Atmospheric Elemental Dispersion

Maria do Carmo Freitas

The aim of this unit is research related to environment (mainly atmosphere). Related also to atmospheric environment is nutrition and health. These are the main interests of the group: environment, nutrition and health. It is a natural application of the potentialities of k_0-INAA (instrumental neutron activation analysis using the k_0-method). The development of this nuclear analytical technique runs in parallel with their applications. The research unit activities include six main lines:

Monitoring, Biomonitoring, Quality Control, and Data Handling aiming at characterising areas of Portugal (continent and islands) 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 atmopsphere, both locally and by long-range transport. In conjunction to this, data analysis methods and development are very important due to the multielement nature of the analytical techniques used. This nature makes that specific methods can and are being used and developed to profit the most out of this type of data. 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 is currently done: services to industry (monitoring), project research (biomonitoring) and training (one PhD thesis in monitoring finished this year and one PhD thesis in 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 to be initiated next year are dedicated to this subject.

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 onvestigates 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 and air particulate matter the state valence of the chemical elements, which is the subject of another PhD thesis.

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 another PhD thesis.

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 just started, aiming at a submission of a project (FCT and/or Azores regional collaboration).

Training. The research unit has a strong component in training: five PhDs, one MSc, and one graduation thesis are ongoing; four graduation theses and one PhD were completed this year. Also a 1-year training for an IAEA fellow was completed this year.

Services: Analytical services were also provided under request (private companies), and under a contract initiated in 1999 (IDAD/ValorSul).

Atmospheric Elemental Dispersion

Research Team

Researchers

- M.C. FREITAS, Aggregation principal researcher
- A.M.G. PACHECO, Auxiliary professor (15%)[1]
- RANJITH JAYASEKERA, IAEA fellow (83%)[4]

Students

- S.M. ALMEIDA, PhD student, Aveiro Univ., PRAXIS grant; post-doctorate in 2004, PRAXIS grant
- R. GODINHO, PhD student, Delft Univ. Tech., PRAXIS grant
- S. SARMENTO, PhD student, Delft Univ. Tech., PRAXIS grant
- A.P. MARQUES, PhD student, Delft Univ. Tech., ITN grant
- M.M. FARINHA, PhD student, Delft Univ. Tech., ITN grant
- M.G. VENTURA, PhD student, IST, Lisbon Technical Univ., PRAXIS grant
- E. SOUSA, Graduation student, Azores Univ.
- A.S. AMARAL, Graduation student, Azores Univ.
- C. RODRIGUES, Graduation student, Azores Univ.
- E. FERREIRA, Graduation student, Trás-os Montes Univ. (17%)

Technical Personnel

- A. MACHADO, POCTI
- B. VIEIRA, POCTI
- I. DIONÍSIO

Funding (€)

Research Projects:	0
Industry Contracts:	37 328
Services:	2 580
Total:	**39.908**

Publications

Books:		0	
Journals:		7	and 8 in press
Proceedings:		22	
Conf. Communications:		3	
Other publications (reports):		3	
Theses:	PhD	1	
	MSc	0	
	LIC.	5	
IAEA training:		1	

[1] CVRM-IST
[2] IRI/Delft Univ. Tech.
[3] DCA/Azores University
[4] On leave from Sri Lanka University

Lichen Transplants in the Assessment of the Dispersion of Atmospheric Pollutants: Effects of Positioning Towards Wind Direction

A.P. Marques, M.C.Freitas, M.A. Reis, H.Th. Wolterbeek[1], T. Verburg[1], J. de Goeij[1]

Objectives

Analysis of the enhancement by wind direction differential exposure of biomonitors in particular for the lichen transplant study in Sado estuary.

Results

The trace element monitoring was carried out with epiphytic lichen transplants of Parmelia sulcata Taylor. The transplants were suspended in December 1997 according to a grid in the Sado estuary area. They were oriented facing (F) and opposing the wind direction (T) and exposed in a special device built for the purpose.

The obtained results indicate that F (facing the wind) and T (opposing the wind) positioned transplants do not differ regarding the accumulation of Na, Mg, P, Cl, K, Fe, Co, Ni, Ga, Se, Br, Sr, Ba, La, Nd, Sm, Lu and Ta, regardless of the examined periods of exposure. Differences between F and T transplants were obtained for Cr and Zn (see fig. 1 for facing/opposing the wind ratio). For the remaining elements, high variability is observed.

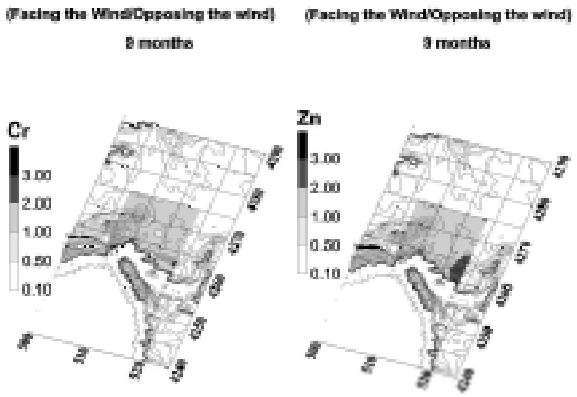

Fig. 1 – Contour plots (Surfer, Golden Software Inc) of transplants ratio (facing/opposing the wind) for Cr (3, 6 and 9 months exposure) and Zn (6 and 9 months exposure). These plots are based in a 1/r3 extinction rule.

Nine factors were identified using all Sado data sets (three soil factors, sea spray, physiological, oil combustion, iron and steel processing and handling, agricultural activities and one unknown factor) and seven factors were identified using F and T data separately. Two factors are only identified in all data combination. Five factors were identified for the three combinations performed, oil combustion, 2 soils, marine and physiological factors. The factors identified as agricultural activities and ferrous metal processing and handling, could be transplant specific (Table I). For these 2 factors, F data presents better correlation with all data than T data. Overall the relative strength of the factors is similar for F and T in common sources.

Table I – Cos(N-dimensional vector angles) between the MCTTFA factors for the three different combinations performed; all data (A), facing the wind transplants data (F) and opposing the wind transplants data (T). Only values greater than 0.75 are marked black.

T \ F	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Factor 1	0.87	0.32	0.36	0.39	0.09	0.50	0.49
Factor 2	0.38	0.50	0.22	0.88	0.20	0.48	0.63
Factor 3	0.37	0.25	0.96	0.21	0.17	0.25	0.38
Factor 4	0.35	0.95	0.24	0.46	0.19	0.53	0.28
Factor 5	0.05	0.21	0.01	0.27	0.93	0.21	0.26
Factor 6	0.37	0.23	0.30	0.43	0.36	0.70	0.58
Factor 7	0.59	0.26	0.54	0.62	0.13	0.49	0.36

All in all, for the majority of elements determined, the data indicate the absence of any significant differences in the behaviour of F and T positioned transplants. F and T positioned transplants accumulate elements to similar levels, and they both don't show any appreciable accumulation of litophylic elements. Moreover, F and T positioned transplants both don't show appreciable losses of K and P, and in general they show similar source profiles in MCATTFA approaches and similar outcomes on calculated source-contributions to total element concentrations, although there are some particular exceptions.

Published, accepted or in press work

1. A.P. Marques, M.C. Freitas, M.A. Reis, H.Th. Wolterbeek, T. Verburg, "MCTTFA applied to differential biomonitoring in Sado estuary region", Journal of Radioanalytical Nuclear Chemistry, Vol. 259, Nº 1 (2004) (in press).
2. A.P. Marques, M.C. Freitas, M.A. Reis, H.Th.Wolterbeek, T. Verburg, J.M.M. De Goeij, "Biomonitoring-transplants in the assessment of the dispersion of atmospheric pollutants: effects of positioning towards wind direction", proceedings of the 3rd International Workshop on Biomonitoring of Atmospheris Pollution, September 21-25, Slovenia, 2003 (in press).

[1] Interfaculty Reactor Institute – IRI, Netherlands

Evaluation of Airborne Trace Elements in Azores and Madeira Archipelago Through Biomonitoring

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

Objectives

This study is the first study of atmospheric elemental pollution using biomonitors in Azores (Terceira, Santa Maria, São Jorge and São Miguel islands) and Madeira archipelagos. It aims to identify species of lichens, bryophytes and tree bark and to evaluate their capacity as bioaccumulators in those islands and to evaluate the spatial distribution of a few trace elements, identified as originated from local and/or remote emission sources.

Results

The species were selected according their abundance and distribution in each island. The lichens species selected were *Flavoparmelia caperata*, *Parmotrema crinitum*, *Parmotrema robustum*, *Parmotrema bangii*, *Usnea dasaea*, *Usnea esperantiana*, *Usnea cornuta*, *Usnea rubicunda*, *Usnea hirta*, *Usnea subfloridana*, *Ramalina canariensis*, *Ramalina farinacea*, *Ramalina implectens*, *Ramalina pussilla*, *Cladonia coccifera*, *Cladonia coniocraea*, *Cladonia fimbriata*, *Cladonia furcata*, *Cladonia glauca*, *Platismatia glauca*, *Hypotrachyna rockii*, *Parmelinopsis horrescens*, *Parmelinopsis minarum*, *Pyrrhospora quernea*, *Heterodermia leucomelos*, *Pyxine subcinerea*,

The bryophytes species selected were *Frullania tamarisci*, *Sphagnum palustre*, *Orthodicranum scottianum*, *Hypnum uncinulatum*, *Fissidens taxiofolius*, *Andoa berthelotiana*, *Campylopus pyriformis*, *Eurhynchium praelongum*.

Because bryophytes species were collected near the ground level the analysis showed a significant contamination by soil particles. As a result bryophytes species were excluded in the latest studies. Tree bark (*Cryptomeria japonica*) and lichens species showed good agreement. Their high elemental contents are mostly naturally originated from the soil (volcanic, more or less recent). Mercury, bromine and antimony, among others, were enriched in Azores Archipelago.

Fig. 1- *Cladonea coccifera* collected at S. Miguel Island (16x).

Fig. 2 - *Ramalina pusilla* collected at Terceira and Santa Maria Island (40x).

Fig. 3 - *Parmotrema bangii* collected in Azores and Madeira archipelagos (40x).

Published, accepted or in press work

1. B.J. Vieira, 2002. Trace Element Evaluation in Terceira Island, using Biomonitoring. Graduation Thesis. ITN/DCA-Azores University, Angra do Heroísmo.
2. P.M. Soares, 2003. Trace Element Evaluation in Santa Maria Island, using Biomonitoring. Graduation Thesis. ITN/DCA-Azores University, Angra do Heroísmo.
3. N. Correia, 2003. Trace Element Evaluation in Santa Maria Island, using Biomonitoring. Graduation Thesis. ITN/DCA-Azores University, Angra do Heroísmo.
4. 4 E. Sousa, 2003. Trace Element Evaluation in São Jorge Island, using Biomonitoring. Graduation Thesis. ITN/DCA-Azores University, Angra do Heroísmo.
5. S. Amaral, 2003. Trace Element Evaluation in São Miguel Island, using Biomonitoring. Graduation Thesis. ITN/DCA-Azores University, Angra do Heroísmo.
6. C. Rodrigues, 2003. Trace Element Evaluation in Pico Island, using Biomonitoring. Graduation Thesis. ITN/DCA-Azores University, Angra do Heroísmo.

[1] – DCA-University of Azores.

Biomonitoring in Azores and Madeira Archipelagos (Portugal) Using Lichens, Bryophytes and Tree-Bark

B.J. Vieira, M.C. Freitas, A.F. Rodrigues[1], P.M. Soares[1], A.M.G. Pacheco[2], M.I. Prudêncio, N. Correia[1], R. Gabriel[1], A. Aptroot[3]

Objectives

Biomonitors to be used in upcoming surveys in Azores and Madeira archipelagos were studied Different species of lichens, bryophytes and tree bark were collected in Terceira and Santa Maria (Azores) and Madeira Island and their contents were determined by instrumental neutron activation analysis (INAA). Superficial soils were also collected to evaluate the influence in biomonitores.

Results

The chemical characterization of surface soils showed that the superficial layer of the soil is correlated with the type of initial material. The projection material being richer in Hf, Ta and Se, as well as rare earth elements, Th, Zn, Rb and Mn and basalts have higher concentrations of Sc, Ti, V, Cr, Fe and Co. The more relevant differences found between the two islands are: (1) existence of positive Ce anomaly in two soils from Santa Maria Island, (2) higher contents of Cr in Santa Maria Island; and (3) Br is more concentrated in Terceira Island and shows an increasing gradient from East to West.

Results obtained for genera with different species of lichens were compared, as well as results of foliose and fruticose lichens, with the purpose of calibration. The results correlate well (see for example Fig. 1), even if fruticose species take up more Cl, Na, Mn, and Zn. Foliose lichens generally show higher contents than fruticose lichens, roughly a half factor. Generally speaking, and in what concerns lichen bioindication, morphological aspects and habitat features appear more relevant than mere interspecies, taxonomic distinction. The element contents of such species show that even if the contents are generally low, and in that sense comparable what has been found in other remote areas, they differentiate between spatial patterns with indications of effects of some sources.

Hg and Se contents were emphasized and it was hypothesized that Se blocks the mercury uptake in lichens and bryophytes once a very threshold concentration is exceeded. Local burning of fossil fuels contributes in a very small extent to Hg atmospheric contents of the Azores and Madeira Islands. Possible major airborne sources of Hg in the islands include long-range transports, marine emissions, volcanic fluxes, crustal degassing and weathering degassing, or combination of these.

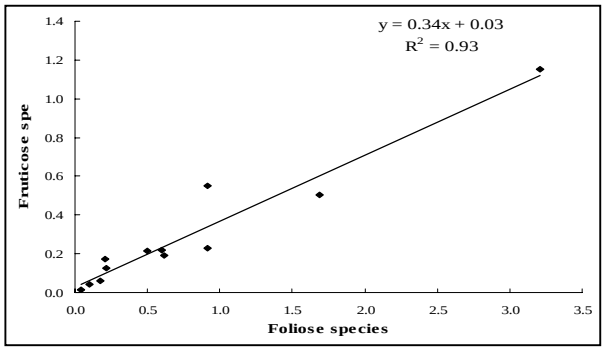

Fig.1 - Calibration of foliose and fruticose lichens collected in Santa Maria Island Centre.

Published, accepted or in press work

1. 1.B.J. Vieira, P.M. Soares, M.I. Prudêncio, M.C. Freitas, A.F. Rodrigues, Caracterização química (terras raras e outros elementos) de solos das Ilhas de Santa Maria e Terceira (Açores, Portugal), Geociências (accepted).

2. B.J. Vieira, F. Rodrigues, M.C. Freitas, P.M. Soares, N. Correia, Determination of minor and trace elements in lichens of Terceira, Santa Maria (Azores) and Madeira Islands. 3rd Int. Workshop on Biomonitoring of Atmospheric Pollution, September 21-25, Slovenia, 2003 (in press). *Journal of Atmospheric Chemistry* (submitted).

3. 3.Rodrigues, A.F., Freitas, M.C., Vieira, B.J., Soares, P.M., Correia, N., Gabriel, R., Mercury in lichens, bryophytes and tree bark in the Central North Atlantic islands, 3rd Int. Workshop on Biomonitoring of Atmospheric Pollution, September 21-25, Slovenia, 2003 (in press). *Journal of Atmospheric Chemistry* (submitted)

[1] DCA-University of Azores
[2] CRVM-Technical University of Lisbon
[3] CBS - Royal Netherlands Academy of Arts and Sciences

Calibration of in Situ Biomonitors for Quantification of the Atmospheric Dispersion of Heavy Metals

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

Objectives

Within BIOCAL project (POCTI/38411/CTA/2001, financed by FCT with FEDER funds) a study was conducted in spring and summer of 2003 (two months each). The principal aim of this study consisted in evaluating the performance of non-biological monitors exposure modes as alternative to the already demonstrated performance of biological monitors.

Results

Three sampling sites (Viana do Castelo, Porto and Sines) were selected in view of the existence of meteorological station, high levels of pollution and accessibility. Especial attention was taken in Sines due to the wide variety of anthropogenic sources. This area is a typical industrial zone, where a refinery, a thermo-electrical power station and a petrol-chemical industry are located among other industries. Also vehicle and boat traffic are significant. Lichen biomass (*Flavoparmelia caperata*) and tree-bark biomass (*Platanus hybrida*) – together with prospective, non-biological monitors – cellulose acetate and Chelex-100™ resin – were exposed with conventional transplants of the same species. The conventional biological transplants consisted in *Flavoparmelia caperata* and *Platanus hybrida* in square pieces. The device used to expose the samples (except tree bark, consisting of square pieces exposed inside 2 mm grid nylon bags) consisted in a plastic petri-slide, polyamide linen (61 μm porosity) and the biological and non-biological monitors to be exposed. (see figure 1). The polyamide linen is used to keep the material inside the specified exposure area, allowing the determination of the exact exposed area. Biological and non-biological monitors were exposed in triplicate, protected from direct rain.

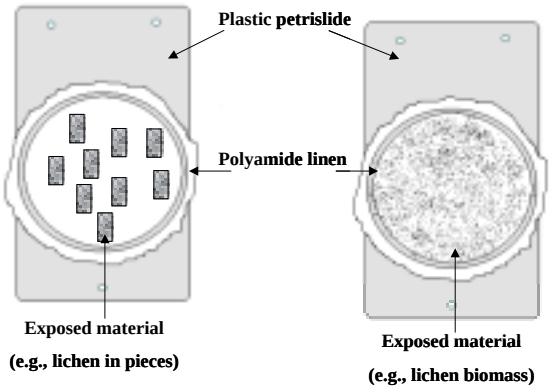

Fig. 1 - Exposure device for lichens (square pieces and biomass), tree bark (biomass) and polymeric monitors – cellulose acetate and Chelex-100™ resin.

After exposure, the samples contents in chemical elements were determined by instrumental neutron activation analysis (INAA). Sines results were analyzed using manganese as a crustal reference for data normalization.

The elements contents determined revealed a high variability, limiting the biological and non-biological monitors comparison. Even though, it was clear that higher element accumulation was obtained in spring. When comparing the two expositions (spring and summer) for the biological monitors data (pieces and biomass), good reproducibility and consistency was found. For the lichen case, higher element accumulations were determined in the biomass; the opposite behaviour occurred with the tree bark. This may indicate that increasing the exposure area has benefits in the lichen case, but it has no influence when tree bark is concerned. When comparing lichen with tree bark, it appeared that lichen (in pieces or biomass), was a more consistent bioaccumulator than bark (in pieces and biomass). Even though, for K determination, bark in pieces was advisable. For the resin and cellulose acetate data, fewer elements were detected, reducing the chance of these monitors to be alternative to the traditional ones. In the resin case, the high affinity to Na might explain the limited elements accumulation. The Cl vs. Na correlations evidenced a good reliability of the biological monitors and cellulose acetate data. It also indicated that the seawater was the elements source. Therefore, concerning Cl and Na, lichen biomass, bark biomass and cellulose acetate might be used as alternative to lichen and bark transplant. In the Mg case, correction of total element content in the exposed samples for soil contamination, by Mn normalization, turned possible more effective comparisons. The Mg correlations results indicated soil and seawater contribution and confirmed Mn as a good soil tracer.

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, Proceedings of BIOMAP-3, Bled, Slovenia, September 21-25, 2003. *Journal of Atmospheric Chemistry (*submitted*).*

[1] CIIMAR (Centro Interdisciplinar de Investigação Marinha e Ambiental)
[2] CVRM-IST (Centro de Valorização de Recursos Minerais-Instituto Superior Técnico)
[3] LAQUIPAI (Laboratório de Química Inorgânica Pura e de Aplicação Interdisciplinar)

Assessment of Lichen Vitality During Transplantation to a Polluted Site

R. M. Godinho, M. C. Freitas, H. Th. Wolterbeek[1]

Objectives

This experiment intents to examine the short time accumulation behaviour of lichen thalli exposed to a known source of air pollution in terms of physiological parameters and metal accumulation.

It was studied: 1) the influence of thalli morphology using to different species, one foliose (*Parmelia caperata*) and other fruticose (*Evernia prunastri*). 2) The influence of tissue age, exposing separately old and new parts of the thalli. 3) The influence of the process of transplantation, transplanting lichens from the same place were they would be exposed.

Results

Lichen samples were collected in a clean area and transplanted 1) to the same zone nearby were they were collected, and 2) to a polluted area under the influence of an industrial complex. Transplant samples were taken periodically during four months in both places. At the same time lichen samples from Tomar native populations were also collected. Lichen vitality was evaluated by the following physiological parameters: chlorophyll content, the chlorophyll degradation (expressed as change in the $A_{435nm}/A_{415\ nm}$ ratio), and the cell membrane integrity (represented by K^+ leakage measured by electric conductivity) Total metal concentrations were determined by INAA.

Fig. 1- Hanging method and exposure device.

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Lichen vitality

Lichen vitality, as measured with the studied parameters, showed to have seasonal fluctuations related mainly with temperature and humidity. Differences could be found between Sines and Tomar, indicating a possible charge effect. There seems to be more sensibility during summer hot and drier months, although previous studies indicate that lichens are more sensitive to air pollution in the hydrated, physiologically active state.

The similar behaviour in Tomar of native and transplanted species indicates that the process of transplanting itself did not affect seriously lichens health, although in the summer native lichens seem to present better indices.

From the chosen parameters, the leachate conductivity was the most sensitive. Total chlorophyll concentration only shows a decrease in *E. prunastri*, and A_{435nm}/A_{415nm} values only vary in the summer. This agrees with previous reports of sensitive order of lichen physiological response to air pollution.

The values A_{435nm}/A_{415nm} of the present study, even ones from the control site, were low when compared with literature indicating some degree of phaeophytinization

E. prunastri was the most sensitive species. When transplanted to Sines it showed an immediate rise on conductivity values while *P. caperata* managed to recover initial values during spring, just being more affected at the driest and hot period. Also *E. prunastri* was the only to show a reduction in the total chlorophyll concentration, although that was not corresponding with A_{435nm}/A_{415nm} values indicating molecule degradation.

Elements concentration

Preliminary results indicate different accumulation behaviour either between species or in different parts of the thallus. However results are still missing for analysis in course

Published, accepted or in press work

1. Godinho R. M., Freitas M. C. E Wolterbeek H. Th. 2003. “Assessment of lichen vitality during transplantation to a polluted site”, Proceedings of BIOMAP-3, Bled, Slovenia, September 21-25, 2003. *Journal of Atmospheric Chemistry* (submitted).

[1] IRI – Delft University of Technology, Delft, The Netherlands

Monitoring of Trace Elements Through Vascular Plants

M.C. Freitas, A.M.G. Pacheco[1], A.P. Marques, B. Vieira, I. Dionísio

Objectives

Vegetation, other than lichens, is being collected either related to industry contracts (ValorSul trace element monitoring) or research. Leaves of vascular plants and tree bark are routinely analysed.

Results

Since 1999 services are being provided in the framework of the S. João da Talha Urban Residue Incinerator air quality monitoring program.

ValorSul contract with biomonitors foresees a twice a year sampling, in Spring and in Autumn, in order to monitor the trace element eventual increase due to the laboration of S. João da Talha urban waste incinerator. Three biomonitors were chosen. Fig. 1 shows some results for Zn an element associated with incinerators.

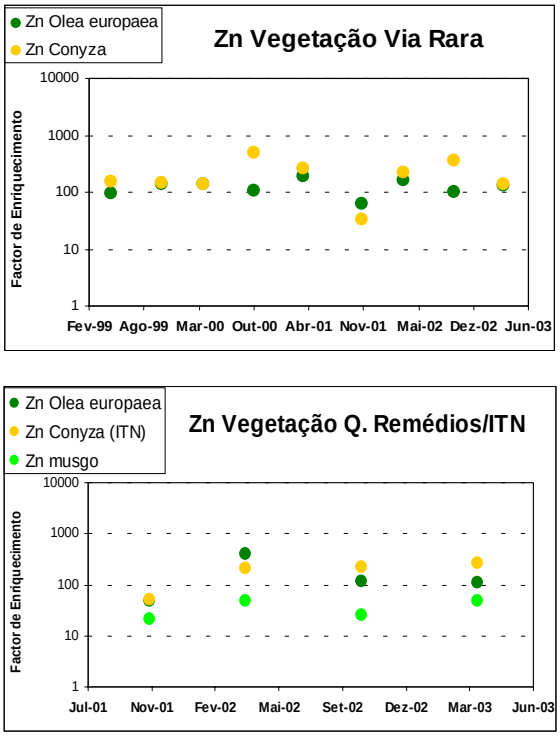

Fig. 1 - Results for Zn in two sampling stations, Via Rara and Q.R./ITN.

Fig. 2 shows the enrichment factors (EF) for bark (*Cryptomeria japonica*) collected in Terceira island. Efs are compared with the results of well known bioaacumulators (lichens) collected from the bark samples. For saline elements both biomonitors gave identical response, pointing out enrichment. Bark of *Cryptomeria japonica* appeared to be a better biomonitor than either *Parmotrema* sp. or *Ramalina* sp.. This was also found that *Olea europaea* bark showed higher EF than *Parmelia sulcata* lichen, appearing also as a better biomonitor (see Fig. 3).

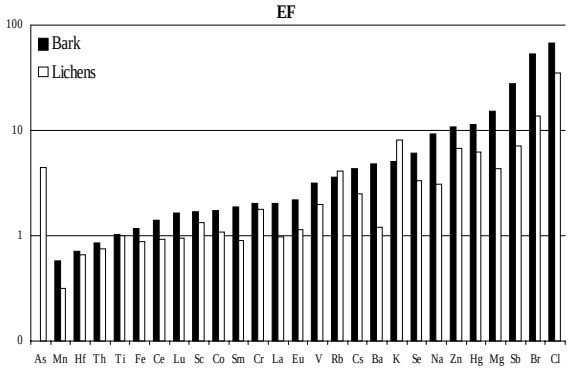

Fig. 2 – Enrichment factors of elements in lichens and tree bark of Terceira Island.

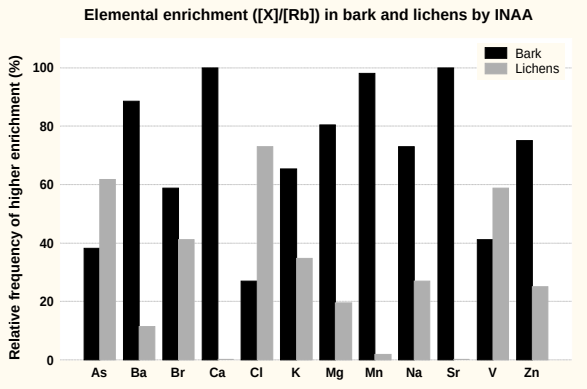

Fig. 3 - Nonparametric trends of enrichment in related samples of *Olea europaea* bark and *Parmelia* spp. thalli across the study area in Portugal Continental.

Published, accepted or in press work

1. A.M.G. Pacheco, M.C. Freitas, M.A. Reis, Trace-Element Measurements in Atmospheric Biomonitors – A Look at the Relative Performance of Inaa and Pixe on Olive Tree Bark, *Nucl. Inst. and Meth. A* 505 (2003) 425-429.
2. 2.M.C. Freitas, M.A. Reis, A.P. Marques, S.M. Almeida, M.M. Farinha, O.R. Oliveira, M.G. Ventura, A.M.G. Pacheco, L.I.C. Barros, Monitoring of Environmental Contaminants: 10 Years of Application

[1] CVRM/IST

of k0-INAA, *J. Radioanal. Nucl. Chem.* 257(3) (2003)
621-625.

Sources and events affecting air particulate matter in an industrialized/urban area located at the north of Lisbon

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

Objectives

Air particulate matter (APM) was measured in an industrial/urban area, situated in the North of Lisbon, in different air masses trajectories episodes, in order to evaluate the contribution of long range transport in their physico-chemical characteristics. Principal Component Analysis (PCA) and Multilinear Regression Analysis (MLRA) were used to identify possible sources of aerosol and determine their contribution for APM mass.

Results

Aerosol particles were collected in two fractions – AD (aerodynamic diameter) < 2.5 μm and 2.5 μm < DA < 10 μm - and analysed in relation to total mass, trace elements, water soluble ions and organic and black carbon. The analysis of samples according to air mass characteristics shows the importance of the Atlantic Ocean in Lisbon air quality. Maritime episodes present the lowest anthropogenic and mineral aerosol concentrations, due to the sea unpolluted air masses transport and the increase of the dispersion conditions associated to these scenarios. The highest mineral and anthropogenic loads in PM10 and PM2.5 were recorded in South Continental air masses due to the transport of dust from Africa and polluted air from Europe and due to the local emissions. In 2001 50% of the PM10 EU limit values exceeded was measured during African dust events.

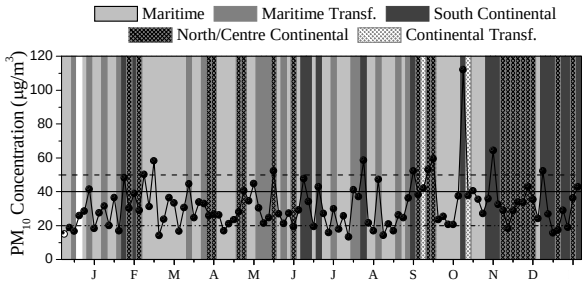

Fig. 1 - PM10 concentration discriminated by air mass type. EU Directive 1999/30/CE limit values --- 24h limit value (50 μg/m^3); __annual limit value for 2005 (40 μg/m^3); _.._ annual limit value for 2010 (20 μg/m^3).

Seven main groups of sources were identified: soil, sea, secondary aerosols, road traffic, fuel-oil and coal combustion and metal works. In PM2.5 secondary aerosol, road traffic and fuel oil combustion contribute on average, and respectively, with 22%, 19% and 17% of the total fine aerosol mass; while sea spray and soil represent, respectively, 39% and 25% of the coarse fraction mass loading. Seasonal variations with maxima during the summer and minimum in winter were observed for sulphate. Seasonal variations for most of the other anthropogenic species had a maxima in cooler seasons.

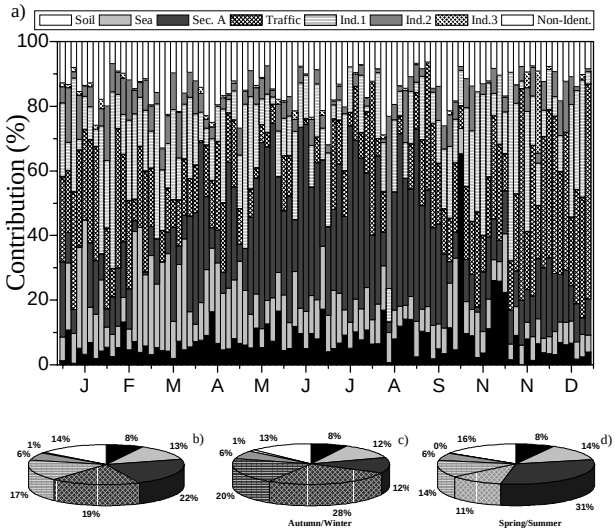

Fig. 2 - Relative source contribution for PM2.5 total mass concentration (%) time series. Average relative source contribution for PM2.5 total mass concentration during all the year (b), autumn/winter (c) and spring/summer (d).

Published, accepted or in press work

1. 1.S.M. Almeida, M.A. Reis, M.C. Freitas, C.A. Pio, Quality assurance in elemental analysis of airborne particles, *Nuclear Instruments and Methods in Physics Research B* 505 (2003) 609-613.
2. 2.S.M. Almeida, M.C. Freitas, M.A. Reis, C.A. Pio, Quality assessment on airborne particulate matter of k_0-INAA, *Journal of Radioanalytical and Nuclear Chemistry* 257 (3) (2003) 609-613.
3. S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis Events Affecting Air Particulate Matter in Lisbon,– European Aerosol Conference, Madrid, Spain, 31 August-5 September 2003. *Journal of Aerosol Science* (submitted).

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Arsenic Speciation in Lichens and in Coarse and Fine Air Particulate Matter

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

Objectives

This is part of the PhD work of M.M. Farinha. The objective of this work is the arsenic speciation and multi-element analysis in transplant lichens and fine and coarse air particulate matter using several extracts solution. Comparison of the two different monitoring systems was made.

Results

Parmelia sulcata transplants and coarse and fine air particulate matter used in this study are from an experiment held in Portugal in the period of 1994-95. Two sampling sites were chosen for this study, Tapada do Outeiro and Sines. Tapada do Outeiro is a rural site located in the north of Portugal with an old power station (100 MW) burning 80% national coal and 20% of fuel oil during the sampling period. Sines is a small town located south of Lisbon in an industrial area including the largest and more modern coal-powered station of the country (1256 MW) during the sampling time.

For total arsenic content, samples were analysed by instrumental neutron activation analysis (INAA) in the Portuguese Research Reactor and concentrations were calculated by the k_0-method.

In order to extract the arsenic present in the samples a three-step sequential extraction procedure with Milli-Q, $CaCl_2$ and H_3PO_4 was applied. The arsenic species identification was made in the Josef Stefan Institute in Slovenia using HPLC-UV-HG-AFS.

The extractability of arsenic in both monitoring systems is shown in the Fig. 1 and Fig. 2.

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 a total As concentration after exposure being similar 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.

Concluding we may say that in lichens the presence of organic arsenic may indicate the biotransformation of inorganic As, since in the fine and coarse aerosol fractions these species were not identified.

Table 1 Total amount of As, and the extracted amount with Milli-Q and $CaCl_2$+H_3PO_4 from coarse and fine fractions collected at Tapada do Outeiro and Sines.

Sampling site	Size fraction	Total As conc. (ng/m^3)	(mg/Kg)	Extractability of As Milli-Q	$CaCl_2$+H_3PO_4	refractory (in % of total As)
Tapada Outeiro	Fine	2.71	135	14.1	31.6	54.3
	Coarse	0.69	51	8.5	71.3	20.2
Sines	Fine	1.90	116	6.2	15.8	78.0
	Coarse	0.15	10	-	52.5	47.5

Table 2 Total As concentrations and sequential arsenic extractability in Milli-Q and in $CaCl_2$+H_3PO_4 extracts for lichens exposed at Tapada do Outeiro and Sines (a and b denote duplicate lichen transplant and in situ samples)

	Total As conc. mg kg^{-1}	Extractability of As Milli-Q	$CaCl_2$+H_3PO_4	refractory (in % of total As)
Reference a	0.82	≈ 3	1.5	96
Reference b	0.97	2.6 - 6.2	-	94 - 97
Tapada Outeiro a	2.8	≈ 7	4.6 - 6.2	≈ 88
Tapada Outeiro b	1.6	7.5 - 9.3	1.0 - 1.8	≈ 90
Sines a	2.1	≈ 2	-	≈ 98
Sines b	2.3	≈ 2	0.7	≈ 97

Published, accepted or in press work

1. 1.M.M. Farinha, Z. Šlejkovec, J.T. van Elteren, H.Th. Wolterbeek, M.C. Freitas, Arsenic Speciation in Lichens and in Coarse and Fine Air Particulate Matter by HPLC-UV-HG-AFS, Proceedings of 3rd Int. Workshop on Biomonitoring of Atmospheric Pollution, September 21-25, 2003, Slovenia. Journal of Atmospheric Chemistry (submitted).
2. 2.Z. Šlejkovec, M M. Farinha, Z. Jeran, J. T. van Elteren "Arsenic Speciation in Lichen Samples, Proceedings of 3rd International Workshop on Biomonitoring of Atmospheric Pollution, September 21-25, 2003, Slovenia. Journal of Atmospheric Chemistry (submitted).
3. 3.Z. Šlejkovec, M.M. Farinha, J.T. van Elteren, H.Th. Wolterbeek. Arsenic speciation in lichen samples. In: Report of research co-ordination meeting held at the Institute for Chemical Technology and Analytics, Vienna, Austria, 18-22 November 2002. Development and validation of speciation analysis using nuclear techniques. Vienna: IAEA, 2003, p. 17-24.

[1] Jožef Stefan Institute, Slovenia
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Levels of Selenium in Portugal

M.G.Ventura, M.C. Freitas, A.M.G. Pacheco[1]

Objectives

More than other nutrient, selenium illustrates the dichotomy between essentiality and toxicity. For this fact selenium constitutes an interesting subject for environmental and health related studies. At ITN, selenium is determined by instrumental neutron activation analysis (INAA), based on measurement of the long-lived ^{75}Se nuclide. Aiming the estimation of selenium contents distribution in Portuguese territory, selenium results are compiled, resulting from a few environmental studies using lichens, vascular plants, soils and air particulate matter (APM) held since 1990. A comparative study for selenium deposition between the lichen Parmelia sulcata and APM for two Portuguese locations is presented and discussed.A comparative study for selenium deposition between the lichen Parmelia sulcata and APM for two Portuguese locations is presented and discussed.

Results

Mean or range in contents of Se were determined for locations: Tapada do Outeiro, Carregado, Bobadela, Faralhão, Palmela, Abrantes, Sines and Monchique.

Contents found for Se in soil are inside the typical range for most soils. Mean values for soil were calculated for two different depths. At all cases, the difference between the depths 0-10 cm and 10-20 cm was not significant.

The determined values in plants are within the range 0.01-2 mg/kg given in the literature as being the normal quantities for Se on mature leaf tissue for various species of plants. The results obtained are different depending on the analysed plant. Comparatively to vascular plants, lichens have higher contents at the same places.

Concentration of selenium for atmospheric particulate matter given in the literature can vary between 0.3 and 5.7 ng/m3 in urban areas and, between 0.03 and 1.6 ng/m3 in rural areas. All studied sites have typical values of urban areas; Monchique and Palmela are in the lowest level of the range while Sines is in the highest. APM Se values in Carregado and Bobadela located at North of Lisbon area are of the same magnitude of those obtained for Faralhão located at Setúbal Peninsula.

Air particulate matter and its deposition over lichens have been related in a few publications.

In qualitative terms, apparently there is a good agreement between the distribution of Se in APM and the Se found in the native lichens (Parmelia sulcata), visible from the Se mapping shown by Freitas et al., 2000. The correlation between Se in the lichen transplants (in ng/cm^2) and the cumulative Se contents in APM (in ng/cm^2) during the lichen exposure time was determined for Carregado and Monchique and is quite satisfactory for both stations (see figure 1).

Transplants from Monchique accumulate much more Se than the Carregado transplants, fact that can be attributed to the better physiological conditions of Monchique transplants and to an inferior number of atmospheric components in that place.

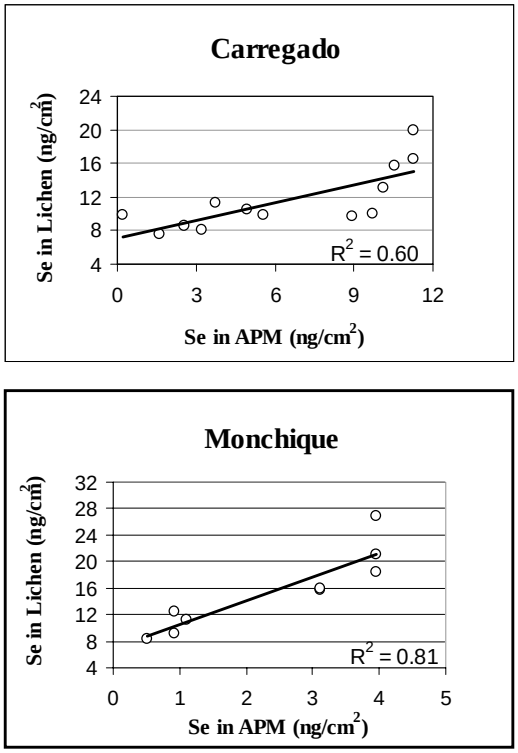

Fig. 1 - Correlation between Se in the lichen transplants and the cumulative Se contents in APM during the exposure time for Carregado and Monchique.

Published, accepted or in press work

1. 1.M. G. Ventura, M. C. Freitas, A. M. G. Pacheco; Levels of Selenium in Portugal. Proceedings of the 3rd International Workshop on Biomonitoring of Atmospheric Pollution; Bled, Slovenia, September 21-25, 2003. Submitted to Journal of Atmospheric Chemistry.

[1] CVRM-IST

Monitoring of Trace Elements in the Atmosphere Using Nuclear Analytical Techniques

M.C. Freitas, M.M. Farinha, M.G. Ventura, B. Vieira, I. Dionísio, M.A. Reis, O.R. Oliveira, R. Pinheiro, P.C. Chaves, M. Coutinho[1], M. Pereira[1], C. Borrego[1]

Objectives

This program combines both research and services to the community. The objectives are the direct monitoring of concentrations of trace metals in the atmosphere, a field where nuclear techniques can play an important role, and a field in which much support to the general society can be provided.

Results

Within this program, and since 1999 services are being provided in the framework of the S. João da Talha Urban Residue Incinerator air quality monitoring program. Data on elemental contents in PM2.5 and PM10-2.5 are determined. In Figs. 1 and 2 it is shown the concentrations found for some of the main pollutants.

Results shown in Figs. 1 and 2 indicate that lead concentrations tend to decrease as a consequence of unleaded gasoline, arsenic concentrations are seasonal, being higher in autumn/winter, mercury can reach very high levels and then also enormous amounts of selenium are emitted. Beyond these elements also Cd, Cr, Cu, K, Mn, Ni, Sb, V, and Zn were reported for the same period (1999-2003).

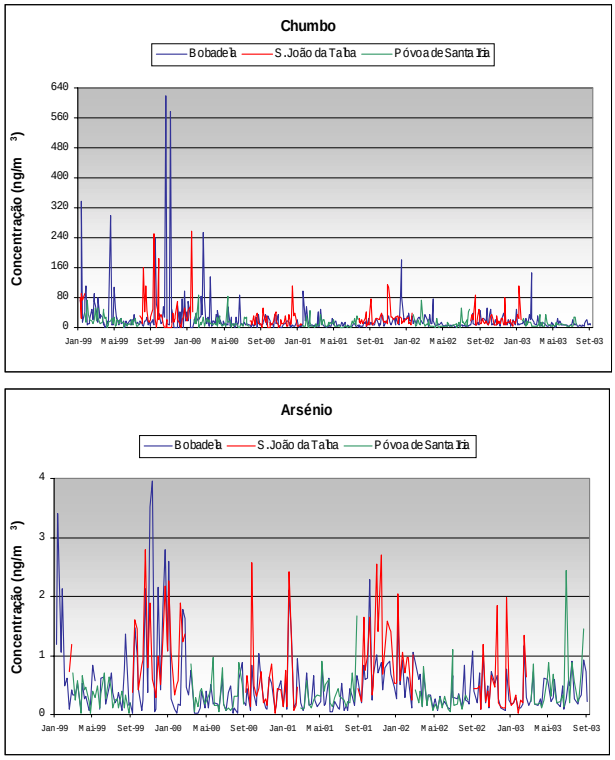

Fig. 1 – Pb and As concentration evolution in PM10 in Lisbon area (1999-2003).

[1] IDAD – Instituto do Ambiente e Desenvolvimento

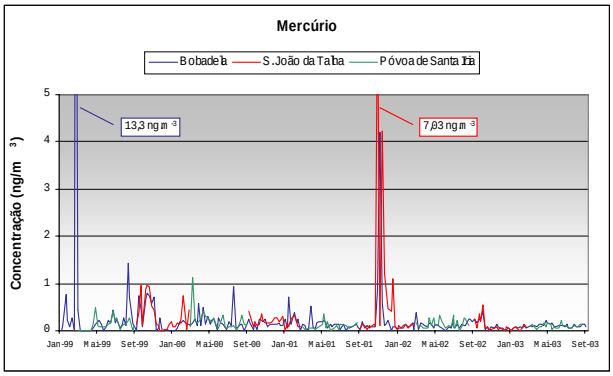

Fig. 2 – Mercury concentration evolution in PM10 in Lisbon area (1999-2003).

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2. 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* (in press).
3. 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* (in press).
4. M.M. Farinha, M.C. Freitas, S.M. Almeida, Studies of Air Quality Control Monitoring of an Urban Waste Incinerator, *J. Radioanal. Nucl. Chem* (in press).
5. M. Coutinho, M. Pereira, C. Borrego, M.C. Freitas, M.A. Reis, M.M. Farinha, P.C. Chaves, O. Reis, B. Vieira, I. Dionísio, R. Pinheiro, Monitoring of Air Quality - Program of CTRSU Monitoring of Air Quality – Valorsul, IDAD/ITN Report (2003) (in Portuguese).

Major and Trace Element Analysis of Spices and Rice. The Applicability of k_0-Standardization and Energy Dispersive X-Ray Fluorescence

Ranjith Jayasekera[1],*, M.C. Freitas, M.F. Araújo

[1] On leave from Sri Lanka University, Colombo.

Objectives

The fellowship programme was focused on a well-organized research plan on the major and trace elements in some foodstuffs from Sri Lanka. The main objective of the research programme was to obtain data on the elemental concentrations, including those of the potentially toxic elements, in some foodstuffs (rice and some spices), and to compare them with maximum permissible levels specified in international guidelines. The results of this study are intended to be used as baseline values for future comparisons.

Results

The levels found for a number of major and trace elements in the above investigation were either lower than or consistent with general values published for food plants.

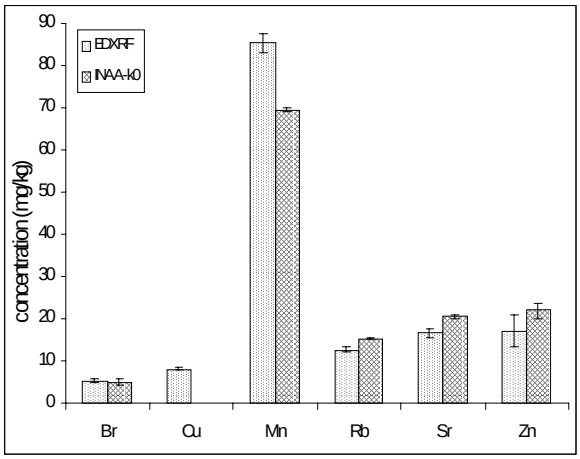

Fig. 1 - Comparison of the concentration values (with ± SD) obtained by EDXRF and INAA-k_0 for turmeric powder.

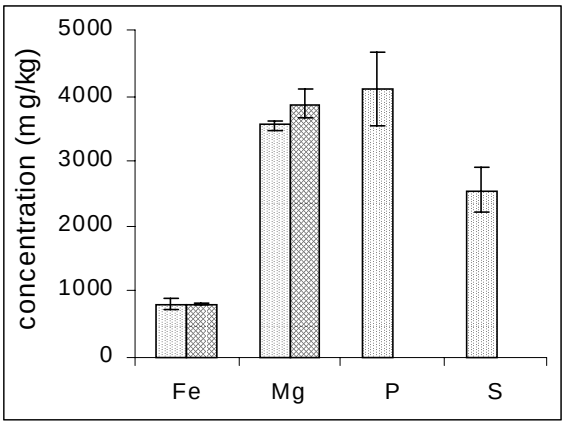

Fig. 2 - Comparison of the concentration values (with ± SD) obtained by EDXRF and INAA-k0 for curry powder 1.

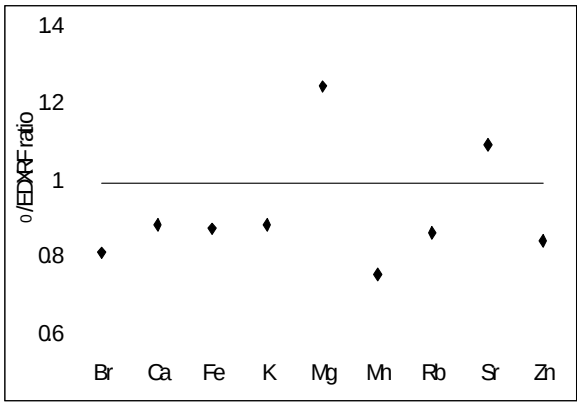

Fig. 3 - Concentration ratio (INAA-k0/EDXRF) for nine elements analysed both by INAA-k0 and EDXRF in curry powder 4.

For the degree of accuracy required in the analysis of spices, the two techniques are suitable, as can be inferred from the results obtained for the SRM 1572.The k_0 standardization method is particularly suitable as a multi-element technique, because by using several combinations of irradiations and decay times, the number of elements that can be detected and determined with adequate accuracy and precision is increased considerably.Since the spices of tropical origin are of particular chemical composition, specially the curry powder with several plant ingredients, the development of a suitable reference material is of utmost importance.

Table 1 Approximate daily dietary intake supplied through rice

Element	Raw rice (200g/day)	Daily dietary
Ca	28.3 mg	0.8 g
Cu	1.01 mg	3 mg
Fe	5.16 mg	10-20 mg
Mn	3.18 mg	4 mg
Na	3.9 mg	1-2 mg
Zn	6.5 mg	15 mg
Co	21 µg	3 µg
Se	65.1 µg	0.1 g

Published, accepted or in press work

1. R. Jayasekera , M.C. Freitas, M.F. Araújo, Major and trace element analysis of spices. The applicability of k_0-standardization and energy dispersive X-ray fluorescence, Journal of Trace Elements in Medicine and Biology (accepted).