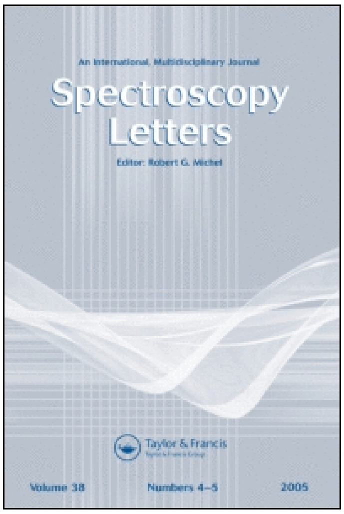

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Determination of Trace Elements in Bouregreg River Water by Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT This paper describes a method for the multielement determination of Ti, V, Cr, Co, Ni, As, Rb, Sr, Ba, Th, and U in water from the Bouregreg River (Morocco) by use of inductively coupled plasma mass spectrometry (ICP-MS). The distribution of trace elements in water samples of the Bouregreg River and its tributaries was determined by measurements at 10 sampling sites. The data obtained show that the spectrum of normalized concentrations with regard to concentrations found at the reference station (site AGL1) have rather identical forms for sites located downstream in the river, wheres a certain dispersal was observed for sites situated upstream in the river (BLH, KSK1 , KSK2, and AGL2). The concentrations of most elements are particularly low at the reference station (site AGL1). The elements Co, As, and Rb show a maximum concentration at the site AGL2 situated downstream of Aguelmous and close to a public discharge; this is explained by an anthropogenic origin for the concentrations of these elements.

KEYWORDS bouregreg River, ICP-MS, multielement analysis trace elements

INTRODUCTION

During the past decades, most of the rivers of the world saw their quality degrading. This degradation is due to urbanization, and industrial and agricultural activities.

In this context, studies on the chemistry of rivers have attracted attention for several years.[1–7] These studies follow natural processes as well as contributions of human activities along rivers. The determination of the concentrations of elements can contribute to a better understanding of these processes.

In Morocco, the region of Rabat is developing very quickly around the cities of Rabat and Sale, near the estuary of the Bouregreg River.

Along the Bouregreg River, the draining of pollutants is found not only near these two cities but also further upstream. Indeed, agricultural

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development in the Mâaziz and Larbaâ Shoul plains implies the use of chemical products (fertilizing, pesticides, etc.). Featilizers and pesticides are found directly in the main river or in one of the tributaries. In addition to this agricultural waste, there is domestic waste represented especially by uncontrolled discharges situated in the immediate vicinity of the river or sometimes directly in the river stream, as is the case of the garbage dump of the city Aguelmous, which is situated in on the river bank.

The current work is dedicated to study the spatial distribution of some trace elements in the water samples taken at 10 sites along the Bouregreg River by application of the ICP-MS technique. Discussion is provided on the following elements: Ti, V, Mn, Co, As, Rb, Sr, Ba, Th, and U.[8]

MATERIALS AND METHODS

Catchment Area

The Bouregreg River is one of the main streams of Morocco. Its source is located in the Moroccan Central Massif and flows toward the Atlantic coast through the coastal Meseta. The Bouregreg River Basin is located in the Moroccan Central Massif, which consists mainly of Paleozoic formations. 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 with the Ment, Oulmès, and Moulay Bou Azza granites.

The 10 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

Water samples were carried out and stored in polyethylene bottles of 2000 mL initially washed with concentrated HNO_3 and rinsed 3 times with the sample to be taken.

After filtration on cellulose nitrate filters of porosity $0.22\,\mu$m and of diameter 47 mm, the water was acidified with Normatom concentrated HNO_3 (2 to 3 drops). The obtained solution represents the mother solution intended for the analysis.

Water samples analysis was carried out by inductively coupled plasma mass spectrometry (ICP-MS) in the Pierre Sue Laboratory of the Saclay CEA Center (Saclay, France).

ICP-MS Measurements

Samples were introduced as solutions. The filtered and acidified water samples were directly analyzed.

From the mother solutions, several dilutions (10, 100, and 1000) were prepared and analyzed. Mass calibration of the apparatus is made with a solution that represents a range of elements from the light masses to the heavy masses.[9]

Aqueous CRM (SLRS-4 (River water reference material for trace metals from the National Research Council Canada) and NIST 1640 (natural fresh water from the National Institute of Standards and Technology, USA)) and blank samples were pre-

TABLE 1 **Results Obtained by ICP-MS for NIST 1640 and SLRS4 (Certified Reference Material) (μg/L).**

	NIST 1640		SLRS4	
Element	ICP-MS	Certified value	ICP-MS	Certified value
V	12.99±2.44	12.99±0.37	0.34±0.01	0.32±0.03
Mn	117.50±2.36	121.50±1.10	3.42±0.11	3.37±0.18
Co	20.03±2.66	20.28±0.31	0.042±0.01	0.033±0.06
As	24.90±1.86	26.67±0.41	0.62±0.02	0.68±0.06
Rb	2.04±1.96	2.00±0.02	—	—
Sr	124.40±1.44	124.20±0.70	28.04±0.84	26.3±3.2
Ba	148.00±0.83	148.00±2.20	12.35±0.37	12.2±0.6
U	—	—	0.051±0.001	0.050±0.003

Values are means ± SD of three determinations (n = 3).

pared in the same manner. All measurements were carried out by a THERMO-ELEMENTAL X7 series Inductively Coupled Plasma Mass Spectrometer provided by Thermo Scientific in Courtaboeuf, France.

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.

A mother multielement standard solution was prepared by mixing four multielement standard solutions (Jobin Yvon, SPEX) having concentration of $10.0\,\mu g\,ml^{-1}$ for each element. Thus, this mother solution containing 100 ppb of all elements was used to prepare a set of 0 to 4 ppb multielement standard for ICP-MS analysis. Reagent blanks were prepared prior to the corresponding samples. A standard solution was analyzed periodically and at the end of the series to check any drift during the run.

Some limitations occur in ICP-MS measurements because of various interferences. The main one is due to the recombination in the plasma of argon with elements such as O, N, H coming from air or water but also with major elements of the dissolved Matrix: Cl, C, and so on. A Collision Cell Technology (CCT) has been developed by ICPHMS engineers. It consists in introducing a stable gas like He or H_2, with kinetic energy sufficient to break the $ArM+$ ions. Our device was fitted with a CCT apparatus, allowing the determination of ^{56}Fe (cancelling the $^{40}Ar^{16}O$ interference) and of ^{75}As (cancelling the $^{40}Ar^{35}Cl$). However, other interferences such as recombinations as oxides of major elements and isobaric interferences still exist. Particularly, it was not possible to determine ^{80}Se, due to the existence of high concentrations of Ca (interference of $^{40}Ar^{40}Ca$ or recombinations such as $^{40}Ca^{40}Ca$ still may disturb the analysis).

RESULTS AND DISCUSSION

Prior to the analysis of unknown samples, the ICP-MS method was validated by analyzing water reference materials. SLRS-4 (River water reference material for trace metals, distributed by the National Research Council of Canada) and NIST 1640 (distributed by the National Institute of Standards and Technology, USA) were used. During the course of the study, the control materials were run every 5 samples to ensure analytical accuracy.

Table 1 shows the results obtained by ICP-MS for the two CRM used. Most of the values agree well with the certified values.

In this articles, we present the results of the sampling campaign carried out in winter 2004. The elements discussed are Ti, V, Mn, Co, As, Rb, Sr, Ba, Th, and U. Their concentrations are measured with relative errors less than 10%. These results are summarized in Table 2.

The results of Table 1 show that Mn, Co, As, and Rb present a high concentration at the AGL2 site. After strongly increase at the AGL2 site, the content of Mn decreases along all others sites and stabilizes from the MAZ1 site, whereas for Co, As, and Rb the concentrations decrease at the KSK1 site before increasing again at the KSK2 site and continue to decrease progressively at the other sites before stabilizing at LSH1. The concentration of Ti varies little from AGL1 to AGL2 to reach the maximal value, which is 73.7 $\mu g/l$ at the KSK1 site. It can be explained by the lithology of the catchement area, which is more enriched in granitic rocks. For the vanadium, it grows from uphill until the downstream where it records its maximal level (1.4 $\mu g/l$). For Th and U, they have the same behavior along the four first sites with a remarkable increase in KSK1 (0,007 $\mu g/L$ for Th and 1,00 $\mu g/L$ for U); after decrease of the concentrations of these two elements at KSK2, one notes a stabilization of the concentration of Th until the LSH1 site, which has a light increase followed by a maximal value recorded downstream (LHS2 site); whereas the concentration of U continues to increase until it reaches the maximal value at LSH2. A little variation for Sr is mentioned, the concentrations of this element very from uphill until its maximal value recorded at MAZ1, then it decreases at MAZ2 before stabilizing at the rest of the other sites (Figure 1). Concentrations of Ba remain steady and vary little from one site to the other before recording its maximal value at LSH1.

In order to have a general view on the differences between the stations and to discover possible enrichments or depletions between elements, the concentrations of the elements are normalized to the concentrations registered in the reference station (AGL1 site) localized more upstream of the river (Figure 1). The diagrams of concentrations normalized to the reference station (AGL1 site) are represented in Figure 2.

TABLE 2 Concentrations of the different water samples (μg/L)

Element	AGL1 %	AGL2 %	KSK1 %	KSK2 %	BLH %	MAZ1 %	MAZ2 %	MAZ3 %	LSH2 %	LSH1 %
Ti	25.14±1.44	48.3±2.10	73.74±1.65	30.79±0.89	26.51±1.69	9.70±0.92	12.27±1.35	9.109±1.87	7.68±0.38	8.10±0.69
V	0.207±1.44	0.68±1.43	0.83±1.27	0.76±0.91	0.79±1.37	0.91±1.30	1.16±0.76	1.28±0.22	1.37±3.39	1.33±1.24
Mn	1.33±0.80	68.1±1.27	56.46±0.96	42.81±0.75	9.75±1.20	1.86±2.32	3.94±0.63	0.26±5.20	6.12±1.48	9.12±1.00
Co	0.04±1.94	0.46±3.76	0.23±6.30	0.36±1.56	0.23±2.50	0.28±0.76	0.21±2.41	0.24±1.20	0.28±0.58	0.30±0.34
As	0.46±9.09	5.02±1.97	0.97±2.31	4.74±1.75	3.99±0.99	1.20±1.05	1.82±1.09	1.67±3.17	1.64±1.78	1.64±0.36
Rb	0.43±0.51	3.52±0.67	0.48±0.46	2.79±0.72	0.77±0.58	0.63±0.36	1.45±0.58	1.63±1.02	1.12±1.04	1.03±1.50
Sr	36.03±0.69	73.64±0.56	98.02±257	71.85±0.33	193±0.25	423±0.29	267±0.38	348±0.31	349±0.57	365±0.67
Ba	29.24±0.54	36.92±0.48	30.07±0.50	33.5±0.46	65.7±0.44	58.7±0.18	50.8±0.57	58.9±0.25	93.2±0.12	98.2±0.25
Th	0.001±2.74	0.002±2.88	0.007±2.89	0.003±7.12	0.002±11.3	0.002±0.64	0.002±5.74	0.002±5.46	0.013±6.88	0.004±15.3
U	0.004±4.51	0.08±4.77	1.006±2.79	0.31±1.05	1.08±4.88	1.37±2.62	1.25±4.42	1.33±4.43	1.52±2.09	1.48±3.65

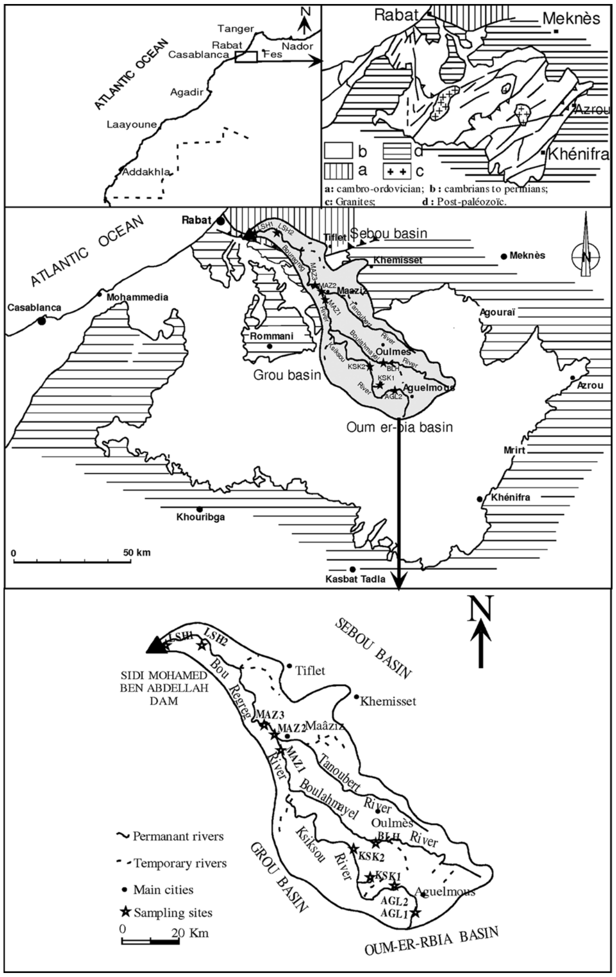
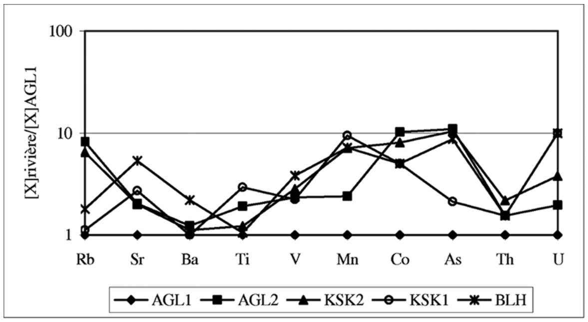
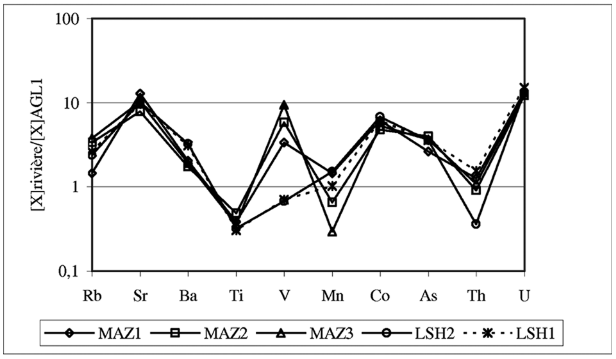


FIGURE 1 Location of the Bouregreg River basin in the Moroccan Central Massif and Sampling points.



(a) Sites localised upstream of the river



(b) Sites localised downstream of the river

FIGURE 2 Diagram of the concentrations normalized to the reference site concentrations (AGL1) in the Bouregreg river water.

Several remarks are provided below.

- For most elements, all stations localized upstream present higher concentrations than does the reference site (AGL1) (ratio > 1),
- Ti, V, Mn, and Th present, at some stations localized downstream (MAZ1, MAZ2, MAZ3, LSH2, and LSH1), values below those recorded more upstream at the reference station.
- One also notes that in the sites localized downstream (MAZ1, MAZ2, MAZ3, LSH2, and LSH1), the set of diagrams, represented in Fig. 2, has identical forms. On the other hand, one notes a certain scattering of the diagrams in the sites localized upstream (BLH, KSK1, KSK2, and AGL2). The regularity of the diagrams downstream could be explained by the localization of these sites in plains where the altitudes decrease slowly from the inside toward the Atlantic ocean, from 400 m to a few score of meters, which makes the sedimentation phenomenon more favored than at the sites situated upstream where the strong slopes dominate but the shelf areas with average slopes in undulating relief step in for the characterization of the part of the basin.
- However the diagrams are not flat (recall that if the elements were in the same proportions in the waters of every station of the basin of the Bouregreg, the diagram would be flat). Considerable differences are notable, especially for Sr, V, Co, As and U. These elements are enriched systematically in relation to their neighbors, while Ti, Mn, and Th are depleted.

CONCLUSION

In this work, we used the ICP-MS technique for the determination of the concentrations of a range of elements in the water samples collected at 10 sites along the Bouregreg River. The analysis by ICP-MS allows estimating the degree of pollution of the Bouregreg River.

The diagrams of concentrations normalized to the concentrations registered in the reference station (site AGL1) allowed us to pull the following conclusions:

- For the most part of the elements, all the stations present concentrations superior to that of the reference (AGL1) site (ratio > 1),
- Ti, V, Mn, and Th present, in some stations localized downstream (MAZ1, MAZ2, MAZ3, LSH2, and LSH1), values below those registered upstream.
- In stations localized downstream (MAZ1, MAZ2, MAZ3, LSH2, and LSH1), the diagram has rather identical forms. On the other hand, a certain dispersal of diagram at the level of sites situated upstream (BLH, KSK1, KSK2, and AGL2) is noticed.

However, diagrams are not flat, there are so considerable differences, notably for Sr, V, Co, As, and U. These elements are systematically enriched with regard to their neighbors, whereas Ti, Mn, and Th are depleted.

On the other hand, the concentrations of most of the elements are particularly weak at the reference station (site AGL1). Some elements such as Mn, Co, As, and Rb all present a maximum of concentration at the AGL2 site situated downstream to Aguelmous and near a garbage dump, which suggests an anthropogenic origin of concentrations of these elements. Th and U have the same behavior on the set of sites with a net increase in the KSK1 site. A mainly natural origin is very likely considering the granitic aspect of the region of MENT crossing by the river.

For a better understanding of the studies of pollution of this region, it would be necessary to identify for every sample a wide palette of elements to allow elaborating of a multielementary "signature."

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REFERENCES

1. Edmond, J. M.; Palmer, M. R.; Measures, C. I.; Brown, E. T.; Huh, Y. Fluvial geochemistry of the eastern slope of the northeastern Andes and its foredeep in the drainage of the Orinoco in Columbia and Venezuela. Geochim. Cosmochim. Acta **1996**, *60*, 2949–2976.
2. Gislason, S. R.; Arnorsson, S.; Armannsson, H. Chemical weathering of basalt in southwest Iceland: effects of runoff, age of rocks and vegetative/glacial cover. Am. J. Sci. **1996**, *296*, 837–907.
3. White, A. F.; Blum, A. E.; Schulz, M. S.; Vivit, D. V.; Larsen, M.; Murphy, S. F. Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: I. Long term versus short-term chemical fluxes. Geochim. Cosmochim. Acta **1998**, *62*, 209–226.
4. Land, M.; Ingri, J.; Ohlander, B. Past and present weathering rates in northern Sweden. Appl. Geochem. **1999**, *14*, 761–774.
5. Azzaoui, S.; El Hanbali, M.; Leblanc, M. Copper, lead, iron and manganese in the Sebou Drainage Basin: sources and impact on surface water quality. Water Quality Res. J. Canada **2002**, *37*(4), 773–784.
6. Zahry, F.; Labraimi, M.; Bilal, E.; Gruffat, J. J.; Moutte, J.; Garcia, D.; Bounakhla, M. Heavy metals assessment in Oum Er Rbia basin using WD-XRF and ICP-AES. J. Phys. IV **2003**, *107*, 1401–1402.
7. Bounakhla, M.; Tahri, M.; Benyaïch, F.; Zahry, F.; Bilal, E.; Gruffat, J. J.; Moutte, J.; Garcia, D. Heavy metals analysis of water, soils and sediments along the Oued Boufakrane River (central Morocco) using WD-XRF and ICP-AES. J. Phys. IV **2003**, *107*, 207–210.
8. Khalis, M. Etude de l'influence du milieu environnant sur la composition minérale d'une rivière marocaine, Thèse d'Etat, Université Moulay Ismail, Meknès, Maroc, **1997**, 152 pp.
9. Veado, M. A. Application de l'analyse par activation neutronique et de la spectrométrie de masse associée à un plasma d'argon pour l'identification et le dosage des éléments métalliques apportés par les rejets miniers dans la rivière DAS VELHAS – Brésil, Thèse de Doctorat, Université Paris XI, Orsay, **1997**, 154 pp.