Atmospheric Elemental Dispersion

Maria do Carmo Freitas

The research is focused on studies of atmospheric environment, nutrition and health. The investigation appeared as a natural application of the potentialities of k_0-INAA (instrumental neutron activation analysis using the k_0-method). The unit activities include six main lines:

1-Monitoring, Biomonitoring, Quality Control, and Data Handling aiming at characterising areas of Portugal using lichen transplants, air particulate matter collection, and (wet+dry) deposition. The data are analysed for factors aiming at identifying emission sources and the spread of elements through the atmosphere, both locally and by long-range transport. Data analysis methods and their development are very important due to the multielement nature of the analytical technique used. To assure the quality of the data, accuracy and precision studies are being performed, both in biomonitoring and monitoring fields, aiming at better understanding differences found in the results for the same element and sample. Air particulate matter obtained by different air samplers is compared. So-called conventional analytical techniques are applied to complement the research unit's results. Within this activity line, the following are being done: services to industry (monitoring), FCT funded project research (biomonitoring) and training (one PhD thesis on monitoring finished this year and two current PhD theses on biomonitoring).

2-Epidemiological studies include health related problems. The objective is to link biomonitoring and monitoring to epidemiological studies, at local, regional and European scale. Currently, one PhD and one post-doctorate initiated on March 2004 are dedicated to this subject.

3-Chemical Element Speciation aims at obtaining a better knowledge of the chemical state of the elements, its bioavailability towards the environment and its toxicity to the human being. Current biochemical, toxicological and physiological studies are focused not only on the overall occurrence of the element but also on their chemical forms. The work investigates the relationships between elemental occurrences in lichens and in selected particulate matter size classes, thereby also considering elemental solubilities and extractabilities in both lichens and particulate matter. Current work also concerns identifying in lichens, air particulate matter, and food items the state valence of the chemical elements, which is the subject of two PhD theses and one research project, funded by FCT.

4-Element Uptake Processes. The group also enters the plant physiology looking for effects on plants due to atmospheric chemical components. The underlying questions are related to the extent in which lichens may reflect the element contents of particulate matter, which may possibly be dominated by its soluble element concentration fractions. This is the subject of one PhD thesis.

5-Nutrition. The group initiated this year nutrition studies through a PhD thesis aiming at a better knowledge of selenium in the Portuguese diets. Selenium is a nutrient, which should be included in the human organism within a very narrow mass a mount range, otherwise severe diseases should be expected. Also nutrition contents in spices and rice originated from Sri Lanka were studied, within a IAEA fellowship. Honey analysis was surveyed for Azores islands and Portugal mainland, a more complete study is foreseen.

6-Training. The research unit has a strong component in training.

7-Services: Analytical services were also provided under request (private companies).

Atmospheric Elemental Dispersion

Research Team

Researchers

- M.C. FREITAS, Principal Researcher with Aggregation, Group leader

Students

- S.M. ALMEIDA, PhD Student, Aveiro Univ., FCT Grant; Post-Doctorate after March 2004, FCT Grant
- R. GODINHO, PhD Student, Delft Univ. Tech., FCT Grant
- S. SARMENTO, PhD Student, Delft Univ. Tech., FCT Grant
- A.P. MARQUES, PhD Student, Delft Univ. Tech., ITN Grant (17%)
- M.M. FARINHA, PhD Student, Delft Univ. Tech., ITN Grant (25%)
- M.G. VENTURA, PhD Student, IST, Lisbon Technical Univ., FCT Grant
- E. FERREIRA, Graduation Student, Trás-Os-Montes Univ. (33%)
- A. MACHADO, POCTI/CTA/38411/2001 BioCal project
- B. VIEIRA, POCTI/CTA/38411/2001 BioCal project

Technical Personnel

- I. DIONÍSIO, Auxiliary Technician

Funding (€)

Research Projects:	9.286,75
Services:	33.445,93
Total:	**57.445,93**

Publications

Books:		0
Journals:		7 and 13 in press
Proceedings:		8
Conf. Communications:		15
Other publications:		6
Theses:	PhD	1
	MSc	2
	Grad	1

Accumulation Behaviour of Lichen Thalli Exposed to Known Source of Air Pollution

R.M. Godinho, A.P. Marques, M.C. Freitas, H.Th. Wolterbeek[1], O.M. Steinebach[1], T. Verburg[1], J.J.M. De Goeij[1]

Objectives

During this year work in this area, aimed 1) to examine the short time element accumulation behaviour of lichen thalli exposed to a known source of air pollution compared with total deposition and deposition in aerosol filters, 2) to relate physiological parameters with accumulated elements, 3) to focus on the possible effects from lichen-transplants positioning on element influx and subsequent element accumulation, as related to the monitored total-element deposition and precipitation volumes.

Results

Lichen vitality, as measured with the studied parameters, showed seasonal fluctuations related principally with temperature and humidity. Lichens seemed more sensitive during summer hot and drier months, although previous studies indicate that lichens are more sensitive to air pollution in the hydrated, physiologically active state. From the chosen parameters, the leachate conductivity was the most sensitive, in the sense that it showed higher variability between site and season.

Lichen element content was determined by INAA and ICP-OES. Fig. 1 illustrates the ratios between the INAA element concentrations in exposed lichen thalli in the beginning and the end of an experiment.

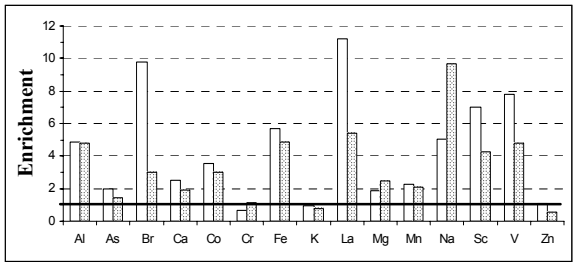

Fig. 1. Enrichment factor in exposed lichen thalli

Significant enrichments were observed for Al, Br, Cl, Co, Fe, La, Na, Sc e V.

When normalized to distinguish the atmospheric contribution from the influence of the soil particles resuspension due to local winds, it was observed that the samples were only enriched with Br, Cl e Mg, all elements present in maritime spray. This means that the other accumulated elements may have origin in the soil, revealing some soil particles content.

P. sulcata Taylor was exposed in different conditions towards the air influx: Hi – horizontal influx only; Vi – vertical influx only; Fi – horizontal + vertical influxes, as shown in Fig. 2. What criteria can be used for selection a particular hanging system? In general the lichen should display a rapid and strong accumulation over the background value leading to a constant (plateau) value (saturation curve). As it comes to a choice for a particular system, it depends on what one is measuring and also what one wants to measure (for instance as to source). In the Fi system the influx of elements is not hampered in horizontal or vertical direction, and for most elements, that Hi and Vi accumulate less than Fi when going from an unpolluted to a polluted area. Exceptions to this general trend are interesting like K, Pb and Se.

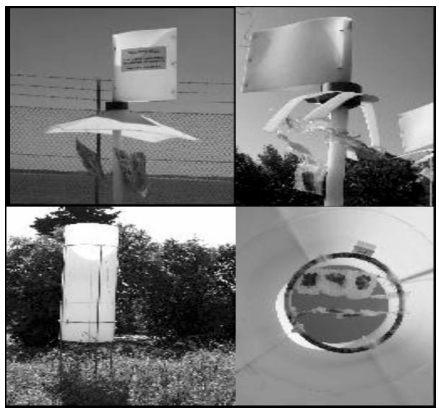

Fig. 2. Lichen exposure in different conditions towards the air influx.

Published, accepted or in press work

1. R.M. Godinho, M.C. Freitas, H.Th. Wolterbeek, Assessment of lichen vitality during transplantation to a polluted site, *J. Atmos. Chem.* (in press).
2. R.M. Godinho, M.C. Freitas, H.Th. Wolterbeek, Estudo do comportamento de duas espécies de líquenes epifíticos usados como biomonitores de poluição atmosférica, *Proc. 8th Conf. Nac. de Ambiente*, UNL, Lisboa, 27-29 October 2004.
3. A.P. Marques, M.C. Freitas, M.A. Reis, H.Th. Wolterbeek, T. Verburg, MCCTFA Applied to Differential Biomonitoring in Sado Estuary Region, *J. Radioanal. Nucl. Chem*. **259**/1 (2004) 35-40.
4. A.P. Marques, M.C. Freitas, H.Th. Wolterbeek, O.M. Steinebach, T. Verburg, J.J.M. De Goeij, Cell-Membrane Damage and Element Leaching in Transplanted *Parmelia sulcata* Lichen Related to Ambient SO_2, Temperature and Precipitation", *Env. Sci. Techn*. (in press).
5. M.C. Freitas, A.M.G. Pacheco, Bioaccumulation of Co in *Parmelia sulcata*, *J. Atmos. Chem*. (in press).

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Arsenic Speciation in Atmospheric Monitors

M.M. Farinha, A. Machado, M.C. Freitas, Z. Šlejkovec[1], J.T. van Elteren[2], H.Th. Wolterbeek[3], A.M.G. Pacheco[4]

Objectives

Within a bilateral cooperation between Portugal (ITN-Instituto Tecnologic e Nuclear) and Slovenia (IJS-Jožef Stefan Institute), arsenic species were determined on transplanted lichens (*Flavoparmelia caperata* (L.) Hale) and tree bark (*Platanus hybrida*, Brot.) after high performance liquid chromatography (HPLC) separation and hydride generation atomic fluorescence spectrometry (HG-AFS) analysis. Also, arsenic speciation and multi-element analysis was performed in *Parmelia sulcata* Taylor (native and transplant lichens), and fine and coarse air particulate matter using several solution extracts.

Results

In order to extract the arsenic present in *Parmelia sulcata* transplants and coarse and fine air particulate matter, a three-step sequential extraction procedure with Milli-Q, $CaCl_2$ and H_3PO_4 was applied. The arsenic species identification used was HPLC-UV-HG-AFS. The sequential extraction procedure was different from the conventional: the extractant was not replaced in each step but additions were made to the extractant to increase gradually the extractability of arsenic; in each step small aliquots were withdrawn for analysis. For this procedure, two *in situ* lichens, two exposed lichens transplants from Tapada do Outeiro and two from Sines were prepared. Lichen transplant samples used were exposed during 1-year aerosol sampling period. Composite filters were made up of 47 and 43 filters quarters (both fine and coarse) from Tapada do Outeiro and Sines, respectively.

The As species concentrations in aerosols from Tapada do Outeiro were higher than from Sines, for both fine and coarse fractions, which agrees with the total arsenic concentrations. For both size fractions, only inorganic As was found (As(III) and As(V)) for the applied sequential extraction procedure. For lichens, in spite of the similarity of the total As concentration after exposure for both sampling sites, the extractability of As species was more extensive for Tapada do Outeiro. Four arsenic species were found, two inorganic species (As(III) and As(V)) and two organic species (DMAA and MMAA) for both sampling sites and for Milli-Q extractions. In conclusion, the presence of organic arsenic in lichens may indicate the biotransformation of inorganic As, since in the fine and coarse aerosol fractions these species were not identified.

Within the BIOCAL project (FCT, co-funded by the EU through FEDER), arsenic species were determined on transplanted lichens and tree bark after high performance liquid chromatography (HPLC) separation and hydride generation atomic fluorescence spectrometry (HG-AFS) analysis. The lichens and tree bark were exposed in Sines and Lisboa for 2 months. Characteristic anionic species chromatogram is shown in Fig. 1 for both standard and sample.

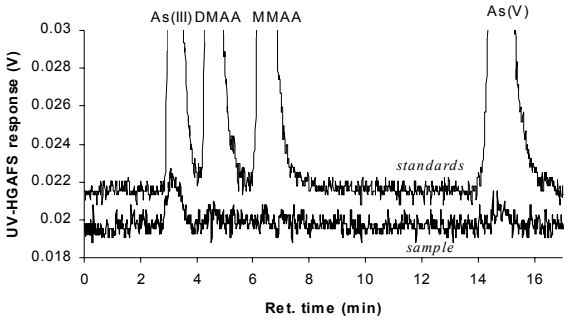

Fig. 1. Standard and sample anionic chromatograms

The selected extraction method and determination system (HPLC-HG-AFS) was appropriated to lichen samples. The results obtained clearly indicate the presence of As (III) in all the samples, As (V) in all but two, and DMAA in Sines lichen samples. This difference between Lisbon and Sines may be related to the presence of higher total As concentration in this last one environment. The extraction method was applied for the first time to tree bark. The experiments were not conclusive, only in one sample it was possible to determine As (III) and DMAA but the results were not confirmed by the second measurement. A possible explanation for these results may be the low total As concentration present in these samples. The species may be present in solution but their concentrations could be below detection limit. Further studies should be conducted in order to clarify this issue.

Published, accepted or in press work

1. M. M. Farinha, Z. Slejkovec, J. T. van Elteren, H. Th. Wolterbeek, M.C. Freitas, "Arsenic Speciation in Lichens and in Coarse and Fine Airborne Particulate Matter by HPLC-UV-HG-AFS", *J. Atmos. Chem*. (in press).

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[2] National Institute of Chemistry, Slovenia.
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Calibration of *in situ* Biomonitors for Quantification of the Atmospheric Dispersion of Heavy Metals

A. Machado, M.C. Freitas, A.M.G. Pacheco[1], M. Baptista[2], J.P. Cabral[3], M.T. Vasconcelos[3]

Objectives

Within the framework of BioCAL project (POCTI/CTA/38411/2001, co-funded by the EU through FEDER), a full study was conducted in three different locations in Portugal - Lisbon, Viana do Castelo and Sines - in order to compare responses of biological (lichen *Parmelia caperata* and tree bark of *Platanus hybrida*) and non-biological (cellulose acetate) monitors. Alternate forms of lichen exposure were also tested (with substrate and in roughly square pieces). The study was based on the total amounts of pollution-related chemical elements, among others.

Results

The exposed material was collected in a clean area in the North of Portugal (Baião). Lichen *Flavoparmelia caperat*a (L.) Hale was collected from pine trees substrates 1.5 m height above the ground and pieces of *Platanus hybrida* Brot. tree bark were also collected at the same height. The cleaned lichen was then cut in square pieces. The lichen material thus prepared is referred as lichen in pieces. The rest of the lichen was kept with substrate and was exposed. The samples were exposed sheltered from direct rainfall, at a height of ca. 1.5 m above ground, for periods of two months starting November 2003 (discontinuous accumulation). At the same time a continuous experiment was performed during one year with periodic sampling each two months (continuous accumulation). Lichen transplant and tree bark were laid open inside nylon bags (mesh º 2 mm), while lichen in pieces and cellulose acetate were exposed in a device consisting of petrislides with polyamide linen. Total (wet+dry) deposition was sampled every 2 months as well, and analysed by ICP-MS.

After exposure, the samples contents were determined by INAA. As examples, Fig. 1 shows the results for vanadium content in the lichen (L) and tree bark (TB) transplants exposed in Sines in 2003/2004, in both continuous and discontinuous forms, and the vanadium contents of unexposed lichen and bark. The results clearly show the vanadium uptake. Both biomonitors up took vanadium and the lichen had a better yield.

In the discontinuous mode, for both biomonitors the vanadium uptake was similar for each 2 months exposure May/July, July/August and August/ September, indicating that the most important factor was the exposure time and that the vanadium in the atmosphere was practically constant. Furthermore the vanadium levels in lichens in 2004 were similar to the ones obtained in a similar experiment performed in 2003.

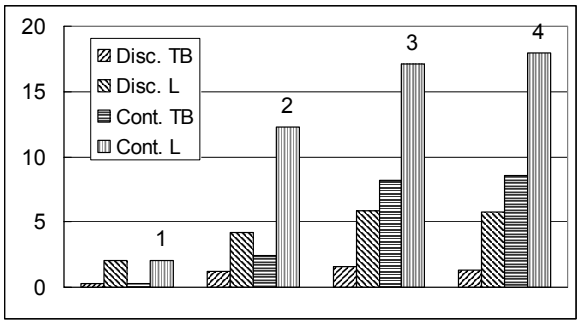

Fig. 1. Content (in mg kg^{-1}) of vanadium in *Parmelia caperata* and *Platanus hybrida* transplants, exposed continuously (1: 0 months, 2: 6 months, 3: 8 months, and 4: 10 months) and discontinuously (2 months each).

From the available atmospheric vanadium, lichen had a better yield than tree bark. It is concluded that the vanadium source in Sines is constant and seasonality seems not influencing the sampling area.

In the continuous mode, the vanadium accumulation increased exponentially, reaching equilibrium after 8-10 months of exposure for both biomonitors. After 10 months both up took well the vanadium available in the atmosphere, a better yield was obtained for the lichen.

Native lichens collected in the vicinity of the experiment during the same period of the experiment, proved to be in equilibrium in what vanadium is concerned (constant value along the experiment).

Published, accepted or in press work

1. Machado, M.C. Freitas, A.M.G. Pacheco, Relative Response of Biological and Non-Biological Monitors in a Coastal Environment, *J. Atmos. Chem.* (in press).

2. Machado, M.C. Freitas, A.M.G. Pacheco, M. Baptista, J.P. Cabral, M.T. Vasconcelos, Resposta de Monitores Biológicos e não Biológicos a Elementos Químicos numa Atmosfera Industrial e Urbana, Proc. 8th Conf. Nac. de Ambiente, UNL, Lisboa, 27-29 October 2004, 485-486.

3. M. Baptista, J.P. Cabral, M.T Vasconcelos A. Machado, M.C. Freitas, A.M.G. Pacheco, Comparação entre Capacidade em Acumular Chumbo, Cobre, Níquel e Estrôncio da Atmosfera, por parte de Materiais Biológicos e Substratos Orgânicos Sintéticos, Proc. 8th Conf. Nac. de Ambiente, UNL, Lisboa, Oct. 2004, 194.

[1] CRVM-IST, Technical University of Lisbon, Portugal.
[2]CIIMAR-Centro de Interdisciplinar de Investigação Marinha e Ambiental, Portugal.
[3]LAQUIPAI-Lab. Química Inorgânica Pura e Aplicação Interdisciplinar, Portugal.

New Lichen Flora Found on *Cryptomeria japonica* D. Don in Azores

B.J. Vieira, M.C. Freitas, A.F. Rodrigues[1], A. Aptroot[2],
E. Sousa[1], C. Rodrigues[1], A.S. Amaral[1], P.M. Soares[1]

Objectives

This work is based primarily on specimens collected in the Azores Islands during biomonitoring work carried out in 2002-2003. The collections were made in Terceira, Pico, São Jorge, São Miguel and Santa Maria. The reported specimens were collected in Terceira, Santa Maria, Pico, S. Jorge, Santa Maria and S. Miguel.

Results

Twenty-nine lichen species, mostly foliose and fruticose, were found on *Cryptomeria japonica* D. Don in the Azores. The species *Ramalina peruviana* Ach. was newly recorded on the Macaronesian Region, and 7 new records, were added to the Azorean lichen checklist published by HAFFELNER (1995, 2002). The following is a list of lichens species found in each island, followed by the citation of the specimen on witch the record is based (only for the new records).

Pico: *Cladonia coniocraea* (Floerke) Sprengel, *Heterodermia leucomelos* (L.) Poelt, *Parmelinopsis horrescens* (Taylor) Elix & Hale, *Parmelinopsis minarum* (Vainio) Elix & Hale, *Parmotrema bangii* (Vain.) Hale, *Parmotrema robustum* (Degel.) Hale, *Pyrrospora quernea* (Dickson) Körber, *Pyxine subcinerea* Stirt, *Rimelia reticulata* (Taylor) Hale & Fletcher, *Usnea hirta* (L.) Weber & F. H. Wigg., *Usnea florida* (L.) Weber & F. H. Wigg. and *Usnea subfloridana* Stirton.

Parmotrema bangii (Vain.) Hale – Rodrigues (2002:01) was reported only from Terceira and Santa Maria but it is widespread in the studied Azorean islands over 200-600 m above sea level.

Pyrrospora quernea (Dickson) Körber – Rodrigues (2003:01), a farinaceous granular lichen, was found in S. Miguel and Pico Islands. This specie is a new record for the Azores. Both species are sterile.

Pyxine subcinerea Stirt – Rodrigues (2003:02) is also a new record for Azores from Pico.

Santa Maria: *Cladonia coniocraea* (Floerke) Sprengel, *Flavoparmelia caperata* (L.) Hale, *Parmotrema bangii* (Vain.) Hale, *Ramalina canariensis* J. Steiner, *Ramalina farinacea* L. (Arch.), *Ramalina implectens* Nyl. and *Ramalina pusilla* Le Prévost ex Duby.

Ramalina implectens Nyl. - Rodrigues (2002:02) was newly recorded for the Azores from Santa Maria.

S. Jorge: *Cladonia coniocraea* (Floerke) Sprengel, *Parmotrema bangii* (Vain.) Hale, *Parmotrema crinitum* (Ach.) M. Choisy, *Parmotrema robustum* (Degel.) Hale, *Physcia adscendens* (Fr.) H. Olivier, *Ramalina peruviana* Ach., *Rimelia reticulata* (Taylor) Hale & Fletcher, *Usnea subfloridana* Stirton and *Xanthoria parietina* (L.) Th. Fr..

Parmotrema crinitum (Ach.) M. Choisy – It is absent in S. Miguel, Santa Maria and Pico, but newly reported in São Jorge. In S. Jorge, the observed habitat for *P. crinitum* varied from shaded to open humid conifer forests.

Ramalina peruviana Ach. – Rodrigues (2003:04) is reported as new to the Macaronesian Region.

S. Miguel: *Cladonia coniocraea* (Floerke) Sprengel, *Chrysothrix candelaris* (L.) J.R. Laundon, *Flavoparmelia caperata* (L.) Hale, Graphis scripta (L.) Arch., *Hypotrachyna rockii* (Zahlbr.) Hale, *Parmelinopsis horrescens* (Taylor) Elix & Hale, *Parmelinopsis minarum* (Vainio) Elix & Hale, *Parmotrema bangii* (Vain.) Hale, *Parmotrema robustum* (Degel.) Hale, *Pyrrospora quernea* (Dickson) Körber, *Usnea cornuta* Köber and *Usnea rubicunda* Sirton.

Terceira: *Cladonia coniocraea* (Floerke) Sprengel, *Chrysothrix candelaris* (L.) J.R. Laundon, *Flavoparmelia caperata* (L.) Hale, *Parmotrema bangii* (Vain.) Hale, *Parmotrema crinitum* (Ach.) M. Choisy, *Parmotrema robustum* (Degel.) Hale, *Ramalina canariensis* J. Steiner, *Ramalina pusilla* Le Prévost ex Duby, *Usnea dasaea* Stirton and *Usnea esperantiana* P. Clerc.

Usnea dasaea Stirton – Rodrigues (2002:03) and *Usnea esperantiana* P. Clerc – Rodrigues (2002:04) were collected in Terceira Island, at 500 m above sea level. The species are new records for the Azores from Terceira.

Published, accepted or in press work

1. F. Rodrigues, A. Aptroot, M.C. Freitas, E. Sousa, C. Rodrigues, A.S. Amaral, B.J. Vieira, P. Soares, Additions to the Lichen Flora Found on *Cryptomeria japonica* D. Don growing in the Azores, *Rev. Arquipélago-Life and Marine Sci.*
2. F. Rodrigues, M.C. Freitas, B.J. Vieira, P. Soares, E. Sousa, A.S. Amaral, C. Rodrigues, A. Aptroot, Mercury Levels on the Eastern Flanks of the Mid-Atlantic Ridge (Azores Region), Proc. 7th Int. Conf. on Mercury as a Global Pollutant, Ljubljana, ed. *RMZ-Materials & Geoenvironment*, **51**/2, Ljubljana, June 2004.

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Epithermal Neutron Activation Analysis (ENAA) and Compton Suppression Applied to Neutron Activation Analysis

B.Vieira, M.C. Freitas, S. Landsberger[1], S.R. Biegalski[1]

Objectives

The aim was to study the effect of Epithermal NAA and Compton suppression in trace elements NAA in presence of higher amounts of marine elements (Br, Cl, and Na. A set of samples were analysed at The University of Texas at Austin TRIGA research reactor located at the Nuclear Engineering Teaching Laboratory (NETL), within the IAEA C6/POR/03003 fellowship training. The gamma-ray detection system utilised had the ability to simultaneously collect spectra in normal and suppressed Compton.

Results

Fig. 1 shows a very significant reduction in the background continuum between normal INAA, normal ENAA and Compton suppressed INAA. In the sample, Cl and Na are present at high concentrations and because they have considerable thermal neutron absorption cross-section they generate a high Compton background on the gamma-ray spectra.

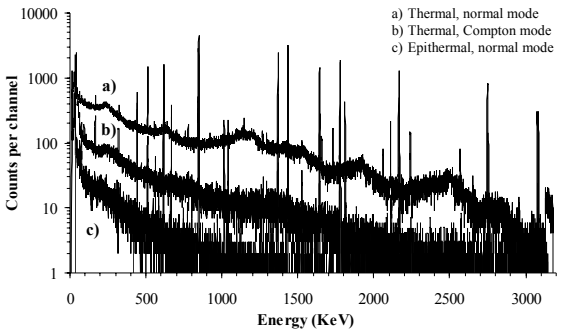

Fig. 1. Comparison of spectral background in Nucleopore® polycarbonate filters with particulate matter enriched in marine elements

Comparing with the analyses (INAA) carried out at the DEA group, the facilities used in this work (ENAA and Compton Suppression) contribute with extra elements: I, In, Si. Furthermore the sensitivity of As, Cu and Ni is significantly improved allowing to increase the quality of results. The elements Al, Cl, Cu, Mg, Mn, Ni, Si, and V, which are determined by PIXE at the DEA group, could also be analysed using the facilities in this work. This improves the quality of results since PIXE is a technique, which uses only a very small area of the filter for analysis, inducing heterogeneity trends.

A comparison of the 442.9 keV from ^{128}I in short-thermal with normal mode, short-epithermal with normal mode and short-epithermal with Compton mode is shown in Fig. 2. Since this gamma-ray peak is from non-cascade emission and located on the Compton continuum of high energy from ^{38}Cl and ^{24}Na, the use of Compton suppression can reduce significantly the background of gamma-ray spectra. That background reduction is more than one order of magnitude when compared with thermal irradiation in normal mode.

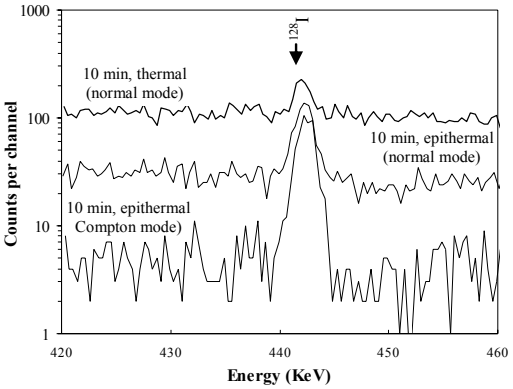

Fig. 2. Spectra comparison of ^{128}I peak with the various conditions.

Table 1 shows concentrations as determined by ENAA and Compton suppression.

Table 1. Descriptive statistics of some elements (ng.m^{-3})

	Mean	SD	Maximum	Minimum
Al	510	234	1090	209
Cl	931	854	3040	206
Cu	27.5	10.8	48.2	5.25
I	2.58	1.32	6.79	1.20
Si	295	111	508	178
Ti	185	166	302	67.2
V	80.1	60.3	202	11.2

Published, accepted or in press work

1. M.C. Freitas, A.M.G. Pacheco, M.G. Ventura, Anthropogenic Sources of PM2.5's Arsenic, Lead, Mercury and Nickel in Northern Metropolitan Lisbon, Portugal, *Nucl. Inst. and Meth.* **B 219-220** (2004) 153-156.

2. M.C. Freitas, S.M. Almeida, M.A. Reis, M.G. Ventura, Neutron Activation Analysis: Still a Reference Method for Air Particulate Matter Measurements, *J. Radioanal. Nucl. Chem*. **262/1** (2004) 235-239.

3. M.C. Freitas, M.M. Farinha, M G. Ventura, S.M. Almeida, M.A. Reis, A.M.G. Pacheco, Atmospheric Selenium in an Industrialized Area of Portugal, *J. Radioanal. Nucl. Chem*. (in press).

[1] University of Austin, Texas, U.S.A.

Air Particulate Matter: Emission Sources, Morbidity and Mortality

S.M. Almeida, C.A. Pio[1], M.C. Freitas, M.A. Trancoso[2]

Objectives

The main objective of this area was to assess the relationship between long term exposure to Air Particulate Matter (APM) and the incidence of Asthma, Chronic Obstructive Pulmonary Disease (COPD) and mortality.

It was expected, not only to find that relationship for the total APM mass concentration, but also for some particle toxic chemical constituents levels (for instance, Pb, Ni, Cd, As, Hg and Cr). The determination of the health risk for different concentrations of total APM and for some of their constituents was also aimed.

The study of the chemical particles species allows the determination of the main sources of particles to the atmosphere, using receptor models. This project assesses the direct relationship between the pollutant sources and the health impacts. With this information, it was possible to suggest abatement strategies perfectly adapted to the studied area, in order to improve the air quality and, consequently, to decrease the impacts on human health.

Results

Aerosol chemical composition data for $PM_{2.5}$ and $PM_{10-2.5}$, was acquired during the year 2001 at a sub-urban area located in the north outskirts of Lisbon. An association of complementary tools, including Principal Component Analysis (PCA), Multilinear Regression Analysis (MLRA), enrichment factors, air mass back trajectories analyses, meteorological data and particle size distribution, was applied to understand, how sources, which are directly accessible to the local authorities, contribute to the APM pollution and what sort of additional actions should be taken at regional, national, EC and worldwide levels to control particulate air pollution. PCA and MLRA were used to identify possible sources of APM and to determine their mass contribution. Seven main groups of sources were identified: soil, sea, secondary aerosols, road traffic, fuel-oil combustion, coal combustion and a Se/Hg emission source. In $PM_{2.5}$, secondary aerosol and vehicle exhaust contributed on average, with 25% and 22% to total mass, respectively, while sea spray and soil represented respectively, 47% and 20% of the coarse fraction mass loading, as shown in Fig. 1. Details of this work are in a PhD thesis concluded in March 2004 at Aveiro University and a current PhD thesis at Technical University of Delft. A (SFRH/BPD/14479/2003) fellowship was attributed for the study of the relationship between long term exposure to APM, sources and the incidence of morbidity and mortality. Results are not yet available.

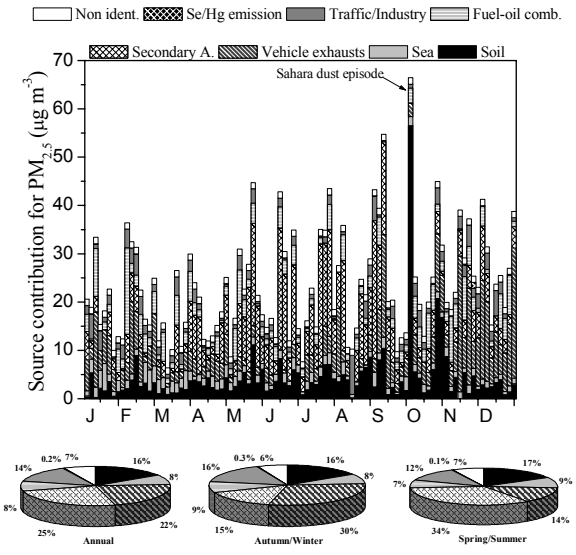

Fig. 1. Identified sources in $PM_{2.5}$ collected in the north outskirts of Lisbonand their contribution.

Published, accepted or in press work

1. S.M. Almeida, Composition and sources of atmospheric aerosol in an urban/industrial region, Ph.D. thesis, Aveiro University, Portugal, 2004.
2. S.M. Almeida, CA. Pio, M.C. Freitas, M.A. Reis, M.A. Trancoso, Contribuição da Circulação Automóvel para o Aerossol Atmosférico na Zona Norte de Lisboa, *Proc. 8th Conf. Nac. Ambiente*, Lisboa, 27-29 Oct.2004, (ed. CD-ROM).
3. S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, M.A. Trancoso, Source Apportionment of Fine and Coarse Particulate Matter in a Sub-Urban Area at the Western European Coast, *Atmos. Environ.* (in press).
4. M.M. Farinha, M.C. Freitas, S.M. Almeida, Air Quality Control Monitoring at an Urban and Industrialized Area, *J. Radioanal. Nucl. Chem.* **259/2** (2004) 203-207.
5. M.C. Freitas, M.M. Farinha, M.G. Ventura, S.M. Almeida, M.A. Reis, A.M.G. Pacheco, Gravimetric and Chemical Features of Airborne PM_{10} and $PM_{2.5}$ in Mainland Portugal, *Env. Monit. and Assess.* (in press).

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Total Selenium Determination and Selenium Speciation in Typical Constituents of Portuguese diets

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Objectives

The first step of this study consisted on selenium determination in individual food items commonly associated with Portuguese food consumption habits. Total selenium was determined by instrumental neutron activation analysis (INAA), through the short-lived nuclide ^{77m}Se. Measurements were performed with a 'fast rabbit system', available at the Interfaculty Reactor Institute (Delft University of Technology, Delft, The Netherlands). The second step was a preliminary study, which aimed the determination and quantification of selenium species existing in one sample of sword fish (*Aphanopus carbo*) obtained on a local market from Coimbra and with origin from Atlantic northwest. For determination of selenium species, an HPLC-UV-HG-AFS system was used. Experiments were performed at the JSI- Jožef Stefan Institute.

Results

On Table 1 values for total selenium determined on food items collected at two different regions are presented.

Table 1. Selenium contents in food items collected in Coimbra and Évora areas.

	Samples from Évora		Samples from Coimbra	
	Se concentration (mg/kg) n=3	Stdev (%)	Se concentration (mg/kg) n=3	Stdev (%)
Cereals and beans				
Rice I (carolino)	0.03	12	0.03	11
Rice II (agulha)	0.03	-	0.05	-
Bean I (manteiga)	0.20	5	0.26	8
Bean II (frade)	0.40	9	0.48	3
Meat				
Chiken	0.34	7	0.59	3
Chicken trifles	2.27	0.4	2.19	2
Pork	0.54	5	0.63	3
Bovine	0.24	6	0.46	3
Fish				
Saurel	13.37	3	6.87	6
Sword fish	3.44	1	3.26	5
Squids	1.81	1		
Octupus	-	-	1.15	9
Sardine	-	-	2.14	5
Eggs	1.05	1	0.98	10
Vegetables				
Broccoli	0.06	37	nd	-
Cabbage	0.09	15	nd	-

The highest values were found, as expected, in protein-rich food such as fish, meat and eggs. A detection limit of 0.05 mg kg^{-1} for the used technique was not enough to determine selenium on vegetables and fruit, which have usually concentrations below or at the same order than this value. When compared with values presented in the literature, very high values were found on fish samples. No significant differences between samples obtained in the two different sampling sites were found.

The total selenium on supernatant from sword fish samples was determined by HG-AFS. The extraction yield was around 80%. This value is 10-15 % inferior to the value pointed out in the literature, where the same type of fish and a similar extraction procedure were used. A chromatogram obtained from sword fish sample with an anion exchange column can be observed on Fig. 1. First results gave indication on the presence of three species, selenometionine (SeMet), selenocystine (SeCys2) and Se-methylselenocysteine (SeMetSeCys). Peaks were all confirmed on the chromatogram obtained by a cation exchange column. The SeMet found in sword fish samples corresponds approximately to 50% of the total selenium extracted.

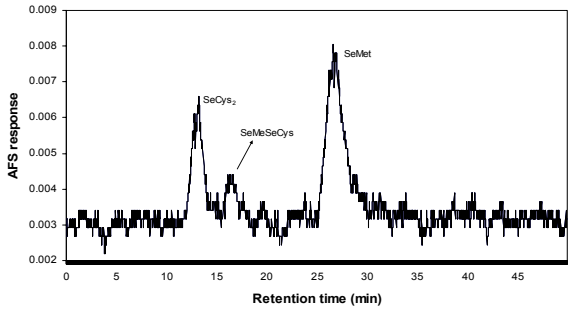

Fig. 1. A chromatogram obtained from sword fish sample with an anion exchange column

In Table 2, speciation analysis results are presented. Values between [] correspond to peaks that appear only in one replicate. Dolt-2 is the reference material (Dogfish liver, National Research Council of Canada), ProXIV and ProVIII are both enzymes used in the digestion process.

Table 2. Speciation analysis results in sword fish

	Sword fish/ProXIV *(n=3)*	*Dolt2/ProXIV* *(n=2)*	*Dolt2/ProXIV/ProVIII* *(n=2)*
Total Se on supernatants (ng)	799.5 ± 62	1482.9 ± 160	1613.9 ± 8
Extraction yield (%)	80 ± 12	54 ± 11	58 ± 2
Species concentration (ng/g sample)			
SeMet	1353.1 ± 138	[411.5]	167.8 ± 78
SeIV	-	[62.5]	-
SeVI	-	-	-
SeMetSeCys	[155.8]	[120.9]	133.6 ± 25
SeCys2	426.8 ± 184	452.7 ± 152	[232.4]
Sum for species detected	1935.8	1047.6	533.8
% from total on sample	59 ± 4	17 ± 10	9 ± 4

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1. M.G. Ventura, M.C. Freitas, A.M.G. Pacheco, Selenium Contents in Typical Constituents of Portuguese Diets, *2nd Int. IUPAC Symp. on Trace Elements in Food*, Oct. 2004, Brussels, Belgium.

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