

# Environmental Analytical Chemistry

*Maria de Fátima Araújo*

The “Environmental Analytical Chemistry” research group is mainly dedicated to the study of the distribution and behaviour of chemical elements and light isotopes in Environmental Sciences. The main analytical facilities available within the EAC group are the Energy-Dispersive X-Ray Fluorescence Spectrometer, the Tritium Dating Unit and the Mass Spectrometers for Light Isotopes. These methods, which allow the multielemental analyses and the light isotopic determinations, combined with dating techniques are being primarily directed into the *Environmental and Marine Geochemistry and Isotope Hydrology* areas.

The research developed in Environmental and Marine Geochemistry is being mostly directed to the **Biogeochemical Cycles of Elements and Light Isotopes in river basins and coastal zones**. Our main goal is the understanding of the consequences of the modification of the sediment load carried by large rivers to estuaries and to the continental shelf due to diverse anthropogenic activities. These alterations, caused by a wide range of factors, in a seasonal and temporal scale, are responsible for important environmental alterations in the coastal area.

The isotope data obtained in the framework of the national network for isotopes in precipitation provides important information for **hydrological investigations relevant for water resources management and development**. Research studies in Isotope Hydrology aim to contribute to a better understanding of the dynamic evolution response in time of aquifer systems. The flow velocities and the chemical evolution of the groundwater give valuable information about the aquifers response to Human influences and to the climatic evolution.

During the current year, the main goals within the group were the development and strengthen of the research on the above mentioned areas, which has included:

1. The preparation of several project proposals to obtain financial support to reinforce our activities. Applications were submitted to the research programmes of the National Science Foundation (in Marine Sciences and Technologies and Earth,

Sea and Air Sciences) and IAEA (Isotope Hydrology).

2. The upgrade of some Laboratories and Equipment.

The Portuguese Science Foundation has approved two projects that will start in 2001:

1. A large **multidisciplinary project in the Marine Sciences and Technologies Program** will be coordinated, by this group. The project is focused on the **consequences caused by the changes in runoff and sediment load during the last century in the main Iberian river basins**. Besides, being the *Principal Research Unit*, the ITN group will focus on the studies of *Sedimentary Geochemistry*.
2. The second project “**Aquifers as archives of palaeoclimate and indicators of future climatic scenarios – Sado/Sines system and Bairrada carsic aquifer**” is dedicated to the study of groundwater resources, in two different hydrogeological systems in Portugal. This group will be responsible by the *Isotope Hydrology* studies.

These financed projects will permit to reinforce the research team by new positions of research and Post-Doctoral students. However, the maintenance and development of these activities are largely dependent on the increase of the permanent staff within the research group.

Another project, a Coordinated Research Program (CRP) “**The Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate**” financed by the IAEA was initiated by the end of the year. The main objective of the CRP is to acquire a climate and hydrogeological data set to achieve a better understanding of the Mediterranean atmospheric circulation.

Besides, due to the available equipment, analytical techniques and expertise within the EAC group (multielemental, isotopic and dating) technical services are provided to Universities, Institutes and Public and Private Institutions.

## Research Team

### Researchers

- Maria de Fátima Araújo (Aux. Researcher) **(Group leader)**
- Paula Carreira (Aux. Researcher) Isotope Hydrologist, Hydrogeologist

### Technical personnel

- Pedro Valério (Chemical Engineer, TS) X-Ray Fluorescence Spectrometry, Tritium Dating
- Dina Nunes (Chemist, TS) Mass Spectrometry for Light Isotopes
- Maria Manuela Correia (Laboratory, Technician)

### Students

- Paula Galego Fernandes (**PhD** student - Hydrogeology)
- Ana Catarina Correadeira (**MSc** student – Marine Resources)
- Teresa Barbosa (Chemist, Research student)
- Ana Cristina Tavares Teixeira (**Last year BSc** student – Chemistry)
- Ana Sofia da Conceição (**Last year BSc** student – Chemistry)
- Susana Alves de Sousa e Silva Gomes (**Last year BSc** student – Chemistry)

## Publications

Journals:	2	and 4 in press
Proceedings:	6	
Conf. Communications:	2	
Book Chapters:	1	

## Funding

	×10 <sup>3</sup> PTE
<b>Research Projects<sup>(a)</sup>:</b>	24 297
<b>Services:</b>	7237
<b>TOTAL:</b>	<b>31 534</b>

(a)

	×10 <sup>3</sup> PTE
- Environmental and marine studies using nuclear related techniques (IAEA TC/POR/7/003) <sup>(1)</sup> ITN/Co-ordinator: <b>M. Fátima Araújo</b>	23 000
- Ocean Margin Exchange – OMEX, European Project ~36 partners (MAS3-CT97-0076) (1998-2000) (ITN – 2 000 × 10 <sup>3</sup> PTE) ITN/Co-ordinator: <b>M. Fátima Araújo</b> .....	500
- Geochemical Anthropogenic Signatures on the Fine Sediments at the Northwestern Continental Portuguese Margin (Bilateral Collaboration ITN/Bordeaux Univ.) (225 × 10 <sup>3</sup> PTE) ITN/Co-ordinator: <b>M.Fátima Araújo</b> .....	225
- The Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate (IAEA/CRP/POR/11368RO) (572 × 10 <sup>3</sup> PTE) ITN/Co-ordinator: <b>Paula Carreira Paquete</b> .....	572
- Environmental Isotopes and Noble Gas Palaeothermometers in the Study of Climatic Change Encoded in the Palaeowaters of the Aveiro Aquifer (PRAXIS/2/2.1/CTA/321/94) (1996-2000) (Total - 10 <sup>6</sup> PTE; ITN - 5 610 × 10 <sup>3</sup> PTE) ITN/Co-ordinator: <b>Paula Carreira Paquete</b> , Partners: Univ. Aveiro, IST .....	—

<sup>(1)</sup> Technical Co-Operation Project. The financial support includes the purchase/repairing of equipment, training and expert missions.

## Environmental and Marine Geochemistry

M.F. Araújo, J.-M. Jouanneau<sup>1</sup>, P. Valério, T. Barbosa, Â. Gouveia<sup>2</sup>, P. Carreira, O. Weber<sup>1</sup>, J.M.A. Dias<sup>3</sup>, A. Oliveira<sup>4</sup>, A. Rodrigues<sup>4</sup>, A.C. Corredeira, F. Rocha<sup>5</sup>

### Objectives

Studies in Environmental and Marine Geochemistry are being mostly directed to the Biogeochemical Cycles in sediments in Portuguese river basins and coastal zones. In this scope, we aim to contribute to the understanding of the modification of the sediment load carried by rivers to estuaries and to the continental shelf due to a range of anthropogenic activities (e.g. damming, mining, urbanisation). The large river basins of the West Iberian margin are excellent examples for these modifications responsible by important environmental alterations. Several projects were run within the group for the last ten years and the origin and dispersal of fine sediments at the shelf could be evaluated by multidisciplinary approaches including chemical, sedimentological, and dating studies.

### Results

A geochemical study on the major, minor and trace elements has been performed all over the sediment cover, with particular relevance at fine deposits and at the adjacent estuaries (Minho, Douro and Tagus). Chemical and mineralogical composition of superficial sediments collected all over the northern Portuguese shelf and from the Minho and Douro river basins were performed [1]. In the case of the Tagus, it was demonstrated that offshore the estuary in the marine environment, the anthropogenic and lithological influences of the river basin are clearly identified along the sedimentary deposit [2]. Statistical evaluation of the shelf sediment database allows the identification of elements with similar behaviour and to distinguish different sediment types along the shelf and evaluate their origin [3]. Downcore profiles on the chemical composition of dated fine sediments could not identify any recent records of Human activities. To assess the influence of those river basins in the fine sedimentary formations, elemental distribution patterns of selected sediments collected at these formations were compared with estuarine fine sediments. Several approaches were applied, namely: normalisation to Al of groups of lithogenic and anthropogenic elements and the shale normalised REE distributions. Results on the lithogenic and rare earth elements of fine sediments put in evidence similarities between the Douro sediment composition and the Douro and also Galicia sedimentary deposits. However, none of the Douro estuarine heavy metal contamination is detected in the shelf, probably due the complex physico-chemical processes namely: resuspension, complexation and bioturbation occurring during transport [3].

In general it could be concluded that, sediments provided by the Portuguese River basins, mainly the Douro and Minho is distributed throughout the shelf area [4]. The main mechanism of sediment input are floods. Sediment provenient from the Galician hinterland is trapped in the Galician Rías. The sediments deposited on the shelf are frequently remobilised by waves and storms. Fine-grained sediments are transported northwards by poleward flowing bottom currents while still in suspension. They are deposited in the Douro and Galicia mud patches, which lie in areas that act as sediment traps. Transport by the northward flowing bottom currents explains why both Mud Patches lie to the North of their main sediment sources [5].

### Published (or in press) work

- [1] Araújo, M.F., Marques, R., Rocha, F., Caracterização química e mineralógica da fracção silto-argilosa de sedimentos dos rios Minho, Lima, Cávado, Ave e Douro. 3<sup>o</sup> *Simpósio sobre a Margem Ibérica Atlântica*. Faro, 2000, pp.97-98.
- [2] Valério P., Barbosa, T., Araújo, M.F., Jouanneau, J.-M., A Geochemical comparison of the sedimentary deposits off the major Iberian rivers: Tagus and Douro (Portugal). 3<sup>o</sup> *Simpósio sobre a Margem Ibérica Atlântica*. Faro, 2000, pp.233-234.
- [3] Araújo, M.F., Jouanneau, J.-M., Valério, P., Barbosa, T., Gouveia, A., Weber, O., Oliveira, A., Rodrigues, A., Dias, J.M.A., Geochemical Tracers of Northern Portuguese Estuarine Sediments on the Shelf. *Progress in Oceanography*, in press.
- [4] Dias, J.M.A., Jouanneau, J.-M., Weber, O., Araújo, M.F., Drago, T., Garcia, C., Oliveira, A., Rodrigues, A., Vitorino, Processos sedimentares recentes na plataforma Norte Ibérica. 3<sup>o</sup> *Simpósio sobre a Margem Ibérica Atlântica*. Faro, 2000, pp. 273-274.
- [5] Dias, J.M.A., Jouanneau, J.-M., Araújo, M.F., Drago, T., Garcia, C., Gonzalez, R., Oliveira, A., Rodrigues, A., Vitorino, J., Weber, O., Present Day Sedimentary Processes on the Northern Iberian Shelf. *Progress in Oceanography*, in press.

### Further Work

Some work is still going on mainly concerning the sedimentary geochemistry of the Minho/Galician shelf. However, in this area the research work for the next years will be developed under the following research contract to start in 2001 "Consequences of River Discharge Modifications on Coastal Zone and Continental Shelf".

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<sup>4</sup> Instituto Hidrográfico, Rua das Trinas 49, 1249-093 Lisboa, Portugal.

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## Isotope Hydrology

P.M. Carreira, M.A. Marques da Silva<sup>1</sup>, T. Condesso de Melo<sup>1</sup>, L. Aráguas- Aráguas<sup>2</sup>, L. Gourcy<sup>2</sup>, M.F. Araújo, M. Stute<sup>3</sup>, D. Nunes, P. Valério, P.G. Fernandes, S. Gomes

### Objectives

This research area aims to contribute to a better understanding of the dynamic evolution response in time of aquifer systems, using chemical, physical and isotopic determinations. The apparent flow velocities and the chemical evolution of the groundwater give valuable information about the aquifers response to Human influences (pollution, over exploitation, etc.) and to the climatic evolution (palaeohydrology). The several projects carried out within the group for the last twelve years have allowed giving answer to relevant scientific issues, such as the identification of the salts contamination sources in groundwater and the reconstruction of the palaeoclimatic environments.

The isotope data obtained in the framework of the national network for isotopes in precipitation provides important information for hydrological investigations relevant for water resources inventory, planning and development.

During 2000, the project "Environmental Isotopes and Noble Gas Palaeothermometers in the Study of Climatic Change Encoded in Palaeowaters of Aveiro Aquifer" was concluded. The CRP/IAEA project "The Isotopic Composition of Precipitation in the Mediterranean basin in Relation to Air Circulation Patterns and Climate" was initiated by end of the year.

<sup>1</sup>University of Aveiro – Department of Earth Sciences;

<sup>2</sup>IAEA – Isotope Hydrology Section;

<sup>3</sup>University of Columbia – Lamont-Doherty Earth Observatory.

### a) - Palaeowaters of the Aveiro aquifer

P.M. Carreira, M.A. Marques da Silva<sup>1</sup>, T. Condesso de Melo<sup>1</sup>,  
L. Aráguas- Aráguas<sup>2</sup>, M. Stute<sup>3</sup>, D. Nunes

The main goal of this work was the reconstruction of the palaeoclimatic environment in the Aveiro region, until *c.* 30 000 years ago through the isotopic record within the groundwater of the Quaternary and Cretaceous aquifer.

The carbon-14 determinations carried out in groundwater samples in the Cretaceous aquifer indicate apparent ages that range from 2 000 to 30 000 years BP. The <sup>14</sup>C results in TDIC measured in groundwater samples of the Cretaceous aquifer also reveal an interesting pattern: between km 5 and 8 the <sup>14</sup>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 <sup>14</sup>C remains almost constant, indicating a much higher apparent flow velocity of groundwater. This flushing was most probably induced by the decrease in the sea level by about 100 m during the last glacial period about 18 ka BP.

The apparent carbon-14 ages of groundwater (<sup>13</sup>C corrections and assuming initial radiocarbon content equal to 100 pmc), between 8 and 16 Km from the recharge area, cluster around 18 ka BP pointing to glacial origin of this water. The <sup>14</sup>C trend for older waters, with apparent <sup>14</sup>C ages between 22 and 35 ka

BP, suggests a flow regime similar to that prevailing during Holocene.

The increase of ages from the recharge area to the line coast observed in Aveiro Cretaceous aquifer is accompanied also by enrichment in heavy isotopes (<sup>18</sup>O and <sup>2</sup>H) in the groundwater samples. Also, these samples are enriched in heavy isotopes when compared with modern precipitation in the region. This stable isotope enrichment (<sup>18</sup>O and <sup>2</sup>H) found in Aveiro palaeowaters is unique on the European continent: groundwater from UK and from western and central Europe, that were recharged during the last glaciation, like the Aveiro aquifer, show a depletion in both <sup>18</sup>O and <sup>2</sup>H. One possible explanation of this phenomenon is that coastal aquifers respond more to the changes in the isotopic composition of the ocean than to changes in surface air temperature induced by fluctuations of climate.

Noble gas determinations (He, Ne, Ar, Kr and Xe) as a palaeoclimatic indicators were carried out on these waters. The palaeotemperature results (groundwater with Pliocene ages) give an average temperature of 5°C lower than the water samples collected either in the shallow system or in the deep aquifer zone with Holocene ages [1].

**Book Chapter**

- [1] Condesso de Melo, M.T.; Carreira, P.M.M., Marques da Silva, M.A., Evolution of the Aveiro Cretaceous aquifer (NW Portugal) during the Late Pleistocene and present day: evidence from chemical and isotopic data, *in* Paleowaters in Europe, W.M. Edmunds and C.J. Milne (eds.), Geological Society, London, Special Publications, in press.

**Further Work**

This work was developed in the framework of a research project that was concluded in March 2000. However, some fieldwork is still running in the area of most intense exploitation of the aquifer. It is plausible that intensive pumping introduces additional mixing in this sector of the aquifer, leading to apparent high flow velocities derived from the radiocarbon data.

<sup>1</sup>University of Aveiro – Department of Earth Sciences;

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**b) National Network for Isotopes in Precipitation**

P.M. Carreira, L. Gourcy<sup>1</sup>, M.F. Araújo, D. Nunes, P. Valério, S. Gomes

Portugal through ITN/Environmental Analytical Chemistry Group has been participating in the IAEA/WMO (International Atomic Energy Agency/World Meteorological Organisation) in the *Global Network for Isotopes in Precipitation* (GNIP). The GNIP main objective is the systematic collection of basic data on isotope content of precipitation on a global scale. The work developed aims to provide basic isotope data for hydrological investigations, by determining the temporal and spatial variations of environmental isotopes (oxygen-18, deuterium and tritium). The data can be used as tracers of the isotopic composition of past and present precipitation, giving an opportunity for climate and water studies, all this information are very relevant for water resources inventory, planning and development.

Since 1988 the ITN team at the Chemistry Sector has been responsible for the monthly isotopic measurements (<sup>2</sup>H, <sup>3</sup>H and <sup>18</sup>O) in precipitation samples collected in five meteorological stations all over Portugal (Oporto, Penhas Douradas, Portalegre,

Faro and Funchal-Madeira). Results show that the signatures of isotopes in precipitation are not static. They respond to both, synoptic climatology and global climate change.

The observed isotope distribution in space and time can be related to a number of environmental parameters, which characterise not only the source region but also a given sampling site. Seasonality, amount of precipitation, altitude dependence, continentality, the role of local temperature, together with the source specific fractionation between <sup>18</sup>O and <sup>2</sup>H: all these effects can contribute to the isotope content of precipitation.

The use of stable isotopes in palaeoclimatic studies has mainly derived from their relation to atmospheric temperature.

Isotopic results are compiled and gathered in the IAEA Data Base and disseminated via IAEA publications ([www.iaea.org/programs/ri/gnip/gnipmain.htm](http://www.iaea.org/programs/ri/gnip/gnipmain.htm)) to be used in hydrogeological and climatological studies.

<sup>1</sup>IAEA – Isotope Hydrology Section.

## Services

The facilities available and the expertise within the members of the research team are often requested to provide services to Universities, Laboratories and Public and Private Institutions, either as analytical results or as consultants. The main analytical requests involve the following facilities:

- Energy-dispersive X-ray fluorescence spectrometry, for multielemental (e.g. quality control, environmental monitoring) and non-destructive analysis (e.g. archaeometry).
- Mass spectrometry for light isotope determinations in water samples and sediments ( $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$ ).
- $^3\text{H}$  determination in water samples.