

# Environmental Analytical Chemistry

The “Environmental Analytical Chemistry” research group is dedicated to the development of analytical technique as well as their applications in the study of the distribution and behaviour of chemical elements and isotopes in Environmental Sciences. This team has been created in October 1998 as a result of a reorganization within the Chemistry Section.

The main analytical facilities within the group are based on the Energy-Dispersive X-Ray Fluorescence Spectrometer, the Mass Spectrometers for Light Isotopes and the Tritium Dating Unit.

Multielemental analytical methods and isotopic ratios ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$ ) combined with other techniques such as  $^{210}\text{Pb}$ , radiocarbon and tritium dating are being applied in studies of *Pollution Monitoring, Sedimentary Dynamics and Natural Resources*. Some research projects with financial support have been recently carried out, namely: Heavy Metal Pollution in the Trancão River Basin - Soils, Sediments and Water Resources (PEAM/P/GAG/226/93 - DGA 33/95) and Ocean Margin EXchange - OMEX (MAST Program). Some other studies aiming at the pollution assessment and remediation are being developed namely on the dispersal pathways and transfer mechanisms on soil/plant systems focused on mining areas (pyrites) .

Environmental isotopes (H, C, O) are giving a significant contribution to study and characterise present and ancient environments, namely in the fields of *Isotope Hydrology, Palaeohydrology, Palaeoclimatology and Water Resources*. The main current research projects are: Management of Coastal Aquifers in Europe: Paleowaters, Natural Controls and Human Influence - Palaeaux (ENV4-CT95-0156) and 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). A systematic study of precipitation waters collected in five meteorological stations located all over the country and in Madeira island is being carried out since 1988. This study is being developed within a worldwide network to obtain spacial and temporal variations on the light isotopes and tritium distribution. Patterns obtained are of a large significance on the interpretation of the current data on hydrological studies and on a long term prediction of climatic changes.

Finally, X-ray fluorescence spectrometry, because of being a multielemental and non-destructive technique, is being applied in collaboration with museologists and archaeologists in studies of Paleometallurgy.

Research projects are usually developed in partnership with National and International teams from Universities and Research Laboratories.

A major difficulty is related with the available analytical capabilities. Up to now, it is not possible to determine trace elements in liquid samples. Our research field would significantly improve with this natural expansion. It is worth noting that the studies on Isotope Hydrology (unique in the country) are of an enormous importance at the National and International level on Water Resources Management and they would highly benefit if complemented by the chemical composition determination of the groundwaters. Also, in pollution studies and biogeochemical cycles, the bioavailable phases which can move up the biological chain (and reach the human), can not be determined without having such capacity. In fact the development of this research area, as well as some other research activities within the ITN would highly benefit from an equipment that can perform these analyses. The conclusions of the first “Evaluation Panel” organised by the ITN Directive Board in 1997 pointed out the lack of such type of equipment and they have suggested the acquisition of an ICP-MS. Therefore, during the current year, a proposal has been prepared and presented to the ITN Directive Board for an acquisition of an ICP-MS spectrometer to be shared with other researchers. This project has been associated with a “Multidisciplinary Laboratory” proposal, where it should be properly installed.

## Heavy Metal Pollution in the Trancão River Basin - Soils, Sediments and Water Resources \*

M.F. Araújo, T. Pinheiro, P.M. Carreira, P. Valério, L.C. Alves, D. Nunes

### Objectives

This project aims at the study of the heavy metal contamination of surface and groundwaters, sediments and soils in a polluted river basin - the Trancão river. Data from isotopic ratios of surface and groundwaters, together with the trace metal contents of water and sediments were used to identify pollutants and trace their possible sources.

### Results

Superficial sediments and water dry residue (WDR) collected in Trancão river basin (Fig. 1) show a general downstream increase of trace metal concentrations. This behavior seems to be controlled mainly by sediment grain size distribution and organic matter content, as well as by the cumulative effect of the different anthropogenic inputs along the river basin.

Surface water isotopic ratio patterns, electrical conductivity and WDR compositions suggest an important pollution contribution from Póvoa river.

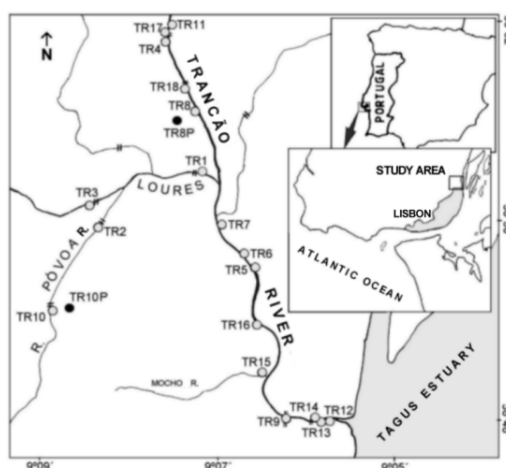


Fig.1. Trancão river basin and sampling sites locations.

As the early results suggested (M.F. Araújo *et al.*, *Nucl. Instr. and Meth. B* **136** (1998) 1005-1012; P. Valério *et al.*, *Actas do 1º Simpósio Interdisciplinar de Processos Estuarinos* (1998) 186-189) the pollution sources in the Trancão river basin can be characterized by enhanced contents of Cl, Mn, Cu, Zn, Br and Pb. In some locations the marked increase of pollutants indicate very localised effluents of industrial, domestic and agricultural origin, as is the case for As and I in the WDR from the upstream Trancão sites, high organic matter sediment contents and local increase of the Cr, Mn, Cu, Zn and Pb concentrations [1,2,3].

The only identified pollution sources at the Trancão river are a paper plant (site TR4) and a metal processing industry in the Mocho stream (site TR15). These can be clearly distinguished by the enhanced Ca concentrations in sediments from TR4 site and by the high Cr and Zn levels in both sediments and WDR at the TR15 sampling site [1,2,3].

### References

1. Pinheiro, T., Araújo, M.F., Carreira, P.M., Valério, P., Nunes, D., Alves, L.C., Pollution assessment in the Trancão river basin (Portugal) by PIXE, EDXRF and isotopic analysis, *Nucl. Instr. and Meth. B* **150** (1999) 306-311.
2. Araújo, M.F., Pinheiro, T., Carreira, P.M., Valério, P., Nunes, D., Alves, L.C., Heavy Metal Pollution in the Trancão River Basin - Soils, Sediments and Water Resources, Final Project Report, ITN (1999) 59pp.
3. Carreira, P.M., Araújo, M.F., Pinheiro, T., Valério, P., Nunes, D., Alves, L.C., Métodos isotópicos e de análise multielementar na identificação de poluentes. Exemplo: a bacia do rio Trancão, *Actas do II Congresso Ibérico de Geoquímica / XI Semana da Geoquímica* (1999), Lisboa, Portugal, 14-17 Junho.

### Further Work

The contract was concluded during 1999.

\*Funding: Ministry of Environment (DGA), Contract PEAM/P/GAG/226/93;  $4.8 \times 10^6$  PTE.

## Ocean Margin EXchange - OMEX \*

M.F. Araújo, T. Barbosa, P. Valério, J.-M. Jouanneau<sup>1</sup>, O. Weber<sup>1</sup>, J.M.A. Dias<sup>2</sup>

### Objectives

This study is an attempt to contribute to the knowledge of the sedimentary dynamics along the Portuguese shelf, focused on sediments from the two fine sedimentary deposits, located at about 100 m depth and lying off two main estuaries: Douro and Minho.

### Results

Geochemical study of superficial sediments and cores, with depths ranging from 6 down to 14 cm, collected at mid shelf all over the sedimentary deposits (Fig. 1), have been carried out. Chemical analyses (major, minor and trace elements) by using EDXRF technique and sedimentological analyses combined with sedimentation rates (by using the <sup>210</sup>Pb method) were carried out by studying core segments of 1 cm.

The elemental analysis of the superficial sediments allow to differentiate several types of sediments, which composition is related with the origin of the deposited material (terrigenous and biogenic) and its grain size distribution. High contents on Si and Ca are associated with low contents on Al and with coarser particles. The transition elements contents is controlled by the grain size distribution and no anthropogenic influences could be detected (T.Barbosa, Caracterização química de sedimentos da plataforma continental a norte de Espinho. (1997) *Tese de Licenciatura, Universidade de Lisboa*; T. Barbosa et al., *Actas do 1º Simpósio Interdisciplinar de Processos Estuarinos* (1998) 91-94).

Granulometric distribution showed that sediments from the northern deposit are slightly coarser. The superficial layers of the sediment cores were apparently mixed due to storm effects and bioturbation which did not allow the determination of the accumulation rates by the <sup>210</sup>Pb method. It is worth noting that those mixing processes could hide the presence of an anthropogenic signature.

Previous work has shown that the shale normalised REE distribution of selected superficial sediments revealed that both fine deposits are similar to shales, being the sediments deposited at the northern formation enriched in LREE (M.F. Araújo & M.A.Gouveia, REE distribution in fine-grained sediments from the Portuguese Atlantic shelf, *Proceedings of the 9th International Symposium on water-Rock interaction* (1998), New Zealand).

The downcore profiles of the elemental composition are flat which might be due to a mixing of the materials caused by a storm event and/or bioturbation effect. Both phenomena have been detected by the radiographic studies particularly for the upper layers (~7cm) [1,2,3].

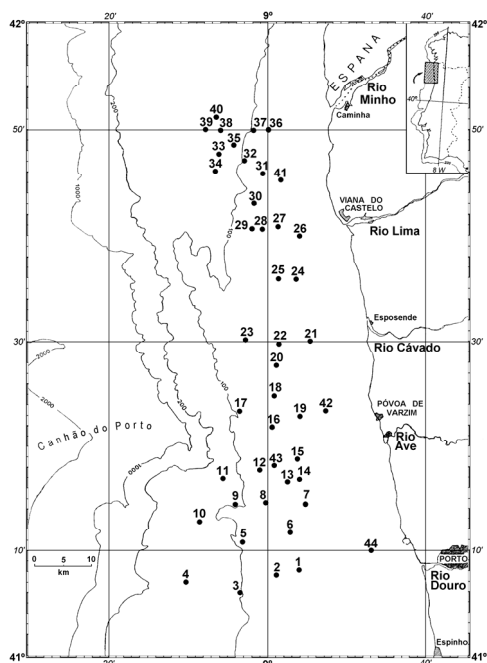


Fig. 1. Sampling locations on the northern Portuguese shelf

### References

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2. Garcia, C., Martins, V., Araújo, F., Jouanneau, J.-M., Barbosa, T., Dias, J.M.A., Weber, O., Gouveia, A., Carapito, C. e Boski, T., The Galicia Mud Patch. OMEX II-II Annual Workshop - The Carbon Cycle at the Iberian Margin (1999), Plymouth, UK, 27-29 April.
3. T. Barbosa, M.F. Araújo, J.-M. Jouanneau, A. Gouveia, O. Weber & J.M.A. Dias (1999). Geochemistry of the sediments from the Portuguese shelf. II Congresso Ibérico de Geoquímica / XI Semana de Geoquímica (1999), Lisboa, Portugal, 14-17 de Junho, 437-440.

### Further Work

Geochemical study of sediment cores collected at the Galician shelf, off Minho and Galician rias.

\*Funding: EEC (Sub. Contract - Universidade do Algarve);  $2 \times 10^6$  PTE.

<sup>1</sup> Département de Géologie et Océanographie, Université Bordeaux I, France.

<sup>2</sup> UCTRA, Universidade do Algarve.

# Management of Coastal Aquifers in Europe: Palaeowaters, Natural Controls and Human Influence - Palaeaux\*

P.M. Carreira; D. Nunes

## Objectives

This project intends to study the paleowaters of the Miocene aquifer where a strong increase of groundwater mineralization has been verified. In order to find out the origin of salts in this area, that can be related to seawater encroachment, to a brine dissolution, or to active seawater intrusion, isotopic, physical and chemical analyses have been performed in water samples between Troia and Alcochete.

## Results

A strong increase of groundwater mineralization has been verified in the Lower Sado Miocene aquifer, which represent a vital water resource of an important industrialised region, isotopic ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $^3\text{H}$  and  $^{14}\text{C}$ ), physical and chemical analyses has been carried out in groundwater samples. The lack of relation between the increase of salinization and the  $^{14}\text{C}$  content, in the S part of the lower Sado basin put clearly in evidence a brine dissolution mechanism, or mixing with ancient seawater trapped in the sediments during the basin formation. On the other hand in Almada region the strong correlation between these parameters point out to recent sea water intrusion in this area.

The hydrochemical evolution of the groundwater is characterized by a progressive increase in the total dissolved solids, ranging from 80 mg/l up to 2565mg/l in the Pliocene aquifer, while in the Miocene the mineralization varies from 200 mg/l up to 7800 mg/. Cl contents show an increase of salinization in the central part of the basin, near Pinhal Novo, where Cl-Na water is being exploited for agriculture and public supply from Mio-Pliocene units. This occurrence is most probably related to the graben structure responsible for the rising to shallow depths of a brine or ancient seawater within the sediments.

The nitrate content was an important tool in the characterization of the two main aquifers and in the identification of mixing between these units. No nitrate was detected in the deeper aquifer although in the Pliocene the  $\text{NO}_3$  content varying from 7mg/l up to 93 mg/l, associated to agricultural activities.

Tritium contents in the upper aquifer vary from 1 to 3 TU, and no  $^3\text{H}$  were found in the Miocene water samples. Radiocarbon was measured on the total dissolved inorganic carbon, in 12 wells. The values obtained range between 71.9 up to 88.1 pmc in the Pliocene aquifer, and between 2.9 pmc up to 45.6 pmc in the Miocene. The lack of relationship between the increase of the salt content and  $^{14}\text{C}$  values in the groundwater, collected in the Southern part of the basin seem to confirm the brine dilution mechanism. The opposite pattern was found in the Almada region (North part of the basin) where a strong relation between the  $^{14}\text{C}$  and Cl content is observed, pointing to recent seawater intrusion in the area.

A small difference of about 2 ‰ in deuterium and 0.2 ‰ in oxygen-18 was found in the mean isotopic composition between the two main aquifers. The small enrichment in heavy isotopes observed in the Miocene groundwater samples, when compared with values obtained in the Pliocene system, may be related to the isotopically heavier ocean during late glacial time

## References

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2. Carreira, P.M. - Evidence for Paleowater in the Lower Tagus and Lower Sado aquifers, Portugal. Final Report, EC Fourth Framework Programme (Climatology and Natural Hazards), 1999, pp. 84–87.

## Further Work

The contract was concluded in March 1999.

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# Environmental Isotopes and Noble Gas Palaeothermometers in the Study of Climatic Change Encoded in Paleowaters of Aveiro Aquifer\*

P.M. Carreira; M.A. Marques da Silva<sup>1</sup>; D. Nunes

## Objectives

The main goal of this project is to reconstruct the palaeoclimatic environment of the Aveiro region, from today until *c.* 30 000 years ago, through the isotopic composition of the groundwater in the Quaternary and Cretaceous aquifer.

## Results

The ages obtain in the groundwater of the Cretaceous aquifer range from 2 000 to *c.* 30 000 years BP. The increase of ages corresponds to enrichment in heavy isotopes in the groundwater samples. On the other hand, groundwater 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: groundwaters from UK and from western and central Europe, which were recharged during the last glaciation, like the Aveiro aquifer, area depleted 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 [1].

The <sup>14</sup>C results in TDIC measured in groundwater samples of the Cretaceous aquifer 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, resulting from intense flushing of the aquifer during the last glacial period about 18 ka. This flushing was induced by the decrease in the sea level by about 100 m.

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.

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 [1,2].

## References

1. Carreira, P.M. – Paleoáguas de Aveiro. Tese de Doutoramento. Universidade de Aveiro, 377 pp.
2. Carreira, P.M.; Soares, A.M.; Marques da Silva, M.A.; Araguás-Araguás, L.; Rozanski, K.; Stute, Martin – Isótopos ambientais na caracterização de paleoáguas do Cretácico de Aveiro, Actas II Congresso Ibérico de Geoquímica / XI Semana de Geoquímica. 213-216.

## Further Work

The project will be concluded in March 2000. However, some field work is still running in the area of most intense exploitation of the aquifer (near Aveiro city), that coincides with the region of apparent high flow rate. 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. Thus a confirmation of these data will be performed.

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<sup>1</sup> Departamento de Geociências, Universidade de Aveiro.

