Atmospheric Elemental Dispersion

The aim of this scientific line is the evaluation of elemental concentrations in suspension in the atmosphere and the characterisation of atmospheric dispersion of chemical elements either local, mesoscale or long-range transport. For this, both monitoring (air filtering and deposition sampling) and biomonitoring are used. The field is a natural application of the potentialities of k_0-INAA and PIXE. Development of these two nuclear analytical techniques runs in parallel allowing for a double faced research that provides a more immediate use of the developments made in each area.

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
- Techniques development and chemical element speciation
- Transfer of know-how and technology in the role of CPLP (Portuguese Speaking Countries Community)

The analytical techniques available within the group are suitable for services and collaborations. Therefore, activities such as:

- INAA and PIXE applications for the scientific community
- INAA and PIXE applications for the industry

are also made in a routine basis.

Monitoring and biomonitoring of atmospheric dispersion of elements

The atmospheric biomonitoring program essentially started with a campaign held in the Summer of 1993, although some related work had been already made before.

Biomonitor response quantification for about 20 elements were achieved for lichen *Parmelia sulcata* and results are reported in a PhD thesis just finished on that subject (scheduled to be presented in the Summer of 2000).

A local scale environment impact study using biomonitor transplants and air particulate matter collection was carried out and data are now being thoroughly explored.

Direct monitoring of elemental air pollution was also started essentially at the same time as the biomonitoring program. The group applied his know-how in this field to the outside of the scientific community, being involved in the evaluation of the effects on the air quality, since the start-up (May 1999) 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 sample changer has been planned. Recently a laboratory version of a low cost system was used and it was shown to provide results otherwise difficult to obtain. Changes for robustness of the apparatus are now being implemented. The know-how accumulated in this development will be used to develop INAA and PIXE automatic sample changing units.

Techniques development and chemical element speciation

Contacts were made with Dr. Maria Teresa Vasconcelos of LAQUIPAI (Porto University) for supervising one PhD thesis on chemical element speciation in biomonitors; and with Dr. H.Th. Wolterbeek of IRI (Delft Technical University) for supervising a 3-month training on this subject in the last trimester of 2000.

Future perspectives

In the near future, integration of biomonitoring with standard monitoring will be continued as a research topic.

Services will continue to be provided. With the expected new European regulations for control of atmospheric pollutants, the unit is in position of expanding this type of work, as long as it does not become limited by infrastructures throughput (namely accelerator beam time, reactor useful time and gamma detectors free time).

At the frontier of international research the search for methods of chemical element speciation in airborne particles and biomonitors, using the techniques available in ITN as well as its combination with other techniques, will be the main goal.

Biomonitors Faint Memory Effects upon Calibration of Lichens *Parmelia sulcata*[*]

M.A.Reis, L.C.Alves, M.C.Freitas, B.van Os[1], H.Th.Wolterbeek[2] , J. de Goeij[2]

Objectives

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. In this work, an uptake experiment using transplants of lichen *Parmelia sulcata* was held in Portugal during a two years period (1994/95) and their calibration was carried out considering faint memory effects from the phenomenological point of view. The project is the main component of the PhD Thesis of M.A.Reis, scheduled to be presented in the Technical University of Delft in the year 2000.

Results

Faint memory effects were introduced into calibration by two ways. In the first the amount of element available for the biomonitor (availability) is weighted prior to the calculation of average:

$$LEC_i^{\ell} = a_m \langle A \rangle_i^{\ell} + b_m \quad ; \quad \langle A \rangle_i = \sum_{j=1}^{i} \left(e^{-\frac{T_i^{\ell} - T_j^{\ell}}{\lambda}} A_i \, \Delta T_i^{\ell} \right) \Bigg/ \sum_{j=1}^{i} \left(e^{-\frac{T_i^{\ell} - T_j^{\ell}}{\lambda}} \Delta T_i \right) \tag{4}$$

where LEC_i^{ℓ} is the element content in the lichen at time instant i , $\langle A \rangle_i^{\ell}$ the average availability in the time period before i and ΔT_i^{ℓ} the time interval for the i^{th} month period at station ℓ . It was shown that such an expression still allows a pure regression calculation of a_m and b_m parameters on the minimisation of the sum of squares, although λ is unknown. This parameter is the solution of equation:

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

to be found numerically.

The second method to account for faint memory effects makes use of both availability average or maxima data and simultaneously, of the standard variation of availability. It was shown that by using both these terms in a linear regression, much better results were achieved.

Both approaches provide information on the biological response of the organism to availability. This leads to the introduction of a new concept which is Equivalent Constant Availability and allows to group different availability time series into a common class, represented by the effect that the sequence of availability events has upon an organism.

Using these approaches it was possible to model lichen response out from availability for 20 elements out of a list of 25. The traditional linear regression method only allows for 11 recoveries and several with worse statistical significance.

[*] This project was funded in previous years by the IAEA TC-POR/8/006 (15x10^6 PTE)

[1] National Geological Survey, Haarlen, The Netherlands
[2] IRI-TUDelft, Mekelweg 15, 2629 JB Delft, The Netherlands

Lichens Time Response Model and Gravitational Fitting*

M.A.Reis, L.C.Alves, M.C.Freitas, B.van Os[1], H.Th.Wolterbeek[2], J. de Goeij[2]

Objectives

To understand the behaviour of biomonitors from a physical point of view, it is necessary to test the physical model used against real data. This project starts with the second approach to quantification of lichens response used for the PhD thesis of M.A.Reis (the main topic is described also in this section), but extends much beyond that. The final goal is to have a complete model which describes the dynamics of uptake of elements by lichens (applicable also to other organisms) under any condition of climate and for any element.

Results

So far a a model was proposed and shown to contain two limit cases one of which is the ad-hoc expected response of biomonitor. The second limit case was shown to provide better results in some cases. These results were published in [1].

For the test of the whole model it was necessary to implement a fitting algorithm to obtain physical meaningful values for the parameters. After a search in the literature of fitting algorithms and methods, it was realised that the best selection should be for Simulated Annealing methods. The fact that these methods were originally devised to solve problems in discrete parameter spaces, leads to the proposal of a new fitting algorithm which uses some of the reasoning behind simulated annealing methods but is specially developed to approach problems where the parameter space is continuous.

The method is based in a random generator that provides a distribution of random points in the parameter space, centered in a given set of coordinates and with a variable density. The shape of the density is controlled by a single number, described as the gravitational parameter.

References

1. .Reis, M.A., Alves, L.C, Freitas, M.C., van Os, B., Wolterbeek, H.Th. , Lichen (*Parmelia sulcata*) time response model to environmental availability, *The Science of Total Environment* **232** (1999) 105-115.

Further work

So far results were obtained for all elements and both the model and the fitting routine were shown to provide good results. The physical meaning of the values of the parameters obtained, nevertheless, needs the introduction of new approaches, namely Maximum Entropy Methods and Bayesian Inference, as well as a more extensive solution of the integral equation to provide the lichen response time model. So far these equations were solved only in a mean field approach but the full blown equations are stochastic and should be dealt with in their full potential.

*

* This project has been funded in previous years by the IAEA TC-POR/8/006 (15×10^6 PTE).

[1] National Geological Survey, Haarlen, The Netherlands.
[2] IRI-TUDelft, Mekelweg 15, 2629 JB Delft, The Netherlands.

Automatic Filter Changer Aerosol Sampler*

R. Mateus[1], M.A. Reis, L.C. Alves, M.C. Freitas, A.P. Jesus[2]

Objectives

Building of a robust, low cost atmospheric aerosol aparatus capable of replacing filter units automatically.

Results

After the identification in 1993 of the need for samplers capable of replacing automatically filter units for atmospheric aerosol collection, the construction of a prototype was started at ITN. The project suffered various delays, but as much as possible it was possible to maintain a (although slow) steady improving rate. Three main lines were initially established and are now all accomplished. First, the system had to be vacuum tight under operation conditions. This step implied redesign of some parts several times. Second the system must be low cost (otherwise it would have not been necessary to redesign items, but a simpler solution of more expensive design would have been adopted). Third the system must be capable of withstanding long energy breakdowns, be robust and reliable.

Presently, only the last two items of the third condition are not yet achieved. The prototype in its first version was tested by comparison with two Gent samplers. Results obtained are presented in Fig.1. It can be seen that the differences observed between the automatic system (SARA) and the Gent samplers are similar to those determined between Gent samplers.

One of the most complex components of this system, the PM10 separator head was designed by the team and built at ITN. The results presented Fig.1 also assure it works as well as the Gent separator. Furthermore, from the theoretical point of view, the ITN separator should be better because it is built in metal and therefore, no electrostatic charge occurs during operation.

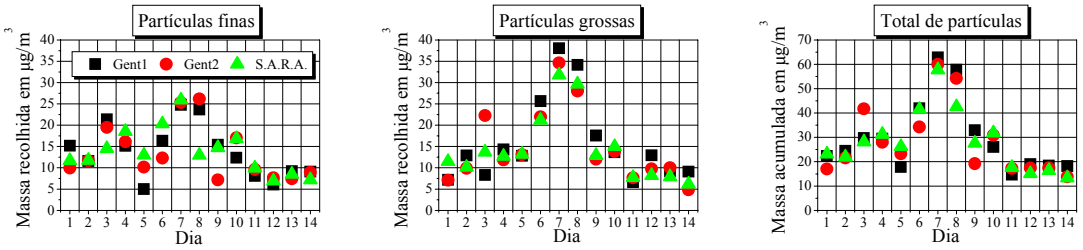

Fig. 1 – Gravimetric mesurement of collected masses by the three samplers, S.A.R.A. being the automatic filter change system and the others two identical Gent PM10 samplers. Data are shown for fine particles (partículas finas), coarse particles (partículas grossas) and the sum of both (Total de partículas).

Future work

The system has now gone through a major redesign of the structural parts looking for larger robustness and size reduction. Originally designed in a single block unit, the philosophy was changed and it will now be a multi-block system. The team believes this will improve both the robustness and the transport facility.

* Contracts: DGA No. 26/96 - 5,6 × 10^6 PTE; IAEA CRP 9938 - 4,8 ×10^6 PTE;
IDAD /Valor Sul - 16,6 ×10^6 PTE/year.

[1] PRAXIS PhD student.
[2] Dep. de Física, Faculdade de Ciências, Universidade de Lisboa; Centro de Física Nuclear da Univ. Lisboa.

Wind Differential Biomonitoring and Integration with Direct Aerosol Characterization*

A.P.Marques[1], C.Costa, R.Mateus[2], M.A.Reis, M.C.Freitas

Objectives

This project aims:

(i) the demonstration of the potentialities of the integration of biomonitoring and standard aerosol monitoring taken simultaneously;

(ii) the verification of the enhancement in biomonitoring by wind direction differential exposure of biomonitors.

Results

The region of Lisbon and south of Lisbon (Sado estuary) is densely industrialised, and therefore air pollution should be studied in more detail there transplants of lichen *Parmelia pulcara Taylor* were suspended in nylon bags in this region following a certain grid. In each of the 47 places two sets of four transplants each were hanged. Samples of about 2 grams of lichen were put in nylon bags and suspended at about 1.5 meters above the soil, within a rectangle 15 km wide and 25 km long on a 2.5 km × 2.5 km grid, centred in the Setúbal power station. Fig.1 shows the area under study and the transplant grid.

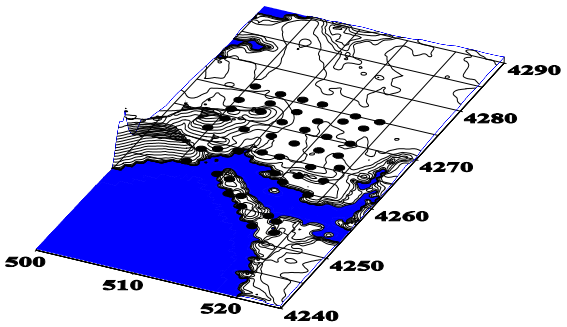

Fig. 1 - Collecting sites grid.

For a 9-months period and every 3 months, one transplant of each set was collected. In the laboratory, the nylon were removed, the lichens were cleaned, washed in distilled water, freeze-dried and ground in a teflon wild. The sample power was analysed by INAA and PIXE in pellet form.

So far, it was possible to show the potentialities of wind differential biomonitoring differentiates local from remote sources and three months exposure of lichen is enough for such differentiation. Evidence of large seasonal changes on patterns was also identified along the 9-months exposure period.

The data and conclusions so far obtained were included in DGA 26/96 contract, ended in October 1999.

Future work

Aerosol data are not yet all processed, therefore analysis will be finished and in integration of aerosol data and biomonitoring will be performed. This will be done within the IAEA CRP 9938 contract. Also, it was observed that INAA and PIXE results of lichen samples do not fit each other very often. The reason may be the heterogeneity of the samples which may be solved by griding to smaller grain size. This investigation will be an important part of the PhD program of Ana Paula Marques. Samples and data from this project will be the major component of her thesis

* Contract DGA nº26/96 5.5 × 10^6 PTE, Contract IAEA CRP9938 4.5 × 10^6 PTE.

[1] PRAXIS XXI fellowship 4/4.1/BIC/3573 starting March 1997.

[2] PRAXIS PhD student.

Air Particulate Matter Characterization of an Industrial Area at North Of Lisbon*

S.M.Almeida[1], M.M.Farinha[2], R.Mateus, R.Pinheiro, I.Dionísio, M.A.Reis, M.C.Freitas

Objectives

This is a project based in a contract for analytical services mainly, but from the data collected under this protocol, scientific work will also be performed, including PhD thesis.

Results

Table I: Average and maxima concentration of some elements in suspension in the fine particles mode for the period between the Jan.28 to Nov 7 for Bobadela; March and Sep. 26 to Nov 7 for S.João da Talha; Mar. 22 to Sep. 22 for Qta da Piedade. Samples are collected twice a week for 16 hours out of 24h to assure that filters do not become blocked.

Bobadela	P	S	Cl	Mn	V	Ni	Cu	Zn	Pb
Num.of Samples	7	59	57	7	76	73	67	65	77
Average (ng/m^3)	7.2	996.8	74.1	7.2	8.0	3.3	3.1	46.3	21.2
Maxima (ng/m^3)	11.5	5370.0	535.1	11.5	33.6	17.3	7.9	314.7	152.7
S. João da Talha	P	S	Cl	Mn	V	Ni	Cu	Zn	Pb
Num.of Samples	3	14	14	3	14	16	18	18	18
Average (ng/m^3)	9.2	1049.5	141.2	9.2	25.9	7.9	4.4	34.0	31.6
Maxima (ng/m^3)	10.7	2725.0	857.0	10.7	84.6	28.3	10.2	83.6	94.1
Qta da Piedade	P	S	Cl	Mn	V	Ni	Cu	Zn	Pb
Num.of Samples	1	34	34	1	43	40	40	31	48
Average (ng/m^3)	6.7	1124.8	48.2	6.7	6.1	2.4	1.7	14.6	12.5
Maxima (ng/m^3)	6.7	5020.0	243.9	6.7	17.4	5.7	6.6	70.2	35.8

Further work

The raw data presented here will be submitted to further analysis. It is clear that some high levels of S, Zn and Pb were detected and the causes can eventually be determined once there is enough data to proceed with multivariate statistical analysis.

*

* Contract for analytical services 16.6 × 10^6 PTE/ano (a complement including consultancy is under discussion).
[1] PRAXIS PhD student.
[2] Fellowship for Professional Degree.