

Neutron Activation in Environment, Nutrition and Epidemiology

Marta Almeida

The research in NANE group is focused on the development of the NAA (Neutron Activation Analysis) methodologies and on their application to environment, nutrition and epidemiology studies. NANE is a multidisciplinary group that has the collaboration of researchers from different fields of science: environment, chemistry, physics, environmental health, biology, biochemistry and geology. The capability of NAA techniques at RPI is based on irradiation and measurement facilities that allow the utilization of the entire neutron spectrum of the reactor, epithermal neutrons (ENAA), cyclic irradiations (CNA), Compton suppression spectroscopy (CSS), automatic sampling changers (ASCs) and prompt gamma (PGAA) (ongoing work). Nowadays, the combination of NAA techniques in ITN permits the determination of the elements Ag, Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, F, Fe, Hf, Hg, I, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Ti, U, V, Yb, Zn and Zr in biological, environmental and material samples.

The unit activities include the following scientific interests:

Quality assurance and quality control (QA/QC), development of methodologies and automatization.

The principal objective of the group is to assure the quality of the results given by the NAA techniques. Within the activities of the NANE group, a large number of researchers/students is involved, principally doing temporary studies. These researchers deal with a big number of samples and with several equipments and softwares in order to generate large databases. For this reason, the QA/QC is essential to guarantee the quality of the generated data. To accomplish this objective Inter and Intra- laboratory exercises are performed in a routine basis. This line also aims to optimize the analytical techniques *in* order to improve the analysis of the samples, to speed the calculations and to simplify the handling of the data.

Environment

Over the last two decades, NANE group have developed aerosol sampling and analysis

instrumentation, which nowadays are applied successfully for measurements of various physical and chemical aerosol parameters. NANE research have already shown that NAA can be advantageously used in aerosol studies because many elements are determined, high accuracy and precision are obtained, many samples are analyzed and little sample preparation is necessary.

At the moment, the complete characterization of the particles and biomonitoring at the receptor is advantageously used by NANE group to elucidate the sources of the pollutants and the processes associated with their formation, to assess local, regional and long-range transport and, finally, to identify mitigation options focusing on the reduction of the air pollutant concentrations.

Epidemiological studies

The objective of this research line is to establish unequivocal associations between pollution, morbidity and mortality. Respiratory problems, cardiovascular disease and carcinogenic incidence in the Portuguese population have been studied in association with chemical elements measured by NAA.

Nutrition

Selenium has been the target of NANE research in the nutrition field because it is an essential element to humans and, in Portugal, its contents in diet are deficient. NANE group is studying different types of Selenium supplementation and is evaluating their efficiency.

Training

The research unit has a strong component in graduation and post-graduation training (B.Sc., M.Sc., Ph.D., post-Ph.D.).

Services

NANE provide analytical services under request for private national and international companies and universities. In these services NAA characterize materials and environmental samples.

Research Team

Researchers

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Selenium distribution in cereals and portuguese cultivation soils. Interactions between selenium and iodine uptake by cereals - a case study.

C. Galinha¹, M.C. Freitas, A.M.G. Pacheco¹, J. Coutinho², B. Maçãs², A.S. Almeida²

Objectives

Selenium is a trace element essential to the well-being and health quality of humankind. This project focuses on determining the ability of bread (*Triticum aestivum* L.) and durum wheat (*Triticum durum* Desf.) to accumulate selenium after supplementation.

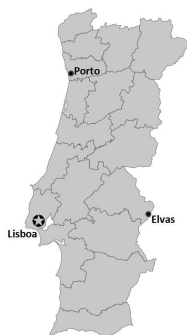


Fig. 1 - Outline of mainland Portugal, showing the approximate location of the experimental fields.

Two of the most representative wheat cultivars in the country -- Jordão (bread) and Marialva (durum) -- have been selected for field trials, following the same agronomic practices and schedules as the regular (non-supplemented) crops of those varieties. Soil supplements were applied at the sowing time, whereas foliar additions were performed at the booting and grain-filling stages, in either case by using sodium selenate and sodium selenite solutions at three different Se concentrations, equivalent to field supplementation rates of 4, 20 and 100 g of Se per ha (with and without potassium iodide, as a joint additive). All field experiments were done in south areas of mainland Portugal (Fig. 1).

Results

Seed enrichment may be viewed as an alternative to classical biofortification strategies, such as soil amendments or foliar treatments. A study has dealt with the first phase of such an alternative, that is, with the preparation of Se-enriched seeds of wheat by optimizing both their soaking time (in an active Se solution) and washing time (in bidistilled water), through detection of a Se radiotracer (⁷⁵Se). The study has been designed to conform to realistic Se-supplementation rates and to have an extension in actual field trials. The optimized times for administering Se to seeds (soaking time) and ensuring inner-seed levels only (washing time) are 48 and 24 h, respectively.

After harvesting, Se contents in these cereal grains were compared to data from regular wheat samples (field blanks) grown at the same soil/time, yet devoid of any supplements. Total Se in all field samples -- a three-fold replication, in a full-factorial design -- have been determined by instrumental neutron activation analysis, via the short-lived nuclide ^{77m}Se (half-life time: 17.5 s).

The results show that foliar additions can increase Se contents in mature grains up to 35 times, when compared to non-supplemented crops, and that selenate-based treatments seem more effective in enhancing such contents (Fig. 2 and 3). Jordão and Marialva may respond differently to the stage of application though.

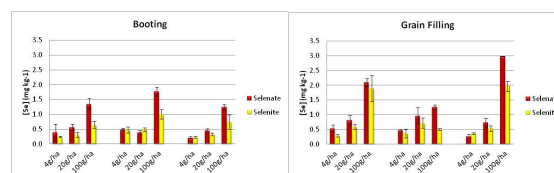


Fig. 2 Selenium results for foliar supplementation in Marialva.

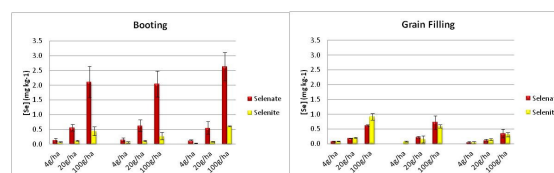


Fig. 3 Selenium results for foliar supplementation in Jordão.

Overall, for any given field supplementation rate, foliar application appears to translate into higher Se concentrations in wheat grains than each soil counterpart.

Published work

C. Galinha, M.C. Freitas, A.M.G. Pacheco, J. Kameník, J. Kucera, H.M. Anawar, J. Coutinho, B. Maçãs, A.S. Almeida (2011) Selenium in cereal plants and cultivation soils by radiochemical neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, doi: 10.1007/s10967-011-1262-0

C. Galinha, M.C. Freitas, A.M.G. Pacheco, J. Coutinho, B. Maçãs, A.S. Almeida Radiotracing selenium in bread-wheat seeds for a Se-biofortification program: an optimization study in seed enrichment. *Journal of Radioanalytical and Nuclear Chemistry*, 291(2011) 193-195.

C. Galinha, M.C. Freitas, A.M.G. Pacheco, J. Coutinho, B. Maçãs, A.S. Almeida, Determination of selenium in bread-wheat samples grown under a Se-supplementation regime in actual field conditions. *Journal of Radioanalytical and Nuclear Chemistry*, 291(2011) 231-235.

C. Galinha, H.M. Anawar, M.C. Freitas, A.M.G. Pacheco, M. Almeida-Silva, J. Coutinho, B. Maçãs, A.S. Almeida, Neutron activation analysis of wheat samples, *Applied Radiation and Isotopes*, 69 (2011) 1596-1604.

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Development of k_0 -based cyclic NAA for short-lived radionuclides

H.M. Dung, S.M. Almeida, I. Dionisio, D.G. Beasley, M.C. Freitas, J. Marques

The k_0 -based cyclic neutron activation analysis (k_0 -CNAA) technique has been studied at the Portuguese research reactor (RPI) for the determination of elements which form short-lived radionuclides, particularly fluorine (^{20}F , 11.16 s half-life) and selenium ($^{77\text{m}}\text{Se}$, 17.36 s half-life) in polymer, biological and environmental samples. The detection limits obtained for F and Se were about 50 and 0.01 mg kg⁻¹, respectively, in the investigated materials. The timing parameters for the procedure were 10 to 20 s for irradiation, 5 s decay, 10 to 20 s counting, and 5 s waiting and performed with 8 cycles. The k_0 -IAEA program was modified to use millisecond time resolution for irradiation, decay and counting times as needed for interpreting k_0 -CNAA data in terms of concentration, accuracy and detection limit. The analytical quality of the procedure was evaluated by the analysis of standard reference materials with the accuracy within 15% for F and Se and within 12% for other elements producing short-lived or detectable radionuclides, i.e. Al, Ca, Cl, Cu, Dy, I, Mg, Mn, Ti, and V.

Quality control of k_0 -NAA by participating in the inter-comparison study (WEPAL, the Netherlands)

H.M. Dung, S.M. Almeida, I. Dionisio, M.C. Freitas

A total of 8 dried samples of plant (IPE) and soil (ISE) materials have been received via an IAEA proficiency test programme organised by WEPAL, the Netherlands. The samples were analysed with 6 replicates for each sample by the k_0 -NAA procedures developed at RPI. The average results of the determinations have been reported to the IAEA and the WEPAL after 6 weeks of the arrival of the samples. The results have been processed at Wageningen University and published under code names. Determinations were made for the following elements: Ag, Al, As, Ba, Br, Ca, Ce, Co, Cr, Cs, Cu, F, Fe, Ga, Hg, I, K, La, Mg, Mn, Mo, Na, Nb, Nd, Pd, Rb, Sb, Sc, Se, Sn, Sr, Th, Ti, U, V, W, Y, Zn and Zr.

Optimization of the Neutron Activation Analysis capabilities

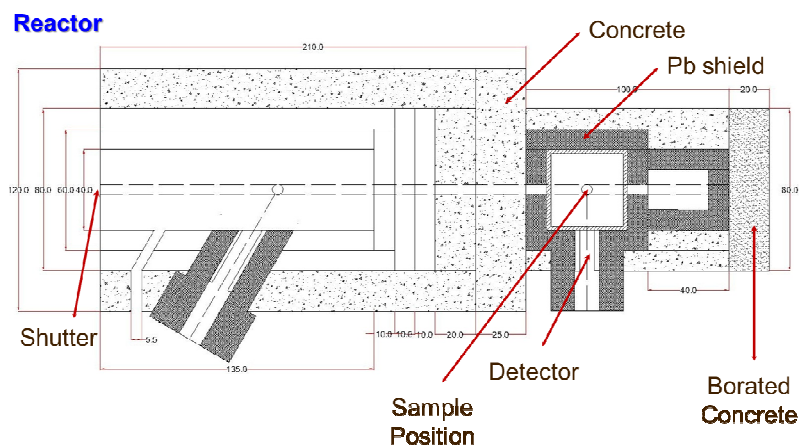
H.M. Dung, S.M. Almeida, M.C. Freitas

A new CANBERRA detector (GC-3018) was purchased and installed in one of the automatic sample changers (ASC2-N#2). The dead time of the gamma-ray spectrometers has been improved after re-design the ground system between DSspecs and the ASC2s. The spectrometers' electronic parameters have also been optimized in order to enhance the spectral quality and stability. The permanent database used for k_0 -IAEA software has regularly been updated in order to meet the requirements of the applications of interest.

Enhancing the sustainability of RR & their safe operation through regional cooperation, networking & coalitions, IAEA TC Regional Project RER/4/032

N. Canha, H.M. Dung, M.C. Freitas, S.M. Almeida, J. Marques, Zs. Révay¹

This project supported by the IAEA has the goal to implement a PGNA (Prompt Gamma Neutron Activation Analysis) facility at the RPI-ITN. A new design of the facility was created to overcome several problems detected in preliminary studies (such as high background) and the necessary materials to build it were acquired. In October 2011, a visit from an IAEA team was conducted to ITN to discuss this project and its achievements and to define further timelines.



¹KFKI, Budapest, Hungary

Impact of atmospheric indoor aerosol in human health, PTDC/SAU-ESA/65597/2006

N. Canha, M. Almeida-Silva, S.M. Almeida, M.C. Freitas, M. Martinho¹, P. Pegas², C. Alves², C. Pio², M. Trancoso³, R. Sousa³, F. Mouro³, T. Contreiras⁴

A statistical treatment was conducted over the database of indoor air parameters and the primary schools where these parameters were sampled (urban area of Lisbon, Portugal). The aim of this study was to assess the associations between indoor air parameters with the schools building characteristics, through the use of statistical methods. Several associations were found and allow pointing out several recommendations to improve the classrooms IAQ. Overall, the conclusions of this study point to the following recommendations: 1) classrooms should face streets rather than patios and should not be located in basements, 2) the density of students can affect the indoor environment and should be limited, 3) wooden materials appear to have advantages as building materials due to a lower input of contaminants. Other factors, like ventilation, cleanings and use chalk versus whiteboard pens, can reduce or increase specific contaminants inside the classrooms.

¹United Nations-NY/USA, ²UA/CESAM, ³LNEG/UB-LBA, ⁴INSA/ONSA

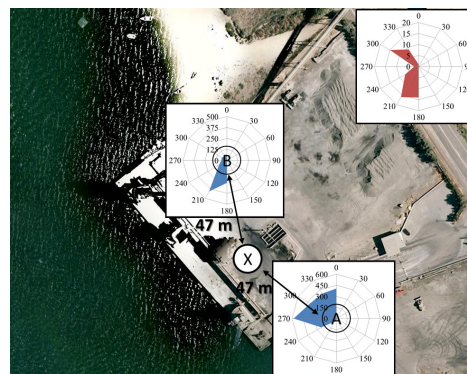
Measurement of fugitive emissions during harbour operations, PTDC/AAC-AMB/098825/2008

A.V. Silva, S.M. Almeida, A.M. Marques¹, A.I. Silva, C.A. Ramos¹, S. Almeida¹, A. Lopes¹, A.I. Pedro¹, A. Ferreira¹, T. Pinheiro, S. M. Garcia², G. Domingues², A.I. Miranda³

Fugitive emissions pose problems both for general air quality management and for the operational management of the facilities. In harbours, activities such as loading, unloading and transport of dusty materials are important sources of particles fugitive emissions.

The aim of this study was to estimate the impact of harbour activities on Air Particulate Matter (APM) levels and composition. This work was based on experimental campaigns carried out in a Portuguese harbour when three types of bulk materials – fertilizer, phosphorite from Syria and phosphorite from Morocco - were handled. High time resolution monitors were installed close to the unloaded area and recorded APM concentrations and meteorological variables. PM_{2.5} and PM_{2.5-10} were also collected during unloading operations, in polycarbonate filters by Gent samplers. A complete chemical characterization of collected samples was made by the techniques Instrumental Neutron Activation Analysis and Particle Induced X-Ray Emission.

Results showed that manipulation of materials during harbour operations resulted in high emissions of particles, especially from the coarse fraction. These emissions were very affected by the granulometry of the handled materials and by the meteorological conditions.



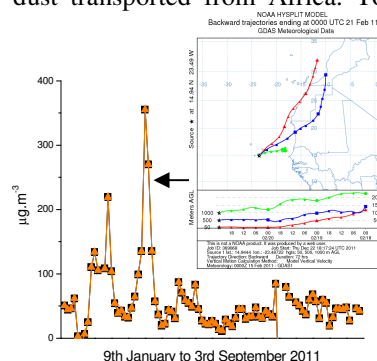
¹Escola Superior de Tecnologia da Saúde de Lisboa ²Instituto de Soldadura e Qualidade ³CESAM, Universidade de Aveiro.

CV-Dust - Atmospheric aerosol in Cape Verde region: seasonal evaluation of composition, sources and transport, PTDC/AAC-CLI/100331/2008

M. Almeida-Silva, S.M. Almeida, T. Sítio, M.C. Freitas, C. A. Pio¹, T. Fernandes¹, D. Custódio¹, J. Cardoso²

Cape Verde is located in an area of massive dust transport from land to ocean. Thus, it is ideal to set up sampling devices that will allow the characterization and the quantification of the dust transported from Africa. To characterize the chemical composition of dust transported from Africa, a total of 100 Nucleopore and Teflon filters were sampled in Praia, Cape Verde. All filters were weighted by gravimetry in a controlled clean room (class 10,000) with a semi-micro balance. Filter mass before and after sampling was obtained as the average of three measurements, when observed variations were less than 1%.

Hysplit Model, ending in Praia in 3rd February 2011 confirms an air mass transported from Sahara Desert localized in the Center of Africa. Other higher peak of particles concentrations happened in 21st February 2011 and the Hysplit Model confirms an air mass transported from Sahara Desert but also from Atlas Mountains located in the North of Africa.



¹CESAM – Aveiro University
²Cape Verde University

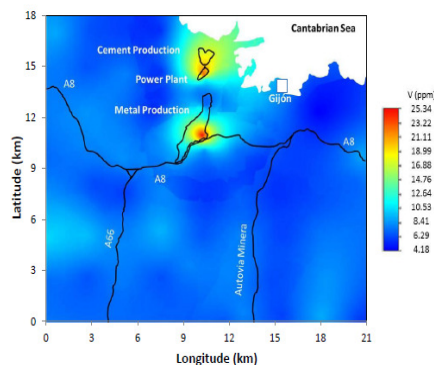
Integration of biomonitoring and instrumental techniques to assess the air quality in an industrial area located in the coastal of central Asturias, Spain, RFSR-CT-2009-00029

S.M. Almeida M.C. Freitas, A.I. Pedro, T. Ribeiro, J. Lage, A. V. Silva, N. Canha, M. Almeida-Silva, T. Siteo, I. Dionisio, S. Garcia¹, G. Domingues¹, J. Perim de Faria², B. González Fernández², D. Ciaparra³

A biomonitoring study was 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.

Lichens were transplanted from a clean background site, exposed in an industrial area in Gijon, and collected after 5 months. After lichens exposure, the study had three objectives: 1) to explore spatial patterns of lichens conductivity in order to identify the impact of the industrial studied area; 2) to study the spatial distribution of chemical elements determined by INAA technique; 3) to establish a relationship between the distribution of conductivity and the concentrations measured in lichens and the characteristics of local sources.

Results showed that the values of conductivity and antropogenic elements were significantly higher near the main industries (a steel plant, a power plant and a cement plant).

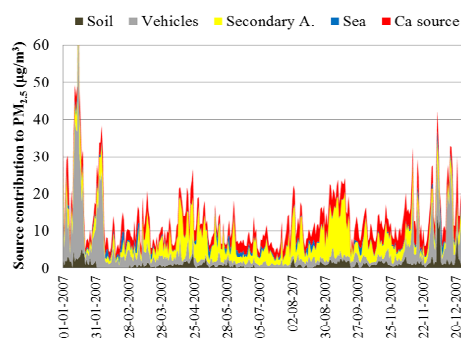


¹ISQ, ²Arcelor Mittal Spain, ³Tata Steel,

Characterizing seasonal variations in elemental particulate matter concentrations in european urban and rural areas under different climatic conditions, IAEA RER/2/005

S.M. Almeida, N. Canha, M.C. Freitas, I. Dionisio, T. Siteo, J. Cardoso¹, A. Caseiro¹, C.A. Pio¹, H.Th. Wolerbeek²

The aim of the project is to apply non-destructive and multi-elemental nuclear techniques to characterize APM in different countries in Central and Western Europe, to contrast the results for areas with a continental and a marine climate and to compare them with the acceptable standards for particulate matter and elemental concentrations as defined by European countries. The meteorological parameters have also been measured and correlated with the element concentrations. In Portugal, APM was collected in 1 rural (Fors do Arão) and 2 urban (Lisbon and Setúbal) areas and element concentrations were measured by Neutron Activation Analysis in ITN. APM and element concentrations showed a seasonality characterized by higher contributions of secondary aerosol during summer/spring and higher contributions of vehicles during autumn/winter. Several approaches were used in order to identify the emission sources: receptor models, air mass trajectory analysis; weekday/weekend ratios; hourly variations and comparison between stations.



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

(Hyper)accumulation of arsenic and other elements in plants adapted to sites impacted by mining and smelting activities (HYPERAS), PTDC/AMB/65462/2006

N. Canha, H.M. Anawar, M.C. Freitas, S.M. Almeida, A.I. Dionísio, H.M. Dung, M.G. Pacheco¹, C.J. Pinto-Gomes², A. Bettencourt³

This study aimed to find out a vascular plant species that accumulate relatively high concentrations of arsenic (As) for its use as phytoremediator at abandoned and contaminated mining areas, such as São Domingos mines (1), Portugal. The assessment of As contamination levels in soils and plants of other similar sites in the north of the country (Castromil-2 and Poço de Freitas-3) was also conducted; and the sample analyses were made by instrumental neutron activation analysis. *Agrostis* genera have shown higher As transfer coefficients than other studied plant species and, in particular, *Agrostis curtisii* has shown a reasonable ability to accumulate high concentration of this toxic element.



¹CERENA/IST, ²ICAM - Évora University, ³CMA-IMAR, Évora Univ