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Multielement analytical procedure coupling INAA, ICP-MS and ICP-AES: Application to the determination of major and trace elements in sediment samples of the Bouregreg river (Morocco)

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Instrumental neutron activation analysis (INAA), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) were used for the determination of major and trace elements in sediment samples of the Bouregreg river (Morocco). The reliability of the results was checked, by using IAEA Soil-7 certified reference material. Results obtained by the three techniques were compared to control digestions efficiencies. A general good agreement was found between INAA and both ICP-MS and ICP-AES after alkaline fusion (ICPf). The ICP-MS technique used after acid attack (ICPa) was satisfactory for a few elements. A principal component analysis (PCA) has been used for analyzing the variability of concentrations, and defining the most influential sites with respect to the general variation trends. Three groups of elements could be distinguished. For these groups a normalization of concentrations to the central element concentration (that means Mn, Si or Al) is proposed.

Introduction

Since the last decades, the knowledge of the water quality became more important, due to the development of irrigation and to the refinement of concentration criteria of heavy metals for drinkable water. The quality must be controlled and monitored, because the demographic pressure tends to increase the human presence along the rivers, everywhere. Various heavy metal pollutions may appear, due to human activities such as industry, agriculture, domestic wastes and mine workings.[1] All along the river basin, heavy metals can be carried either dissolved in water, or in suspended particles. They can also be found in the sediment at the bottom of the river.

Small amounts of many trace elements are of ecological interest due to their usefulness as nutrients or their toxicity as pollutants. Nutrient trace elements include Mg, Mn, Cu and Zn, some of which become toxic at high concentrations. Others, including the heavy elements such as Hg, Cd, As and Pb are of environmental concern due to their high toxicity and widespread industrial use.

Rivers carry various heavy metal species either in dissolved aqueous forms, or included in particulate suspended matter. The bigger particles can accumulate in the sediment. Conversely, under certain conditions (temperature, pH, anion concentrations, etc.), part of heavy metal from the sediments could be sometimes released into the water, so that the sediments could be considered as sources and sinks of heavy metals.[2] Aqueous concentrations are sensitive to fast inputs of pollutants. Sediments integrate slow but significant modifications of sources or sinks of heavy metals. They keep a memory of the various long term inputs. Thus, sediments are particularly suitable for studying long term evolution of concentrations due to changes of the input functions.

Certain elements are mainly brought by natural geochemical processes. Each geological area crossed by the river, can provide a particular signature in concentration ratios of various trace elements. Furthermore, certain elements like Fe, Mn and Al play an important role on the formation of colloids, able to include other trace elements, then along long distance transports. Finally, some other elements, for instance, Pb, As, Cu, Cd, Ni, etc., can reach too high concentrations and become toxic. Consequently, it is useful to survey a large set of elements. It is also important to study the precisions of analytical techniques, in order to interpret variations in term of geological or human activities inputs, above the natural background.

As a result of these concerns, field studies have been actively developed to measure the levels of trace metals in the environment, over the last two decades in urban, rural and remote sites at different parts of the world using different analytical techniques.[3–9]

In Morocco, the region of Rabat is now developing very quickly, around the cities of Rabat and Sale and their suburbans, near the Bouregreg river estuary.

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The need of water for irrigation and urban facilities increased drastically. Along the Bouregreg basin, pollutants may be introduced not only near these important cities, but further upstream, by extensive agricultural development and various human activities, all along the river, but also from the erosion and dissolution processes of the various geological materials.

Three multi-element analytical techniques appear well suited for multi-element analysis of inorganic trace concentrations: inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA).

INAA is a very accurate method for the analysis of solid samples. It has also been widely used for river pollution studies.[10–12] On the other hand, multi-element analysis by means of inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) are routinely applied in laboratories to monitor the water quality. They were recently used to determine the composition of river water and sediments for trace analysis.[13–15] These multi-element techniques allow high-sensitivity trace determinations of several heavy metals.[16]

In Morocco, Khalis et al.[17] used INAA and ICP-MS to study the contamination of toxic heavy metals in water and sediments of the Boufakrane river, near Meknès city (Morocco). They found high concentrations of toxic elements such as As and Sb that may explain disturbances on normal aquatic life in the river.

Marques et al.[18] compared INAA and ICP-MS techniques in order to determine trace elements in coastal marine sediment samples. They found that both techniques gave corresponding results for most of elements. However, ICP-MS values for Fe, Mn and Co were lower than those found by INAA showing the need for improving the sample digestion.

Pinte et al.[16] showed that INAA and ICP-MS concentrations agree generally well in the water and sediment analysis. The concentrations obtained by ICP-MS for certain elements (e.g., Zr) were lower than the certified values and the INAA results were not complete, probably because the dissolution of their natural forms.

In this work, three techniques were used: INAA, ICP-MS and ICP-AES to analyze sediment samples collected from nine locations along the Bouregreg river basin. For ICP-MS, two dissolution methods were tested, either by alkaline fusion, or by using an acid mixture.

The aim of this work was to intercompare the performances of these techniques when applied to the determination of major and trace element concentrations in real sediment samples, in order to provide accurate data, allowing consistent geochemical interpretations of observed variations that will be described in another paper. It was also to define the possible element concentrations able to be determined when using only INAA and ICP-MS after acid attack, which are commonly used at Laboratoire Pierre Süe. Both techniques were also applied to the analysis of particulate suspended matter (PSM).

A statistical treatment of data is proposed to define the main features in the concentration variations.

Experimental

Sampling

Sediment samples were collected from nine locations along the 200 km course of the Bouregreg river (Morocco) from its source to the vicinity of its estuary, near Rabat (Fig. 1).

The Bouregreg river is one of the main streams of Morocco. Its source is located in the Moroccan Central Massif and flows towards the Atlantic coast through the coastal Meseta. The Bouregreg river basin is located in the Moroccan Central Massif which consists mainly of Palaeozoic formations (essentially combro-ordovician detrital formations).[19] Furthermore, the Central Moroccan Massif is characterized by the presence of many plutonic Hercynian granites covering a rather wide geographical area. Those localized in the Bouregreg river basin correspond to the Ment, Oulmès and Moulay Bou Azza granites.

Table 1 shows the sampling sites with their lithological forms. Whereas, Fig. 1 displays the Bouregreg river basin in the Moroccan Central Massif and sampling points (details in Table 1). Sampling sites were selected in order to represent most of the main lithological heterogeneities and the distribution of the anthropogenic activities along the Bouregreg basin.

Sample preparation

Sediment samples were collected at distances of 20 cm from the banks of the river, using polyethylene bags. Samples were dried during 24 hours in an oven at 105 °C, then crushed in an agate mortar, homogeneized and stored in polyethylene bags until analyses. Care was taken to avoid contamination during sampling, drying, grinding, sieving and storage. The particles less than 100 μm were used for analysis. Then, samples were stored in a closed container, waiting later different treatments depending on the analytical techniques.

INAA measurements: Samples were irradiated at the Laboratoire Pierre Süe (LPS), directly connected to the two nuclear reactors (OSIRIS and ORPHÉE) of the CEA Saclay Center (France).

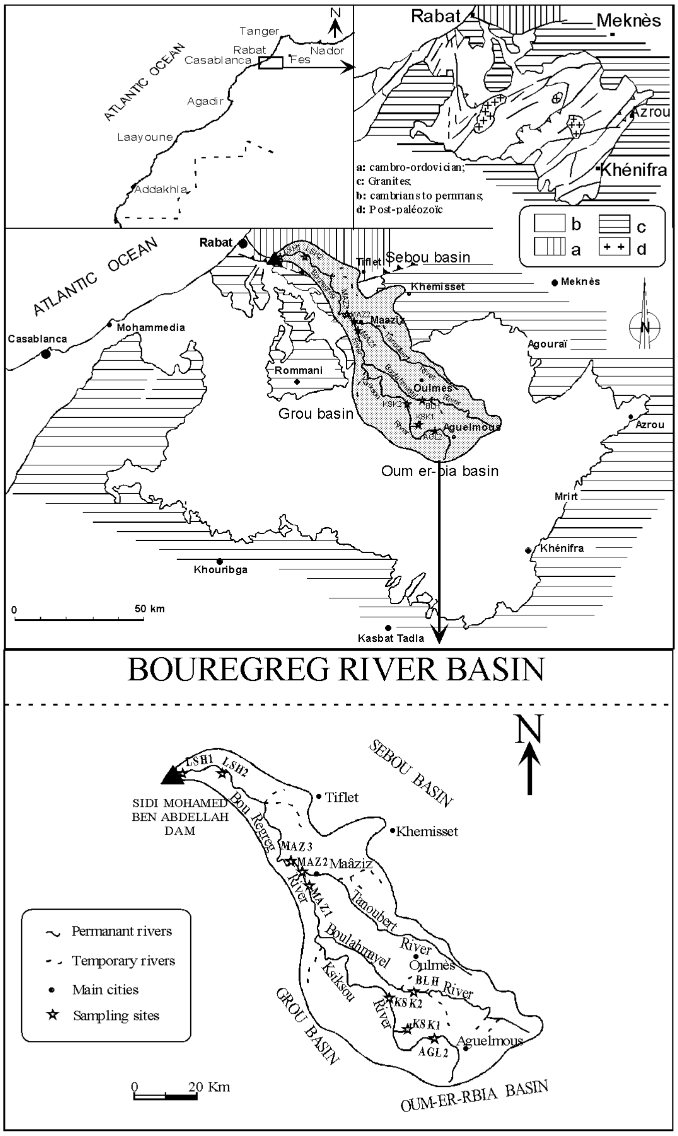

Fig. 1. Location of the Bouregreg river basin in the Moroccan Central Massif and sampling points

Table 1. Mineralogy of the sediment samples collected along the Bouregreg river

Sample	Mineralogical form
ALG 2	Sandy pelites, micaceous pelites
KSK 1	Sandy pelites, micaceous pelites and quartzites
KSK 2	Micaceous pelites and quartzites
BLH	Micaceous pelites, quartzites, microconglomerats and sandy pelites
MAZ 1	Sandy pelites, pelites, red shales and dolorites
MAZ 2	Sandy pelites, pelites, red shales and dolorites
MAZ 3	Sandy pelites, pelites, limestones, red shales and dolorites
LSH 2	Sandy pelites
LSH 1	Sandy pelites

The ORPHEE reactor provides mainly thermal neutrons, with fluxes ranging from $1.2\cdot10^{13}$ to $2\cdot10^{13}\ \text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ according to the channels. Since it is possible to recover the irradiated samples within a few minutes, short half-life radioisotopes can be reached. Long half-life radioisotopes can also be measured, through long irradiation times and suited decay times.

The OSIRIS reactor provides a more complex neutron spectrum composed of thermal neutrons (from $7\cdot10^{13}$ to $9\cdot10^{13}\ \text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$), and important epithermal and fast neutrons components. Several additional nuclear reactions like (n,p), (n,2n) and (n,α) can occur. Furthermore, the existence of high epithermal fluxes allows a better determination of elements having high integral resonances.

For short irradiations, in the ORPHEE channels, about 100 mg of sample were sealed into a pure polyethylene container and placed with 3 to 6 mg of IRMM-530 gold wire (Al/Au alloy containing certified 0.100% Au) as a neutron flux monitor in a polyethylene shuttle and irradiated from 30 seconds to 2 minutes. After irradiation, four countings were carried out for each sample for 2, 5, 15 and 60 minutes, respectively. This procedure allowed the determination of Na, K, Ti, Al, V, Mn, and Dy.

For long irradiations, in the ORPHEE channels, 100 mg samples each were wrapped in high purity aluminum foil. They were placed in an aluminum shuttle which contained up to 10 samples. A Fe flux monitor and one 100 mg sample of the Certified Reference Material (Soil-7), provided by the International Atomic Energy Agency were prepared similarly. The irradiation time was 7 hours. After irradiation, samples were measured three times on an HPGe detector after 7, 15 and 30 days decay time.

For certain elements (Rb, Cs, Ba, Sr, Ni, Tb, Zr, Hf, Th and U), irradiations were also performed under a cadmium wall (epithermal neutron activation analysis, or ENAA) to select epithermal and rapid neutrons in the OSIRIS reactor.

Such thermal and epithermal irradiations were developed at LPS by JORON at al.,[20] CHAYLA at al.[21] and RAIMBAULT at al.,[22] applied for the determination of Rb, Cs, Ba, Sc, Cr, Fe, Co, Ni, Zn, As, Sb, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Zr, Hf, Ta, Mo, W, Th and U, by using both reactors.

The concentrations were calculated using the K_0 LABSUE software.[23] The compilation data (mean and standard deviation) were calculated from the average values taking into account the number of results. In general, results are given with 3 times the standard deviation (3σ), corresponding to a confidence interval of 99%.

Table 2 shows the average element concentrations, obtained by INAA and ICPa from 10 repeats on certified reference material IAEA Soil-7.

The accuracy of measurement is defined by the closeness of the assessment between the result obtained by INAA and the certified (or recommended) IAEA concentrations of the Soil-7 used as a measurand. (VIM: 1993, 3.5 amplified by ISO 5725-1 to 6).

Most of the element concentrations are consistent within 10%. The concentrations of some elements (Ti, Cr, Zn, Sr, Zr and Nd) obtained by INAA were a little different than the IAEA recommended values. However, Ti, Cr, Zn, Zr and Nd concentrations within the 3σ interval confidence remains inside the confidence interval defined by IAEA. For Sr, the concentration interval did not agree with the IAEA interval. The Sr determination is not recommended by INAA of this kind of material.

In order to statistically evaluate the results obtained for elements determined by both techniques, the paired *t*-test was applied.[24] As shown in Table 3, for a 95% confidence level the two techniques do not give significantly different values for most of the elements. Zr and Hf were significantly different by both techniques. This indicates that ICPa gives lower values than INAA that could be explained by the incomplete dissolution of the sample.

ICP-MS and ICP-AES measurements: The ICP-MS technique developed at LPS is involved in several different programmes like environmental pollution, earth sciences and biological sciences.

In order to avoid the pollution of the device by elements like B and Li, it was decided not to use alkaline fusion processes to dissolve samples. It was preferred to try using acid attacks for the dissolution of sediments (that way is designed as ICPa, below). However, it was expected that some elements in some sediment samples need more efficient techniques. This is the reason why samples were also analyzed after digestion by alkaline fusion at the CRPG/SARM (Centre de Recherche Pétrographique et Géologique/Service d’Analyse et de Recherche sur les Minéraux) at Vandoeuvre-lès-Nancy, France, by ICP-MS for trace elements and ICP-AES for major elements (both techniques applied after alkaline fusion are designed as ICPf below). This was the opportunity to intercompare INAA, ICPa and ICPf, when applied to the Bouregreg sediment samples.

Alkaline digestion: The devices used at CRPG/SARM were a Jobin-Yvon JY 70 ICP-AES and a Thermo-elemental X7-series ICP-MS. All samples were routinely digested by the alkaline fusion procedure described by GOVINDARAJU et al.,[24] and summarized by the followings.

One gram of each sample was accurately weighed into a porcelain crucible and placed into a muffle furnace at 1000 °C for 4 hours, to remove most of its organic matrix. After cooling down in a drier, about 200 mg of dry sample was weighed into a gold-platinum crucible and 600 mg of lithium metaborate was added. The crucible was then covered and heated again at 1000 °C in order to carry out an alkaline fusion of the sample. After cooling to 600 °C, the sample was quickly sunk in a 10% (v/v) nitric acid. The solution was made up to 250 ml with ultrapure water. This sample solution was then ready after appropriate dilution for ICP-AES and ICP-MS measurements. Reagent blanks were prepared following the same procedure. The reliability of this technique was regularly checked by international standards.[24]

Major and minor elements in solutions, Si, Al, Fe, Mn, Mg, Ca, Na, K, P, and Ti were determined by ICP-AES, while the measurements of As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Ta, Tb, Th, U, V, W, Y, Yb, Zn, and Zr were achieved by ICP-MS.

Acid digestion: A temperature and pressure controlled microwave digestion system (®Milestones Ethos+) was used for sample dissolution. A carousel allowed the digestion of twelve samples in Teflon vessels of 120-cm^3 volume each, in a run.

A 100 mg sediment sample was weighed in one Teflon vessel. Then, 6 cm^3 HNO_3 (65% v/v), 3 cm^3 HF (40% v/v), and 3 cm^3 HCl (30% v/v) were added. Ten Teflon vessels contained the sediment samples and the acid mixture. One Teflon vessel contained only the acid mixture for a blank and a last one contained the CRM Soil-7. The microwave digestion system was operated by three steps: first, an increase of the temperature during 5-minutes to 130 °C, second, a new increase from 130 to 210 °C during 15 minutes, and third, a temperature plateau during 20 minutes at 210 °C.

Table 2. Results obtained by INAA and ICPa for IAEA certified reference material Soil-7 (in mg/kg)

Element	INAA (10)	ICPa (4)	Certified values	Confidence interval
Na	2300 ± 69		**2400	2300–2500
Al	48000 ± 1440	43000 ± 1290	**47000	44000–51000
K	12000 ± 1080		**12100	11300–12700
Ca	163000 ± 6520		**163000	157000–74000
Sc	8.5 ± 0.3		*8.3	6.9–9.0
Ti	2600 ± 312	2600 ± 208	**3000	2600–3700
V	67 ± 5	67 ± 3	*66	59–73
Cr	69 ± 3	67 ± 2	*60	49–74
Mn	625 ± 19	630 ± 25	*631	604–650
Fe	26000 ± 1040		**25700	25200–26300
Co	8.5 ± 0.3	10.2 ± 0.4	*8.9	8.4–10.1
Ni		28 ± 1	**26	21–37
Cu		11.0 ± 0.4	*11	9–13
Zn	116 ± 7	103 ± 4	*104	101–113
As	13.5 ± 0.7		*13.4	12.5–14.2
Rb	53 ± 4	58 ± 2	*51	47–56
Sr	76 ± 21	104 ± 4	*108	103–114
Y		21.0 ± 0.8	*21	15–27
Zr	220 ± 64	140 ± 10	*185	180–201
Nb		12.0 ± 0.5	**12	7–17
Cd		1.30 ± 0.06	**1.3	1.1–2.7
Sb	1.7 ± 0.2	1.70 ± 0.07	*1.7	1.4–1.8
Cs	5.4 ± 0.2	5.0 ± 0.1	*5.4	4.9–6.4
Ba	160 ± 30	151 ± 5	**159	131–196
La	27 ± 1	28 ± 2	*28	27–29
Ce	58 ± 2	56 ± 2	*61	50–63
Nd	24 ± 3	29.5 ± 0.9	*30	22–34
Sm	4.6 ± 0.2	5.2 ± 0.2	*5.1	4.8–5.5
Eu	0.90 ± 0.06	1.05 ± 0.05	*1	0.9–1.3
Tb	0.60 ± 0.07	0.62 ± 0.01	*0.6	0.5–0.9
Dy	3.7 ± 0.6	4.6 ± 0.2	*3.9	3.2–5.3
Yb	2.3 ± 0.2	2.35 ± 0.07	*2.4	1.9–2.6
Lu	0.30 ± 0.02	0.305 ± 0.009	**0.3	0.1–0.4
Hf	4.9 ± 0.3	3.66 ± 0.14	*5.1	4.8–5.5
Ta	0.8 ± 0.1	0.84 ± 0.06	*0.8	0.6–1.0
Pb		64 ± 2	*60	55–71
Th	8.1 ± 0.4	8.2 ± 0.3	*8.2	6.5–8.7
U	2.4 ± 0.8	2.75 ± 0.08	*2.6	2.2–3.3

( ) Number of analyses.
** Certified values.
* Recommended values.

Table 3. Comparison of INAA and ICPa by mean of the paired *t*-test

Element	Mean difference, mg/kg	S.D. of the mean, mg/kg	Calculated $\lvert t \rvert$
Ti	1130.1394	270.4162	3.1454
V	12.1582	4.0691	0.3197
Cr	10.9705	6.7087	0.2077
Mn	138.1018	75.7706	2.1856
Co	1.5809	0.7472	0.5206
Zn	21.1921	18.5728	2.2803
Rb	19.2346	12.4278	2.9654
Sr	33.3278	29.1860	1.2814
Zr	129.1707	39.0884	3.6123
Sb	0.2990	0.1416	0.9387
Cs	1.3367	0.5062	1.4299
Ba	70.8017	77.9803	0.1175
La	3.2529	2.0057	0.9163
Ce	6.5078	1.0926	0.0405
Nd	4.5173	2.3582	0.8731
Sm	0.8649	0.4163	1.1634
Eu	0.1588	0.0486	1.4951
Tb	0.0812	0.0725	0.2225
Dy	0.2928	0.1982	0.2789
Yb	0.3620	0.3180	1.8475
Lu	0.0655	0.0432	2.8527
Hf	2.2956	1.1530	3.8228
Ta	0.8408	1.1469	1.1605
Th	0.9810	0.6465	0.1721
U	0.5130	0.2786	0.7271

Then, the samples were transferred in 50-ml Teflon beakers and reduced to near dryness. A volume of 3 cm^3 HNO_3, was added, and then evaporated again to near dryness, two times. Finally a last volume of 1 cm^3 HNO_3 is added and then made up to 50 ml by using high purity water provided by a Milli-Q-Element system designed for ultra-trace analysis was used. All measurements were carried out by a THERMO-ELEMENTAL® X7 series inductively coupled plasma mass spectrometer. The signal drift was monitored by adding internal standards (1 ppb) to the samples and standard solutions. Be, In and Re were used because they cover the whole mass range. The concentrations of these three elements were previously determined in a first run of sample analyses without internal standard. When significant concentration was measured, the internal standard was corrected. A mother solution containing 100 ppb of all elements was used to prepare a set of 0 to 4 ppb multi-element standard for ICP-MS analysis. A calibration curve of the ICP-MS signal versus concentrations was established by linear regression. Reagent blanks were prepared similarly.

Some limitations occur in ICP-MS measurements, because of various interferences. The main of them are due to the recombination in the plasma of argon with elements like O, N, H coming from air or water, but also with major elements of the dissolved matrix. In order to decrease the Argon recombination interferences, a Collision Cell Technology (CCT), developed by Thermo-Elemental was used. It consists in introducing a stable gas like He or H_2, which kinetic energy is sufficient to break the ArM+ ions. The determination of ^{56}Fe (cancelling of the ^{40}Ar^{16}O interference) and of ^{75}As (cancelling the ^{40}Ar^{35}Cl) becomes possible. However, other interferences like recombinations as oxides of major elements and isobaric interferences still exist. It was not possible to determine ^{80}Se, due to high concentrations of Ca.

Concentrations were calculated from the average values taking into account the number of results. Results are given with a confidence interval corresponding to 3 times the standard deviation (3σ). Averages of the four analyses were carried out on the CRM Soil-7 of IAEA. Results are shown in Table 2. Most of the element concentrations are consistent with the recommended values within 10%. Some elements display concentrations obtained by ICPa rather different than the value recommended by IAEA: Ti, Cr, Co, Rb, Zr and Hf. For Ti, Cr and Co, concentrations remain in the confidence interval given by IAEA. For Rb, concentrations are a little higher than the maximum proposed value, while Zr and Hf, concentrations were in significant default, when determined by ICPa. For the last two elements, the chemical yield of dissolution is not efficient enough.

Thus, by using INAA or ICPa techniques or both, all element concentrations of Table 2 except Zr can be accurately determined on the Soil-7 CRM material.

Results and discussion

Sediments are complex mixtures with crystalline structures, more or less easy to dissolve. It is expected that important composition differences may occur all along the Bouregreg river, due to the diversity of geological structures that it crosses. The same remark can be made about the reference materials coming from very different origins. Thus, when applying a same chemical treatment leading to good reliabilities on one reference material do not proves that the reliability will be the same for all sediments. INAA presents a great advantage for sediments. There is no need of any chemical treatment that decreases the confidence level. However, some elements are not determined at all by INAA, like Cu, Pb, Cd, some rare earth elements. For them, the use of digestion procedures associated to other analytical techniques like ICP-MS or ICP-AES are needed.

The techniques applied to sediments from 9 sites in this work are INAA, ICPf and ICPa, previously described.

Concentrations are intercompared by couples of techniques, called 1 and 2. The Techniques 1 and 2 give concentrations $C1,j,k$ and $C2,j,k$ for each element (j), at each site (k). The average concentration is $Cj,k=(1/2)(C1,j,k+C2,j,k)$.

The deviation of the results from Technique 1 from the average is $\Delta 1,j,k(\%)$ expressed as:

$$\Delta 1, j, k(\%) = \frac{C1, j, k - Cj, k}{Cj, k} \times 100$$

or

$$\Delta 1, j, k(\%) = \frac{C2, j, k - Cj, k}{Cj, k} \times 100$$

The average of $\Delta 1,j,k$ on the 9 sites gives the mean concentration $D1,j$ for each element (j), and an absolute standard deviation $\sigma 1,j$. Thus, it is possible to define an interval with a minimum deviation $\%(D1,j-\sigma 1,j)$ and a maximum deviation $\%(D1,j+\sigma 1,j)$, obtained for the Technique 1 or 2, when compared to the average of the two techniques.

All data are given in Table 4. Three couples of comparisons are performed: ICPf and INAA, ICPa and INAA, ICPf and ICPa.

When the absolute values of the minimum and maximum deviations in % are less than 10%, the agreement between both techniques is considered acceptable (sign Y in columns of Table 4). When, both extrema are less than –10%, Technique 1 is considered as giving systematic default results. Cases with extreme deviations % having two different figures correspond to a lack of precision by using one technique or both. The choice of one technique is then based on the experimental knowledge of each technique. The most precise technique is preferred.

Table 4. Deviation percentage of the results obtained by the three used techniques

Element	1:ICPf; 2:INAA				
	*D*1,*j*	StD	Min	Max	|*D*|<10%
Be					
Na	1	4	–3	5	Y
Al	–1	3	–4	2	Y
K	–2	4	–6	2	Y
Ti	–7	4	–11	–3	ICPf default
V	–7	5	–12	–2	ICPf default
Cr	–7	5	–12	–2	ICPf default
Mn	2	5	–3	7	Y
Fe	3	2	1	5	Y
Co	–5	2	–7	–3	Y
Ni	–5	2	–7	–3	Y
Cu					
Zn	–9	3	–12	–6	ICPf default
As	–8	2	–10	–6	ICPf default
Rb	–5	2	–7	–3	Y
Sr	–19	4	–23	–15	ICPf default
Y					
Zr	–19	6	–25	–13	ICPf default
Nb					
Mo	–19	9	–28	–10	ICPf default
Cd					
In					
Sn					
Sb	4	10	–6	14	
Cs	–12	7	–19	–5	ICPf default
Ba	–7	3	–10	–4	ICPf default
La	–3	9	–12	6	ICPf default
Ce	–5	12	–17	7	ICPf default
Pr					
Nd	–4	11	–15	7	ICPf default
Sm	6	8	–2	14	
Eu	2	9	–7	11	
Gd					
Tb	–5	7	–12	2	ICPf default
Dy	–1	7	–8	6	Y
Ho					
Er					
Tm					
Yb	–4	3	–7	–1	Y
Lu	–2	3	–5	1	Y
Hf	–6	4	–10	–2	ICPf default
Ta	–3	5	–8	2	Y
W	–5	7	–12	2	ICPf default
Pb					
Bi					
Th	–7	4	–11	–3	ICPf default
U	–3	2	–5	–1	Y

Table 4. Continued

Element	1:ICPa; 2:INAA				
	*D*1,*j*	StD	Min	Max	|*D*|<10%
Be					
Na					
Al	–29	43	–72	14	ICPa default
K					
Ti	1	15	–14	16	
V	–6	5	–11	–1	ICPa default
Cr	–6	6	–12	0	ICPa default
Mn	4	7	–3	11	ICPa default
Fe					
Co	–4	2	–6	–2	Y
Ni	–3	7	–10	4	ICPa default
Cu					
Zn	–8	5	–13	–3	ICPa default
As			0		
Rb	–6	22	–28	16	ICPa default
Sr	–27	18	–45	–9	ICPa default
Y					
Zr	–38	14	–52	–24	ICPa default
Nb					
Mo	–14	26	–40	12	ICPa default
Cd					
In					
Sn					
Sb	–3	10	–13	7	ICPa default
Cs	–21	9	–30	–12	ICPa default
Ba	–11	10	–21	–1	ICPa default
La	–9	15	–24	6	ICPa default
Ce	–11	14	–25	3	ICPa default
Pr					
Nd	–8	20	–28	12	ICPa default
Sm	0	17	–17	17	ICPa default
Eu	–1	23	–24	22	ICPa default
Gd					
Tb	–21	14	–35	–7	ICPa default
Dy	–14	14	–28	0	ICPa default
Ho					
Er					
Tm					
Yb	–29	20	–49	–9	ICPa default
Lu	–32	20	–52	–12	ICPa default
Hf	–29	12	–41	–17	ICPa default
Ta	–2	15	–17	13	ICPa default
W	4	37	–33	41	
Pb					
Bi					
Th	–15	13	–28	–2	ICPa default
U	–9	8	–17	–1	ICPa default

Table 4. Continued

Element	1:ICPa; 2:ICPf				
	*D*1,*j*	StD	Min	Max	|*D*|<10%
Be	11	27	–16	38	
Na					
Al	15	35	–20	50	
K					
Ti	–8	13	–21	5	ICPa default
V	–1	4	–5	3	Y
Cr	0	4	–4	4	Y
Mn	–2	4	–6	2	Y
Fe					
Co	0	3	–3	3	Y
Ni	–1	6	–7	5	Y
Cu	0	4	–4	4	Y
Zn	–1	3	–4	2	Y
As					
Rb	1	22	–21	23	
Sr	9	20	–11	29	
Y	29	13	16	42	ICPa default
Zr	20	15	5	35	ICPa default
Nb	–4	6	–10	2	ICPa default
Mo	–5	24	–29	19	ICPa default
Cd	14	9	5	23	ICPa default
In	34	67	–33	101	
Sn	17	18	–1	35	
Sb	7	9	–2	16	
Cs	6	8	–2	14	
Ba	3	10	–7	13	
La	7	8	–1	15	
Ce	6	8	–2	14	
Pr	3	8	–5	11	
Nd	3	9	–6	12	
Sm	6	9	–3	15	
Eu	3	21	–18	24	
Gd	6	7	–1	13	
Tb	14	13	1	27	ICPa default
Dy	21	9	12	30	ICPa default
Ho	23	13	10	36	ICPa default
Er	24	10	14	34	ICPa default
Tm	28	16	12	44	ICPa default
Yb	23	14	9	37	ICPa default
Lu	28	15	13	43	ICPa default
Hf	24	12	12	36	ICPa default
Ta	–1	16	–17	15	ICPa default
W	–3	18	–21	15	ICPa default
Pb	–1	3	–4	2	ICPa default
Bi	–6	40	–46	34	ICPa default
Th	9	14	–5	23	
U	6	8	–2	14	

$D1,j$ = Mean concentration of $\Delta 1,j,k$ obtained from 9 sites for each element (j).
StD = Absolute standard deviation of the 9 values ($\sigma 1,j$).
Min = Minimum deviation % ($D1,j-\sigma 1,j$) obtained for the Technique 1 or 2, when compared to the average of the two techniques.
Max = Maximum deviation % ($D1,j+\sigma 1,j$), obtained for the Technique 1 or 2, when compared to the average of the two techniques.
$|D|$ = Absolute values of the minimum and maximum deviations.
Y = Agreement between both techniques considered acceptable (the absolute values of the minimum and maximum deviations % are less than 10%).

Comparison between ICPf (Technique 1) and INAA (Technique 2)

The condition $D1,j<10\%$ is fulfilled for Na, Al, K, Ti, Mn, Fe, Co, Ni, Rb, Tb, Dy, Yb, Lu, Hf, Ta, W and U. For these elements, ICPf or INAA can be used as well. The ICPf technique gives values less than INAA for V, Cr, Zn, As, Sr, Zr, Mo, Cs, Ba, La and Th. For these elements INAA concentrations are preferred.

According to the Table 4, the $D1,j$ is overwhelming negative. This means that results obtained by ICPf are negatively biased. The determination of Sb is always preferred by INAA, because two different determinations are performed by two different radioisotopes ^{122}Sb and ^{124}Sb with a good agreement. Rare earth element concentrations are preferred by ICPf, because, the chemical behavior is more similar when using a same technique, and more rare earth elements are determined.

Comparison between ICPa (Technique 1) and INAA (Technique 2)

The condition $D1,j<10\%$ is only fulfilled for Co. Most element concentrations present default values for ICPa with respect to INAA. This is explained by the fact that those elements are supported in inorganic phases, incompletely dissolved by acid attack.

Comparison between ICPf (Technique 1) and ICPa (Technique 2)

The ICP-MS technique offer the possibility to determine additional element concentrations than INAA. This is interesting to compare the two dissolution techniques, both followed by ICP-MS measurements, applied to the nine Bouregreg sediments. The condition $D1,j<10\%$ is found for V, Cr, Mn, Co, Ni, Cu, Zn, Nb and Pb.

When the alkaline fusion is avoided in order to preserve the device from pollution effects, acid attack is used. This way is chosen at LPS, besides INAA. Thus with ICPa and INAA, it is possible to determine the concentrations of the following elements: Na, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Nb, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Lu, Ta, W, Pb, Th and U. Both techniques were used also to determine the same elements in suspended matter fixed on filters from water samples. Results will be presented elsewhere. For sediments, ICPf (joining AES and MS), is considered an additional technique, making possible the determination of more element concentrations, besides the list above described, and comprising: Y, Cd, Sn, the total set of rare earth elements, Bi, P, Si, and Ga.

For Zr a poor intercomparison is remarked. This element is probably included in inorganic phases, especially difficult to dissolve either by alkaline fusion, or by acid attack. Some problems exist also for the Zr determination by INAA: lack of sensitivity, interferences with ^{152}Eu, ^{95}Nb, U fission in thermal neutrons. Another specific technique should be applied for an accurate and precise determination of Zr.

Principal component analysis (PCA)

Elements determined in different sediment samples, collected in January 2004, are indicated in Table 5. The average concentration calculated on the nine sites is given for each element, with their absolute and relative standard deviation. This last parameter gives an estimate of the variability of element concentrations along the Bouregreg river. A few elements present a weak variability less than 25%: Si, Al, V, Fe, Mn, Ti, P, Zn, Mo, Cs, Ba, Ga. The highest variability observed is 73% for U. The average variability for all elements is 35% with a standard deviation of 14%.

Despite the number of elements is higher than the number of sites (observations), it has been attempted to perform a principal component analysis. The PCA used in this work is carried out by the XLSTAT program. Most part of the variability (93%) is supported along 5 axes: F1, F2, F3, F4 and F5. The coordinates of the couples F1–F2, F1–F3, F1–F4 and F1–F5 are given in Fig. 2 (a, b, c, d). The projection of the observations are represented in Fig. 3 (a, b, c, d). Some features can be described.

As shown in Fig. 2a, a strong association is found along F1 axis for the following elements: Mn, Na, K, Ti, Be, Rb, Y, Nb, Mo, Ce, Sm, Gd, Tb, Ho, Er, Tm, Yb, Lu, Ta, W, Th and U. The F1–F2 projection of the observations is shown in Fig. 3a. It can be pointed out that two sites KSK1 and KSK2 display the most important influence on those elements. Minimum concentrations are revealed in AGL2 and MAZ2, along F1 axis. In this series of elements, Mn has the highest concentration. If these correlations between concentrations have a geological signification, the ratio of one element concentration to Mn concentration may give information on the residual variability not supported by Mn. Table 6 gives some examples of such normalization for Sm/Mn and Yb/Mn. A reverse ratio is given for Mn/Th and Mn/Ta. The variability of these ratios observed for the 9 observations vary from 15% to 28%. It becomes easier in the new series of normalized figures to detect any anomalous variation with respect to the average, the variability of which coming from another cause than the average associated to the Mn concentration variations. When two elements of the series have a similar behavior, their concentrations ratio may also have a weak variability.

Table 5. Results obtained for sediment samples of Bouregreg river (in mg/kg)

Element	AGl2	KSK2	KSK1	BLH	MAZ1	MAZ2	MAZ3	LSH2	LSH1	Mean	SD	SD%
Li	55.5	63.3	68.7	70.8	96.7	147	106	48.1	64.3	80.04	31.22	39.01
Be	2.2	3.1	4.1	2.7	1.9	2.6	2.6	1.6	2.1	2.54	0.74	29.09
Na	3290	6420	14600	5940	4240	4870	8710	5950	5040	6562	3378	51.48
Mg	3180	4020	3300	6480	9180	8100	8820	6300	6960	6260	2299	36.72
Al	62000	64400	80800	77500	75600	81200	77200	60300	56000	70556	9774	13.85
Si	347000	327000	302000	314000	286000	295000	292000	312000	327000	311333	19812	6.36
P	780	1200	1020	900	960	1080	1020	900	960	980	120	12.24
K	27400	27800	51200	17500	20700	24300	22500	17100	18100	25178	10555	41.92
Ca	3620	5680	4900	4400	17500	12600	16100	20500	12800	10900	6401	58.72
Sc	13.5	10.3	12.4	33	14.9	26.5	15	12.3	11.9	16.64	7.75	46.53
Ti	2990	4100	6350	4620	4520	4810	5300	4805	4760	4695	897	19.10
V	75.3	67.3	51.6	114	108	119	100	93.5	101	92.19	22.74	24.67
Cr	50.6	46.4	18.4	79.9	91.5	102	80.3	77.2	95.5	71.31	27.32	38.32
Mn	422	898	880	690	735	694	739	773	848	742.11	142.76	19.24
Fe	29000	33000	33000	47000	44000	55000	46800	39000	50000	41867	8838	21.11
Co	8.2	10.9	6.8	15.2	17.5	18.6	15.2	13.9	16.6	13.66	4.14	30.31
Ni	19.6	20.5	8	37.9	34.8	42.1	36.6	31.2	35.5	29.58	11.11	37.57
Cu	13.6	18.9	7.9	27.8	26.8	31	29.1	23.2	23.2	22.39	7.65	34.18
Zn	101	134	72.8	181	116	140	112	107	114	119.76	29.98	25.03
Ga	14.6	16.9	23.7	20.7	20.7	21.8	19.4	15.9	15.7	18.82	3.16	16.79
As	37.4	44	13.1	40.9	20.2	33.8	27.8	24.5	22.2	29.32	10.35	35.31
Rb	125.7	138	233	139	108	133	110	84.8	84.9	128.49	44.33	34.50
Sr	47.6	72.7	105	85.4	129	131	146	129	106	105.74	32.07	30.33
Y	19.4	42.5	68.5	13.7	31.1	16.7	26.9	39.6	29.3	31.97	16.82	52.60
Nb	9.6	17.4	27.1	16.2	19.6	18.4	18.7	22.3	18.1	18.60	4.68	25.18
Mo	0.5	0.6	0.9	1.1	0.7	1.1	1	0.9	0.9	0.86	0.21	24.87
Cd	0.3	0.9	0.5	0.5	0.4	0.5	0.3	0.7	0.3	0.49	0.20	41.47
Sn	22.2	15.4	8.8	7.8	2.8	4.3	3.5	5.9	11.6	9.14	6.36	69.56
Sb	4.2	4	1.1	5.7	1.5	10.3	4	4.3	4.4	4.39	2.65	60.37
Cs	6.4	6.5	9.7	7.2	9.1	7.3	6.8	5.6	5.2	7.09	1.48	20.93
Ba	401	434	513	533	544	512	481	426	401	471.67	56.91	12.07
La	30.6	47.3	63.8	50.9	46.8	44.9	40.4	43.4	80.6	49.86	14.50	29.09
Ce	68	107	154	108	87.5	92.7	82.6	90.3	144	103.79	28.43	27.39
Pr	6.7	11.2	16	10.9	11.4	10.7	9.5	10.4	20.7	11.94	4.07	34.07
Nd	26	45.9	62.4	46.3	38.6	39.6	35.6	39.3	77.3	45.67	15.40	33.72
Sm	4.8	8.6	12.7	7.7	7.4	7.5	6.7	6.6	14	8.44	2.98	35.34
Eu	1	1.2	1.3	1.6	1.6	1.6	1.4	1.5	2.2	1.49	0.34	22.64
Gd	3.8	7.1	10.8	6.3	6.2	5.9	5.5	6.7	9.2	6.83	2.06	30.15
Tb	0.6	1.2	1.9	1.1	1	0.9	0.9	1.1	1.2	1.10	0.35	32.14
Dy	3.6	7.3	11.5	3.7	4.4	5	4.9	6.5	4.1	5.67	2.52	44.39
Ho	0.7	1.5	2.3	1.2	1.1	1	0.9	1.4	1	1.23	0.47	38.03
Er	2	4.4	6.8	3.4	3.1	1.6	2.4	4	2.8	3.39	1.56	46.15

Table 5. Continued

Element	AGl2	KSK2	KSK1	BLH	MAZ1	MAZ2	MAZ3	LSH2	LSH1	Mean	SD	SD%
Tm	0.3	0.7	1	0.5	0.5	0.4	0.3	0.6	0.4	0.52	0.22	42.58
Yb	2.2	5.4	7.1	3.6	3.2	2.9	2.7	4.2	2.8	3.79	1.56	41.30
Lu	0.3	0.8	1.1	0.6	0.5	0.4	0.4	0.7	0.4	0.58	0.25	43.94
Hf	6.9	15.1	10.5	9.2	8.5	5.2	6.6	15	7.6	9.40	3.55	37.78
Ta	1.1	2.5	2.8	1.5	1.6	1.6	1.7	1.9	1.6	1.81	0.53	29.01
W	2.7	4.5	5.4	3	1.5	2	2.1	2.8	3.5	3.06	1.25	40.78
Pb	42.5	61.3	33.5	105	29.8	46.3	45.9	49	40.4	50.41	22.39	44.42
Bi	0.6	0.7	0.2	0.2	0.3	0.4	0.4	0.3	0.3	0.38	0.17	45.42
Th	9.8	20.6	28.8	14	13.8	14.4	13.6	13.2	11.3	15.50	5.79	37.36
U	2.3	5.8	11.5	3.3	2.8	2.6	2.6	3.5	2.5	4.10	2.97	72.48

Table 6. Concentration ratios of some elements of geochemical interest

Ratio	AGl2	KSK2	KSK1	BLH	MAZ1	MAZ2	MAZ3	LSH2	LSH1	Moyenne	StD	StD%
K/Mn	65	31	58	25	28	35	30	22	21	35	16	45
Rb/Mn	0.3	0.2	0.3	0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1	37
Y/Mn	0.05	0.05	0.08	0.02	0.04	0.02	0.04	0.05	0.03	0.04	0.02	40
Sm/Mn	0.011	0.010	0.014	0.011	0.010	0.011	0.009	0.009	0.017	0.011	0.003	23
Yb/Mn	0.005	0.006	0.008	0.005	0.004	0.004	0.004	0.005	0.003	0.005	0.001	28
Mn/Ta	384	359	314	460	459	434	435	407	530	420	63	15
Mn/Th	43	44	31	49	53	48	54	59	75	51	12	24
Th/Ta	8.91	8.24	10.29	9.33	8.63	9.00	8.00	6.95	7.06	8.49	1.07	13
Yb/Ta	2.00	2.16	2.54	2.40	2.00	1.81	1.59	2.21	1.75	2.05	0.31	15
Ba/Al	0.00646	0.00674	0.00635	0.00687	0.00719	0.00631	0.00623	0.00706	0.00716	0.00671	0.00038	6
Ga/Al	0.00024	0.00026	0.00029	0.00027	0.00027	0.00027	0.00025	0.00026	0.00028	0.00027	0.00002	6
Cs/Al	0.00010	0.00010	0.00012	0.00009	0.00012	0.00009	0.00009	0.00009	0.00009	0.00010	0.00001	12
Pb/Zn	0.4	0.5	0.5	0.6	0.3	0.3	0.4	0.5	0.4	0.4	0.1	22
As/Zn	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	27
Cd/Hf	0.04	0.06	0.05	0.05	0.05	0.10	0.05	0.05	0.04	0.05	0.02	32

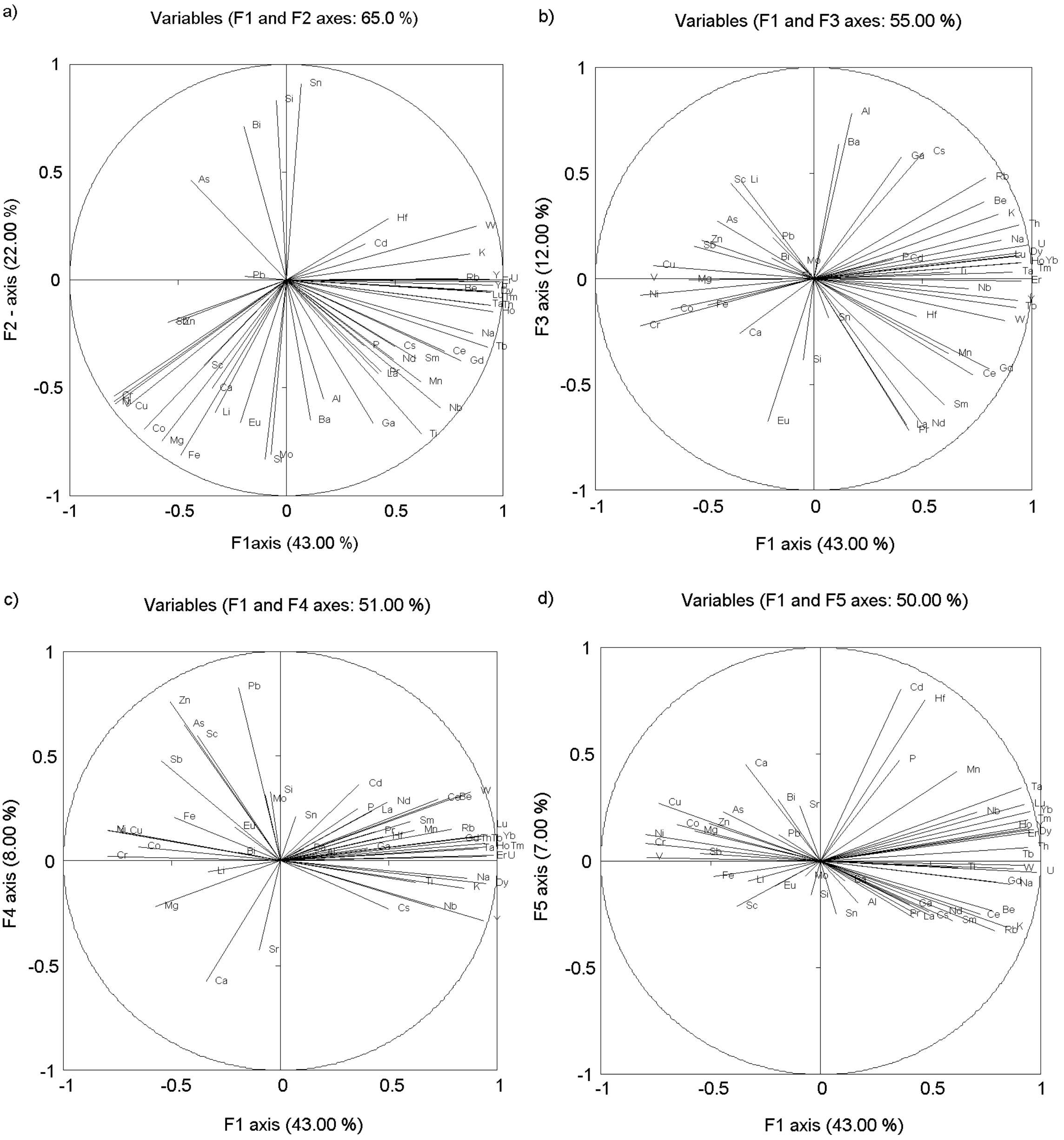

Fig. 2. Partitioning of the variables in the PCA F1 and F2 axes (a); in the PCA F1 and F3 axes (b); in the PCA F1 and F4 axes (c); in the PCA F1 and F5 axes (d)

Two examples are given in Table 6, by comparing Th and Ta and Yb and Ta. The Th/Ta and Yb/Ta have variabilities of 13% and 15%, respectively. Such ratios can be considered constant in that geochemical series. It can be interpreted as an identification of an homogeneous geochemistry of the Bouregreg river basin (formations with dominant detrital materials resulting of successive reorganizations of an ancient continental platform).

A strong association is found along the F2 axis (Fig. 2a) between Si, Sn and Bi. The individuals AGL2 and KSK2 (Fig. 3a) are the most representative of such association. Silicium is generally associated either to silica (SiO_2) or to silicates having various contents of Fe, Mg, and Al. Those three elements are not associated along the F2 axis. Then it is supposed that Sn and Bi are rather related to silica. Conversely, Fe, Al, Mg are anti-correlated with Si along the F2 axis. This fact should be explained by a source of silicates located around sites MAZ1, MAZ2, MAZ3, partly replacing silica compounds with increases of concentrations of elements associated to silicates and a decrease of concentrations of elements associated to silica.

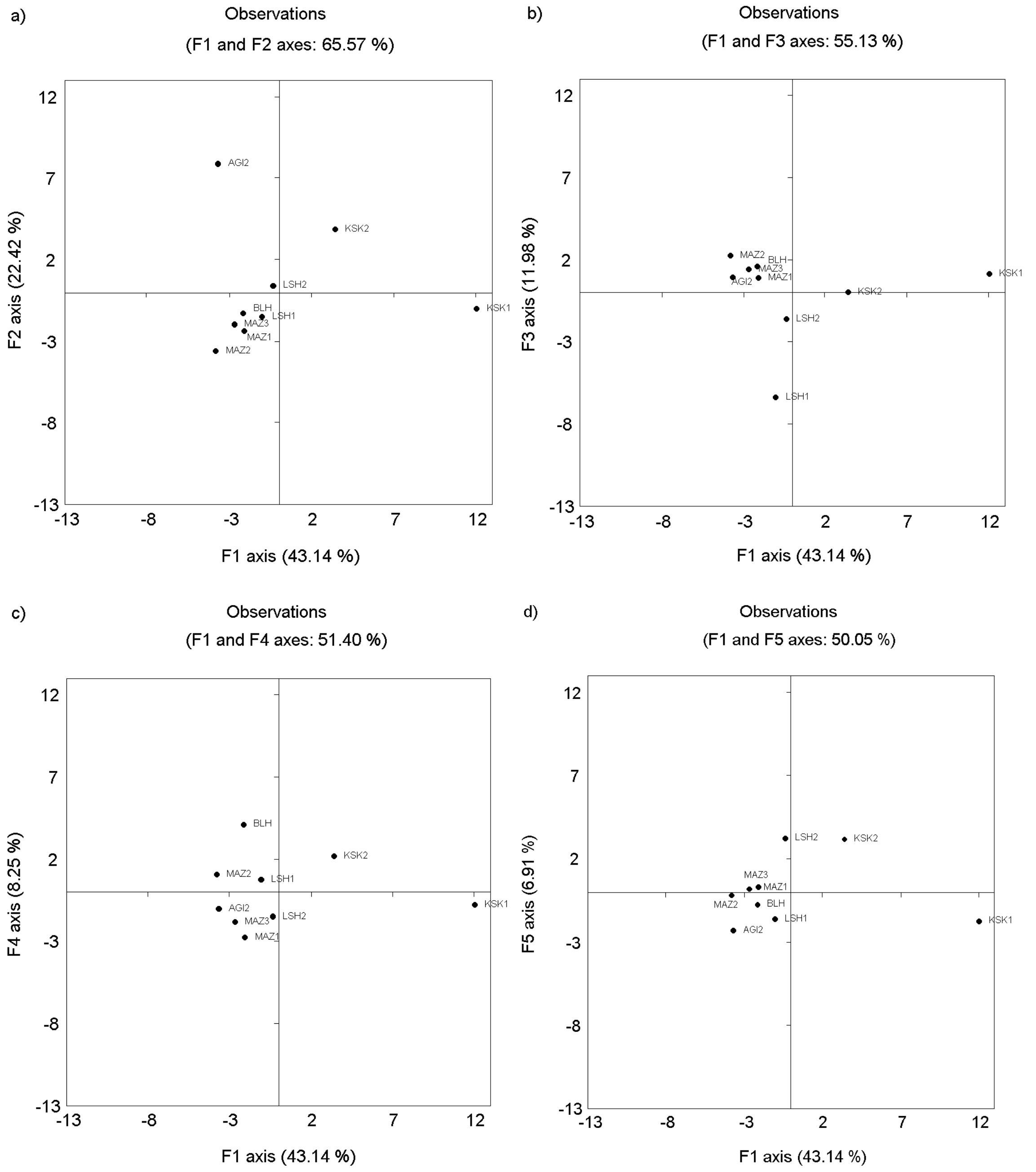

Fig. 3. Partitioning of the observations in the PCA F1 and F2 axes (a); in the PCA F1 and F3 axes (b); in the PCA F1 and F3 axes (c); in the PCA F1 and F5 axes (d)

However, because silicates are mixtures of complex compounds, the variabilities of Fe, Al and Mg are not completely similar. For that class of elements (Sn, Bi), it has been attempted to calculate a normalization of their concentrations to those of Si, in Table 6. The standard deviations remain quite high: 63% and 41%, respectively. However, whether sites AGL2 and KSK2 are excluded, then the variabilities become weaker: 49 and 28%, respectively.

A strong association between Ba, Al, Ga and Cs is observed along the F3 axis (Fig. 2b). All these elements were already observed as having weak variabilities all along the Bouregreg river in Table 5. The projection of observations on the F1-F3 plan (Fig. 3b) display that LSH1 and LSH2 are distinguished by their lowest concentrations. The highest concentrations are observed in Table 5 at sites KSK1, BLH and MAZ2, but their variability is too weak to be denoted in Fig. 3b.

It has been attempted to calculate a normalization of Ba, Ga and Cs concentrations to Al concentrations in Table 6. The variabilities of Ba/Al, Ga/Al and Cs/Al are as weak as 6%, 6% and 12%, respectively. Thus, the variability of Ba, Ga and Cs, could be well explained by the variability of Al.

An association between Zn, As and Pb is observed along the F4 axis (Fig. 2c). The projection on the F1–F4 plan (Fig. 3c) shows that BLH and KSK2 are the most influent sites. BLH and KSK2 are on two different tributaries, but located in a similar geological formation. Furthermore, BLH is near the town of Oulmes. Anthropogenic sources of those elements may be suggested since these elements often are associated to human activities. However, As, Zn and Pb are geochemically associated to sulphide species, so that such a natural source may be also evoked near the sites of BLH and KSK2. Elements Pb, Zn and As are trace compounds in the geochemical materials. For each of these three elements a comparison (Student test) was performed between concentrations found at KSK2 and BLH and the average concentration calculated from the 7 other sites, and defining a geochemical background. The concentrations at KSK2 and BLH were significantly different than the geochemical average at a level of 95%. At MAZ2, the Zn concentration was also significantly different by using the same criteria. However, it is not certain that the origin of such signals is from anthropogenic activities.

An association between Cd and Hf is observed along the F5 axis (Fig. 2d). The projection on the F1–F5 plan (Fig. 3d) shows that the sites LSH2 and KSK2 are the most influent. No interpretation can be yet hypothetized.

Conclusions

Three techniques were used to analyze sediment samples collected from nine locations along the Bouregreg river basin: instrumental neutron activation analysis (INAA), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES).

For ICP-MS, two dissolution procedures were tested: the alkaline fusion (ICPf) and the acid digestion (ICPa). For ICP-AES, only the fusion procedure was applied.

At LPS, two techniques were available: INAA and ICP-MS by using acid attacks. Both techniques were successfully applied to the reference material Soil-7, a certified reference material, provided by IAEA. However, sediments are very often difficult to dissolve, this is true also for sediment reference materials. It has been preferred to check the quality by intercomparisons of the 3 analytical techniques applied to real sediments.

Results obtained in this work show that LPs results for INAA showed no significant bias with respect to recommended values for IAEA Soil-7; as except ICPa showed a significant negative bias for elements that may be present in acid-insoluble compounds. Results for sediments obtained by ICPf are negatively biased in comparison with INAA, but deviations are on the average less than 10%. However, results obtained by ICPa are consistently positively biased in comparison to ICPf.

A general good agreement was found between INAA and ICPf techniques, while, the ICPa technique has been revealed useful only for a few elements. Thus, when only INAA and ICPa techniques are available, like at LPS, it was possible to determine concentrations for the 33 following elements: Na, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Nb, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Lu, Ta, W, Pb, Th and U.

Suspended particulate materials (PSM) have similar nature than that of sediments. Both techniques can be applied to the other kind of materials, for the determination of the same elements. Results for PSM are not provided here but will be published elsewhere. For sediments, the additional techniques ICPf (MS and AES) allow the determination of other elements: Li, Be, Mg, Si, P, Ga, Y, Cd, Sn, Pr, Gd, Ho, Er, Tm and Bi.

A principal component analysis has been used for analyzing the variability of concentrations, and defining what are the most influent sites with respect to the general variation trends. A first group of element is linked to the Mn concentration variations. It is composed of Mn, Na, K, Ti, Be, Rb, Y, Nb, Mo, Ce, Sm, Gd, Tb, Ho, Er, Tm, Yb, Lu, Ta, W, Th and U. A second group composed of only Sn and Bi linked to Si concentration variations. Fe, Mg and Al are anti-correlated with that group. A third group composed of Ba, Ga and Cs is linked to Al concentration variations. For these three groups a concentration normalization is proposed to the central element concentration (that means Mn, Si or Al). The new set of data has less variability and it is easier to define some sites where the behavior of the elements significantly differ due to specific sources. As and Pb have a Zn concentration variability pattern and composed the fourth group. Cd is linked to the fifth behavior pattern looking like those of Hf. Regarding Pb, As and Zn, a significant signal to the background is revealed at two sites, one of them being close to a small town. Since these elements are often associated to human activities, the link between the concentration variations of these three elements to anthropogenic sources can be suggested at one site at least. Another possible hypothesis is the existence of natural sulphide in the region of interest, since all these three elements can be associated to weakly soluble sulphide. Through the concentration variability studies in sediments, revealed by the PCA, it appears that the Bouregreg river basin is geochemically homogeneous.

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