

Environmental and Analytical Chemistry

Maria de Fátima Araújo

The activities of the Environmental and Analytical Chemistry Group (EAC) combine fundamental and methodological research related to **Elemental and Isotopic Analysis** as well as their applications in the fields of **Environmental Geochemistry, Isotope Hydrology, Oceanography and Archaeometry**.

Research is developed by a multidisciplinary team constituted by Analytical and Inorganic Chemists, Geologists, Biologists and Conservation scientists. Different facilities have been implemented and maintained by the team: **Energy-Dispersive X-Ray Fluorescence, Light Isotope Mass Spectrometers, Radiocarbon Dating, Tritium Unit and High Performance Liquid Chromatograph/Inductively Coupled Plasma Mass Spectrometer**.

During the current year, by using the HPLC/ICPMS facility (installed in 2008) new studies in the Environmental and Biomedical (in collaboration with the Biomedical Studies Group/IBL/UFA) fields were implemented. The acquisition of the stable isotopic ratio mass spectrometer to be associated with the sample preparation for AMS (Accelerator Mass Spectrometry) measurements (in collaboration with the Ion Beam Laboratory Group/UFA) was finished.

Environmental Geochemistry and Oceanographic research was carried out under a multi-proxy approach, including sedimentology, geochronology, absolute dating and paleoecology. Research focused in Sedimentary Geochemistry aimed at the palaeoenvironmental reconstruction along the Holocene on the Portuguese coastal area, in particular at the Minho and Douro drainage basins and at the assessment of ecological effects of the metal contents on Sado tidal marshes. Oceanographic studies concerning the marine reservoir effect, based on **Radiocarbon Dating** of pairs of samples (terrestrial and marine) were enlarged to new regions off the W margin of Iberian Peninsula – Aveiro / mouth of Minho river and Faro / Mouth of Guadiana river.

Isotope Hydrology research studies have been developed aiming at to contribute to a sustainable regional development and appropriate use of the water resources. Investigations were carried out in different environments: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in CO₂-rich Thermomineral Waters, including the geothermal potential evaluation and the seismo-volcanic hazard assessment at Azores archipelago. These investigations have significantly contributed to the exploitation and development of regional water resources and to the delimitation of protection areas.

The **archaeometallurgical research** was focused on materials characterization, involving different analytical techniques (EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) of Cu and Au-based artefacts and other remains recovered in different archaeological sites from Portuguese territory. Results have shown that reduction, alloying and recycling operations were probably undertaken in several sites, and that artefact shaping was performed by diverse methods. Another study dedicated to the Chinese brass coins belonging to the collection of Macau Scientific and Cultural Centre Museum (Lisbon, Portugal) proposes to correlate the alloy elemental composition with the metallic phases. Present observations show that minor elements as Pb, Sn, Sb, Fe and As are structurally significant in these cast coins.

A study of the Macao Scientific and Cultural Center Museum **Chinese copper cash** was focused on the correlation of the alloy elemental composition with the metallic phases. Current observations showed that minor elements as Pb, Sn, Sb, Fe and As are structurally significant in these cast coins

The EAC group is highly engaged in education and training of MSc and PhD students in collaboration with different Universities.

Technical services are also available to Universities and to Public and Private Institutions.

Research Team

Researchers

M.F. ARAÚJO, Princ., Group Leader

A.M.M. SOARES, Princ.

P. CARREIRA, Aux.

J.M. DE LA ROSA, Aux. (Contract, after October)

P. G. FERNANDES, Post-Doctoral, FCT grant (till July)

M. G. SANTOS, Post-Doctoral, FCT grant

Students

C. CORREDEIRA, PhD student, FCT grant

E. FIGUEIREDO, PhD student, FCT grant

M. J. FURTADO, PhD student, FCT grant

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P. PORTELA, Graduate student, FCT grant

Technical Personnel

D. NUNES, Graduate technician

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Collaborators

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Environmental Geochemistry – Elemental and Isotopic Research

M.F. Araújo, P. Carreira, A.M. Monge Soares, P.G. Fernandes, P. Alvarez-Iglésias, M. G. Santos, J.-M. Rosa, D. Nunes, P. Valério, J. Martins, P. Portela

Objectives

Activities aim at the development and promotion of coordinate research on Earth and Environmental Sciences in conjunction with the implementation of analytical and absolute dating techniques:

1. Multielemental characterization ($Z > 10$) using X-Ray Fluorescence spectrometry;
2. Light isotope determination ($\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$);
3. Radiocarbon dating;
4. Tritium dating.
5. High Performance Liquid Chromatography coupled to an Inductively Coupled Plasma Mass Spectrometry

Elemental, isotopic and dating techniques are being used in the understanding of natural environments, particularly aquifers, rivers, estuaries, lagoons, coastal waters and continental shelf. Our main goals are:

- 1) to establish the evolutionary patterns of coastal environments since the Holocene; identify sediment sources and evaluate the major driving factors controlling its distribution and composition; setting up regional backgrounds and the beginning and origin of anthropogenic inputs;
- 2) to determine the origin of different groundwater systems; identify the recharge areas; calculate mixture between different water bodies; assess the vulnerability of groundwater to surface pollution; understand and determine the origin of pollution in hydric systems;
- 3) to assess the variability of the W Iberian coastal upwelling during the Holocene; identify episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Results

Geochemical and dating studies carried out in estuarine and tidal marshes sediments revealed to be essential tools in the study of transitional and marine environments, providing indication about the marine/terrestrial origin of the deposited materials and allowing to recognise and evaluate changes occurred during the Holocene. During 2009, studies were mainly focused on: Minho/Coura and Douro estuaries. Results obtained in the study the radiocarbon dated sedimentary sequences reveal the influence of relative sea-level rise during the Holocene. The geochemical signatures of the drainage basins as well as the different natural (regional) background could also be identified. Metal contents on sediments showed to be a result of a wide variety of factors, including the lithology of the drainage basin and the sediment grain size distribution. In addition, preliminary studies on

the organic fraction of estuarine sediments, indicate that humic acids are usually heavy metal enriched, although they seem to preferentially accumulate specific metals, in particular Cu.

Hydrological aspects such as origin and magnitude of recharge, groundwater, dynamics, nitrate pollution, interaction between surface and groundwaters, and water quality issues have been one of the main goals, highlighted through the use of environmental isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}_{(\text{SO}_4)}$, $\delta^{18}\text{O}_{(\text{SO}_4)}$ and ^3H). During 2009 the collected gases in the CO_2 rich mineral waters N of Portugal reflect the pristine isotope composition of the C source. The measured $\delta^{13}\text{C}_{\text{CO}_2}$ values around -6‰ are consistent with a mixing between crustal marine plus metamorphic gases and mantle-derived volatiles. All the free gases measured fall very close to the field of the gas typical of a mantle origin. Release of deep-seated fluids having a mantle-derived component in a region without recent volcanic activity indicates that extensive neo-tectonic structures originating during the Alpine Orogeny are still active.



Radiocarbon dating is an important tool to set up chronological frameworks for the past environmental changes. As usual, it is of much use in several fields of our research. A new step in the study of the marine reservoir effect was implemented since 2008 in order to get reliable ΔR values for two coastal zones in the Atlantic Iberia badly sampled previously – Aveiro / mouth of the river Minho and Faro / mouth of river Guadiana. A significant number of ΔR values were determined for the second zone showing that this coastal region seems to have not been affected during the Holocene by an active upwelling. As the phenomenon is a wind-driven process, a nonexistent upwelling in the region probably means that westerlies were weak or not predominant during the Holocene.

Geochemical record of environmental changes in Portuguese coastal areaM.F. Araújo, C. Corredeira, M. Santos, S. Moreira¹, F. Fatela¹

The overall objectives of this current work are the recognition of recent environmental changes which have occurred at the main Portuguese estuaries and adjacent shelf, by using a multi-proxy geochemical approach to characterize and trace the history of the sedimentary record. Studies were mainly focused on estuarine sediments from Sado tidal marshes and from Guadiana downstream basin and adjacent shelf along the Northern Gulf of Cadiz. Elemental distribution patterns on Guadiana river sediments showed heavy metal enriched sediment in specific locations, most likely related to the long exploitation of mineral resources and other recent anthropogenic activities. However, metal contamination is much more significant at the shelf due to the particular run-off behaviour of Guadiana river system induced by specific hydrographic and climate characteristics that clearly induce a major sediment exportation towards the continental shelf. On Sado tidal marshes relations between foraminiferal assemblages distribution and respective sediment contents of Cr, Cu, Zn, Pb, Ca and organic matter, coarse fraction proportion and pH, were assessed using a detrended canonical correspondence analysis ordination technique (DCCA). Considering the values measured in Sado estuary these sediment features do not seem to directly affect the distribution of marsh foraminifera. The influence of such parameters is exceeded by the marine influence and time submersion. The adaptation of foraminiferal species to these main ecological factors of tidal marshes, seems to mask the effect of other ecological and anthropogenic factors.



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The marine reservoir effect – its quantification and variabilityA.M. Monge Soares, J.M. Matos Martins, J.M. Alveirinho Dias¹, A. Mederos Martín²

Following previous research (see 2007 and 2008 ITN Reports) concerning the upwelling phenomenon off the Iberian coast of the Gulf of Cadiz it was determined that ΔR , a parameter that quantifies the marine reservoir effect, takes positive values with a weighted mean of 65 ± 20 ¹⁴C yr (south-western Portuguese coast) or negative values with a weighted mean of -135 ± 20 ¹⁴C yr (Andalusian coast). Nevertheless, between 4400 BP and 4000 BP ΔR values are strongly positive. Positive ΔR values can be correlated with an active upwelling, while negative ΔR values correspond usually to a nonexistent upwelling. Those strongly positive values suggest a very strong upwelling existed in the entire region of the Gulf of Cadiz. This does not reflect wind-driven processes, but probably an eastward extension of the Azores Front, which is characterized by locally intense upwelling, along the Azores Current that penetrated into the Gulf of Cadiz. Concerning the coastal waters of Canary Islands, another region object of our research in the same field, ΔR values that were determined are consistent with the hydrodynamic system present off Canary Islands. The eastern islands (Fuerteventura and Lanzarote) are affected by the coastal upwelling regime prevailing over the north-western African continental shelf, conversely to what happens off the other islands of the archipelago, namely off Tenerife Island, where the upwelling effect does not prevail. For Fuerteventura Island ΔR takes a positive mean value of 150 ± 40 ¹⁴C yr, while for Tenerife Island a range of negative values was obtained resulting on a mean value of -10 ± 50 ¹⁴C yr.

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Groundwater resources assessment by anthropogenic and natural contamination sourcesP.M. Carreira, P.A. Fernandes, D. Nunes, L. Ribeiro¹, M.A. Marques da Silva², M.T.C. Melo²

The application of stable nitrogen isotopes (¹⁵N/¹⁴N ratios) offers a direct way to identify the pollutant sources in groundwater systems. In Aveiro region the isotope techniques were used to evaluate the aquifer vulnerability to nitrate contamination. Groundwater samples were collected from wells and springs for isotopic analysis ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from NO_3 and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from H_2O). Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contribution to nitrogen cycle in Aveiro ecosystem, based on the fact that the main sources of nitrate in the area have isotopic distinct $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ signatures.



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Hydrology in urban areas

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Environmental isotopes, such as $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}_{(\text{SO}_4)}$, $\delta^{18}\text{O}_{(\text{SO}_4)}$ and ^3H , are one of the tools that can be used to complement the conventional hydrogeological and geochemical approach to evaluate the impact of urban recharge in groundwater. A multidisciplinary approach, using hydrogeochemical, isotopic and ecotoxicological analyses, performed to assess the nature and suitability for use of Paranhos and Salgueiros spring waters (Porto city, NW Portugal). Based on the surface activities located along the course of the springs, twenty-three water samples were collected. All the samples have been analysed for major element concentrations. The isotopic techniques employed included $\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H . Standard acute bioassays with *Daphnia magna* were also performed. The hydrogeochemical analyses showed a nitrate and sulphate-enriched composition for these groundwaters, resulting mainly from urban drainage and sewer leakage. Concerning the ecotoxicological analyses, no significant mortality was observed in any of the tests performed. The results obtained in this study suggest that Porto urban groundwater could be suitable for irrigation uses.

Aquifers located in urban environments for the sustainable development and management of groundwater resources requires a precise assessment of its occurrence, availability and vulnerability to deterioration.

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Arid /semi arid zones hydrology

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Overexploitation of coastal aquifers and pollution are among the main problems related to groundwater resources assessment and management. Isotopic techniques combined with geochemistry and geophysical investigations, provided comprehensive information on groundwater recharge, as well as on the identification of salinization mechanisms (e.g. seawater intrusion, salt dissolution, and marine aerosols) of the groundwater systems, at Cap Bon Area, Northern Tunisia. In addition, at Essaouira Basin (Morocco) also a multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones.



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Gas geochemistry in CO₂-rich thermomineral waters a contribution to the geothermal potential evaluation and the seismic-volcanic hazard assessment

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Three sampling campaigns were performed in Azores archipelago in order to: i) characterize the chemical and isotopic composition of ground waters, fumaroles and gas emissions related with hydrothermal/geothermal systems and volcanologic/seismic settings. A continuous-flow GC/IRMS technique has been developed to analyse $\delta^{15}\text{N}$ values for molecular nitrogen in gas samples. The method was tested on magmatic and hydrothermal gases as well as on soil gas samples. The analysis of nitrogen isotope composition may be prone to atmospheric contamination mainly in samples with low N_2 concentration; based on the simultaneously determined $\text{N}_2/^{36}\text{Ar}$ ratios and assuming that ^{36}Ar content in crustal and mantle-derived fluids is negligible with respect to ^{36}Ar concentration in the atmosphere, for each sample, the degree of atmospheric contamination can be accurately evaluated.

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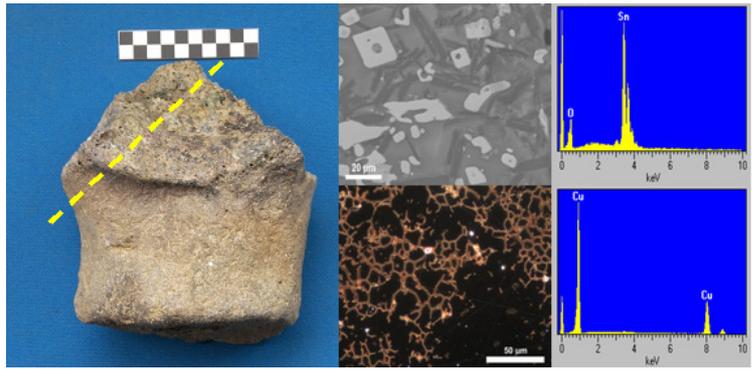
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Archaeometallurgy – Provenance, technology and use of metallic artefacts

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The archaeometallurgical research combines material characterization (involving different analytical techniques as EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) with archaeological evidences, to investigate the evolution of ancient metallurgical operations and artefact production in the Portuguese territory. Metallic artefacts from Castro dos Ratinhos and Entre Águas 5 indicate that the inland region of the Southern Portuguese territory exhibits a



metallurgy of binary bronzes with “suitable” tin contents (~8-12%) at least until the end of the 8th century BC. Conversely, later bronze artefacts from Palhais (7th-6th centuries BC) present lower tin contents, which are comparable with the coeval Mediterranean tradition, perhaps pointing out to imports from this region. Furthermore, the characterization of slagged remains from Entre Águas 5 seems to indicate that a cementation process was used when the introduction of bronze in Southern Portugal occurred. The use of hammering and annealing cycles was confirmed in the production of thin gold sheets from the Chalcolithic site of Perdigões, while the solid state diffusion process had been identified for joining components at Early Iron Age gold buttons from Outeiro da Cabeça. Regarding the Central and Northern Portuguese regions a large set of artefacts, fragments, scraps, and other metallurgical remains (recovered at various archaeological sites, as Castro de Nossa Senhora da Guia de Baiões, Castro de São Romão and Medronhal) have been analysed and results have been interpreted. Analyses showed that during the Late Bronze Age artefacts had generally very low Pb contents (Pb<1%) and that the tin content is regularly around 9-15%. The microstructural studies show that different thermo-mechanical treatments were performed in the artefacts, regarding their shape. Also, some metallurgical remains from Baiões/Santa Luzia cultural group point out to various metallurgical operations, involving smelting and recycling, performed inside the settlements.

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