Atmospheric Elemental Dispersion

Introduction

This group was created, with proper identity, during the year of 1998 as a result of a natural evolution of the work done previously in this field. The field is a natural application of the potencialities of both k_0-INAA and PIXE to environmental air pollution and atmospheric chemical and physical processes. The aim of this line ranges from the simple and direct evaluation of elemental concentrations in suspension in the atmosphere to the caracterization of local and mesoscale dispersion patterns. For this both air filtering and biomonitoring techniques are used. Also the nuclear measuring techniques development runs in parallel with the subject oriented work, allowing for a double faced research that provides a more immediate use of the developments made in each area.
The state of art well defined procedures are also made available to the general non-scientific community as service provider.
In the next 5 to 10 years the activities in this area are planned to develop along four main lines:

- Monitoring and biomonitoring of atmospheric dispersion of elements
- Prototype development
- Heavy metal speciation
- Transfer of know-how and technology in the role of CPLP

Monitoring and biomonitoring of atmospheric dispersion of elements

The atmospheric biomonitoring program essencially started with a campaign held in the Summer of 1993, although some related work had been already made before. Presently, data from a quantification experiment are being deeply explored and a PhD thesis is just about finished on that subject. A local scale environment impact study using trasnplants was launched and the sample collection part is completed, data are now going for evaluation. Some of the data here colected were already subject of a presentation in an International Conference.
Direct monitoring of elemental air pollution was also started essencially at the same time as the biomonitoring program. The group is now in conditions of making the know-how available to the outside of the scientific community, being involved in the evaluation of the effects on the air quality of the start-up of an Urban Solid Residue Incinerator placed in the vicinity of the laboratory.

Prototype development

Since the end of 1993, the construction of an automatic air filtering units changer has been planned. Recently it was possible to come to a laboratory version of a low cost system, which will now enter the stage of optimisation towards a pre-comercial version. The know-how accumulated in this development will be used to develop INAA and PIXE automatic sample changing units.

The remain topics titles both speak for themselves and correspond to activities which will be launched in a near future.

Research Team

Researchers –	2 (1 PhD)
Research Students –	4
Technicians –	3

Publications

Journals –	3	and 6 in press
Conf. Commun.:	3	
Theses:		
Lic. –	1	

	10^3 PTE
Expenditure:	**3 337**
Missions:	2 154
Other Expenses:	753
Hardware & Software:	430
Other Equipment:	0

		10^3 PTE
Funding:		**4 250**
External Projects:	1997	-572
	1998	4 700
Others		122

Response of Lichen *Parmelia sulcata* to Environmental Pollutants in Portugal

***M.A.Reis*[1], *M.C.Freitas*[1], *L.C.Alves*[1], *B.van Os*[2], *H.Th.Wolterbeek*[3]**
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Abstract
Transplants of lichen *Parmelia sulcata* collected in an area previously identified as non polluted, were placed at six stations, five of which were near Power Plants and the other in an area expected to be pollution free. Together with the lichen transplants, two total deposition collection buckets and an aerosol sampler were installed. Lichens were recollected two every month from each station. At the same time new ones replaced the water collection buckets. The aerosol sampler filter was replaced every week, collection being effective only for 10 minutes out of every two hours, in the remote station, aerosol filters were replaced only once a month, the collection rate being kept. Each station was run for a period of one year. Both lichens and aerosol filters were analysed by PIXE and INAA at ITN. Total deposition samples were dried under an infrared lamp, and afterwards acid digested and analysed by ICP-MS at the National Geological Survey of the Netherlands. Data for the three types of samples were then produced for a total of 16 elements. Use was made of the data set thus obtained to test a model for the time response of this lichen to a new environment. Application of the model to a national survey based on *Parmelia sulcata* performed in 1993 is discussed.

Environmental Pollution (in press).

Mean Annual Response of Lichens *Parmelia sulcata* to Environmental Elemental Availability

***M.A.Reis*[1], *L.C.Alves*[1], *M.C.Freitas*[1], *B.van Os*[2], *H.Th.Wolterbeek*[3]**
[1] *ITN, EN10 Sacavém, 2685 Sacavém, PORTUGAL*
[2] *National Geological Survey, Haarlen, The Netherlands*
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Abstract
Lichens collected in an area previously identified as unpolluted, were transplanted to six different places located in polluted areas near Power Plants (both fuel and coal powered). A total of 26 lichen transplants were made for each place, each transplant weighing about 2g. Two were analysed as zero or reference and the remain 24 were hanged in nylon net bags in order to be able to collect two transplants each month, out of every station. Besides the 24 lichen samples, each station was provided with two total deposition collection 10 litter buckets (with 25 cm diameter funnels) and an aerosol sampler. Concentration in both lichens and aerosols were measured by PIXE and INAA at ITN. Total deposition residues were analysed by ICP-MS at the The Netherlands Geological Survey. On this work we present the results obtained by looking for correlation between lichens elemental concentrations and annual averages of elemental availability variables such as concentration in suspension in the atmosphere and concentration in total

deposition samples, for a total of 40 elements. In order to access both the limitations and the reliability of the results a discussion on the details of handling this data set is presented. A mathematical function which tentatively represents the lichen up-take response to water availability is also proposed.

IAEA TECDOC (in press).

Lichens *Parmelia sulcata* Time Response Model to Environmental Elemental Availability

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Abstract
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IAEA TECDOC (in press).

Lichens *Parmelia sulcata* Time Response Model to Environmental Elemental Availability

M.A.Reis[1], L.C.Alves[1], M.C.Freitas[1], B.van Os[2], H.Th.Wolterbeek[3]
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Abstract
Parmelia sulcata transplants, collected in a non-polluted area, were exposed to new atmospheric conditions at six stations, of which five were located near power plants; the last one was located in an unpolluted area. Data were collected for a one-year period, on rainfall, and on elemental composition in total deposition, aerosols and lichen materials. The experiment was carried out to quantify the relationships between elemental

environmental availability and elemental accumulation in lichens. A mathematical model was developed, including a simple representation of the lichen, and a memory loss function which describes the time relations for the lichen's progressive reflection of new ambient conditions. The data set obtained for the various stations was used to test the model. The results indicate that the environmental data on Na, Al and Pb could be reproduced and model-predicted, including occurring fast variability patterns. Half-memory times were calculated for Na, Al and Pb as 200, 500 and 600 days respectively, based on using all station data simultanuously in fitting procedures. However, the data also show that further improvements are still needed, including the clarification of differences in model outcomes between stations.

The Science of the Total Environment (in press).

Current Work

Some Applications of Nuclear Techniques to Environmental Studies

M.C. Freitas, M.A. Reis, L.C. Alves
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Abstract
In our Institute environmental studies are being performed for more than one decade. Lichens were collected in 1993 within a national survey programme, pollution sources were identified using multivariate factor analysis. Results on lichen transplants were conjugated with total deposition and air particulate matter to study the time response of the lichens to the surrounding environment. Particular regions of the country, intensively industrialised, are being studied in detail, for modelling. PIXE and INAA were applied in combination, giving a quite good panoramic of the elemental composition of the different samples. In this work, examples of the environmental applications of these two techniques within the mentioned projects will be presented.

This work was submitted for presentation at the 6th Int. Conf. on Applications of Nuclear Techniques, Creta, Grécia, 20-26 de Junho de 1999.

Dispersion of Chemical Elements in an Urban Atmosphere using Parmelia sulcata

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Abstract
The region of Lisbon and south of Lisbon (Sado estuary) is densely industrialised, and therefore air pollution should be studied in a more detailed scale there. The topography of the Sado estuary region and the predominant wind direction from north-west contribute to the influence in this region of the industries located north. The region selected includes an oil power station.
Transplants of the lichen *Parmelia sulcata* were suspended in nylon bags in that region within a rectangle of 15 km wide and 25 km long on a grid 2.5 km $\times$ 2.5 km; centred in the power station. In each of the 47 places two sets of four transplants each were hanged. Care was taken i) in covering the sets with a polyethylene roof to prevent leaching of elements in the lichen, ii) in building a hanging system which could rotate according to the wind direction, iii) in orienting each one set towards the wind and the other set against the wind.
For one-year period and every three months, one transplant of each set is collected. The lichen transplants are cleaned, freeze-dried, and ground in a Teflon mill. Pellets are prepared for INAA and PIXE analysis.
The data obtained by both techniques are submitted to Monte Carlo factor analysis in order to identify pollution sources. The elemental concentrations are mapped and discussed. As far as we know it is the first study on differentiation of elemental uptake of *Parmelia sulcata* according to wind direction; this study can furnish some insight towards the phenomena behind lichen elemental uptake. At the same time, also information upon local and distant sources is expected to be accessible. The absence of direct rainwater on the lichens during this study must be stressed too. In a previous work these two conditions - wind direction and absence of direct rainwater - were not taken into account, therefore we also aim to compare the results of both studies.

This work will be presented at the MTAA-10 in Washington, April 1999, and it will be submitted to the Journal of Radioanalytical Nuclear Chemistry, Articles.

Biomonitors Memory Effects upon Calibration of Lichens Parmelia sulcata

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Abstract
One of the most important steps which provides a qualitative improvement upon the use of biomonitors is their calibration against more traditional element availability variables like deposition or airborne concentration. On doing this, a very simple approach is usually used. It requires the measurement of some availability variable, say deposition, during a given time interval, say one year, and a set of biomonitors exposed to environments presenting different availability environments. It is also assumed that a linear regression between biomonitors concentration and availability average values does provide a good calibration. Once memory times different from zero or infinity are considered this approach becomes erroneous. In this work, an uptake experiment using transplants of lichen *Parmelia sulcata* held in Portugal during a two years period (1994/95) is described. The problem of calibrating biomonitors considering memory effects is discussed and possible solutions proposed. The important role of rainfall is also addressed.

Calibration Methods

As opposed to moss calibration procedures, which allow a straightforward calibration procedure, some care must be taken to calibrate lichens out of an uptake experiment. This is due to the fact that: lichens exposed for, say two month, cannot have any information of what append afterwards; lichens exposed for long periods are exposed to a mean availability value different from the average value of the time step period prior to its collection from the experiment site. Besides this the calculus of the linear interpolation parameters must also take into consideration that the data set is not ideal. In order to proceed with a straightforward linear calibration the following expressions were thus used:

$$\langle LEC \rangle_\ell = a \cdot \overline{A}_\ell + b \quad \text{being} \quad \overline{A}_\ell = \frac{1}{N}\sum_{i=1}^{N} \langle A \rangle_i^\ell = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\sum_{j=1}^{i}\left(\Delta T_j^\ell \cdot A_j^\ell\right)}{\sum_{j=1}^{i} \Delta T_j^\ell} \right) \tag{1}$$

Where $\langle LEC \rangle_\ell$ is the algebraic mean value of element content of 24 lichen transplants exposed during the experiment, $\overline{A}_\ell$ the average of the $\langle A \rangle_i^\ell$ availability, being ΔT_i^ℓ the time interval for the i^{th} month period at station ℓ. The calibration parameters were obtained by interpolation based on the minimisation of the sum of squares and the mathematical expressions used accounted for the existence of cases of missing data. Both missing data and values bellow detection limit were not replaced by zero but overlooked.
Once obtained the values for a and b, the determination of the average availability from an individual lichen elemental content value is straightforward:

$$\overline{A} = (LEC - b)/a \quad \text{being now generaly} \quad \overline{A} = \int_{-\infty}^{0} A(t)\, dt \Big/ \int_{-\infty}^{0} dt \tag{2}$$

where the right hand side of the second equation of (2) must only be understood from the formal point of view, of course.
This formal expression of (2) allows a fast, simple and clear introduction of the need for a memory correction term. In fact, if had it be written as:

$$\overline{A} = \int_{-\infty}^{0} e^{\frac{t}{l}} A(t)\,dt \Big/ \int_{-\infty}^{0} e^{\frac{t}{l}}\,dt \tag{3}$$

and the need for formal interpretation can be dropped, because (3) is meaningful by itself, even in a strict mathematical sense, as long as l , the memory period, is positive but not infinity.
In order to accommodate such a concept into the simple calibration procedure, we can simply replace the individual lichen concentration expression by:

$$LEC_i = a_m \langle A \rangle_i + b_m \quad \text{making now} \quad \langle A \rangle_i = \sum_{j=1}^{i} \left(e^{-\frac{T_i - Tj}{l}} A_i \, \Delta T_i \right) \Bigg/ \sum_{j=1}^{i} \left(e^{-\frac{T_i - Tj}{l}} \Delta T_i \right) \tag{4}$$

in order to allow numerical calculations.
Equation (1) is then just slightly changed to accommodate the additional exponential term.
After solving the system of equation extreme values of the sum of squares of the difference between measure and model, this approach leads to an equation in l , namely:

$$\sum_{l,m=1}^{N_{lm}} \left(\langle LEC \rangle_l - \overline{\langle LEC \rangle} \right) \cdot \left(\overline{A}_m - \overline{\overline{A}_m} \right) \cdot \left(\overline{A}_l \frac{\partial \overline{A}_m}{\partial l} - \overline{A}_m \frac{\partial \overline{A}_l}{\partial l} \right) = 0 \tag{5}$$

which solutions can be found numerically.

This paper is about to be finished and is planed to be submitted to the environmental issue journal “The Science of Total Environment”. In this resume we present only the main ideas for considering memory effects while calibrating lichens uptake.

Gravitational Fitting
A Procedure Based on the Collapse of the Parameter Space

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Abstract

The major problems that must be faced when attempting to fit a non linear model to data are: the setting of the initial values of the parameters, the selection of the merit function and the belief that the results obtained really correspond to absolute extreme of this function and not to a local extreme. Although several methods were developed to approach this problem, like Markquardt-Lavenberg, Simplex, Simulated Annealing and others, most of them are based either in a good initial parameter values or in an optimisation around a first good set of values. Another group of optimisation procedures exists which like Simulated Annealing makes use of Maximum Entropy Bayesian Methods but in a more complex way, thus being not a good choice if the fitting is expected in useful time and a good knowledge of these methods is not already available. The method here proposed allows for a fast and simple implementation, makes very simple use of any desired merit function, being even applicable under conditions were chaotic behaviour of the model can not be excluded.

The Model

The model is based on a random search for parameter values. Initially the whole parameter hiperspace is searched using a log-uniform grid. The uses of a log uniform distribution for the points to calculate the merit function, imply that a higher density of points is found near a reference value. If there is any hint to what the fitting parameter value should be, then this value should be given as starting reference, but this is not an essential input. In the first iteration the merit function is thus determined in a defined (not necessarily vary big) number of points and a set of points presenting the best merit function results is selected.

In the specific implementation made, a set of 20 points is selected out of a total of 2401 points in the parameter hiperspace. The point presenting the best merit function result is used as reference point for the second iteration. In the first five iterations nothing else is made. After these, the values for each of the parameters are limited to the interval centred in the value assumed at the best point and having an amplitude equal to twice the range of values for that same parameter in the set of the 20 bets points. This process is then repeated until the hipercube of values allowed for the parameters is considered small enough or there is no evidence that additional improvement can be obtained.

In the particular implementation used, a variable merit function was used. For every odd iteration the ratio of the correlation between model and data to the product of normalised chi-square and maximum absolute difference was used as merit function. In the even iterations, only the correlation or the inverse of the maximum absolute difference was used in an alternate faction. In this way a consistency between different merit functions results was also accessed.

This model is now under improvement while it is being applied to the study of a lichen time response model. The major problems are faced on the exit conditions which must be not strict enough so that the cycle is endless repeated but cannot be also much too loose so that the shrinking process gets not effective enough.

Lichens Time Response Model

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Abstract

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Under this subject one paper was accepted for publication in an IAEA TECDOC (Proceedings of the International Workshop in Atmospheric Biomonitoring) and a deep revised version was already accepted to publication in "The Science of Total Environment". The application of the fitting procedure described above to this subject is planed to be presented in the next year.

Comparison of air filtered volume and collected mass between GENT and S.A.R.A. samplers

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Abstract

The automatic system for replacement of aerossol stacked filter units (S.A.R.A.) was idealised from the "Gent" stacked filter unit sampler. Sofar discussion were made concerning automatic SFU replacement, the vacuum air tightness, the robustness of the system and the mechanism to avoid contamination problems. The last experiment aims to compare the air filtered volume and the collected mass between S.A.R.A. and two "Gent" machines, for some sample sets. The three samplers were installed close to each other, in the Physics Department building. The experiments occurred out of the time schedule in order to avoid the influence of some possible emissions. In this experiment, we installed a new PM10 inlet in S.A.R.A. machine. It was developed to ensure a better efficiency in the separation of particles around 10 μm of "equivalent aerodynamic diameter".

The results obtained, presented in the table, shows that the new machine results are in good agreement with the values obtained with the "Gent" samplers.

amostra	tempo de acumulação (horas)	volume de ar filtrado (m^3)	massa retida filtro fino (μm)	massa retida filtro grosso (μm)	massa total retida (μm)
GENT a 1	16.04	16.723	263.3	190.0	453.3
GENT b 1	16.02	16.231	256.7	193.3	450.0
S.A.R.A. 1	16.00	15.356	296.7	190.0	486.7
GENT a 2	16.02	17.282	286.7	106.7	393.3
GENT b 2	16.01	15.922	223.3	106.7	330.0
S.A.R.A. 2	16.00	14.858	226.7	133.3	360.0
GENT a 3	16.03	15.884	276.7	140.0	416.7
GENT b 3	16.00	16.240	370.0	236.7	606.7
S.A.R.A. 3	16.00	15.336	290.0	153.3	443.3
GENT a 4	16.28	15.955	443.3	160.0	603.3
GENT b 4	16.25	15.826	463.3	126.7	590.0
S.A.R.A. 4	16.00	14.152	363.3	103.3	466.7