Environmental Analytical Chemistry

Introduction

The “Environmental Analytical Chemistry” research group aims the development of analytical techniques as well as its applications in the study of the distribution and behaviour of chemical elements and isotopes in the field of Environmental Sciences. This team has resulted from the reorganization of the “Applied Chemistry to the Earth and Environmental Sciences” and the “Archaeometry” groups carried out in October 1998.

The main analytical activities within the group are based on the energy-dispersive X-ray fluorescence spectrometer, two mass spectrometers for light isotopes and the tritium dating unit. These techniques have been mainly applied in studies of pollution monitoring, transfer mechanisms in soil/plant systems, sedimentary dynamics, water resources, palaeohidrology and palaeoclimatology. Environmental isotopes (C, O, H) have been used to study and characterize present and ancient environments, namely in the fields of isotope hydrology, palaeohidrology and palaeoclimatology. Also, multielemental analytical methods and isotopic ratios ($\delta^{18}O$, $\delta^{13}C$, $\delta^{2}H$) combined with other techniques such as ^{210}Pb, radiocarbon and tritium dating have been applied in studies of pollution monitoring, sedimentary dynamics, and natural resources. As a consequence, these particular capabilities have led to an active engagement of the staff of this group in several research projects in partnership with national and international teams from Universities and Research Laboratories. Besides, X-ray fluorescence spectrometry, because of being a multielemental and non-destructive, has been giving significant contribution in the studies of Monetary History as well as a regular collaboration with archaeologists in studies of primitive metallurgy.

Research Team

Researchers –	2	(1PhD, 1 research assistant)
Research Students –	3	
Undergraduate Students –	1	
Technicians –	1	

Publications

Journals –	9	and 5 in press
Proceedings –	8	and 2 in press
Conf. Commun. –	4	
Theses:		
PhD –	1	
Lic. –	1	

	10^3 PTE
Expenditure:	**5 037**
Missions:	694
Other Expenses:	3894
Hardware & Software:	23
Other Equipment:	426

		10^3 PTE
Funding:		**5 855**
External Projects:	1997	-2 524
	1998	7 706
Others		673

About the Origin of CO_2 in some HCO_3/Na/CO_2-rich Portuguese Mineral Waters

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Abstract

The present paper aims at increasing knowledge on the origin of CO_2 in hot and cold HCO_3/Na/CO_2-rich mineral waters issuing in the northern part of the Portuguese mainland. The main chemical and isotopic signatures of these waters are presented. $\delta^{13}C_{(TIDC)}$ values observed in hot and cold mineral groundwaters range between -6.00 $^{o}/_{oo}$ and 1.00 $^{o}/_{oo}$ *vs* PDB indicating a deep-seated (mantle) origin for most of the CO_2. In the case of the heavier $\delta^{13}C_{(TIDC)}$ values, the contribution of metamorphic CO_2 or the dissolution of carbonate rock levels at depth cannot be excluded. Concerning the hot waters, the lack of a positive ^{18}O-shift should be attributed to water-rock interaction with short contact times, rather than to the isotopic influence of CO_2 on the $\delta^{18}O$-values of the waters.

Geothermal Resources Council Transactions, **Vol 22** (1998) 113-117.

Pollution Assessment in the Trancão River Basin (Portugal) by PIXE, EDXRF and Isotopic Analysis

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Abstract

This paper reports on the inorganic contamination assessment of a river basin and local water resources in order to establish quality standards. PIXE was applied to the elemental determination of the freeze-dried water dry residue and EDXRF was used for the evaluation of elemental content of sediments. To infer the water provenance the electrical conductivity was measured as well as the isotopic composition of surface waters using the $^{18}O/^{16}O$ ratio. The combined isotopic and elemental composition information enables to establish dominant contamination contributions from the several tributaries. Moreover, the variability observed for certain parameters, associates them with specific basin regions as for instance, dry residue mass, conductivity and Br, or S, Cl and As or Cr, Ni, Zn and Pb which permit to establish both pollution characterisation and their origin (agriculture, industrial, etc.). At certain locations, enhanced concentrations of elements as Cr, Cu, Zn and Pb are observed both in sediments and in the surface water. The elemental particular associations also permit to characterise pollution sources.

Nucl. Instrum. Methods, (in press).

Bronze Axe from Santo Tirso

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Abstract

The present paper is a descriptive study of an axe from Santo Tirso, of the *Museu Nacional de Arqueologia* (Lisbon) collection. Non-destructive analysis carried out by energy-dispersive X-ray fluorescence spectrometry revealed that the axe is a bronze with high lead content. This axe may be classified as belonging to the Late Bronze Age of Atlantic Europe.

Santo Tirso Arqueologica, Vol 2, 2^{a} Série, (in press).

Geomorphological Control of Fine Sedimentation on the Northern Portuguese Shelf

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Abstract

Six cores sampled in the two mud fields located at the northern continental Portuguese shelf have been studied in order to evaluate the control processes of the fine sedimentation. The southern mud patch, offshore Douro river is limited in the western side by some Cretaceous and Paleocene outcrops that constitute reliefs of 5-30m amplitude; on the contrary, the northern mud patch, offshore the Minho river extends along a flat region. Granulometric distribution shows that the sediments from Minho mud patch are coarser than the Douro mud patch, where the grain size diminishes towards West. Also, carbonate content is higher in Minho mud field. The sediment organization in fining-up sequences in Minho mud patch and in the eastern part of Douro mud patch indicates sediment remobilization by storm events. The Douro mud patch has higher sedimentation rates than the Minho mud patch. The highest values are probably related with the existence of reliefs, which may offer an hydrodynamic protection or functioning as fine sediment barrier. The elemental distribution for chemicals elements was determined in different fractions of these cores. Geochemical patterns are in general rather similar for both mud fields, pointing out to a common continental origin of the sediments. The main differences in the chemical composition are mainly controlled by the grain size distribution, either for the presence of coarse quartz particles or a local enrichment in biogenic material.

Publicación Especial del Instituto Español de Oceanografia (in press).

Use of Environmental Isotopes in the Study of the Aquifers Systems from Maciço das Setes Cidades (Azores) - Preliminary Results

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[3]*Departamento de Geologia da FCUL - Centro de Geologia da Universidade de Lisboa*

Abstract

The results obtained with the isotope analyses ($\delta^{2}H$ and $\delta^{18}O$) performed in groundwater samples collected in springs, wells, in a lake and two lakelets at Sete Cidades Massif (Azores), allow the identification of a mixing mechanism between surface water and groundwater. In view of these results there is also the possibility of recharge of the aquifers systems by fog that surrounds the island approximately during all the year.

The springs located near the coastline, at low altitude, have a residence time in the order of 5 to 10 years based in the tritium content. The ^{3}H values stand for a recharge area located relatively far away from the outlet.

Revista da Associação Portuguesa dos Recursos Hídricos (APRH), (in press).

Chemical Characterization of Sediments from the Portuguese Shelf (North of Espinho)

T. Barbosa[1], M.F. Araújo[1], P. Valério[1] & A.P. Carvalho[2]

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[2]*Departamento de Química e Bioquímica, FCUL, Campo Grande, 1700 Lisboa*

Abstract

This work reports on the geochemical study of 44 samples (Figure 1) of superficial sediments were collected at the Portuguese shelf (between 41° 05’ and 41° 52’) during the cruise CORVET 96, in November 1996, on board of the research vessel *R.V. Almeida Carvalho*. Sample preparation and analytical procedures were accomplished according to a previously reported procedure (Araújo *et al.*,1994).

Chemical analyses have been carried out by energy-dispersive X-ray fluorescence spectrometry (EDXRF) for 16 elements (Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr and Pb). The accuracy and precision of the overall procedure are usually better than 10%.

Mineralogical analyses and semi-quantitative determination of the minerals quartz and calcite have been also carried out in 8 selected samples by X-ray powder diffraction located along two perpendicular profiles to the coast line, on the two shelf mud fields, from the inner to the outer shelf.

Results show that sediment composition is dominated by terrigeneous materials. A general decrease on the Si content is observed with the distance from the coast, due to the size of particles and the increasing of biogenic activities. High percentages in Ca at high depths are of biogenic origin. No significant differences are found in the trace element distribution, which content is mainly related with the grain size distribution.

Elemental distribution in the two mud fields seem to be rather identical for all major, minor and trace elements suggesting a similar origin of the deposited material.

Proceedings 1º Simpósio interdisciplinar sobre processos estuarinos – Sipres 98, Faro, 15-17 Junho, pg. 91-94.

Heavy Metal Contamination along the Trancão River Basin

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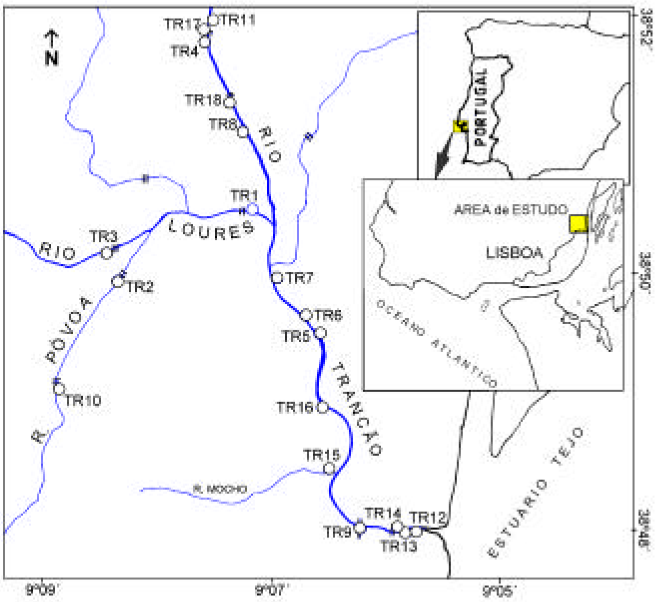
Abstract

This work aims at the heavy metal assessment all over the Trancão river basin by the multielemental analysis of sediments and surficial waters. Sediments and waters were sampled in 18 stations in April 1997. Sediments were analysed by EDXRF while the analysis of the waters dry residue was carried out by PIXE. Results showed local enrichments in Cr, Cu, Zn and Pb, particularly in the region located upstream the confluence with the Loures river. In general, Cr, Cu, Zn and Pb content exhibit similar distribution patterns in sediments and waters. In sediments, the metal distribution is controlled by grain size distribution but determined values are rather high when compared with other published for non-polluted areas.

Some pollution sources could be identified, namely a paper treatment plant and some a metal industry, which were the origin of anomalously high values of Ca and Cr. The domestic contamination, responsible by the elevated concentrations of Cu, Zn and Pb measured all over the basin present higher levels downstream the confluence with the Loures river.



Map of the Trancão river basin with the information of the sample points.

Proceedings 1º Simpósio interdisciplinar sobre processos estuarinos – Sipres 98, Faro, 15-17 Junho, pg. 186-189.

Heavy Metal (Cu, Zn, Pb) Assessment in Sediments from the Minho, Lima, Cávado, Ave and Douro Rivers

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Abstract

This work reports on the metal contamination (Cu, Zn and Pb) in sediments collected along the Minho, Lima, Cávado, Ave e Douro river courses and estuaries. These five major rivers drain rather populated and industrialized regions in the northern Portugal. In order to normalize the metal concentrations, because of the different grain size distributions of sediments, the clay/silt size fraction was separed by wet sieving and analysed by EDXRF.

Cu, Zn and Pb distribution along these basins exhibit rather different patterns, probably due to the different industries, mining and agricultural activities along the different regions. Sediments collected Minho and Lima rivers showed to be less enriched in heavy metals. In the Cávdo river basin the existence of the mining regions of Borralha and Borrageiro seem to explain the anomalously high levels in Cu and Pb. Ave is the more contaminated river basin probably mainly because of the large number of industries located along the river course. In the Douro river basin the industrial, domestic and agricultural activities cause an enrichment in those metals.

Proceedings 1º Simpósio interdisciplinar sobre processos estuarinos – Sipres 98, Faro, 15-17 Junho, pg. 159-162.

Pollution Assessment in a Contaminated River Basin by Multielemental and Isotopical Analyses – Effects in the Groundwater System

M.F. Araújo, T. Pinheiro, P.M. Carreira, P.M. Valério, L.C. Alves, A.M. Soares
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Abstract

The Trancão river drains a small basin into the Tagus inner estuary, one of the largest on the West Coast of Europe in the Lisbon surroundings. During the last two decades a disordered populational and industrial boom have transformed the river into an open air sewer. However, in spite of the obvious contamination along the river basin, river water is currently used to irrigation purposes.

This work aims at the study of the contamination (inorganic) of sediments, surface and groundwaters in the Trancão river basin. Samples of surface sediments and waters were collected at the river main course and tributaries, in different seasons during 1996 and 1997, to account for local influences and seasonal variabilities. Measurements of pH, temperature and electrical conductivity were carried out at each location.

Sediments were analysed for 17 elements by EDXRF (Energy-Dispersive X-Ray Fluorescence spectrometry) and the waters freeze-dried residue analysed by PIXE (Particle Induced X-ray Emission) and about 20 elements could be detected. Isotopic composition: $^{2}H/^{1}H$, $^{18}O/^{16}O$ ratios and tritium contents were performed in the surface waters and groundwaters to better understand the dynamics and interaction between these systems.

By the combination of the chemical and isotopical analyses, we can stress the following points:

- high concentrations levels of Cr, Cu, Zn and Pb (indicating a serious contamination) were

found in sediments and surface waters, highly dependent on the season and sediment type;

- elements usually associated with fertilizers (e.g. As and Br) were detected in waters;
- an enrichment in ^3H was measured, ranging from 20 to 30 TU above the values considered as background in this region, which can not be attributed to evaporation;
- apparently, due to the low water flow that characterizes the entire basin, any local (e.g. effluents discharges) and seasonal variation directly influences the sediments (particularly the metal contents) and waters compositions (the high differences in conductivity measured can not be a result of the mixing with sea water).

Proceedings "The PITTSBURGH CONFERENCE - PITTCON 98", New Orleans, USA,
1-5 March 1998, contribution n°948.

Elemental Distribution in Sediment cores from Two Fine Sedimentary Deposits on the Portuguese Northwestern Shelf

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Abstract

This work reports on the results of the geochemical study of six cores with different depths collected all over two fine sedimentary deposits located at the Portuguese Northwestern Atlantique shelf. The higher accumulation rates measured for the southern deposit by the ^{210}Pb technique (Drago *et al.*, 1997) are explained by the differences on the geomorphology along the shelf. In fact, the presence of Cretaceous and Paleocene outcrops along the shelf, off Douro, act as barriers forcing sediment particles to deposit, while the northern deposit is settled on a non steep large region of the shelf. Downcore profiles on the elemental distribution were obtained by analysing subsamples of the bulk sediment cores selected at different depths.

Chemical analyses have been carried out by energy-dispersive X-ray fluorescence spectrometry (EDXRF) for 18 elements (Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr and Pb).

Elemental distribution for the lithogenic elements points out to their continental source. The marine influence is visible by some higher concentrations in Ca and Sr associated with an increasing of the granulometry. The largest variations observed on the elements are highly correlated with grain size distribution. Concentrations in trace metals are rather low, however in marine sediments their distribution is usually determined by inorganic detrital materials which main constituents, quartz, felspars and carbonates, are poor in trace elements and serve to dilute other phases richer in these elements (e.g. clay minerals).

Generally, the geochemical patterns of the cores collected from both fine sedimentary deposits are very similar, pointing out to a common continental origin of the sediments. Some differences in composition are mainly controlled by either grain size distribution or the presence of biogenic material. Moreover, they do not exhibit variations in the case of cores with comparable sedimentation rates, even if the conditions that cause the sediment particles to deposit are apparently rather different.

Proceedings 2° Simpósio Sobre a Margem Continental Ibérica Atlântica, 17 -20 Setembro, Cadiz, Espanha.

Palaeoclimatic and Palaeodynamic Characterization of the Aveiro Cretaceous Multiaquifer Trough the Application of Environmental Isotopes

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[1] *Instituto Tecnológico e Nuclear, Laboratório de Isótopos Ambientais. Estrada Nacional Nº 10 2886 Sacavém, Portugal*

[2] *Universidade de Aveiro, Departamento de Geociências. 3800 Aveiro, Portugal*

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Abstract

Through the application of isotope and hydrochemical techniques in the study of Cretaceous multiaquifer system of the Lower Vouga Basin, we try to evaluate the effect of the high exploitation of groundwater of this system along the last 4 decades.

Between km 5 and 8 the ^{14}C content of the groundwater decrease almost linearly with the increasing distance, along the general direction of groundwater flow. However, between km 8 and 16 the concentration of ^{14}C remains almost constant, indicating a much higher apparent flow velocity of groundwater, resulting from intense flushing of the aquifer during the last glacial period about 18 ka . This flushing was induced by the decrease in the sea level by about 100 m.

On the other hand, an enrichment in ^{18}O and in ^{2}H downgradient from the recharge area can be observed along the flow paths, with more positive δ values for higher apparent ^{14}C ages. This apparent enrichment in heavy isotopes observed for Aveiro palaeowaters is unique in the European continent, and probably reflects the fact that the global ocean was enriched in both ^{18}O and ^{2}H during the glacial period.

Noble gas determinations (He, Ne, Ar, Kr and Xe) as a palaeoclimatic indicators were carried out on these waters. The palaeotemperature results (groundwater with Pleistocene ages) give an average temperature of 5ºC lower than the water samples collected either in the shallow system or in the deep aquifer zone with Holocene ages.

Proceedings of *4º Congresso da Água. "A Água Como Recurso Estruturante do Desenvolvimento*". Lisboa, Portugal (1998).

Use of Stable Carbon and Oxygen Mass Spectrometry and Neutron Activation Analysis in Determining Provenance of Some Roman Works of Art in Portuguese Museums

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[1]*Instituto Tecnológico e Nuclear, Departamento de Química. Estrada Nacional nº 10, 2686 Sacavém, Portugal*
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(see Cultural Heritage and Sciences)

Phytoremediation: A study of Metals on the Soil-plant System in the Aljustrel Mining Area Regarding *Cistus ladanifer* L.

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Abstract

The soils in the Aljustrel mining area and *Cistus ladanifer* L., an autochthonal aromatic plant, often the unique coloniser in this type of soils, have been analysed with the following objectives: to survey the soils and plants chemical composition; to quantify the most abundant elements particularly those having a greater pollutant potential, as well as their bioavailability; to evaluate the capacity of plants in accumulating specific elements and their contribution to a possible phytoremediation of that area.

The multielemental (Mg, S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn, As, Br and Pb) characterisation of the soils and *C. ladanifer* leaves was carried out by Energy-Dispersive X-Ray Fluorescence spectrometry (EDXRF). Results evidence the *C. ladanifer* capacity to resist to unfavourable soil conditions, highly enriched in toxic elements, pointing out to its potential application in a phytoremediation strategy for that mining zone.

Proceedings “*1st International Meeting of Aromatic and Mediterranean Plants*”, Conimbriga, 1998, (in press).

Contribution to the Hydrogeological Study of the Lower Tagus and Lower Sado Miocene Aquifer Through the Application of Isotopic Techniques

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A strong increase of groundwater mineralization has been verified in the Lower Tagus and Lower Sado Miocene aquifer, which represent a vital water resource of an important industrialized region. In order to find out the source of salinization, which can be related to seawater encroachment, to a brine dissolution (detected in depth), or to active seawater intrusion, isotope (δ^2H, δ^{18}O, ^{3}H and ^{14}C), physical and chemical analyses has been carried out in groundwater samples. The lack of relation between the increase of salinization and the 14c content, in the S part of the lower Sado basin put clearly in evidence a brine dissolution mechanism, or mixing with ancient seawater trapped in the sediments during the basin formation. On the other hand in Almada region the strong correlation between these parameters point out to recent sea water intrusion in this area.

Submitted to *II Congresso Ibérico de Geoquímica. XI Semana de Geoquímica.* Lisboa. Portugal, 1999.