

Environmental Analytical Chemistry

Maria de Fátima Araújo

The activities within the Environmental Analytical Chemistry Research Group involve the study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. Our main skills are in the fields of Instrumental Analytical Chemistry, Environmental Geochemistry, Isotope Hydrology, Oceanography, ^{14}C Dating and Archaeometallurgy.

Instrumental Analytical Chemistry is based on the implementation of Energy Dispersive X-Ray Fluorescence Spectrometry, Mass-Spectrometry for Light Isotopes, Elemental Analysis coupled to Mass Spectrometry, ^{14}C and ^3H Dating techniques. These are being utilised in studies involving quantitative elemental analysis, isotopic determinations and dating of environmental and archaeological samples.

During the current year we have reinforced our skills, by the implementation of new techniques and through new approved proposals. The installation of the ICP-MS, financed by the “*Programa Nacional de Re-Equipamento Científico*” is being initiated. Besides, the operation of the Elemental Analyser coupled to mass spectrometer unit allowed the development of new fields of study by isotopic techniques ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in nitrates and determination of organic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in sediment and water samples), leading to the expansion of different working domains in Isotope Hydrology and Isotope Geochemistry.

Environmental Geochemistry and Oceanographic research was developed under a multidisciplinary approach, including sedimentology, geochronology, absolute dating, meteorology and paleoecology. Research was focused in Sedimentary Geochemistry financed by several research projects, particularly the *CRIDA* project, to evaluate the consequences caused by the changes that occurred during the last centuries in the main Iberian river basins. Further studies have contributed to assess the stratigraphic succession of the sedimentary record of Minho estuary, lagoons and

interdune depressions of the SW coast to recognize the environmental changes occurred during the Late Quaternary. Moreover, studies concerning the marine reservoir effect off the W margin of Iberian Peninsula, based on ^{14}C dating of marine shells and charred wood or bones closely associated, have enabled the clarification of the variability of the coastal upwelling off Atlantic Iberia and the identification of episodes of abrupt shifts in oceanic circulation.

The expansion of the Isotope Hydrology domain was achieved by the approval and financial support of four new research projects in new fields of Isotope Hydrology, namely: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in CO_2 -rich Thermomineral Waters. These important environmental issues are being addressed in the exploitation and future development of regional water resources and the delimitation of protection areas.

The development of research projects have given support to political decisions, taking into account the sustainable regional development and the appropriate use of the water resources and management on the basis of several European and national directives, namely vulnerable regions and EC Water Framework. Research on pre-historical metallic artefacts has been enlarged by using other techniques (Metalography, Microfluorescence). Besides, a new project was approved by the FCT, in order to characterize the technological and social conditions of Late Bronze Age metal production, circulation and consumption in Central Portugal.

Due to the specificity of the available equipment and expertise within the group, technical services are provided to Universities and Public and Private Institutions.

Research Team

Researchers

M.F. ARAÚJO, Aux., Group Leader
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Students

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Collaborators

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Environmental Geochemistry – Elemental and Isotopical Research

M.F.Araújo, P. Carreira, A.M. Monge Soares, D. Burdloff, P.G. Fernandes, F. Moreno, C. Corredeira, D. Nunes, P. Valério, O. Margo, M. Correia, A. Amaro

Objectives

The improvement, promotion and coordinate research on Earth and Environmental Sciences using and implementing the following analytical techniques:

1. Multielemental characterization ($Z > 10$) using X-Ray Fluorescence spectrometry in solid samples;
2. Light isotope ($\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) determination in liquid and solid samples, including organic matter;
3. Radiocarbon dating;
4. Tritium dating of water samples.

The elemental, isotopic and dating techniques are being broadly applied to the understanding and management of natural coastal environments, particularly aquifers, rivers, lagoons, estuaries and continental shelf. Our main goals are:

- 1) to establish the evolutionary patterns of these environments since the Last Glacial Maximum; define geochemical signatures for different marine and terrestrial contributions; evaluate changes in sediment sources; delineate local fossil background values;
- 2) to determine the origin of different groundwater systems; 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; identify episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Results

A multidisciplinary study on the stratigraphic succession of Holocene sedimentary records of Minho estuary allowed the recognition and distinction of relevant palaeoenvironmental units belonging to the Late Quaternary. Geochemistry studies have revealed to be an important tool in the study of transitional environments, giving particular indications in the marine/terrigeneous origin of the deposited materials and allowing to recognise and evaluate some temporal changes occurred during the last 11000 years.

The assessment of terrigenous and marine supplies during the last centuries in muddy deposits on the middle shelf off the three largest Iberian river mouths (Douro, Tejo and Guadiana) was obtained by the study of large size sediment cores collected at similar depths at the Portuguese Continental Shelf. According to our data, 20 to 70 %, 50 to 80 % and 60 to 100 % of fine-sized organic matter is derived from terrestrial sources, respectively for Guadiana, Tagus and Douro.

Douro river load has the most significant contribution to the North-western sedimentary deposits, although an absence of heavy metal enrichment, suggests that it was depleted in metals during transport. The narrow shelf adjacent to Tagus and the local circulation pattern favours the deposition of sediments directly from the river discharge and an anthropogenic continental signature is measurable as a result of urban wastes and industrial effluents due to the presence of naval construction works and several industries settled in a high-populated region. Guadiana shelf sediments exhibit an important continental contribution. The main sources of pollution are the mineral wastes of mining activities resulting from the ore exploitation along the Iberian Pyrite Belt. Also, a gradually decreasing sedimentation rate (N towards S) is in agreement with the continental supply decrease with respect to those of marine source.

Besides, environmental isotope techniques applied to surface waters have identified and characterised sources of pollution: natural, industrial, agricultural, and domestic. Isotope techniques have allowed recognising incipient pollution, providing an early warning although the chemical and biological indicators did not point to any mixture of systems or pollutants contribution (Sado/Sines basins). Agricultural practices and high industrial areas with over exploitation of the systems were identified as sources of pollution to the environment: sediment and hydrological domains (Porto region and Sado basin).



Radiocarbon dating has been used as a tool to set up chronological frameworks for the past environmental changes identified in our research. Besides this, several pairs of samples of marine shells and charred wood or bones closely associated collected at several Iberian archaeological sites, representing different periods of time in the Holocene, were radiocarbon dated and the regional reservoir effect, ΔR , was calculated. The results enable not only a clarification of the variability of the coastal upwelling off Atlantic Iberia but also the identification of episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Geochemistry of fine sediments deposited along the Portuguese continental shelf*M. Fátima Araújo, C. Corredeira, A. Gouveia¹*

The geochemical characterisation of fine sediments collected along the Portuguese Continental Shelf and adjacent to main Iberian river basins (Douro, Tagus and Guadiana), was used to assess the influence of the river sediment load into the coastal marine environment. Douro is the main source of the shelf fine sediments, although sediments do not present signals of anthropogenic contamination. Probably, sediments pass through many remobilisation and mixing processes during a long transport until being deposited in the shelf. Since Douro River seems to have a substantial contribution to the sedimentary deposit located in the middle of the adjacent shelf, the absence of heavy metal enrichment suggests their depletion by geochemical processes, during the long suspension time before deposition. In case of Tagus, the narrow shelf and the local circulation pattern favour the deposition of sediments directly from the river discharge and anthropogenic contamination is observed at the shelf, probably as a result of urban wastes and industrial effluents due to the presence of naval construction works and several industries settled in a high-populated region. Southwards, at Guadiana, shelf sediments present an important continental contribution. The main sources of pollution are probably the mineral wastes of mining activities resulting from the ore exploitation along the Iberian Pyrite Belt. Contaminated sediments have been transported, probably by Guadiana River and the anthropogenic signatures at the shelf sediments seem to be able to last for several centuries.

¹ Cultural Heritage and Sciences group, ITN.

Organic carbon sources to the northern and southwestern Portuguese shelf sediments*M. Fátima Araújo, D. Burdloff, J-M. Jouanneau¹*

In this study, we provide an elemental (organic carbon and total nitrogen) and isotopic ($\delta^{13}\text{C}$) record of fine-sized ($<63\mu\text{m}$) particulate organic matter in Portuguese continental shelf sediments. Studies were carried out in large size sediment cores ($\sim 3\text{ m}$) collected at similar depths. The aim of the work is the assessment of terrigenous and marine supplies in muddy deposits on the middle shelf off the three largest Iberian river mouths during the last centuries. The first-order linear correlations displayed between $\delta^{13}\text{C}$ values and OC/TN ratios for each core is usually interpreted as a mixing trend between terrestrial and marine sources of organic matter, providing depleted and enriched isotope ratios, respectively. Assuming constant $\delta^{13}\text{C}$ end-member values for marine (-20‰) and terrestrial (-27‰) fine-sized organic matter supply along each core, we can make a semi quantitative estimation of the continental contribution. According to our data, 20 to 70 %, 50 to 80 % and 60 to 100 % of fine-sized organic matter is derived from terrestrial sources, respectively in cores CRIDA 05, MD 992332 and KSGX 57. Thus, the gradually increasing trend of sedimentation rate: $0.12\text{-}0.13\text{ cm.yr}^{-1}$, $0.20\text{-}0.24\text{ cm.yr}^{-1}$ and 0.45 cm.yr^{-1} , respectively, goes with an increase of supplies coming from continent with respect to those of marine source. The variability on the sedimentary organic matter supply results from differences in the transported sediment load, hydrodynamism and morphological environment along the continental shelf.

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Palaeoenvironmental geochemical patterns in the Holocene evolution of Minho estuary*M. Fátima Araújo, A. Lobato, A. Cruces, T. Drago¹*

A multidisciplinary study on the stratigraphic succession of Holocene sedimentary records of Minho estuary permitted the recognition of relevant palaeoenvironmental units. The cores reached the regional substrate rock (granite) and the sedimentological infill begins with a gravelly basal unit (Unit I), constituted essentially by quartzite and round gravels and particulate OM that correspond to a fluvial environment ($11380\pm 60\text{BP}$). After $8090\pm 60\text{BP}$, there are variations in Al and Si related to alternate layers of sandy and muddy sediments. These units have higher concentrations Ca, Sr, Cl and Br suggesting a major marine influence. In unit III this marine signal decreases and in core 1 at the top of the unit (Unit IIIB) a sudden impoverishment in these “marine” elements is observed. The topmost unit (Unit IV) is constituted by a monotonous sequence of sands (high Si and low Al contents) disturbed by a singular event: a muddy organic layer with fragments of charcoal, low contents of Si, K and Rb (terrigenous), high contents of S, Cl and Br. Geochemistry contribution is an important tool in the study of transitional environments giving particular indications in the marine/terrigenous origin of the deposited materials and allowing to evaluate some temporal changes occurred during the last 11000 years.

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Groundwater resources as indicators and archives of palaeoclimatic changes

P.M. Carreira, P.G. Fernandes, J.M. Marques¹, F. Monteiro Santos², M.O. Silva³, D. Nunes

The regional geomorphology of the region seems to favour a conceptual circulation model for Caldas de Monção thermomineral system where the recharge area is located at south of Caldas de Monção, up hill between 300 and 600 m a.s.l (based on $\delta^{18}\text{O}$ values). The underground flow paths are associated with the NNE-SSW fault systems and their NW-SE associated systems, issuing these waters when appropriate conditions are found. The geophysical models suggest that those tectonic systems may be deep and filled with mineralized water. The low ^{14}C content (between 4.82 ± 1.00 pmc and 7.43 ± 0.34 pmc) of Caldas de Monção thermomineral waters (TDIC) together with the absence of ^3H support the hypothesis of a long circulation path through the subsurface rocks. This hypothesis is corroborated by the minimum depth reached by the Caldas de Monção thermomineral water system (2.2 km) estimated by the geothermometric approach. The $\delta^{13}\text{C}$ determinations give values in the range of -7 to -6 ‰, indicating a “complex” origin for the CO_2 in these waters (mixture between atmospheric CO_2 , decay of organic matter and upper mantle CO_2). Geophysical, isotopic and geochemical studies performed at Caldas de Monção region have increase knowledge on the interaction between local shallow cold groundwater systems and the low-temperature geothermal waters. This important environmental issue should be addressed either in the exploitation and future development of these low-temperature geothermal resources or/and in the delimitation of well-head protection areas.

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High mountain areas in catchment water resources

P.M. Carreira, D. Nunes, J.M. Marques¹, J. Espinha Marques², H. Chaminé³, P. Fonseca⁴

Mountainous areas are usually the source of most of the larger river systems all over the world, and represent some of the “black boxes” in the hydrological cycle. The seasonality and spatial variability of local groundwaters and the complex role of soils, geomorphology, geology, climate, land use and Human activities on the hydrology of mountain areas are rather particular. Special emphasis is dedicated on high mountains and their role and impact on surface water/groundwater interaction at Serra da Estrela region - Central Portugal in order to i) increase knowledge on recharge and discharge processes in this high mountain area and ii) assess snow as a source of thermal water resources, with the aid of isotopic techniques.

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National network for isotopes in precipitation

P.M. Carreira, M. Fátima Araújo, D. Nunes, P. Valério, M. Correia, L. Gourcy¹

Interpretation of the isotopic composition in terrestrial water (groundwater and superficial waters) requires knowledge about the meteoric water that feeds them: rain and snow. Their isotopic composition is quite variable in time and space, and depends on climate, geography, nuclear fallout and other factors. In the follow up of these factors for more than a decade we are participating in the Global Network for Isotopes in Precipitation (GNIP) in a close collaboration with the Isotope Hydrology Section of the IAEA. The work carried out aims to provide basic isotope data (^2H , ^3H and ^{18}O) and to establish temporal and spatial variations for hydrological investigations. The large depletion in the isotopic composition in vapour and rain events are associated to the depressions over the Atlantic (Mid North Atlantic) or over the British Islands. Regional variations in the ^3H between littoral and interior stations are probably a result of the oceanic dilution of the ^3H in the atmospheric water vapour. Isotopic results are used in international hydrogeological and climatologic studies, being compiled in the IAEA Data Base and disseminated via IAEA publications (www.iaea.org/programs/ri/gnip/gnipmain.htm).

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Hydrology in urban areas

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One of the most crucial water-related research issues at the turn of the millennium “Water and Society” with special emphasis dedicated on “Land habitat hydrology in urban areas” and their role and environmental impact on surface water/groundwater recharge and circulation. In urban regions the application of environmental isotope geochemistry includes the assessment of recharge from leaking water mains and sewers, from in situ sanitation, from waste water and from influent surface watercourses. The isotopic techniques most commonly employed are ^2H and ^{18}O in water and ^{15}N and ^{18}O in nitrate (in liquid and solid samples), in combination with major and trace hydrogeochemical indicators. Thus, one question may arise: what is the relative importance of these several potential sources of recharge to assess the quality/quantity based in hydrogeochemical, isotopic and ecotoxicological parameters and related them with the underground circulation with the main goal to provide information to support water management and land use planning. A better understanding of urban hydrological cycle will contribute to a proactive management of urban groundwater resources.

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Groundwater resources assessment by anthropogenic and natural contamination sources

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The work is focused on the study of the quality of groundwater sources for Human supply and groundwater resource protection and management, through the identification and quantification of pollution sources traced by environmental isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^3H). Isotope techniques can assess the vulnerability of groundwater to pollution from the surface by determining how rapidly it moves and where it is being recharged. Surface pollution can then be determined, e.g. natural, industrial, agricultural or domestic. Isotope techniques can also identify incipient pollution, providing an early warning before chemical or biological indicators. Agricultural practices and high industrial areas must be seen as new inputs of pollution in the environment (sediment and hydrological domains) through demographic density increase and growing of organic and toxic contamination. In the particular case of nitrogen isotopes, this tool can offer a direct mean of source identification. The relative contribution of these two sources to groundwater or surface water can be estimated by mass balance. The analysis of $\delta^{18}\text{O}$ of nitrate in conjunction with $\delta^{15}\text{N}$ improves the ability to trace nitrate sources and cycling. This area of work will give scientific proves to support political decisions, taking into account the sustainable development of the region and the appropriate use of Nitrogen fertilizers on the basis of several European and national directives, namely the establishment of vulnerable regions.

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Gas Geochemistry in CO₂-rich Thermomineral Waters

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In Portuguese mainland, the greatest number of hot (~76 °C) and cold (17 °C) CO₂-rich thermomineral waters are situated in the Northern part of the country, occurring along or near major faults. Such faults should be considered important targets for geothermal exploration in Portugal. A new geochemical approach on the study of the nature of these thermomineral waters will be focused on the geochemistry of the gas associated with those waters. Gas isotopes will give new insights on the sources of gas constituents (crustal rocks, mantle, etc.) and reservoir temperatures. Chemical and isotopic water signatures, together with the gas characteristics, will be used to confirm and/or update the preliminary conceptual models of the local and regional fluid circulation, producing new data on the geothermal potential of the northern part of Portuguese mainland. Trace elements in waters will expand the possibilities of quantitative interpretation of specific mineral-solution equilibrium conditions.

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Arid /semi arid zones hydrology

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A multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones and environmental / climatic changes at Santiago Island (Cabo Verde). The combination of these different methodologies have been applied in this island with the goal of monitoring fresh-water – salt water interface. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data will be used to identify and characterize the recharge areas and also to quantify the percentage of mixture between seawater and fresh water. Besides, tritium measurements will allow obtaining the mean residence time of the water system. ^3H and stable isotope data, together with the accumulation of chloride in the unsaturated zone, can be applied (under piston flow conditions) to provide a record of past recharge and help to reconstruct the antecedent climatic conditions. The obtained data may act as an additional climatic archive of the region. It is important to have in mind that the hydrological balance shows that the rainfall at the islands is distributed in the following medium periods: 67 % is evaporated, 20 % is drained away as superficial drainage and only 13 % recharges the aquifers.

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Archaeometallurgy – Provenance, technology and use of metallic artefacts

M. Fátima Araújo, P. Valério, E. Figueiredo, A.M.M. Soares, J.C. Senna-Martinez¹, A. Ávila de Melo²

This field combines analytical and archaeological studies concerning the metallurgical activities of the Copper and Bronze Ages in the Portuguese territory. The relationship between archaeometallurgy research with historical, cultural and economical contexts will ultimately enhance our knowledge of those prehistoric societies. The research conducted in Late Bronze Age sites from *Beira Alta* (*Castro da Senhora da Guia*, *Castro de Santa Luzia*, *Castro do Outeiro dos Castelos de Beijós*, *Canedotes* e *Castro da Senhora das Necessidades*) establishes the preponderance of artefacts with an Atlantic typology although constituted by copper-tin alloys instead of the typical Atlantic leaded bronzes. The latter alloy is particularly scarce in this region, probably due to the fact that this is an area exceptionally rich in tin ores, namely cassiterite (SnO_2). The absence of leaded bronze artefacts in Late Bronze Age *Beira Alta* is also a proof of the reduced exchange system of metallic commodities with the Atlantic world. Contacts with Oriental Mediterranean Cultures are also established by the presence of a few characteristic copper-tin artefacts, namely from the *Castro da Senhora da Guia* (*Baiões*).

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Non invasive elemental characterization of pre-historic copper-based artefacts

P. Valério, M. Fátima Araújo, A.M.M. Soares, I. Silva

Research concerning Cultural Heritage items requires the use of non invasive techniques in order to protect this significant part of our collective History. Energy Dispersive X-Ray Fluorescence spectrometry is therefore being used in the Archaeometallurgy field. Our work involves the elemental characterization of copper-based artefacts and related materials (e.g. crucibles, slags, etc.) from the Portuguese territory dated from the end of the IV millennium BC until the first half of I millennium BC. Several metallic artefacts from *Castro de Palheiros* (*Vila Real*) were analysed in order to establish the type of alloy, as well as its major impurities. Chalcolithic materials could be divided into copper with low and high arsenic content, as well as copper with different impurities of tin. Artefacts from the Iron Age occupation of the site are made from copper-tin alloys with low and high lead contents. In a different study, Copper Age materials from *Porto das Carretas* (*Évora*) provide significant results regarding the arsenical copper metallurgy of this period – artefacts are made from copper with high arsenic content, whereas analysed ore fragments from the same period, are constituted by copper without any traces of arsenic. The slag composition from *Castelo Velho de Safara* (*Moura*) point out to the local smelting of lead ores.

The reservoir effect of coastal waters off the western margin of the Iberian Peninsula*A.M.M. Soares, J.A. Alveirinho Dias¹*

Marine shells have not been used as extensively as charcoal or bone samples in absolute chronologies due to the unknown variability of past oceanographic conditions. At present, along the western coasts of Europe active upwelling is restricted to the western margin of the Iberian Peninsula. ¹⁴C content of marine shells can be used a proxy of the upwelling intensity. However, present and past oceanographic conditions must be known in order to use radiocarbon dating of marine shells accurately. Sample pairs (marine shell – charred wood or bone) collected at the same stratigraphic level (and closely associated) from several western Iberian archaeological sites, representing different periods of time, were dated and the regional reservoir effect (ΔR) calculated: 940 ± 50 to -160 ± 40 ¹⁴C years. This considerable variation suggests a significant fluctuation in the strength of the Iberian coastal upwelling, which may be the result of fluctuations in the latitudinal migration of the subtropical front or of the North Atlantic Oscillation – the strength of northerly and northwesterly winds depends on these factors – or on the summer insolation – higher summer insolation results in increased sea breezes that strengthen the northerly component of the wind. Those data also enable, not only a clarification of the eventual variability of the coastal upwelling off Atlantic Iberia, but also the identification of episodes of abrupt shifts in oceanic circulation, probably coupled with sudden climatic changes. On the other hand, the viability of using radiocarbon dating of marine shells in order to get reliable chronologies was consequently tested out in this research.

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