Environmental Analytical Chemistry

Maria de Fátima Araújo

The research within the Environmental Analytical Chemistry Group has been dedicated to the study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. In the last years the main goal of the Group, constituted by chemists, geologists and biologists, has been the reinforcement of the analytical capabilities and enlargement of the expertise towards a strengthening on the Environmental and Analytical fields. The most important available equipments are the Energy-Dispersive X-Ray Fluorescence Spectrometer, Tritium Dating Unit and Mass Spectrometers for Light Isotopes. During this year, an Elemental Analyser coupled to a Mass Spectrometer was installed, commencing the investigation on Isotope Biogeochemistry of Organic Carbon and Nitrogen.

The work was carried out in the framework of projects previously approved and externally financed, run in collaboration with other research teams and different National and International Institutions.

During the current year, our research work was focused on the following areas:

- Environmental Geochemistry
- Isotope Hydrology
- Palaeoenvironments
- Archaeometallurgy

The major domain of research has been in the Environmental Geochemistry, focused in the Sedimentary Geochemistry and Isotope Hydrology fields:

1. Sedimentary Geochemistry – Particularly in the framework of the project "Consequences of River Discharge Modifications on Coastal Zone and Continental Shelf (CRIDA)", aiming at the evaluation of the consequences caused by the changes that occurred during the last decades in the main Iberian river basins. Studies on multielemental and isotopical composition, as well as geochronology and dating, combined with meteorological, climatic, oceanographic, sedimentological and historical aspects are being applied to understand the evolution of those basins and to assess the continental influence in the coastal marine environment. The set of obtained data will allow suggestions concerning legislation involving river basins, their estuaries, adjacent shelves and coastlines.
2. Isotope Hydrology – Studies aiming to contribute to a better understanding of the dynamic evolution response of groundwater systems to Human influences and climatic changes. These resources have become progressively more endangered by accelerated modification of the natural conditions. A national network for isotopes in precipitation provides important information for hydrological investigations, relevant for the management, protection and development of water resources.

The non-invasive characteristic of the EDXRF method has been driving for years some of our research to the study of metallic artefacts with museological and archaeological interest aiming to identify their Provenance, Technology and Use. In recent years, Archaeometallurgy has had a growing relevant interest in our research activities. The absence of research teams in this area within the country and the significance of the obtained results are justifying the expansion of our research on this subject.

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

An important achievement was the coupling of the mass spectrometer SIRA 10 with an Elemental Analyser dedicated to the $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ isotopic determinations in solid and liquid samples. This system was funded by the projects and services rendered by the group. The new equipment is of utmost importance in Environmental Geochemistry (sources of pollutants, e.g. fertilisers, pesticides, industrial), Palaeoceanographic and Palaeobiological domains.

Concerning the reinforcement of analytical capabilities, we have been making proposals in order to install a Mass–Spectrometer in particular an HR-ICP-MS (High Resolution, Inductively Coupled Plasma-Mass Spectrometer). The International Advisory Board that followed the ITN activities for the last years has repeatedly supported this proposal. During the call of the "Fundação da Ciência e Tecnologia" within the "Programa Nacional de Re-Equipamento Científico", in 2002 we have led a National proposal, aiming at the implementation of a "Centre of Elemental and Isotrace Analysis", located at the ITN, which includes this equipment.

Another important goal within the group is the training of young research students and the enlargement and reinforcement of collaboration with other research groups and Institutions. However, it is worth noting in spite of our efforts in enlarging the group with graduated and post-doctoral students, the permanent staff is fairly small and in order to strengthen our research it is becoming urgent the contract of at least one more researcher.

Environmental Analytical Chemistry

Research Team

Researchers

- M.F. ARAÚJO, Auxiliary researcher, (Group Leader)
- P.M. CARREIRA, Auxiliary researcher
- D. BURDLOFF, Post-Doctoral FCT grant
- L.R. JAYASEKERA[1], Professor, IAEA grant

Students

- P.G. FERNANDES, PhD student, FCT grant
- C. CORREDEIRA, MSc student, FCT grant
- M. ANDRADE[2], MSc student, FCT grant
- M. LAMBÉRIA[3], MSc student
- E. FIGUEIREDO, PRODEP grant
- A.R. MIRANDA, PRODEP grant

Collaborators

- A. CRUCES, Collaborator, FCUL
- F. MORENO, Collaborator, Univ. Minho

Technical Personnel

- P. VALÉRIO
- D. NUNES
- M. CORREIA

[1] On leave from Kelaniya University (Sri Lanka) until Nov., 2003.
[2] MSc degree obtained in June, 2003.
[3] MSc degree obtained in June, 2003.

Funding (€)

Research Projects:	23.309,88
Services:	4.634,70
Total:	**27.944,58**

Publications

Journals:	7 and 7 in press
Proceedings:	21
Conf. Communications:	4
Theses: MSc	2

Sediment Geochemistry on the Iberian Coastal Zone and Continental Shelf

M.F. Araújo, C. Corredeira, D. Burdloff, P.M. Carreira,
P. Valério, A. Gouveia[1], J.-M. Jouanneau[2]

Objectives

The Portuguese coastal zone is characterised by the presence of large Iberian river basins: Minho and Douro at the northern zone, Tagus at the central-west and Guadiana at the southern area. These rivers drain regions with different lithologies, and types of Human occupation and industrialisation. The Iberian coastal area presents extreme annual climate variability and a high inter-annual variability of the flows carried by those rivers. This work aim at the evaluation of the consequences caused by the changes that occurred during the last decades in the Minho, Douro, Tejo and Guadiana river basins. Studies are based on geochemical determinations (elemental and isotopical), within an interdisciplinary approach which combines mineralogy, nanoplankton, meteorology, climate, oceanography, dating, sedimentology and historical aspects.

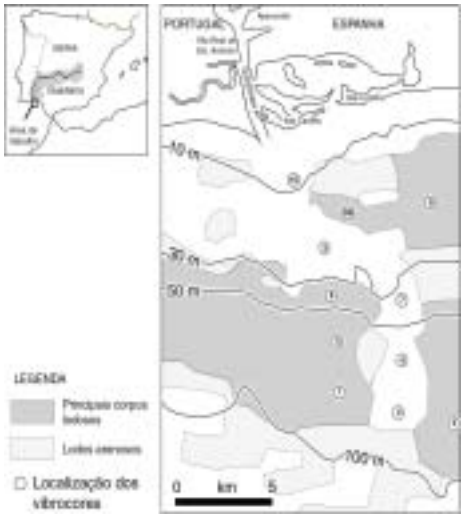

Fig.1 - Guadiana river basin.

Results

At the northern region the work was focused in the area between the mouth of Minho River and the Finisterra Cape at the Iberian NW Coastal Zone and Shelf, aiming to investigate the Minho/Galiza Shelf sedimentary dynamics. Geochemical characterisation of the collected samples indicates that sediments deposited at the Northern Iberian Shelf have three different sources: lithogenic, anthropogenic and biogenic. Apparently, there is no local contamination in the coastal zone, with the exception of areas off the Rias, which have clearly been exposed to some recent local anthropogenic contamination (Zn and As). Zirconium distribution patterns observed for the Vigo coastal area indicate that the possible exchange of sediments is from the Continental Shelf to the Rias.

At the Southwestern Iberian Continental Shelf, the temporal and spatial elemental and mineralogical distribution patterns were established along the shelf between the Guadiana and Tinto/Odiel rivers. In general, distinct characteristic materials were identified off the Guadiana, Tinto-Odiel and Guadalquivir estuaries defining sediment signatures attributable to the river influence.
Major element distribution patterns along the Southwestern Iberian Continental shelf indicate a decrease on the alumino-silicates and iron oxides phase, and an opposite behaviour on the calcium (carbonates) contents. Cu, Zn and Pb contents on the shelf surface sediments evidence the existence of pollution from the coast till the latitude of about 36° 54′ for the entire studied region. Metal profiles determined in cores collected on the region present identical values at the surface, although reaching background values at ~40cm depth. The Cu, Zn and Pb enrichment can be associated to sulphide minerals related to the presence of the Iberian Pyrite Belt and/or to the mineral wastes of industrial plants.

Published, accepted or in press work

1. A. Machado, F. Rocha, M.F. Araújo, F. Vitali, C. Gomes, J.A. Dias, Geochemical Characterisation of Surficial Sediments from the Southwestern Iberian Continental Shelf, *Ciencias Mariñas* (*in press*).
2. J. Ferreira, M. Cachão, F. Araújo, Calcareous Nannoplankton from the Eastern Algarve Offshore and the Guadiana Estuary, *Proceedings of the 4th Symposium on the Iberian Atlantic Margin*, Vigo, 7-10 July (2003) 174-175.
3. C. Corredeira, M. F. Araújo, A. Gouveia, J.-M. Jouanneau. Geochemical characterisation of sediment cores of the Minho/Galicia coastal zone and Continental shelf, *Ciencias Mariñas* (*in press*).
4. M.F. Araújo, F. Vitali, C. Corredeira, D. Burdloff, Elemental Geochemistry of Sediments from the Southwestern Iberian Continental Shelf, *Proceedings of the IV Congresso Ibérico de Geoquímica*, Coimbra, 14-18 July (2003) 273-275.

[1] Grupo Património Cultural e Ciências, ITN.
[2] Université Bordeaux I, Bordeaux, France.

Geochemical and Mineralogical Palaeoenvironmental Patterns in the Douro Estuary

M.F. Araújo, F. Rocha [1], M. Lambéria, P. Valério, A.Gouveia[2], T. Drago[3]

Objectives

A recent sedimentary study on the stratigraphic succession of the sedimentary record of Douro estuary is being carried out aiming at the recognition and distinction of the environmental changes, which have occurred during the Late Quaternary. Results obtained on the sedimentology, carbonates, organic matter, mineralogy, foraminifera, nanoplancton and polen have permitted to recognise the geological record of the area, including the shift of fluvial to marine facies.

Results

This work is based on the study of three cores, which were obtained by rotary drilling in the Douro estuary: one in the barrier (core 2) known as Cabedelo and two in the back-barrier (cores 1 and 1B, 50 cm apart), inside de S. Paio Bay (Fig. 1).

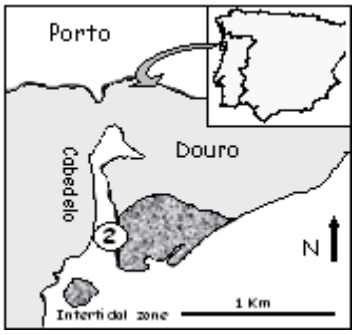

Fig.1 – Douro estuary.

The core 2 is divided in two units – SED1 and SED2. The lower unit (SED1), comprised between the core bottom and ~-34m and aged between 13750 and 10310 BP, consists of a muddy sand/sandy mud sequence. SED2, comprised between ~-34m and -20m and aged between 10310 and 8930 BP, is constituted by a mud and sandy mud sequence.

In both units, sediment major and minor elemental composition is in general similar to published values for the mean crust, mean sediment and average shale. The most striking differences are the low contents in Ca and Sr, which is a consequence of the major occurrence of granitic rocks in the region, which is confirmed by the high negative correlation with the Zr contents.

Downcore elemental distribution of some lithogenic elements revealed a slight downcore (corresponding to SED1 levels) increase in some lithogenic elements (Al and K), usually associated with the finer grain size fractions. Mineralogical data show an increase in feldspars, and in lesser scale, in some clay minerals (mainly illite and kaolinite). Calcium contents are general below 0.40%, although considerably higher concentrations have been measured at the sections (-20.53 to -22.74m, corresponding to the upper levels of SED2) in which a slight increase of carbonates was determined. At a much deeper layer (39.46m), considerable higher concentrations of Ca and Zr were measured. Ca values must probably relate to the increase of plagioclases and/or smectites, whereas Zr values may be the signature of the fluvial detrital supply. The Ca increasing tendency in the upper layers of SED2 unit reflects a marine influence, corroborating the results obtained by the calcareous nannoplankton analyses.

The REE distribution patterns may reflect the provenance of sedimentary rocks, since REE are not easily fractionated during sedimentation. The average shale-normalised REE distribution patterns determined along the unit SED 2 exhibit a strong Eu negative anomaly and are slightly LREE enriched. At the lower section the REE patterns become comparable, probably due the homogeneity of sedimentary materials. The Eu depletion in sedimentary rocks is due to chemical fractionation related to production of K-rich granitic rocks, which typically possess negative Eu-anomalies.

Published, accepted or in press work

1. Oliveira, M.F. Araújo, F. Rocha, Mineralogy and Geochemistry of Bottom Sediments from NW Iberian Shelf, *Proceedings of the 4th Symposium on the Iberian Atlantic Margin*, Vigo, 7-10 July (2003) 68-70.
2. M.F. Araújo, F. Rocha, M. Lambéria A. Gouveia, T. Drago, Geochemical and Mineralogical Palaeoenvironmental Patterns in the Douro Estuary, *Proceedings of the IV Congresso Ibérico de Geoquímica*, Coimbra, 14-18 July (2003), 146-148.
3. T. Drago, C. Freitas, F. Rocha, M. Cachão, J. Moreno, F. Naughton, C. Fradique, F. Araújo, T. Silveira, A. Oliveira, J. Cascalho, F. Fatela, Paleoenvironmental Evolution of Estuarine Systems During the Last 14000 Years – the Case of Douro Estuary (NW Portugal), *Journal of Coastal Research*.

[1] MIA, Centro Minerais Industriais e Argilas, Univ. de Aveiro, Aveiro, Portugal.
[2] Grupo Património Cultural e Ciências, ITN.
[3] IPIMAR, Instituto de Investigação das Pescas e do Mar, Olhão, Portugal.

Sources of Fine Organic Matter on the Southwestern Iberian Continental Shelf: $\delta^{13}C$ and $\delta^{15}N$ Isotope Tracers

D. Burdloff, M.F. Araújo, P. Carreira, J.-M. Jouanneau[1]

Objectives

In order to better constrain the origin, dispersal pathways and modification of the sediment load carried by the large Iberian river basins to the Portuguese shelf, detailed investigations have been carried out, both on the mineralogical and on the chemical composition of the fine sediment supply. However, no study has yet investigated the change in source of organic matter, possibly induced by river discharge modifications on the coastal zone and continental shelf. Recently, we have started to investigate the $\delta^{13}C$ and $\delta^{15}N$ of organic matter in marine environments for the study of paleoceanographic and paleobiogeochemical changes. Applications to preserved sedimentary organic matter in sediment of river basins and coastal zones can reflect provenance sources when marked differences exist between the contributing organic matter pools of the mixtures.

Results

Eleven cores have been collected along the Guadiana continental shelf. The following results concern more particularly the upper layers of core 5. It is located at 72 m depth and the fine size fraction (<63 μm) in the upper layers represent more than 99% of sediment weight.

Using the ^{210}Pb-excess profile (Fig. 1), an average sedimentation rate of 0.13 cm.yr^{-1} can be estimated for the 6 first centimetres of core. This value is consistent with the average values reported in the Tagus, Galicia and Douro mud adjacent deposits.

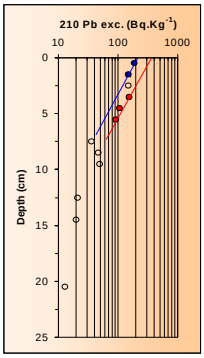

Fig. 1 - ^{210}Pb-excess profile in the core 5.

The downcore variations of organic carbon (OC), organic carbon mass accumulation rates (CAR) and $\delta^{13}C$ isotope ratios are displayed for fine sedimentary organic matter (Fig. 2).

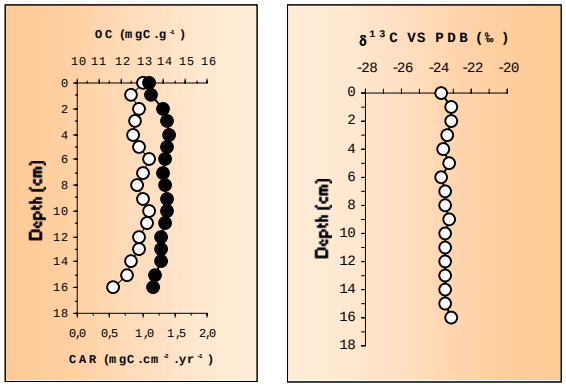

Fig. 2 - Down-core variation of organic carbon concentration, carbon mass accumulation rate and $\delta^{13}C$ for fine-sized fraction of carbonate-free samples.

Surface sediment record display roughly constant organic carbon concentrations with depth (OC ranging between 12 and 13 mgC.g^{-1}). Due to the permanent feature of sediment density and sedimentation rate in the top of the core, CAR remains constant along the depth (CAR ranging between 1 - 1.5 mgC.cm^{-2}.yr^{-1}).

The down-core variation of $\delta^{13}C$ values for fine-sized organic matter range from -24 to -23‰. As for both organic carbon concentrations and CAR, the isotopic values measured do not show significant deviations. Sedimentary organic matter in Guadiana continental margin sediments can be derived from several possibles sources: 1) terrestrial biological, soil and lithic material supplied by river discharges and, 2) marine organic matter derived from planktonic and benthic sources. A linear relationship corresponding to a binary mixture in which one end-member is best represented by terrestrial organic sources ($\delta^{13}C$ between –29 and –27‰), the second being a marine organic source enriched in ^{13}C ($\delta^{13}C$ between –22 and –20‰), is expected in our samples. We can make a semi-quantitative estimate of the proportion of continental derived organic matter at core 5 location. Results indicate than 60% of fine-sized organic matter in the top sixteen centimetres of the core is derived from marine sources.

Published, accepted or in press work

1. D. Burdloff and M.F. Araújo. Orígenes de los sedimentos depositados sobre la plataforma continental adyacente al estuario del Guadiana: utilización de los marcadores isotópicos $\delta^{13}C$ y $\delta^{15}N$ de la materia orgánica. *Thalassas*, **19** (2b) (2003) 33.

2. P.M. Carreira, D. Burdloff and M.F. Araújo. Razões isotópicas de oxigénio ($\delta^{18}O$), carbono ($\delta^{13}C$) e azoto ($\delta^{15}N$) em hidrologia e geoquímica sedimentar. *Abstracts of the IV Iberian Geochemistry Meeting* (2003) 344-346.

[1] Université Bordeaux I, Bordeaux, France.

Groundwater Resources as Indicators and Archives of Palaeoclimatic Changes

P.M. Carreira, P.A. Fernandes, M.P.L. Andrade,
J.M. Marques[1], M.O. Silva[2], D. Nunes

Objectives

Scarcity of fresh water, degradation of its quality and increasing demands has fostered interest in isotope methods as tools to characterise and manage freshwater resources. In the last decades, the groundwater resources have become progressively more endangered, by accelerated modification of their natural conditions due to industrial development associated with the growing of population and intensive agriculture.

The origin of different groundwater systems located at the Northern Portugal is being assessed by isotopic and geochemical parameters. Work is focused on the characterisation of the deep aquifers in relation to the shallow groundwater and definition of the groundwater characteristics with respect to environmental issues.

Results

In the aquifers under investigation, a comprehensive study has accomplished the following main parameters: delimitation of recharge zones for protection of the water resources, identification of groundwater mixtures between different types of aquifer systems and estimations of residence time. Our study areas were mainly developed at Caldas do Moledo geothermal mineral water (Monção), Caldelas and Gerês Spas. Groundwater systems of Vilarelho da Raia / Chaves group, Vidago / Pedras Salgadas group and Caldas do Moledo are also being investigated.

The low-resistivity zones detected in the profiles southwards of Caldas de Monção spa corroborate the circulation paths (from recharge to discharge) identified through the isotopic signatures of the thermomineral waters. The obtained models suggest that the fault systems should go deep into the granite body as predicted by geological studies.

Thermomineral and cold dilute waters present similar hydrogeochemical signatures (mainly HCO_3-Na type). However, in a Piper Diagram, the groundwater samples from the shallow cold dilute systems show some dispersion, probably related to the collection sites. Water samples were collected in springs located down hill (in areas of intensive agricultural activities) where the Human impact is enhanced by the increase in Cl and SO_4 concentrations.

The isotopic gradient for $\delta^{18}O$ was estimated using the discharge altitude of the shallow cold dilute groundwater from springs and $\delta^{18}O$ signatures. The obtained gradient for $\delta^{18}O$ (–0.18 $^{o}/_{oo}$ per 100 m of altitude), indicates that the recharge altitude of Caldas de Monção system is between 400 and 700 m a.s.l..

A close system model was used to calculate the apparent carbon-14 age of the thermomineral waters. The apparent groundwater ages obtained for AC2 and AC1 thermomineral waters were 14.11 ± 1.69 ka BP and 18.56 ± 2.32 ka BP, respectively.

Published, accepted or in press work

1. J.M. Marques, M. Andrade, F. Goff, M.J. Basto, M.J. Matias, R.C. Graça, P.M. Carreira, L. Aires-Barros and L. Rocha. Origin and evolution of high pH mineral waters (S-Portugal) traced by isotope geochemistry. *Proceedings of the International Symposium on Isotope Hydrology and Integrated Water Resources Management* (2003) 180-181.
2. J.M. Marques, J. Espinha Marques, P.M. Carreira, R.C. Graça, L. Aires-Barros, J.M. Carvalho and H.I. Chaminé. Geothermal fluids circulation at Caldas do Moledo area, Northern Portugal: geochemical and isotopic signatures. *Geofluids Journal*, **3**, 189-201.
3. J.M. Marques, J.E. Marques, P.M. Carreira, M. Andrade, R.C. Graça, L. Aires-Barros, J.M. Carvalho, H.I. Chaminé and F.S. Borges. An isotopic approach to sustain recharge sources of low temperature geothermal waters. *Proceedings of International Conference on Groundwater in Fractured Rocks* (2003) CD-ROM.
4. J.E. Marques, J.M. Marques, H.I. Chaminé, A.A. Gomes, P.E. Fonseca, J.M. Carvalho, P.M. Carreira, R.C. Graça, L. Aires-Barros and F.S. Borges. Poço Quente thermal spring (Granjão–Caldas do Moledo Northern Portugal): morphostructure, geochemistry and hydrology. *Series Cadernos do Laboratorio de Laxe*, 28, 147-172.
5. P.M. Carreira, J.M. Marques, R.C. Graça and L. Aires-Barros. Isotopic constraints in ^{14}C dating CO_2-rich mineral waters: a case study of some hydromineral systems of N-Portugal. *Submited to IAH - Hydrogeology Journal.*

[1] Laboratório de Mineralogia e Petrologia (LAMPIST). Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.
[2] Centro de Geologia. Faculdade de Ciências da Universidade de Lisboa, Campo Grande C2, 5º Piso, 1749-016 Lisboa, Portugal.

Groundwater resources assessment by anthropogenic and natural contamination sources

P.M. Carreira, P.A. Fernandes, M.F. Araújo, , D. Burdloff,
M.P.L. Andrade, M.O. Silva[1], D. Nunes

Objectives

Groundwater resources in Portugal have been utilized locally and slowly, resulting in a natural regeneration which balances the Human exploitation. In the last decades, local water resources have become progressively more endangered, both in quality and quantity, by accelerated modification of their natural conditions due to industrial and/or agricultural activities. The work is focused on the study of the quality of groundwater sources for Human supply, through the identification and quantification of pollution sources traced by environmental isotopes ($\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$).

Results

The combination of different geochemical isotopic parameters as environmental-tracers is an important tool to resolve changing inputs within fields as diverse as, identification of pollution sources and alterations of water resources. Agricultural practices and high industrial areas must be seen as new inputs of pollution in the environment (sediments and hydrological domains) through demographic density increase and growing of organics and toxic contamination. Among others, pollution associated to agriculture influences the rate and composition of groundwater recharge and aquifer biogeochemistry. Some direct effects include dissolution and transport of fertilisers.

The study performed at Sado-Sines coastal aquifers (systems located at coastal regions) deal with the increase of salinisation and pollution. The first is usually associated to the effects of seawater intrusion by overexploitation of the groundwater system and by sea-salt spray. Then again, the anthropogenic activities such as domestic wastes, agriculture and industry can induce a degradation of the water quality.

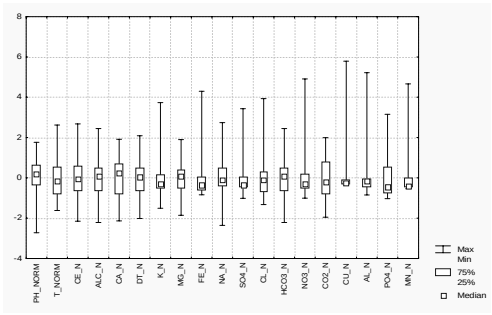

Fig. 1 - Boxplot of standardised parameters in Sines basin.

In Sado Miocene Aquifer the isotopic data carried out in this basin reveal a strong increase of groundwater mineralization that have lead to a degradation of these natural resources. The isotopic results have shown that the salt increase is related with seawater encroachment in Setubal and Troia area. In Sines basin anthropogenic contamination of the groundwater systems by fertilizers was observed.

Published, accepted or in press work

1. P.G. Fernandes, P.M. Carreira, D. André and M. Oliveira da Silva. Modelo de funcionamento do sistema aquífero da Bacia do sado: Resultados isotópicos e físico-químicos. *Actas das Jornadas Luso-Espanholas sobre as Águas Subterrâneas no Sul da Península Ibérica* (2003).
2. P.G. Fernandes, P.M. Carreira and M. Oliveira da Silva. Análise multivariada (ACP) na identificação da contaminações por actividades agrícolas e pecuárias – sistema aquífero da Bacia de Sines. *Actas das Jornadas Luso-Espanholas sobre as Águas Subterrâneas no Sul da Península Ibérica* (2003).
3. P.M. Carreira, D. Burdloff and M.F. Araújo. Razões isotópicas de oxigénio ($\delta^{18}O$), Carbono ($\delta^{13}C$) e azoto ($\delta^{15}N$) em hidrologia e geoquímica sedimentar. *Actas do IV Congresso Ibérico de Geoquímica* (2003) 344-346.
4. P.G. Fernandes, P.M. Carreira and M. Oliveira da Silva. Groundwater evolution traced by environmental isotopes (^{2}H, ^{18}O, ^{3}H and ^{14}C): Sado and Sines coastal aquifers. *Actas do IV Congresso Ibérico de Geoquímica* (2003) 350-352.
5. P.G. Fernandes, M. Bahir, J. Mendonça, P.M. Carreira, Y. Fakir and M.O. Silva. Anthropenic features within Sines (Portugal) and Essaouira (Morocco) coastal aquifers by PCA – Hydrochemical evolution comparative study. *Submitted to IAH - Hydrogeology Journal*.

[1] Instituto de Ciências da Terra e do Espaço. Rua da Escola Politécnica 58, 1296-102 Lisboa, Portugal.

National Network for Isotopes in Precipitation

P.M. Carreira, M.F. Araújo, D. Nunes, P. Valério, M.Correia, L. Gourcy[1]

Objectives

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 for hydrological investigations, by determining the temporal and spatial variations of environmental isotopes (oxygen-18, deuterium and tritium). The obtained data can be used as tracers of the isotopic composition of past and present precipitation, which are essential in climate and water studies. The database provides relevant information for water resources inventory, management, planning and development.

Results

The isotope spatial and temporal distributions in precipitation can be related to a number of environmental parameters, which characterise the source region and also a given sampling site. Seasonality, amount of precipitation, altitude, continentality, temperature, together with the source specific fractionation between ^{18}O and ^{2}H, all contribute to the establishment of the isotope signatures of precipitation, which is of great importance in hydrogeological research studies.

Temporal and spatial variations of the tritium (^{3}H) concentrations in the precipitation over Portugal are also being determined. The monthly variations on the ^{3}H content determined on the precipitation samples allowed the establishment of distinct tritium distribution patterns for three meteorological stations: Porto, Penhas Douradas and Portalegre (Fig. 1).

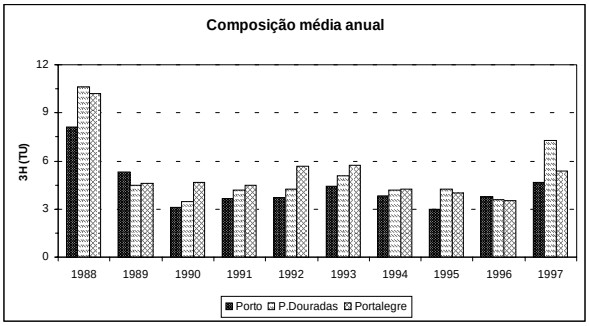

Figure -Tritium variation in precipitation since 1988.

Regional variations between littoral and interior stations are probably a result of the oceanic dilution of the tritium content in the atmospheric water vapour. Also the stratosphere-to-troposphere transport is visible in the results by a marked seasonality effect in the ^{3}H precipitation cycle contents - the so-called "spring leak effect".

We are also participating in an IAEA Coordinated Research Programme "Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate", which includes the determination of the isotopic composition in precipitation in daily and monthly events. This study involves also the investigation of the isotopic variation and evolution of atmospheric water vapour in the Lisbon area (ITN campus).

The Isotopic results are compiled and gathered in the IAEA Data Base and disseminated via IAEA publications to be used in international hydrogeological and climatologic studies (www.iaea.org/programs/ri/gnip/gnipmain.htm).

Published, accepted or in press work

1. P.M. Carreira, T. Barbosa, P. Valério and M.F. Araújo. Teores em trítio nas águas de precipitação em Portugal Continental: variabilidade e factores condicionantes. *Actas do IV Congresso Ibérico de Geoquímica - XIII Semana de Geoquímica* (2003) 353-355.
2. P.M. Carreira, D. Burdloff and M.F. Araújo. Razões isotópicas de oxigénio ($\delta^{18}O$), carbono ($\delta^{13}C$) e azoto ($\delta^{15}N$) em hidrologia e geoquímica sedimentar. *Actas do IV Congresso Ibérico de Geoquímica - XIII Semana de Geoquímica* (2003) 344-346.
3. www.iaea.org/programs/ri/gnip/gnipmain.htm

[1] Isotope Hydrology Section, IAEA,Wagramerstrasse 5, PO Box 100, A-1400 Vienna, Austria

Archaeometallurgy – Provenance, Technology and Use of Metallic Artefacts

M.F. Araújo, P. Valério, E. Figueiredo, A.A. de Melo[1],
A.C. Sousa[2], J.S. Martinez[3], L. de Barros[4]

Objectives

Central Portugal was an important area for the production of tin and gold during the pre-history. The investigation of production, circulation and use of metallic artefacts is a major subject in the study of the Pre-historic Age populations. Differences in the elemental composition of Chalcolithic till Iron Age metallic artefacts from sites in the Portuguese Estremadura and Beira Alta can provide significant information regarding this issue. The interdisciplinary studies (e.g. chemical composition, chronological and typological data), carried out in close collaboration with archaeologists, intend to establish the technology and evolution of metal fabrication, as well as, the amounts of metal production, circulation and the socio-economic implications in the dynamics of the Pre-historic Age peoples of Central Portugal.

Results

During 2003, more than one hundred artefacts from different sites in Central Portugal were studied:

Estremadura - Previous investigations have identified bronze (with low and high lead content) and iron artefacts in the archaeological site of Quinta do Almaraz. The additional remains studied identified bronze artefacts, as well as, one copper and one arsenical copper[1-3]. Crucible and slag fragments provide important evidences of the silver production by the cupellation process in the Portuguese territory before the Roman period.

The analysed metallic remains from Quinta do Marcelo are mainly binary bronzes. Also, a copper artefact, one lead and several iron artefacts were also investigated. Despite the possible connection between the two sites, the bronzes from this location present a rather higher tin content than the alloys from Quinta do Almaraz, difference that probably can not be explained only by the corrosion processes.

Another metallic collection from the Penedo do Lexim is composed by artefacts with simple forms and which chemical composition is representative of the metallurgical evolution of the pre-historic man in the site: coppers, arsenical coppers, binary bronzes and bronzes with high lead content[4].

Recently a large set of metallic artefacts from Pragança, part of the collection of the National Archaeological Museum is under investigation. Currently several artefacts made of copper, arsenical copper, binary and ternary bronze alloys were identified.

Beira Alta - The studied archaeological sites from Beira Alta belong to the cultural group of "Baiões/Santa Luzia". The metallic collection from Senhora da Guia de Baiões is the most significant collection from the Late Bronze Age in Portugal. In the analysed group, containing more than 70 artefacts, the majority proved to be composed by binary bronze alloys. Nevertheless, some bronze artefacts with high lead contents were also identified.

Published, accepted or in press work

1. P. Valério, A.A. de Melo, L. de Barros and M.F. Araújo. Archaeometallurgical study of pre-historical artefacts from Quinta do Almaraz (Cacilhas, Portugal), *Proceedings of the International Conference Archaeometallurgy in Europe*, **I** (2003) 327-336.
2. M.F. Araújo, L. de Barros, A.C. Teixeira and A.A. de Melo. EDXRF study of Prehistoric artefacts from Quinta do Almaraz (Cacilhas, Portugal), *Nuclear Instruments and Methods in Physics Research B* (*in press*).
3. M.F. Araújo, L. de Barros and A.A. de Melo. Archaeometallurgical investigations on the metal production in the "Quinta do Almaraz" (Cacilhas, Portugal), *Proceedings of the Radiation Physics for the Preservation of the Cultural Heritage Conference* (*in press*).
4. M.F. Araújo, P. Valério, A.C. Teixeira and A.C. Sousa. EDXRF study of archaeological metallic artefacts from Penedo do Lexim (Portugal), *Proceedings of the International Conference Archaeometallurgy in Europe*, **II** (2003)591-597.
5. M.F. Araújo, T. Pinheiro, P. Valério, A. Barreiros, A. Simionovici, S. Bohic and A. Melo. Analysis of a roman *Centaurus* from Canas de Senhorim (Portugal) - comparative study using EDXRF and SRXRF, *Journal de Physique IV*, **104** (2003)523-526.
6. M.F. Araújo, T. Pinheiro, P. Valério, A. Melo, A. Barreiros, A. Simionovici and S. Bohic. Bronze romano de Canas de Senhorim: estudo arqueometalúrgico por métodos de análise não destrutiva, *Trabalhos de Arqueologia da EAM*, **6** (2003) 89-97.

[1] Museu Nacional de Arqueologia, Praça do Império, 1400-206 Lisboa.
[2] Câmara Municipal de Mafra, Praça do Município, 2644-001 Mafra.
[3] Faculdade de Letras da Universidade de Lisboa, Alameda da Universidade, 1600-214 Lisboa.
[4] Museu Municipal de Almada, Olho de Boi, 2800 Almada.