

Spatio-temporal evaluation of air quality and its influence on morbidity

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**SPATIO -TEMPORAL
EVALUATION OF AIR QUALITY
AND ITS INFLUENCE ON MORBIDITY**

Ana Margarida Januário Cruz

RADIATION SCIENCE AND TECHNOLOGY DEPARTMENT

Propositions accompanying the thesis
“Spatio-Temporal Evaluation of Air Quality and its Influence on Morbidity”
by Ana Cruz

1. Throughout the 2006-2008 monitoring period, the Council Directive 2008/50/EC and WHO guidelines for airborne particulate matter (PM₁₀ and PM_{2.5}) were exceeded in several monitoring stations. *This thesis (Chapter 2)*
2. Results obtained from the urban traffic monitoring station of Vermoin, located in the Oporto metropolitan area, suggest that that site should be re-classified in the context of ambient environmental effects. *This thesis (Chapter 2)*
3. In analysing the spatial representativeness of the measurement-data from a single sampling station, it is essential to understand the distribution of pollutants in larger geographical areas (Almeida SM, Farinha MM, Ventura MG, Pio CA, Freitas MC, Reis MA, Trancoso MA (2007) Measuring Air Particulate Matter in Large Urban Areas for Health Effect Assessment. *Water Air Soil Poll.* 179:43-55). *This thesis (Chapter 3)*
4. Although PM appears to have small but consistent and significant effects on human health, more study is needed to clarify the relationship between PM and cerebrovascular disease. (*in: J.O. Anderson et al., J. Med. Toxicol.* 8: 166-175, 2012)
5. Both lichen and bark accumulate chemical elements from the atmosphere. However, bark is less sensitive to pollution than lichen, suggesting that bark may have a more general usability. *This thesis (Chapter 3)*
6. High electric conductivity values indicate damaged cell membranes. (*in: J. Garty et al., Responses Environm. Res.* 85A: 159-176, 2001)
7. There are many hypotheses in science that are wrong. That is not a problem, because they are the aperture to find out what is right. Science is a self-correcting process. To be accepted, new ideas must survive the most rigorous standards of scrutiny and evidence.
Carl Sagan
8. Nothing in life is to be feared, it is only to be understood. Now it is the time to understand more, so that we may fear less.
Marie Curie
9. The most important thing about goals is having one.
Geoffrey F. Abert
10. Love does not consist of gazing at each other, but in looking outward together in the same direction.
Antoine de Saint-Exupéry, Airman's Odyssey

These propositions are regarded as opposable and defensible, and have been approved as such by the supervisors Prof. Dr. H. Th. Wolterbeek, Dr.ir. C. Alves and Prof. Dr.ir. M. C. Freitas.

Stellingen behorende bij het proefschrift
“Spatio-Temporal Evaluation of Air Quality and its Influence on Morbidity”
door Ana Cruz

1. Gedurende de 2006-2008 monitoring periode werden de Council Directive 2008/50/EC en WHO richtlijnen voor atmosferische vaste stofdeeltjes (PM₁₀ en PM_{2,5}) in verschillende monitoring stations overschreden. *Dit proefschrift (Hoofdstuk 2)*
2. De resultaten verkregen vanuit het monitoring station voor stedelijk verkeer in Vermoin, gesitueerd in de Oporto stadsregio, suggereren dat deze plek zou moeten worden gereclassificeerd in verband met de milieu-effecten in de onmiddellijke omgeving. *Dit proefschrift (Hoofdstuk 2)*
3. Bij de analyse van de ruimtelijke representativiteit van de meetdata van een enkel meetstation is het noodzakelijk de verspreiding te begrijpen van verontreinigingen in grotere geografische gebieden (Almeida SM, Farinha MM, Ventura MG, Pio CA, Freitas MC, Reis MA, Trancoso MA (2007) Measuring Air Particulate Matter in Large Urban Areas for Health Effect Assessment. *Water Air Soil Poll.* 179:43-55). *Dit proefschrift (Hoofdstuk 3)*
4. Hoewel PM een klein maar consistent en significant effect op humane gezondheid lijkt te hebben, is meer studie nodig om de relatie op te helderen tussen PM en cerebrovasculaire aandoeningen (*in: J.O. Anderson et al., J. Med. Toxicol.* 8: 166-175, 2012)
5. Zowel korstmos als boombast accumuleren chemische elementen vanuit de lucht. Boombast is echter minder gevoelig voor luchtverontreiniging dan korstmos, waardoor boombast een meer algemene toepasbaarheid lijkt te hebben. *Dit proefschrift (Hoofdstuk 3)*
6. Hoge elektrische geleidbaarheid wijst op beschadigde celmembranen. (*in J.Garty et al., Responses Environm. Res.* 85A: 159-176, 2001)
7. Veel wetenschappelijke hypothesen zijn onjuist. Dat is geen probleem, want zij zijn de opening naar het vinden van wat juist is. Wetenschap is een zelfcorrigerend proces. Om geaccepteerd te worden moeten nieuwe ideeën rigoureuze standaarden overleven van onderzoek en bewijsvoering
Carl Sagan
8. Er is niets in het leven om bang voor te zijn, het moet alleen begrepen worden. Nu is de tijd om meer te begrijpen, zodat we voor minder bang hoeven te zijn.
Marie Curie
9. Het meest belangrijke aan doelen is er eentje te hebben.
Geoffrey F. Abert
10. Liefde bestaat niet uit naar elkaar staren, maar uit het gezamenlijk uitkijken in dezelfde richting.
Antoine de Saint-Exupéry, Airman's Odyssey

Deze stellingen worden opponeerbaar en verdedigbaar geacht en zijn als zodanig goedgekeurd door de promotoren Prof. Dr. H. Th. Wolterbeek, Dr.ir. C. Alves and Prof. Dr.ir. M. C. Freitas.

**SPATIO-TEMPORAL EVALUATION OF
AIR QUALITY AND ITS INFLUENCE ON
MORBIDITY**

SPATIO-TEMPORAL EVALUATION OF AIR QUALITY AND ITS INFLUENCE ON MORBIDITY

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof.ir. K.C.A.M Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op
donderdag 23 juni 2016 om 10:00 uur

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*To the memory of my
dear grand mother*

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1 Introduction

1.1 Motivation

Epidemiological studies have consistently shown an association between the incidence of cardiovascular and respiratory diseases and air pollution. The main goals of the study described in the present thesis are to characterise the air quality in Portugal, with a special focus on Lisbon, and to estimate the health risks associated with exposure to atmospheric pollution. Monitoring data from the Portuguese air quality network are used to investigate the spatio-temporal behaviour of air pollutants (AP) and to analyse their relationships. Particular emphasis is on particulate matter (PM), since, on the one hand, it is a constituent less studied than traditional gaseous pollutants and, on the other hand, PM has recently been classified as carcinogenic to humans (Group 1).

Within the thesis, various models are adjusted to air pollution time series in order to have reasonable spatial and temporal short-term outcomes. A biomonitoring survey of Lisbon is carried out to obtain a spatial screening of atmospheric pollution. Considering the uncertainties in judging health effects of AP and given the fact that this kind of investigation is rather inexistent in Portugal, a study is carried out using time series regression models for the entire patient population, and for subgroups, admitted to hospital emergencies for cardiorespiratory illness in Lisbon, during the 2006-2008 period. The thesis is to yield information that supports measures for stricter control at (emission) sources, whether by transport policies or regulatory changes, which in turn should decrease the concentrations of the main atmospheric pollutants and reduce morbidities.

For this purpose, the thesis addresses 3 primary goals:

- 1) Characterisation of air pollution in Portugal with a special focus on PM (mainland and islands);
- 2) Use of biomonitors to assess air pollution in large geographical areas, with a focus on Lisbon;
- 3) New methodologies to evaluate air quality in terms of its associations with diseases, with a focus on Lisbon.

The following paragraphs of Chapter 1 summarise issues in air pollutants and health effects, the air quality in Portugal and Lisbon, the biomonitoring approach in assessing air pollution, and gives a brief design and set-up of the thesis.

1.2 Air Pollutants and Health Effects

Most sources of outdoor air pollution are related to economic activities, such as industry, transport, energy and agriculture, as well as some domestic household activities like heating. This situation is well beyond the control of individuals and demand action by national and international policymakers in sectors like transport, energy waste management, buildings and agriculture.

The air is cleaner today than it has been the last two decades—policy actions and international co-operation have reduced air pollution significantly. For example, sulphur dioxide emissions—the main cause of acid rain—have been cut by more than 80-90%, as stated by the European Commission’s work on "Cleaner air for all", but more action is needed to make further progress as fine particles and ground-level ozone (O₃) still create serious health problems, and emissions continue to harm many natural environments. The same work suggests that, as a result, 420000 Europeans died prematurely from air pollution in 2010 and 6000 in Portugal in 2012.

Although the present study is focused on the 2006-2008 period, outdoor air pollution in both urban and rural areas was estimated to cause 3.7 million premature deaths worldwide per year, still in 2012 (WHO 2015); this mortality is due to exposure to small particulate matter of 10 microns or less in diameter (PM₁₀), which causes stroke, cardiovascular diseases, lung cancer, and both chronic and acute respiratory diseases, including asthma. (WHO 2015) estimates that some 80% of outdoor air pollution-related premature deaths were due to ischaemic heart disease and strokes, while 14% of deaths were due to chronic obstructive pulmonary disease or acute lower respiratory infections; and 6% of deaths were due to lung cancer.

There are many examples of successful policies in transport, urban planning, power generation and industry that cut air pollution: 1) for industry and other economic sectors—clean technologies that reduce smokestack emissions, improved management of urban and agricultural waste, including capture of methane emitted from waste sites as an alternative to incineration (for use as biogas); 2) for transport—shifting to clean modes of power generation, prioritising rapid urban transit, walking and cycling networks in cities as well as rail interurban freight and passenger travel, shifting to cleaner heavy duty diesel vehicles and low-emissions vehicles and fuels, including fuels with reduced sulphur content; 3) for urban planning—improving the energy efficiency of buildings and making cities more compact, and thus energy efficient; 4) for power generation—increased use of low-emission fuels and renewable combustion-free power sources (like solar, wind or hydropower) and co-generation of heat and power, and distributed energy generation (e.g. mini-grids and rooftop solar power generation); 5) for municipal and agricultural waste management—strategies for waste reduction, waste separation, recycling and reuse or waste reprocessing, as well as

Chapter 1 – Introduction

improved methods of biological waste management such as anaerobic waste digestion to produce biogas, low cost alternatives to the open incineration of solid waste; where incineration is unavoidable, then combustion technologies with strict emission controls are critical.

PM affects more people than any other pollutant. The major components of PM are organic carbon, sulphates, nitrates, ammonia, sodium chloride, black carbon, mineral dust and water. The most health-damaging particles are those with a diameter of 10 microns or less (PM₁₀), which can penetrate and lodge deep inside the lungs. Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases, as well as lung cancer.

Air quality measurements are typically reported in terms of daily or annual mean concentrations of PM₁₀ per cubic meter of air volume (m³). Routine air quality measurements typically describe such PM concentrations in terms of micrograms per cubic meter (µg/m³). When sufficiently sensitive measurement tools are available, concentrations of fine particles (PM_{2.5} or smaller) are also reported.

There is a close quantitative relationship between exposure to high concentrations of small particulates (PM₁₀ and PM_{2.5}) and increased mortality or morbidity, both daily and over time. Conversely, when concentrations of fine particulates are reduced, related mortality will also go down—presuming other factors remain the same. This allows policymakers to project the population health improvements that could be expected if particulate air pollution is reduced.

Small particulate pollution have health impacts even at very low concentrations—indeed no threshold has been identified below which no damage to health is observed.

Therefore, the World Health Organisation (WHO) Air Quality Guideline (AQG), published in 2005, aimed to achieve the lowest concentrations of PM possible. The European Member States are required to draw up plans to guarantee compliance with the defined limit values set by the Air Quality Council Directive 2008/50/EC for PM but also other AP. Table 1.2.1 summarizes air quality standards according to European legislation and WHO AQG for PM₁₀, PM_{2.5}, O₃, carbon oxide (CO), nitrogen oxides (NO_x), nitrogen dioxide (NO₂) and sulphur dioxide (SO₂).

If table 1.2.1 interim targets were to be achieved, significant reductions in risks for acute and chronic health effects from air pollution can be expected. Progress towards the guideline values, however, should be the ultimate objective.

The effects of PM on health occur at levels of exposure currently being experienced by many people both in urban and rural areas and in developed and developing countries (WHO 2014a)—although exposures in many fast-developing cities today are often far higher than in developed cities of comparable size.

Table 1.2.1 – Air quality standards according to European legislation and WHO AQG for PM and AP.

		Air Quality Directive (2008/50/EC)	WHO AQG
PM₁₀	Annual mean	Limit value: 40 µg/m ³	20 µg/m ³
	24h-mean	Limit value: 50 µg/m ³ (not to be exceeded on more than 35 times per year)	50 µg/m ³
PM_{2.5}	Annual mean	Target value: 25 µg/m ³	10 µg/m ³
	24h-mean		25 µg/m ³
	8-hour mean		100 µg/m ³
O₃	Maximum daily 8-hour mean	Target value: 120 µg/m ³ (not to be exceeded on more than 25 times per year averaged over three years)	
CO	maximum daily eight hour mean	Limit value: 10 mg/m ³	10 mg/m ³
NO_x	annual limit value for the protection of vegetation		30 µg/m ³
NO₂	Annual mean	Limit value: 40 µg/m ³	40 µg/m ³
	1-hour mean	Limit value: 200 µg/m ³ (not to be exceeded more than 18 times per year)	200 µg/m ³
SO₂	24-hour mean	Limit value: 125 µg/m ³ (not to be exceeded more than 3 times per year)	20 µg/m ³
	1-hour mean	Limit value: 350 µg/m ³ (not to be exceeded more than 24 times per year)	
	10-minutes mean		500 µg/m ³

WHO AQG estimate that reducing annual average of PM₁₀ concentrations from levels of 70 µg/m³, common in many developing cities, to the WHO AQG level of 20 µg/m³, could reduce air pollution-related deaths by around 15%. However, even in the European Union, where PM concentrations in many cities do comply with guideline levels, it is estimated that average life expectancy is 8.6 months lower than it would otherwise be, due to PM exposures from human sources (WHO 2014a). There are serious risks to health not only from exposure to PM, but also from exposure to O₃, NO₂ and SO₂. As with PM, concentrations are often high in the urban areas of low-and middle-income countries. Ozone is a major factor in asthma morbidity and mortality, while NO₂ and SO₂ can also play a role in asthma, bronchial symptoms, lung inflammation and reduced lung function.

The recommended O₃ limit in the 2005 WHO AQG was reduced from the previous level of 120 µg/m³ based on recent conclusive associations between daily mortality and lower O₃ concentrations. Ozone at ground level—not to be confused with the O₃ layer in the upper atmosphere—is one of the major constituents of photochemical smog. It is formed by the reaction with sunlight (photochemical reaction) of pollutants such as NO_x from vehicle and industry emissions and volatile organic compounds (VOCs) emitted by vehicles, solvents and industry. As a result, the highest levels of O₃ pollution occur during periods of sunny weather. Excessive O₃ in the air harm human health, as it can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases. In Europe it is currently one of the AP of most concern. Several European studies have reported that the daily mortality rises by 0.3% and that for heart diseases by 0.4%, per 10 µg/m³ increase in O₃ exposure.

Carbon monoxide is a gas produced by the incomplete combustion of fossil fuels and biofuels. The introduction of catalytic converters in road transport reduced substantially what was once a significant source of CO emissions. Day traffic patterns determine different carbon monoxide concentrations. Urban areas, typically during rush hour at traffic locations, present the highest CO levels. EEA (2014) refers that the CO emission reduction in the 2003–2012 period was 32 % in the 28 European Member States (EU-28) and 27 % in the member countries of the European Environment Agency (EEA-33)¹. In 2012, Europe's main CO source was commercial, institutional and household fuel combustion, responsible for 44 % of total EU-28 countries CO emissions, which rose by 9 %, in the period from 2003 to 2012. The transport sector, which was once the main emitter of CO, present a significant lower value of its CO emissions (61 % from 2003 to 2012), due to the application of the Air Quality Council Directive 2008/50/EC. In contrast to the situation for the NO₂ annual limit value, high concentration levels of CO are few and not widespread. EEA 2014 shows that, with exception for rural stations, where concentrations are very low and close to the detection limit, average CO concentrations have diminished at all monitoring station types. Over the last decade, the CO daily 8-hour maximum concentrations reduced, on average, to approximately one third in Europe. These reductions are in accordance with the reported reduction in total emissions. EEA 2014, based on the available measurements, concluded that the European population's exposure to CO ambient concentrations above the limit value is very localized and infrequent, and is limited to very few areas near traffic and industry and it may lead to heart disease and damage to the nervous system; it can also cause headache and fatigue.

¹ EEA-33 member countries (the EU Member States Belgium, Bulgaria, the Czech Republic, Denmark, Germany, Estonia, Ireland, Greece, Spain, France, Croatia, Italy, Cyprus, Latvia, Lithuania, Luxembourg, Hungary, Malta, the Netherlands, Austria, Poland, Portugal, Romania, Slovenia, Slovakia, Finland, Sweden and the United Kingdom, plus the remaining five EEA member countries, Iceland, Liechtenstein, Norway, Switzerland and Turkey).

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Nitrogen oxides (NO) are a family of gases collectively known as NO_x. EEA 2014 summarize that NO_x emissions and the subsequent deposition of nitrogen contribute to both eutrophication and acidification of ecosystems, which is a bigger problem than the exposure to NO_x ambient concentrations. Contributes to the formation of O₃, with associated climate effects. It also contributes to the formation of nitrate particles, cooling the atmosphere and can lead to damage to buildings.

As an air pollutant, NO₂ has several correlated activities. According to WHO 2014a, short-term concentrations exceeding 200 µg/m³, it is a toxic gas which causes significant inflammation of the airways. Nitrogen dioxide is the main source of nitrate aerosols, which form an important fraction of PM_{2.5} and, in the presence of ultraviolet light, of O₃. The major sources of anthropogenic emissions of NO₂ are combustion processes (heating, power generation, and engines in vehicles and ships). Epidemiological studies have shown that symptoms of bronchitis in asthmatic children increase in association with long-term exposure to NO₂. Reduced lung function growth is also linked to NO₂ at concentrations currently measured (or observed) in cities of Europe and North America (WHO 2014a).

WHO's work on "Ambient (outdoor) air quality and health" (WHO 313 2014) indicate that a proportion of people with asthma experience changes in pulmonary function and respiratory symptoms after periods of exposure to SO₂ as short as 10 minutes. The WHO AQG revision in 2005 of the 24-hour guideline for SO₂ concentrations from 125 to 20 µg/m³ was based on the following considerations: 1) health effects are now known to be associated with much lower levels of SO₂ than previously believed; 2) a greater degree of protection is needed. Although the causality of the effects of low concentrations of SO₂ is still uncertain, reducing SO₂ concentrations is likely to decrease exposure to co-pollutants. According to WHO 2014a, SO₂ is a colourless gas with a sharp odour. It is produced from the burning of fossil fuels (coal and oil) and the smelting of mineral ores that contain sulphur. The main anthropogenic source of SO₂ is the burning of sulphur-containing fossil fuels for domestic heating, power generation and motor vehicles. Sulphur dioxide can affect the respiratory system and the functions of the lungs, and causes irritation of the eyes. Inflammation of the respiratory tract causes coughing, mucus secretion, aggravation of asthma and chronic bronchitis and makes people more prone to infections of the respiratory tract. Hospital admissions (HA) for cardiac disease and mortality increase on days with higher SO₂ levels. When SO₂ combines with water, it forms sulphuric acid; this is the main component of acid rain, which is a cause of deforestation (WHO 2014a).

EEA (2014) argues that to minimise air pollution and its impacts, action at international, European Commission's, national, regional and local levels is required. The national and subnational authorities are very important actors in implementing European legislation. Moreover, these authorities can adopt additional measures to further protect their populations and the environment.

WHO's work on "Measuring health gains from sustainable development" has proposed air pollution indicators as a marker of progress for development goals related to sustainable development in cities and the energy sector and assists Member States in sharing information on successful approaches, on methods of exposure assessment and monitoring of health impacts of pollution.

1.3 Air Quality in Portugal

1.3.1 Preamble

In recent decades, Europe has improved the air quality. Emissions of many air pollutants were controlled and reduced successfully, converging to meet the World Health Organization (WHO), Air Quality Guidelines (AQG) and the Air Quality Directive (2008/50/EC) limit values. The European Directive was transposed into the national ruling in the form of Decree-Law n.º 102/2010, of September 23th. A set of actions settled in four pillars were defined: 1) improvement of evaluation processes of air quality; 2) geo-referenced and stored information with transparency criterion; 3) information availability in almost real time and simplified reporting ; 4) improvement measures of air quality and verification of indicators.

Despite the implemented strategies, several studies and reports (e.g. EEA 2015) show that many cities are still exposed to air pollutants in harmful levels, and that the most dangerous pollutants are fine particles, ozone and nitrogen dioxide. Nevertheless, comparing with the rest of Europe, Portugal is among those with lower PM concentrations, below the European average (EEA 2015).

As referred previously in section 1.2 of this thesis, the Air Quality Council Directive 2008/50/EC and WHO AQG recommend monitoring PM, O₃, CO, NO_x, NO₂ and SO₂ for sustainable ambient air quality assessment and management. Nevertheless, in Portugal, particularly in Lisbon, the priority strategy is to mitigate PM. Several studies show that PM still need special attention due to high concentrations, especially in urban (traffic) and industrial areas (Ramos et al. 2016). SO₂ and CO concentrations have been decreasing to levels that are not a threat to human health (e.g. Cruz et al. 2014). The present preliminary study was performed to accomplish a spatial distribution of PM₁₀, PM_{2.5}, NO₂ and O₃ concentrations and to compare their concentrations with the Air Quality Directive (2008/50/EC) and WHO AQG, for the period of 2006-2008.

1.3.2 Data Treatment

The data used throughout the present thesis were supplied by the Air Quality Monitoring Network (QualAr) of the Portuguese Environment Agency (APA), which provides hourly data of the main atmospheric pollutants, such as PM, NO₂ and O₃ . The database for all

monitoring stations was processed according to the following criteria: 1) Concerning the temporal variability, year by year (2006, 2007 and 2008); 2) type of influence (background, industrial and traffic); 3) type of environment (Oporto and Lisbon-urban and industrial areas, Remaining Areas-rural areas and Islands); 4) geographical perspective: Coastline, Mainland and Islands. Figure 1.3.1 shows the differences between types of studied areas, namely Coastline/Mainland/Islands and Oporto/Lisbon/Remaining Areas. The analysis of variance of four different ways of aggregating data was performed by nonparametrics statistics for a significance level of 0.050. The Kruskal–Wallis test was used for multiple independent groups, whilst the Mann–Whitney test was applied to binary independent groups. All the tests were conducted using the statistical software and data analysis in Excel – XLSTAT, 2013 version. Maps were done using the software ArcGis 9.3. Air mass trajectories were performed by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. Annual means were calculated using Excel.

1.3.3 PM₁₀

The Kruskal–Wallis test was applied to each PM₁₀ annual mean concentration data set. The results demonstrated a significantly statistic p -value = 0.00 for four different ways of aggregating data (Figure 1.3.2) that prove that these new data groups were different from each other. The Mann–Whitney test was applied to compare PM₁₀ concentrations in the different pair groups that are possible to obtain: 1) type of influence (background, industrial and traffic), all had a significantly different statistic value ($p = 0.00$), except for industrial vs traffic ($p = 0.28$); 2) type of environment (Oporto, Lisbon, Remaining Areas and Islands) had a significantly statistic under p -value of 0.05 for Oporto vs Remaining Areas, Oporto vs Islands, Lisbon vs Remaining Areas and Lisbon vs Island, but the results are not statistically different for Oporto vs Lisbon ($p = 0.34$) and Remaining Areas vs Islands ($p = 0.16$); 3) geographical perspective had a significantly different statistic value with $p = 0.00$ in Coastline vs Mainland and Coastline vs Islands. The result was not statistically different in Mainland and Islands ($p = 0.27$); 4) the temporal variability, year by year, had a significantly different statistic value with $p=0.00$ in 2006 vs 2008 and 2007 vs 2008, only 2006 vs 2007 was not statistically different ($p = 0.87$).

Concerning the temporal variability, year by year, the PM₁₀ mean concentrations showed a decreasing trend from 2006 to 2008, as other works demonstrated (e.g. Alves et al. 2010b; Sarmiento et al. 2009; Almeida et al. 2014; Cruz et al. 2014).

Considering the type of influence (background, industrial and traffic), traffic areas present higher PM₁₀ mean concentrations, followed by industrial areas, whilst the lowest values were registered in background areas.

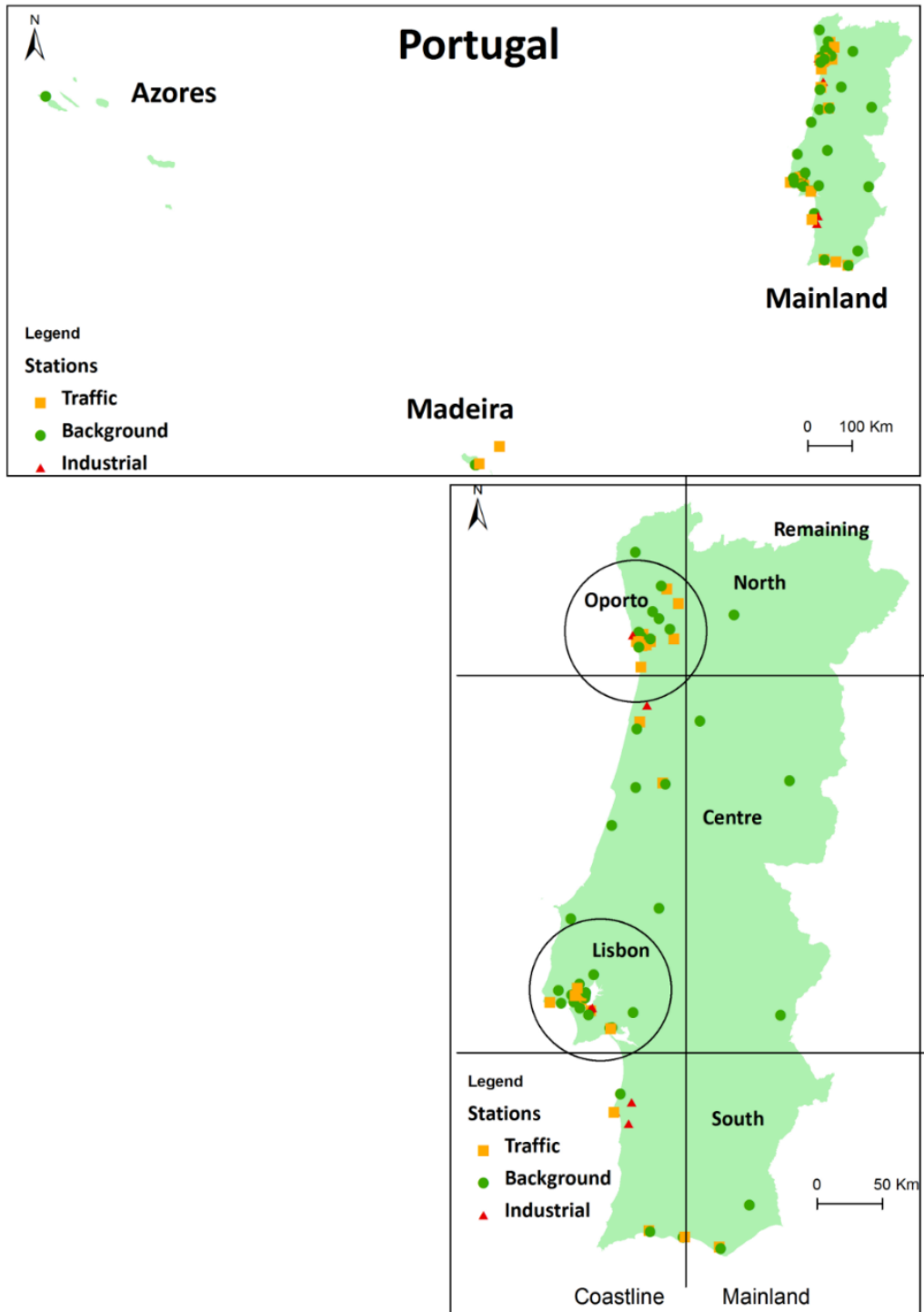


Figure 1.3.1 – Air quality monitoring stations the Portuguese Air Quality Network (QualAr from APA) according to each type of influence.

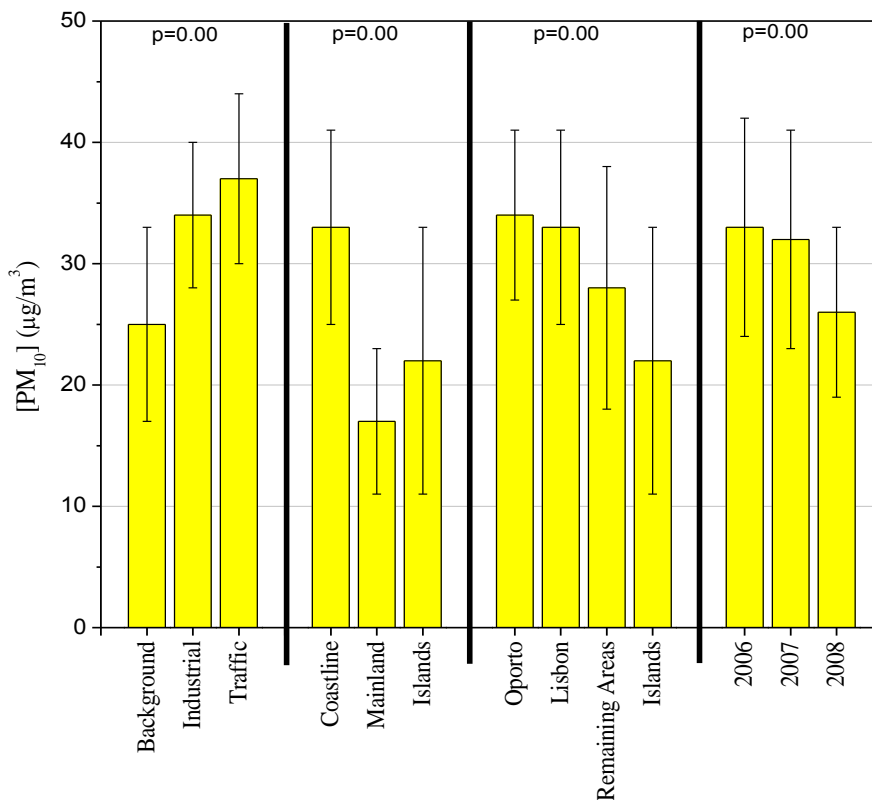


Figure 1.3.2 - Mean PM₁₀ concentrations in each cluster and *p*-value obtained from the Kruskal–Wallis test in each data set.

According to the type of environment, Oporto and Lisbon-urban and industrial areas–presented the highest PM₁₀ mean concentrations compared with remaining areas. Islands registered the lowest PM₁₀ mean concentrations, probably due to the influence of clean air masses over the Atlantic. The high population density and industrial areas concentrated in the Portuguese coast justify the higher PM₁₀ mean concentrations (Cachorro et al. 2006, Cruz et al. 2016 in press).

Some exceedances to the EU limit values and WHO AQG were observed for the annual mean concentrations of PM₁₀ in some of the monitoring stations(mainland and islands), as shown in Figures 1.3.3 and 1.3.4.

Figure 1.3.3 and 1.3.4 show that, regarding PM₁₀ concentrations: 1) in 2006, 21% of the monitoring stations exceeded the PM₁₀ limit value (40 µg/m³). In 2007 and 2008 this percentage decreased to 13% and 3%, respectively; 2) Only Circular Sul, in 2007, surpassed the concentration of 50 µg/m³ for PM₁₀. This monitoring station is influenced by traffic.

The daily time trend of PM₁₀ hourly mean was studied for each type of influence (Figure 1.3.5). Traffic and industrial sites show a typical variability (e.g. Vecchi et al. 2007;

Balakrishnaiah et al. 2011, Carvalho and Prior 1994), with peaks between 10:00 and 13:00 and between 21:00 to 24:00. Often, industrial areas take longer to decrease PM₁₀ concentrations during the night period than traffic areas (Vecchi et al. 2007; Balakrishnaiah et al. 2011; Carvalho and Prior 1994). Traffic areas present higher PM₁₀ concentrations than industrial areas after 21:00. Background areas present smooth daily variability compared with the other two types of influence. This behaviour is typical, as shown in several studies (e.g. Almeida et al. 2011).

The time trends for PM₁₀ daily mean concentrations, during the period of study, are shown in Figure 1.3.6, for each type of influence: traffic, industrial and background. The highest values were registered in traffic influenced areas.

During the studied period, were identified also the days with PM₁₀ mean concentrations higher than the daily limit value (50 µg/m³)² in more than 50% of the monitoring stations of Portugal (mainland and islands).

Air mass trajectories, given by Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPIT) developed by NOAA's Air Resources Laboratory (Draxler et al. 2014), were computed for four days whose PM₁₀ mean concentrations were significantly higher than those stipulated by the European legislation, in more than 80% of the monitoring stations, during the studied period (Figure 1.3.7). There are periods that clearly present simultaneously the highest concentrations for the majority of the national stations. The transport of maritime air mass is usually associated with cleaner air masses from the Atlantic Ocean and with better dispersion conditions of pollutants coming from industrial areas (Almeida et al. 2013b). Nevertheless, high concentrations of AP can be registered under adverse meteorological conditions and low dispersion conditions. This fact can be associated with the transport of Saharan dust or polluted air masses from the West or Southwest of the Iberian Peninsula (Rodríguez et al. 2001). However, high concentrations were also observed for other types of air mass trajectories. In several regions, atmospheric dynamics present specific characteristics that may also cause high levels of PM as a result of the air mass recirculation processes under local and regional cycles. For example, in Spain, Saharan dust outbreaks from long range transport processes have been found to play a key role on the observed levels and exceedances (Querol et al. 2008; Querol et al. 2009; Jiménez et al. 2010; Díaz et al. 2012; Querol et al. 2014; Notario et al. 2014), at least in rural and urban background stations.

Besides the reduction of PM₁₀ in some sampling stations, more mitigation strategies should be applied in order to reduce the PM levels in Portugal. These strategies should focus on traffic and industrial emissions.

² set by the Air Quality Directive (2008/50/EC).

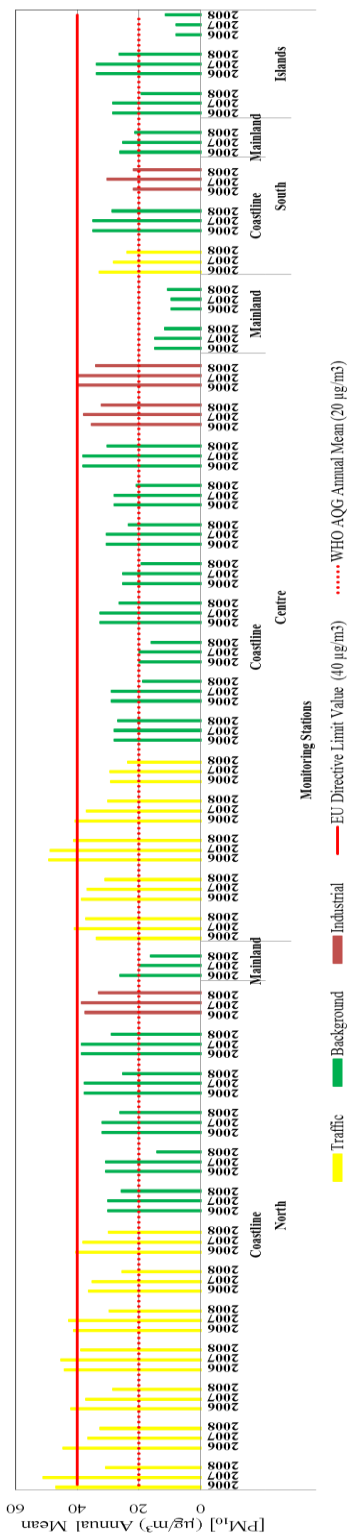


Figure 1.3.3 - Annual mean PM₁₀ concentrations in the years of 2006, 2007 and 2008.

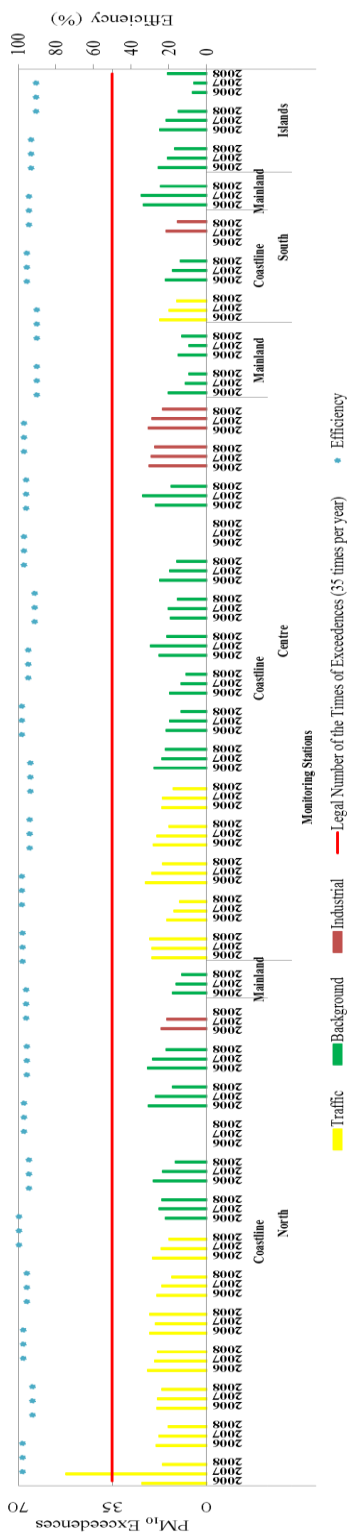


Figure 1.3.4 - Number of days exceeding the daily PM₁₀ concentration limit in the studied cluster (type of influence). Red dash line is the maximum value of exceedences allowed by year.

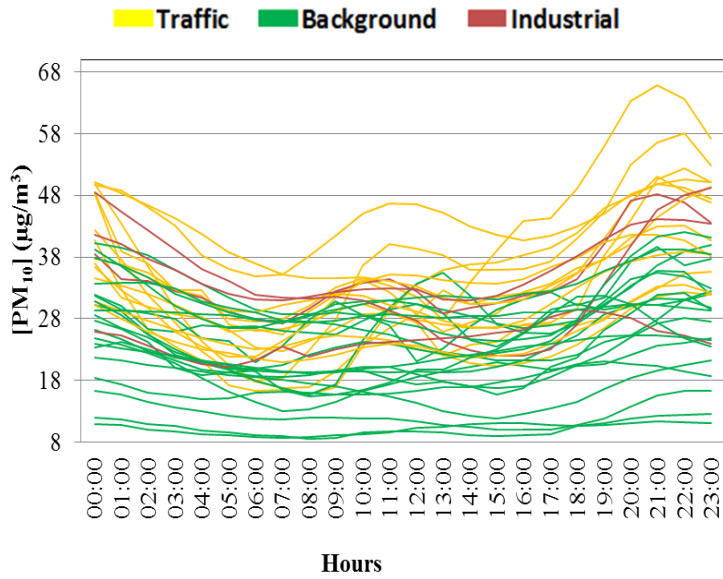


Figure 1.3.5 - Hourly PM₁₀ mean concentrations in the studied cluster (type of influence), for a 24 hours period.

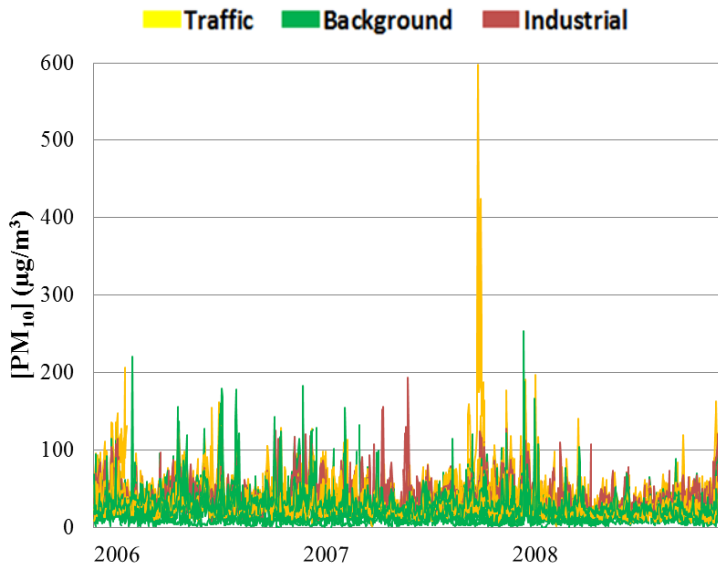


Figure 1.3.6 - Daily PM₁₀ concentrations during the 3 years of the studied period in each cluster (type of influence).

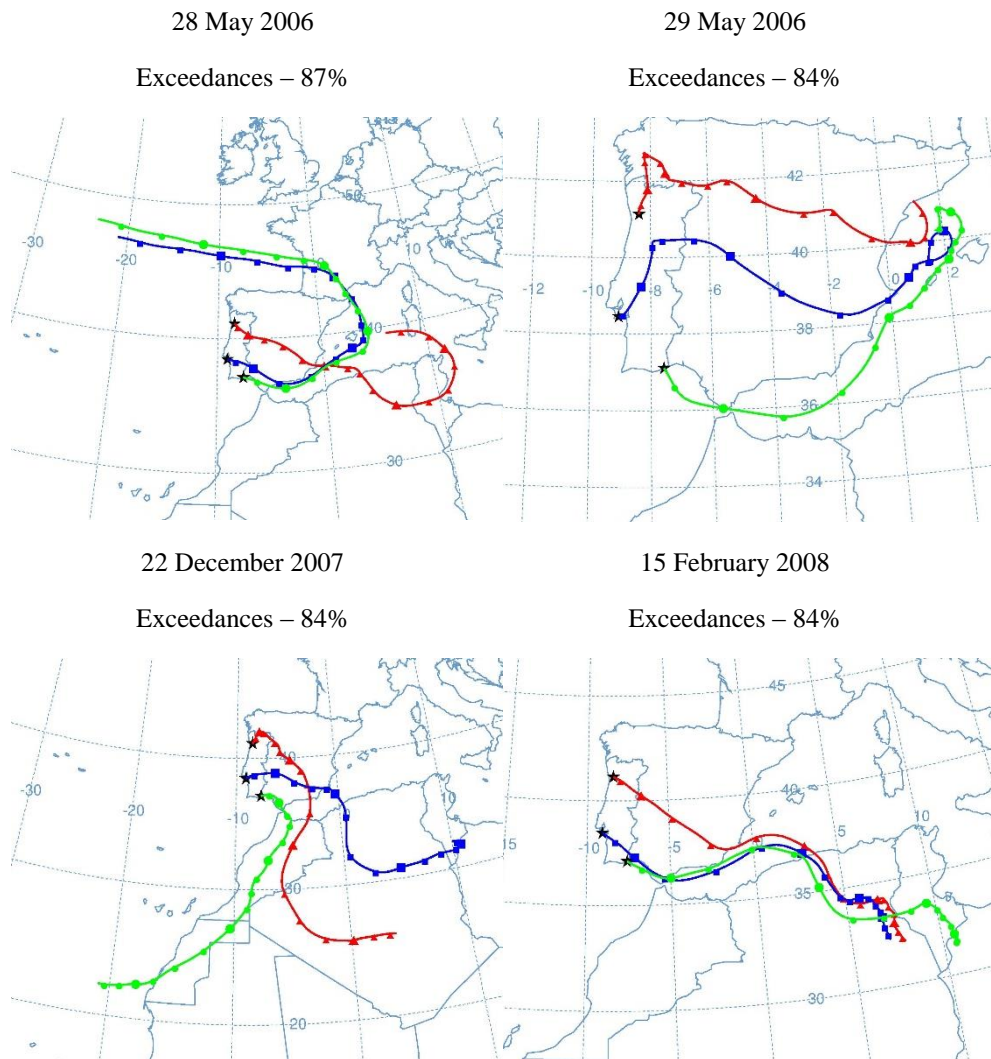


Figure 1.3.7 - Air mass trajectories in days for which the limit value of $50 \mu\text{g}/\text{m}^3$ for PM_{10} was exceeded simultaneously in more than 80% of the monitoring stations.

The present study focused on Lisbon because several studies indicate that it is the urban area most densely populated in Portugal with relevant peaks of pollution (Cachorro et al. 2006; Alves et al. 2010, Almeida et al. 2011). Lisbon is the capital of Portugal, it is the largest city of the country and it is also the westernmost capital in mainland Europe.

In Lisbon, PM_{10} concentrations (Figure 1.3.8) exceeded the annual limit value ($40 \mu\text{g}/\text{m}^3$) set by the Air Quality Directive (2008/50/EC), in 40 % of stations, in 2006, and 20% of the stations, in 2007 and 2008. It was verified that: 1) the monitoring stations are located in the

centre of Lisbon, near important streets; 2) $PM_{2.5}$ concentrations did not exceed the limit value ($25 \mu g/m^3$) established by Air Quality Directive.

Figure 1.3.8 shows the spatial distribution of monitoring stations of Lisbon and the PM_{10} annual mean concentrations.

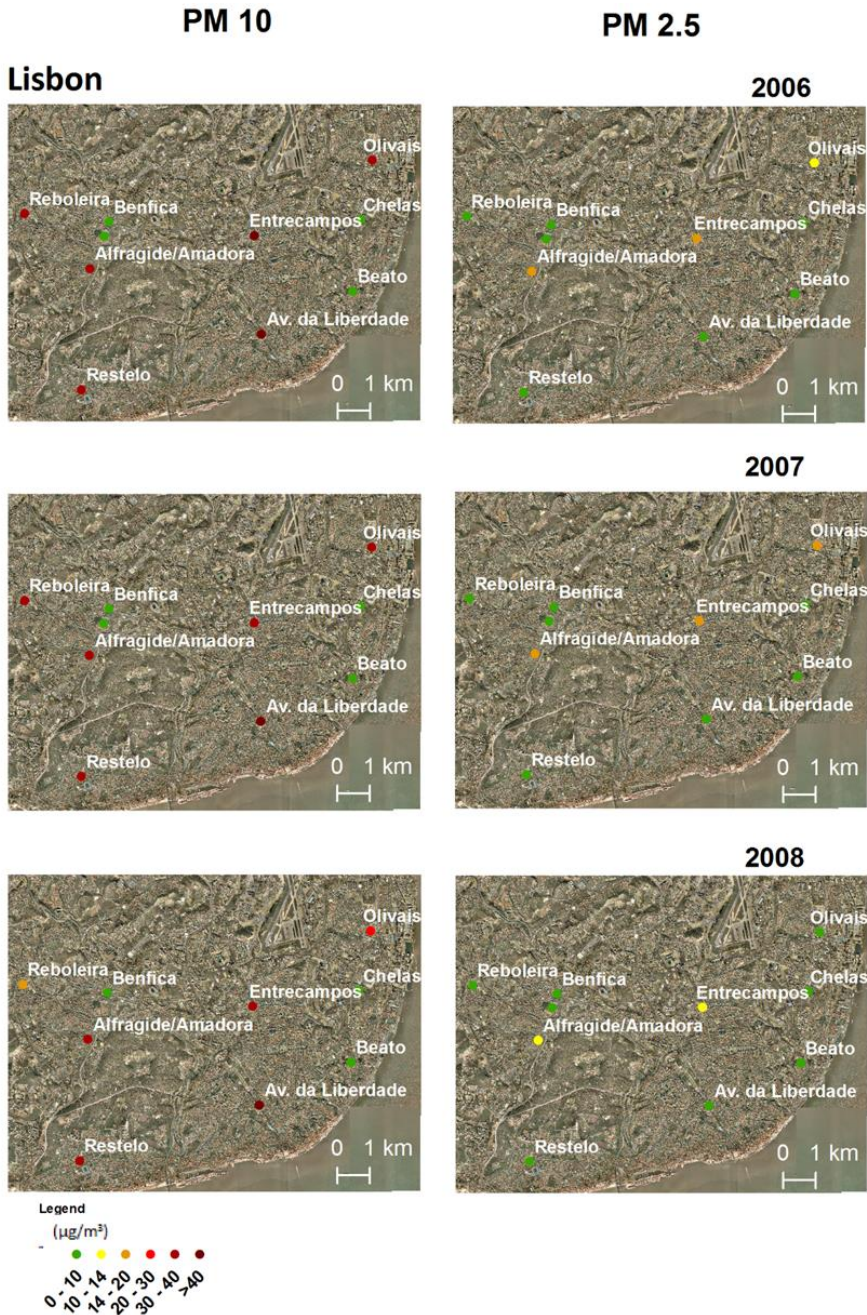


Figure 1.3.8 – Spatial distribution of PM_{10} concentrations in Lisbon.

1.3.4 PM_{2.5}

PM_{2.5} concentrations were aggregated according to temporal variability, year by year, type of influence and environment, as it was done to PM₁₀. The results are in Figure 1.3.9.

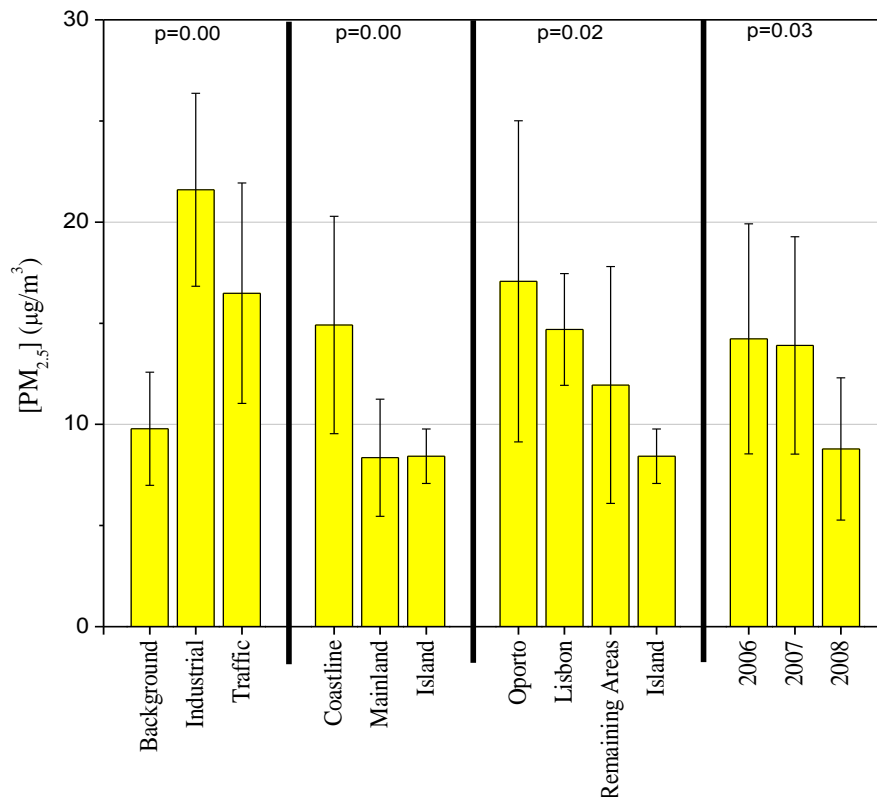


Figure 1.3.9 - Mean PM_{2.5} concentrations in each cluster and p-value obtained from the Kruskal–Wallis test for each data set.

The Kruskal–Wallis test was applied to each PM_{2.5} annual mean concentration data set. The results demonstrated a significantly statistic value for all different ways of aggregating data with p -value < 0.05 (Figure 1.3.9). The Mann–Whitney test was also applied to compare PM_{2.5} concentrations for the different pair groups that was possible to obtain: 1) type of influence, all had a significantly different statistic value ($p = 0.00$), except for industrial vs traffic ($p = 0.25$); 2) type of environment had a significantly different statistic value (p -value < 0.05) for Lisbon vs Remaining Areas, Lisbon vs Islands and Remaining Areas vs Islands, but the results were not statistically different in Oporto vs Lisbon ($p = 0.52$), Oporto vs Remaining Areas ($p = 0.48$) and Oporto vs Islands ($p = 0.16$); 3) geographical perspective had a significantly different statistic value ($p = 0.00$) for Coastline vs Mainland and Coastline vs Islands. The result was not statistically different for Mainland compared to Islands ($p = 0.69$); 4) the temporal variability, year by year, had a significantly different statistic value (p -

value < 0.05) in 2006 vs 2008 and 2007 and 2008, only 2006 vs 2007 was not statistically different ($p = 0.91$).

The results obtained for $PM_{2.5}$ were a little different than the ones obtained for PM_{10} in type of environment in Oporto vs Remaining Areas and Oporto vs Islands. Probably the number of $PM_{2.5}$ data was too small and thus less representative compared to the much larger database of PM_{10} concentrations for the same groups.

Regarding temporal variability, it is possible to observe that all $PM_{2.5}$ concentrations were below $20 \mu\text{g}/\text{m}^3$ and that there was a decreasing of concentrations in 2008. Of the three types of influence, only industrial presented higher $PM_{2.5}$ concentrations, while the lowest was background, as expected. Oporto presented higher $PM_{2.5}$ concentrations than Lisbon, followed by the remaining areas and islands with lower values. Coastline presented higher $PM_{2.5}$ concentrations, as Oporto and Lisbon are located at seaside. Mainland and islands presented similar concentrations.

Figure 1.3.10 indicates that, regarding $PM_{2.5}$ concentrations: 1) All monitoring stations presented concentrations below $25 \mu\text{g}/\text{m}^3$ in all studied years; 2) In 2006, except in Vermoim–North of mainland Portugal and Estarreja-Centre of mainland Portugal, all the stations presented concentrations lower than $20 \mu\text{g}/\text{m}^3$. Vermoim is a monitoring station influenced by traffic and Estarreja by industries; 3) In 2007, only Vermoim and Estarreja still presented concentrations higher than $20 \mu\text{g}/\text{m}^3$; 4) In 2008, there was a decrease of the concentrations and the target value to 2020 was not exceeded in any stations.

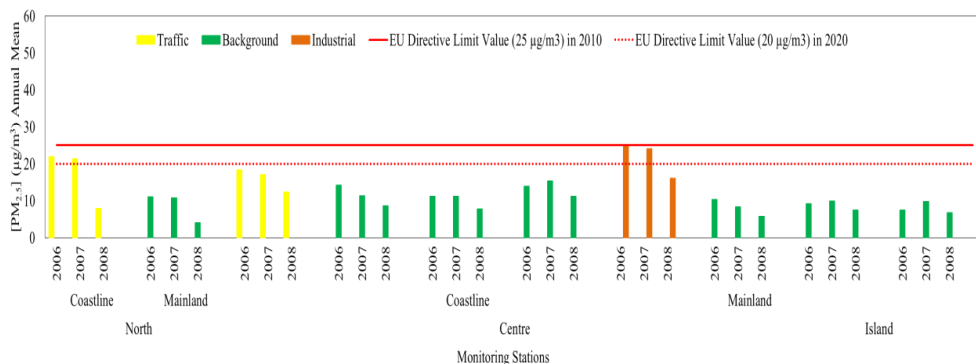


Figure 1.3.10 - Annual Mean $PM_{2.5}$ concentrations for the years of 2006, 2007 and 2008.

1.3.5 NO_2

Similarly to PM, NO_2 concentrations were analysed considering temporal variability, type of influence and environment and the results are shown in figure 1.3.11.

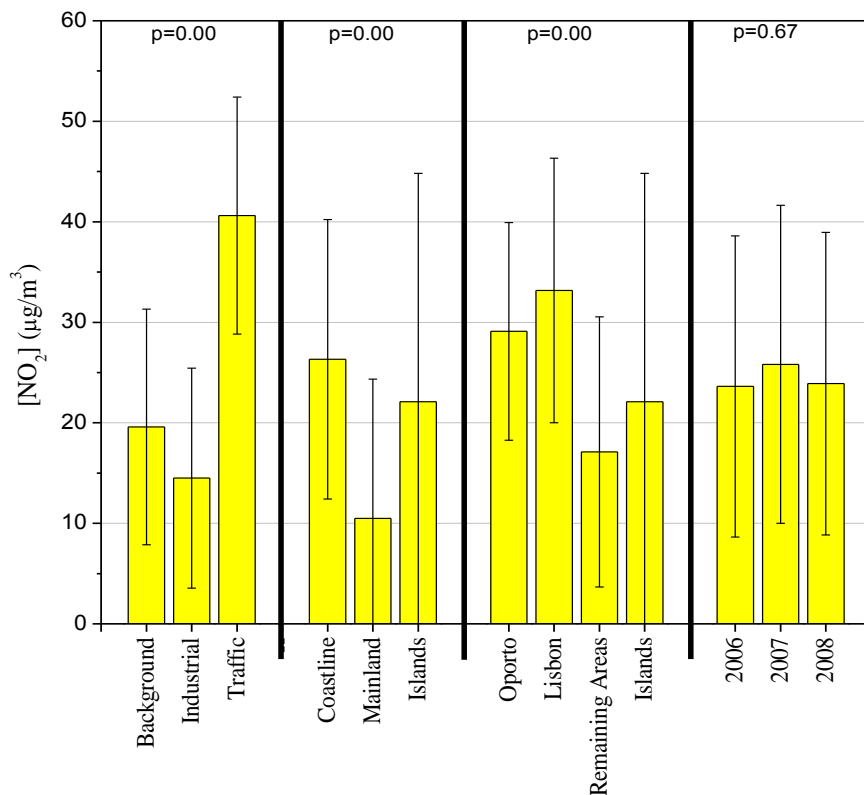


Figure 1.3.11 - Mean NO₂ concentrations in each cluster and p -value obtained from the Kruskal–Wallis test for each data set.

The Kruskal-Wallis test was applied to each NO₂ annual mean concentration data set. The results demonstrated a significantly different statistic value for all different ways of aggregating data with p -value = 0.00 (Figure 1.3.11), except the temporal variability ($p=0.67$). The Mann-Whitney test was also applied to the different pair groups that were possible to obtain. The results were: 1) type of influence, all had a significantly different statistic value ($p = 0.00$), except for background vs industrial ($p = 0.08$); 2) type of environment had a significantly different statistic value with p -value = 0.00 for Oporto vs Remaining Areas and Lisbon vs Remaining Areas, while the pairs were not statistically different for Oporto vs Lisbon ($p = 0.27$), Oporto vs Islands ($p = 0.16$), Lisbon vs Islands ($p = 0.08$) and Remaining Areas vs Islands ($p = 0.99$); 3) geographical perspective had a significantly different statistic value with $p = 0.00$ for Coastline vs Mainland. The result was not statistically different for Coastline vs Islands ($p = 0.26$) and Mainland vs Islands ($p = 0.69$); 4) the temporal variability, year by year, had not a significantly different statistic value for any pair. NO₂ concentrations do not present significant variability or decreasing trend, as it happened for PM concentrations, year by year.

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The highest NO₂ concentrations were associated with traffic, as expected. Background presented higher concentrations in industrial areas, probably influenced by the road network, in addition to combustion processes in some plants. Coastline, including Lisbon and Oporto, presented the highest concentrations. Although in the islands concentrations were higher than in mainland, both were clearly below 40 µg/m³, the annual mean proposed by the WHO AQG and Air Quality Directive (2008/50/EC).

Figure 1.3.12 shows the time trend of NO₂ concentrations, year by year, and the comparison with the WHO AQG and Air Quality Directive (2008/50/EC). The EU limit value (40 µg/m³) was surpassed in 13% of the monitoring stations in Portugal (mainland and islands). Figure 1.3.13 shows that only 10% of the monitoring stations exceeded more than 18 times per year the limit value (200 µg/m³). The highest NO₂ concentrations were found in the monitoring stations with traffic influence, which accounted for 84% of all monitoring stations that surpassed the limit value. The other 16% were background monitoring stations located in North Coastline and Centre (Lisbon).

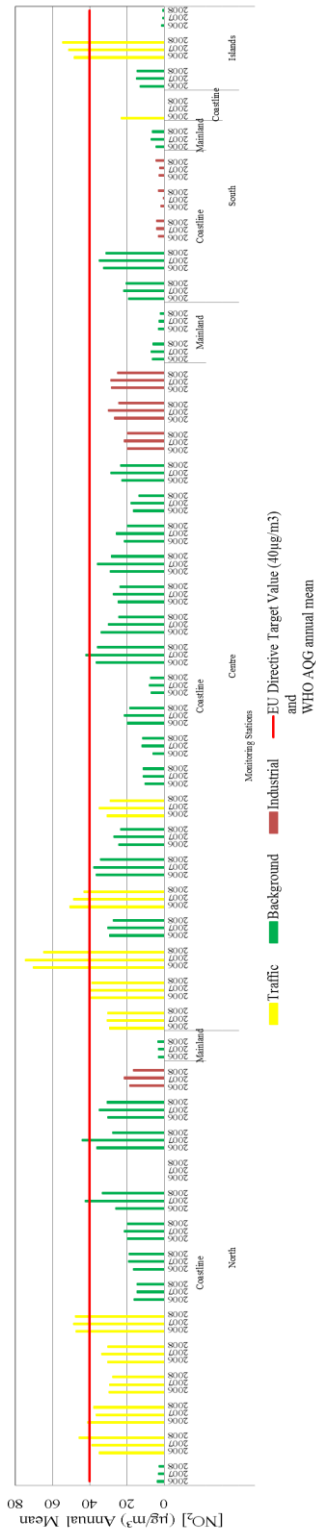


Figure 1.3.12 – NO₂ concentrations annual mean for the years of 2006, 2007 and 2008.

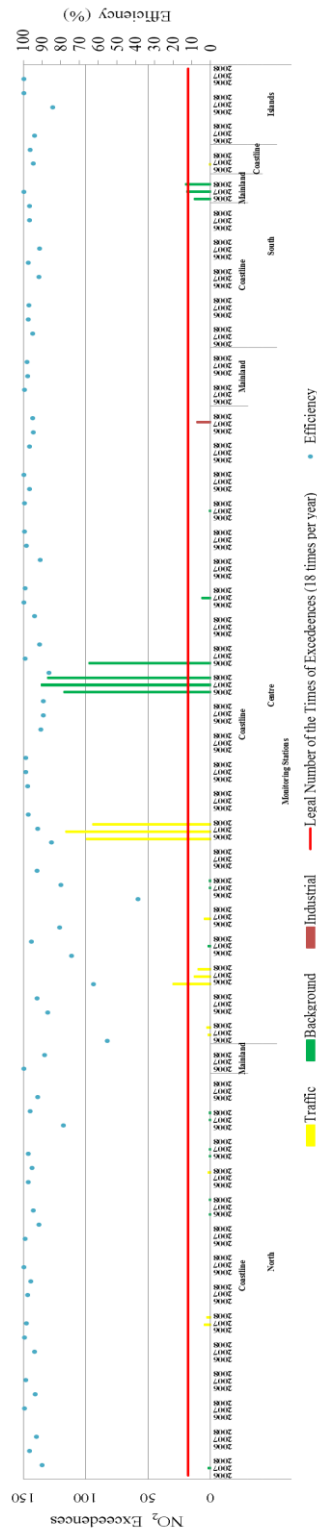


Figure 1.3.13 - Number of days exceeding the 1h mean of NO₂ concentrations. Red dash line is the limit value of exceedances allowed by year, according to the Air Quality Directive (2008/50/EC).

1.3.6 O₃

Ozone concentrations data were also aggregated according to temporal variability, type of influence and environment. The results are shown in figure 1.3.14.

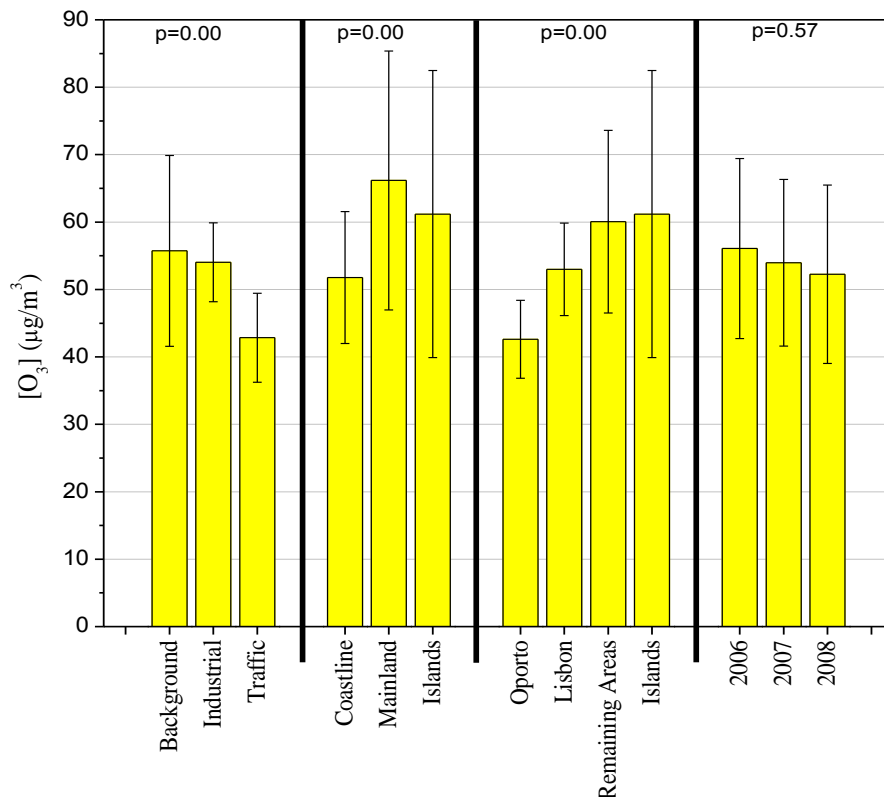


Figure 1.3.14 - 8-hour mean O₃ concentrations in each cluster and p-value obtained from the Mann-Whitney test in each data set.

The Kruskal–Wallis test was applied to each O₃ 8h mean concentration data set. The results demonstrated a significantly different statistic value for all groups ($p = 0.00$) except for the temporal variability group ($p = 0.57$) (Figure 1.3.14). The Mann–Whitney test was also applied to the different paired groups that were possible to obtain and the results were: 1) type of environment-Oporto vs Lisbon ($p = 0.00$), Oporto vs Remaining Areas ($p = 0.00$), Oporto vs Islands ($p = 0.03$), Lisbon vs Remaining Areas ($p = 0.01$) presented a significantly different statistic value, but Lisbon vs Islands ($p = 0.40$) and Remaining Areas vs Islands ($p = 0.89$) did not; 2) geographical perspective-significantly different statistic value for Coastline vs Islands ($p = 0.00$), whereas Coastline vs Mainland ($p = 0.79$) and Mainland vs Islands ($p = 0.79$) did not reveal a significantly different statistic value; 4) the temporal variability, year by year, had not a significantly different statistic value in any paired group.

Ozone concentrations vary with several factors that are linked in a complex way: 1) NO_x emissions; 2) VOCs; 3) CH₄ in lower quantities; 4) CO; 5) meteorological factors like sun radiation and temperature that regulate processes of O₃ photochemical production and destruction; 6) factors with influence on vertical and horizontal transport of this pollutant and its precursors from place to place (Fowler et al., 2008; Guicherit and Roemer, 2000).

All O₃ concentrations were low, showing a decreasing trend from 2006 to 2008. The lowest values were registered at traffic sites, followed by industrial and background stations. Coastline presents lower O₃ concentrations than islands and mainland, respectively. Oporto and Lisbon present lower values than the remaining areas. The O₃ concentrations in urban areas (Oporto and Lisbon) presented lowest than rural areas. Ozone is a pollutant of both rural and urban areas and it is possible to find higher ozone concentrations in some rural areas. This can be explained for two reasons: 1) in city centres, some pollutants, like nitric oxide or alkenes remove ozone from the air; 2) VOCs vary in their degree of reactivity in a way that photochemical reactions that lead to ozone formation may take hours to operate. During the time taken to create ozone urban plume of precursor pollutants may have drifted many tens of kilometres downwind of cities, increasing rural ozone concentrations there by as much as 70 ppb (140 µg/m³). Ozone may continue to be created hundreds of kilometres downwind of major cities during daylight hours.

Concerning O₃, the 8-hour mean never surpassed 100 µg/m³ per year, the limit value established by WHO AQG (Figure 1.3.15) in any monitoring station.

Air Quality Directive (2008/50/EC) sets a target value for O₃: the maximum daily eight-hour mean may not exceed 120 µg/m³ on more than 25 days per calendar year averaged over three years. Figure 1.3.16 shows that 23% of the monitoring stations did not fulfil this criterion. Among these stations, 13% were influenced by traffic and 87% were background monitoring sites.

In spite of the effort in reducing O₃ precursor emissions, these will probably continue in line with economic development and the rise of world population. Natural source emissions will mostly be influenced by climate and land use changes, while the increase of energy needs, transport, nutritional and non-nutritional items and other resources will influence emissions from human activities. Nevertheless, it is expected that legal actions and new emission production and control technologies will contribute to go against the relation between O₃ and the economic development (Fowler et al. 2008; Meehl et al. 2007; Olivier et al. 2005).

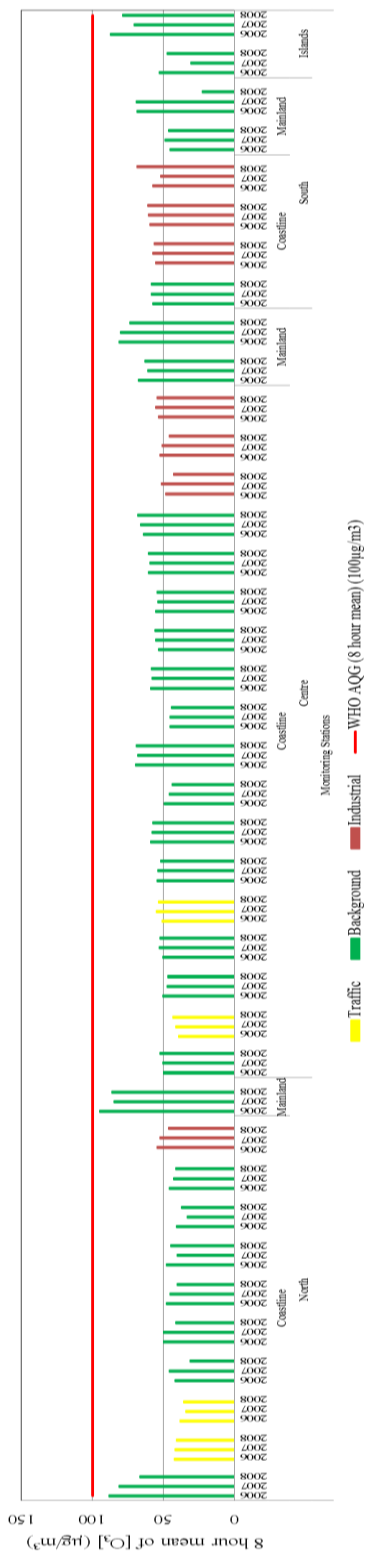


Figure 1.3.15 - 8h-mean O₃ concentrations for the years 2006, 2007 and 2008 comparing with WHO AQG.

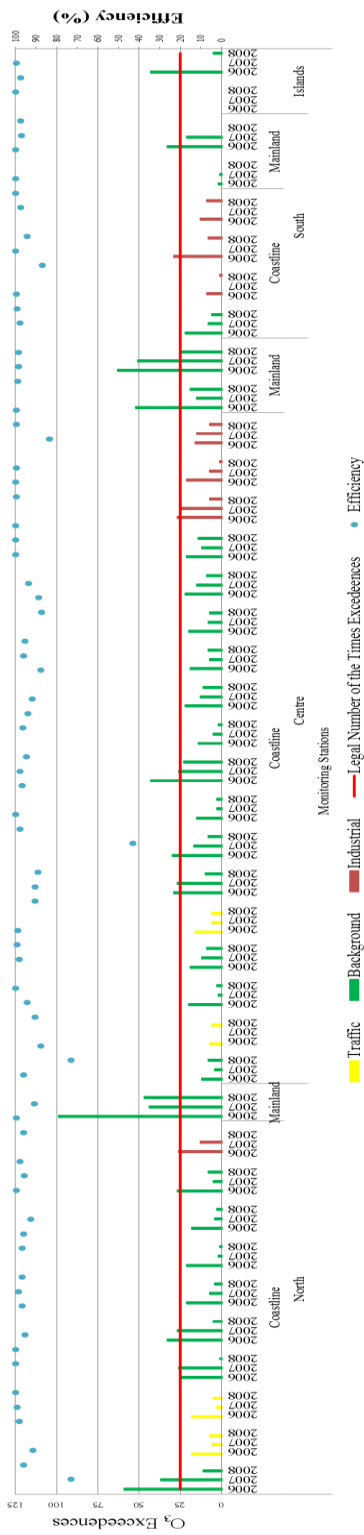


Figure 1.3.16 - Number of days exceeding the target value allowed by year, according to the Air Quality Directive (2008/50/EC).

1.3.7 Outcomes

The study revealed that high concentrations of PM₁₀ and PM_{2.5} were registered in the coastal region, where the main urban and industry areas are located in Portugal. NO₂ concentrations were associated with traffic essentially in Coastline, also where the main road network is implemented. O₃ concentrations are in general low, regardless the temporal variability, the type of influence and environment.

Oporto presented higher PM₁₀ and PM_{2.5} concentrations than Lisbon, mostly correlated with the traffic pattern in the city, suggesting that Oporto air quality is strongly influenced by the traffic emissions but other sources should also be considered, namely the high concentrations of sea salts included in PM₁₀ measurements, related to the coastal localization of Oporto. Lisbon is the urban (traffic/industrial) area chosen in this work because it presented many AP concentrations higher than WHO AQG and Air Quality Directive (2008/50/EC) propose. It is reasonably covered with air quality monitoring stations, providing long term datasets, and it is the capital of Portugal, where the largest fringe of the Portuguese population lives.

The classifications are made according to the type of influence and environment of monitoring stations from Air Quality Monitoring Network (QualAr) of the Portuguese Environment Agency (APA). Nowadays some of the monitoring stations have an inadequate classification.

Air pollution levels in Portugal, comparing with the rest of Europe, are not that high, but they are still a matter of concern considering health effects. Considering all AP referred in the Directive and WHO APG, PM are still the ones to be a target of mitigation strategies, mainly in urban areas (influenced by traffic and industries) where there is a higher population density, increasing the probability of exposure to pollution.

Other pollutants to be dealt with in chapters 5 and 6 (CO, NO, SO₂) are not discussed in 1.3 because their concentrations were observed to be very low in Portugal (mainland and islands) compared to the EU legislation. Their values will be shown in those chapters.

1.4 Lichen Biomonitoring of Air Pollution

Monitoring air pollution is difficult for several reasons (Nimis et al. 2000; Wolterbeek 2002) namely the large number of potentially dangerous substances released into the atmosphere, the difficulty in estimating their synergic and antagonic effects, the large spatial and temporal variations of pollution, the high costs of measurement instruments and because of that few places where biomonitoring stations can be installed. So, along with the traditional instrumental monitoring, biomonitoring techniques allow for the mapping of pollution effects over wide areas with a high sampling density (Almeida et al. 2012; Wolterbeek et al. 2002) and study the time trend concentrations (Fрати et al. 2005). Long term biomonitoring can be

useful in determining tendencies and correlations of the main chemical elements present in the atmosphere. It is important to have in mind that it is possible to biomonitor a vast area, in which there is no conventional air quality network and assess the contribution of human activities to air pollution. For that reason, lichen biomonitoring can be useful in assessing the risks for human health, and can be a powerful tool for environmental planning (Brunialti and Frati 2007). In fact, the use of live organisms as an environmental stability indicator has been widely recognised in the past. In the last decades, several plants, animals, moss, fungus and bacteria have been used as bioindicators and biomonitors in air, soil and water pollution studies (Freitas et al. 1997; Wolterbeek 2002; Batzias and Siontorou 2007). The terms bioindicator and biomonitor should not be used indistinctively. While the term bioindicator refers to organisms that present a different response to the different pollution exposition levels, the term biomonitor is related to bioindicators and bioaccumulators (Garty 2001). Lichens are some of the most important long term biomonitors (Wolterbeek 2002, Batzias and Siontorou 2007) and can be used as sensitive indicators to estimate pollutants biological effects, measuring the alive organisms of a population according with pollution levels or as cumulative organisms of pollutant chemical elements, using concentrations levels measured in a very small part of the lichen. It is also possible to consider the bark where the lichen is attached as a biomonitor (Wolterbeek 2002) to assess the atmospheric levels.

Another aspect related to the atmospheric pollution levels is the electric conductivity of the extract obtained when the lichen is put under water, which was described as the most sensitive parameter to determine the response of these organisms to the environmental stress (Mulgrew and Williams 2000). The importance of lichens as bioindicators and biomonitors is related to its abundance, not only in distant areas, but also in areas close to pollutant sources, where the variety of the response of the different species to pollution provides detailed variation patterns, even with low pollution levels (Batzias and Siontorou 2007). The possibility of using bioindicators to assess regional patterns of ecosystems impact was legislated in Portugal through the Decree-Law n.º 351/2007 of 23 October. Most lichens are constituted by a fungus and a microscope algae that appear to be a single organism in a symbiotic association. Lichens do not have roots and absorb nearly all air nutrients. Measuring a vast sample of pollutants allows the assessment of the source profiles and to study if a pollutant or an emission profile can be related to a human health effect for which it is responsible (Sarmiento et al. 2008). Multi-elementary analysis techniques are usually applied on these studies. In environmental biomonitoring of chemical elements, nuclear techniques are usually seen as very useful to analyse large quantities of samples (Freitas et al. 2000; Smodis 2007), as solid samples do not need to be transformed in solutions and sensibility, precision and accuracy are adequate to the quantity of the available sample to the analysis.

The Instrumental Neutron Activation Analysis (INAA) and all its variations allow the quantification of all the chemical elements that are important to the atmospheric

biomonitoring (Ventura et al. 2007). Some of the most important actors of global change, as climate, pollution and eutrophication are factors that influence lichen communities and they respond to them in only a few years and lichen physiology in few weeks (Brown 1985). Since the nineteenth century, people have been using lichen community composition and species frequency for biomonitoring purposes (Godinho et al. 2008; Marques 2008). It is possible to obtain useful information on the status of the environment and its changes over time and space, by analysing lichens, as they are amongst the most sensitive organisms to environmental changes. In particular, species composition may be a suitable indicator for climate and landuse effects as well. Further interpretation of lichen diversity requires careful data analysis for providing affirmative results related to ambient air quality. There are other ecological factors, like tree species, forest structure and microclimatic conditions that can influence lichen communities (Brown 1985; Giordani and Brunialti 2015).

Newly developed physiological methods allow us to assess lichen's response to the rapidly changing environmental conditions (Upreti et al. 2015). A trustable base for the development of environmental policies can be achieved by connecting physiological mechanisms, functional diversity and ecological impacts.

1.5 Thesis outline

The first step of this study was to characterise PM_{10} , $PM_{2.5}$, NO_2 and O_3 , as the pollutants of concern in Portugal (mainland and islands). The IARC, which is part of the WHO, has recently considered that PM is the most dangerous air pollutant. It has been classified as a carcinogenic contaminant. On the other hand, while traditional gaseous pollutants in Portugal have received considerable attention over the last years (Barros et al. 2015; Borrego et al. 2015; Carvalho et al. 2010; Monteiro et al. 2007), atmospheric particulate matter has been much less studied. The data used were provided by the Portuguese Environmental Agency (APA) for a 3-year period (2006-2008). Although there are 78 monitoring stations in Portugal, only 11 measure simultaneously PM_{10} and $PM_{2.5}$. Paired values are necessary to apply wavelet analysis (Percival and Walden 2006) in order to build a variance/covariance profile of the studied monitoring stations across time scales with direct connection with the main periodicities observed in $PM_{2.5}$ and PM_{10} time series.

The study then focused in Lisbon. Five main reasons justify the selection of this geographical area: 1) together with some industrial sites, it is the region with highest pollution levels; 2) it is the capital and largest city of the country, where the largest fringe of the Portuguese population live; 3) contrary to what is observed in the 2nd largest metropolitan area (Oporto), Lisbon is reasonably covered with air quality monitoring stations, providing long term datasets; 4) there are more available databases regarding HA; 5) the monitoring stations to be considered in this study are in municipalities whose population is served by the hospitals

where the HA data were collected. It is the westernmost large city located in Europe and the only one along the Atlantic coast (Almeida et al. 2013b), with a population of 564 657 inhabitants, according to *Census 2001* provided by Instituto Nacional de Estatística (INE) in Portugal. In the city, traffic is the main source of atmospheric pollution (Almeida et al. 2009a, b). Industries include textiles, chemicals, steel, oil, cement, sugar refining, shipbuilding, soap and flour production (Almeida et al. 2007, 2013a; Farinha et al. 2004a). Due to the geographic position of Lisbon and to the dominant western wind regime, influenced by the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean, the expected high levels of pollutants are uncommon. The transport of maritime air mass is usually associated with cleaner air masses from the Atlantic Ocean and with better dispersion conditions of pollutants coming from the industrial areas (Almeida et al. 2013b). Nevertheless, high concentrations of AP can be registered under adverse meteorological conditions, low dispersion conditions and thermic inversions.

Lisbon is committed in the improvement of air quality with mitigation measures regarding air pollution concentrations. Political programmes of the Lisbon City Hall have this goal, namely: 1) Low Emission Zones (LEZ), which prohibit the circulation of vehicles prior to 1996 and 2000 in the city centre; 2) Renovation of the municipal vehicle fleet with the acquisition of “cleaner” vehicles; 3) promoting public transport; 4) parking management with fees; 5) creating bike paths; 6) creating pedestrians circuits; 7) urban traffic management.

To complete this study, a biomonitoring survey was carried out aiming at allowing to enlarge the density of the monitored area, regarding atmospheric pollution. Bark and lichen, brought from clean areas, were transplanted and exposed in Lisbon to inter-compare their response effectiveness to atmospheric pollution levels.

Finally, associations between pollutants and the probability of occurrence of diseases were studied, using two different, but complementary, statistical methods. The first one OLS enabled to define the best way of aggregating data and to define the best temporal scale. The second one COM-Poisson generalises the Poisson distribution by adding a parameter to model overdispersion and underdispersion, allowing for time trends of morbidity to detect the long-term effects of common levels of air pollution and/or meteorological parameters.

Figure 1.5.1 shows the scheme of the design of this thesis.

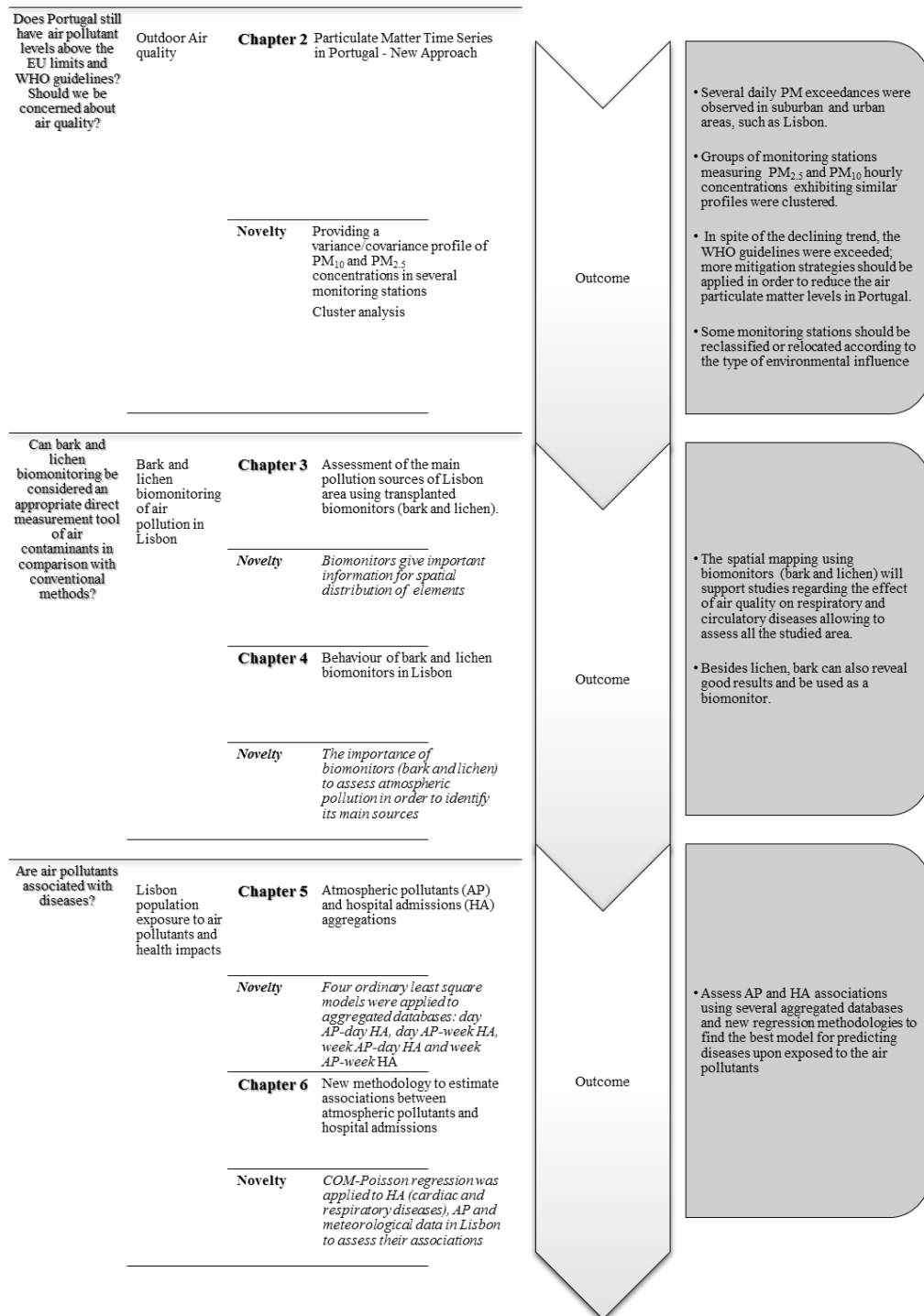


Figure 1.5.1 - Scheme of the thesis.

Chapter 1 – Introduction

Chapter 2 includes the evaluation of PM₁₀ and PM_{2.5} levels measured by the air quality monitoring station (mainland and islands) belonging to the APA. The databases contributed to assess the contribution of the main emission sources or processes affecting the PM levels and their diurnal and seasonal profiles. Back-trajectories were simulated by using the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) developed by NOAA's Air Resources Laboratory (Draxler et al. 2014) and their influence on PM levels was discussed. This chapter also aims at providing a variance/covariance profile of a set of 11 monitoring stations measuring simultaneously PM₁₀ and PM_{2.5} hourly concentrations.

Chapter 3 describes the creation of a database corresponding to the concentration of 30 chemical elements present in lichens collected outdoor at 22 elementary schools of Lisbon-city from January 2008 to May 2008 and from June 2008 to October 2008. This permitted the drawing of maps portraying the outdoor spatial distribution of 30 chemical elements in lichens as a result of transplanting from unpolluted to air polluted areas.

Chapter 4 shows the emission source profiles of chemical elements using biomonitoring. The selected lichen and bark were respectively, *Parmotrema bangii* and *Criptomeira Japonica*, picked up from a pollution-free atmosphere of Azores, which were then placed in the courtyards of 22 elementary schools of Lisbon.

Chapter 5 analyses the associations between AP and HA in Lisbon, for cardiac diseases, circulatory and respiratory diseases, compiled by ages: < 15; 15-64; ≥ 64 years old, using OLS regression.

Chapter 6 focuses on the COM-Poisson distribution that is used to assess the magnitude of the association between hospital admission counts, air pollutant concentrations and temperature and relative humidity.

2 A Wavelet-based Approach Applied to Suspended Particulate Matter Times Series in Portugal

Based on article of the same title:

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2.1 Abstract

This study intends to analyse the particulate matter (PM) levels in Portugal (mainland and islands) throughout a 3-year period. Although a decreasing trend has been observed, the WHO guidelines for the PM₁₀ and PM_{2.5} annual mean concentrations have been exceeded in all monitoring stations. Most inland urban, rural and suburban sites follow a pronounced seasonal variation with much higher values in winter than in summer. Lower levels and a weak seasonal variability were registered in the two urban background stations of Madeira island, which are permanently under the influence of clean air masses over the Atlantic. Receiving long range transported pollution, rural stations located in mountain sites, presented an opposite seasonal pattern, with higher levels in summer. Diurnal profiles were also analysed and compared between stations. A mining process was also carried out, consisting in the application of multi-scale wavelet transforms, data pattern identification using cluster analysis, and examination of the contribution to the total variance/covariance of the time series per wavelet scale for all stations. Groups of stations exhibiting similar variance/covariance profiles were identified. One group contains urban and rural stations with diurnal and daily time scales. Urban background stations located in the island of Madeira constitute another cluster, corresponding to higher wavelet scales (lower periodicity phenomena). One traffic station in the Oporto metropolitan area was grouped with a suburban/industrial station of central Portugal, suggesting the need for reclassification in what concerns the type of environmental influence.

2.2 Introduction

In spite of all strategies and policies to improve air quality in Europe, particulate matter (PM) concentrations remain an issue of concern considering human health effects (Solomon et al. 2012; EEA 2014; Schachter *et al.* 2015). In 2013, reports from the International Agency for Research on Cancer (IARC), which is part of the World Health Organisation (WHO), have recognised that outdoor air pollution may be classified as a carcinogenic agent. Among the criteria air pollutants, PM was considered to have the highest carcinogenic risk, being responsible for the increased incidence of lung cancer. Recent studies (e.g. Brook *et al.* 2010;

WHO 2014) demonstrate that air pollution, and principally PM, plays a much stronger role in cardiovascular illness and premature deaths than previously thought. Although PM concentrations in many EU cities do not surpass the guideline levels, the average life expectancy is not as high as it would be predictable because of PM exposure. Even with PM_{2.5} levels lower than the current annual WHO air quality guideline level (10 µg/m³), recent long-term studies (e.g. Hoek *et al.* 2013; WHO 2014; Chung *et al.* 2015) still show associations between PM and mortality. It has been estimated that a decrease of the annual average particulate matter (PM₁₀) levels of 70 µg/m³, which are frequent in many growing cities of developing countries, to the WHO guideline level of 20 µg/m³, could signify a 15% decrease in mortality due to atmospheric pollution (WHO 2014). Mitigation measures applied to PM pollution are also effective in reducing concentrations of greenhouse gases and other contributors to the global warming (e.g. soot), since many of the emission sources are common.

Traffic exhaust emissions have long been considered as the main PM source (Charron *et al.* 2007; Oliveira *et al.* 2010; Andrade *et al.* 2012; Pant and Harrison 2013; Keuken *et al.* 2013; Kimbrough *et al.* 2013; Mirante *et al.* 2014), but recent studies show that non-exhaust emissions from road traffic (Thorpe and Harrison 2008; Harrison *et al.* 2012; Pant and Harrison 2013; Amato *et al.* 2014), biomass burning and cooking (Allan *et al.* 2010; Alves *et al.* 2012; Gonçalves *et al.* 2012; Mohr *et al.* 2012) are also key sources of this pollutant. While control technologies have led to substantial reductions in exhaust emissions, non-exhaust and non-traffic emissions remain the same. In many regions, atmospheric dynamics, mainly related to local and regional air mass recirculation processes, may contribute to high levels of PM. For example, in Spain, long range transport of Saharan dust have been found to play a key role on the observed levels and exceedances (Querol *et al.* 2008; Querol *et al.* 2009; Jiménez *et al.* 2010; Díaz *et al.* 2012; Querol *et al.* 2014; Notario *et al.* 2014), especially in rural and urban background stations.

The European Member States are required to draw up plans to guarantee compliance with the limit values set by the Air Quality Council Directive 2008/50/EC. However, the current policy efforts, at both European and national levels, have not reached the expected results. A number of studies demonstrated that the limit values are exceeded in Portugal (Khan *et al.* 2007; Lage *et al.* 2014), although PM₁₀ and PM_{2.5} concentrations reflect a decreasing trend, probably resulting from more efficient environmental technologies applied in industries and vehicles, together with a fall of the economic activities due to the financial crisis. Nevertheless, as shown by estimates of the health impacts associated with exposure to air pollution, despite substantial improvements in recent decades, Portugal is still far from attaining levels of air quality to ensure adequate public health and environmental protection (Alves *et al.* 2010b; Sarmiento *et al.* 2009; Almeida *et al.* 2014; Cruz *et al.* 2014).

Given the growing evidence of increased mortality and morbidity upon exposure to PM, Cruz *et al.* (2014) evaluated the relationships between air pollutant levels and hospital admissions due to cardiac, respiratory and circulatory diseases in Lisbon, by Ordinary Least Squares Linear Regression, between 2006–2008. The results of this study showed significant positive associations between PM₁₀ and PM_{2.5} and circulatory diseases for ages ranging from 15 to 64 and respiratory diseases for ages below 15. The present study intends to expand the evaluation of the PM levels, recorded in the same period, to the entire Portuguese territory and to classify monitoring stations, measuring simultaneously PM₁₀ and PM_{2.5}, via homogeneous clusters in an attempt of identifying spatial patterns and similarities in pollution or atmospheric dynamics. By providing variance/covariance profiles of a set of monitoring stations, it is possible to incorporate these profiles in a wavelet decomposition-based clustering algorithm in order to point out groups of stations exhibiting similar profiles. Wavelets-based clustering of air quality monitoring sites in Portugal have been successfully applied to ozone and nitrogen oxides (Gouveia *et al.* 2015), but not to PM levels. This mathematical tool helps to choose the most representative stations in each area for later use in epidemiological studies. Air quality monitoring sites are classified according to “Type of area” (urban, suburban, rural) and/or “Type of station” (traffic, industrial, background). When performing air quality evaluations at macro-scales, it is frequent to choose one type of area or one type of station to represent an entire region. However, it is recommended to develop or refine other selection schemes which reflect not only geographical characteristics and the most influencing sources, but also intra-diurnal, daily or longer cycles due to regional atmospheric circulation patterns. Statistical techniques, such as clustering analysis, also identify sites whose classification needs revision according to the type of environment influence.

2.3 Methodology

2.3.1 Air Quality Data and Monitoring Stations

Data collected from eleven Portuguese monitoring stations (Figure 2.3.1), during a 3-year period (2006-2008) were provided by the Portuguese Environmental Agency (APA), through the QualAr air quality databases, available at www.qualar.com (Table 2.3.1). Monitoring stations are classified by APA, following criteria proposed by the European Environmental Agency (EEA), as rural remote area (natural background), rural regional area (rural background), rural near-city area (suburban background), suburban, urban background, urban traffic and industrial area. The data quality control is based on common methods and criteria for diagnosing and assessing the ambient air quality in Member States (Council Directive 2008/50/EC).

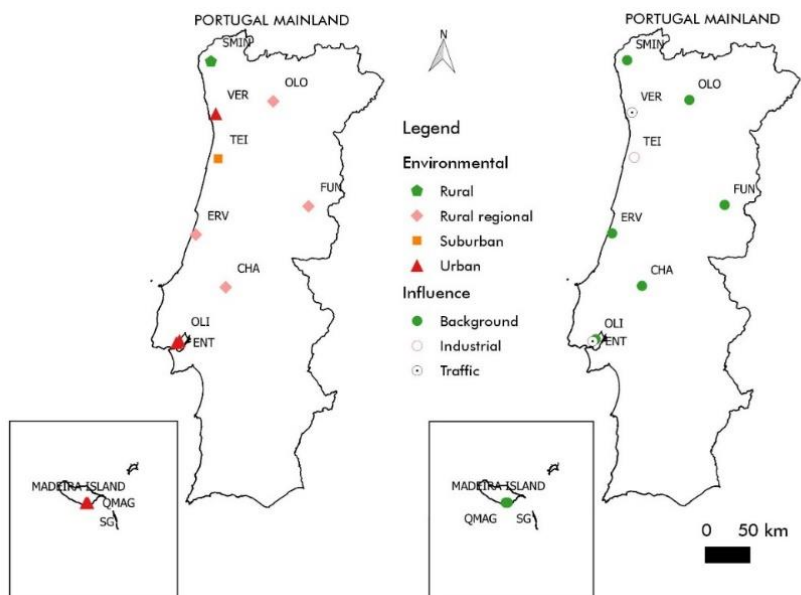


Figure 2.3.1 – Spatial location and classification (environment and influence) of the air quality monitoring stations.

The air quality data used in this work consists of 11 pairs of PM₁₀ and PM_{2.5} hourly series. Only stations with data collection efficiency $\geq 75\%$ have been considered.

Table 2.3.1 – Stations from the Portuguese air quality monitoring network (www.qualar.com), with data coverage higher than 75%.

Monitoring station	Code	Environment	Influence	Geographical		Altitude (m)
				Lat.	Long.	
Estarreja/Teixugueira	TEI	Suburban	industrial	40°45'24"	-8°34'22"	20
Olivais	OLI	Urban	background	38°46'08"	-9°06'29"	32
Entrecampos	ENT	Urban	traffic	38°44'55"	-9°08'56"	86
Quinta Magnólia	QMAG	Urban	background	32°38'30"	-16°55'15"	0
Chamusca	CHA	Rural	background	39°21'09"	-8°27'58"	143
Fundão	FUN	Rural	background	40°13'59"	-7°18'07"	473
Vermoim	VER	Urban	traffic	41°14'08"	-8°37'07"	90
São Gonçalo	SG	Urban	background	32°38'59"	-16°55'06"	0
Senhora do Minho	SMIN	Rural	background	41°48'08"	-8°41'38"	777
Lamas de Olo	OLO	Rural	background	41°22'17"	-7°47'27"	1086
Ervedeira	ERV	Rural	background	39°55'26"	-8°53'30"	60

Note: Classification schemes for Air Quality Stations, covered by the Exchange of Information Decision and the Implementing Decision for Reporting (2011/850/EU), refer to two different spatial scales:

1. “Type of area” or “Environment” (urban, suburban, rural) refers to the environment on a scale of several kilometers;

2.3.2 Air Mass Trajectories

The Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPIT) developed by NOAA’s Air Resources Laboratory (Draxler et al. 2014) that uses meteorological data from GDAS (Global Data Analysis System) was used to simulate back-trajectories. Ninety two hours (four days) backward trajectories arriving at distinct hours at every monitoring station were calculated individually, using different heights, for each one of the 1096 days of the study period. Air trajectories were then clustered. Each cluster is formed by similar trajectories and represents a possible pattern of air-mass movement over the studied area. HYSPLIT has a module for applying cluster techniques based the Total Spatial Variation (TSV) between different formed clusters and on the spatial variance (SPVAR) between each cluster component (Draxler et al. 2014).

2.3.3 Wavelet Analysis

In the current study, discrete wavelet analysis (Percival and Walden 2006) was applied in order to build a variance/covariance profile of the studied monitoring stations across time scales with direct connection with the main periodicities observed in PM_{2.5} and PM₁₀ time series. Afterwards, the individual profiles were used to identify groups of similar stations and to investigate the classification (environment and influence) of the monitoring sites by a Wavelet decomposition-based Clustering (WdC). This type of analysis follows a two steps strategy: 1) wavelet decomposition by Maximal Overlap Discrete Wavelet Transform (MODWT) is applied to the PM_{2.5} and PM₁₀ time series in order to identify the most pertinent scales regarding variability and joint variability to each station; 2) application of WdC method for grouping the monitoring stations regarding the similarity of their profiles. This method is fully described in Gouveia et al. (2015). MODWT is the base of an additive decomposition of a time series X_t ($t = 1, \dots, T$) in two: D_j with wavelet coefficients for the pass-band filtering scales $\tau_j = 2^{j-1}$ and S_j with scaling coefficients for the remaining parcel of the decomposition.

$$X_t = \sum_{j=1}^J D_j + S_J \quad \text{[Equation 2.3-1]}$$

The wavelet coefficients D_j are associated with frequencies in the interval $\left[1/2^{j+1}, 1/2^j\right]$ and scale τ_j captures dynamics in the time interval $\left[2^j, 2^{j+1}\right]$, with S_J associated with all scales above. The stochastic process with the MODWT filter $\delta_{j,t}$ associated with the scale τ_j , is given by:

$$W_{j,t}^X = \sum_{l=0}^{L_j-1} \delta_{j,t} X_{t-l} \quad L_j = (2^j - 1)(L-1) + 1; L: \text{base filter width for } j = 1 \quad [\text{Equation 2.3-2}]$$

The time independent MODWT wavelet variance at scale τ_j is:

$$v_X^2(\tau_j) := V(W_{j,t}^X) [\text{Equation 2.3-3}]$$

The wavelet analysis decomposes the variance of X_t across wavelet scales:

$$V(X_t) = \sum_{j=1}^{\infty} v_X^2(\tau_j) [\text{Equation 2.3-4}]$$

The covariance between two stochastic processes X_t and Y_t can be decomposed similarly, being V_{XY} the covariance between $W_{j,t}^X$ and $W_{j,t}^Y$ wavelet scales:

$$\text{Cov}(X_t, Y_t) = \sum_{j=1}^{\infty} v_{XY}(\tau_j) [\text{Equation 2.3-5}]$$

The scale-by-scale wavelet variance/covariance quantification can be rearranged:

$$C(\tau_j) := \begin{pmatrix} v_X^2(\tau_j) & v_{XY}(\tau_j) \\ v_{YX}(\tau_j) & v_Y^2(\tau_j) \end{pmatrix} [\text{Equation 2.3-6}]$$

$C(\tau_j)$ is estimated through the unbiased empirical counterpart of its components, being $M_j = T - L_j + 1$ the number of wavelet coefficients excluding the boundary coefficients:

$$\hat{v}_X^2(\tau_j) := \frac{1}{M_j} \sum_{t=L_j-1}^{T-1} (\hat{W}_{j,t}^X)^2 \quad \text{and} \quad \hat{v}_{XY}(\tau_j) \equiv \hat{v}_{YX}(\tau_j) := \frac{1}{M_j} \sum_{t=L_j-1}^{T-1} \hat{W}_{j,t}^X \hat{W}_{j,t}^Y [\text{Equation 2.3-7}]$$

The least asymmetric (LA) filter is used to obtain an adequate decomposition and estimation, and for better visualisation purposes. The number of scales J is restricted to the length of the time series (T) and the filter width (L), resulting in $J \leq 11$ (analysis includes annual periodicity).

The PM_{10} and $\text{PM}_{2.5}$ time series were previously normalised, with variance corresponding to the respective percentage of X_t variance.

The clustering procedure uses a dissimilarity measure and a group linkage criterion (Everitt et al. 2011). The dissimilarity matrix (d_w) compares pairwise objects i and i' , based on their wavelet variance/covariance matrices, using the distance measure (D'Urso et al. 2014):

$$d_w(i, i') = \left\{ \left[0.5 \cdot d_{vv}(i, i') \right]^2 + \left[0.5 \cdot d_{wc}(i, i') \right]^2 \right\}^{1/2} [\text{Equation 2.3-8}]$$

taking into account sum of the squared differences between both objects across scales, in terms of wavelet variance (term d_{wv}) and in terms of wavelet covariance (term d_{wc}).

The procedure creates a dendrogram, in which different group linkage criteria were considered, choosing those maximising the dendrogram's goodness-of-fit, measured by the cophenetic correlation coefficient (Everitt et al. 2011).

2.4 Results and Discussion

2.4.1 PM Mass Concentrations

Table 2.4.1 shows the mean concentrations of PM_{10} and $PM_{2.5}$ ($\mu\text{g}/\text{m}^3$) and number of exceedances according with the defined limit values set by the Air Quality Council Directive 2008/50/EC. In general, PM_{10} and $PM_{2.5}$ concentrations decreased from 2006 to 2008 as has occurred in other countries (Baldasano et al. 2003; Aldabe et al. 2011; Wang et al. 2012). It has been reported that emissions of primary PM_{10} and $PM_{2.5}$ decreased by 14% and 16% respectively in the EU-27 between 2002 and 2011 (Guerreiro et al. 2014). The reductions in the same period for the EEA-32 member countries were 9% for PM_{10} and 16% for $PM_{2.5}$.

Throughout the monitoring period, only Entrecampos (ENT), classified as a traffic station, exceeded in 2006 the PM_{10} limit value of $40 \mu\text{g}/\text{m}^3$ set by the Council Directive 2008/50/EC. All the other monitoring stations registered annual means below the limit value. However, the PM_{10} daily limit value ($50 \mu\text{g}/\text{m}^3$) was surpassed in 5, 4 and 1 stations out of 11 more than 35 times in 2006, 2007 and 2008, respectively. These stations are located in urban areas, with industrial and traffic influence. The highest annual values were recorded in Estarreja/Teixugueira (TEI) and VER, although these stations have not exceeded the legal limit. TEI is located in the region of Estarreja, where since the middle of the XX century it has settled one of the largest complexes of food and chemical industries in Portugal. VER belongs to the air quality network of the Oporto Metropolitan Area. Despite the fact that this station is classified as urban traffic, it is likely under the influence of strong emission sources, such as the Oporto international airport, the huge oil refinery of Petrogal, and the large and rather grubby commercial harbour of Leixões, among others.

The $PM_{2.5}$ annual mean concentrations in all monitoring stations were lower than $25 \mu\text{g}/\text{m}^3$, the target value that came into force on 1st January 2015. The target value for 2015 of $20 \mu\text{g}/\text{m}^3$, reviewed in 2013 by the European Commission to protect human health, in background rural and urban areas, has been generally reached. The exceptions are TEI and VER, which are classified as industrial and traffic monitoring stations, respectively.

The WHO guidelines for the PM₁₀ and PM_{2.5} annual mean concentrations are 20 µg/m³ and 10 µg/m³, respectively. These guidelines were exceeded in all monitoring sites, although the percentage of stations surpassing the WHO recommended values decreased along the years: 82%, 64% and 45% in 2006, 2007 and 2008, respectively, for PM₁₀, and 82%, 73% and 27%, in the case of PM_{2.5}.

Table 2.4.1 – Annual mean concentrations of PM₁₀ and PM_{2.5} (µg/m³) and number of exceedances according to the limit values set by the Air Quality Council Directive 2008/50/EC: (a) the PM₁₀ 24-hour limit value of 50 µg/m³ must not be exceeded more than 35 times per year; (b) the PM_{2.5} target value (annual mean) is 25 µg/m³ since 2010.

(a)					(b)			
	PM ₁₀	2006	2007	2008		Annual mean		
					PM _{2.5}	2006	2007	2008
TEI	Annual mean	35.5	37.9	32.3	TEI	24.7	23.9	16.3
	Exceedances	75	78	40		OLI	13.9	15.3
OLI	Annual mean	30.7	28.0	23.7	ENT		18.5	17.0
	Exceedances	47	20	13	QMAG	7.6	9.7	6.8
ENT	Annual mean	40.5	36.9	30.2	CHA	11.0	11.2	7.7
	Exceedances	81	68	19	FUN	10.4	8.4	5.7
QMAG	Annual mean	35.1	33.5	26.0	VER	22.0	21.3	7.8
	Exceedances	36	41	19	SG	9.2	9.9	7.5
CHA	Annual mean	22.6	20.0	16.1	SMIN	11.0	10.6	8.4
	Exceedances	16	1	1	OLO	10.9	10.7	4.0
FUN	Annual mean	21.8	14.9	11.6	ERV	14.4	11.3	8.7
	Exceedances	14	1	0				
VER	Annual mean	37.7	39.0	25.8				
	Exceedances	86	87	28				
SG	Annual mean	20.0	22.8	19.7				
	Exceedances	17	17	9				
SMIN	Annual mean	14.4	16.1	14.2				
	Exceedances	4	2	4				
OLO	Annual mean	26.0	19.4	15.6				
	Exceedances	16	2	4				
ERV	Annual mean	25.5	25.4	15.5				
	Exceedances	23	17	4				

PM concentrations follow a pronounced seasonal variation (Figure 2.4.1) with much higher values in winter than in summer. Higher PM levels in winter can be attributed to increased emitting activities (e.g. residential heating) together with more stable atmospheric conditions, leading to poor dispersion. This seasonality is, at least in part, also explained by a greater partitioning of secondary compounds (e.g. nitrates) in the aerosol phase during colder periods (Donahue et al. 2006). FUN and Lamas de OLO (OLO), two high altitude mountain stations, represent exceptions. These two sites are particularly known by the extremely high ozone

levels during summer (e.g. Carvalho et al. 2010) and the intense photochemically-driven secondary formation of aerosols (e.g. Alves et al. 2010a) from biogenic volatile organic compounds (VOCs), which react with anthropogenic gaseous precursors from long range transport. As can be seen for OLO (Figure 2.4.2), these sites are influenced by a cluster of air mass trajectories that originates in the Bay of Biscay, following a northeast transport pathway from the north of the Iberian Peninsula or through the centre of the Iberian Peninsula, which likely contributes to the influx of more pollution. The mountain stations are also influenced by a north flow regime from the region of Galicia, which brings NO_x emissions from several thermal power plants located in that Spanish region. The highest concentrations are concurrently registered under the influence of air masses from the neighbour country or passing by the metropolitan area of Oporto, while the lowest correspond to periods in which air masses originate in the NE Atlantic.

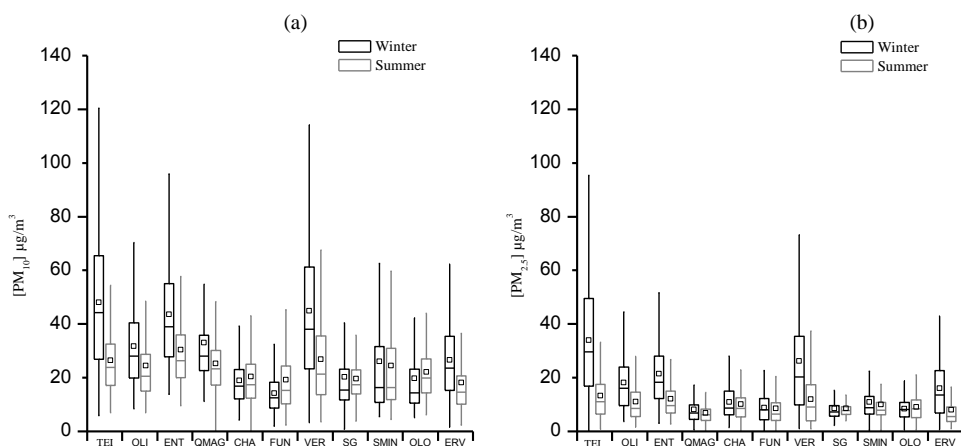


Figure 2.4.1 – Seasonal concentrations: (a) PM_{10} ; (b) $\text{PM}_{2.5}$. Each box is determined by the 25th and 75th percentiles and the whiskers are determined by 5th and 95th percentiles.

The lowest $\text{PM}_{2.5}$ levels and a weak seasonal variability were registered in the two urban background stations of Madeira Island (Quinta Magnólia-QMAG and São Gonçalo-SG). Clean air masses over the Atlantic (Figure 2.4.3) and a very mild climate justify this observation. Regardless of the cluster, concentrations do not vary much, and only a slight increase is observed for trajectories closer to the Portuguese and African coast. However, these island stations do not register the lowest PM_{10} levels. Due to the strong Atlantic influence, relatively high levels of sea salt particles are expected, which dominate the coarse mode. On the other hand, in winter, sporadic African dust outbreaks reach the island (Cachorro et al. 2006). The dominance of coarse particles is expressed by high annual $\text{PM}_{10}/\text{PM}_{2.5}$ ratios, which reached values up to 4.6 in QMAG.

As observed for background stations, the lowest PM concentrations at traffic and industrial sites, such as ENT (Figure A1) and TEI (Figure A2), respectively, were registered under the

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influence of westerly and northerly Atlantic flows, while higher values are attained when air masses follow a northeast transport pathway from the north or through the centre of the Iberian Peninsula. These continental air masses bring aged aerosol pollution, which joint the freshly emitted or formed particles from local sources.

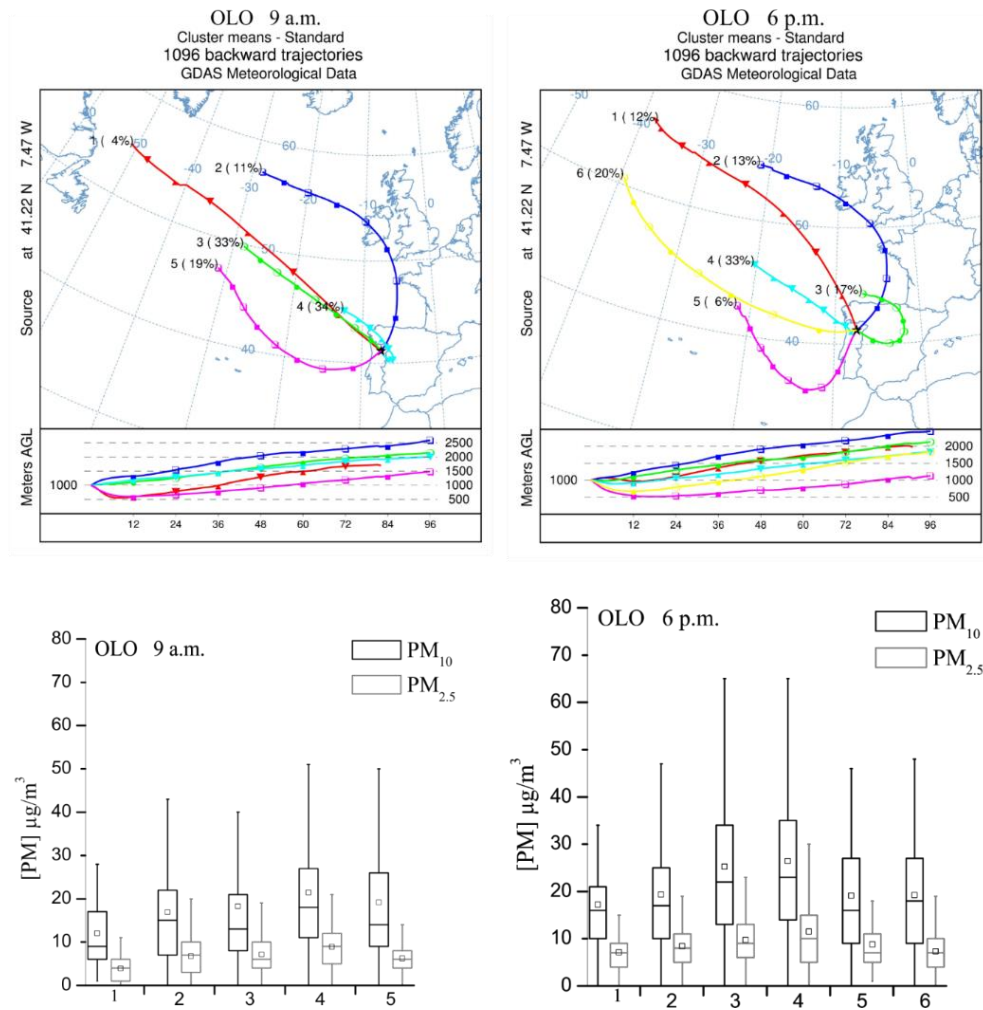


Figure 2.4.2 – Clusters of air backward trajectories and PM levels for OLO.

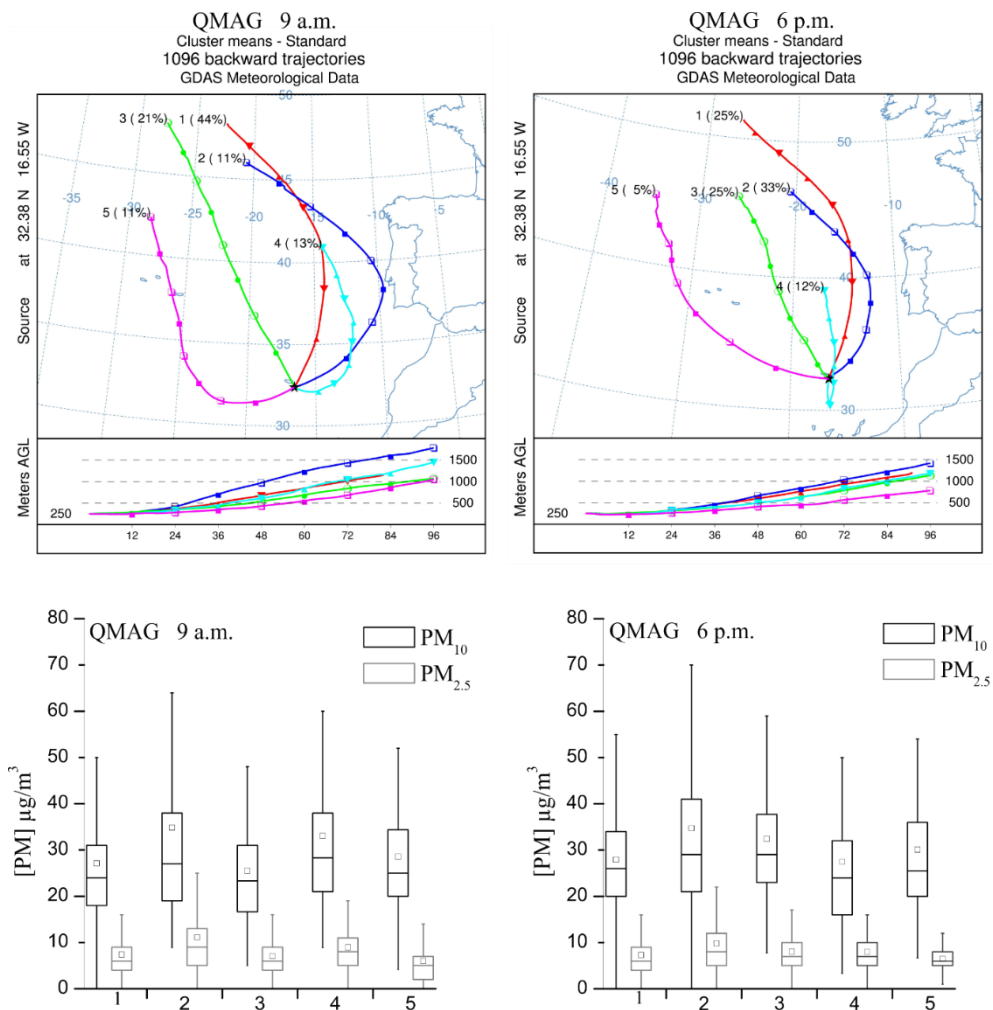


Figure 2.4.3 – Clusters of air backward trajectories and PM levels for QMAG.

In general, an increase in both PM_{10} and $PM_{2.5}$ concentrations are observed in the early evening (Figures 2.4.4 and 2.4.5). During night-time the wind speed is generally slower and the nocturnal boundary layer shallower, decreasing the dispersion of pollutants. This causes the confinement of aerosols and manifest as an increase of concentrations in the early night period. As night advances, there is a substantial decrease in aerosol generation, while particles tend to settle to the ground by gravity, resulting in a decrease of concentrations in the early morning hours. Similar nocturnal behaviour has been reported for many other regions (Vecchi et al. 2007; Balakrishnaiah et al. 2011). It should be noted, however, that in mainland Portugal, in wintertime, residential biomass burning may represent a very significant emission source contributing to the enhancement of PM levels in the early evening (Gonçalves et al. 2012). An early morning rush hour peak is well established in the diurnal profiles of traffic sites, such as ENT. A decrease of concentrations in the early afternoon is

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observed, especially at coastline stations. This may be a “cleansing” effect of sea breezes, a frequent mesoscale phenomenon that develops during the late morning and early afternoon (Carvalho and Prior 1994).

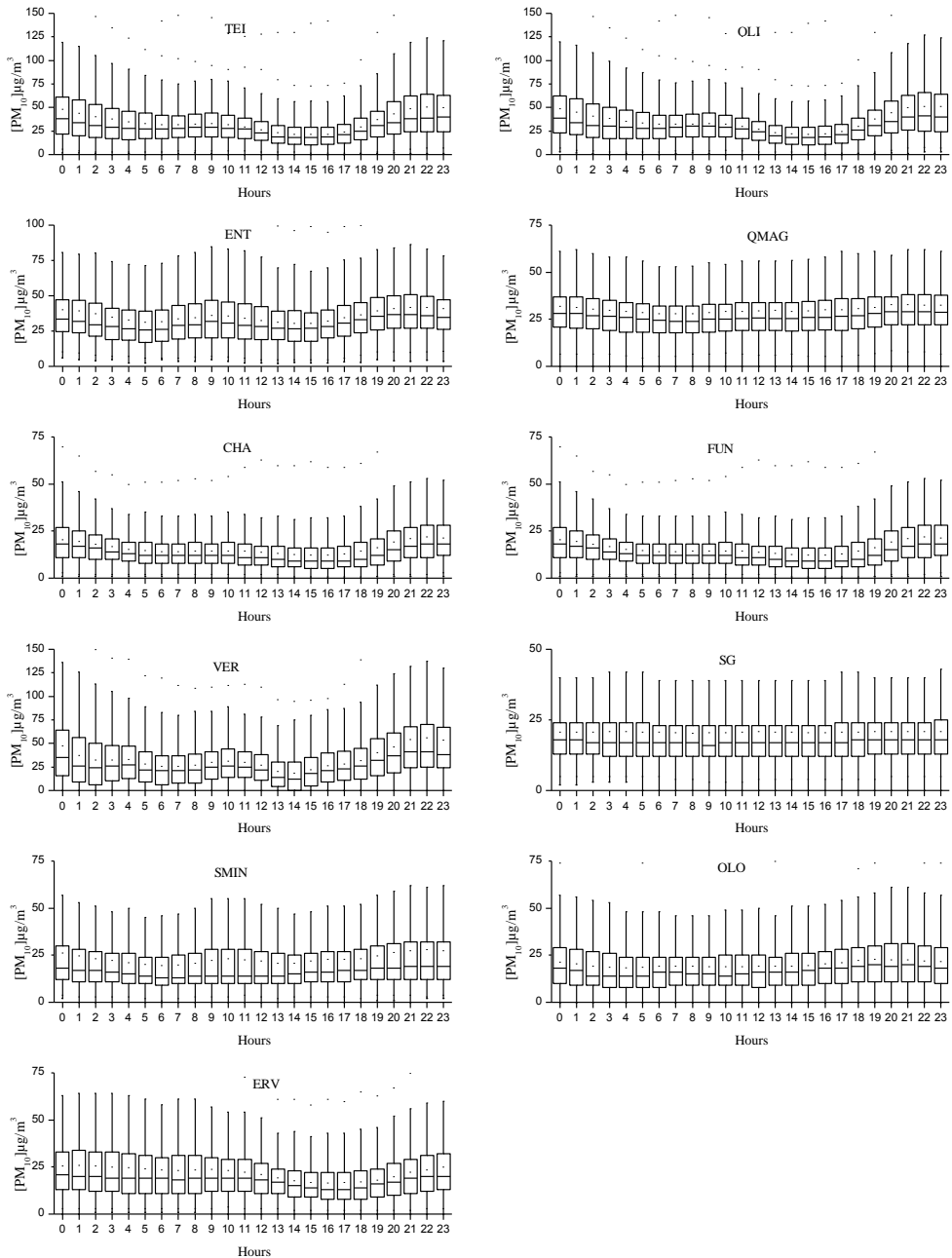


Figure 2.4.4 – Daily variability of PM₁₀ concentrations.

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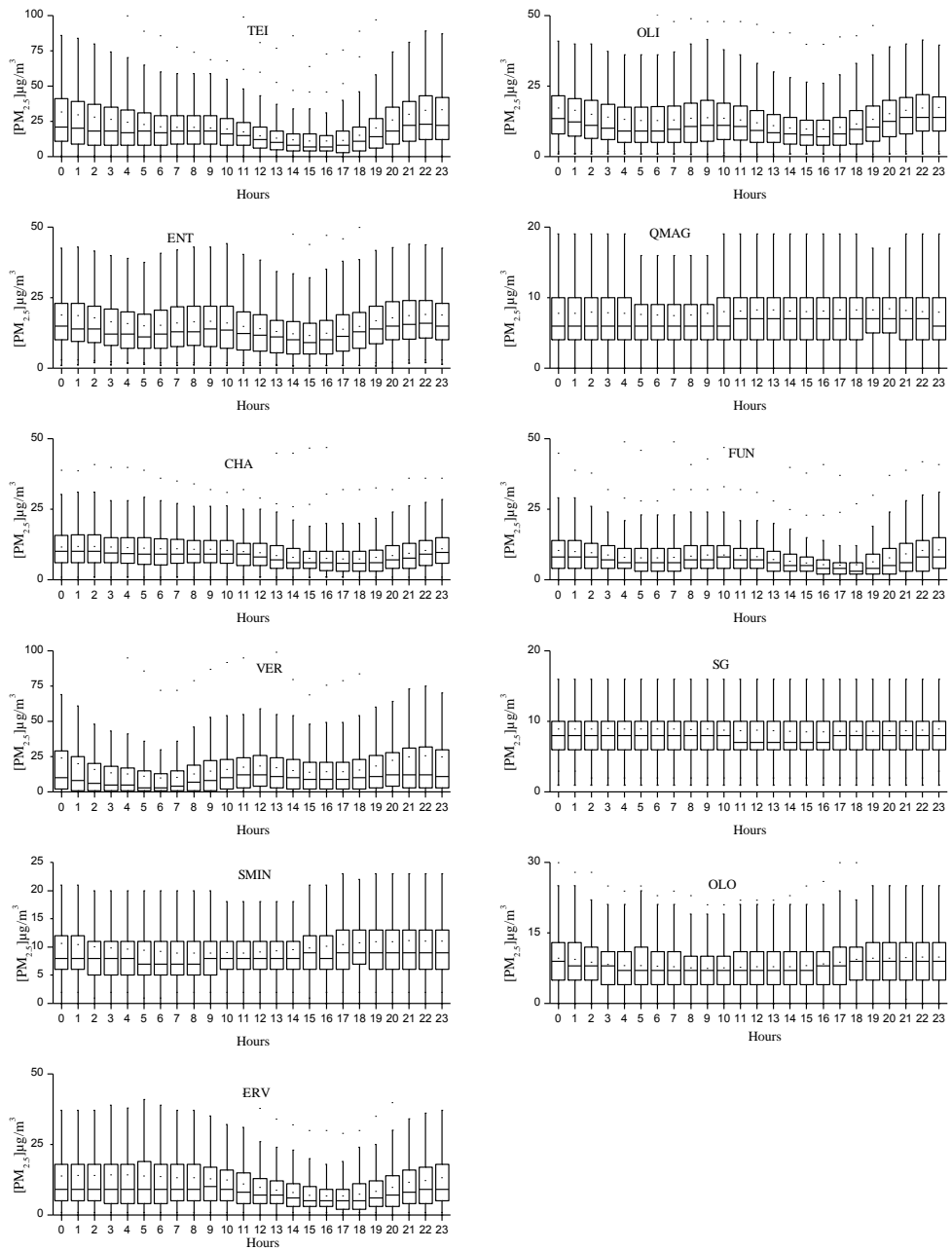


Figure 2.4.5 – Daily variability of $PM_{2.5}$ concentrations.

2.4.2 Wavelets

The distance function is given by $dw(i,i')$ where the smaller is $dw(i,i')$ the closer are the stations in terms of variance/covariance profile. Figure 2.4.6 presents dendrograms where stations with closer profiles stay together.

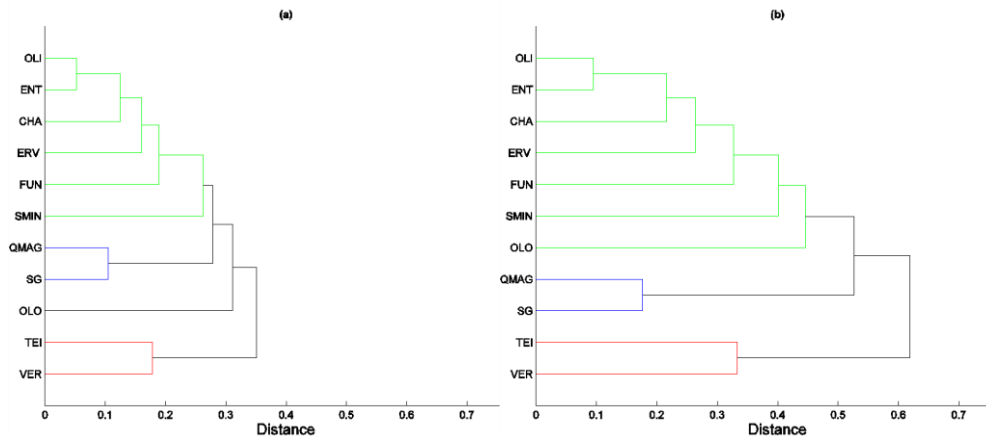


Figure 2.4.6 – Dendrogram showing the hierarchical clustering of the monitoring stations (average link criteria). The classification is based on the distance metric d that is a weighted combination of the variance profile d_{vv} and covariance profile d_{wc} : (a) the weight is 0.5 in variance and 0.5 in covariance; (b) the weight is 1 in variance and 0 in covariance.

Depending on the weights in variance and covariance, the dendrograms clearly distinguishes three or four groups of similar monitoring stations. The island urban background stations, QMAG and SG, are always merged into the same group. TEI (industrial station) and Vermoim (VER) (urban traffic station) are embedded in another cluster. It should be recalled that the highest PM concentrations have been registered in these two stations and that VER is under the influence of intense emission sources (e.g. oil refinery, commercial harbour, etc.), which gives it a more industrial character. Thus, this latter station should probably be categorised as a suburban industrial or, in alternative, be relocated if the goal is to capture effectively urban traffic emissions. Another cluster is formed by the rural stations of Chamusca (CHA), Ervedeira (ERV), Fundão (FUN) and Senhora do Minho (SMN) and by the two urban stations of Lisbon (ENT and Olivais-OLI). These two are the stations that have the most similar variance/covariance profiles among all. Depending on the weights in variance and covariance, OLO may be included in this group or come alone. Dissimilarities between rural stations increase with increasing geographical distance to Lisbon.

Each wavelet scale corresponds to a certain time scale, where scale τ_j captures the dynamics over intervals with duration from 2^j to 2^{j+1} time units, as described by Gouveia et al. (2015). The rural sites of CHA, ERV, FUN, OLO and Senhora do Minho (SMN), as well the urban monitoring stations of OLI and ENT, present a $j = 4$ scale that contains variance/covariance associated with phenomena with a time duration between 2^4 and 2^5 units (Figure 2.4.7). This represents physical phenomena with duration between 16 and 32

hours, which include the daily cycles typical of PM_{10} and $PM_{2.5}$ (Figures 2.4.4 and 2.4.5). In the same way, TEI and VER also seem to have a clear daily cycle ($j = 4$). QMAG and SG present relevant variance/covariance in higher wavelet scales ($j = 5, 6, 7, 8, 9$) that correspond to lower periodicity phenomena, between 32 and 1024 hours, which include a weekly and a monthly variation. This suggests that Madeira island is under the influence of meteorological and circulation phenomena over the Atlantic having seasonal and subseasonal time scales, such as changes in the trade winds associated with the Azorean high and the Intertropical Convergence Zone (Cropper 2013). These phenomena will probably have reflexes on PM levels that override the diurnal cycle of emission sources, contributing to very smooth daily concentration profiles (Figures 2.4.4 and 2.4.5).

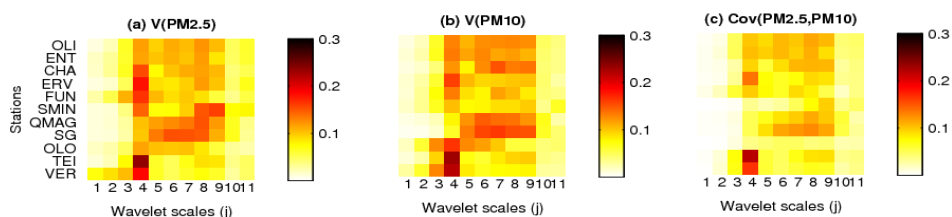


Figure 2.4.7 – Mosaic plot representing the contribution to the total variance/covariance of the time series *per* wavelet scale for all stations (darker colours indicate higher absolute values).

Figure 2.4.7c shows that PM_{10} and $PM_{2.5}$ are positively associated for all the clusters and for all scales. The best association was obtained for TEI and VER, suggesting common emission sources or formation processes. The similarity between these two stations raises again the possibility of misclassification of VER. These stations started monitoring in the early 1990s and urban and industrial areas have greatly expanded since then. It is necessary to update the classification of monitoring stations according to the type of environmental influence.

2.5 Conclusions

Three-year data sets of simultaneous measurements of PM_{10} and $PM_{2.5}$ in different mainland and insular air quality stations in Portugal were analysed in this study. Although a decreasing trend in concentrations has been observed, the WHO guidelines were surpassed in all monitoring sites. The highest levels were registered in stations classified as “urban traffic” or “suburban industrial”. This means that additional abatement measures should be adopted, including restrictions to the circulation of heavy vehicles, street washing, incentives to the replacement of traditional woodstoves and fireplaces by certified residential combustion equipment or by gas central heating, creation of low-emission zones in city centres, implementation of no-drive days based on license numbers, adoption of the best available technologies by industries, etc.

In addition to local sources, meteorology and long range circulation patterns also influence the seasonal and daily concentration profiles. Clean air masses from the Atlantic and mild year-round temperatures contribute to relatively low concentrations and to very smooth daily and seasonal variation profiles in urban background stations of Madeira island. Contrary to that observed in other mainland stations, high altitude mountain sites present higher summer concentrations, probably due to enhanced formation of secondary aerosol arising from photochemical reactions between biogenic compounds and anthropogenic precursors transported from the north or through the centre of the Iberian Peninsula or from the metropolitan area of Oporto.

The variance/covariance profiles were embedded in a wavelet decomposition-based clustering algorithm to identify groups of monitoring sites exhibiting similar profiles, thus representing the same type of area or station. Insular stations, which were grouped into the same cluster, presented relevant variance/covariance in higher wavelet scales that correspond to lower periodicity phenomena (weekly and monthly variation). The cluster composed of rural stations and the urban sites of Lisbon revealed wavelet scales corresponding to the daily cycles. The urban traffic site of VER was clustered with an industrial station, showing significant variance/covariance for time scales also encompassing the daily cycle. Thus, VER probably needs revision in what respects its classification according to the type of environment and influence. Together with other criteria or methods, this data mining process can help government agencies in air pollution management.

2.6 Appendix

Additional information concerning the monitoring stations, such as ENT (Figure A1) and TEI (Figure A2), respectively.

3 Spatial Mapping of the City of Lisbon using Biomonitors

Based on article of same title:

Cruz AMJ, Freitas MC, Canha N, Verburg TG, Almeida SM, Wolterbeek HT
Int. J. of Environment and Health (2012) Vol.6, No.1:1 – 17.
DOI: 10.1504/IJENVH.2012.046852

3.1 Abstract

Biomonitoring is used to study the performance of a single air sampler as representing air elemental concentrations in Lisbon. A database of chemical elements' concentrations was obtained by analysing exposed lichens and bark, hung on courtyards trees of 22 Lisbon basic schools from January to May 2008 and June to October 2008 (winter and summer campaigns). Electric conductivity was also measured in lichens, as a sensitive indicator of lichen vitality and, indirectly, of air pollution. This work also enabled evaluation of stress effects in lichens as a result of transplanting from unpolluted to air-polluted areas, the adaptation of transplanted biomonitors into new meteorological and physical-chemical conditions, and the comparison of performance of both biomonitors.

3.2 Introduction

Almeida et al. (2007) concluded that it is essential to understand the distribution of pollutants in larger geographical boundaries to analyse the spatial representativeness of the measurements provided from one single sampling station. If the data of the latter are used to estimate an entire city population exposure, the potential health effect of individual particulate matter species with low station-to-station correlation would be underestimated or overestimated compared to the species that have high station-to-station correlation. The use of biomonitors to evaluate spatially large geographical areas is now a well-established method (Marques 2008).

The extraordinary capability of some lichen species to grow at large geographical areas and to accumulate chemical elements far above their need, rank them among the best bioindicators of air pollution. Biomonitors could be advantageously used to apportion the distribution of element concentrations in such large areas (Farinha et al. 2004b).

Electric conductivity was pointed out as the most sensitive parameter for physiological response of lichens to environmental stress, when compared to Normalized Difference Vegetation Index (NDVI) and chlorophyll degradation, being also related to the whole lichen and not to just the photobiont as are many other parameters (Marques et al. 2005).

Parmotrema bangii is used in this work because previous studies indicated it as an adequate choice in biomonitoring studies (Vieira et al. 2007). *Cryptomeria japonica* is also an alternative to epiphytic lichens for air-monitoring purposes (Freitas et al. 2003). The main implicit assumption in these studies is that the *P. bangii* and *C. japonica* response behaviour can be compared throughout the whole investigated area, irrespective of variances in ambient conditions (Pacheco and Freitas 2004).

In this work, *P. bangii* epiphytic lichen and *C. japonica* tree bark were transplanted from Azores to 22 school courtyards of Lisbon, from January to May 2008 (winter campaign) and from June to October 2008 (summer campaign).

3.3 Methodology

3.3.1 Sampling and Chemical Analysis

Parmotrema bangii was collected from *Cryptomeria japonica* in São Miguel, Azores islands (WGS84: N37°47'25,6";W25°38'12,8"; elevation: 261 m). For the summer campaign, the time between the collection of the biomonitors and its exposure was about eight days, including 3-4 days for the transport and 3-4 days for the laboratory preparation. For the winter campaign, the time between sampling and exposure was around three weeks.

In the laboratory, the samples were cut in pieces of around 6 cm x 6 cm, composed of the lichen over the bark; the sets were air-dried for 24 h and hung in school courtyard trees using nylon strings. Each courtyard of the 22 Lisbon schools had four sets exposed. Figure 3.3.1 shows the distribution of the selected Lisbon schools.

Ten unexposed samples of either lichen or bark, in each of the campaigns, were kept for measuring the initial conditions prior to exposure.

Table 3.3.1 shows the number of prepared samples, the number of selected schools and the number of samples collected after exposure. At the exposure end of experiments, some replicates could not be found (due to cutting of the tree branches, vandalism, fall, etc.).

After exposure, bark was separated from lichen in all replicates, both cleaned from dust, leaf debris, fungus contamination and degraded material, rinsed three times for 5 s in double distilled water (Garty et al. 2001; Godinho et al. 2004), freeze-dried and ground in Teflon™ (balls and capsules) mills under liquid nitrogen. After homogenisation, pellets of 250-300 mg were prepared and put into polyethylene vials for neutron irradiation. Each vial contained up to ten pellets.

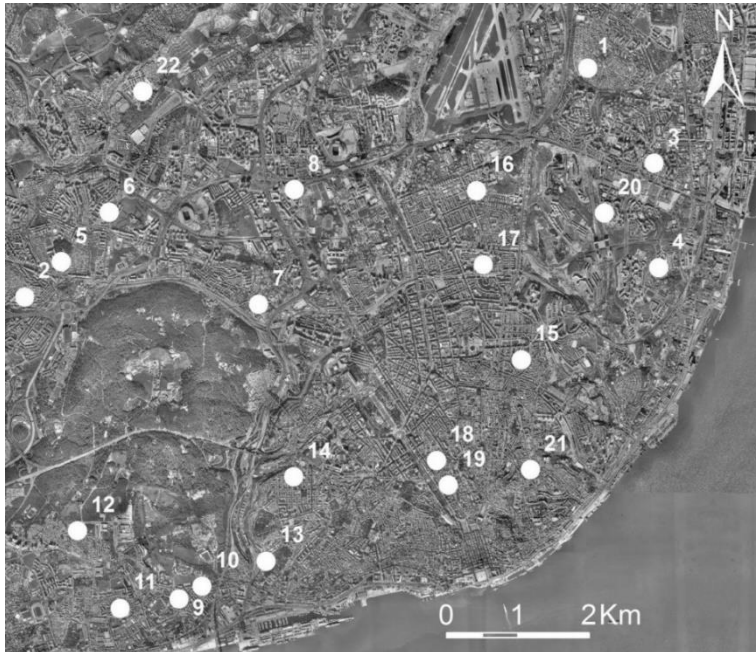


Figure 3.3.1 – Location of the 22 Lisbon schools where bark and lichens were exposed in winter and in summer campaigns.

Table 3.3.1 – Number of prepared samples, selected schools and samples collected after exposure in winter and summer campaigns.

Campaign	Number of studied schools		Number of prepared samples			Number of collected samples		
	Total	Collection of Effective biomonitor	<i>Parmotrema bangii</i>	<i>Criptomeria japonica</i>	Total	<i>Parmotrema bangii</i>	<i>Criptomeria japonica</i>	Total
Winter	22	14	88	88	176	41	38	79
Summer	22	20	88	88	176	66	60	126

Elemental chemical content was determined by Instrumental Neutron Activation Analysis (INAA). The samples were irradiated at the Portuguese Research Reactor (RPI; ITN-Sacavém). The long (7 h) irradiations were performed at a thermal neutron flux of 2.88×10^{12} n.cm⁻².s⁻¹. Gamma-spectra of the irradiated samples were acquired with high-resolution, hyperpure-Ge detectors, after 4 days and 4 weeks with a counting time of 2 h and 3.5 h, respectively. The samples were analysed by the k_0 -standardized neutron activation analysis (De Corte 1987; Freitas and Martinho 1989; De Corte et al. 1993) using 0.1% Au–Al discs were as comparators.

Quality control was asserted by analysing certified reference materials IAEA-336. Deviations from certified values were generally within 1–15%, except for Sb, which exceeded this range (Vieira et al. 2007).

Lichen samples of 100 mg each were immersed in 10 ml double-distilled water for 60 min to determine the lichen vitality (Godinho et al. 2004). The electric conductivity of the water before and after the lichen immersion was measured with an electric conductivity meter (*Mettler Toledo*).

3.3.2 Meteorological data and data processing

Lisbon meteorological data (pressure, humidity, temperature and wind direction) was measured by Gago Coutinho meteorological station (N38°46'; W9°08') and supplied by the Portuguese Meteorological Institute.

Student's t-tests, Z-tests and Pearson correlations were applied to the data. All statistical tests were performed using Microsoft Excel and a 95% significance level was chosen.

Frequency distribution of wind direction normalized to a total of 100 per season followed a radar diagram using a *Excel* software. Chemical elements spatial distribution mapping used *ArcGis 9.2* software.

3.4 Results and Discussion

3.4.1 Conductivity

Statistically significant difference ($p = 0.00$) in humidity and temperature parameters between winter (73%; 14⁰C) and summer (67%; 20⁰C), were registered, with a warmer and drier period in summer. Figure 3.4.1 shows the distribution of wind predominant directions during the studied periods. Summer has wind predominance from WNW and NNW; in winter, two main directions dominate: WNW and ENE.

Conductivity is related with the health/vitality of lichens. Larger conductivity means higher number of damaged cell membranes and, consequently, a lower level of lichen vitality. Concerning the unexposed lichens, no statistically significant difference between lichen conductivity in winter and summer (14±12 and 28±11 mS/(mg.cm), respectively) was found ($p = 0.2$). This means that both Azores lichen sets were part of the same population and that the eight days and three weeks between sampling and exposure did not affect differently the unexposed lichens.

The spatial distribution of lichen conductivity at the end of the winter and summer campaigns for 12 locations in Lisbon (Figure 3.4.2) show variability between the two campaigns and variability across the studied area. Conductivity was significantly higher at the end of summer than at the end of winter ($p = 0.00$), which is explained by the significantly lower humidity and higher temperatures in summer (see above). The lichens' stress during summer months

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has been observed before in Portugal (Reis 2001; Freitas and Pacheco, 2004; Marques et al. 2005; Godinho et al. 2008; Marques 2008). Furthermore, in winter exposed and unexposed lichens showed significant differences ($p = 0.00$), while in summer no differentiation was observed ($p = 0.14$). It is then concluded that, in Lisbon, conductivity is suitable for studying spatial differentiation of air pollution in winter, but not in summer.

Comparing Figures 3.4.1 and 3.4.2, it may be concluded that: 1) during the summer campaign, the humidity comes from WNW/NNW where the Atlantic Ocean is. It would be expected that the lichens positioned over that direction might have lower conductivity; this is actually observed. The lichens positioned towards east present higher conductivity; 2) the lichens exposed during winter had humidity the whole period and the conductivity is low at all sites when compared with the summer period.

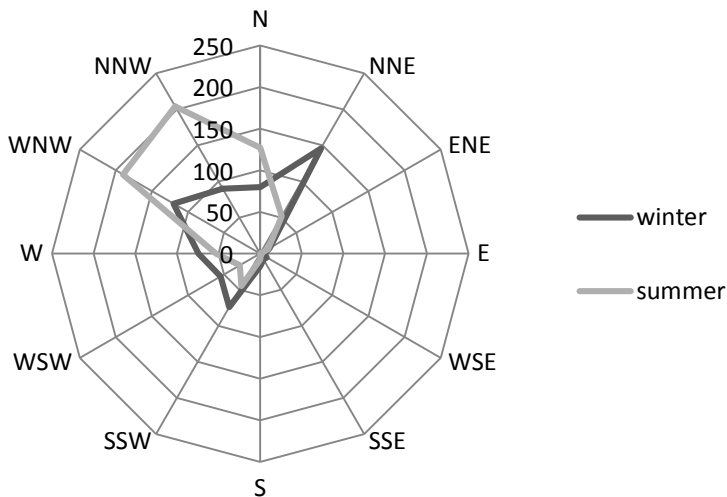


Figure 3.4.1 – Frequency of wind direction normalized to a total of 100 per season, in Lisbon city, 2008.

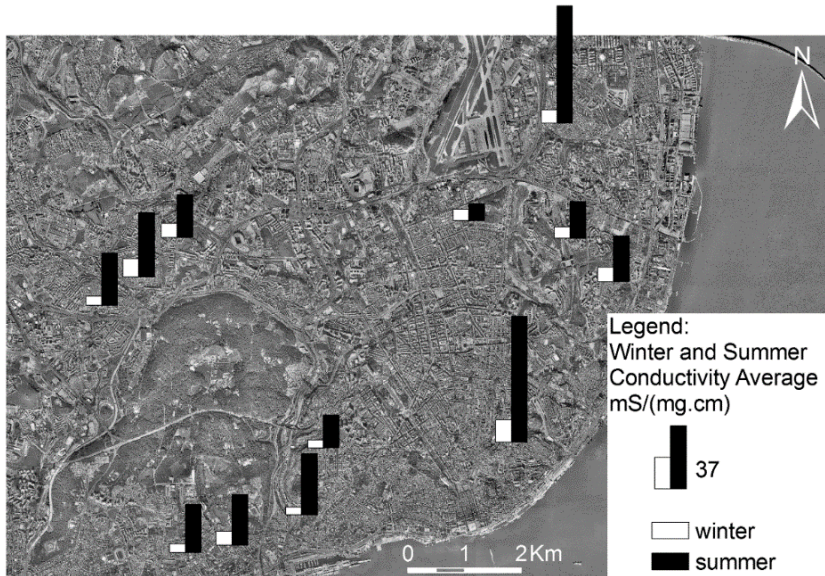


Figure 3.4.2 – Conductivity spatial distribution obtained in lichens at the end of the winter and summer campaigns.

3.4.2 Chemical Elements

In order to verify eventual element release or accumulation in bark and lichen, the (exposed/unexposed) concentration ratios was calculated at the end of the campaigns, the results are presented in Tables 3.4.1 and 3.4.2.

In bark, the concentration of the elements Br, Co, Hf, Rb, Sb increased significantly during winter campaign. Rb, Sb, Zn showed a significant accumulation during summer. It may be concluded that sources with Rb and Sb are present the whole year. Br ratios were significantly different at the end of the two campaigns, with higher element accumulation during the winter season.

Concerning the lichen samples, significant accumulation of the elements Ce, Co, Eu, Fe, Sb, Sm, Sc, and Zn during the summer campaign is observed. Sb shows a significant accumulation in both campaigns, indicating a Sb source the whole year as concluded above for bark. Zn in bark and lichens was behaving identically during summer. Sb and Zn are indicative sources of traffic (Nriagu 1989; Sternbeck et al. 2002; Almeida et al. 2009). Sodium concentrations showed a significant release during winter. Leaching of Na in lichens by rainfall is a known fact (Reis 2001; Reis et al. 2002). Between campaigns, there are significant differences in accumulation for the elements Ce, Fe, Sb, and Sc, with higher values during summer campaign; mostly they are soil-related and soil dust is more resuspended in summer than in winter.

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Table 3.4.1 – Average (exposed/unexposed) concentration ratios in bark at the end of the winter and summer campaigns. Comparison between exposed and unexposed values (same campaign) and between campaign ratios.

	<i>Bark</i>									
	<i>Winter</i>				<i>Summer</i>				<i>Winter-Summer</i>	
	<i>N</i>	<i>Aver</i>	<i>Stdev</i>	<i>P Z-test</i>	<i>N</i>	<i>Aver</i>	<i>Stdev</i>	<i>P Z-test</i>	<i>P t-test</i>	
Br	12	1.97	0.33	0.00	15	1.07	0.22	0.75	0.02	
Ce	12	3.15	1.25	0.08	15	2.90	1.34	0.16	0.83	
Co	12	5.27	1.92	0.03	15	2.30	0.88	0.14	0.07	
Cr	11	3.42	1.46	0.10	15	4.17	2.23	0.15	0.65	
Eu	12	0.67	0.32	0.31	15	2.40	1.38	0.31	0.10	
Fe	12	2.65	1.15	0.15	15	3.05	1.61	0.20	0.74	
Hf	12	4.20	1.52	0.04	15	3.27	2.23	0.31	0.58	
La	12	2.32	0.89	0.14	15	2.16	0.88	0.19	0.84	
Na	12	1.04	0.18	0.83	15	0.77	0.17	0.18	0.14	
Rb	9	2.43	0.66	0.03	14	3.01	0.92	0.03	0.42	
Sb	12	4.59	1.79	0.05	15	3.04	1.00	0.04	0.26	
Sc	12	3.59	1.56	0.10	15	3.06	1.82	0.26	0.72	
Sm	12	3.64	1.53	0.08	15	3.00	1.35	0.14	0.62	
Sr	11	1.47	0.31	0.13	14	2.04	1.00	0.30	0.40	
Zn	12	3.48	1.44	0.08	15	2.96	0.90	0.03	0.63	

Note: Values significantly different at 95% level (*p* value) are in bold.

Table 3.4.2 - Average (exposed/unexposed) concentration ratios in lichen at the end of the winter and summer campaigns. Comparison between exposed and unexposed values (same campaign) and between campaign ratios.

	<i>Lichen</i>									
	<i>Winter</i>				<i>Summer</i>				<i>Winter-Summer</i>	
	<i>N</i>	<i>Aver</i>	<i>Stdev</i>	<i>P Z-test</i>	<i>N</i>	<i>Aver</i>	<i>Stdev</i>	<i>P Z-test</i>	<i>P t-test</i>	
Br	14	0.70	0.16	0.06	15	0.84	0.23	0.47	0.44	
Ce	14	1.01	0.21	0.96	15	1.65	0.30	0.03	0.04	
Co	14	1.46	0.27	0.09	15	1.73	0.28	0.01	0.29	
Cr	14	0.88	0.35	0.74	15	1.25	0.28	0.38	0.23	
Eu	14	1.10	0.28	0.73	15	1.75	0.33	0.02	0.06	
Fe	14	1.46	0.30	0.12	15	2.33	0.41	0.00	0.04	
Hf	14	0.78	0.17	0.19	15	1.30	0.29	0.30	0.06	
La	14	0.80	0.16	0.22	15	1.20	0.25	0.41	0.08	
Na	14	0.66	0.14	0.01	15	0.72	0.16	0.08	0.64	
Rb	14	0.93	0.22	0.74	15	1.61	0.46	0.19	0.08	
Sb	14	3.39	0.93	0.01	15	7.22	1.38	0.00	0.02	
Sc	14	1.13	0.24	0.60	15	2.01	0.40	0.01	0.03	
Sm	14	1.12	0.24	0.63	15	1.74	0.37	0.05	0.07	
Sr	8	0.89	0.28	0.69	14	1.52	0.85	0.54	0.29	
Zn	14	3.55	5.50	0.64	15	2.93	0.33	0.00	0.85	

Note: Values significantly different at 95% level (*p* value) are in bold.

To check whether there is a significant relationship between the element concentrations in exposed bark and lichen, Pearson's correlation coefficients were calculated for both campaigns. The results are shown in Table 3.4.3. A positive and statistically significant

Chapter 3 – Assessment of the main pollution sources of Lisbon area using transplanted biomonitors (bark and lichen)

correlation between the concentrations of Ce, Eu, Fe, La, Na, Sm, during winter was found. These are essentially elements related to natural sources: soil and sea. During the summer campaign, none of the relationships were statistically significant, most probably due to the lichen damage during that season as demonstrated by the high conductivity values, as discussed above.

Figures 3.4.3 and 3.4.4 show the concentrations of a few chemical elements in bark and lichen at the end of the campaigns. The first conclusion from visualisation is that bark accumulates more than lichen in absolute terms. In general, higher values of bark correspond to higher values of lichen.

Figure 3.4.3 relates soil-related elements; their patterns are very similar indicating same source. Since they result from soil resuspension, it is expected that they are higher in summer than in winter and that they increase with the wind direction. This occurs more in bark than in lichen.

Figure 3.4.4 shows the chemical elements related to traffic/industry and sea-spray. Bark was less sensitive to Na while lichen was less sensitive to Zn. The highest concentrations of Na are in NNE directions, related to winter directions.

Table 3.4.3 - Calculated correlation (*R*) between element concentrations in exposed bark and lichen at the end of the campaigns.

	Winter			Summer		
	N	R	P value	N	R	P value
Br	12	0.19	0.56	14	0.10	0.74
Ce	12	0.75	0.01	14	-0.20	0.49
Co	12	-0.04	0.89	14	0.17	0.57
Cr	11	0.48	0.14	14	0.28	0.34
Eu	12	0.75	0.00	14	0.00	1.00
Fe	12	0.61	0.03	14	0.14	0.64
Hf	12	0.54	0.07	14	0.01	0.96
La	12	0.76	0.00	14	-0.14	0.63
Na	12	0.58	0.05	14	-0.12	0.69
Rb	9	0.20	0.62	13	-0.19	0.55
Sb	12	0.33	0.29	14	0.39	0.17
Sc	12	0.56	0.06	14	0.15	0.61
Sm	12	0.77	0.00	14	-0.16	0.57
Sr	5	-0.08	0.90	12	0.09	0.79
Zn	11	0.32	0.34	14	0.29	0.31

Note: Significant correlations (*p* value) at 95% confidence level are given in bold

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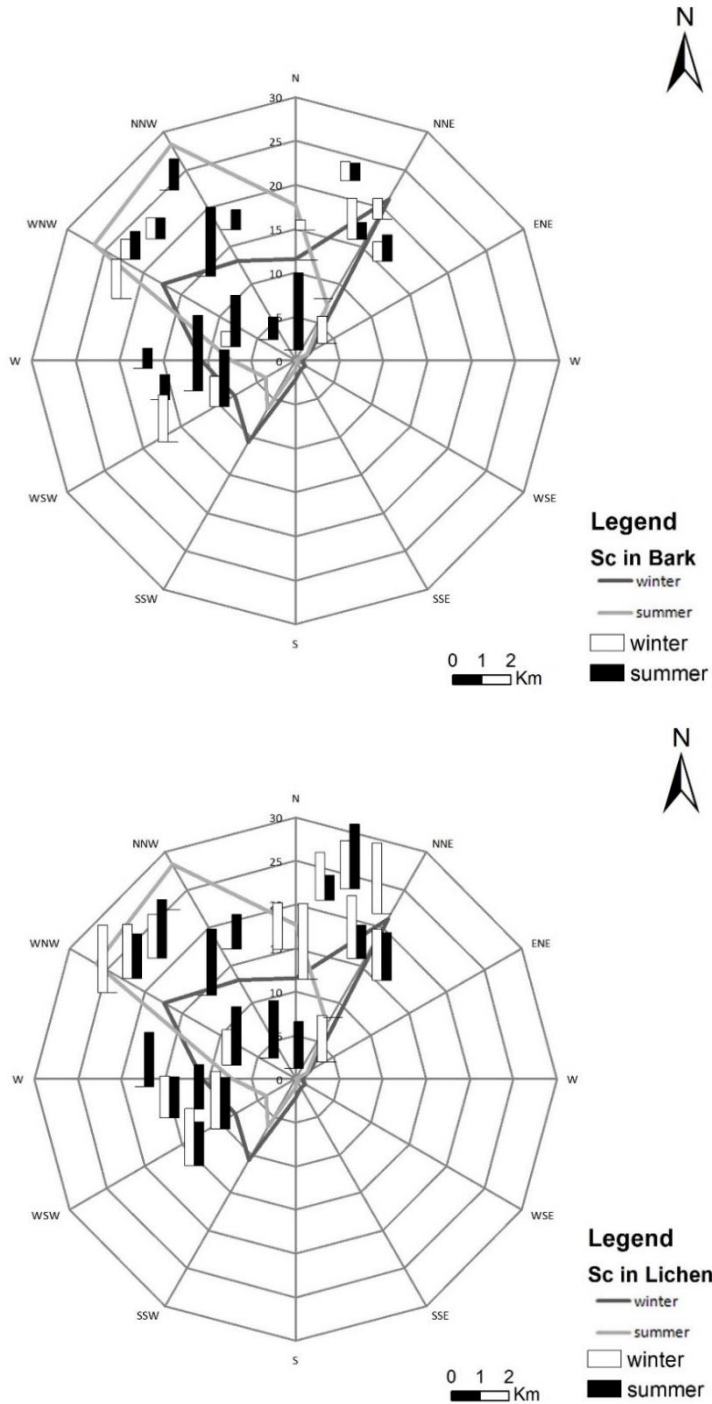


Figure 3.4.3 – Concentrations of Sc, Hf and Fe in bark and lichens exposed during winter and summer campaigns, over the wind direction map of Lisbon city.

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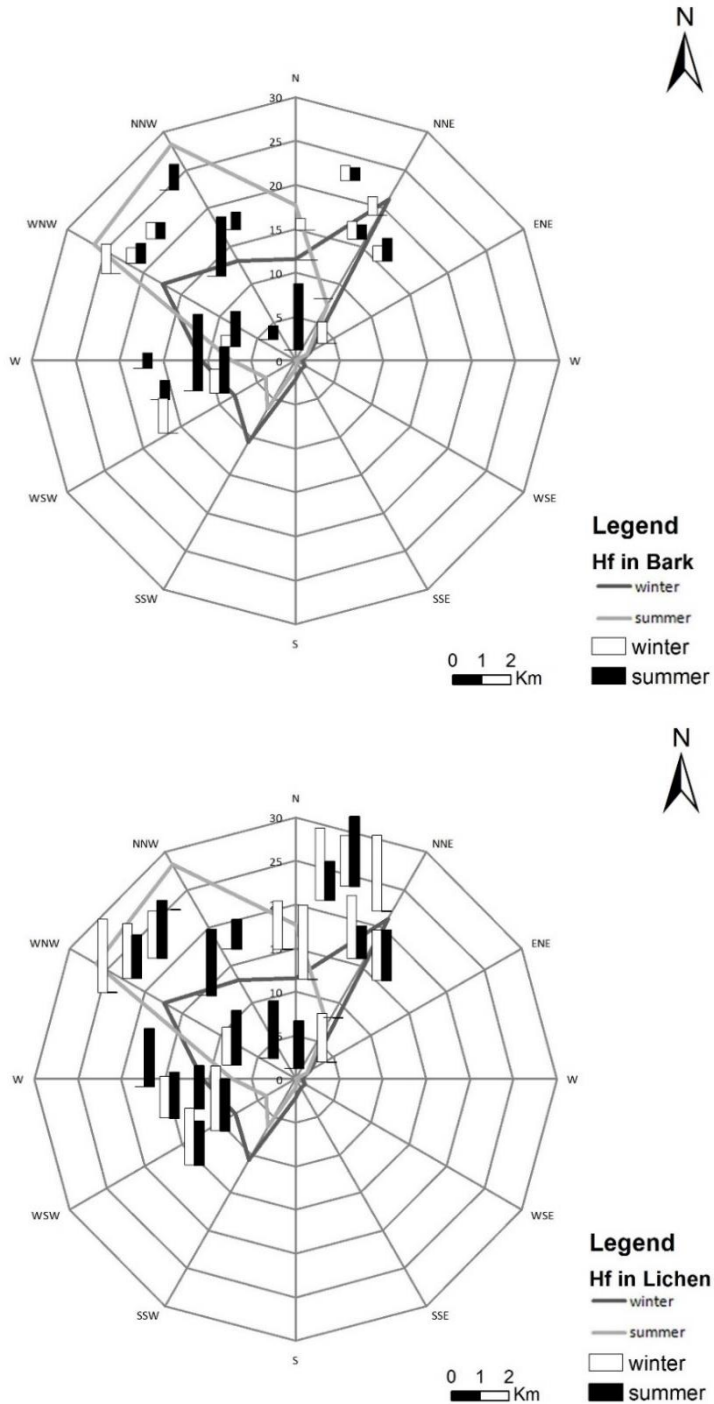


Figure 3.4.3 – Concentrations of Sc, Hf and Fe in bark and lichens exposed during winter and summer campaigns, over the wind direction map of Lisbon city (continued).

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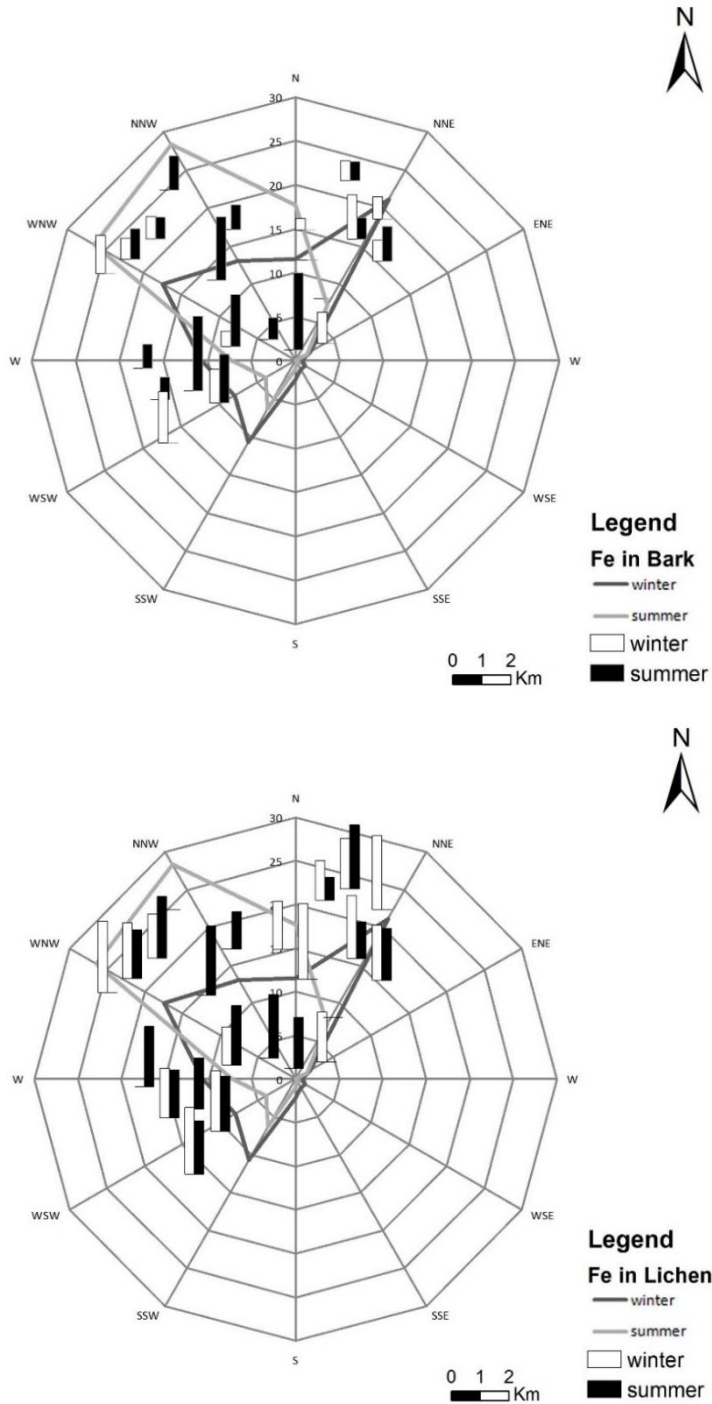


Figure 3.4.3 – Concentrations of Sc, Hf and Fe in bark and lichens exposed during winter and summer campaigns, over the wind direction map of Lisbon city (continued).

Chapter 3 – Assessment of the main pollution sources of Lisbon area using transplanted biomonitors (bark and lichen)

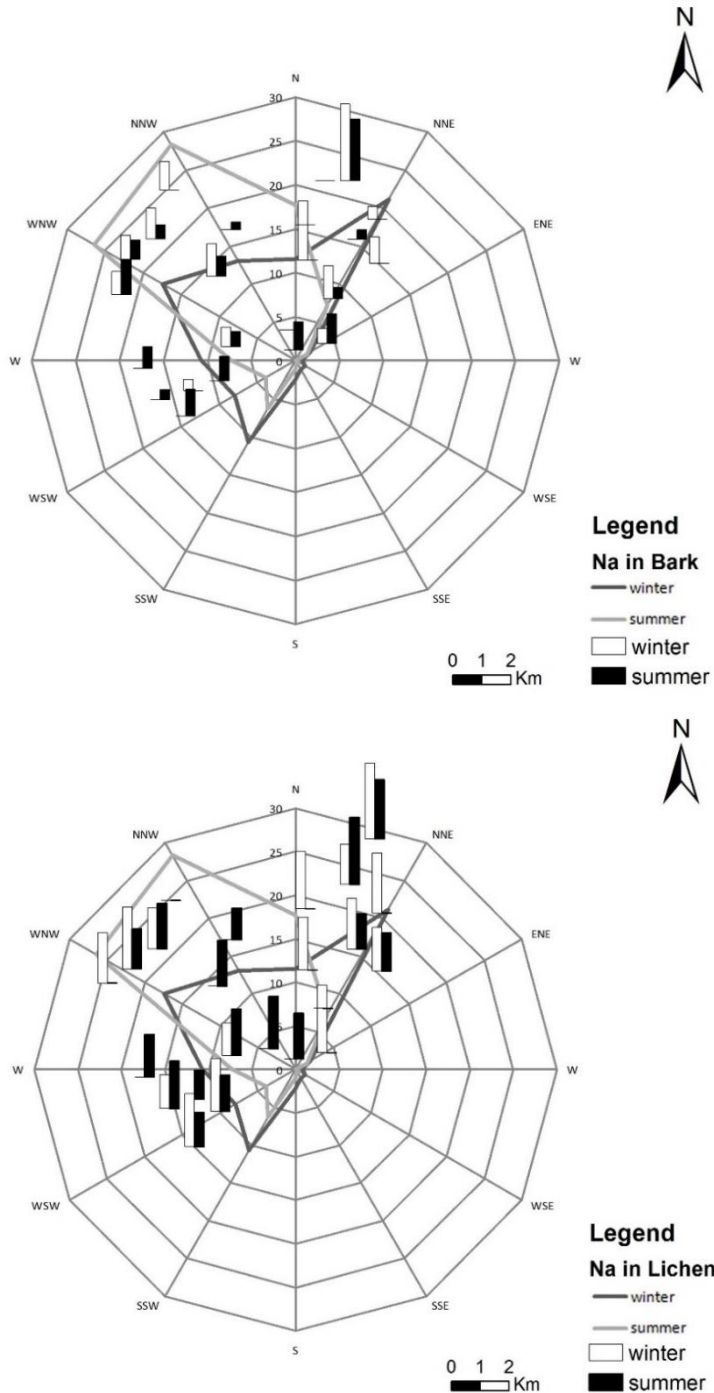


Figure 3.4.4 – Concentrations of Na, Sb and Zn in bark and lichens exposed during winter and summer campaigns, over the wind direction map of Lisbon city.

Chapter 3 – Assessment of the main pollution sources of Lisbon area using transplanted biomonitors (bark and lichen)

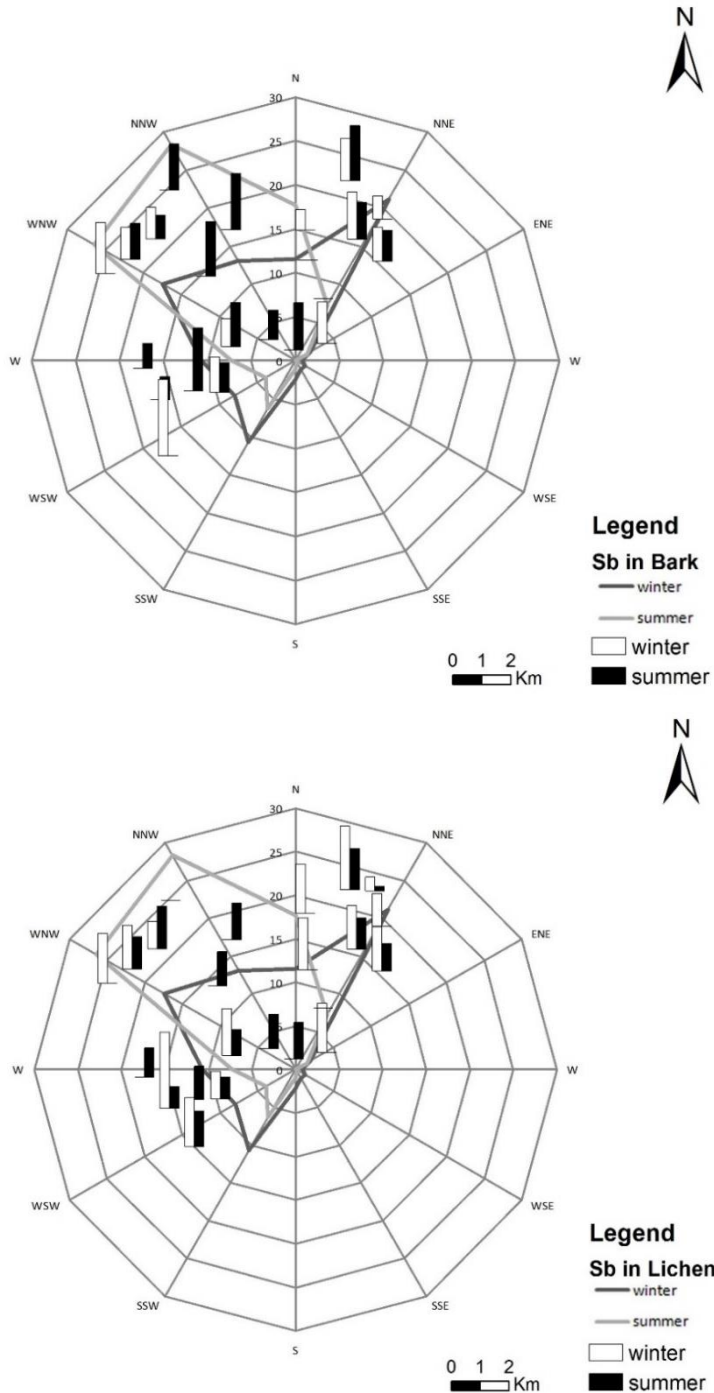


Figure 3.4.4 – Concentrations of Na, Sb and Zn in bark and lichens exposed during winter and summer campaigns, over the wind direction map of Lisbon city (continued).

Chapter 3 – Assessment of the main pollution sources of Lisbon area using transplanted biomonitors (bark and lichen)

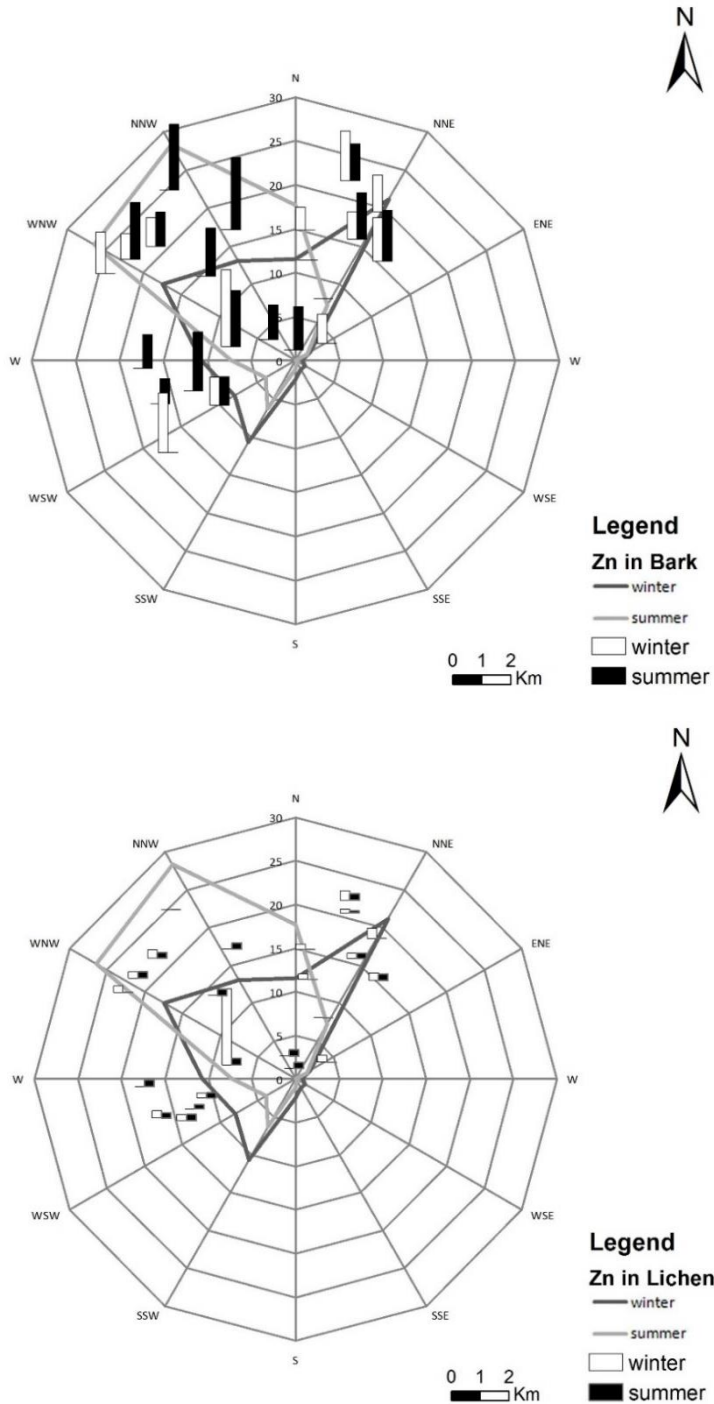


Figure 3.4.4 – Concentrations of Na, Sb and Zn in bark and lichens exposed during winter and summer campaigns, over the wind direction map of Lisbon city (continued).

3.5 Conclusions

Electric conductivity measured in lichens give a spatial response in winter and not in summer. Bark and lichen responded similarly towards Sb and Zn availability, chemical elements related to traffic. There is an excellent correlation between exposed bark and lichen concentrations of natural sources at the end of the winter campaign. This is not observed in summer, neither other correlation, most probably due to lichen damage by lack of humidity and higher temperatures. The spatial distribution of elemental concentrations in bark presents more broadened ranges than the ones for lichens, showing that bark exposure in polluted urban areas might be more adequate than lichens to get responses.

4 Response of Exposed Bark and Exposed Lichen to an Urban Area

Based on article of same title:

Cruz AMJ, Freitas MC, Verburg TG, Canha, N, Wolterbeek HT

Proc. Radiochim. Acta (2011) Vol.1, Issue 1: 363-369.

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4.1 Abstract

The aim of this study is to understand emission sources of chemical elements using biomonitoring as a tool. The selected lichen and bark were respectively *Parmotrema bangii* and *Cryptomeria japonica*, sampled in the pollution-free atmosphere of Azores (Sao Miguel island), Portugal, and were exposed in the courtyards of 22 basic schools of Lisbon. The exposure was from January to May 2008 and from June to October 2008 (designated through the text as winter and summer respectively). The chemical element concentrations were determined by INAA. Conductivity of the lichen samples was measured. Monte Carlo Target Transformed Factor Analysis (MCTTFA) was applied to winter/summer bark/lichen exposed datasets. Arsenic emission sources, soil with anthropogenic contamination, a Se source, traffic, industry, and a sea contribution, were identified. In lichens, a physiological source based on the conductivity values was found. The spatial study showed contribution of sources to specific school positioning. Conductivity values were high in summer in locations as international Lisbon airport and downtown. Lisbon is spatially influenced by marine air mass transportation. It is concluded that one air sampler in Lisbon might be enough to define the emission sources under which they are influenced.

4.2 Introduction

Biomonitoring studies using lichens to measure their pollutant-specific response are commonly used to indicate geographical variances in trace-element air pollution because they depend mainly on the input of the atmospheric mineral nutrients (Marques 2008). Lichens could be advantageously used to apportion the distribution of element concentrations in big areas (Farinha et al. 2004b). A key lichen parameter is the lichen physiological vitality, sometimes analysed by determination of the lichen membrane permeability. Although there are several experimental procedures to test the impact of environmental pollution on lichen vitality, measuring either the conductivity or the K^+ content of a leachate with an appropriate electrode is the easiest way of monitoring the membrane integrity (Marques et al. 2005). Electric conductivity of lichen was pointed out as the most sensitive parameter for its physiological response to environmental stress, when compared to the normalized difference

vegetation index and chlorophyll degradation. Bark has equally been used as biomonitor and a few publications confirm its good performance when compared to lichens (Chiarenzelli et al. 2001; Freitas et al. 2006a, b).

The presence of chemical elements in biomonitors may depend on several inputs, namely from local and long-range air pollution, natural cycling processes (airborne sea-salt, volcanic sources, biogenic emissions from marine and terrestrial environments), throughfall/stemflow leaching from vascular plants into epiphytic organisms, and mineral particles, mainly wind-blown soil dusts (Bargagli 1998; Rahn et al. 1999; Vieira et al. 2007; Pacheco et al. 2009).

Epiphytic *Parmotrema bangii* was used in this study because it is an adequate choice for further lichen-based (Vieira et al. 2007, 2004, 2006). *Cryptomeria japonica*, the tree from where *Parmotrema bangii* was collected, is also an alternative to epiphytic lichens for air-monitoring purposes as concluded in previous studies (Freitas et al. 2003; Pacheco et al. 2008, 2009). Using these two biomonitors we aim to get answers to the following questions: 1) how conductivity can be a measure of pollution through Lisbon city when compared to the elemental concentrations, 2) how bark compare with lichen, 3) which sources are visualized by the biomonitors, 4) how representative is a unique air sampler in Lisbon.

4.3 Methodology

Samples of the lichen species *Parmotrema bangii* were collected from *Criptomeria japonica* trunks (Japanese cedar trees) in São Miguel, in the Azores islands (N37°47'25,6";W25°38'12,8"; elevation: 261 m), in January and May 2008. All bark and samples collected in January, and more than 50% of those collected in May, were from the same tree; these samples are designated in this study by unexposed lichen samples and unexposed bark samples, respectively. The periods between sampling in the Azores and exposure in Lisbon were 2 and 3 weeks, in winter and summer campaigns respectively.

On arrival from Azores, the samples were distributed in 98 pieces of bark with the lichen over them. Ten of these pieces were kept in the laboratory, unexposed to Lisbon air pollution to estimate the baseline of bark and lichen samples, and they were immediately processed as explained below. The other pieces were exposed to Lisbon air pollution by suspending them with a nylon string from the trees of the courtyards of 22 elementary school in Lisbon (figure 4.3.1), four replicates in each courtyard, in a total of 88 pieces. The pieces were exposed from January to May 2008 (designated by winter or winter campaign) and from June to October 2008 (designated by summer or summer campaign), because it is known from other publications that air pollutants may be different and may have different sources in the considered periods (Almeida et al. 2005; Freitas et al. 2009a). At the end of the winter campaign, 41 lichen samples and 38 bark samples could be recovered from 14 schools; at the

end of the summer campaign, 66 lichen samples and 60 bark samples could be recovered from 20 schools.

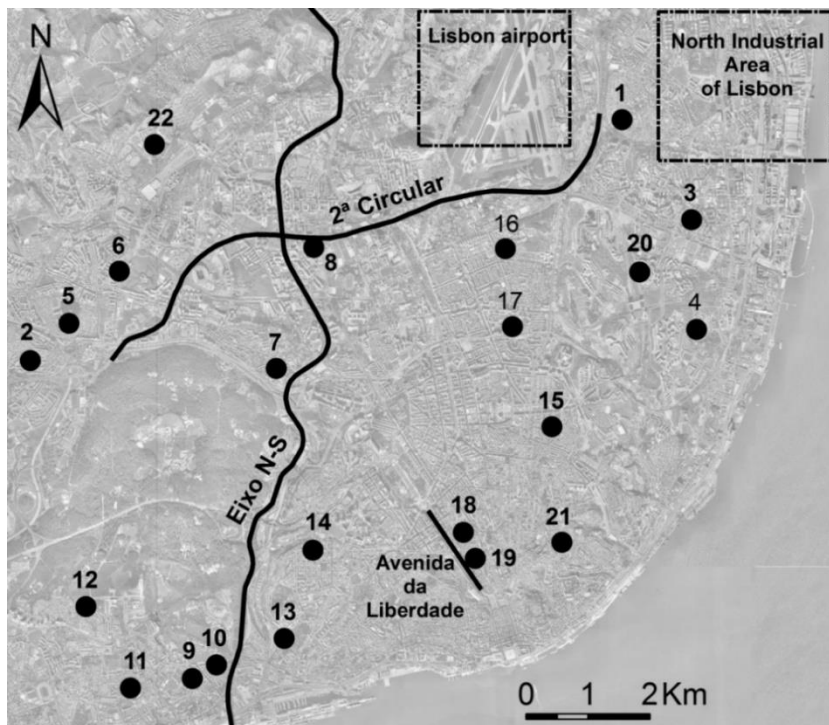


Figure 4.3.1 – Location of the Lisbon schools where bark and lichens were exposed in winter and in summer campaigns.

The unexposed and exposed lichens were separated from the exposed barks; both were cleaned from dust, leaf debris, fungus contamination and degraded material. Then they were rinsed three times for 5 s, in 18 M Ω water (Garty et al. 2001; Godinho, et al. 2004), freeze-dried, and ground by vibration inside PTFE capsules under liquid nitrogen. Pellets of around 250 mg were prepared.

The chemical content was determined by Instrumental Neutron Activation Analysis (INAA). The pellets were irradiated during 5 h in the Portuguese Research Reactor (RPI) at a thermal neutron flux of about $3 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Gamma-spectra of the irradiated samples were acquired with high-resolution hyperpure germanium detectors, after 4 days and 4 weeks. A comparator –an Al-0.1% Au disc–was irradiated together with the samples and measured for application of the k_0 -INAA methodology (De Corte et al. 1987; Freitas et al. 1989). More details of the analytical procedure may be found in (Vieira et al. 2004; Freitas et al. 2006a, b; Pacheco et al. 2009).

Quality control was asserted by analysing 9 subsamples of the certified reference material IAEA-336 lichen following similar procedures to the ones described for the bark and lichen samples.

The electric conductivity was measured in unexposed and exposed lichens. The electric conductivity of the 18 M Ω water was measured before each lichen conductivity measurement – blank value. Lichen samples of about 100 mg, 24 h air dried material, were immersed in 10 ml 18 M Ω water for 60 min following the procedure described in (Godinho et al. 2004), and the conductivity was measured with an electric conductivity meter (*Mettler Toledo*). All results were subtracted from the blank values.

Meteorological data during the exposure periods were 73.4 \pm 15.1% (humidity) and 14.0 \pm 3.2 $^{\circ}$ C (temperature) and 66.9 \pm 16.3% (humidity) and 20.2 \pm 3.5 $^{\circ}$ C (temperature for the winter and summer campaigns respectively). The temperature and the humidity values of the two campaigns are significantly different at 95% confidence level ($P = 0.000$).

4.4 Results and Discussion

The mean of the conductivity values obtained in the 10 unexposed samples was 0.14 \pm 0.12 mS/m.g and 0.28 \pm 0.11 mSm $^{-1}$.g $^{-1}$ in winter and summer respectively. These values were of the order of magnitude of the ones obtained in (Godinho et al. 2004) in *Flavoparmelia caperata* collected at Tomar region (mainland Portugal), considered an unpolluted area. The lichen conductivity averages were higher during the summer than during the winter, as might be expected because of the warmth in summer (Freitas et al. 2004; Marques 2008). However, the difference was not statistically significant at 95% confidence level ($P = 0.203$). Therefore, it may be considered that the lichen vitality at the start of both campaigns was identical. The conductivity mean values after exposure were 0.071 \pm 0.025 mS/m.g and 0.32 \pm 0.17 mS/m.g, in winter and summer respectively. The averages were considered statistically different ($P = 0.000$), meaning that the lichen vitality was influenced by the exposure as concluded before by other authors (Freitas et al. 2004; Godinho et al. 2004).

Figure 4.4.1 shows the ratio of the mean values obtained in this work for the reference material IAEA-336 lichen and its certified values. Results are within \pm 22% of agreement with the certified values. Taking into account the uncertainties, all values are in good agreement, therefore the quality of the analytical procedure was assured.

Table 4.4.1 shows the mean and its standard deviation of selected chemical elements determined by INAA in unexposed samples, and exposed samples in both campaigns. To check whether there are significant differences in the element concentrations between the campaigns, an unpaired Student's *t*-test (independent samples) was conducted and the results are shown in Table 4.4.1, as well.

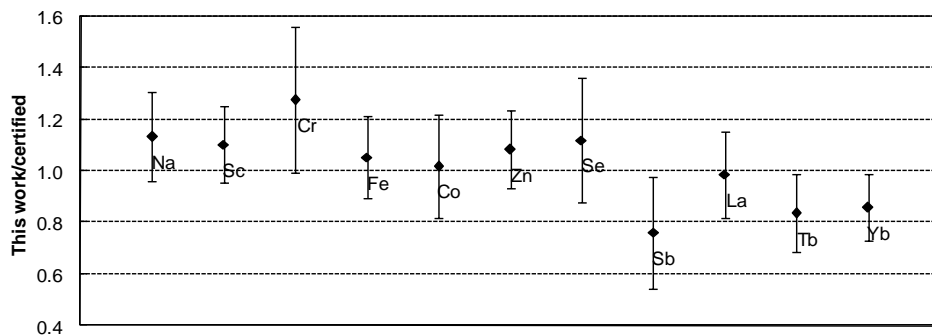


Figure 4.4.1 – Ratio between the mean of 9 replicates obtained in this work for IAEA-336 lichen reference material and its reported certified values. Ratio uncertainties include both the ones of the mean values and the certified values, and are at 95% confidence level. No informative or certified value is reported for Hf.

In unexposed lichens, the ones coming from Azores island, statistically significant differences (95%) were found between the concentrations of Cr, Hf, La, and Na, obtained in summer and winter. These elements are usually soil-related; Na is also a marine component when there is close proximity of oceans (Nriagu et al. 1989; Almeida et al. 2009) which is the case. For all of them, the concentrations were higher in winter than summer, meaning larger uptake during winter. According to other publications (Almeida et al. 2005; Freitas et al. 2009a), the soil resuspension by traffic is higher in winter than summer.

Table 4.4.1 - Chemical element's mean concentration and standard deviation in unexposed and exposed (all schools as a set) bark and lichen samples, calculated for winter and summer campaigns. Statistical differentiation between summer and winter is presented by the P value, obtained using an unpaired Student's t-test. Significant different concentrations at 95% confidence level are given in bold.

Element	Unexposed									
	Bark					Lichen				
	Winter		Summer		P value	Winter		Summer		P value
Aver.	St. Dev.	Aver.	St. Dev.	Aver.		St. Dev.	Aver.	St. Dev.		
Na	800	100	1086	31	0.009	1678	84	1310	110	0.010
Sc	0.040	0.008	0.067	0.002	0.006	0.37	0.02	0.19	0.16	0.132
Cr	0.40	0.07	0.50	0.08	0.186	6.0	0.4	3.0	1.2	0.016
Fe	279	178	333	15	0.630	1089	54	642	562	0.243
Co	0.05	0.04	0.125	0.007	0.038	0.34	0.02	0.27	0.07	0.204
Zn	3.8	1.4	5.22	0.48	0.177	21.7	1.7	13	12	0.286
Se	0.15	0.04	0.107	0.008	0.166	--	--	0.4	0.1	--
Sb	0.04	0.04	0.067	0.004	0.351	0.08	0.03	0.03	0.03	0.067
La	0.64	0.18	0.79	0.04	0.232	2.7	0.1	1.8	0.2	0.002
Hf	0.021	0.008	0.043	0.003	0.010	0.38	0.05	0.20	0.01	0.004
Tb	0.0100	0.0009	0.009	0.001	0.514	--	--	--	--	--
Yb	0.014	0.002	0.020	0.003	0.067	--	--	--	--	--

Chapter 4 – Behaviour of bark and lichen biomonitors in Lisbon

Table 4.4.1 - Chemical element's mean concentration and standard deviation in unexposed and exposed (all schools as a set) bark and lichen samples, calculated for winter and summer campaigns. Statistical differentiation between summer and winter is presented by the P value, obtained using an unpaired Student's t-test. Significant different concentrations at 95% confidence level are given in bold (continued).

Exposed										
	Bark					Lichen				
	Winter		Summer		P value	Winter		Summer		P value
Element	Aver.	St. Dev.	Aver.	St. Dev.	P value	Aver.	St. Dev.	Aver.	St. Dev.	P value
Na	831	147	840	183	0.946	1100	231	941	208	0.720
Sc	0.14	0.06	0.2	0.1	0.359	0.42	0.09	0.38	0.08	0.872
Cr	1.4	0.6	2.1	1.1	0.030	5.3	2.1	3.8	0.8	0.048
Fe	741	322	1020	536	0.342	1590	322	1490	260	0.875
Co	0.26	0.09	0.3	0.1	0.675	0.49	0.09	0.46	0.07	0.398
Zn	13.1	5.4	15.5	4.7	0.548	45	10	39.0	4.4	0.060
Se	0.35	0.15	0.4	0.1	0.752	0.65	0.12	0.62	0.09	0.613
Sb	0.20	0.08	0.21	0.07	0.834	0.28	0.08	0.19	0.04	0.031
La	1.5	0.6	1.7	0.7	0.480	2.1	0.4	2.2	0.4	0.526
Hf	0.09	0.03	0.14	0.10	0.128	0.30	0.06	0.27	0.06	0.712
Tb	0.02	0.01	0.02	0.01	0.962	0.03	0.01	0.03	0.01	0.544
Yb	0.04	0.02	0.05	0.02	0.627	0.08	0.02	0.07	0.02	0.832

Furthermore, larger entrances of sea spray are observed during winter as compared to summer (Vieira, et al. 2004; Almeida et al. 2005). Selenium, Tb, and Yb in the unexposed bark samples were below the detection limit of INAA. Statistically significant differences (95%) of elements concentrations between summer and winter were found for Co, Hf, Na, Sc. The concentrations of Co and Sc were higher in summer than in winter, while the one of Hf was higher in winter than in summer (similar result to unexposed lichen); the Na concentrations in lichen were higher in summer than in winter while in bark it was the other way around. The different behaviour towards soil and sea-spray related elements indicates that the differences at the start of exposure, either for lichen or bark, must be taken into account in the discussion of the results of exposed samples. All the other elements were not statistically different in the two sampling periods.

Table 4.4.2 shows the mean and standard deviation for the same set of chemical elements in exposed lichen and exposed bark during the campaigns. The latter showed significant differences (95%) between summer and winter for Cr with higher concentrations during summer. Since this element presented statistically identical values at exposure start, it may be concluded that Cr was uptaken in both winter and summer, and more during the latter—it is concluded that one Cr source influences Lisbon the whole year although with higher intensity during summer. The elements Co, Hf, Na, Sc whose concentrations in bark were different at the start, turned out equal at the end of the exposures. It is then concluded that these elements are in sources which influence Lisbon. As for the lichen samples, there were

statistically significant differences (95%) between summer and winter campaigns in the concentrations of Cr and Sb, with lower levels during summer. A conclusion that can be taken here is that Cr is an element for which bark and lichen respond differently, since the Cr uptake in bark was higher in summer while in lichen was lower. Concerning Sb, related to traffic in Lisbon (Sternbeck et al. 2002; Almeida et al. 2009; Freitas et al. 2009a), it is expected that values are lower in summer because the traffic is drastically reduced due to the end of the school year (most of the parents use private cars as transport just because they need to take their children to school, otherwise they use public transportation) and the commuter summer vacation period (Freitas et al. 2009a).

For lichen, ratios between averages in winter and summer were higher than unity (winter > summer) for Co, Cr, Fe, Hf, Na, Sb, Sc, Se, Tb, Yb, Zn. For bark, ratios larger than unity were not found in any of the elements, this is, most of the elements showed higher concentrations in summer.

When the ratios (exposed/unexposed) are considered, a P z-score test applied to lichen results showed that statistically significant differences (95%) were found for Na (<1), Sb and Zn (both >1) in winter, and Co, Fe, Sb, Sc, Se, Zn (all >1) in summer. This means that 1) the lichen samples lost Na which is understandable because they came from a more enriched Na environment (one small island in the middle of North Atlantic Ocean); this release after accumulation was also observed in (Godinho et al. 2011) in an experiment where lichens were exposed to a polluted area and later to an unpolluted environment; 2) they uptook Sb and Zn from vehicles tires wear out; 3) they uptook Co, Fe, Sc from soil particles and soil resuspension; 4) uptook Sb, Se, Zn from industrial areas (Freitas et al. 2005; Almeida et al. 2007; Farinha et al. 2009a). If the ratios (exposed/unexposed) in winter and summer are compared (P t-test, 95%), only Fe, Sb, and Sc (all higher in summer than winter) are statistically different, maybe indicating Sahara dust (Almeida et al. 2005).

For bark, statistically significant differences (P z-score test, 95%) between exposed and unexposed means were found for Co, Hf, Sb (all >1) in winter, and Sb, Se, and Zn (all >1) in summer. When summer and winter campaigns are compared, statistically significant differences (P t-test, 95%) were not found for any of the elements. Different responses of bark and lichen are therefore obtained, when the average of the values is considered. Similar differences were pointed out previously (Kuik et al. 1993; Farinha et al. 2009; Pacheco et al. 2009).

To check whether there is a significant relationship between the elemental concentrations in exposed bark and lichen, Pearson correlations were calculated for both campaigns (not shown). Positive and statistically significant correlations (95%) between the elemental concentrations of exposed lichen and exposed bark were found during winter for Fe ($r = 0.61$,

$p = 0.034$), La ($r = 0.76$, $p = 0.004$), Na ($r = 0.58$, $p = 0.048$), and Yb ($r = 0.74$, $p = 0.006$) – all might be considered natural source related (marine and soil), and no correlations were observed with the summer data.

Pearson correlations were also calculated between conductivity determined in exposed lichen and its elemental concentrations. Only Tb ($r = -0.56$, $p = 0.037$) and Yb ($r = -0.56$, $p = 0.040$) determined in winter showed statistically significant correlations (95%). No explanation was found for the selective preference to these two elements.

MCTTFA factor analysis was applied to winter and summer bark and lichen exposed datasets. The most significant element (the pilot element) in a factor is marked with P. MCTTFA (Kuik et al. 1993; Pacheco et al. 2004) approach consists of: 1) the data set is first transformed into standardized variables which are assumed to be a linear sum of factors (emission sources); 2) a unique contribution, specific for each individual sampling site is calculated depending of coefficients designated by loadings of the factors, representing the correlation of elements with factors, and of coefficients symbolizing the contribution of factors to samples; 3) the target transformation is an iterative method to satisfy the condition that the loadings should not contain negative values; 4) the uncertainties in the obtained loadings are estimated using a Monte Carlo approach. In order to choose the optimal number of factors for both bark and lichen, use was made of the number of factor identification conflicts (FIC) (Kuik et al. 1993; Pacheco et al. 2004). In case of bark an increase of FIC can be observed at 5 factors (data not shown). For lichen the FIC show a sharp rise at 6 factors. Therefore respectively 4 and 5 factors were chosen as the optimal number of factors to be used.

The mean values contributions (%) to total element occurrence calculated for bark and lichen on both campaigns are presented in Table 4.4.2. With the bark dataset, 4 factors were obtained. Soil with some anthropogenic contamination (Co, Cr, Fe, Hf-pilot element, Na, La, Sb, Sc, Se) was identified by factor 1. Factor 2 indicates an anthropogenic source with Zn as pilot element, Sb, Co, and also soil-related Cr, Fe, Hf, La, Sc. These elements are associated with different sources namely coal combustion, cement production, incineration (Nriagu et al. 1989) and traffic (mainly tires and brakes' wear out, rather than combustion processes) (Sternbeck et al. 2002). The association between Zn and Sb with vehicles and the importance of this source in the centre of Lisbon has been demonstrated before (Almeida et al. 2005; Freitas et al. 2009a). A Se source, containing also Co, Fe, Hf, La, Sb, Sc, was identified in Factor 3. In the north of Lisbon, Se contents 1000 higher in PM₁₀ and PM_{2.5} were registered in 2001, compared with Se concentrations measured in other urban and industrialized areas of Portugal (0.5-1 ng/m³) (Freitas et al. 2005). Factor 4 represents the sea contribution, with high factor loading for Na (pilot element), and also Co, Fe, Hf, La, Sc, Se.

Table 4.4.2 - Mean values contributions (%) of the factors (obtained by MCTTFA) to total element occurrence calculated for bark and lichen in both campaigns. Elements with significant positive loadings are marked: + means $95\% < P < 99\%$, * means $P > 99\%$. The most significant element (the pilot element) in a factor is marked with *P*.

Bark						
	Factor 1	Factor 2	Factor 3	Factor 4	Total	
Na	0.03*	0.00	0.04⁺	0.32P	0.39	
Sc	0.28*	0.25*	0.32*	0.32*	1.17	
Cr	0.27*	0.29*	0.00	0.00	0.56	
Fe	0.25*	0.30*	0.34*	0.23*	1.12	
Co	0.13*	0.48*	0.08*	0.22*	0.91	
Zn	0.00	0.84P	0.00	0.04	0.89	
Se	0.08*	0.00	0.54P	0.25*	0.87	
Sb	0.06*	0.59*	0.31*	0.00	0.97	
La	0.17*	0.13*	0.36*	0.08*	0.75	
Hf	0.33P	0.38*	0.14*	0.41*	1.26	
Lichen						
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Total
Na	0.55*	0.01	0.00	0.02	0.41P	0.98
Sc	0.97*	0.04*	0.00	0.02 ⁺	0.10*	1.13
Cr	0.61*	0.51P	0.00	0.09 ⁺	0.01	1.22
Fe	0.88P	0.03*	0.00	0.05*	0.05*	1.01
Co	0.58*	0.00	0.00	0.16*	0.01	0.75
Zn	0.03	0.23*	0.00	0.00	0.05 ⁺	0.31
Se	0.55*	0.00	0.00	0.03 ⁺	0.01	0.59
Sb	0.00	0.21*	0.00	0.74P	0.11 ⁺	1.05
La	0.75*	0.00	0.00	0.05*	0.00	0.80
Hf	1.03*	0.05*	0.00	0.00	0.13*	1.21
Conductivity	0.00	0.00	1.00P	0.00	0.00	1.00

Figure 4.4.2 shows the factor values calculated for bark for both winter and summer campaigns, by school site (C1...C22). No significant differences (using a paired Student's *t*-test, 95%) were found between campaigns.

Figure 4.4.3 shows the factor values calculated for lichen for both winter and summer campaigns, by school site (L1...L22). A significant difference (using a paired Student's *t*-test) was found for factor 3 only with higher factor values in summer. When the circles which represent winter campaign values or the squares which represent summer campaign values are not shown, that means lost sample.

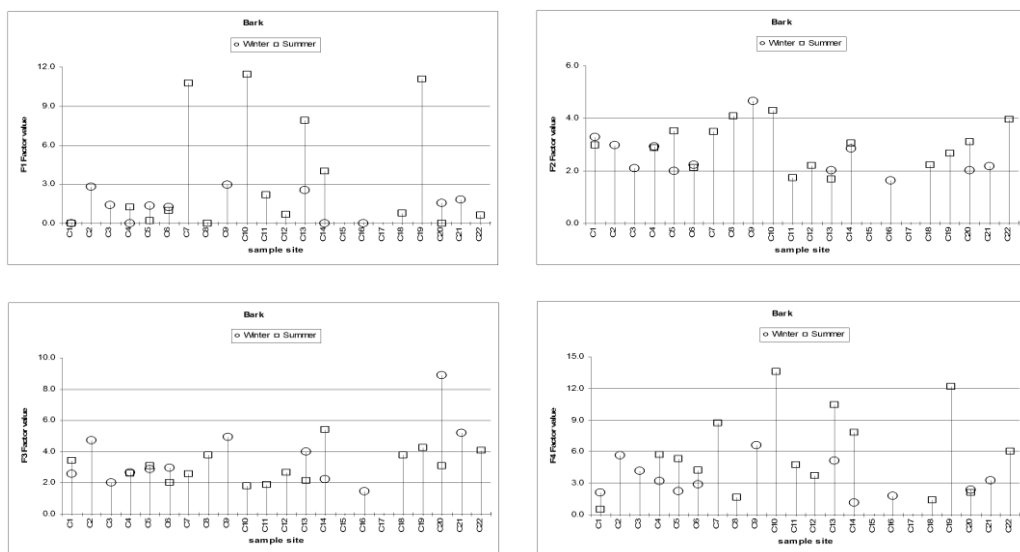


Figure 4.4.2 – Contribution of each sampling site to the Factors F1, F2, F3, F4 obtained by MCTTFA, using bark as biomonitor exposed in summer and winter periods. C1, ..., C22 refer the bark samples exposed in Lisbon school sites 1, ..., 22.

Higher element contributions for Factor 1 (Figure 4.4.2) were by traffic from schools 7, 10, 13, 14, and 19. Schools 7, 10, 13, and 14 are near the busy road *Eixo Norte-Sul*, which crosses Lisbon from north to south to distribute more efficiently the traffic through the city; school 19 is near *Avenida da Liberdade*, the main via to downtown area. It was expected similarity between contributions of schools 18 and 19, because of their closeness but this was not observed, maybe due to specific school characteristics of the courtyards where bark was exposed. School 18 is inside a building, surrounded by compact buildings area (it is the only one with these characteristics among the studied ones). Factor 2 is similar for all studied area in winter and summer. Lisbon is then a large urban area with an anthropogenic source influencing the whole area. This may indicate traffic as the main source in Factor 2. School 20 is a site with Se source identified in Factor 3. It is situated (see Figure 4.3.1) near an industrial area in the north of Lisbon. In this case, there is a local source with higher contribution in winter when the industrial sources are more active, thus emitting higher levels of Se. The schools with higher contribution to Factor 4 are the same as in Factor 1, also with higher contribution in summer than in winter. These schools are positioned from north to south (see Figure 4.3.1) and Na is carried in sea-spray brought by the northern winds (predominant direction in summer). With the lichen dataset (Table 4.4.2), the number of factors given by MCTTFA was 5, one more than for bark due to conductivity. Except for the physiological source, the factors given by lichen dataset do not differ from the ones by bark. Soil source was identified in Factor 1 which is associated to Fe – pilot element, Co, Cr, Hf, La, Na, Sc, Se; traffic was identified in Factor 2 which is associated with Cr – pilot element,

Fe, Hf, Sb, Sc, Zn. Conductivity, a physiological source, was identified in Factor 3. A Se source was identified in Factor 4, with Se as a pilot element, and Co, Fe, La. Factor 5 represents the sea contribution, with Na as pilot element, and Fe, Hf, Sc. A significant difference (using a paired Student's *t*-test, 95%) was found for factor 3 with higher factor values in summer. This result shows that lichens in summer presented less vitality (higher conductivity) than in winter. This may be due to the higher temperature and lower humidity (Marques et al. 2005), and probably not to air pollution. The most significant element contribution to Factor 1 (Figure 4.4.2) was Fe. Table 4.4.1 shows that Fe increased from summer to winter for both bark and lichen. Bark and lichen can absorb Fe in the same conditions (Pacheco et al. 2009). In soils with different Fe concentrations, lichen has the same Fe enrichment, whereas bark can take different Fe concentrations (Kuik et al. 1993). This explains why different bark locations present different Fe absorption and the same locations present the same Fe uptake by lichens. Pacheco et al. 2002 verified that bark and lichen absorbed Fe in the same conditions, and that there was a good correlation between Fe absorption by bark or by lichen. Godinho et al. 2011 observed elemental enrichments of factors during lichen exposure to contaminated areas and their loss during sequent exposure to clean areas. This explains Fe concentrations growth from the unexposed samples to exposed samples. The spatial distribution of schools shows that factor 2 is traffic contaminated soil resuspension School 1 (see Figure 4.3.1) is near 2^a Circular (the main internal Lisbon surrounding via) and also near an *industrial area in the North of Lisbon*. School 4 (see Figure 4.3.1) is near *Avenida Infante D. Henrique* (main road along the Tagus river) and the *industrial area of the North of Lisbon*. School 3 might have presented a differentiation too because it was located close to schools 1 and 4; however, this differentiation was not observed probably because school 3 is located away from the higher traffic roads and avenues, surrounded by buildings. Seasonal differentiation was observed with higher values in winter. The activity of factories and intensity of traffic on those roads is higher in winter leading to seasonal differentiation. Freitas et al. 2009b) verified that all the soil resuspension elements have higher levels in the atmosphere during the winter. The conductivity of exposed lichens was higher in schools 1 and 18 in summer. School 1 is near the international airport of Lisbon, therefore lichen conductivity is higher during summer probably due to the increased air traffic during this season. School 18 is located not far from downtown, surrounded by buildings, making it a confined space where chemical element concentrations and climatic conditions cannot vary much. Selenium (Factor 4) concentrations are higher in winter (see Table 4.4.2), increases from the unexposed to the exposed lichens and decreases from winter to summer (see Table 4.4.1). School 11 shows the highest contribution to Factor 4; it is close to Tagus river and the influence may be from south-western winds which bring Se from the Atlantic Ocean. All the other schools present equivalent contributions which are most probably caused by the Se source at the northern industrial area (Freitas et al. 2005).

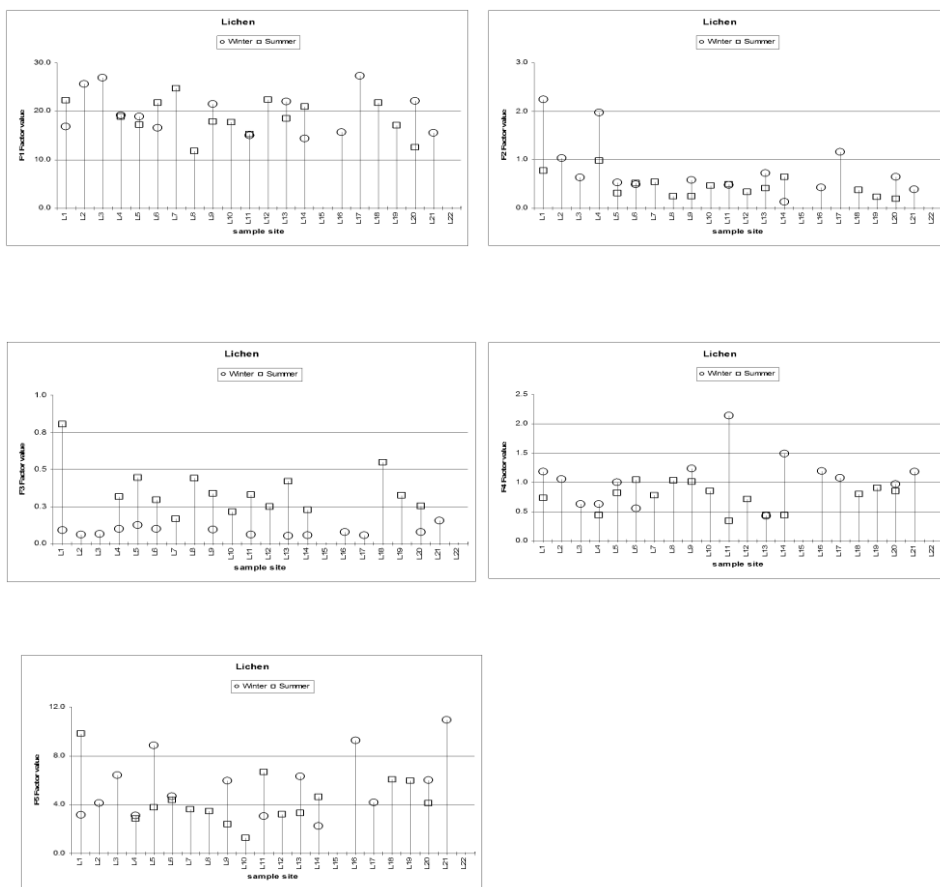


Figure 4.4.3 – Contribution of each sampling site to the Factors F1, F2, F3, F4 obtained by MCTTFA, using lichen as biomonitors exposed in summer and winter periods. L1, ..., L22 refer the lichen samples exposed at Lisbon school sites 1, ..., 22.

4.5 Conclusions

In this work we conclude that lichen conductivity can be a measure of different meteorological conditions but it was not demonstrated that it might be a measure of air pollution. Conductivity was found to be correlated with Tb and Yb in winter, very few elements to proof the good performance of conductivity vs the elemental concentrations. Bark and lichen, when averages were considered, had mostly different responses even sometimes reversed; however both gave the same information on emission sources in Lisbon. The visualized sources relate soil, traffic, Se source and sea spray; however they are not pure, they show contamination of the natural sources by the anthropogenic and the other way around. Considering the kind of study done, it can be said that one aerosol sampler in Lisbon might be enough to define the emission sources.

5 Association between Atmospheric Pollutants and Hospital Admissions in Lisbon

Based on article of same title:

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5.1 Abstract

Ambient air pollution is recognised as one of the potential environmental risk factors causing health hazards to the exposed population, demonstrated in numerous previous studies. Several longitudinal, ecological and epidemiological studies have shown associations between outdoor levels of outdoor atmospheric pollutants and adverse health effects, especially associated with respiratory and cardiovascular hospital admissions (HA). The aim of this work is to assess the influence of atmospheric pollutants over the HA in Lisbon, by Ordinary Least Squares Linear Regression. The pollutants (CO, NO, NO₂, SO₂, O₃, PM₁₀ and PM_{2.5}) were obtained from 13 monitoring stations of the Portuguese Environmental Agency, which provide hourly observations. Hospital admission data were collected from the Central Administration of the Health System (ACSS) and were compiled by age: < 15, 15-64, ≥ 64 years old. The study period was 2006-2008. Results showed significant positive associations between: 1) the pollutants CO, NO, NO₂, SO₂, PM₁₀ and PM_{2.5} and circulatory diseases for ages between 15 and 64 years (0.5% HA increase with 10 µg/m³ NO increase) and above 64 years (1.0% stroke admission increase with 10 µg/m³ NO₂ increase); 2) the pollutants CO, NO, NO₂, SO₂, PM₁₀ and PM_{2.5} and respiratory diseases for ages below 15 years (up to 1.9% HA increase with 10 µg/m³ pollutant increase); 3) the pollutants NO, NO₂ and SO₂ and respiratory diseases for ages above 64 years (1.3% HA increase with 10 µg/m³ CO increase).

5.2 Introduction

Links between air pollution, especially atmospheric particles and sulphur dioxide (SO₂), and the number of hospital admissions (HA) have been established in studies in North America (Burnett 1997; Lipfert 1997; Middleton et al. 2008; Pope et al. 2004, 2008; Roemer et al. 1998; Zanobetti and Schwartz 2005; Wilson et al. 2004), South America (Lumley and Sheppard 2000; Roberts 2005), Asia (Cameron and Trivedi 1998; Luvsan et al. 2012), Australia (Hansen et al. 2012) and Europe (Almeida et al. 2014, Alves et al. 2010b, Freitas et al. 2010, Pablo Dávila et al. 2013, Pascal et al. 2013, Neuberger 2007 and Ayres-Sampaio et al. 2014). However, still many efforts to clarify pollution-health associations are necessary,

including the separation of the short-term and long-term health effects of individual air pollutants (AP) and those of complex pollutant mixtures. Additionally, more research is needed to infer specific regional links between air pollution and adverse health effects. As the composition of the air pollution mixture differs between locations, the health risks associated with the pollutant of interest may vary over time and space (Almeida et al. 2011; Shin et al. 2008).

Recent studies, in Spain, demonstrate that the levels of the finest PM fractions are important risk factors for daily cardiovascular mortality (Maté et al. 2010; Pérez et al. 2012) and increase the number of HA (Linares and Díaz 2010; Linares et al. 2010). Including HA in studies related to the short term effects of air pollution on human health is particularly valuable since such studies may refer to large parts of the population and, consequently, constitute the most direct way of accessing the cardio-respiratory health burdens imposed by the complex air pollution mixtures to the exposed communities (Delfino et al. 2009). According to this assumption, a lot of remarkable studies have been conducted in order to define the association among one or more pollutants and the number of daily HA (Atkinson et al. 2001; Kan and Chen. 2004; Katsouyanni et al. 2001; Moshhammer et al. 1987, 2006; Morawska et al. 2002; Neuberger et al. 2007, 2013). Apart from particulates, ozone (O₃) and a wider range of pollutants, including monoxide carbon (CO), nitrogen dioxide (NO₂) and SO₂, play a very significant role in the public health decline (Katsouyanni et al. 1997; McConnell et al. 2002). Furthermore, most models only estimate the short-run impact of air pollution and do not account for the possibility that a high number of HA on a certain day might be followed by an off-setting reduction in the number of HA spread over the following weeks and months (Maddison 2005). Recognising the importance of this issue, some researchers (Schwartz 2000a, 2001; Zeger et al. 1999) have thought to provide what they refer as ‘harvesting resistant’ estimates of the health effects of air pollution. The approach adopted by Schwartz (2001) involves analysing the association between 15 day moving averages of air pollution and mortality counts and HA. Adopting an alternative approach, Zanobetti et al. (2002) used polynomial lags to explore the short-term mortality displacement issue. Based on the above remarks, it is obvious that the question of how to best aggregate exposure and health variables over time and estimate the unique effect of single pollutants remains an open issue, given that there is a lot of speculation about the suitability of the applied methodologies, or the special conditions of the urban area under study.

Time-series analysis usually performed linear regression when data are normally distributed and, more recently, Poisson regression. Usually models include only one pollutant. Additional covariates denote, on the one hand, temporal patterns in diseases (long-term trends, seasonality and weekday trends) and, on the other hand, meteorological indicators and seasonal indicators (Smith et al. 2000). Most time-series studies use days as the units of comparison which is the minimum time period for which hospitalisation data are recorded.

Such data usually contains very low counts of health events, it is thus very noisy and it is necessary to adjust for weekly averages as well as consider potential lag effects. The daily data may consist of the actual daily values of health and pollution or some form of average over a number of days. Some studies have modelled single day health events with exposure averages over multiple days (Lipfert 1993; Lumley and Sheppard 2000; Roberts 2005; Sarmiento et al. 2009; Smith et al. 2000) and a minority has modelled the health events also as averages over multiple days, while preserving the days as units of comparison (Schwartz 2000a,b).

Recent epidemiological studies have consistently shown positive associations between low-level exposure to AP and health outcomes. In Portugal, very few studies have analysed the acute effect of AP on public health (Almeida et al. 2011, 2014; Alves et al. 2010b; Freitas et al. 2009a). In this study, an attempt is made to find the short-term associations between HA for diseases: all circulatory, cardiac, ischaemic heart, stroke, all respiratory diseases, asthma, and AP: CO, nitrogen monoxide-NO, NO₂, SO₂, O₃, particles with aerodynamic equivalent diameter of 10 µm-PM₁₀ and particles with aerodynamic equivalent diameter of 2.5 µm-PM_{2.5}, in the area of Lisbon, Portugal, for a three year period, from 2006 to 2008.

5.3 Data

Lisbon is the capital and largest city of Portugal, with a population of 564 657 within its administrative boundaries on a land area of 84.8 km². Lisbon is the westernmost large city located in Europe, as well as the westernmost capital city and the only one along the Atlantic coast (Almeida et al. 2010). The urban area of Lisbon extends beyond the administrative city limits and this study includes the neighbour municipalities of Loures, Odivelas, Amadora, Oeiras and Cascais, with a total area of 448 km² and a resident population of 1 378 868 inhabitants (average over 2006-2008) (Figure 4.3.1).

The industrial area includes textiles, chemicals, steel, oil, cement, sugar refining, shipbuilding, soap and flour production (Almeida et al. 2007, Almeida et al. 2013a; Farinha et al. 2004a). In the city, traffic is the main source of atmospheric pollution (Almeida et al. 2009a, b). Due to the geographic position of Lisbon and to the dominant western wind regime, influenced by the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean, the expected high levels of pollutants are uncommon. The transport of maritime air mass is usually associated with cleaner air masses from the Atlantic Ocean and with better dispersion conditions of pollutants coming from the industrial areas (Almeida et al. 2013b). Nevertheless, under adverse meteorological conditions, low dispersion conditions and thermic inversions, high concentrations of AP can be registered.

In this study, the measuring stations to be considered are in municipalities whose population is served by the hospitals where the HA data were collected.

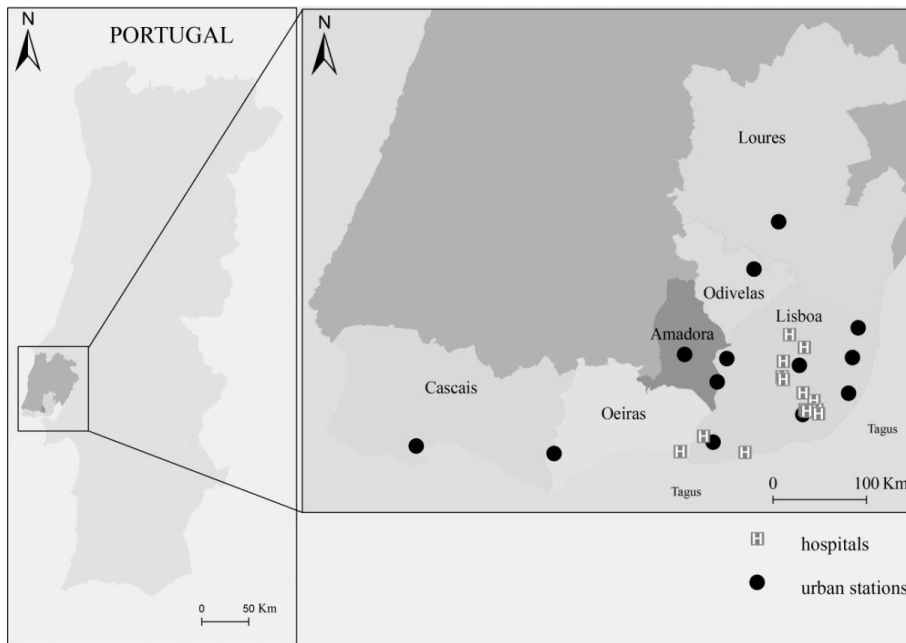


Figure 5.3.1 – The studied area: spatial distribution of the main hospitals and air quality monitoring stations.

5.3.1 Air Pollutants

Data on regulated AP (CO, NO, NO₂, SO₂, O₃, PM₁₀ and PM_{2.5}) were obtained for all the monitoring urban stations in the studied area: in Loures, Odivelas, Cascais and Oeiras one station each, in Amadora two stations and Lisbon seven stations. All the stations are considered as background (areas not directly influenced by traffic) stations except for the one in Odivelas, Cascais and three in Lisbon with intense traffic. This monitoring network is assumed to represent the exposure of the population served by the 13 hospitals from which health data were collected.

The data, provided by the Portuguese Environmental Agency (QUALAR network), consisted of hourly measurements, over the years 2006-2008. Daily averages were calculated for each pollutant in each of the 13 monitoring stations following the recommendations of Directive 2008/50/CE of 21 May 2008. Daily values were calculated as the 24 hour-average for SO₂, PM₁₀, and PM_{2.5}, as the daily 1 hour-maximum for NO, NO₂ and as 1 hour-maximum of octo-hourly moving averages for CO and O₃. Daily values were calculated only when at least 75% of the hourly values on a particular day were non-missing.

The daily values of each pollutant were then averaged over the 13 monitoring stations as a criteria to obtain a daily single value of AP which may represent a daily pollutant measure for the whole studied area.

5.3.2 Hospital Admissions

The HA database was provided by the Central Administration of the Health System (ACSS). It consists of daily counts of hospitals admissions, over the years 2006-2008 in 13 public hospitals, all in Lisbon municipalities (Figure 5.3.1). In HA database it was observed that hospital admission counts tend to be lower on weekends as compared to working days, as already concluded by Sarmiento et al. (2009), suggesting that either weekend admissions are registered on Mondays only or patients wait for Monday to go to hospital if the symptoms are not so severe or the number of doctors in hospital is reduced during weekend and people may wait to Monday to be assisted. This is visible in Figure 5.3.2 which shows a HA week study for the diseases under study from 2006-2008.

Daily HA database were aggregated by age group (< 15, 15-64, 64 years old). These age groups were adopted for consistency with former studies in Portugal (Sarmiento et al. 2009 and Almeida et al. 2014). The studied causes of HA classified according to the World Health Organisation’s International Statistical Classification of Diseases by the, 9th Revision (ICD-9) and 10th Revision (ICD-10) endorsed by the Forty-third World Health Assembly in May 1990, came into use in WHO Member States since 1994 (WHO 2014b): all circulatory (ICD-9: 390-459; ICD-10: I00-I99), cardiac (ICD-9: 390-429; ICD-10: I30-I52), ischaemic heart (ICD-9: 410-414; ICD-10: I20-I25), stroke (ICD-9: 430-438; ICD-10: I60-I69); all respiratory (ICD-9: 460-519; ICD-10: J00-J99), asthma (ICD-9: 493; ICD-10: J45).

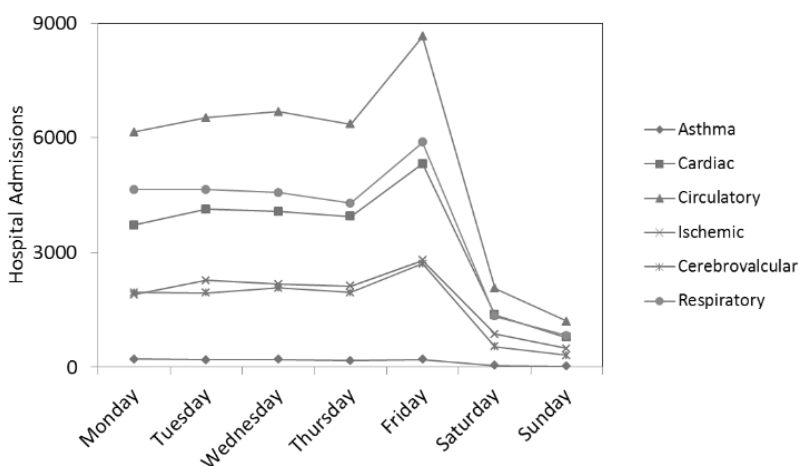


Figure 5.3.2 - Weekly study of HA, for all diseases, from 2006 to 2008.

5.3.3 Methodology

In an attempt to better understand the effect of the pollutants on HA for the different diseases, four different ways of aggregating atmospheric pollutants and hospital admission variables, were considered over time. Studies on human health effects usually use daily data; although, recent epidemiological studies have been using exposures in the form of moving averages, distributed lags or data aggregated over several days or even weeks (Schwartz 2000b; Sarmiento et al. 2009).

In this study, we followed the methodology applied by Sarmiento et al. (2009) and Almeida et al. (2014). The AP and HA daily databases were joined in into one (DAY database-N equals 1096) and from it, we generated other three differently aggregated databases:

WEEK (both AP an HA are expressed as 7-day averages). The number of observations is thus 7 times less than the number of observations in the DAY database (N reduced from 1096 to 156);

O&MA (HA are expressed with the original daily values, AP are expressed as a prior 7-day moving average, this is the seventh HA value connects with the average of the first seven AP values; the HA eighth value connects with the average of the AP seven values, from the second to the eight – moving average – from AP and so on. The number of observations is thus equal to the number of observations in the DAY database minus 6);

MA&MA connects the average from the eight to the fourteenth HA values with the average from the first to the seventh AP value. The next value results from the average from the ninth to the fifteenth HA value with the average from the second to the eight AP value, and so on. The number of observations is thus equal to the number of observations in the DAY database minus 12.

WEEK and MA&MA databases aimed to control the effect of weekday on HA, to mitigate the influence of potential peaks on the evaluation of associations, and to account for lagged health responses which was considered to be 7 days (Sarmiento et al. 2009, Almeida et al. 2014).

Averages of 7 days were selected in agreement with Sarmiento et al. (2009) and Almeida et al. (2014) because 7 days is still considered an acute time-scale for associations (WHO 1999; WHO 2006), and averages of 7 days in both AP and HA can adjust for biases arising from weekly fluctuations.

To control the seasonal variability of AP data 12 dummy variables (one per month) were added. The dummy variables took either the zero value or the average value of the daily observations of each month (considering all the years). For instance, the dummy variable for January assumed the value of zero for all observations, except for January, for which the month averages were considered; the same applies for February, March and so on.

Weekend effects were over HA data were controlled, in models DAY and O&MA (not necessary in WEEK and MA&MA, because already week aggregated), by including a weekend dummy, zero on weekends and 1 on weekdays.

Ordinary Least Squares Linear Regression (OLS) was applied to DAY, WEEK, O&MA and MA&MA databases and was performed with Excel 2007 and SPSS 17.0 software packages. In OLS, HA and AP were the dependent and independent variables, respectively. OLS was applied to be consistent with similar former studies in Portugal (Sarmiento et al. 2009 and Almeida et al. 2014).

Pearson correlation was applied to verify linearity of models following the requirements of OLS: 1) the normality of residuals was observed in these histograms; 2) the constant variance of residuals was checked using appropriate graph (scatter plot between standard and variable waste); 3) zero waste covariance was verified by the Durbin-Watson test.

The associations obtained with OLS and Poisson regression for the WEEK database were compared.

5.4 Results and Discussion

All AP present a seasonal pattern with high winter levels and low summer levels, except O₃ (not shown). The summer higher values of O₃ could be explained by the adequate weather conditions for its formation-sunlight, warm temperatures and high emission of precursor pollutants (nitrogen oxides and volatile organic compounds) lead to high levels of this atmospheric oxidant during the summer season (Karr et al. 2007; Alves et al. 2010b).

The AP descriptive statistics is shown in Table 5.4.1. Comparing with the Europe Union air quality guidelines suggested in Directive 2008/50/EC, it is possible to verify that, over the period 2006-2008: 1) CO average annual concentration did not exceed the maximum daily 8-h average (10 mg/m³); 2) NO₂ and PM₁₀ average annual concentrations exceeded the annual limit of 40 µg/m³; 3) SO₂ concentrations were very low over the studied period as compared to the daily average legal value (125 µg/m³ – not to be exceeded more than 3 days per year); 4) O₃ concentrations were under the maximum of octo-hourly of 120 µg/m³ (not to be exceeded more than 25 days per year); 5) Daily averages of PM₁₀ concentrations exceeded the limit value of 50 µg/m³ in 2006 (58 times) and 2007 (37 times), although PM₁₀ concentrations decreased to values under the daily limit established by the Directive; 6) PM_{2.5} annual concentrations were under the annual limit established by the Directive (25 µg/m³). Comparing AP descriptive statistics with Alves et al. (2010b) in 1999-2004 for the same area, all AP decreased, except O₃ and NO₂; the standard deviations were in the same order of magnitude. Average and median values are similar indicating a reasonable normality of the data. Histograms are included in the Table 5.4.1. Differences between minima and maxima are quite large, as it is expected in AP values; consequently, standard deviations are high too.

Table 5.4.1 also shows the statistical values for winter and summer. Only summer and winter are shown because these seasons have the extreme climacteric conditions considering temperature and humidity. The seasonality is evident.

Statistics for the daily HA in the studied area is presented in Table 5.4.2. Except for asthma, higher values were recorded for people ≥ 64 than for < 64 years old. For asthma, annual HA do not appear to vary much with age. Averages and medians are mostly different for circulatory and cardiac diseases, which show bimodal histograms. For these diseases, either there are very low HA values or very high HA values. This may already give an indication of high associations with AP peaks. Stroke and respiratory diseases are also bimodal but not so sharp as the previous ones. Ischaemic heart and asthma diseases may be considered normal. Table 5.4.2 also shows the statistical values for winter and summer. Seasonal variation appears to be evident.

Table 5.4.3 shows the associations that were significant ($p < 0.05$) at least for one model (DAY, WEEK, O&MA, MA&MA) after applying OLS, as well as their semi-elasticity, expressed in % of variation in HA per $10 \mu\text{g}/\text{m}^3$ increase in the atmospheric pollutants. They are 37 out of a total of 126 ($6 \text{ HA} \times 3 \text{ age-groups} \times 7 \text{ AP}$) associations. It was observed that statistical significance and semi-elasticity were highly sensitive to the study design issues defined by the four models.

According to Lipfert (1993, 1997), the semi-elasticity at the average of both atmospheric pollutant and hospital admission was calculated from the risk difference provided by the slope of the linear regression. The use of the semi-elasticity makes it easier to compare our results, obtained from a linear model, with those obtained from time-series studies using Poisson (Cameron and Trivedi 1998) and log-linear models, which use the Risk Ratio as the measure of effect.

Comparing the results of OLS and Poisson for the WEEK database, we obtained similar results even considering that OLS get more associations than the Poisson regression. For instance, the increase of $10 \mu\text{g}/\text{m}^3$ in Lisbon of the PM_{10} was associated with an increase in circulatory diseases, for 15-64 years of the 0.6 % with OLS while Poisson was 1% and an increase in cardiac diseases, for 15-64 years, 0.7% and 1%, respectively. The increase of $10 \mu\text{g}/\text{m}^3$ of the $\text{PM}_{2.5}$ was associated with an increase in stroke diseases, over 64 years, is respectively 0.9% and 0.6% and an increase in cardiac diseases, for 15-64 years of the 0.6% and 0.3 %, respectively. Sarmiento et al. (2009) has already concluded the same for O&MA and MA&MA databases.

Comparing the models applied, more numerous statistically significant associations with MA&MA were observed, followed by the DAY models, decreasing to about half in WEEK and O&MA models. The fact that the WEEK model yields a lower number of significant

associations can simply be due to a much smaller number of observations ($N = 156$) than in all other models (N around 1096).

The results in Table 5.4.3 indicate positive significant associations: 1) between CO, NO, NO₂, SO₂, PM₁₀, PM_{2.5} and respiratory diseases for ages below 15 years; 2) CO and stroke and ischaemic above 64 years; NO and cardiac, circulatory, and ischaemic diseases for ages between 15 and 64 years; 3) cardiac, stroke, circulatory, ischaemic and respiratory above 64 years; NO₂ and ischaemic diseases for ages between 15 and 64 years and stroke, circulatory and respiratory diseases above 64 years; 4) SO₂ and cardiac, circulatory and ischaemic diseases ages between 15 and 64 years and stroke, circulatory, ischaemic and respiratory diseases above 64 years; 5) PM₁₀ and cardiac, stroke, circulatory and ischaemic diseases for ages between 15 and 64 years and stroke and ischaemic diseases above 64 years; 6) PM_{2.5} and cardiac and circulatory diseases for ages between 15 and 64 years and stroke and ischaemic diseases above 64 years.

The most relevant results ($p = 0.000$ and highest $E(\%)$) in Lisbon were obtained in MA&MA model, in which the increase of 10 $\mu\text{g}/\text{m}^3$ in NO₂ and PM₁₀ concentrations was associated with an increase in HA of about 1.9% due to respiratory causes, for individuals under 15 years.

The association between NO and HA due to respiratory diseases for individuals under 15 years was significant for all applied models. Results showed that an increase of 10 $\mu\text{g}/\text{m}^3$ in this pollutant concentration is associated with an increase in HA of 1.2%, 1.8%, 1.8% and 0.9%, for the different models. This shows that roughly 1 to 2% effect might be supported.

The significance of the associations between other AP and HA due to the different diseases depends of the applied model.

Wong et al. (2002) used Poisson regression to compare HA and air quality between Hong Kong and London. They found that respiratory admissions (≥ 64 years of age) were related to NO₂ and SO₂ in both cities. Significant associations were also found between PM₁₀ and SO₂ for cardiac admissions. Wilson et al. (2004) concluded that air pollution has significant and remarkably similar effects in both cities, regardless of differences in social, lifestyle and environmental factors, suggesting that the association is casual.

In Valencia (Spain), Ballester et al. 2001 shown a rise in SO₂ levels of 10 $\mu\text{g}/\text{m}^3$ was significantly associated with an increment of 3.0% and 3.6% in the expected number of all cardiovascular and heart diseases admissions, respectively. A similar increase in NO₂ was associated with an increment of 3.6% in the expected number of admissions for stroke diseases.

Alves et al. (2010b) found that, in Lisbon, the risk for circulatory diseases increased by 0.8%, 0.5% and 2.2% per 10 $\mu\text{g}/\text{m}^3$ increase in NO₂ for the under 15, 15-64 and over 64 age groups,

respectively. A $10 \mu\text{g}/\text{m}^3$ increase in the same atmospheric pollutant, increases the risk due to respiratory diseases for the < 15 and ≥ 64 age groups by 1.2% and 2.0%, respectively. The results obtained in Lisbon are in the same range of values reported by other studies carried out in the US and Europe. The association between PM_{10} and $\text{PM}_{2.5}$ and the HA due to stroke and ischaemic diseases for individuals over 64 years was significant for all models. Results showed that an increase of $10 \mu\text{g}/\text{m}^3$ in PM_{10} is associated with an increase in that typology of HA between 0.7% and 1.0% for stroke and from 0.4% to 1.0% for ischaemic diseases; the same increment in $\text{PM}_{2.5}$ is associated with an increase of that typology of HA that ranged between 0.3% and 0.9% for stroke and between 0.2% and 0.8% for ischaemic diseases.

The studies reviewed here encompass a variety of methodologies to investigate the short-term impact of atmospheric pollutants and public health. Each of the studies reported a significant association with at least one atmospheric pollutant. For respiratory admissions, Schwartz (1997) summarised a selection of US studies and reported increases in respiratory admissions of 1.3% for $10 \mu\text{g}/\text{m}^3$ increases in PM_{10} . In 26 US communities, and for a $10 \mu\text{g}/\text{m}^3$ increase in $\text{PM}_{2.5}$ concentration, Zanobetti et al. (2009) found an increase of 2.07% in respiratory admissions. The United States Environmental Protection (US EPA) reviewed the evidence for health effects of particles, including admission time-series studies, and tabulated results from a large number of works. The US EPA reports that particle effects ranged from approximately 1% to 5% for $10 \mu\text{g}/\text{m}^3$ increases (Chapman et al. 1996). Results obtained for 8 European cities within the APHEA project showed an increase in respiratory admissions of 0.9% for $10 \mu\text{g}/\text{m}^3$ increases in PM_{10} , for individuals over 64 years (Atkinson et al. 2001). Wellenius et al. (2006) found in six US cities that a $10 \mu\text{g}/\text{m}^3$ increase in PM_{10} was associated with an increase of 0.72% in HA due to cardiac diseases. In Hong Kong, Hong et al. (2013) obtained, for an increase of $10 \mu\text{g}/\text{m}^3$ in $\text{PM}_{2.5}$ levels, an increase of 1.86% in HA due to circulatory diseases.

In Lisbon, no significant correlations between PM_{10} and HA due to respiratory diseases for individuals between 15 and 64 years and over 64 years was found in this study; in Setúbal (Almeida et al. 2014), the increase of $10 \mu\text{g}/\text{m}^3$ in PM_{10} was associated with an increase in HA of 1.6% for respiratory diseases for individuals under 15 years as observed in our study by the WEEK model. Our results point out 1.6 to 2.1%, for $10 \mu\text{g}/\text{m}^3$ increases of PM_{10} and 1.3 to 1.6% for $10 \mu\text{g}/\text{m}^3$ increases of $\text{PM}_{2.5}$. These increases are for below 15 years only (the significant one).

Chapter 5 – Atmospheric pollutants (AP) and hospital admissions (HA) aggregations

Table 5.4.1 - Summary statistics of AP daily average concentrations ($\mu\text{g}/\text{m}^3$) for the period 2006-2008.

Pollutant	Year	Average		Median		SD		Min.		Max.		Histogram
CO	2006	522.82		420.55		303.29		213.64		2229.93		
	winter/summer station	796.24	363.93	728.06	328.56	360.51	151.67	269.05	213.64	2229.93	1305.45	
	2007	516.16		419.29		294.48		184.63		1688.17		
	winter/summer station	810.30	311.36	744.37	288.01	328.92	83.05	309.62	184.63	1688.17	717.04	
	2008	449.86		373.02		245.21		170.51		1549.73		
	winter/summer station	677.46	282.03	635.17	267.80	277.53	62.00	274.66	170.51	1549.73	484.48	
NO	2006-2008	496.24		401.78		283.79		170.51		2229.93		
	winter/summer station	761.10	319.11	707.22	294.23	328.58	111.08	269.05	170.51	2229.93	1305.45	
	2006	78.61		51.57		69.38		6.83		351.57		
	winter/summer station	134.57	39.75	113.00	30.06	83.58	27.94	19.95	6.83	351.57	140.54	
	2007	80.05		50.78		71.34		10.67		346.49		
	winter/summer station	138.62	38.62	122.14	31.54	84.01	27.42	12.84	10.67	346.49	197.20	
NO ₂	2008	66.62		40.58		63.30		7.98		367.67		
	winter/summer station	115.78	27.31	98.48	24.83	77.91	13.79	12.82	7.98	367.67	101.19	
	2006-2008	75.08		46.40		68.29		6.83		367.67		
	winter/summer station	129.62	35.22	112.85	28.55	82.25	24.55	12.82	6.83	367.67	197.20	
	2006	70.17		68.94		28.32		17.72		158.22		
	winter/summer station	90.02	56.12	91.37	46.35	23.91	28.06	38.19	17.72	158.22	153.71	
SO ₂	2007	73.87		72.25		30.75		18.28		194.60		
	winter/summer station	93.17	50.93	90.79	46.62	26.71	23.66	25.81	18.28	194.60	153.62	
	2008	67.49		66.18		28.94		14.67		148.29		
	winter/summer station	89.44	44.24	87.74	38.35	24.47	18.88	31.62	14.67	148.29	104.99	
	2006-2008	70.51		69.32		29.44		14.67		194.60		
	winter/summer station	90.87	50.43	90.67	42.50	25.04	24.26	25.81	14.67	194.60	153.71	
SO ₂	2006	2.46		2.01		1.81		0.09		20.26		
	winter/summer station	2.97	2.30	2.80	1.98	2.32	1.51	0.09	0.41	20.26	6.80	
	2007	2.09		1.72		1.40		0.21		8.26		
	winter/summer station	2.64	1.77	2.28	1.44	1.64	1.37	0.21	0.35	8.06	8.26	
	2008	1.23		0.99		0.92		0.15		5.39		
	winter/summer station	1.67	0.85	1.36	0.71	1.12	0.57	0.35	0.15	5.34	4.35	
SO ₂	2006-2008	1.93		1.48		1.51		0.09		20.26		
	winter/summer station	2.42	1.64	1.94	1.12	1.84	1.36	0.09	0.15	20.26	8.26	

In histograms, x represents the daily averages AP concentrations and y their frequencies. SD: mean standard deviation.

Chapter 5 – Atmospheric pollutants (AP) and hospital admissions (HA) aggregations

Table 5.4.1 - Summary statistics of AP daily average concentrations ($\mu\text{g}/\text{m}^3$) for the period 2006-2008 (continued).

Pollutant	Year	Average		Median		SD		Min.		Max.		Histogram
O ₃	2006	68.93		67.06		27.04		13.63		181.19		
	winter/summer station	47.92	88.30	49.63	80.67	17.18	27.79	15.43	36.58	85.57	181.19	
	2007	70.20		70.85		24.56		10.74		145.62		
	winter/summer station	45.78	81.29	43.60	78.31	17.58	18.88	10.74	45.60	83.84	145.62	
	2008	69.15		68.25		21.64		12.19		153.09		
	winter/summer station	49.79	80.70	52.97	77.28	13.89	20.89	12.19	39.28	80.12	153.09	
	2006-2008	69.43		68.30		24.49		10.74		181.19		
winter/summer station	47.84	83.43	49.57	78.37	16.33	23.04	10.74	36.58	85.57	181.19		
PM ₁₀	2006	34.87		30.98		16.50		10.72		106.55		
	winter/summer station	39.25	34.69	35.44	28.61	15.43	19.91	13.01	10.72	86.67	106.55	
	2007	32.69		30.50		13.80		10.02		107.77		
	winter/summer station	39.30	25.96	38.18	24.78	17.06	9.16	11.80	10.02	107.77	57.11	
	2008	26.78		24.26		10.62		9.98		81.97		
	winter/summer station	31.24	22.58	27.96	20.67	13.00	7.81	13.59	9.98	81.97	50.55	
	2006-2008	31.44		27.90		14.25		9.98		107.77		
winter/summer station	36.58	27.74	32.90	24.20	15.67	14.34	11.80	9.98	107.77	106.55		
PM _{2.5}	2006	16.13		12.60		10.40		2.66		62.13		
	winter/summer station	21.44	15.04	19.03	12.60	11.85	9.95	5.71	2.66	62.13	46.45	
	2007	16.09		13.62		10.19		3.05		72.14		
	winter/summer station	22.02	10.83	19.51	8.64	12.62	6.19	5.25	3.05	72.14	35.78	
	2008	11.89		9.67		7.17		2.96		49.65		
	winter/summer station	16.02	8.82	14.04	7.29	8.83	4.46	4.88	2.96	49.65	23.51	
	2006-2008	14.70		11.79		9.57		2.66		72.14		
winter/summer station	19.82	11.56	16.83	8.85	11.51	7.67	4.88	2.66	72.14	46.45		

In histograms, x represents the daily averages AP concentrations and y their frequencies. SD: mean standard deviation.

Chapter 5 – Atmospheric pollutants (AP) and hospital admissions (HA) aggregations

Table 5.4.2 - Summary statistics of daily HA values for the period 2006-2008.

Disease	Age	Year	Count.	Average	Med.	SD	Min.	Max.	Histogram		
All Circulatory	all ages	2006-2008	37622	11.44	6	13.72	0	75			
		winter/summer	83 59	0.23 0.16	0 0	0.92 0.40	0 0	13 2			
	< 15	2006-2008	186	0.17	0	0.41	0	2			
		winter/summer	61 59	0.17 0.16	0 0	0.42 0.40	0 0	2 2			
	15-64	2006-2008	9580	8.74	9	5.60	0	30			
		winter/summer	3285 3059	9.10 8.29	9 9	6.01 5.16	0 0	28 23			
	≥ 64	2006-2008	27856	25.42	28	14.27	1	75			
		winter/summer	10026 8762	27.77 23.75	31 26	15.42 13.25	1 2	74 54			
	Cardiac	all ages	2006-2008	23314	7.09	4	8.67	0		50	
			winter/summer	49 38	0.13 0.10	0 0	0.67 0.32	0 0		10 2	
< 15		2006-2008	115	0.10	0	0.32	0	2			
		winter/summer	33 38	0.09 0.10	0 0	0.29 0.32	0 0	1 2			
15-64		2006-2008	5902	5.39	5	3.67	0	21			
		winter/summer	2080 1844	9.10 8.29	9 9	6.01 5.16	0 0	28 23			
≥ 64		2006-2008	17297	15.78	17	9.21	0	50			
		winter/summer	6300 5381	17.45 14.58	18 15	10.03 8.35	0 0	48 34			
Ischaemic Heart		all ages	2006-2008	12610	3.84	3	3.72	0	25		
			winter/summer	545 464	1.50 1.26	1 1	1.45 1.25	0 0	7 6		
	< 15	2006-2008	1456	1.33	1	1.33	0	8			
		winter/summer	535 464	1.48 1.26	1 1	1.44 1.25	0 0	7 6			
	15-64	2006-2008	3818	3.48	3	2.59	0	17			
		winter/summer	1406 1160	3.89 3.14	4 3	2.83 2.36	0 0	17 11			
	≥ 64	2006-2008	7336	6.69	6	4.29	0	25			
		winter/summer	2756 2199	7.63 5.96	7 6	4.81 3.68	0 0	25 23			
	Stroke	all ages	2006-2008	11477	3.49	1	4.62	0	27		
			winter/summer	16 7	0.04 0.02	0 0	0.25 0.14	0 0	3 1		
< 15		2006-2008	31	0.03	0	0.17	0	2			
		winter/summer	12 7	0.03 0.02	0 0	0.19 0.14	0 0	2 1			
15-64		2006-2008	2741	2.50	2	2.12	0	11			
		winter/summer	919 921	2.55 2.50	2 2	2.22 2.01	0 0	9 9			
≥ 64		2006-2008	8705	7.94	8	5.18	0	27			
		winter/summer	3097 2795	8.58 7.57	9 8	5.58 4.92	0 0	27 22			
All Respiratory		all ages	2006-2008	26180	7.96	5	8.65	0	55		
			winter/summer	1778 667	4.88 1.81	4 1	3.50 1.67	0 0	18 9		
	< 15	2006-2008	3366	3.07	2	2.88	0	18			
		winter/summer	1764 667	4.89 1.81	4 1	3.50 1.67	0 0	18 9			
	15-64	2006-2008	5734	5.23	5	4.10	0	24			
		winter/summer	2327 1611	6.45 4.37	6 4	4.69 3.41	0 0	24 17			
	≥ 64	2006-2008	17080	15.58	15	10.48	0	55			
		winter/summer	7037 4569	19.49 12.38	19 13	12.42 7.45	0 0	54 31			

Chapter 5 – Atmospheric pollutants (AP) and hospital admissions (HA) aggregations

Table 5.4.2 - Summary statistics of daily HA values for the period 2006-2008 (continued).

Disease	Age	Year	Count.	Average	Med	SD	Min.	Max.	Histogram
Asthma	all ages	2006-2008	1046	0.32	0	0.63	0	4	
		winter/summer	139 68	0.38 0.18	0 0	0.61 0.45	0 0	3 2	
	< 15	2006-2008	326	0.30	0	0.55	0	3	
		winter/summer	139 68	0.39 0.18	0 0	0.61 0.45	0 0	3 2	
	15-64	2006-2008	430	0.39	0	0.69	0	4	
		winter/summer	182 112	0.50 0.30	0 0	0.78 0.62	0 0	4 4	
	≥ 64	2006-2008	290	0.26	0	0.54	0	3	
		winter/summer	136 67	0.38 0.18	0 0	0.65 0.44	0 0	3 2	

In histograms, x represents HA values and y their frequencies. SD: mean standard deviation.

Chapter 5 – Atmospheric pollutants (AP) and hospital admissions (HA) aggregations

Table 5.4.3 - Statistically significant ($p < 0.05$) positive relationships between AP and HA, at least in one of the four models (DAY, WEEK, O&MA, MA&MA).

Pollutant	Disease	Age	DAY	WEEK	O&MA	MA&MA	DAY	WEEK	O&MA	MA&MA
			$p(B)$				$E (\%)*$			
CO	Stroke	≥ 64	-	0.045	-	0.000	-	0.919	-	0.940
	Ischaemic	≥ 64	-	-	0.044	0.023	-	-	1.167	0.450
	Respiratory	< 15	-	0.031	0.003	0.000	-	2.104	2.390	1.311
NO	Cardiac	15-64	0.006	-	-	-	0.639	-	-	-
		≥ 64	0.013	-	-	-	0.414	-	-	-
	Stroke	≥ 64	0.045	-	0.017	0.000	0.407	-	0.878	0.674
		15-64	0.020	-	-	-	0.469	-	-	-
	Circulatory	≥ 64	0.011	-	0.045	0.000	0.377	-	0.543	0.277
		15-64	0.016	-	-	0.009	0.655	-	-	0.463
	Ischaemic	≥ 64	0.026	-	-	0.029	0.483	-	-	0.291
		< 15	0.000	0.007	0.001	0.000	1.264	1.756	1.786	0.924
	Respiratory	≥ 64	0.050	-	-	0.010	0.361	-	-	0.309
Stroke		≥ 64	0.016	-	-	0.000	1.007	-	-	0.862
NO ₂	Circulatory	≥ 64	0.005	-	-	-	0.861	-	-	-
		15-64	0.000	-	-	-	2.031	-	-	-
	Respiratory	< 15	0.006	0.014	0.006	0.000	1.728	2.860	2.713	1.945
		≥ 64	0.006	-	-	0.000	1.037	-	-	0.847
	Cardiac	15-64	0.019	-	-	0.046	0.538	-	-	0.212
SO ₂	Stroke	≥ 64	0.037	0.010	-	0.000	0.416	0.607	-	0.428
		15-64	-	-	-	0.000	-	-	-	0.320
	Circulatory	≥ 64	-	0.028	-	-	-	0.341	-	-
PM ₁₀	Ischaemic	15-64	0.017	0.016	0.002	0.000	0.638	0.918	1.174	0.881
		≥ 64	0.006	0.002	0.001	0.000	0.580	0.878	0.964	0.639
	Respiratory	< 15	0.002	0.002	0.003	0.000	0.900	1.557	1.267	0.913
		≥ 64	-	-	-	0.001	-	-	-	0.300
	PM _{2.5}	Cardiac	15-64	0.019	-	-	0.009	0.877	-	-
≥ 64			-	-	-	0.002	-	-	-	0.769
Stroke		≥ 64	0.014	0.008	0.021	0.000	0.792	1.043	1.076	0.761
		15-64	0.047	-	-	0.000	0.640	-	-	0.597
Circulatory		15-64	0.002	0.021	0.044	0.009	1.374	1.478	1.264	0.582
		≥ 64	0.005	0.016	0.030	0.021	0.964	1.152	1.073	0.388
Respiratory		< 15	-	0.046	0.003	0.000	-	1.687	2.077	1.922
PM _{2.5}	Cardiac	15-64	-	-	-	0.018	-	-	-	0.307
		≥ 64	-	0.003	0.009	0.000	-	0.861	0.912	0.706
	Circulatory	15-64	-	-	-	0.006	-	-	-	0.308
		≥ 64	-	0.019	-	0.043	-	0.833	-	0.255
	Respiratory	< 15	-	0.039	0.002	0.000	-	1.291	1.585	1.195

This table shows the statistical significance of the association (p) and semi-elasticity (E) in %.

*(For each 10 $\mu\text{g}/\text{m}^3$ of AP a certain % of HA changes).

5.5 Conclusions

In this study, we have studied potential AP and HA associations in Lisbon urban area, from 2006 to 2008. AP values in this study presented higher values during winter than in summer, except O₃ which was the other way around; these are expected observations. Only NO₂ and PM₁₀ exceeded the annual limit as given by Directive 2008/50/EC of European Union. AP averaged over the stations present normality in all cases; HA averaged over the hospitals are bimodal for the studied diseases, except asthma.

Four models were applied using OLS, following previous studies, considering the databases day AP-day HA, day AP-week HA, week AP-day HA and week AP-week HA. The later was the one leading to a larger number of significant associations. The increase of HA with the increase of 10 µg/m³ in AP, given by the different models, are of the same order of magnitude; however the week-week models gave in general lower values, most probably due to the smoothing of both AP and HA data. The increases go up to 3%, considering all the models. It may be concluded that any of the models can be adopted, because they lead to similar conclusions. However, since the week-week models produces a larger number of associations might be suggested the use of this one.

Three ranges of age were studied: < 15, between 15 and 64, ≥ 64.

For < 15, all models showed significant associations between respiratory diseases and all AP except the day-day model for PM₁₀ and PM_{2.5}. For this age range, no more associations were found between AP and the other studied diseases. For the other age ranges, associations depended of the disease and the pollutant.

For ≥ 64, similar associations as for other authors were found between respiratory diseases and NO₂, SO₂ and PM₁₀. This age range is sensitive to all diseases associated with almost all pollutants. For stroke, 1% increase when NO₂ increase of 10 µg/m³ was found in this work: other authors pointed out 3.6%. No association between PM₁₀ and respiratory disease was observed, as other authors have found.

For individuals between 15 and 64, HA due to cardiac, stroke, circulatory and ischaemic diseases are associated to most of the pollutants. No association was found between respiratory disease HA and AP. Also no association was found between NO₂ and HA by circulatory diseases as pointed out by other authors as 0.5% increase in HA when the pollutant increase 10 µg/m³; this value was obtained in this work with NO.

The followed methodology was validated by comparison, with comparison of some data with Poisson regression, and it was sustained by previous publications.

6 COM-Poisson Regression Applied to Hospital Admissions (Cardiac and Respiratory Diseases), Air pollutants and Meteorological Data in Lisbon

Based on article of same title:

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6.1 Abstract

Air pollutants are recognised as one of the potential environmental risk factors causing health hazards to the exposed population. This study aims to investigate associations between hospital admissions, air pollutants and meteorological data in Lisbon (Portugal), focusing on weekly databases, between 2006 and 2008. Hospital admissions of cardiac diseases, circulatory and respiratory diseases, aggregated into 3 age classes (<15; 15-64; >64 years old) were the responses. Air pollutants (CO, NO, NO₂, SO₂, O₃, PM₁₀ and PM_{2.5}) and meteorological data (temperature and relative humidity) were the predictors variables. Since data exhibit under-dispersion, the Conway-Maxwell-Poisson distribution (COM-Poisson) was used to estimate the magnitude of the association between hospital admission counts, air pollutant concentrations and temperature and relative humidity. The most relevant statistical significant associations were obtained between: 1) circulatory diseases, in adults, and PM₁₀, temperature and humidity simultaneously present in the atmosphere; 2) cardiac diseases, in adults, and PM₁₀, temperature and humidity simultaneously present in the atmosphere; 3) ischaemic diseases, in elderly people, and PM₁₀, temperature and humidity simultaneously present in the atmosphere; 4) respiratory diseases in elderly people, and PM₁₀, PM_{2.5} and temperature simultaneously present in the atmosphere; 5) circulatory diseases in adults and PM₁₀, PM_{2.5} and temperature simultaneously present in the atmosphere; 6) ischaemic diseases, in adults and PM₁₀, PM_{2.5} and temperature simultaneously present in the atmosphere.

6.2 Introduction

Air pollution has been studied for many years because it poses a health risk in many regions worldwide, including developed countries (Ballester et al. 2006). Interest in this phenomenon is reflected by the high number of studies in several regions. Epidemiological studies, have consistently shown positive associations between hospital admissions and atmospheric particulate matter (particles with aerodynamic equivalent diameter of 10 and 2.5 μm -PM₁₀ and PM_{2.5}, respectively), a wide range of other pollutants, including carbon monoxide (CO),

nitrogen oxide (NO), nitrogen dioxide (NO₂) and sulphur dioxide (SO₂), and weather conditions (temperature and relative humidity) in different continents: North America (Burnett 1997; Lipfert 1997; Middleton et al. 2008; Pope et al. 2004, 2008; Rodopoulou et al. 2014; Roemer et al. 1998; Wilson et al. 2004; Zanobetti and Schwartz 2005), South America (Lumley and Sheppard 2000; Roberts 2005), Asia (Cameron and Trivedi 1998; Hosseinpoor et al. 2005; Katsouyanni et al. 1997; Lin et al. 2013; Luvsan et al. 2012; McConnell et al. 2002; Qiu et al. 2013; Yu et al. 2013; Tao et al. 2014; Yang et al. 2015), Australia (Chen et al. 2007; Hansen et al. 2012) and Europe (Almeida et al. 2014; Alves et al. 2010b; Ayres-Sampaio et al. 2014, Freitas et al. 2010; Kalantzi et al. 2011; Linares and Díaz 2009, 2010; Neuberger 2007; Pablo Dávila et al. 2013; Pascal et al. 2013; Perez et al. 2012).

In Portugal, however, very few studies have assessed the acute effect of air pollutants on public health (Almeida et al. 2013a, 2014; Alves et al. 2010b; Cruz et al. 2014, Freitas et al. 2009a; Sarmiento et al. 2009; Vasconcelos et al. 2013). Both ambient air pollution and extreme temperatures are risk hazards for human health (Barnett 2007; Kan et al. 2008; Qian et al.; 2008, Romieu et al.; 2012, Tong et al.; 2012; Yang et al.; 2012). It is widely accepted that effects of air pollution and temperature on mortality may confound each other (Qian et al. 2008; Romieu et al. 2012; Wu et al. 2013; Yang et al. 2012). Studies examining acute health endpoints have reported the simultaneous effects of both weather variables and air pollutants on health. Ren et al. (2006) found that airborne particles significantly modified the effects of air temperature on respiratory and cardiovascular hospital admissions in Brisbane, Australia.

Li et al. (2011) used time-series analysis to explore the modification effects of temperature on the association between PM₁₀ and the cause-specific mortality for cardiovascular, respiratory, cardiopulmonary, stroke and ischemic heart diseases, as well as non-accidental mortality in Tianjin between 2007 and 2009. Results showed that the PM₁₀ effects were stronger on high temperature level days than that on low temperature level days. This suggests that the modifying effects of the temperature should be considered when analysing health impacts of ambient PM₁₀. Vasconcelos et al. (2013) investigated the effects of air temperature on acute myocardial infarction morbidity in the two most populated areas in Portugal (Oporto and Lisbon) and concluded that cold weather is associated with an increased risk of hospitalisations. These results demonstrated that cold weather is an important environmental hazard in Portugal, where low temperatures are generally under-rated compared to high temperatures during summer periods drawing attention to the negative effect that exposure to cold weather during winter can have on human health.

Including hospital admissions in studies related to the short term effects of air pollution on human health is particularly valuable since such studies may refer to large parts of the

population even though, only a small portion of population is admitted to hospital; this criterion constitutes the most direct way of accessing the cardio-respiratory health burdens imposed by the complex air pollution mixtures to the exposed communities (Delfino et al. 2009). According to this assumption, a lot of remarkable studies have been conducted in order to define the association between one or more pollutants and the number of daily hospital admissions (Atkinson et al. 2001; Kan and Chen 2004; Katsouyanni et al. 2001; Moshhammer et al. 1987, 2006; Morawska et al. 2002, Neuberger et al. 2007, 2013).

Multiple Poisson regression models constitute one of most widely used statistical techniques for analysing associations between hospital admissions and air pollutants. This is a powerful tool is since the relationships between the responses and the predictors are a straight-line, polynomial, or exponential. In many applications, however, the reliance on a defined mathematical function is difficult. Many phenomena do not have a relationship that can be easily defined (Terzi and Cengiz 2009). Real data are often over-or under-dispersed and, thus not conducive to Poisson regression. To tackle this problem, a regression model based on the Conway-Maxwell-Poisson (COM-Poisson) distribution provides a more suitable framework (Sellers and Shmueli 2010).

Most time-series studies use days as the units of comparison, which is the minimum time period for which hospitalisation data are recorded. Some studies have modelled single day health events with exposure averages over multiple days (Lipfert 1993; Lumley and Sheppard 2000; Roberts 2005; Sarmiento et al. 2009; Smith et al. 2000) and a minority has modelled the health events also as averages over multiple days, while preserving the days as units of comparison (Schwartz 2000a,b). This study used weekly database because it has been previously found that this temporal cycle is the one leading to a larger number of significant associations (Cruz et al. 2014).

Usually models include only one pollutant. Investigating multivariate relationships will enhance our understanding of the interaction between pollutants, as well as the human health effects related to these complex mixtures. Additional covariates denote, on the one hand, temporal patterns in diseases (long-term trends, seasonality and weekly trends) and, on the other hand, meteorological indicators and seasonal indicators (Chen et al. 2007; Katsouyanni 1996, 2001; Samet et al. 1997; Smith et al. 2000; Walters et al. 1994).

To elucidate the association between air pollutants and health effects on people attending emergency rooms in hospitals from Lisbon, from 2006 to 2008, a Conway-Maxwell-Poisson distribution (COM-Poisson) analysis was applied to weekly databases. Responses were all circulatory, cardiac, ischaemic heart, stroke and all respiratory diseases by three age groups (<15, 15-64; >64 years old). Air pollutants and meteorological variables, CO, NO, NO₂, SO₂, O₃, PM₁₀, PM_{2.5}, temperature and relative humidity, were the predictors. This innovative

work will contribute to bridge a gap in what concerns simultaneous multiple associations between environmental parameters and health outcomes in a country where the scarcity of studies is still evident.

6.3 Data

6.3.1 Description of Study Area

Lisbon is the westernmost large city located in Europe, as well as the westernmost capital city and the only one along the Atlantic coast (Almeida et al. 2013b). The studied urban area of Lisbon, with a total area of 448 km², has a resident population of 1 378 868 inhabitants (average over 2006-2008) (Figure 6.3.1). In the city, traffic is the main source of atmospheric pollution (Almeida et al. 2009a,b). Industries includes textiles, chemicals, steel, oil, cement, sugar refining, shipbuilding, soap and flour production (Almeida et al. 2007, 2013a; Farinha et al. 2004a). Due to the geographic position of Lisbon and to the dominant western wind regime, influenced by the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean, the expected high levels of pollutants are uncommon. The transport of maritime air mass is usually associated with cleaner air masses from the Atlantic Ocean and with better dispersion conditions of pollutants coming from the industrial areas (Almeida et al. 2013b). Nevertheless, high concentrations of air pollutants (AP) can be registered under adverse meteorological conditions, low dispersion and thermic inversions. The monitoring stations to be considered in this study are in municipalities whose population is served by the health units where the hospital admissions data (HA) were collected. Information on the municipalities and resident population was obtained from the National Institute of Statistics of Portugal (INE).

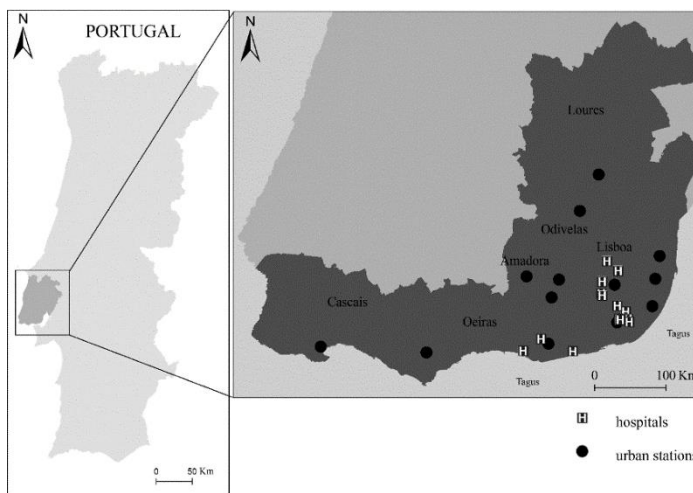


Figure 6.3.1 – Spatial distribution of the main hospitals and air quality monitoring stations.

6.3.2 Hospital Admissions

The Central Administration of the Health System (ACSS) provided the HA databases, which consist of daily counts of hospital admissions, from 2006 to 2008, in 13 public hospitals from Lisbon (Figure 6.3.1). HA were arranged according to the World Health Organisation's International Statistical Classification of Diseases (9th and 10th Revisions, ICD-9 and ICD-10, respectively) endorsed by the Forty-third World Health Assembly in May 1990, which came into use in WHO Member States since 1994 (WHO 2014b): circulatory (ICD-9: 390-459; ICD-10: I00-I99), cardiac (ICD-9: 390-429; ICD-10: I30-I52), ischaemic heart (ICD-9: 410-414; ICD-10: I20-I25), stroke (ICD-9: 430-438; ICD-10: I60-I69) and all respiratory (ICD-9: 460-519; ICD-10: J00-J99) diseases.

HA weekly databases were rounded to unit values to maintain counts for dependent variables. The criterion used in HA weekly databases has been used in former studies in Portugal (Almeida et al. 2014; Cruz et al. 2014; Sarmiento et al. 2009). It consists in aggregating HA by age group (<15, 15-64, >64 years old). Sarmiento et al. (2009) and Cruz et al. (2014) analysed the seasonal trends in the HA daily databases, during the period under study, and associated these trends with weather conditions. It was also observed that HA tend to be lower on weekends as compared to working days, suggesting that: 1) weekend health outcomes are only registered on Mondays, 2) patients wait for Monday to go to hospital if the symptoms are not so severe, or 3) the number of doctors in hospitals is reduced during weekend and people may wait to Monday to be assisted.

6.3.3 Air Pollutants

The AP concentrations (CO, NO, NO₂, SO₂, O₃, PM₁₀ and PM_{2.5}) (in µg/m³) were obtained from 13 monitoring urban stations in the studied area of the Portuguese Environmental Agency (QualAr network). Three are considered background monitoring stations and the remaining are classified as urban, influenced by traffic. This monitoring network is assumed to represent the exposure of the population served by the 13 hospitals from which health data were collected. From the hourly data, daily averages were calculated for each pollutant in each of the 13 monitoring stations following the recommendations of the European Commission (Directive 2008/50/CE). Daily values were calculated as the 24 hour-average for SO₂, PM₁₀, and PM_{2.5}, as the daily 1 hour-maximum for NO, NO₂ and as 1 hour-maximum of octo-hourly moving averages for CO and O₃. The condition to choose the monitoring station data to this study was that at least 75% of the hourly values on a particular day were non-missing. The COM-Poisson regression was applied using the weekly average of the 13 monitoring stations of each AP.

6.3.4 Meteorological data

The temperature (in degree Celsius) and relative humidity (in percentage) were downloaded from weather archive data (<http://meteo.infospace.ru>) from Lisboa/Gago Coutinho station, which provide hourly observations. Data from this meteorological station are widely used as representative of the entire metropolitan area. The hourly database was converted to a weekly database.

6.4 Methodology

6.4.1 Databases

Epidemiological studies have been using exposures in the form of moving averages, distributed lags or data aggregated over several days or even weeks (Schwartz 2000b; Sarmiento et al. 2009).

In an attempt to better understand the effect of AP, temperature and relative humidity on HA for the cardiac, circulatory and respiratory diseases organised in three age groups, averages of 7 days were selected in agreement with Sarmiento et al. (2009), Almeida et al. (2014) and Cruz et al. (2014), for the period from 2006 to 2008. Seven days is still considered an acute time-scale for associations (WHO 1999; WHO 2006). Averages of 7 days of both AP and HA can adjust for biases arising from weekly fluctuations, to mitigate the influence of potential peaks on the evaluation of associations, and to account for lagged health responses and autocorrelation at frequencies ≤ 7 days (part of their variability may be noise) (Sarmiento et al. 2009, Cruz et al. 2014). HA weekly database were rounded to unit values. The diagnoses with only zero or one counts were excluded from this study: circulatory, cardiac, stroke and asthma in people under 15 years old; asthma in people between 15 and 64 years and elder than 64 years old.

The averages of temperature and relative humidity were included in the model to adjust for the potential nonlinear confounding effects of weather conditions (Chen 2012). To smooth the temperature as confounder, HA, AP and meteorological databases were aggregated in winter and summer databases ($N = 51$ and $N = 52$, respectively), for the period of study. The winter database corresponds to months with temperatures lower than 16°C , while the summer database includes months with temperatures higher than 16°C . For each database only months with over 75% readings were considered. The winter database comprises November, December, January and February and to summer database encompasses May, June, July and August.

Recorded variables usually present different unities, scales and ranges (Table 6.4.1).

Table 6.4.1 – Descriptive statistics for the variables.

	PM ₁₀	PM _{2.5}	SO ₂	NO	NO ₂	CO	O ₃	Temp.	Humid.
Min.	15	5	0.4	19	27	218	23	7	43
1st Qu.	25	9	1	36	54	331	55	13	66
Median	29	13	2	59	72	412	70	16	73
Mean	31	15	2	75	70	495	70	16	73
3rd Qu.	36	18	2	100	84	606	85	19	80
Max.	73	46	7	225	150	1243	154	27	90
Range	58	41	6	206	122	1026	131	20	47
IC 0.05	11	9	1	64	30	276	30	7	13
%IC	20	34	35	55	21	34	22	22	9

In order to allow proper assessment of variable interdependencies and avoid suppressing their magnitude, any eventual distortion or scale effects, an initial transformation of sample i ($1 \leq i \leq 151$) of variable j ($1 \leq j \leq 9$), χ_{ij} , was performed for all i, j , using the transform $x_{ij} = \frac{\chi_{ij} - \chi_{m_j}}{\chi_{M_j} - \chi_{m_j}}$, where x_{ij} is the value of χ_{ij} scaled to the [0,1] interval and χ_{M_j} and χ_{m_j} are maximum and minimum values of the j -th variable, respectively.

6.4.2 Modelling Approach

Associations between HA and AP and meteorological data were performed with a generalised linear model (GLM) following the Conway-Maxwell-Poisson (COM-Poisson) distribution.

HA are the dependent variables, whilst AP and meteorological data are both covariates. Scaled weekly mean data during 2006-2008 were performed.

Usually, data used in these studies, present overdispersion (Alves et al. 2010b), but in the case of the present matrix, the variance of counts was less than the mean (under-dispersion) in all cases, except respiratory diseases, elderly. COM-Poisson distribution is used for modelling count data and presents useful, flexible and elegant characteristics in dealing with over or under-dispersion (Shmueli et al. 2005; Kadane et al. 2006; Guikema and Coffelt 2008). This method is a two-parameter generalisation of the Poisson distribution that also includes, in special cases, the geometric distribution and in limit cases, the Bernoulli distribution.

The COM-Poisson probability distribution function is given by:

$$P(Y = y) = \frac{\lambda^y}{(y!)^\nu Z(\lambda, \nu)} \quad y = 0, 1, 2, \dots; \quad \lambda > 0; \nu \geq 0 \text{ [Equation 6.4-1]}$$

for a random variable Y , where $Z(\lambda, \nu) = \sum_{s=0}^{\infty} \lambda^s / (s!)^\nu$ is a normalising constant; λ is a centering parameter and ν is the dispersion parameter such that $\nu > 1$ indicates under-dispersion and $\nu < 1$ indicates over dispersion.

Approximations for the first two central moments of the COM-Poisson distribution can be used (McCullagh and Nelder 1997; Shmueli et al. 2005):

$$E[Y] \approx \lambda^{1/\nu} + \frac{1}{2\nu} - \frac{1}{2} \text{ and } \text{Var}[Y] \approx \frac{1}{\nu} \lambda^{1/\nu} [\text{Equation 6.4-2}]$$

These approximations must be used with caution since, in particular, they may not be accurate for $\nu > 1$ or for $\lambda^{1/\nu} < 10$ (Shmueli et al. 2005).

GLM models the relation between a response variable Y and a set of regressors X. In GLMs the dependence of the mean, $E(Y)$, on the regressors is of the linear type

$$g(E(Y)) = \beta_0 + \beta_1 X_1 + \dots + \beta_p X_p [\text{Equation 6.4-3}]$$

where $g(E(Y))$ is a known link function.

The COM-Poisson regression model was developed from an ordinary Poisson regression, which can be viewed as a special case of a loglinear model taking the form of a Poisson regression (McCullagh and Nelder 1997). In this case the link function is $\log(\lambda)$, and, therefore, the model specializes into

$$\log(\lambda) = \beta_0 + \beta_1 X_1 + \dots + \beta_p X_p [\text{Equation 6.4-4}]$$

In this study the GLM model was used to explain the occurrence of diseases caused by a combination of pollutants and atmospheric conditions. It was applied for all COM-Poisson distributions, except for Circ <15; Card >15, Str <15, Ast <15, Ast 15-64 and Ast >64, because these series almost only have 0 and 1 counts.

Relative risk (RR) was calculated from simply division of the COM-Poisson coefficients by ν . This of a crude comparison reasonable to approach because $E(Y\nu) = \lambda$ (Sellers and Shmueli 2010). In the COM-Poisson regression case, it is not use the first approach that compares conditional means directly, because the relationship between the conditional mean and the predictors is neither additive nor multiplicative and coefficients from a COM-Poisson regression model are on a different scale than those from an ordinary Poisson model.

6.5 Results and Discussion

6.5.1 Hospital Admissions

As expected, the number of emergency room visits for people older than 64 years old was significantly higher than for the other age groups (Figure 6.5.1). Seasonality can be observed with higher number of admissions during the winter. A long term trend across the years could not be observed, so it is enough to control fluctuations associated with seasons and day of the week.

HA averaged over the hospitals are bimodal for the studied diseases. During weekends the HA counts decreased (Cruz et al. 2014).

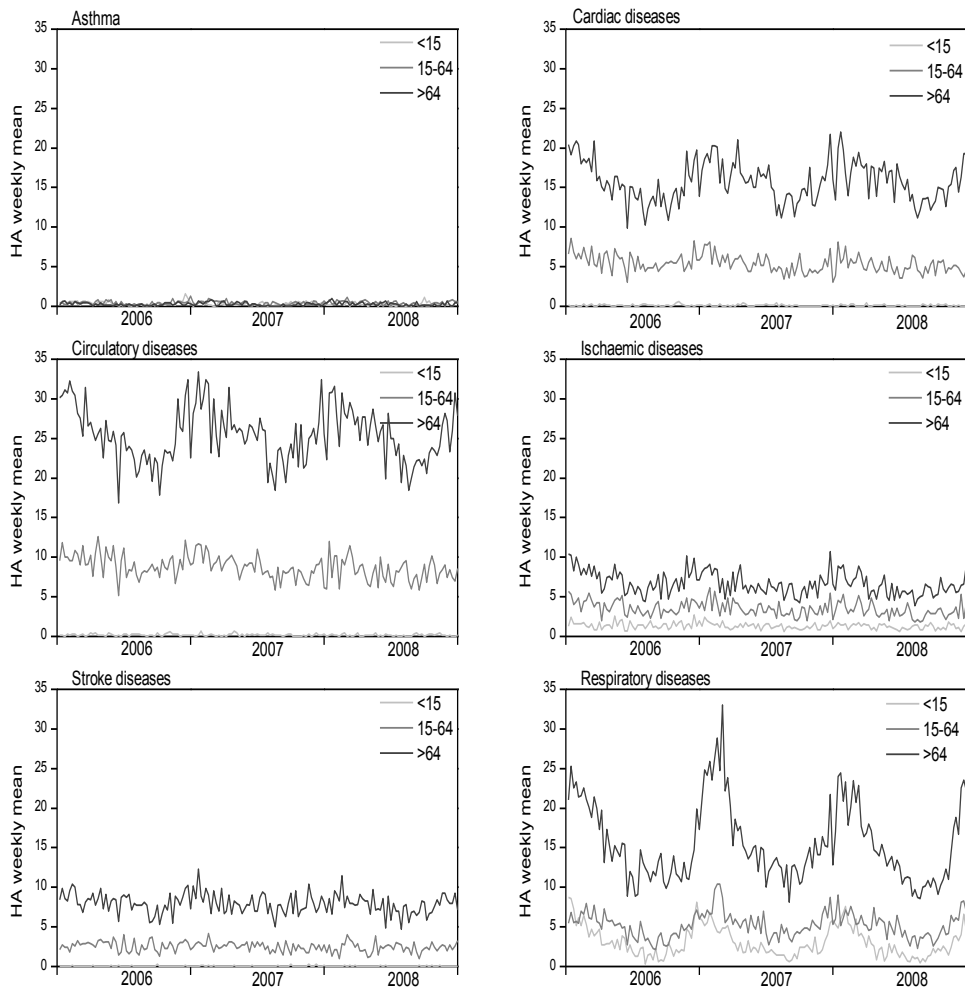


Figure 6.5.1 – Time trend of Hospital Admissions (HA).

6.5.2 Air Pollutants

The time series of AP weekly concentrations is shown in Figure 6.5.2. CO, NO and NO₂ present a seasonal pattern with high winter and low summer levels, except O₃ that presents an antagonistic behaviour. The summer higher values of O₃ could be explained by the adequate weather conditions for its formation. Sunlight, warm temperatures and high emission of precursor pollutants (nitrogen oxides and volatile organic compounds) lead to high levels of this atmospheric oxidant during the summer season (Alves et al. 2010b; Karr et al. 2007). PM₁₀, PM_{2.5} and SO₂ present smoothie seasonality. SO₂ showed lower

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concentrations than other AP, with a mean of 2.42 $\mu\text{g}/\text{m}^3$ in winter and a lower value of 1.64 $\mu\text{g}/\text{m}^3$ in summer.

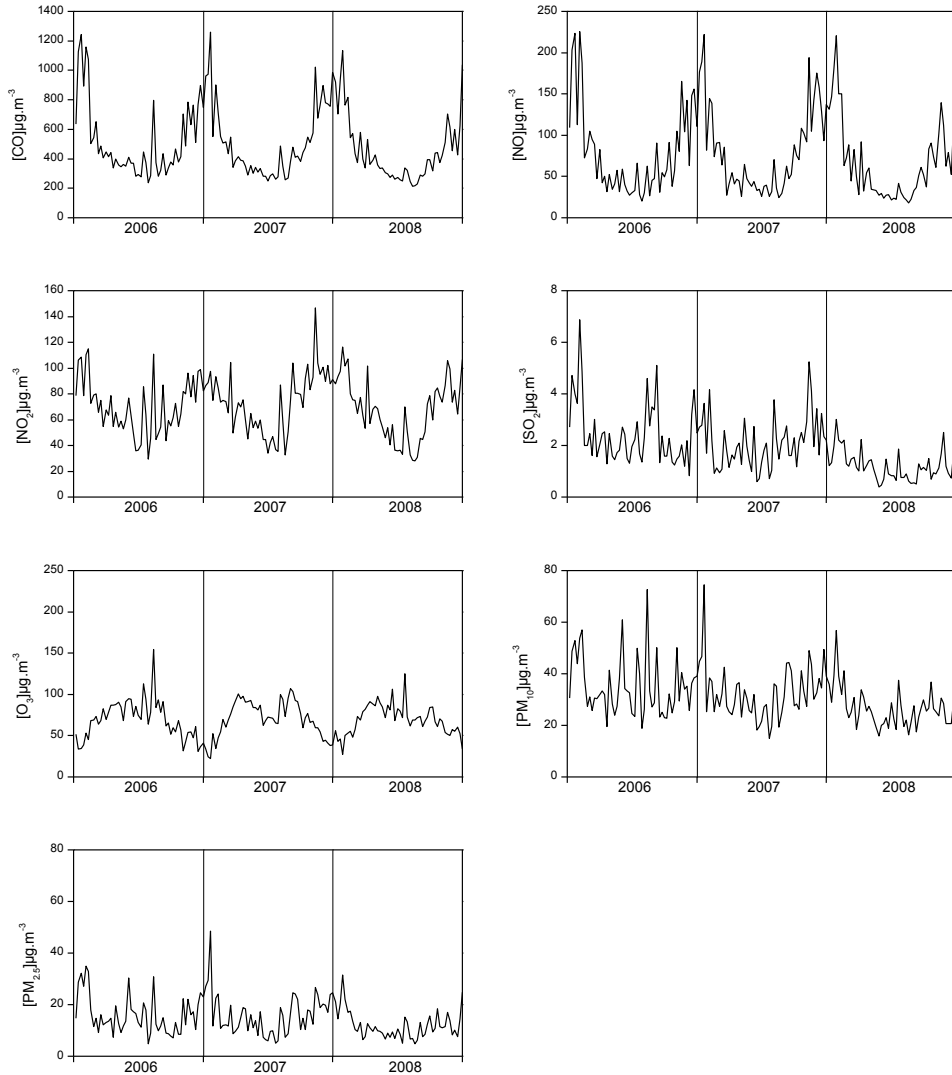


Figure 6.5.2 – Air pollutants (AP) time-trend.

6.5.3 Meteorological Data

The time series of meteorological hourly data (Figure 6.5.3) shows, as expected, higher temperature values in summer than in winter, as well as higher relative humidity in winter and more fluctuations in summer. The average temperature (minimum-maximum) and

humidity (minimum-maximum) for winter and summer periods of hourly data were 11.84°C (-0.10°C to 24. 0°C) and 20.0°C (9.60°C to 40, 0°C), 78.5% (28.0% to 100%) and 20.0% (9.60% to 40.0%), respectively.

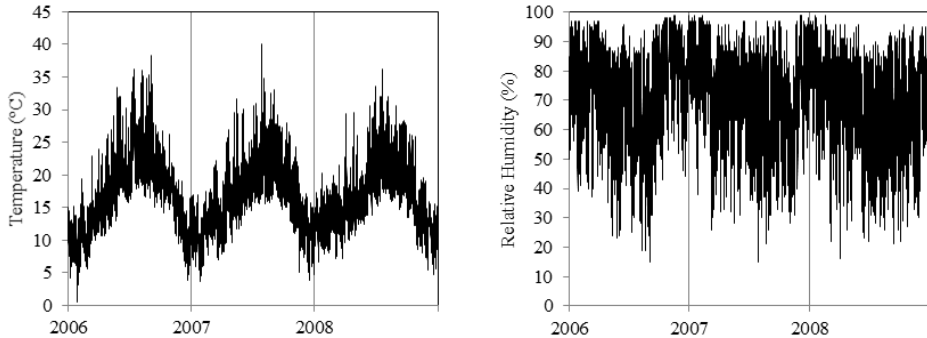


Figure 6.5.3 - Time trend of Meteorological (temperature and relative humidity) daily database.

6.5.4 COM-POISSON Regression

The results of the approach of COM-Poisson are shown in Table 6.5.1.

Respiratory diseases in all ages present statistical significant associations simultaneously with PM₁₀ and temperature. The same association was founded in circulatory and cardiac diseases, in elderly people and just ischaemic diseases, in adults.

Concerning circulatory and cardiac diseases in adults, statistical significant associations with PM₁₀ temperature and humidity at the same time in atmosphere were observed, as well ischaemic diseases in elderly people.

Humidity was only statistically correlated with ischaemic diseases, in childhood and stroke diseases in elderly people seems to be only correlated with temperature. When temperature was presented in a model, their coefficient (β) were always negative, these means that when increase temperature, the hospital admissions declined significantly.

In Cruz et al. (2014) also presented positive statistical significant associations between PM₁₀ and respiratory in children, circulatory, cardiac and ischaemic diseases, in adults, although, with ischaemic diseases in elderly people.

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Table 6.5.1 – Statistical significant relationships between HA and covariates AP and meteorological data obtained from COM-Poisson distribution.

	Dispersion	Coefficient (β)	Standard error
< 15 years old - Respiratory diseases			
Intercept		5.60	0.83
x(PM ₁₀)		4.37	1.51
x(Temp)		-6.65	0.89
v	3.45		0.40
15-64 years old - Respiratory diseases			
Intercept		9.48	1.18
x(PM ₁₀)		4.17	1.34
x(Temp)		-4.53	0.66
v	4.41		0.51
> 64 years old - Respiratory diseases			
Intercept		5.07	0.61
x(PM ₁₀)		1.87	0.50
x(Temp)		-1.77	0.25
v	1.67		0.19
15-64 years old - Circulatory diseases			
Intercept		9.99	1.20
x(PM ₁₀)		2.74	1.04
x(Temp)		-1.04	0.36
x(Humid)		0.86	0.38
v	4.68		0.53
> 64 years old - Circulatory diseases			
Intercept		13.65	1.57
x(PM ₁₀)		1.16	0.57
x(Temp)		-1.65	0.26
v	4.07		0.46
15-64 years old - Cardiac diseases			
Intercept		8.53	1.10
x(PM ₁₀)		3.03	1.36
x(Temp)		-1.34	0.47
x(Humid)		1.19	0.51
v	5.20		0.60

Chapter 6 - New methodology to estimate associations between atmospheric pollutants and hospital admissions

Table 6.5.1 – Statistical significant relationships between HA and covariates AP and meteorological data obtained from COM-Poisson distribution (continued).

	Dispersion	Coefficient (β)	Standard error
> 64 years old - Cardiac diseases			
Intercept		12.06	1.40
x(PM ₁₀)		1.38	0.73
x(Temp)		-2.11	0.34
v	4.12		0.47
< 15 years old - Ischaemic diseases			
Intercept		1.99	1.17
x(Humid)		2.64	1.12
v	7.29		0.90
15-64 years old - Ischaemic diseases			
Intercept		7.71	1.08
x(PM ₁₀)		4.80	1.71
x(Temp)		-2.63	0.63
v	5.41		0.62
> 64 Years old - Ischaemic diseases			
Intercept		9.23	1.15
x(PM ₁₀)		2.78	1.20
x(Temp)		-2.06	0.45
x(Humid)		0.98	0.44
v	4.87		0.56
> 64 Years old - Stroke diseases			
Intercept		14.69	1.74
x(Temp)		-1.57	0.46
v	6.82		0.78

6.6 Conclusions

In this study, statistical significant associations between hospital admissions and air pollutants and meteorological data of a Lisbon (Portugal) were obtained through the application of COM-Poisson regression. Results show relevant associations between circulatory, cardiac and ischaemic diseases, in adults and respiratory and ischaemic diseases in elderly people, and, jointly, particulate matter and weather variables.

Europe has achieved great improvements in air quality over recent decades, but much more remains to be done. The described associations add that air pollution, even at low levels, and weather conditions promote cardiac, circulatory and respiratory diseases in exposed people. These results suggest that it is still necessary to invest in strategies and awareness to reduce levels of atmospheric pollutants in densely populated urban and industrial areas, to improve exposed people's health.

Further studies involving the same approach in other areas with high population density areas (e.g. Oporto) are warranted.

7 General Discussion

This thesis presents several studies that characterise the outdoor air quality in Portugal and Islands, bark and lichen biomonitors in Lisbon and the association between air pollutants (AP) and hospital admissions (HA) in this city, between 2006 and 2008.

Throughout the monitoring period, legal limits were sometimes surpassed, in urban areas with industrial and traffic influence, indicating the need to adopt additional mitigation measures. Methodological approaches comprised mining techniques, wavelets and data clustering. The results suggest that the reclassification of some monitoring stations of atmospheric pollutants in Portugal is probably required.

Statistical techniques were used such as Ordinary Least Square Linear Regression (OLS) and Conway-Maxwell-Poisson distribution (COM-Poisson), which demonstrated significant associations between AP and HA, for both children and elderly people.

Lichens and barks were shown to be good biomonitors, as they allowed the identification of chemical elements and their sources in vast and dense areas.

7.1 Overview

Chapter 1 presents the thesis scheme, a brief introduction to air pollutants and a general overview and spatial distribution of PM₁₀, PM_{2.5}, NO₂ and O₃ in Portugal (mainland and islands). The spatial and temporal variability of PM concentrations need to be carefully studied to understand possibilities for mitigation measures. The PM spatial distribution was also assessed in more detail in Lisbon, because this metropolitan area is the focus of chapters 5 and 6, in which correlations between air pollution and emergency room admissions have been established.

Chapter 2 provides a comparative analysis of the air quality in Portugal, focused on PM₁₀ and PM_{2.5}, using a wavelet based approach. The most relevant conclusion of the study is the suggestion of a reclassification of one traffic station in the Oporto metropolitan area that was grouped with a suburban/industrial station of central Portugal, considering the type of environmental influence. The PM source-clustering suggest both source-combined impact at stations, and that more effort may be necessary to clarify source-specific contributions (also shown in Chapter 3).

Chapter 3 focused on the set-up of a spatial mapping of chemical elements in the atmosphere using biomonitors as a tool. The selected lichen and bark were *Parmotrema bangii* and *Cryptomeria japonica* respectively, sampled in the pollution-free Azores (Sao Miguel island),

Portugal, which were then exposed in the courtyards of 22 basic schools of Lisbon. The exposure period was from January to May 2008 and from June to October 2008 (indicated throughout the text as winter and summer, respectively). The chemical element concentrations were determined by Instrumental Neutron Activation Analysis (INAA). The conductivity of the lichen samples was measured to assess stress effects. Monte Carlo Target Transformed Factor Analysis (MCTTFA) was applied to winter/summer bark/lichen datasets. Emission sources that were identified comprised soil with anthropogenic contamination, a Se source, traffic, industry, and a sea contribution. In lichens, a physiological factor was recognised. The spatial study showed variable contributions of sources in dependence of specific school locations. Conductivity values were high in summer in locations such as the international Lisbon airport and downtown Lisbon. Lisbon is spatially influenced by marine air mass transport. It was concluded that a single air sampler in Lisbon may be enough to define the emission sources and that lichen conductivity may be used as a measure of differential meteorological conditions; conductivity could not be demonstrated to reflect variable levels of air pollution (see also Chapter 4). The visualised sources relate to soil, traffic, Se emission and sea spray; nevertheless, they are not pure: natural sources show up as mixed-up with anthropogenic sources and vice-versa. More study is needed to find out what a best-possible approach may be to reduce the mix-up of (emission) sources as showing up in MCTTFA factors.

Chapter 4 aimed at the evaluation of stress effects in lichens as a result of transplanting from unpolluted to air-polluted areas, the adaptation of transplanted biomonitors to new meteorological and physical-chemical conditions, and the comparison of the performance of both biomonitors. The selected lichen and bark were *Parmotrema bangii* and *Cryptomeria japonica* respectively, in the same studied area, in the same exposure period as indicated in Chapter 3. Bark and lichen, when outcome-averages were considered, had mostly different responses, but both gave the same information on emission sources in Lisbon. More study is needed to further investigate the differences between lichens and bark, with respect to both their baseline (background) element levels, the changes in levels after exposure, the dynamics in accumulation and release, and their *sensitivities* in indicating real changes in ambient environmental conditions.

In Chapters 3 and 4, biomonitoring was used to assess the chemical elements present in the atmosphere during the period of study and to link them to their emission sources. The lichen vitality was also measured in order to understand the physiological response during the transplant period. Two campaigns (winter and summer) were carried out to assess seasonality. The biomonitor approach proved very useful for mapping the Lisbon area, and permitted monitoring at sites where it may be difficult to make use of conventional monitoring stations. The seasonality of lichen conductivity data, the relationship of conductivity with physiology, and the possible effect of physiology on lichen element

accumulative behaviour, however, makes that more study is needed to clarify the (possibly element-specific) conductivity relationships with lichen monitoring performance, this notwithstanding the Chapter 3 data that suggest that lichen conductivity may be seen as more reflecting meteorological ambient conditions than be of effect on element accumulation.

In Chapter 5 the effects of air quality on respiratory and circulatory diseases were assessed, using Ordinary Least Squares (OLS) regression. The studied area was Lisbon, the period considered was 2006-2008. The pollutants (CO, NO, NO₂, SO₂, O₃, PM₁₀ and PM_{2.5}) were obtained from 13 monitoring stations, which provide hourly observations. Hospital admission data were compiled by age: < 15, 15-64, ≥ 64 years old. Results showed significant positive associations between: 1) the pollutants CO, NO, NO₂, SO₂, PM₁₀ and PM_{2.5} and circulatory diseases for ages between 15 and 64 years (0.5% HA increase with 10 µg/m³ NO increase) and above 64 years (1.0% stroke HA increase with 10 µg/m³ NO₂ increase); 2) the pollutants CO, NO, NO₂, SO₂, PM₁₀ and PM_{2.5} and respiratory diseases for ages below 15 years (up to 1.9% HA increase with 10 µg/m³ pollutant increase); 3) the pollutants NO, NO₂ and SO₂ and respiratory diseases for ages above 64 years (1.3% HA increase with 10 µg/m³ CO increase). One of the main issues for future study is the dependence of associations observed on the models that are used to track AP-HA correlations.

In Chapter 6 the associations between air quality and hospital admissions in Lisbon were studied, using COM-Poisson regression. The most relevant statistically significant associations that showed-up were those between circulatory diseases, cardiac diseases, both in adults, and elderly people with ischaemic diseases, with PM₁₀, temperature and humidity. Further statistically significant associations that were observed were associations between respiratory diseases in elderly people, circulatory diseases and ischaemic diseases, (the latter both in adults), and PM₁₀, PM_{2.5} and temperature. In Chapter 6, the technique applied was used with the same database as in Chapter 5, to consolidate the results obtained with OLS data regression.

7.2 Final Remarks

This thesis underlines that the work of worldwide-and European organisations of environmental and health protection have had and will continue to play an important role in maintaining and increasing public awareness, in order to comply with legislation and recommendations to preserve the air quality and diminish exposure to pollution, thus preventing associated diseases. Nevertheless, there is still a lot of work to do to mitigate pollutant concentrations in the atmosphere. The implementation of environmental technologies in industry and the automotive sector is crucial, as is the replacement of raw material to less harmful products to the environment, investment in the right routing and

treatment of residues (solid, liquid and gaseous), certification of both biofuels and residential combustion appliances, etc. Bark and lichen biomonitoring may serve as an important assessment tool in environmental studies for the several advantages that they present. In fact, it is a passive and economic technique and allows monitoring in dense, vast, and both urban and remote study areas.

The knowledge related to the relationships between pollutants and the probability of diseases is very relevant; however, new statistical techniques and mathematical models are needed to further substantiate the value of these modelled associations. Considering the new techniques applied in the present work on PM in Portugal, new classifications of the monitoring stations can be set up, implementing more precise accounting of their ambient surroundings.

7.3 Future Research

Biomonitoring studies, as presently carried out in e.g. Lisbon, as well as tracking possible associations between AP and HA, should be repeated and continued on a regular basis, to monitor changes possibly occurring in relation with the here-followed 2006-2008 period.

Presently, Lisbon was selected as the city to be monitored: more cities should be included (e.g. Oporto), and also other urban (and remote) areas, to assess effect-variabilities related to the differences in environmental conditions: this could lead to a necessary country-wide monitoring strategy, based on which more dedicated mitigation measures may be defined by environmental and governmental agencies.

Bringing this line of reasoning to a European or global level, it should be noted that Europe has achieved significant improvement in general air quality over recent decades, but much more remains to be done. The development and expression of even more ambitious goals for air quality requires the development and application of new (monitoring and mitigation) strategies.

List of Abbreviations

Chapter 1

PM – particulate matter

PM₁₀ – particulate matter of aerodynamic diameter 10 µm or less

PM_{2.5} - particulate matter of aerodynamic diameter 2.5 µm or less

WHO – World Health Organisation

AQG – Air Quality Guideline

CO – Carbon Monoxide

NO – Nitrogen Oxide

NO_x – Monoxide Oxides

NO₂ – Nitrogen Dioxide

O₃ – Ozone

SO₂ – Sulphur Oxide

VOCs - Volatile Organic Compounds

EU – European Union

EU-28 - the 28 EU Member States

EEA - European Environment Agency

INAA - Instrumental Neutron Activation Analysis

OLS - Ordinary Least Square Linear Regression

COM-Poisson - Conway-Maxwell-Poisson distribution

IARC - International Agency for Research on Cancer

APA - Portuguese Environmental Agency

INE - Instituto Nacional de Estatística (INE)

AP – Air Pollutants

HA – Hospital Admission

HYSPIT - Hybrid Single Particle Lagrangian Integrated Trajectory model

MCTTFA - Monte Carlo Target Transformed Factor Analysis

Chapter 2

PM – particulate matter

PM₁₀ – particulate matter of aerodynamic diameter 10 µm or less

PM_{2.5} - particulate matter of aerodynamic diameter 2.5 µm or less

WHO – World Health Organisation

AQG – Air Quality Guideline

NO_x – Monoxide Oxides

VOCs - volatile organic compounds

EEA - European Environment Agency

OLS - Ordinary Least Square Linear Regression

IARC - International Agency for Research on Cancer

APA - Portuguese Environmental Agency

HYSPIT - Hybrid Single Particle Lagrangian Integrated Trajectory model

GDAS – Global Data Analysis System

TSV – Total Spatial Variation

SPVAR – Spatial Variance

WdC - Wavelet decomposition-based Clustering

MODWT - Maximal Overlap Discrete Wavelet Transform

LA – Least asymmetric

NE – North-East

Chapter 3

NDVI - Normalised Difference Vegetation Index

INAA - Instrumental Neutron Activation Analysis

RPI – Portuguese Research Reactor

WNW - West-northwest

ENE - East-northeast

NNW - North-northwest

List of Abbreviations

NNE - North-northeast

Br - Bromine

Ce - Cerium

Co - Cobalt

Cr - Chromium

Eu - Europium

Fe - Iron

Hf - Hafnium

La - Lanthanum

Na - Sodium

Rb - Rubidium

Sb - Antimony

Sc – Scandium

Sm - Samarium

Sr - Strontium

Zn - Zinc

Chapter 4

INAA - Instrumental Neutron Activation Analysis

RPI – Portuguese Research Reactor

MCTTFA - Monte Carlo Target Transformed Factor Analysis

Na - Sodium

Sc - Scandium

Cr - Chromium

Fe - Iron

Co - Cobalt

Zn - Zinc

Se - Selenium

List of Abbreviations

Sb - Antimony

La - Lanthanum

Hf - Hafnium

Tb - Terbium

Yb - Ytterbium

Chapter 5

AP – Air Pollutants

HA – Hospital Admission

CO – Carbon Monoxide

NO – Nitrogen Oxide

NO₂ – Nitrogen Dioxide

O₃ – Ozone

SO₂ – Sulphur Oxide

PM₁₀ – particulate matter of aerodynamic diameter 10 µm or less

PM_{2.5} - particulate matter of aerodynamic diameter 2.5 µm or less

OLS - Ordinary Least Square Linear Regression

APA - Portuguese Environmental Agency

Health System Central Administration (ACSS)

ICD – International Statistical Classification of Diseases

Chapter 6

AP – Air Pollutants

HA – Hospital Admission

PM₁₀ – particulate matter of aerodynamic diameter 10 µm or less

PM_{2.5} - particulate matter of aerodynamic diameter 2.5 µm or less

CO – Carbon Monoxide

NO – Nitrogen Oxide

NO₂ – Nitrogen Dioxide

List of Abbreviations

O₃ – Ozone

SO₂ – Sulphur Oxide

OLS - Ordinary Least Square Linear Regression

COM-Poisson - Conway-Maxwell-Poisson distribution

Se – Selenium

Tb - Terbium

Yb - Ytterbium

PM – particulate matter

Chapter 7

AP – Air Pollutants

HA – Hospital Admission

CO – Carbon Monoxide

COM-Poisson - Conway-Maxwell-Poisson distribution

NO – Monoxide Oxide

NO₂ – Nitrogen Dioxide

O₃ – Ozone

PM – particulate matter

PM₁₀ – particulate matter of aerodynamic diameter 10 µm or less

PM_{2.5} - particulate matter of aerodynamic diameter 2.5 µm or less

SO₂ – Sulphur Oxide

References

- Aldabe, J, Elustondo D, Santamaría C, Lasheras E, Pandolfi M, Alastuey A, Querol X, Santamaría JM (2011) Chemical Characterisation and Source Apportionment of PM_{2.5} and PM₁₀ at Rural, Urban and Traffic Sites in Navarra (North of Spain). *Atmos. Res.* 102(1-2):191–205.
- Allan JD, Williams PI, Morgan WT, Martin CL, Flynn MJ, Lee J, Nemitz E, Phillips GJ (2010) Contributions from Transport, Solid Fuel Burning and Cooking to Primary Organic Aerosols in Two UK Cities. *Atmos. Chem. Phys.* 10:647–668.
- Almeida SM, Pio CA, Freitas MC, Reis MA, Trancoso MA (2005) Source Apportionment of fine and Coarse Particulate Matter in a Sub-urban Area at the Western European Coast. *Atmos. Environ.* 39:3127–3138.
- Almeida SM, Farinha MM, Ventura MG, Pio CA, Freitas MC, Reis MA, Trancoso MA (2007) Measuring Air Particulate Matter in Large Urban Areas for Health Effect Assessment. *Water Air Soil Poll.* 179:43-55.
- Almeida, SM, Freitas MC, Repolho C, Dionísio I, Dung HM, Caseiro A, Alves C, Pio CA, Pacheco AMG (2009a) Characterizing Air Particulate Matter Composition and Sources in Lisbon, Portugal. *J. Radioanal. Nucl. Chem.* 281: 215-218.
- Almeida SM, Freitas MC, Repolho C, Dionísio I, Dung, HM, Pio CA, Alves C, Caseiro A, Pacheco AMG (2009b) Evaluating Children Exposure to air Pollutants for an Epidemiological Study. *J. Radioanal. Nucl. Chem.* 280(2):405-409.
- Almeida SM, Canha N, Silva A, Freitas MC, Pegas P, Alves C, Evtyugina M, Pio AC (2010) Children Exposure to Atmospheric Particles in Indoor of Lisbon Primary Schools. *Atmos. Environ.* 45(2011):7594-7599.
- Almeida SP, Casimiro E, Calheiros J (2011) Short-term Association between Exposure to Ozone and Mortality in Oporto, Portugal. *Environ. Res.* 111:406-410.
- Almeida SM, Lage J, Freitas MC, Pedro AI, Ribeiro T, Silva AV, Canha N, Almeida-Silva M, Siteo T, Dionisio I, Garcia S, Domingues G, Perim de Faria J, Fernández BG, Ciaparra D, Wolterbeek HT (2012) Integration of Biomonitoring and Instrumental Techniques to Assess the air Quality in An Industrial Area Located in the Coastal of Central Asturias. Spain. *J. Toxicol. Environ. Health Part A Current Issues* 75(22-23):1391-1403.
- Almeida SM, Freitas MC, Reis M, Pinheiro T, Felix PM, Pio CA (2013a) Fifteen Years of Nuclear Techniques Application to Suspended Particulate Matter Studies. *J. Radioanal. Nucl. Chem.* 297(3):347-356.
- Almeida, SM, Silva AI, Freitas MC, Dung HM, Caseiro A, Pio AC (2013b) Impact of Maritime Air Mass Trajectories on the Western European Coast Urban Aerosol. *J. Toxicol. Environ. Health Part A* 76(4-5): 252-262.

References

- Almeida SM, Silva AV and Sarmento S (2014) Effects of Exposure to Particles and Ozone on Hospital Admissions for Cardiorespiratory Diseases in Setúbal, Portugal. *J. Toxicol. Environ. Health Part A*. 77(14-16):837–848.
- Alves CA, Gonçalves C, Mirante F, Nunes T, Evtyugina M, Sánchez de la Campa A, Rocha AC, Marques MC (2010a) Organic Speciation of Atmospheric Particles in Alvão Natural Park (Portugal). *Environ. Monit. Assess.* 168:321–337.
- Alves CA, Scotto MG and Freitas MC (2010b) Air Pollution and Emergency Admissions for Cardiorespiratory Diseases in Lisbon (Portugal). *Quim. Nova* 33(2):337–344.
- Alves C, Vicente A, Pio C, Kiss G, Hoffer A, Decesari S, Prevôt ASH, Minguillón MC, Querol X, Hillamo R, Spindler G, Swietlicki E (2012) Organic Compounds in Aerosols from Selected European Sites – Biogenic versus Anthropogenic Sources. *Atmos. Environ.* 59:243–255.
- Amato F, Cassee FR, Denier van der Gon HAC, Gehrig R, Gustafsson M, Hafner W, Harrison RM, Jozwicka M, Kelly FJ, Moreno T, Prevot ASH, Schaap M, Sunyer J, Querol X (2014) Urban Air Quality: The Challenge of Traffic Non-exhaust Emissions. *J. Hazard. Mater.* 275:31–36.
- Andrade MF, Miranda RM, Fornaro A, Kerr A, Oyama B, Andre PA, Saldiva P (2012) Vehicle emissions and PM_{2.5} mass concentrations in six Brazilian cities. *Air Qual. Atmos. Health* 5(1):79-88.
- Atkinson RW, Anderson HR, Sunyer J, Ayres J, Baccini M, Vonk JM, Boumghar A, Forastiere F, Forsberg B, Touloumi G, Schwartz J, Katsouyanni K (2001) Acute Effects of Particulate air Pollution on Respiratory Admissions: Results from APHEA 2 Project. *Air Pollution and Health: A European Approach. Am. J. Respir. Crit. Care Med.* 164(10):1860–1866.
- Ayres-Sampaio D, Teodoro A C, Sillero N, Santos C, Fonseca J, Freitas A (2014) An Investigation of the Environmental Determinants of Asthma Hospitalizations: An Applied Spatial Approach. *Applied Geography* 47 10-19.
- Balakrishnaiah G, Kumar, KR, Reddy BSK, Gopal KR, Reddy RR, Reddy LSS (2011) Characterization of PM, PM₁₀ and PM_{2.5} Mass Concentrations at a Tropical Semi-arid Station in Anantapur, India. *Indian J. Rad. Space Phys.* 40(April):95–104.
- Baldasano JM, Valera E, Jiménez P (2003) Air Quality Data from Large Cities. *Sci. Total Environ.* 307(1-3):141–165.
- Ballester F, Tenías JM, Pérez-Hoyos S (2001) Air Pollution and Emergency Hospital Admissions for Cardiovascular Diseases in Valencia, Spain. *J. Epidemiol. Community Health* 55:57-65.
- Ballester F, Rodríguez P, Iñíguez C, Saez M, Daponte A, Galán I, Taracido M, Arribas F, Bellido J, Cirarda FB, Cañada A, Guillén JJ, Guillén-Grima F, López E, Pérez-Hoyos S,

References

- Lertxundi A, Toro S (2006). Air Pollution and Cardiovascular Admissions Association in Spain: Results within the EMECAS Project. *Epidemiol. Community Health* 60:328-336.
- Bargagli R (1998) Trace Elements in Terrestrial Plants: An Ecophysiological Approach to Biomonitoring and Biorecovery. *Springer-Verlag*: Berlin.
- Barnett AG (2007) Temperature and Cardiovascular Deaths in the US Elderly: Changes Over Time. *Epidemiology* 18(3):369–372.
- Barros N, Fontes T, Silva MP, Manso MC, Carvalho AC (2015) Analysis of the Effectiveness of the NEC Directive on the Tropospheric Ozone Levels in Portugal. *Atmos. Envir.* 106: 80-91.
- Batzias F and Siontorou C (2007) A Novel System for Environmental Monitoring through a Cooperative/Synergistic Scheme between Bioindicators and Biosensors. *Environ. Manage.* 82:221-239.
- Borrego C, Coutinho M, Costa AM, Ginja J, Ribeiro C, Monteiro A, Ribeiro I, Valente J, Amorim JH, Martins H, Lopes D, Miranda AI (2015) Challenges for a New Air Quality Directive: The Role of Monitoring and Modelling Techniques, *Urban Climate* 14(3):328-341.
- Brook RD, Rajagopalan S, Pope CA, Brook JR, Bhatnagar A, Diez-Roux AV et al. (2010) Particulate Matter Air Pollution and Cardiovascular Disease: An Update to the Scientific Statement from the American Heart Association. *Circulation* 121(21):2331–2378.
- Brown DH (1985) Lichen Physiology and Cell Biology. *Springer U.S.* 247-258.
- Brunialti G and Frati L (2007) Biomonitoring of Nine Elements by the Lichen *Xanthoria parietina* in Adriatic Italy: A Retrospective Study over a 7-year Time Span. *Sci. Total Environ.* 387:289-300.
- Burnett, R, Brook JR, Yung WT, Dales RE, Krewski D (1997) Association between Ozone and Hospitalization for Respiratory Diseases in 16 Canadian Cities. *Environ. Res.* 72:24-31.
- Cachorro VE, Vergaz R, de Frutos AM, Vilaplana JM, Henriques D, Laulainen N, Toledano C (2006) Study of Desert Dust Events Over the Southwestern Iberian Peninsula in Year 2000: Two Case Studies. *Ann. Geophys.* 24:1493–1510.
- Cameron CA and Trivedi PK (1998) Regression Analysis of Count Data (Econometric Society Monographs). 30 p. 89.
- Carvalho A, Monteiro A, Ribeiro I, Tchepel O, Miranda, AI, Borrego C, Saavedra S, Souto JA, Casares JJ (2010) High Ozone Levels in the Northeast of Portugal: Analysis and Characterization. *Atmos. Environ.* 44(8):1020–1031.

References

Carvalho RAC, Prior V (1994) Sea Breeze in Summer, Along the West Coast of Portugal. Air Pollution Modeling and Its Application. NATO Challenges of Modern Society series X(18):637-638.

Chapman R, Grant LD, Hasselblad V, Ito K, Kalkstein L, Kotchmar D, Lipfert FW, Marcus A, Thurston GD (1996) Air Quality Criteria for Particulate Matter. EPA/600/P-95/001cF. U.S. Environmental Protection Agency.

Charron A, Harrison RM, Quincey P (2007) What are the Sources and Conditions Responsible for Exceedences of the 24h PM₁₀ Limit Value (50 µg m⁻³) at a Heavily Trafficked London Site? *Atmos. Environ.* 41(9):1960-1975.

Chen L, Mengersen K, Tong S (2007) Spatiotemporal Relationship between Particle Air Pollution and Respiratory Emergency Hospital Admissions in Brisbane, Australia. Original Research Article *Science of The Total Environment* 373(1):57-67.

Chen R, Kan H, Chen B, Huang W, Bai Z, Song G, Pan G (2012) Association of Particulate Air Pollution with Daily Mortality: the China Air Pollution and Health Effects Study. *Am. J. Epidemiol.* 175:1173–1181.

Chiarenzelli JR, Aspler LB, Dunn C, Cousens B, Ozarko DL, Powis KB (2001) Multi-element and Rare Earth Element Composition of Lichens, Mosses, and Vascular Plants from the Central Barrenlands, Nunavut, Canada. *Appl. Geochem.* 16(2):245-270.

Chung Y, Dominici F, Wang Y, Coull BA, Bell ML (2015) Associations between Long-term Exposure to Chemical Constituents of Fine Particulate Matter (PM_{2.5}) and Mortality in Medicare Enrollees in the Eastern United States. *Environ. Health Persp.* 123(5):467–474.

Council Directive EU (2008) Directive 2008/50/EC of The European Parliament and of the Council of 21 May 2008 on Ambient Air Quality and Cleaner air for Europe. *Official Journal of the European Union* 51: L152:1-44.

Cropper T (2013) The Weather and Climate of Macaronesia: Past, Present and Future. *Weather* 68(11):300–307.

Cruz AMJ, Sarmiento S, Almeida SM, Silva AV, Alves C, Freitas MC, Wolterbeek HT (2014) Association between Atmospheric Pollutants and Hospital Admissions in Lisbon. *Environ. Sci. Pollution Res.* 22(7):5500–5510.

De Corte F (1987) The k₀-Standardization Method — A Move to the Optimization of Neutron Activation Analysis. Aggrégé Thesis. Gent University. Belgium.

De Corte F, Simonits A, Bellemans F, Freitas MC, Jovanovic S, Smodis B, Erdtmann G, Petri H, De Wispelaere A (1993) Recent advances in the k₀-standardization of Neutron Activation Analysis: Extensions, Applications, Prospects. *J. Radioanal. Nucl. Chem.* 169:125-158.

References

- Delfino RJ, Brummel S, Wu J, Stern H, Ostro B, Lipsett M (2009). The Relationship of Respiratory and Cardio Vascular Hospital Admissions to the Southern California Wildfires of 2003. *Occup. Environ. Med.* 66(3):189–197.
- Díaz J, Tobías A and Linares C (2012) Saharan Dust and Association between Particulate Matter and Case-Specific Mortality: a Case-crossover Analysis in Madrid (Spain). *Environ. Health: A Global Access Science Source* 11(1):11.
- Donahue NM, Robinson AL, Stanier CO, Pandis SN (2006) Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ. Sci. Technol.* 40(8):2635–2643.
- D’Urso P, de Giovanni L, Maharaj EA (2014) Wavelet-based Self-organizing Maps for Classifying Multivariate Time Series. *J. Chemometr.* 28:28–51.
- Draxler R, Stunder B, Rolph G, Stein A, Taylor A (2014) HYSPLIT4 User’s Guide, Air Resources Laboratory. NOAA. http://www.arl.noaa.gov/documents/reports/hysplit_user_guide.pdf.
- EEA (2014) Air quality in Europe - 2014 Report. European Environment Agency, Copenhagen. <http://www.eea.europa.eu/publications/air-quality-in-europe-2014>.
- Everitt BS, Landau S, Leese M, Stahl D (2011) Cluster Analysis. *Wiley*. Chichester. UK.
- Farinha MM, Freitas MC, Almeida SM (2004a) Air Quality Control Monitoring at an Urban and Industrialized Area. *J. Radioanal. Nucl. Chem.* 259(2): 203-207.
- Farinha MM, Slejkovec Z, Van Elteren JT, Wolterbeek HT, Freitas MC (2004b) Arsenic Speciation in Lichens and in Coarse and Fine Airborne Particulate Matter by HPLC–UV–HG–AFS. *J. Atmos. Chem.* 49:343–353.
- Farinha MM, Verburg TG, Freitas MC, Wolterbeek HT, (2009) Local and Regional Sources as Given by Aerosol Measurements and Biomonitoring at Sado Estuary Area, Portugal. *J. Radioanal. Nucl. Chem.* 281: 299-305.
- Fowler D et al. (2008). Ground-level ozone in the 21st century: future trends, impacts and policy implications. (RS1276 ed.) *Royal Society Policy Document 15/08*. London: The Royal Society.
- Fрати L, Brunialti G, Loppi S (2005) Problems Related to Lichen Transplants to Monitor Trace Element Deposition in Repetead Surveys: A Case Study from Central Italy. *J. Atmos. Chem.* 49:67-82.
- Freitas MC and Martinho E (1989) Accuracy and Precision in Instrumental Neutron Activation Analysis of Reference Materials and Lake Sediments. *Analytica Chimica Acta* 223: 287-292.

References

- Freitas MC, Reis MA, Marques AP, Almeida SM, Farinha MM, Oliveira O, Ventura MG, Pacheco AMG, Barros LIC (2003) Monitoring of Environmental Contaminants, 10 years of use k_0 INAA. *J. Atmos. Chem.* 257:621-625.
- Freitas MC, Pacheco AMG (2004) Bioaccumulation of Cobalt in *Parmelia sulcata*. *J. Atmos. Chem.* 49:67-82.
- Freitas MC, Farinha MM, Ventura MG, Almeida SM, Reis MA, Pacheco AMG (2005) Atmospheric Selenium in an Industrialized Area of Portugal. *J. Radioanal. Nucl. Chem.* 263(3):710-720.
- Freitas MC, Pacheco AMG, Vieira BJ, Rodrigues AF (2006a) Neutron Activation Analysis of Atmospheric Biomonitoring from the Azores: A comparative study of lower and higher plants. *J. Radioanal. Nucl. Chem.* 270(1): 21-27.
- Freitas MC, Pacheco AMG, Dionísio I, Sarmiento S, Baptista MS, Vasconcelos MTSD, Cabral JP (2006b) Multianalytical Determination of Trace Elements in Atmospheric Biomonitoring by k_0 -INAA, ICP-MS and AAS, *Nucl. Instrum. Meth. in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment.* 564(2):733 – 742.
- Freitas MC, Almeida SM, Pacheco AMG, Dionísio I, Repolho C, Caseiro A, Pio CA, Alves C (2009a) Characterization of the Seasonal Exposure to Air Pollutants for a Respiratory Epidemiological Study. *J. Radioanal. Nucl. Chem.* 281: 219-223.
- Freitas MC, Dionísio I, Beasley DG, Almeida SM, Dung HM, Repolho C, Pacheco AMG, Caseiro A, Pio CA, Alves C (2009b) Association between Monthly-reported Rhinitis by Children from Elementary School and Monthly-averaged Air Pollutants, at Lisbon (Portugal). *J. Radioanal. Nucl. Chem.* 282:15-20.
- Freitas MC, Pacheco AMG, Verburg TG, Wolterbeek, HT (2010) Effect of Particulate Matter, Atmospheric Gases, Temperature, and Humidity on Respiratory and Circulatory Diseases' Trends in Lisbon, Portugal. *Environ. Monit. Assess.* 162:113-121.
- Garty J, Tamir O, Hassid I, Eshel A, Cohen Y, Karnieli A, Orlovsky L (2001) Photosynthesis, Chlorophyll Integrity, and Spectral Reflectance in Lichens Exposed to Air Pollution. *Journal of Environmental Quality.* 30:884-893.
- Giordani P and Brunialti G (2015) Sampling and Interpreting Lichen Diversity Data for Biomonitoring Purposes. In *Recent Advances in Lichenology. Springer India.* 19–47.
- Godinho RM, Freitas MC and Wolterbeek HT (2004) Assessment of Lichen Vitality during a Transplantation Experiment to a Polluted Site. *J. Atmos. Chem.* 49: 355-361.
- Godinho RM, Wolterbeek HT, Verburg TG, Freitas MC (2008) Bioaccumulation Behaviour of Transplants of the Lichen *Flavoparmelia caperata* in Relation to Total Deposition at a Polluted Location in Portugal. *Environmental Pollution* 151:318-325.

References

- Godinho RM, Verburg TG, Freitas MDC and Wolterbeek HT (2011) Dynamics of Element Accumulation and Release of *Flavoparmelia caperata* during a Long-term Field Transplant Experiment. *Environ. Health* 5(1-2):49-59.
- Gonçalves C, Alves C, Pio C (2012) Inventory of Fine Particulate Organic Compound Emissions from Residential Wood Combustion in Portugal. *Atmos. Environ.* 50:297–306.
- Gouveia S, Scotto, MG, Monteiro A, Alonso AM (2015) Wavelets-based Clustering of Air Quality Monitoring Sites. *Environ. Monit. Assess.* 187(11):693:1-14.
- Guerreiro CB, Foltescu V and de Leeuw F (2014) Air Quality Status and Trends in Europe. *Atmos. Environ.* 98:376-384.
- Guicherit R and Roemer M (2000). Tropospheric ozone trends. *Chemosphere - Global Change Science.* 2:167-183.
- Guikema SD and Coffelt JP (2008) A Flexible Count Data Regression Model for Risk Analysis. *Risk Analysis* 28:213-223.
- Hansen A, Peng B, Monika N, Dino P, Philip R, Thomas S, Adrian GA (2012) Particulate Air Pollution and Cardiorespiratory Hospital Admissions in a Temperate Australian City: A Case-crossover Analysis. *Sci. Total Environ.* 16:48–52.
- Harrison RM, Jones AM, Gietl J, Yin J, Green DC (2012) Estimation of the Contributions of Brake Dust, Tire Wear, and Resuspension to Nonexhaust Traffic Particles Derived from Atmospheric Measurements. *Environ. Sci. Technol.* 46:6523–6529.
- Hoek G, Krishnan RM, Beelen R, Peters A, Ostro B, Brunekreef B and Kaufman JD (2013) Long-term Air Pollution Exposure and Cardio-respiratory Mortality: a Review. *Environ. Health.* 12(1):43.
- Hosseinpoor AR, Forouzanfar MH, YunesianM, Asghari F, Naieni KH, Farhood D (2005) Air pollution and hospitalization due to angina pectoris in Tehran, Iran: A time-series study. *Environ. Res.* 99:126-131.
- Jiménez E, Linares C, Martínez D, Díaz J (2010) Role of Saharan Dust in the Relationship between Particulate Matter and Short-term Daily Mortality Among the Elderly in Madrid (Spain). *Sci. The Total Environ.* 408(23):5729–5736.
- Kadane JB, Krishnan R. and Shmueli G (2006). A Data Disclosure Policy for Count Data Based on the COM-Poisson Distribution. *Management Science* 52:1610–1617.
- Kalantzi EG, Demosthenes M, Duquenne MN, Kaklamani S, Stapountzis H, Gourgoulianis KI (2011) Air pollutants and morbidity of cardiopulmonary diseases in a semi-urban Greek peninsula. *Atmos. Environ.* 55(39):7121-7126.
- Kan H and Chen B (2004) Particulate Air Pollution in Urban Areas of Shanghai, China: Health-based Economic Assessment. *Sci. Total Environ.* 322(1–3):71–79.

References

- Kan H, London SJ, Chen G, Zhang Y, Song G, Zhao N, Jiang L, Chen B (2008) Season, sex, age, and education as modifiers of the effects of outdoor air pollution on daily mortality in Shanghai, China: the public health and air pollution in Asia (PAPA) Study *Environ. Health Perspect.* 116 (9):1183–1188.
- Karr C, Lumley T, Schreuder A, Davis R, Larson T, Ritz B, Kaufman J (2007) Effects of Subchronic and Chronic Exposure to Ambient Air Pollutants on Infant Bronchiolitis. *Am. J. Epidemiol.* 165:553-60.
- Katsouyanni K, Schwartz J, Spix C, et al. (1996) Short term effects of air pollution on health: a European approach using epidemiologic time series data: the APHEA protocol. *J. Epidemiol. Community Health* 50:S12–18.
- Katsouyanni K, Touloumi G, Spix C, Schwartz J, Balducci F, Medina S, Rossi G, Wojtyniak B, Sunyer J, Bacharova L, Schouten JP, Ponka A, Anderson HR (1997) Short-term Effects of Ambient Sulphur Dioxide and Particulate Matter on Mortality in 12 European Cities: Results from Time Series Data from the APHEA Project. *Air Pollution and Health: a European Approach* *BMJ* 314(7095):1658.
- Katsouyanni K, Touloumi G, Samoli E, Gryparis A, Le Tertre A, Monopoli Y, Rossi G, Zmirou D, Ballester F, Boumghar A, Anderson H, Wojtyniak B, Paldy A, Braunstein R, Pekkanen J, Schindler C, Schwartz J (2001) Confounding and Effect Modification in the Short-term Effects of Ambient Particles on Total Mortality: Results from 29 European Cities within the APHEA2 Project. *Epidemiology.* 12(5):521–531.
- Keuken MP, Moerman M, Voogt M, Blom M, Weijers EP, Röckmann T, Dusek U (2013) Source Contributions to PM_{2.5} and PM₁₀ at an Urban Background and a Street Location. *Atmos. Environ.* 71: 26–35.
- Khan IR, Freitas C, Pacheco AMG (2007) Particulate Matter Levels in Portugal (mainland and islands). A Preliminary Study for Outdoor/indoor Environment in Basic Schools. *Proceedings of Clima 2007 WellBeing Indoors.*
- Kimbrough S, Baldauf RW, Hagler GSW, Shores RC, Mitchell W, Whitaker DA, Croghan DW., Vallero DA (2013) Long-term Continuous Measurement of Near-road Air Pollution in Las Vegas: Seasonal Variability in Traffic Emissions Impact on Local Air Quality. *Air Qual. Atmos. Health* 6(1): 295-305.
- Kuik P, Blaauw M, Sloof JE and Wolterbeek HT (1993) The Use of Monte Carlo Methods in Factor Analysis. *Atmos. Environ.* 13:1967-1974.
- Kuik P, Sloof JE, Wolterbeek HT (1993) Application of Monte Carlo Assisted Factor Analysis to Large Sets of Environmental Pollution Data. *Atmos. Environ.* 13:1975-1983.
- Lage J, Almeida SM, Reis MA, Chaves PC, Ribeiro T, Garcia S et al. (2014) Levels and Spatial Distribution of Airborne Chemical Elements in a Heavy Industrial Area Located in the North of Spain. *J. Toxicol. Environ. Health Part A* 77(14-16):856–66.

References

- Li G., M. Zhou, Y. Cai, Y. Zhang, X. Pan (2011) Does temperature enhance acute mortality effects of ambient particle pollution in Tianjin City, China. *Sci. Total Environ.*, 409(10):1811–1817.
- Lin, Yu-Kai, Yu-Chun Wang, Tsung-Jung Ho, Chensheng (Alex) Lu. (2013) Temperature effects on hospital admissions for kidney morbidity in Taiwan Original Research Article *Science of The Total Environment* 443:812-820.
- Linares C and Díaz J (2009) Efecto de las Partículas de Diámetro Inferior a 2.5 Micras (PM_{2.5}) sobre los Ingresos Hospitalarios en Niños Menores de 10 Años en Madrid. *Original Research Article Gaceta Sanitaria* 23(3):192-197.
- Linares C and Díaz J (2010) Short-term Effect of Concentrations of Fine Particulate Matter on Hospital Admissions Due to Cardiovascular and Respiratory Causes among the Over-75 Age Group in Madrid, Spain. *Public Health* 124(1):28-36.
- Linares C, Tobías A, Díaz J (2010) Is there New Scientific Evidence to Justify Reconsideration of the Current WHO Guidelines for Particulate Matter during Dust Intrusions? *Sci. Total Environ.* 408(10): 2283-2284.
- Lipfert FW (1993) A Critical Review of Studies of the Association between Demands for Hospital Services and Air Pollution. *Environ. Health Persp.* 101(Suppl. 2): 229–268.
- Lipfert FW (1997) Air Pollution and Human Health: Perspectives for the '90s and Beyond. *Risk Anal.* 17:137-46.
- Lumley T and Sheppard L (2000) Assessing Seasonal Confounding And Model Selection Bias In Air Pollution Epidemiology Using Positive And Negative Control Analyses. *Environmetrics* 11:705–717.
- Luvsan M-E, Ruel-Hao S, Tseden P, Lkhagvasuren B, Barkhasragchaa B, Chang-Chuan C (2012) The Influence of Emission Sources and Meteorological Conditions on SO₂ Pollution in Mongolia. *Atmos. Environ.* 61:542-549.
- Maddison D (2005) Air Pollution and Hospital Admissions: an ARMAX Modelling Approach. *J. Environ. Econ. Manag.* 49(1):116-131.
- Marques AP, Freitas MC, Wolterbeek HT, Steinebach OM, Verburg TG, DeGoeij JJM (2005) Cell-Membrane Damage and Element Leaching in Transplanted *Parmelia sulcata* Lichen Related to Ambient SO₂, Temperature, and Precipitation. *Environmental Science and Technology* 39:2624-2630.
- Marques AP (2008) Positional Responses in Lichen Transplant Biomonitoring of Trace Element Air Pollution. PhD Thesis. Department of Radiation, Radionuclides & Reactors. Faculty of Applied Sciences. Delft University of Technology.

References

- Máté B, Roland B, Zsófia AG, Brigitta T, Márk M (2010) Age Dependent Correlation between the CNV Amplitude and Heart Rate Change. *International Journal of Psychophysiology* 77(3):258-258.
- McConnel R, Berhane K, Gilliland F, London SJ, Islam T, Gauderman WJ, Avol E, Margolis HG, Peters JM (2002) Asthma in Exercising Children Exposed to Ozone: a Cohort Study. *Lancet* 359(9304):386-391.
- Mccullagh, P and Nelder, JA (1997). *Generalized Linear Models*, 2nd ed. Chapman & Hall/CRC, London.
- Meehl GA, Stocker TF, Collins WD, Friedlingstein P, Gaye AT, Gregory JM, Kitoh A, Knutti R, Murphy JM, Noda A, Raper SCB, Watterson IG, Weaver AJ, Zhao Z-C (2007) Global Climate Projections. *Climate Change 2007: Mitigation of Climate Change. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, EUA.
- Meehl, GA, Stocker TF, Collins WD, Friedlingstein P, Gaye AT, Gregory JM, Kitoh A, Knutti R, Murphy JM, Noda A, Raper SCB, Watterson IG, Weaver AJ, Zhao Z-C (2007) Global Climate Projections. In: *Climate Change 2007: The Physical. Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Middleton N, Yiallourous P, Kleanthous S, Kolokotroni O, Schwartz J, Dockery D, Demokritou P, Koutrakis P (2008) A 10-year Time-series Analysis of Respiratory and Cardiovascular Morbidity in Nicosia, Cyprus: the Effect of Short-term Changes in Air Pollution and Dust Storms. *Environ. Health Middleton: BioMed Central Ltd*.
- Mirante F, Salvador P, Pio C, Alves C, Artiñano B, Caseiro A, Revuelta MA (2014) Size Fractionated Aerosol Composition at Roadside and Background Environments in the Madrid Urban Atmosphere. *Atmos. Res.* 138:278–292.
- Mohr C, De Carlo PF, Heringa MF, Chirico R, Slowik JG, Richter R et al. (2012) Identification and Quantification of Organic Aerosol from Cooking and Other Sources in Barcelona Using Aerosol Mass Spectrometer Data. *Atmos. Chem. Phys.* 12(4):1649–1665.
- Monteiro A, Miranda AI, Borrego C, Vautard R (2007) Air Quality Assessment for Portugal. *Sci. Total Environ.* 373:22-31.
- Morawska L, Jayaratnea ER, Mengersenb K, Jamriskaa M, Thomasa S (2002) Differences in Airborne Particle and Gaseous Concentrations in Urban Air between Weekdays and Weekends. *Atmos. Environ.* 36:4375-4383.
- Moshhammer H, Hutter HP, Hauck H, Neuberger M et al. (1987) Grippe, Luftverunreinigung und Mortalität in Wien. *Forum Städtehygiene* 38:7-11.

References

- Moshhammer H, Hutter HP, Hauck H, Neuberger M (2006) Low Levels of Air Pollution Induce Changes of Lung Function in a Panel of School Children. *Eur. Respir. J.* 27:1138-1143.
- Mulgrew A and Williams P (2000) Biomonitoring of Air Quality using Plants, WHO Collaborating Centre for Air Quality Management and Air Pollution Control. Berlin 165.
- Neuberger M, Daniel R, Moshhammer H (2007) Extended Effects of Air Pollution on Cardiopulmonary Mortality in Vienna. *Atmos. Environ.* 41:8549–8556.
- Neuberger M, Moshhammer H, Rabczenko D (2013) Acute and Subacute Effects of Urban Air Pollution on Cardiopulmonary Emergencies and Mortality: Time Series Studies in Austrian Cities. *International Journal of Environmental Research and Public Health* 10(10):4728-4751.
- Nimis PL, Lazzarin G, Lazzarin A, Skert N (2000) Biomonitoring of Trace Elements with Lichens in Veneto (NE Italy) *Sci. Total Environ.* 255:97-111.
- Nriagu JO (1989) Natural Versus Anthropogenic Emissions of Trace Metals to the Atmosphere, in Pacyna. J.M. and Ottar B (Eds.). Control and Fate of Atmospheric Trace Metals. NATO ASI Series. Kluwer Academic Publishers. The Netherlands 3-13.
- Notario A, Adame JA, Bravo I, Cuevas CA, Aranda A, Díaz-de-Mera Y, Rodríguez A (2014) Air Pollution in the Plateau of the Iberian Peninsula. *Atmos. Res.* 145-146:92–104.
- Oliveira C, Pio C, Caseiro A, Santos P, Nunes T, Mao H et al. (2010) Road Traffic Impact on Urban Atmospheric Aerosol Loading at Oporto, Portugal. *Atmos. Environ.* 44(26):3147–3158.
- Olivier JGJ, Van Aardenne JA, Dentener FJ, Pagliari V, Ganzeveld LN, Peters JAHW (2005) Recent trends in global greenhouse gas emissions: regional trends 1970–2000 and spatial distribution of key sources in 2000. *Environ. Sci.*, 2(2-3):81-99.
- Pablo Dávila FL, Soriano LR, Sánchez-Llorente JM, Nájera-López A (2013) Effects of Weather Types on Hospital Admissions for Respiratory Diseases in Castilla-La Mancha, Spain. *Atmósfera* 26(1):95–107.
- Pacheco AMG, Barros LIC, Freitas MC, Reis MA, Hipólito C, Oliveira OR (2002) An Evaluation of Olive-tree Bark for the Biological Monitoring of Airborne Trace-elements at Ground Level. *Atmos. Environ.* 120:79–86.
- Pacheco AMG, Freitas MC (2004) Are Lower Epiphytes Really that Better than Higher Plants for Indicating Airborne Contaminants? An Insight Into the Elemental Contents of Lichen Thalli and Tree Bark by INAA, *J. Radioanal. Nucl. Chem.* 259:27-33.
- Pacheco AMG, Freitas MC, Sarmiento S, Baptista MS, Vasconcelos MTSD, Cabral JP (2008) Elemental Levels in Tree-bark and Epiphytic-lichen Transplants at Mixed Environments in Mainland Portugal, and Comparisons with an in Situ Lichen. *Environ. Pollut.* 151(2):326-33.

References

- Pacheco AMG, Freitas MC (2009) Trace-element Enrichment in Epiphytic Lichens and Tree Bark at Pico Island, Azores, Portugal. *J. Air & Waste Manage. Assoc.* 59:411-418.
- Pant P and Harrison RM (2013) Estimation of the Contribution of Road Traffic Emissions to Particulate Matter Concentrations from Field Measurements: A review. *Atmos. Environ.* 77:78–97.
- Pascal M, Corso M, Channel O, Declercq C, Badaloni C, Cesaroni G, Henschel S, Meister K, Haluza D, Martin-Olmedo P, Medina S and on behalf of the Aphekom group (2013) Assessing the Public Health Impacts of Urban Air Pollution in 25 European Cities: Results of the Aphekom Project. *Sci. Total Environ.* 449:390–400.
- Percival DB and Walden AT (2006) Wavelet Methods for Time Series Analysis. Cambridge University Press. Cambridge.
- Perez L, Tobías A, Querol X, Pey J, Alastuey A, Díaz J, Sunyere J (2012) Saharan Dust, Particulate Matter and Cause-specific Mortality: a Case–crossover Study in Barcelona (Spain). *Environ. Int.* 48:150–155.
- Pope CA III, Burnett RT, Thurston GD, Thun MJ, Calle EE, Krewski D, Godleski JJ (2004) Cardiovascular Mortality and Long Term Exposure to Particulate Air Pollution: Epidemiological Evidence of General Pathophysiological Pathways of Disease. *Circulation* 109:71-77.
- Pope CA III, Renlund DG, Kfoury AG, May HT, Horne BD (2008) Relation of Heart Failure Hospitalization to Exposure to Fine Particulate Air Pollution. *Am. J. Cardiol.* 102(9):1230-4.
- Qian Z, He Q, Lin H, Kong L, Bentley CM, Liu W, Zhou D (2008) High temperatures enhanced acute mortality effects of ambient particle pollution in the “oven” city of Wuhan, China. *Environ. Health Perspect.* 116(9):1172–1178.
- Qiu H, Yu IT, Wang X, Tian L, Tse LA, Wong TW (2013) Season and Humidity Dependence of the Effects of Air Pollution on COPD Hospitalizations in Hong Kong. *Atmos. Environ.* 76:74-80.
- Querol X, Alastuey A, Moreno T, Viana MM, Castillo S, Pey J et al. (2008) Spatial and Temporal Variations in Airborne Particulate Matter (PM₁₀ and PM_{2.5}) Across Spain 1999–2005. *Atmos. Environ.* 42(17):3964–3979.
- Querol X, Pey J, Pandolfi M, Alastuey A, Cusack M, Pérez N, Moreno T, Viana M, Mihalopoulos N, Kallos G, Kleanthous S (2009) African Dust Contributions to Mean Ambient PM₁₀ Mass-levels Across the Mediterranean Basin. *Atmos. Environ.* 43(28):4266–4277.

References

- Querol X, Alastuey A, Pandolfi M, Reche C, Pérez N, Minguillón MC, Moreno T, Viana M, Escudero M, Orío A, Pallarés M, Reina F (2014) 2001-2012 Trends on Air Quality in Spain. *Sci. Total Environ.* 490:957–69.
- Rahn KA, Huang S (1999) A Graphical Technique for Distinguishing Soil and Atmospheric Deposition in Biomonitors from the Plant Material. *Sci. Total Environ.* 232(1–2):79-104.
- Ramos C, Wolterbeek HT, Almeida SM (2016) Air Pollutant Exposure and Inhaled Dose during Urban Commuting: a Comparison between Cycling and Motorized Modes. *Air Qual. Atmos. Health* 1-13.
- Reis MA (2001) Biomonitoring and Assessment of Atmospheric Trace Elements in Portugal. PhD Thesis. Department of Radiation. Radionuclides & Reactors. Faculty of Applied Sciences. Delft University of Technology.
- Reis MA, Alves LC, Freitas MC, Van Os B, de Goeij J, Wolterbeek HT (2002) Calibration of Lichen Transplants Considering Faint Memory Effects. *Environmental Pollution.* 120(1):87–95.
- Ren, C., Williams, G.M., Tong, S., 2006. Does particulate matter modify the association between temperature and cardiorespiratory diseases? *Environ. Health Perspect.* 1690, 1690 e 1696.
- Roberts S (2005) Using Moving Total Mortality Counts to Obtain Improved Estimates for the Effect of Air Pollution on Mortality. *Environ. Health Persp.* 113:1148–1152.
- Rodríguez S, Querol X, Alastuey A, Kallos G, Kakaliagou O (2001) Saharan dust contributions to PM₁₀ and TSP levels in Southern and Eastern Spain. *Atmos. Environ.* 35(14):2433-2447.
- Rodopoulou Sophia, Marie-Cecile Chalbot, Evangelia Samoli, David W. DuBois, Bruce D. San Filippo, Ilias G. Kavouras Air pollution and hospital emergency room and admissions for cardiovascular and respiratory diseases in Doña Ana County, New Mexico *Environ. Res.* 129:39-46.
- Roemer W, Hoek G, Brunekreef B, Haluszka J, Kalandidi A, Pekkanen J (1998) Daily Variations in air Pollution and Respiratory Health in a Multicentre Study: the PEACE Project. Pollution Effects on Asthmatic Children in Europe. *Eur. Resp. J.* 12:1354-61.
- Roemer W, Hoek G, Brunekreef B, Haluszka J, Kalandidi A, Pekkanen J (1998) Daily variations in air pollution and respiratory health in a multicentre study: the PEACE project. Pollution Effects on Asthmatic Children in Europe. *Eur Resp J* 12:1354-61.
- Romieu I., N. Gouveia, L.A. Cifuentes, A.P. de Leon, W. Junger, J. Vera, et al. (2012) Multicity study of air pollution and mortality in Latin America (the ESCALA study) *Res. Rep. Health Eff. Inst.* 171:5–86.

References

- Samet JM, Zeger SL, et al. Particulate air pollution and daily mortality: analysis of the effects of weather and multiple air pollutants. The Phase I.B Report of the particle epidemiology evaluation project. Cambridge MA: *Health Effects Institute* 1997:14–21.
- Sarmiento S, Wolterbeek HT, Verburg TG, Freitas MC (2008) Correlating Element Atmospheric Deposition and Cancer Mortality in Portugal: Data Handling and preliminary Results *Environ. Pollut.* 151:341-351.
- Sarmiento S, Verburg TG, Almeida SM, Freitas MC, Wolterbeek HT (2009) Robustness of Different Regression Modelling Strategies in Epidemiology: a Time-series Analysis of Hospital Admissions and Air Pollutants in Lisbon (1999–2004). *Environmetrics* 22:86–97.
- Schachter EN, Moshier E, Habre R, Rohr A., Godbold J, Nath A, Grunin A, Coull B, Koutrakis P, Kattan M (2015) Outdoor Air Pollution and Health Effects in Urban Children with Moderate to Severe Asthma. *Air Qual. Atmos. Health* 1-13.
- Schwartz J (1997) Health Effects of Air Pollution from Traffic: Ozone and Particulate Matter. In: Fletcher T, McMichael AJ, editors. *Health at the Crossroads: Transport Policy and Urban Health*. Chichester, England: *John Wiley & Sons* 61-82.
- Schwartz J (2000a) Assessing Confounding, Effect Modification and Thresholds in the Association between Ambient Particles and Daily Deaths. *Environ. Health Persp.* 108:563–568.
- Schwartz J (2000b) Harvesting and Long-term Exposure Effects in the Relation between Air Pollution and Mortality. *Am. J. Epidemiol.* 151:440–448.
- Schwartz J (2001) Is There Harvesting Association of Airborne Particles with Daily Deaths and Hospital Admissions? *Epidemiology* 12:55–61.
- Sellers KF and Shmueli G (2010) A Flexible Regression Model for Count Data. *The Annals of Applied Statistics* 4(2):943–961.
- Shin H, Stieb AM, Jessiman B, Goldberg MS, Brion O, Brook J, Ramsay T, Burnett RT (2008) A Temporal, Multicity Model to Estimate the Effects of Short-term Exposure to Ambient Air Pollution on Health. *Environ. Health Persp.* 116(9):1147–1153.
- Smith RL, Davis JM, Sacks J, Speckman P, Styer P (2000) Regression Models for Air Pollution and Daily Mortality: Analysis of Data from Birmingham, Alabama. *Environmetric* 11:719-743.
- Smodis B (2007) Investigation of Trace Element Atmospheric Pollution by Nuclear Analytical Techniques at a Global Scale: Harmonised Approaches Supported by the IAEA. *Environ. Manage.* 85:121-128.
- Shmueli G, Minka TP, Kadane JB, Borle S and Boatwright P (2005) A Useful Distribution for Fitting Discrete Data: Revival of the Conway–Maxwell–Poisson Distribution. *Appl. Statist.* 54 127–142.

References

- Solomon PA, Costantini M, Grahame TJ, Gerlofs-Nijland ME, Cassee FR, Russell AG, Brook JR, Hopke PK, Hidy G, Phalen RF, Saldiva P, Sarnat SE, Balmes JR, Tager IB, Özkaynak H, Vedal S, Wierman SSG, Costa DL (2012) Air Pollution and Health: Bridging the Gap from Sources to Health Outcomes: Conference Summary. *Air Qual. Atmos. Health* 5:9–62.
- Sternbeck J, Ake S, Kenth A (2002) Metal Emission from Road Traffic and the Influence of Resuspension-results from Two Tunnel Studies. *Atmos. Environ.* 36:4735–4744.
- Tao Y, Mi S, Zhou S, Wang S, Xie X (2014) Air Pollution and Hospital Admissions for Respiratory Diseases in Lanzhou, China *Original Research Article Environmental Pollution* 185:196-201.
- Terzi Y and Cengiz MA (2009) Using of Generalized Additive Model for Model Selection in Multiple Poisson Regression for Air Pollution data. *Sci. Res. and Essay* 4(9):867-871.
- Thorpe A, Harrison RM (2008) Sources and Properties of Non-exhaust Particulate Matter from Road Traffic: A review. *Sci. Total Environ.* 400(1-3):270–282.
- Tong S., X.Y. Wang, Y. Guo (2012) Assessing the short-term effects of heatwaves on mortality and morbidity in Brisbane, Australia: comparison of case-crossover and time series analyses PLoS One, 7 (5), p. e37500.
- Upreti DK, Divakar PK, Shukla V, Bajpai R (2015) Recent Advances in Lichenology: Modern Methods and Approaches in Biomonitoring and Biospection, volume 1, *Springer India*.
- Vasconcelos J, Freire E, Almendra R, Silva GL, Santana P (2013) The Impact of Winter Cold Weather on Acute Myocardial Infarctions in Portugal, *Environmental Pollution* 183:14-18.
- Vecchi R, Marazzan G, Valli G (2007) A Study on Nighttime – Daytime PM₁₀ Concentration and Elemental Composition in Relation to Atmospheric Dispersion in the Urban Area of Milan (Italy). *Atmos. Environ.* 41:2136–2144.
- Ventura MG and Pacheco AMG (2007) Selenium Content in Selected Portuguese Foodstuffs, *European Food Rese. and Technol.* 224:395-401.
- Vieira BJ, Freitas MC, Rodrigues AF, Pacheco AMG, Soares PM, Correia N (2004) Element-enrichment Factors in Lichens from Terceira, Santa Maria and Madeira Islands (Azores and Madeira archipelagoes). *J. Atmos. Chem.* 49(1):231-249.
- Vieira BJ, Biegalski SR, Freitas MC, Landsberger S (2006) Atmospheric Trace Metal Characterization in Industrial Area of Lisbon, Portugal. *J. Radioanal. Nucl. Chem.* 270(1):55-62.

References

- Vieira BJ, Freitas MC, Rodrigues AF, Pacheco AMG, Soares PM (2007) An INAA-based Evaluation of the Responses of Epiphytic Lichens to Elemental Inputs in an Oceanic Environment (Azores). *J. Radioanal. Nucl. Chem.* 271:377–385.
- Walters S, Griffiths RK, Ayres JG (1994) Temporal Association between Hospital Admissions for Asthma in Birmingham and Ambient Levels of Sulphur Dioxide and Smoke. *Thorax* 49:133–40.
- Wang KC, Dickinson RC, Su L, Trenberth KE (2012) Contrasting Trends of Mass and Optical Properties of Aerosols Over the Northern Hemisphere from 1992 to 2011. *Atmos. Chem. Phys.* 12(19):9387–9398.
- Wellenius GA, Schwartz J, Murray AM (2006) Particulate Air Pollution and Hospital Admissions for Congestive Heart Failure in Seven United States Cities. *Am. J. Cardiol.* 97(3):404-408.
- Wilson A, Salloway JC, Wake CP, Kelly T (2004) Air Pollution and the Demand for Hospital Services: A review. *Environ. Int.* 30(8):1109-1118.
- WHO (1999) Monitoring Ambient Air Quality for Health Impact Assessment. WHO Regional Series. European Series. No. 85. World Health Organisation: Copenhagen.
- WHO (2006) WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. Global update 2005. WHO/SDE/PHE/EH/06.02. Available at http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf.
- WHO (2014a) Ambient (Outdoor) Air Quality and Health. Fact Sheet N°313, Updated March 2014. World Health Organisation (<http://www.who.int/mediacentre/factsheets/fs313/en/>). Accessed 8 October 2015.
- WHO (2014b) International Classification of Diseases (ICD), Available at <http://www.who.int/classifications/icd/en/>.
- WHO 2015. The European Health Report 2015 Targets and Beyond – Reaching New Frontiers in Evidence - Highlights.
- Wolterbeek HT (2002) Biomonitoring of Trace Element Air Pollution: Principles, Possibilities and Perspectives. *Environ. Pollut.* 120:11-21.
- Wolterbeek HT, Garty J, Reis MA, Freitas MC (2002) Biomonitors in Use: Lichens and Metal Air Pollution. In: B.A. Markert, A.M. Breure and H.G. Zechmeister, Editor(s), Trace Metals and other Contaminants in the Environment. *Elsevier* 6:377-419.
- Wong CS, Waser NAD, Whitney FA, Johnson WK, Page JS (2002) Time-series Study of the Biogeochemistry of the North East Subarctic Pacific: Reconciliation of the Corg/N Remineralization and Uptake Ratios with the Redfield Ratios. *Deep Sea Research Part II: Topical Studies in Oceanography* 49, (24–25):5717-5738.

References

- Wu W, Xiaoc Y, Li G, Zenga W, Lin H, Rutherford S, et al., Xub Y, Luo Y, Xub X, Chue C, Ma W (2013) Temperature-mortality Relationship in Four Subtropical Chinese Cities: a Time-series Study using a Distributed Lag Non-linear Model *Sci. Total Environ.* 449:355–362.
- Yang J, Ou CQ, Ding Y, Zhou YX, Chen PY (2012) Daily Temperature and Mortality: a Study of Distributed Lag Non-linear Effect and Effect Modification in Guangzhou *Environ. Health* 11:63.
- Yang Y, Cao Y, Li W, Li R, Wang M, Wu Z, Xu Q (2015) Multi-site time series analysis of acute effects of multiple air pollutants on respiratory mortality: A population-based study in Beijing, China *Sci. Total Environ.* 508:178-187.
- Yu IT, Qiu H, Wang X, Tian L, Tse LA (2013) Synergy between Particles and Nitrogen Dioxide on Emergency Hospital Admissions for Cardiac Diseases in Hong Kong *International Journal of Cardiology*, 168(3):2831-2836.
- Zanobetti A, Schwartz J, Samoli E, Gryparis A, Touloumi G, Atkinson R, Le Tertre A, Bobros J, Celko M, Goren A, Forsberg B, Michelozzi P, Rabczenko D, Aranguez Ruiz E, Katsouyanni K (2002) The Temporal Pattern of Mortality Responses to Air Pollution: a Multicity Assessment of Mortality Displacement. *Epidemiology* 13:87–93.
- Zanobetti A and Schwartz J (2005) The Effect of Particulate Air Pollution on Emergency Admissions for Myocardial Infarction: A Multicity Case-crossover Analysis. *Environ. Health Persp.* 8(113):978-982.
- Zanobetti, A, Franklin M, Koutrakis, P, Schwartz J (2009) Fine Particulate Air Pollution and its Components in Association with Cause-specific Emergency Admissions. *Environ. Health* 8:58.
- Zeger SL, Dominici F, Samet JM (1999) Harvesting-resistant Estimates of Pollution Effects on Mortality. *Epidemiology* 89:171–5.

Summary

The context of the study described in this thesis is the concern that exposure to environmental air pollution causes adverse health effects. The research focused on three main issues:

- 1) Comparative analysis of the air quality in Portugal (mainland and islands);
- 2) Biomonitoring of air pollution in Lisbon
- 3) New methodologies to judge air quality in terms of its associations with disease.

The data for these studies were supplied by the Air Quality Monitoring Network (QualAr) of the Portuguese Environment Agency (APA) (air pollutants such as particulate matter (PM), ozone, nitrogen- and sulphur oxides, carbon monoxide), were obtained by biomonitoring studies with both lichens and tree bark (a multitude of chemical elements, as obtained by Instrumental Neutron Activation Analysis (INAA)), and were provided by the Portuguese Central Administration of the Health System (ACSS) (Hospital Admissions (HA)).

Chapter 1 summarises 1) some of the most important issues in air pollution in Portugal and particularly in Lisbon, 2) biomonitoring and epidemiology, and 3) presents the main issues of the thesis. Air quality in Portugal is not “as bad” as in many other regions of Europe, but it is still a matter of concern considering health effects. Lisbon was the city chosen to apply the various techniques, because Lisbon is the largest (urban) area, reasonably covered by monitoring stations and with the highest population density in Portugal.

Chapter 2 presents a wavelet-based approach in analysing atmospheric PM time series ($PM < 10 \mu m$ (PM_{10}) and $2.5 \mu m$ ($PM_{2.5}$)) through the mainland of Portugal, including islands, measured by APA-QualAr. The databases were analysed to assess the contribution of main emission sources and their diurnal profiles. Back-trajectories were simulated by using the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPIT) developed by NOAA’s Air Resources Laboratory (Draxler et al. 2014) that uses meteorological data from GDAS (Global Data Analysis System). Chapter 2 further provides a variance/covariance profile of a set of 11 monitoring stations measuring simultaneously PM_{10} and $PM_{2.5}$ hourly concentrations. Groups of stations of similar profiles were identified, one station (Oporto metropolitan area) is discussed as needing to be re-classified with respect to its ambient environmental impact.

Chapter 3 addresses the Lisbon-city biomonitoring by lichens and tree bark (originally collected from Azores islands background areas), and describes the set-up of a data-base of 30 chemical elements (INAA analysis), after exposure as transplants in the courtyards of 22 elementary schools of Lisbon-city from January 2008 to May 2008 and from June 2008 to October 2008. This study permitted the spatial mapping of the distribution of the chemical elements. Furthermore, the Chapter’s focus was on lichen conductivity, which is a measure

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of the lichen's physiological status quo. The underlying reasoning was that data comparability should be ensured during all exposure conditions. Transplanting did not have any effect on conductivity, but season appeared to have effect, as end-of-summer lichen transplants did show increased conductivity values.

Chapter 4 presents emission source profiles, as obtained by applying Monte Carlo Target Transformed Factor Analysis (MCTTFA) to the element data from the biomonitoring. The selected lichen and bark were *Parmotrema bangii* and *Criptomeira Japonica* respectively, were picked up from pollution background sites in Azores and placed in the courtyards of 22 elementary schools of Lisbon. The results indicate that although element concentration averages differed for lichen and bark, they yield similar source profiles from MCTTFA.

Chapter 5 shows the associations between atmospheric pollutants (AP) and the hospital admissions in Lisbon (HA), based on data from APA-QUALAR (AP data) and ACSS (HA data), compiled over a 2006-2008 period, and aggregated by age-groups: < 15; 15-64; ≥ 64 years old. Data processing was by Ordinary Least Squares Linear Regression (OLS). HA increased up to 3 % per 10 $\mu\text{g}\cdot\text{m}^{-3}$ rise in AP, with variable age/disease-differentiated outcomes, also depending on the models used.

Chapter 6 focuses on the Conway-Maxwell-Poisson distribution (COM-Poisson) that is used to assess the magnitude of the association between HA, air pollutants (CO, NO, NO₂, SO₂, O₃, PM₁₀ and PM_{2.5}) and temperature and relative humidity. The results indicate relevant association between PM and weather variables and HA due to circulatory, cardiac and ischaemic diseases.

Chapter 7 gives a general discussion, and conclusions from the thesis.

Samenvatting

De context van de studie, beschreven in dit proefschrift, is de bezorgdheid dat blootstelling aan luchtverontreiniging negatieve gezondheidseffecten veroorzaakt. Het proefschrift is gericht op drie belangrijke aandachtspunten:

- 1) Vergelijkende analyse van de luchtkwaliteit in Portugal (vaste land en eilanden);
- 2) Biomonitoring van de luchtkwaliteit in Lissabon;
- 3) Nieuwe methodologieën om luchtkwaliteit te beoordelen in termen van de associatie met ziekte.

De gegevens voor deze studies werden geleverd door de Air Quality Monitoring Network (QualAr) van het Portugese Milieuagentschap APA (luchtverontreinigingen zoals vaste deeltjes (PM), ozon, stikstof- en zwaveloxiden, koolmonoxide), werden verkregen uit biomonitoring studies met zowel korstmos als boombast (een veelheid aan chemische elementen, zoals verkregen via Instrumentele Neutronen Activeringanalyse (INAA), en werden beschikbaar gesteld door de Portugese Centrale Administratie van het Gezondheidssysteem (ACSS) (Ziekenhuisopnames (HA).

Hoofdstuk 1 geeft een samenvatting van 1) enige van de meest belangrijke aandachtspunten ten aanzien van de luchtverontreiniging in Portugal en met name in Lissabon, 2) biomonitoring en epidemiologie, en 3) presenteert de belangrijkste aandachtspunten van het proefschrift. De luchtkwaliteit in Portugal is niet “zo slecht” als in vele andere regio’s in Europa, maar het is wel nog een reden tot zorg als gezondheidseffecten worden beschouwd. Lissabon is de stad die gekozen is om de diverse technieken toe te passen, omdat Lissabon het grootste verstedelijkte gebied is, omdat het redelijk is gedekt met monitoring stations, en het de grootste bevolkingsdichtheid heeft in Portugal.

Hoofdstuk 2 geeft een wavelet-aanpak in het analyseren van atmosferische PM tijdseries (PM < 10 μm (PM₁₀) en 2.5 μm (PM_{2.5}) door het vasteland van Portugal, de eilanden inbegrepen, zoals gemeten door QualAr. De databases werden geanalyseerd om de contributies te bepalen van de belangrijkste bronnen en hun dagelijkse profielen. Back-trajectories werden gesimuleerd via het gebruik van het Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPIT), zoals ontwikkeld door NOAA’s Air Resources Laboratory (Draxler et al. 2014), waarbij gebruik wordt gemaakt van meteorologische gegevens van het GDAS (Global Data Analysis System). Hoofdstuk 2 geeft verder een variantie/covariantie-profiel van een set van 11 monitoring stations waar simultane metingen werden gedaan aan PM₁₀ en PM_{2.5} uurs-concentraties. Groepen van stations met vergelijkbare profielen konden worden geïdentificeerd, en één station (Oporto stadsregio) is bediscussieerd in verband met een nodige re-classificatie in relatie tot de lokale omgevings-impact.

Samenvatting

Hoofdstuk 3 richt zich op de biomonitoring van de stad Lissabon door korstmoss en boombast (verzameld in achtergrondgebieden op de Azoren eilanden), en beschrijft de opzet van een database van 30 chemische elementen (INAA analyse), na blootstelling als transplanten in de binnenplaatsen van 22 lagere scholen in Lissabon, van Januari 2008 tot Mei 2008 en van Juni 2008 tot Oktober 2008. Deze studie maakte het ruimtelijk weergeven van de distributie van de chemische elementen mogelijk. Het hoofdstuk was verder gericht op de conductiviteit van de korstmoss, wat een maat is voor de fysiologische status quo van de korstmoss. De redenering hierbij was dat de vergelijkbaarheid van data moest worden gewaarborgd voor alle expositiecondities. Transplanteren had geen effect op conductiviteit, maar het seizoen leek effect te hebben, omdat korstmossen aan het eind van de zomer verhoogde conductiviteit lieten zien.

Hoofdstuk 4 presenteert emissiebronprofielen, zoals verkregen via Monte Carlo Target Transformed Factor Analysis (MCTTFA) van de elementgegevens van de biomonitoring. De geselecteerde korstmoss en boombast waren respectievelijk *Parmotrema bangii* en *Criptomeira Japonica*, gemonsterd in verontreinigings-achtergrondgebieden op de Azoren, en geplaatst in de binnenplaatsen van 22 lagere scholen in Lissabon. De resultaten geven aan dat hoewel de gemiddelde elementconcentraties verschillend waren voor korstmoss en boombast, ze beiden vergelijkbare bronprofielen opleverden vanuit MCTTFA.

Hoofdstuk 5 geeft de associaties tussen atmosferische verontreinigingen (AP) en de ziekenhuisopnames (HA) in Lissabon, gebaseerd op data van APA-QualAr (AP data) en ACSS (HA data), gecompileerd voor een 2006-2008 periode, en geaggregeerd naar leeftijdsgroepen: < 15, 15-64, ≥ 64 jaar oud. Data verwerking werd uitgevoerd via Ordinary Least Squares Regression (OLS). HA nam toe tot op 3 % per toename met 10 µg.m⁻³ in AP, met variabele leeftijds/ziekte-gedifferentieerde uitkomsten, ook afhankelijk van het gebruikte model.

Hoofdstuk 6 is gericht op de Conway-Maxwell-Poisson distributie (COM-Poisson), die is gebruikt om de omvang van de associatie tussen HA, luchtverontreinigingen (CO, NO, NO₂, SO₂, O₃, PM₁₀ en PM_{2.5}), temperatuur en luchtvochtigheid vast te stellen. De resultaten geven associaties aan tussen PM en weer-variabelen en HA als gevolg van bloedsomloop-, hart- en ischaemische ziekten.

Hoofdstuk 7 geeft een algemene discussie, en conclusies van het proefschrift.

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Curriculum Vitae

Ana Margarida Januário Cruz was born on 2nd May 1978 in Coimbra, Portugal. She obtained high school degree at Escola Secundária Avelar Brotero in Coimbra. Subsequently she studied Geology at Universidade de Coimbra and later she obtained a Master degree in Geosciences with a thesis entitled “Distribution of uranium in Shear Bands Fragile and Implications for Risk Maps of Radon: The Case of Baroque Mine (Gouveia - Portugal Central)” (“Distribuição do Urânio em Bandas de Cisalhamento Frágil e Implicações para os Mapas de Risco do Radão: O Caso da Mina do Barroco (Gouveia – Portugal Central)”).

She started her work career in 2001 as high school teacher but in 2002 she moved to the *Instituto Politécnico* de Coimbra, Portugal, where she has been adjunct professor until our days.

In 2009 she started a PhD at Department of Radiation Science & Technology (RST) of the Delft University of Technology, where her main research area was outdoor air quality environments. The results of her research are presented in this book.

List of publications

Dissertations

Cruz, AMJ (2006) Distribuição do Urânio em Bandas de Cisalhamento Frágil e Implicações para os Mapas de Risco do Radão: O Caso da Mina do Barroco (Gouveia – Portugal Central), dissertação submetida para obtenção do grau de Mestre em Geociências, na área de especialização em Ambiente e Ordenamento do Território, da Faculdade de Ciências e Tecnologia, da Universidade de Coimbra, Coimbra.

Journal articles

Cruz AMJ, Scotto MG, Alves C, Freitas MC, Wolterbeek HT (2016) Com-Poisson Regression Applied To Hospital Admissions (Cardiac And Respiratory Diseases), Air Pollutants And Meteorological Data In Lisbon. *Environ Sci Pollut Res. Submitted.*

Cruz AMJ, Alves C, Gouveia S, Scotto MG, Freitas MC, Wolterbeek HT (2016) A Wavelet-Based Approach Applied To Suspended Particulate Matter Time Series In Portugal. *Air Quality, Atmosphere and Health 1-13.*

Cruz AMJ, Sarmiento S, Almeida SM, Silva A, Alves C, Freitas MC and Wolterbeek HT (2014) Association between atmospheric pollutants and hospital admissions in Lisbon. *Environmental Science and Pollution Research 22(7):5500-5510.*

Cruz AMJ, Freitas MC, Verburg TG, Canha N, Almeida SM and Wolterbeek HT (2012) Spatial mapping of the city of Lisbon using biomonitors. *Int. J. Environment and Health 6(1):1-17.*

Cruz AMJ, Freitas MC, Verburg TG, Canha N and Wolterbeek HT (2011) Response of exposed bark and exposed lichen to an urban area. *Proceedings in Radiochemistry - A Supplement to Radiochimica Acta 1:1:363-369.*

Oral presentations

Cruz AMJ, Almeida SM, Freitas MC, Alves A, Wolterbeek HT (2014) Association between atmospheric pollutants and hospital admissions in Lisbon. 3rd International Congress Environmental Health (ICEH2014), Porto, 24th to 26th September.

Cruz AMJ, Freitas MC, Verburg TG, Canha N, Wolterbeek HT (2009) Response of bark and lichen exposed to an urban area. APSORC'09 Asia-Pacific Symposium on Radiochemistry'09, 29th November to 4th December.

List of publications

Cruz AMJ, Freitas MC, Canha N, Dung HM, Beasley DG, Wolterbeek HT (2009) Spatial Mapping of the City of Lisbon Using Biomonitoring. Workshop Biomap-5, Buenos Aires – Argentina, 20th to 24th September.

Posters

Cruz AMJ, Almeida SM, Canha N, Alves C., Freitas MC, Wolterbeek HT (2012) Spatial distribution of the air quality in Portugal (concerning traffic, industrial and background areas). European Aerosol Conference (EAC 2012), Granada, 2th to 7th September.

Ramos CA, Almeida SM, Paulino A, Cruz AMJ, Alves F, Wolterbeek HT (2012) Indoor Air Quality in Gymnasiums. European Aerosol Conference (EAC 2012), Granada, 2th to 7th September.

Cruz AMJ, Canha N, Freitas MC, Almeida SM, Verburg TG, Wolterbeek HT (2012) Assessment of the meteorological conditions influence on spatial and temporal variation of biomonitoring conductivity at Lisbon city, Portugal. International Congress on Environmental Health (ICEH 2012), Lisboa, 29-Maio a 02-Junho de 2012.

Cruz AMJ, Freitas MC, Canha N, Verburg TG, Almeida SM, Alves CA, Wolterbeek HT (2010) Spatial distribution of particulate matter levels in Portugal (Mainland, islands and a large urban area - Lisbon) Urban Environmental Pollution Conference, 20th to 23th June.

Cruz AMJ, Pereira, AJSC & Pereira, LCG (2007) Distribuição do Urânio em Bandas de Cisalhamento Frágil e Implicações para os Mapas de Risco de Radão: o Caso da Mina do Barroco (Gouveia – Portugal Central) 9^a Conferência Nacional do Ambiente (Um futuro sustentável: Ambiente, Sociedade e Desenvolvimento), vol. IV, p. 1283, Universidade de Aveiro, Aveiro.

Appendix

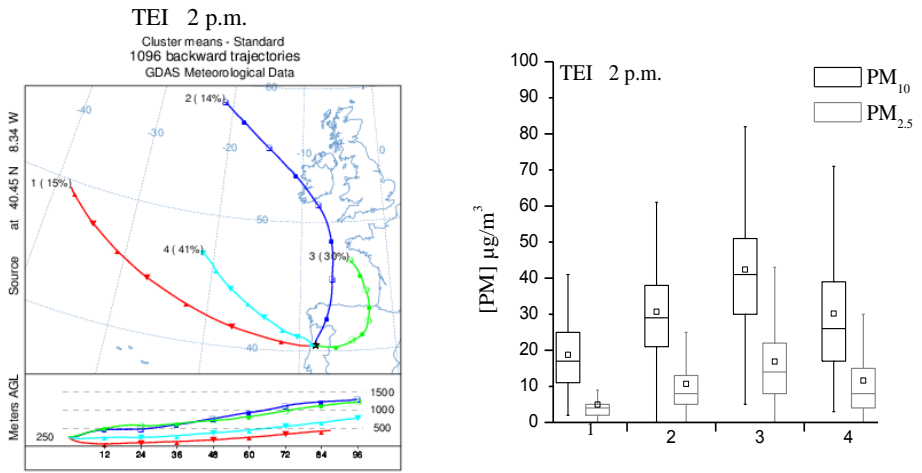


Figure A1 – Clusters of air backward trajectories and PM levels by cluster for ENT.

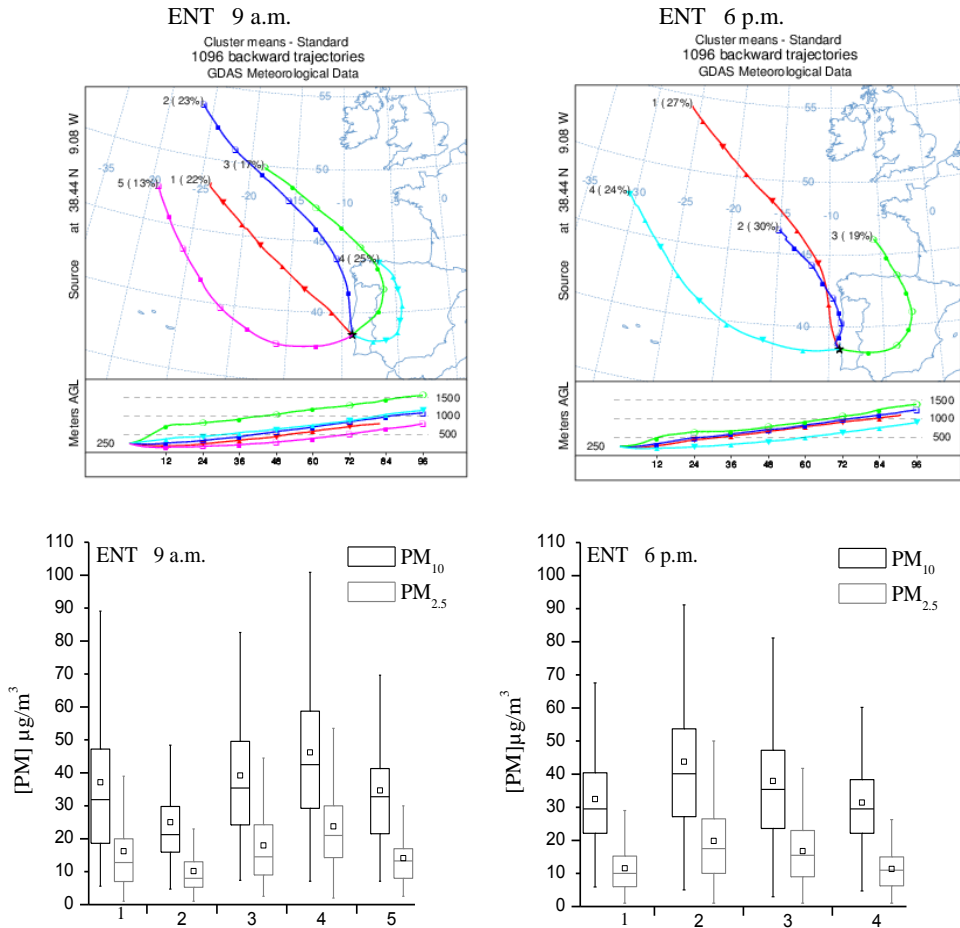


Figure A2 – Clusters of air backward trajectories and PM levels by cluster for TEI.



INVITATION

to the public defence
of my doctoral thesis
entitled

SPATIO-TEMPORAL EVALUATION OF AIR QUALITY AND ITS INFLUENCE ON MORBIDITY

Thursday 23rd of
June 2016 at 10:00
Senaatszaal of the Aula,
Delft University of
Technology
(Mekelweg 5 Delft)

You are
most welcome!

Ana M. J. Cruz



REACTOR INSTITUTE DELFT

