Neutron Activation in Environment, Nutrition and Epidemiology

Maria do Carmo Freitas

The research is focused on development of methodologies in neutron activation analysis and their application to studies of atmospheric environment, nutrition and epidemiology. 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 the following scientific interests:

Development of Methodologies, Quality Control, Automatization, Data Handling

This line aims to optimize the analytical technique in order to facilitate the analysis of the samples of the different projects, to speed the calculation and to improve the handling of the data. It also aims to implement methodologies to improve the detection limits for important pollutant chemical elements such as cadmium, arsenic, nickel, and to determine lead and the light elements. Interlaboratory exercises are targets, aiming at analytical quality control.

Monitoring, Biomonitoring

This line aims to characterise areas of Portugal using biomonitors and air particulate matter collection. The data are analysed for factors aiming at identifying emission sources and the air mass trajectories, including local, regional and long-range transport. To assure the quality of the data, accuracy and precision studies are being performed. So-called conventional analytical techniques are applied to complement the research unit's results. Cooperation with Cabo Verde entities started in 2010 within a FCT project; the cooperation with Azores University continued aiming studies of long-range transport at Pico summit.

Epidemiological studies

The objective of this line is to link biomonitoring and monitoring to epidemiological studies. Children respiratory problems, cardiovascular diseases and carcinogenic incidence in the Portuguese population are being studied in association to chemical elements, pollutant gases and meteorological data. New methodologies are suggested to smooth health and environment data.

Element Uptake Processes

Plant physiology is also one of the group aims, looking for effects on plants due to atmospheric chemical components. The underlying questions are related to the extent in which biomonitors may reflect the element contents of particulate matter. Bioremediation at mining abandoned areas is being studied aiming to select strong accumulators of arsenic.

Nutrition

So far, selenium has been the target. It is an essential element to humans and in Portugal its contents in diet is deficient. Therefore, we are supplementing it to cereals and studying its absorption in the cereal plant and the cereal grains. The experiments on foliar selenium spray performed in 2010 were a success, since selenium enriched wheat grains were cropped. We proceed with other two methods (soil and enriched seeds). Cooperation with INIA/Elvas strongly started.

Training

The research unit has a strong component in graduation and post graduation training (BSc, MSc, PhD, post-PhD). A training course was held for the research unit's newcomers, to uniform the basic knowledge. Courses are attended in order to improve and update the team´s knowledge knowledge.

Participation in intercomparison exercises

Whenever offered, the group collaborates in intercomparison exercises, to improve its analytical quality.

Services

Analytical services are provided under request. Fluorine is being determined for a German company. Portuguese universities requested analysis. Services are being done for a private Portuguese company.

Research Team

Researchers

M. CARMO FREITAS, Princ. (Agreg), Group Leader
S.M. ALMEIDA, Aux. (Contract)
H.M. DUNG, Aux. (Contract)
A. HOSSAIN, Post-Doc. grant

Technical Personnel

I. DIONISIO
T. SITOE, PTDC/AAC-CLI/100331/2008 fellow (since Aug. 2010)

Students

R. GODINHO, PhD student
S. SARMENTO, PhD student
N. CANHA
A. SILVA,
M.A. SILVA, (since Aug. 2010), FCT PhD

Collaborators

A.M.G. PACHECO, Aux. Professor, CERENA/IST, Portugal
H.TH. WOLTERBEEK, Sen. Res., TUDelft, The Netherlands
M.M. FARINHA, ISQ-Portugal, PhD student
A. CRUZ, CERNAS/ESAC/IPC-Portugal, PhD student
B. VIEIRA, AmbiGovernance, PhD student
C. GALINHA, DEQ/IST

Impact of Atmospheric Indoor Aerosol in Human Health, (PTDC/SAU-ESA/65597/2006)

N. Canha, M. Almeida Silva, M.C. Freitas, S.M. Almeida, H.M. Dung, I. Dionísio, T. Sitoe, C.A. Pio[1], M.A. Trancoso[2], H.Th. Wolterbeek[3]

Objectives

Most individuals spend about 80% of their time indoors and, consequently, the exposure to the indoor environment is much higher than to the outdoors. Furthermore, children spend most of their time at home or at school and study at these localities are important to evaluate their time-weighted exposure.

Due to their underdeveloped airways, children constitute a sensitive group with a higher risk than adults. The higher impact in health and educational performance of children reveals the importance of indoor air quality studies of schools.

The aim of this study was to assess the children exposure, at elementary schools of the Lisbon urban area (Fig. 1), to bioaerosols (fungi, bacteria and pollens) and to total particulate matter – TPM (its natural radioactivity, elemental and soluble ions composition) by using passive methods.

Fig. 1. Studied elementary schools at urban area of Lisbon.

Methods

Polycarbonate and quartz filters were passively exposed at two classrooms of each of the 14 Lisbon primary schools, for periods of 1-3 months (Fig. 2), to collect TPM. Three sampling campaigns were done: Spring 2009, Autumn 2009 and Winter 2010.

Fig. 2. Placement of the passive filters in the classrooms.

Bioaerosols were collected passively at the indoor of the classrooms of 3 schools and, for bacteria and fungi, as well at the outdoor to determinate the ratio indoor/outdoor and to assess the level of outdoor contamination of the indoor environment.

Results

Passive sampling showed its feasibility to evaluate TPM in a spatially large scale. Furthermore, it was demonstrated that passive sampling is an easier and cheaper method than the use of automatic samplers. Quartz and polycarbonate collected masses were significantly correlated (Fig. 3).Higher TPM mass values were obtained in autumn (0.97-4.55mg) and winter (0.81-4.42mg) than in spring (0.27-2.23mg) and a correlation between autumn and winter was found. This suggests a significant difference towards spring, probably due to insufficient ventilation, especially in winter.
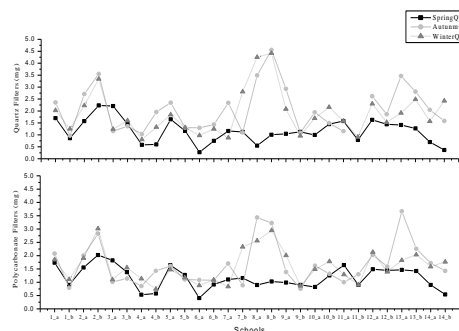

Fig. 3. TPM mass collected in schools.

Fungi levels were usually higher at outdoor environments. Seasonally, fungi were higher in spring and lower in winter due to the outdoor atmospheric conditions, especially temperature and relative humidity. Bacteria levels were higher indoors due to the children presence and a seasonal variation was not found. The indoor bacterial level was associated with the occupancy of the classroom.

TPM elemental composition was assessed by Instrumental Neutron Activation Analysis (INAA), natural radioactivity by gamma measurement using a HPGe detector and the soluble ions content (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, PO_4^{3-}, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-) by ionic chromatography, atomic absorption and UV spectroscopy.

Further work will evaluate TPM source apportionment, the correlation between the indoor parameters and the children allergenic symptoms (assessed by inquiries applied to the children).

Published work

N. Canha, M.C. Freitas, S.M. Almeida, M. Almeida Silva, M. Ribeiro, C. Galinha, H.Th. Wolterbeek. Indoor school environment: easy and low cost to assess inorganic pollutants. J. Radioanal. Nucl. Chem. 286 (2): 495-500.

N. Canha, M. Ribeiro, M. C. Freitas, S. M. Almeida, S. Cabo, H.Th. Wolterbeek, M. Almeida Silva, Fungi, bacteria and pollens seasonally quantified at 3 basic schools in Lisbon, 2010. ASHRAE, IAQ Conference, Malaysia 2010, CDROM.
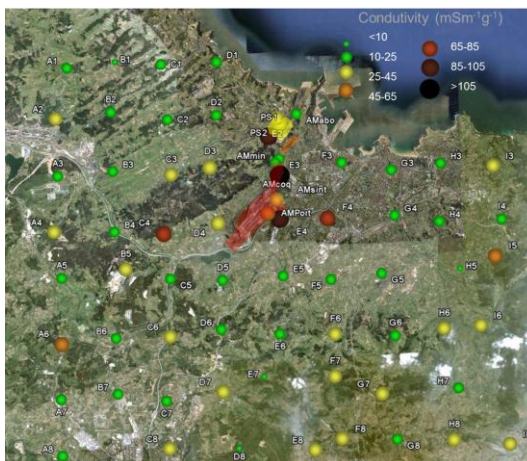
N. Canha, M. Almeida Silva, M.C. Freitas, S.M. Almeida, Seasonal variation of total particulate matter and children respiratory diseases at Lisbon basic schools using passive Methods, Procedia Environmental Sciences (in press).

[1]CESAM/Aveiro University; [2]LNEG; [3]Dept. Radiation, Radionuclides & Reactors, Delft, The Netherlands

Biomonitoring of Metal Deposition in the Vicinity of a Spanish Steel Plant, RFSR-CT-2009-00029

S.M. Almeida, M.C. Freitas, A. Silva, N. Canha, M. Almeida Silva, C. Galinha, T. Sitoe, I. Dionisio, J. Perim de Faria[1], V. Torre Suarez[1], S. Garcia[2], G. Domingues[2]

A biomonitoring study is being performed within the European Project "Assessment of Emissions and Impact of Steel Processes" in order to indicate geographical variances in trace-element air pollution around the Arcelor Mittal steelwork placed in Gijon, Spain. In 2010, lichens were transplanted from a clean background site, exposed in an industrial area in Gijon, and collected after 5 months 1) to verify membrane damage during the exposure by measuring the electric conductivity and 2) to determine trace element concentrations. The main objective was to relate variability in lichen vitality to variability in ambient conditions. Results showed that the values of conductivity from the transplants were significantly higher near the main industries (a steel plant, a power plant and a cement plant) revealing the existence of a physiological response to environmental stress.

[1]Arcelor Mittal Spain, [2]ISQ

Characterization of Dust Material emitted during Setúbal Harbour Activities by INAA and PIXE, PTDC/AAC-AMB/098825/2008

S.M. Almeida, A. Silva, M.C. Freitas, T. Pinheiro, A.M. Marques[1], A.I. Silva[2], C.A. Ramos[1], S. Garcia[3], G. Domingues[3], I. Abreu dos Santos[4]

Activities in the Setúbal harbour such as loading, unloading and transport of materials may be an important source of Atmospheric Particulate Matter (APM). Depending on the materials, type of operation and meteorological conditions, these activities may have an impact on the levels of APM around harbour areas. The aim of this work was to characterize the emissions of dust originating from different handling operations. The techniques INAA and PIXE were applied as sensitive analytical tools for the determination of heavy metals and rare earth elements in the APM sampled in the harbour during the unloading operations. Results showed that manipulation of bulk materials during harbour operations resulted in high emissions of particles, principally from the coarse fraction. These emissions were enriched in rare earth elements and heavy metals and were very affected by the provenience of the material.
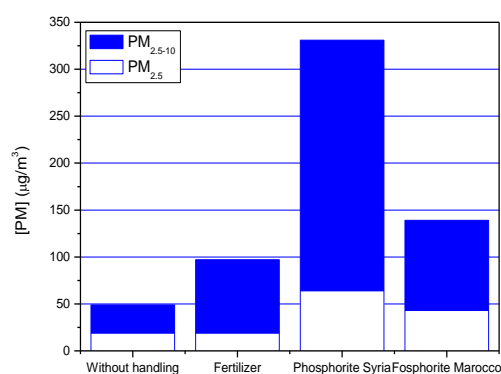
[1]ESTeSL, [2]ISEL, [3]ISQ, [4]SAPEC PI

CV-Dust - Atmospheric Aerosol in Cape Verde Region: Seasonal Evaluation of Composition, Sources and Transport, PTDC/AAC-CLI/100331/2008

M. Almeida Silva, M.C. Freitas, S.M. Almeida, H.M. Anawar, I. Dionísio, T. Sitoe, J. Cardoso[1], C. A. Pio[1]

A total of 100 filters of Nucleopore polycarbonate were weighed and sent to Aveiro University together with a Partisol (*Plus Sequential Air Sampler*). This equipment is used for sampling the particulate air matter in Cape Verde, Santiago island. The sampling is taking place at the Praia airport area. One sampling campaign of biomonitors was done in Fogo Island[a1,a2], Cape Verde. A total of 37 samples of 7 different biomonitors were collected from 23 sites. The main species found were *Acacia albida[b]*, *Ficus sycomorus ssp. Gnaphalocarpa[c]*, *Eucalyptus*, *Oleandro*, and *Apple Tree*. Bark from these species is being processed aiming site differentiation. Also the lichen *Usnea* sp. Was collected at one site.
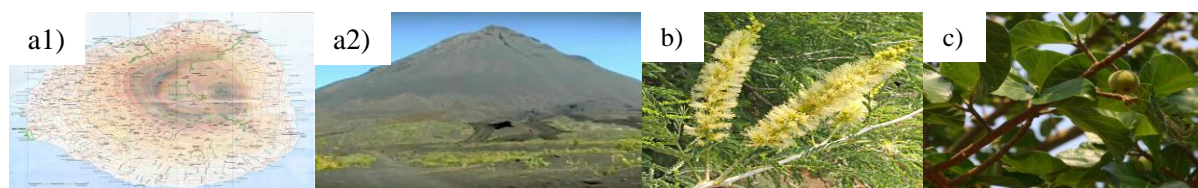
[1]CECESAM/Aveiro University

Selenium Distribution in Cereals and Portuguese Cultivation Soils. Interactions between Selenium and Iodine Uptake by Cereals - A case study, PTDC/QUI/65618/2006

C. Galinha[1], A.M.G. Pacheco[1], M.C. Freitas, H.M. Anawar, H.M. Dung, I. Dionísio, T. Sitoe, A.S. Almeida[2], J. Coutinho[2], B. Maçãs[2]

This project is a joint initiative of ITN and IST. Selenium in soil and cereal samples were analyzed by INAA. Due to the very low concentrations of selenium in several samples Radiochemistry was also done in Řež - Czech Republic. So far selenium results were within the range of 100-225ppb for soils; 3-55ppb for durum wheat; 6-80ppb for bread wheat and 4-30ppb for rye. Bread and durum wheat were seeded, grown and collected with the collaboration of INRB/INIA – Elvas. These crops were used to study the biofortification of selenium using foliar supplementation at different stages of plant growing. These supplemented samples are being analyzed by INAA on the fast pneumatic system (SIPRA). It was shown that Rye collected in Portugal has a Transfer Coefficient from soil (TC) above 10% for Zn and K and around 100% for Br. Also for wheat (bread and durum wheat) it was found a TC relative to soil above 10% for K. Some cereal cultivation soils near Elvas area showed a deficiency in zinc, below the detection limit of the analytical technique, around 20 mg/kg.

[1]CERENA/IST; [2]INRB/INIA - Elvas

(Hyper)accumulation of Arsenic and other Elements by Plants adapted to Sites impacted by Mining and Smelting Activities, PTDC/AMB/65462/2006

M.C. Freitas, H.M. Anawar, N. Canha, I. Dionísio, H.M. Dung, A.M.G. Pacheco[1], C. Pinto-Gomes[2], A. Bettencourt[3]

The objective was to characterize the elemental composition of mine tailings in order to evaluate the environmental hazards, and to identify the metal accumulation potential of native plant species from São Domingos mine, one of the oldest massive sulphide deposits of Portugal that belongs to the Iberian Pyrite Belt. The mine tailings are highly contaminated by As and Sb (main contaminants), Ag, Cr, Hg, Sn, Fe and Zn. Among the plant species, higher concentrations of all the metals were noted in *Erica andevalensis*, *Erica australis*, *Echium plantagium* and *Lavandula luisierra*. Considering the tolerant behavior and abundant growth, the plant species *Erica australis*, *Erica andevalensis*, *Lavandula luisierra*, *Daphne gnidium*, *Rumex induratus*, and *Juncus* are important for the rehabilitation and recovery of the degraded São Domingos mining area. Water flows are also highly contaminated with hazardous pollutants, the contamination decreasing with distance to the main well.
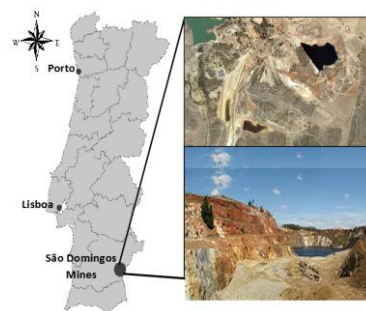
[1]CERENA/IST; [2]ICAM – Évora University; [3]CMA-IMAR, Évora University

Characterizing Seasonal Variations in Elemental Particulate Matter Concentrations in European Urban and Rural Areas under Different Climatic Conditions, IAEA RER/2/005

N. Canha, M.C. Freitas. S.M. Almeida, H.M. Dung, I. Dionisio, T. Sitoe, J. Cardoso[1], A. Caseiro[1], C.A. Pio[1], H.Th. Wolerbeek[2]
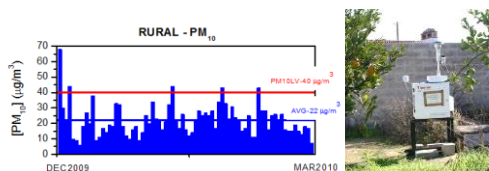
The aim was to characterize air particulate matter (APM) pollution, to identify the pollution sources and to prepare guidelines/recommendations to reduce APM. A Partisol sequential air sampler was put in a rural area (Foros de Arrão, Ponte Sor - 39°10'39 N; 8°14'25 W) for 3 months (December 2009 – March 2010), the Portuguese colder winter months. In this area, burning wood for heating and cooking is a common practice and no other anthropogenic source is known except for small village traffic. PM_{10} average concentration in the rural area was 22 $\mu g/m^3$ (with values in a range of 6 – 68$\mu g/m^3$), which did not exceed the limit values established by the EC legislation. High K concentrations were found in the APM probably due to the wood combustion. $PM_{2.5}$ was sampled inside a classroom of a primary school at the rural area for 2 weeks (in March 2010). The obtained $PM_{2.5}$ average concentration was 67 $\mu g/m^3$ (range 13-201 $\mu g/m^3$). Comparing with $PM_{2.5}$ sampling performed at a classroom in the Lisbon urban area (average value of 10 $\mu g/m^3$), it is obvious the higher concentrations of $PM_{2.5}$ that children are exposed in the school located at the rural area, where wood is used to heat the classroom.

[1]CESAM/Aveiro University; [2]Dept. Radiation, Radionuclides & Reactors, Delft, The Netherlands

Enhancement of Capability of the NAA Techniques at RPI

H.M. Dung, M.C. Freitas, S.M. Almeida, N. Canha, C. Galinha, I. Dionísio, J. Marques
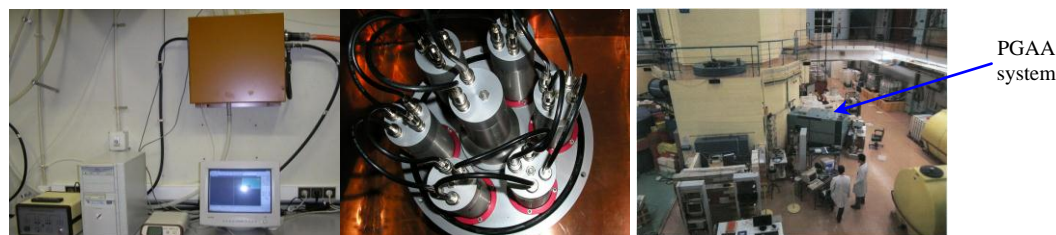

PGAA system

Fig. 1. From left to right, the SIPRA, CSS and PGAA systems.

The capability of Neutron Activation Analysis (NAA) techniques at RPI (some of the equipment discussed is shown in Fig. 1) is based upon irradiation and measurement facilities that permit to utilize the entire neutron spectrum of the reactor, epithermal neutrons (ENAA), cyclic irradiations (CNAA), Compton suppression spectroscopy (CSS), automatic sample changers (ASCs) and prompt gamma (PGAA). The existing NAA techniques must be combined in order to improve the analytical capabilities for the intended applications. Three different modes of combination were studied: 1) Normal short and long irradiations; 2) ENAA counted with and without CSS; and 3) CNAA. Computer software NAA-PRO, in which a linear system of differential equations are solved to obtain the radionuclides in modelled gamma-ray spectrum, predicting the best conditions for the detection of radionuclides of interest prior to carrying out the experiments. The combination of NAA techniques allows to determine the elements: Ag, Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, Hg, I, K, La, Mn, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, Zn and Zr by using the above mentioned first mode; by the second mode: As, Cu, I, K, La, Lu, Sm, Sr and U; and the third mode: F, Al, Ca, Cl, Cu, Se, Ti and V in biological, environmental and material (polymer) samples. The experimental results were in a good agreement with the certified or consensus values, with biases lower than 12% for most elements. The combination of Cyclic NAA with cumulative/replicate NAA was also studied, and the detection limits of selenium (^{77m}Se) in biological and fluorine (^{20}F) in polymer samples were improved by a factor of 1.7 and 1.9, respectively. The implementation of PGAA is being carried out within a regional IAEA project.

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Enhancing the sustainability of Research Reactors and their safe operation through regional cooperation, networking and coalition, IAEA-TCR-05632 RER/4/032

N. Canha, M.C. Freitas. S.M. Almeida, H.M. Dung, J. Marques, Z. Révay[1]

This project is supported by the IAEA - International Atomic Energy Agency and its main goal is to implement a PGNAA (Prompt Gamma Neutron Activation Analysis) facility at the RPI-ITN in order to enhancing its facilities and experimental techniques offer to the users. In January 2010, three members of the group went for one month training on this technique at the Budapest PGNAA facility at the Nuclear Research Department from the Institute of Isotopes and Surface Chemistry of the Hungarian Academy of Sciences. It was possible to learn about the technique and to understand the processes of irradiation, measurement, spectra analysis (by Hypermet-PC software) and the results calculations. PGAA analysis of soil samples allowed obtaining information for light elements, such as B and Si. Possibilities of setups for the future PGNAA facility at ITN were designed and the materials required were discussed. In October 2010, Dr. Zsolt Révay (IAEA specialist for PGAA technique) visited the RPI and several designs

for the PGAA facility were evaluated by doing some experiments (different reactor power and different setups of the shielding material of the bunker proposed for the facility). The measured beam background was above 1000 cps (too high) which does not allow installing a versatile PGAA facility at the bunker, in which the facility was planned. It was proposed to position the detector at the end of the neutron beam line, aiming at a larger distance between the detector and the reactor wall. Further work will be developed where a new design of the facility will be created (with the detector located far away from the reactor face).

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[1]KFKI, Budapest, Hungary