

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:

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 (both biomonitoring and aerosol monitoring) and training (one post-doctorate on monitoring and two current PhD theses on biomonitoring).

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 are dedicated to this subject.

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.

Nutrition. The group is increasing the investigation in 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 amount range, otherwise severe diseases should be expected. Also nutrition contents in spices and rice originated from Sri Lanka are still being studied, following a IAEA fellowship. Honey analysis is being surveyed for Azores islands and Portugal mainland, a more complete study is now taken in Algarve region.

Training. The research unit has a strong component in post graduation training.

Services. Analytical services are also provided under request (private companies).

Research Team

Researchers

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Students

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Calibration of *in situ* Biomonitoring for Quantification of the Atmospheric Dispersion of Heavy Metals

M.C. Freitas, A.M.G. Pacheco, S. Sarmento, I. Dionísio, M.S. Baptista,
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Objectives

Within BioCAL project (POCTI/CTA/38411/2001, co-funded by 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).

Results

Two-month exposures, performed during Winter, Spring and Summer, at three Portuguese coastal cities, revealed that airborne accumulations of copper, lead, nickel and strontium were partially dependent of meteorological conditions but essentially dependent of nature of exposed material. No reduction in variability of standardized synthetic materials or homogenized biomasses was shown when compared to lichen. The synthetic materials only accumulated Cu and Ni, being therefore considered an alternative to traditional transplants when these are the elements of interest. The biological materials accumulation of studied elements was comparable to lichen transplant accumulation. The tested biomasses did not present higher ability to accumulate metals, thus their replacement of the traditional transplants was not considered advantageous since their attainment is a time-consuming process. Lichen exposure in detached form was suitable in biomonitoring studies instead of traditional transplants and accurate measurement of area/volume is useful to relate atmospheric deposition rates with lichen metal content.

For lichens, low-methylated arsenic species were found in long-term exposure experiments, whereas in short-term exposure experiments no increase in total arsenic concentration was observed although some degree of biomethylation occurred. Tree bark experiments were not conclusive; no arsenic species could be determined due to too low initial total arsenic concentrations. It was concluded that transplanted lichens can only be used for long-term exposure studies. Looking at the extent of methylation seems probable that lichens do not act as simple passive biomonitoring but are actively involved in uptake, accumulation and/or biotransformation of arsenic, possibly other elements as well.

The exposed samples were analysed by INAA, ICP-MS, AAS. It could be concluded that analytical precision was similar for all elements but Br, Cu, Na by INAA, which also did not agree with their certified values in first place. A nonparametric assessment of

correlation between field replicates by paired techniques showed that Spearman coefficients could be asserted at any significance level (asymptotic $p = 0.000$), in all cases and elements. Identical results – based on Wilcoxon's T statistic at $p < 0.05$ – were only found for Na by INAA, Mg, Mn, Ti by INAA and ICP-MS, and Cu by ICP-MS and AAS. In a few cases, biological-matrix effects appeared to underlie the results of the techniques' intercomparison, such as for Ca and Sr (unbiased results for lichen set alone, when separated from bark set) and Pb (unbiased results for bark set alone, when separated from the lichen set).

Significantly higher contents were determined by ICP-MS for As, Ba, Cr, Cs, La, Sc, Ta whereas a few others resulted higher by INAA (Ce, Hf, Se, Zn). Statistically convincing evidence of difference in techniques' output could not be found for Ca, Co, Fe, K, Na, Rb, Sb, Sm, Tb, Th, U, at stringent significance levels. Residual variability may reach 37 % (*P. caperata* thalli) or even 57 % (*P. hybrida* bark), not to mention the biological variability in accumulation during the period(s) of exposure (or assessment, in native lichens). For some elements, experimental issues may arise from digestion procedures (ICP-MS) and/or sample heterogeneity (INAA).

Published or in press work

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2. M.C. Freitas, A.M.G. Pacheco, I. Dionísio, S. Sarmento, M.S. Baptista, M.T. Vasconcelos, J.P. Cabral. Multianalytical determination of trace elements in atmospheric biomonitoring by INAA, ICP/MS and AAS, *Nuclear Instruments and Methods in Physics Research A* (in press).
3. M.C. Freitas, A.M.G. Pacheco, I. Dionísio, S. Sarmento, M.S. Baptista, M.T. Vasconcelos, J.P. Cabral, Instrumental neutron activation analysis and inductively coupled plasma mass spectrometry on atmospheric biomonitoring, *J. Radioanalytical and Nuclear Chemistry* (in press).
4. A. Machado, Z. Šlejkovec, J.T. van Elteren, M.C. Freitas, M.S. Baptista, Arsenic speciation in transplanted lichens and tree bark in the framework of a biomonitoring scenario, *J. Atmospheric Chemistry* (in press)

Atmospheric Aerosol Impacts on Human Health*S.M. Almeida, M.C. Freitas, S. Sarmiento, C.A. Pio¹*

This work is supported by the project POCI/AMB/55878/2004. The main objective is 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, for both total APM mass concentration and particle toxic chemical constituents' levels (as Pb, Ni, Cd, As, Hg, Cr). Health risk will be followed relating different concentrations of total APM and some of their constituents. The study of the chemical particles species allowed determining the main sources of particles to atmosphere, using receptor models. The direct relationship between pollutant sources and health impacts will be assessed. From this information, it will be 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. Time series related to APM concentrations are correlated with asthma and COPD hospital admissions. In 2005, Hospital admission for the respiratory diseases was obtained by analysing the hospital check-out lists from Instituto for Informatic and Financial Management for Health. The health data are analyzed by time series methods in order to exclude potential confounders as seasonal and long term patterns, daily temperature, humidity, precipitation, other pollutants (SO₂, O₃, NO_x) concentration and influenza epidemics. Meteorological and air quality data are obtained in Meteorological and Environment Institutes.

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Studies for the Evaluation of Selenium (and Other) Levels in Typical Constituents of Portuguese Diets*M.G. Ventura, M.C. Freitas, A.M.G. Pacheco¹, H.T. Wolterbeek²*

The aim is to determine the selenium content in a few selected food items commonly consumed and produced in Portugal. Selenium is an essential trace element of fundamental importance to human health. Despite its biological importance, data on selenium in foods are still limited for Portugal. Selenium levels in foods are affected by both content and availability of the element in soil or feed which vary geographically between and within countries. This study provided basic information on selenium content in various foods which can contribute to build a national database. The latter combined with national consumption data can be used to estimate the selenium intake by Portuguese population. Rich protein food, i.e., meat, fish, eggs contribute mostly to the daily dietary Se intake. Vegetables, fruits, cereals, with lower contents on selenium can be an important source on the Mediterranean type diet, where its consumption is considered high. Total selenium content in selected food items have been determined using nuclear activation analysis (NAA) in both versions instrumental (INAA) and replicate sample (RSINAA) through the short-lived nuclide ^{77m}Se, respectively at Interfaculty Reactor Institute/Delft and developed at ITN. Selenium daily intake for two geographically distinct population groups and on selenium species determination in fish samples with high consumption in Portugal, are followed.

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Biomonitoring of trace element air pollution*A.P. Marques, R.M. Godinho, M.C. Freitas, H.Th. Wolterbeek¹*

This study is about the use of lichens in air pollution studies. Lichens are used in all experiments and elemental analyses are performed by nuclear multi-elemental techniques. One project aimed this year to understand the differences in the results obtained by two elemental techniques in two replicates of the same sample – it was concluded that statistically they do not differ, and to focus on elemental accumulation differentiation in the possible set-ups in transplant monitoring. The other project focus on the (bio)assessment of the elemental burden from selected APM's size classes. The issue is to relate lichen elemental occurrences to elemental occurrences in selected atmospheric size PM, thereby discriminating towards solubility and extractability. Results should make out the usability of lichens in fast and easy estimates of integrative atmospheric. The attention is focused on the multi-element solubility and extractability in both lichens and selected PM size classes, obtained from the same exposure sites. The issue is that lichens may reflect soluble and /or extractable fractions of atmospheric PM's in various or specific size classes. Positive results may lead to an extensive use of lichens in easy, cheap, geographically large scaled and first-line screening of elemental burden from atmospheric particles.

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