furnace (PANalytical Perl'X 3), yielding beads 30 mm in diameter (Figures 7h and 7i). For other elements (Ag, As, Ba, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, Hf, I, La, Mo, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Te, Th, Tl, U, V, W, Y, Yb, Zn, and Zr), 6.0 g of the

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dried sediment was mixed with 2 ml of synthetic resin (20% Elvacite 2044 dissolved in acetone), transferred to an agate mortar, and then compacted using a Herzog press at 200 kN of pressure for 60 s (Figure 8). Quantification of the elements was achieved by means of linear calibrations employing geological reference materials, following the same sample preparation procedures. The protocols were in line with procedures widely described by organizations worldwide: ANRT - Association Nationale de la Recherche Technique, France; BCS - British Chemical Standards; BAS - Bureau of Analysed Samples, England; CCRMP - Canadian Center for Mineral and Energy Technology; CRPG - Centre de Recherches Pétrographiques et Géochimiques, CNRS, France; IGGE - Institute of Geophysical and Geochemical Prospection, Ministry of Geology, China; IWG-GIT - International Working Group, Analytical Standards of Minerals, Ores and Rocks, France; MISC - Geological Research Laboratory, Bulgaria; NIST - National Institute of Standards and Technology, USA; NIM - SABS, South Africa; NRC - National Research Council, Institute for Environmental Chemistry, Canada; USGS - United States Geological Survey, USA; GSJ - Geological Survey of Japan. Possible interferences and matrix effects were corrected using the PANalytical PROTRACE program. The analyses were performed using a PANalytical Axios Advanced wavelength dispersive X-ray fluorescence (WDXRF) spectrophotometer. The following equation was used to calculate the linear calibration:

$$ S = \sqrt{\frac{\sum_n (cc + dc)^2}{n - k}} $$

where S = sigma of the linear calibration; n = patterns; k = regression coefficient; cc = chemical concentration; dc = calculated concentration.
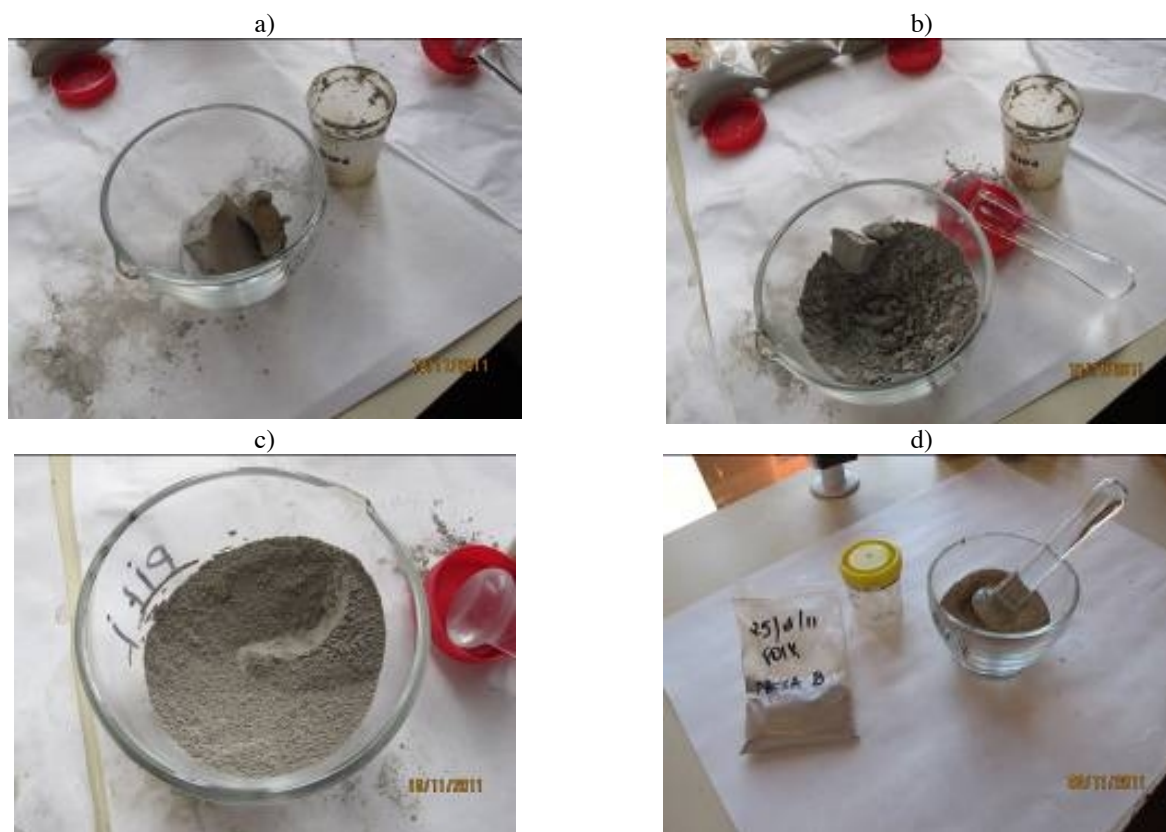
Figure 6: Crushing of the dry sediment using a glass mortar: Removal of the sample from the bottle (a); different stages of grinding (b and c); packing the material in Ziploc bags (d).
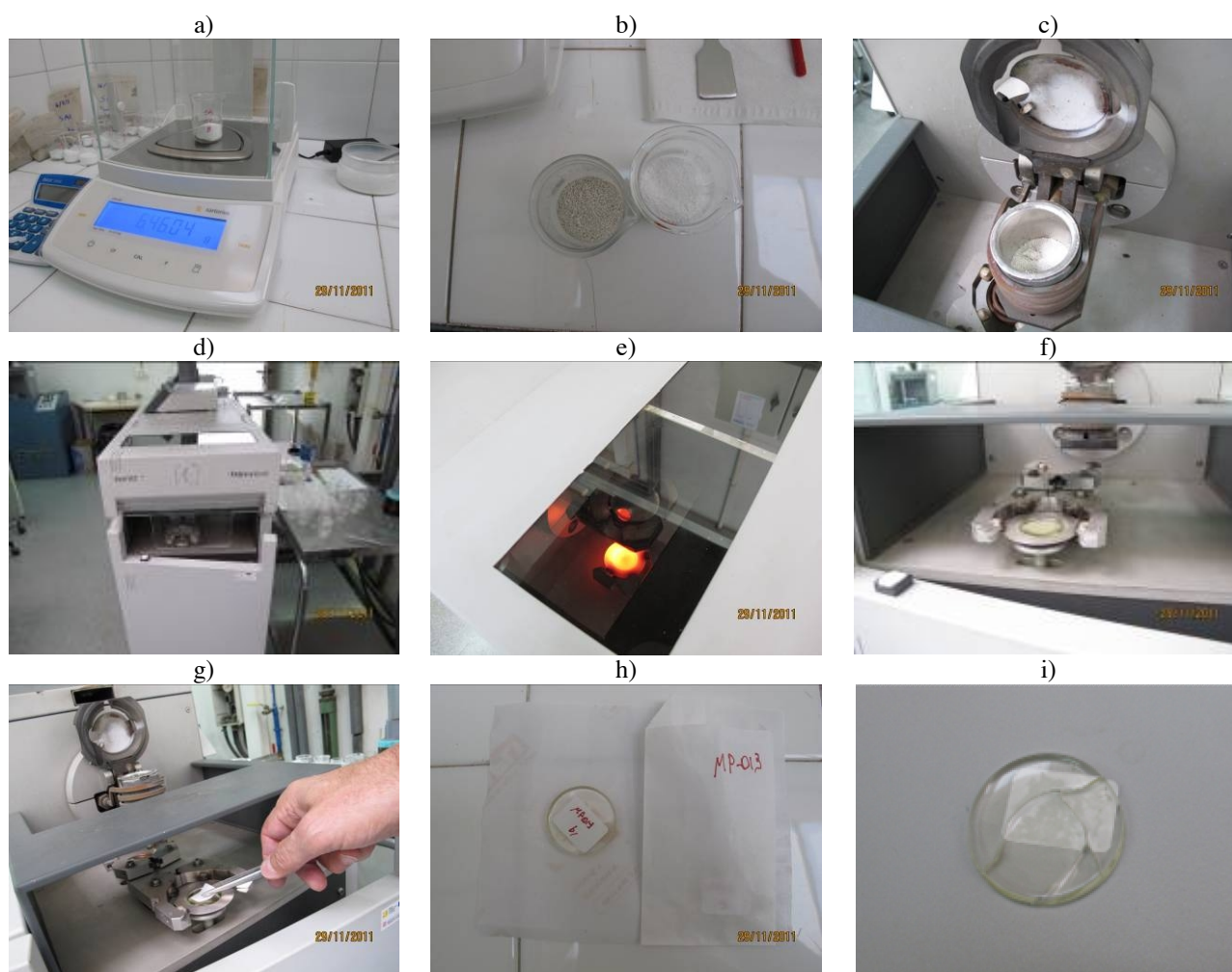
Figure 7: Procedure for the preparation of pearls for the determination of major elements by X-ray fluorescence: (a) weighing of the sediment and lithium tetraborate; (b) lithium tetraborate homogenate with the sediment (left-hand beaker); (c) platinum vase wrapped in resistance wire; (d) PANalytical Perl'X 3 instrument; (e) smelting procedure; (f) cooling of the pearl in a platinum dish; (g) pearl removal; (h) labeled pearl and storage envelope; (i) malformed pearl (cracked).

All the reagents used were of high purity, and the results were expressed as the concentrations of the elements based on the dry weights of the pellets and beads.

The sediment samples were also analyzed following microwave digestion in closed Teflon flasks, using an Etho Plus oven (Milestone), following a standard procedure at the University of Barcelona. Portions of 0.5 g of dry sediment were placed in the flasks, to which were added 6 ml of HCl and 2 ml of HNO_3. The flasks were sealed, placed in the microwave oven, and heated to 200 °C in a series of steps. They were then allowed to cool to below 80 °C, removed from the oven, and cooled to room temperature before opening. The contents were filtered (Whatman 589/2), transferred to 50 ml volumetric flasks, and the volumes made up with 0.5 M HNO_3. The samples were then transferred to pre-cleaned plastic bottles and stored in a refrigerator prior to analysis. Before use for new samples, the Teflon flasks were cleaned by heating for 20 minutes in the microwave oven, using 6 ml of HNO_3, 2 ml of HCl, and 2 ml of HF. After cooling, the acid was removed and the flasks were rinsed ten times with deionized water and three times with ultra-pure water. They were then dried (60 °C). The volumetric flasks were washed with 50% HNO_3 (v/v), with sonication for 10 minutes (Selecta ultrasonic bath), then rinsed ten times with deionized water and three times with ultra-pure water. The concentrations of Fe were measured using Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) (Optima 3200 RL, Perkin Elmer). All other elements were determined using Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) (Elan 6000, Perkin Elmer). For each element, four standards and a blank were prepared, with

relative concentrations of 0:1:2:5:10. For example, in the case of Fe, for which the detection limit was 0.01 ppm, the concentrations used were 0, 0.2, 0.4, 1, and 2 ppm. Analytical grade reagents were used (Merck), together with distilled and ultra-pure water (18 MΩ-cm) (Purelab Ultra, ELGA).

Figure 8: Sediment pastille used for the analysis of trace elements by X-ray fluorescence.

3.3 DATA ANALYSIS

The XRF data were normalized in order to identify anthropic contributions, minimizing the variations derived from natural causes such as differences in the sizes of the grains. Al was used as the conservative element, dividing the concentration of a given element ($[element_i]$) by the corresponding concentration of the conservative element ($[Al_i]$) in the same sample (COAKLEY et al., 1993; COAKLEY; POULTON, 1993; LUOMA; RAINBOW, 2008). For statistical analysis of the horizontal spatial heterogeneity of the chemical elements, the values were calculated as follows: $\log(([element_i]/[Al_i])*1000 +1)$. The statistical procedures employed were linear regression, cluster analysis, principal component analysis (PCA), and one-way ANOVA, performed with PAST v. 2.17c software (HAMMER et al., 2001). For each sampling station, the three fractions Ⓐ, Ⓑ, and Ⓒ were used (as shown in Figure 4).

Investigation of differences between the reservoirs employed two multiple discriminant analyses (MDA) (LEGENDRE; LEGENDRE, 1998), one based on the XRF data for Fe, Mn, Ti, K, P, Mg, Ca, and Si, and the other based on the XRF data for Ba, Ce, Co, Cr, Cu, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, and Zr. Investigation of differences between the regions (river, center, and dam locations) of the Barasona, Foix, and Sau reservoirs was performed using the same procedures (in this analysis, the Santa Fe and Susqueda reservoirs were excluded, because samples were only collected at one location). The MDA analysis enabled identification of the variables (chemical elements) responsible for differences between the reservoirs (VALENTIN, 2000). The data used in these analyses were normalized (using $[Me]/[Al]$) and then log-transformed using $[\log(x+1)]$. The MDAs were performed with Statistica v. 7.0 software (STATSOFT, 2004).

4 RESULTS AND DISCUSSION

The ranges of concentrations of the elements analyzed by XRF and ICP are shown in Table 2. The smallest variation was found for Sn (XRF), with a coefficient of variation (CV) of 8.7%, and the largest variation was obtained for Mn (XRF and ICP), with CV values of 120-130%. Also shown are the detection limits (DL), where available. In the case of the ICP analyses, the values are only indicative (provided by the Technical Services Laboratory of the University of Barcelona).

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Table 2: Concentrations of elements in the sediments of the Spanish reservoirs: minimum, maximum, and average values, standard deviations (SD), coefficients of variation (CV), and detection limits (DL), using two different analytical methods (XRF and ICP). The background (B) values for shales (Turekian; Wedepohl, 1961). The data were calculated considering all the sampling locations

Element	Method	Minimum mg/kgDW	Maximum mg/kgDW	Average[1] mg/kgDW	SD mg/kgDW	CV (%)	DL mg/kgDW	B mg/kgDW
Ag	XRF	2.28	4.02	**3.15**	0.40	12.8	*	0.07
As	XRF	4.92	38.66	13.83	7.16	51.8	*	13
	ICP	7.1	39.7	16.7	6.71	40.1	1.00 *	
Ba	XRF	215.60	821.83	450.55	181.05	40.2	25.1	580
Br	XRF	1.53	29.09	**10.39**	8.19	78.8	*	4
Cd	XRF	0.98	2.64	**1.84**	0.43	23.1	*	0.3
	ICP	0.158	0.963	0.436	0.243	55.7	0.04 *	
Ce	XRF	41.77	119.10	62.17	23.60	38.0	8.5	59
Co	XRF	7.15	15.33	11.21	1.95	17.4	2.8	19
	ICP	6.96	14.27	9.98	2.14	21.4	0.20*	
Cr	XRF	19.61	108.83	55.49	17.42	31.4	12.7	90
	ICP	27.45	107.93	52.33	16.28	31.1	1.00 *	
Cs	XRF	1.34	12.42	6.62	2.93	44.2	*	5
Cu	XRF	11.42	101.63	44.00	29.12	66.2	8.3	45
	ICP	9.98	92.73	40.95	26.68	65.2	0.40 *	
Ga	XRF	10.33	22.71	16.29	3.31	20.3	1.4	19
Hf	XRF	0.90	5.53	2.87	1.10	38.2	*	2.8
Hg	ICP	< 0.40	0.302	0.114	0.0612	54.1	0.40 *	0.4
I	XRF	**	14.17	**8.15**	3.39	41.6	*	2.2
La	XRF	22.66	66.06	32.53	11.25	34.6	*	92
Mo	XRF	< 0.5	1.51	0.89	0.26	29.2	0.5	2.6
Nb	XRF	9.93	18.15	12.89	2.01	15.6	8.5	11
Nd	XRF	17.34	56.78	26.83	9.31	34.7	*	24
Ni	XRF	16.96	36.73	26.53	4.53	17.1	6.5	68
	ICP	17.18	66.29	29.79	11.62	39.0	0.40 *	
Pb	XRF	15.84	68.40	31.74	14.09	44.4	11.6	20
	ICP	11.65	65.05	29.51	13.54	45.9	0.1 *	
Rb	XRF	60.58	146.99	107.47	21.23	19.8	11.3	140
Sb	XRF	1.69	6.35	**4.16**	1.00	24.1	*	1.5
Sc	XRF	13.36	43.08	**34.53**	8.47	24.5	*	13
Se	XRF	**	1.03	0.41	0.28	68.8	*	0.6
Sm	XRF	0.58	11.65	6.22	2.52	40.5	*	6.4
Sn	XRF	< 7.2	9.75	8.47	0.74	8.7	7.2	6
Sr	XRF	80.33	586.71	321.68	149.61	46.5	13.8	300
Ta	XRF	**	1.84	0.74	0.44	60.1	*	0.8
Te	XRF	**	2.49	1.20	0.81	66.9	*	D
Th	XRF	4.65	19.14	8.61	4.26	49.5	3.5	12
Tl	XRF	**	2.12	1.12	0.51	45.6	*	1.4
U	XRF	0.24	4.49	2.40	0.84	35.1	*	3.7
V	XRF	65.38	139.94	102.39	18.10	17.7	7.8	130
W	XRF	< 4.5	6.46	**5.82**	1.05	18.0	4.5	1.8
Y	XRF	17.97	37.79	22.89	6.12	26.7	5.1	26
Yb	XRF	2.05	5.98	4.21	0.83	19.7	*	2,6
Zn	XRF	49.18	142.79	99.51	29.99	30.1	18.3	95
	ICP	52.57	156.37	106.82	32.99	30.9	1.0 *	
Zr	XRF	87.12	196.60	124.31	26.93	21.7	18.4	160
		g/kgDW	g/kgDW	g/kgDW	g/kgDW	(%)	mg/kgDW	g/kgDW
Fe	XRF	22.00	51.06	33.44	7.57	22.6	0.629	47.20
	ICP	19.37	42.00	29.83	5.63	18.9	0.02 *	
Mn	XRF	0.39	4.88	0.73	0.90	123.4	0.310	0.85
	ICP	0.33	4.95	0.69	0.92	132.7	0.02 *	
Ti	XRF	2.52	6.41	3.49	0.97	27.8	0.120	4.6
K	XRF	15.73	28.64	23.22	3.30	14.2	0.572	26.6
P	XRF	0.74	1.46	1.17	0.26	22.0	0.332	0,70
Mg	XRF	9.62	26.23	14.30	4.61	32.3	0.043	15.0
	ICP	6.41	22.85	12.29	4.30	35.0	0.1 *	
Ca	XRF	8.72	170.63	**117.22**	45.87	39.1	3.739	22.1
	ICP	4.17	158.06	104.44	41.90	40.1	0.1 *	
Si	XRF	151.20	276.86	**190.90**	31.30	16.4	1.164	73.0
Al	XRF	43.48	125.53	79.29	19.86	25.0	1.447	80.0

*Values not certified (guideline values only); **Negative values; D – data missing or unreliable (TUREKIAN; WEDEPOHL, 1961); [1]Bold type indicates average values at least twice those established by Turekian; Wedepohl (1961).

The greater range of values obtained for Mn were mainly due to the high concentrations found for the dam zone of the Susqueda reservoir (Table 3). The lower range observed for Sn probably reflected minor anthropogenic emissions in the region, with only 13 samples presenting values above the limit of detection, and the maximum and mean values being close to the detection limit of the method. For both Sn and Mn, the mean values were close to the background values established for crustal shales (TUREKIAN; WEDEPOHL, 1961), of 850 and 6 mg/kg, respectively. Only a few of the elements determined in the present work showed concentrations that were slightly greater than the average shale geogenic background (Table 2).

Table 3: Mean values (X) and standard deviations (SD) for concentrations of major and trace elements in the sediments of the Spanish reservoirs (Barasona, Foix, Sau, Santa Fe, and Susqueda). The lowest concentrations are indicated in bold type and the highest values are underlined. E – element, M - method

E	Unit	M	Barasona		Foix		Sau		Santa Fe		Susqueda	
			X	SD	X	SD	X	SD	X	SD	X	SD
Fe	g/kgDW	XRF	**27.86**	2.11	30.69	4.77	35.15	5.47	50.28	0.74	40.69	3.14
		ICP	**24.96**	2.21	28.26	4.20	32.70	4.87	35.55	0.37	39.74	3.19
Mn	g/kgDW	XRF	**0.39**	0.02	0.46	0.07	0.62	0.24	0.74	0.04	4.07	1.15
		ICP	**0.35**	0.03	0.46	0.06	0.61	0.23	0.51	0.00	4.11	1.20
Ca	g/kgDW	XRF	146.68	11.73	147.98	11.53	97.15	28.30	**8.78**	0.07	84.42	19.18
		ICP	128.32	10.49	134.61	12.32	86.79	26.40	**4.28**	0.10	79.06	17.95
Mg	g/kgDW	XRF	10.75	0.50	20.81	2.61	13.96	1.98	**9.70**	0.14	11.13	0.94
		ICP	9.13	0.77	18.16	2.16	12.39	1.77	**6.47**	0.06	9.92	1.07
Co	mg/kgDW	XRF	**9.63**	0.57	10.87	2.12	12.15	1.58	12.61	1.04	14.25	1.53
		ICP	**7.99**	0.44	9.49	1.37	10.96	1.87	12.36	0.33	14.08	0.27
Cr	mg/kgDW	XRF	61.09	6.21	46.54	2.89	69.94	19.58	**22.43**	2.50	52.27	1.94
		ICP	54.37	11.47	41.67	6.76	66.40	16.19	**28.52**	0.92	62.43	8.92
Cu	mg/kgDW	XRF	**13.34**	1.69	82.78	11.93	47.26	13.46	21.84	0.31	41.38	3.41
		ICP	**11.48**	1.28	75.62	10.66	44.77	13.10	24.30	1.45	40.09	3.47
Ni	mg/kgDW	XRF	27.23	2.51	25.34	3.69	29.34	4.01	**17.31**	0.50	29.51	0.44
		ICP	27.10	3.65	28.59	11.47	33.90	11.95	**17.74**	0.60	48.28	25.47
Pb	mg/kgDW	XRF	**16.97**	0.74	32.41	3.27	33.77	4.88	66.69	1.58	41.01	2.86
		ICP	**15.06**	1.29	30.35	3.16	31.44	4.24	62.55	2.22	39.68	3.17
Zn	mg/kgDW	XRF	**60.02**	4.68	100.16	8.45	123.84	12.16	130.35	2.41	138.28	6.37
		ICP	**63.96**	5.66	105.31	7.38	133.78	11.40	144.22	5.66	150.45	8.37

The Mn/Al and Mn/Fe elemental ratios (in mg-at.g^{-1}*1000), calculated as described by LÓPEZ et al. (2006), were 4.51 and 22.19, respectively, slightly higher than the values found by LÓPEZ et al. (op cit.), of 3.72 for Mn/Al and 16.25 for Mn/Fe. López et al. also studied the East Catalonian region, including the Sau, Susqueda, Foix, and Santa Fe reservoirs, and found the highest Mn/Al ratio (7.11) at Susqueda, where the average oxygen saturation in the bottom was below 8%. The concentrations and ratios of sedimentary Mn are also very sensitive to other factors (such as the mineralogy of the catchments and carbonate equilibrium, for example) in addition to the redox conditions, as observed previously (LÓPEZ et al., op cit.).

Table 3 shows the mean concentrations (X) and standard deviations (SD) of the elements (E) for each reservoir, corresponding to the XRF and ICP analyses (with DLs for XRF). Elements for which DLs were not available were not included in Table 3. It can be seen that the lowest concentrations in sediment were obtained for the Barasona and Santa Fe reservoirs, probably due to smaller anthropogenic inputs into these systems. The Barasona reservoir is mesotrophic and receives little anthropic material (INFRAECO, 2006; ALATORRE, 2010). The Santa Fe reservoir is classified as mesoeutrophic, although this is not due to human activity because the reservoir is in a protected location at 1080 m altitude and receives virtually no anthropic inputs (GENERALITAT DE CATALUNYA, 2005; MAGRAMA, 2014). On the other hand, the Foix, Sau, and Susqueda reservoirs are considered more eutrophic. The Foix reservoir is hypereutrophic (MARCÉ et al., 2000), the Sau is eutrophic (FEIJOÓ et al., 2008), and the Susqueda is mesoeutrophic (PALAU et al., 2010), due to intense anthropogenic activities in these hydrographic basins.

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In the case of cascade reservoirs located along the Tietê River (São Paulo State, Brazil), Rodgher et al. (2005) associated high levels of bioavailable metals in the sediments with anthropic contributions, with higher levels of Cr, Cu, and Zn in the first reservoirs of the system. In another system of cascade reservoirs along the Paranapanema River (Brazil), Jorcin; Nogueira (2005) attributed high levels of N and P in the sediment to anthropic activity. Similar findings were reported for the estuary of the Sergipe River (Sergipe State, Brazil), with higher average metal concentrations because greater anthropogenic inputs (ALVES et al., 2007).

The concentrations of Cd, Cu, Cr, Ni, Pb, Zn, and Mn determined in this work were similar to those reported for the superficial sediments of reservoirs and lakes in other regions (Table 4), most of which showed medium to high levels of anthropogenic impacts, which supports the notion that anthropic sources were predominant at the Spanish reservoirs. From Table 4, it can be seen that high levels of Cu were found at the Guarapiranga reservoir (POMPÊO et al., 2013) and the Billings reservoir, especially for the Rio Grande arm (MARIANI; POMPÊO, 2008). Both of these reservoirs are located in São Paulo State (Brazil). In order to control potentially toxic algae, for around 40 years these reservoirs have been treated with heavy dosages of copper sulfate pentahydrate (CALEFFI, 2000), with application of around 440 and 360 tons respectively in 2007 alone (CETESB, 2008). This is reflected in horizontal spatial heterogeneity of Cu concentrations in these reservoirs, with much higher sediment Cu levels towards the dam zones.

Table 4: Concentrations of Cd, Cu, Cr, Ni, Pb, and Zn obtained under different environmental conditions and anthropogenic contributions

Reference	Elements (mg/kg)							Impact (c)	Type	Location
	Cd	Cu	Cr	Ni	Pb	Zn	Mn			
1 (*)	9.7	1157.2 (b)	59.6	57.3	<0.048	223.74		H	R	Brazil
2 (*)	9.7	1644.1 (b)	56.7	74.4	765.9	128.6		H	R	Brazil
3 (**)	0.1–0.6	0.9-30.5	2–28	2.2–29.6	0.9–31.2	11–402	67-397	M	R	Turkey
4 (**)	0.02–0.31	5.46–61.8	16.0< -66.5	4.0< -31.1	5.0< -45.7	21.7-161.0	110-506	M	B	Spain
5 (**)	0.01-0.12	5.6–18.7	8.7–19.6		1.6-65	24.8–99.0		L	LS	Brazil
6 (**)	0.47–0.9	72-4830				88–1600		L-H (a)	R	USA
7 (**)	5.3–7.8	151.6–233.9	80.1–119.5		17.0–31.6	177.5–307.6		L-H	R	Brazil
8 (**)		20-460	90-2800		20-240	20-990		H	R	Poland
9 (*)		5.82			0.44	11.91		M	R	Niger
10 (**)						189-406		L/M	R	Spain
11 (**)		16.1-44.2	17.8-74.0		20.1-78.9	70.1-164.6		M	R	Poland
12 (**)	0.08-0.42	5.0-30		7.1-32	9.9-36		340-2060	H/M	R	Lithuania
13 (**)	5-6	17-25		57-83	38-50	30-40	250-270	M	R	Iran
14 (**)		12-52			10-126	9-169	83-439	M	R / L	Poland
15 (**)	0.98-2.64	11.4-101.6	19.6-108.8	16.9-36.7	15.8-68.4	49.2-142.3	390-4880	L/H	R	Spain

1 - Pompêo et al., 2013 (Guarapiranga reservoir); 2 – Mariani; Pompêo, 2008 (Billings reservoir, Rio Grande arm); 3 - Keskin, 2012 (Akkaya dam); 4 - Rodriguez-Barroso et al., 2010 (Cádiz bay); 5 - Santos et al., 2003 (Lagoa Mirim); 6 - Finlayson et al., 2000; 7 - Bonai et al., 2009; 8 – Dojlido; Taboryska, 1991; 9 - Olutona et al., 2012; 10 - Lopéz et al., 2006; 11 - Senze et al., 2008; 12 – Kruopiene, 2007; 13 - Karbassi et al., 2011; 14 – Solecki; Chibowski, 2000 (Kowsar dam: Zalew Zemborzycki reservoir and Masluchowskie and Piaseczno lakes); 15 - This work.
* average values; ** ranges; (a) compartmentalized reservoir, with a portion receiving acid mining drainage; (b) reservoir with copper sulfate application for control of phytoplankton growth; (c) information inferred from the manuscript; R = reservoir; B = bay; L = lake; LS = lagoon system; H = high anthropogenic impact; M = medium anthropogenic impact; L = low anthropogenic impact.

In terms of land use and occupation (Table 5, Figure 9), the Barasona basin is the most protected, with around 82% covered by semi-natural areas and forest. The Foix hydrographic basin has the highest fraction devoted to agriculture, accounting for almost 54% of the area, with 42% of forest and semi-natural land cover. The Sau reservoir has an intermediate profile, with 22.6% of agricultural use and 75% of forests and semi-natural areas. These percentages, especially the high values for forests and semi-natural areas, corroborate the low metal concentrations found in the Barasona reservoir sediment, due to the lower intensity of anthropogenic activity and associated low emissions of metals to the atmosphere and aquatic systems of the region. Conversely, the higher concentrations found in the sediment of the Foix reservoir were in agreement with the higher level of anthropic activity and smaller proportion of protected areas in this basin. From comparison of the Foix and Barasona reservoirs (Figure 9), it can be concluded that anthropic contributions

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were responsible for the higher sediment concentrations measured for the former, especially in the case of elements attributed to anthropogenic contamination (such as Co, Cr, Cu, Ni, and Zn).

Table 5: Classification criteria for land use and occupation in the basins of the Foix, Barasona, and Sau reservoirs

Level 1	Level 2	Level 3
1. Artificial surfaces	1.1 Urban fabric	1.1.1 Continuous urban fabric
		1.1.2 Discontinuous urban fabric
	1.2 Industrial, commercial, transport	1.2.1 Industrial or commercial units
	1.3 Mines, dumps, construction sites	1.3.1 Mineral extraction sites
2. Agricultural areas	2.1 Arable land	2.1.1 Non-irrigated arable land
		2.1.2 Permanently irrigated land
	2.2 Permanent crops	2.2.1 Vineyards
		2.2.2 Fruit trees and berry plantations
		2.2.3 Olive groves
	2.3 Pastures	2.3.1 Pastures
	2.4 Heterogeneous agricultural areas	2.4.2 Complex cultivation patterns
		2.4.3 Mainly agriculture, significant areas of natural
3. Forest, semi-natural areas	3.1 Forests	3.1.1 Broad-leaved forest
		3.1.2 Coniferous forest
		3.1.3 Mixed forest
	3.2 Scrub and/or herbaceous vegetation	3.2.1 Natural grasslands
		3.2.2 Moors and heathland
		3.2.3 Sclerophyllous vegetation
		3.2.4 Transitional woodland, shrubs
	3.3 Open spaces, little or no vegetation	3.3.1 Beaches, dunes, sands
		3.3.2 Bare rocks
		3.3.3 Sparsely vegetated areas
		3.3.4 Burnt
		3.3.5 Glaciers and perpetual snow
4. Wetlands	4.1 Inland wetlands	4.1.2 Peat bogs
5. Water bodies	5.1 Inland waters	5.1.1 Water courses
		5.1.2 Water bodies

Figure 9: Land use and occupation in the watersheds of the Foix, Sau, and Barasona reservoirs. The criteria used are given in Table 5.

In terms of the toxicity potentials of the sediments (Table 6), values between the interim sediment quality guideline (ISQG) and probable effect level (PEL) values (CCME, 2003) were obtained for Pb, Cu, and Zn in sediments from the Sau (dam region), Susqueda, and Santa Fe reservoirs. For Cr (determined using both ICP and XRF), almost all the sites showed values between the ISQG and the PEL, although at the Santa Fe reservoir the concentrations were below the ISQG value. Values slightly above the PEL were only observed for Cr in sediment from the Sau reservoir (samples B and C). Since the concentrations obtained using the XRF and ICP techniques considered the total amounts of the metals, rather than the bioavailable fractions as defined by CCME (2003), the sediments from the Sau, Foix, Susqueda, Santa Fe, and Barasona reservoirs could be considered to have low toxicity potentials in terms of the individual metals. Nonetheless, values above the PEL for some elements, even considering that these reflected total amounts, indicated that greater attention should be paid to the sediments from the Sau, Susqueda, and Foix reservoirs, compared to those from the Barasona and Santa Fe reservoirs.

Table 6: Sediment quality guidelines for the protection of aquatic life and human health. These values are used to define toxicity potential, according to CCME (2003). ISQG: Interim sediment quality guideline; PEL: Probable effect level

Element	ISQG mg/kg	PEL mg/kg
Cd	0.6	3.5
Cr	37.3	90
Cu	35.7	197
Pb	35	91.3
Zn	123	315

It can be seen from Figures 10 and 11 that the Barasona sediment presented lower average values for the elements Fe, Ti, Mn, Ba, Pb, Th, Y, and Zn, while the Santa Fe sediment showed lower values for K, Mg, Ca, Cr, Ni, Si, and V. The concentrations of the elements in the sediments from the Foix, Sau, and Susqueda reservoirs were generally higher than in the Barasona and Santa Fe sediments. The concentrations of Mn and Ce were notably higher in the Susqueda sediment. The data therefore provided further evidence for the low anthropic inputs of metals at the Barasona and Santa Fe reservoirs (despite a high Sr concentration at Barasona). The Foix, Sau, and Susqueda reservoirs showed greater anthropic contributions, corroborated by their higher trophic states and their records of eutrophication due to inputs of nutrients derived from anthropogenic activities in the hydrographic basins.

In terms of spatial heterogeneity, cluster analysis (performed using the XRF data) revealed the existence of reservoir groupings, especially for the major elements but also for the trace elements (Figures 12a and 13a). The Barasona and Santa Fe reservoirs showed the least similarity to the other reservoirs, while the Sau (collection site in the dam zone) and Susqueda reservoirs showed the greatest similarity. Grouping was also observed between the Sau and Foix reservoirs, probably due to their similar trophic levels. The existence of the different groupings could be explained by the different anthropic inputs, reflected in the different trophic levels (Barasona is oligotrophic, Santa Fe is considered mesoeutrophic, and Sau, Susqueda, and Foix (especially) are eutrophic). The dendrograms obtained for the Barasona, Foix, and Sau reservoirs were indicative of intra-reservoir heterogeneity for the major elements as well as the trace elements, with discrimination amongst the sites at the river (R), center (C), and dam (D) locations.

The Sau and Susqueda reservoirs comprise a cascade system, whereby several reservoirs are constructed in sequence along the same river (STRAŠKRABA et al., 1993; STRAŠKRABA; TUNDISI, 2000; TUNDISI; MATSUMURA-TUNDISI, 2008). In this configuration, the characteristics of an upstream reservoir can influence those downstream, with deep and stratified reservoirs likely to exert greater effects than shallow reservoirs. Other factors influencing such systems include the classification (type) of the river connecting the water bodies, the trophic levels of the reservoirs, and the distances between them. The latter factor is an important consideration, because after a distance of several hundred kilometers from the upstream reservoir, the river returns to its natural state, so the effects on the downstream reservoir are much less significant, compared to a system where the reservoirs are closer together. In the present case, the similarity between the Sau and Susqueda reservoirs, observed in the PCA and cluster analyses, can be explained by the effects of the upstream reservoir (Sau) on the downstream reservoir (Susqueda). The effect was heightened by the close proximity of the two water bodies, with the water leaving the Sau reservoir at a short distance from the river zone of the Susqueda reservoir.

The PCA results for the major elements (Figure 12b) showed that the first and second components explained 48.32 and 23.95% of the variance, respectively. The corresponding values for the trace elements (Figure 13b) were 58.66 and 24.64%, respectively. Low values were obtained for the major elements Fe and Ti (Barasona) and Ca, K, and P (Santa Fe). For the trace elements, low values were obtained for Th, Ce, Pb, Ba, and Zn (Barasona) and V, Cr, and Ni (Santa Fe). Higher values for the elements analyzed (with the exception of Sr) were obtained for the Foix, Sau, and Susqueda reservoirs.

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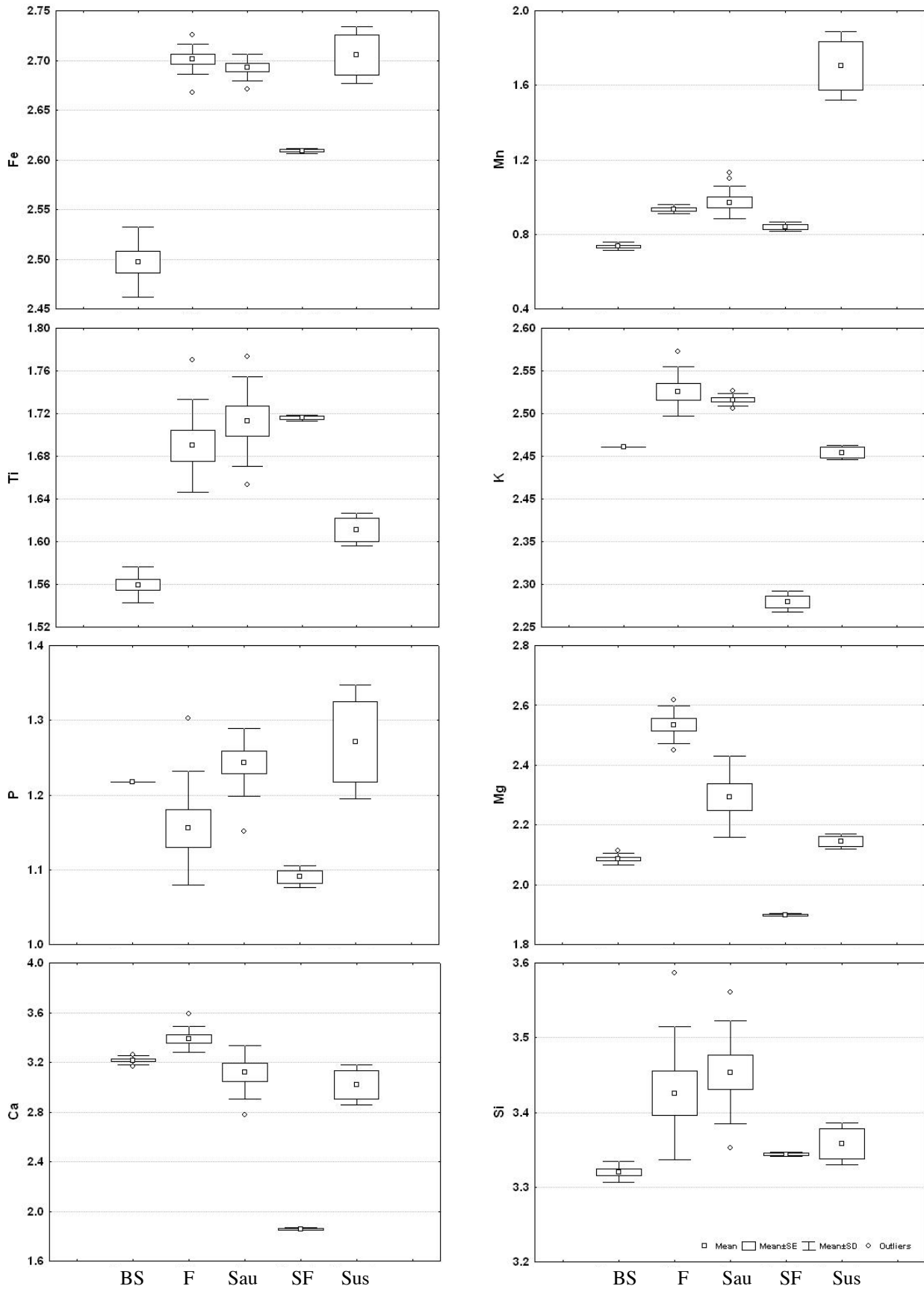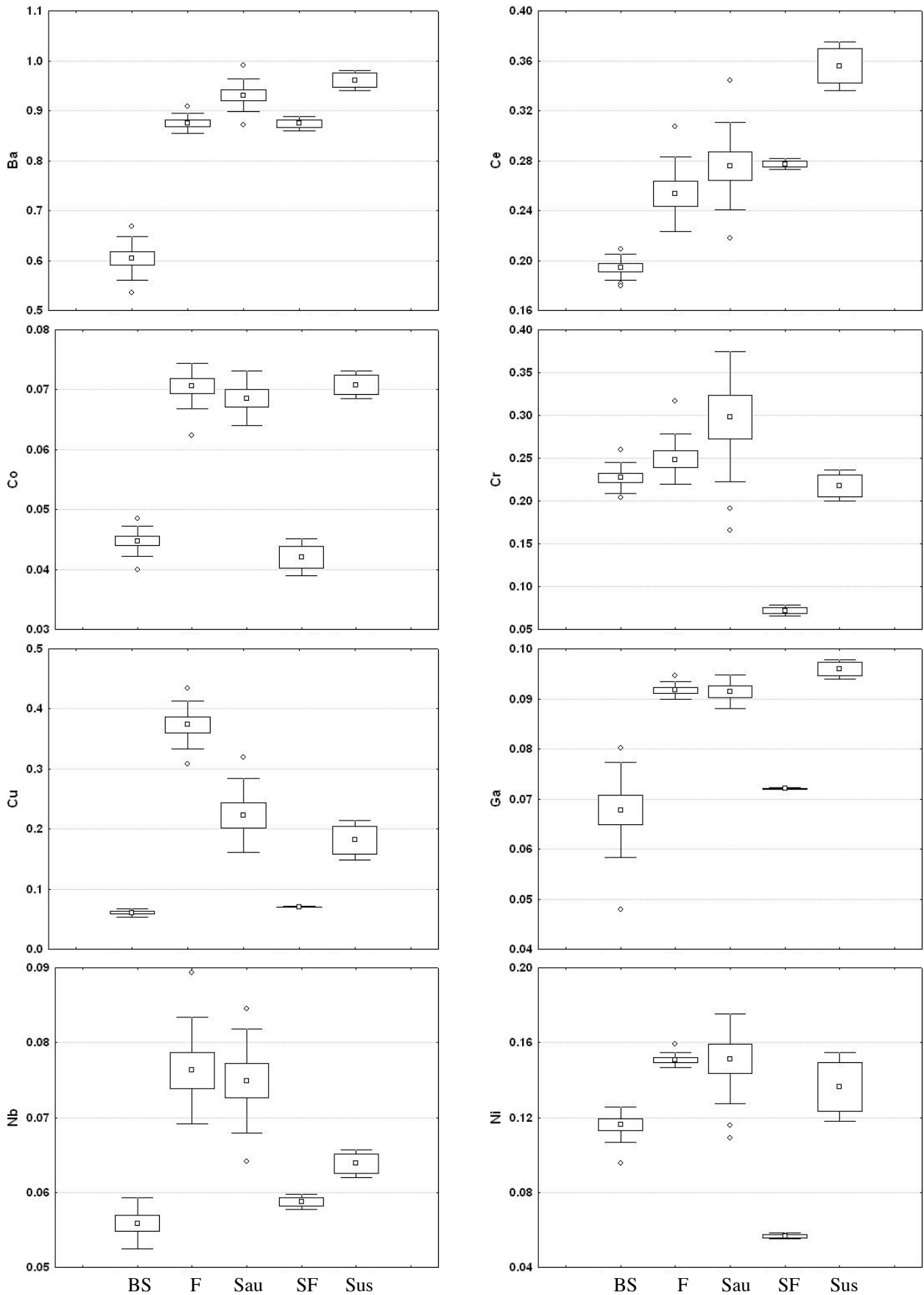
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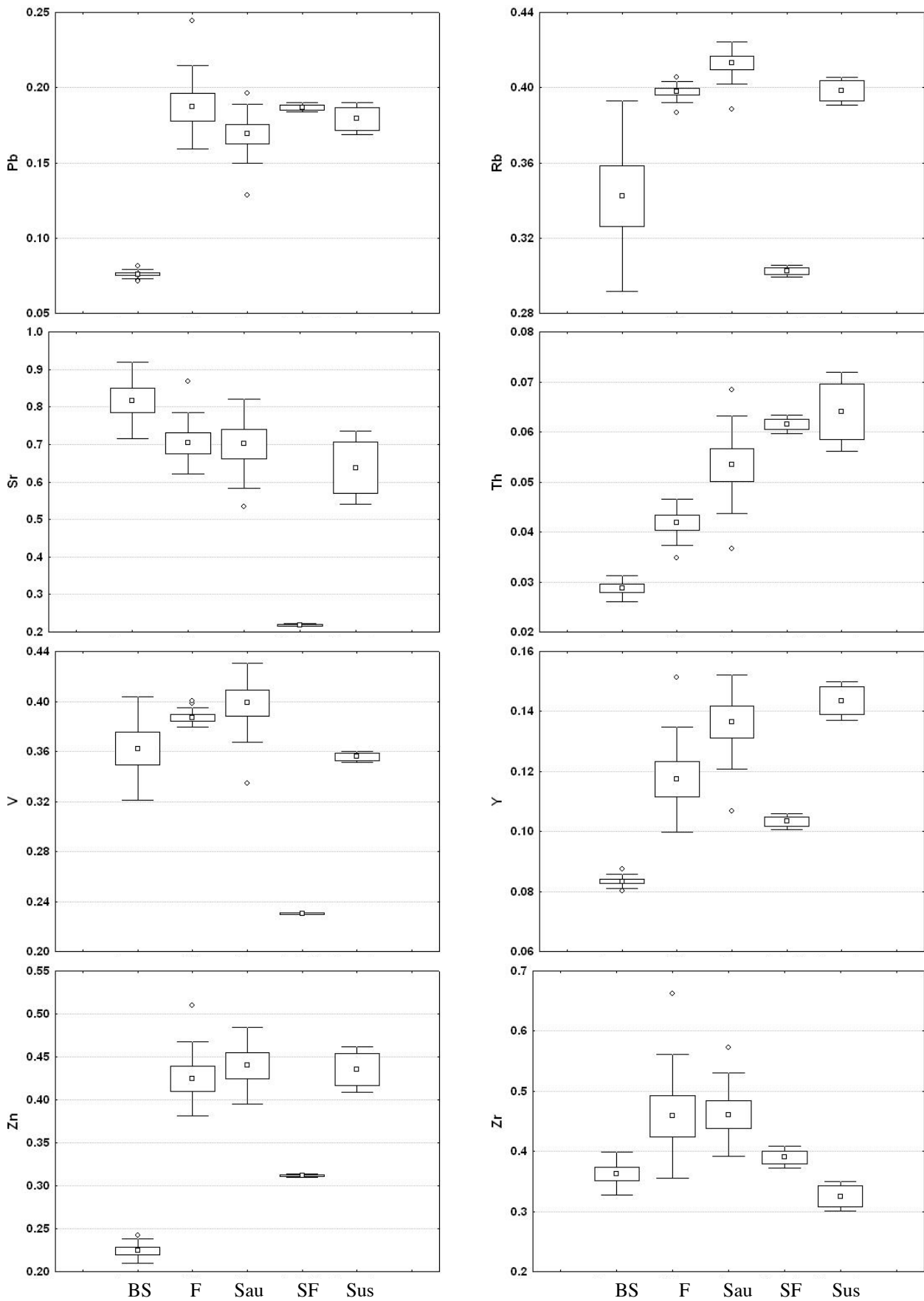
Figure 10: Box-and-whisker plots for major elements in the sediments of the five Spanish reservoirs. The values shown on the Y-axes are the element concentrations divided by the corresponding concentrations of Al and then log-transformed (log (([E] / [Al]) * 1000 +1)). BS – Barasona, F – Foix, SF – Santa Fe, Sus – Susqueda.

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Figure 11: Box-and-whisker plots for trace elements in the sediments of the five Spanish reservoirs. The values shown on the Y-axes are the element concentrations divided by the corresponding concentrations of Al and then log-transformed (log (([E] / [Al]) * 1000 +1)). BS – Barasona, F – Foix, SF – Santa Fe, Sus – Susqueda. (Continue).

(Continuation)

Figure 11: (Continuation) Box-and-whisker plots for trace elements in the sediments of the five Spanish reservoirs. The values shown on the Y-axes are the element concentrations divided by the corresponding concentrations of Al and then log-transformed (log (([E] / [Al]) * 1000 +1)). BS – Barasona, F – Foix, SF – Santa Fe, Sus – Susqueda.

Application of the centralization technique and one-way ANOVA was used to provide confirmation of the trends indicated in Figures 12a and 13a, considering differences among the river, center, and dam sites for the Foix, Sau, and Barasona reservoirs. These analyses employed the standardized and normalized average values of the elements (log ([element]/[Al])*1000 + 1), for each individual trace element (Ba, Ce, Co, Cr, Cu, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, and Zr). Statistically significant differences were only found for Sr and Zr (Table 7), with differences between the river and dam sites. No statistically significant differences were found for the other elements.
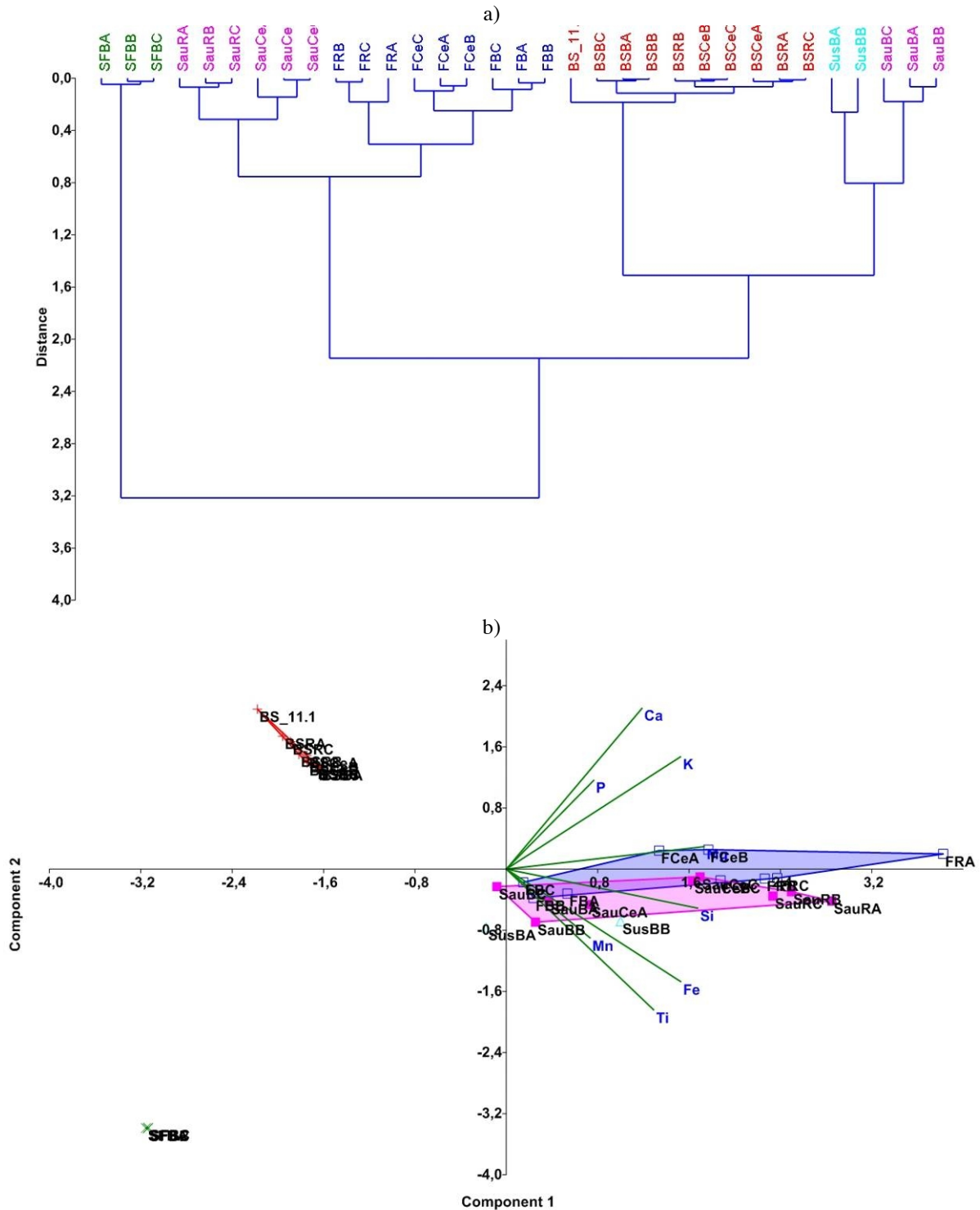
Figure 12: (a) Cluster analysis and (b) PCA analysis of major elements. Labels: according to Table 1 and Figure 4.
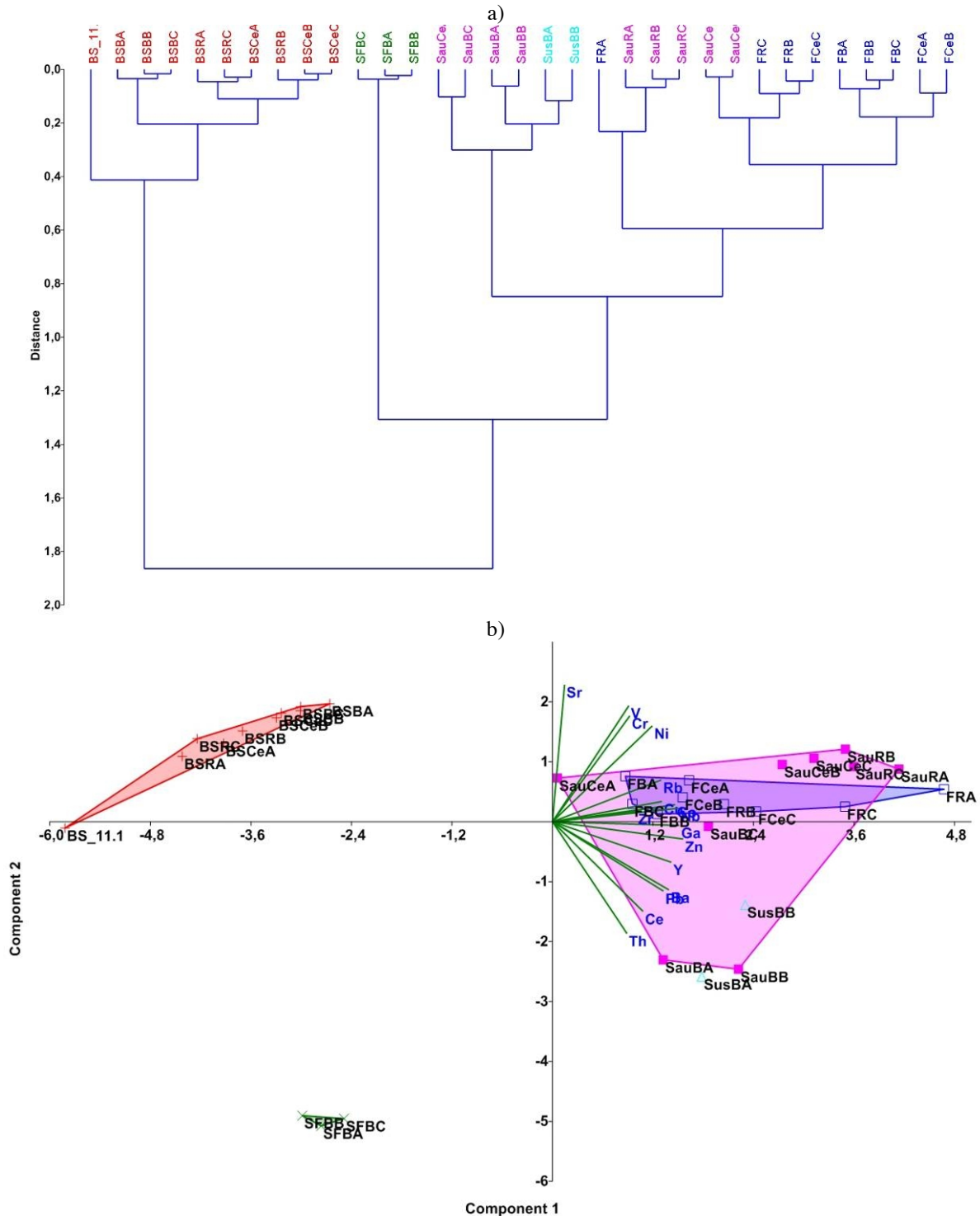
Figure 13: (a) Cluster analysis and (b) PCA analysis of trace elements. Labels: according to Table 1 and Figure 4.

Comparing the reservoirs, the MDA analyses revealed differences for both the major elements (Wilks' Lambda: 0.0000018; $p < 0.0000$) and the trace elements (Wilks' Lambda: 0.0000002; $p < 0.001$). The most important major elements for discrimination between the reservoirs were Mn ($p = 0.001$), K ($p < 0.001$), P ($p = 0.0344$), Mg ($p < 0.001$), and Ca ($p < 0.001$). The most important trace elements were Ba ($p = 0.0062$), Cu ($p = 0.0183$), Nb ($p = 0.0224$), Rb ($p = 0.0042$), V ($p = 0.0417$), and Zn ($p = 0.0429$). In this case, MDA was employed to compare all the reservoirs. When only data for the Sau, Foix, and Barasona reservoirs were used in the analysis, substantial differences were observed for both the major elements (Wilks' Lambda: 0.1656754; $p < 0.0028$) and the trace

elements (Wilks' Lambda: 0.0230437; p < 0.0064). Comparison of the different reservoir compartments indicated that only the river and center locations showed no differences, for both the major (p = 0.1347) and trace elements (p = 0.08608). The most important major and trace elements for discrimination between the sites were K (p = 0.0295) and Zn (p = 0.0244), respectively. The MDA procedure therefore showed that the region close to the dam differed from the river and center locations. Different to the centralization technique, described above, ADM integrated all the elements, rather than treating them one by one.
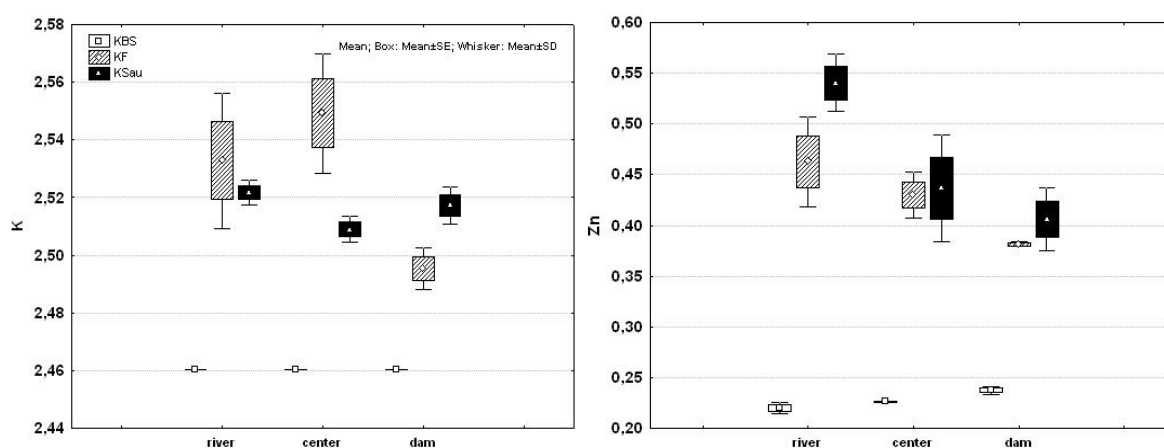
Figure 14 shows the values of K and Zn for the river, center, and dam locations, from which it can be seen that there was a tendency towards smaller values in the direction of the dam, especially for the Foix and Sau reservoirs.

Table 7: One-way ANOVA comparison of the values for Sr and Zr, normalized and standardized by the centering technique

One-way ANOVA (Sr)			
F=5.601, df=2.946, p=0.099			
	River	center	dam
river		0.136	0.010
center	3.221		0.156
dam	6.287	3.066	
One-way ANOVA (Zr)			
F=5.612, df=3.62, p=0.077			
	River	center	dam
river		0.094	0.014
center	3.629		0.316
dam	5.894	2.265	

Figure 14: Mean values of K and Zn for the river, dam, and center regions of the Barasona, Foix, and Sau reservoirs. The values shown on the Y-axes are the element concentrations divided by the corresponding concentrations of Al and then log-transformed (log (([E] / [Al]) * 1000 +1)).

5 FINAL CONSIDERATIONS

The data obtained in this work indicated the existence of differences in the concentrations of elements measured in the superficial sediments of the Foix, Santa Fe, Barasona, Sau, and Susqueda reservoirs. The Barasona and Santa Fe reservoirs, located in protected hydrographic basins with limited human occupation and activity, showed lower concentrations due to smaller anthropic contributions. Higher values were obtained for the Foix, Sau, and Susqueda sediments, due to the inputs from anthropogenic activity in the respective hydrographic basins. This effect was greatest for the Foix reservoir, and elements including Co, Cr, Cu, Ni, and Zn showed the greatest anthropic

contributions. Despite the higher concentrations measured in the Foix, Susqueda, and Sau sediments, the data indicated that the reservoirs did not present high toxicity potentials for the elements analyzed. The data also revealed intra-reservoir variability, with smaller anthropic contributions in the dam zones, compared to the river and center sections.

The findings suggested that for management purposes, monitoring should be undertaken at different locations of the Foix, Sau, and Susqueda reservoirs. Given the higher levels of major and trace elements at these reservoirs, monitoring should be implemented using shorter sampling intervals, compared to the Santa Fe and Barasona reservoirs, which are currently better protected against anthropogenic impacts.

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