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Biomonitor-Reflection of Large-Distance Air Mass Transported Trace Elements

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Doctoral Thesis

Biomonitor-Reflection of Large-Distance Air Mass Transported Trace Elements

Radiation Science & Technology

Bruno José Henriques Vieira

Biomonitor-Reflection of Large-Distance Air Mass Transported Trace Elements

Biomonitor-Reflection of Large-Distance Air Mass Transported Trace Elements

Proefschrift

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Door

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Keywords: Neutron Activation Analysis, air pollution, aerosols, trace elements, biomonitoring, lichen transplants, long-range transport, North Atlantic, low troposphere.

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To Maria, the force that encourages me

(Para a Maria, a força que me encoraja)

And to the star in the sky that guides me, Rodrigo.

(e para a estrela no céu que me guia, Rodrigo)

Contents

Chapter 1

GENERAL INTRODUCTION

1.1. Atmospheric aerosol

1.1.1. Introduction

Over the last decades the interest on atmospheric pollution has grown, due to the confirmation of the influence that aerosol particles have on the earth-ocean-atmosphere system and on human health[1-8]. This influence often implies irreversible changes in ecosystems and serious respiratory and cardiovascular diseases. In turn, the measurement of the behaviour of atmospheric elements in terms of transport, physics and chemistry, is of major importance both for the emission sources (e.g. industries, transport, agriculture), and for governments, the latter especially for establishing control strategies. Recognition of emission sources that are responsible for contamination of air quality is of cource important. Most of the work done in that respect is in the perspective of local and regional sources and focuses on the source characterization, on the quantification of deposition, air quality evaluation and impact of element deposition in the surroundings of the emitters. However, as the links between pollutants, sources and effects are more and more found and indicated at a global scale, there is now a growing recognition of the importance of the transport of air pollutants over much longer distances. Intercontinental transport of air pollutants, especially particulate matter, has been established as an important factor in air quality management.

Understanding this long-range transport better and charactering it at the level of what is happening in the North Atlantic will certainly help to understand the consequences of the passive contamination of some territories by polluters present in nations at long distances.

1.1.2. Atmospheric dynamics of long-range transport

Aerosol plumes (both natural and anthropogenic) may rise aloft, delivering significant pollutant concentrations to a downwind continent sometimes in a matter of a few days[9,10]. Under some conditions diffuse export can lead to an overall increase in tropospheric pollutant abundance, thus increasing pollution in background clean air[11]. In all cases the ultimate impact will depend on how aerosols being transported aloft are mixed down to the surface.

Most meteorological phenomena that affect long-range aerosol transport occur in the troposphere. The chemical elements transported from the emitter sources into the lower free troposphere (LFT) often travel great distances because of the strong winds aloft, including the jet streams, the strong rivers of atmosphere flow that encircle the earth. The mechanisms producing upward transport into the LFT play important roles in determining whether or not long-range aerosol transport will occur. This depends on the occurrence of localized thunderstorms and low pressure systems[12]. The long-distance transports can move the aerosols large distances either with minimal dilution or mixed with the background air masses; the latter turns identification of the source more difficult. The differentiation of these two mechanisms is necessary in the indentification and quantification of the aerosol source contributions.

The long-range aerosol transport in the LFT in the central North Atlantic in middle latitudes is from west to east due to the prevailing westerly winds, greatly influenced by the transient low pressure system. The North Atlantic Oscillation (NAO) is the dominant mode of winter atmospheric circulation variability in the Northern Atlantic, which affects the position, strength and trajectories of low pressure-systems[13]. These eastward moving storms transport surface-based aerosol from the industrialized North America east coast to higher altitudes and then toward Europe[14,15]. At lower latitudes the prevailing wind typically flows east to west bringing Saharan dust from northern African into the North Atlantic region.

1.1.3. General Characterization

Other important factors affecting aerosol transport, in addition to atmospheric dynamics, are the size, morphology and chemical composition of the aerosol particle.

The size and morphology of an airborne particle control much of the particle dynamics as well as its biological, chemical and physical effects upon the environment. Many effects of particles or elements present in the particles depend on particle shape. According to Reis[16] particles shape and density have different consequences for their aerodynamic behaviour and therefore different important influences on the aerosol transport in the atmosphere. Aerosols are classified in terms of their aerodynamic diameter. The coarse particle (PM10) is the mass of particle matter with diameter smaller than 10 µm, and fine particles (PM2.5) designate the particulate fraction with aerodynamic diameter smaller than 2.5 µm. With lifetimes in the atmosphere in the order of days to weeks, fine particle matter can undergo long-range transport, producing global aerosol deposition.

The chemical composition of aerosols depends on the emitting sources or particles precursors and on atmospheric conditions. Aerosols could have a natural or anthropogenic origin, and their composition can be derived from direct emissions (primary aerosol) or be the result of primary aerosols transformed in the atmosphere into secondary aerosols, thru photochemical reactions. In general, long-range transport can be more significant when aerosol transformation rates are slow relative to long-distance transport times[17].

Long-range aerosol transport is directly dependent on the magnitude of emission fluxes of primary aerosol in upwind source regions. Understanding their temporal and spatial distribution is an important challenge to detect and quantify the impact of long-range transport on downwind receptor regions. In general, this can be predicted with a combination of chemical analyses of aerosol and geographic dynamic models. This approach is described in this thesis in Chapter 5.

1.1.4. Transport and deposition in central North Atlantic

Pico Island is the Portuguese highest peak placed in the Atlantic Ocean. The contribution of local anthropogenic sources is very low and the long-range transports result mostly in background increases with natural and anthropogenic aerosols from the surrounding mainlands[18-21]. Relevant features that make this location unique for assessing regional and hemispheric impacts from measurements within the lower free troposphere (LFT) or the marine boundary layer (MBL) have already been highlighted[22].Even though this region is of great importance for long-range transport studies, not many studies have been done into the aerosol characterization. It is important to characterize aerosol physical and chemical properties and in order to do that, aerosol samples were collected at the PICO-NARE observatory at the summit of the Pico mountain[23]. The PICO-NARE station was established to study the composition of the lower free troposphere in the central North Atlantic region, with an emphasis on the impact of pollution outflows from the surrounding continents[24]. The station is located on the summit caldera of Pico Mountain (38.470ºN, 28.404ºW; 2225 m above medium sea level - AMSL). The station is located at an elevation that allows sampling of air in the LFT. It includes the seven-wavelength aethalometer (model AE31), and it is an automated, self-contained, experimental station.

As already mentioned the aerosols emitted at the surface could enter into the LFT. Thus, understanding the aerosol composition at the ground/sea level is also very important to infer the possible local contribution on aerosol present in the LFT.

The cost and complexity of this type of monitoring on such remote places makes that biomonitoring could be a possible alternative, given that biomonitoring is cost effective as it does not require specialised or technically sophisticated monitoring equipment and it is also effective in large scale air pollution monitoring programmes both in spatial or time scale[25-27].

1.2. Biomonitoring

1.2.1. Introduction

The environmental and health concern related to atmospheric pollutants is increasing[28-33] and all countries at a global scale underline the efforts to establish control programs either by field measurements of the several emission sources or by dispersion models based on quantitative measurements. However, monitoring anthropogenic air pollution is a very complex problem due to 1) the great number of potentially dangerous substances, 2) the difficulty in estimating bioavailability, 3) the large spatial and temporal variation of pollution phenomena and 4) the high costs of the recording instruments and hence the low sampling density of a purely instrumental approach[26,27]. These difficulties are more evident when monitoring air samples at remote places are needed. Due to these difficulties and from the derivation of advantages in other methodologies, the feasibility of bio-indicators/monitors was demonstrated in studies to establish geographical and/or temporal variation in the bioavailability of pollutants. Since the very early 1860's rather scattered observations with bioindicators were associated to environmental induced stress in urban and industrial areas[34] (the term bioindicator refers to organisms that undergo modification as a response to atmospheric pollution: they could be associated to qualitative assessment of the presence of a certain amount of atmospheric pollutants[26]). However, only in the late 1960's, after extended work with mosses[35], the bioindicator approach has grown in the next decades into a serious alternative to instrumental methods[27,36-38] thereby evolving into the biomonitoring method (the term biomonitor refers to organisms used for the quantitative determination of atmospheric pollutants). Nowadays, these methods are widely accepted in many countries, especially as a support for the limited data derived from instrumental measurements.

Biomonitoring of atmospheric elements is based on the use of organisms that are able to absorb and retain a certain amount of chemical element in their tissues. They can reflect the deposition of atmospheric elements as well as its biological impact in the organism itself[39,40]. Biomonitoring also permits the study of possible synergies among different pollutants[41]. Needed biomonitor characteristics are 1) a wide geographical distribution; 2) a large anbundance; 3) all year availability; 4) easy to collect; 5) high tolerance for the elements in the atmosphere; 6) a significant correlation between the element quantity in their tissues and the element quantities in the atmosphere[42]. In the last decades lichens were the most used organisms in monitoring atmospheric deposition[39].

1.2.2. Lichens

Lichens are stable synergistic associations between a fungal (mycobiont) and algal or cyanobcterial species (phycobionts). They are perennial, and grow slowly on soil (epigeic), rocks (epilithic) and trees (epiphytic). The fact that lichens do not possess roots and cuticle, explains their major dependence on atmospheric sources of nutrients. Because atmospheric sources of nutrients are poor, nutrient concentrating mechanisms are critical for lichen survival[43]. They absorb the water, minerals and other nutrients from wet, dry and occult atmospheric deposition over the entire surface of the thallus. These phenomena explain the specific sensitivity of lichen in studying air pollution[44], especially inorganic contaminants. Contaminants may occur in lichens as: a) particles absorbed onto the thallus surface or within intercellular spaces; b) ions bound to extra or intracellular exchange sites; c) soluble intracellular ions[45-47].

All biomonitoring methods using lichens are based on the pollutant equilibrium process of the biotic and abiotic components of ecosystems involving uptake/loss from/to the surrounding environment[46,48]. This equilibrium depends on the ecological variables such as climate, substrate, etc, which may influence element uptake and physiological processes. The use of exposed-to-control ratio (EC ratios) allows interpretation of changes in element concentrations[46,49].

1.2.3. Studies using lichens transplants

As indicated in the previous paragraphs, lichens have been extensively used for the evaluation of anthropogenic pollution (urban and industrial)[38,50-54] and their use also yielded information on background levels in remote places[55-57], both approaches in native (passive monitoring) as well as in transplanted (active monitoring) samples[58-62]. Transplanted lichens can be put to use in areas in which hardly any native lichen species occur, by transplanting thalli of suitable lichen species from an uncontaminated area. Additional advantages are: a) the lichen material can be exposed according to a rational scheme; b) it’s possible to calculate enrichment rates and ratios since values before exposition can be determined; c) the monitoring can be in patterns of time and space[46]; and d) the exposure time can be controlled[36]. The usability of lichen transplants to monitor atmospheric elements depends of several factors, as:

a) The level and variability of the background concentration of the elements in control samples (before exposure);
b) The period and impact of exposure as it can affect the vitality of thalli and consequently the active process of element uptake[46]; In repeated surveys, it is mandatory to transplant lichen samples for the same duration because bioaccumulation rates can vary according to differences

in viability[63]; According to some authors the equilibrium levels are reached by the transplant lichen between 12-15 months for industrial sites and 6-9 months to clean site. The higher the atmospheric pollution the longer should be the exposition time[25].

c) The memory loss concept describes the time during which the biomonitor preserves a "memory" of a given environmental availability condition; that could be longer or shorter than the exposure time period[60] and depend on the element release rate, that in turn most probably is specific for individual or groups of chemical elements and also depends on ambient and lichen morpho-physiological conditions[27].

Meteorological conditions may affect the accumulation capacity of lichens[64]. Some authors report a decrease in the elemental concentration in lichens with increasing rainfall and wet days due to a release of particles from the thallus surface[37,65] and others report the opposite, because rainfall and wet weather favour active metabolism and consequently the uptake of minerals[66]. In this context, is very important to understand what the effects are on lichen elemental uptake, especially when in the same dimensional survey lichen samples are under varying weather conditions as rainfall, humidity and temperature.

1.2.4. Long distance transported elements studies

Most of the biomonitoring surveys are performed in low elevation sites. Very few lichen surveys have been performed along elevational gradients in order to study long-range transport and deposition of elements. Although this is a major environmental issue in some policies developed under the Convention on Long-range Transboundary Air Pollution in European Union[67,68] since 1979, it has received not enough attention. Remote high-altitude environments have been recognized as ideal sites for the investigation of transboundary air pollution associated with the global distribution of pollutants. There are some studies in mountain areas (between 1300m and 5200m)[69-73], mainly in the last decade, allowing the generation of evidence of long-range transported elements. The results of these studies suggested that the origins of pollutants are not local but remote, mainly by long-distance atmospheric transport. The presence in lichens of elements such As, Br, Cd, Cu, Pb, Sb and Zn are reported in accordance with elemental contents of samples collected with instrumental aerosol collectors. This suggests the capability of using biomonitors in long-range aerosol transport studies. However, the calibration of the biomonitor's elemental content to atmospheric element dispersion asks for a clear understanding of bioconcentration and biomagnification. This is essential to understand the monitoring data, and may lead to a clearer interpretation of observed results, eventually even allowing for transport estimates to be made.

1.3. NAA methodologies

1.3.1. Introduction

During the 1960s Neutron Activation Analysis (NAA) was unsurpassed as a technique in achieving excellent sensitivity for a wide range of trace elements while having unique characteristic of being non-destructive. There are many methods to determine the elemental concentration in environmental samples. NAA is a method for the measurement of chemical elements by activating the stable nuclides in the sample with neutrons (produced in a nuclear reactor facility) and measuring the induced radioactivity of the new radionuclides[74]. Is one of the most sensitive methods for multielement analysis without the problems associated with chemical separation based techniques[75,76]. By NAA, up to 30-40 elements are commonly observed in environmental samples[77]. Advantages above other analytical methods are: samples can be liquids, solids or powders; NAA is non-destructive; no pre-chemistry is required; NAA is a multi-elemental analytical technique, with sensitivity that permits the assessment of trace-level elements; is totally unaffected by the presence of organic material in the sample. The neutrons used in NAA are usually produced in a fission reactor, mostly using thermal and epithermal energies. Epithermal neutrons can be obtained by using a filter which is made of material with high neutron absorption for low energy neutrons. Therefore, only higher energy neutrons (epithermal neutrons) activate the sample. The use of epithermal neutrons (ENAA) gives an advantage in reducing an interfering reaction by thermal neutrons. This advantage only can be taken if the element of interest has a high ratio of the neutron radioactive capture resonance integral (I_0) to the thermal cross-section (σ_{th}), whereas the element producing the interference reaction has the low ratio. It essentially results in a lower background and better sensitivities for some nuclides[78-81]. NAA can be ranked among the most precise and accurate of all analytical methods for the determination of trace elements. In using NAA, however, choosing a best suitable reaction, or reducing the interference reaction must be seriously considered.

The selection of an analytical method should be closely linked to the objectives of the study, be practical in costs and throughput, being in concordance with the number of samples to be analysed. Thus, the principal choice maybe the method with high level of accuracy and sensitivity, which allows to obtain the results in a reasonable period, especially when many samples are to be handled.

The following paragraphs describe a few general characteristics of NAA methodologies used in this thesis, since more detailed information will be indicated in Chapter 2.

1.3.2. Accuracy

NAA has on many occasions proven to be a potentially accurate technique for trace element analysis. Intercomparisons however reveal large discrepancies between the results obtained by different methods, which are sometimes element-specific.

An estimate of the accuracy of the measurement is achieved by analysing certified reference materials. This indicates how good one's technique and methods are when the results are compared with known concentrations of major, minor and trace elements in similar or other matrices. There are several factors which can severely limit the accuracy of NAA, including:

1) Changes in neutron flux profile which are not carefully monitored;
2) Inaccurate placement of samples in front of detectors, including variations between standards and samples. This is particularly significant when counting at short distances form the detector. Automatic turning of the sample in front of the detector can also be used to ensure better reproducibility of the counting;
3) Inaccurate correction for deadtime losses and pulse file-up by either software or hardware methods;
4) Poor deconvolution or overlapping peaks by computer programs;
5) Nuclear or spectral interferences;
6) Human factor errors;
7) Trace impurities in counting vials;
8) Volatilization of certain elements during irradiation;
9) Incorrect drying procedures;

Another consideration is the presence of elements in samples with large activation cross-sections that contribute to the high background resulting from the Compton effect.

1.3.3. Sensitivity

In many NAA applications the detection of trace elements can be limited by Compton scattering. Lower energy peaks can often exhibit a poor-signal-to-noise ratio, making the analysis of these peaks difficult. In particular, this is a result of Al, Br, Cl, Co, Fe, Na, Mn, Sc and Zn. Most NAA methods to enhance elemental sensitivities usually revolve around optimizing irradiation, decay and counting times, employing loss-free counters, larger detectors, using alternative photopeaks or using radiochemical means to isolate the radionuclide of interest.

Compton scattering occurs when a photon loses some of its energy when colliding with an electron. This results in an increased background from the multiple scatterings, which generates a decrease of analytical sensitivity for the determination of gamma-rays. The application of Compton suppression systems (CSS) is more advantageous for isotopes which emit single gamma rays or those having cascading disintegration schemes with low coincident yield. The background of the Compton continuum in the spectrum is reduced to a level much lower than in a normal spectrum, and the analytical sensitivity is drastically improved[82-84].

For gamma ray spectrum acquisition, Ge semiconductor detectors are used. Their high energy resolution allows for the conversion of the spectrum to a list of photopeak energies and net peak areas. The energies identify the radionuclides, the net areas are proportional to the amount of the elements present in the sample. To improve detection limits by signal improvement, larger efficiency detectors will be advantageous. This could be achieved using other detectors than the usual (coaxial Ge-detector) or using well-type detectors. Detection limits are determined by the counting efficiency and the spectral background, which both are related to the characteristic of the detector[85].

1.4. Motivation and Objectives of the present Thesis

The focus of the present thesis is the biomonitoring of atmospheric trace elements with the attention on the long-range transported trace elements. In the context of the above many questions exist, such as:

a) What are the possible effects of the environmental factors associated with altitude on biomonitors vitality?
b) What are the possibilities to use biomonitors to reflect large-distances air masses transported elements? They could be a valid alternative to instrumental aerosol analysis?
c) What is the chemical composition of LFT in terms of trace elements? Is its composition distinct from the marine layer, or is there any mixture of elements between the two layers?
d) What are the main characteristics that distinguish aerosols of different origins in LFT in terms of shape and size?
e) What is the chemical composition of aerosols of different emission sources and resulting from long transport? What is the geographical prevalence of aerosols in the North Atlantic?
f) What are the effects (advantages or disadvantages) on accuracy and sensitivity of using INAA with and without CSS, using ENAA, using coaxial detectors or well-type detectors on the analysis of a large set of environmental samples?

Therefore, in order to gain some understanding about these questions, the overall major objectives of these thesis were to: a) compare analytical aspects of NAA, in terms of accuracy, sensitivity and flexibility in routine applications to decide which has the most appropriate performance when a large set of environmental samples (lichens and coal fly ash) is considered, and identify the advantages and disadvantages of each method; b) increase knowledge of aerosol composition in terms of chemical and physical (size and shape) composition at different altitude layers (marine boundary layer - MBL and LFT) of the atmosphere at the middle North Atlantic; c) identify and characterize the main sources of pollution and its contribution to background concentrations on LFT in the middle North Atlantic. Is this area contaminated with aerosols from long-distances pollution sources?; and d) evaluate the usability of lichens transplants to monitor long-range transported elements at different altitudes between the MBL and LFT.

The Thesis consists of 8 Chapters. Chapter 1 is a general introduction to all issues of the Thesis' focus, Chapters 2-7 are in three main parts: the first part is about the comparison of NAA methods (Chapter 2); the second part (Chapter 3-5) is about aerosol characterization and source apportionment; and the third part (Chapters 6,7) focuses on the vitality of transplanted lichens, and their use in a case study at several altitude transects at Pico mountain, the case study aimed at the possible recognition of elemental deposition from long-range pollution sources, and Chapter 8 gives a general discussion and outlook.

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Chapter 2

NEUTRON ACTIVATION METHODOLOGIES ON ENVIRONMENTAL SAMPLES – QUALITY OF CALIBRATION AND DETECTION LIMITS COMPARISON[1]

2.1. Introduction

The obvious increment of environmental problems in the world, resulting from the interaction of anthropogenic activities to bio-systems, increasingly called for the necessity of monitoring such negative impacts, mainly on soil, atmosphere and aquatic systems. Evaluation of chemical element amounts is part of this and the selection of an appropriate method of analysis is crucial for the quality of the results. This selection is essentially dependent on e.g. the required elements, degree of trueness, metrological traceability the limits of detection, the uncertainty of measurement, the sample mass, level of instrumentation automation and financial aspects.

The neutron and charged particle activation analysis have been applied in many fields of science in the last 80 years[1,34-39] and, in spite of the non-nuclear multielement technique development (ICP-ES, AAS and XRF), the nuclear ones still have an important role when their complementary advantages are taken into account[2-4]. Comparing with mass spectrometry techniques as ICP-ES with growing use, NAA has the advantages of not being based on digestion of samples and the opportunity of analyzing material for which matrix-resembling calibrators do not exist. With respect to trueness and precision, the analytical results by NAA can be even better to those obtained by other analytical methods as atomic absorption spectrometry, atomic emission spectrometry or mass spectrometry[5,40].

NAA measurements are nearly independent on the effect arising from the sample matrix when compared with other non-nuclear methods. Detection limits can be improved controlling some

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[1] *This Chapter is a modified version of:*
B.J. Vieira, P. Bode, H.Th. Wolterbeek, M.C. Freitas, "Inter-comparisons analysis – assessment of optimum instruments for minimum detectable amounts in multi-element techniques", oral presented on the "Ninth International Conference on Nuclear Analytical Methods in the Life Sciences" placed in Lisbon, Portugal (2008).

factors that affect the signal-to-noise ratio: photopeak efficiency, cross section, neutron flux, sample mass, Compton scattering and detector resolution[6,7].

2.1.1. Neutron Activation Analysis - NAA

NAA is a method for the measurement of chemical elements by activating the stable nuclides in the sample with neutrons and measuring the induced radioactivity of the new radionuclides. The number of radionuclides produced will depend basically on the number of target nuclei (mass of sample), the number of neutrons (neutron fluency during a given irradiation time) and the probability of activation occurring (cross-section of nuclei). The growth of activity during irradiation depends on the half-life of the radionuclide. As each radionuclide has its energy of emitted radiation and specific decay constant, gamma-ray spectrometry can be used to measure their activities by converting the energy quantum of the respective radiations - usually by emission of a gamma-ray, a proton or an alpha particle - in impulses by electronic means. The reaction most often used in NAA is radioactive capture,

$$n + {}^{A}Z \rightarrow {}^{A+1}Z^{*} \rightarrow {}^{A+1}Z + \gamma \,,$$

where ${}^{A}Z$ is the irradiated isotope, n the neutron, ${}^{A+1}Z^{*}$ is the compound nucleus in the excited state, and γ is the secondary gamma radiation.

The formation of a radionuclide by neutron activation is dependent of several factors which the most relevant are: 1) Neutron flux: the larger the neutron flux, the greater the rate at which interaction occurs; 2) Target nuclei: the activation rate is directly proportional to the number of target nuclei present; 3) Mass: the activation rate is proportional to the mass of the element; 4) the probability of the nuclei targeted by the neutron flux to be activated is the thermal cross section or the resonance integral for thermal or epithermal neutron respectively; 5) Resonance integral: lighter elements have thermal cross sections and resonance integrals in the same order of magnitude. Other isotopes have very large resonance integrals even larger than their thermal cross sections, indicating strong resonances in the region above the cadmium cut-off energy (may be considered the frontier between thermal and epithermal neutrons); 6) Decay rate: the radionuclide will decay already during irradiation with a characteristic half-life, this is, the time the activated nuclei take to be reduced to a half; 7) Nuclear interferences: some radionuclides can be produced by different nuclear reactions or by decay of isotopes of different chemical elements, such nuclear interferences have an impact.

As a result of the irradiation with neutrons, several radionuclides are formed with emissions of photons with discrete energies which usually are characteristic for the decaying nucleus. The conversion of the energy deposited by an incident photon to an electric pulse of proportional height can be measured by gamma ray spectrometry detectors and calculated from the net peak area for each gamma ray line.

The number of nuclei (ΔN) disintegrating during the measurement is given by:

$$\Delta N(t_{ir}, t_d, t_m) = \frac{RN_0}{\lambda}(1-e^{-\lambda t_{ir}})e^{-\lambda t_d}(1-e^{\lambda t_m})$$

t_{ir} – duration of irradiation

t_{d} – duration of decay

t_{d} – duration of measurement

R – reaction rate per nucleus capturing a neutron

N_0 – number of target nuclei

λ – decay constant

The resulting net area (A) of a photopeak for a given photon energy in the gamma ray spectrum is approximated by the following activation equation:

$$A = \Delta N \gamma \varepsilon = \Phi_{th} \sigma_{eff} \frac{N_A \theta w}{M}(1-e^{-\lambda t_{ir}})e^{-\lambda t_d}\frac{(1-e^{\lambda t_m})}{\lambda}\gamma\varepsilon$$

Φ_{th} - neutron flux

σ_{eff} - cross-section

N_A – Avogadro's number

θ - isotopic abundance

w – mass of the element

M – atomic mass

γ - gamma-ray abundance

ε – detector efficiency

All the factors determining the detection limits in NAA can be applied under different experimental conditions, background conditions, photopeak efficiency, peak-to-Compton ratio and resolution which all can be derived from detectors specifications. The signal strength in NAA is influenced by, among others, the photopeak efficiency. The photopeak efficiency is a function of photon energy and source-to-detector distance. The irradiated sample may be counted closer to the detector – and thus at a higher efficiency without problems associated to high dead time - is often the first step towards better detection limits.

2.1.2. Epithermal Neutron Activation Analysis - ENAA

Neutron energy distributions and fluxes are considerably varied in different types of reactors and at different positions within a reactor. Neutron energy distributions are usually described via three principal energy components: thermal, epithermal and fast (Figure 2.1).

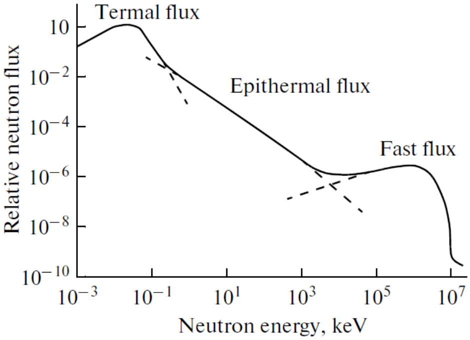

Figure 2.1. Representation of the nuclear-reactor neutron spectrum[44].

The irradiation condition chosen under NAA depend on the element to be measured and the type of matrix of the sample. NAA with thermal neutrons, usually loosely referred as INAA, in general provides the largest scan of elements determined simultaneously by a single irradiation, as other NAA types can only provide concentrations of a few specific elements.

Neutrons with moderated energy from 0.5 eV to about 1 MeV are used for ENAA. With increasing neutron energy, the cross-section values decrease for some nuclear reactions, while other exhibit significant resonances. As the amount of epithermal neutrons in general is about 10 % of the total neutron flux, it is necessary to remove the thermal neutrons using cadmium or boron as a filter. The cadmium ratio (activity induced by the total neutron flux divided by the activity induced after cadmium filtering) of the element of interest can be evaluated to decide when ENAA is meaningful to enhance the detectability of the element of interest. Typically, it will be only advantageous if the element of interest has a high ratio of the neutron radioactive capture resonance integral to the thermal cross-section, whereas the element producing the interference reaction has the lowest ratio. Irradiation of such nuclides by epithermal neutrons allows selective activation to be carried out and specific element determination techniques to be developed. It also become possible to effectively suppress the induced activity of some matrix elements in samples of environmental and biological nature as ^{28}Al, ^{56}Mn, ^{24}Na, ^{35}Cl, ^{45}Sc and others, that have large cross sections for thermal neutron absorption and reduce the number of competing reactions and it becomes possible to determine small concentrations of trace elements.

2.1.3. Detectors

The analysis of gamma-ray spectra can be considered to consist of spectrum reduction, standardization and spectrum interpretation. For gamma ray spectrum acquisition, Ge semiconductor detectors are used. Their high energy resolution allows for the conversion of the spectrum to a list of photopeak energies and net areas. The energies identify the radionuclides, the net area is proportional to the amount of the elements present in the sample.

To improve detection limits by signal improvement, either higher neutron fluxes or larger efficiency detectors or both will be advantageous. This could be achieved using other detectors than the usual (coaxial Ge-detector), sometimes longer irradiation times or using well-type detectors[7,32]. Coaxial detectors have a cylindrical shape. The lower part of the central cylinder may be removed to improve the ratio of the active volume vs the dead volume. Coaxial detectors are made from either n-type or from p-type germanium. Well-type detectors are commonly made from p-type germanium. By placing the irradiated sample inside the hole or “well” in the crystal, an almost 4π surrounding with active detector material is accomplished, which has favourable consequences for the effectiveness of detection. Moreover, it also reduces the geometrical errors that occur with imprecise positioning and differences between sources and standards when counting close to the end-cap of a common coaxial detector[43]. It has been shown, both theoretically and experimentally[6,7,19,20] that the well-type detector offers the best outlook for attaining better detection limits. The almost 4π geometry of the source of well-type detector favourably influences the photopeak efficiency. In general, the energy resolution of a well type detector is approximately 10% poorer than of a 20% coaxial detector. In spite of that, when larger distances have to be applied due to geometrical reasons[7] for example, counting in the well-type detector always results in the highest absolute efficiency.

2.1.4. Compton Suppression System - CSS

The background under the photopeak is the ‘noise’. Except for the contribution of the natural background radiation, the background under the peak mainly stems from Compton scattering. It is one of the interaction mechanisms of photons with matter, which can be: 1)the photoelectric effect, in which the photon transfers all of its energy to an atomic electron; 2) Compton scattering, in which the photon loses part of its energy to an atomic electron and is deflected from its original path; 3) Pair production, in which a photon with an energy > 1022 MeV interacts with the electric field of the nucleus and creates an electron-positron pair; the positron annihilates with a free electron resulting in the emission of two 511 keV photons.

Compton scattering results in an increased background by the multiple scatterings, which causes a worsening of the detection limit and precision for the determination of gamma-rays, particularly for lower gamma energy emitters. The use of CSS reduces the Compton continuum from high-energy γ-rays resulting in advantageous measurement of lower-energy γ-rays for some emitters[8-12] (e.g. As, Ba, Ce, Ni, Rb, Se, Th and Zn). CSS can usually reduce the background, depending on the distance of the sample from the detector and the energy of the gamma-ray of interest, by a factor of 2 to 8-9[9-13]. Consequently, the improvement in detection limits is maximum 1.4 to 3 (square root of the background) or often less because the photopeak may be reduced due to coincidence summing losses. Other advantage of CSS is the reduction of contributions for the spectrum of radionuclides decaying with two or more γ-rays emitted in coincidence as the emitters of Br as an example[9]. In several studies, with results obtained in the same irradiation and measurements conditions with and without the CSS, it was demonstrated the compatibility of CSS in analysing environmental samples. In biological material, the use of CSS showed significant reduction in the detection limit of As, Ca, Cd, Cr, Fe, Hg, K, Rb, Sr and Zn[13,25]. In aerosols, it improved the detection limits of Al, Ba, Ce, Cr, Ni, Rb, Ti, V and Zn[8,10].

The noise can also be improved by reducing the neutron activation of interfering radionuclides via ENAA. Most of the studies using ENAA focus on the analysis of soil samples[3,14], mainly on measurements of nuclides with half-lives of 10-15 minutes or more. The possibility of combination of ENAA and CSS is in well advance for elements as As, Au, Ba, Cd, Ga, I, K, Mo, Si and W[9,8,14]. ENAA has found numerous applications, namely for analysis of geological and biological samples with matrix rich in Al, Na or Br, due to the background activity in spectrum caused by these elements and, as a consequence, it improves the detection limits. Several studies[3,41,42] demonstrate the compatibility of ENAA especially in conjunction with CSS in analysing environmental samples. In biological material, it was confirmed the improvement in determination of As, Au, Ba, Gd, Ho, Mo, Rb, Sb, Sn, Sr, Th, Tm, U and W. In aerosols, it can be effectively used for the determination of elements such as As, Cd and Sb[26-27]. In water samples, it is indicated to determine Br, Cl and I[28,29].

To improve detection limits via noise reduction, the use of ENAA or CSS or both in simultaneous could be advantageous. Some other characteristics of the spectrometric techniques were widely studied by some authors and comparative advantages are presented in Table 2.1. In spite of comparisons between analytical techniques are often done, the most relevant aspects affecting the results obtained depend on a such wide variety of experimental conditions that quantitative comparison is almost impossible to carried. However, some authors[2,30,36,48] report NAA as the most accurate, reliable and effective technique, especially when multielement analysis of a great deal of samples is required.

Table 2.1. Comparison of some spectrometric methods of trace element analysis (adapted from M. De Bruin, 1992[45]).

	Accuracy	Sensitivity	Distribution	Multi-element	Sample Size	Routine	Turn-around time	Accessibility	Costs
INAA	+	0	-	+	S, l	+	-	-	0
RNAA	+	+	-	0	S, m	+	-	-	-
XRF	0	-	-	+	s	+	+	+	
TXRF	0	0	-	+	S, m	+	+	+	+
SXRF	0	+	+	+	s	-	-	-	
PIXE	-	0	+	+	s	+	-	-	
ICP-ES	0	0	-	+	S, m	+	+	+	+
AAS	-	0	-		S, m	+	+	+	+
ICP-MS	0	0	-	+	S, m	+	+	0	0
ICP-IDMS	+	0	-		S, m	0	+	0	-
SSMS	-	0	-	+	s	+	+	+	

Scores: (+ positive; 0 average; - negative); sample size (s ~mg; m ~g; l ~kg).

For the research described in this chapter, INAA and ENAA were applied; different detector types (coaxial and well-type detectors) were available for use; CSS was also used for both methods. To evaluate the performance between these different analytical techniques the results obtained by the various methods in different experimental protocols were compared. These experiments were done by analysing lichens - IAEA 336 and coal fly ash NIST 1633a reference material.

Comparing the quality of calibration parameters and detection limits achieved, we will discuss which could be more appropriate for selected environmental matrices in a routine perspective.

2.2. Experimental

The comparison in this study is based on the results obtained with some analysis done under different experimental conditions as well as other results obtained in studies already performed by other researchers. This is due to a huge difficult to compare different techniques with such a wide variety of assumption and different experimental conditions.

2.2.1. Sample preparation

Two certified reference materials Lichen IAEA 336 and Coal Fly Ash NIST-1633a were prepared with amounts as shown in Table 2.2. Material was placed inside ultra pure polyethylene vials filled to 8 mm high in case of lichen material and 5 mm high in case of coal fly ash. For each type of sample and for each technique, three replicates were prepared

In this study, the analysis considered the realization of different experiments, as shown in Figure 2.2, that is: A) INAA for short and medium-long-lived nuclides, with and without CSS. In this experiment, the measurement without CSS were carried on coaxial-type detectors and the measurement with CSS using NaI(Tl) detectors; B) INAA for medium-long-lived nuclides using well-type detector; C) ENAA for short-lived nuclides with CSS.

2.2.2. Description of experimental conditions: INAA with and without CSS

For short-lived nuclides, SIPRA, was used. This system was specially designed to rapidly transfer samples to and from an irradiation terminal for use in the NAA application. Irradiation was done in cell 26 of the RPI, an open pool-type with 1 MW power. Parameters of irradiation and measurement of samples are shown in Table 2.2. The samples were measured simultaneously in the device consisting of a primary Canberra GX-3518 HPGe detector with a 35% relative efficiency and 1.8 keV resolution for the 1332.5 keV photopeak of ^{60}Co and a total of seven NaI(Tl) detectors. Six NaI(Tl) detectors are mounted on the surrounding annulus while the 7th is used as a plug. All detectors are coupled to model Canberra 2026 spectroscopy amplifier, Canberra Model 2040 coincidence analyser and Canberra MultiPort-II (USB) operated by Genie-2000 software. Samples were submitted to different short irradiation times according Table 2.2. The computation of all parameters for the calibration of energy, peak-shape and full-energy peak detection efficiency in order to calculate elemental concentration was carried out by k_0-IAEA software based on k_0-method[23,31].

Table 2.2. Parameters of irradiation and measurement for lichen and coal fly ash samples of the different NAA methods compared.

NAA method	Irradiation facility	Type of Sample	Sample mass (mg)	Irradiation and measurement parameters				
				Flux (n.cm^{-2}.s^{-1})	**Irradiation Time**	**Decay Time**	**Counting Time**	**Sample-to-detector distance (mm)**
ENAA	PRR/ITN – Sacavém, Portugal	Lichen – IAEA336	350-450	$1.17E^{+11}$	90-150 s	300-1400 s	600 s	49.8
	1 MW natural water open pool-type	Coal Fly Ash - NIST 1633a	850-950	$1.17E^{+11}$	10-18 s	600-1700 s	600 s	49.8
INAA[a]	PRR – Sacavém, Portugal 1 MW natural water open pool-type	Lichen – IAEA336	100-120	Short: $2.68E^{+12}$	90-150 s	300 s	600 s	49.8 (10)
				Long: $5.12E^{+12}$	5 h	96-816 h	2- 8 h	38.8
		Coal Fly Ash - NIST 1633a	150-200	Short: $2.68E^{+12}$	18-30 s	600 s	600 s	93.8 (5)
				Long: $4.12E^{+12}$	3 h	144-984 h	2-8 h	71.8
INAA[b]	HOR – Delft, Netherlands	Lichen – IAEA336	100-120	$5.10E^{+12}$	4 h	122-528 h	1 h	0
	2 MW natural water open pool-type	Coal Fly Ash - NIST 1633a	200-230	$5.10E^{+12}$	1.5 h	192-528 h	1 h	0

[a] – Method with the use of CS system and coaxial-type detector; [b] - Method with the use of well-type detector.; values in parenthesis correspond to distance in CSS.

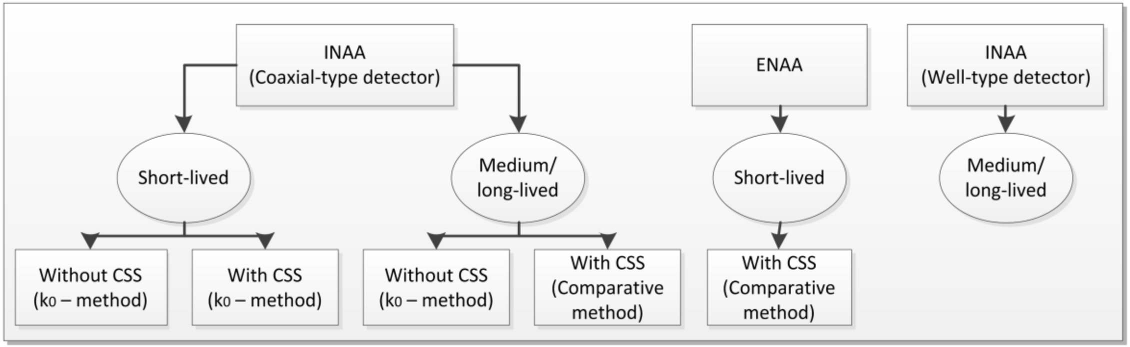

Figure 2.2. Representation of the different experiments.

For medium and long-lived nuclides, irradiations and measurements were done according parameters shown in Table 2.2. Using coaxial detector, samples were measured on a calibrated detector, an ORTEC GEM-30185-P with relative efficiency of 30% and resolution 1.85 keV (^{60}Co – 1332.5 keV), and signals processed by NIM using ND AccuSpec software. Samples were counted using an automatic sample changer coupled to the measurement facility to determine radioisotopes with medium half-lives. The measurements with CSS for intermediate and long half-life radionuclides obtained with thermal neutrons were done in the NaI(Tl) detectors, after measurement in the coaxial detector. Elemental concentrations were calculated on basis of k_0-method[23] using gold as the single comparator element. With CSS elemental concentrations were calculated using the comparative method using concentration of the estuarine sediment reference material NIST-1646-SRM as a standard.

2.2.3. Description of experimental conditions: INAA using well-type detector

For the analysis, the samples were irradiated at the research reactor HOR, an open pool-type with 2 MW power in the Reactor Institute Delft at the Delft University of Technology. For medium and long-lived nuclides irradiations and measurements were done according Table 2.2. A well-type detector was used in other to compare with measurements obtained in coaxial detectors. The measurement with well-type used the slow pneumatic pool-side rabbit system with each rabbit loaded with 14 samples stacked in 4 columns. The 250 cm^3 well-type semiconductor detector is equipped with automated sample changer with signal processed by standard NIM electronics. The NIM ADC’s are linked to the local area components network via an in-house developed 8K-buffered interface NIM models[30]. Elemental concentrations were calculated on basis of k_0-method[23] using zinc as the single comparator element.

2.2.4. Description of experimental conditions: ENAA without CSS

The ENAA for short-lived nuclides with CSS in this work was done using the pneumatic system, SIPRA (described above). The irradiations and measurements were done according Table 2.2. Irradiation was done in cell 26 in RPI were the irradiation terminal was previously covered with a Cd ring. The samples were measured on a device consists of a primary Canberra GX-3518 HPGe detector with a 35% relative efficiency and 1.8 keV resolution for the 1332.5 keV photopeak of ^{60}Co and a total of seven NaI(Tl) detectors. Six NaI(Tl) detectors are mounted on the surrounding annulus while the 7th is used as a plug. All detectors are coupled to model Canberra 2026 spectroscopy amplifier, Canberra Model 2040 coincidence analyzer and Canberra MultiPort-II operated by Genie-2000 software.

The measurements were done only with CSS and the elemental concentrations were calculated using the comparative method using elemental concentrations of the estuarine sediment NIST-1646-SRM as a standard.

2.3. Results and Discussion

2.3.1. Accuracy

Due to the strongly variation on composition of environmental samples, in mostly of the studies the consistency of the absolute values of the results is more important than the degree of uncertainty. Therefore, the agreement between the result of a measurement and a certified value obtained between the different analytical methods is mandatory to the assessment of the accuracy of the results. This is verified via the analysis of reference materials and through intercomparisons. To compare the results produced with the several techniques, *Z*-score tests were applied. This method obtains an estimation of the experimental results tendencies and allows comparing it to a target standard deviation. A *Z*-score is defined as:

$$Z = \frac{C_x - C_r}{\sqrt{S_x^2 + S_r^2}}$$

where $C_{x,r}$ and $S_{x,r}$ are the mass fraction and uncertainties of experiments (*x*) and of certified values (*r*). Results for which $|Z| \geq 3$ are not accepted, if $2 < |Z| < 3$ results are questionable and if $|Z| \leq 2$ results are considered acceptable for approval of the results at the 95% confidence level[30,33].

The Z-score for all elements determined with the different NAA techniques are shown in Table 2.3. For the same elements analysed with well-type and coaxial detectors, after thermal irradiation, Z-scores are lightly better on well-type detector for lichen IAEA-336 and for coal fly ash NIST-1633a in coaxial detectors. Only a few elements present |Z-scores| > 2 in coaxial detector: Th and Cl in lichen IAEA-336 and Fe in coal fly ash NIST-1633a-SRM. Measurements in well-type are all within |z-scores| < 2 for lichen IAEA-336 and for coal fly ash NIST-1633a-SRM, the elements presenting |Z-scores| > 2 are Fe and Rb only. In terms of using different types of detectors, in spite of results were slightly better in well-type measurement, there are not a significantly increasing in the accuracy of results and the selection between them should consider other different factors.

Despite using different irradiation conditions and different measurement parameters, in general results in both types of detectors are considered acceptable, despite of some deviation in the elements referred above.

Analysing Table 2.3, it is possible to verify that the results of thermal irradiation do not improve with the use of CSS. There are some elements for which the results obtained with CSS have |Z-score| > 2: La for lichen IAEA-336 and Fe and Mn for Coal Fly Ash NIST1633aSRM.

In all the elements determined with ENAA with CSS the Z-score values are on the level of acceptable (|Z-scores| < 2), which means good element calibration of the single comparator method.

In all NAA methods, values are acceptable which demonstrates a high level of accuracy. For some elements that are the exceptions, it could be attributed to sources of errors that could be annulated with preventive assurance. According to some authors[7,30,48], the sources could be associated with samples preparation errors, experimental process inconformity or sample inhomogeneity. Comparatively to other analytical methods, in NAA, samples can be irradiated directly without any procedures of extraction, so common errors due to such procedure can be complete eliminated. So all the NAA are advantageous in terms of accuracy as demonstrated in Table 2.3.

2.3.2. Sensitivity

In terms of sensitivity, under the NAA methods and in the last decades was a significant effort to develop some systems that allows to analyze many trace elements in concentration under the 10^{-6} ppm, making NAA one of the most effective methods in life sciences. Figure2.3 refers to the short-lived gamma-ray spectra of the techniques included in the comparison of this study. A significant reduction in the background continuum for the same sample measured with CSS either in the irradiation with thermal neutrons or with irradiation with epithermal neutrons result in a better detection limits that can be advantageous when determining trace elements in environmental samples with some unwanted elements in sample matrix, that generate a high Compton background on the gamma-ray spectra. In CSS, the reduction of background is mainly a consequence of the reduction of the continuum due to the coincidence of gamma-rays of some nuclides as an effect of the suppression mode. In epithermal spectra, the reduction is mainly because target nuclides in samples have relevant thermal neutron absorption cross-sections less activated with epithermal neutrons.

The potential of the use of different detector types (coaxial or well-type) in order to increase sensitivity was evaluate comparing results of detection limits (irradiation and measurements parameters according to Table 2.2). It was calculated an improvement factor dividing the results of detection limits, in $mg.kg^{-1}$of both detectors. In Table 2.4 comparison shown that, in general, well-type detector improves sensitivity for almost elements under this analysis. In fact, the improvement is light (1.0-3.0) for Co, Cs, Eu, Fe, Rb, Sm, Th, Yb and Zn and strong (>3.0) for Ce, Lu, Sb, Sc and Tb. The few situations that coaxial detector improves the detection limits was for As, Cr, K, La and Na. This observation agrees well with some reports from other authors[7,10,13]. They report a 2-3 times better detection limits at 5 cm source-to-detector spacing. Therefore, when distances are close to 0 improvements are not effective. In practice, the advantage of well-type against coaxial detectors in terms of sensitivity improvements increase rapidly with the distance between sample and the endcap. This should be considered when considering samples with isotopes as ^{24}Na, ^{28}Al, ^{56}Mn, ^{59}Fe (ex.: soil, aerosol filters) which by the thermal irradiation generate a large activity via thermal (n, α) irradiation that affect the real time counting and need to be at high distances from the face of detector. Other reasons are related to type of samples (size, morphology).

In some other studies was observed that the suppression factor with CSS is variable according to the energy range of the Compton continuum and is influenced by the configuration of the CSS instrumentation. The advantage of use CSS is especially important for elements with small amounts in samples, that are usually below the detection limits with normal INAA. This analytical methodology is not possible for nuclides that have cascade events occurring in the decay from other nuclides, as ^{82}Br, ^{60}Co, ^{140}La, ^{46}Sc and ^{75}Se. Considering these constraints, the performance of CSS is very influenced of the sample composition. In this experiment, the reduction observed in the background continuum by using CSS in INAA (see Figure 2.3) that was caused by the photopeak of ^{82}Br, ^{38}Cl and ^{24}Na present in the sample. As these elements are at high concentration in lichen IAEA 336 samples and having considerable thermal neutron absorption cross section they generate high Compton background. The CSS reduces the continuum from the coincidence summing out gamma-rays.

The use of CSS for ^{76}As determination using the ^{75}As(n,γ)^{76}As reaction analysing the 559 keV gamma-ray peak can be helpful mainly because of two factors. First it reduces the signals coming from the 1368 keV gamma-ray coincidence peak from ^{24}Na and second it reduces the signal from the coincident 554 keV gamma-ray peak belonging to ^{82}Br, and so the possibility of overlap. Our results of detection limits with and without CSS of coal fly ash NIST-1633a shown an improvement factor of 1.6 using CSS (without CSS, 66.6 mg.kg^{-1}; with CSS, 41 mg.kg^{-1}). This shown and advantage of using CSS in samples with high concentrations of Br and Na (marine contaminated samples).

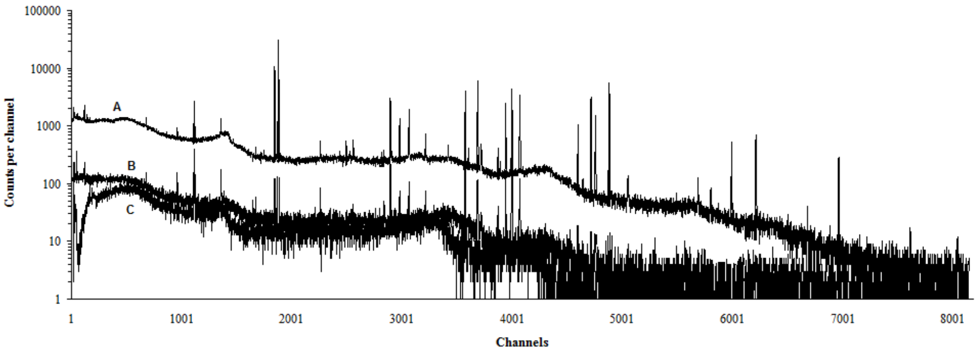

Figure 2.3. Short-lived gama-ray spectrum of lichen sample (IAEA 336) showing the Compton continuum reduction. A - INAA without CSS; B - INAA with CSS; C - ENAA with CSS.

There are other nuclides that can present poor statistical results when analysed with INAA without CSS, as ^{66}Cu and ^{86}Rb. The use of CSS can decrease the statistical errors and sensitivities are much better for the 1039keV photopeak from ^{66}Cu with improvement factor of 5.7 (without CSS, 0.23 mg.kg^{-1}; with CSS, 0.04 mg.kg^{-1}) and for 1077 keV photopeak from ^{86}Rb with improvement factor of 3.3 (without CSS, 1.44 mg.kg^{-1}; with CSS, 0.43 mg.kg^{-1}) on lichen IAEA-336 sample.

All the results obtained show improvement of sensitivity when using CSS and agreed well with other studies[7,10,13]. Anyways, should be noted that results of detection limit depends on the experimental parameters used.

The combination of the CSS and ENAA proved to be efficient in analysis of several elements in environmental samples[8-10,28,46-48], as As, I, K, Si and W. According to the authors this combination can decrease the background by a factor of 5 to 10 depending of the experimental parameters.

One element with high I_0/σ_{th} value where ENAA with CSS show an advantage is ^{128}I. Since the gamma-ray 443 keV is from non-cascade emission and the located on the Compton continuum of high energy from ^{38}Cl and ^{24}Na, the use of ENAA with CSS can significantly reduce the background of gamma-ray spectra. A comparison of gamma-ray spectra of lichen IAEA 336 obtained in this study is presented in Figure 2.4.

Table 2.3. Calculated z-scores for elements in lichen samples (IAEA-336) an in coal fly ash (NIST-1633a-SRM) using different NAA methods. (n=3). |z-scores| ≥ 2 in bold.

Reference Material	**Elements**	**Certified value** (mg/kg)	**|z-score|**			
			INAA (coaxial detector)	**INAA** (well-type)	**INAA-CSS**	**ENAA-CSS**
Lichen IAEA-336	As	0.63 ± 0.08	0.29	0.48	**2.50**	
	Ba	6.4 ± 1.1		0.65		
	Br	12.9 ± 1.7	0.16^a		**4.93**	0.13^a
	Ce	1.28 ± 0.17	0.35	1.40	1.25	
	Co	0.29 ± 0.05	0.06	0.45	0.57	
	Cs	0.110 ± 0.04	0.45	0.62		
	Fe	430 ± 50	0.41	0.52	0.50	
	K	1840 ± 200	0.64/1.14^a	0.89	0.10^a	1.75 ^{a}
	La	0.66 ± 0.1	1.55	1.56	**2.62**	
	Mn	63 ± 7	1.08^a		0.22^a	0.26^a
	Na	320 ± 40	0.32/0.49^a	0.85	1.39^a	0.13^a
	Nd	0.6 ± 0.18		0.54		
	Sb	0.073 ± 0.01	**3.32**	0.54	1.17	
	Se	0.22 ± 0.04	**3.88**	0.99		
	Sm	0.106 ± 0.014	0.43	0.71		
	Th	0.14 ± 0.02	**4.10**	1.73		
	Zn	30.4 ± 3.4	0.13	0.15		
	Al*	680	1.86^a			0.19^a
	Cl*	1900	**2.02**^{a}		0.03^a	0.52^a
	Cr*	1.06	**5.39**/0.30^a	0.35	0.31	
	Eu*	0.023	0.30	1.17		
	Lu*	0.0066		1.08		
	Rb*	1.76	0.36	0.50	0.58	
	Sc*	0.17	0.07	0.34		
	Tb*	0.014		1.79		
	V*	1.47	1.98^a			1.36^a
	Yb*	0.037	0.01	0.13	0.01	
Coal Fly Ash NIST 1633a	Al	143000 ± 10000	1.33^a			0.54^a
	As	145 ± 15	0.04	0.27	**3.89**/0.47^a	1.12^a
	Ca	11100 ± 1000	0.32^a	1.02		
	Cr	196 ± 6	0.58			
	Fe	94000 ± 1000	**5.81**	**2.04**	**2.73**	
	K	18800 ± 600	0.21/0.46^a	0.66	0.52^a	1.99^a
	Mg	4550 ± 100	0.13^a			
	Mn	179 ± 8	0.46^a		**3.63**^{a}	0.01^a
	Na	1700 ± 100	1.77/1.55^a	0.78	**7.56**/1.52^a	0.23^a
	Rb	131 ± 2	0.30	**8.37**	0.24	
	Sb	6.8 ± 0.4	1.07	1.34	0.70	
	Se	10.3 ± 0.6	0.64	0.20	0.76	
	Th	24.7 ± 0.3	1.16	0.72		
	V	297 ± 6	1.82^a			0.24^a
	Zn	220 ± 10	0.36	2.07		
	Ba*	1500	*0.80/0.98*^{a}	*0.83*		
	Ce*	180	*0.82*	*0.94*	*0.98*	
	Co*	46	*0.90*	*1.02*	*0.98*	
	Cs*	11	*0.81*	*0.96*	*0.96*	
	Eu*	4	*0.76*	*0.98*	*0.99*	
	Ga*	58	*0.85*	*1.67*		
	Hf*	7.6	*0.69*	*0.99*		
	Mo*	29		*0.83*		
	Ni*	127		*1.97*		
	Sc*	40	*0.93*	*1.03*	*0.99*	
	Ti*	8000	*1.01*^{a}			

*Empty cells means data not available; * - Elements with information values only (noncertified);^{a}Results from short lived radionuclides;Values in italic represent the simple ratio between obtained and informative concentrations.*

Table 2.4. Detection limits (mg.kg^{-1}) and improvement factor comparison of INAA medium and long-lived elements on lichen IAEA 336 obtained on Coaxial and Well-type detector (according to irradiation and measurements parameters described in Table 2.2). Improvement Factor (IF) of the detection limits, between Well-type and Coaxial detector.

	Coaxial	**Well-type**	***IF***
As	0.037	0.038	0.9
Ce	0.44	0.12	3.5
Co	0.065	0.061	1.1
Cr	2.1	3.8	0.6
Cs	0.07	0.05	1.3
Eu	0.01	0.007	1.3
Fe	43.6	23.6	1.8
K	11.1	65.9	0.2
La	0.016	0.021	0.8
Lu	0.012	0.0028	4.4
Na	0.12	2.4	0.1
Rb	1.4	1.3	1.1
Sb	0.05	0.01	4.4
Sc	0.011	0.0035	3.1
Se	0.19	0.19	1.0
Sm	0.0023	0.0014	1.7
Tb	0.21	0.02	12.5
Th	0.029	0.019	1.5
Yb	0.024	0.013	1.8
Zn	3.1	1.2	2.6

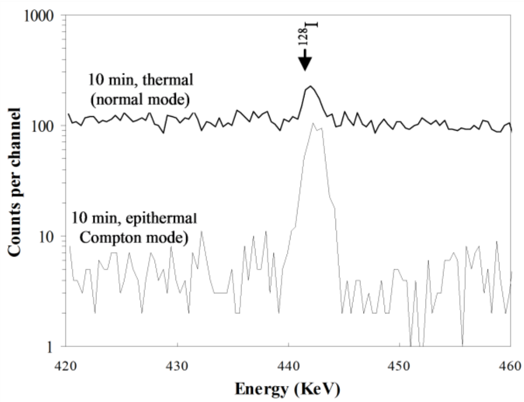

Figure 2.4. Spectra comparison of ^{128}I peak with ENAA with and without CSS.

The ENAA ca also be favourable for elements analysed with (n,p) reaction as Si, since a threshold energy of neutron is required for such nuclear reaction. The ^{29}Si(n,p)^{29}Al reaction was used to the determination of Si using the 1273 keV gamma-ray. The use of ENAA with CSS significantly reduces the background as depicted in Figure 2.5, representing comparison of gamma-ray spectra of coal fly ash NIST-1633a obtained in this study.

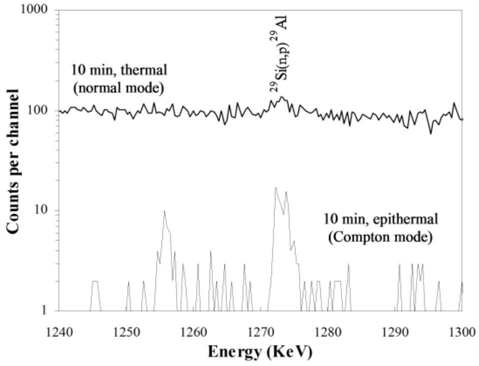

Figure 2.5. Spectra comparison of ^{29}Al peak from ^{29}Si activation with ENAA with and without CSS.

2.3.3. Flexibility in Routine application

Despite mostly of the analytical methods present a high degree of development, some present advantages comparatively with each other, especially when large amounts of samples are considered to analyze in routine perspective.

The use of coaxial detectors in INAA has an advantage related to the possibility to place samples on any distance from the face of the detector. This flexibility allows to easily associate automated samples changer devices. On other hand adjustments of counting in function of the total-rate could be done, increasing the performance in terms of sensitivity. These both aspects could be very important when a large set of samples are considered.

Using well-type detectors one advantage comparatively with coaxial detector is the smaller dependence to the size and geometry of the sample due to the almost 4π geometry. This is more relevant when sample measurement is done closer to the face of coaxial detector.

The use of CSS could have significantly advantages on the sensitivity of measurement of some elements as discussed above. However, some consideration should be considerate when samples have some specific characteristics. For example, when counting-rate exists it affect the difference in dead-time between Compton and anti-Compton mode. This affects the performance. For a large set of samples, the difficult in sample automation could be also a disadvantage.

2.4. Conclusions

Should be noted that the conclusion presented represent an analysis from a set of results from a specific experimental protocol, and also some similar approaches from studies reported in bibliography.

One first point of this study was that the use of the various NAA methods experimented turns possible to determine almost all the significant trace elements with environmental interest and can prevent the need for complementary, non-nuclear techniques.

The result of the calculation of the sensitivity improvement factor should be used together with all experimental considerations, and expectation with respect to the type of spectra to be analysed and the need for a high energy resolution.

When comparing INAA with and without CSS, using different detectors (coaxial and well-type) and ENAA with CSS in different experimental parameters, several advantages and drawbacks become evident. It has been shown that there is an obvious unique advantage in the utilization of a CSS and ENAA for determination of some specific elements. This was confirmed by the significant decrease of the background in gamma-ray spectra and, so the detection limits, originated mainly in the presence of nuclides with a coincidence gamma-ray. According with our results and other authors[9,10,13] the CSS results in the increase of the analytical sensitivities using thermal neutrons of Al, Ba, Ce, Cr, Cu, Fe, Hg, Ni, Rb, Sc, Se, Th, Ti, V and Zn. The use of CSS also with ENAA significantly reduces the detection limits for As, I, K, Si and W[8,49]. The results also confirmed that the composition of the sample is mandatory of using the CSS, mainly because of the implication on the sample-detector distance affection. The use of CSS introduces additional problems as the complicated sample changing of samples and more complex data acquisition.

The well-type detector improves the accuracy and sensitivity of a large number of elements comparatively to coaxial detector, when samples need to be at 4 to 9 cm distance from the face of detector. However, well-type is less flexible with respect to sample changer design and automatization. That aspect makes coaxial detectors the most profitable choice for processing a set of large number of samples with great variety in composition.

Mostly of the analytical techniques used in this comparison are optimized allowing obtaining the maximum of it performance, with levels of accuracy and sensitivity, for a large range of elements, giving the capability of these NAA techniques to achieve some levels that sometimes cannot be obtained by other analytical techniques. Maybe further development on ENAA with CSS by absolute methods (k_0-compton suppression with ENAA)[31] could be enhanced for elemental analysis of nuclides with half-lives of 5-10 min and longer, because of ^{28}Al, the 1780 keV gamma-ray is monoenergetic and its suppression fails.

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Chapter 3

ELEMENTAL COMPOSITION OF AIR MASS UNDER DIFFERENT ALTITUDES IN AZORES, CENTRAL NORTH ATLANTIC[2]

Abstract

Between 8th July 2002 and 18th June 2004, aerosol samples were collected for elemental concentration analysis in Azores, in both the Marine Boundary Layer (MBL) and the Lower Free Troposphere (LFT), to study the differences of aerosols in different atmospheric altitudes of the Central North Atlantic. PICO-NARE observatory is an experimental site on Pico mountain summit (38,470ºN, 28,404ºW, 2225m a.s.l.) in Pico Island, Azores, where air masses from the surrounding continents (Africa, Europe, Central and North America) carrying aerosols with anthropogenic (Sb, Br, Mo, U, Se and Tb) and/or natural emissions (Fe, Co, La, Na, Sm, Cr, Zn, Hf, K and Th), pass through. At Serreta, Terceira Island, Azores (38,69ºN, 27,36ºW, 50 m a.s.l.) in TERCEIRA-NARE, natural aerosols (I, Cl, Na, Br and other soil related elements) are predominant, but combined interpretation of the data (mean comparison and EF factors) of MBL show a co-existence of the anthropogenic elements Sb and Mo, eventually with similar origins as the ones passing Pico Mountain summit. Very high concentrations and EF for Sb, Mo and Br in LFT, higher than other globe areas, confirm atmospheric long-range transport mainly from west boundary of North Atlantic, and gives the possible accumulation and persistence of those elements in the area due to the presence of Azores high pressures or the Hadley cells effect. A correlation agreement between Fe and Yb and enrichment of rare earth elements (La, Sm, Tb and Yb) and Th in LFT aerosols, reflects a mineral dust intrusions from North Africa (Sahara and Sahel region).

3.1. Introduction

The last few decades have witnessed an increased interest in the occurrence, magnitude and distributions of natural and anthropogenic aerosols. This is due to their known direct and indirect

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[2] *B.J. VIEIRA, M.C. FREITAS, H.TH. WOLTERBEEK, "Elemental composition of air masses under different altitudes in Azores, central north Atlantic", J Radioanal Nucl Chem 291 (2012) pp.63–69. DOI:10.1007/s10967-011-1308-3*

effects on the earth's climate and thus their influence on the earth–ocean–atmosphere system[1-6], and to the role that the aerosol particles may have on human health[7-8].

The atmospheric aerosol contributes to about 10^{-9} – 10^{-7} of the air mass, with 80 % of the mass in the troposphere and more than half of their mass is concentrated in the first 5 km layer[9]. In the North Atlantic it is estimated that about 96 % of the total aerosols emissions are from natural emissions, where marine salt, biogenic elements and natural mineral dust are the main contributors. Volcanic emission is also significant. The other 4 % of emission result from anthropogenic emissions from long-range transport, including biomass combustion, fossil combustion and other anthropogenic indirect activities[10]. The marine aerosol is characteristic of North Atlantic atmosphere, but its appearance is restricted to the MBL that ranges altitudes between 850 m and 2000 m, depending on the latitude and the annual period. In Azores area, in summer, MBL ranges between 850 m and 1100 m and in winter between 900 m and 1700 m[11-13]. Usually the MBL is separated from the lower troposphere, avoiding the mixture with upper layers. The composition of marine aerosol usually reflects the composition of seawater that exists in the surface layer of the oceans; as it is usually associated with larger water fractions, which results in physical changes as volume modification, aerodynamic diameter and optical properties, the marine aerosol easily changes its chemical composition by reacting with other different element sources[14-15]. Marine aerosol in North Atlantic is commonly associated to high concentration of sulphur possibly from biogenic emissions, from anthropogenic sulphur and from volcanic emissions observed on the Atlantic Mid-ridge[5,16]. Mineral aerosol has its main source the dust of Sahara and also of Sahel region in North Africa which contributes with approximately half of all mineral aerosols present in North Atlantic atmospheres[17-21]. The altitude of the dust layer could reach up to 6 km, but over the Central Atlantic Ocean it is developed mainly in the first 4 km layer[18]. Silicate is the most abundant particle type (65-85%), however dust also carries large amounts of other elements (REE, Al, Ca, Fe, Sc and Sm)[20-21]. With particular weather conditions dust from arid and semi-arid regions of central Asia could also reach the North Atlantic, through the dust transported over Greenland[22]. Dust from Sahara/Sahel region could also transport particles with origin other than the geological one. High enrichment factors of some pollutant elements (Sulphur) in dust from Sahara/Sahel suggest a mixing process of the pollution aerosols from Europe with the mineral aerosols[18]. Volcanic emissions also contribute with significant impact to the mineral emissions in North Atlantic. In the Azores area volcanoes from the Mid-Atlantic Ridge are mainly basaltic with magmas rich in Mg and Fe and poor in Si[23]. The West and East boundary of North Atlantic are extremely industrialized and urbanized, and atmospheric long-range transport could affect aerosol increment through some particularly events with the direct plume transport from those affected areas. Among the anthropogenic emissions biomass combustion is one of the most important sources of aerosols. The seasonality of concentrations of aerosols from biomass combustion on North Atlantic depends on the source area. During summer months in the Boreal forest of North America and South Europe forest fires occur bringing carbonaceous aerosols and other particles to the North Atlantic[24-25]. Some plums from Siberian forests have also been reported to reach North Atlantic[26]. In winter period, in Florida Peninsula, particularly dry weather favors the increase of forest fires[27]. It is also during winter that aerosols from biomass combustion are higher in Europe mainly because of the combustion for heat production[26].

In general, aerosols reach the Central North Atlantic in different vertical layers, dependent of air mass origins and aerosol characteristics[28]. However, mechanisms of mass compensation could favor the penetration of particles in the anticyclone and their deposition over Central North Atlantic. The maximum annual aerosol concentrations are in the North Atlantic in summer[19,27].

This study intends to discuss elemental concentrations of air masses, which reached the Central North Atlantic (Azores) in both the LFT and MBL. The climate is oceanic temperate, strongly influenced by the Azores anticyclone and the North Atlantic Drift of the Gulf Stream, with high humidity and precipitation, and much milder temperatures as other regions in same latitude.

Pico Mountain in Pico Island is the Portuguese highest peak placed in the Atlantic Ocean. Aerosols were collected at PICO-NARE observatory summit. The contribution of local anthropogenic sources is very low if not null, and the long-range transport observation is expected to be obtained since the site is in the pathway of air masses travelling in LFT (2225 m) from the surrounding continents (Europe, North Africa, North and Central America). TERCEIRA-NARE Station is located in the western coast of Terceira Island, in the basis of MBL (50 m high) and at 100 m from the coast line. This station provides measurements complementary to low troposphere observations and allows studying the importance of long-range transport in the MBL and giving information on atmospheric composition. TERCEIRA-NARE station is 100 km away from PICO-NARE observatory, based on their longitudes.

3.2. Experimental

In PICO-NARE station (Figure 3.1), the aerosol samples with particles with all ranges of aerodynamic diameters were continuously collected in quartz filters (manufacturer: Pallflex®; type: Q250F) by the automated, self-contained Aethalometer (model AE31), for periods of approximately 24 h, from 8 July 2002 to 18 June 2004. The total number of analyzed filters (384) corresponds to the days of sampling working with an irregular periodicity (27% in Spring; 41% in Summer; 20% in Autumn; 12% in Winter). As a consequence, the air-intake volume varied between 0.21 m^3 and 80.9 m^3. The average air volume, sampled for each filter, was 4.31±0.07 m^3 to an average flow rate close to 3.3 L.min^{-1} for the period between 8 July 2002 and 17 September 2003, and 8.47±0.44 m^3 and an average flow rate close to 5.9 L.min^{-1} for the period between 18 September 2003 and 18 June 2004. Due to the remote setting of PICO-NARE and local weather conditions, instrumental maintenance was performed 1-2 times/year[29].

Aerosol particles were weekly (7-day samples) collected on pre-fired quartz fibre filters with a high-volume sampler, from 8 July 2002 to 22 June 2004, the same collection period of PICO-NARE station. The total number of analyzed filters (62) corresponds to the days of sampling working with some sporadic interruptions between October 2002 and June 2004. The average air volume, sampled by filter, was 10.1±3.1 m^3.

The filters from PICO-NARE station (blanks and samples) were cut from the strips in circular forms with an area of 0.950±0.086 cm^2 each. The exposed side of each spot was covered with a piece of unexposed blank filter, to avoid contamination of the sample with the polyethylene top cover; the same procedure was applied to each blank in order to obtain identical geometry. Each sample or blank sandwiched set was irradiated for 7h with a neutron thermal flux of 3 x 10^{12}.cm^{-2} s^{-1} together with one disc (125 µm thick and 5 mm diameter) of a 0.1% Au-Al alloy as comparator. After irradiation, samples and blanks decayed for 4 to 6 days and were then measured for 7 h; after this measurement samples decayed for 4 weeks more and were again measured for 7 h. For samples from Terceira (Figure 3.1), besides similar long irradiations and measurements as described for PICO-NARE station, short irradiations with neutron thermal flux of 6 x 10^{11} cm^{-2} s^{-1} were done using the SIPRA for determination of elements with short life time.

All gamma spectra measurements were done using liquid nitrogen cooled hyperpure germanium detector (1.8 keV resolution at 1.33 MeV and 30% relative efficiency), connected to 4096 multi-channel analyzers. The gold alloy discs were measured for 5 minutes, also with the same detector, 7 days after the end of the irradiations. The elemental composition of the aerosol samples in Pico summit and Terceira was determined by k_0-standardised, k_0-INAA[30-33] and calculations of elemental concentration with the k_0-IAEA software[34].

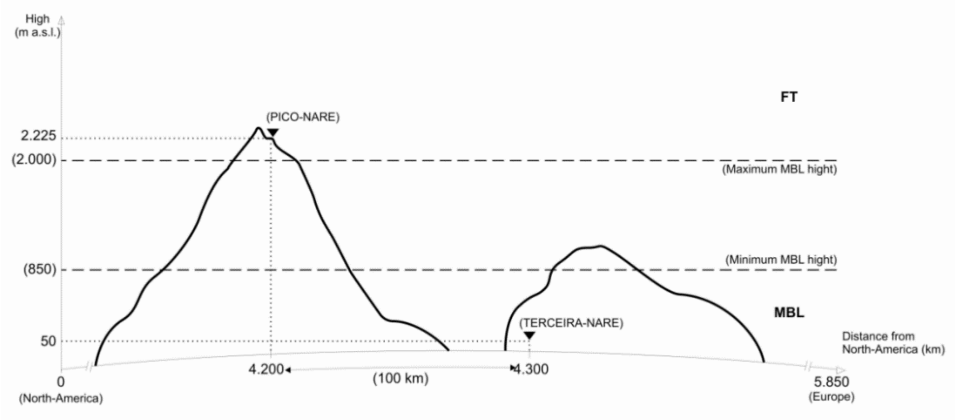

Figure 3.1. Representation of the experimental stations in the context of North-America and Europe boundary and in the atmosphere layers.

In order to evaluate the anthropogenic and marine influence at PICO-NARE and TERCEIRA-NARE the enrichment factors of the aerosols relatively to the soil were calculated using Sc as the normalizing element. For the calculation of each EF value, the elemental content in each sample was related to the elemental content in the soil collected at the same site[35]. The EF value for an element X was computed according to EFx=[X/REF]sample/[X/REF]ref.sample, where REF is Sc. Values of “ref.sample” were calculated from soil sample collected at each site, one out of the superficial (0–10 cm depth) layer. Standard packages from exploratory, correlation and multivariate data analyses were STATISTICA® StatSoft Inc. 8.0.

For the reference material “Air Particulate on Filter Media” (NIST-SRM® 2783; PM2.5 on a polycarbonate filter membrane) measured by INAA, the reproducibility was within 5-15%[36].

3.3. Results and Discussion

Table 3.1 shows the elemental concentrations found in the analyzed samples of PICO-NARE in LFT and from TERCEIRA-NARE in MBL. Concentrations of 33 different elements could be determined in MBL and 19 in LFT. In both layers, results show high amplitude between minimum and maximum concentrations and considerable high variation in concentrations along the sampling period. This reflects an atmosphere subjected to constant influence from several different factors, as diversified aerosols particles origin, changes in meteorological conditions, particularly particles emissions events or seasonality influences. The exceptions are K, As, Se, Sb, Cs, Tb, Yb, W, Th, Al, V and I in MBL and K in LFT. These elements have low variations.

A study of air-masses trajectories in all sampling days was done, by displaying 10 days backtrajectory in order to establish their main directions[37]. In LFT, origin of air masses is attributed to long-range transport from North-America (49%), Arctic (12%), local marine area (10%), Europe (9%), Central America (9%), Tropic-Cancer (7%) and Africa (3%). In MBL, origin of air masses is mainly from local marine area (90%), Tropic-Cancer (8%) and Europe (2%). These distinct characteristics could explain the high ratios between element concentrations means of the two layers. With exception of Sb, all elements have higher mean concentrations in MBL, particularly Na with almost 2 orders of magnitude difference. This was expected at this localization and altitude and in accordance to the reported in other studies in ocean area. Other elements higher than 1 order of magnitude in MBL are Sc, Br, Mo, La and Hf. On other hand, Sb has much higher concentration in LFT. This divergence may be to the accumulation of anthropogenic aerosol deposit of undergoing long-range transport in LFT. This issue (seasonal variation and air masses origins) will be discussed in more in future publications.

The daily aerosol concentrations of PICO-NARE observatory were arranged in week concentrations through the average of the week values of the correspondent TERCEIRA-NARE sampling periods. Correlation analysis between data of both stations show no significant correlation in all chemical elements (not shown), suggesting that air masses in both LFT and MBL have different element enrichments sources.

The EF was calculated in both datasets to determine which elements in aerosols composition have other origin than crustal one. The results for the EF referred to Sc are shown in Figure 3.2 for TERCEIRA-NARE and PICO-NARE respectively. Considering that concentration data show high variability, many EF values would be produced for each element. So, graphic presentation identifies the amplitude between 25%-75% of the EF values on the non-outlier range, the outliers and the extreme values. In this approach, we focus on the mean, however further publications will discuss the events related with the extreme values. The EF factors below 10 are considered to show a strong correlation to the crustal signature. The EFs between 10 and 100 indicate a moderate enrichment above crustal levels and EFs above 100 indicate that the element is significantly enriched and that it is originated from other natural or anthropogenic emissions. Concerning the MBL, the elements I, Cl and Mo show high EFs and Sb, Na, Au, Cr, Br and Ba moderately EFs. I, Cl, Na and Br have potential marine origin. Some studies refer some photoreactions and low residence times in atmosphere that explain the results [38]. The Sb values are moderately enriched, however in some sporadic events extreme values reflecting an enrichment of 2 or 3 order of magnitude higher, suggesting depositions from LFT coming from high altitude long-range transportation processes. Sb may also be due to local traffic.

In LFT, with exception of Fe, Co and La, all other elements present EF above 100. Nevertheless, only Th, Yb, Tb, Se, U, Mo, Br and Sb are highly enriched. In case of Sb and Br, the EF values reach 100,000, putting in evidence the large influence of anthropogenic emissions from polluted areas reaching the Azores area that contribute to contamination levels higher than some high polluted areas, reflecting some type of accumulation process. This phenomenon was previously referred by Freitas et al. (2009). Comparing the minimum and maximum EF values, Br with higher amplitude than Sb could mean that Br concentrations are more related with particularly emission events, while Sb values suggest background enrichment. An identical trend is observed for Se. Fossile combustion and traffic, both long transported, may be the origin[39-40].

The magnitude of enrichment between the two layers is different, but when comparing EF of the two aerosol datasets, Sb and Mo are common elements with high enrichment. This fact put in evidence the possibility of aerosol co-existence and same origins in North Atlantic atmosphere at different altitudes.

Table 3.2 shows the concentrations of elements that are enriched in both layers and concentrations of these elements in other remote and urban areas of the globe. Comparing to total suspended particles at remote site such Himalayan Mountains (Pakistan)[41] or Beiring Sea (Arctic)[42] the concentrations at PICO-NARE are 2 orders of magnitude higher for Sb and Mo, one order of magnitude higher for Br and Tb and similar to U. The Se and Th concentrations are lower in PICO-NARE when compared with other remote areas. The Sb and Mo have higher concentrations in this location (one order of magnitude) even when compared with urban areas of North-America[43] and Europe[44].

In TERCEIRA-NARE, high concentrations of I and Cl confirm the marine suspended aerosols that influences atmosphere at this altitude. Concentrations of Mo are even higher than in PICO-NARE, but lower EFs also means a crustal influence in aerosol contents.

All the extreme concentration values observed in the enriched elements in LFT occur in summer season, particularly between July and August, in accordance with other authors that identify high aerosol concentrations in that period[19,45-46]. On other hand, concentration values of high enriched elements in MBL were identified in winter season, particularly during March and October, when the weather conditions favor the suspension of marine aerosols from ocean surface.

Table 3.1. Descriptive statistics of aerosol samples from the MBL and LFT on North-Atlantic for the period between 8th July 2002 and 18th June 2004 (ng.m^{-3}). Mean; N – number of samples for an element, median, minimum, maximum and STDEV – standard deviation. Last column refers to the ratio between mean of MBL and mean of LFT.

	TERCEIRA-NARE (MBL)						**PICO-NARE (LL)**						**Mean Ratio**
	Mean	**N**	**Med**	**Min**	**Max**	**STDEV**	**Mean**	**N**	**Med**	**Min**	**Max**	**STDEV**	(MBL/LFT)
Na	39,923	53	22,214	85.4	215,544	48,996	599	123	77.3	0.12	8,341	1,316	**66.6**
K	2,318	42	1,577	14.9	10,488	2,241	635	9	841	22.8	959	363	**3.7**
Sc	0.29	60	0.15	0.0025	4.30	0.60	0.027	73	0.0095	0.00025	0.32	0.056	**10.7**
Cr	58.5	40	21.2	0.65	415	89.0	6.08	28	0.544	0.037	74.4	15.1	**9.6**
Fe	1,227	70	696	1.23	23,188	2,888	182	128	60.7	6.71	1,909	306	**6.7**
Co	1.24	65	0.58	0.044	8.60	1.70	0.75	131	0.34	0.00047	5.51	1.02	**1.7**
Zn	88.6	70	47.2	1.06	1,315	172	12.3	35	3.20	0.092	219	37.1	**7.2**
As	1.64	19	1.50	0.53	3.60	0.80							
Se	2.36	37	1.78	0.377	8.90	1.99	0.76	43	0.44	0.15	5.88	0.97	**3.0**
Br	165	67	62.2	10.3	1,420	248	13.8	253	6.79	0.049	167	25.4	**11.9**
Rb	3.73	54	2.24	0.14	27.5	4.80							
Mo	115	52	92.9	3.92	859	125	5.63	25	2.54	0.023	24.2	5.94	**20.4**
Sb	0.73	66	0.62	0.017	2.80	0.60	20.9	43	9.72	0.0013	152	32.5	**0.03**
Cs	0.15	31	0.13	0.039	0.40	0.10							
Ba	334	28	114	7.58	2024	514							
La	2.42	23	1.50	0.04	22.0	4.50	0.16	80	0.061	0.00032	1.55	0.27	**15.6**
Ce	9.91	7	2.49	0.77	49.3	17.5							
Nd	6.24	6	3.20	0.82	17.1	6.60							
Sm	1.30	34	0.55	0.00090	15.5	2.70	0.24	29	0.059	0.0076	2.97	0.58	**5.5**
Eu	0.14	49	0.11	0.0087	1.10	0.20							
Tb	0.15	22	0.10	0.011	0.40	0.10	0.064	34	0.026	0.0070	0.66	0.12	**2.3**
Yb	0.42	6	0.45	0.14	0.70	0.20	0.18	36	0.037	0.0040	3.18	0.54	**2.3**
Hf	1.87	23	0.94	0.050	9.80	2.40	0.15	28	0.060	0.0092	0.71	0.20	**12.7**
Hg							0.91	14	0.060	0.037	8.51	2.34	
Ta	0.16	26	0.07	0.00040	1.70	0.30							
W	1.27	15	1.07	0.50	3.20	0.70							
Th	0.88	13	0.73	0.15	2.90	0.80	0.19	14	0.083	0.0019	0.78	0.23	**4.6**
U	1.12	37	0.69	0.078	6.60	1.20	0.86	160	0.39	0.031	9.86	1.48	**1.3**
Al	9,057	35	6,206	291	30,963	8,319							
Cl	65,552	48	16,191	233	636,029	123,001							
Mg	487	47	194	14.4	12,071	1,814							
Ti	769	35	349	3.56	6,529	1,241							
V	17.3	43	15.2	1.50	51.9	10.8							
I	22.0	19	15.9	7.34	60.3	15.2							

Table 3.2. Elemental concentrations ($ng.m^3$) in aerosol samples of elements with EF higher than 100 on MBL and LFT, and in other remote and urban areas of globe.

	This Study		**Remote area**			**Urban area**	
	PICO-NARE	**TERCEIRA-NARE**	**Himalayan Pakistan**	**Bering Sea Artic**	**Mace Head Ireland**	**New York St. USA**	**Lisbon Portugal**
Sb	20.9±32.5	-	0.54	0.206		0.4	2.3
Br	13.8±25.4	-		1.416		1.7	13.4
U	0.86±1.48	-		0.178		0.010	
Se	0.76±0.97	-	2.35			0.91	17.4
Tb	0.064±0.12	-		0.007		0.058	
Th	0.19±0.23	-	1.45	0.112		0.012	
Mo	5.63±5.94	115±125		0.090		0.20	
I	-	220±15.2			36.2		2.6
Cl	-	65,000±123,000	692	1585		25	930

3.5. Conclusions

In Central North Atlantic elemental concentration of 384 daily aerosol samples collected at the lower LFT (PICO-NARE) and 62 aerosol samples weekly collected at the MBL (TERCEIRA-NARE) between 8th July 2002 and 18th June 2004 resulted in data set of 33 major, minor and trace chemical elements.

In the LFT, the air masses were classified as contaminated by anthropogenic elements coming from North-America and Europe, taking into account the aerosol enrichment in some tracer elements and their high concentrations when compared with similar data from moderately-polluted urban and industrialized areas of North Atlantic coastal areas of Europe and America continent. Very high concentrations, and EFs for Sb, Mo and Br higher than other globe areas, confirm atmospheric long-range transport mainly from west boundary of North Atlantic, not only by the direct plume transport from that extremely industrialized and urbanized areas, but particularly by the indirect via of possible accumulation and persistent emission of those elements in the area, due to the presence of Azores high pressures or the Hadley cells. Europe also contributes with similar components as well, although not that often due to the preferential wind directions from west. An additional class, but with less predominance, reflects influence of mineral dust intrusions from North Africa (Sahara and Sahel region) by the enrichment of some typical elements in the air masses, as the rare earth elements (La, Sm, Tb and Yb) and Th.

Based on EF values, the MBL is mainly dominated by marine elements (I, Cl, Na and Br) and local suspended soil particles. This cleaner layer of atmosphere, when compared with LFT, is influenced by two other factors with non-natural origin. One is the high enrichment and elemental concentrations of Mo. In Freitas et al. (2009), it is referred the strong association with U in a compositional profile that could fit a number of uranium processing operations in North America. Mo is also present in LFT, but in much less amount. The other common enriched element in MBL is Sb. This fact put in evidence the possibility of aerosol co-existence and reflection of the same air masses origins in North Atlantic atmosphere at different altitudes, with respect to these two high-pollution related elements.

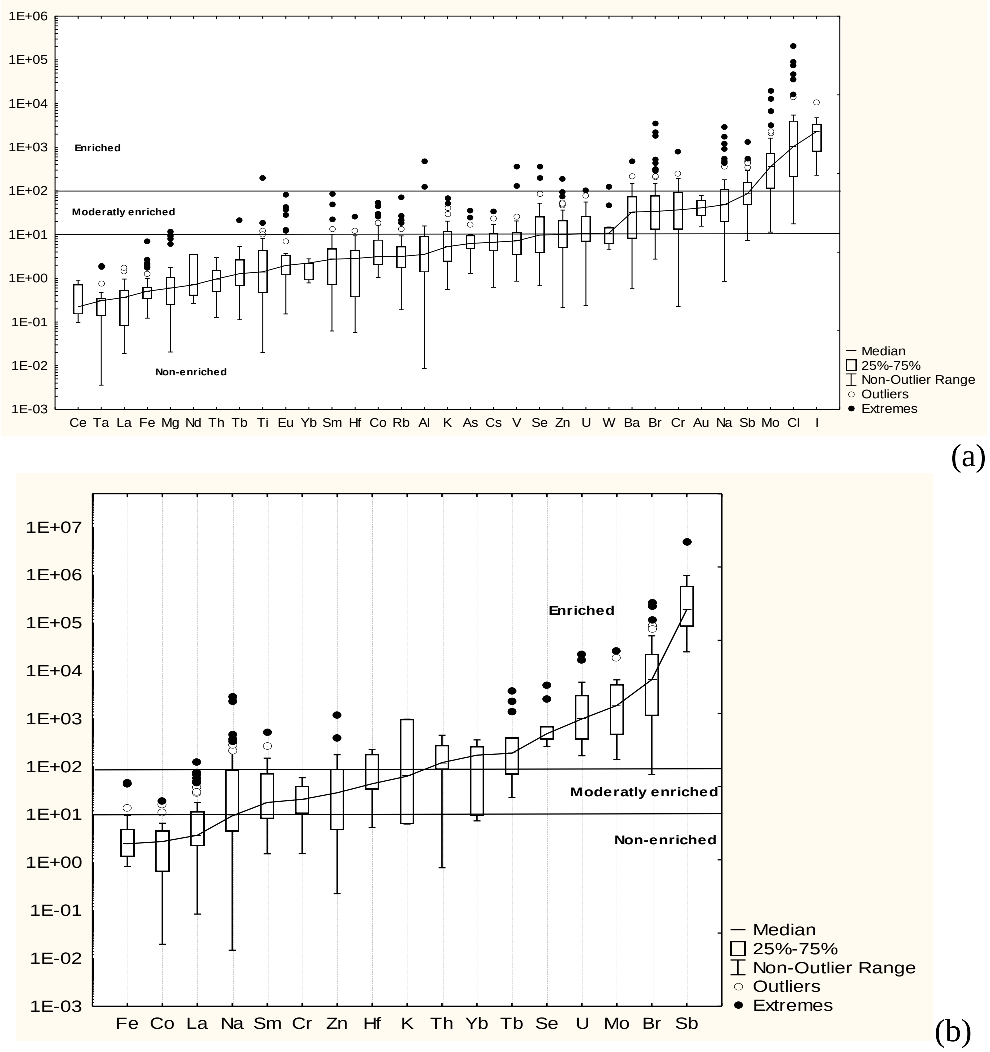

Figure 3.2. (a) Crustal enrichment factors relative to scandium as the reference element in MBL (TERCEIRA-NARE) at 50m a.s.l. The bar in the middle of each box represents the median of the data. The range of the box is from the 25 to 75 percentile. The whiskers extending from the box range from the down to the 10 and up to the 90 percentile, respectively. Points lower than the 10 percentile and points above the 90 percentile are plotted individually as outliers and extremes. (b) Crustal enrichment factors relative to scandium as the reference element in LFT (PICO-NARE) at 2225m a.s.l. The bar in the middle of each box represents the median of the data. The range of the box is from the 25 to 75 percentile. The whiskers extending from the box range from the down to the 10 and up to the 90 percentile, respectively. Points lower than the 10 percentile and points above the 90 percentile are plotted individually as outliers and extremes.

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Chapter 4

THE INDIVIDUAL PARTICLE ANALYSIS OF ATMOSPHERIC AEROSOLS FROM PICO MOUNTAIN, AZORES[3]

4.1. Introduction

Atmospheric aerosols are recognized as a major problem of air pollution around the world, due to their known direct and indirect adverse effects on the climate[1-3], environment[4-7] and human health[8-11]. Their impact on the earth-ocean-atmospheric-human health-systems depend on the extremely variable particle chemical composition and size-morphology, in turn depending on factors such as climatic conditions, emission sources and geographical location.

The atmospheric aerosols are a significant mass of the atmosphere, where 80% are within the troposphere and more than half of their mass is concentrated in the first 5 km layer[12]. In the North Atlantic atmosphere is estimated that about 96% of the total atmospheric aerosols are from natural emissions, with marine salt elements from the Atlantic Ocean[13] and mineral dusts from North Africa[14-16] as the main contributors, but volcanic and biogenic emissions are also considered as significant[17,18]. The other 4% of atmospheric emissions result from anthropogenic activities such as biomass combustion, fossil combustion and other industrial activities[2,19,20].

In the Azores Islands, situated within the North Atlantic, where the present study was carried out, relevant human activity is almost non-existent. This makes these Islands very well fitted to investigate long-range transport of aerosols that may originate from various continents. The West

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This Chapter is a modified version of

[3] *B.J. VIEIRA, M.C. FREITAS, H.TH. WOLTERBEEK (2011) Individual particle analysis of atmospheric aerosols from Pico mountain, Azores. Global Conference on Global Warming-2011 (GCGW11), 11-14 July, Lisbon, Portugal.*

and East boundaries of the North Atlantic are extremely industrialized and urbanized, and analysis of long-range transport of aerosols (plumes and aerosol characterization) could give clear indications as to their (emission) origin. Since the main atmospheric transport pathway over the North Atlantic is from West to East, its troposphere is most affected by anthropogenic aerosols from North America[20]. In these air masses, high concentrations were found of typical anthropogenic chemical elements such as As, Br, Mo, Sb, U, and Zn[21,22].

Earliest studies indicated that dusts observed in the Central Atlantic areas were mainly transported from Sahara and Sahel regions in North Africa[23,24]. Mineral aerosols from this dust cross the Atlantic in 5-7 days. The altitude of the dust layer may be up to 6 km, but over the Central Atlantic the layer develops mainly in the first 4 km altitude[14,15]. Silicates are the most abundant particles, however dust also carries large amounts of other mineral elements such as lanthanides, Al, Ca, Fe, Sc and Sm[16]. Volcanic emissions also contribute to the mineral emissions over the North Atlantic. In the Azores the volcanic emissions from the Mid-Atlantic ridge are mainly basaltic with magma rich in Fe and Mg and poor in Si[25].

Ongoing Azores-based studies of air-mass trajectories in 2 year periods suggested that the origin of air masses should be attributed to long-range transports from North-America (49%), Arctic (12%), Local marine area (10%), Europe (9%), Central America (9%), Tropic-Cancer (7%) and Africa (3%).

The intercontinental aerosols transport over the North Atlantic is strongly affected both by the horizontal transport conditions for air masses over long-range distances and the source-local vertical transport conditions. These complex and dynamic processes strongly affect the atmospheric residence time of atmospheric aerosols, which in turn affects the enrichment of pollutant elements in natural aerosols.

Up to today, the chemical inorganic composition is determined of atmospheric aerosols, sampled in mixed samples on Pico Island, Azores (Lower Free Troposphere). However, the bulk analysis of mixed samples[21,22] makes that no information can be gathered from the size and morphology of the various aerosol particles: it is these aerosol characteristics that should be added to the information on their composition that may strengthen our insights in both transport, origin and source apportionment.

The present study, undertaken on the Azores Islands, Pico mountain, was carried out to characterize single atmospheric particles, both with respect with to their elemental composition and to their size and morphology. The aim was to investigate whether the combined analysis, on single particle level, would increase opportunities to relate aerosols to their origins and emission sources.

Mixed sample element composition was determined by INAA, single-particle analysis was carried out by SEM-EDX: INAA is a well-established method for multi-element analyses, SEM-EDX is often used as the optical/X-ray technique in particle characterization. INAA and X-ray spectroscopy may be regarded as complementary techniques, applying both of them serves to ensure best possible and complete outcomes in aerosol elemental composition[26-30].

4.2. Experimental

4.2.1. Sampling

In PICO-NARE station, the aerosol samples with particles with all ranges of aerodynamic diameters were collected in quartz filters (manufacturer: Pallflex®; type: Q250F) by the automated, self-contained Aethalometer (model AE31), for periods of approximately 24 h[32]. The air-intake volume was around 7.6 m^3±0.3 m^3 to an average flow rate close to 8.47±0.44 $L.min^{-1}$. For this study, based on the backward trajectories, only 4 samples were selected, each one representing different air masses origins. The selected filter for Europe air masses was collected on 14th July 2005, for North America on 19th of May 2005, for North Africa on 8th April 2005 and for Tropic Cancer on 11th July 2005.

The filters from PICO-NARE station (blanks and samples) were cut from the strips in circular forms with an area of 0.950±0.086 cm^2 each. Then, half of the set was cut for each one of the analysis.

4.2.2. SEM-EDX analysis

A FEG Scanning Electron Microscope (JEOL 7001) coupled with an Energy Dispersive X-ray Spectrometry (Oxford light elements INCA Energy 250) equipped with backscattered and secondary electron detectors and in EDS detection system (EBSD detector) at IST-UTL was employed to obtain the morphology and chemical composition of individual atmospheric particles. The filters were mounted into an aluminium FEG-SEM stub using conducting top. It was coated with a thin Au-Pd film (<10µm) to achieve higher quality secondary electron images. An accelerating voltage of 15kV beam and accumulation time of 20s was used. The acquisition time was 30-80s. The control software localises the particles from the image and performs an x-ray measurement within each particle. The intensities of the characterising peak in the spectra are determined by the top-hat filter method. In the 4 samples, 27 representative images were taken randomly at a magnification of 3.000-30.000 for SEM image analysis.

4.2.3. INAA

Each sample was irradiated for 7h with a neutron thermal flux of 3 x $10^{12}.cm^{-2}.s^{-1}$ together with one disc (125 µm thick and 5 mm diameter) of a 0.1% Au-Al alloy as comparator. After irradiation, samples and blanks decayed for 4 to 6 days and were then measured for 7 h; after this measurement samples decayed for 4 weeks more and were again measured for 7 h. All gamma spectra measurements were done using liquid nitrogen cooled hyperpure germanium detector (1.8 keV resolution at 1.33 MeV and 30% relative efficiency), connected to 4096 multi-channel analysers. The gold alloy discs were measured for 5 minutes, also with the same detector, 7 days after the end of the irradiations. The elemental composition of the aerosol samples was determined by k_0-standardised, instrumental neutron activation analysis – k_0-INAA[33-36] and calculations of elemental concentration with the k_0-IAEA software[37].

4.3. Results and Discussion

Three-dimensional back trajectory (10 days) of each day of the 2005 aerosol campaign was determined using the NOAA HYSPLIT model[38]. According to the trajectories obtained, a representative day for the four most relevant air masses origins in terms of aerosol deposition was selected for the analysis. Figure 4.1 confirms these events.

Despite their complementary technique, chemical characterization should be done in association, because the scanning electron microscopy method as some limitation, as the fact that it loss volatile compounds due to the vacuum inside of the microscope, the fact that it affects the shape due to the electron beam interferences and particle chemistry can be ambiguous due to the matrix effects.

Based on their morphology and elemental composition, individual atmospheric particles could be classified into four types: a) *soot aggregate* are usually formed from ultrafine particles (< 1 µm) and readily aggregate together, from small chains into large chains. They are usually originated from combustion sources; b) *mineral* exists in irregular and regular shapes. The regular shaped particles are from geological sources while the elongated particles are generally formed by secondary atmospheric reaction. Are mainly from dust carried by wind; c) *fly ash* are spherical particles with smooth surface with different range of size. They are normally derived from coal combustion, industries emissions and automobile exhaust[31]. The analyses of all sample images show that most of the aerosols particles were found to be 1-20 µm in diameter. In the four samples, we found several different particle shapes. However irregular shapes of mineral particles are the most abundant.

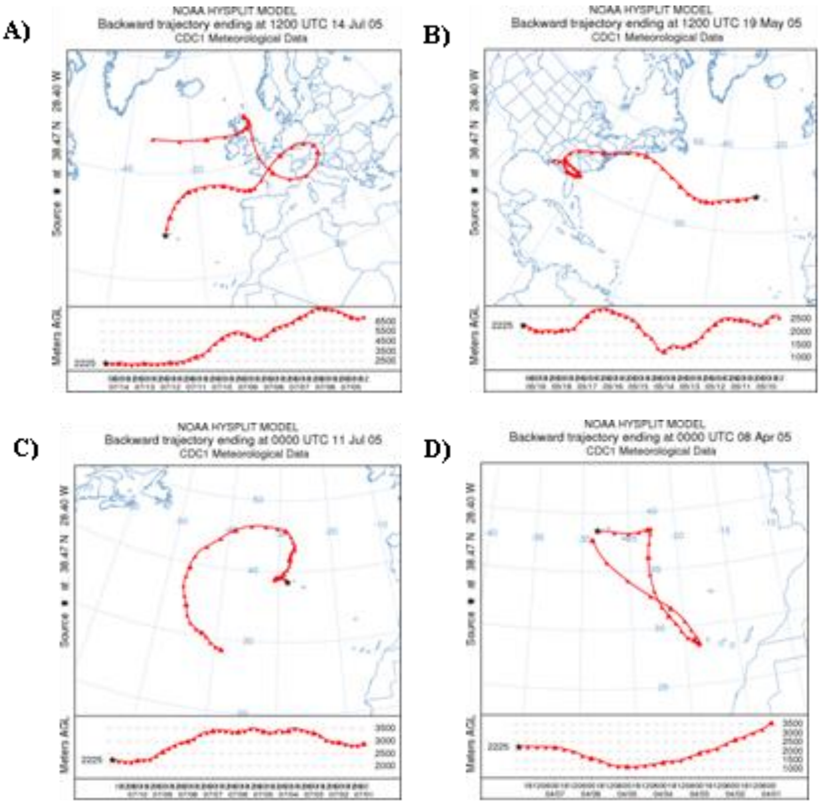

Figure 4.1. Backward trajectories ending in PICO-NARE station (Midle North Atlantic), calculated with HYSPLIT model from NOAA. A) Europe air mass origins ending in 14th July 2005; B) North America air mass origins ending in 19th of May 2005; C) Tropic Cancer air mass origins ending in 11th of July 2005; D) North Africa air mass origins ending in 8th of April 2005.

4.3.1. Europe

The Figure 4.2, representing particles from Europe show typical example of SEM images and X-ray spectra of particles collected. The irregular shapes reflected in this figure were frequently displayed by mineral particles. Comparing elemental abundance of particles collected, expressed in Table 4.1, we found that they are consistently different. Particle 1 appears with a confidante mineral origin due to the high enrichment of Al, Ca, Ti and Fe, all typical in mineral particulate. Particle 2 with a more spherical shape, which is associated to fly ash, appear also with C-rich, S-rich, Br-rich particles, which corroborates a probable anthropogenic origin. Biological material was also found in European air mass as show in Figure 4.3.

Chemical concentrations of 14 different elements determined by INAA are summarized in Table 4.5. Concentrations are higher for Co, Cr when compared with the other samples, which according to previous studies are related to oil combustion[21]. However, as the concentrations is one the average it is not clear whether the Br, C and S from individual particulate analysis are derived from anthropogenic source. Good agreement was found for the presence of mineral elements such Cr, Fe and Sc. Low concentrations of Br and Na when compared to average values of previous studies suggest a non-marine origin for these elements.

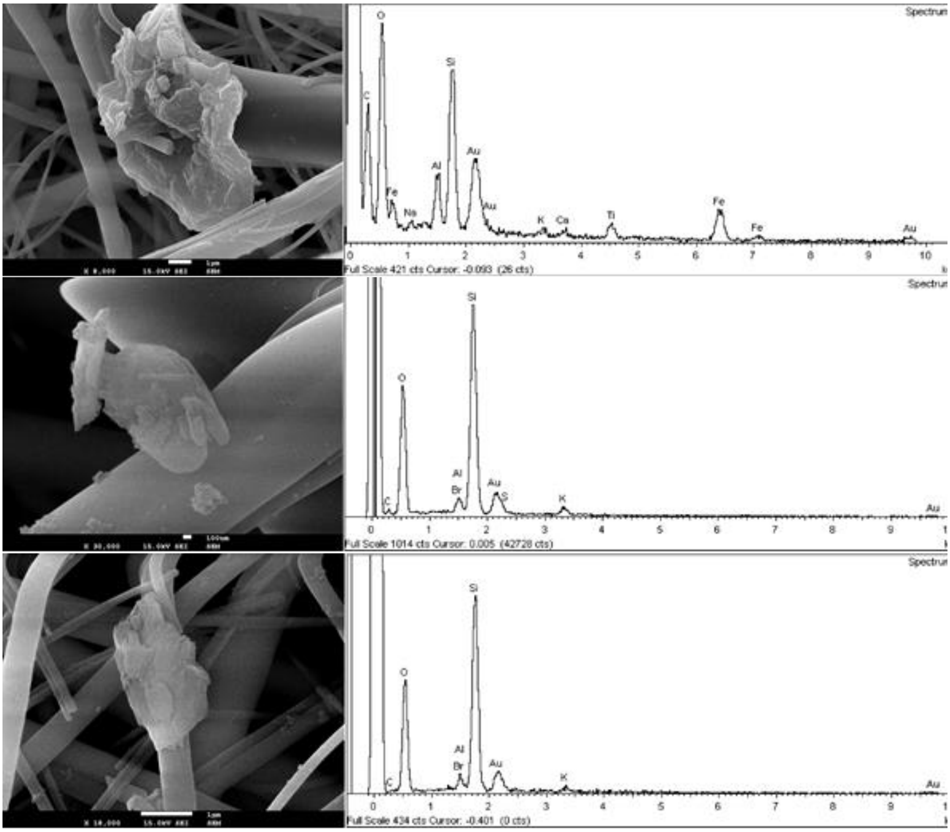

Figure 4.2. Typical examples of SEM images and X-ray spectra of particles collected on Europe origin sample (14th July 2005).

Table 4.1. Classification of particles according to elements relative abundance (weigh %) in Europe origin sample.

Abundance (weight%)		Particle classes	Abundance (weight%)		Particle classes	Abundance (weight%)		Particle classes
Particle 1			**Particle 2**			**Particle 3**		
O	54,90	SiO_2	C	21,97	$CaCO_3$	O	45,78	SiO_2
Na	1,09	Albite	O	45,75	SiO_2	Si	28,46	SiO_2
Al	4,55	Al_2O_3	Si	26,16	SiO_2	Br	6,89	KBr
Si	15,28	SiO_2	S	0,45	FeS_2	W	20,02	W
K	1,07	Feldspar	K	1,64	Feldspar			
Ca	0,78	Wollastonite	Br	4,70	KBr			
Ti	3,68	Ti						
Fe	18,65	Fe						

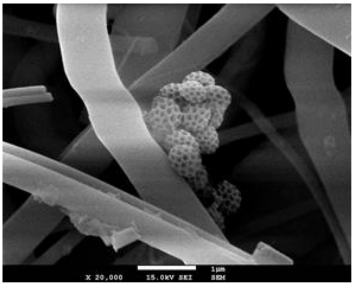

Figure 4.3. Example of biological particulate (pollen) SEM images found on Europe origin sample.

4.3.2. North America

The Figure 4.4, representing particles from North America show typical example of SEM images and X-ray spectra of particles collected. In that sample we found that morphology of particles are mainly soot aggregate (Particle 3 on the right) and fly ash (Particulate 2). Less abundant but also present particles with irregular shape are also present (Particle 1). As shown in Table 4.2, high values of C abundance in Particle 2 and 3 are consistently with the shape of particle, namely anthropogenic emissions. The C-rich is suggested to be $CaCO_3$, but in fact could probable be originated from long range transported pollution from combustion process in North America. This is in consonance with the chemical concentration presented in Table 4.5 for sample with North America origin. The high concentration of Sb and U, a well know elements associated with oil combustion, which was already associated with origins in North America[21,22], when compared with the other samples and inclusively with values of previous studies demonstrate that.

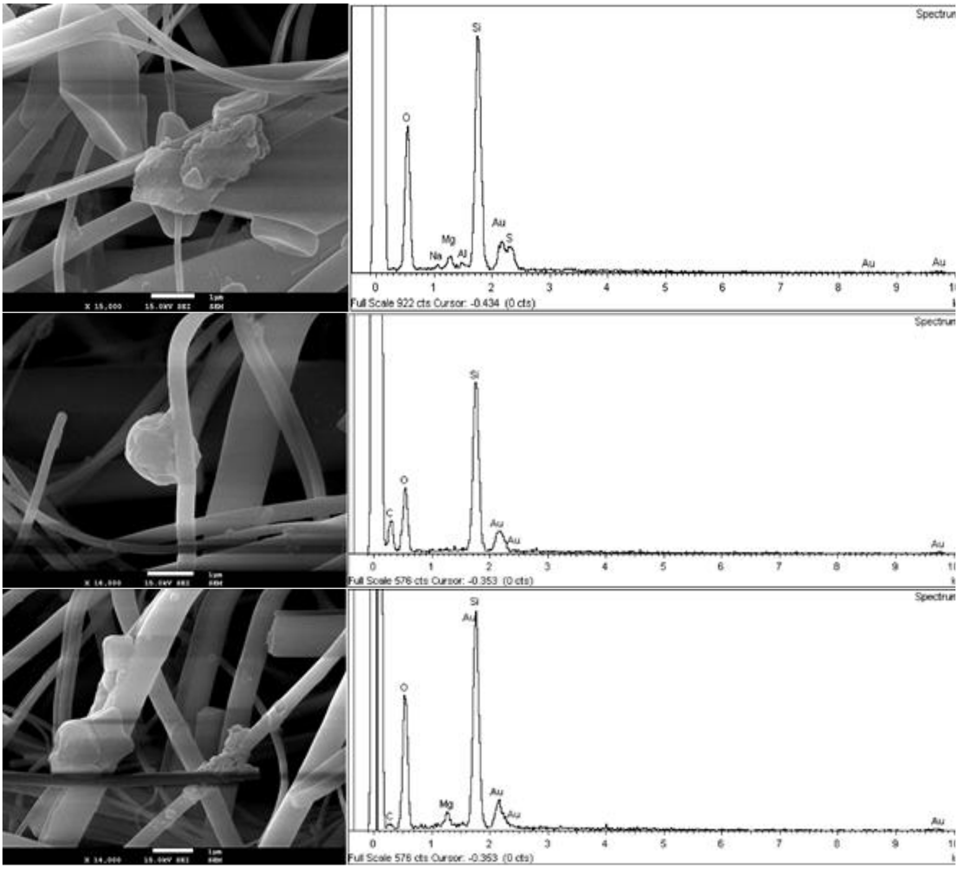

Figure 4.4. Typical examples of SEM images and X-ray spectra of particles collected on North America origin sample (19th May 2005).

Table 4.2. Classification of particles according to elements relative abundance (weigh %) in North America origin sample.

Abundance (weight%)		**Particle classes**	**Abundance (weight%)**		**Particle classes**	**Abundance (weight%)**		**Particle classes**
Particle 1			**Particle 2**			**Particle 3**		
O	45,78	SiO_2	C	39,30	$CaCO_3$	C	10,64	$CaCO_3$
Si	28,46	SiO_2	O	35,00	SiO_2	O	53,84	SiO_2
Br	6,89	KBr	Si	25,68	SiO_2	Mg	2,13	MgO
W	20,02	W				Si	33,41	SiO_2

4.3.3. Tropic Cancer

The Figure 4.5, representing particles from Tropic Cancer origin shown typical example of SEM images and X-ray spectra of particles collected. The irregular shapes reflected in the figure were frequently displayed by mineral particles. Particle 3 which appear with elongated shape are generally associated with mineral particle with secondary atmospheric reactions. In fact, comparing elemental abundance of particle collected expressed in Table 4.3, we found that they are considerable similar and consistence with that evidence. All particles are from mineral origin with typically marine elements association (Br, Cl and Na). It is clear that in the sample, particles have a mineral origin, probably from North Africa, due to Fe presence, with enrichment of marine elements, resulting is secondary aerosols. Maybe this fact justifies the high size of this articles which generally are higher than 10 µm.

The chemical concentrations determined by INAA (Table 4.5) clearly give the same indication as the individual particle analyses. Higher concentrations of marine elements (Br and Na) comparing all samples, with evident presence of high concentrations of Fe and Sc.

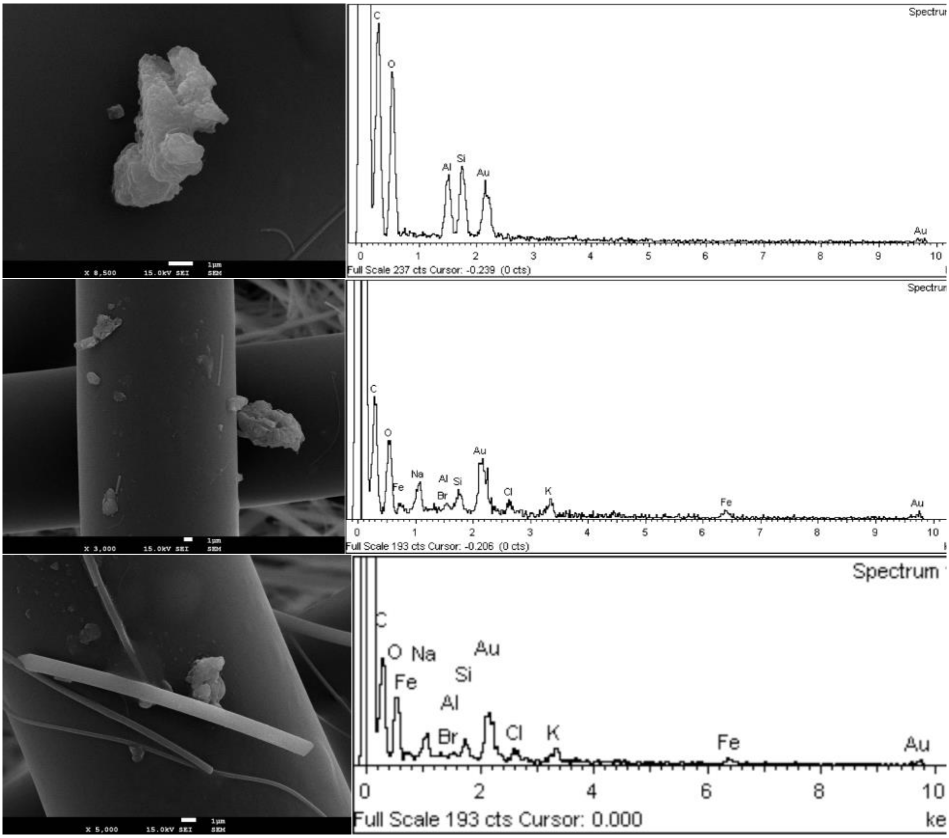

Figure 4.5. Typical examples of SEM images and X-ray spectra of particles collected on Tropic Cancer origin sample (11th July 2005).

Table 4.3. Classification of particles according to elements relative abundance (weigh %) in Tropic Cancer origin sample.

Abundance (weight%)		**Particle classes**	**Abundance (weight%)**		**Particle classes**	**Abundance (weight%)**		**Particle classes**
Particle 1			**Particle 2**			**Particle 3**		
C	9,03	$CaCO_3$	C	62,97	$CaCO_3$	C	36,01	$CaCO_3$
O	52,66	SiO_2	O	25,80	SiO_2	O	37,19	SiO_2
Na	2,26	Albite	Na	0,76	Albite	Na	4,73	Albite
Si	17,27	SiO_2	Si	2,73	SiO_2	Al	2,84	Al_2O_3
K	3,39	Feldspar	Cl	1,00	KCl	Si	2,11	SiO_2
Ca	0,36	Wollastonite	K	0,91	Feldspar	Cl	2,44	KCl
Ti	0,72	Ti	Ca	0,71	Wollastonite	K	2,91	Feldspar
Fe	1,95	Fe	Fe	1,98	Fe	Fe	5,39	Fe
Br	13,62	KBr	Br	3,13	KBr	Br	7,09	KBr

4.3.4. North Africa

The Figure 4.6, representing particles from North Africa origin, show typical example of SEM images and X-ray spectra of particles collected. Particle shapes in that sample are mainly spherical with some irregular too. Sizes varies between 1 µm and 5 µm. Comparing elemental abundance of particles collected, expressed in Table 4.4, we found that they all have mineral basis compositions with enrichment in Mg (suggested to be MgO), K (suggested to be feldspar), Ca (suggested to be wollastonite) and in Fe. Figure of Particle 2 and 3 shows an S-rich particle. It is not clear whether the S is derived from mineral or anthropogenic source. Nonetheless, Particle 3, an association of S with Mg could be from volcanic emissions, as these two elements are associated to volcano emissions locally existing. Mineral source of Particle 1 seem to be different than the others as the presence of Fe is more evident than in Si. In this particle the presence of Co, Mn and Zn suggests an influence of secondary reaction with pollutant elements.

The chemical concentrations determined by INAA also give an indication of mineral origin of air mass, due to the higher concentrations of some mineral elements in North Africa sample. As the Sb concentration is also high when compared to average value in previous studies, a presence of anthropogenic pollutants could not be discharge.

Table 4.4. Classification of particles according to elements relative abundance (weigh %) in North Africa origin sample.

Abundance (weight%)		**Particle classes**	**Abundance (weight%)**		**Particle classes**	**Abundance (weight%)**		**Particle classes**
Particle 1			**Particle 2**			**Particle 3**		
O	29,42	SiO_2	O	53,34	SiO_2	O	54,22	SiO_2
Mg	1,53	MgO	Al	0,85	Al_2O_3	Na	1,25	Albite
Si	8,63	SiO_2	Si	33,94	SiO_2	Mg	0,59	MgO
K	0,37	Feldspar	S	6,03	FeS_2	Si	33,55	SiO_2
Ca	1,93	Wollastonite	K	2,07	Feldspar	S	2,47	FeS_2
Mn	2,81	Mn	Ca	3,40	Wollastonite	K	0,49	Feldspar
Fe	37,89	Fe	Fe	0,37	Fe	Fe	1,65	Fe
Co	0,84	Co				Br	7,55	KBr
Zn	15,44	Zn						
Br	1,16	KBr						

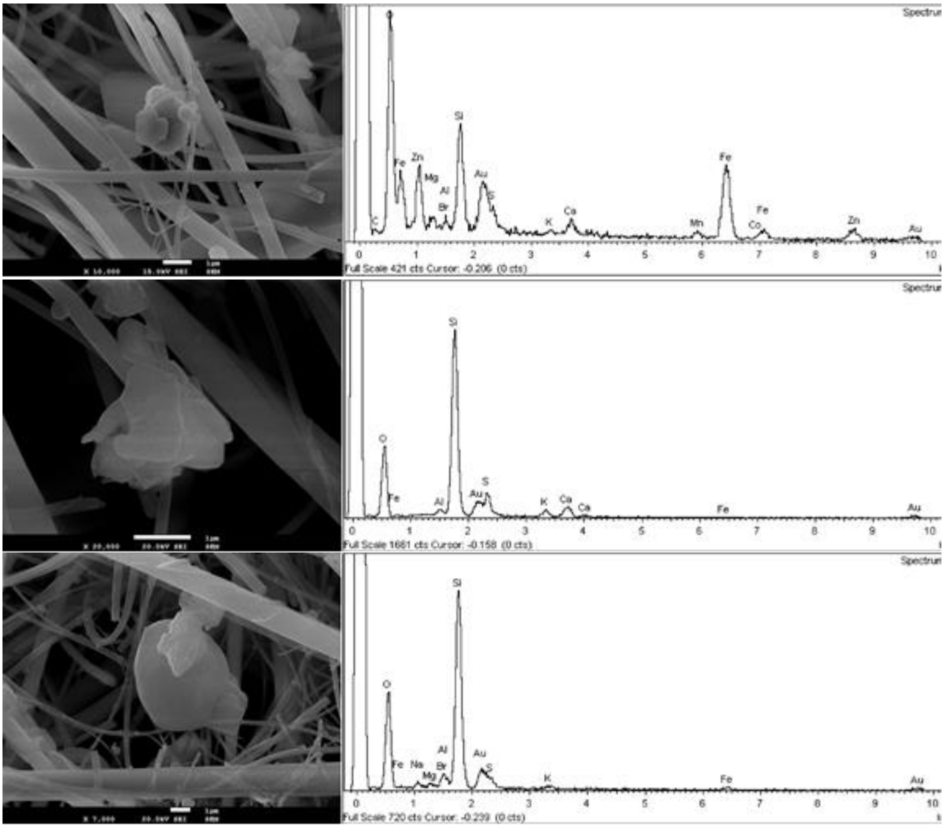

Figure 4.5. Typical examples of SEM images and X-ray spectra of particles collected on North Africa origin sample (8th April 2005).

Table 4.5. Elemental concentrations (ng.m^3±%) in aerosol samples of the different air masses episodes. EU – Europe; AM – North America; TC – Tropic cancer; AF – North Africa.

	EU	**AM**	**TC**	**AF**	**Previous studies[21]**
Br	10.4±(25)	0.4±(43)	99.1±(40)	13.2±(17)	17.1
Co	0.834±(5)	0.650±(7)	0.644±(6)	0.434±(6)	0.83
Cr	128±(4)	122±(3)	119±(3)	116±(3)	2.24
Cs	-	0.098±(28)	-	0.041±(37)	-
Eu	-	0.036±(41)	0.032±(23)	-	0.053
Fe	423±(20)	444±(10)	711±(28)	772±(19)	275
Hf	0.09±(41)	-	0.18±(17)	0.49±(38)	0.13
La	-	-	-	1.10±(27)	0.23
Na	398±(32)	-	553±(38)	121±(33)	477
Rb	-	-	-	1.41±(33)	-
Sb	12.2±(9)	49.3±(3)	0.87±(20)	32.8±(7)	22.8
Sc	0.42±(30)	0.39±(45)	0.43±(26)	0.37±(17)	0.054
U	0.087±(20)	0.18±(16)	0.079±(23)	0.23±(21)	0.78
Zn	30.9±(7)	27.8±(13)	29.9±(11)	33.0±(11)	10.4

Missing values correspond to not detected concentrations.

4.4. Conclusion

Based on the lower size (<5 µm) and irregular morphology, the single particle contribution of mineral elements and chemical concentration of the sample, suggest that dust particles constantly exist in the lower free troposphere over the Central North Atlantic especially in air masses with origin in North Africa (more evident), Tropic Cancer, and Europe (less evident). However, it seems that all the samples from the different air masses have distinct compositions and characteristic.

In Europe single-particles also show a C-rich, S-rich and Br-rich in some particles with smooth and spherical shape which evidences a contamination of pollutants elements with anthropogenic origin. As expected, in Tropic Cancer air masses all the results confirm a marine influence. Single-particles with elongate shape and higher sizes (> 10 µm), rich in Br, Cl, Na and are very typical in this sample. In spite of a clear of mineral source, some single-particles from North Africa sample have some aggregates with sulphur. It was suggested that this contamination in mineral dust results from secondary process occurring during the transport caused by atmospheric pollution. In North America sample, particles morphology is mainly soot aggregate and fly ash with high abundance of C. The high concentration of Sb and U, confirms a clear anthropogenic origin of particles with origin in this region.

The results obtained in this study provide very useful information about the single-particle characterization, which in a manner of fact could give an approach on prediction of the origin of aerosols in lower free troposphere in Central North Atlantic. As the results show, the particle types which were found in the four individual samples could in general will be related with the transport pathway and source regions.

To better understanding eventual seasonal distribution of single-particles and how it influences the chemical composition its needs some more extended study.

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Chapter 5

AEROSOL CONCENTRATIONS AND REMOTE SOURCES OF AIRBORNE ELEMENTS OVER PICO MOUNTAIN, AZORES, PORTUGAL[4]

Abstract

Aerosol samples were collected using an aethalometer from 15 July 2001 to 18 April 2004 at the PICO-NARE site in Pico island, Azores, Portugal. The aethalometer is at an altitude of 2225 m AMSL, and sampled for 24 h in most cases, and for a few periods continuously. Samples were assessed through instrumental neutron activation analysis (k0-variant), and concentrations of up to 15 airborne elements were determined. Concentrations are in the order of magnitude of a moderately polluted urban-industrial site. Elements are predominantly entrained by air masses from North-Central America, and to a lesser extent from Europe and North Africa. PCA and PMF assigned sources related to pollution (traffic, fossil-fuel combustion, mining, industrial processing) and to natural occurrences (crustal, Saharan episodes, marine). Although data uncertainties are relatively high due to the small masses collected in the filters and impurities in them, PMF – which includes the uncertainty – did not prove better than PCA when missing data are replaced by arithmetic means of the determined values for each element.

5.1. Introduction

The Azores archipelago comprises nine islands (2335 km^2), geographically split into three groups – Eastern (Santa Maria, São Miguel), Central (Terceira, Graciosa, São Jorge, Pico, Faial) and Western (Flores, Corvo) – which span over 600 km in an overall ESE-WNW direction (36º55'-39º43' N; 25º00'-31º15' W), as outlined in Figure 5.1. The climate is oceanic temperate, strongly influenced by the Azores anticyclone – often referred to as Azores High – and the North Atlantic Drift of the Gulf Stream, with high humidity and precipitation, and much milder temperatures (average- and amplitude-wise) than Lisbon or New York City, NY, both at roughly the same latitude.

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[4] *M.C. FREITAS, A.M.G. PACHECO, I. DIONÍSIO, B.J. VIEIRA, "Aerosol concentrations and remote sources of airborne elements over Pico mountain, Azores, Portugal in Kim, Y.J., Platt, U., Gu, Y.J., Iwahashi, H. eds. – Atmospheric and Bilogical environmental Monitoring (2009) pp.153-157 Springer, Dordercht, The Netherlands. DOI: 10.1007/978-1-4020-9674-7_9*

All islands have volcanic origins, with some sedimentary (reef) contribution for Santa Maria, the oldest, formed some 7 million years ago. Geological-age estimates widely differ though, and an abundance of marine fossils in Santa Maria's rocks imply that, at some point, the island may have sunk and then resurfaced. The youngest island is Pico, only about 300 thousand years old. The archipelago lies on the Mid-Atlantic Ridge, near the so-called Azores triple-junction[79], in an area of confluence of three major tectonic plates – the North American Plate, the Eurasian (or Euroasian) Plate and the African (or Nubian) Plate – complete with the local Azores Microplate. The two westernmost islands (Flores, Corvo) actually lie on the North American Plate. Tectonic patterns/geodynamics and geochemical aspects relating to the formation of the Azores plateau have been extensively discussed[24,27,79,80,86].

Figure 5.1. The Azores archipelago in the context of the North Atlantic Ocean.

The archipelago sits directly on the pathway of long-range transport of airborne species over the North Atlantic Ocean, namely mineral particles from Africa's Sahara and Sahel[17] – arguably, the world's largest sources of Aeolian soil dusts – and non-natural contaminants from the United States' eastern seaboard down to Central America and the Caribbean. The transport mechanisms and remote impacts of African dust have been clearly established[70-74]. African-dust events have been shown not only to affect coastal North America and the Caribbean basin[52,53,71-74], but also to reach deep into the continent, to the point that African-dust incursions could be discerned over much of the eastern half of the United States, including areas that make up the so-called "dust bowl"[67]. In what concerns the Azores proper, contamination of African dust with polluted aerosols from Europe has been observed as well[77], in line with similar mixing processes detected in the North-Eastern Atlantic Ocean[21].

The archipelago is thus an ideal platform for watching significant deposition episodes in the area and, especially, for tracking the regular oceanic transit of air masses from the surrounding continents – Africa, Europe and North-Central America. Furthermore, the Pico mountain, rising up to 2351 m

AMSL in Pico island – Figure 5.2 – is high enough to enable land-based access to the lower free troposphere, which means that contaminant loads from afar can be detected over the altitude range of significant removal by (sinking into) the ocean, and that their trajectories may be appraised without accounting for the influence of the marine boundary layer. This work addresses the former issues, by looking into the characteristics of aerosol samples collected through a seven-wavelength aethalometer at the PICO-NARE observatory.

Figure 5.2. Pico mountain (2351 m AMSL) in Pico island (Azores' Central group).

5.2. Experimental

5.2.1. Instrumental aspects

The PICO-NARE observatory (38.470ºN, 28.404ºW; 2225 m AMSL), which includes the seven-wavelength aethalometer (model AE31), is an automated, self-contained, experimental station located near the summit of the Pico mountain – Figure 5.3. Relevant features that make this location unique for assessing regional and hemispheric impacts from measurements within the lower free troposphere or the marine boundary layer have already been highlighted[38]. In particular, measurements of aerosol absorption coefficients have been made at the observatory since July 2001. Details on the operation and calibration of the aethalometer system, as well as a few examples of its use on the characterization of biomass-burning plumes and Saharan-dust aerosols, can be found elsewhere[25,26,33,39].

All elemental determinations for the present study were carried out at the RPI (pool-type reactor; maximum nominal power: 1 MW) of the ITN-Sacavém, Portugal, through k_0-standardised, instrumental neutron activation analysis – k_0-INAA[19,20,28-30]. An excellent account of fundamentals and techniques of activation analysis with thermal (low energy) neutrons was given in a review by Erdtmann and Petri[23].

In brief, this methodology uses the production of artificial radionuclides from stable elements for their identification and quantitative determination. Samples are irradiated with a neutron beam produced along the nuclear fission of ^{235}U nuclei in a nuclear reactor, thermalised by a moderator in order to induce the nuclear reaction type (n, γ). The latter consists in the capture of a thermal neutron by the nucleus of an atom with simultaneous emission of gamma radiation that hits an electron of the atom of the material which makes up the counting detectors (germanium). The full energy is absorbed by the electron that gets ejected, and its energy is collected as an electronic impulse with the same energy of the gamma radiation emitted. The result is a spectrum of several full-energy peaks, which enables an identification of elements whose atoms were involved in the former neutron captures. The peak areas provide the numerical bases for assessing the corresponding amounts of elements present in the irradiated sample.

As mentioned above, all calculations for this work were based on the k_0-variant of INAA, which includes a comparator – usually gold, to obtain the radionuclide ^{198}Au – to be irradiated together with the sample. Elemental concentrations are then calculated by comparing the full-energy peaks present in the spectra of the sample and comparator. Irradiation conditions and reactor parameters for the current implementation of the k_0-INAA methodology at ITN have been previously reported[32,63].

The results herein refer to 425 aerosol samples collected from July 15, 2001, until April 18, 2004, with an irregular periodicity. As a consequence, the air-intake volume varied between 0.12 m^3 and 81 m^3. Most frequent values were around 8 m^3, which may be seen to correspond to an average flow rate close to 5.5 L·min-1, on a 24-hour sampling basis. The AE31 instrument has been operated with quartz-fibre filter tapes, reinforced with a non-woven polyester support layer as a strength binder (manufacturer: Pallflex®; type: Q250F) – Figure 5.4a. The increase in tensile strength regarding similar, binder-free media has been found quite significant[84]. Due to the remote setting of PICO-NARE and local weather conditions, instrumental maintenance has been performed once-twice a year.

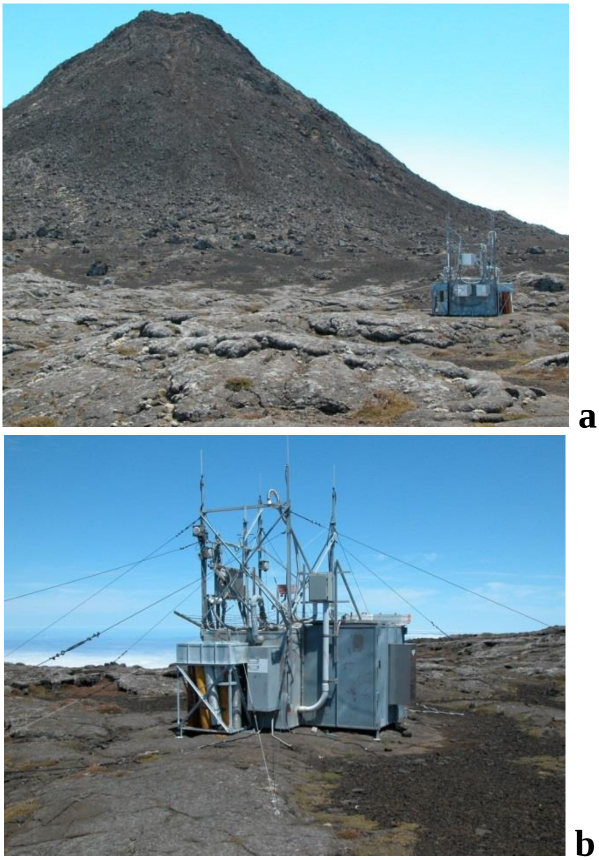


Figure 5.3. a) PICO-NARE experimental site (2225 m AMSL) near the summit of the Pico mountain (2351 m AMSL); and b) a closer view of the automated observatory.

Aerosol-laden spots were identified after removing the tape from the aethalometer – see Figure 5.4b for an example – and packed together with unexposed portions of the tape (as blanks) for elemental analysis. Upon removal, each tape was first cut into segments of ca. 20 cm, which were photographed for archival backups, and then sealed into polyethylene sleeves for shipping purposes. At ITN, both samples and blanks were carefully cut from the quartz-fibre strips in circular shapes with an area of 0.950±0.086 cm^2, the former centred on the selected-spot area (0.50±0.05 cm^2). The exposed side of each cut-out was protected with an identical piece of blank filter, to avoid contamination of the sample with the polyethylene top cover. The same procedure was also applied to every actual blank, to obtain an identical geometry. All sandwich-like sets were packed into aluminium sheets for further irradiation.

Each sample or blank set was irradiated for 5-7 hours at a thermal-neutron flux of about $10^{13}.n.cm^{-2}.s^{-1}$, together with one disc (thickness: 125 µm; diameter: 0.5 cm) of an Al-0.1 % Au alloy as comparator. After irradiation, sets were allowed to decay for 4 to 6 days and then measured; after this, they kept on decaying for an additional 2-3 weeks, and were measured again. All gamma spectra were acquired on a liquid nitrogen-cooled, ORTEC®-calibrated, high-purity germanium detector (1.85 keV resolution at 1.33 MeV; 30 % relative efficiency), connected to a 4096 multi-channel analyser. The comparator disc was measured in the same detector 7 days after the end of an irradiation.

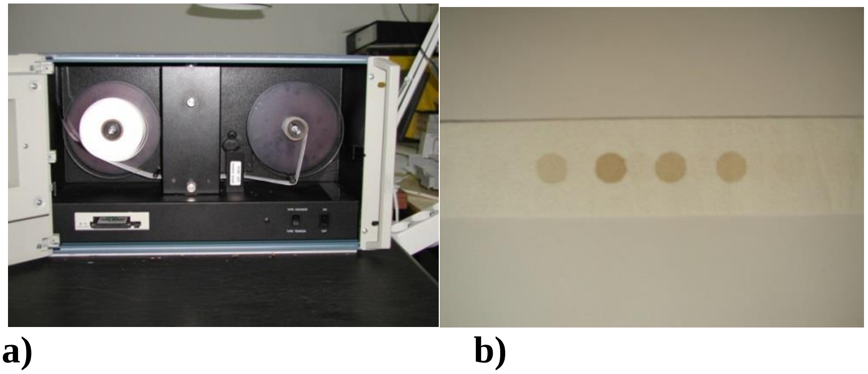


Figure 5.4. a) Instrumental set-up for the quartz-fibre filter tape on site (continuous strip); and b) an exposed section of the tape after removal at the laboratory (four identifiable spots).

5.2.2. Data analysis, quality control and elemental uncertainties

Elemental concentrations in loaded and blank media were assessed with the current version of the "k_0-IAEA" software, that has been developed by Blaauw[11] with an endorsement by the IAEA. Standard packages for exploratory, correlation and multivariate data analyses were STATISTICA® 6.0 (StatSoft Inc.) and SPSS 11.0 for Windows© (SPSS Inc.). Backward trajectories of air masses reaching the Azores above PICO-NARE were produced in isentropic mode with HYSPLIT from NOAA ARL READY Website[22,78].

Filters are made from quartz, and their dimensions are reduced. Their main constituent – silicon – does not activate that much with thermal neutrons; however, impurities are significant for a few elements. Unfortunately, aerosol reference materials with a quartz matrix are not commercially available, the only ones existing are polycarbonate membrane filters, such as the Nuclepore® brand. The latter are composed mainly of C and O, which do not activate, and they feature lower impurities than the quartz filters. For the reference material 'Air Particulate on Filter Media' (NIST-SRM® 2783; PM2.5 on a polycarbonate filter membrane) measured by INAA, the reproducibility was within 5-15 %[3]. Impurity amounts found in the present quartz filters were, in $\mu g.cm^{-2}$: As: 0.02; Br: 0.002; Co: 0.007; Cr: 0.02; Fe: 0; Hf: 0.002; K: 5; La: 0.001; Mo: 0.2; Na: 6.8; Sb: 0.5; Sc: 0.0001; Sm: 0.0006; U: 0.003; Yb: 0; Zn: 0.07.

The ratio of an elemental (typical) mass determined in loaded filters to its occurrence (as an impurity) in blank filters is 2 for most elements, except for Br (ratio: 90), La, K, Sc and U (ratio: 4), and Na (ratio: 9). Iron and ytterbium are not present in the blanks. The uncertainties from the analysis proper, which arise mainly from the measurements of full-peak areas, are, typically: 2 % for Br and Sb; 10-15 % for Mo, Na and U; 15-20 % for Co, K and La; 25-35 % for Cr, Fe, Hf, Sc, Sm, Yb and Zn; and 70 % for As.

5.3. Results and Discussion

5.3.1. Concentrations of elements at PICO-NARE

Table 5.1 shows the elemental concentrations found in the analysed samples. Only the elements detected in at least 25 % of the cases are shown. Other elements with a ratio of determination under 25 % were: As (5 %; average: 2.0 ng·m^{-3}), Cr (24 %; average: 1.9 ng·m^{-3}), K (18 %; average: 376 ng·m^{-3}), Se (8 %; average: 1.3 ng·m^{-3}), Tb (0.2 %; average: 2.0 ng·m^{-3}), Yb (5 %; average: ng·m^{-3}), and Th (3 %; average: 0.4 ng·m^{-3}). When compared by their absolute magnitude of concentrations, the average data can be grouped as 1) above 100 ng·m^{-3}: Fe, Na; 2) between 100 and 10 ng·m^{-3}: Br, Mo, Sb, Zn; 3) between 1 and 0.1 ng·m^{-3}: Co, Hf, La, Sm, U; and 4) below 0.1 ng·m^{-3}: Sc.

Comparing to total suspended particles at a remote site such as the Antarctic Peninsula (King Sejong station), the concentrations at PICO-NARE are three orders of magnitude higher for Zn and U, two orders of magnitude higher for Co, and one order of magnitude higher for Cr[58]. A similar comparison with PM_{10} from McMurdo station, Antarctica, results in three orders of magnitude for Fe, two orders of magnitude for As, and one order of magnitude for Co, Cr, K, Se and Zn[57]. Therefore, the Pico summit has no characteristics of a remote clean area.

At Bobadela – an urban-industrial neighbourhood in the northern outskirts of Lisboa, Portugal, some 20 km straight from the open Atlantic Ocean – the following elemental concentrations, in ng·m^{-3}, were found in PM_{10}[4]: As: 0.43; Br: 4.3; Co: 0.2; Fe: 400; K: 270; La: 0.23; Na: 1500; Sb: 2.6; Sc: 0.061; Se: 4.4; Sm: 0.041; Zn: 36. The present results compare well for Co, Fe, La, Sc and Sm, which were crustal elements for the PM_{10} fraction[4], even if higher values could occur due to Saharan-dust episodes[5].

As to (potential) marine elements, the present work found higher concentrations of Br (one order of magnitude) and lower concentrations of Na (one order of magnitude). This divergence may be due to an added anthropogenic component of Br (volatile element) in Pico[83]; see also further) and a stronger marine component of Na in Bobadela, since sea-salt advection inland over a flat terrain is likely easier than the vertical mixing or upslope flow of salt-laden air into the high reaches of Pico mountain. Actually, enrichment data for a major sea-salt tracer (Cl) in biomonitors from a high-altitude site in Pico island (Cabeço Redondo; 1000 m AMSL) strongly suggests that such an enrichment may be due to deposition of salt undergoing long-range transport through the upper troposphere (or lower stratosphere, for finer particles), rather than to the direct advection of locally-produced, marine aerosol[64].

Table 5.1. Number of samples for an element (N), proportion of samples for an element to the total analysed samples (in %), mean, median, standard deviation (SD), minimum and maximum (all in ng m^{-3}), referring to the whole collection from the PICO-NARE site, July 15, 2001, through April 18, 2004 (425 aerosol samples).

	Br	**Co**	**Fe**	**Hf**	**Mo**	**La**
N	302	233	154	152	120	170
% Total	71	55	36	36	28	40
Mean	17.1	0.83	275	0.13	13.6	0.23
Median	1.34	0.49	85.8	0.090	8.94	0.094
SD	88.6	2.01	711	0.15	42.5	0.51
Minimum	0.015	0.00048	6.71	0.00093	0.023	0.0016
Maximum	1227	28.6	7978	1.35	469	4.40

	Na	**Sb**	**Sc**	**Sm**	**U**	**Zn**
N	186	154	136	127	256	145
% Total	44	36	32	30	60	34
Mean	477	22.8	0.054	0.14	0.78	10.4
Median	789	16.2	0.012	0.048	0.34	5.63
SD	1129	28.6	0.20	0.44	1.94	27.3
Minimum	1.40	0.0013	0.00037	0.0015	0.0022	0.059
Maximum	8341	257	2.23	3.81	20.0	276

The anthropogenic elements As and Sb (volatile elements) show higher concentrations at the Pico summit, while Zn has a higher concentration in Bobadela. Fugitive emissions from an urban-waste incinerator nearby may not be ruled out for Bobadela though, for Zn has been widely regarded as the prime indicator for refuse incineration[75]. As a conclusion, the site at the Pico summit seems largely influenced by anthropogenic emissions as well as by natural sources, and thus may be viewed as close to an urban-industrial location in what concerns the more volatile elements and the African-dust occurrences.

In an earlier study[33], 109 aerosol filters collected from July 2001 through July 2008 at PICO-NARE were dealt with, and a correlation analysis suggested the existence of 5 groups: G.I, split into groups G.Ia with Fe and Ce, and G.Ib with Sm, La and Sc; G.II, with Co, Hf, Sb and Th; G.III, with Br, W and Zn; G.IV, with Br and Na; and G.V, with Mo and U. The application of such grouping to the extended data-set of 425 aerosol filters is shown in Table 5.2.

Purely crustal before, G.I now contains a larger number of elements with good or even excellent correlation related to an anthropogenic origin, such as Br, Sb and Zn, as well as Co, Mo and U of probable crustal sources. Other than good correlations between Hf and Sb, and Co and Sb, G.II includes also good correlations for Mo, Na, U and Zn. The former high degree of association between Br and Zn in G.III still exists, and now Br appears highly correlated with Co, Mo and U too. There are no significant associations within G.IV and G.V though.

Table 5.2. Significant results of the correlation-coefficient matrix ($r \geq 0.5$) for elements associated into the five identified groups at PICO-NARE[33].

G.I	Sm	La	Fe	**G.II**	Hf	Co	**G.III**	Br	**G.IV**	Br	**G.V**	Mo
La	0.93	–	0.87	Na	–	0.51	–	–	Na	–	U	–
Sc	0.69	0.87	0.98	–	–	–	–	–	–	–	–	–
Fe	0.69	–	–	–	–	–	–	–	–	–	–	–
Co	0.96	0.86	–	–	–	–	Co	0.96	–	–	–	–
Zn	0.49	–	–	Zn	–	0.48	Zn	0.50	–	–	–	–
Br	0.97	0.85	–	–	–	–	–	–	–	–	–	–
Mo	0.99	0.86	–	Mo	–	0.97	Mo	1.00	–	–	–	–
Sb	0.52	–	–	Sb	0.68	0.56	–	–	–	–	–	–
U	0.80	–	–	U	–	0.70	U	0.81	–	–	–	–

5.3.2. Enrichment factors at PICO-NARE

To look into the status of relative pollution at the PICO-NARE site, crustal, marine and aerosol EFs were calculated. The EF value for an element X was computed according to $EF_X = X/REF_{sample}/X/REF_{ref.sample}$, where REF is Sc when "ref. sample" is a crustal reference value or an aerosol reference value, and REF is Na when "ref. sample" is a marine reference value. Sodium is a primary (cationic) sea-salt tracer. Even if Al is the historical and, arguably, most used element to account for soil-dust inputs or even correct for them[9,49,88], there is no such thing as an established crustal reference[56]. Besides, Sc has already been deemed an optimal choice for that purpose[15]. Values of "ref. sample" were taken from Bowen[12]. For crustal and marine cases, average data are available; for aerosols, data ranges (minima and maxima) are given. Therefore, the latter have two calculated values, using the extremes of the corresponding aerosol ranges. Considering that many EF values would be produced for each element, the criterion was to calculate minimum and maximum concentrations of each element in the whole set of concentrations for that element, and then compute the minimum and the maximum enrichment factors for the same element.

Figure 5.5 illustrates the results for crustal and marine enrichment factors, respectively referred to Sc and Na as reference elements. Concerning the crustal EFs, there is some depletion of As, Br, K, Na, Mo, Se and U relatively to the reference soil values, which seems inconclusive at best. On the contrary, EFs for Br and K of potential marine origin (relative to sodium, in grey colour) may span several decades. Even if EFs are crude indices, not to be taken strictly at face value, some concentrations of Br and K in the samples can hardly be ascribed to oceanic inputs, and likely are of anthropogenic origin.

The elements Cr and Zn show no significant enrichment, or are depleted relative to their soil-reference values; no enrichment is observed for Yb and Hg either. All these four elements are likely coming from crustal sources. Clearly enriched samples do exist for Co, Hf, Fe, La, Sb, Sm, Tb and Th, though, some of which have been associated with Saharan-dust events – Fe, La, Sm[5,26]. When the present EFs relative to soil, with Sc as the crustal reference, are matched against former ones from Bobadela[2], it results that Sb is enriched at both places, although to a lesser extent in Pico summit (one order of magnitude lower), while As, Br, and Zn present no enrichment relative to soil in Pico summit (EFs > 100 at Bobadela for all these elements).

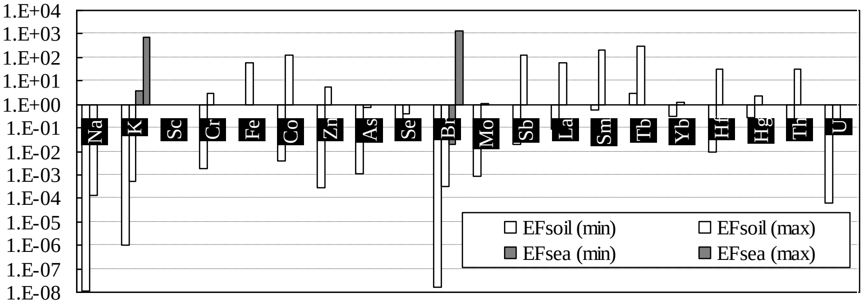


Figure 5.5. Crustal enrichment factors relative to scandium as the reference element. Marine enrichment factors of bromine and potassium relative to sodium as the reference element are also shown. Reference values were taken from Bowen[12].

Enrichment results relative to aerosol reference compositions, again using Sc as the normalising element, are summarised in Figure 5.6. An identical trend is observed whether one takes the minimum or the maximum of the reference range, that is the aerosols from PICO-NARE are enriched in As, Co, Na, Hf, K, La, Mo, Sb, Sm, Tb, Th, U and Zn, when comparing to aerosol-reference data. The magnitude of enrichment is actually strong for all elements but Br, Cr, Fe, Hg, Se and Yb.

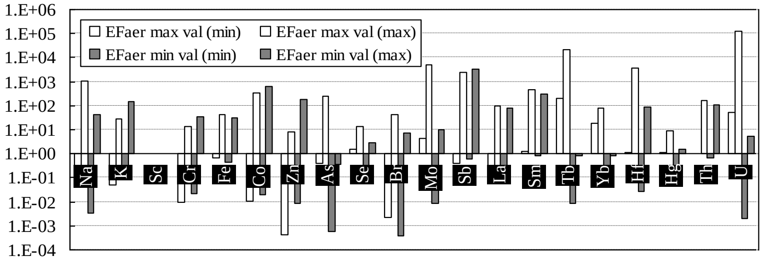


Figure 5.6. Aerosol enrichment factors relative to scandium as the reference element. Reference ranges were taken from Bowen[12].

5.3.3. Multivariate statistical analysis of aerosol data from PICO-NARE

Source categories for PM constituents were tentatively identified through PCA. This was carried out by using the orthogonal transformation method with Varimax rotation[43,44] and retention of principal components whose eigenvalues were greater than unity. Factor loadings indicate the correlation of each pollutant species with each component, and are related to the emission-source composition.

PCA has been commonly used in environmental studies[2,13,37]. Only the species assessed in more than 28 % of the samples were considered for PCA. The whole data-set was included in the analysis; missing values were replaced by detection limits for the corresponding elements. Results are listed in Table 5.3, where four factors (principal components) can be seen to account for about 79 % of the total variability in the data.

*Table 5.3. Factor structure for elemental concentrations in aerosol samples from PICO-NARE (whole data-set), after extracting PC from the correlation matrix and rotating axes to maximum variance for each factor. Missing values were replaced by detection limits. Bold figures - factor loadings > **0.60**.*

Variable (Element)	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Br	**0.96**	-0.04	0.13	0.12	0.97
Co	**0.93**	-0.03	0.22	0.17	0.94
Fe	0.08	**0.92**	0.09	0.19	0.78
Hf	0.22	-0.03	**0.80**	-0.08	0.36
La	**0.70**	0.26	-0.11	0.22	0.54
Mo	**0.96**	-0.10	0.07	-0.03	0.92
Na	0.12	-0.03	-0.22	**0.81**	0.39
Sb	-0.01	0.22	**0.85**	0.06	0.50
Sc	0.08	**0.94**	0.10	0.02	0.79
Sm	**0.94**	0.11	0.18	-0.02	0.94
U	0.00	0.28	0.24	**0.69**	0.51
Zn	**0.60**	0.24	-0.08	-0.16	0.34
Eigenvalue	4.5	2.0	1.6	1.3	–
% Variance	39.70	17.81	12.16	8.90	78.57
Probable Source	Crustal Traffic	Crustal (Saharan)	Combustion (Oil)	Marine	–

The first factor appears strongly loaded by traffic- (Br, Zn) and soil-derived elements (Co, La, Mo, Sm), suggesting that the former may have resulted from re-suspension processes[8]. The representation of different source processes in a single factor may be explained by the relatively well-mixed nature of the oceanic troposphere, and by regional phenomena responsible for the aerosol mixing[36]. Apart from refuse burning, Zn has been related to vehicle wear[41,81] while Br, even if prevalent in the marine environment, has long been viewed as an elemental marker for mobile sources after the phasing-out of leaded gasoline[41].

The second factor stands for a crustal contribution, given that it shows high loadings for Fe and Sc, typical soil elements. African dust is likely the main contributor to this component, the highest concentrations of which may have been reached at PICO-NARE from October 31 through November 5, 2001[26]. It should be recalled that the Sahara desert alone is responsible for the emission of 50 % of the total mass of mineral aerosols to the atmosphere[65].

The third component, with high loadings for Sb and Hf, suggests oil combustion. The lack of determination of Ni and V in the filters precludes an unequivocally confirmation of that source though. Still, the source was confirmed in the Azores atmosphere by the composition of organic matter in carbonaceous aerosols[6].

Moreover, the same filters – sampled in Terceira island, at sea level – were recently re-analysed for V and U, and some degree of association is apparent between these elements, of the order of magnitude of the uranium loading in the factor[34].

The fourth factor relates to marine sources. Other than sodium, there is a significant loading for uranium. This might be typical of high altitudes in oceanic environments, since no association of Na and U could be confirmed at sea level[34].

As an alternative approach to the former analysis, and instead of replacing missing values by detection limits, replacements were made in terms of averages of determined data, which may seem more reasonable (see below). The alternative results are listed in Table 5.4.

The communality increased with an almost total explanation for all elements (only U is below 0.90). There are still four factors, yet a few changes did occur in between. Now, Sc, Fe, La and Sm – elements strongly associated with Saharan events[5] – are grouped together. Antimony and hafnium still make up a likely oil-burning component, but now joined by cobalt, which is not unheard of from previous studies[2,31]. The marine factor included Na and U (Table 5.3). Sodium is now well correlated with Br and Zn (traffic tracers), and the fourth factor implies an association of U and Mo that may stem from uranium mining/milling and nuclear-waste processing (more further).

*Table 5.4. Factor structure for elemental concentrations in aerosol samples from PICO-NARE (whole data-set), after extracting principal components from the correlation matrix and rotating axes to maximum variance for each factor. Missing values were replaced by averages of determined values. Bold figures indicate factor loadings higher than **0.60**.*

Variable (Element)	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Br	0.01	-0.01	**0.98**	-0.15	0.99
Co	0.30	**0.78**	0.22	0.24	0.87
Fe	**0.98**	0.05	0.16	-0.07	1.00
Hf	-0.10	**0.93**	-0.10	0.00	0.90
La	**0.98**	-0.06	0.16	0.04	1.00
Mo	0.01	0.31	-0.22	**0.83**	0.95
Na	0.09	-0.05	**0.79**	0.31	0.99
Sb	-0.10	**0.96**	-0.09	0.20	0.96
Sc	**0.99**	-0.01	0.02	0.08	1.00
Sm	**0.93**	0.03	-0.04	0.33	0.99
U	0.25	0.11	0.08	**0.87**	0.77
Zn	0.17	0.03	**0.68**	-0.39	0.97
Eigenvalue	4.0	2.5	2.2	1.9	–
% Variance	33.16	20.91	18.55	16.19	88.81
Probable Source	Crustal (Saharan)	Combustion (Oil)	Marine Traffic	Uranium (Processes)	–

Generally speaking, this second approach to filling in the missing values with average data not only objectively decreases the unexplained variance, but may conceptually be closer to the actual reason why such missing data did occur in the first place. In fact, close values in blank and loaded samples may yield a null result for an element when accounting for its concentration in blanks, thus making justifiable a replacement by the limit of detection. There are, however, other missing data due to the radioactivity decay along the first week of measurements, and, for these ones, an average of the determined values could be more reasonable.

The results of cluster analysis are shown in Figure 5.7, for the situation of filling in missing values with detection limits. Two main clusters are apparent: one with Na only, isolated from the other that contains the remaining elements, which is in itself an indication of the large oceanic influence at Pico summit. The mixed group is split into two parts. One subgroup has Fe isolated, indicating the high concentrations of this element during the Saharan events, whereas the anthropogenic elements Br, Co, Mo, Sb, U and Zn from another subgroup. There is also a crustal subgroup made up of La, Sm, Hf and Sc. Changing the replacement mode (detection limits by averaged data), just like before, would mainly affect the U positioning, putting it in aside the crustal elements Hf, La, Sc and Sm.

Since the error estimates of the present aerosol data broadly vary, and also to avoid the occurrence of negative loadings within the former factor structures (by PCA followed by rotations), a more robust approach may be convenient. PMF is a multivariate receptor model that uses an inversely-weighted, least-squares methodology, and an iterative re-weighting algorithm, to provide a factor structure that is essentially non-negative. The factor-analysis solution by PMF is thus constrained so that both matrices of source contributions (scores) and source profiles (loadings) are required to be non-negative. In brief, that means neither negative source contributions to the samples, nor negative species concentrations at the sources – which, by the way, seems perfectly reasonable an assumption on phenomenological grounds.

The PMF technique was developed by Paatero and Tapper[60,62] from their own stance on factor analyses as least-squares-fit problems[61]. Since its inception – and first application to environmental (precipitation) data by Juntto and Paatero[42] – PMF has been extensively used in receptor-modelling and source-attribution studies[7,10,14,16,18,45,46,51,54,55,66,69,85,87]. A comprehensive review of methods for apportioning sources of ambient particulate matter through the PMF algorithm – with an emphasis on procedural decisions and parameter selection – was recently given by Reff et al.[76].

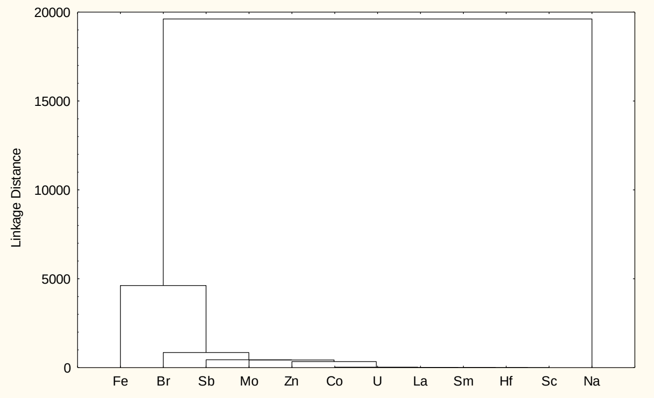


Figure 5.7. Results of cluster analysis for elemental concentrations in aerosol samples from PICO-NARE (single linkage; Euclidean distances). Missing values were replaced by detection limits.

In practical terms, PMF is a trial-and-error procedure where data uncertainties play a key role for obtaining an optimal – and physically significant – solution with a given number of factors. Error estimates of the data points not only provide the residual sum of squares with (inverse) weights for the optimization (minimization) process of an objective function Q – a goodness-of-fit index – but also enable an adequate handling of missing and below-detection-limit values[60,68]. The criteria adopted here to fill in blanks and attribute uncertainties was based in Hopke et al.[40]. For determined values, the concentration stands as it is, with the uncertainty as it is plus one third of the LOD. For values below LOD, the concentration is half of LOD, and the uncertainty is an arithmetic mean of elemental LODs in the sampling site, divided by 2, plus one third of LOD. For missing values, the concentration is the geometric mean of the determined values, and the uncertainty is 4 times the geometric mean of the determined values.

Table 5.5 shows the results of a six-factor PMF analysis upon data from aerosol samples collected between July 2001 and July 2002, accounting for the above criteria. This data-set had 15 chemical elements determined for 135 sampling days. The calculated Q value was 2172, which is fairly close to the {[number of chemical elements]•[number of sampling days]} = 2072 (theoretical, optimized Q). Still, comparing the PMF results to the ones given by PCA (Tables 5.3-5.4) – which does not include uncertainties, and either fills the missing data with arithmetic means and/or LODs – it may be concluded that they do not actually differ.

Table 5.5. Six-factor structure for elemental concentrations in aerosol samples from PICO-NARE (partial data-set: July 2001-July 2002; number of sampling days: 135), by positive matrix factorization. Bold figures indicate factor loadings ≥ ***0.30****.*

Variable (Element)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
As	0.00	0.16	0.00	0.00	0.01	**0.36**
Br	0.00	0.17	0.08	0.17	0.07	**0.30**
Co	0.06	0.06	0.00	**0.55**	0.01	0.00
Cr	0.00	0.00	0.00	0.26	0.10	0.19
Fe	**0.66**	0.00	0.00	0.10	0.00	0.16
Hf	0.00	0.00	0.05	**0.33**	0.02	**0.32**
K	0.13	0.00	0.00	0.17	**0.64**	0.00
La	**0.30**	**0.31**	0.19	0.05	0.04	0.01
Mo	0.00	**0.41**	**0.55**	0.01	0.00	0.28
Na	0.12	0.12	0.00	0.00	**0.32**	0.19
Sb	0.00	0.00	0.03	**0.53**	0.17	0.00
Sc	**0.82**	0.00	0.00	0.00	0.00	0.02
Sm	0.22	0.00	**0.67**	0.00	0.05	0.00
U	0.01	**0.82**	0.00	0.00	0.00	0.00
Zn	0.01	0.00	0.05	**0.33**	0.02	**0.32**
Probable Source	Crustal (Saharan)	Uranium (Processes)	Crustal	Combustion (Oil)	Marine	Traffic

5.3.4. Directional predominance of air masses and continental provenance of airborne elements at PICO-NARE

The air-mass trajectories for the studied period, as given by back analysis (HYSPLIT model), were associated in order to establish their main directions. The trajectories were requested 5 days backwards, for 100, 500 and 1000 m above the sampling site (AGL), in an isentropic mode due to the complete oceanic situation of the sampling site. As no differences were found for the three altitudes, the 100 m AGL was selected thereafter. This trajectory height appears to be more than enough to ensure a transport pathway well above the MBL, that is within the LFT, an essential attribute to assess long-range impacts of upwind source regions. It should be emphasized that the PICO-NARE station itself (2225 m AMSL) already lies above the regional MBL[50], which is typically less than 1000 m high in summer[59,82]. Subtropical MBLs are usually found between 800 m and 1600 m AMSL, supporting the lower-stratocumulus cloud layer[1,39] – and in Pico, more often than not, such cloud-topped, visually-apparent boundary is situated well below the mountain summit. Therefore, despite some possibility of marine upslope flows[47,48], trajectories whose end-point altitudes run at least above the mountain-top height most likely stand for transport phenomena within free tropospheric air.

The trajectories were split for seasonal study into summer – April to September – and winter – October to March. Figure 5.8 shows the directional predominance for summer and winter, as well as for the whole period.

There are no significant differences between the three outputs by MapInfo Professional v7.5. Most air masses originate in North-Central America, followed by Europe, North Africa and Greenland. Less frequent are the ones coming from South America, Central Africa and South Africa. Such pattern is not surprising and likely explains why the area is under the influence of anthropogenic emissions from North America and Europe[6].

This is the first study on the concentrations of chemical elements at an altitude of more than 2000 m AMSL, in the middle of the North Atlantic Ocean. A previous study using the same filters dealt with black carbon and PM concentrations[25]. So the next question would be which trajectories bring As, Br, Sb, U, etc, detected in the analysed filters. To answer that, each elemental data-set was put in increasing order of concentrations, and the 20 % highest values were selected. The latter corresponded to particular sampling times. Synoptic, 5-day backward trajectories were then computed in isentropic mode, for the highest concentrations of elements entrained by air masses arriving at 100 m above PICO-NARE at those particular times. This is illustrated by Figure 5.9 for arsenic, antimony and uranium (drawings by MapInfo Professional v7.5).

Even if the assignment of remote sources is always debatable, arsenic clearly originates from the Canada/United States of America (USA) border, where high-stack smelters are in operation. Antimony is of continental origin: all trajectories that carry the highest concentrations of this element can be traced back to North-Central America or Western Europe. The highest concentrations of uranium come in from well-defined directions: Canada/USA, Caribbean basin and Central-Eastern Europe.

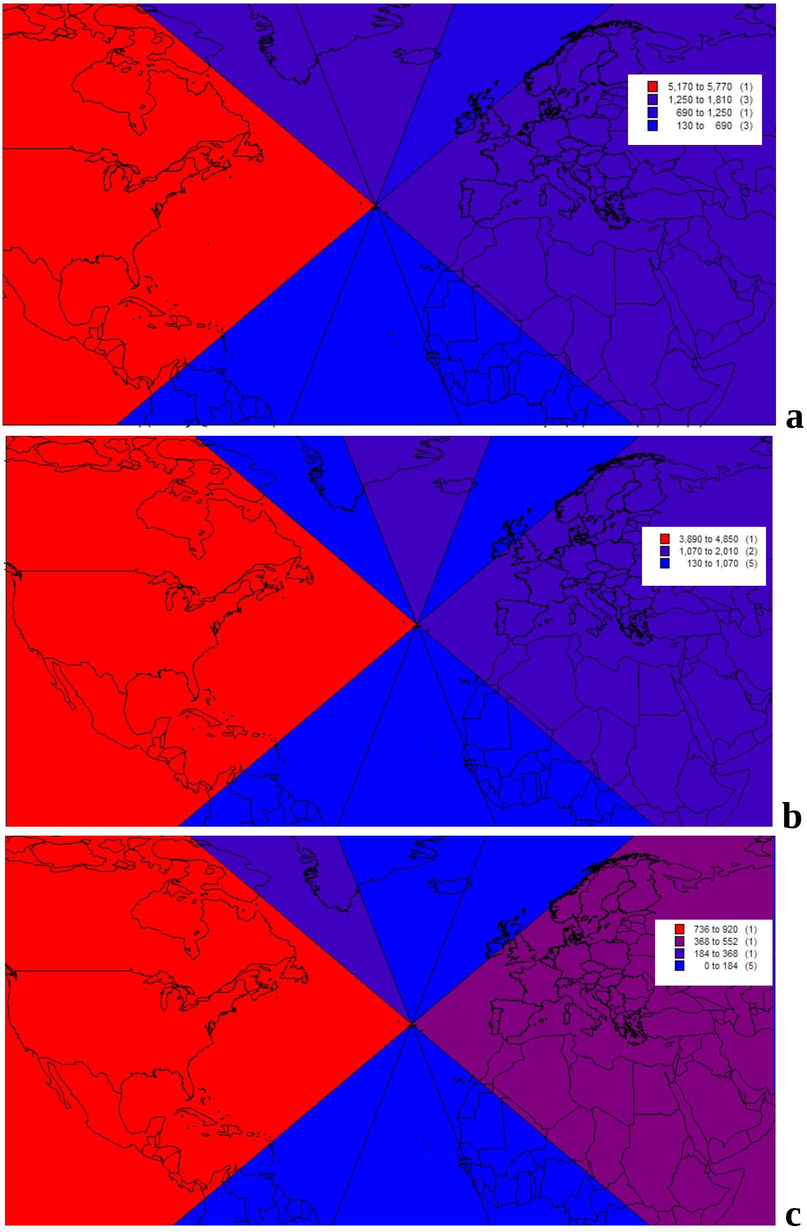


Figure 5.8. Directional prevalence of air masses reaching the Azores at 100 m above the PICO-NARE. a): annual; b): summer; c): winter.

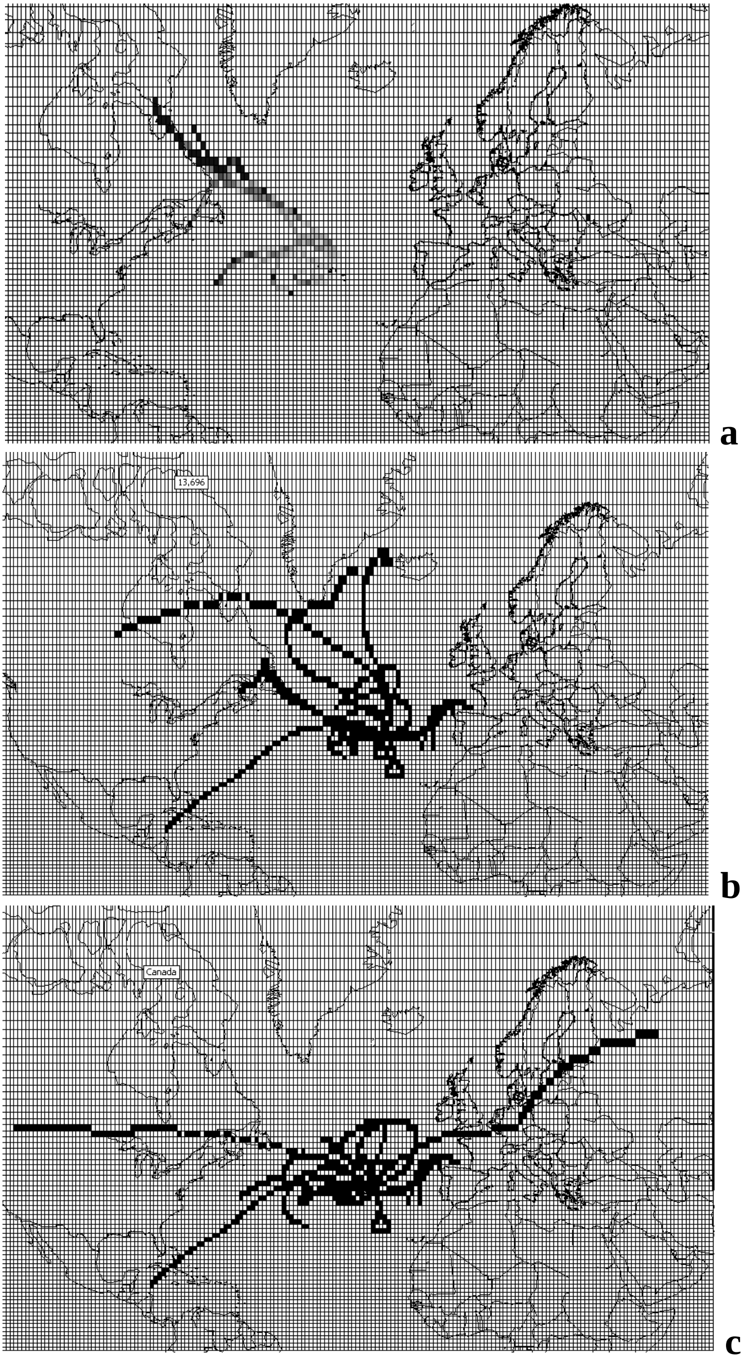


Figure 5.9. Directional prevalence of air masses with high elemental loads, reaching the Azores at 100 m above the PICO-NARE observatory. a): arsenic; b): antimony; c): uranium.

A few examples of 5-day backward trajectories (100, 500 and 1000 m AGL), ending at times when high concentrations of an element (or elements) was (were) observed, are given in Figures. 5.10-5.11. Such examples include:

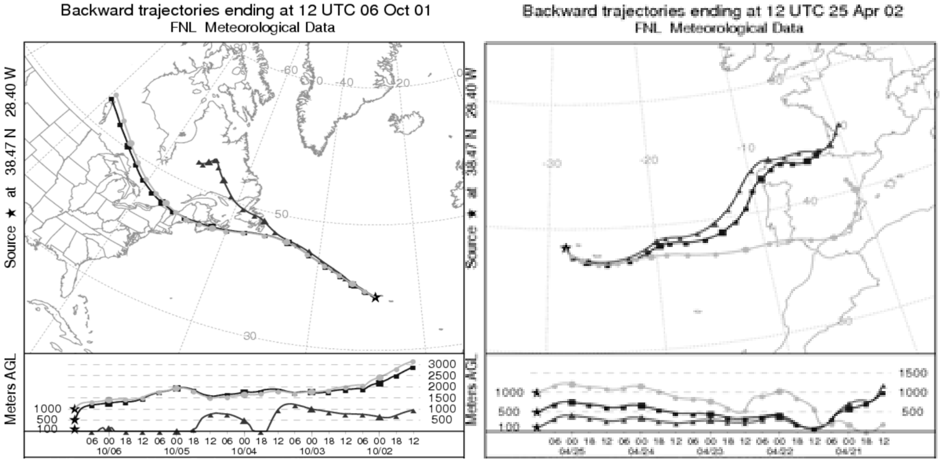
October 6, 2001: from the North American continent, across Canada; 25 ng·m^{-3} of Mo;

April 25, 2002: from the European continent, north-south Iberian peninsula; 21.7 ng.m^{-3} of Mo, 50.8 ng.m^{-3} of Sb, 0.8 ng.m^{-3} of La, 0.3 ng.m^{-3} of Sm;

September 2, 2003: from the European continent, Ireland and United Kingdom; 0.3 ng.m^{-3} of Hf;

February 19, 2004: from the North American continent, across USA and Canadian border; 20 ng.m^{-3} of U.

Some of the former values are considerably higher than those obtained almost a decade ago from PM10 at the vicinity of an oil-fired power plant in Setúbal, mainland Portugal[35]: La: 0.3 ng.m^{-3}; Sb: 1.8 ng.m^{-3}; Sm: 0.07 ng.m^{-3}; U: 0.4 ng.m^{-3}.



Backward trajectories ending at 12 UTC 06 Oct 01
FNL Meteorological Data

Backward trajectories ending at 12 UTC 25 Apr 02
FNL Meteorological Data

Figure 5.10. Five-day synoptic back trajectories arriving at PICO-NARE on October 6, 2001, and April 25, 2002, at three different heights – 100, 500 and 1000 m AGL. Calculations were done in isentropic mode with the HYSPLIT model, via the NOAA ARL READY Website.

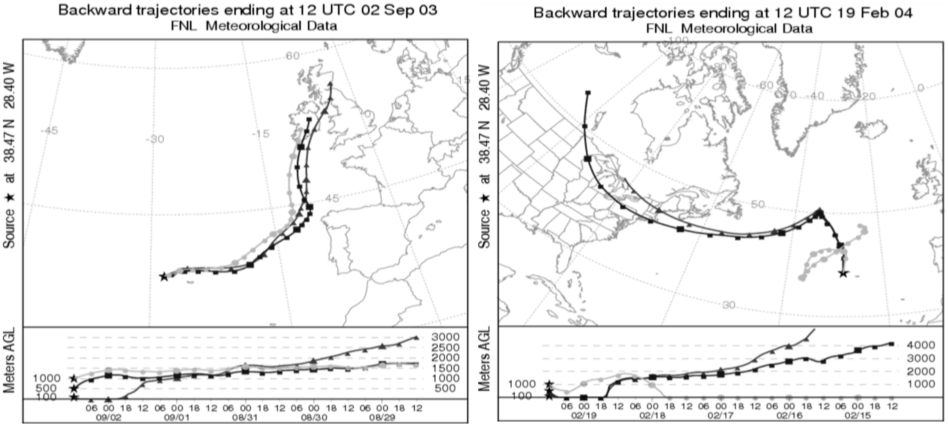


Figure 5.11. Five-day synoptic back trajectories arriving at PICO-NARE on September 2, 2003, and February 19, 2004, at three different heights – 100, 500 and 1000 m AGL. Calculations were done in isentropic mode with the HYSPLIT model, via the NOAA ARL READY Website.

5.4. Summary

The chemical composition of 425 aerosol samples collected on quartz-fibre filter tapes by a seven-wavelength aethalometer from 15 July 2001 to 18 April 2004 at the PICO-NARE observatory, Pico island, Azores, was assessed by k_0-standardised, k_0-INAA. Generally speaking, elemental concentrations do not comply with the features of a clean, remote area, as would be expected for a high-altitude location in the middle of the North Atlantic Ocean. Instead, and for a few determined elements, they may even be seen to compare with similar data from moderately-polluted, urban-industrial areas in mainland Portugal. This is likely due to an influence of air masses originated in the three surrounding continents, which entrain anthropogenic and crustal elements from sources afar, the latter more intensely from North Africa when Saharan-dust episodes happen to occur. Still, the predominance of air masses reaching – and crossing over – the Pico-summit area is from North and Central America. Enrichment of pollutants like antimony, arsenic, bromine, uranium and zinc – relative to crustal/marine (gross) averages or aerosol (reference) data – may thus be assigned to those continental areas. Europe contributes with similar components as well, albeit not that often due to the preferential wind direction.

Factor analyses by extracting principal components from the correlation matrix for the whole data-set – and rotating axes to maximum variance for each factor – did not result in major differences between the factor solutions corresponding to different ways of handling missing data, that is filling in blanks with LODs or averages of existing values. The second approach, though, leads to an almost general enhancement of the proportion of the variables' (elements') variances accounted for by the four-factor structure, except for Co, with a substantial decrease of the total unexplained variance. Uranium appears strongly associated with molybdenum in a compositional profile that could fit a number of U-processing operations (mining, milling, recycling), instead of showing up in a marine profile – with Na, that has been clearly segregated by cluster analysis. Other than crustal/marine sources, and notwithstanding minor variations, both PCA analyses point to significant inputs from far-flung, traffic- and combustion-related sources to the Pico atmosphere.

Since uncertainties can be relatively high, yet readily available – 5-15 % for the method alone, based on quality control of k_0-INAA through a surrogate reference material (NIST-SRM® 2783), plus individual (elemental) errors in the counting (spectral) statistics – a factor-analysis solution by PMF was sought. An optimal six-factor solution by PMF all but confirms the former PCA results. Again, an U-Mo association is clearly apparent in a factor that fits a compositional profile akin to U-processing operations; the remaining factors stand for probable sources already identified by PCA – soil dusts (atypical and Saharan), marine salts, traffic and oil combustion, both (the latter two) of remote origin.

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Chapter 6

VITALITY ASSESSMENT OF EXPOSED LICHENS ALONG DIFFERENT ALTITUDES. INFLUENCE OF WEATHER CONDITIONS[5]

Abstract

To evaluate the effects of the ambient climatic conditions in lichens vitality along some well oriented transect in different altitudes, lichen transplants of Parmotrema bangii were exposed approximately every 250 m starting from 50 m to 1,500 m during one year period in 3 transect along Pico mountain at Azores; Electric conductivity of leachates, elemental concentrations and the ambient conditions such as temperature, precipitation, humidity and altitude were the compared parameters. According to the obtained values of electric conductivity it is credible to consider that vitality was not seriously affected under different altitudes. In accordance with previous studies, electric conductivity values in this study show high negative correlation with precipitation and humidity. The significantly high differences between minimum and maximum electric conductivity values found along the altitude transect makes that, when comparing elemental concentrations in time or spatial series it is required a comparison with lichen vitality, because the different vitality stages could induce variability in metal uptake.

6.1. Introduction

Lichens are well documented indicators of anthropogenic disturbances which are not immediately discernible by remote sensing techniques. This potential of bioindicating, using in-situ or transplanted lichen species in exposure studies, was demonstrated over the past years: it showed the lichens to reflect the variance in ambient conditions[9,12,14,32,33].

Lichens are symbiotic (fungii + algae) organisms, able to adapt and colonize many habitats that largely vary in environmental characteristics; they are generally more resilient than many other organisms[31]. Apart from their resistance to a wide range of environment stress factors, lichens are

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[5] *B.J. VIEIRA, M.C. FREITAS, H.TH. WOLTERBEEK, "Vitality assessment of exposed lichens along different altitudes. Influence of weather conditions", Environ Sci Pollut Res (2017) 24:pp.11991–11997. DOI: 10.1007/s11356-016-6868-x*

also known to strongly accumulate chemical elements from the atmosphere, especially when fully hydrated[21,22,25]. They do so by a variety of mechanisms, including particulate trapping, ion exchange, extracellular electrolyte absorption, hydrolysis and intracellular uptake[17].

The elemental uptake by the lichen transplants during the exposure period is highly dependent on lichen physiological conditions and may not exclusively reflect the ambient element availability[8,20,26]. The differences in meteorological conditions among the various exposure sites should also be considered as of possible effect to both the accumulated chemical element content of the lichens[7,17] and to the lichens' physiological vitality[8,10,16,19,27]. The lichen vitality is relevant for their growth rates and therefore for their biomass increase or decrease, which, in turn, may lead to dilution-enrichment effects; the latter may influence the element uptake and ion-cation competition inside the lichen[29]. There are sensitive parameters reported that may be used to track physiological responses to environmental stress: several studies indicate the usability of determining the release of potassium ions (K^+) to indicate loss of membrane integrity. The release of the mobile potassium may be evaluated by determining the electric conductivity of a water solution in which the lichen material is immersed during a preset period of time[18]. Any progressive loss in membrane integrity, leading to an increase in cell permeability, results in the release of potassium and the subsequent increase of the solution's electrical conductivity[1,28]. Ion release is reported as mainly related to wet-dry cycles, but many studies also show correlations with the deposition of pollutants such as Ba, Cl, Cr, Cu, Na, Ni, Tb, or Yb[9,11,14,19,24,26,30]. A study with transplants, conducted by Marques et al.[26], suggested that the obtained concentrations for Na, Cl and K could be considered as largely determining the conductivity. This might be considered in this study as the samples were collected in a marine environment. The electric conductivity of the leakage water in which lichens are immersed is a result of the degree of damage caused on cell membranes. Garty et al.[15] found differences of approximately factor of 2 in electric conductivity in lichens from industrial polluted sites in Israel compared with those from rural sites; however, in some cases, the K loss in the lichen was not due to reduced air pollution but a consequence of wet-dry cycles. Other studies to evaluate the extent of cell membrane integrity loss report differences of a factor of 2-4[1].

Investigation on influence of elemental concentration and weather conditions in lichen vitality is abundant, mainly in the perspective of survey studies. However, with respect to a well oriented transect along different altitudes, it seems to be necessary to increase the knowledge on all factors affecting lichen as a biomonitor. Altitude is directly related with the temperature, precipitation, humidity and also wet deposition, all parameters which potentially influences the lichen vitality and thus, the bioaccumulation capabilities. As demonstrated by some studies using mosses in different altitudes, this approach could also be very important on defining the main patterns which affects elemental contents in lichens as they can provide altitude-dependent information, giving some perspective of element increase from long-range transport[23,29,34].

The aim of the present study was to evaluate the effects of the ambient climatic conditions and elemental content in lichen vitality along some well oriented transect in different altitudes in an exposure experiment. The electric conductivity is assessed to evaluate the response behavior throughout the exposure area. Lichens were transplanted from a clean background site and exposed on Pico mountain, Pico Island, Azores; they were collected after a winter- and a one-year exposure periods, to judge whether the observed variances in lichen vitality advises the use of lichens at higher altitude areas. Recorded and determined parameters were the electric conductivity of leachates and the ambient conditions such as temperature, precipitation, humidity and altitude.

6.2. Materials and Methods

6.2.1. Sampling

Samples of lichen *Parmotrema bangii (Vain.) Hale* were collected in May 2007 from four Japanese cedar trees (*Cryptomeria japonica D.Don*) growing in São Miguel island, Azores (37º47’26’’N; 25º38’13’’W; elevation 207 m), in a pollution-free area. The lichens were collected with their substrates up to 1.5 m above ground level and transported in the same day to the laboratory into clean polyethylene bags. In the laboratory, dead tissues and any extraneous material (large soil particles, litter) were removed. The lichens were not separated from their substrates. In September 2007, the same procedure was done for different time exposure experiment.

Each lichen transplant with a total contour surface area of 350 cm^2, still attached to its tree bark substrate, was put on a 20 cm x 25 cm wood support and fixed with 0.5 mm thick nylon strings, as shown in Figure 6.1. A total of 21 of these sets were prepared for exposure. In each support, a sample of bark devoid of tree lichens was also included to conduct a study on the deposition of heavy metals to be published in a future article.

6.2.2. Field experiment

In May 2007, the lichen transplants were taken to the Pico mountain in Pico island, Azores (North Atlantic Ocean). The period between sampling in São Miguel island and exposure in Pico island was one week for both exposure times. They were exposed in northern, southern and western directions, along the mountain at varying altitudes (approximately every 250 m starting from 50 m above sea level and then at 250 m, 500 m, 750 m, 1,000 m, 1,250 m and 1,500 m whenever possible) during one year period (May 2007 to May 2008). Due to difficulties in accessing the eastern direction, this latter direction was not used. The supports were fixed on trees whenever available, above 1.5 m from the soil; otherwise, because of the absence of trees (mostly above 1,000 m), the supports were fixed on rocks.

On the western side, in September 2007, half of the exposed sample was collected and replaced by a new transplant sample, collected at the same background site (São Miguel island). It was placed on the support for an exposure period of 8 months, mainly in the winter period (September 2007-May 2008).This last experiment was done to compare results with all year exposure and it was done only for western direction.

None of the transplanted samples from all year and winter periods were exposed above 1,500 m altitude because of the snow and ice in this period of the year.

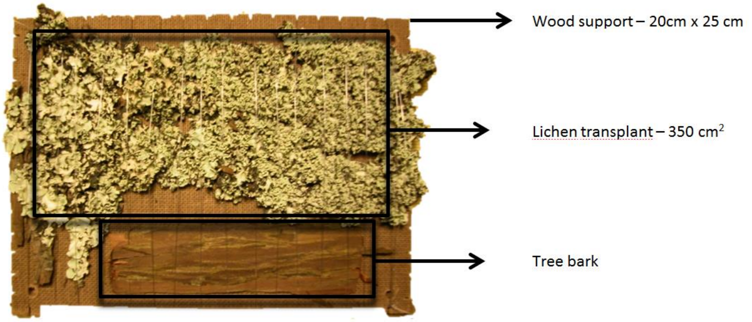

Figure 6.1. *Support with transplanted lichen Parmotrema bangii and tree bark of Cryptomeria japonica.*

6.2.3. Meteorological data

Precipitation, humidity and temperature for each exposure site, and for each exposure period, were taken from the CIELO model[3,6] and are shown in Table 6.1.

6.2.4. Analytical procedures

The electric conductivity of the unexposed and exposed lichens was measured in the laboratory one week after collection. Approximately 100 mg of material was cleaned, rinsed 2 times for 5 s each with demineralized water to avoid any interference on the conductivity values derived from particulate matter deposited on the lichen talus surface, then air dried for 24 h and immersed in 10 ml of demineralized water for 1 h. After removal of the lichen material, the electrical conductivity of the water solution was measured three times with a conductivity meter OAKTON WD-35607-10 CON110 Standard[17,19]. For blank values, the electric conductivity of the 18MΩ water was measured before each lichen conductivity measurement.

Conductivity values are given relative to the dry mass of the lichen used in the leachate experiments, and the electric conductivity of blank values was subtracted from the observed values before further comparisons were made.

Elemental concentrations were determined by k_0-standardised, k_0-INAA following procedures described in Freitas et al.[13].

6.3. Results and discussion

The pH of the solution was measured to track any possible acidity effect on the electric conductivity. Values were very steady between samples (pH=6.3±0.1), discarding any conductivity pH influence on conductivity values from the H^+ ion.

The electric conductivity of the lichens before exposure (background values) was measured and the average for the 8 samples collected from the 8 trees (4 referring to May 2007 sampling – all year exposure; 4 referring to September 2007 sampling – winter period) was determined as 0.02±0.001 $mSm^{-1}g^{-1}$. These values are much lower than the ones obtained elsewhere for background values (i) in *Flavoparmelia caperata* collected in Tomar region, mainland Portugal: between 0.15 - 0.25 $mSm^{-1}g^{-1}$ (12), (ii) in *Parmotrema bangii* collected also in São Miguel island in 2008: between 0.14 - 0.28 $mSm^{-1}g^{-1}$ (20) and (iii) in *Parmelia sulcata* collected in Mafra/Ericeira region, mainland Portugal: 2.822 $mSm^{-1}g^{-1}$ (26). All these places are considered unpolluted areas. The obtained values were similar in both collections periods, meaning that lichen vitality was identical at the start of both exposure experiments and at the different directions.

Figure 6.2 presents the electric conductivity data for the whole year exposure period for the northern, southern and western directions and for the winter time exposure period for the western direction. The electric conductivity mean values after exposure were, in ascending order, of 0.022±0.008 $mSm^{-1}g^{-1}$ at western direction in winter period, of 0.108±0.056 $mSm^{-1}g^{-1}$ at western direction in all year period, of 0.368±0.351 $mSm^{-1}g^{-1}$ at northern direction in all year period and of 0.389±0.478 $mSm^{-1}g^{-1}$ at southern direction in all year period. The results in the western direction exposed for the whole year and the winter periods are in the same order of those reported in unpolluted areas of Portugal[19,26] and much lower compared to rural-unpolluted area in Israel[14] which are generally higher than 2.14 $mSm^{-1}g^{-1}$.

Table 6.1. Meteorological data of Pico Mountain exposure sites in Pico island, Azores. All year exposure time corresponds to the period between May 2007 and May 2008; the winter exposure time corresponds to the period between September 2007 and May 2008. N, S and W correspond to the northern, southern and western sides of the mountain. Values represent the average of the whole considered period.

Altitude (m)	**Coordinates**			**Precipitation (mm)**				**Humidity (%)**				**Temperature (ºC)**			
				All year			**Winter**	**All year**			**Winter**	**All year**			**Winter**
	N	**S**	**W**	**N**	**S**	**W**	**W**	**N**	**S**	**W**	**W**	**N**	**S**	**W**	**W**
50	N38º32’58’’ W28º25’40’’	N38º25’29’’ W28º26’45’’	N38º30’23’’ W28º31’56’’	89	80	80	102	83.2	78.8	87.3	87.4	18.1	19.2	17.5	15.6
250	N38º31’53’’ W28º25’35’’	N38º26’20’’ W28º26’54’’	N38º30’07’’ W28º30’00’’	123	278	148	172	86.3	86.2	93.2	93.2	17.0	16.6	15.3	13.4
500	N38º31’08’’ W28º26’07’’	a)	N38º29’29’’ W28º28’20’’	186	-	281	363	90.9	-	97.5	97.4	15.3	-	13.3	11.4
750	N38º30’04’’ W28º25’12’’	N38º27’01’’ W28º26’17’’	N38º28’52’’ W28º26’59’’	338	268	338	434	95.4	95.5	93.9	91.4	13.5	12.8	12.9	10.9
1,000	N38º28’58’’ W28º25’47’’	N38º27’54’’ W28º26’22’’	N38º28’08’’ W28º26’24’’	416	314	324	399	96.8	97.9	94.4	98.2	12.3	11.5	11.7	9.6
1,250	N38º28’29’’ W28º25’25’’	N38º28’07’’ W28º25’39’’	N38º28’19’’ W28º25’32’’	428	428	428	538	98.3	98.3	98.3	98.3	10.2	10.2	10.2	8.1
1,500	N38º28’11’’ W28º25’19’’	N38º28’08’’ W28º25’21’’	N38º28’11’’ W28º25’19’’	443	443	499	628	97.8	97.8	98.6	98.6	9.4	9.4	8.7	7.1

The lichen electric conductivity mean values were higher during the all year exposure than the winter time exposure. All the electric conductivity mean values are higher after exposure at confidence level 95% (P<0.001), except for western direction in winter period. In this case the difference was not statistically significant (P=0.5411), which put in evidence that the increase between low altitude values (0.018±0.002 $mSm^{-1}g^{-1}$) and high altitude (0.037±0.001 $mSm^{-1}g^{-1}$), by a factor of 2.1, observed in the right graphic at Figure 6.2, is mainly related to natural variance of the lichen vitality. This means that the lichen vitality is indeed influenced by the exposure factors but only in all year experiment. As winter period coincides with the last 8 months of the all year exposure time, the main factors influencing the lichen vitality seem to occur in the period between May 2007 and September 2007 (summer period). According to some authors, this summer negative influence on lichen vitality, was mostly associated with meteorological causes (temperature, precipitation and humidity)[19,25,26]. The fact that the lichens exposed during the whole year present higher mean values than the ones for winter also suggest that, in general, no re-establishment of the membrane integrity occurs as observed in previous studies[26,27,33].

Considering the whole year transplants, the electric conductivity differences between the different altitudes are significant for all the directions at a 95% confidence level. This puts in evidence a clear difference between the different altitudes. Garty et al.[15] reported differences of a factor of 2 in electric conductivity of lichens batches from industrial polluted sites compared with those from rural sites. In western direction, values range on a factor of 4.2 between 1,000 m (lower electric conductivity value) and 50 m (higher electric conductivity level). In northern direction, values range of a factor of 17.8 between 1,500 m (lower electric conductivity value) and 500 m (higher electric conductivity level). According to the correlation coefficients between meteorological factors and electric conductivity values for these two directions (Table 6.2), there is a high negative correlation with precipitation, humidity and altitude and a positive one with temperature. Godinho et al.[19] also reported similar correlation with temperature and humidity. This suggests that the best (meaning the minimum values) lichen vitality of the transplanted lichens under study might be due to the increase of precipitation and humidity, which in fact is also related with the altitude increase. In southern direction, values range of a factor of 13.7 between 50 m (lower electric conductivity value) and 750 m (higher electric conductivity value).

Results of electric conductivity are not correlated with any meteorological parameters which puts in evidence a potential existence of other factors influencing the lichen vitality. In general, for all the directions, higher electric conductivity values are obtained in the first 500 m (750 m in case of south direction) followed by a decrease tending to constant values until 1,500 m. In fact the differences between these two levels are significant, with differences in the average electric conductivity by factors of 3.9, 4.9 and 8.7 in the southern, western and northern directions respectively. These results suggest that the best performance of exposed lichens is in high altitudes when considering a whole year exposure. At lower altitudes, lichens' membrane seems to reflect some damage. This might be due to lower humidity, lower precipitation and higher temperatures levels during the summer period.

In spite of these results being correlated with weather conditions, it should be considered that other extraneous factor could influence the lichen vitality under these altitudes.

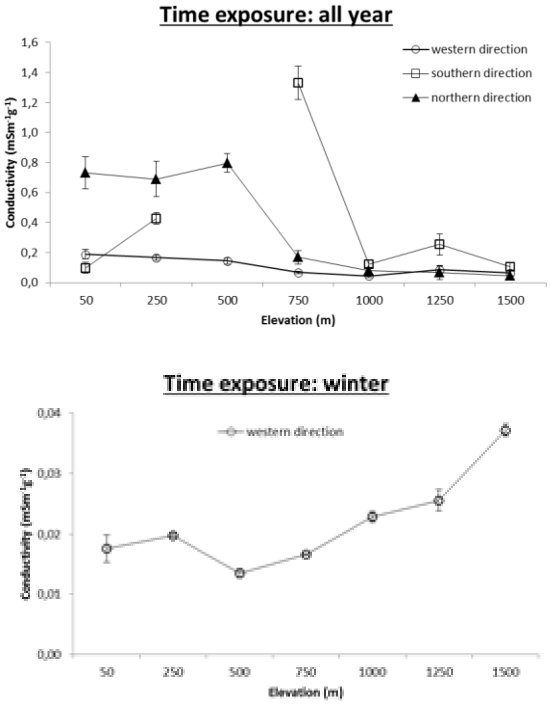

Fig. 6.2. Electric conductivity of the water solutions expressing leakage in thalli of transplanted lichens Parmotrema bangii in the northern, southern and western directions for the whole year time exposure and for the winter period in the western vector along the Pico mountain. Each point represents the mean of three replicates.

Considering the whole year transplants, the electric conductivity differences between the different directions are significant for all the altitudes at a 95% confidence level, mainly because of the differences in the electric conductivity in the first 750 m, due to the influences explained below. Lower difference was between northern and western direction (P=0.077). When considering the same exposure local at 1,500 m, the results of electric conductivity for all directions are very similar (0.045±0.001 $mSm^{-1}g^{-1}$ – northern; 0.064±0.021 $mSm^{-1}g^{-1}$ - western; and 0.106±0.026 $mSm^{-1}g^{-1}$ – southern).

The elemental concentrations of the lichen thalli (not shown) were correlated with electric conductivity. Significant correlations were only found for K and Se in all year period at west direction and Rb in all year period at north direction, which suggest the absence of any further effect from other elements. The increase of K and Rb concentrations with the increase of electric conductivity cannot be explained by the leakage of this ion due to membrane disruption. As the correlation between K and Rb is positively related with precipitation and humidity (Table 6.2), these weather parameters can induce the lichen biomass growth and so the increase of these elements. For Se, its correlation with electric conductivity is in the reverse side, which suggests the increase of chemical atmospheric element uptake with the increase of lichen vitality. Some previous studies indicate that lichens are more sensitive to air pollution in the hydrated, physiologically active state[22].

Table 6.2. Correlation coefficients (R) between meteorological factors (precipitation, humidity, temperature) and electric conductivity values (mSm^{-1}g^{-1}) measured in water solution, expressing leakage in thalli of transplanted lichens P. bangii at the 7 different altitudes. In addition, P values are presented for all correlations; the significant ones (threshold P<0.05) are given in bold italic.

			Western direction		
		Elevation	*Precipitation (mm)*	*Humidity (%)*	*Temperature (ºC)*
Time exposure: the whole year	R	-0.71	***-0.76***	***-0.83***	***0.79***
	P	0.073	***0.047***	***0.021***	***0.035***
Time exposure: winter	R	***0.80***	0.68	0.53	-0.73
	P	***0.032***	0.096	0.224	0.066
			Northern direction		
Time exposure: the whole year	R	***-0.88***	***-0.96***	***-0.90***	***0.89***
	P	***0.009***	***0.001***	***0.006***	***0.007***
			Southern direction		
Time exposure: the whole year	R	-0.13	-0.10	0.14	0.00
	P	0.810	0.853	0.788	0.993

Garty et al.[16] takes as a reference a value about 6-7 mSm^{-1}g^{-1} to consider injury on lichen cell membranes. The maximum value obtained in this study (1.330±0.111 mSm^{-1}g^{-1} at 1,000 m in southern direction) is much lower; it is then credible to consider that vitality was not seriously affected under the different altitudes and directions, and lichens could be considered physiologically active. The highest difference factors between lower and higher electric conductivity values obtained (4.2 in western direction; 17.8 in northern; 13.7 in southern) are significantly higher when compared to those reported in Garty et al.[15] and Alebic-Jurtic and Arko-Pijevac[2] and it may be due to a much lower level of the minima, rather than some severe damage in lichen membrane.

Results of electric conductivity show high negative correlation with precipitation and humidity for the whole year period in the northern and western directions in accordance with previous studies[19]. Electric conductivity is also lower in southern direction above 750 m where values of precipitation and humidity are higher. These results suggest that the best performance of the exposed lichens is at high altitudes when considering a whole year exposure. In lower altitudes (below 500 m) lichens seem to reflect some damage during the summer period as a result of lower humidity and lower precipitation conditions. In winter period, lichen vitality was not significantly affected by ambient conditions and its values are lower when compared to the ones of whole year period.

6.4. Conclusions

The differences in electric conductivity found along the altitude transect and at the different directions reflect different stages of lichen vitality. These occurrences may influence the lichen growth conditions and therefore its biomass increase. This may lead to dilution concentration effects at high altitudes and to influences over deposited elemental uptake. It was also observed a positive correlation between the elemental concentrations of K, Rb and lichen vitality. This behavior was observed in a similar study done with mosses, where bioaccumulation of metals vary depending on ecological influence factors like precipitation[25,29]. However, it also depends of the total amount of atmospheric deposition elements. In such case, the obtained elemental concentrations should be considered underestimated, compared to other samples. This was considered in previous studies related to altitude[23,34].

Our results show that it is very important to take into account the lichen vitality information when elemental concentrations results are obtained in time or spatial series in lichen surveys along altitude transects. Due to the inexistence of vitality data above 1,500 m, it is not possible to infer if temperature could negatively influence lichen membrane permeability above this altitude.

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Chapter 7

LICHENS AS BIOMONITORS OF LONG-RANGE TRANSPORTED TRACE ELEMENTS: ELEMENTAL CONCENTRATIONS UNDER DIFFERENT ALTITUDES AND DIFFERENT AIR MASSES INFLUENCES[6]

7.1. Introduction

The growing interest raised by the study of atmospheric pollution is due to its impact on human health, air quality and global climate change[1-3]. In this field, atmospheric particles play a key role also because they may contain high concentrations of several trace elements, known to have toxic effects on human health and environment due to their nonbiodegradable nature and their long biological half-life[4-6].In the North Atlantic it is estimated that about 96% of the total aerosol emissions are mainly from natural process: marine salt, biogenic elements and natural mineral dust. Volcanic emission is also significant. The remaining 4% result from long-range transport anthropogenic emissions, including biomass combustion, fossile combustion and other anthropogenic indirect activities[7]. The deposition rate on the environment depends on several factors such as emission (pollutant species and their amount), characteristic of both the transport schemes and the receiving landscapes[8]. Concentrations of various pollutants (primary and/or secondary) are found to be significant in remote locations as well as in multiple-layer structures up to several kilometers above the surface. Recent studies focus on the importance of long-range transport patterns of aerosols of anthropogenic and natural origin[9-11]. The Azores archipelago stretches across a sizeable longitude span and sits directly on the pathway of long-range transport for natural and anthropogenic aerosols species over the North Atlantic Ocean, between western and eastern boundaries extremely industrialized and urbanized that contribute to its aerosol increment. Therefore, it is an ideal platform for watching significant deposition episodes in the area and/or

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[6] *B.J. VIEIRA, M.C. FREITAS, H.TH. WOLTERBEEK, "Lichens as biomonitors of long-range transported trace elements: Elemental concentrations under different altitudes and different air masses influences", (To be submitted).*

simply keeping track of regular downward plumes at ground level, through either conventional or biological air-monitoring approaches. Moreover, the Pico Mountain at 2,351 m AMSL is high enough to enable land based access to the lower free troposphere, which means that contaminants loads from afar can be detected over the altitude range of influence of the marine boundary layer[12].

Monitoring anthropogenic air pollution, performed through instrumental techniques, is a very complex task due to a variety of reasons: the great number of potentially dangerous substances; the large spatial and temporal variation of pollution phenomena; the large human and economic efforts and hence the low sampling density[13,14]. Through the last decades, the biomonitoring approach has grown into a serious alternative – or, at least, a useful complement – to traditional (instrumental) methods of assessing contaminants from natural or anthropogenic sources[15]. Regardless of the species involved, most biomonitoring studies use lichen species because they readily accumulate pollutants in their thallus in line with atmospheric concentrations, allowing to obtain results that are complementary to chemico-physical monitoring methods[14,16-23]. Lichens are perennial, slow-growing organisms that maintain a fairly uniform morphology in time, highly dependent on the atmosphere for nutrients[29]. Lichens intercept atmospheric pollutants dissolved in wet precipitation (normal precipitation and occult precipitation – fog and dew), dry deposition and gaseous emissions[30]. Occult precipitation is a phenomenon almost permanent in Azores, occurs under very stable atmospheric conditions and contains concentrations of nutrients and contaminants orders of magnitude higher than normal precipitation[19]. Three mechanisms can explain the accumulation of pollutants in the lichen thallus: 1) particulate materials absorbed onto the thallus surface or within intercellular spaces; 2) extra-cellular binding of cations; and 3) intracellular uptake[20,26-28]. Accumulated pollutants show a close correlation with their atmospheric levels and have proved the lichen's capability as an effective biomonitor in general[24-26] and to monitor spatial and/or temporal deposition patterns of trace elements[31-33].

Whereas in situ lichen are not available, or the heterogeneity of factors that affect lichen uptake are predictable, the use of lichen transplantation has additional important advantages: lichens can be exposed in a predefined scheme, the pre-exposure values are known, they are comparable with further studies and the exposure time is known[15,34,35]. Thalli are usually collected from remote background areas and transplanted to a given area to monitor changes in trace element concentrations over time/space. The elemental uptake by the lichen transplants during the exposure period is highly dependent on lichen physiological conditions and may not exclusively reflect the ambient element availability[32,35,36]. The differences in meteorological conditions among the various exposure sites should also be considered as of possible effect to both the accumulated chemical element content of the lichens[21,37], and to the lichens' physiological vitality[34,36,38-40]. The lichen vitality is relevant for their growth rates and therefore for their biomass increase or decrease, which, in turn, may lead to dilution-enrichment effects in rain or dry seasons, respectively[44]; the latter may also influence the element uptake and ion-cation competition inside the lichen[41]. A relatively short exposure period under 3 months are generally suggested to reduce these possible influences[42,43,45]. In a study at Pico mountain lichen transplants exposed along different altitudes (50m to 1,500m) were not seriously affected by the different weather conditions under the different altitudes; however a high negative correlation with precipitation and humidity means that metabolism under wet conditions are favorable to growth which affects elemental concentration estimation[61].

In order to evaluate the impact of pollutants using lichens, it is necessary to identify the possible sources of pollution and to determine the elemental composition of these sources as well as the contribution of each source to the total pollution level. For a significant number of environmental pollution studies, the EF[49,50] or multivariate statistical methods such as factor analysis[46-48] have been frequently applied. Values of EF indicate that sources of enrichment are either natural or anthropogenic (both local and remote). Factor analysis is the most appropriate choice to obtain the desired information in cases where no previous information about the source is available.

The relation between chemical elements in atmospheric particulate matter and lichen thalli are not widespread. Therefore, this work aims to make a contribution to the establishment of valid relations between lichen content and average concentration of chemical elements in atmospheric particulate matter to discern about the possibility of using lichen transplants on a remote area (North Atlantic Ocean) under the influence of long-range transported elements to identify possible sources of elements, using varying altitudes.

7.2. Materials and Methods

7.2.1. Study area

The study was carried in Pico mountain, located on Pico island in Azores archipelago, hence the Portuguese highest peak. It is situated in the North mid-Atlantic Ocean at 2,351m AMSL. With non-volcanic activity in the last 3 centuries, there is, on top of Pico, an area of permanent degasification characterized by the emission of water vapor at a temperature of between 50 °C and 75 °C. The climate is ocean temperate climate with low temperature amplitude, high precipitation and humidity, strongly influenced by the Azores anticyclone (North Atlantic low pressure) and North Atlantic drift of the Gulf Stream, with high humidity and precipitation, which induce much milder temperatures than in other regions at the same latitude. The mean annual temperature is 17.5º C, though very dependent on the altitude. Precipitation builds up towards west, and its amount roughly increases 25 % per 100 m height. The mean annual rainfall ranges between 100 mm and 1,200 mm, more intense in December and January and humidity between 78% and 99%. Prevailing winds are from the west-southwest[51]. More detailed information on weather conditions was previously published[61].

The archipelago sits directly on the pathway of long-range transport of airborne species over the North Atlantic Ocean, namely mineral particles from Africa's Sahara and Sahel and non-natural contaminants from the North America eastern seaboard down to Central America and the Caribbean. In what concerns the Azores proper, contamination of African dust with polluted aerosols from Europe has been observed as well. The archipelago is thus an ideal platform for watching significant deposition episodes in the area and, especially, for tracking the regular oceanic transit of air masses from the surrounding continents – Africa, Europe and North-Central America, both in the marine layer and LFT layer. More detailed information about air masses influences was previous published[52].

7.2.2. Lichen transplants preparation

Samples of lichen *Parmotrema bangii (Vain.) Hale* were collected for the first transplant experiment (summer period – May to September 2007; all year period – May 2007 to May 2008) in May 2007 from four Japanese cedar trees *(Cryptomeria japonica D.Don*) growing in São Miguel island, Azores (37º47'26''N; 25º38'13''W; elevation 207 m), in a pollution-free area. The lichens were collected with their substrates up to 1.5 m above ground level and transported in the same day to the laboratory inside clean polyethylene bags. In the laboratory, dead tissues and any extraneous material (large soil particles, litter) were removed. The lichens were not separated from their substrates. In September 2007, the same procedure was done for the second transplant experiment (winter period – September 2007 to May 2008). Each lichen transplant with a total contact surface area of approximately 350 cm^2, still attached to its tree bark substrate, was put on a 20 cm x 25 cm wood support and fixed with 0.5 mm thick nylon strings, as shown in Figure 6.1, Chapter 6. A total of 28 of these sets were prepared for exposure in summer and all year period transplant experiment. For winter period only 21 sets were prepared, because the experiment was done below 1,500m altitude only.

7.2.3. Experimental design

Transplanted samples were exposed in northern, southern and western surface, along a transept from the base to the summit, every 250 m altitude up to 1,500 m, and above every 150 m, starting from 50 m up to 2,250 m AMSL (see Table 7.1). Due to access difficulties, the eastern surface was not considered in this study except for one sample in Pico summit and northern and southern between 1,500 m and 2,050 m. The supports with transplanted lichens were fixed on trees whenever available, above 1.5 m from the soil; otherwise, because of the absence of trees (mostly above 1,000 m), the supports were fixed on rocks.

Table 7.1.Localization of the transplanted exposed samples in Pico mountain, Azores (Altitude Above Medium Sea Level; Coordinates according DATUM WGS84).

Altitude AMSL (m)	**Coordinates**			
	North	**South**	**West**	**East**
50	N38º32’58’’ W28º25’40’’	N38º25’29’’ W28º26’45’’	N38º30’23’’ W28º31’56’’	-
250	N38º31’53’’ W28º25’35’’	N38º26’20’’ W28º26’54’’	N38º30’07’’ W28º30’00’’	-
500	N38º31’08’’ W28º26’07’’	N38º27’08’’ W28º27’26’’	N38º29’29’’ W28º28’20’’	-
750	N38º30’04’’ W28º25’12’’	N38º27’01’’ W28º26’17’’	N38º28’52’’ W28º26’59’’	-
1,000	N38º28’58’’ W28º25’47’’	N38º27’54’’ W28º26’22’’	N38º28’08’’ W28º26’24’’	-
1,250	N38º28’29’’ W28º25’25’’	N38º28’07’’ W28º25’39’’	N38º28’19’’ W28º25’32’’	-
1,500	N38º28’11’’ W28º25’19’’	N38º28’08’’ W28º25’21’’	N38º28’11’’ W28º25’19’’	-
1,700	-	-	N38º27’54’’ W28º24’54’’	-
1,850	-	-	N38º27’55’’ W28º24’42’’	-
2,050	-	-	N38º27’54’’ W28º24’28’’	-
2,250	N38º28’09’’ W28º24’13’’	N38º27’53’’ W28º24’04’’	N38º27’56’’ W28º24’12’’	N38º28’10’’ W28º24’11’’

The transplant experiment was performed according the scheme in Figure 7.1. The first transplant experiment was exposed in May 2007 during a 5 months summer period. After this period half of the lichen material was collected for analysis and the other half was kept for further accumulative exposure during the winter period, making a time of 12 months of exposure (May 2007 to May 2008).I n September 2007, a new transplant sample was exposed at the same sites for a period of 7 months, mainly in the winter period (September 2007-May 2008). None of the transplanted samples from all year and winter periods were exposed above 1,500 m altitude because of the almost permanent snow and ice in this period of the year, and hence the expected inactivity of lichens.

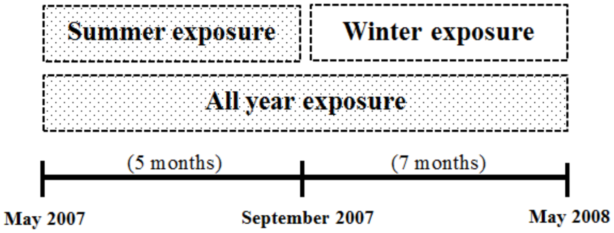


Figure 7.1*.Time representation of the exposure periods of the three lichen transplant experiments (summer, winter and all year).*

7.2.4. Trace elements analysis

In the laboratory, unwashed samples of lichens were separated from the bark substrate, and thoroughly sorted to remove dead tissue and extraneous material (remaining bark, large soil particles, litter, bugs, etc.). Samples were first freeze-dried, then ground in Teflon (balls and capsule) mills. The subsequent powder was homogenized and then samples weighed about 200 mg each were packaged in ultra-pure polyethylene containers. Due to the large number of samples only one replicate was done for each sample. At the locations, soil samples were collected out of the superficial layer (0-10 cm depth) in all sampling points. The samples were oven dried at 40ºC for 48h and sieved (nylon net) to separate the 64 µm fraction in order to normalize the soil grain size for analysis. Samples of about 100-150 mg of material each was prepared.

Element determinations were carried out at the Portuguese Research Reactor of the ITN-Sacavém; maximum nominal power 1 MW, by k_0-standardized, k_0-INAA (53 - 56). Irradiations were done during 5 h for lichen samples and 3 h for soil samples, together with one disc (thickness: 125 µm; diameter: 5 mm) of an aluminum 0.1% gold alloy (Al-0.1% Au) as comparator for the k0-methodology,with a thermal neutron flux of 5.10 x1012 n.cm–2.s–1.Using coaxial detector, samples of lichen were measured at a distance of 38.8 - 49.8 mm from the face of calibrated detector, an ORTEC GEM-30185-P with relative efficiency of 30% and resolution 1.85 keV (^{60}Co – 1332.5 keV), and signals processed by NIM using ND AccuSpec software. Samples were counted using an automatic sample changer coupled to the measurement facility to determine radioisotopes with medium and long half-lives. Elemental concentrations were calculated on basis of k_0-method using gold as the single comparator element. The decay time was 85-95 h and the counting time 2-3 h. The computation of all parameters for the calibration of energy, peak-shape and full-energy peak detection efficiency were carried out by k_0-IAEA software. Parameters of irradiation and measurement were selected according to a previously optimization study done in different facilities.

For short-lived elements, determinations were carried out in the research pulsed fast reactor IBR-2 of the FLNP, JINR, in Dubna (maximum nominal power 2 MW), using the pneumatic system REGATA for irradiation of lichen, soil and reference materials samples as well as gold monitors of neutron flux density. Therefore, a relative method (comparison with the standard) of INAA is used. Irradiations were done during 180 s for lichen and reference material samples and 60 s for soil, with a thermal neutron flux of 1.5 x10^{12} n.cm^{-2}.s^{-1}. Using coaxial detector, samples of lichen were measured at a distance of 200 mm from the face of calibrated detector, a Canberra GC4019-7500SL with relative efficiency of 41.8% and resolution 1.74 keV (^{60}Co – 1332.5 keV). To evaluate the gamma spectra the program «Measurement» was applied which used software Genie-2000 S500 and Batch Support Tools S561 by Canberra's and database of NAA. The decay time was 10-20 s and the counting time 15 min.. Additional details on irradiation and measurements conditions and reactor parameters can be found elsewhere[57,58].

Quality control of the procedures and determination of elements was asserted by parallel analyses of certified reference materials. Deviations from certified values were within 1-15 % range.

7.2.5. Enrichment factors

In order to evaluate the incidence of soil contamination of the lichen samples, an EF was calculated for each element by normalizing the element concentration in the lichen to the concentration in the local soil data for each sampling location, according to the formula:

$$EFX=([X]/[Ref.])lichen/([X]/[Ref.])soil$$

where EFX stands for the EF of an element X in lichen sample, “X” is the concentration of the investigated element and “Ref.” is the concentration of the reference element. Sc was used as reference soil element. As a rule, the more EF approaches 1, the higher is the probability that the element in lichen originates from the soil; values higher than1 can be considered not originated from the local soil background and may be attributed to long transportation phenomena from other natural and/or anthropogenic sources, or, in some cases, to a possible preferential uptake[59].

7.2.6. Factor analysis

Descriptive statistics, correlation coefficients for variables and factor analysis were calculated using IBM SPSS Statistics[23]. The mathematical details of the factor analysis model used in the present study were in accordance with Kuik et al., 1993[60]. The analytical data were represented in a multidimensional space with variables defining the axis, and projected into a few principal components that were linear combination of the original variables and described the maximum variation within the data. To validate the factor analysis method in terms of its ability to produce the correct source profile and to evaluate the independence of the correlation matrix between the initial variables, it was performed and conducted a Bartlett's test to check for intercorrelation between variables, measuring the percentage of no redundant residuals. The Kaiser-Meyer-Olkin measure of sampling adequacy (KMO) was computed to determine adequacy of sample size and the internal consistency of the scale. Then, a PCA of compositional data was performed in order to reduce the size of the data set by highlighting factors that explain variation in the composition of the lichen samples. Communality was calculated to show the proportion of variance explained by the extracted factors. To determine the most appropriate number of factors, we used an eigen value of 1 in combination with scree plots. After that pattern and structure matrices were compared to reveal the influence of shared variance of the different variables (different directions; different layers; different deposition time; different altitudes).

7.3. Results and Discussion

The analytical results of the 36 chemical elements in lichen transplanted samples exposed in Pico mountain during 5 months in summer, 7 months in winter and during all year, along with the elemental contents of control samples (before exposure), are summarized in Table 7.2. The comparison of the results of lichens before exposure (background), with previously published values from remote areas, including mountains regions[49,62,63], showed that most elements are in the same order of magnitude. The elements Co, Cs, Eu, Hg, K, Mn, Rb, Sb, Th, U and Zn are much lower than the previously reported. For the elements Al, Br, Ce, Cl, Cr, Hf, La, Na and V, which are commonly related with soil and marine origins, the values are in the higher. This confirms that background lichen samples are under elemental composition of other pristine places in the world, but with small influences of marine environment and deposition of particles from pedogenic origin. For south and north surfaces in winter exposure period and west surface in all year exposure, almost all the minimum concentrations are higher compared with the levels of control sample, meaning that all samples along the altitude transept accumulate elements during the exposure time.

Table 7.2a. Mean,maximum and minimum elemental contents (mg/kg) in each surface of the Pico mountain in summer exposure period obtained for the transplanted lichen data set. First column results of background concentration (mean value - standard deviation) of lichen collected in an unpolluted area of São Miguel island – Azores. N = 3 for lichen set before exposure (except for elements without STDV, where N = 1, due to values below the limit detection in two samples); N = 1 for transplanted lichens.

	Before-Exposure	**Summer exposure**					
		West		**South**		**North**	
	Mean±STDV	**Mean**	**max-min**	**Mean**	**max-min**	**Mean**	**max-min**
Al	2264±98	2714	4370-1800	2817	4400-1530	3213	4480-1520
As	0.18	0.23	0.34-0.17	0.26	0.40-0.17	0.26	0.40-0.16
Ba	14.99	19.9	28.5-13.7	22.5	33.6-15.4	23.8	32.7-17.2
Br	25.0±3.8	26.0	30.6-22.0	26.8	32.3-20.6	29.5	35.2-19.4
Ca	1692±426	1854	2630-1340	2999	5510-1490	3861	14900-1500
Ce	3.52	4.77	7.17-2.99	5.31	7.59-3.37	5.81	7.88-2.70
Cl	651±22	724	1300-482	696	943-431	721	1310-451
Co	0.31±0.03	0.42	0.65-0.25	0.48	0.73-0.27	0.54	0.67-0.33
Cr	2.86±0.14	3.61	6.56-2.35	3.92	6.10-1.85	4.60	5.79-3.01
Cs	0.068	0.088	0.134-0.061	0.088	0.113-0.066	0.098	0.119-0.073
Eu	0.078	0.088	0.123-0.065	0.099	0.142-0.057	0.107	0.132-0.059
Fe	992±255	1560	2489-972	1724	2588-834	1972	2572-1126
Ga	NA	1.25	1.92-0.67	1.40	2.05-1.04	1.63	2.65-0.66
Hf	0.28±0.07	0.33	0.59-0.18	0.35	0.53-0.16	0.42	0.58-0.24
Hg	0.14	0.194	0.270-0.119	0.170	0.244-0.090	0.179	0.246-0.108
I	11.7±2.1	13.6	16.5-9.8	12.8	15.5-7.6	14.2	19.2-8.8
K	2094	2052	2715-857	2615	3214-1115	2632	3261-2222
La	2.09±0.43	2.19	3.13-1.58	2.46	3.36-1.48	2.70	3.37-1.51
Lu	0.011	0.014	0.019-0.011	0.017	0.024-0.010	0.018	0.023-0.010
Mg	1276±424	1611	2240-1040	1704	2170-1270	1797	2140-1090
Mn	19.7±0.08	46.1	63.4-28.5	51.4	58.8-46.2	46.7	70.1-21.2
Na	1015±182	774	1301-486	820	1166-393	1077	1454-762
Nd	1.50	1.85	2.69-1.21	1.97	2.93-1.15	2.10	3.04-1.18
Rb	3.89	4.75	6.38-2.74	6.06	7.90-2.83	6.24	7.60-5.04
Sb	0.080±0.040	0.11	0.15-0.09	0.11	0.15-0.07	0.11	0.16-0.08
Sc	0.30±0.08	0.44	0.72-0.27	0.48	0.70-0.23	0.54	0.71-0.30
Se	0.52±0.12	0.63	0.78-0.47	0.63	0.87-0.48	0.69	0.81-0.49
Sm	0.31	0.36	0.49-0.26	0.40	0.56-0.23	0.44	0.55-0.24
Sr	14.02	24.3	32.6-18.4	27.7	36.2-16.9	29.2	41.6-17.8
Ta	0.14	0.174	0.341-0.093	0.187	0.292-0.093	0.227	0.319-0.121
Tb	0.036	0.043	0.060-0.031	0.045	0.062-0.024	0.050	0.075-0.025
Th	0.23	0.27	0.48-0.16	0.27	0.42-0.13	0.33	0.45-0.19
Ti	343±20	418	705-273	439	671-211	515	774-258
U	0.17±0.004	0.12	0.15-0.10	0.17	0.18-0.15	0.15	0.22-0.12
V	5.59±0.11	6.20	9.75-4.26	6.70	9.50-5.54	7.03	9.25-3.86
Yb	0.065	0.099	0.126-0.069	0.110	0.151-0.074	0.121	0.151-0.067
Zn	20.1±5.2	29.2	41.9-23.7	32.4	52.6-21.3	31.2	40.1-26.2
Zr	13.4	16.1	32.0-6.9	15.0	22.1-7.7	17.1	23.7-9.5

NA: Not available.

Table 7.2b. Mean,maximum and minimum elemental contents (mg/kg) in each surface of the Pico mountain in winter exposure period obtained for the transplanted lichen data set. First column results of background concentration (mean value - standard deviation) of lichen collected in an unpolluted area of São Miguel island – Azores. N = 3 for lichen set before exposure (except for elements without STDV, where N = 1, due to values below the limit detection in two samples); N = 1 for transplanted lichens.

	Before-Exposure	**Winter exposure**					
		West		**South**		**North**	
	Mean±STDV	**Mean**	**max-min**	**Mean**	**max-min**	**Mean**	**max-min**
Al	2264±98	3482	4840-1650	3955	6310-2580	5984	10900-3650
As	0.18	0.31	0.47-0.17	0.40	0.74-0.25	0.48	0.76-0.32
Ba	14.99	32.3	47.3-11.8	36.5	48.6-30.3	52.1	80.9-34.9
Br	25.0±3.8	33.5	39.2-22.2	36.4	41.3-31.1	45.5	58.2-32.5
Ca	1692±426	4463	6620-1560	7598	20600-3970	6744	13000-2990
Ce	3.52	5.85	10.18-2.66	8.04	12.19-5.60	9.93	14.4-5.56
Cl	651±22	1073	1860-670	989	2130-516	1385	2810-625
Co	0.31±0.03	0.61	1.03-0.24	0.70	1.27-0.45	1.58	5.92-0.52
Cr	2.86±0.14	5.56	9.36-2.24	5.72	10.46-3.37	19.58	94.2-4.64
Cs	0.068	0.121	0.183-0.052	0.126	0.184-0.084	0.154	0.194-0.126
Eu	0.078	0.113	0.190-0.056	0.146	0.220-0.105	0.208	0.395-0.112
Fe	992±255	2151	3698-937	2536	4497-1521	4528	11930-2098
Ga	NA	1.32	2.06-0.39	1.63	2.48-1.01	2.52	3.89-1.75
Hf	0.28±0.07	0.44	0.73-0.18	0.50	0.90-0.31	0.76	1.07-0.44
Hg	0.14	0.245	0.365-0.153	0.209	0.246-0.147	0.276	0.369-0.160
I	11.7±2.1	18.8	26.1-13.8	18.8	21.9-11.4	21.3	25.8-16.6
K	2094	1743	2474-1214	1920	3001-1332	2271	2940-1656
La	2.09±0.43	2.88	4.75-1.32	3.79	5.56-2.91	4.71	6.39-2.82
Lu	0.011	0.018	0.027-0.010	0.026	0.038-0.017	0.031	0.054-0.020
Mg	1276±424	2215	3090-1390	2375	3070-1830	3936	10500-2150
Mn	19.7±0.08	54.2	88.6-18.0	73.9	99.1-44.5	98.8	192.0-64.5
Na	1015±182	1502	2092-1031	1275	2089-785	2328	3830-1130
Nd	1.50	2.39	3.78-1.07	3.17	5.64-2.08	3.76	4.62-2.35
Rb	3.89	4.74	7.39-3.05	5.57	7.97-3.74	6.62	9.56-4.09
Sb	0.080±0.040	0.13	0.22-0.08	0.16	0.20-0.11	0.20	0.28-0.14
Sc	0.30±0.08	0.61	1.03-0.25	0.71	1.26-0.43	1.43	4.68-0.58
Se	0.52±0.12	0.81	1.03-0.45	0.99	1.65-0.69	1.03	1.48-0.81
Sm	0.31	0.44	0.76-0.22	0.63	0.92-0.45	0.80	1.25-0.46
Sr	14.02	40.7	54.0-15.7	49.2	61.2-38.1	65.3	93.2-50.4
Ta	0.14	0.240	0.408-0.100	0.262	0.466-0.158	0.408	0.613-0.242
Tb	0.036	0.053	0.087-0.023	0.072	0.110-0.050	0.095	0.171-0.050
Th	0.23	0.37	0.61-0.17	0.43	0.70-0.26	0.58	0.78-0.36
Ti	343±20	505	789-209	592	1030-362	1019	2280-500
U	0.17±0.004	0.19	0.26-0.14	0.24	0.29-0.16	0.24	0.35-0.15
V	5.59±0.11	7.51	9.80-4.07	8.28	11.80-6.64	14.36	36.40-7.12
Yb	0.065	0.120	0.190-0.063	0.173	0.263-0.124	0.218	0.348-0.129
Zn	20.1±5.2	28.5	35.8-17.9	35.8	60.6-17.6	32.9	47.3-23.8
Zr	13.4	18.4	33.7-9.1	23.2	39.9-13.3	33.1	46.2-21.0

NA: Not available.

Table 7.2c. Mean,maximum and minimum elemental contents (mg/kg) in each surface of the Pico mountain in the all year exposure period obtained for the transplanted lichen data set. First column results of background concentration (mean value - standard deviation) of lichen collected in an unpolluted area of São Miguel island – Azores. N = 3 for lichen set before exposure (except for elements without STDV, where N = 1, due to values below the limit detection in two samples); N = 1 for transplanted lichens.

	Before-Exposure	**AllYearexposure**					
		West		**South**		**North**	
	Mean±STDV	**Mean**	**max-min**	**Mean**	**max-min**	**Mean**	**max-min**
Al	2264±98	NA	NA	2920	4230-1900	3841	7970-1760
As	0.18	0.37	0.48-0.29	0.32	0.51-0.15	0.36	0.62-0.25
Ba	14.99	36.3	48.2-23.1	24.3	33.9-19.1	38.7	60.5-25.5
Br	25.0±3.8	38.1	48.8-29.9	26.7	36.0-17.6	33.6	43.9-27.5
Ca	1692±426	4613	7495-2280	4877	6620-2170	7781	15200-2690
Ce	3.52	7.86	10.5-5.49	5.00	6.42-3.28	6.66	9.62-3.50
Cl	651±22	NA	NA	904	1460-540	1816	4410-714
Co	0.31±0.03	0.73	1.01-0.53	0.49	0.65-0.33	1.14	4.60-0.34
Cr	2.86±0.14	6.42	9.59-4.08	4.02	5.71-2.48	12.75	61.5-2.45
Cs	0.068	0.111	0.138-0.087	0.100	0.152-0.052	0.107	0.141-0.075
Eu	0.078	0.147	0.20-0.11	0.100	0.136-0.061	0.139	0.29-0.068
Fe	992±255	2623	3783-1852	1817	2479-1172	3041	9265-1092
Ga	NA	1.88	2.16-1.51	1.53	2.16-1.11	2.52	3.78-1.26
Hf	0.28±0.07	0.56	0.84-0.38	0.37	0.53-0.24	0.44	0.68-0.22
Hg	0.14	0.219	0.30-0.17	0.162	0.224-0.125	0.175	0.24-0.11
I	11.7±2.1	NA	NA	14.7	25.9-7.8	17.8	28.7-10.9
K	2094	2113	3011-1240	1848	2627-1171	1789	3280-1103
La	2.09±0.43	3.79	5.47-2.69	2.39	3.19-1.52	3.08	4.83-1.68
Lu	0.011	0.022	0.029-0.016	0.016	0.024-0.008	0.022	0.040-0.013
Mg	1276±424	NA	NA	1941	2480-1230	2893	7070-1610
Mn	19.7±0.08	NA	NA	45.4	81.4-23.1	82.6	133-54.4
Na	1015±182	1676	2973-1160	1060	1351-736	1745	2949-915
Nd	1.50	2.98	3.99-2.22	1.95	2.67-1.34	2.66	4.52-1.50
Rb	3.89	5.24	7.23-3.18	5.03	6.83-3.70	5.02	8.79-2.18
Sb	0.080±0.040	0.14	0.19-0.12	0.11	0.13-0.08	0.13	0.17-0.08
Sc	0.30±0.08	0.72	1.01-0.50	0.49	0.67-0.29	0.99	3.78-0.28
Se	0.52±0.12	0.79	1.02-0.60	0.90	1.76-0.42	0.86	1.15-0.61
Sm	0.31	0.59	0.79-0.41	0.41	0.58-0.25	0.54	1.01-0.28
Sr	14.02	45.8	64.3-30.5	34.1	45.0-20.7	52.3	77.5-31.6
Ta	0.14	0.298	0.447-0.206	0.190	0.279-0.136	0.222	0.306-0.108
Tb	0.036	0.068	0.088-0.048	0.048	0.061-0.027	0.060	0.109-0.031
Th	0.23	0.45	0.66-0.32	0.31	0.43-0.20	0.33	0.45-0.18
Ti	343±20	NA	NA	461	613-344	636	1600-291
U	0.17±0.004	0.21	0.30-0.15	0.20	NA	0.19	0.22-0.16
V	5.59±0.11	NA	NA	5.85	9.07-3.51	9.80	25.80-4.50
Yb	0.065	0.158	0.206-0.113	0.118	0.162-0.078	0.153	0.312-0.080
Zn	20.1±5.2	27.3	33.3-17.3	33.2	47.4-24.8	26.5	39.7-16.4
Zr	13.4	23.4	36.3-16.4	15.9	26.4-9.4	19.6	36.9-10.1

NA: Not available.

The ratio between the concentration of each element in exposed samples to that of control samples before exposure was used to investigate the accumulation rate of lichens thalli, as well as to compare the results of the three exposure periods at the different exposed surfaces along the altitude transept on Pico mountain, in order to detect any underlying trend between them[64]. Data were interpreted on the EC, assumed to be 30% from the ratio of 1, corresponding to a difference higher than, at least, one STDV of the mean value of background value. i.e: 0-0.3 correspond to severe loss of elements in exposed lichens; 0.3-0-7 correspond to loss; 0.7-1.3 correspond to normal; 1.3-1.8 correspond to accumulation; and >1.8 correspond to severe accumulation.

According to the EC ratios expressed in Table 7.3, the concentrations of transplanted lichens in winter time of exposure present accumulation or sever accumulation in all the surfaces of the mountain, in all elements except K. Furthermore, K was the only case of loss in all year period at 750 m and 1,000 m. In north surface, the EC ratio for most elements is higher compared with the other surfaces, presenting accumulation or severe accumulation for almost all of the elements except Br, Cl, I and Na, which are all marine related elements. At this same period, accumulation is higher in south surface for Ca, Fe and Zn only. The accumulation is less prominent on west surface. The summer period has the lowest EC ratios, however correspond to levels considered accumulated or sever accumulated in west surface on 17 elements (As, Ba, Ce, Co, Cr, Cs, Fe, Hg, Lu, Mg, Mn, Sb, Sc, Sr, Ta, Yb and Zn); in south surface on 23 elements (except Al, Br, Cl, Hg, I, K, La, Na, Sc, Tb, Th, V and Zr); and in north surface on all elements except Br, Cl, I and Na, similar to winter period.

In all year period, lichen transplants do not reflect an increment of accumulation relatively to each partial periods of exposure. Although, they present higher EC ratio than the corresponding first part of the exposure time (summer period), but lower when compared with winter period. This might mean that the 12 months period (all year) exceeds the time at which the long-term transplant accumulates the chemical elements, equalizing the concentrations that in situ lichen takes, i.e. the 'equilibrium time'[65]. An influence of drier weather in first part of exposure time, or an influence of the time to preserve the "memory" of a given environmental availability condition[32] or saturation due to an accumulation of some particular chemical element could explain that fact. The exception to the last is the progressive accumulation in the west surface of Ba, Ca, Ce, Eu, Hf, La, Lu, Na, Nd, Rb, Sb, Sm, Sr, Ta, Tb, Th, Yb and Zr and in the south surface of Cl and Mg. The explanation for higher accumulation in winter time of exposure is probably related to the higher lichen vitality in this period of the year, due to propitious weather conditions, namely higher levels of precipitation and humidity, which is in agreement with a previously study at Pico mountain in terms of lichen vitality[61]. These conditions are favorable to the growth and mineral uptake of lichen transplants.

The EC ratios determined in function of the different altitudes at the three periods of exposure are presented in Table 7.4. The values along the altitude present significant heterogeneity between them.

Table 7.3.Average values of exposed-to-control ratio (EC) of the transept in west, south and north surface of the Pico mountain in summer, winter and all year exposure periods. Underlined values correspond to accumulation during exposure and bold values correspond to severe accumulation. Data for Ga and U was not presented due to values below detection limit in the lichens before exposure and in most of the transplanted samples.

	Al			**As**			**Ba**			**Br**			**Ca**			**Ce**			**Cl**			**Co**			**Cr**		
	W	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**	**W**	**S**	**N**
Summer	1.2	1.2	1.4	1.3	1.5	1.5	1.3	1.5	1.6	1.0	1.1	1.2	1.1	**1.8**	**2.3**	1.4	1.5	1.7	1.1	1.1	1.1	1.3	1.5	1.7	1.3	1.4	1.6
Winter	1.5	1.7	**2.6**	1.7	**2.3**	**2.7**	**2.2**	**2.4**	**3.5**	1.3	1.5	**1.8**	**2.6**	**4.5**	**4.0**	1.7	**2.3**	**2.8**	1.6	1.5	**2.1**	**1.9**	**2.2**	**5.0**	**1.9**	**2.0**	**6.8**
AllYear	1.3	1.7	NA	**2.1**	**1.8**	**2.1**	**2.4**	1.6	**2.6**	1.5	1.1	1.3	**2.7**	**2.9**	**4.6**	**2.2**	1.4	**1.9**	1.4	**2.8**	NA	**2.3**	1.6	**3.6**	**2.2**	1.4	**4.5**
		Cs			**Eu**			**Fe**			**Hf**			**Hg**			**I**			**K**			**La**			**Lu**	
Summer	1.3	1.3	1.4	1.1	1.3	1.4	1.6	1.7	1.7	1.2	1.3	1.5	1.4	1.2	1.3	1.2	1.1	1.2	1.0	1.2	1.3	1.0	1.2	1.3	1.3	1.6	1.7
Winter	**1.8**	**1.9**	**2.3**	1.5	**1.9**	**2.7**	**2.2**	**2.6**	**4.6**	1.6	**1.8**	**2.7**	1.7	1.5	**2.0**	1.6	1.6	**1.8**	0.8	0.9	1.1	1.4	**1.8**	**2.3**	1.7	**2.4**	**3.0**
AllYear	1.6	1.5	1.4	**1.9**	1.3	**1.8**	**2.6**	**1.8**	**3.1**	**2.0**	1.3	1.6	1.6	1.2	1.2	NA	1.3	1.5	1.0	0.9	0.9	**1.8**	1.1	1.5	**2.1**	1.5	**2.1**
		Mg			**Mn**			**Na**			**Nd**			**Rb**			**Sb**			**Sc**			**Se**			**Sm**	
Summer	1.3	1.3	1.4	**2.3**	**2.6**	**2.4**	0.8	0.8	0.9	1.2	1.3	1.4	1.2	1.6	1.6	1.3	1.3	1.4	1.5	1.6	**1.8**	1.2	1.2	1.3	1.2	1.3	1.4
Winter	1.7	**1.9**	**3.1**	**2.8**	**3.8**	**5.0**	1.5	1.3	**2.3**	1.6	**2.1**	**2.5**	1.2	1.4	1.7	1.6	**2.0**	**2.5**	**2.0**	**2.4**	**4.8**	1.6	**1.9**	**2.0**	1.4	**2.0**	**2.6**
AllYear	1.5	**2.3**	NA	NA	**2.3**	**4.2**	1.7	1.0	1.7	**2.0**	1.3	**1.8**	1.3	1.3	1.3	1.7	1.4	1.6	**2.4**	1.6	**3.3**	1.5	1.7	1.7	**1.9**	1.3	1.7
		Sr			**Ta**			**Tb**			**Th**			**Ti**			**V**			**Yb**			**Zn**			**Zr**	
Summer	1.7	**2.0**	**2.1**	1.3	1.4	1.7	1.2	1.2	1.4	1.2	1.2	1.4	1.2	1.3	1.5	1.1	1.2	1.3	1.5	1.7	**1.9**	1.5	1.6	1.6	1.2	1.1	1.3
Winter	**2.9**	**3.5**	**4.7**	**1.8**	**1.9**	**3.0**	1.5	**2.0**	**2.6**	1.6	**1.8**	**2.5**	1.5	1.7	**3.0**	1.3	1.5	**2.6**	**1.9**	**2.7**	**3.4**	1.4	**1.8**	1.6	1.4	1.7	**2.5**
AllYear	**3.3**	**2.4**	**3.7**	**2.2**	1.4	1.6	**1.9**	1.3	1.7	**1.9**	1.3	1.4	NA	1.3	**1.9**	NA	1.0	**1.8**	**2.4**	**1.8**	**2.4**	1.4	1.7	1.3	**1.8**	1.2	1.5

NA: Notavailable

Table 7.4. Average values of exposed-to-control ratio (EC) of the three surfaces (west, south and north) along the different altitudes at the Pico mountain in summer, winter and all year exposure periods. Underlined values correspond to accumulation during exposure and bold values correspond to severe accumulation. Data for Ga and U were not presented due to values below detection limit in the lichens before exposure and in most of the transplanted samples.

		Altitude (m)										
		50	**250**	**500**	**750**	**1,000**	**1,250**	**1,500**	**1,750**	**1,900**	**2,050**	**2,250**
Al	**Summer**	1.1	1.1	1.5	1.3	1.7	1.0	1.2	1.3	1.1	**1.9**	1.1
	Winter	**2.4**	**1.8**	**1.8**	1.4	**2.0**	**2.7**	**1.9**				
	AllYear	1.5	1.3	1.1	1.5	1.3	**2.2**	1.6				
As	**Summer**	1.3	1.2	1.4	1.2	1.7	1.5	**1.9**	1.1	1.4	1.4	1.1
	Winter	**2.0**	**1.8**	**2.3**	1.6	**2.6**	**2.6**	**3.4**				
	AllYear	1.6	1.4	**2.3**	**1.8**	**2.0**	**2.4**	**2.6**				
Ba	**Summer**	1.5	1.2	**1.8**	1.3	1.7	1.3	1.6	**1.9**	1.0	1.3	1.3
	Winter	**3.6**	**2.3**	**2.6**	**2.3**	**2.6**	**2.9**	**2.6**				
	AllYear	**1.9**	**1.8**	**2.4**	**2.2**	**2.0**	**2.7**	**2.4**				
Br	**Summer**	1.0	1.2	1.2	1.1	1.2	0.9	1.2	1.1	0.9	1.2	1.0
	Winter	1.4	1.5	**1.9**	1.5	1.6	1.4	1.7				
	AllYear	1.0	1.2	1.4	1.3	1.4	1.3	1.6				
Ca	**Summer**	1.6	1.0	1.1	1.1	1.2	**4.4**	1.3	1.1	1.6	1.3	1.0
	Winter	**3.3**	**2.0**	**2.2**	**3.1**	**3.5**	**7.9**	**3.5**				
	AllYear	**2.6**	1.4	**3.1**	**4.5**	**3.8**	**5.7**	**2.7**				
Ce	**Summer**	1.3	1.5	1.4	1.4	**1.9**	1.3	1.7	1.2	1.5	1.7	1.2
	Winter	**2.9**	**2.0**	**2.1**	1.5	**2.1**	**2.6**	**3.1**				
	AllYear	1.6	1.6	**1.9**	1.6	1.6	**2.4**	**2.4**				
Cl	**Summer**	0.9	**1.8**	1.1	1.1	1.0	1.2	0.8	1.0	0.9	1.1	1.0
	Winter	1.5	**2.6**	**2.7**	**2.1**	1.4	1.3	0.9				
	AllYear	**2.1**	**3.9**	1.3	**2.8**	1.7	1.1	**1.8**				
Co	**Summer**	1.5	1.3	1.6	1.4	**1.9**	1.4	1.5	1.4	1.4	1.6	1.3
	Winter	**3.4**	**1.9**	**2.3**	1.7	**2.2**	**7.6**	**2.5**				
	AllYear	**2.0**	1.6	**2.1**	1.7	1.6	**6.3**	**2.2**				
Cr	**Summer**	1.4	1.1	1.5	1.3	**1.9**	1.2	1.6	1.3	1.2	1.5	1.2
	Winter	**3.2**	**1.8**	**2.1**	1.6	**2.2**	**12.0**	**2.5**				
	AllYear	**1.8**	1.4	**2.1**	1.5	1.4	**8.6**	**2.1**				
Cs	**Summer**	1.2	1.2	1.5	1.4	**1.8**	1.3	1.5	1.2	1.1	1.2	1.1
	Winter	**2.4**	1.6	**2.0**	**1.8**	**2.0**	**1.8**	**2.5**				
	AllYear	1.5	1.5	1.6	1.5	1.6	0.9	1.8				
Eu	**Summer**	1.2	1.2	1.3	1.1	1.6	1.0	1.3	1.2	1.3	1.4	1.0
	Winter	**2.5**	1.7	**1.8**	1.3	**1.8**	**2.7**	**2.4**				
	AllYear	1.4	1.2	1.6	1.4	1.4	**2.5**	**2.0**				
Fe	**Summer**	1.6	1.5	**1.9**	1.7	**2.4**	1.3	**1.9**	**1.8**	1.7	**2.0**	1.0
	Winter	**3.9**	**2.3**	**2.8**	**1.9**	**2.7**	**5.4**	**3.1**				
	AllYear	**2.2**	**1.9**	**2.6**	**1.9**	**1.8**	**4.8**	**2.5**				
Hf	**Summer**	1.1	1.1	1.5	1.3	**1.8**	0.8	1.5	1.3	1.3	1.4	1.0
	Winter	**2.8**	**1.8**	**2.1**	1.3	**2.0**	**2.2**	**2.3**				
	AllYear	1.5	1.4	**1.9**	1.4	1.3	**2.0**	**1.8**				
Hg	**Summer**	0.8	1.1	1.6	1.3	1.6	0.8	1.4	1.4	1.2	1.7	**1.8**
	Winter	1.3	1.5	**2.3**	**1.8**	**2.2**	1.5	1.7				
	AllYear	1.2	1.2	1.5	1.2	1.2	1.3	1.5				
I	**Summer**	1.0	1.3	1.1	1.3	1.3	0.9	1.1	1.4	0.9	1.3	1.2
	Winter	**1.8**	1.7	1.7	1.5	**1.9**	1.4	**1.8**				
	AllYear	1.4	1.1	1.3	**1.9**	1.1	1.0	**1.9**				
K	**Summer**	1.3	1.4	1.3	1.2	1.1	1.2	1.3	0.8	0.9	0.7	0.5
	Winter	1.2	1.1	1.0	0.7	0.9	0.8	1.0				
	AllYear	1.1	1.3	1.1	0.6	0.6	0.8	0.8				
La	**Summer**	1.1	1.2	1.2	1.1	1.5	1.0	1.3	1.1	1.2	1.2	0.9
	Winter	**2.3**	1.6	1.7	1.2	1.7	**2.1**	**2.2**				
	AllYear	1.3	1.2	1.5	1.3	1.3	**1.9**	**1.8**				

Table 7.4. (continuation)

		50	**250**	**500**	**750**	**1,000**	**1,250**	**1,500**	**1,750**	**1,900**	**2,050**	**2,250**
Lu	**Summer**	1.3	1.6	1.5	1.4	**1.8**	1.3	**1.9**	1.4	1.5	1.4	1.2
	Winter	**3.0**	**1.9**	**2.1**	1.7	**2.1**	**3.1**	**3.0**				
	AllYear	1.5	1.4	**2.1**	1.5	**1.8**	**2.6**	**2.3**				
Mg	**Summer**	1.2	1.3	1.4	1.3	1.5	1.4	1.3	1.4	0.8	**1.8**	1.3
	Winter	**2.4**	**1.8**	**1.8**	1.6	**2.1**	**4.0**	**1.9**				
	AllYear	1.7	1.7	1.4	1.7	1.5	**3.3**	**1.9**				
Mn	**Summer**	1.7	**2.1**	**2.4**	**2.8**	**2.6**	**2.4**	**2.4**	**3.0**	**2.3**	**3.2**	**2.5**
	Winter	**3.4**	**3.8**	**2.9**	**3.6**	**3.7**	**6.1**	**3.1**				
	AllYear	**2.7**	**2.9**	**2.0**	**3.8**	**3.4**	**4.8**	**3.3**				
Na	**Summer**	0.8	1.0	1.1	0.9	1.1	0.6	0.9	0.8	0.7	0.8	0.4
	Winter	**2.1**	1.7	**2.4**	1.1	1.6	**1.9**	1.4				
	AllYear	1.4	1.7	**2.0**	1.1	1.1	1.7	1.3				
Nd	**Summer**	1.2	1.3	1.4	1.3	1.7	1.0	1.5	1.3	1.2	1.2	1.1
	Winter	**2.9**	**1.8**	**1.8**	1.5	**1.8**	**2.3**	**2.7**				
	AllYear	1.3	1.5	1.6	1.4	1.5	**2.2**	**2.2**				
Rb	**Summer**	1.7	1.5	1.7	1.6	1.5	1.6	1.4	1.0	1.1	0.9	0.7
	Winter	**1.9**	**1.8**	1.6	1.0	1.2	1.2	1.4				
	AllYear	1.5	**1.9**	1.7	0.9	0.8	1.1	1.2				
Sb	**Summer**	1.3	1.4	1.4	1.3	1.4	1.1	1.6	1.2	1.4	1.4	1.4
	Winter	**2.4**	**2.3**	**2.2**	1.7	**1.9**	1.7	**2.4**				
	AllYear	1.6	1.6	**1.8**	1.4	1.5	1.4	**1.9**				
Sc	**Summer**	1.5	1.3	**1.8**	1.6	**2.2**	1.2	1.7	1.6	1.5	**1.8**	1.4
	Winter	**3.6**	**2.1**	**2.6**	**1.8**	**2.4**	**6.4**	**2.9**				
	AllYear	**2.0**	1.6	**2.2**	1.7	1.6	**5.7**	**2.3**				
Se	**Summer**	1.1	1.1	1.4	1.3	1.6	1.2	1.3	1.4	0.9	1.3	1.1
	Winter	**1.8**	1.4	1.7	1.7	**2.3**	1.6	**2.5**				
	AllYear	1.2	1.2	1.7	1.7	**1.9**	1.4	**2.5**				
Sm	**Summer**	1.2	1.3	1.3	1.2	1.6	1.0	1.5	1.2	1.3	1.4	1.0
	Winter	**2.6**	**1.8**	**1.9**	1.4	**1.8**	**2.4**	**2.6**				
	AllYear	1.4	1.3	1.6	1.5	1.5	**2.3**	**2.1**				
Sr	**Summer**	1.7	1.7	**1.9**	**1.8**	**2.2**	**2.2**	**2.1**	**2.0**	**2.0**	**1.8**	1.6
	Winter	**4.0**	**2.6**	**3.6**	**3.4**	**3.9**	**4.9**	**3.7**				
	AllYear	**2.5**	**2.0**	**3.4**	**3.2**	**3.3**	**4.4**	**3.2**				
Ta	**Summer**	1.2	1.3	**1.8**	1.5	**2.1**	0.9	1.6	1.4	1.3	1.5	1.2
	Winter	**3.0**	**2.0**	**2.4**	1.5	**2.3**	**2.5**	**2.5**				
	AllYear	1.7	1.6	**2.1**	1.6	1.4	**2.1**	**1.9**				
Tb	**Summer**	1.2	1.2	1.2	1.2	1.5	1.1	1.5	1.2	1.4	1.4	0.9
	Winter	**2.6**	**1.8**	**1.9**	1.3	1.7	**2.7**	**2.5**				
	AllYear	1.4	1.2	1.6	1.4	1.4	**2.2**	**2.1**				
Th	**Summer**	1.0	1.1	1.5	1.3	**1.8**	0.8	1.3	1.3	1.2	1.3	1.1
	Winter	**2.6**	**1.8**	**2.1**	1.4	**2.0**	**2.0**	**2.3**				
	AllYear	1.5	1.3	1.8	1.4	1.4	**1.8**	**1.8**				
Ti	**Summer**	1.2	1.1	1.6	1.3	**1.8**	1.0	1.3	1.3	1.1	**2.1**	1.1
	Winter	**2.5**	**1.9**	**1.8**	1.2	**2.0**	**3.2**	**2.0**				
	AllYear	1.3	1.4	1.2	1.4	1.3	**2.8**	1.7				
V	**Summer**	1.0	1.2	1.2	1.2	1.4	1.2	1.0	1.2	0.9	1.7	1.2
	Winter	**1.9**	1.7	1.6	1.3	1.6	**3.1**	1.3				
	AllYear	1.3	1.2	0.9	1.4	1.1	**2.6**	1.2				
Yb	**Summer**	1.6	1.7	1.7	1.6	**2.0**	1.4	**1.9**	1.5	1.6	**1.8**	1.4
	Winter	3.3	2.4	**2.4**	**1.9**	**2.4**	**3.2**	**3.3**				
	AllYear	**1.9**	1.6	**2.2**	**2.0**	**1.9**	**3.1**	**2.7**				
Zn	**Summer**	1.5	1.3	1.5	1.5	1.6	1.5	**2.2**	1.4	1.3	1.4	1.3
	Winter	1.6	1.2	1.5	1.4	**2.0**	1.4	**2.5**				
	AllYear	1.4	1.2	1.7	1.3	1.4	1.7	1.5				
Zr	**Summer**	1.0	1.1	1.4	1.2	**1.8**	0.8	1.2	1.4	1.2	1.4	0.9
	Winter	**2.5**	**1.8**	**1.9**	1.3	1.7	**1.9**	**2.2**				
	AllYear	1.3	1.2	1.7	1.4	1.1	**1.9**	1.5				

In Table 7.5 there is an indication of the altitude where the maximum accumulation was reached for each period of lichen exposure. As expected, and in accordance with previous studies on air masses characterization in Pico mountain[12], the EC ratios below 750 m (under the marine layer), represent an accumulation or sever accumulation in Br, Cl, I and Na. At 50 m, in winter period, high EC ratios of Ba, Eu, Hf, La, Nd, Rb, Sm, Ta, Th, Yb and Zr indicate a potential influence of local soil contamination. This also occurs at 1,250 m in samples from winter and all year period, and at 2,050 m in summer period. At 1,500 m, due to a high accumulation of some anthropogenic related elements (As, Br, Ce, Cs, Hg, Lu, Sb, Se and Zn), all the three exposure periods indicate that the environments to which the transplanted thalli were exposed, were polluted by the elements from an anthropogenic source from long-range transport. Figure 7.2 represents the accumulation of these elements in the different surfaces for the three periods of exposure at 1,500 m. In all year period the values are in the same order of magnitude for all elements except for Se, which is higher in south. That diference is determined during winter period. In fact, in winter period, the influence from south is higher for all elements (As, Ce, Cs, Se and Zn) except for Sb, which is more accumulated in north In summer, the higher influence is from north for As and Sb, and from south for Lu and Zn. Despite the prevailing winds being from west, there may be an influence of soil particles suspended over the other mountain surfaces that can explain the above mentioned. These observations and conclusions will be discussed below in the perspective of elemental enrichment. In all year period, EC ratios are higher in north surface for Br and Sb and in south for As and Cs. In Pico summit (2,250 m) there is a possible contamination of Hg from local volcanic emissions.

The verified significant differences in elemental concentrations among almost all the exposure areas may further emphasize the adequacy of using lichen transplant to monitor pollutants from the atmosphere in high altitudes in remote areas.

In order to evaluate the possibility of local soil particles contribute to the elemental content of transposed lichens, the EF was calculated for 12 elements (Figure 7.3). The EFs between 1 and 10 indicate a moderate enrichment above crustal levels and EFs above 10 indicate that the element is significantly enriched and is originated from natural or anthropogenic emissions other than soil. Only As and Se showed EFs close to 1, suggesting that they were essentially due to soil contamination of the samples. All the other elements with EF higher than 1 cannot be considered strictly related to airborne particles originating from local soils and may be related to long-distance transport from other natural and/or anthropogenic sources or even to a possible selective uptake from the lichen. Ba, Br, Ce, Cl, I, Hg, Sb and Zn display EFs which are significantly enriched at some altitudes of the exposed periods. The Ba values are significantly higher than 1 for all the altitudes except in north surface at 250-750-1,250 m. This element has been used as aproxy for soil dust, but as Pico soils are very poor in Ba when compared with worldwide averages, it is most probable to be viewed as a reliable tracer for automotive emissions in an era of lead banned fuels from long range transport[66]. This is more evident in north surface at 500 and 1,000 m in all year period of exposure. Br, Cl and, at a lesser extent, the I are substantially enriched, especially at lower altitudes. The origin of these elements is most certainly marine and has been invariably found in aerosol samples from the marine and lower troposphere layer in Pico mountain[11,12]. For Cl and I in west and south surface, values of EF follow a descending gradient along the increase of altitude relatively to the sea. Values are higher in winter period, reflecting higher marine resuspension from sea surface due to adverse weather conditions (wind, waves). The transplants display an almost homogeneous enrichment for Hg along all the samples areas, with slight emphasis in west at 500 and 1,000 m and in north at 500 and 1,000 m, confirming the ability of the transplanted lichens to be able to accumulate atmospheric Hg. Usually, it is considered an element of relevant environmental concern with origin on combustion processes. However, in Azores volcanic islands, a natural origin should also be considered. Sb might be associated to the finest airborne particles and can be subjected to long transport phenomena in the higher tropospheric stratus as it was demonstrated in a previously study carried in Pico mountain[11,12] where significant high concentrations of Sb were found especially at high altitudes. Due to the high EFs in this experiment, transplanted lichens also demonstrate the ability to absorb fine particles containing Sb and their potential to evaluate depositional fluxes following airborne transfer from the basis of troposphere. Zn is typically an anthropogenic element, widely regarded as the prime indicator for waste incineration[67]. Because there are no such facilities on Pico Island, and given the relatively strong presence of Zn in the Pico mountain aerosol[11,12] a remote source and further transport into fine particles may certainly account for its enrichment.

The prevailing winds in Pico mountain are from the west and consequently the pathway of polluted air masses arrive from North America. In accordance with EC ratios, discussed above, the highest accumulation of elements occurs in north surface in winter period of exposure. However, as the lichens seem to be significantly enriched with local soil particles due to the wind suspension, it was done a further analysis to the above studied elements concerning the values of EF in the different surfaces (see Table 7.6) and it was found a very clear tendency of enrichment with atmospheric aerosol in the west surface. Indeed, for Hg, Sb and Zn it is the only surface with significant enrichment. The same was observed in Pico summit (2,250 m) for Sb, Hg and Th. This is in agreement with the aerosol study in the same area (11, 12) and puts in evidence the capability of lichen transplants exposed in this area reflecting the long-range transport from anthropogenic pollutants from North America.

Table 7.5., For each exposure period, representation of the altitude where each element reaches the maximum value for EC ratio.

Altitude (m)	**Exposure Period**		
	Summer	**Winter**	**All Year**
50		Ba, Eu, Hf, La, Nd, Rb, Sm, Ta, Th, Yb, Zr	
250	Cl, Na		Cl, Rb
500	Rb	Br, Cl, Hg, Na	Na
750	Ce		I
1,000	Co, Cr, Cs, Eu, Fe, Hf, Na, Nd, Sc, Se, Sm, Sr, Ta, Tb, Th, Yb, Zr,	I	
1,250		Al, Ca, Co, Cr, Fe, Lu, Mg, Mn, Sc, Sr, Tb, Ti, V	Al, Ba, Ca, Ce, Co, Cr, Eu, Fe, Hf, La, Lu, Mg, Mn, Nd, Sc, Sm, Sr, Ta, Tb, Th, Ti, V, Zn
1,500	As, Lu, Sb, Zn	As, Ce, Cs, Sb, Se, Zn	As, Br, Se, Cs, Hg, Sb
1,650	Ba, I		
1,850			
2,050	Al, Mg, Mn, Ti, V		
2,250	Hg		

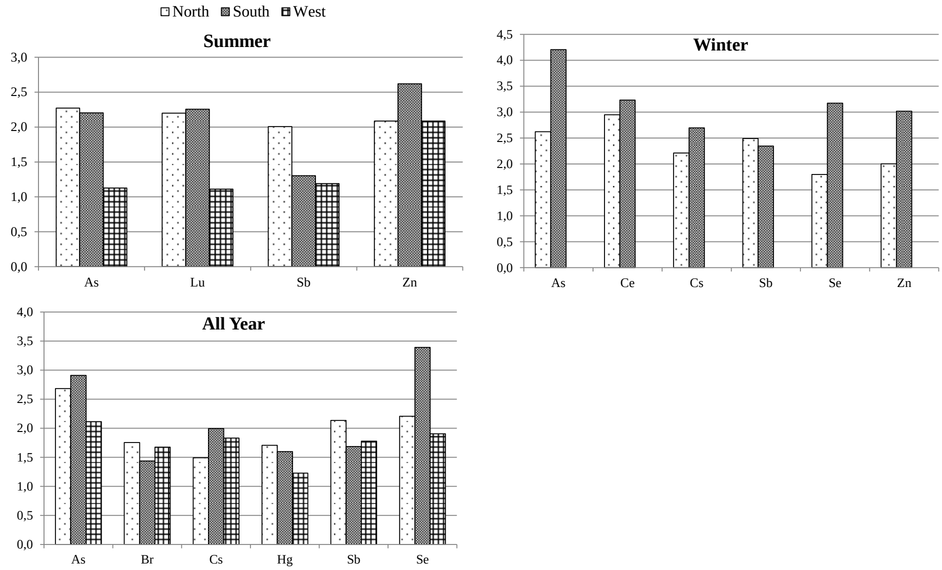


Figure 7.2.*Comparison of EC ratios of some anthropogenic elements at an altitude where values are maxima (1,500 m) at the different surfaces of Pico mountain in the three periods of exposure. No results from west in winter because inadvertently samples lost in the laboratory.*

Table 7.6.Values of EF for elements with maximum EC ratios at 1,500 m in winter period of exposure. Bold values correspond to higher EF values.

Surface	**Elements**								
	As	**Br**	**Ce**	**Cs**	**Hg**	**Lu**	**Sb**	**Se**	**Zn**
North	0.7	2.7	3.8	0.8	4.6	2.5	7.4	1.3	4.8
South	0.8	2.7	3.5	0.8	5.6	2.9	7.0	1.3	7.1
West	**1.3**	**4.9**	**6.2**	**2.0**	**15.3**	**3.9**	**16.4**	**4.1**	**18.4**

In order to better describe the relationship between the elemental concentrations and samples, PCA was performed with varimax rotation and it was assumed that the uncertainties in the elemental concentrations were mainly by local variations in the lichens rather than from analysis. The correlation matrix was created from the values of the variables for 22 elements in the 64 samples in the same data set (42% of soil elements were removed to reduce the amount of variance of these elements in the associated factor). Preliminary tests did not show significant differences between the different exposure periods. The KMO with value of 0.80 confirms the sampling adequacy for the analysis. Bartlett's test of sphericity indicates that correlations between items were sufficiently large for PCA ($p < 0.01$ for the chi-square). An initial analysis was conducted to obtain eigenvalues for each component in the data. Four components had eigenvalues over Kaiser's criterion of 1 and together they explained 83.3% of the variance. Table 7.7 shows the obtained loadings.

Table 7.7.PCA results after normalized varimax rotation for elemental concentration in all lichen transplant data set (N = 64) for 22 elements (variables). Loading and percentage of explained variance (P %) are reported for principal components with eigenvalue >1.

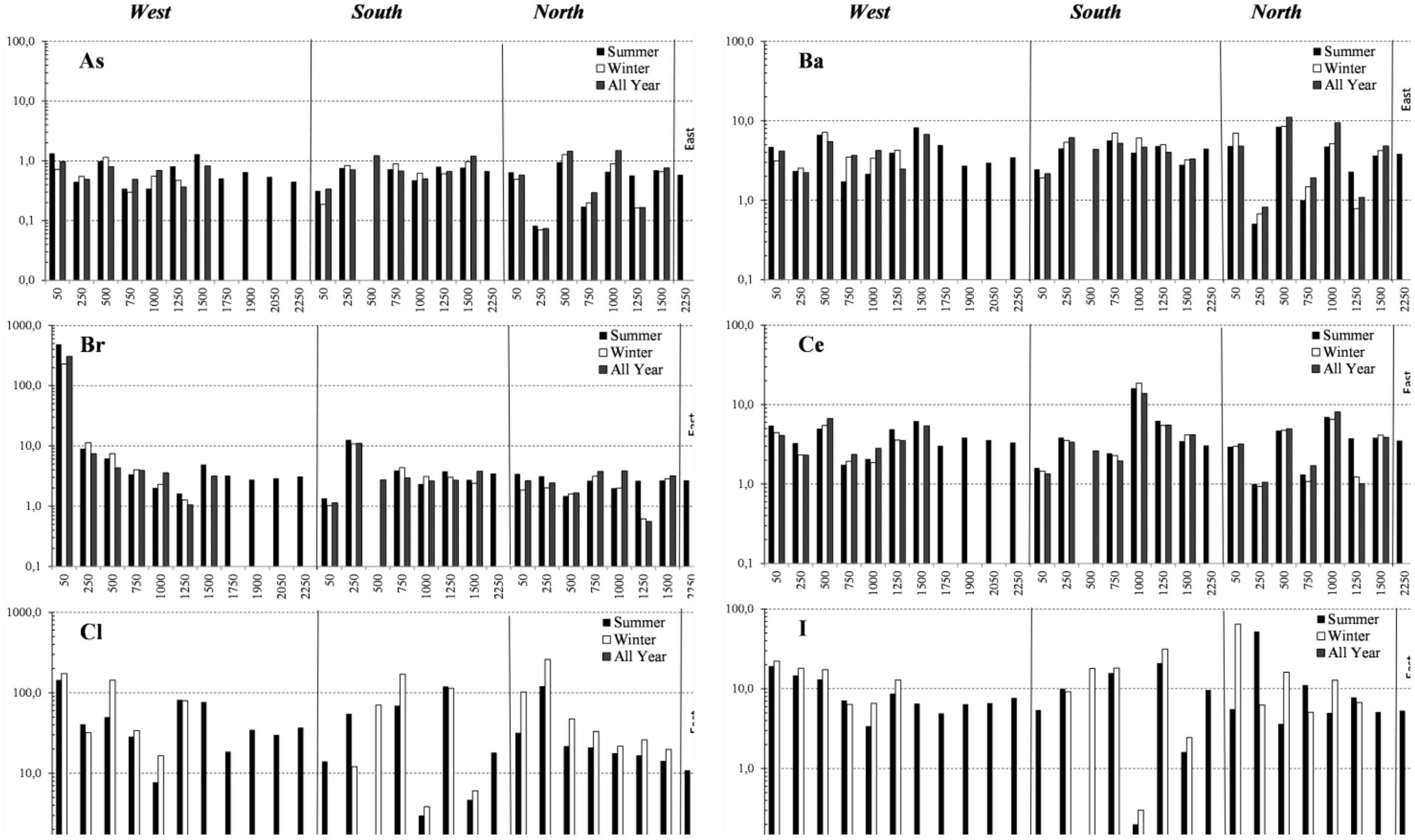
PC1		**PC2**		**PC3**		**PC4**	
(P = 34.5%)		(P = 28.6%)		(P = 11.0%)		(P = 9.3%)	
As	0.69	Co	0.97	K	0.94	Cl	0.80
Ba	0.71	Mg	0.93	Rb	0.91	Zn	-0.87
Br	0.88	Mn	0.76				
Ce	0.72	Sc	0.94				
Cs	0.84	V	0.92				
Hg	0.68						
I	0.78						
La	0.74						
Sb	0.83						
Se	0.79						
Th	0.78						

PC 1 is characterized by high loadings of As, Ba, Br, Ce, Cs, Hg, I, La, Sb, Se and Th and it seems to be a combination of three source types, i.e.: 1) La and Th are elements strongly associated with Saharan dust events[69] and they present severe accumulation along the transplant period of exposure. In the previous studies on aerosols analysis[12], it was also demonstrated a high enrichment of these elements in relation to the soil, especially in the lower free troposphere; 2) Hg is associated with volcanic emissions which in fact are present at this area; 3) Br, I and even Se[70] could be associated with marine origin although it does not appear associated with PC 4. These elements have high enrichment in aerosols from Pico mountain[11,12] and accumulation in transplanted lichen, as seen above, with high EF values; 3) Ba, Ce and Sb, discussed in previous sections, are associated with As and Cs which correspond to elements with no significant accumulation in lichens and with no relevant enrichment, thus it could be associated to local soil origin. Due to influence of air masses originated in the three surrounding continents, which entrain anthropogenic and crustal elements from sources afar, this factor seems to reflect some mineral source probably from Sahara-Sahel region enrichment with secondary pollutants from anthropogenic sources acquired during the transport.

PC 2 is related to Co, Mg, Mn, Sc and V, all soil derived elements, put in evidence the possible resuspension of soil particles of these elements. Emphasis should be done to V because it can also be associated with fuel derivate combustion. Moreover the aerosols at marine boundary in Pico island are frequently enriched with this element[12]; furthermore also the transplanted lichens present high EC ratios in some samples, especially in winter when the wind increases the influence of re-suspended soil. A possible soil contamination with V in Pico mountain should be suggested to further investigation to corroborate this fact.

PC 3 is characterized by high loadings of K and Rb. Judging from the lack of major sea-salt tracers and an absence of accumulation for K in lichen transplanted samples, there is no influence of marine or soil related contamination origin. In Figure 7.4 it is shown the correlation between the PC 3 factor and the altitude. There is a decreasing gradient along the Pico mountain that seems to be negatively related to lichen vitality. The latter is associated to favorable weather conditions for lichens with the increase of altitude, which increase their biomass production inducing a dilution effect of K and Rb concentrations. This is in accordance with a previously study in lichen vitality[61]. In spite of being hardly ascribed, this descending gradient could also be attributed to some marine influence because the EFs for these two elements show significant high values at lower altitudes. This hypothesis was put in evidence before in previous studies[11,12], where aerosols from marine boundary at this area appear with moderate enrichment assigned to marine elements. Concerning Rb, there is no association with major anthropogenic emissions.

Figure 7.3. EFs normalized to Sc of some elements in transplanted lichens at different altitudes (m) and surfaces of Pico mountain, during the three different times of exposure. Calculated using the elemental concentrations of local soils. Between 1,500 -2,050 m only results from west surface are presented and at Pico Summit (2,351 m) North surface is not available (see experimental protocol). Results of all year period for Cl and I are not available.



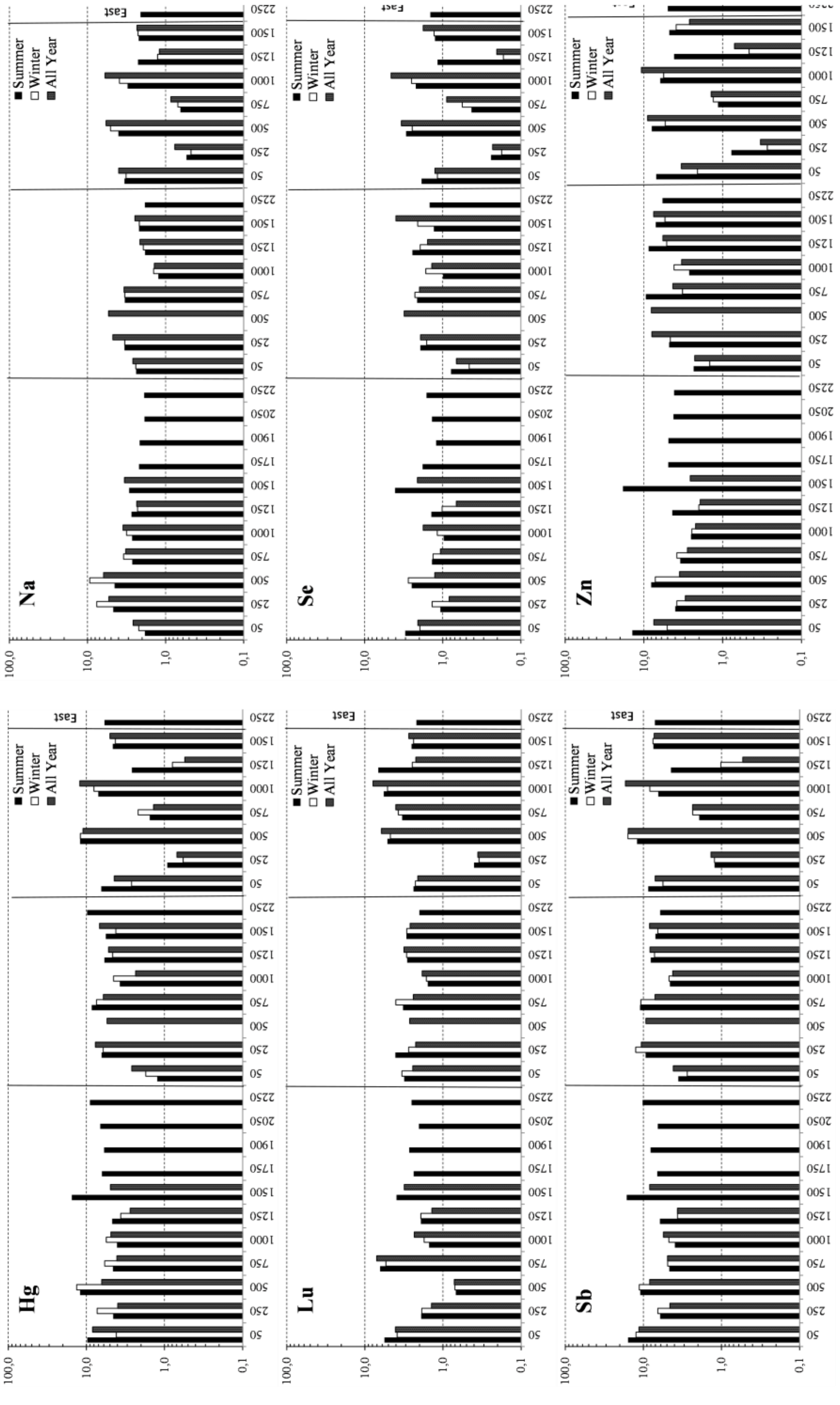


Figure 7.3. (continuation)

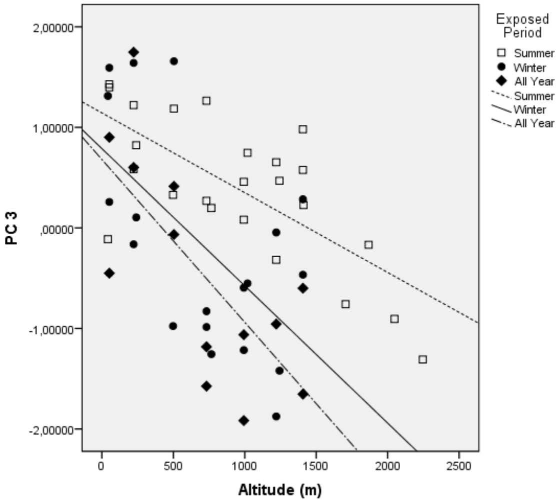


Figure 7.4.Correlation among altitude and the effect of PC 3 (biological or marine related). Variable plots highlighting the three exposure times. Lines represents their relationship (summer: R^2 = 0.51; winter: R^2 = 0.36; all year = R^2 = 0.50).

PC 4 is characterized by high loadings of Cl and Zn (at negative opposition). Zn is typically an anthropogenic element, and widely regarded as the prime indicator for waste incineration[67] or motor vehicle emissions, wear of tires and tear of brake linings and other vehicle metallic parts[68]. Because there are no such activities in relevance in Pico Island or even in Azores area, and given the significant enrichment of Zn in transplanted lichen from Pico mountain, a remote source with further transport and contamination of marine Cl certainly account for its behavior. High enrichment of Zn and Cl in marine layer aerosols were previously reported being thus in agreement with this study[12].

All the extracted factors from PCA were inter-correlated and correlated to the several variables associated (time of exposure, altitude, surface) and none of them show significant differences. However, in accordance with the study done with aerosol analysis which showed a distinct elemental content under two different layers (marine and low troposphere) at Pico mountain, the factors obtained in this study were correlated and it was observed in this lichen data set approximately the same distinction in terms of atmospheric elemental deposition. In Figure 7.5 it is possible to distinguish between the accumulation in marine layer and in lower free troposphere layer.

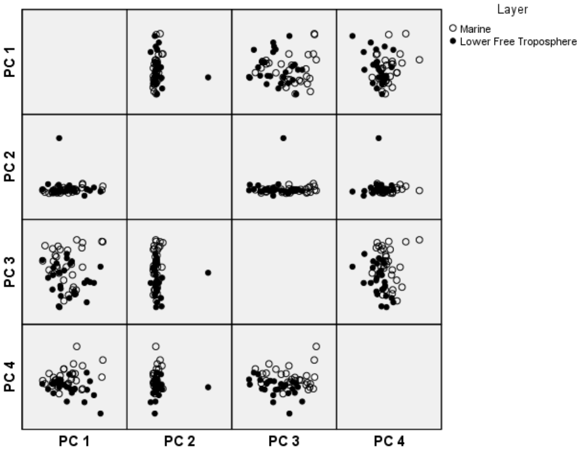


Figure 7.5. *Correlation between the four principal components of factor analysis of the whole lichen data set. Variable plots highlighting the two distinct atmospheric layers at Pico mountain (marine Layer ~0 to 850 m AMSL; Lower Free Troposphere above 850 m AMSL).*

7.4. Conclusions

The present experiments show that lichen transplants could be used to study the elemental atmospheric deposition in altitude transepts, ideally after 6 months of exposure. They also show a distinct elemental accumulation of atmospheric element between two different atmospheric layers (marine and low free troposphere), reflecting a correspondence of an aerosol composition study at the same location. This demonstrates a capability for transplanted lichen to be used as biomonitors of long-range transported elements at high altitudes.

Results of elemental accumulation are dependent of the transplant orientation, meaning that the study of origin of sources of long-range transported elements should consider different types of orientation of the exposure samples to the air masses. In this study high levels of contamination were found mainly in the western surface, corresponding to the prevailing air masses from North America. This samples show high EF values for Ba, Br, Ce, Cl, I, Hg, Sb, Th and Zn.

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Chapter 8

GENERAL DISCUSSION AND OUTLOOK

8.1. Discussion

The first part of the Thesis handled analytical methods. Heavy metals are within the group of agents that are usually harmful to the environment and human health[1,2]. Nowadays, chemical analysis of metals and other elements in environmental samples is carried out using not only classical methods but also nuclear-physics techniques such as NAA[3-5]. NAA is particularly effective when multielemental analysis of a large set of samples is required. NAA has been developed since the middle of the XX century; nowadays there are several improved NAA techniques that allow determining a large range of elements. NAA has been applied in many fields of science in the last 90 years[6-10] due to their complementary advantages compared to other non-nuclear multielement techniques. However, each of the NAA approaches has either advantages or drawbacks: the selection of an appropriate method of analysis is essentially dependent on the required elements, the necessary degree of accuracy, the limits of detection and the flexibility in routine applications. Chapter 2 focused on the study of the performance of several NAA techniques available at the Reactor Institute of Delft and at the Nuclear and Technological Campus in Lisbon, in order to sense accuracy and sensitivity by controlling some experimental parameters. Two different types of samples (lichen and coal fly ash) were used; two different irradiation conditions (thermal neutrons (INAA) and epithermal neutrons (ENAA); measurements were performed with and without CSS, and with different type of detectors (coaxial and well-type). The various NAA approaches permitted the determination of almost all environmentally significant trace elements, however, each approach with different affinity for specific elements. The study indicated that much effort should be devoted to harmonize analytical techniques, in the sense that protocols should be developed and tested ensuring the technique's comparability under all experimental conditions. The general level of performance of each analytical methodology depended on the elements of interest of the sample material. More attention should be paid to obtain better accuracy. Different approaches to the quality control of analyses affected the accuracy, sometimes more than the variance of analytical different methodologies[11].

Considering all the specificities of the different methodologies, the elemental composition of the sample is of effect in improving sensitivity. If samples contain isotopes such as Al, Br, Cl, Co, Fe, Na, Mn, Sc and Zn, the thermal irradiation generates a large activity that affects real time counting, which implies a necessary large distance from the sample to the face of the detector. Distance related improvements of factor 2-3 for several elements at distances between 4 to 9 cm from the face of detector were obtained. However, well-type is less flexible than coaxial when automatization is considered. The use of CSS in samples with these elements with considerable thermal neutron absorption cross section is also advantageous, because of the reduction of signals related to the Compton Effect. However, this analytical methodology is not possible for nuclides that have cascade events occurring in the decay from other nuclides.

If samples have elements with a high ratio of the neutron radioactive capture resonance integral integral (I_0) to the thermal cross-section (σ_{th}), whereas the element producing the interference reaction has a low ratio, using epithermal neutrons in irradiation is advantageous. The results obtained shown a significant decrease of the spectrum background in both type of samples. The use of ENAA with CSS is advantageous in terms of sensitivity to analyze As, I, K, Si and W; NAA with CSS to analyze the Al, Ba, Ce, Cr, Cu, Fe, Hg, Ni, Rb, Sc, Se, Th, Ti, V and Zn.

Depending on the elements of interest an improvement in sensitivity may be accomplished with one of these different methodologies applying optimized experimental conditions. The potential improvement is highly dependent on elemental sample composition. On the other hand, when studies include a large set of samples and the sample variance is unknown, the use of these methodologies could not contribute dramatically to an improvement of the performance of the results. This suggests that more flexibility and routine application could be most advantageous for a set of large numbers of samples instead of purely focusing on more accuracy or sensitivity.

The second part of the present thesis focused on the study of aerosol chemical and morphology characteristics of aerosol in North Atlantic Area (Azores) at LFT and at MBL and to understand the importance of long-range transport from the surrounding continents (Europe, North Africa and Central and North America) on the atmospheric composition, in terms of natural or anthropogenic origin. A further objective was to gain more understanding of physical properties of aerosol (shape and size) that are an important factors for elucidating the mechanism of the long-range transport due to different aerodynamics types[12,13]. Two approaches were followed: 1) In Chapter 3 mean comparisons and EF factors were determined for chemical element concentrations of samples collected on Pico mountain summit (2,225 m AMSL) at LFT and on Serreta-Terceira, Azores (50 m AMSL.) at MBL; 2) In Chapter 4 aerosol particles from samples collected at Pico mountain summit, Azores with origins in North America, Europe, North Africa and Atlantic ocean were analyzed with SEM-EDX methodology. Several chemical elements were detected and a morphological identification was carried out. Overall results from Chapters 3 to 5 suggest that the high-altitude location in the middle of North Atlantic Ocean does not comply with the features of an unpolluted and remote area: this puts on evidence on the existence of a strong transfer of chemical elements between the 3 surroundings continents.

At the same geographic area, the different layers of atmosphere have distinct chemical compositions and the obtained results show that they, somehow, do not significantly mix. The MBL is mainly dominated by marine elements (Br, Cl, I and Na) and local soil particles reflecting the influence of local seawater and soil contamination, and LFT reflects different types of long-range aerosols sources either with natural or anthropogenic origin depending on the geographical orientation of the samples collected. This clearly indicates the possibility of using the PICO-NARE station to study the transport of anthropogenic and natural elements in the central North Atlantic from the surrounding continents. The distinct chemical composition of the two different layers of atmosphere, also suggests the importance of the altitude on the sample collection when the objective is to study the long-range transport of pollution. To understand how aerosols being transported aloft are mixed down to the local surface and in what extent, more efforts should be made to study chemical or physical mixing processes, identify possible local anthropogenic emitters and understand the occurrence of some localized vertical weather mechanisms.

Particle shape affects the aerosol aerodynamic behavior influencing the transport in the atmosphere and therefore the residence time in the atmosphere. Fine particles with spherical shape are expected to have favorable aerodynamic behavior getting more important in terms of long-range transport. The individual particle analysis presented in Chapter 4 suggests that size and shape of aerosols is distinctly different depending on the origin of such aerosols. The aerosol with origin in the Europe region is mainly smaller than 1 µm and appears as smooth and with spherical shape associated to elements typically with anthropogenic origins (Br, C and S). In the North America sample, particles shape is mainly soot aggregate with particulates smaller than 1 µm and rich in some anthropogenic pollutants (Br and U). Single-particles from North Africa are mainly irregularly shaped with diameters less than 5 µm. It appeared that some aggregates with spherical shape and smaller than 1 µm associated to S composition. In the air masses with more local origin (Tropic Cancer area) particles observed have diameters larger than 10 µm with elongate shape. Results confirmed a marine influence. As the particle size is smaller, the greater the distance from the emission source, and the results suggest that the size is determinant with regard to the aerodynamics of the particles and as such the influence on their transport over long distances. The recognition of the particle shape from the source emission could give an approach on prediction of the residence time of aerosols in LFT and its impact on long-distance transport. However, more effort should be devoted to develop model associations and more extended study is needed to effectively support the association between size and shape, and their influence in long-range transport.

The intercontinental aerosol transport over the North Atlantic is a result of the horizontal transport conditions and the vertical transport conditions which are strongly influenced by the Azores anticyclone and the North Atlantic Drift of the Gulf steam. As a result the main atmospheric pathway is from West to East and so the troposphere is most affected by anthropogenic aerosols from North America[14-16]. Also some transport mechanisms and remote impact of African dust exist[17-19]. Considering the many reports in literature, in the North Atlantic atmosphere is estimated that about 96% of the total aerosols are from natural emissions (marine salt, mineral dusts, volcanic and biogenic emissions) and the other 4% result from anthropogenic activities such as biomass combustion and other industrial activities[20]. The chemical data of the 425 aerosol samples, corresponding to a 3 years period, presented in Chapter 5, clearly indicate that, over that period, the predominance of air masses reaching Pico island area is from North and central America, and in general samples are contaminated with several anthropogenic related elements such as As, Br, Mo, Sb, U and Zn. Air masses with a Europe origin contribute with similar chemicals as well, albeit not that often, due to much less prevailing wind from west direction. Crustal associated elements (La, Sm, Hf and Sc) occur associated to Sahara-dust episodes. The association with some anthropogenic elements suggest that North African aerosol is resulting from primary aerosol (mineral origin) transformed in the atmosphere thru photochemical reactions into secondary contaminated aerosol. Instead, and for a few determined elements, the air masses at LFT may even be seen to compare with similar data from moderately-polluted, urban-industrial areas. This knowledge is essential to understand the transport dynamics and main composition of aerosols originating from long distances over central North Atlantic. However, it is important to understand the correspondence of some specific events at the predominant origins from specific emitters and the related chemical composition obtained at the receptor, in order to improve source-recognition. Due to the very high concentrations and EFs for Br, Mo and Sb, higher than other globe areas or higher than surface polluted areas, more effort should be devoted to study the possible progressive increase in troposphere abundance of these high-pollution related elements.

In the third part of the thesis the biomonitoring approach was tested in order to evaluate the use of lichens as an alternative for monitoring air pollution through instrumental techniques. This approach was tested at Pico mountain along different altitudes (50m to 2,050m) in order to get insight into the possibility to identify possible sources of long-range transported elements. This is important because monitoring air pollution through instrumental techniques could be a very complex task to do in remote places where the possibility to study the atmosphere at LFT level exists, and, at the same time, lichens species are generally abundant at different altitudes. This is unprecedented in studies carried out at these altitudes and in this geographic location and could complement several studies that have already demonstrated the usability of this type of biomonitors[21-26].

Chapter 6 focuses on the vitality of exposed lichen samples, which was studied with the aim to evaluate the influence of the different weather conditions (humidity, temperature and precipitation) under different altitudes on the results of elemental accumulation in lichen transplants. The results of electric conductivity measurements[27] suggest that the comparability of lichen vitality may be slightly affected in terms of precipitation, humidity and time to exposure. The high negative correlation with precipitation and humidity suggest that the vitality of the exposed lichens increases as altitude increases and therefore humidity and precipitation. In the most dry season or in the longest series involving the dry season the values of vitality seem to be affected. These observations suggest that any comparison of element concentrations for time-or altitude series should be compared in the ambient conditions corroborating with the many approaches that are reported in bibliography concerning the lichen response in terms of element accumulation/release dependence on vitality[28-30]. However, notwithstanding these fluctuations in electric conductivity values, even in situations of lower vitality, all the present results are in the same order of those reported in unpolluted areas[25,27,30]. In view of this, the vitality influence on the variance of the concentrations of the elements observed between transects at different altitudes may be seen as of limited significance in this study. The elemental uptake can also be affected by the presence of other elements present in the environment. As the concentrations of some pollutants vary with the altitude, more study should be carried out in order to evaluate this influence on elemental uptake. Furthermore, the "memory" of the lichen should be better understood for all the elements of interest[31].

Chapter 7 presents and discusses the results obtained on the 3 different altitude transects. Results show that lichen transplants can be used to study the elemental atmospheric deposition at high altitudes. The concentrations of transplanted lichens present accumulation or sever accumulation at all the surfaces of the mountain. High levels of contamination were found mainly in the western surface, corresponding to the deposition from prevailing air masses from North America. This samples show high EF values for Ba, Br, Ce, Cl, I, Hg, Sb, Th and Zn. The distinct elemental accumulation of atmospheric elements along the different altitudes related to the different atmospheric layers (MBL and LFT), overall reflects a correspondence to the aerosol composition study at the same location, and demonstrates the usability for transplanted lichen to be used as biomonitors of long-range transported elements. In 12 months' time of exposure, lichen transplants do not reflect an increment of accumulation relatively to each 6 months periods of exposure. This data suggest that the lichen elemental uptake is reaching the equilibrium in less than 12 months for most of the elements. An influence of drier weather in the first part of exposure time, or an influence of the time to preserve the "memory" of a given environmental availability condition or saturation due to an accumulation of some particular chemical element could explain that fact[31]. Increasing the knowledge of the evolution of the absorption rate of chemical elements and their relationship with the presence of these elements in the atmosphere would be quite important. Data indicate that higher accumulation occurs in winter time of exposure when higher lichen vitality is observed due to propitious weather conditions, namely higher levels of precipitation and humidity. These conditions are favorable for the growth and mineral uptake of lichen transplants. However, more effort should be made to study the effective influence in elemental concentration variance.

Taking into account the lichen's distinguishing between the concentrations observed in the MBL and the LFT, in agreement with the analysis of the aerosols, the possibility of observing results with periods of exposure up to 6 months, the possibility of using lichens at altitudes above 800 m and up to 2,050 m without major influences on vitality and as such in the variation of the absorption of chemical elements, all suggest the usability of biomonitors to evaluate elemental deposition from long-range air masses transport. The approach may be regarded as effective and advantageous, taking into account that this study was carried out in remote environments with inherent adversities, as far as instrumental monitoring is concerned. The results obtained in this thesis contribute to the increase of biomonitoring approaches. However, further improvements are fundamental on comparability in uptake behavior according to external factors, the study of the correlation between aerosol elemental concentration and finally the study of the lichen dynamics associated to the uptake and release metabolic processes.

The present thesis gives the first approach of using lichens as biomonitors of long-range transported elements at LFT and indicates the possibility to use this methodology at a global scale in order to gain insight about global pollution dynamics.

8.2. Outlook

On basis of the obtained results, the thesis generates several thoughts on approaches in future lichen-based long-range air pollution studies as well the aerosols transport dynamics:

- Comparative studies integrating data of concentrations of the sources present in the main geographical emitting areas and the correspondence to the events verified in the Pico mountain, in order to correlate the occurrence of events;
- Raising this research to a global scale by integrating the values of different similar locations in low troposphere zones, integrating the data in a network;
- Evaluating the effect of the different morphological and chemical characteristics of the particles on the biological mechanisms of absorption that occur in lichens;

- Better understanding models, allowing correlating the elemental concentration in lichens under the different weather conditions with chemical concentrations in the atmosphere;
- Developing statistical models allowing to correlate the elemental concentration in lichens with the aerosol deposition rate at the different altitudes;
- Studying the effect of the element deposition of long-range transported elements on human health;
- Extending this study to the investigation of depositions of other chemical compounds with long-range transport origins.

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LIST OF ABBREVIATIOS

AAS - Atomic Absorption Spectrometry

AGL - Above the Ground Level

AMSL - Above Medium Sea Level

CIELO - Clima Insular à Escala Local

CSS – Compton Suppression System

EC ratio - Exposed-To-Control Ratio

EF - Enrichment Factors

ENAA – Epithermal Neutron Activation Analysis

FEG-SEM - Field Emission Gun - Scanning Electron Microscope

FT - Free Troposphere

HYSPLIT - Hybrid Single-Particle Lagrangian Integrated Trajectory

I_0 – Resonance Integral

IAEA – International Atomic Energy Agency

ICP-ES - Inductively Coupled Plasma-Emission Spectroscopy

ICP-IDMS - Inductively Coupled Plasma - Isotope Dilution Mass Spectrometry

ICP-MS - Inductively Coupled Plasma - Mass Spectrometry

INAA – Instrumental Neutron Activation Analysis

IST-UTL - Instituto Superior Técnico – Technical University of Lisbon

ITN - Technological and Nuclear Institute

k_0-INAA – INAA using k_0 method

KMO - Kaiser-Meyer-Olkin

LFT - Lower Free Troposphere

LOD - Limit of Detection

MBL - Marine Boundary Layer

NAA – Neutron Activation Analysis

NAO - North Atlantic Oscillation

NIST-SRM – National Institute of Standards and Technology - Standard Reference Material

NOAA – National Oceanic and Atmospheric Administration

PC - Principal Component

PCA – Principal Component Analysis

PIXE- Particle Induced X-ray Emission Analysis

PM – Particullate Matter

PMF - Positive Matrix Factorization

REE – Rare Earth Elements

RNAA - Radiochemical NAA

RPI - Portuguese Research Reactor

SEM-EDX - Scanning Electron Microscopy Coupled With Energy Dispersive X-ray Spectrometry

SIPRA – Pneumatic Transfer System

SSMS - Spark Source Mass Spectrometry

STDV – Standard Deviation

SXRF - Synchrotron Radiation XRF

TXRF - Total Reflection XRF

XRF - X-ray Fluorescence Analysis

σ_{th} – thermal cross-section

SUMMARY

The present thesis' topic is the biomonitoring of atmospheric trace elements with attention focused on the long-range transported trace elements. The aim was to provide improved understanding of aerosol characteristics under the atmospheric transport dynamics of Central North Atlantic at different altitudes, and also evaluate the usability of lichen transplants to monitor those long-range transported elements. The study was carried out at Pico mountain in Azores, Portugal. The high altitude of this mountain reaching the Low Free Troposphere and its position in the central North Atlantic were the decisive factors for the selection of this sample site, because it was possible to analyze aerosol deposition from surrounding continents (Africa, Europe and Central-North America) at the layer of the atmosphere where the aerosol transportation occurs, both with sample collectors (active sampling) and with biomonitors (passive sampling). Since the number of samples was several hundreds, the thesis also includes a study on analytical aspects: a comparison of Nuclear Activation Analysis methods, in terms of accuracy, sensitivity and flexibility in routine application. The thesis comprises three main parts, divided in 8 chapters, including the general introduction and the general discussion and outlook: the first part is about a comparison of several NAA approaches under different experimental conditions; the second part is about aerosol characterization and source apportionment; and the third part focused on vitality of transplanted lichens and their usability, the latter in the case study implying several altitudes transects at Pico mountain, aiming at the possible recognition of elemental deposition from long-range pollution sources.

The organization of the 8 chapters in the thesis is as follows:

Chapter 1 is the Introduction of the thesis and presents the current state of the art of NAA methodologies, of aerosol dynamics at the North Atlantic area, and of biomonitoring, and introduces the main issues of the thesis and also presents the corresponding objectives.

Chapter 2 discusses the quality of calibration and detection limits comparing some NAA methodologies, applied with environmental samples. The use of NAA methods and their applications in the life sciences has been on-going for more than six decades. In this chapter emphasis is placed on thermal and epithermal activation with reactor neutrons using Ge semi-conductor detectors (coaxial and well-type) with and without Compton Suppression.

The results of NAA measurements for different types of samples (lichen and coal fly ash) indicated that coaxial detectors in thermal irradiation without Compton Suppression System are the most reasonable choice for processing a set of a large number of samples with large variety in composition.

Chapter 3 is the study of elemental composition of air masses under different altitudes at Azores, Central North Atlantic. Between 8th July 2002 and 18th June 2004, aerosol samples were collected for elemental concentration analysis in Azores, in both the MBL and the LFT, to study the differences of aerosols in different atmospheric altitudes of the Central North Atlantic. On the Pico mountain summit air masses carrying aerosols with anthropogenic (Sb, Br, Mo, U, Se and Tb) and/or natural emissions (Fe, Co, La, Na, Sm, Cr, Zn, Hf, K and Th) were sampled. At the marine boundary layer (Serreta, Terceira Island, Azores), natural aerosols (I, Cl, Na, Br and other soil related elements) were predominant, but combined interpretation of the data (mean comparison and EF factors) of MBL showed a co-existence of the anthropogenic elements Sb and Mo, eventually with similar origins as the ones passing the Pico Mountain summit. Very high concentrations and EF for Sb, Mo and Br in the LFT, higher than other globe areas, confirmed atmospheric long-range transport mainly from west boundary of North Atlantic, and shows the possible accumulation and persistence of those elements in the area due to the presence of Azores high pressures or the Hadley cells effect. A correlation agreement between Fe and Yb and enrichment of rare earth elements (La, Sm, Tb and Yb) and Th in LFT aerosols, reflected mineral dust intrusions from North Africa (Sahara and Sahel region).

Chapter 4 characterizes the individual particles of atmospheric aerosols from Pico mountain. The size, morphology and elemental composition of both mixed samples and single particles were determined with NAA and SEM-EDX in order to achieve any possible consistent relation between their characteristics and the corresponding aerosol’s source origins. Single particles from Europe were shown to reflect contamination with pollutant elements of anthropogenic origin. In the Tropic Cancer air masses all the results confirmed a marine influence. In spite of a clear mineral source, some single-particles from North Africa have aggregates with Sulphur. In the North America sample, particles morphology is mainly soot aggregate and fly ash and rich in pollutants confirming a clear anthropogenic origin. Results from the chemical sample analysis, complemented by single particle analysis with SEM-EDX confirmed that the particle types which were found in the four individual samples could in general be related with the transport pathway and source regions.

Chapter 5 studies the aerosol concentration from remote sources of airborne elements over Pico mountain. Aerosol samples were collected using an aethalometer from 15 July 2001 to 18 April 2004 at the PICO-NARE site in Pico island summit. Concentrations were in the order of magnitude of a moderately polluted urban-industrial site. Elements were predominantly entrained by air masses from North-Central America, and to a lesser extent from Europe and North Africa. PCA and PMF assigned sources related to pollution (traffic, fossil-fuel combustion, mining, industrial processing) and to natural occurrences (crustal, Saharan episodes, marine). Although data uncertainties are relatively high due to the small masses collected in the filters and impurities in them, PMF – which includes the uncertainty – did not prove better than PCA when missing data are replaced by arithmetic means of the determined values for each element.

Chapter 6 reflects the evaluation of the vitality assessment of exposed lichens along different altitudes with the influence of weather conditions. To evaluate the effects of the ambient climatic conditions in lichens vitality along some well oriented transects in different altitudes, lichen transplants of Parmotrema bangii were exposed approximately every 250 m starting from 50 m to 1,500 m during one year period in 3 transects along Pico mountain at Azores; Electric conductivity of leachates, elemental concentrations and the ambient conditions such as temperature, precipitation, humidity and altitude were the compared parameters. According to the obtained values of electric conductivity, vitality may be considered as not seriously affected under different altitudes. In accordance with previous studies, electric conductivity values in the present study showed high negative correlations with precipitation and humidity. The significantly high differences between minimum and maximum electric conductivity values found along the altitude transect prompts the idea that, when comparing elemental concentrations in time or spatial series d a comparison with lichen vitality is required, because the different vitality stages could induce variability in metal uptake.

Chapter 7 addresses the study of lichens as biomonitors of long-range transported trace elements under different altitudes and different air mass influences. A set of transplanted lichen Parmotrema bangii were exposed for 5, 7 and 12 months to assess the deposition of trace elements and their possible origins in Pico mountain. The elemental concentrations of 38 elements were determined in 28 locations over the mountain surface between sea level (50 m – baseline of marine layer) up to the summit (2,250 m - low free troposphere). The EC ratio showed that the concentrations of almost all the elements increased with respect to the control, at all mountain surfaces, especially during winter, with winds causing soil re-suspension and consequent accumulation. Local soil was also analyzed to calculate EF to further assess atmospheric pollution. Samples showed high soil enrichment with exception of Ba, Br, Ce, Cl, I, Hg, Sb, Th and Zn, for which high values were found mainly in the western surface, corresponding to the prevailing air masses origins from North America. Moreover, PCA results showed that major sources of atmospheric elements are soil with anthropogenic contamination, Sahara particles from dust events, re-suspension of local soil, marine elements. Transplanted lichens showed a distinct accumulation of atmospheric elements under the two different layers in accordance with aerosols studies previously completed, suggesting the usability of transplanted lichen as biomonitors of long-range transported elements at high altitudes (LFT).

Chapter 8 presents a brief general discussion and conclusion, and an outline is given for possible future work.

SAMENVATTING

Het onderwerp van dit proefschrift is de biomonitoring van atmosferische spore-elementen waarbij de aandacht is gericht op het lange afstands transport van deze spore-elementen. Het doel was meer inzicht te verkrijgen in de aerosol karakeristieken en de atmospherische transport dynamica van het Centraal Noord Atlantisch gebied, voor diverse hoogten, en ook de evaluatie van de bruikbaarheid van korstmos-transplanten om het lange afstands transport van deze elementen te monitoren.

De studie werd uitgevoerd op Pico Mountain, op de Azoren, Portugal. De grote hoogte van deze berg, die tot aan de "Low Free Troposphere" (LFT) reikt, en zijn positie in de Noord Atlantische Oceaan ware de doorslaggevende factoren om deze bemonsterings-plaats te selecteren, omdat deze het mogelijk maakt aersol depositie te analyseren van omringende continenten (Afrika, Europa en Centraal Noord-Amerika) binnen de atmospherische lagen waar het aerosol transport plaatsvindt, zowel met monster collectors (actieve bemonstering), als met biomonitors (passieve bemonstering). Omdat het om honderden monsters ging, omvat het proefschrift ook een studie naar analytische aspecten: een vergelijking van Neutronen Activerings Analytische (NAA) benaderingen, in termen van accuratesse, gevoeligheid en flexibiliteit in routinematige toepassingen.

Het proefschrift bestaat uit drie delen, opgesplitst in 8 Hoofdstukken, met inbegrip van de Algemene Inleiding en de Algemene Discussie en Vooruitzichten: het eerste deel is over de vergelijking van verschillende NAA benaderingen onder verschillende experimentele omstandigheden, het tweede deel is over de karakteriseringen van aerosolen en brontoekenning, en het derde deel richt zich op de vitaliteit van getransplanteerde korstmossen en hun bruikbaarheid, het laatstgenoemde in een case-studie die verscheidene hoogte-transecten bij Pico-Mountain omvatte, met als doel de mogelijke herkenning van element-depositie vanuit lange afstands verontreinigingsbronnen.

De organisatie van het proefschrift is als volgt:

Hoofdstuk 1 is de Inleiding van het proefschrift en presenteert de huidige state-of-the-art van NAA methodieken, van aerosol dynamica in het Noord Atlantisch gebied, en van biomonitoring, introduceert de voornaamste punten van aandacht van het proefschrift, en geeft de corresponderende doelen.

Hoofdstuk 2 bediscussieert de NAA kwaliteit van kalibratie en detektielimieten, daarbij enige NAA methodieken vergelijkend, toegepast op milieumonsters. Het gebruik van NAA methoden en hun toepassingen in de levenswetenschappen omvat meer dan zes decades. In hoofdstuk 2 wordt de nadruk gelegd op thermische- en epithermische activering met reactor neutronen gebruikmakend van Ge halfgeleider detectoren (coaxiaal en put-type) met- en zonder Compton suppressie.

De resultaten van de NAA metingen voor verschillende monstertypen (korstmos en vliegas) lieten zien dat coaxiale detectoren in thermische activering zonder Compton onderdrukking-systemen de meest redelijke keuze zijn om grote aantallen monsters met grote variabiliteit in samenstelling te hanteren.

Hoofdstuk 3 is de studie naar de element-samenstelling van aerosolen bij verschillende hoogten op de Azoren in het Centraal Atlantisch gebied. Tussen 8 Juli 2002 en 18 Juni 2004 werden aerosol samples verzameld voor de analyse van hun elementsamenstelling op de Azoren, in zowel de Marine Boundary Layer (MBL) als de Lower Free Troposphere (LFT), om de verschillen in aerosolen te bestuderen op diverse hoogten in het Centraal Atlantisch gebied. Op de Pico Mountain werden lucht massa’s met aerosolen gesampled met anthropogene (Sb, Br, Mo, U, Se en Tb) en/of natuurlijke emissies (Fe, Co, La, Na, Sm, Cr, Zn, Hf, K en Th). Bij de MBL (Serrete, Terceira Islands, Azores) waren natuurlijke aerosolen (I, Cl, Na, Br en overige grond-gerelateerde elementen) dominant, maar gecombineerde data-interpretatie (vergelijking van gemiddelden en EF factoren) van de MBL lieten een co-aanwezigheid zien van de anthropogene elementen Sb en Mo, uiteindelijk met dezelfde oorsprong als die die de Pico Mountain top passeren. Heel hoge concentraties en EFs voor Sb, Mo en Br in de LFT, hoger dan in andere wereld-gebieden, bevestigden het atmospherisch lange-afstands transport met name vanuit de westgrenzen van het Noord Atlantisch gebied, en laten de mogelijke accumulatie en persistentie in het gebied zien van deze elementen, vanwege het bestaan van de Azoren hoge druk of het Hadley cells effect. De correlatie tussen Fe en Yb en de verrijking van zeldzame aarden (La, Sm, Tb en Yb) en Th in LFT aerosolen reflecteerden minerale stofintrusies vanuit Noord Afrika (Sahara en Sahel regio’s).

Hoofdstuk 4 behandelt de karakterisering van individuele deeltjes van atmospherische aerosolen van Pico Mountain. De grootte, morfologie en elementsamenstelling van zowel gemengde monsters en individuele deeltjes werden gedetermineerd via NAA en SEM-EDX, om ieder mogelijke consistente relatie te verkrijgen tussen hun karakteristieken en de corresponderende aerosol bron-origine. Van individuele deeltjes vanuit Europa werd aangetoond dat zij contaminatie met verontreinigings-elementen vanuit anthropogene oorsprong reflecteren. In de Kreeftskeerkring-luchtmassa’s bevestigden alle resultaten een mariene invloed. Ondanks een duidelijke minerale bron, bleken sommige individuele deeltjes vanuit Noord Afrika aggregaten te bevatten met zwavel. In het Noord Amerikaanse monster, de deeltjes morfologie is voornamelijk roet en vliegas en het is rijk aan verontreinigingen, welke een anthropogene bron bevestigen. Resultaten van de chemische monsteranalyse, gecomplementeerd met SEM-EDX aan individuele deeltjes, bevestigden dat de deeltjes-typen die gevonden werden in de vier individuele monsters in het algemeen konden worden met deze transportwegen en bron regio's.

In hoofdstuk 5 worden de aerosol concentraties van ververwijderde bronnen van atmosferische elementen over Pico Mountain bestudeerd. Aerosol monsters werden verzameld gebruikmakend van een aethalometer, van 15 Juli 2001 tot 18 April 2004, bij de PICO-NARE plaats bij de PICO eiland top. Concentraties waren in de orde van een gematigd verontreinigde stedelijk-industriele plek. Elementen werden voornamelijk voortgebracht via luchtmassa's vanuit Noord-Centraal Amerika, en in mindere mate vanuit Europa en Noord Afrika. Via PCA en PMF toegekende bronnen waren gerelateerd aan verontreiniging (verkeer, verbranding van fossiele brandstoffen, mijnbouw, industriele processen) en aan natuurlijke aanwezigheid (aardkorst, Sahara episodes, marien). Hoewel de onzekerheid in de data relatief groot was als gevolg van de kleine bemonsterde massa's die gecollecteerd werden in de filters, en de daarin aanwezige onzuiverheden, bleek PMF (die onzekerheid omvatte), niet beter dan PCA als ontbrekende data werden vervangen door aritmetische gemiddelde waarden zoals bepaald voor ieder element.

Hoofdstuk 6 reflecteert de evaluatie van de vitaliteitsbepalingen van op verschillende hoogten blootgestelde korstmossen in relatie met de weersomstandigheden. Om de effecten van de locale klimaatomstandigheden bij enige goed-georienteerde transsecten bij verschillende hoogten op de korstmosvitaliteit te evalueren, werden korstmostransplanten van Parmotrema bangii blootgesteld op ongeveer iedere 250 m, startend bij 50 m tot aan 1,500 m hoogte, gedurende een jaarsperiode in 3 transsecten langs Pico Mountain op de Azoren. De electrische conductiviteit van uitspoelvloeistoffen, elementconcentraties en de locale omstandigheden zoals temperatuur, neerslag, luchtvochtigheid en hoogte waren de te vergelijken parameters. Volgens de verkregen waarden van de elektrische conductiviteit mag vitaliteit als niet serieus beinvloed worden beschouwd bij verschillende hoogten. In overeenstemming met eerdere studies liet de electrische conductiviteit in de huidige studie sterk negatieve correlaties zien met neerslag en met luchtvochtigheid. De significant grote verschillen tussen minimum en maximum waarden voor de electrische conductiviteit zoals gevonden langs hoogte-transsecten geeft voeding aan het idee dat, wanneer elementconcentraties worden vergeleken in tijd- of ruimteseries, een vergelijking met korstmosvitaliteit nodig is, omdat de verschillende vitaliteitsniveaus aanleiding kunnen zijn tot variabiliteit in metaalopname.

Hoofdstuk 7 adresseert de studie naar korstmossen als biomonitors van lange afstands-getransporteerde elementen op verschillende hoogten en verschillende luchtmassa invloeden. Een set van getransplanteerde korstmossen Parmotrema bangii werd blootgesteld in Pico Mountain voor 5,7 en 12 maanden om de depositie van spore-elementen en hun mogelijke origine te bepalen. De elementconcentraties voor 38 elementen werden bepaald op 28 locaties over het bergoppervlak, tussen zeeniveau (50 m – basislaag van de marine laag) tot op de top (2,250 m, LFT). De EC ratio liet een verhoging zien van de concentraties voor nagenoeg alle elementen vergeleken met de controles, op alle bergoppervlakken, met name gedurende de winter, wanner de wind grondresuspensie veroorzaakte en daarmee samengaande accumulatie. Locale grond werd ook geanalyseerd om EF’s te berekenen en atmospherische verontreiniging te determineren. Monsters lieten hoge grondverrijking zien met uitzondering van Ba, Br, Ce, Cl, I, Hg, Sb, Th en Zn, waarvoor hoge waarden voornamelijk werden gevonden in het west-bergoppervlak, corresponderend met de heersende luchtmassa’s afkomstig uit met Noord Amerika.

Bovendien lieten PCA resultaten zien dat belangrijke bronnen van atmospherische elementen bestaan uit grond met anthropogene contaminastier, Sahara deeltjes van stofgebeurtenissen, re-suspensie van locale grond, mariene elementen. Getransplanteerde korstmossen lieten een duidelijke accumulatie zien van atmosferische elementen in de twee lagen, in overeenstemming met de eerder afgeronde studies met aerosols, welke de bruikbaarheid suggereert van getransplanteerde korstmos als biomonitor van lange afstands getransporteerde elementen op grote hoogten (LFT).

Hoofdstuk 8 presenteert een koorte algemene discussie en conclusie en een outline wordrdt gegeven voor moge toekomstig onderzoek.

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CURRICULUM VITAE

Bruno José Henriques Vieira was born on the 29th October 1979 in Ourém, Portugal. He obtained the secondary school level in Natural Sciences. In 2002 he graduated in Environmental Engineering at the University of the Azores. It included a six months period of training that was performed at the Reactor Department of the Nuclear and Technological Institute (ITN) at Sacavém, under the supervision of Prof. M.C. Freitas, where he developed a study and present the final thesis "Analysis of atmospheric trace elements on Terceira Island by biomonitoring". Is also qualified by the University of the Azores in Quality Management (in 2006) and as an Occupational Health and Safety Technician (in 2016).

In 2002 he started research work at ITN, integrated on Atmospheric Elementary Dispersion group, where he developed until 2005 her professional abilities on K_0-INAA (Instrumental Nuclear Activation Analysis) applied to several environmental samples. During this period, in addition to the collaboration in several public and private research projects in the field of Environmental Pollution, he was award with an IAEA (International Atomic Energy Agency) fellowship on Environmental, Health and Nutrition Studies. Was carried out at the "Nuclear Engineering Teaching Laboratory" at the University of Texas at Austin in USA, under the supervision of Prof. Sheldon Landsberger. During this period, he developed her skill and published several papers on the area of biomonitoring, atmospheric aerosols, INAA, ENAA and Compton Suppression System.

During 2005 and 2006 he worked as Air Traffic Official in the SATA airline company. In 2006 he won a fellowship from FCT (portugues Foundation for Science and Technology) to develop her PhD Work as TU Delft student in Environmental Sciences with the thesis "Biomonitor-Reflection of Large-Distance air masses transported trace elements". The work was developed at ITN, supervised by Prof. M.C. Freitas and at the Radiation and Isotopes from Health section of the Department of Radiation Science & Technology at the Faculty of Applied Sciences of the Delft University of Technology (TU Delft) under the supervision of Prof. H.Th. Wolterbeek.

During the PhD journey he developed full time professional activity at some industries in the field of Environmental and Quality management. Between 2006 and 2015 worked as head of Department, supervising several projects related to the ISO 9001, ISO 14001, EMAS III and ISO 12647-2:2007. The results of their work in environmental terms were recognized by obtaining 3 national awards in the industrial area. Since 2015 until now he works at Energy Production Industry (EDA –

Electricidade dos Açores), coordinating and participating in several projects in the area of Environmental and Quality Management. Since 2006 he also performs, as freelancer, activities of Quality and Environmental auditing, studies, projects, consulting and training. He lectured at the University of the Azores as also in other professional schools the subject “Environmental Management”.

B.J. Vieira is author of 9 papers (two are submitted) and co-author of 6 papers in international peer review journals, with about 180 citations. Between 2003 until now he attends to several international conferences in this scientific field where he made 5 oral presentation and 6 poster presentations. Is reviewer of several publications on international scientific journals: Journal of Radioanalytical Nuclear Chemistry, Ecological Indicators, Journal of Environmental Management and Journal of Environment and Bio Research.

In 2011 he was award with the prize “Young Scientist and Student Competitive Award” attributed by the Texas A&M University at the conference “Modern Trends in Activation Analysis-13 (Houston, Texas, USA, 12-20 March).

Her main scientific interests are atmospheric aerosols, biomonitoring, NAA and Environmental and Quality Management.

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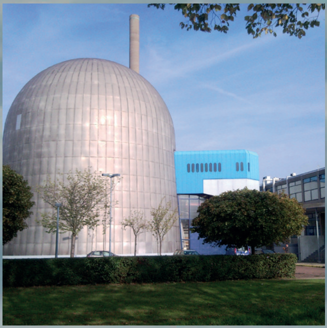

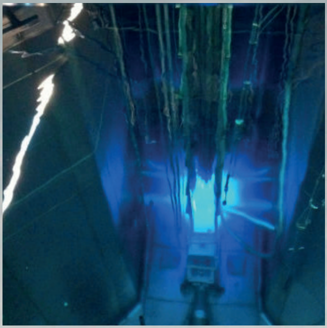

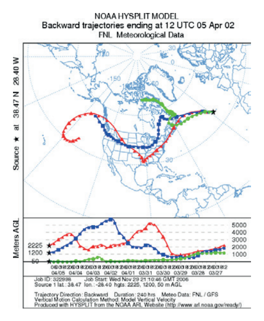

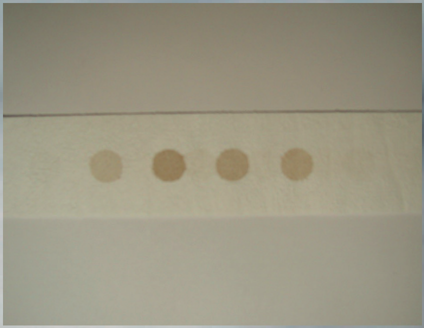

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