

# Atmospheric Elemental Dispersion

*Maria do Carmo Freitas*

## Scientific Goals

The aim of this research group is the evaluation of elemental concentrations in suspension in the atmosphere, the characterisation of atmospheric dispersion of chemical elements subjected to local, mesoscale or long-range transport, and its effects or impacts upon the biosphere, including Man. For this, both monitoring (air filtering and deposition sampling) and biomonitoring are used. The field is both a natural application of the potentialities of  $k_0$ -INAA and PIXE techniques, which are the historical roots of the group, and a key-subject in environmental problems. The development of these two nuclear analytical techniques used, runs in parallel with their applications, allowing for a double faced research that provides a more immediate use of the developments made in each area and thus allows the preservation and enhancement of the capacity to provide highly qualified services to the scientific community and to the society in general.

The atmospheric monitoring and biomonitoring program essentially started with a campaign held in the summer of 1993, although some related work had been already made before. Under this scope, the team is providing measurements of atmospheric trace elements concentrations to those entities requesting them, as well as carrying out its own research projects. In order to improve both the assurance of quality of established procedures, and the quality of scientifically new approaches, the team is also involved in quality control studies, which are still rare in this field. Up to now this line has been the major source of external financing.

In the framework of this main line, during the year of 2000 the following specific programs were running and results were achieved and/or compiled within them:

- a) Analysis of biomonitors and aerosol samples around the Sado estuary was completed. Data is now being thoroughly exploited.
- b) Since January 1999 the team is involved in the non-continuous monitoring of atmosphere around the S. João de Talha urban incinerator, involving also airborne particle and biomonitor measurements. In connection, quality control of PIXE and INAA analysis of biomonitor and aerosol samples is being

investigated thoroughly and is now a significant part of two PhD works under development. One in cooperation with University of Aveiro – Portugal, and another in cooperation with the Technical University of Delft.

- c) Study of the possibility of using other biomonitors different from lichens or mosses.

These specific programs and the results in 2000 are treated in the following pages.

Research and development were not strictly connected to specific funded projects so the work developed independently of the specific funding obtained.

## Future Perspectives

In the near future, integration of biomonitoring with standard monitoring will be continued as a main research topic, but the element speciation, and the quantification of the impact of trace element upon the biosphere, will gain importance. The study of correlations between element dispersion impact in biomonitors and in human population will be addressed. Receptor models will be tentatively used for inference of air mass long-range transport. Air sampling prototypes developed are expected to become in use in the next year, but also to become available as an ITN product. Services will continue to be provided. With the expected in a near future European regulations for control of atmospheric pollutants, the group is in a particular good position to expand this type of work, of major importance at the level of services, for the community, and to support the other public entities.

Due to the natural growth of a group working in a highly dynamic area of research, and where the requests from the outside also increase from day to day, the output of the team is now becoming limited by infrastructures throughput. It is therefore urgent that throughput capabilities are increased in order to be able to respond in a very near future to an expected large increase in requests. In the direction of the solution of this problem, the team is intensifying the interactions with other groups of ITN.

## Research Team

### Researchers

- Maria do Carmo Freitas, (Principal Researcher with Habilitation) (**Group Leader**)
- Miguel A. Reis (Research Assistant)<sup>1,3</sup>

### Technical Personnel

- Isabel Dionísio (Technician)
- Rute Pinheiro (Technician) (20%)

### Students

- Ana Paula Marques (**PhD** Student)
- Carla Hipólito Gomes (**PhD** Student)
- Susana Marta Almeida (**PhD** Student)
- Carlos Costa (**MSc** Student)<sup>2</sup>
- Carla Mustra (**MSc** Student) (since Sept. 2000)
- Maria Manuel Farinha (**BSc** ITN Grant)
- Lia Barros (Graduate Student, from Jan until Jun2000)
- Rodrigo Mateus (**PhD** Student of CFNUL)
- Orlando Reis de Oliveira (**BSc**, ITN Grant)

<sup>1</sup> Doing PhD.

<sup>2</sup> Secondary School Teacher, on leave.

<sup>3</sup> Also member of CFNUL (Centro de Física Nuclear da Universidade de Lisboa).

## Publications

Journals:	2 and 4 in press
Proceedings:	3 and 1 in press
Conf. Communications:	10
Book Chapters:	1

## Funding

	×10 <sup>3</sup> PTE
<b>Research Projects<sup>(a)</sup>:</b>	13 068
<b>Services:</b>	1313
<b>TOTAL:</b>	14381

(a)

	×10 <sup>3</sup> PTE
- ValorSul - Monitoring of Air Quality at the Incinerator of S. João da Talha (Renewed Nov./99, and Nov./2000) ITN/Co-ordinator: <b>M. Carmo Freitas</b> , Partners: IDAD .....	12 036
- Study of Atmospheric Dispersion of Pollutants in the Industrial Region of the Sado Estuary using Biomonitoring (contract IAEA-CRP9938) (Dec.1997 - Dec. 2001) ITN/Co-ordinator: <b>M. Carmo Freitas</b> , Partners: IAEA and other 14 International Laboratories/ Institutions .....	—
- PERM-Polymeric Elemental Reference Material (SMT4/CT95-2034 - UE Contract) (Mar. 1996-Dec. 2000) ITN/Co-ordinator: <b>M. Carmo Freitas</b> , Partners: DSM Research and other 16 International Laboratories/ Institutions .....	1032
-	

## Wind Differential Biomonitoring and Integration with Direct Aerosol Characterisation

A.P. Marques, C. Costa, I. Dionísio, O.R. Oliveira, R. Mateus, R. Pinheiro, M.A. Reis, M.C. Freitas, H.Th. Wolterbeek\*, A. Jesus\*\*

### Objectives

There are two main points in this project: (i) to show the potentialities of the integration of biomonitoring and standard aerosol monitoring taken simultaneously; (ii) to verify the enhancement in biomonitoring by wind direction differential exposure of biomonitors. It includes one PhD Thesis and one Master.

### Results

In this project, transplants of lichen *Parmelia sulcata* Taylor were suspended in nylon bags in Sado estuary region within a rectangle 15 km wide and 25 km long on a 2.5 km x 2.5 km grid, centred in the Setúbal power station. In each place two sets of four transplants each were suspended at about 1.5 meters above the soil, one permanently facing the wind and the other permanently opposing the wind direction. In the laboratory, the lichens were taken off the nylon bags, cleaned, rinsed in distilled water, freeze-dried, and ground in a Teflon® mill. The sample powder was analysed by INAA and PIXE in pellet form. In Fig. 1 the zinc deposition pattern determined in wind facing and opposite wind facing lichens are presented in units of the standard deviation of the reference lichen set.

An influx of Zn onto the estuary with atmospheric origin can be inferred from these results, and the differences between patterns show that there are important local sources (enhanced effect on wind facing samples), although remote sources cannot be discarded. Local sources can be traced to industries located at the shore area. The urban area (about 510E by the shore) is seen to be not particularly affected.

Week averaged airborne particles data from Faralhão station is presented in Fig. 2 right. Zn levels up to 40ng/m<sup>3</sup> in PM2.5 (fine mode) and up to 80 ng/m<sup>3</sup> in PM10 were found. Due to its location in an averaged affected area (orange), conditions worse than these can be expected for all areas marked in red and black in Fig.1.

### Published (or in press) work

- [1] Freitas; M.C., *et al.*, *J.Radioanal.Nucl.Chem.* **244** (2000) 109-113.
- [2] Freitas, M.C., *et al.*, *J.Radioanal.Nucl.Chem.*, in press.
- [3] Jesus, A.P., *et al.*, *Nucl.Instr.Methods* **B161-163** (2000) 120-124.

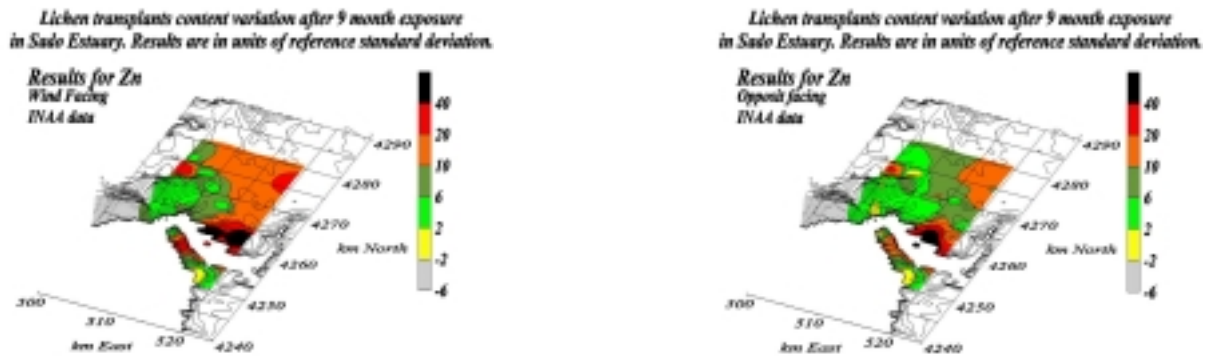


Fig.1: Zinc deposition pattern in Sado estuary (units of reference standard deviation).

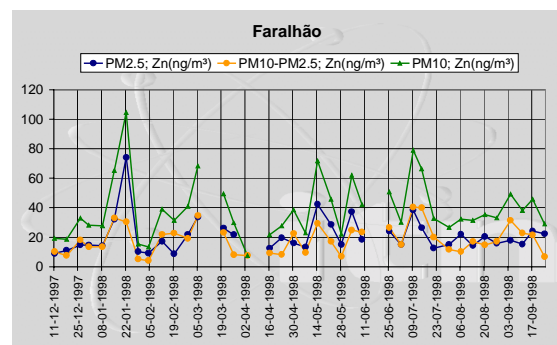


Fig.2: Left – Air sampler and biomonitoring transplants support (Troia station, 4257N, 515E). Right – Time series of concentrations of suspended Zinc at Faralhão station (4265N, 520E).

\* Delft Technical University

\*\* Universidade Nova de Lisboa.

## Characterisation of an Industrial Area at North of Lisbon and Quality Control

A.P.Marques, I.Dionísio, M.M.Farinha, O.R. Oliveira, R.Mateus, R.Pinheiro, C. Mustra, S.M.Almeida, C.S. Hipólito, M.A.Reis, M.C.Freitas, C. Pio\*, M. Coutinho\*\*, P. Gomes\*\*, M.T. Vasconcelos\*\*\*

### Objectives

This project makes use of data gathered in the framework of a contract for analytical services. It includes two PhD theses and one Master. Within this project both airborne particles and biomonitors are analysed and quality control tests are carried out.

### Results

In Fig. 1 the time series of PM<sub>2.5</sub> and PM<sub>10</sub> masses gathered since January 1999 are presented. These correspond to 24h measurements. These results on suspended mass couple with data for about 25 elements covering the same period. In the results of Fig. 1 a comparison to recent US-EPA standards shows that quality of life in ITN vicinity may be affected due to the high PM<sub>2.5</sub> levels measured. At an EU level there is yet no standard for this variable. Relative to EU PM<sub>10</sub> standards, the year average of 40µg/m<sup>3</sup> is not reached until November 2000. Relative to quality control results on aerosol measurements,

two samplers were run simultaneously, side by side at a distance of about 4m. The filters were then cut in four and the eight 1/4<sup>th</sup> were analysed and the standard deviation for each determined element was calculated and plotted against suspended concentration. The results are presented in Fig.2. Quality control of biomonitor sample materials analysis has also been made. In Fig. 2 a comparison of the potassium determinations made by INAA and PIXE in six certified reference materials is presented. A new procedure was established to improve Cd measurements in airborne particles, by looking for the 336.2keV gamma line of In-115m besides the gamma line 527.9keV in the detection of Cd-115. Chemical speciation of air particulate matter has started and some preliminary results were published.

### Published (or in press) work

[1] Farinha, M.M., *et al.*, accepted for publication in *Radiation Phys. and Chem.*

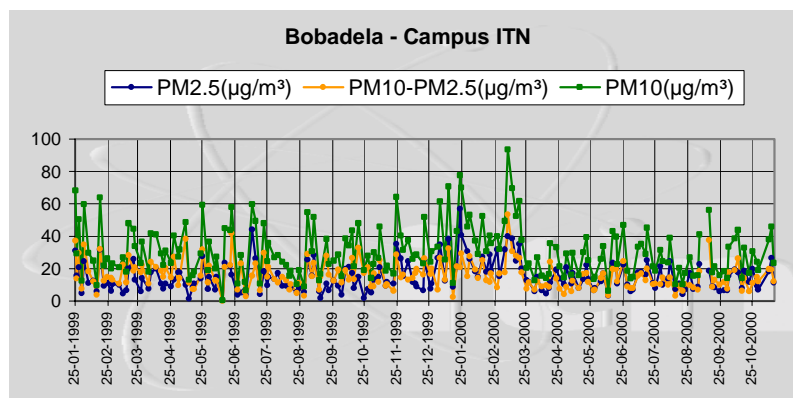


Fig.1: Suspended mass in fine mode (PM<sub>2.5</sub>) coarse mode (PM<sub>10</sub>-PM<sub>2.5</sub>) and PM<sub>10</sub> measured at ITN twice a week. The whole database corresponding to these results contains data for about 25 different chemical elements.

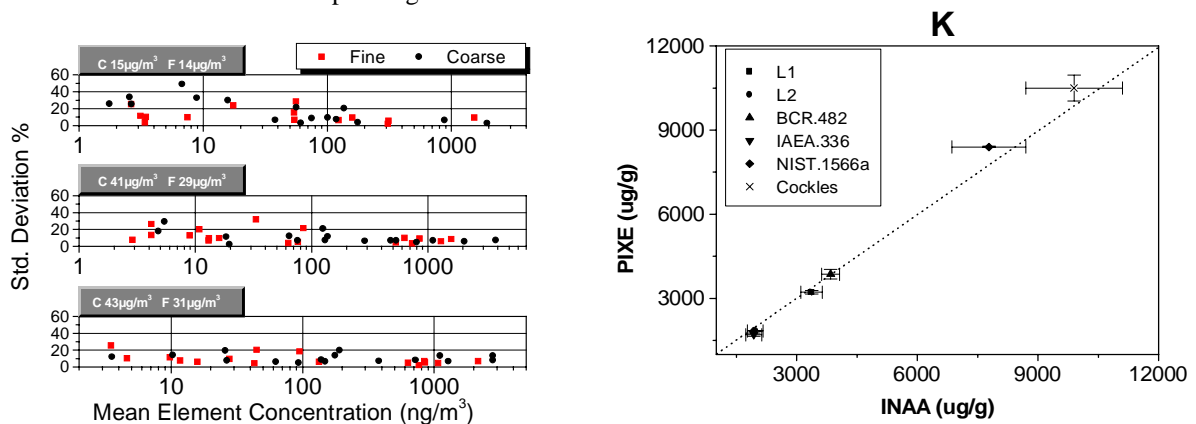


Fig.2: Left - Quality control data on airborne particles. Right – Comparison between PIXE and INAA potassium determinations in lichen Certified Reference Materials.

\* Universidade de Aveiro.

\*\* IDAD.

\*\*\*Universidade do Porto.

## Olive-Tree Bark as an Air-Pollution Biomonitor

A.M.G. Pacheco\*, L.I.C. Barros\*, R. Figueira\*, A.P. Marques, C.S. Hipólito,  
O.R. Oliveira, M.A. Reis, M.C. Freitas

### Objectives

The use of biomaterial in air-pollution studies has gone through major developments, but tree bark has been used far less than lichens, bryophytes and non-lichenised fungi. And yet, lichens are known for their slow regeneration, so an intensive sampling may put them in the threshold of extinction. Mosses appear rather unsuitable for large-scale surveys in drier regions. In this work, olive-tree bark is suggested as an alternative to lichens and mosses, at least in Mediterranean countries.

### Results

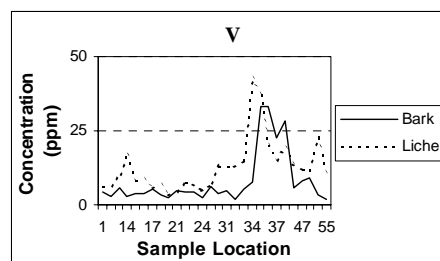
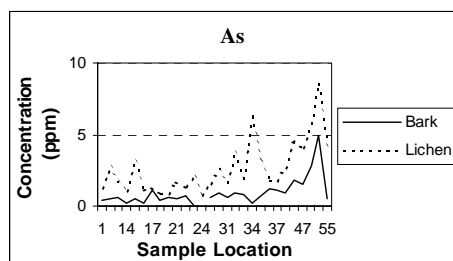
Olive-tree (*Olea europaea*) bark samples have been collected across a field grid of 10x10 km along the Portuguese northwest coast. Samples were analysed by means of Instrumental Neutron Activation Analysis (INAA) for short and long-lived nuclides, using the  $k_0$ -standardization method, and by PIXE. Certified reference material BCR-62 (*Olea europaea* leaves) and IAEA-336 (epiphytic lichen *Evernia prunastri* (L.) Ach.) were used for quality control. Experimental data for reference materials reveal an acceptable agreement with their certified values for either element.

Basic statistics show bark data as being fairly

unskewed, allowance made for a relatively wider gap between central-tendency measures in vanadium. The situation with comparative measures in epiphytes is by no means different. Generally speaking, concentrations in bark samples are lower than in lichen thalli from the same spot, with the noteworthy exceptions of Mn and Cu. Nonparametric statistical results are highly significant for a marine element – Na – and for a rare earth – La – associated with the soil. The potential of olive-tree bark for monitoring typical elements from industrial sources seems promising as well. Below, results for arsenic and vanadium are shown. These elements are normally associated to emissions from coal-fired and fuel-fired power plants. The correlations determined between bark and lichen are still significant beyond the 0.02 level.

### Published (or in press) work

- [1] Freitas, M.C., *et al.*, *J. American Institute of Physics*, accepted for publication.
- [2] Pacheco, A.M.G. *et al.*, *J. Radioanal. Nucl. Chem.*, accepted for publication.



Nonparametric statistics and associate probability levels for the concentrations  
of arsenic and vanadium in *Olea europaea* bark and *Parmelia* spp. thalli

	Spearman $R_S$ (p-level)	Kendall $R_K$ (p-level)	gamma G (p-level)
$[As]_{BARK}$ vs $[As]_{LICHEN}$	0.487 (.012)	0.370 (.008)	0.370 (.008)
$[V]_{BARK}$ vs $[V]_{LICHEN}$	0.446 (.017)	0.331 (.013)	0.332 (.013)

\* CVRM/Universidade Técnica de Lisboa.

## Effects of Atmospheric Trace Elements upon the Biosphere

M.A. Reis, M.C. Freitas, H.Th. Wolterbeek\*

### Objectives

The aim of this line is to study the response of biomonitors to general element availability in the environment, in order to promote the use of biomonitoring as a standard environmental method to assess the dispersion of chemical elements through the atmosphere. As upon doing this additional knowledge is gained on the behaviour of biomonitors and living organisms in general, the methods developed will eventually also be used to infer possible new methods for risk assessment of human populations, or eventually ecosystems stress conditions. It includes one PhD.

### Results

The results obtained and/compiled in this main line during 2000 are contained in the PhD thesis, entitled "Biomonitoring and Assessment of Atmospheric Trace Elements in Portugal, methods response modelling and nuclear analytical techniques" expected to be defended in the Technical University of Delft in June 2001. This comprises:

- New methods for calibrating biomonitors against element availability, where the dynamic response of biomonitors to exterior changes is incorporated.
- A three compartments free parameter model for lichen uptake, which can be tentatively applied to other organisms.
- The development of a computer code capable of handling and fitting the model to the data providing results without any initial values for the parameters.

A new method single airborne particles sample source apportionment, named ECRA – Element Content Ratio Analysis - has been improved to provide time

resolved data. A major paper on ECRA is now under preparation. The method will also continue to be improved. In tight connection to this ECRA project, collaboration with the University of Azores was started with the purpose of establishing methods for identification of long-range transport based in correlations between sample signatures. This collaboration and work will be continued during 2001 and eventually pursued further. The collaboration to the Technical University of Delft was very important, and the search for other collaborations was started. The application of the free parameter values to other organisms other than lichens are being attempted, and the exploitation of the capacities of the computer code and specific algorithm used was initiated. As shown in the table (extracted from public domain data of the Portuguese National Statistics Institute) the number of deaths per capita due to ischemic heart disease is larger in "Lisboa e Vale do Tejo" and in "Alentejo" and "Açores", than it is in the North (Norte), although this area is dominated in population by the second biggest city in Portugal. This is from our point of view a curious result and it might be compared with the pattern of Ni deposition found in the 1993 lichen survey. Research towards finding if there is a true correlation between these results or if it is just a mere coincidence will be investigated.

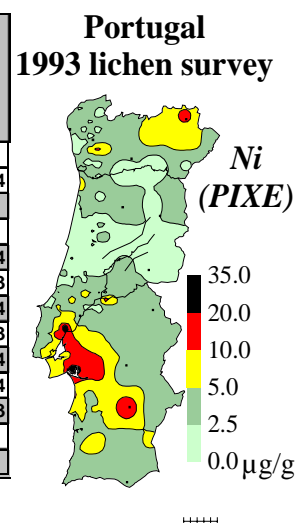
### Published (or in press) work

- [1] Reis, M.A., *et al.*, *Environ.Poll.*, in press.

Deaths per capita in Portugal in 1998, main death causes (GRUPOS DA LISTA BÁSICA DA CID-9)	Population	Ischemic hart disease	Lung circulation and other forms of hart disease
<b>Total</b>	<b>9 979 450</b>	<b>9.4E-04</b>	<b>7.9E-04</b>
<b>Residentes em Portugal</b>			
<b>Continente</b>			
Norte	3 578 310	5.8E-04	6.5E-04
Centro	1 710 330	7.9E-04	1.2E-03
Lisboa e Vale do Tejo	3 326 460	1.3E-03	6.8E-04
Alentejo	510 320	1.5E-03	1.0E-03
Algarve	348 650	7.8E-04	6.0E-04
<b>Açores</b>	<b>244 940</b>	<b>1.6E-03</b>	<b>8.3E-04</b>
<b>Madeira</b>	<b>260 440</b>	<b>7.9E-04</b>	<b>1.0E-03</b>
<b>Residências Ignoradas</b>			
<b>Estrangeiro</b>			

Total de óbitos (1998): 106 574

\* Delft Technical University.



## Prototype Development

M.A. Reis, R. Mateus, O.R. Oliveira, M.C. Freitas  
L.C. Alves<sup>1</sup>, R. C. da Silva<sup>1</sup>

### Objectives

This line of research provides the necessary improvement in automation for improvement of analysis throughput, methods of sampling and eventually other matters requiring design and construction of equipment.

### Results

During 2000 the following systems were made, assembled or just designed:

- A system for automatic replacement of targets during PIXE analysis was designed and constructed. Fig.I presents a photograph of the mechanical part.



Fig. I

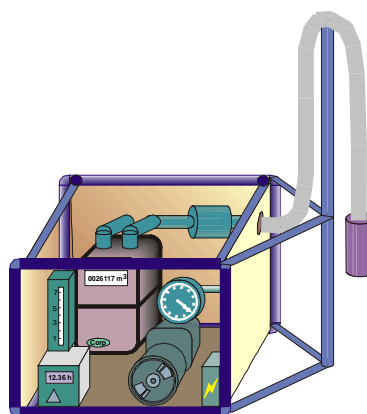


Fig. II

- A system for aerosol sampling with manual replacement of filters was designed introducing improvements relative to the presently used Gent samplers. A scheme is presented in Fig.II
- Since the end of 1993, the construction of a low cost automatic filter replacement air sampler is being constructed. During 2000 the prototype was submitted to robustness reshaping and power requirements reduction. Changes for robustness of the apparatus were implemented and a series of field experiments is being planned for 2001.

<sup>1</sup> Nuclear Solid State Physics Using Ion Beams Group.

## Services

### **INAA and PIXE applications for the scientific community and industry upon request**

In the year 2000 the following services were carried out:

- Technical support to Cláudia Umbelino\* from Coimbra University for  $k_0$ INAA analysis of archaeological human bones, for studies of Paleodietary.
- $k_0$ INAA analysis of samples, for the Nuclear Solid State Physics Using Ion Beams group.
- $k_0$ INAA analysis of trace elements in vegetation around the S. João da Talha incinerator, for the Chemistry Environmental Group.
- $k_0$ INAA analysis of a bone, for the Coimbra University.
- $k_0$ INAA analysis of the sea water, for the “Oceanário de Lisboa”.

\* Universidade de Coimbra.