

Impact of Ozone on the Prevalence of Childhood Asthma

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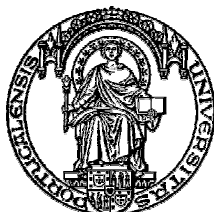
Dissertation presented by

Sofia Isabel Vieira de Sousa

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Thesis supervised by

Professor Maria da Conceição Machado Alvim Ferraz

Professor Fernando Gomes Martins

Chemical Engineering Department

To Mom,
for the eternal love and support

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ABSTRACT

It is well documented that high ozone levels can adversely affect many human body systems and that they are a particular threat especially among risk groups, such as persons with respiratory problems, children and elderly.

The objectives of this thesis were: i) to evaluate and interpret the evolution of ozone concentrations in northern Portugal; ii) to develop statistical models to predict ozone concentrations aiming the implementation of anticipated strategies for the protection of human health, when high concentrations of ozone are previewed; and iii) to evaluate the specific impact of ozone concentrations on the prevalence of childhood asthma without the confounding effects of other pollutants.

Pre-industrial and recent data series were used to assess the evolution of ozone concentrations in northern Portugal, being the results analysed according to the atmospheric chemistry. Compared to the nineteenth century, current concentrations were in average 147% higher due to the increased photochemical production, associated with the increased anthropogenic emissions. The prediction of ozone concentrations was based on the comparison of time-series, multiple linear regression, principal component regression, artificial neural networks and quantile regression models. Principal components application on feedforward artificial neural networks was the better approach to predict ozone concentrations. Quantile regression model also showed high efficiency especially in the prediction of extreme values which are very useful on days with peak ozone episodes. The models developed were considered valuable tools for public health protection because they could make efficient predictions of ozone levels, thus allowing to provide early warnings to the population. The impact of ozone concentrations on the prevalence of childhood asthma was assessed eliminating confounding effects by the assessment of the influence of ozone on biological pollutants and by selecting an area to perform the study with high ozone concentrations and low of other pollutants (exposed area). Children with 6 to 13 years old, living at the exposed area were compared with those living at an area without significant pollutant concentrations, including ozone (unexposed area). Asthma prevalence was in a first phase evaluated through the completion of questionnaires, aiming the identification of asthmatic symptoms on children. Asthmatic children were identified when dyspnoea and wheezing were simultaneously mentioned in the absence of upper respiratory infections. These asthmatic symptoms were re-evaluated in a second phase through spirometric tests performed by medical doctors. According to that, the lifetime prevalence of asthma at the exposed sites was 9.2%, considerably higher than the prevalence rate for asthmatic symptoms at the unexposed area (3.2 to 3.5%).

Children living at the exposed area had a 3 times higher risk (relative risk 2.84; odds ratio 3.02) of having asthma than those living at the unexposed area.

Keywords: Ground-level O₃; NO_x; VOC; Predictive models; MLR; PCR; FANN; Asthmatic symptoms; Childhood asthma prevalence; Spirometric tests.

RESUMO

As concentrações elevadas de ozono podem afectar negativamente diversos sistemas do corpo humano, em especial em grupos de risco, como são as pessoas com problemas respiratórios, crianças e idosos.

Esta tese teve como objectivos i) avaliar e interpretar a evolução das concentrações de ozono no Norte de Portugal; ii) desenvolver modelos estatísticos de previsão das concentrações de ozono, de modo a permitir a implementação de estratégias para protecção da saúde humana, quando forem previstas concentrações elevadas; e iii) avaliar o impacte específico do ozono na prevalência de asma infantil.

A evolução das concentrações de ozono no Norte de Portugal foi avaliada comparando dados recentes com os da era pré-industrial, tendo a análise sido baseada na química atmosférica. Os resultados mostraram aumentos médios de cerca de 147%, relativamente ao século XIX, associados ao aumento das emissões antropogénicas. A previsão das concentrações de ozono baseou-se no desenvolvimento e comparação dos seguintes modelos: séries temporais, regressões lineares múltiplas, regressões por componentes principais, redes neuronais artificiais e regressões por percentis. A aplicação de componentes principais como variáveis de entrada nas redes neuronais artificiais foi dos modelos utilizados o que demonstrou ser mais eficaz. O modelo de regressão por percentis mostrou-se também eficaz, especialmente na previsão de valores extremos, sendo bastante útil em dias com “episódios de ozono”. Os modelos desenvolvidos mostraram ser ferramentas de elevada relevância na protecção da saúde pública, uma vez que foram capazes de prever as concentrações de ozono com eficácia, podendo contribuir para a comunicação de avisos prévios à população. O impacte das concentrações de ozono na prevalência de asma infantil foi avaliado eliminando factores confundidores, através da avaliação da influência do ozono nos poluentes biológicos e da selecção de uma área com concentrações elevadas de ozono e muito baixas de outros poluentes para efectuar o estudo (área exposta). A prevalência de asma em crianças dos 6 aos 13 anos que vivem na área exposta foi comparada com a de crianças da mesma faixa etária que vivem numa área com concentrações não significativas de poluentes, incluindo ozono (área não exposta). A prevalência de asma foi avaliada numa primeira fase através de questionários para a identificação de sintomas asmáticos nas crianças. Estas foram consideradas asmáticas quando mencionaram, simultaneamente, dispneia e pieira na ausência de infecções respiratórias superiores. Estes sintomas foram reavaliados numa segunda fase através de testes espirométricos efectuados por médicos. De acordo com estes testes, a prevalência de asma durante a vida nas áreas expostas foi 9,2%, consideravelmente superior à prevalência de sintomas asmáticos na área não exposta (3,2 a 3,5%).

As crianças que residem na área exposta apresentaram um risco 3 vezes superior (risco relativo 2,84; razão de probabilidades 3,02) de desenvolverem asma do que as que residem na área não exposta.

Palavras chave: O₃ superficial; NO_x; VOC; Modelos de previsão; MLR; PCR; ANN; Sintomas asmáticos; Prevalência de asma; Crianças; Testes espirométricos.

RÉSUMÉ

Les concentrations élevées d'ozone peuvent affecter négativement des différents systèmes du corps humain, surtout chez les sujets à risque, comme sont les personnes qui portent des problèmes respiratoires, les enfants et les âgés.

Les objectives de cette thèse sont: i) évaluer et interpréter l'évolution des concentrations d'ozone du Nord du Portugal; ii) développer des modèles statistique qui puissent aider à faire une prévision des concentrations elles mêmes, de façon à permettre l'établissement de stratégies pour la protection de la santé humaine; iii) évaluer l'impact spécifique d'ozone dans la prévalence de l'asthme infantile.

L'évaluation des les concentrations au Nord du Portugal fut estimée à dater d'un étude récent par rapport à un autre étude concernant l'ère préindustrielle, et dont l'analyse a été basée sur la chimie atmosphérique. Les résultats ont montré que les augmentations globales sont environ 147%, par rapport au XIX siècle, et les résultats sont associés à l'augmentation des émissions anthropogéniques. La prévision des concentrations d'ozone s'est basée sur le développement et la comparaison des modèles suivants: des séries temporelles, des régressions linéaires multiples, des régressions sur composantes principales, tels que réseaux de neurones artificiels et des régressions quantiles. L'application des composantes principales comme variable d'accès aux réseaux de neurones artificiels, a été de tout les méthodes utilisées celui qui s'est montré plus efficace. Quoique la méthode de régression quantile soit aussi efficace, notamment dans la prévision des valeurs extrêmes ce qui est très utile du cours des jours où il y a des épisodes d'ozone. Les modèles développés ont montré qu'ils sont des outillages très importants dans ce qui concerne la protection de la santé publique, vu qu'ils ont été capable de prévoir les concentrations d'ozone avec efficace, pouvant de cette façon contribuer à faire une communication d'avis préalable aux populations. L'impact des concentrations d'ozone dans la prévalence de l'asthme infantile fut évaluée, en écoutant de les facteurs embarrassants, en travers l'évolution de l'influence d'ozone dans les polluants biologiques ainsi que le triage d'une area où il y a des concentrations élevées d'ozone et existent très basses d'autres polluants (area exposée) afin de faire l'étude. La prévalence d'asthme chez les enfants dont l'âge est entre 6 et 13 ans qui habitent dans une area exposée, a été confrontée à des enfants des mêmes âges mais qui habitent une area où les concentrations des polluants incluant l'ozone n'ont aucune signification (area non exposée). La prévalence d'asthme fut évaluée dans une première phase à partir de questionnaires afin d'identifier des symptômes asthmatiques chez les enfants. Ceux-ci furent considérés asthmatiques au moment où ils avaient à la fois, dyspnée et rôle mais ils n'avaient pas d'autres infections respiratoires supérieures. Ces symptômes furent réappréciés dans une deuxième phase à partir des tests spirométriques effectués par des médecins. Après ces tests, la prévalence d'asthme durant la vie dans les areas exposées était 9.2%, assez supérieure à la prévalence des symptômes asthmatiques dans la area qui n'était pas exposée (3.2 à 3.5%).

Les infants qui habitent dans l'area exposée sont en risque de développer l'asthme, 3 fois supérieure à ceux qui habitent dans l'area qui n'est pas exposée (Risque Relatif 2.84; odds ratio 3.02).

Mots-Clés: O₃ superficiel; NO_x; VOC; Modèles de prévision; MLR; PCR; ANN; Symptômes asthmatiques; Prévalence d'asthme; Enfants; Tests spirométriques.

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LIST OF ACRONYMS

6 th EAP	Sixth Environment Action Programme
ANN	Artificial Neural Networks
AQG	Air Quality Guidelines
AT	Alert Threshold
BG ₁	Bragança district background remote site 1
BG ₂	Bragança district background remote site 2
BG ₃	Bragança district background remote site 3
BG ₄	Bragança district background remote site 4
BG ₅	Bragança district background remote site 5
BG _{rur}	Background rural site (Oporto Metropolitan Area)
BG _{sub1}	Background suburban site 1 (Oporto Metropolitan Area)
BG _{sub2}	Background suburban site 2 (Oporto Metropolitan Area)
CAFE	Clean Air For Europe
CI	Confidence Interval
COPD	Chronic Obstructive Pulmonary Disease
d ₂	Index of agreement
DL	Decreto-Lei
DS _{old}	Old data series
DS _{rec}	Recent data series
EC	European community
EEA	Environmental European Agency
EU	European Union
FANN	Feedforward Artificial Neural Network
FEF _{25%-75%}	Forced Expiratory Flow over the mid-range of expiration
FEV ₁	Forced Expiratory Volume in the 1 st second
FVC	Forced Vital Capacity
HC	Hydrocarbons
IND	Industrial suburban site
ISAAC	International Study of Asthma and Allergies in Childhood
IT	Information Threshold

LO	Lamas d'Olo background remote site
MAE	Mean Absolute Error
MBE	Mean Bias Error
MG ₁	Mogadouro background remote site 1
MG ₂	Mogadouro background remote site 2
MLR	Multiple Linear Regression
MSE	Mean Squared Error
n	Data number
NECD	National Emission Ceilings Directive
NMHC	Non-Methane Hydrocarbons
NMVOC	Non-Methane Volatile Organic Compounds
OECD	Organisation for Economic Co-operation and Development
Oporto-MA	Oporto Metropolitan Area
OR	Odds Ratio
P	Pressure
P ₁ to P ₁₀	Periods 1 to 10
P ₉₀ (R ² _{aj})	90 th Percentil of the adjusted correlation of determination
PAH	Poliaromatic Hydrocarbons
PC	Principal Components
PCA	Principal Component Analysis
PC-FANN	Feedforward Artificial Neural Networks based on Principal Components
PCR	Principal Component Regression
PM	Particulate Matter
PM ₁₀	Particulate Matter with aerodynamic diameters smaller than or equal to 10 µm
PM _{2.5}	Particulate Matter with aerodynamic diameters smaller than or equal to 2.5 µm
PP	Precipitation
QR	Quantile Regression
R	Correlation coefficient
R'	Goodness of fit
R ²	Coefficient of determination
R ² _{aj}	Adjusted correlation of determination

R_{crit}	Critical correlation coefficient
RH	Relative Humidity
RMSE	Root Mean Squared Error
RR	Risk Ratio
SATSA	Sequential Approach to Time-Series Analysis
SP	Serra do Pilar
SR	Solar Radiation
T	Average temperature
TF ₁	Traffic site 1 (Oporto Metropolitan Area)
TF ₂	Traffic site 2 (Oporto Metropolitan Area)
TF ₃	Traffic site 3 (Oporto Metropolitan Area)
TM ₁	Torre de Moncorvo background remote site 1
TM ₂	Torre de Moncorvo background remote site 2
TM ₃	Torre de Moncorvo background remote site 3
T _{Max}	Maximum temperature
T _{Mim}	Minimum temperature
TS	Time Series
TSP	Total Suspended Particles
TVPHH	Target Value for the Protection of Human Health
UNECE	United Nations Economic Commission for Europe
US	United States
US EPA	US Environmental Protection Agency
UTC	Universal Time Coordinated
VOC	Volatile Organic Compounds
WD	Wind Direction
WHO	World Health Organization
WV	Wind Velocity

PART I
INTRODUCTION

Chapter 1

Framework

This thesis was carried out between 2006 and 2009 at the Laboratory for Process, Environmental and Energy Engineering (LEPAE) in the Chemical Engineering Department of the Faculty of Engineering, University of Porto. This work allowed the publication of seven papers in international periodicals included in the scientific citation index, having one more been submitted.

1.1 Relevance

To protect human health from the harmful effects of ozone, air quality legislation sets a target value of $120 \mu\text{g m}^{-3}$ (daily maximum of 8-hour averages) that should not be exceeded more than 25 days per year (Directive 2008/50/EC). According to the Environmental European Agency (EEA), in 2005, 38% of the European population was exposed to ozone levels above this target value, as can be seen by Figure 1.1.

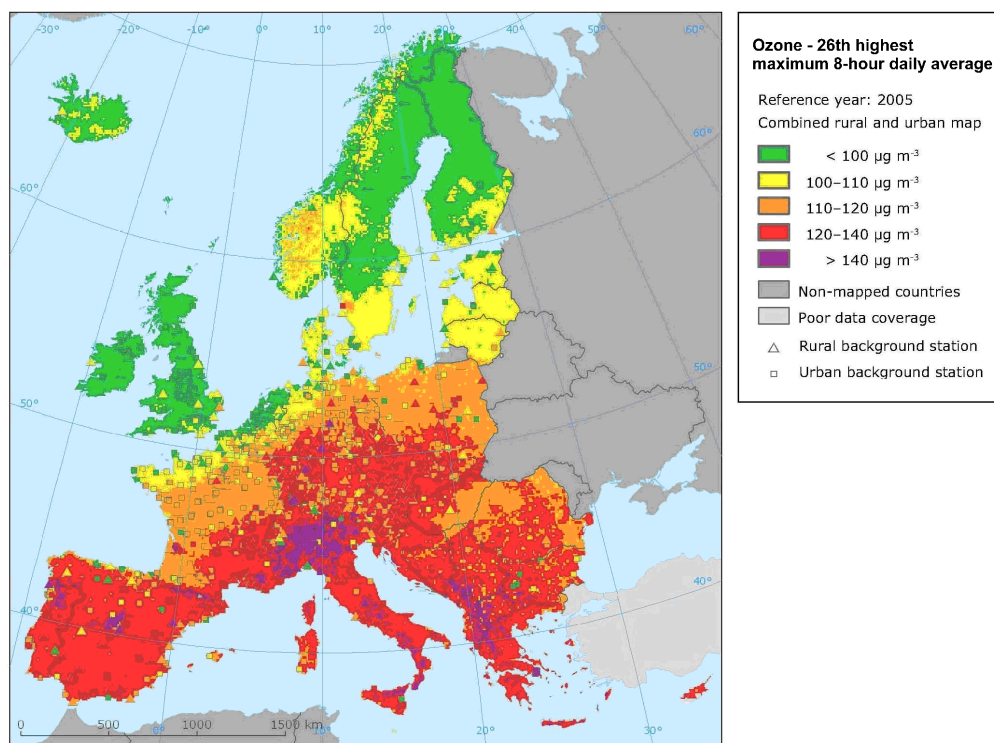


Figure 1.1 Combined maps of rural and urban concentration of the ozone health indicators - 26th highest daily maximum of 8-hour averages ($\mu\text{g m}^{-3}$), in 2005 (EEA, 2009).

This percentage varies strongly from country to country; the population living in southern, central and eastern European countries, especially in Mediterranean ones, are those exposed to the highest concentrations, with results showing areas with non-compliances, while those living at northern European countries are exposed to considerably lower concentrations, with results showing no exceedances in most of the countries. The estimated probability of exceeding the target value for the protection of human health is higher than 50% south of the line Biarritz - Basel - Luxemburg - Hannover - Lodz, being in some Mediterranean countries and in northern Portugal higher than 75%. North of the line referred above, the probability of exceeding the target values is much lower, between 25 and 50%, and north of the border running La Rochelle - Rostock - Vilnius, that probability is generally lower than 25% (EEA, 2009).

Ozone, as a strong photochemical oxidant, impairs biological tissues namely of the lungs, causing increased medication use, illness and death (OECD, 2008). According to EEA health impact assessment (EEA, 2009), south-eastern and southern Europe have an average of 75

deaths per million inhabitants due to elevated ozone concentrations, being around 44 deaths per million inhabitants in Portugal, and less than 10 deaths per million inhabitants for northern and north-western Europe. It is even suggested that there is no safe level for ozone exposure, posing a health risk even at concentrations below the legislated (OECD, 2008). Concerning these strongly negative impacts on health, the development of models to predict ozone concentrations is crucial, because preventing exposure is the most effective way of protecting human health from environmental threats.

The population at higher risk is the elderly, children and persons with respiratory diseases. Children are highly vulnerable to environmental hazards, being considered a risk group for several reasons including their relative higher amount of air inhalation (the air intake per weight unit of a resting infant is twice that of an adult), their not fully developed immune system and lungs and also their higher amount of time spent outdoors. As a result, children will have substantially higher exposures to air pollutants than adults (Schwartz, 2004; WHO, 2004).

Protecting the health of children and the environment is an essential objective for the health policies of any modern society, being also crucial for a sustainable development. Evaluating the risk of developing childhood asthma is one of the four priority issues identified by the European Commission, according to the European Union Environment and Health Action Plan (EEA, 2005a).

Several studies have demonstrated a strong association between the exposure to ozone and asthma, even more significant in asthmatic children (Salvi, 2007; Macdonnell et al., 1997). However, the complexity of exposure patterns, the changes in the vulnerability of children at various stages of development, and the practical limitations of research, lead to a still incomplete understanding of the ozone impact on the health of children. Difficulties on the interpretation of epidemiological studies to evaluate chronic effects are mainly due to an absence of studies designed specifically to address this question and to inherent limitations in characterizing exposure. The more rigorous studies provided new evidences for chronic effects of ozone on small airway function and possibly on asthma, but substantial uncertainties remain (WHO, 2006).

A key issue affecting ozone epidemiological studies concerns the evaluation of the extent to which other air pollutants may confound or modify the specific ozone impact. The use of multi-pollutant regression models is nowadays the prevailing approach for controlling potential confounding by co-pollutants (USEPA, 2006).

Based on the development of models to predict ozone concentrations and on the elimination of possible confounding effects, the work reported in this thesis aimed to evaluate the specific impacts of ozone on childhood asthma, allowing further advances on the field.

1.2 Objectives

The main objective of this thesis was to evaluate the impact of ozone on the prevalence of childhood asthma. This was accomplished by:

- 1 - Evaluating and interpreting the evolution of ground-level ozone concentrations in northern Portugal;
- 2 - Developing statistical models (based on time-series, multiple linear regressions, principal component regressions, quantile regressions and artificial neural networks) to predict ozone concentrations, aiming the implementation of anticipated strategies for the protection of human health, when high concentrations of ozone are previewed.
- 3 - Evaluating the specific impact of ozone concentrations on the prevalence of childhood asthma without the confounding effects of other pollutants.

1.3 Outline

The work presented in this thesis linked three main scientific topics: environment, statistics and epidemiology.

This Part I is an introduction describing the subject relevance, work objectives and thesis structure (Chapter 1); it also provides an overall view of atmospheric pollution including a general description of atmospheric pollutants, namely its sources and average levels, health impacts and legislation that is nowadays applied concerning this issue (Chapter 2).

Part II introduces the evolution and photochemical formation of ground-level ozone and also deals with the evaluation and interpretation of these topics for northern Portugal (Chapter 3).

Part III provides an overview on the field of ozone concentration prediction referring to work already performed and also to the use of statistical models, namely time-series, multiple

linear regressions, principal component regressions, quantile regressions, and artificial neural networks (Chapters 4 to 6 compare the different applications of the models above referred).

Part IV addresses the health impacts of ozone, namely the evaluation of the specific impact of ozone on the prevalence of childhood asthma without the confounding effects of other pollutants (described through the evaluation of the influence of ozone on the concentrations of pollen and fungal spores and through the identification of a region mainly polluted by ozone). It starts by referring to work already performed, followed by the analysis of the influence of ozone on biological pollutants and the identification of a region in northern Portugal with high ozone concentrations and very low concentrations of other pollutants (Chapter 7), ending with the evaluation of asthma prevalence (Chapter 8).

Part V goes over the main conclusions referring future work lines to complement the present study (Chapter 9).

Chapter 2

Atmospheric Pollution

Atmospheric pollution is the presence in the outdoor atmosphere of any dust, fumes, mist, smoke, other particulate matter, vapour, gas, odorous substances, energy, or a combination thereof, in sufficient quantities and of such characteristics and duration as to be, or likely to be, injurious to human health or welfare, animal or plant life, or property, or as to interfere with the enjoyment of life or property (Peavy et al., 1985).

Human beings can survive some weeks without eating and some days without drinking, but cannot survive some minutes without breathing. The daily requirements for food, drinks and air are about, 0.5 kg, 1.5 kg and 15 kg, respectively, highlighting the importance of air quality (Alvim-Ferraz and Melo, 2005). The general feeling is not always according to what is shown by these figures, probably because air is the most available natural resource, not having the leading role of the scarce goods. Nevertheless, all people should have conscience that the free access to air of acceptable quality is a fundamental human right.

Air contamination by human activities has existed at least since people learned how to use fire, although different aspects have been important at different times.

2.1 Past, Present and Future

When Prometheus stole fire from the gods, he simultaneously got a blessing and a curse. The early smoke from isolated wood-burning fires of cave dwellers, with time became the smoke from coal-burning furnaces of heavily populated cities, early recognized to have negative impacts on the inhabitants of those cities (Peavy et al., 1985). In AD 61 the philosopher Seneca, who suffered from asthma and was often in poor health, referred the “heavy air of Rome” and “stink of the smoky chimneys thereof”; the sooner he was out of Rome (ordered by his doctor) the better he felt (Brimblecombe, 1999). In 1273, the burning of “sea coal” was forbidden by King Edward I from England, after being associated with the smoke and fog mixture that covered London many times in winter, due to the burning of that kind of coal for heating. Although, as a heavy deforestation made wood a scarce good, the London heating in winter became more and more dependent on coal burning. Apparently, Queen Elizabeth I from England and Scotland (1558-1603) had an allergy to coal smoke, reason why she moved out of the city. Consequently, about three hundred years after the first law, a new one was promulgated forbidding coal burning when Parliament was sitting, to be possible for the Queen to take the chair of the sessions (Peavy et al., 1985). According to the tradition, during her reign, one man was executed by breaking that law (Borrego et al., 2002). By 1661, over a century later, it seems that the obedience to the law was still not acquired. At that time, the removal of all smoke-producing plants and the planting of greenbelts around London were suggested, solutions thoroughly actual. Nevertheless, those suggestions seem to fell on empty.

The Industrial Revolution brought to Western Civilization richness and social transformations that completely changed the human life. The severe increase of air contamination, associated with the extensive use of coal as energy source, was the downside of the industrial development. Consequently, the impacts on health of sulphur dioxide and suspended particles became more and more evident, waking up the social conscience to the progress counterpart.

During the first half of the twentieth century, a new kind of pollutants appeared as protagonists: those emitted by the combustion of oil products, namely the ones associated with vehicle fuels. Industrial and traffic emissions led to several acute episodes with mortality consequences since the first half of the twentieth century (1930: Belgium; 1948: Donora; 1948: London; 1952: London). For example in 1952, the increase of sulphur dioxide and particle concentrations in London during 5 days in December was clearly associated with

more than 4000 extra deaths (Brimblecombe, 1999). Stringent laws were implemented only after this disaster, leading to a real improvement of London air quality. It should be enhanced that the implementation of procedures to control the obedience of the laws is at least as important as their implementation.

The raise of personal or commercial vehicles all over the world strongly increased the amount of emitted pollutants to the atmosphere and the impacts of atmosphere contamination. In addition to sulphur dioxide and suspended particles, carbon and nitrogen oxides, hydrocarbons and other organic and halogenated-organic compounds were more and more released to the atmosphere by traffic emissions. To control this kind of contamination, the introduction of new transport policies, the generation of cleaner combustion engines and the introduction of alternative clean energy sources have been considered (Brimblecombe, 1999).

During the last thirty years of the twentieth century, the long-range transport of pollutants was studied being shown that it is responsible for the appearance of global impacts that might be felt sometimes very far from the places where pollutants were emitted. Ionizing radiation and acid deposition began belonging to the list, more and more enlarged, of environmental concerns. It was noted that there was a depletion of ozone in the stratosphere, but curiously, it was noted at the same time, that ozone in the troposphere was increasing. The depletion of ozone in the stratosphere and the increasing of ozone and other photochemical pollutants in the troposphere became a worldwide problem at regional and continental scales. Studies were carried out to increase the understanding about accumulation of persistent inorganic pollutants (heavy metals) and persistent organic pollutants (polyaromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo dioxins, polychlorinated dibenzo furans) and their impacts on the human health and environment. The overstated utilization of fertilizers (excess nutrient loading), herbicides and pesticides led to their atmospheric transport, fate and deposition, with impacts on ground quality, surface water quality, and environmental toxicology (Krupa, 2002).

By the end of the twentieth century, the emission of greenhouse gases and the associated climate change turned out to be one of the environmental problems of major concern.

At the beginning of the twenty first century, there is an increased interest in indoor air quality (homes, services, work and leisure spaces). The atmospheric pollutants with more negative effects on human health are suspended particles, ozone, organic and halogenated-organic compounds (WHO, 2000; WHO, 2006). On a global perspective, research is needed to

determine the relationship between greenhouse gases, aerosols and surface temperature; the study of climatic implications of these are more urgent than ever (Austin et al., 2002).

Europe has been making a great effort and has reduced many forms of air pollution; it has eliminated smog in many areas and it has reduced acid rain. However, high concentrations of fine particulates and tropospheric ozone in particular, are still causing health problems in urban and rural areas. Tropospheric ozone is also damaging for ecosystem health and for crops across large areas of rural Europe. Regardless of the emissions reduction, concentrations of these pollutants remain high, often above existing standards (EEA, 2003). Exposure to high concentrations leads to reduced life expectancy and causes premature death and extensive aggravation in health (EEA, 2005a).

2.2 Atmospheric Pollutants

Atmosphere is constituted by nitrogen (78.1%), oxygen (20.9%) and a number of trace gases (1%) which can be present in almost invariable concentrations such as argon, neon, helium and others that vary temporally and spatially, such as water vapour, carbon dioxide, carbon monoxide, sulphur dioxide, nitrogen oxides and ozone (Colls, 2002; Godish, 2004).

Air pollutants may be primary, which are emitted into the atmosphere, or secondary which are formed in it. Primary air pollutants include sulphur dioxide, nitrogen oxides, volatile organic compounds, and carbonaceous and non-carbonaceous particles and are released into the atmosphere from road transport emissions, stationary combustion sources and from natural emissions. Secondary air pollutants are formed from chemical reactions of primary pollutants in the atmosphere. Sources of primary pollutants may be classified as mobile (automobiles, industrial vehicles, trains, all types of vessels and airplanes) or stationary (petroleum refineries, petrochemical plants, fossil fuel power plants, food processing plants, other large and small industries and home heating) (Godish, 2004).

The lifetime of air pollutants interferes with the spatial scales on which air pollution occurs. Thus, pollutants can be classified in local, urban, regional and global scale. On a local scale pollutants such as hydrogen fluoride and 1,3-butadiene have a very short atmospheric lifetime (generally less than one hour) and considerable concentrations close to their point source, therefore having low background concentration in the atmosphere. On an urban scale, pollutants such as nitrogen oxides and carbon monoxide have, in general, atmospheric lifetimes of hours and high concentrations. On a regional scale, pollutants such as ozone and

fine particles have atmospheric lifetimes of a few days to several weeks, allowing the long-range transport (thousands of kilometres, being possible to cross national boundaries). On a global scale, pollutants such as carbon dioxide and methane have atmospheric lifetimes of years (being capable of circulating all over a hemisphere) and concentrations close to the emission sources only slightly higher than those at background atmosphere (Seinfeld and Pandis, 1998; Colls, 2002; WHO 2006).

2.2.1 Particulate Pollutants

Particulate air pollution is a mixture of solid, liquid or solid and liquid particles suspended in the air. Particles differ in size, mass, density, morphology and chemical and physical properties. The term “aerosol” is often used synonymously with particulate matter (PM), but an aerosol includes both the particles and all gaseous components of air (Vallero, 2008).

Atmospheric particles may be primary or secondary depending on their origin and formation processes. Primary particles are emitted directly into the atmosphere from natural and anthropogenic sources. In the former case, these include volcanoes, forest fires, ocean spray, biologic sources (mold, pollen, bacteria, plant parts), and meteoric debris; anthropogenic sources include transports, fuel combustion in stationary sources, a variety of industrial processes, solid waste disposal, and miscellaneous sources such as agricultural activities and fugitive emissions from roadways. Secondary particles are produced from both naturally emitted gaseous substances and anthropogenic sources as a result of chemical processes involving gases, aerosol particles and water vapour. These particles include sulphates, nitrates, and oxyhydrocarbons produced by direct, catalytic, and photochemical oxidation of sulphur, nitrogen, and volatile non-methane hydrocarbons (WHO, 2003; Godish, 2004; Vallero, 2008). Indoor sources of PM include tobacco smoking, unvented heaters, cooking, candles and incense, and particles coming from outdoors.

Particles are usually classified through their aerodynamic properties due to its relation with: i) the transport and removal from the air; ii) their deposition within the respiratory system; and iii) the chemical composition and sources. Accordingly, sampling covers a wide range of sizes, from a few nm (1-2 nm) to several μm (100 μm); however these very large particles tend to drop out rapidly through gravity. Thus, in practice there are few particles exceeding 20 μm of diameter in the atmosphere (WHO, 2003).

The largest particles, called the coarse fraction, are mechanically produced by the break-up of larger solid particles. These particles are often of natural origin and can include wind-blown dust from agricultural processes, uncovered soil, unpaved roads or mining operations. Traffic produces road dust and air turbulence that can stir up road dust. Near coasts, evaporation of sea spray can produce large particles. Pollen grains, mould spores, and plant and insect parts are all in this larger size range. Most coarse particles are in the 2.5-10 μm size range, but they can be as large as 30 μm . Smaller particles, called the fine fraction are predominantly of anthropogenic origin (Fenger, 2002) and comprise one third of the particulate mass found in nonurban areas and one half in urban ones being largely formed from gases (Godish, 2004; WHO, 2003). The smallest particles, called ultrafine particles are less than 0.1 μm and are formed by nucleation, that is, condensation of low-vapour-pressure substances formed by high-temperature vaporization or by chemical reactions in the atmosphere. Both fine and coarse particles up to 10 μm tend to remain suspended in the atmosphere being called suspended particles (suspension times depending on size).

Figure 2.1 shows the different sizes of tropospheric particles in relation with their formation process, sources and number.

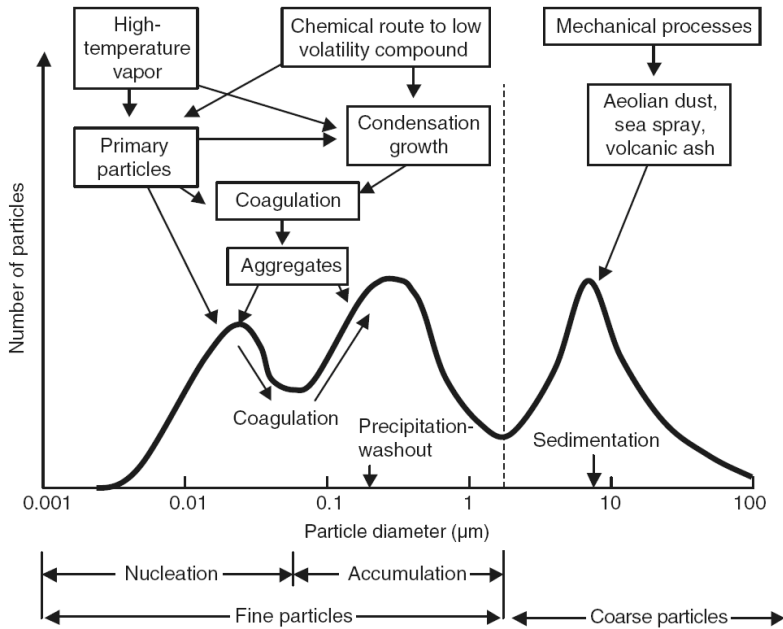


Figure 2.1 Prototypical size distribution of tropospheric particles with selected sources and pathways of how the particles are formed. Dashed line is approximately 2.5 μm diameter (Vallero, 2008).

Suspended particles are also highlighted because of their associated health effects. Particle size classes have been identified reflecting particle penetration and deposition in the human respiratory system. Thus, PM_{10} or “thoracic particles” are particulates with aerodynamic diameters smaller than or equal to $10\ \mu\text{m}$ that deposit within the deeper respiratory tract and $PM_{2.5}$ or “respirable particles”, are particulates with aerodynamic diameters smaller than or equal to $2.5\ \mu\text{m}$ that penetrate to the gas-exchange region of the lungs (WHO, 2003; Brunekreef and Holgate, 2002). Thus, $PM_{2.5}$ are an important indicator of risk to health from particulate pollution once they can penetrate deeper in the lungs, being possible their trapping in alveoli and worse effects on human health.

As well as other components of the atmosphere, particles move in both horizontal and vertical dimensions. Smaller particles can be particularly problematic from a pollutant transport perspective because of their ability to travel longer distances (Vallero, 2008). They are carried downwind by advective airflows and transported both upward and downward by convective air motion (Godish, 2004).

The main removal processes of aerosol particles from the atmosphere are rainout, sedimentation and dry deposition (Jacobson, 2002).

The most frequently used indicator for suspended particles in the air has been PM_{10} . The World Health Organization (WHO) reported that the general levels of suspended PM_{10} in Asia and Latin America are higher than those in Europe and North America (WHO, 2006). In Europe, WHO reported PM_{10} levels for 2002 (data from more than 1100 monitoring sites in 24 countries, including around 550 in urban areas) of $26.3\ \mu\text{g m}^{-3}$ for the annual average and $43.2\ \mu\text{g m}^{-3}$ for the 36th highest value of the daily averages in urban background. In rural areas the concentrations were of $21.7\ \mu\text{g m}^{-3}$ for the annual average and $38.1\ \mu\text{g m}^{-3}$, for the 36th highest value of the daily averages. The highest annual average concentrations measured exceeded $80\ \mu\text{g m}^{-3}$, while the highest daily average concentrations exceeded $150\ \mu\text{g m}^{-3}$.

Towns in arid areas with surrounding deserts frequently receive a considerable amount of dust from wind-blown fine sand. In Cairo it was found that large fractions of the PM_{10} might be attributed to fine sand particles (WHO, 2006).

The annual averaged PM_{10} concentrations in the analysed Asian cities ranged from about $35\ \mu\text{g m}^{-3}$ to $220\ \mu\text{g m}^{-3}$ and in Latin America from about $30\ \mu\text{g m}^{-3}$ to $129\ \mu\text{g m}^{-3}$, while in Europe and North America the typical range was $15\text{--}60\ \mu\text{g m}^{-3}$. The high concentrations over

Asia might be due to the well-known springtime meteorological phenomenon, causing the Asian dust cloud, which comes from windblown dust of Mongolia and China.

Massive forest fires have also caused significant increases in PM concentrations, for example in a two and a half weeks fire in California 1987, concentrations reached $237 \mu\text{g m}^{-3}$ and in another one lasting 10 weeks in the United States they reached $500 \mu\text{g m}^{-3}$ in two days (WHO, 2006).

Although evidence is growing that $\text{PM}_{2.5}$ and smaller fractions are the most important PM, measurements and emissions in Europe are often only available for PM_{10} . Available $\text{PM}_{2.5}$ annual average concentrations at rural background sites in Europe are in general between $11 \mu\text{g m}^{-3}$ and $13 \mu\text{g m}^{-3}$, being considerably lower than urban background levels (around $15\text{-}20 \mu\text{g m}^{-3}$), which are also lower than $\text{PM}_{2.5}$ at traffic sites (typical range $20\text{-}30 \mu\text{g m}^{-3}$). In Portugal, studies showed concentrations of $\text{PM}_{2.5}$ significantly lower for background sites ($8 \mu\text{g m}^{-3}$) than for traffic ones ($42 \mu\text{g m}^{-3}$) (Slezakova, 2007). The $\text{PM}_{2.5}/\text{PM}_{10}$ ratio has been reported in many cities worldwide. The PM_{10} fraction includes particles smaller than $2.5 \mu\text{m}$, thus $\text{PM}_{2.5}/\text{PM}_{10}$ ratio shows which fraction is the dominant. Data from 119 $\text{PM}_{2.5}$ measuring sites in Europe showed an average $\text{PM}_{2.5}/\text{PM}_{10}$ ratio of 0.65 ranging between 0.42-0.82; in African dust outbreaks over eastern and northern Spain reported $\text{PM}_{2.5}/\text{PM}_{10}$ ratios, respectively, from 0.4-0.8 and 0.7-0.9 (EEA, 2007a; WHO, 2006). Reported ratios in Portugal were very similar, being for background sites 0.7-0.9 and for traffic ones of 0.8 (Slezakova, 2007).

Figure 2.2 shows the Portuguese emissions of $\text{PM}_{2.5}$, PM_{10} and Total Suspended Particles (TSP) between 1990 and 2006, according to the national report for the United Nations Economic Commission for Europe (UNECE) and the United Nations Framework Convention on Climate Change.

It is clear that the emissions of PM in Portugal have an increasing tendency.

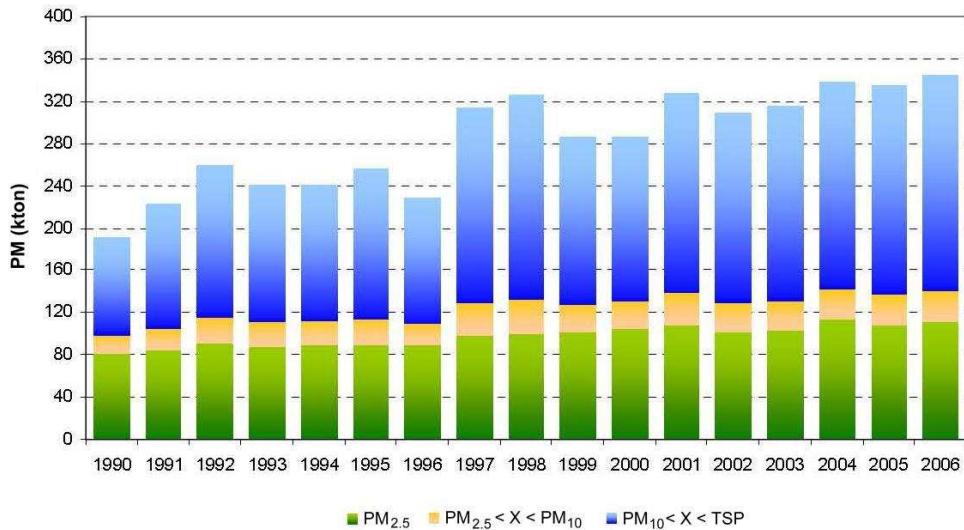


Figure 2.2 Evolution of PM_{2.5}, PM₁₀ and TSP emissions in Portugal between 1990 and 2006 (adapted from CCDRN, 2009).

Figure 2.3 shows the evolution of annual PM concentration for the Portuguese northern region: (a) PM₁₀ at traffic sites (between 1999 and 2006); (b) PM₁₀ at background sites (between 1999 and 2006); and (c) PM_{2.5} at traffic and background sites (between 2004 and 2006). Controversially with the increase in emissions, a decline on concentrations was observed since 1999, however with a tendency to maintain the levels in the last years. A peak was observed generally for the sites in and close to Oporto city (especially at *Antas*) in 2001 due to civil construction operations of huge dimension that occurred at this city (CCDRN, 2008). It is important to refer that the concentrations of PM₁₀ are in general not significantly different at traffic and background sites, enhancing the significance of regional transport. This is not the case of *Lamas*, *Sra. Minho* and *Horto* which are considered remote background sites. Concerning PM_{2.5}, it is clear the higher levels at the traffic site than at the remote background ones.

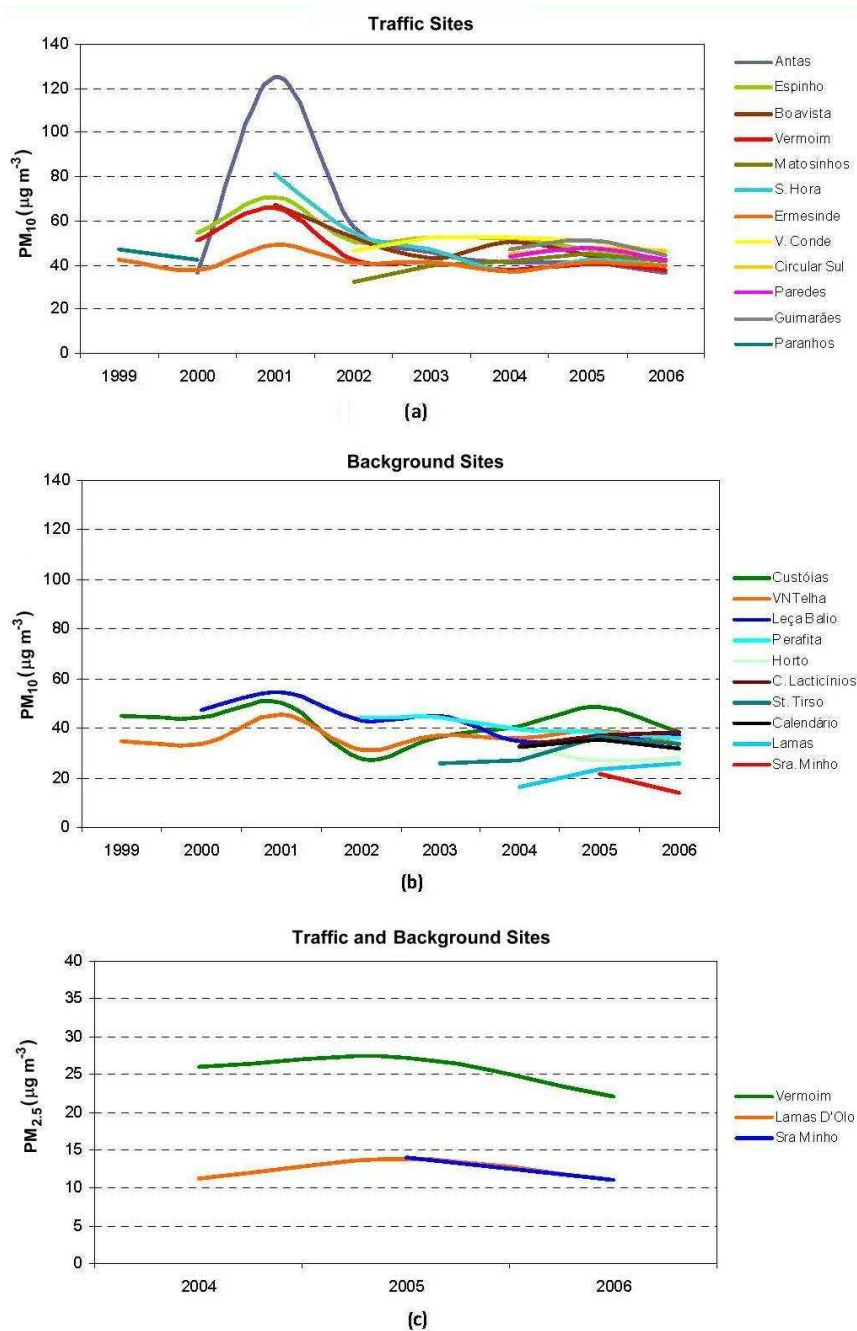


Figure 2.3 Evolution of annual PM average concentrations in northern Portugal: (a) PM₁₀ (between 1999 and 2006) at traffic sites; (b) PM₁₀ (between 1999 and 2006) at background sites; and (c) PM_{2.5} (between 2004 and 2006) at one traffic site (green line) and two remote background sites (orange and blue lines) (adapted from CCDRN, 2008).

2.2.2 Gaseous Pollutants

A large variety of gaseous substances is emitted to the atmosphere from both anthropogenic and natural sources (Godish, 2004). Gaseous pollutants are those capable of passing through filters and can rapidly pass into the respiratory system (WHO, 2006).

The major groups of gaseous air pollutants, due to their historical importance, concentration and overall effects on plants and animals (including people) are sulphur dioxide (SO_2), carbon monoxide (CO), volatile organic compounds (VOC), nitrogen oxides (NO_x), which represent the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2), and ozone (O_3).

Sulphur Dioxide

SO_2 is a colourless gas, soluble in water and with a strong pungent odour at high concentrations (detected at 0.9 mg m^{-3}). This gas can be released directly into the atmosphere by natural sources, such as volcanoes or as the oxidation product of the dimethyl sulphide released by oceanic phytoplankton. Anthropogenic formation of SO_2 is generally due to the combustion of fuels containing sulphur (oil, coal and natural gas) both for domestic heating and motor vehicles. Power stations burning coal or oil, industrial combustion plants and sulphuric acid works, though often fitted with flue gas desulfurization technology designed to limit SO_2 releases, discharge concentrated plumes of pollution which can lead to highly elevated ground-level concentrations over quite short periods (Colls, 2002; WHO, 2006).

Oxidation of SO_2 , especially at the surface of particles in the presence of metallic catalysts, leads to the formation of sulphurous and sulphuric acids. Neutralization, by ammonia, leads to the production of bisulphates and sulphates. In recent years the use of high sulphur coal for domestic heating has declined in many European countries, being now power generation the predominant source. Thus, cities such as London, which were once heavily polluted, have continued to reduce the levels of SO_2 . The use of tall chimneys at power stations has led to wider dispersion and dilution of SO_2 . These changes in pattern of usage have led to urban and rural concentrations becoming more similar in the economically developed countries; indeed, in some areas, rural concentrations can even be higher than those in urban areas. In many developing countries, however, the use of high-sulphur coal is increasing in power production, as well as for domestic heating and cooking, and ground-level SO_2 concentrations remain at very high levels (WHO, 2006, Harrison, 1999; Seinfeld and Pandis, 2006).

Also in most North America and in many locations in Asia, levels of SO_2 have markedly decreased. The highest SO_2 concentrations are being recorded in some of the megacities in developing countries, although some large urban areas have quite low concentrations. While typical annual average concentrations of SO_2 in urban areas in developing countries are $40\text{--}80\ \mu\text{g m}^{-3}$, those in North America and Europe are $10\text{--}30\ \mu\text{g m}^{-3}$, and in cities in the European Union (EU) are $6\text{--}35\ \mu\text{g m}^{-3}$. In Africa some of the urban areas, especially industrial ones, still experience high concentrations of SO_2 . Also, some of the heavily industrialized areas in Europe may still be experiencing high levels of SO_2 , such as the north-western corner of the Russian Federation, close to large primary smelters, where daily concentrations of SO_2 exceed $1000\ \mu\text{g m}^{-3}$ (WHO, 2006).

In Portugal, SO_2 emissions have been decreasing in the last years, due to the growing use of less sulphurous substances and also because industry moves towards the use of natural gas instead of other more pollutant combustibles. Figure 2.4 represents the evolution of national emissions of SO_2 between 1990 and 2006 compared with the emission ceiling for 2010 (Directive 2001/81/EC, *Decreto-Lei* 193/2003).

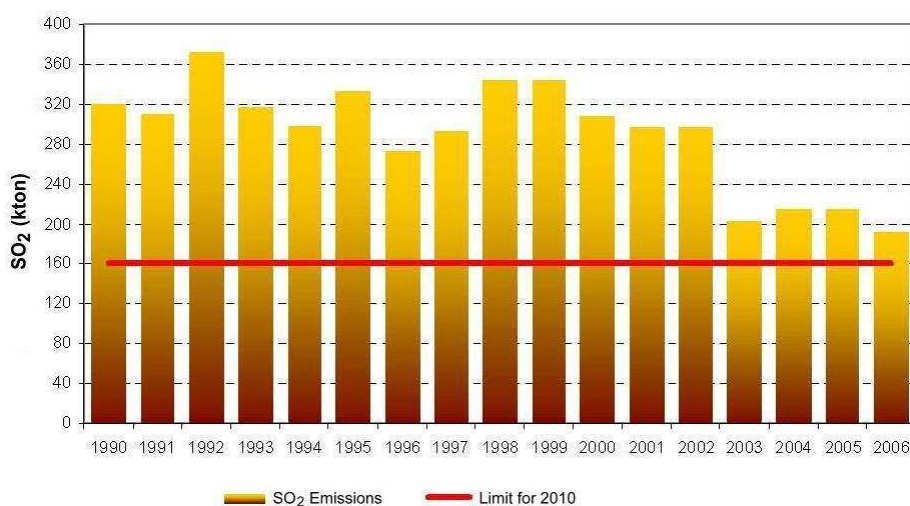


Figure 2.4 Evolution of SO_2 emissions in Portugal between 1990 and 2006 compared with the limit for 2010 (adapted from CCDRN, 2009).

There was a decrease in the emissions, although they continued above emissions ceiling for 2010 (Directive 2001/81/EC, *Decreto-Lei* 193/2003). The reduction in the emission had a consequent effect in the average concentrations measured in the air. Figure 2.5 shows the

annual average concentrations of SO_2 in northern Portugal for (a) traffic sites between 1995 and 2006 and (b) background sites between 1999 and 2006.

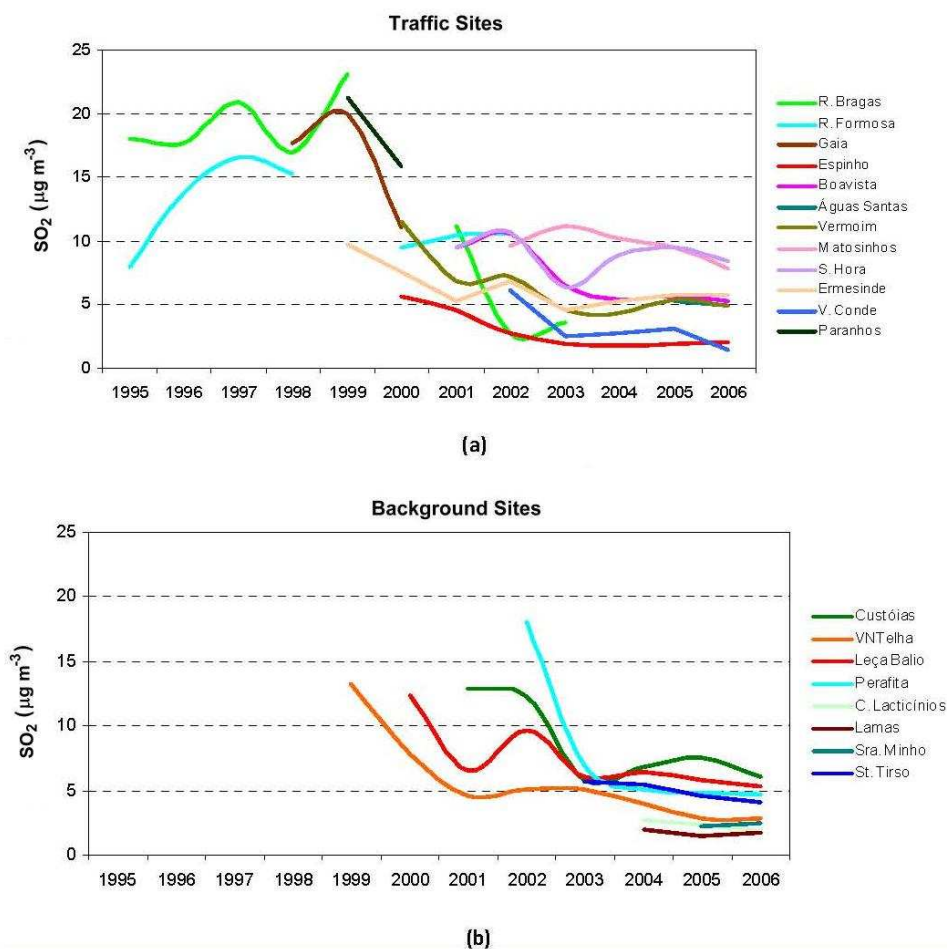


Figure 2.5 Evolution of annual SO_2 average concentrations in northern Portugal: (a) traffic sites between 1995 and 2006 and (b) background sites between 1999 and 2006 (adapted from CCDRN, 2008).

Levels of SO_2 decreased until 2003 and afterwards can be considered stable. In general, the concentrations were low for all sites (traffic and background).

Carbon Monoxide

CO is a colourless, odourless and tasteless gas that is poorly soluble in water and has a slightly lower density than air. In the human body, it reacts readily with haemoglobin to form carboxyhaemoglobin. Small amounts of CO are also produced endogenously. CO

exposure is still one of the leading causes of unintentional and suicidal poisonings, and it causes a large number of deaths annually both in Europe and in the United States (US) (WHO, 2000; Godish, 2004).

The annual global emissions of CO into the atmosphere have been estimated to be as high as 2600 million tonnes, of which about 60% are from human activities and about 40% from natural processes.

Some widespread natural non-biological and biological sources, such as plants, oceans and oxidation of hydrocarbons, give rise to the background concentrations outside urban areas. Anthropogenic emissions of CO are mainly from incomplete combustion of carbonaceous materials. The largest proportion of these emissions is produced as exhausts of internal combustion engines, mainly by gasoline powered vehicles. Other common sources include various industrial processes, power plants using coal, and waste incinerators. Petroleum-derived emissions have greatly increased during the past few decades. In various indoor environments, space heaters fuelled with oil, gas or kerosene, gas stoves and some other combustion appliances, and tobacco smoking cause significant emissions of CO (Holman, 1999; Maynard and Waller, 1999; WHO, 2000).

Major sink processes of CO are uptake by soil microorganisms and reaction with atmospheric hydroxyl (OH) radicals, affecting the tropospheric concentrations of O₃. For each molecule of CO oxidized, one molecule of O₃ is formed. As such, oxidation of CO in the troposphere is an important (but low-level) source of O₃ (USEPA, 2000; Godish, 2004).

Global background concentrations of CO range between 0.06 mg m⁻³ and 0.14 mg m⁻³. During the early 1980s, there was an annual 1-2% increase in nonurban tropospheric concentrations of CO, while between 1989 and 1992 concentrations began declining rapidly. The ambient concentrations measured in urban areas depend greatly on the density of combustion powered vehicles, and are influenced by topography and weather conditions. In the streets, the CO concentration varies greatly according to the distance from the traffic; in large European cities, 8-hour average concentrations are generally lower than 20 mg m⁻³ with short peaks below 60 mg m⁻³ (WHO, 2000).

In Portugal CO emissions had an overall decrease of 20% between 1990 and 2006, Figure 2.6.

Generally, a decrease was also noticed in the average concentrations between 1990 and 2003 in northern Portugal, both in traffic and background sites, becoming relatively stable in

the last 4 years, Figure 2.7. The concentrations at traffic sites are considerably higher than those at background, confirming the traffic influence in the emissions of this pollutant.

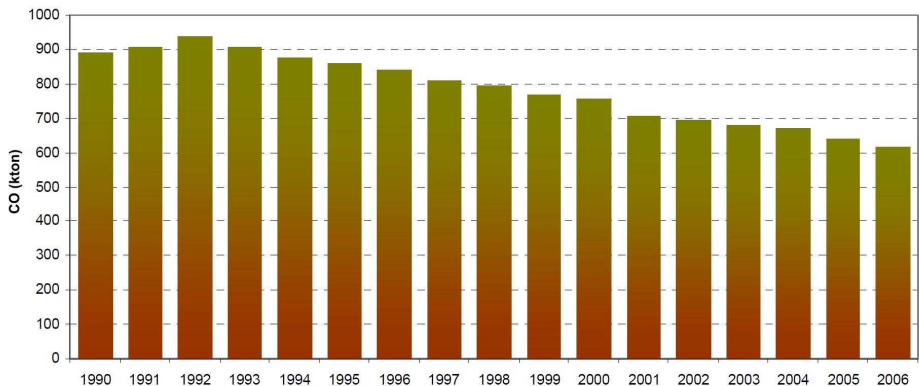


Figure 2.6 Evolution of CO emissions in Portugal between 1990 and 2006 (adapted from CCDRN, 2009).

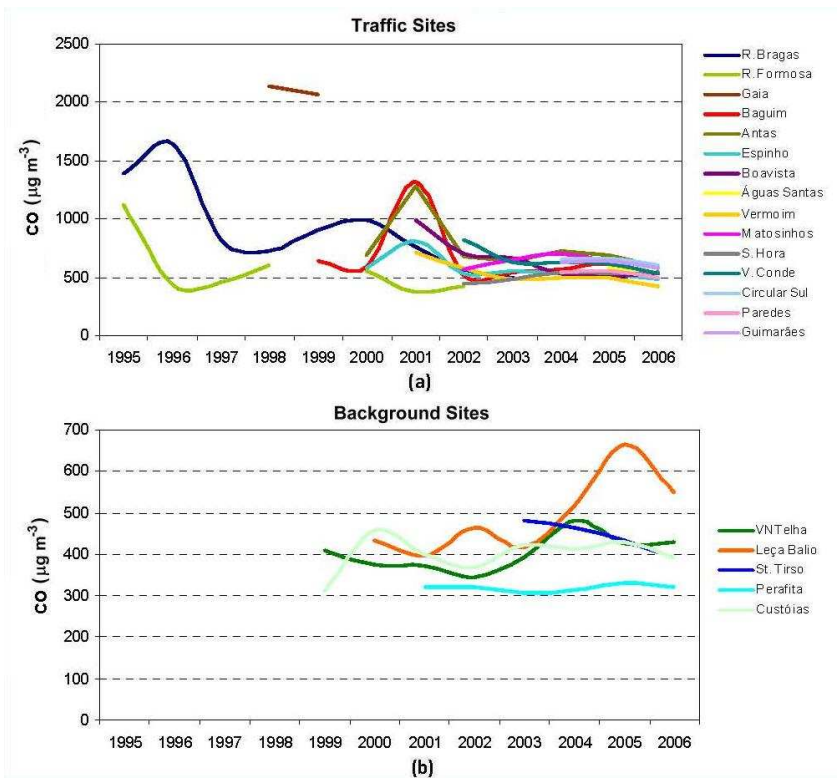


Figure 2.7 Evolution of annual CO average concentrations in northern Portugal: (a) traffic sites between 1995 and 2006 and (b) background sites between 1999 and 2006 (adapted from CCDRN, 2008).

Volatile Organic Compounds

The general category of VOC includes methane (CH_4) and non-methane hydrocarbons (NMHC), such as alkanes, alkenes and aromatics; halocarbons, such as trichloroethylene; and oxygenates such as alcohols, aldehydes and ketones (Colls, 2002; Holman, 1999).

Historically, measurements of atmospheric hydrocarbons (HC) concentration have been expressed in terms of the non-methane component, because the CH_4 concentration was regarded as a stable natural background. However, it is now recognised that CH_4 is also a man-made pollutant from intensive animal and rice production, that the concentration is increasing globally, and that it plays an important role in O_3 photochemistry. Within the VOC, HC have received the most attention for their role in photochemistry. The VOC protocol of the UNECE identifies three groups of VOC according to their potential for photochemical O_3 production. Group I (highest potential) includes alkenes, aromatics, low alkanes and isoprene; Group II ethanol and high alkanes; and Group III methanol, acetone, benzene and acetylene (Colls, 2002). More recently, the range of molecules of concern has expanded to include other groups such as chlorinated and oxygenated HC. NMHC can undergo many transformations in the atmosphere, most of which involve reactions with nitrate (NO_3) or OH radicals, or with O_3 ; during these reactions, the NMHC may form more stable or soluble species, or may become converted from gas to particle or vice versa (Colls, 2002; Holman, 1999).

Plants synthesise many organic molecules as an essential part of their biochemistry. Vegetation, mostly forests, emits large amounts of VOC when temperatures are high: i) HC including hemiterpenes such as isoprene (C_5H_8), monoterpenes ($\text{C}_{10}\text{H}_{16}$) such as α -pinene and β -pinene, sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) such as humulene; and ii) oxygenated compounds with one carbon atom such as methanol (CH_3OH) and formaldehyde (HCHO), with two carbon atoms such as ethanol ($\text{C}_2\text{H}_5\text{OH}$), and with three carbon atoms such as acetone (CH_3COCH_3). Some of these VOC are released to the atmosphere: the turpentine smell characteristic of pine forests, the monoterpenes from mint and the aldehydes from mown grass are well-known examples.

Isoprene is the most reactive and has been found to play a significant role in O_3 formation in the US. Although the EU emission inventory includes natural sources, there is considerable uncertainty over the results obtained in predicting O_3 formation.

Anthropogenic VOC emissions occur during processes such as painting (evaporation of solvents), oil production (flaring and venting of gas), oil refining (flaring and fugitive

emissions), distribution of oil or refinery products (evaporation from storage, displacement losses when venting tanks), dry cleaning (final drying of clothes), use of aerosol sprays (both in the product and from the propellant), inefficient combustion of bituminous coal in domestic grates, production of alcoholic drinks (breweries and distilleries) and arable farming (crop growing, silage manufacture, sludge spreading) (Colls, 2002). Poliaromatic hydrocarbons (PAH) are formed by more than one ring of benzene and are solids under ambient atmospheric conditions. The best-known compound in this group is benzo- α -pyrene, which contains five benzene rings. The PAH are produced in the combustion chemistry of organic fuel and materials and are commonly found as constituents of atmospheric aerosol (Godish, 2004).

The EU-27 Member States have, in general, made good progress towards reducing emissions in line with their obligations under the National Emission Ceilings Directive (NECD). However, Belgium, Denmark, Greece, Hungary, Portugal and Spain have emissions still significantly above their respective emission ceilings and thus must make significant reductions over the coming years if they are to comply with the NECD (EEA, 2007b).

Figure 2.8 shows the evolution of national emissions of non-methane volatile organic compounds (NMVOC) between 1990 and 2006, compared with the emissions ceiling for 2010 (Directive 2001/81/EC, *Decreto-Lei* 193/2003). In Portugal emissions are somehow constant since 1990 and always exceeding the emission ceiling for 2010, being generally above 300 kton.

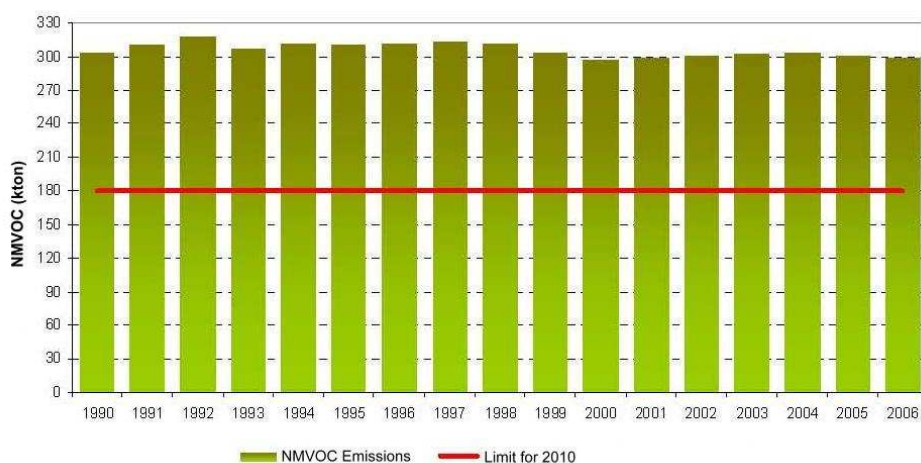


Figure 2.8 Evolution of NMVOC emissions in Portugal between 1990 and 2006 and comparison with the limit for 2010 (adapted from CCDRN, 2009).

Nitrogen Oxides

Many chemical species of NO_x exist, but the air pollutant species of most interest from the point of view of human health are NO and NO_2 . NO is a colourless, odourless, tasteless, relatively nontoxic gas. It is produced naturally in soil through biological nitrification and denitrification processes and as a result of biomass burning, lightning and oxidation of ammonia by photochemical processes. It is also transported from the stratosphere into the troposphere. Anthropogenically it is produced in high-temperature combustion processes. NO concentrations are not generally reported separately from those of NO_2 , because it spontaneously produces the dioxide when exposed to air. Studies indicate that NO concentrations have a peak during the early-morning rush hour (6h to 9h) and then are rapidly depleted by oxidation to NO_2 and other processes (Godish, 2004). NO_2 is a reddish brown gas with a characteristic pungent odour being a strong oxidant that reacts with water to produce nitric acid (HNO_3) and NO. NO_2 is an important atmospheric trace gas not only because of its health effects but also because: (a) it absorbs visible solar radiation, contributing to reduce atmospheric visibility; (b) it has a potentially direct role in global climate change; (c) it is, along with NO, a chief regulator of the oxidizing capacity of the free troposphere by controlling the build-up and fate of radical species, including OH radicals; and (d) it plays a critical role in determining O_3 concentrations in the troposphere because the photolysis of NO_2 is the only key initiator of the photochemical formation of O_3 , whether in polluted or in non-polluted atmospheres (WHO, 2006).

Natural sources include intrusion of stratospheric NO_x , bacterial activity in soils, volcanic action and lightning. The major sources of anthropogenic emissions of NO_x into the atmosphere are the combustion processes in stationary sources (heating, power generation) and in mobile sources (internal combustion engines in vehicles and ships). Indoor sources include tobacco smoking and the use of gas-fired appliances and oil stoves (WHO, 2006; Godish, 2004).

NO_2 can be produced in a number of atmospheric processes. These include the relatively slow, direct oxidation of NO (Reaction 2.1) and more rapid photochemical reactions involving O_3 , RO_2 radicals, and hydrogen species, such as hydrogen peroxide (H_2O_2) and OH and hydro-peroxile (HO_2) radicals, as follows:





Sink processes for NO and NO₂ involve chemical reactions that convert NO to NO₂ and NO₂ to HNO₃, being the latter the major sink process:



NO₂ is also converted to HNO₃ by night-time reactions involving O₃:



Reactions between O₃ and NO₂ produce NO₃ radical that subsequently reacts with NO₂ to produce N₂O₅, which reacts rapidly with H₂O vapour to produce HNO₃. This acid is also produced in reactions involving NO₃ radical and formaldehyde (HCHO) or HC radicals:



NO₃ radical plays a significant role in night-time oxidation of biogenically produced VOC such as isoprene and pinenes, as referred above. NO₃ radical is rapidly photolyzed at sunrise by a shift in the equilibrium between NO₂, NO₃ radical and N₂O₅ toward NO₂. HNO₃ remains in the gas phase until it reacts with NH₃ to form ammonium salts:



Nitric acid and its salts are removed from the atmosphere by wet and dry deposition processes. In the lower troposphere the atmospheric lifetime of nitrates is approximately one week. Because of their low solubility, NO and NO₂ are readily transported to the upper troposphere, with the subsequent production of HNO₃ on reaction with OH radical. HNO₃ produced in the upper troposphere is not subject to dry deposition, and generally not to wet deposition. It can be transformed to NO₂ by photolysis and, to a lesser extent, oxidation by OH radical:



Because these reactions are relatively slow, HNO₃ serves as a reservoir species and carrier for NO_x in atmospheric transport (Godish, 2004). Reactions involving O₃ will be further discussed in Part II.

Over the past few decades an increase in emissions of NO_x resulting from the increase in traffic activity has been noticed (Williams, 1999). Annual average NO_2 concentrations in urban areas throughout the world are generally in the range of $20\text{--}90\ \mu\text{g m}^{-3}$. Diurnal variations in NO_x concentration are also to be expected because of the season of the year, variations in traffic flow and atmospheric dispersion. Winter NO is around twice summer NO, but NO_2 does not vary much with season; short-term episodes of high NO_2 lasting from a few hours to a few days, can occur in either summer or winter via different mechanisms. In the summer, high NO_2 levels are formed by rapid photochemistry, and are therefore associated with low NO levels. In the winter, high NO concentrations are observed due to the trapping of emissions beneath temperature inversions (Colls, 2002). Typical daily patterns include a low background level of NO_2 , upon which is superimposed one or two peaks of higher levels that correspond to rush-hour traffic emissions of NO_x . Several studies have measured ambient concentrations in road tunnels in Europe and the US and have shown that personal exposures in vehicles using these tunnels can be high (ranging $179\text{--}688\ \mu\text{g m}^{-3}$). A particularly severe NO_x smog occurred in London between 12 and 15 December 1991: the average NO_2 concentration were around $280\ \mu\text{g m}^{-3}$ with a peak rising to around $800\ \mu\text{g m}^{-3}$, which stood out from the typical concentrations that year ($57\text{--}95\ \mu\text{g m}^{-3}$). NO concentrations were of around $2290\ \mu\text{g m}^{-3}$; 160 deaths could be attributed to the incident (Colls, 2002).

According to the emissions report of the northern region of Portugal, based on 2003 data, this region contributes with about 28% of the total national emissions. Figure 2.9 shows the evolution of NO_x emissions in Portugal between 1990 and 2006, compared with the emissions ceiling for 2010 (Directive 2001/81/EC, *Decreto-Lei* 193/2003).

Portugal emissions were higher between 1999 and 2002 and decreased since 2003, however still exceeding the emissions ceiling imposed for 2010. Figure 2.10 shows the NO_2 concentrations in the northern region of Portugal for (a) traffic sites between 1995 and 2006 and (b) background sites between 1999 and 2006.

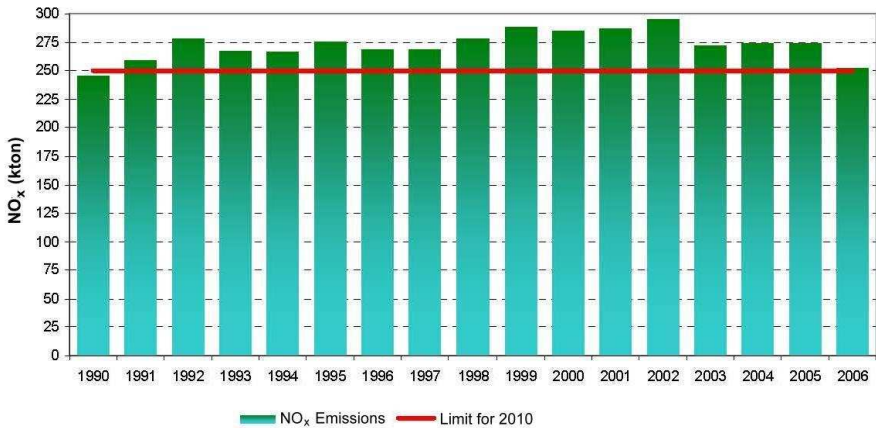


Figure 2.9 Evolution of NO_x emissions in Portugal between 1990 and 2006 and comparison with the limit for 2010 (adapted from CCDRN, 2009).

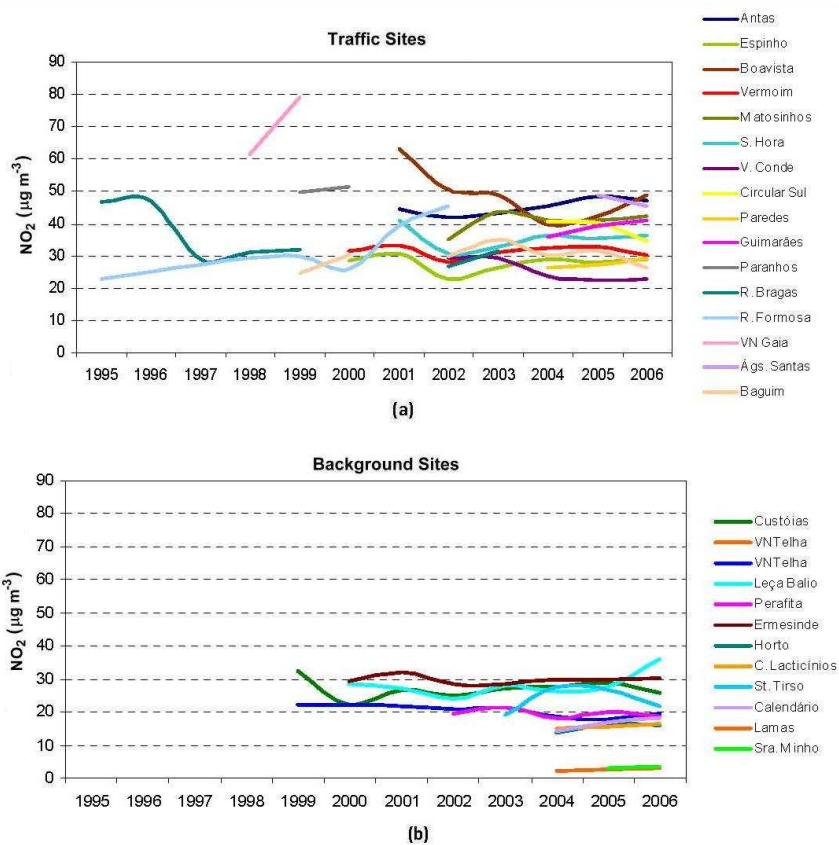


Figure 2.10 Evolution of annual NO₂ average concentrations in northern Portugal: (a) traffic sites between 1995 and 2006 and (b) background sites between 1999 and 2006 (adapted from CCDRN, 2008).

NO₂ concentrations maintained in general the same behaviour over the last few years, being between 20-50 µg m⁻³ in the traffic sites and between 3-35 µg m⁻³ in the background sites (CCDRN, 2008).

Ozone

O₃ is a colourless gas and a strong oxidizing agent. As already referred, O₃ is a normal constituent of the atmosphere, with peak concentrations in the middle stratosphere. As a consequence of anthropogenic activities, O₃ represents two major and distinct environmental concerns: in the stratosphere, because of its concentration decrease and near surface, because of its concentrations increase (Godish, 2004). It differs from the other tropospheric pollutants because it is of secondary origin (it is formed in the atmosphere rather than being emitted). Major sources of ground-level O₃ concentrations are stratospheric intrusions, particularly during spring months, and photochemical processes. The latter involve a complex series of reactions relating the action of sunlight with NO₂ and HC. This pollutant photochemical formation will be discussed in more detail in Part II. Major sink processes of O₃ are photochemical processes, transport by wind and deposition (USEPA, 2006 Colls, 2002; Godish, 2004).

Ground-level O₃ concentrations have a seasonal pattern, having its higher values in summer. The daily profile also presents a pattern following the daily solar cycle and also the variations of anthropogenic activities. Figure 2.11 shows the daily profile for traffic, industrial and background sites of northern Portugal in 2006.

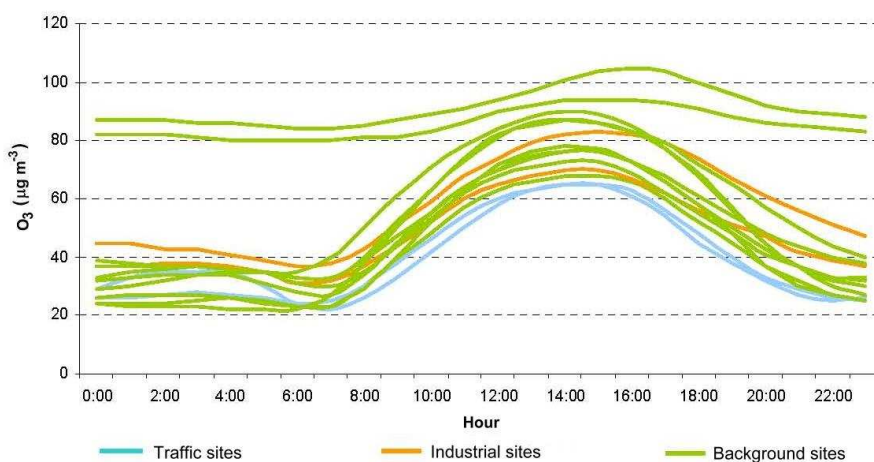


Figure 2.11 Daily profile of O₃ for traffic, industrial and background sites of northern Portugal in 2006 (adapted from CCDRN, 2008).

Several studies have concluded that O_3 concentrations are clearly higher at rural areas than at urban ones (Bayer-Oglesby et al., 2004; Dueñas et al., 2004; Syri et al., 2001). Figure 2.11 shows a similar tendency, with background sites having higher concentrations mainly due to lower NO_x concentrations. The two background sites with the highest concentrations have specific behaviours probably due to other factors that increase even more the concentrations, such as altitude, vertical or horizontal transport and natural emissions from vegetation. Both seasonal and daily cycles of O_3 will be discussed in more detail in the next chapter.

2.3 Human Exposure

The basic concepts used in exposure assessments were developed in the early 1980s by Duan and Ott (Monn, 2002). Their introduction of the term human exposure emphasises that the human being is the most important receptor of pollutants in the environment. Ott elaborated a system of definitions for the term exposure and defined exposure as "an event that occurs when a person comes in contact with the pollutant" (Monn, 2002). This definition refers to a contact with a pollutant, but it is not necessary that the person inhales or ingests the pollutant. Once the pollutant has crossed a physical boundary (e.g. skin, alveolar epithelial cells), the concept of dose is used. Dose is the amount of material absorbed or deposited in the body for an interval of time and is measured in units of mass (or mass per volume of body fluid in a biomarker measurement) (WHO, 2006; Monn, 2002).

An exposure assessment evaluates the relationship between the source of a pollutant and its health effect. Figure 2.12 describes the route of a contaminant from its source into the body.

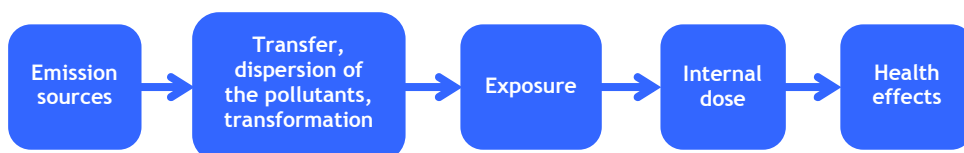


Figure 2.12 Sequence of exposure from source to health effects.

Personal exposure measurements can be performed directly, by determining levels of individual exposure, using a personal passive sampler or through a biological marker, or indirectly, through stationary monitors or determined by models (Monn, 2002). The assessment of exposure data from a large number of individuals (necessary to infer for the

general population) is an expensive undertaking so, generally health impact studies use pollutant concentrations in ambient air as exposure data.

Questionnaires are also important tools for assessing exposure. They can be used for identifying contact with emissions, socioeconomic status and other helpful data for a complete understanding of the exposure.

A difficulty in an exposure assessment for air pollutants is related to the fact that pollutants are present as mixtures, making the evaluation of exposure effects to one specific pollutant complex, because co-pollutants can be potential confounders. Confounding factors include also the interaction between pollutants and meteorological variables (temperature and relative humidity), other exposures (occupational, smoking, and indoor air pollution) and infectious disease. Such interactions may, in part, explain differences observed between epidemiological and toxicological studies. Other confounding factors are individual sensitivity, age, existing disease, gender, race, socioeconomic status, tobacco smoking and lifestyle (Godish, 2004; Monn, 2002).

2.4 Health Effects

A 2001 review from the Organisation for Economic Co-operation and Development (OECD) estimated that 5-8 % of all health problems in the high- and middle-income OECD countries, and more than 13 % in non-OECD countries were environment-related (EEA, 2005b; EEA, 2007a).

Exposure to air pollution has been related with the most varied adverse health outcomes. The impacts of air pollution on human health can be expressed in terms of a reduction in average life expectancy, additional premature deaths and hospital admissions, and increased use of medication and days of restricted activity (EEA, 2007a). The proportion of the exposed population affected by the less severe health effects, such as subclinical and asymptomatic events, is much larger than that affected by more severe events such as emergency admission to hospital and death. Thus, the frequency of occurrence of a health effect associated with exposure to air pollution is inversely related to its severity (Figure 2.13).

Air pollution principally affects the respiratory, cardiovascular and nervous systems. The respiratory system is the principal route of entry for air pollutants, however, any system can be affected.

Two important measures of diseases in populations are incidence and prevalence. The former is the number of newly reported cases in a population over time and the latter the total number of cases in a population at a particular point in time (WHO, 2006).

Short-term as well as long-term effects of air pollution are presented in Table 2.1 (WHO, 2006).

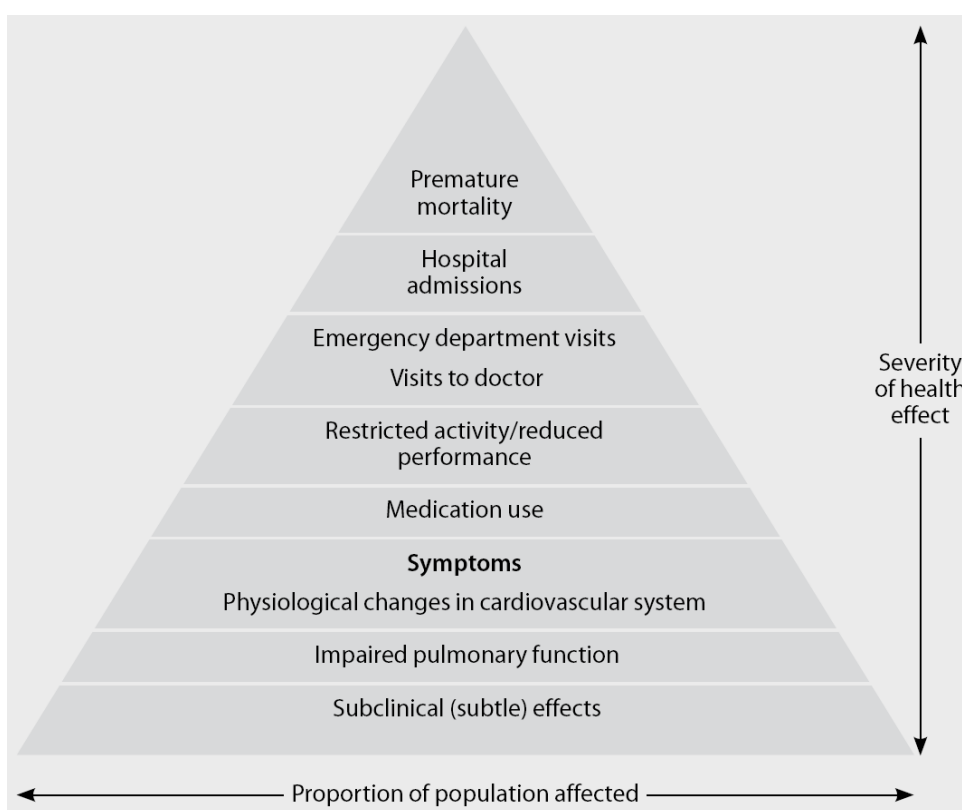


Figure 2.13 Pyramid of health effects associated with air pollution (WHO, 2006).

Data for health impact assessment come from experimental (clinical and toxicological) and epidemiological studies. Clinical and epidemiological studies focus on humans and

toxicological approaches are based on studies conducted on animals or simpler cellular systems. Clinical studies provide evidence on the effects of air pollutants under reproducible laboratory conditions. Ethical considerations limit human exposure to levels of air pollutants which do not have irreversible effects. Epidemiological studies focus on the distribution and determinants of conditions or events related to health in specific populations.

In air pollution epidemiology there are three very important types of approaches: cohort, case-control and cross-sectional studies.

Table 2.1 Health effects of air pollution (WHO, 2006).

Effects attributed to short-term exposure
Daily mortality
Respiratory and cardiovascular hospital admissions
Respiratory and cardiovascular emergency department visits
Respiratory and cardiovascular primary care visits
Use of respiratory and cardiovascular medications
Days of restricted activity
Work absenteeism
School absenteeism
Acute symptoms (wheezing, coughing, phlegm production, respiratory infections)
Physiological changes (e.g. lung function)
Effects attributed to long-term exposure
Mortality due to cardiovascular and respiratory disease
Chronic respiratory disease incidence and prevalence (asthma, chronic obstructive pulmonary disease (COPD), chronic pathological changes)
Chronic changes in physiologic functions
Lung cancer
Chronic cardiovascular disease
Intrauterine growth restriction (low birth weight at term, intrauterine growth retardation, small for gestational age)

Cohort studies are in general longitudinal, following populations and subpopulations to relate different exposures and diseases to specific changes induced in the population and subpopulations over a specified period. These studies can be either prospective (a group is

identified and then followed for years after), or retrospective (a group is identified and the investigators try to determine which risk factors and exposures appear to be associated with the present health status of the group) (WHO, 2006; Morgenstern and Thomas, 1993).

In case-control studies researchers identify one group of people who already have the health outcome (cases), and another group of people who do not have the outcome (controls). The two groups are studied to determine the extent to which an exposure was more prevalent in the past history in comparison to the other group, thus being retrospective. These studies can be either longitudinal (following the population through a certain period) or cross-sectional (assessing the population in one determined period) (Morgenstern and Thomas, 1993).

A cross-sectional study involves a single determination of disease prevalence in a population. Usually, exposure is ascertained simultaneously with the disease, and different exposure subpopulations are compared with respect to their disease prevalence (Morgenstern and Thomas, 1993).

In epidemiological studies two parameters are fundamental to evaluate the association between exposure and disease: the relative risk or risk ratio (RR) and odds ratio (OR). Both RR and OR compare the relative likelihood of an event occurring between two distinct groups, exposed and unexposed. The risk is the number of persons having disease divided by the total population and the odds are the number of persons having disease divided by the number of persons not having disease. The main differences between RR and OR are: i) when the outcome is common, RR is constrained but OR are not; and ii) for OR the conclusions are identical either considering the outcome as the occurrence of an event, or the absence of the event, which does not happen with RR. When the outcome is rare, the OR is the same as the RR. Ratios of 1.0 indicate no association; ratios higher than 1 indicate positive associations and ratios less than 1.0 indicate decreased risk and protective effects (Kirkwood and Sterne, 2003).

Particulate air pollution was one of the first types of pollution demonstrated to have serious health effects, thus having greatest evidence of consistent short and long-term health effects even at low ambient levels. The weight of evidence from numerous epidemiological studies on short-term responses indicated that an increase of approximately $10 \mu\text{g m}^{-3}$ in daily PM_{10} average concentration is associated with an increase of approximately 0.9% in daily mortality, related with cardiovascular system and of 1.3% related with respiratory system. Also increased hospitalizations and related health care visits are significant for

various respiratory diseases and, to a lesser extent, for cardiovascular disease. Increased symptom prevalence including lower respiratory system symptoms, asthma, and cough were associated with PM_{10} as well (WHO, 2006).

Studies on long-term exposure to $PM_{2.5}$, showed an association with different cardiac and pulmonary health effects. Total mortality appears to increase approximately 2 to 4% for every $5 \mu g m^{-3}$ increase in $PM_{2.5}$, associated in a higher extent with cardiopulmonary system. Also significant increases in respiratory disease (bronchitis) and small decreases in lung function have been reported. Though strong epidemiological evidence links both acute and chronic PM exposures to significant health effects; toxicological mechanisms for these effects are less clear (WHO, 2006).

SO_2 available information about acute and chronic effects is mostly from toxicological studies. Inhalation is the only route of exposure to SO_2 that is of interest regarding its effects on health. SO_2 solubility characteristic turns its removal from the upper respiratory system efficient, thus less than 1% of the SO_2 inhaled reaches alveoli. Exposure of the lower airways and alveoli increases during exercise and mouth breathing. The major physiological effects of SO_2 are changes in mechanical function of the upper airways, including an increase in nasal flow resistance and a decrease in nasal mucus flow rate. There is some evidence that exposures may cause chronic bronchitis. Studies performed on asthmatic individuals have shown that after briefly exposure to high SO_2 concentrations they exhibit acute responses characterized by bronchoconstriction (airway narrowing) with clinical symptoms of shortness of breath and wheezing. Such responses also occur at low SO_2 levels during moderate exercise, being asthmatic children and adults at higher risk. Available epidemiological data do not show any evidence of excess on asthma mortality associated with SO_2 exposures in urban areas (Godish, 2004; WHO 2006).

Exposure to CO may be lethal at very high concentrations, with death as a result from hypoxia. At lower concentrations CO may cause neurological-type symptoms, including headache, fatigue, nausea, and, in some cases, vomiting. CO poisoning is due to exposures that are considerably higher than those that occur in ambient air of cities. Generally, the mechanism of CO toxicity is tissue hypoxia which results from the favoured bonding of CO to haemoglobin forming carboxyhaemoglobin. CO has an haemoglobin affinity 240 times that of oxygen. Effects are particularly severe at tissues where partial pressures of oxygen are already low. The quantity of carboxyhaemoglobin formed depends on a variety of factors, such as, the concentration and duration of CO exposure, temperature, health status, and metabolism of the individual exposed. Effects of CO on the cardiovascular system are well-

documented; nevertheless some studies have been confounded by the effects of cigarette smoking. There has been relatively little recent research into the potential health effects of low level CO exposure (Godish, 2004; Maynard and Coster, 1999).

NMHC causes two major exposure and health concerns. The most important one is related with being a precursor of O₃. Generally, exposures to individual NMHC species are relatively low and health risks on a community-wide basis are considered to be small to negligible. Many NMHC are regulated as hazardous or toxic air pollutants, such as benzene. Many are suspected human carcinogens, mutagens, teratogens, and some are irritants and neurotoxic. NMHC such as the aldehydes and acrolein are strong irritants and exposure to these substances, individually or collectively, may cause eye, nose, throat, and sinus irritation. Such symptoms are transitory, resulting in no apparent long-term adverse health effects. PAH are of high health concern; these compounds are carcinogenic, with benzo- α -pyrene being one of the most potent carcinogens and common PAH found in aerosol samples (Godish, 2004).

NO is though to cause no health risk at ambient exposure levels, because it is a relatively non-irritating gas, being its major problem the almost instantaneous oxidization to NO₂, which is a much more toxic gas. NO₂ is less soluble than SO₂, thus passes into the pulmonary region, by inhalation. Approximately 70-90% of NO₂ inhaled can be absorbed from the respiratory tract of humans, and this increases further with exercise (Godish, 2004). Experimental studies have shown that NO₂ or its chemical products can remain within the lung for prolonged periods. HNO₃ and nitrous acids (HNO₂) or their salts have been observed in the blood and urine after exposure to NO₂. Evidence from animal toxicological studies indicates that long-term exposure to NO₂ at concentrations above current ambient concentrations has adverse effects (pathological changes have included destruction of cilia, alveolar tissue disruption, and obstruction of respiratory bronchioles). In human studies, NO₂ has been associated with adverse health effects even at low ambient concentrations. Exposure to high NO₂ levels, resulting from occupational exposure may have adverse effects such as pulmonary edema which it is only visible hours after exposure has ended (WHO, 2006; Godish, 2004). Asthmatics are the most reactive group to NO₂ studied to date, although controlled studies on the effects of short-term exposure on the symptoms and severity of asthma have not led to clear findings (WHO, 2006; Ackermann-Liebrich and Rapp, 1999).

Short-term exposure to high O₃ concentration includes effects on the pulmonary and cardiovascular systems, counting evidence of both morbidity and mortality. Long-term

exposure to relatively low levels is also of concern, because it can lead to the development of atherosclerosis and asthma, reduction in lung function and life expectancy (WHO, 2006). The health effects of this pollutant will be discussed with more detail in Part IV.

There is a need for more research, particularly into the quantification of both individual and public health effects of air pollution, to guide those who need to control pollution.

2.4 National and International Legislation

World Health Organization - Air Quality Guidelines

The WHO Regional Office for Europe, in Copenhagen, had undertaken an earlier, highly successful effort at providing very concise assessments of a number of air pollutants considered to pose health and/or environmental threats for European countries. Those assessments, and Air Quality Guidelines (AQG) based on them, were published in 1987 in a WHO publication entitled AQG for Europe, which has found wide use not only in Europe but elsewhere, in helping to provide support for development of air standards in various nations (WHO, 1987). The process employed in producing the AQG was by organizing task groups, during a few years, to review sets of individual chapters dealing with certain categories of pollutants, such as the task group for major air pollutants (PM, O₃, NO₂, CO and SO₂), another for certain inorganic substances and another for certain organic compounds. During the past several years, the process has been repeated, resulting in revised and updated versions of the AQG for Europe published in 2000 and in 2006, including assessment of an expanded list of air pollutants beyond those addressed in the 1987 edition (WHO 2006; WHO, 2000). It is however important to emphasize that the air quality guidelines, above referred as being generated under WHO responsibility, are not air quality standards; rather, the guidelines represent concentrations appropriate for certain averaging times (1-hour, 24-hour, 1-year) recommended by international experts for consideration by national or international authorities in promulgating air quality standards (Grant et al., 1999).

European Union - Europe Environmental Action Programme

The issue of air quality is one of the areas in which the EU has been most active. Since the early 1970s, the EU has been working to improve air quality by controlling emissions of harmful substances into the atmosphere, improving fuel quality, and by integrating

environmental protection requirements into the transport and energy sectors. Thirty years of environment policy has led to a comprehensive system of environmental controls.

The Sixth Environment Action Programme (6th EAP) - “Environment 2010: Our future, Our choice”, effectively set the environmental objectives and priorities that are being an integral part of the strategy of the European Community (EC) for sustainable development, between 2002 and 2012. The programme sets out the major priorities and objectives for environmental policy over the following five to ten years and detailed measures to be taken.

Concerning exposure to air pollution the EU has been acting through: i) EC legislation, ii) work at international level to reduce cross-border pollution, iii) cooperation with sectors responsible for air pollution, iv) national and regional authorities as well as non-governmental organizations; and v) research and development of thematic strategies on air pollution under the title “Clean Air For Europe (CAFE)” (COM (2001) 31 final).

The CAFE initiative has led to thematic strategies setting out the objectives and measures for the next phase of European air quality policy. Its specific objectives, communicated in 2005 (COM (2001) 245 final) are:

- i) to develop, collect and validate scientific information relating to the effects of air pollution, (outdoor air pollution, emission inventories, air quality assessment, emission and air quality projections, cost-effectiveness studies and integrated assessment modelling) leading to the development and updating of air quality and deposition objectives and indicators and identification of the measures required to reduce emissions;
- ii) to support the implementation and review the effectiveness of existing legislation (in particular the air quality daughter directives), to support the decision on information exchange and to support national emission ceilings (as set out in recent legislation) as well as to contribute to the review of international protocols and to develop new proposals as and when necessary;
- iii) to ensure that the measures that will be needed to achieve air quality and deposition objectives cost-effectively are taken at the relevant level through the development of efficient structural links with the relevant policy areas;
- iv) to determine an overall, integrated strategy at regular intervals which defines appropriate air quality objectives for the future and cost-effective measures for meeting those objectives;

v) to widely disseminate the technical and policy information arising from implementation of the programme.

Following its communication on the CAFE programme, the EC has examined whether current legislation is sufficient to achieve the 6th EAP objectives by 2020. This analysis foreseen future emissions and impacts on health and the environment and has used the best available scientific and health information. It showed that significant negative impacts will persist even with effective implementation of current legislation, with PM and ground level O₃ being the principal problems.

Concerning health impacts, the EU assessment concluded that the reduction in life expectancy due to PM_{2.5} would be from 8 to 5.5 months (equivalent to 272 000 premature deaths). For O₃, it was estimated to be around 21 000 cases of premature mortality in 2020. The severe consequences on life quality are even worst for children and elderly, as well as for citizens suffering of asthma and cardiovascular diseases because of their particular vulnerability. In monetary terms, for 2020 the damage to human health alone was estimated between €189 - 609 billion per year.

Considering the conclusions reached, strategies were defined to comply with the 6th EAP objective of attaining “levels of air quality that do not give rise to significant negative impacts on, and risks to human health and the environment” (COM (2005) 446 final). The chosen strategy set health and environmental objectives and emission reduction targets for the main pollutants, to be delivered in stages. By setting objectives to be attained by 2020, EU citizens will be protected from exposure to PM and O₃ in air (PM_{2.5} concentration would be reduced by 75% and ground-level O₃ by 60% from what is technically feasible by 2020). In order to attain these strategic objectives, further initiatives should also be taken indirectly by considering energy, transports and agriculture; current air quality legislation should be simplified and other legislation revised where appropriate (COM (2005) 446 final). Thus, the new Directive on Ambient Air Quality and Cleaner Air for Europe of 21 May 2008 (Directive 2008/50/EC) emerged and entered into force, including the following key elements: i) the merging of most of existing legislation into a single directive (except for the fourth daughter directive) with no change to existing air quality objectives (Directive 96/62/EC, 1-3 daughter Directives 1999/30/EC, 2000/69/EC, 2002/3/EC, and Decision on Exchange of Information 97/101/EC); ii) new air quality objectives for PM_{2.5} including the limit value and exposure related objectives - exposure concentration obligation and exposure reduction target; iii) the possibility to discount natural sources of pollution when assessing compliance

against limit values; and iv) the possibility for time extensions of three years (PM_{10}) or up to five years (NO_2 , benzene) for complying with limit values (based on EC evaluation).

The Member States have 2 years to transpose the new Directive, until then the existing legislation applies. Some provisions of the new Directive such as $PM_{2.5}$ monitoring requirements have to be implemented sooner. It is expected that the provision enabling notifications of postponements or exemptions, in respect of the limit values for PM_{10} , NO_2 or benzene, will be applied before the end of the 2 year transposition deadline. Portugal still has not transposed Directive 2008/50/EC, thus the former legislation still applies:

1. *Decreto-Lei* 276/99 of July 23rd 1999 and its first amendment, *Decreto-Lei* 279/2007, of August 6th 2007 transposed from Council Directive 96/62/EC on ambient air quality assessment and management that is commonly referred to as the Air Quality Framework Directive. It describes the basic principles as to how air quality should be assessed and managed in the Member States listing the pollutants for which air quality standards and objectives will be developed and specified.

2. *Decreto-Lei* 111/2002 of April 16th 2002 transposed from Council Directive 1999/30/EC relating to limit values for SO_2 , NO_2 and NO_x , PM and lead in ambient air and from Directive 2000/69/EC of the European Parliament and of the Council relating to limit values for benzene and CO in ambient air. The former directive was the so-called "First Daughter Directive" and describes the numerical limits and thresholds required to assess and manage air quality for the mentioned pollutants, addressing both PM_{10} and $PM_{2.5}$, but for $PM_{2.5}$ only establishing monitoring requirements. The latter directive was the "Second Daughter Directive" and established the numerical criteria relating to the assessment and management of the pollutant above referred.

3. *Decreto-Lei* 320/2003 of December 20th 2003 transposed from Directive 2002/3/EC of the European Parliament and of the Council relating to O_3 in ambient air. This was the "Third Daughter Directive" and established target values and long term objectives for the concentration of O_3 in air. As already referred, O_3 is a secondary pollutant formed in the atmosphere by the chemical reaction of HC and NO_x in the presence of sunlight. As such, the directive also describes certain monitoring requirements relating to VOC and NO_x in air.

4. *Decreto-Lei* 351/2007 of October 23rd 2007 transposed from Directive 2004/107/EC of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel and PAH in ambient air. This is the "Fourth Daughter Directive" and completes the list of pollutants initially described in the Framework Directive. Target values for all pollutants

except mercury, that only has specified monitoring requirements, are defined, though for PAH, the target is defined in terms of concentration of benzo- α -pyrene which is generally used as a marker substance for PAH.

It should be also referred *Decreto-Lei* 193/2003 of August 22nd 2003 transposed from Directive 2001/81/EC of the European Parliament and of the Council on national emission ceilings for certain atmospheric pollutants, namely SO₂, NO_x, VOC and NH₃.

Figure 2.14 summarizes the air quality European Directives and respective transposed Portuguese laws.

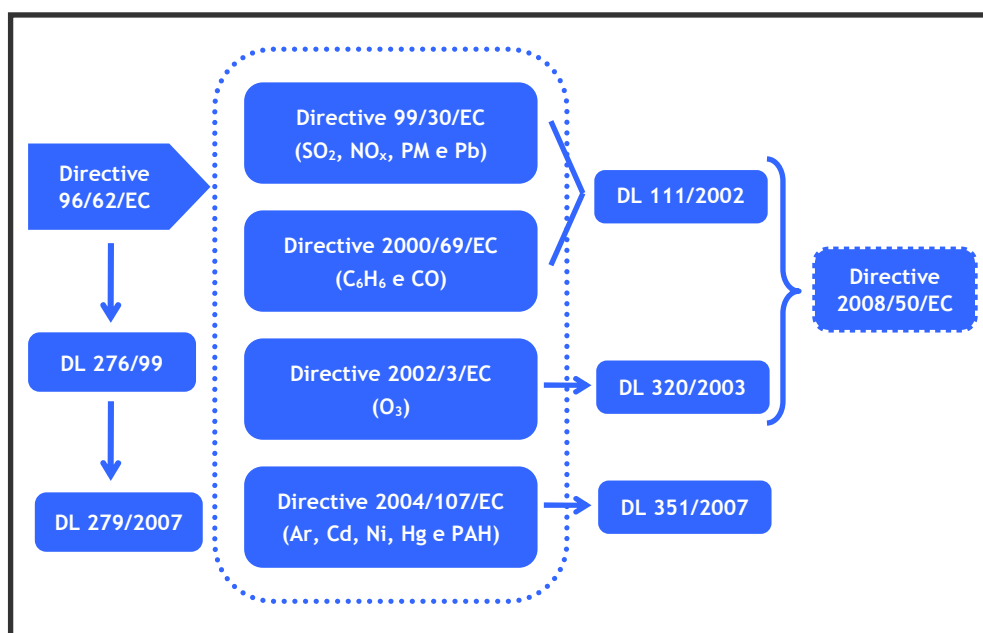


Figure 2.14 Air quality European Directives and respective transposed Portuguese laws (DL - *Decreto-Lei*).

The air quality health standards and objectives are summarised in Table 2.2. These apply over different periods because health impacts depend on exposure times.

Under EU law a limit value is legally binding from the date it enters into force subject to any exceedances permitted by the legislation. A target value is to be attained as far as possible by the attainment date and so is less strict than a limit value.

Table 2.2 Air quality health standards and objectives.

Pollutant	Concentration	Period	Legal nature	Permitted exceedances each year
O ₃	120 µg m ⁻³	Maximum daily 8 hour average	Target value enters into force 01.01.2010	25 days averaged over 3 years
PM _{2.5}	25 µg m ⁻³	1 year	Target value enters into force 01.01.2010; Limit value enters into force 01.01.2015	n/a
PM ₁₀	50 µg m ⁻³	24 hours	Limit value enters into force 01.01.2005	35
	40 µg m ⁻³	1 year	Limit value enters into force 01.01.2005	n/a
SO ₂	350 µg m ⁻³	1 hour	Limit value enters into force 01.01.2005	24
	125 µg m ⁻³	24 hours	Limit value enters into force 01.01.2005	3
NO ₂	200 µg m ⁻³	1 hour	Limit value enters into force 01.01.2010	18
	40 µg m ⁻³	1 year	Limit value enters into force 01.01.2010	n/a
Pb	0.5 µg m ⁻³	1 year	Limit value enters into force 01.01.2005 (or 01.01.2010 in the immediate vicinity of specific, notified industrial sources; a 1.0 µg m ⁻³ limit value applies from 01.01.2005 to 31.12.2009)	n/a
CO	10 mg m ⁻³	Maximum daily 8 hour average	Limit value enters into force 01.01.2005	n/a
Benzene	5 µg m ⁻³	1 year	Limit value enters into force 01.01.2010	n/a
Arsenic (As)	6 ng m ⁻³	1 year	Target value enters into force 01.01.2012	n/a
Cadmium (Cd)	5 ng m ⁻³	1 year	Target value enters into force 01.01.2012	n/a
Nickel (Ni)	20 ng m ⁻³	1 year	Target value enters into force 1.1.2012	n/a
PAH	1 ng m ⁻³ (expressed as concentration of benzo- α -pyrene)	1 year	Target value enters into force 01.01.2012	n/a

Ozone Standards and Objectives

Standards and objectives for O₃ are defined in 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, former Directive 2002/3/EC of the European Parliament and of the Council relating to O₃ in ambient air and in Portuguese law by the transposed *Decreto-Lei* 320/2003.

Annex I of the Directive 2008/50/EC defines data quality objectives for ambient air quality assessment, being for O₃ the following:

- considering fixed measurements, the minimum data capture should be 90% during summer (April to September) and 75% during winter (January to March, October to December);
- considering indicative measurements, at least 90% of data should be captured with more than 10% during summer.
- considering modelling uncertainty, at least 50% of hourly and eight-hour averages should be captured.

Annex VII of the Directive defines O₃ target values and long-term objectives. Table 2.3 presents the criteria that should be used for checking validity when aggregating data and calculating statistical parameters and Table 2.4 shows the target values and long-term objectives.

Table 2.3 Criteria used for checking validity when aggregating data and calculating statistical parameters (Directive 2008/50/EC).

Parameter	Required proportion of valid data
1 hour average	75% (i. e. 45 minutes)
8 hour average	75% (i. e. six hours)
Maximum daily 8 hours average (running average)	75% of the hourly running eight hours averages (i.e. 18 eight-hourly averages per day)
AOT40	90% of the one hour averages over the period defined for calculating the AOT40* average
Annual average	75% of the one hour averages summer and 75% over winter seasons separately
Number of exceedances and maximum average per month	90% of daily maximum eight hours average (27 available daily averages per month)
	90% of one hour averages between 8.00 and 20.00 Central European Time (CET)
Number of exceedances and maximum average per year	Five out of six months over the summer season (April to September)

*AOT40 (expressed in $\mu\text{g m}^{-3}\cdot\text{h}$) averages the sum of the difference between hourly concentrations greater than $80 \mu\text{g m}^{-3}$ and $80 \mu\text{g m}^{-3}$ over a given period using only the one-hour averages measured between 8.00 and 20.00 CET each day.

Table 2.4 Target values and long-term objectives for O₃ (Directive 2008/50/EC).

Target Values			
Aim	Averaging period	Target value	Date by which target value should be met
Protection of human health	Maximum daily eight-hour average	120 µg m ⁻³ not to be exceeded on more than 25 days per calendar year averaged over three years	01.01.2010
Protection of vegetation	May to July	AOT40 (calculated from 1 h averages) 18000 µg m ⁻³ .h averaged over five years	01.01.2010
Long-term Objectives			
Aim	Averaging period	Long-term value	Date by which target value should be met
Protection of human health	Maximum daily 8-hour average within a calendar year	120 µg m ⁻³	Not defined
Protection of vegetation	May to July	AOT40 (calculated from 1 h averages) 6000 µg m ⁻³ .h	Not defined

Annex XII of the Directive defines information and alert thresholds for O₃ (Table 2.5).

Table 2.5 Information and alert thresholds (Directive 2008/50/EC).

Purpose	Averaging Period	Threshold
Information	1 hour	180 µg m ⁻³
Alert	1 hour (for 3 consecutive hours)	240 µg m ⁻³

In Europe, emissions of many air pollutants have fallen substantially since 1990, resulting in improved air quality over the region. However, since 1997, measured concentrations of particulate matter and O₃ in the air have not shown any significant improvement despite the decrease in emissions. A significant proportion of the urban population of Europe still live in cities where EU air quality limits set for the protection of human health are exceeded. A number of countries are also likely to miss one or more legally binding 2010 emission ceilings. Consequently, the need to reduce exposure to air pollution remains an important issue.

PART II
GROUND-LEVEL OZONE SINCE
PRE-INDUSTRIAL ERA

Although O₃ is now considered a pollutant in the troposphere, when it was identified as an atmospheric trace constituent, by F. Schönbein around 1840, medical doctors considered it as an index of healthy air, attributing to it an important role on the control of epidemic diseases due to its strong oxidative properties. Therefore, many O₃ monitoring sites were installed in places that people wished to be considered healthy. During the 50's and 60's decades of the 19th century, O₃ was a fashionable subject. Many meteorologists, physicians, chemists and medical doctors developed studies to prove its existence, to discover its function in the atmosphere and to evaluate its erroneously presumed role in the spread of epidemics. The first semi-quantitative analytical methodology for measuring O₃ concentrations in the atmosphere, expressed in ozonometric degrees, was developed by Schönbein. Improved versions were first introduced by Bérigny in France, 1856, being used until early 20th century. Albert-Lévy began O₃ measurements at Parc Montsouris (Paris) in 1876 using simultaneously a new quantitative method and the improved method of Schönbein. These simultaneous measurements, which were conducted for 34 years, allowed the conversion between the units of the two methods, being from then on the basis of all the methods to convert ozonometric degrees into modern units (Pavelin et al., 1999). The Schönbein-type tests have recognized interferences that were attempted to compensate for their effects, in order to improve the quality of the measurements (Bojkov, 1986; Volz and Kley, 1988). Humidity is the most important interference that was analysed by Linvill et al. (1980) who obtained a chart, later modified by Anfossi et al. (1991), relating O₃ levels and relative humidity (Pavelin et al., 1999; Marengo et al., 1994). A precision between 25% and 33% can be expected for the O₃ concentrations deduced from ozonometric degrees (Anfossi and Sandroni, 1997; Marengo et al., 1994). The increased ground-level O₃ enhanced the relevance of pre-industrial O₃ levels. Therefore, in spite of the conversion precision, the pre-industrial data are of great interest if they are used cautiously. Several studies have been carried out showing the increase of ground-level O₃ concentrations (Baldassano et al., 2003; Dueñas et al., 2002; Guicherit and Roemer, 2000). Some scientists have pointed out the need for more detailed studies about ground-level O₃, not only because the actual knowledge of its effects, but also because the chemical processes in the troposphere are

important to interpret stratospheric processes (Bojkov, 1986). Furthermore, as pre-industrial O_3 data were measured in an atmosphere not significantly influenced by human activities, the interest in the search of those data was strongly stimulated since they can provide a reference for the levels and behaviour of O_3 (Anfossi et al., 1991).

Photochemical Formation

During the pre-industrial era, the O_3 found in the troposphere came essentially from the stratosphere, through intrusion of stratospheric air. Recent estimates indicate that stratospheric-tropospheric exchanges only account for 20% of the current total ground-level O_3 , because now it is mainly produced by complex photochemical reactions involving solar radiation and anthropogenic pollutants (Marenco et al., 1994). Hence increased ground-level O_3 levels of photochemical origin can be correlated with the increased emissions of anthropogenic pollutants.

Photochemical O_3 is formed by reactions involving solar radiation and anthropogenic pollutants (CH_4 , NMVOC, CO) in the presence of NO_x .

In less polluted environments, O_3 is produced in the presence of sunlight (at wavelengths <424 nm), through the photolysis of NO_2 :



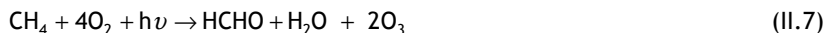
where M represents N_2 , O_2 or other molecules that can absorb the excess of vibrational energy, allowing the stabilization of O_3 . Once formed, O_3 quickly reacts with NO regenerating NO_2 :



In the absence of other chemical species this cycle reaches a photo-stationary equilibrium between NO, NO_2 and O_3 , without effective O_3 formation, and with an O_3 concentration proportional to the ratio $[NO_2]/[NO]$. In less polluted environments O_3 production may also involve the radicals HO_2 and methyl peroxy (CH_3O_2), intermediate products of CO and CH_4 oxidation:



These reactions with NO occur when the ratio [NO]/[O₃] is significantly high. The global reactions of oxidation of CO to CO₂ and CH₄ to HCHO are the following:

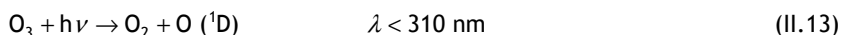


In polluted environments the photochemical production of O₃ cannot be explained solely by the CO-CH₄-NO_x equilibrium, mainly due to the additional presence of VOC. The VOC oxidation cycle disturbs the natural equilibrium NO_x-O₃, allowing alternative paths for the oxidation of NO to NO₂ without consumption of O₃. VOC oxidation mechanisms are mainly induced by OH radical during the day and by NO₃ radical during the night, leading to the production of HO₂ and RO₂ radicals. These radicals are able to oxidize NO to NO₂ avoiding Reaction II.3, and leading to the accumulation of O₃ through Reactions II.1 and II.2. These mechanisms explain the high concentrations of O₃ in polluted areas, whenever the radiation is high enough to initiate the photodissociation process. The reactions involved can be simplified as follows:



where CARB is either a carbonyl species (RCHO) or a ketone (RCRO).

The destruction of O₃ is accomplished by chemical and photochemical degradation, by the oxidative cycle of CO and CH₄, and by dry deposition on the soil. The main reactions are the following:



Previous studies showed that NO_x emissions are mainly responsible for O₃ formation in rural areas, whilst VOC are responsible in urban areas (EEA, 1998). There is a competition between VOC and NO_x for the OH radical. When [VOC]/[NO_x] is high, OH will react mainly with VOC (NO_x limited), generating new radicals and accelerating O₃ production. Under

these conditions, typical of rural areas, an increase in NO_x concentration accelerates O_3 formation. When $[\text{VOC}]/[\text{NO}_x]$ is low, the reaction of OH with NO_x can predominate (VOC limited), removing OH from the VOC oxidation cycle and retarding the further production of O_3 . Under these conditions, typical of polluted areas, an increase in NO_x concentration leads to O_3 decrease. Therefore, while increasing of VOC concentration always increases O_3 formation, increasing of NO_x leads to more or less O_3 , depending on the prevailing ratio between $[\text{VOC}]$ and $[\text{NO}_x]$ (Pereira et al., 2005; Sadanga et al., 2003; Guicherit and Roemer, 2000; Barros, 1999; Seinfeld and Pandis, 1998).

Chapter 3

Increase of Ground-level O₃ in the Oporto Metropolitan Area since the 19th Century*

The main purpose of this study was to evaluate the contribution of anthropogenic pollutants to the increase of ground-level O₃ concentration in the Oporto Metropolitan Area (Oporto-MA) since the 19th century. The study developed was based on pre-industrial and recent data series. The results were analysed according to the atmospheric chemistry characteristic of the periods corresponding to the two series. The treatment of O₃ and meteorological data was performed by classical statistics and time-series analysis.

* adapted from: Alvim-Ferraz MCM, Sousa SIV, Pereira MC, Martins FG, 2006. Contribution of anthropogenic pollutants for the increasing of tropospheric ozone levels in the Oporto Metropolitan Area since the nineteenth century. *Environmental Pollution* 140: 516-524.

3.1. Methodology

The data considered in this study were collected in the Oporto-MA. With the aim of evaluating the influence of anthropogenic pollutants to the increase of ground-level O₃ levels two data series were selected, corresponding to completely different atmospheric emissions: i) one old data series collected between 1861 and 1897 (DS_{old}) before the industrial development of the area; and ii) one recent data series (DS_{rec}) collected between 1999 and 2003.

3.1.1 Characterization of the Region

Oporto is the second largest Portuguese city, being located in the North, at a latitude and longitude of approximately 41°10' N and 8°40'W, respectively. Industries related to wine, textile, footwear, metal and mechanics were the first to be installed in the city, but acquiring significant importance only around the end of the 19th century. This means that industrial emissions, as well as traffic emissions, did not significantly influence the air quality until the end of the 19th century.

Nowadays, Oporto belongs to the Oporto-MA that includes the municipalities shown in Figure 3.1 (Oporto-MA, 2004). Oporto-MA has about 1.2 million inhabitants and a population density of 540 inhab km⁻².

The region is limited on the west by Atlantic Ocean with 50 km of coastline and crossed by Douro River (between Porto/Gondomar and Vila Nova de Gaia). Topographically the zone is rather uneven, with a maximum altitude of about 400 m that decreases with the proximity of the coast. In climatic terms this area is designated by North maritime (Ribeiro et al., 1987), characterized by warm and dry summers and mild and wet winters with two transition seasons: spring and autumn. The annual average temperature is around 15°C and the difference between warmer and colder monthly averages is less than 10°C. Annual air humidity is between 75% and 80%, and the total annual average precipitation varies between 1000 mm and 1200 mm, with about 40% in the winter season, and with more than one hundred days per year with precipitation equal to or higher than 1.0 mm. Prevailing winds are from W and NW in summer and from E and SE in winter (Santos et al., 2002; Monteiro, 1997). In the North of Portugal, Oporto-MA is the region with the highest power consumption per capita and per industry, which is related to a relatively high industrial density. The

motorization rate is the second highest in Portugal. In Oporto-MA the most important stationary sources of atmospheric pollutants are one oil refinery, one petrochemical plant, one thermoelectric plant working with natural gas, one waste incineration unit and one international shipping port. Nevertheless, motor traffic is supposed to be responsible for a significant amount of the pollutants emitted to the atmosphere. Previous studies showed that in Oporto-MA special care must be taken with atmospheric concentrations of PM₁₀ and O₃ (Pereira et al., 2002).

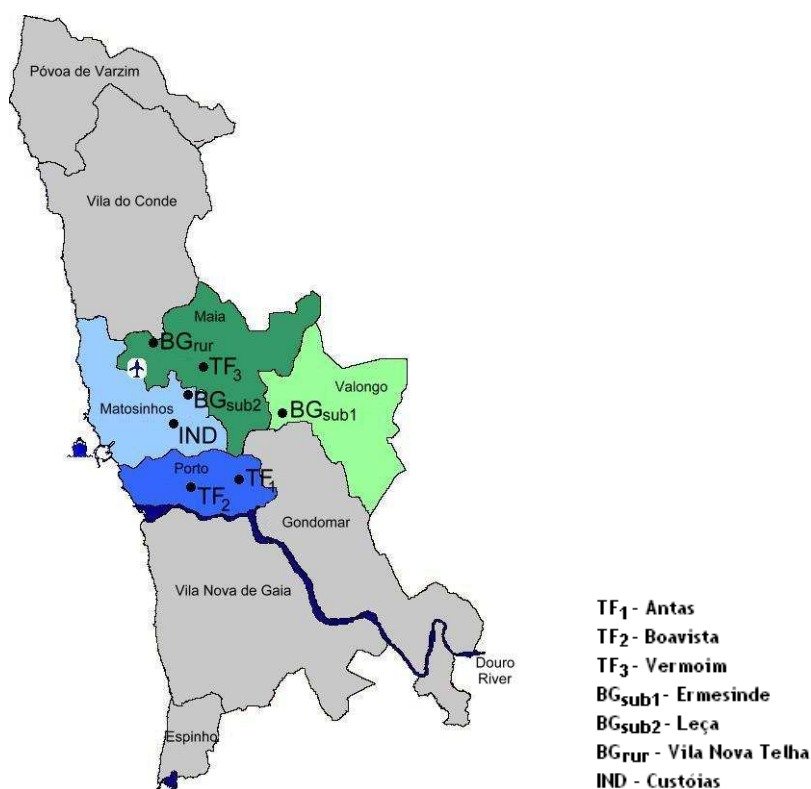


Figure 3.1 Oporto Metropolitan Area.

3.1.2 Characterization of the Monitoring Sites

Atmospheric O₃ quantification in Oporto started in December 1859, being performed uninterruptedly for more than 37 years under the responsibility of *Observatório Meteorológico da Eschola Medico -Cirurgica do Porto*. Atmospheric pressure, temperature, wind direction and velocity, precipitation, hygrometric conditions of air, and the sky

characteristics were simultaneously evaluated. The monitoring site was located in the urban centre, with a latitude of $41^{\circ} 8' 54''\text{N}$, a longitude of $8^{\circ} 27' \text{W}$ and an altitude of 84.8 m (Fradesso da Silveira, 1864).

The O_3 evaluation in Oporto was restarted in 1994, integrated in the measurements conducted by the Air Quality Monitoring Network of Oporto-MA, managed by the Regional Commission of Coordination and Development of northern Portugal (*Comissão de Coordenação e Desenvolvimento Regional do Norte*, CCDRN), under the responsibility of the Ministry of the Environment. The study here reported considered three urban sites with traffic influences (TF_1 , TF_2 and TF_3), one suburban site with industrial influences (IND), two suburban background sites (BG_{sub1} and BG_{sub2}) and one rural background site (BG_{rur}). The meteorological parameters were measured at *Serra do Pilar* (SP) on the left edge of Douro River, at an approximate altitude of 90 m, by the Geophysical Institute of Oporto University (*Instituto Geofísico da Universidade do Porto*). The analysis of the wind patterns in different places of the city, allowed concluding that the wind pattern at *Serra do Pilar* can be considered representative of the wind patterns at the sites here considered (Mesquita, 2007).

The study considered the minimum, medium and maximum temperatures (T_{Min} , T and T_{Max} , respectively), pressure (P), relative humidity (RH), precipitation (PP) and wind velocity (WV).

3.1.3 Analytical Methodologies

In the 19th century the O_3 evaluation was made by a Schönbein-type method, based on the air exposure of paper strips impregnated with a solution of potassium iodide and starch (Pavelin et al., 1999; Marengo et al., 1994). The paper strips developed a bluish colour whose intensity depends on the O_3 levels in the air. After that, the colour of the paper strips was compared with a standard chromatic scale, graduated from 0 to 21. The paper strips were exposed for 12 hours (from 9 am to 9 pm and from this hour until next day at 9 am). With these two values a daily average was calculated, expressing the results in ozonometric degrees. The writing records were so carefully made that valid data series can be expected. In fact, it is possible to know the details concerning filter and reagent quality, material and equipment maintenance, and analytical procedure. To convert ozonometric degrees into modern units, the scale of ozonometric degrees was first adjusted to the scale used on the modified Linvill chart that relates O_3 levels to RH. This chart was digitalized in order to

elaborate artificial neural networks (ANN) as a model to predict the volumetric ratio adjusted to humidity at reference pressure and temperature (Alvim-Ferraz et al., 2001).

Nowadays, O₃ concentration is continuously monitored by UV-absorption photometry using the equipment 41M UV Photometric O₃ Analyzer from Environment S.A., according to ISO 13964, Portuguese Portaria n° 623/96 and EU Directive 2002/3/CE. Hourly averages are recorded expressing the concentration in $\mu\text{g m}^{-3}$. All the equipments were submitted to a rigid maintenance program and were periodically calibrated.

The meteorological parameters were measured continuously and the study was based on the hourly averages.

3.1.4 Data Treatment

The daily averages of O₃ concentration were calculated for both recent and old data set (DS_{rec} and DS_{old}). The monthly averages were also calculated in order to analyze the seasonal variations. To evaluate the influence of relative humidity on O₃ concentration, the respective monthly averages were correlated.

The time-series analysis allows the identification of deterministic behaviours hidden by the large variability of air quality data and by the low signal-to-noise ratio of the measurements. Thus, this kind of data treatment contributes to a deeper understanding of cause/effect relationship in environmental problems (Sebald et al., 2000; Salcedo et al., 1999; Tetzlaff, 1997). Several studies have been carried out for the identification of cyclic patterns for VOC traffic emissions and for meteorological parameters (Hies et al., 2000; Sebald et al., 2000). The time-series analysis involved the identification of long-term variation of the average and cyclical components. The Sequential Approach to Time-Series Analysis (SATSA) model was applied for determining the trend, cyclical components and noise of O₃ concentration and meteorological data series, based on appropriate observation equations (Salcedo et al., 1999).

3.2 Results and Discussion

3.2.1 Influence of Relative Humidity on Ozone Concentration

Figure 3.2 shows the correlation coefficients between monthly averages of O_3 concentration and RH, for the data series of the 19th century and for the recent data series in a suburban site influenced by industrial emissions.

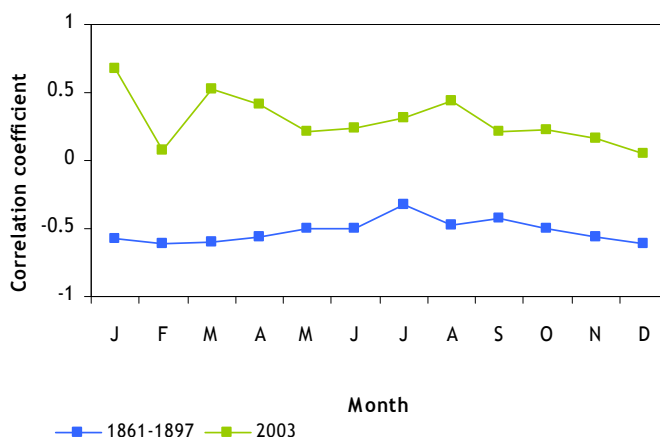


Figure 3.2 Correlation coefficients (monthly averages of O_3 concentrations vs. RH) for the data series of the 19th century and for the recent data series in a suburban site influenced by industrial emissions.

It was possible to observe that for the data series of the 19th century the correlations were always negative with a global average value of -0.52, suggesting that increase of humidity decreased O_3 concentration. On the contrary, for the recent data series (2003) the correlations were positive. The negative correlation coefficients observed in the 19th century may be correlated with meteorological subsidence. Low RH is associated with meteorological subsidence that leads to the transport of air from the upper troposphere towards the surface. O_3 in the troposphere increased with height mainly in the pre-industrial era, because the stratosphere was the main O_3 source. Thus, subsidence originated the transport to the surface of air with higher O_3 concentration, justifying the negative correlation coefficients observed. Nevertheless, atmospheric chemistry may be the better support for the observed correlation coefficients. As already referred, photochemical O_3 is produced by photolysis of NO_x , strongly dependent on NO_x concentrations. For low NO_x concentrations and high humidity levels, the Reactions II.13-II.16 dominate over the Reactions II.8-II.11 (or II.12), meaning that the loss of O_3 dominates over its photochemical

production (Pavelin et al., 1999). In these circumstances, the Reactions II.13 and II.14 lead to a decrease in the O₃ concentration when humidity increases, justifying the negative correlation coefficients observed in the 19th century. For high NO_x concentrations, the Reaction II.12 dominates over the Reactions II.13-II.16, meaning that the photochemical production dominates over its loss, justifying the positive correlation coefficients between monthly averages of O₃ concentration and RH, observed in recent data series. Concluding, the negative correlation observed for the data series of the 19th century showed that the atmosphere was then not significantly influenced by NO_x. Therefore, a negligible amount of photochemical O₃ was present and it was thus possible to consider the old O₃ concentrations as reference values.

3.2.2 Seasonal Variation of Ozone Concentrations

The seasonal variation of O₃ concentrations was analyzed using the values of monthly averages, shown in Figure 3.3 for the data series of the 19th century and for the recent data series (site TF₂ was selected as example).

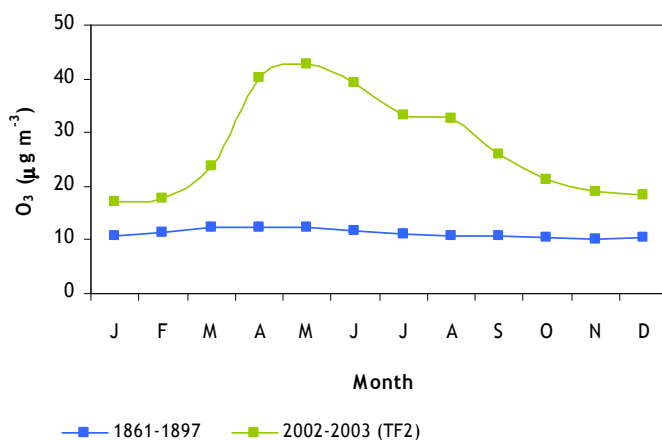


Figure 3.3 Standard seasonal behaviour of monthly averages of O₃ concentration for the data series of the 19th century and for the recent data series in an urban site influenced by traffic.

The seasonal variation for DS_{old} showed no significant differences throughout the year, with a minimum of 10.0 µg m⁻³ in November, a maximum of 12.5 µg m⁻³ in April, and a global average of 11.1 µg m⁻³. A slight increase in concentration was observed in spring and not in

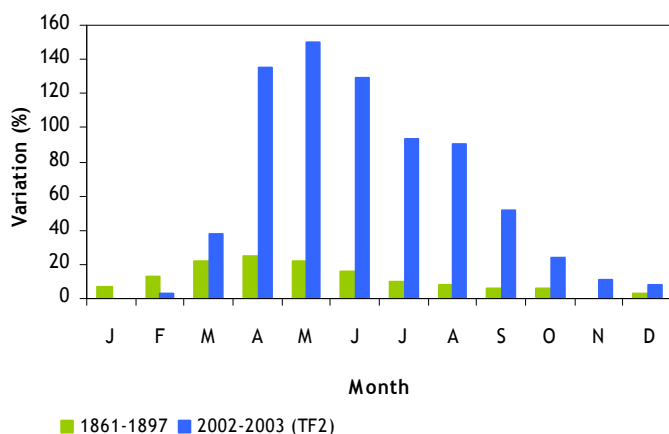
the warmer months. The annual cycles observed in Oporto were similar to those that were observed in Montsouris (1876 - 1886) and Moncalieri (1868-1893) but the annual averages ($16 \mu\text{g m}^{-3}$) were higher there (Anfossi et al., 1991; Volz and Kley, 1988). These extremely low O_3 concentration point to much lower NO_x concentrations than those that are found today, confirming that a negligible amount of photochemical O_3 was present, according to the negative correlation observed between O_3 concentration and RH.

The seasonal variation for DS_{rec} showed big differences throughout the year, with a clear increase of O_3 (and NO_x) concentrations and a broad summer maximum. A minimum of $17.1 \mu\text{g m}^{-3}$ was observed in January and a maximum of $42.8 \mu\text{g m}^{-3}$ was observed in May, for a global annual average of $27.5 \mu\text{g m}^{-3}$, significantly lower than the annual average values ($40\text{--}70 \mu\text{g m}^{-3}$) referred by WHO (2000). The recent annual cycles observed in Oporto showed that the seasonal variation is similar to the one observed in other European locations (Guicherit and Roemer, 2000), namely in a Spanish coastal city (Dueñas et al., 2002). Nevertheless, those authors referred higher monthly averages along the year ranging from 35 to $90 \mu\text{g m}^{-3}$ (Dueñas et al., 2002) and 58 to $86 \mu\text{g m}^{-3}$ (Guicherit and Roemer, 2000).

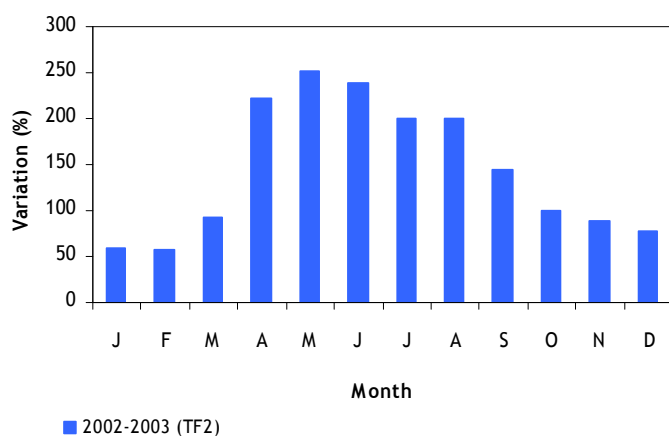
The dependence of photochemical O_3 formation on the sunlight radiation increases O_3 production during summer, due to the increasing of UV radiation and temperature and to the decrease of wind speed (WHO, 2000). Therefore, in the presence of NO_x , the increased radiation during summer leads to an increase in O_3 , according to the Reactions II.8-II.11 (or II.12), as it was observed for the recent data series.

On the contrary, for low NO_x concentrations, like those of the 19th century, the O_3 destruction exceeds the O_3 production; increased radiation during summer leads to a net destruction of O_3 , through Reactions II.13-II.16. Consequently, O_3 maximum should not be expected in the summer. The transport of O_3 from the stratosphere and its possible influence on the annual cycle have been widely studied for many years (Logan et al., 1999; Schultz et al., 1999; Fishman, 1981; Seiler and Fishman, 1981; Liu et al., 1980). As that transport is more efficient in spring (Liu et al., 1980), the maximum may occur in that season as was observed for the data series of the 19th century.

The relative variations of the monthly averages of O_3 concentrations are shown in Figure 3.4 (a) for both data series relative to their minima and (b) for recent data series relative to those of the 19th century.



(a)



(b)

Figure 3.4 Relative variation of monthly averages of O₃ concentrations: (a) for both data series relative to their minimum; (b) for recent data series relative to those of the 19th century.

The results showed that for the recent data series the highest variation was observed in May (150%). For the data series of the 19th century much lower variations were observed with a maximum of 25% in April. The variation of recent data series compared to that of the 19th century was higher than 50% for every month. The maximum rise was observed in May (252%) with a global average increase of 147%. The threshold for health protection ($120 \mu\text{g m}^{-3}$ for 8-hour running averages) and for the population information ($180 \mu\text{g m}^{-3}$ for hourly average), referred in Section 2.5, were generally exceeded in all the sites, with the highest exceedances associated with clear sky and high temperatures, consequently associated with

higher radiation intensity. These results show that contrary to what was observed in the 19th century, the recent increase in O₃ concentration was essentially due to the increased photochemical production associated with the increased of anthropogenic emissions.

3.2.3 Time-series Analysis

The SATSA model was applied to compare the cyclic patterns of time-series of O₃ concentration and of meteorological parameters. The time-series were transformed logarithmically for the variance stabilization; a first order differencing was applied before the Fourier analysis. When there were missing data in the series (10% maximum), the SATSA model replaced them by the linear trend of the available measurements (Salcedo et al., 1999).

Data Series of the 19th Century

To find daily cycles, the daily averages of O₃ concentration from 1861 until 1897 were analyzed. For all the periods considered, no daily cycles were found, the same happening with the meteorological parameters (T_{Max}, T_{Min}, PP and WV). The monthly averages of O₃ concentrations and meteorological parameters were calculated to analyze the existence of monthly cycles. The monthly cycles identified (and the respective periodic variance in percentage) were the following: O₃ concentration - 11.99 (5.38); T_{Max} - 11.92 (47.2); T_{Min} - 11.92 (42.4); PP - 11.92 (4.76); WV - 11.77 (6.15). Annual cycles were identified for all the variables, with the highest periodic variances for both T_{Max} and T_{Min}, because of their stronger seasonal behaviour. No cycle associated with anthropogenic activities (like daily or week/weekend) was found for O₃ concentration, once more proofing that human activities did not significantly influenced the concentrations in the data series of the 19th century.

Recent Data Series

To avoid the impact of data noise in the study, the hourly averages of O₃ concentration were analyzed separately for each month. Figure 3.5 shows, as an example, the time-series of hourly averages of O₃ concentration at TF₂ during the first five days of July 2003.

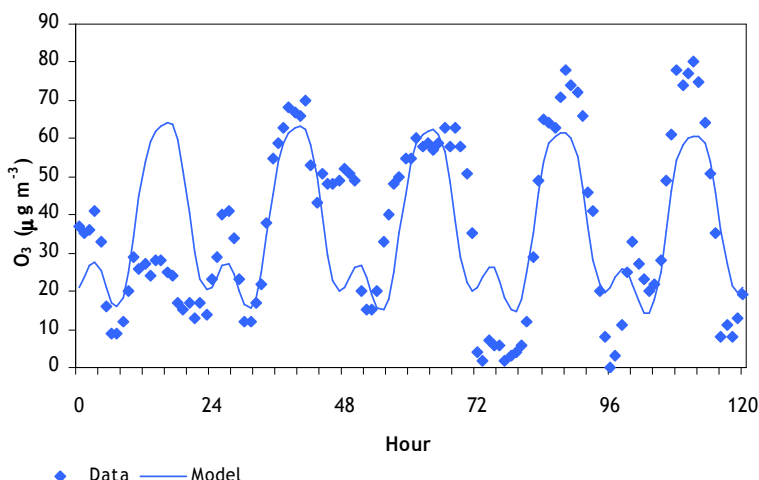


Figure 3.5 Time-series of hourly averages of O₃ concentration at TF₂ since 1st July until 5th July 2003.

The hourly cycles identified (and the respective percentages of significance) are summarized in Table 3.1 for all the sites. This analysis revealed three significant hourly cycles: 24 h, 12 h and 8 h.

Table 3.1 Hourly cycles and respective percentages of significance for each site.

Cycles	Site						
	TF ₁	TF ₂	TF ₃	IND	BG _{sub1}	BG _{sub2}	BG _{rur}
24 h	58.3%	58.3%	75.0%	76.7%	70.0%	61.7%	89.6%
12 h	91.7%	95.8%	77.8%	68.3%	76.7%	43.3%	70.8%
8 h	58.3%	66.7%	44.4%	46.7%	53.3%	25.0%	31.3%

The single meteorological parameter for which hourly averages were supplied was WV. The cycles of 24 h and 12 h observed can also be related with the similar cycles in O₃ concentrations, suggesting that WV and O₃ concentrations can be related. The 24 h cycle of ground-level O₃ concentration can also be associated with similar cycles of photochemical production, directly depending of the 24 h cycle of solar radiation. The 12 h cycle is also

related to the solar radiation that increases during the day and decreases during the night also having a 12 h cycle (Hogrefe et al., 2001).

The 8 h cycle is mainly dependent on the association of traffic emissions and solar radiation, therefore being dependent on anthropogenic activities; this cycle can also be related to vertical and horizontal mixing in the atmosphere. According to the behaviour of VOC limited polluted areas, during the early morning, the fresh NO emissions coming mainly from road traffic lead to the O₃ scavenging and to the production of NO₂ through Reaction II.3. As the day advances and the air mass goes out from the polluted area, the [VOC]/[NO_x] changes due to photochemical reactions, meteorological processes and new emissions. [NO_x] decreases faster than [VOC] due to the quicker oxidation of NO_x to nitrates, leading to a rapid increase in [VOC]/[NO_x] and also to an increase in O₃ until the maximum concentration is reached. Accordingly, a minimum was identified at 8 h and a maximum at 16 h. The relative maximum observed during the night (4 h) has been explained by horizontal transport by land-sea breezes prevailing at night in Oporto-MA (Mesquita et al., 2004). It should be referred that for TF₁ and TF₂, the sites with the strongest traffic influence, the 24 h and the 8 h cycles, have approximately the same significance, suggesting that the influence of traffic emissions on the evolution of O₃ concentration is as important as the solar radiation.

Based on the daily averages, daily cycles were investigated for O₃ concentrations, as well as for the meteorological parameters WV, PP, T_{Max} and T_{Min}, and no significant cycle was observed. Monthly cycles of O₃ concentrations were also analysed based on monthly averages and again no cycles were identified. The 12 months cycles observed for T_{Max} and T_{Min} are directly related with their seasonal profile.

3.3 Conclusions

Data series of the 19th century: A negative correlation between O₃ concentration and RH was observed, meaning that the atmosphere was then not significantly influenced by NO_x. Thus, as the O₃ in the atmosphere was not of photochemical origin, it was possible to consider the respective concentrations as reference values. The seasonal variation of the concentrations was not significant, with a minimum of 10.0 µg m⁻³ in November, a maximum of 12.5 µg m⁻³ in April, and a global average of 11.1 µg m⁻³. The slight increasing in spring was explained by the more efficient transport of O₃ in spring from the stratosphere (the main O₃ source) in

this season. No periodic cycle was identified that could be associated with anthropogenic activities, proving that these activities did not significantly influenced O₃ concentrations.

Recent data series: The seasonal variation of the concentrations was clearly significant, with a minimum of 17.1 µg m⁻³ in January, a maximum of 42.8 µg m⁻³ in May, and a global average of 27.5 µg m⁻³. The broad summer maximum is explained by increased summer radiation in the presence of NO_x, leading to an increase in photochemical O₃ production associated with anthropogenic activities. The 8 h cycle observed for O₃ concentrations could be related to traffic, confirming the dependence on anthropogenic activities. Relative to the 19th century, the current concentrations were in average 147% higher (252% higher in May) due to the increased photochemical production associated with the increased anthropogenic emissions.

PART III
PREDICTION OF OZONE CONCENTRATIONS

The development of mathematical tools able to predict O₃ concentrations has been drawing the attention of many scientists all over the world during the last 20 years. Due to the harmful effects of this gas, the prediction of O₃ concentrations becomes a fundamental tool, concerning the anticipated implementation of strategies to improve public health, namely on providing early warnings to the population, and concerning the reduction of the number of measuring sites. Accordingly, the European Directive on ambient air quality and cleaner air for Europe (Directive 2008/50/EC) enhances the necessity of developing modelling techniques.

Predicting O₃ concentrations is very difficult because of the complex relationships between O₃ and a high number of variables, particularly other pollutants and meteorological factors, which favour or delay its production (Borrego et al., 2003). Recently, attempts have been made to predict O₃ concentrations using different approaches, namely numerical chemistry-transport models, deterministic models based on physic laws, and statistical models. Numerical chemistry-transport models have been applied with very useful results by several authors (Monteiro et al., 2007; Borrego et al., 2006; Monteiro et al., 2005; Bessagnet et al., 2004; Borrego et al., 2003; Schmidt et al., 2001); nevertheless, these models are complex leading sometimes to some uncertainties (Mallet and Sportisse, 2006). The deterministic models are very complex because they require knowledge of particular aspects of the reactions, such as kinetic equations, which are often not known (Soja and Soja, 1999; Ballester et al., 2002). By contrast, the simplicity of statistical models is an advantage for their implementation; statistical models directly adapt to the patterns that arise from the observed data, being therefore very flexible and of fast application (Schlink et al., 2006). Nevertheless, an obvious drawback is that they might be specific for the site analysed because their development is based on local data. This specificity may be also seen as an advantage because of the higher accuracy of the predictions for the specific site.

Concerning statistical approaches, linear and non-linear models have been widely applied to predict O₃ concentrations. Multiple liner regressions (MLR) are one of the methodologies most used. However, this approach can face serious difficulties when the independent

variables are correlated with each other, because it might be difficult to correctly identify the most important contributors to the process in analysis. One of the approaches that have been used to avoid problems of interaction between variables is the principal component analysis (PCA), which has been receiving increased attention as an accepted method in environmental pattern recognition. This multivariate statistical technique transforms the original data set into a set of linear combinations of the original variables. The uncorrelated new variables, designated by principal components (PC), account for the majority of the original variance.

Also quantile regression (QR) model has been applied in environmental studies. QR was first introduced by Koenker and Bassett (1978) to model the relationship between covariates (x) and quantile functions (y). On the contrary, ordinary least squares regression is commonly used to model the relationship between one or more covariates x and the conditional average of y (Cade and Noon, 2003). QR is considered to be particularly important in applications such as environmental studies, where the extreme values are relevant. This model is an extension of the regression models to conditional quantiles of the response variable, and as compared to ordinary least squares regression, it has the advantage of allowing the examination of the entire distribution of the variable of interest rather than measuring the central tendency of its distribution. The application of this method is therefore more flexible to model data with heterogeneous conditional distribution.

Several studies have been reported considering the prediction of O_3 concentrations regarding different kind of models.

Arbilla et al. (2002) developed an empirical kinetic model for the prediction of O_3 concentrations in an urban site. Results showed that the model could be applied in some cases; however, it was generally not a successful approach. Fuzzy techniques were used by Gomez et al. (2001), Heo and Kim (2004) and Mintz et al. (2005) indicating to be useful tools for O_3 modelling. Also the cluster analysis of Davis et al. (1998) tries to solve the problem of O_3 forecasting by distinguishing trends under different meteorological conditions. Dueñas et al. (2005) developed stochastic models, such as auto-regressive integrated moving average (ARIMA), for urban and rural areas that turned out to be site specific. In recent years, principal component regressions (PCR), combining MLR and PCA have being used to model O_3 concentrations. Lengyel et al. (2004) predicted O_3 concentrations at a heavy traffic place using MLR, PCR and partial least squares, reaching to different interpretations depending on the approach; nevertheless considering that the latter two models were very useful tools for grouping the data. Abdul-Wahab et al. (2005) studied the factors contributing to O_3

formation in Kuwait, including environmental pollutants and meteorological variables, by predicting O₃ concentrations using both MLR and PCR methods. Gonçalves et al. (2005) used PCA with the purpose of identifying distinct patterns of respiratory morbidity that occurred in São Paulo and the relative importance of meteorological variables and pollutant concentrations.

Other approaches based on ANN and respective comparisons with linear models have also been presented. Wang et al. (2003) developed an improved ANN made to predict daily maximum O₃ concentration which combines the adaptative radial basis function network with statistical characteristics of O₃ in specific selected areas. The results of this work were good but presented certain limitations such as the application of the model to rural areas. Chaloulakou et al., (2003) compared ANN and MLR models to forecast the next day maximum hourly O₃ concentration in Athens and concluded that ANN provided better estimates of O₃ concentrations, whilst the more often used linear models were less efficient at accurately forecasting high O₃ concentrations. Schlink et al. (2003) performed an inter-comparison of fifteen different statistical techniques for O₃ prediction, including linear and non-linear approaches, demonstrating that ANN and generalized additive models should be used for most situations, as those could handle non-linear associations. The use of ANN was also focused by Libiseller and Grimvall (2003), Abdul-Wahab and Al-Alawi (2002), Wieland et al. (2002), Wieland and Wotawa (1999), Acuna et al. (1996) among others.

Despite of all the advantages of the QR method for predicting O₃ concentrations above referred, the use of this model was only reported in two studies, as far as it is known. Schlinck et al. (2003) neglected some potentialities of this method by using it only as 50% quantile. Baur et al. (2004) used this methodology to interpret nonlinear relationships between the daily maximum of hourly O₃ concentrations and both meteorological and lagged O₃ levels; estimations of the entire conditional O₃ distribution for different values of each explanatory variable (considering them independently) were also performed.

The work specifically developed for this thesis and reported in the following chapters goes further on this field, by focusing on new methodologies. ANN were built based on PC (therefore combining statistical and artificial intelligence techniques) and QR were used considering different quantiles and the prediction based on regression equations (avoiding the problems related with the use of distribution functions) using simultaneously all the statistically significant explanatory variables. Additionally, time-series (TS) was also used for O₃ concentrations prediction. Therefore, Chapter 4 presents a comparison between TS, MLR

and ANN; Chapter 5 presents a comparison between MLR, PCR and ANN based on PC; and Chapter 6 presents a comparison between MLR and QR.

Chapter 4

Comparison of Time-Series, Multiple Linear Regression and Artificial Neural Networks*

As previously referred, this chapter reports the prediction of the daily average of O_3 concentrations using TS, MLR and feedforward artificial neural network models (FANN).

4.1. Methodology

4.1.1 Site Characterization and Data

The study here reported considered one urban site previously characterized (Section 3.1.2) as having traffic influences (TF_1) and one rural reference site previously characterized (Section 3.1.2) as a background site (BG_{rur}) located at Oporto-MA (Figure 3.1). The

* adapted from: Sousa SIV, Martins FG, Pereira MC, Alvim-Ferraz MCM, 2006. Prediction of ozone concentrations in Oporto city with statistical approaches. *Chemosphere* 64: 1141-1149.

meteorological parameters were measured at the representative site SP, (according to what was referred in Section 3.1.2) at 5 km from the TF₁ site and 25 km from the BG_{rur} site.

The study considered daily average concentrations of O₃, NO, NO₂, PM₁₀, SO₂, CO, RH, WV and temperature (T).

The monitoring methodologies of O₃ were performed as described in Section 3.1.3. PM₁₀ concentrations were obtained through the beta radiation attenuation method; SO₂ concentrations were obtained using the UV Fluorescence method; CO concentrations were measured through IR spectroscopy without dispersion; NO and NO₂ concentrations were obtained using a chemiluminescence method. The monitoring was continuous and hourly averages were recorded expressing the concentration in $\mu\text{g m}^{-3}$. Data treatment was based on the hourly averages of pollutant concentrations and meteorological parameters measured during 2002.

4.1.2 Models

The main characteristics of the TS modelling is that it only tries to model the relationship between each observation and previous observations, without using any other variable. Thus, the predicted O₃ concentration is modelled as a function of the previous O₃ concentrations or as a function of the position in time (Slini et al., 2002). One basic and relevant requirement to this model is that the data series must be stationary. This is generally achieved with: i) data transformation; and/or ii) data detrending; and/or iii) data differencing (1st and 2nd order) before applying the Fourier decomposition (Salcedo et al., 1999). As the input variables to TS models are only lagged values of response, the performance of this model concerning O₃ prediction is generally weak.

MLR is a commonly used method to predict O₃ concentrations, as already referred. The measured variable y is given by:

$$y = P_0 + \sum_{i=1}^k P_i x_i + \varepsilon \quad (4.1)$$

where x_i are the predictor variables, P_i the regression coefficients and ε the error associated to the regression (assumed to have expectation of zero). The predicted variable given by the regression model $\hat{y}$ can be written as:

$$\hat{y} = \hat{P}_0 + \sum_{i=1}^k \hat{P}_i x_i \quad (4.2)$$

where the regression coefficients $\hat{P}_0$ and $\hat{P}_i$ are the estimators of P_0 and P_i .

The regression parameters $\hat{P}_i$ are calculated by minimizing the sum of squared errors, through:

$$\hat{P}_i = \arg \min \sum_{i=1}^k (y_i - \hat{y}_i)^2 \quad (4.3)$$

MLR models have been extensively used for O_3 prediction, even though these predictions are simply based on linear and additive associations of the explanatory variables. Thus, these models are not able to incorporate the nonlinearities of O_3 concentrations (Heo and Kim, 2004; Thompson et al., 2001).

An ANN performs a non-linear transformation of input data to approximate output data. It can learn from experimental data examples, exhibiting some ability for generalization beyond the training data. The most common ANN is the FANN where the nodes are grouped into three types of layers, i.e., input layer, hidden layer and output layer, as shown in Figure 4.1. Data are fed into the nodes in the input layer and are then transferred to the subsequent layers. Cybenko (1989) has shown that a FANN with one hidden layer is sufficient to approximate any function if the hidden layer has enough nodes. The topology of the network together with the neuron processing function determines the accuracy and degree of representation of the model developed to correctly represent the system behaviour.

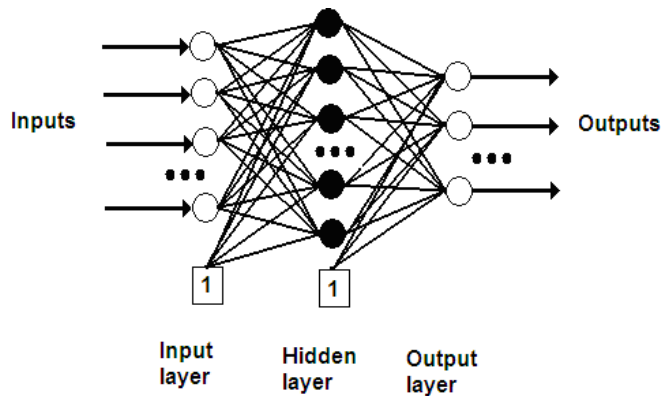


Figure 4.1 A feedforward artificial neural network with three layers.

A nonlinear function, often called an activation function, is applied to obtain the output value of the node. The activation function is usually sigmoid, hyperbolic tangent or linear. Each node in hidden and output layers has a bias value which is known as the activation threshold (Heo and Kim, 2004; Mas et al., 2004; Morabito and Versaci, 2003; Schlink et al., 2003; Aparício et al., 2002; Gardner and Dorling, 2000; Martins and Coelho, 2000; Watanabe et al., 1989).

In most cases, the FANN is achieved using two distinct datasets: training and validation. The training dataset is used to determine the network topology and the associated weights by solving a non-linear optimization problem with the objective function dictated by the mean squared error (MSE). The validation dataset is used to compute the FANN performance.

The overfitting problem that generally appears in applying FANN is usually avoided using cross-validation (Warne et al., 2004; Schenker and Agarwal, 1996). The best network topology corresponds to a FANN which presents a minimum value of MSE for validation dataset.

The non-linear features of FANN model and the possibility of incorporating pollutant concentrations and meteorological parameters as input variables suggest good performance for this model in the prediction of O₃ concentrations.

4.1.3 Performance Indexes

The performance indexes taken into account to evaluate the behaviour of the three models in the two steps of the models implementation (training and validation) were mean bias error (MBE), mean absolute error (MAE) and root mean squared error (RMSE) given by Equations 4.4, 4.5 and 4.6, respectively:

$$MBE = \frac{1}{n} \sum_{i=1}^n (\hat{Y}_i - Y_i) \quad (4.4)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |\hat{Y}_i - Y_i| \quad (4.5)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (Y_i - \hat{Y}_i)^2} \quad (4.6)$$

The MBE indicates whether the predicted concentrations are over or under estimated. The MAE and the RMSE measure residual errors which give a global idea of the difference

between the observed and modelled values (Chaloulakou et al., 2003; Gardner and Dorling, 2000; Ross, 1987).

4.2 Results and Discussion

4.2.1 Data Pre-Processing

Five datasets were considered corresponding to the trimesters (4 datasets), and to the complete year (1 dataset). The validation dataset for each trimester and for the complete year were, respectively, the last 10 and 20 days.

TS Model

TS modelling was carried out using the SATSA program (Salcedo et al., 1999). The data were transformed logarithmically for the variance stabilization and a first-order differencing was applied before Fourier analysis. Where missing data existed in the series (10% maximum), the SATSA program replaced them by the linear trend of the available measurements.

MLR and FANN Models

The MLR and the FANN models were performed using subroutines specifically developed in Microsoft Visual Basic applications for Ms-Excel, to perform this study. The simplex method defined by Nelder and Mead (Press et al., 1986) was considered during the training step of the FANN models.

These models were applied to predict the daily average of O₃ concentrations 1-day ahead. An analysis of the correlation coefficients (R), Equation 4.7, between pollutants and meteorological parameters was performed to evaluate the influence of each variable on the O₃ concentrations. These coefficients provide a measure of the linear relation between the two considered variables.

$$R = \sqrt{\frac{\sum_{i=1}^n (Y_i - \bar{Y}_i)^2 - \sum_{i=1}^n (Y_i - \hat{Y}_i)^2}{\sum_{i=1}^n (Y_i - \bar{Y}_i)^2}} \quad (4.7)$$

Table 4.1 shows the correlation coefficients between O₃ and the other pollutants and the meteorological variables based on the daily averages, as well as the respective total number of considered days (in parenthesis). The statistical significance of the regressions obtained

was analysed calculating the critical correlation coefficient, R_{crit} , with a significance level of 0.05 (two-tailed test). R_{crit} is calculated by Equation 4.8 for $DF = n - k$ degrees of freedom.

$$R_{crit} = \frac{t_{crit}}{\sqrt{DF + t_{crit}^2}} \quad (4.8)$$

The regression is statistically valid if R_{crit} is lower than the absolute value of the correlation coefficient.

Table 4.1 Correlation coefficients between O_3 and its predictors and the respective total number of days considered depending on the valid measured data (in parenthesis).

Variable	Site	R				
		1 st Trim	2 nd Trim	3 rd Trim	4 th Trim	Annual
SO ₂	TF ₁	–	–	–	–	–
	BG _{rur}	-0.14 (86)	-0.09 (88)	0.13 (90)	-0.09 (86)	0.01 (356)
CO	TF ₁	-0.70 (86)	-0.27 (86)	-0.06 (89)	-0.58 (79)	-0.53 (346)
	BG _{rur}	-0.65 (86)	0.01 (84)	0.03 (87)	-0.73 (80)	-0.52 (343)
NO	TF ₁	-0.72 (84)	-0.48 (84)	-0.36 (90)	-0.73 (88)	-0.58 (352)
	BG _{rur}	-0.66 (87)	-0.54 (88)	-0.41 (90)	-0.63 (81)	-0.58 (352)
NO ₂	TF ₁	-0.39 (84)	-0.17 (84)	0.20 (90)	-0.64 (88)	-0.27 (352)
	BG _{rur}	-0.50 (87)	-0.17 (88)	0.09 (90)	-0.79 (81)	-0.43 (352)
PM ₁₀	TF ₁	-0.28 (86)	-0.05 (88)	0.44 (90)	-0.46 (90)	-0.02 (360)
	BG _{rur}	-0.24 (87)	0.12 (88)	0.38 (90)	-0.43 (84)	-0.10 (355)
T	TF ₁	0.47 (86)	-0.01 (88)	0.40 (90)	0.20 (90)	0.33 (360)
	BG _{rur}	0.46 (87)	-0.07 (88)	0.35 (90)	0.29 (86)	0.26 (357)
RH	TF ₁	-0.45 (86)	-0.52 (88)	-0.54 (90)	-0.24 (90)	-0.49 (299)
	BG _{rur}	-0.49 (87)	-0.53 (88)	-0.56 (90)	-0.30 (86)	-0.49 (296)
WV	TF ₁	0.59 (82)	0.47 (88)	0.21 (89)	0.85 (90)	0.49 (355)
	BG _{rur}	0.54 (83)	0.45 (88)	0.26 (89)	0.74 (86)	0.43 (352)

Note: Values in bold: $R > R_{crit}$

The lowest R_{crit} was 0.21, 0.20 and 0.1, respectively, for the 1st and 2nd trimesters, 3rd and 4th trimesters, and annual dataset. The values in bold (Table 4.1) are higher than the respective R_{crit} which means that the linear regressions were statistically significant.

For the annual dataset, the concentrations of CO, NO, NO₂, T, RH and WV showed to have a significant influence on the O₃ concentrations.

The variables used in the MLR and in the FANN models were selected taking in consideration: i) the correlation coefficients as mentioned above; ii) the photochemical production, through the input of temperature and of NO and NO₂ concentrations; iii) the O₃ transport, through the input of WV; and iv) the O₃ accumulation, through the input of O₃ concentrations of one day and two days before the prediction day (the input of the concentration of three days before was tried but no enhancements were achieved). The same procedure was used for the other variables. These assumptions were supported by tests made using MLR and FANN which showed that the correlation coefficients calculated using as inputs data from two days before the prediction day (d-2) were higher than the correlation coefficients obtained when inputs were only from one day before (d-1).

Thus, the variables used to predict the O₃ levels were the concentrations of NO, NO₂ and O₃, T, RH and WV for one and two days before (Figure 4.2). The results showed that no enhancements were obtained in the coefficients when CO concentration was included.

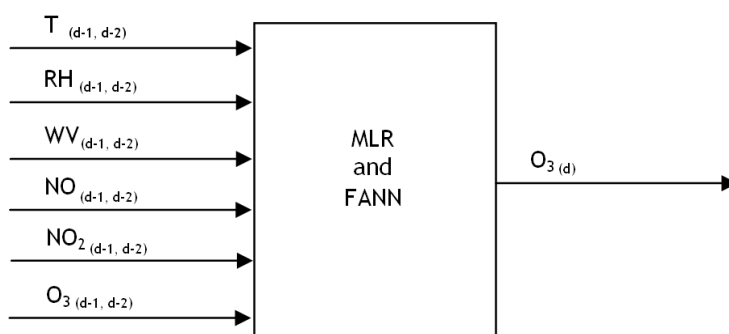


Figure 4.2 Inputs and output for MLR and FANN models.

4.2.2 Models Development

The TS model was applied to calculate the cyclic patterns of time-series of O₃ concentrations. This model applied to the TF₁ site found periods of 3.5 and 4 days for the 1st

and 4th trimesters, respectively. At the BG_{ur} site the cycle of 3.5 days was observed only in the 1st trimester. All of these periods were achieved with a p-value (Gordon and Gordon, 1994) below 0.05. However, these cycles can not be generalized, as they were not obtained for the other datasets.

Although MLR models are simple linear and additive associations of variables, they presented good results. For all datasets, the correlation coefficients were higher than the critical correlation coefficients (0.24-0.28 for trimesters and 0.11 for the complete year), obtained with a significance level of 0.05. An example of the parameters calculated with the MLR as well as the respective lower and upper bounds are shown in Table 4.2, for the 1st trimester at BG_{ur} site.

Table 4.2 MLR parameters and respective lower and upper bounds for the 1st trimester at site BG_{ur}.

	P ₀	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀	P ₁₁	P ₁₂
Parameter	9.155	-0.134	-0.064	0.969	0.162	-0.645	0.181	-0.659	0.713	-2.409	-0.081	0.729	0.467
Lower Bound	-26.066	-0.620	-0.686	-1.300	-0.195	-1.239	-0.294	-1.146	0.130	-4.648	-0.453	0.122	-0.033
Upper Bound	44.376	0.352	0.559	3.237	0.518	-0.050	0.657	-0.172	1.297	-0.170	0.291	1.336	0.967

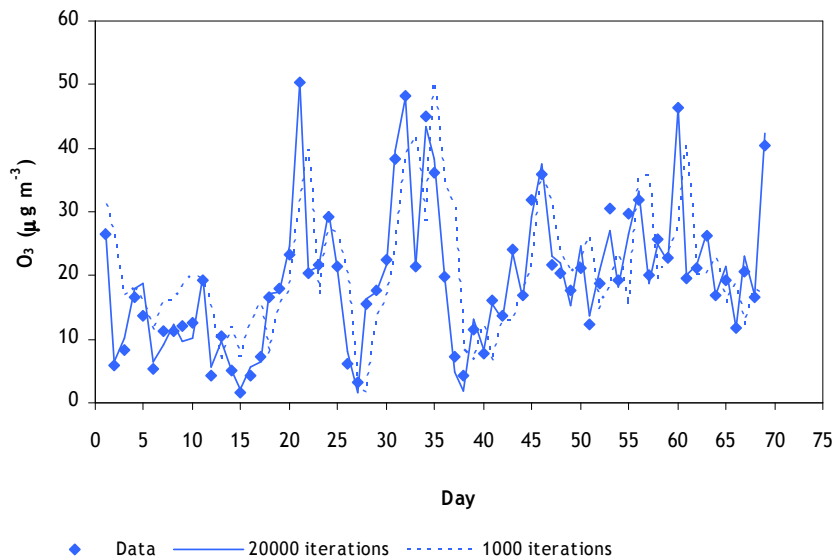
The results showed that some of these parameters might be ignored, because the limits of the confidence intervals presented different signals.

For the application of FANN models, several network structures were tested to find the most appropriate topology for the model. The best architecture, that achieved minimum values of RMSE, consisted of a three-layer network with twelve neurons in the input layer, ten neurons in the hidden layer and one neuron in the output layer. Sigmoid and linear functions were used as activation functions in the neurons of the hidden layer and output neuron, respectively.

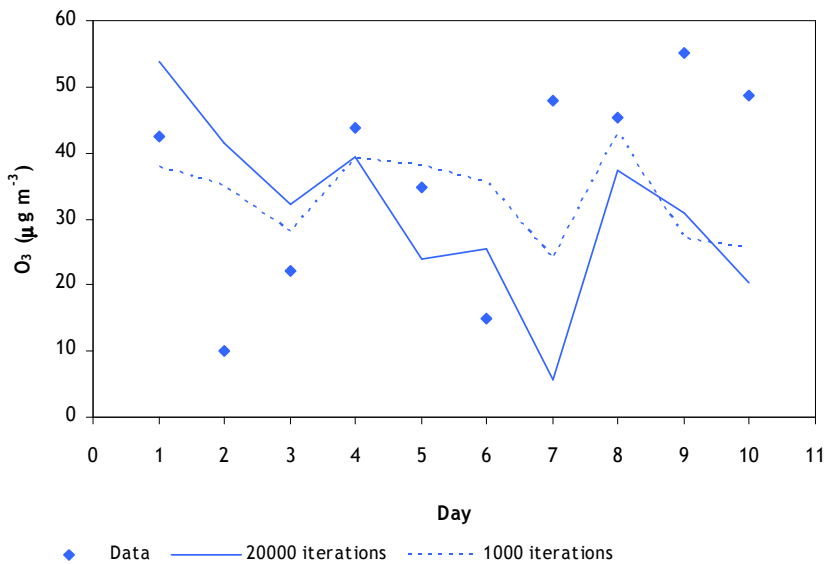
Figure 4.3 (a) and (b) shows, respectively, the results obtained during the training and validation steps for the 1st trimester at the TF₁ site.

This figure presents measured data compared with the values predicted by FANN using 20000 and 1000 iterations (cross-validation). As it can be seen in the training step, a higher number of iterations lead to a better model performance, although this did not occur in the validation step. This can be explained by an overfitting situation when 20000 iterations were

used, because the minimum MSE value in the validation step is achieved for 1000 iterations. Thus, the training step must stop for 1000 iterations.



(a)



(b)

Figure 4.3 Prediction of O_3 concentrations using FANN model: (a) training step and (b) validation step.

The performance indexes calculated in the training step of each model are presented in Table 4.3.

Table 4.3 Performance indexes achieved using TS, MLR and FANN in the development step.

Performance Indexes										
		MBE ($\mu\text{g m}^{-3}$)			MAE ($\mu\text{g m}^{-3}$)			RMSE ($\mu\text{g m}^{-3}$)		
Models		TS	MLR	FANN	TS	MLR	FANN	TS	MLR	FANN
1 st Trim	TF ₁	-2.65	-1.05×10^{-6}	0.99	7.67	6.40	8.23	10.31	8.24	10.32
	BG _{rur}	-3.10	-1.41×10^{-7}	0.96	10.42	8.73	10.06	13.41	10.62	12.49
2 nd Trim	TF ₁	-1.26	-3.50×10^{-6}	-0.73	7.62	6.66	3.41	9.56	8.38	4.33
	BG _{rur}	-1.70	-1.41×10^{-5}	0.23	12.03	10.90	9.14	15.16	13.24	12.23
3 rd Trim	TF ₁	-3.09	-2.69×10^{-7}	-0.82	11.08	9.13	6.78	14.55	10.52	8.59
	BG _{rur}	-2.65	-6.64×10^{-6}	0.64	12.90	10.30	8.71	16.48	12.57	10.93
4 th Trim	TF ₁	-3.09	-5.52×10^{-6}	2.32	9.39	6.90	6.71	12.41	8.64	8.32
	BG _{rur}	-3.81	8.19×10^{-2}	0.66	12.98	10.41	5.58	16.86	13.04	7.60
Annual	TF ₁	-4.10	-5.76×10^{-8}	0.99	11.55	8.36	9.01	14.72	10.37	11.31
	BG _{rur}	-4.74	-2.24×10^{-5}	-0.85	15.67	10.86	10.98	19.92	13.83	13.92

A lower performance was observed with the TS model for both sites. The TS model only considers as input dataset the O₃ concentrations which might be the reason for its poor performance when compared to the other models. The MBE values for this model were always negative, demonstrating that the concentrations were under estimated. Compared with the TS model, the MLR presented better results in fitting the data, having lower MBE, MAE and RMSE for both sites. For the MLR model the MBE were very close to zero for all the datasets, being positive only for the 4th trimester at BG_{rur} site. Thus in this model as well, the concentrations were generally under estimated. The performance indexes obtained with FANN presented similar values to those calculated with MLR, with the exception of MBE which were higher. However, these values were small and in most cases they were positive which demonstrated that the concentrations were overestimated.

The comparison between the site mainly influenced by traffic (TF₁) and the site that characterizes a background rural area (BG_{rur}) showed significant differences. The concentrations at BG_{rur} were generally higher due to lower concentration of nitrogen oxides

which is related with the complex photochemical reactions involved in O_3 formation; the vertical and horizontal transport phenomena also might influence the increase in O_3 concentrations. These phenomena, that affect more strongly the BG_{rur} site, were not well enough contemplated in the models, which justify their worst performance at BG_{rur} site (higher performance indexes). This means that in fact the BG_{rur} site although initially classified as a background reference one has nowadays very different characteristics, being not suitable to use as a reference site.

4.2.3 Models Validation

As it has been referred, the last 10 and 20 days were used, respectively, for each trimester and for the complete year to test the performance of the three models. For the application of MLR and FANN models, the inputs of O_3 concentrations of one and two days before were replaced by the O_3 concentrations predicted by the models.

Table 4.4 shows the MBE, MAE and RMSE calculated for the validation step.

Table 4.4 Performance indexes achieved using TS, MLR and FANN in the validation step.

Perform. Indexes	Model	1 st Trim		2 nd Trim		3 rd Trim		4 th Trim		Annual	
		TF ₁	BG _{rur}	TF ₁	BG _{rur}	TF ₁	BG _{rur}	TF ₁	BG _{rur}	TF ₁	BG _{rur}
MBE ($\mu\text{g m}^{-3}$)	TS	-10.09	3.60	-0.41	3.01	-3.13	-8.78	-16.55	-16.59	-3.99	1.61
	MLR	15.49	-33.09	3.70	-0.74	3.46	0.91	-5.47	-13.59	-11.13	4.25
	FANN	-3.19	-14.85	4.68	10.07	3.94	-2.21	-5.93	-3.53	-6.66	-4.40
MAE ($\mu\text{g m}^{-3}$)	TS	17.90	15.75	8.16	14.00	8.39	13.93	19.42	22.56	11.05	16.03
	MLR	17.78	33.61	8.48	14.73	7.07	11.89	10.86	19.77	13.80	25.74
	FANN	14.15	17.79	7.27	18.15	9.56	8.71	13.40	14.93	10.85	15.52
RMSE ($\mu\text{g m}^{-3}$)	TS	19.51	21.16	10.48	16.32	10.46	15.87	22.84	25.31	14.47	18.12
	MLR	21.19	39.22	10.16	16.77	7.65	16.92	12.11	21.19	18.15	28.45
	FANN	17.40	19.88	9.33	22.40	11.04	10.65	16.93	16.41	12.74	19.21

The results obtained showed that at TF₁ site, using TS model, MBE were always negative. The MLR presented negative MBE values only for the 4th trimester and for the annual

dataset. Considering the FANN model, MBE were negative for the 1st, 4th and annual datasets.

For the BG_{rur} site, the MBE were negative using TS model in the 3rd and 4th trimesters, using MLR in the 1st, 2nd and 4th trimesters, and using FANN in all datasets, except in the 2nd trimester. Thus, the MBE achieved at both sites did not allow differentiation between the models.

The MAE and RMSE were generally higher using TS and MLR models than with FANN models at both sites. This indicates that FANN models presented lower residual errors. However, the models did not fit the daily average of O₃ concentrations as expected.

As an example, Figure 4.4 (a) and (b) shows the predictions with all models and the measured data corresponding to the annual validation period at both sites.

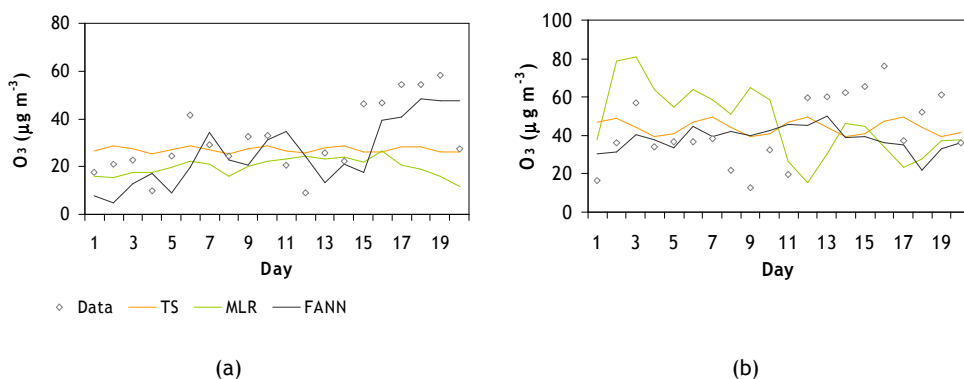


Figure 4.4 Prediction of O₃ concentrations in annual dataset: (a) TF₁ site and (b) BG_{rur} site.

For all models the performance indexes were lower at TF₁ site which was in agreement with the results achieved during the training process.

4.3. Conclusions

The photochemical production, the transport and accumulation of O₃, and the linear correlations between the variables and O₃ concentrations determined the predictors used in MLR and FANN models. Thus, the concentrations of NO, NO₂, O₃, T, RH and WV for one and two days before the prediction day were used.

The study showed that the performance of the models for O_3 forecasting is site specific with more accurate predictions for site TF_1 . This was probably due to the influence of either complex photochemical reactions involved in O_3 formation or the vertical and horizontal transports, more relevant in the BG_{rur} site; these phenomena may not be well enough contemplated in the models, which justify their worst performance at BG_{rur} site.

TS models presented the worst results in the prediction of O_3 concentrations, both in training and validation steps, which may be the result of the absence of the variables used in the other models or the result of the sample time used. FANN models presented lower residual errors in the validation step and a performance equal to MLR models in the training step. Concluding FANN models were the most efficient to predict O_3 concentrations.

Chapter 5

Comparison of Multiple Linear Regression and Artificial Neural Networks based on Principal Components*

In the former chapter it was concluded that FANN was the most efficient model, followed by MLR. These models were used in this chapter for comparison with a new methodology. Thus, as previously mentioned, this chapter reports the prediction of the next day hourly O_3 concentrations, through a new methodology based on FANN using PC as inputs. For that, the relative influence of O_3 precursor concentrations and meteorological variables on O_3 formation was evaluated, using PCA.

* adapted from: Sousa SIV, Martins FG, Pereira MC, Alvim-Ferraz MCM, 2007. Multiple linear regression and artificial neural networks based on principal components to predict ozone concentrations. *Environmental Modelling & Software* 22: 97-103.

5.1 Methodology

5.1.1 Site Characterization and Data

The air quality data were collected at the urban site previously characterized (Section 3.1.2) as having traffic influence (TF₁), situated in Oporto-MA (Figure 3.1). The meteorological parameters were measured at the representative site SP, according to what is referred in Section 3.1.2.

This study considered as predictor variables the hourly concentrations of O₃, NO, NO₂ and hourly averages of T, WV and RH, for July 2003.

O₃, NO and NO₂ concentrations monitoring methods were described in Sections 3.1.3 and 4.1.1.

5.1.2 Models

MLR and FANN (described in Section 4.1.2) were used to predict the next day hourly O₃ concentration, using as predictors air pollutant concentrations (NO, NO₂ and O₃) and meteorological parameters (T, RH and WV). The same models, but based on PCA, were also used, being referred to as principal component regression (PCR) and FANN based on PC (PC-FANN), respectively.

PCA is a multivariate statistical method widely used in air pollution analysis. The objective of PCA, as previously referred, is to reduce the number of predictive variables and transform them into new variables, called PC; these new variables are independent linear combinations of the original data and retain the maximum possible variance of the original set. The eigenvalues of the standardized matrix are calculated by Equation 5.1:

$$|C - \lambda I| = 0 \quad (5.1)$$

where C is the correlation matrix of the standardized data, λ is the eigenvalues and I is the identity matrix. The weights of the variables in the PC are then obtained by Equation 5.2:

$$|C - \lambda I| W = 0 \quad (5.2)$$

where W is the matrix of the weights.

To evaluate the influence of each variable in the PC, varimax rotation was used to obtain values of rotated factor loadings. These loadings represent the contribution of each variable in a specific PC.

The PC used for the prediction of O_3 concentrations were obtained through multiplication of the standardized data matrix by the previously calculated weights (W) (Slini et al., 2006; Çamdevýren et al., 2005).

The applicability of the PCA to the datasets used in this study was verified through the application of modified Bartlett's sphericity test, expressed by the following equation:

$$\chi_k^2 = \left[n \cdot k \cdot \frac{2(p-k) + 7 + 2/(p-k)}{6} + \sum_{j=1}^k \left(\frac{\bar{\lambda}}{\lambda_j - \bar{\lambda}} \right)^2 \right] \times \left[-\ln \prod_{j=k+1}^p \lambda_j + (p-k) \ln \bar{\lambda} \right] \quad (5.3)$$

where p is the number of components, λ_j represents the eigenvalue for the k_j^{th} component, n is the number of observations in the sample and $\bar{\lambda}$ is obtained by the following equation:

$$\bar{\lambda} = \sum_{j=k+1}^p \frac{\lambda_j}{p-k} \quad (5.4)$$

The null hypothesis considered was that all variables were uncorrelated and if non-significant, PCA should be applied (Peres-Neto et al., 2005).

The application of PC in FANN models aims to reduce the collinearity of the datasets, which can lead to worst predictions and also to determine the relevant independent variables for the prediction of O_3 concentrations. The architecture of the PCA based ANN approach is shown in Figure 5.1. The difference between this approach and the simple FANN model is that the input variables used are the PC. Consequently, the network architecture will be less complex due to the decrease of input variables.

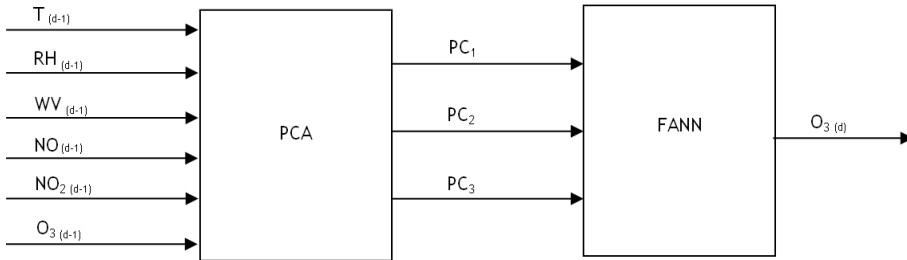


Figure 5.1 Architecture of a PC-FANN model for the prediction of next day O_3 concentrations ($O_{3(d)}$).

According to Warne et al. (2004), the use of PC based ANN eliminates the overfitting problem, i.e., both validation and training MSE continuously decrease.

5.1.3 Performance Indexes

The models behaviour was evaluated in both training and validation steps, as in the previous chapter, by calculating MBE, MAE and RMSE given by Equations 4.4-4.6, and also by the correlation coefficient (Equation 4.7), and the index of agreement (d_2), given by Equation 5.5:

$$d_2 = 1 - \frac{\left[\sum_{i=1}^N |\hat{Y}_i - Y_i|^2 \right]}{\left[\sum_{i=1}^N \left(|\hat{Y}_i - \bar{Y}| + |Y_i - \bar{Y}| \right)^2 \right]} \quad (5.5)$$

The values of d_2 compare the difference between the average, the predicted and the observed concentrations, indicating the degree of error free for the predictions (Chaloulakou et al., 2003; Gardner and Dorling, 2000;).

5.2 Results and Discussion

Correlation coefficients between pollutants and meteorological variables were analysed to evaluate the influence of each variable on O_3 concentrations, as in the previous chapter. These coefficients provide a measure of the linear relation between two variables and also indicate the existence of collinearity between the explanatory variables. The statistical significance of the regressions was analysed by calculating the critical correlation coefficient, R_{crit} , using a significance level of 0.05 (two-tailed test). R_{crit} was calculated by the Equation 4.8.

As already referred, the regression is statistically valid if R_{crit} is lower than the R and results showed that all regressions were statistically valid.

The training dataset included the 26 first days of July (616 data points) whereas the validation dataset was constituted by the last 5 days (118 data points). O_3 concentrations

varied between 0 and 95 $\mu\text{g m}^{-3}$ (average of 36.6 $\mu\text{g m}^{-3}$) and 0 and 180 $\mu\text{g m}^{-3}$ (average of 41.4 $\mu\text{g m}^{-3}$) during training and validation periods, respectively.

High correlation coefficients were found between O_3 and NO , NO_2 , T, WV and RH. Therefore, these variables were used to predict next day hourly O_3 concentrations. Also high values of R were achieved between some O_3 predictors, such as NO and NO_2 (0.56), RH and T (-0.77), demonstrating the existence of collinearity between the variables.

As previously mentioned, MLR and FANN were used to predict the next day hourly O_3 concentrations. These models were based on the original data, as in the previous chapter, (MLR and FANN) and on the PC (PCR and PC-FANN).

Table 5.1 shows the matrix of the weights for the PC, which demonstrates the relative importance of each standardized predictor in the PC calculations.

Table 5.1 Matrix of the weights for the PC.

Variables	PC ₁	PC ₂	PC ₃	PC ₄	PC ₅	PC ₆
NO	-0.325	0.557	-0.555	-0.068	0.410	0.320
NO ₂	-0.275	0.648	0.442	0.429	-0.328	-0.129
O ₃	0.472	0.040	0.234	0.530	0.658	0.086
T	-0.461	0.286	0.281	-0.396	-0.215	0.651
RH	-0.433	-0.427	0.083	0.403	-0.105	0.670
WV	0.441	0.053	-0.596	0.459	-0.484	0.041

To apply the FANN models (based on original data and PC), several network structures were tested to find the most appropriate topology. Using original variables as inputs, the best architecture consisted of a three-layer network with six neurons in the input layer, eight neurons in the hidden layer and one neuron in the output layer. Considering PC as inputs, the best architectures were achieved with different number of neurons in the input layer depending on the number of PC used. The hidden and the output layer consisted of eight and one neurons, respectively. Sigmoid and linear functions were used as activation functions in the neurons of the hidden layer and output neuron, respectively. The training was done for a maximum of 10000 iterations. To avoid the overfitting problem, which generally appears with the application of FANN, cross-validation tests were used as in the

previous chapter. The selection of the network was performed considering a minimum value of MSE for the validation dataset.

Table 5.2 presents the performance indexes using MLR and FANN for both, training and validation steps. A *t*-test (significance level of 0.05) was applied to calculate the statistically valid parameters.

Table 5.2 Performance indexes achieved using MLR and FANN during training and validation steps.

Performance indexes	Training		Validation	
	MLR	FANN	MLR	FANN
R	0.74	0.76	0.70	0.78
MBE	-1.0×10^{-5}	0.66	11.50	2.68
MAE	13.05	12.63	23.61	19.83
RMSE	16.00	15.37	29.50	25.64
d_2	0.83	0.85	0.81	0.84

During the studied period, the coefficient of NO concentrations had a confidence interval [-0.02, 0.08] showing that it was statistically invalid; thus the NO concentrations were removed from the MLR model. The derived model is as follows:

$$[O_3]_{(d)} = -57.0 + 0.16[NO_2]_{(d-1)} + 2.86T_{(d-1)} + 0.14HR_{(d-1)} + 0.54WV_{(d-1)} + 0.40[O_3]_{(d-1)} \quad (5.6)$$

The results obtained during training and validation steps using MLR demonstrated that only the MBE presented a significant difference, which means that although this model is only a simple linear additive association of the variables, it presented reasonable results.

The prediction with FANN model was performed using 2000 iterations (cross-validation). The performance indexes, calculated for the training and validation steps, were quite similar, which indicates that the model performed good predictions. Better performance indexes were achieved with FANN model for both, training and validation steps, with the exception of the MBE that was lower using the MLR in the training period. However, with FANN model, the values of MBE were positive, indicating a slight over prediction.

As previously mentioned, the next day hourly O_3 concentrations were also predicted based on the PC (PCR and PC-FANN models). Bartlett's sphericity test results (Table 5.3) showed

that the PCA was applicable to this dataset; the eigenvalues and respective variances were calculated through the PCA and are shown in Figure 5.2.

Table 5.3 Values of the χ^2 distribution using Bartlett's sphericity test.

Component	$(\chi_c)^2$	χ^2	DF
1	23.7	715	14
2	17.0	208	9
3	11.1	61	5
4	6.0	40	2

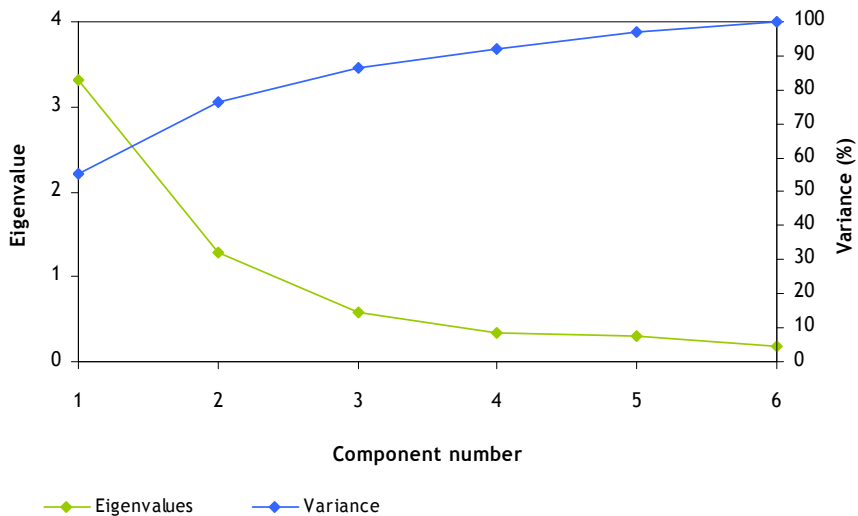


Figure 5.2 Scree plot and respective cumulative variances (%).

For PCR and PC-FANN models, the forecasting was performed considering from two to six PC separately. Considering two PC the eigenvalues were higher than considering one - Kaiser Criterion (Kaiser, 1960) - being responsible for 77% of the total variance (when considering six PC, all the variance was accounted).

A *t*-test was also performed for these regressions, to statistically evaluate the regression parameters. Considering the statistically valid parameters, new regressions were then performed.

Table 5.4 presents the values of performance indexes calculated for both models, using from two to six PC.

Table 5.4 Performance indexes achieved with PCR and PC-FANN during training (Tra) and validation (Val) steps.

PC	Model	Performance Indexes					
			R	MBE	MAE	RMSE	d ₂
Two PC	PCR	Tra	0.70	-3.1×10^{-7}	13.99	16.87	0.81
		Val	0.68	11.33	23.99	29.93	0.79
	PC-FANN	Tra	0.70	-0.04	14.00	16.84	0.81
		Val	0.63	16.18	25.16	31.96	0.82
Three PC	PCR	Tra	0.70	-4.3×10^{-7}	13.82	16.72	0.81
		Val	0.67	12.78	24.04	30.44	0.80
	PC-FANN	Tra	0.73	0.10	13.18	16.12	0.83
		Val	0.65	14.43	24.27	31.13	0.83
Four PC	PCR	Tra	0.72	-1.8×10^{-7}	13.51	16.45	0.82
		Val	0.73	9.13	22.06	28.13	0.82
	PC-FANN	Tra	0.73	0.62	13.24	16.21	0.84
		Val	0.73	6.49	21.84	27.78	0.81
Five PC*	PC-FANN	Tra	0.73	0.74	13.28	16.07	0.84
		Val	0.78	8.49	20.38	25.72	0.86
Six PC	PCR	Tra	0.74	-1.1×10^{-6}	13.02	15.98	0.83
		Val	0.68	12.12	24.04	30.03	0.81
	PC-FANN	Tra	0.77	-0.16	12.18	14.94	0.87
		Val	0.76	5.23	19.79	26.96	0.84

*The performance indexes for PCR using five PC were the same as using four PC.

Using the PCR model, performance indexes for the validation step were generally slightly worse than for the training step. It is important to point out that for this model the MBE were very low in the training step, independently of the number of PC used. The same model was achieved using either four or five PC. Considering all the models achieved with different number of PC, best performance indexes were obtained when prediction was performed using four PC, which corresponds to a cumulative variance of 91.9%. These four PC were then used as predictor variables and the following model was obtained:

$$[O_3]_{(d)} = 38.8 + 9.57PC_1 + 5.24PC_2 + 2.93PC_3 + 5.59PC_4 \quad (5.7)$$

Table 5.5 shows, as an example, the rotated factor loadings and respective communalities using four and two PC, respectively. The bold marked loads indicate the variables that most influenced the correspondent component.

Table 5.5 Rotated factor loadings using four and two PC and respective communalities.

Variables	Four PC					Two PC		
	Rotated factor loadings				Communalities	Rotated factor loadings		Communalities
	PC ₁	PC ₂	PC ₃	PC ₄		PC ₁	PC ₂	
NO	-0.112	0.879	0.376	-0.061	0.93	-0.213	0.838	0.75
NO ₂	-0.023	0.278	0.923	-0.019	0.96	-0.084	0.884	0.79
O ₃	0.486	-0.550	0.011	0.573	0.87	0.774	-0.376	0.74
T	0.885	-0.287	-0.031	0.204	0.91	0.892	-0.123	0.81
RH	-0.897	-0.013	0.044	-0.329	0.91	-0.924	-0.042	0.86
WV	0.383	-0.060	-0.289	0.833	0.93	0.733	-0.336	0.65

Bold marked loads indicate the variables that most influence each parameter

Using four PC, those variables (associated with PC₁, PC₂, PC₃ and PC₄) were: i) T and HR; ii) NO and O₃ concentrations; iii) NO₂ concentration; and iv) WV and O₃ concentration. It was also observed that with lower number of PC, more variables were accounted for each one. In addition, communalities values were higher using four PC.

The validation of PC-FANN models was performed according to the cross-validation, using different number of iterations depending on the number of PC used. The number of iterations, from six to two PC, was 500, 8000, 1000, 1000 and 3500, respectively. Also, the number of neurons in the input layer was different depending on the number of PC used.

The performance indexes, obtained using PC-FANN, were not very different in the training and validation steps, with exception of the MBE values which were slightly different. For this model, the best performance was achieved when five PC were used.

The performance indexes calculated for PCR and PC-FANN showed that the approach using neural networks led to better predictions.

Figure 5.3 shows, as an example, the predictions with all models and the measured data, corresponding to the validation period.

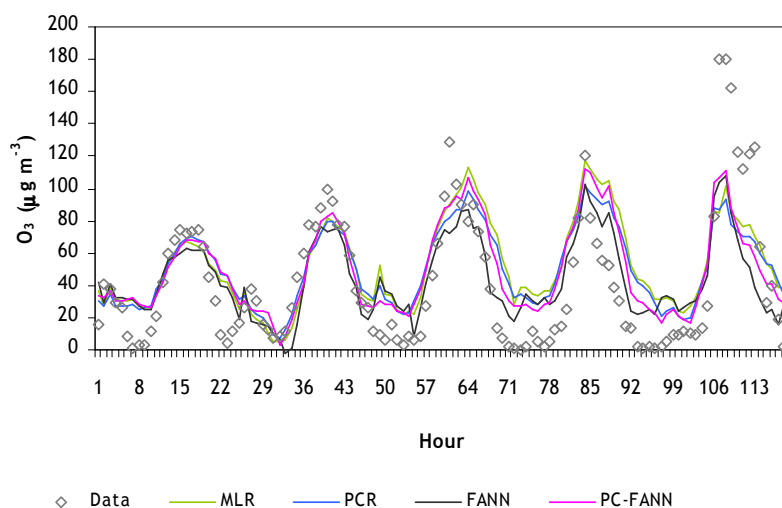


Figure 5.3 Prediction of O_3 concentrations for the first five days of the validation period.

It can be observed that the worst performance occurred with MLR and that neural networks led to better predictions. Although the PC-FANN and the FANN models presented similar results, the first approach was considered to be better, because PCA application led to the introduction of fewer variables and thus less complex networks. Therefore, PC-FANN is considered a promising tool for the prediction of O_3 concentration. It is also important to refer that the neural networks achieved a significant power of generalization beyond the training data, i.e., in validation step they were tested in extrapolated regions being able to predict hourly O_3 concentrations. Although the MBE was generally positive for all the models, meaning that, in average, the predicted O_3 concentrations were overestimated, it can be observed in Figure 5.3 that the highest measured concentrations were underestimated. This problem occurred because the highest concentrations were not contemplated during the training step, which, if possible, should be avoided. Also it was observed that the models were not able to predict lower concentrations. This occurs because, in the validation period, the percentage of data points lower than $20 \mu g m^{-3}$ was 40% and in the training period was of 25%.

5.3. Conclusions

The predictors selected through the calculation of correlation coefficients were: NO, NO₂ and O₃ concentrations and values of T, RH and WV. Two different approaches were used, considering original data and PC as inputs.

During the studied period, the coefficient of NO concentrations was found to be not statistically significant and therefore NO concentrations were removed from MLR model.

Using four PC, the original variables (associated with PC₁, PC₂, PC₃ and PC₄) were: i) T and HR; ii) NO and O₃ concentrations; iii) NO₂ concentration; and iv) WV and O₃ concentration.

The performance indexes achieved using PCR were higher than when using MLR. The use of FANN led to more accurate results than linear models (MLR and PCR), due to the account of non-linearities. The application of PC in this model was considered better than using the original data, because it reduced the number of inputs and therefore decreased the model complexity. The performance indexes were similar using both approaches.

The use of PC based models was considered more efficient, due to elimination of collinearity problems and reduction of the number of predictor variables. It was also verified that the use of PC based artificial neural networks improved the prediction of O₃ concentrations, therefore proving to be a useful tool to public health protection because it can provide early warnings to the population. Although the predicted O₃ concentrations were in average overestimated for all the models, the highest concentrations observed were underestimated, because the highest concentrations were not contemplated during the training step, which should be avoided. Also because the models were very sensitive to the training dataset, they were not able to predict lower concentrations.

Chapter 6

Comparison of Multiple Linear Regression and Quantile Regression*

Considering the difficulties in achieving good predictions for extreme values a new approach based on QR was used to predict next day hourly O₃ concentrations. The performance of this model was compared with that of MLR. Furthermore, the influence of O₃ precursors (meteorological variables and pollutant concentrations) on O₃ concentrations considering different quantiles was analysed.

6.1. Methodology

6.1.1 Site Characterization and Data

Pollutant concentrations were recorded at TF₁, an urban site previously characterized (Section 3.1.2) as having traffic influences located at Oporto-MA (Figure 3.1). Meteorological

* adapted from: Sousa SIV, Pires JCM, Martins FG, Pereira MC, Alvim-Ferraz MCM, 2008. Potentialities of quantile regression to predict ozone concentrations. *Environmetrics* 20: 147-158.

data were recorded at the representative site SP according to what is referred in Section 3.1.2. The hourly averages of T, RH, WV, wind direction (WD) and solar radiation (SR), and also the hourly average concentrations of NO, NO₂ and O₃ were used as predictor variables. O₃, NO and NO₂ concentrations monitoring methods are described in Sections 3.1.3 and 4.1.1.

The study was performed for 2003, being the analysed periods, respectively, June, July, and August separately, and the three months together. The three following datasets were used for each period, referred to the universal time coordinated (UTC): i) daylight (7:00-21:00 UTC); ii) night (22:00-6:00 UTC); and iii) all day.

6.1.2. Models

MLR was used to predict O₃ concentrations as described in Section 4.1.2.

QR was first introduced by Koenker and Bassett (1978), being seen as an extension of the least squares estimation of conditional mean models. To describe the quantile function, a random variable Y with the distribution function $F(y) = \Pr(Y \leq y)$ is considered. The quantile function $Q(\tau)$ with $\tau \in (0, 1)$ is defined as follows:

$$Q(\tau) = \inf \{y : F(y) \geq \tau\} \quad (6.1)$$

The median is $Q(1/2)$, the first quartile is $Q(1/4)$ and the first decile is $Q(1/10)$. The median regression minimizes a sum of the absolute errors. The remaining conditional quantile functions are estimated by minimizing an asymmetrically weighted sum of the absolute errors:

$$\hat{Q}(\tau) = \arg \min_a \left\{ \sum_{i: y_i \geq a} \tau |y_i - a| + \sum_{i: y_i < a} (1 - \tau) |y_i - a| \right\} \quad (6.2)$$

The model parameters, calculated considering quantile regression and a model as presented in Equation 4.2, are given by:

$$\hat{P}(\tau) = \arg \min_{P(\tau)} \left\{ \sum_{i: y_i \geq \hat{y}_i} \tau |y_i - \hat{y}_i| + \sum_{i: y_i < \hat{y}_i} (1 - \tau) |y_i - \hat{y}_i| \right\} \quad (6.3)$$

6.1.3. Performance Indexes

MLR and QR models were compared by calculating the following statistical parameters: MBE, MAE, RMSE, given by Equations 4.4-4.6.

Models behaviour was also analysed by calculating the goodness of fit (R') and the coefficient of determination (R^2), respectively, for the QR and the MLR models:

$$R' = \frac{\left(\sum_{i: y_i \geq \bar{y}_i} \tau |y_i - \bar{y}_i| + \sum_{i: y_i < \bar{y}_i} (1-\tau) |y_i - \bar{y}_i| \right) - \left(\sum_{i: y_i \geq \hat{y}_i} \tau |y_i - \hat{y}_i| + \sum_{i: y_i < \hat{y}_i} (1-\tau) |y_i - \hat{y}_i| \right)}{\sum_{i: y_i \geq \bar{y}_i} \tau |y_i - \bar{y}_i| + \sum_{i: y_i < \bar{y}_i} (1-\tau) |y_i - \bar{y}_i|} \quad (6.4)$$

$$R^2 = \frac{\sum_{i=1}^n (Y_i - \bar{Y}_i)^2 - \sum_{i=1}^n (Y_i - \hat{Y}_i)^2}{\sum_{i=1}^n (Y_i - \bar{Y}_i)^2} \quad (6.5)$$

R' measures the relative success of the corresponding quantile regression models at a specific quantile in terms of an appropriately weighted sum of absolute residuals. Therefore, it represents a local measure of the goodness of fit for a particular quantile rather than a global measure of the goodness of fit over the entire conditional distribution, such as the one represented by the coefficient of determination R^2 . As R^2 , R' is in the interval $[0,1]$ (Koenker and Machado, 1999).

6.2. Results and Discussion

MLR and QR were applied to all datasets. The dependent variables were standardized to have zero mean and unit standard deviation.

Figure 6.1 shows the constants ($\hat{\beta}_0$) generated by the models and the effect of the predictor variables (for all the day of the three months together), using both, MLR (blue bold lines) and QR (green bold lines) models. It also includes information concerning standard errors for the MLR (blue lines) using a significance level of 0.05 (two-tailed t -test), and the bootstrap estimations for QR (green lines), calculated using 1000 times replacements and a significance level of 0.05.

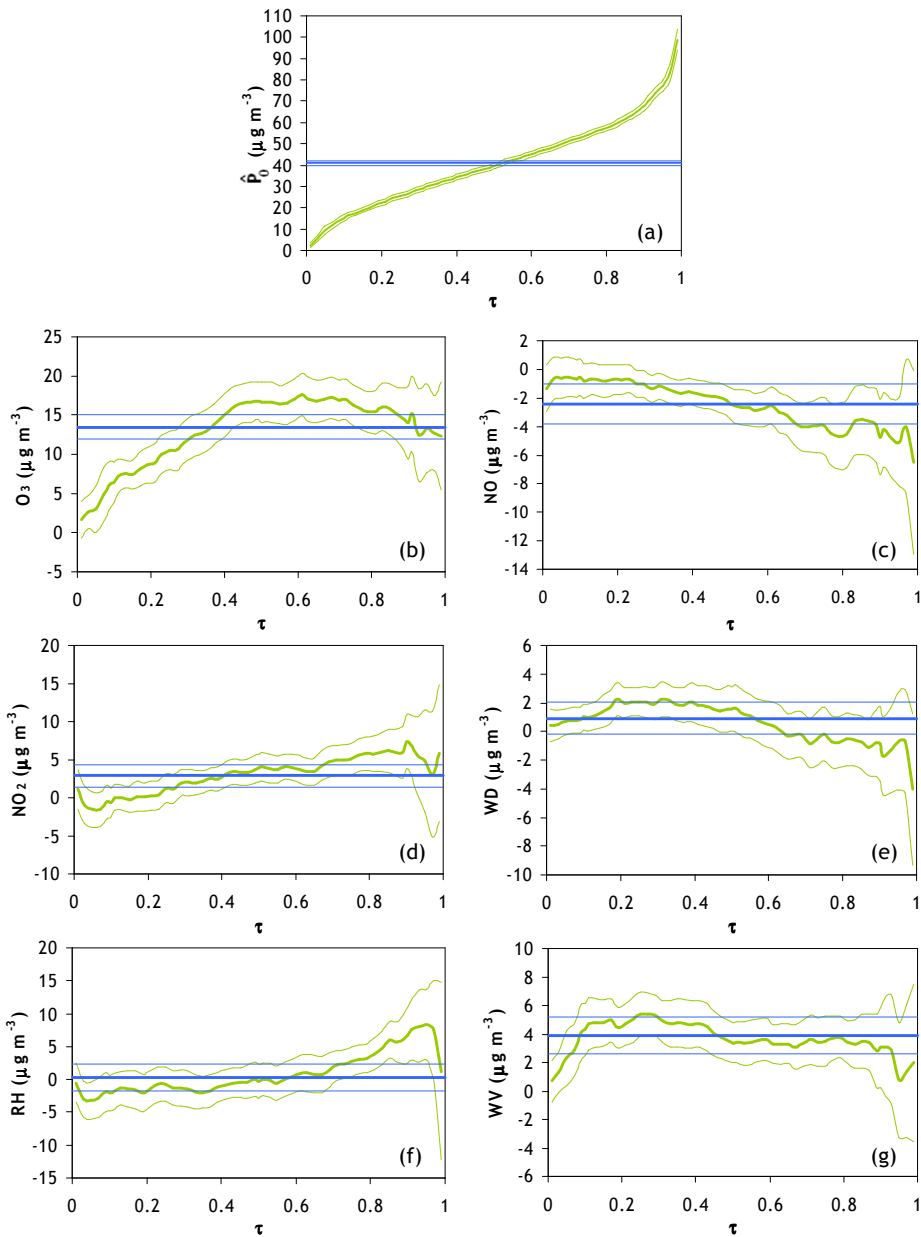


Figure 6.1 Standardized coefficients and confidence intervals estimated using MLR (blue bold lines and blue lines, respectively) and QR (green bold lines and green lines, respectively) models, for both, all day dataset and the three months together.

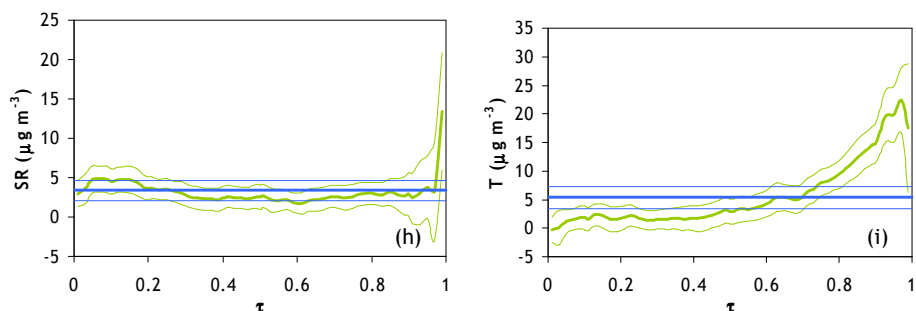


Figure 6.1 (cont.) Standardized coefficients and confidence intervals estimated using MLR (blue bold lines and blue lines, respectively) and QR (green bold lines and green lines, respectively) models, for both, all day dataset and the three months together.

Figure 6.1 (a) shows that the constant $\hat{P}_0$ on the quantile regressions was higher for higher quantiles of O_3 concentrations, with values of about $3 \mu\text{g m}^{-3}$ (0.01 quantile) and $100 \mu\text{g m}^{-3}$ (0.99 quantile). The bounds were very close showing the high confidence in the constant values. The constant behaviour was the same for all the analysed periods, showing similar values. The effect of hourly average concentration of O_3 of the previous day on the next day O_3 concentration is shown in Figure 6.1 (b). It was observed that the effect increased, from about $2 \mu\text{g m}^{-3}$ to $18 \mu\text{g m}^{-3}$, with quantile increasing (until $\tau=0.61$). For the highest quantiles, O_3 concentrations were lower, indicating less influence of this variable. For these quantiles, the analysis was less precise because the confidence interval was larger. The effect of previous NO concentrations was statistically significant from 0.25 to 0.97 quantiles, being higher for the lower quantiles, as shown in Figure 6.1 (c). The values varied between $-1 \mu\text{g m}^{-3}$ and $-5 \mu\text{g m}^{-3}$ revealing a negative effect on the O_3 concentration, with less accurate values for the higher quantiles. The effects of these variables (O_3 and NO concentrations) were statistically significant using the MLR model.

The influence of NO_2 concentrations was statistically significant between 0.3 and 0.95 quantiles and continuously increased with less accurate results for the higher quantiles. Figure 6.1 (d) shows that the standardized coefficients varied between $2.5 \mu\text{g m}^{-3}$ and $7.5 \mu\text{g m}^{-3}$. Using the MLR model, the effect of this parameter was statistically significant.

Figure 6.1 (e) shows that the influence of WD was significant for quantiles higher than 0.1 and lower than 0.53 with all values being about $2 \mu\text{g m}^{-3}$. Considering the RH, in Figure 6.1 (f), the statistically significant quantiles varied between 0.73 and 0.99, and the standardized coefficients showed values between $2.3 \mu\text{g m}^{-3}$ and $8.3 \mu\text{g m}^{-3}$. According to the MLR model, the influences of both, WD and RH were not statistically significant.

The influence of WV was significant between 0.03 and 0.91 quantiles, presenting the highest values between 0.2 and 0.4 quantiles, as it can be observed in Figure 6.1 (g). The MLR model showed that the influence of this parameter was statistically significant. Figure 6.1 (h) shows that the SR profile was very similar using both methods, although it was not statistically significant between 0.89 and 0.99 quantiles.

The influence of temperature was significant for quantiles higher than 0.45, generally increasing for higher quantiles, except for the highest ones where a decrease was observed. The results in the highest quantiles were less accurate as shown in Figure 6.1 (i). According to the MLR model, the effect of this parameter was statistically significant.

Therefore, considering the influence of O₃ precursors, QR models showed that the effects of NO concentrations, WV and WD were higher for lower quantiles. The influence of O₃ concentrations from the previous day was higher in the medium quantiles. In the higher quantiles the variables that most influenced were NO₂ concentrations, RH and T. The effect of SR was similar in all quantiles. Furthermore, the NO concentration was the unique variable with negative influence on O₃ levels. Regarding the MLR model, results showed that WD and RH had no statistically significant influences on O₃ levels.

As an example, Figure 6.2 shows the influence of temperature for the data of the three months together, considering separately the three following periods: (a) all day, (b) daylight and (c) night.

It was observed that using the QR model, the influence of temperature was generally the same, increasing in the higher quantiles. Nevertheless, the night period exhibited a different behaviour, with different statistically significant intervals. For all day and daylight periods the influence of temperature was significant for quantiles higher than 0.02 and lower than 0.43, while for the night period it happened between 0.25 and 0.58 quantiles. The different behaviour during the night period was due to the absence of photochemical production of O₃. Considering the MLR model, this parameter was always statistically significant.

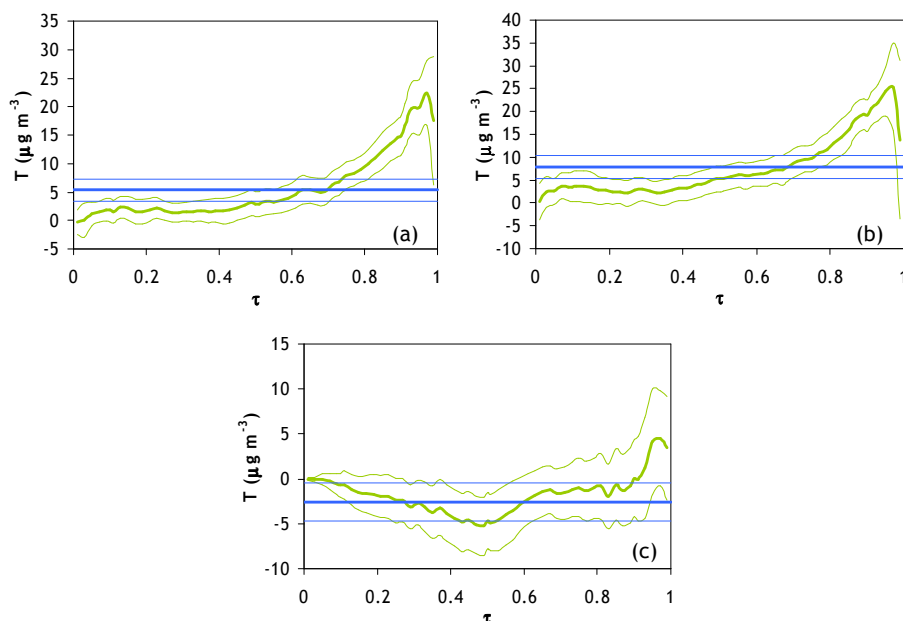


Figure 6.2 Temperature profiles for the three months considering (a) all day, (b) daylight, and (c) night datasets.

Comparing the analysis of the three months together with the analysis of June, July and August separately, it was concluded that the predictor variables showed quite similar influences, with some exceptions for August.

The study for the prediction of next day hourly O_3 concentrations was performed in two distinct steps: training and validation. In the training step, statistical significant model equations were obtained for both MLR and QR models. In the validation step, data from the last 5 days of each month and the last 10 days for the three months together were used.

The model equations for QR were obtained for the quantiles 0.1, 0.3, 0.5, 0.7, and 0.9. To calculate the performance indexes in the training step, the dataset was divided in 5 uniform datasets according to O_3 quantiles. The intervals corresponded to the values of quantiles between the following intervals: $[0, 0.2]$, $[0.2, 0.4]$, $[0.4, 0.6]$, $[0.6, 0.8]$, and $[0.8, 1.0]$, and the model equation used was the one corresponding to the respective mean quantile regression function.

In the validation step, the following procedure was implemented: i) a point that minimizes the sum of the Euclidean distances for all points was determined for each interval; ii) the minimum Euclidean distance between the determined points and each validation point was calculated; and iii) the model equation was selected according to this minimum distance.

The QR models performance in the training step was calculated using the R' (Equation 6.4). As an example, Figure 6.3 shows the values of these coefficients for each O_3 quantile for the three months together.

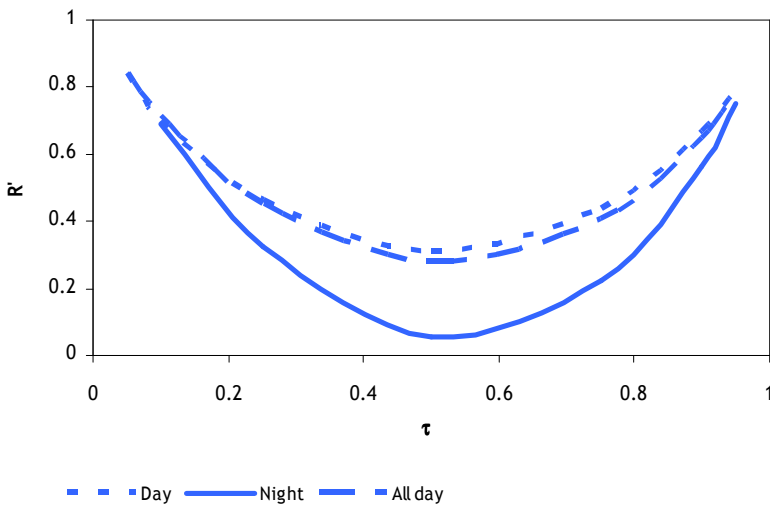


Figure 6.3 Goodness of fit obtained in the training step using QR model for the three months together.

The higher values of R' were achieved for the extreme O_3 quantiles. In addition, the values for daylight and all day datasets were similar with all periods showing the same behaviour.

Table 6.1 shows the performance indexes obtained in the training step using both models.

Concerning the QR model, it was observed that the values of MAE and RMSE were relatively similar for the different periods and datasets being always lower than the ones obtained using the MLR model. The values of R^2 , calculated for MLR approach, were similar for the daylight and the all day datasets, being worst in the night datasets. The values of MBE, MAE and RMSE were similar for all datasets. Better performances were generally achieved in July.

Table 6.1 Performances indexes achieved using MLR and QR models in the training step.

Period		MLR				QR		
		R ²	MBE	MAE	RMSE	MBE	MAE	RMSE
Daylight	June	0.55	3.35	16.90	21.24	6.62	12.27	17.90
	July	0.54	-2.36	14.70	19.02	-2.76	10.26	14.43
	August	0.50	2.59	19.01	25.95	7.47	17.08	27.51
	3 months together	0.52	0.42	16.75	22.46	3.05	13.22	19.29
Night	June	0.13	0.93	15.60	19.03	-0.15	4.47	6.62
	July	0.07	2.07	13.81	16.30	1.76	4.36	6.08
	August	0.03	0.05	15.65	18.94	-0.74	4.28	6.46
	3 months together	0.05	0.33	16.11	19.21	-0.53	5.07	6.92
All day	June	0.49	2.29	16.50	20.95	1.50	11.10	15.57
	July	0.52	3.56	14.66	18.78	0.13	11.05	14.64
	August	0.47	-1.59	18.21	24.65	3.26	13.30	21.76
	3 months together	0.49	-0.21	16.77	21.82	0.85	12.12	16.86

As an example, Figure 6.4 (a) and (b) shows the scatter plots of the O₃ concentrations achieved using, respectively, MLR and QR models, versus the measured hourly O₃ concentrations, for the three months together.

These results are in agreement with the statistical parameters expressed in Table 6.1: MLR model has a tendency to underestimate the highest O₃ concentrations, which did not happen with QR approach. Also, it was observed that the QR model was more efficient to forecast O₃ concentrations.

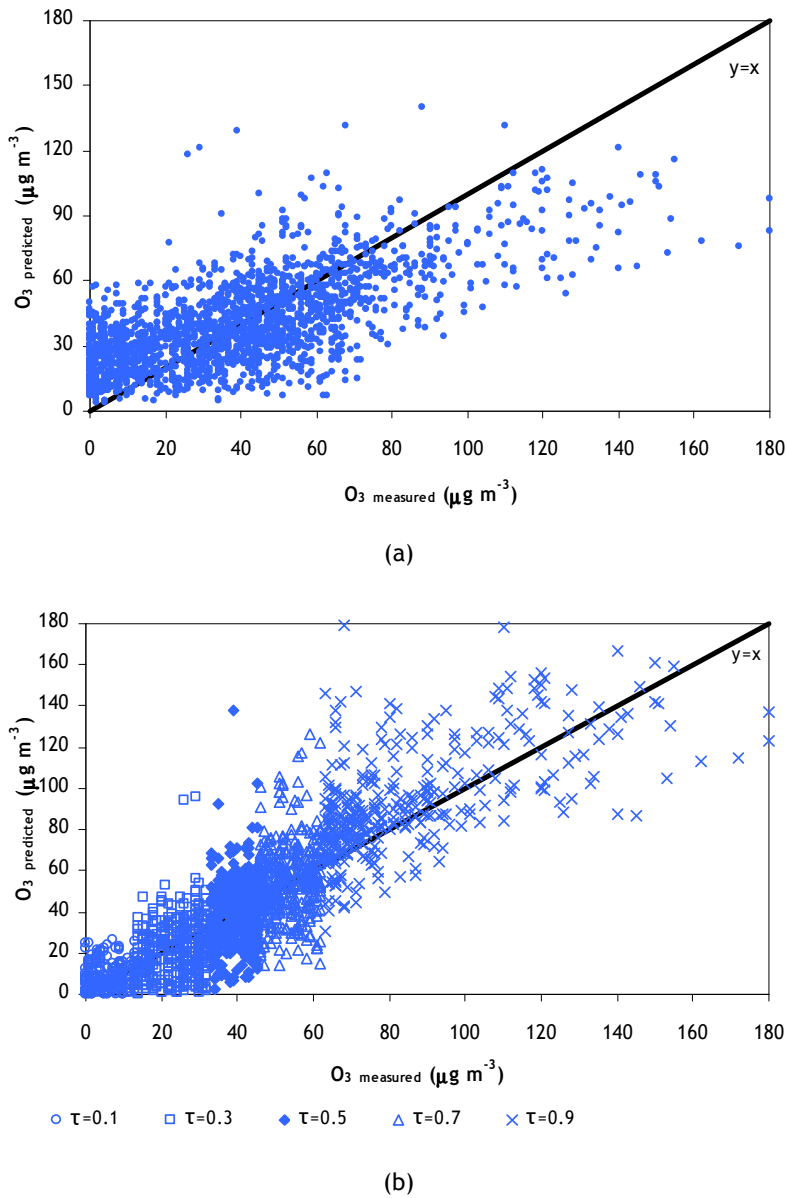


Figure 6.4 Scatter plots of the O_3 concentrations predicted versus the measured hourly ozone concentrations, for the three months together using (a) MLR and (b) QR models.

Figure 6.5 shows the predicted values using both models (MLR and QR) and the measured data in the validation period for July.

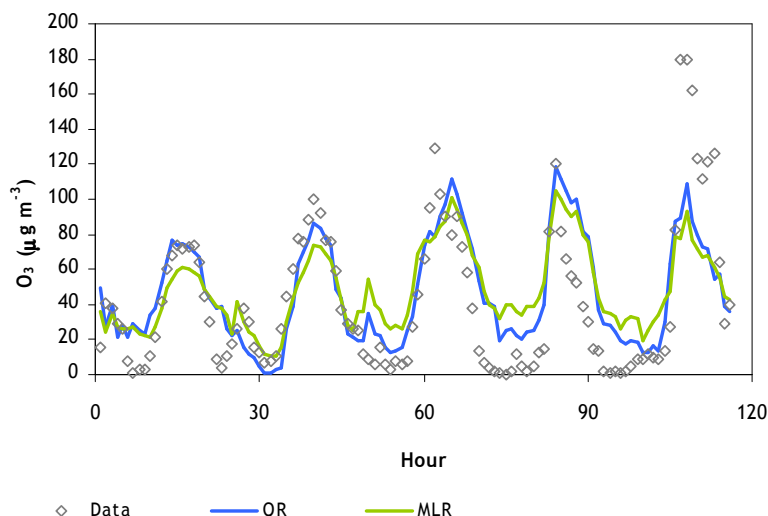


Figure 6.5 Prediction of O_3 concentrations using MLR and QR models, for the all day dataset in July.

The results showed that the QR model was more efficient than MLR model to predict both, high and low extreme values. During the training step, the values of RMSE were significantly lower for QR. Nevertheless, for the validation step they were similar ($28.9 \mu\text{g m}^{-3}$ and $27.0 \mu\text{g m}^{-3}$), meaning that the procedure used to infer which QR model equation would be the most appropriate to predict O_3 was not the most adequate. Even though, QR has proven to be an useful tool to predict O_3 concentrations, allowing more efficient previsions of extreme values which are very useful, because the forecasting of higher concentrations is fundamental for the development of more efficient strategies to protect the public health.

6.3. Conclusions

Results showed that quantile regression is a useful mathematical tool to evidence the heterogeneity of O_3 predictor influences at different O_3 levels. Such heterogeneity is generally hidden if an ordinary least square regression model is used.

Concerning the influences of predictor variables, QR model showed that the effects of NO concentrations, WV and WD were higher for lower quantiles. The influence of O_3 concentrations from the previous day was higher in the in medium quantiles. In the higher quantiles, the variables that most influenced were NO_2 concentrations, RH and T. The effect of SR was the same in all quantiles. Furthermore, the NO concentration was the unique

variable with negative influence on O_3 levels. Regarding MLR model, the results showed that WD and RH had no statistically significant influences on O_3 levels.

The prediction of hourly average O_3 concentrations for the next day showed that the QR model led to an improvement in O_3 predictions. QR model was more efficient than MLR model to predict both high and low extreme values. Nevertheless, for the validation step, the RMSE values were similar, as opposed to the ones obtained in the training step, meaning that the procedure used to infer which QR model equation would be the appropriate to predict O_3 was not the most adequate. Even though, QR has proven to be an useful tool to predict O_3 concentrations, because it allowed more efficient previsions of extreme values which are very useful, because the forecasting of higher concentrations is fundamental to develop efficient strategies to protect the public health.

PART IV
HEALTH IMPACTS OF OZONE

O₃ is a very powerful oxidizing agent and so it can react with a wide range of cellular components and biological materials. There is consistent experimental and observational evidence that O₃ has adverse effects on human health, plausibly promoting both acute and chronic effects (Curtis et al., 2006).

A very large number of studies on the acute effects of O₃ exposure in humans have been performed, employing different experimental approaches, such as single or continuous exposures, controlled exposures at rest or during exercise, exposures at ambient levels and evaluation of effects on subjects with pre-existing pulmonary diseases such as asthma or chronic bronchitis.

Studies on the effects of O₃ on the respiratory system have shown that: i) there is a solid evidence that short-term exposure impairs pulmonary function; ii) transient obstructive pulmonary alterations may occur for 6.6-hour exposures at O₃ levels of 160 µg m⁻³ (controlled exposures), which is a concentration frequently surpassed in many locations in the world; iii) people with asthma and allergic rhinitis are more susceptible to transient alterations in respiratory function due to acute exposure to O₃; iv) changes in pulmonary function and depletion of airway antioxidant defences are immediate consequences of O₃ exposure; v) O₃ enhances airway responsiveness in both healthy individuals and asthmatics. Also, studies conducted under field conditions, such as summer camps, have detected transient functional effects at O₃ levels considerably lower than those observed in controlled exposures. Various factors may account for this discrepancy, like concomitant exposure to other pollutants and difficulties in precisely determining individual exposure. On the other hand, the higher number of days of observation in such studies increases the power of detecting a significant effect (WHO, 2006; USEPA, 2006). The effect of O₃ on respiratory morbidity has also great evidence, being school absenteeism, hospital admissions or emergency department visits for asthma, respiratory tract infections and exacerbation of chronic airway diseases the most common health outcomes studied. A 20% increase in school absenteeism was reported in a study in Mexico City, being associated with ambient O₃ concentrations higher than 260 µg m⁻³ for two consecutive days, being the effect amplified

by low temperature. Also, in northern Nevada, absenteeism was studied in elementary schools and it was estimated an increase of 13% per 100 $\mu\text{g m}^{-3}$ of O_3 increase. There are large multi-city studies relating numbers of hospital admissions for respiratory diseases and COPD to ambient O_3 levels. Such associations were robust enough to persist after controlling for temporal trends in admission rates, day-of-week and seasonal effects, gaseous and particulate air pollution, and climatic factors. Effects of O_3 on respiratory admissions seem stronger during warmer weather. In a study conducted in the Connecticut area, O_3 was significantly associated with respiratory symptoms in asthmatic children; a 100 $\mu\text{g m}^{-3}$ increase in 1-hour O_3 was associated with increased likelihood of wheeze (by 35%) and chest tightness (by 47%). Within a cohort of 846 inner-city asthmatic children aged 4-9 years in seven American communities, an increase in O_3 of 30 $\mu\text{g m}^{-3}$ was associated with a higher risk of morning symptoms (OR 1.16; 95% confidence interval (CI) 1.02-1.30) and with a 0.59% decline in morning peak expiratory flow rates (PEFR) (95% CI 0.13-1.05). The range of relative risks of mortality due to respiratory diseases for an increase of 20 $\mu\text{g m}^{-3}$ in O_3 concentrations was between 0.23% and 6.6%, depending on the age group, season of the year and model specifications (WHO, 2006). Determining the specific cause for mortality is more difficult due to reduced statistical power to examine the associations and the lack of clarifying information of the causes of death (USEPA, 2006).

The effect of short-term exposure to ambient O_3 on cardiovascular function and the initiation and progression of cardiovascular disease in laboratory animals and human populations is an emerging field. Few studies have been conducted in this field, however showing associations of acute effects to O_3 exposure. The vast majority of the studies obtained positive and significant associations between variations in ambient O_3 levels and increased morbidity. The effects were manifested among children, elderly people, asthmatics and those with COPD. A study performed in the Massachusetts area reported reduced heart rate variability (well-documented risk factor for cardiac disease) of 11.5% (95% CI 0.4-21.3) with a 2.6 $\mu\text{g m}^{-3}$ increment in the previous 4-hour average of O_3 , being the effect stronger in men with ischemic heart disease and hypertension. Furthermore, another study performed in the Boston area reported an increased risk of arrhythmia in patients who had implanted defibrillators, associated with short-term increases in ambient O_3 . The OR for a 44 $\mu\text{g m}^{-3}$ increase in O_3 concentration during the hour before the arrhythmia was 2.1 (95% CI 1.2-3.5). These first studies of acute changes in cardiac function associated with ambient O_3 exposures provided biological plausibility for the associations between cardiac morbidity and mortality and O_3 level in the epidemiological studies. Nevertheless, ten out of fifteen studies focusing on cardiovascular diseases (WHO, 2006) showed no significant effects of O_3 .

In addition, there was no clear positive effect of O₃ on any of the particular outcomes evaluated in those studies (myocardial infarction, sudden death, stroke, congestive heart failure and peripheral arterial diseases). Interestingly, in Asia, O₃ was associated with mortality due to stroke.

Evidence for O₃ chronic effects has also been increasing in the last decades (Binková et al., 2004). Preferably, a long-term assessment of O₃ effects in humans should include epidemiological studies investigating cumulative O₃ exposure in association with three types of health outcomes, namely, lung function reduction, development of atherosclerosis, death or reduction on life expectancy and increase of asthma (WHO, 2006). Measures of lung function have most often been used as an objective early marker of chronic pulmonary effects. Several studies have shown associations between O₃ exposure and small airway function and seasonal changes on lung function growth (WHO, 2006). The epidemiologic data, collectively, indicate that the current evidence is suggestive but inconclusive for respiratory health effects from long-term O₃ exposure (USEPA, 2006). The development of atherosclerosis was also studied, but the association with long-term O₃ exposure is not yet quite clear (WHO, 2006). Several studies have reported associations between long-term O₃ concentrations and death rates, being, nevertheless, inconsistent. Recent cohort studies have associated “warm-weather O₃” and cardiopulmonary mortality, with a relative risk of 1.08 (95% CI 1.01-1.16) and a significantly “protective” association for lung cancer. A cohort from the American Cancer Association observed increased mortality from cardiopulmonary diseases but not lung cancer associated with long-term summertime exposure to O₃. In the 15-year follow-up of the Adventist Health Study of Smog (AHSMOG), lung cancer was significantly associated with O₃ level among men; associations were positive for other causes of death but not statistically significant. Nevertheless, cohort studies include, at least in theory, both chronic and acute effects. Thus effects observed in cohort studies may not necessarily be solely due to chronic effects (WHO, 2006). The development of asthma has been also studied in relation with long-term exposures to O₃ (WHO, 2006). Asthma is a complex respiratory disease whose symptoms include dyspnoea, wheezing, chest tightness and recurrent cough (Alvim Ferraz et al., 2005). This is one of the respiratory diseases that has been directly associated with air pollution, featuring an accumulation of inflammatory cells and mucus in the airways, with bronchoconstriction and a generalised airflow limitation (Trasande and Thurston, 2005; Donaldson et al., 2000). Asthma is increasing all over Europe and a large portion of this increase is in childhood, being now the most common respiratory disease in western European children (Anthracopoulos et al., 2007; EEA, 2005b; Jalaludin et al., 2000). On average 7 % of EU-25 children aged 4-10 have problems with asthma although

there is a significant variation between EU countries (EEA, 2005b). Undoubtedly, persons with asthma, especially asthmatic children, are sensitive to air quality and several studies have demonstrated a strong association between exposure to air pollution and worsening of asthma (Ho et al., 2007; Salvi, 2007; D'Amato et al., 2005; Parnia et al., 2002; Friedman et al., 2001; Ramadour et al., 2000; Jedrychowski and Flak, 1998; Leikauf et al., 1995; Ware et al., 1993). Several studies have been conducted regarding the association of O_3 and the respiratory problems in children. A study from California has also indicated O_3 as a trigger of asthma development in non-asthmatic children, which supports a long-favoured assumption that air pollutants play a role in asthma initiation (McConnell et al., 2002). However, in general there is little evidence that air pollution is responsible for the increase in the number of children developing asthma symptoms (asthma prevalence) (EEA, 2005b). Additionally, the comparison between studies is most times a difficult task, because the criteria for analysis are not conveniently established; previous studies considered different criteria, namely concerning the parameters selected for asthma identification, the presence of other pollutants, the age of the children, the exposure assessment and others like the confounding effects of environmental tobacco smoke, and the study power.

Gent et al. (2003) examined during 6 months (from April 1 through September 30, 2001), the simultaneous effect of O_3 and $PM_{2.5}$ at levels below US Environmental Protection Agency (US EPA) standards, on daily respiratory symptoms and rescue medication use. Two hundred, seventy one asthmatic children younger than 12 years old and living in Massachusetts were analysed. Levels for O_3 were $118 \mu g m^{-3}$ (maximum 1-hour average) and $102 \mu g m^{-3}$ (8-hour average) and for $PM_{2.5}$ was $13 \mu g m^{-3}$ (24-hour average). It was concluded that even for O_3 levels below US EPA standards (controlling for fine particle concentration), the children with severe asthma had a significantly increased risk of worsening the respiratory symptoms. Triche et al. (2006) examined respiratory effects of O_3 in infants with asthmatic mothers. The study enrolled 780 women delivering babies between 1994 and 1996 at south-western Virginia. 691 infants, excluding those influenced by environmental tobacco smoke, were followed between 10 June and 31 August 1995 and/or 10 June and 31 August 1996. Measurements of O_3 (24-hour average, peak 1-hour and maximum 8-hour running average), $PM_{2.5}$ and PM_{10} (both 24-hour average) were performed. The 24-hour average O_3 concentration was $70.4 \mu g m^{-3}$. Average concentration of both maximum daily 8-hour running averages ($109 \mu g m^{-3}$) and daily 1-hour peak ($121.6 \mu g m^{-3}$) for the period studied were below the US EPA standards. The average concentration of $PM_{2.5}$ ($23.2 \mu g m^{-3}$) was also below the US EPA standard. Models relating O_3 and respiratory symptoms were developed controlling for temperature, humidity, $PM_{2.5}$ and coarse particles. It was concluded that even at low

levels of O₃ exposure, infants had a significantly increased risk of worsening respiratory symptoms, particularly if their mothers have a history of physician-diagnosed asthma.

Also the differences in the prevalence of asthma in children living in rural and non-rural environments have been target of study; however, different conclusions have been achieved. Priftis et al.(2007) compared, over a period of 8 years, the respiratory health of schoolchildren living at urban (478 children) and rural (342 children) areas, through the assessment of parent completed questionnaire (performed in three phases: 1995/1996; 1999/2000; and 2003/2004) and also by evaluating spirometry indices in the two first phases; concentrations of NO₂, SO₂, O₃ and PM₁₀ were recorded, the annual average concentrations being: i) for NO₂, 31-42 µg m⁻³ (urban) and 4-15 µg m⁻³ (rural); ii) for SO₂, 10-19 µg m⁻³ (urban) and 3-10 µg m⁻³ (rural); iii) for O₃, 60-80 µg m⁻³ (urban) and 40-70 µg m⁻³ (rural); and iv) for PM₁₀, 55 µg m⁻³ (urban, 2001) and 68 µg m⁻³ (urban, 2002); the rates of wheezing for children living in urban and rural areas were similar and remained so for the 8 studied years; children living at rural areas had lower forced vital capacity (FVC) in the first phase and higher forced expiratory flow over the mid-range of expiration (FEF_{25%-75%}) in both phases; this study concluded that in Greece, urban living with long-term exposure to outdoor air pollutants did not result in an increased prevalence of asthma among schoolchildren.

The International Study of Asthma and Allergies in Childhood (ISAAC) was created to maximise the value of epidemiological research into asthma and allergic diseases in children by establishing a standardised methodology and facilitating international collaboration (Asher et al., 1995). This study has been trying to estimate childhood asthma prevalence over 50 countries. Comparisons between rural and urban environments have been also performed. Results have already shown that asthma prevalence has been growing in countries like Scotland, Finland, Australia, Holland, Norway and Portugal (Barros et al., 1999; Chrischilles et al., 2004; SPAIC, 2008).

Gauderman et al.(2004) recruited 1759 children with 10 years old in average, from 12 schools in southern Californian communities and measured air pollutant concentration and lung function annually for eight years; the annual average concentrations of air pollutants in the different communities, from 1994 to 2000 were: i) for O₃ 60-130 µg m⁻³; ii) for NO₂ 8-75 µg m⁻³; iii) for PM₁₀ 15-65 µg m⁻³; and iv) for PM_{2.5} between 5-28 µg m⁻³; results of the study provided evidence that lung development, measured by the growth in FVC, forced expiratory volume in the 1st second (FEV₁) and maximal mid-expiratory flow (MMEF), is

reduced in children with ages between 10 and 18 years old exposed to higher levels of air pollution.

However, these and other studies relating lung function and air pollution mixtures could not discern the independent effects of pollutants because of their common sources and the degree of correlation between them (Lewis et al., 2005; Gauderman et al., 2004; Jedrychowski et al., 1999; Peters et al., 1999). Few other studies have addressed the long-term effects of O₃ on lung function in children, and results have been inconsistent (Gauderman et al., 2004). Thus, research in this field is still a very emerging issue.

Being one of the issues that have more influence on the study of the impacts of air pollution on health, exposure assessment should be carefully studied prior to any study. In National Air Quality Monitoring Networks, O₃ concentrations are measured with monitors working continuously. Data are collected via modem through specific software to calculate and store 15 minute averages. These measurements are costly and essentially designed for measuring at urban and suburban areas. The use of such equipment at remote areas is very difficult, reason why the values of O₃ concentrations at remote areas are almost unknown (Sanz et al., 2007; Manes et al., 2003). Aiming to perform O₃ measurements at remote areas monitoring alternatives were developed. A low-cost alternative and/or complement to continuous monitors is the use of passive samplers. These samplers require no power, are simple to assemble and operate and do not require calibration on the field. Nevertheless, as these measurements are based on sampling periods of some weeks, the results cannot be used to evaluate the exceedances, related to legislated standard values (Section 2.4) (Directive 2002/3/EC). However, the passive samplers can provide a baseline on the O₃ exposures at remote areas, consequently supplying information on the need for additional continuous monitoring at those areas, and they can also provide more personal exposures, as they can be set in the environment of the population in study (Sanz et al., 2007; Manes et al., 2003; Krupa and Legge, 2000; Bernard, et al., 1999; Heal et al., 1999).

Several studies have been published regarding the monitoring of O₃ using passive samplers. Bernard et al. (1999) determined a way of assessing personal exposure to O₃ in all districts in where their study group was living and/or working. Krupa et al. (2003) described a statistical approach to simulate passive O₃ sampler data to mimic the hourly frequency distributions of continuous measurements using climatologic O₃ indicators and passive sampler measurements. Yuska et al. (2003) detected and recorded O₃ concentrations to determine their relationships to O₃-induced foliar injury at numerous remote and forested sites.

The confounding effects of other pollutants are also a subject to consider when assessing the exposure of a population or group. Not only the influence of chemical species is important but also the biological pollutants have to be taken in consideration. In the last decades, epidemiological studies have been showing that those pollutants may be responsible for various pathologies in the respiratory tract (Berico et al., 1997) and an increasing number of aerobiological studies has been conducted around the world (Ridolo et al., 2007; Abreu and Ribeiro, 2005; Oliveira et al., 2005; Smith and Emberlin, 2005; Burge, 2002).

Pollen is the male gametophyte of seed plants and is produced as part of the sexual reproduction cycle. They are inert particles and its dispersion is assured by several biotic and abiotic factors. The wind is the main abiotic transporter carrying these particles along several kilometres. Fungal spores, uni or multicellular, are reproductive or distributional structures produced during the life cycle of fungi. About 100 000 species of fungal spores are known today, being about 80 related with allergic pathologies, whereas allergenic proteins have been identified in 23 fungal genera (Simon-Nobbe et al., 2008). Pollen grains and fungal spores are inert particles being seasonal air pollutants. Their presence and dispersion in the atmosphere depends on a wide range of factors including meteorological (temperature, rain, humidity, wind, etc), biological (physiological state of plants, plant distribution, pollinators, etc) and topographical issues.

Also the relation between meteorological parameters and the biological particles has been worldwide documented (Oliveira et al., 2005; Green et al., 2004; Ribeiro et al., 2003; Vliet et al., 2002; Sabariego et al., 2000; Angulo-Romero et al., 1999; Calderón et al., 1997; Katial et al., 1997). However, studies concerning the relations between non-biological pollutants and biological particles are still few. Adhikari et al. (2006) examined the relationships between inhalable airborne pollen and fungal spores with some chemical air pollutants, using basic linear correlations and linear regression models for different pairs of variables. Ho et al. (2005) analysed correlations between fungal spores (not considering pollens), non-biological pollutants and meteorological factors using correlation coefficients and multiple linear regressions; they concluded that the correlations were complex, showing that further studies are needed on these topics. Furthermore, as far as it is known, the influence of multiple parameters on pollen was not yet studied.

Chapter 7

Elimination of Confounding Effects

7.1. Influence of Atmospheric O₃, PM₁₀ and Meteorological Factors on the Concentration of Airborne Pollen and Fungal Spores^{*}

Considering the potential relevance of crossed effects of non-biological pollutants and pollens and fungal spores on allergy worsening (WHO, 2005), the aims of this work were to evaluate the influence of O₃, PM₁₀ and meteorology on the pollen and fungal spore airborne concentration using linear and multiple linear correlations. The analysis of the seasonal variation of O₃, PM₁₀, pollen and fungal spores were also performed.

^{*} adapted from: Sousa SIV, Martins FG, Pereira MC, Alvim-Ferraz MCM, Ribeiro H, Oliveira M, Abreu I, 2008. Influence of Atmospheric Ozone, PM₁₀ and Meteorological Factors on the Concentration of Airborne Pollen and Fungal Spores. *Atmospheric Environment* 42: 7452-7464 (with collaboration of Instituto de Biologia Molecular e Celular/ Faculdade de Ciências da Universidade do Porto).

7.1.1 Methodology

7.1.1.1 Site Characterization and Data

The data considered in this study were collected in Oporto city (Figure 3.1). Samplers were located at TF₂ (urban site with traffic influences described in Section 3.1.2). O₃ and PM₁₀ samplers were located in the area covered by pollen and fungal spores sampling (approximately 1 km distant). Ornamental and nonornamental trees, shrubs and herbaceous species can be found in the surroundings of the sampling site (some of this species are considered to be allergenic pollen producers and can act as an inoculation source for fungal).

The study here reported considered the daily average of O₃ and PM₁₀ concentrations, T, RH, PP, WV, pollen and fungal spore concentrations, for 2003, 2004 and 2005. The non-biological data were recorded as explained in Section 3.1.2. O₃ measurements were performed as referred in Section 3.1.3 and PM₁₀ concentrations were obtained as referred in Section 4.1.1. The meteorological parameters were continuously measured as referred in Section 3.1.2. The pollutant, pollen and fungal spore monitors were approximately 3 km far from this site.

Airborne pollen and fungal spores were continuously monitored, by *Instituto de Biologia Molecular e Celular*, using a seven day Hirst type volumetric spore trap manufactured by Burkard Manufacturing Company Limited UK. This sampler has a 2x14 mm intake orifice through which the sampled air is impacted onto a drum, rotating once every 7 days. A vane tail keeps the intake orifice facing the wind and a vacuum pump allows a suction of ten litres of air per minute that is equivalent to the human inhalation. Airborne particles were trapped on a Melinex tape coated with silicone oil, which was cut in seven pieces of 48 mm (each one corresponds to one day) and mounted on the slides with a mounting media of glycerol jelly. Pollen grains and fungal spores were identified and counted under an optical microscope (400X) using four and two traverses lines, respectively, evenly spread over the glass slide.

The pollinic types considered in this study were: *Acer* spp., *Alnus* spp., Asteraceae, Betulaceae, Caryophyllaceae, *Castanea* spp., Chenopodiaceae/Amaranthaceae, *Corylus* spp., Cupressaceae, Ericaceae, *Fraxinus* spp., Myrtaceae, *Olea europea*, Pinaceae, *Plantago* spp., *Platanus* spp., Poaceae, *Quercus* spp., *Rumex* spp., *Salix* spp., *Ulmus* spp. and Urticaceae. Due to the difficulty on distinguishing some pollen of plant species belonging to the same

family, because of its similar morphology, it is common to aggregate them by the family names.

The fungal spore types considered were: *Alternaria* spp., Aspergillaceae, *Botrytis* spp., *Cladosporium* spp., *Coprinus* spp., *Corynespora* spp., *Didymella* spp., *Drechslera* spp., *Epicoccum* spp., Rusts, *Fusarium* spp., *Ganoderma* spp., *Leptosphaeria* spp., *Oidium* spp., *Periconia* spp., *Pithomyces* spp., *Pleospora* spp., *Polythrincium* spp., *Rhizopus stolonifer*, *Torula* spp. and *Ustilago* spp.. The sampling method used in this study does not allow the distinction between *Aspergillus* spp. and *Penicillium* spp. spores due to their reduced size (*Aspergillus* spp.: 2-10 µm; *Penicillium* spp.: 3-5 µm), being both spore types included in the category of Aspergillaceae.

7.1.1.2 Statistical Methods

The comparisons of the parameters above described were performed using daily data. Whenever linear correlations and MLR were performed and a data point was not available for a parameter, the correspondent data points of the other were withdrawn from the analysis.

The analysis of the parametric correlation coefficients between non-biological pollutants, meteorological parameters and all the biological pollutants was performed, aiming to evaluate the influence of each variable on the concentrations of pollen and fungal spores. As already referred, these coefficients provide a measure of the linear relation between the two considered variables. As previously, the statistical significance of the correlations obtained was analysed calculating the critical correlation coefficient, R_{crit} (Equation 4.8) with a significance level of 0.05 (two-tailed test).

MLR (described in Section 4.1.2) was also used to model pollen and fungal spores, considering non-biological pollutant concentrations (O_3 and PM_{10}) and meteorological parameters (T, PP, RH and WV) as predictors. The statistical significance of the regressions obtained was also analysed calculating the critical correlation coefficient, R_{crit} . The behaviour of MLR was evaluated calculating the RMSE according to Equation 4.6 and the adjusted correlation of determination (R^2_{aj}), according to the following equation:

$$R^2_{aj} = R^2 - \frac{k-1}{n-k} \times (1-R^2) \quad (7.1)$$

where R^2 is the coefficient of determination.

R^2_{aj} , that is lower than R^2 , adjusts R^2 for the number of explanatory terms in a model. Unlike R^2 , the R^2_{aj} increases only if the new term improves more the model than would be expected by chance. As this test does not give the model accuracy, RMSE was also reported. As already referred, this statistical parameter measures residual errors, which provides a global idea of the difference between the observed and modelled values (Chaloulakou et al., 2003; Gardner and Dorling, 2000).

7.1.2 Results and Discussion

7.1.2.1 Descriptive Statistics and Seasonal Studies

Table 7.1 shows the median, average, minimum and maximum, of the concentrations of O_3 and PM_{10} , meteorological parameters and concentrations of pollen and fungal spores, for 2003, 2004 and 2005. There were 365, 366 and 365 data, respectively for 2003, 2004 and 2005, with exceptions for O_3 and PM_{10} that had, respectively, 351 and 362 in 2003, 364 and 353 in 2004 and 364 both in 2005.

The concentrations of O_3 exceeded the standard values (Directive 2002/3/EC) for the three years and the average concentrations of PM_{10} exceeded the legislated limits (Directive 1999/30/EC) for 2004; the maxima concentrations were always above $120 \mu g m^{-3}$. The meteorological parameters were for these three years according to what was expected, nevertheless with higher temperatures in 2003.

The average and maximum values for each airborne pollen concentration and fungal spore types varied inter-annually, while the minimum values were always zero for each type considered. These minimum values were expected because, just like precipitation, the occurrence of airborne pollen and fungal spores in the atmosphere is seasonal.

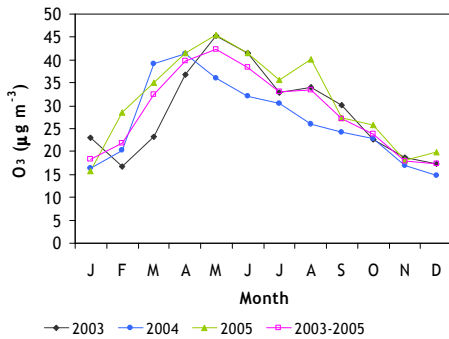
The seasonal evolution of the concentrations of O_3 and PM_{10} , T, RH, PP and WV for 2003, 2004, 2005 and for the global period (2003-2005), based on the monthly averages calculated with the hourly values, are presented in Figure 7.1 (a) to (f).

Table 7.1 Descriptive statistics of non-biological pollutants, meteorological parameters and inhalable bioaerosols (pollen and fungal spores), for 2003, 2004 and 2005.

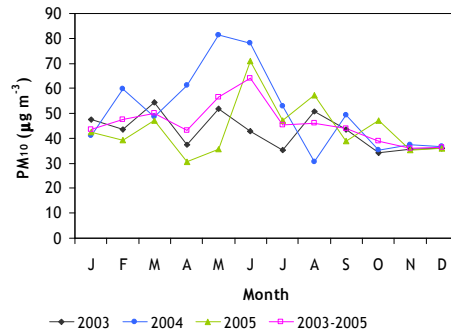
	2003				2004				2005			
Parameter	Median	Average	Min	Max	Median	Average	Min	Max	Median	Average	Min	Max
O ₃ (µg m ⁻³)	27.46	28.75	1.29	75.96	24.44	26.70	1.25	71.96	29.19	31.25	2.91	82.00
PM ₁₀ (µg m ⁻³)	38.46	42.87	0.00	129.79	42.67	50.57	7.13	203.29	38.46	44.08	8.75	165.17
T (°C)	14.93	15.27	4.03	31.06	14.13	14.73	5.52	27.28	15.17	15.03	3.60	29.88
HR (%)	81.75	78.87	34.04	98.17	80.00	77.26	30.67	99.54	76.04	72.47	28.29	96.58
PP (mm)	0.00	3.84	0.00	75.30	0.00	2.60	0.00	76.40	0.00	1.91	0.00	58.10
WV (km h ⁻¹)	14.83	15.90	6.40	37.29	13.46	14.70	2.67	40.54	14.54	15.60	5.79	35.04
Pollen categories (pollen m ⁻³ air)												
Aceraceae	0.00	0.40	0.00	14.88	0.00	1.39	0.00	75.89	0.00	0.68	0.00	43.15
<i>Alnus</i> spp.	0.00	0.17	0.00	5.46	0.00	0.61	0.00	22.32	0.00	0.72	0.00	23.81
Asteraceae	0.00	0.22	0.00	4.96	0.00	0.03	0.00	2.98	0.00	0.01	0.00	1.98
Betulaceae	0.00	0.10	0.00	2.48	0.00	0.56	0.00	34.22	0.00	0.57	0.00	25.79
Caryophyllaceae	0.00	0.06	0.00	2.48	0.00	0.13	0.00	5.95	0.00	0.01	0.00	1.49
<i>Castanea</i> spp.	0.00	0.50	0.00	19.34	0.00	0.53	0.00	29.76	0.00	0.29	0.00	10.91
Chen/Amar	0.00	0.14	0.00	3.47	0.00	0.18	0.00	4.96	0.00	0.07	0.00	2.98
<i>Corylus</i> spp.	0.00	0.06	0.00	1.98	0.00	0.07	0.00	4.96	0.00	0.02	0.00	1.49
Cupressaceae	0.00	0.55	0.00	6.94	0.00	1.02	0.00	16.86	0.00	1.29	0.00	17.36
Ericaceae	0.00	0.07	0.00	1.98	0.00	0.18	0.00	4.46	0.00	0.12	0.00	3.47
<i>Fraxinus</i> spp.	0.00	0.19	0.00	13.89	0.00	0.07	0.00	2.98	0.00	0.13	0.00	2.98
Myrtaceae	0.50	0.66	0.00	9.92	0.00	0.38	0.00	5.95	0.00	0.57	0.00	10.91
<i>Olea europea</i>	0.00	0.45	0.00	49.10	0.00	0.01	0.00	1.49	0.00	0.66	0.00	22.32
Pinaceae	0.00	0.86	0.00	23.81	0.50	3.19	0.00	82.34	0.00	1.88	0.00	52.58
<i>Plantago</i> spp.	0.00	0.57	0.00	4.96	0.00	0.27	0.00	2.48	0.00	0.50	0.00	8.43
Platanaceae	0.00	0.09	0.00	4.96	0.00	1.73	0.00	71.42	0.00	2.51	0.00	162.69
Poaceae	0.50	1.38	0.00	19.34	0.50	1.62	0.00	31.74	0.50	1.41	0.00	31.25
<i>Quercus</i> spp.	0.00	0.18	0.00	5.46	0.00	0.09	0.00	1.98	0.00	0.51	0.00	17.36
<i>Rumex</i> spp.	0.00	0.22	0.00	4.46	0.00	0.20	0.00	7.94	0.00	0.18	0.00	4.46
<i>Salix</i> spp.	0.00	0.06	0.00	2.48	0.00	0.08	0.00	3.97	0.00	0.09	0.00	3.47
<i>Ulmus</i> spp.	0.00	0.04	0.00	2.48	0.00	0.93	0.00	35.71	0.00	0.77	0.00	34.72
Urticaceae	2.48	4.12	0.00	30.26	2.48	4.96	0.00	78.86	0.99	4.36	0.00	58.03
Total	7.44	12.76	0.50	94.74	10.42	19.99	0.50	226.18	6.94	19.25	0.00	229.65

Table 7.1 (cont.) Descriptive statistics of non-biological pollutants, meteorological parameters and inhalable bioaerosols (pollen and fungal spores), for 2003, 2004 and 2005.

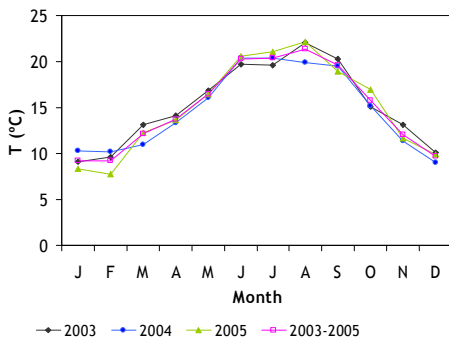
Parameter	2003				2004				2005			
	Median	Average	Min	Max	Median	Average	Min	Max	Median	Average	Min	Max
Fungal spores categories (spores m⁻³air)												
<i>Alternaria</i> spp.	0.99	3.05	0.00	48.61	0.99	2.14	0.00	30.75	1.98	5.41	0.00	47.62
Aspergillaceae	0.00	6.81	0.00	168.64	0.00	6.00	0.00	74.40	0.00	6.62	0.00	151.78
<i>Botrytis</i> spp.	0.00	3.05	0.00	33.73	1.98	5.03	0.00	45.63	1.98	3.10	0.00	52.58
<i>Cladosporium</i> spp.	76.38	175.20	0.00	1785.60	82.34	172.37	0.00	1438.40	133.92	305.58	0.00	2972.03
<i>Coprinus</i> spp.	1.98	3.34	0.00	29.76	2.98	5.37	0.00	139.87	1.98	5.48	0.00	54.56
<i>Corynespora</i> spp.	0.00	0.13	0.00	6.94	0.00	0.31	0.00	6.94	0.00	0.05	0.00	1.98
<i>Didymella</i> spp.	0.00	0.15	0.00	12.90	0.00	0.46	0.00	20.83	0.00	0.24	0.00	8.93
<i>Drechslera</i> spp.	0.00	0.33	0.00	15.87	0.00	0.04	0.00	1.98	0.00	0.15	0.00	3.97
<i>Epicoccum</i> spp.	0.00	1.38	0.00	26.78	0.00	0.92	0.00	9.92	0.99	1.49	0.00	14.88
Rusts	0.99	1.39	0.00	15.87	1.98	4.22	0.00	37.70	2.98	5.37	0.00	97.22
<i>Fusarium</i> spp.	0.00	2.38	0.00	173.60	0.00	0.88	0.00	37.70	0.00	0.26	0.00	11.90
<i>Ganoderma</i> spp.	9.92	27.46	0.00	385.89	10.91	40.82	0.00	719.20	3.97	21.39	0.00	190.46
<i>Leptosphaeria</i> spp.	0.00	0.44	0.00	11.90	0.00	0.39	0.00	18.85	0.00	0.51	0.00	15.87
<i>Oidium</i> spp.	0.00	0.04	0.00	1.98	0.00	0.02	0.00	1.98	0.00	0.08	0.00	5.95
<i>Periconia</i> spp.	0.00	0.03	0.00	3.97	0.00	0.49	0.00	11.90	0.00	0.52	0.00	6.94
<i>Pithomyces</i> spp.	0.00	0.46	0.00	13.89	0.00	0.21	0.00	5.95	0.00	0.24	0.00	9.92
<i>Pleospora</i> spp.	0.00	0.80	0.00	11.90	0.00	0.91	0.00	16.86	0.00	0.40	0.00	4.96
<i>Polythrincium</i> spp.	0.00	0.19	0.00	7.94	0.00	0.12	0.00	3.97	0.00	0.08	0.00	2.98
<i>Rhizopus</i> spp.	0.00	0.41	0.00	9.92	0.00	0.38	0.00	6.94	0.00	0.35	0.00	3.97
<i>Torula</i> spp.	0.00	0.21	0.00	4.96	0.00	0.96	0.00	11.90	0.00	1.09	0.00	14.88
<i>Ustilago</i> spp.	0.00	5.95	0.00	337.28	0.00	0.34	0.00	8.93	0.00	0.69	0.00	18.85
Total	278.75	402.27	1.98	2198.27	304.54	415.78	0.00	2298.46	312.48	494.49	0.00	3247.81



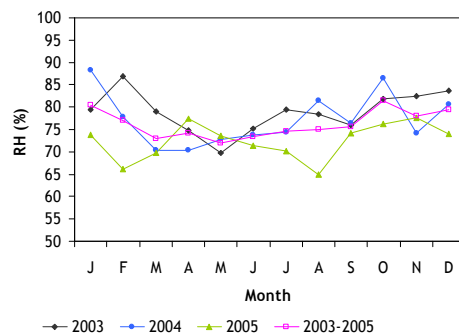
(a)



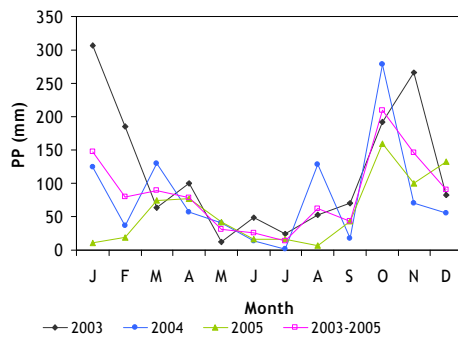
(b)



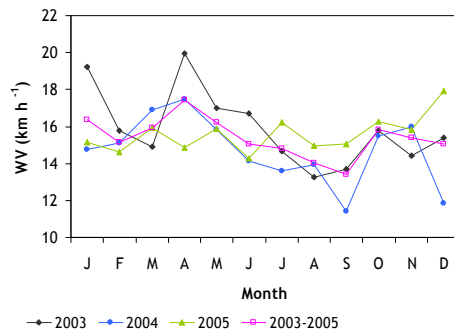
(c)



(d)



(e)



(f)

Figure 7.1 Seasonal evolution of O_3 concentrations (a), PM_{10} concentrations (b), temperature (c), relative humidity (d), precipitation (e) and (f) wind velocity, for 2003, 2004, 2005 and 2003-2005, at a traffic site.

The seasonal variations of O_3 showed differences throughout the year, with a clear increase of O_3 concentrations over the warmer months. For 2003-2005 monthly averages showed a minimum of $17.4 \mu\text{g m}^{-3}$ and a maximum of $42.3 \mu\text{g m}^{-3}$ were observed, respectively, in December and in May, for a global annual average of $28.8 \mu\text{g m}^{-3}$. The seasonal evolution in Oporto was similar to those observed in other European locations (Dueñas et al., 2002; Guicherit and Roemer, 2000). This kind of evolution is justified by the dependence of photochemical O_3 formation on the sunlight radiation; therefore the increases of UV radiation and temperature (and also the decrease of wind speed) have a fundamental role on the increase of O_3 production (WHO, 2000).

The patterns of the seasonal evolution of PM_{10} concentrations were less regular than the ones of O_3 . Some sporadic increases may be associated with forest fires. The annual average concentrations were $43 \mu\text{g m}^{-3}$, $51 \mu\text{g m}^{-3}$ and $44 \mu\text{g m}^{-3}$, respectively, for 2003, 2004 and 2005, showing that the annual limit fixed by the European Union was exceeded. It should be referred that different seasonal evolutions have been reported for PM_{10} concentrations at traffic sites; Latha and Highwood (2006) reported relatively high values during spring season and Artíñano et al. (2004) presented similar values of PM_{10} , during summer and winter.

The seasonal variation of T showed that all the datasets presented a similar profile, with the highest temperatures in August (22°C) and the lowest in January and February (9°C). In average, 2003 was the year with the highest temperatures and the medium temperature for the three years was 15°C .

The RH varied from 65% in August 2005 to 88% in January 2004. In average, the RH during the three years was around 83%.

Generally, higher PP was observed from October to January (during autumn and winter) and lower precipitation was observed between May and August (during spring and summer). The year with the highest total precipitation was 2003.

The WV presented different behaviours depending on the year. Nevertheless, generally, the months with lower velocities were from May to September.

Figures 7.2 (a) and (b) shows the seasonal evolution of pollen and fungal spores for 2003, 2004, 2005 and for the global period (2003-2005), based on the monthly averages calculated with the daily values.

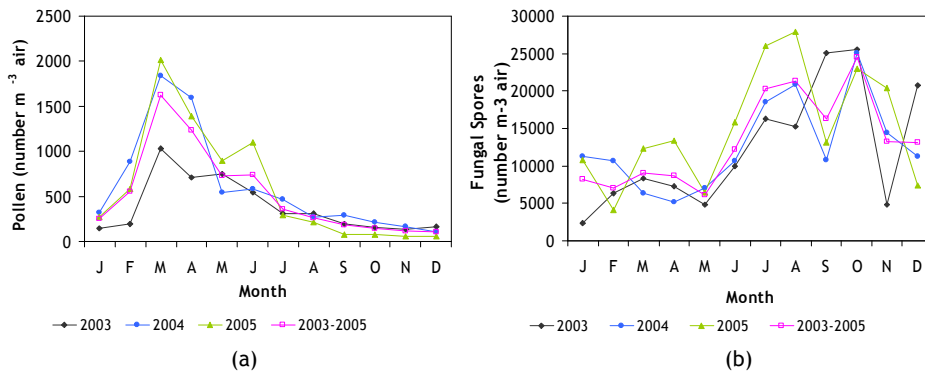


Figure 7.2 Seasonal variation of airborne pollen concentrations (a) and airborne fungal spores concentrations (b), for 2003, 2004, 2005 and 2003-2005.

Fifty different pollen taxa were identified, however, only 22 were considered relevant according to the Portuguese Aerobiology Network. A total average of 6326 pollen grains m^{-3} of air were sampled, mainly distributed from late winter to early summer. These months are the most problematic months for allergic patients. The total annual airborne pollen concentration was minimal in 2003 but very similar in 2004 (7297 pollen grains m^{-3}) and 2005 (7025 pollen grains m^{-3}). In March and April the higher pollen densities were observed and November and December were the months with lower airborne pollen concentration. Urticaceae, Poaceae, Pinaceae and *Platanus* spp. are the most abundant pollen types present in the atmosphere, representing 54% of total annual airborne pollen concentration.

The airborne pollen concentrations started rising in the beginning of the year due to the flowering of Myrtaceae, Cupressaceae, *Fraxinus* spp., *Alnus* spp. and *Salix* spp.. From March to April was found higher airborne pollen concentrations of *Salix* spp., Pinaceae, *Ulmus* spp., Betulaceae, *Corylus* spp., *Acer* spp. and *Platanus* spp. due to the start of their pollination period.

Urticaceae and Poaceae pollen persisted in the atmosphere throughout all year being the former more representative from March-May and the latter from May-August.

The pollens of *Quercus* spp., *Plantago* spp., *Rumex* spp., Caryophyllaceae, Ericaceae, *Olea europea* and *Castanea* spp. were sampled from late April until early July. In the summer pollen of Asteraceae and Poaceae were observed in the air. The pollen of Chenopodiaceae-Amaranthaceae was sampled during late summer until early autumn.

In the urban atmosphere 42 different types of fungal spores were identified, but only 21 were selected based on its abundance and frequency. The most important allergologic spore

types are *Alternaria* spp., Aspergillaceae and *Cladosporium* spp., some other types were included in the study because of their prevalence on Oporto atmosphere (Oliveira et al., 2005). The highest airborne spore concentrations were observed during summer and late autumn (July-October) while the lowest concentrations were found during winter (January-February). In May it was also registered a decrease in the total airborne fungal spores. The most frequent spore was *Cladosporium* spp. and high incidence of *Ganoderma* spp., *Agaricus* spp., Aspergillaceae, *Coprinus* spp., *Alternaria* spp. spores were found.

During the studied period two distinct dispersal patterns of different fungal spore types were registered: i) spores present continuously (during the whole year) in the atmosphere - *Alternaria* spp., Aspergillaceae, *Botrytis* spp., *Cladosporium* spp., *Coprinus* spp., *Epicoccum* spp., *Ganoderma* spp. and Rusts; and ii) spores present sporadically from 1 to 13 consecutive days and usually occurring at low concentrations (1-50 spores/m³) - *Corynespora* spp., *Didymella* spp., *Drechslera* spp., *Fusarium* spp., *Leptosphaeria* spp., *Oidium* spp., *Periconia* spp., *Pithomyces* spp., *Pleospora* spp., *Polythrincium* spp., *Rhizopus* spp., *Torula* spp. and *Ustilago* spp..

Among all the spores continuously observed in the atmosphere, *Cladosporium* spp., *Alternaria* spp., Aspergillaceae, *Botrytis* spp., *Epicoccum* spp. and *Ganoderma* spp. presented peaks spanning from summer to autumn. Spore densities of *Coprinus* spp. were higher during spring while Rusts peaked in autumn-winter. Due to the sporadic occurrence of the remaining spore types, it was not possible to determine a consistent peak season along the three years studied.

7.1.2.2. Linear Correlations

The counts of pollen and fungal spores were respectively expressed as the sum of the average number per cubic meter of air, for a 24 hour period and were normalized, using logarithmic transformation, in order to allow the minimization of errors related to the sampling method.

The main pollination season (period where the majority of pollen is sampled, without taking into consideration pollen recirculation) was defined, as Julian days, when the accumulated sum of pollen reached 10% of the total annual amount and the end of the season was the date when the accumulated sum reached 90% of the total annual pollen.

The pollen data considered for the correlation analysis corresponds to the pre-peak period of the main pollination season. The pre-peak period corresponds to the pollen sampled between the beginning of the main pollination season until the accumulated sum of pollen reached 50%.

The linear correlation coefficients were calculated between the O_3 and PM_{10} concentrations, T, RH, PP, WV, and the concentrations of pollens for 2003, 2004, 2005 and 2003-2005. As example, Table 7.2 shows the linear correlation coefficients for 2003-2005; Appendix A (A1 to A3) shows the linear correlations for 2003, 2004 and 2005. The values in bold represent the statistically significant coefficients and the values in parenthesis represent the data number.

The linear correlation coefficients between O_3 , and *Acer* spp. and Pinaceae were statistically significant and positive during all the periods except for 2005. Some of the statistically significant correlation coefficients were negative, namely for *Alnus* spp. (2003 and 2003-2005) and for Poaceae (2004), suggesting that for those periods the increase of O_3 concentrations decreased the concentration of those pollinic types. In general, the correlation coefficients between O_3 and most pollen were not statistically significant; for Asteraceae, *Fraxinus* spp., *Rumex* spp. and *Salix* spp. they were not significant for all the periods. Even the pollens that had statistically significant correlation coefficients did not show consistent behaviour for the different periods analysed. On the contrary, Adhikari et al. (2006) analysed only one period of two years, publishing statistically significant positive correlations between O_3 and Poaceae and total pollen, not finding correlations with *Acer* spp., Pinaceae, *Quercus* spp. and *Ulmus* spp..

The linear correlations between PM_{10} and pollen were randomly statistically significant, which means that the correlation were not consistent. Pollen have, in general, sizes bigger than 10 μm (Wodehouse, 1935) which means that those can not enter in the device for PM_{10} concentrations monitoring. Therefore, pollen in PM_{10} are not considerable, which explains the inconsistency of statistically significant correlation coefficients. Adhikari et al. (2006) also did not found significant correlations between PM_{10} and pollen.

During all the studied periods, T showed statistically significant positive correlations with some pollen: *Acer* spp., Ericaceae, Pinaceae, *Plantago* spp., Poaceae, *Rumex* spp. and Urticaceae. Adhikari et al. (2006) found statistically significant correlations between temperature and *Acer* spp. and Pinaceae, however they were negative. Some other types of

pollen presented statistically significant correlations with temperature depending on the year, therefore not consistently; these coefficients were always positive, with exception of

Table 7.2 Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the logarithm of pollen concentrations (2003-2005).

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
Aceraceae	0.425 (75)	0.036 (75)	0.422 (75)	-0.167 (75)	-0.036 (75)	0.245 (75)
<i>Alnus</i> spp.	-0.225 (86)	0.133 (83)	-0.070 (86)	-0.247 (86)	-0.332 (86)	-0.309 (86)
Asteraceae	0.021 (378)	-0.009 (375)	0.182 (385)	0.026 (385)	-0.080 (385)	-0.040 (385)
Betulaceae	0.354 (130)	0.105 (130)	0.190 (130)	-0.344 (130)	-0.129 (130)	0.066 (130)
Caryophyllaceae	0.306 (119)	0.216 (119)	0.037 (119)	-0.382 (119)	-0.186 (119)	0.151 (119)
<i>Castanea</i> spp.	0.067 (116)	0.167 (116)	0.433 (116)	-0.237 (116)	-0.199 (116)	0.087 (116)
Chen/Amar	0.054 (403)	0.102 (408)	0.218 (408)	-0.125 (408)	-0.107 (408)	-0.026 (408)
<i>Corylus</i> spp.	0.166 (156)	0.086 (157)	0.194 (157)	-0.052 (157)	-0.107 (157)	-0.008 (157)
Cupressaceae	-0.020 (127)	0.118 (124)	0.074 (127)	-0.299 (127)	-0.304 (127)	-0.181 (127)
Ericaceae	0.139 (262)	0.155 (259)	0.248 (267)	-0.144 (267)	-0.068 (267)	-0.060 (267)
<i>Fraxinus</i> spp.	-0.059 (80)	0.076 (80)	-0.125 (80)	-0.178 (80)	-0.209 (80)	-0.151 (80)
Myrtaceae	-0.045 (222)	-0.007 (214)	-0.104 (225)	-0.178 (225)	-0.129 (225)	-0.016 (225)
<i>Olea europea</i>	0.330 (68)	0.223 (68)	0.200 (68)	-0.262 (68)	-0.009 (68)	-0.066 (68)
Pinaceae	0.390 (142)	0.021 (142)	0.415 (142)	-0.145 (142)	0.001 (142)	0.081 (142)
<i>Plantago</i> spp.	0.186 (317)	0.047 (314)	0.290 (324)	-0.134 (324)	-0.087 (324)	-0.027 (324)
Platanaceae	0.227 (79)	0.246 (84)	0.028 (84)	-0.124 (84)	-0.074 (84)	0.033 (84)
Poaceae	0.019 (208)	0.357 (213)	0.585 (215)	-0.340 (215)	-0.261 (215)	-0.089 (215)
<i>Quercus</i> spp.	0.172 (175)	-0.093 (172)	0.355 (180)	-0.099 (180)	-0.086 (180)	-0.027 (180)
<i>Rumex</i> spp.	0.035 (223)	0.074 (220)	0.342 (230)	-0.027 (230)	-0.106 (230)	-0.044 (230)
<i>Salix</i> spp.	0.008 (132)	0.355 (129)	0.204 (132)	-0.122 (132)	-0.221 (132)	-0.048 (132)
<i>Ulmus</i> spp.	0.227 (94)	0.170 (91)	-0.273 (94)	-0.369 (94)	-0.257 (94)	0.061 (94)
Urticaceae	0.192 (288)	0.245 (282)	0.514 (293)	-0.046 (293)	-0.055 (293)	0.006 (293)

Note: R>R_{crit} in bold; (data number)

Betulaceae for 2005 and *Ulmus* spp. for 2003-2005. No correlation was found between T and *Alnus* spp., *Fraxinus* spp. and Myrtaceae. The influence of T on pollen dispersion along the main pollination season is different, especially for the species with flowering during spring and summer. During these months the temperature shows an increasing tendency. However, the pollination season typically presents a period characterized by an increase in the pollen emission until a peak is reached followed by a pre-peak period with successive decrease of pollen emission. Also pollen production and dispersion are dependent not only on prevailing temperature conditions during flowering (Ribeiro et al., 2003) but also on the temperature regimes observed in the pre-flowering season (Hänninen, 1995). These characteristics can somehow explain the inconsistent results obtained with the linear correlations.

The linear correlations between RH and pollen were different depending both on the year and on the type of pollen. Nevertheless, Poaceae, *Rumex* spp. and *Ulmus* spp. showed negative statistically significant correlation coefficients for all the periods studied, except for Poaceae in 2004 and for *Rumex* spp. and *Ulmus* spp. in 2005. Other studies have shown the influence of humidity on daily Poaceae concentrations (Green et al., 2004). The correlations with *Corylus* spp., *Rumex* spp., *Fraxinus* spp., *Platanus* spp. and *Salix* spp. showed no statistically significant correlation coefficients during the studied periods. Adhikari et al. (2006) found negative statistically significant correlation coefficients between relative humidity and *Acer* spp.. The influence of RH is mainly observed before pollen emission and high RH levels delay anther dehiscence and pollen dispersion (Vázquez et al., 2003). The linear correlations with PP were negative and statistically significant for the following types of pollen: Cupressaceae, (2004, 2005 and 2003-2005); and Poaceae, (2003, 2005 and 2003-2005). The other correlations were, in general, not significant. The linear correlations of WV with pollen showed some randomly statistically significant coefficients. In general, the correlations were not statistically significant.

The linear correlations between O_3 and PM_{10} concentrations, meteorological parameters and some types of fungal spores were also analysed. The linear correlation coefficients were calculated between O_3 and PM_{10} concentrations, T, RH, PP, WV and the concentrations of fungal spores for 2003, 2004, 2005 and 2003-2005. Table 7.3 shows, as example, the linear correlation coefficients for 2003-2005; Appendix A (A4 to A6) shows the linear correlations for 2003, 2004 and 2005. As before, the values in bold represent the statistically significant correlation coefficients and the values in parenthesis represent the data number.

Table 7.3 Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the logarithm of fungal spore concentrations (2003-2005).

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
<i>Alternaria</i> spp.	0.156 (1079)	0.143 (1079)	0.522 (1096)	-0.200 (1096)	-0.174 (1096)	-0.066 (1096)
Aspergillaceae	-0.034 (1079)	-0.021 (1079)	0.008 (1096)	-0.024 (1096)	0.017 (1096)	0.057 (1096)
<i>Botrytis</i> spp.	-0.067 (1079)	-0.011 (1079)	0.048 (1096)	-0.023 (1096)	-0.030 (1096)	-0.020 (1096)
<i>Cladosporium</i> spp.	0.068 (1079)	0.031 (1079)	0.328 (1096)	-0.127 (1096)	-0.105 (1096)	-0.040 (1096)
<i>Coprinus</i> spp.	-0.096 (1079)	-0.104 (1079)	-0.061 (1096)	0.122 (1096)	-0.031 (1096)	-0.081 (1096)
<i>Corynespora</i> spp.	-0.059 (1079)	0.066 (1079)	0.070 (1096)	-0.026 (1096)	-0.046 (1096)	-0.041 (1096)
<i>Didymella</i> spp.	-0.110 (1079)	-0.098 (1079)	-0.136 (1096)	0.165 (1096)	0.133 (1096)	-0.019 (1096)
<i>Drechslera</i> spp.	0.120 (1079)	0.029 (1079)	0.217 (1096)	-0.042 (1096)	-0.060 (1096)	-0.025 (1096)
<i>Epicoccum</i> spp.	0.083 (1079)	0.057 (1079)	0.392 (1096)	-0.110 (1096)	-0.123 (1096)	-0.055 (1096)
Rusts	-0.052 (1079)	-0.146 (1079)	-0.066 (1096)	0.181 (1096)	0.182 (1096)	0.050 (1096)
<i>Fusarium</i> spp.	-0.019 (1079)	0.065 (1079)	0.436 (1096)	0.120 (1096)	-0.076 (1096)	-0.217 (1096)
<i>Ganoderma</i> spp.	-0.026 (1079)	-0.059 (1079)	-0.100 (1096)	0.123 (1096)	0.103 (1096)	0.034 (1096)
<i>Leptosphaeria</i> spp.	0.101 (1079)	0.017 (1079)	0.065 (1096)	-0.027 (1096)	-0.009 (1096)	0.036 (1096)
<i>Oidium</i> spp.	-0.034 (1079)	0.026 (1079)	0.046 (1096)	0.003 (1096)	-0.041 (1096)	-0.014 (1096)
<i>Periconia</i> spp.	0.075 (1079)	0.031 (1079)	0.290 (1096)	-0.001 (1096)	-0.019 (1096)	-0.040 (1096)
<i>Pithomyces</i> spp.	-0.100 (1079)	-0.104 (1079)	-0.172 (1096)	0.215 (1096)	0.212 (1096)	-0.011 (1096)
<i>Pleospora</i> spp.	0.046 (1079)	0.065 (1079)	0.124 (1096)	-0.006 (1096)	-0.032 (1096)	-0.055 (1096)
<i>Polythrincium</i> spp.	0.017 (1079)	0.189 (1079)	0.156 (1096)	-0.133 (1096)	-0.118 (1096)	-0.083 (1096)
<i>Rhizopus</i> spp.	-0.108 (1079)	-0.028 (1079)	-0.121 (1096)	-0.074 (1096)	0.050 (1096)	0.033 (1096)
<i>Torula</i> spp.	0.076 (1079)	0.107 (1079)	-0.082 (1096)	-0.201 (1096)	-0.101 (1096)	0.024 (1096)
<i>Ustilago</i> spp.	0.028 (1079)	0.127 (1079)	-0.048 (1096)	-0.128 (1096)	-0.019 (1096)	0.086 (1096)
Total fungi	-0.098 (1079)	-0.062 (1079)	0.106 (1096)	0.069 (1096)	-0.004 (1096)	-0.046 (1096)

Note: R>R_{crit} in bold; (data number)

The linear correlations between O_3 and fungal spores were statistically significant only in one or two of the four studied periods. The exceptions were: i) *Alternaria* spp., with positive coefficients for 2003, 2005 and 2003-2005; ii) *Didymella* spp. with negative coefficients for 2003, 2004 and 2003-2005; and iii) Rusts with negative coefficients for 2004, 2005 and 2003-2005. These negative correlations might be due to the strong oxidative properties of O_3 that could have destroyed these kinds of spores, leading to lower concentrations when those of O_3 were higher. In general, no important correlations were found between O_3 and fungal spores (coefficients were low or not existent). In contrast, Adhikari et al. (2006) found positive statistically significant correlation coefficients between O_3 and Aspergillaceae and the total fungal spores. Additionally, Ho et al. (2005), who published a study for a three years period (1994-1996), found negative correlations between O_3 and *Ganoderma* spp., total fungal spores, and other fungal spores.

The linear correlations between PM_{10} and *Alternaria* spp. were the only with statistically significant correlation for all the periods studied, being always positive. The fungal spores with statistical significant correlation coefficients for three datasets were: i) *Rhizopus* spp. and *Ustilago* spp., with positive coefficients for 2003, 2005 and 2003-2005; ii) *Torula* spp., with positive coefficients for 2003, 2004 and 2003-2005; iii) *Leptosphaeria* spp., with positive coefficient for 2004 and negative ones for 2003 and 2005; iv) *Didymella* spp., with negative coefficients for 2004, 2005 and 2003-2005; and v) *Pleospora* spp., with negative coefficients for 2003, 2005, and 2003-2005. In general, the linear correlation coefficients between PM_{10} and fungal spores were low or not existent, despite of the small size ($<10\ \mu m$) of the majority of spore types. One explanation for the lack of an important relationship between these two variables may lay on the fact that fungal spore weight was very low not being accounted by the quantification method of PM. Adhikari et al. (2006) found statistically significant positive correlations for Aspergillaceae, *Alternaria* spp. and the total fungal spores. Ho et al. (2005) found positive correlations with *Cladosporium* spp..

The correlations between T and *Alternaria* spp., *Epicocum*, *Ganoderma* spp., *Pithomyces* spp. and *Rhizopus* spp. were statistically significant and positive, for all the studied periods, being *Alternaria* spp. and *Ganoderma* spp. the types with highest coefficients (0.334-0.645). The correlations between T and total fungal spores were statistically significant and positive for 2003, 2005 and 2003-2005. The correlations between T and *Coprinus* spp. were always statistically significant; but positive for 2003 and negative for, 2004, 2005 and 2003-2005. Rusts also presented statistically significant correlation coefficients, but they were positive for 2003 and 2004 and negative for 2005 and 2003-2005. *Didymella* spp. presented

statistically significant negative correlation coefficients for all the periods analysed, meaning that this spore developed better in cold ambient. Also other authors achieved good correlations between temperature and fungal spores (Adhikari et al., 2006; Ho et al., 2005; Sabariego et al., 2000; Angulo-Romero et al., 1999. Katial et al., 1997)

RH showed statistically significant linear correlations with *Fusarium* spp., *Pleospora* spp. and *Torula* spp.; correlations were positive for the first two and negative for the latter, during all the periods analysed. Nevertheless, all the other fungal spores analysed showed to have no linear correlation with RH during the periods analysed.

The linear correlations between PP and *Alternaria* spp. and *Pleospora* spp. were statistically significant for all the studied periods, being positive for the latter and negative for the first one. Studies in US showed that *Cladosporium* spp. and *Alternaria* spp. were negatively associated with PP and positively associated with T and RH (Katial et al., 1997). On the contrary, Ho et al. (2005) and Sabariego et al. (2000) (one year study) found negative correlations between RH and *Alternaria* spp.. Ho et al. (2005) also found negative correlations between PP and *Ganoderma* spp..

The linear correlations between WV and *Ganoderma* spp. were statistically significant for all the periods analysed. The coefficients were negative, meaning that concentrations were higher for low wind velocities. In general, the correlation coefficients were not significant or very low.

The inter-annual inconsistency of the correlation coefficients between the fungal spores of sporadic occurrence and the meteorological factors showed that these last variables are not the most determining factors on the inter-annual distribution. The occurrence of these spores can be associated to other factors such as the vegetative development of plants and the existence of vegetable material in decomposition.

7.1.2.3. Multiple Linear Regressions

The MLR were performed using as input variables the minimum, average and maximum values of O_3 and PM_{10} concentrations, T, RH, PP and WV. For each period, regressions were performed for all types of pollen and fungal spores. Tables 7.4 and 7.5 show the statistically valid MLR, for pollen and fungal spores, respectively, with statistically valid parameters. These parameters were calculated using *t*-test (significance level 0.05); the selection of the

parameters for the best regression was performed using genetic algorithms (Deeb et al., 2007; Broadhurst et al., 1997). The 90th percentiles of R^2_{aj} ($P_{90}(R^2_{aj})$) of MLR were 0.609 and 0.274, respectively, for pollen and fungal spores. As examples, the superior part of the tables shows the regressions achieved above $P_{90}(R^2_{aj})$; the lower part of the tables shows the MLR for some pollen and fungal spores (2003-2005).

Results showed that $P_{90}(R^2_{aj})$ for pollen MLR varied from 0.613 to 0.916. The statistically valid MLR were obtained for: i) *Acer* spp. (2003 and 2005); ii) *Alnus* spp. (2003); iii) Caryophyllaceae (2005); iv) *Castanea* spp. (2003); v) Pinaceae (2005); and vi) *Ulmus* spp. (2004). For these regressions the statistically valid parameters varied with the year and the type of pollen. However, it was possible to perceive that O_3 influenced these types of pollen, with exception of Pinaceae. The influence of PM_{10} was only observed for *Acer* spp. (2005), Caryophyllaceae and Pinaceae. The influence of T was present in almost all the regression models with exception of *Acer* spp. (2003) and Caryophyllaceae. RH influenced *Acer* spp. (2003), Caryophyllaceae and *Castanea* spp.; PP was present on the regressions of *Acer* spp. (2005), Caryophyllaceae and *Ulmus* spp.; and WV influenced *Acer* spp. (2005), Caryophyllaceae and *Castanea* spp..

The pollen MLR models for 2003-2005 presented R^2_{aj} between 0.039 and 0.544. For this period, the parameters that most influenced the airborne pollen were PM_{10} and O_3 , influencing, respectively, 17 and 12 of the 22 pollinic types studied. T was also a parameter with great influence, being present in 17 regression models. The types of pollen without T influence were: Betulaceae, Myrtaceae, *Platanus* spp., *Salix* spp., and *Olea europea*. At a general level, RH, PP and WV presented almost no influence on the pollen. Comparing the linear correlations with MLR, differences were found, especially in what refers to the influences of O_3 and PM_{10} that were more significant when using MLR.

As already referred, pollens in PM_{10} are not considerable, since pollen are larger than 10 μm . Therefore, the use of PM_{10} as independent variable does not seem to be very biologically meaningful, indicating perhaps a coincidence in these particles pattern of occurrence rather than a cause-effect relationship.

Table 7.4 Multiple linear regressions achieved for each type of pollen.

Regression	n	R ² _{aj}	RMSE
2003			
$\text{Aceraceae} = 0.369 + 0.221 \times O_3 - 0.191 \times O_{3\text{Min}} - 0.288 \times RH_{\text{Max}}$	26	0.721	0.231
2005			
$\text{Aceraceae} = 0.644 - 0.216 \times O_{3\text{Max}} + 0.198 \times PM_{10\text{Max}} + 0.907 \times T - 0.594 \times T_{\text{Max}} - 0.173 \times PP_{\text{Max}} + 0.214 \times WV_{\text{Min}}$	20	0.916	0.133
2003			
$\text{Alnus spp.} = 0.201 - 0.079 \times O_3 + 0.142 \times T_{\text{Max}} - 0.062 \times PP_{\text{Min}}$	36	0.680	0.124
2005			
$\text{Caryophyllaceae} = 0.028 - 0.061 \times O_{3\text{Min}} + 0.120 \times O_3 - 0.128 \times O_{3\text{Max}} - 0.066 \times PM_{10\text{Min}} + 0.081 \times PM_{10\text{Max}} - 0.063 \times HR_{\text{Min}} + 0.086 \times HR_{\text{Max}} - 0.026 \times PP_{\text{Min}} - 0.057 \times WV_{\text{Min}} + 0.067 \times WV_{\text{Max}}$	33	0.631	0.042
2003			
$\text{Castanea spp.} = 0.328 - 0.172 \times O_{3\text{Max}} + 0.510 \times T + 0.168 \times HR + 0.225 \times WV_{\text{Max}}$	38	0.634	0.236
2005			
$\text{Pinaceae} = 0.601 - 0.154 \times PM_{10\text{Min}} + 0.393 \times T_{\text{Min}}$	52	0.613	0.314
2004			
$\text{Ulmus spp.} = 0.653 + 0.447 \times O_3 + 0.461 \times PM_{10} + 0.220 \times T_{\text{Min}} - 0.280 \times PP_{\text{Max}}$	26	0.629	0.329
2003-2005			
$\text{Acereceae} = 0.568 + 0.189 \times O_3 - 0.139 \times PM_{10} + 0.118 \times PM_{10\text{Max}} + 0.356 \times T - 0.132 \times PP_{\text{Max}} + 0.141 \times WV_{\text{Max}}$	75	0.544	0.354
$\text{Alnus spp.} = 0.441 - 0.093 \times PM_{10\text{Max}} - 0.153 \times T_{\text{Min}} + 0.180 \times T_{\text{Max}} - 0.075 \times PP_{\text{Min}} - 0.072 \times WV_{\text{Min}}$	83	0.378	0.267
$\text{Betulaceae} = 0.225 + 0.199 \times \text{Avg}O_3 - 0.094 \times \text{Min}PM_{10} + 0.192 \times \text{Avg}PM_{10} - 0.086 \times \text{Max}PM_{10} - 0.103 \times \text{Min}WV$	130	0.254	0.319
$\text{Caryophyllaceae} = 0.107 - 0.047 \times O_{3\text{Min}} + 0.105 \times O_3 - 0.056 \times O_{3\text{Max}} - 0.035 \times PM_{10\text{Min}} + 0.076 \times PM_{10\text{Max}} - 0.101 \times T_{\text{Min}} + 0.095 \times T$	119	0.385	0.139
$\text{Castanea spp.} = 0.264 + 0.251 \times T + 0.119 \times HR + 0.114 \times WV_{\text{Max}}$	116	0.235	0.344
$\text{Olea europea} = 0.348 + 0.221 \times O_3 + 0.131 \times PM_{10} - 0.135 \times WV$	68	0.269	0.320
$\text{Platanaceae} = 0.463 + 0.305 \times O_{3\text{Max}} + 0.144 \times PM_{10\text{Min}} + 0.153 \times PP_{\text{Min}}$	79	0.223	0.582
$\text{Pinaceae} = 0.642 + 0.195 \times O_3 + 0.106 \times PM_{10\text{Max}} + 0.188 \times T_{\text{Min}} - 0.196 \times RH + 0.177 \times RH_{\text{Max}}$	142	0.365	0.388
$\text{Ulmus spp.} = 0.398 + 0.155 \times PM_{10\text{Min}} - 0.099 \times T_{\text{Min}} - 0.196 \times HR_{\text{Max}}$	91	0.265	0.410
$\text{Urticaceae} = 0.809 + 0.102 \times O_3 + 0.086 \times O_{3\text{Max}} + 0.138 \times PM_{10} - 0.068 \times PM_{10\text{Max}} + 0.191 \times T_{\text{Max}} + 0.111 \times HR_{\text{Min}} - 0.048 \times WV_{\text{Max}}$	277	0.385	0.313

Note: logarithm of pollen concentrations were used to develop the regression models; n: data number.

Table 7.5 Multiple linear regressions achieved for each type of fungal spore.

Regression	n	R ² _{aj}	RMSE
2003			
<i>Alternaria</i> spp. = $0.389 - 0.050 \times O_3 - 0.043 \times PM_{10Min} - 0.076 \times PM_{10Max} + 0.147 \times T_{Min} + 0.118 \times T_{Max} - 0.093 \times RH + 0.091 \times RH_{Max} - 0.036 \times PP_{Min} - 0.041 \times PP_{Max}$	351	0.480	0.292
2005			
<i>Alternaria</i> spp. = $0.528 - 0.056 \times O_3 + 0.154 \times T_{Min} + 0.131 \times T_{Max} - 0.062 \times RH$	364	0.325	0.383
2003-2005			
<i>Alternaria</i> spp. = $0.408 - 0.034 \times O_3 - 0.084 \times PM_{10Min} - 0.082 \times PM_{10Max} + 0.217 \times T - 0.071 \times RH + 0.038 \times RH_{Max} - 0.041 \times PP$	1068	0.309	0.354
2003			
<i>Cladosporium</i> spp. = $1.820 + 0.123 \times O_{3Min} - 0.210 \times O_3 - 0.152 \times PM_{10} + 0.519 \times T - 0.118 \times RH - 0.070 \times WV_{Min} - 0.093 \times WV_{Max}$	351	0.500	0.497
2003			
<i>Epicoccum</i> spp. = $0.233 - 0.112 \times O_3 + 0.078 \times O_{3Max} - 0.039 \times PM_{10Max} + 0.149 \times T_{Min} - 0.042 \times PP_{Min} - 0.033 \times PP_{Max}$	351	0.274	0.267
2003			
<i>Ganoderma</i> spp. = $0.915 - 0.162 \times O_3 + 0.156 \times PM_{10Min} - 0.343 \times PM_{10} + 0.497 \times T - 0.108 \times WV_{Min} - 0.146 \times WV_{Max}$	351	0.512	0.517
2005			
<i>Ganoderma</i> spp. = $0.838 + 0.378 \times T_{Min} + 0.171 \times RH - 0.116 \times WV$	364	0.376	0.548
2003-2005			
<i>Ganoderma</i> spp. = $0.944 + 0.051 \times O_{3Max} + 0.382 \times T + 0.140 \times RH - 0.047 \times PP_{Max} - 0.085 \times WV$	1068	0.275	0.625
2003			
Total fungi = $2.410 + 0.064 \times O_{3Min} - 0.179 \times O_3 - 0.099 \times PM_{10Max} + 0.262 \times T - 0.048 \times PP$	351	0.277	0.392
2003-2005			
Aspergillaceae = $0.387 - 0.042 \times O_3 + 0.059 \times WV_{Max}$	1068	0.009	0.570
<i>Botrytis</i> spp. = $0.445 + 0.068 \times O_{3Min} - 0.106 \times O_3 + 0.047 \times T - 0.038 \times RH$	1068	0.024	0.416
<i>Cladosporium</i> spp. = $1.908 + 0.092 \times O_{3Min} + 0.086 \times PM_{10Min} - 0.142 \times PM_{10} + 0.139 \times T_{Min} + 0.142 \times T_{Max} - 0.095 \times RH - 0.048 \times PP$	1068	0.142	0.655
<i>Coprinus</i> spp. = $0.521 + 0.043 \times O_{3Min} - 0.052 \times O_3 - 0.039 \times PM_{10} + 0.033 \times RH - 0.039 \times PP$	1068	0.030	0.424
<i>Epicoccum</i> spp. = $0.230 - 0.028 \times O_3 - 0.024 \times PM_{10Max} + 0.122 \times T + 0.055 \times RH_{Min} - 0.099 \times RH + 0.046 \times RH_{Max}$	1068	0.175	0.270
Rusts = $0.453 - 0.047 \times O_{3Min} + 0.100 \times O_3 + 0.031 \times PM_{10Min} - 0.042 \times PM_{10} - 0.037 \times T - 0.098 \times RH + 0.047 \times PP_{Max}$	1068	0.065	0.391
<i>Fusarium</i> spp. = $0.086 + 0.073 \times T_{Min} - 0.078 \times T + 0.030 \times RH + 0.036 \times PP + 0.021 \times WV_{Max}$	1068	0.060	0.279
<i>Ustilago</i> spp. = $0.131 + 0.034 \times PM_{10} - 0.086 \times T_{Min} + 0.064 \times T_{Max} - 0.044 \times PP - 0.044 \times PP_{Max} + 0.037 \times WV$	1068	0.053	0.307
Total fungi = $2.381 + 0.084 \times O_{3Min} - 0.200 \times O_3 + 0.070 \times O_{3Max} - 0.077 \times PM_{10Max} + 0.115 \times T$	1068	0.055	0.567

Note: logarithm of pollen concentrations were used to develop the regression models; n: data number.

Table 7.5 shows that the values above P_{90} (R^2_{aj}) varied from 0.275 to 0.512, quite inferior to those of pollen. As well as for pollen, the regressions obtained for fungal spores varied with the year and the type of fungal spore. The low values of the R^2_{aj} , obtained during the 2003-2005 period for the fungal spores with sporadic occurrence corroborate the hypothesis, already referred in Section 7.1.1.2, that other variables need to be considered to explain their presence in the atmosphere. Nevertheless, *Alternaria* spp. and *Ganoderma* spp. presented P_{90} (R^2_{aj}) correlations for three periods: 2003, 2005 and 2003-2005. The other fungal spores that showed good R^2_{aj} were *Cladosporium* spp. (2003), *Epicoccum* spp. (2003) and the total fungal spores (2003). In general, O_3 showed considerable negative influence on the concentrations of fungal spores and PM_{10} showed irrelevant influence.

T and RH were the parameters that showed to have more influence. The spores without T influence were Aspergillaceae, *Coprinus* spp. and *Oidium* spp.; and those not influenced by RH were Aspergillaceae, *Corynespora* spp., *Drechslera*, *Oidium* spp., *Ustilago* and the total fungal spores. In general, the other meteorological parameters did not show a great influence.

Ho et al. (2005) achieved similar results for total fungal spores MLR, with contributions of T, PM_{10} and O_3 on the fungal spores. For Aspergillaceae, *Cladosporium* spp. and *Ganoderma* spp., the results were different; even so, the influence of T was frequent on both studies.

Nevertheless, the models for each pollen and fungal spore were different depending on the year, i.e., different influences were found for each year and for 2003-2005, which makes the models somehow inconsistent. Accordingly, it should be remarked that the results previously published supported in only one period, may not be safe enough, which means that the comparison of the results here presented with those obtained by other authors should be made carefully (the differences can also be due to regional specificities, such as climate, vegetation, species diversity and fungal growth substrates).

Nevertheless, in spite of the inconsistent trends between air pollutants and pollen and fungal spores, further research should be made concerning their synergetic effects on health. In fact, pollen and fungal spore allergens may reach peripheral airways, leading to airway reactivity and symptoms exacerbation, due to its transference to other small particles such as PM (Behrendt et al., 1992), especially in regions such as Oporto, where its concentrations exceeded the standard levels (Directive 1999/30/EC). Additionally, the concentrations of other pollutants, such as O_3 , can produce an inflammatory effect on the

airways causing increased permeability and easier penetration of pollen and fungal spore allergens (D'Amato, 2002; Donaldson et al., 2000).

7.1.3. Conclusions

Statistically significant linear correlations were found for all the periods studied between: i) PM_{10} and *Alternaria* spp. spores (positive); ii) Temperature and *Acer* spp., Ericaceae, Pinaceae, *Plantago* spp., Poaceae, *Rumex* spp. and Urticaceae pollen, *Alternaria* spp., *Epicoccum* spp., *Ganoderma* spp., *Pithomyces* spp., *Rhizopus* spp. (positive) and *Didymella* spp. spores (negative); iii) Relative humidity and *Fusarium* spp., *Pleospora* spp. (positive) and *Torula* spp. spores (negative); iv) Precipitation and *Pleospora* spp. (positive) and *Alternaria* spp. spores (negative); v) Wind velocity and *Ganoderma* spp. spores (negative).

Statistically significant linear correlations were found for three of the four periods studied between: i) O_3 and *Acer* spp., Pinaceae pollen, *Alternaria* spp. (positive), *Didymella* spp. and Rusts spores (negative); ii) PM_{10} and Poaceae, *Salix* spp. pollen, *Rhizopus* spp., *Torula* spp., *Ustilago* spp. (positive) and *Didymella* spp. and *Pleospora* spp. spores (negative); iii) Temperature and *Castanea* spp., *Quercus* spp. pollen, *Cladosporium* spp., *Drechslera* spp., *Polythrimum* spp., total fungal spores (positive) and *Coprinus* spp. and *Pleospora* spp. spores (negative); iv) Relative humidity and *Didymella* spp., *Leptosphaeria* spp. spores (positive), Caryophyllaceae, Poaceae, *Ulmus* spp. pollen, *Alternaria* spp. and *Ustilago* spp. spores (negative); v) Precipitation and *Didymella* spores (positive), *Alnus* spp., Cupressae, Poaceae pollen, *Epicoccum* spp. and *Rhizopus* spores (negative).

In general, statistically significant correlations were observed randomly. The parameters that influenced the MLR, performed for each pollen and fungal spore, depended on the analysed period, which means that the correlations identified as statistically significant can be inconsistent. Thus, it seems that the concentrations of O_3 and PM_{10} do not influence most of the airborne pollen and fungal spore concentrations. According to the different conclusions reached, that depended on the periods analysed, it should be remarked that the results previously published supported in only one period, may not be safe enough. Therefore, the comparison of the results here presented with those obtained by other authors should be made carefully, because the differences can also be due to regional specificities, such as climate, vegetation, species diversity and fungal growth substrates.

Nevertheless, in spite of the inconsistent trends between air pollutants and pollen and fungal spores, further research should be made concerning their synergetic effects on health.

7.2. Identification of Regions with High Ozone Concentrations aiming the Impact Assessment on Childhood Asthma^{*}

Considering that the influence of O₃ on biological pollutants was not found, this section reports the work performed to select one area mainly polluted by O₃ (with low concentrations of other chemical pollutants) to perform further studies regarding the specific impact of O₃ exposure on childhood asthma. This study was carried out in two phases; in the first one studies were performed aiming the selection of the area, by i) comparing measurements performed with passive samplers with those performed with continuous monitors; ii) comparing O₃ concentrations at remote areas with the ones measured at an urban area with traffic influence; and iii) evaluating the influence of NO_x and VOC on O₃ concentrations. To confirm the levels of pollutants, in the second phase studies were carried out in sites within the selected area, assessing the concentrations of O₃ and of its precursors (NO_x and VOC).

7.2.1 Methodology

7.2.1.1 First Phase

The study was based on data measured at TF₂ (urban site influenced by traffic in Oporto described in Section 3.1.2) and at six remote sites: five in the Bragança district (BG₁ - Bragança, BG₂ - Vimioso, BG₃ - Miranda do Douro, BG₄ - Torre de Moncorvo, and BG₅ - Macedo de Cavaleiros) and one in the Vila Real district, Lamas d'Olo (LO). The monitoring sites and respective population density are shown in Figure 7.3.

^{*} adapted from: Sousa SIV, Pereira MC, Martins FG, Alvim-Ferraz MCM, 2008. Identification of regions with high ozone concentrations to assess the impact on childhood asthma. *Journal of Human and Ecological Risk Assessment* 14: 610-622.

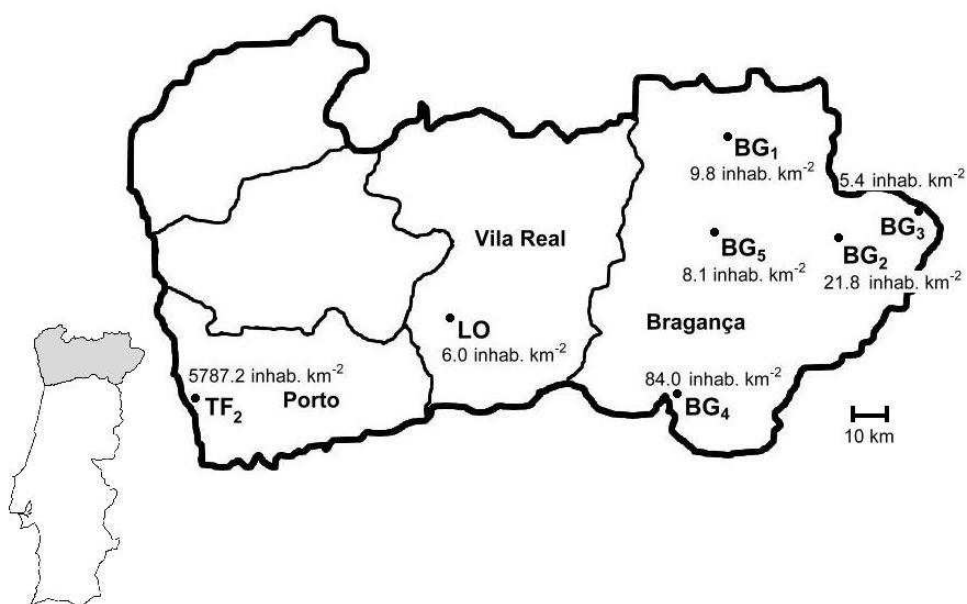


Figure 7.3 Sites location in northern Portugal and respective population density.

Measurements were performed using passive samplers provided by Gradko International Ltd (England), Figure 7.4.

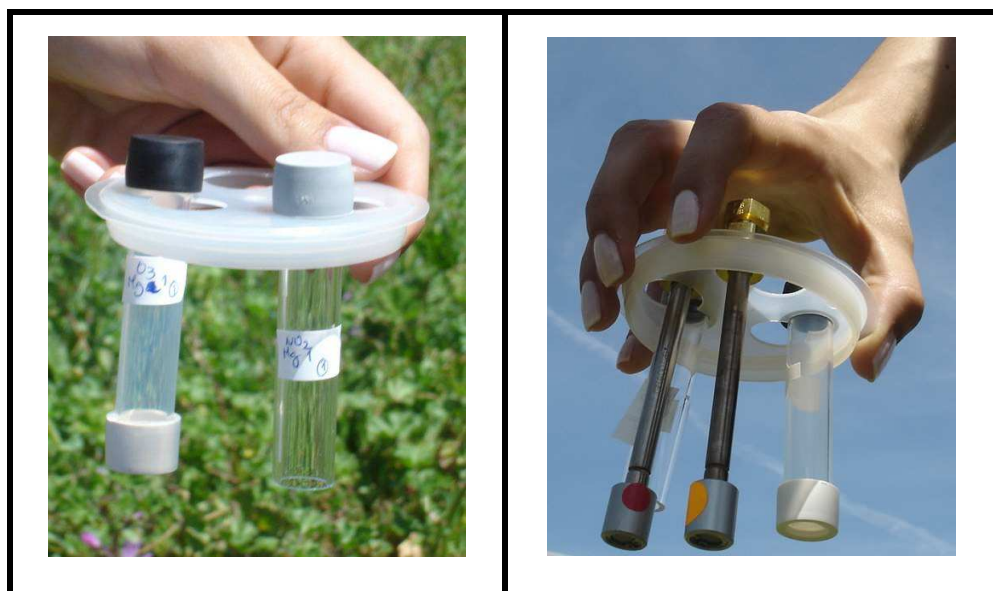


Figure 7.4 O₃, NO₂ and VOC passive samplers used in the field measurements.

To test their performance, the sampling tubes were co-located with continuous monitors (belonging to the Air Quality Monitoring Network) at sites TF₂ and LO.

The TF₂ site is located in a roundabout with several traffic streets, being considered an urban site mainly influenced by traffic. The BG₁, BG₂, BG₃, BG₄, BG₅, and LO sites were located in natural environments not directly influenced by anthropogenic pollution sources and were, therefore, considered background remote sites.

The passive samplers used were provided by Gradko International Ltd (England). According to specified requirements, the sampling tubes were protected from sunlight and heat before and after exposure as well as during storage and transportation. Samplers were placed in an open field at a height of 2-2.5 m and were protected from rain and wind by appropriate shelters, Figure 7.5.



Figure 7.5 Shelters and passive/active samplers location.

Sampling tubes were simultaneously kept without exposure to be used as blanks for future analyses.

Pollutant concentrations were measured with passive samplers in two periods during the summer of 2006: 1st period - between 28/07/2006 and 10/08/2006 for TF₂ and LO sites and between 27/07/2006 and 09/08/2006 for the other sites; and 2nd period - between 10/08/2006 and 05/09/2006 for TF₂ and LO sites and between 09/08/2006 and 05/09/2006

for the other sites. The pollutants measured were O_3 and some precursors (recommended by Directive 2002/3/EC): NO_2 , total VOC (C_5 - C_{12}), and some specific VOC, namely, benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene, and toluene. O_3 , NO_2 , and VOC determination on diffusion tubes was performed, respectively, by ion chromatography, UV spectrophotometry, and Gas Chromatography-Mass Spectrometry (GC-MS). O_3 and NO_2 concentrations were also continuously monitored using the methods described in Sections 3.1.3 and 4.1.1.

7.2.1.2 Second Phase

The study was based on data measured during 2007 summer; five sites were selected, located in two remote areas at the *Bragança* district: *Torre de Moncorvo* (TM_1 , TM_2 , TM_3) and *Mogadouro* (MG_1 , MG_2) with 17.2 inhab km^{-2} and 13.9 inhab km^{-2} , respectively (INE, 2008).

Site TM_1 was located in a natural environment not directly influenced by anthropogenic pollution sources, thus being considered a background remote site. Sites TM_2 , TM_3 , MG_1 and MG_2 were placed in the existing schools of the municipalities, comprising children from 1st to 6th grade, having very low anthropogenic pollution influence, thus being also considered background remote sites.

Measurements were performed using passive samplers (Section 7.2.1.1) and also active samplers for some specific VOC. The data measured at remote sites were also compared to those obtained at TF_2 where O_3 and NO_2 concentrations were continuously monitored, as in the first phase, by the methods described in Sections 3.1.3 and 4.1.1. In this phase, the pollutants measured by passive sampling were the same measured in the first phase (O_3 , NO_2 , total VOC (C_5 - C_{12}), benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene, and toluene) plus some other precursors recommended by Directive 2002/3/EC: total VOC (C_7 - C_{28}), and some specific VOC, namely, α -pinene, β -pinene, 3-carene, limonene and ethane. Also propene, iso-butene, isoprene, 2-methyl-1-butene and 2-methylbutane were measured but by active sampling (pump flow: 0.05 L/min). O_3 , NO_2 , and VOC determination was performed as described in Section 7.2.1.1. Gas Hydrate Separation (GHS) was used for the following specific VOC: ethene, propene, iso-butene, isoprene, 2-methyl-1-butene and 2-methylbutane (C_2 - C_5). All the compounds were measured by exposing the tubes for two or three weeks, except for C_2 - C_5 VOC that were pumped during 10 h and 16 h. The periods of measurement for all the compounds are shown in Table 7.6

Table 7.6 Periods of measurement and respective exposure time for each pollutant.

Pollutants	Periods	Period of Measurement	Exposure time
O ₃ NO ₂ VOC (C ₅ -C ₁₂ and C ₇ -C ₂₈)	1 (P ₁)	16/05/2007-30/05/2007	two weeks
	2 (P ₂)	30/05/2007-13/06/2007	
	3 (P ₃)	13/06/2007-27/06/2007	
	4 (P ₄)	27/06/2007-11/07/2007	
	5 (P ₅)	11/07/2007-25/07/2007	three weeks
	6 (P ₆)	25/07/2007-06/08/2007	
	7 (P ₇)	06/08/2007-28/08/2007	
	8 (P ₈)	28/08/2007-18/09/2007	
	9 (P ₉)	18/09/2007-08/10/2007	
	10 (P ₁₀)	08/10/2007-29/10/2007	
VOC (C ₂ -C ₅)	1 (P ₁)	17/05/2007	10 h
	2 (P ₂)	31/05/2007	10 h
	3 (P ₃)	13/06/2007	16 h

7.2.2 Results and Discussion

7.2.2.1 First Phase

Comparison between Passive and Continuous monitoring

The accuracy of passive samplers was evaluated by comparing the O₃ and NO₂ data obtained using continuous monitors with those using passive samplers at sites TF₂ and LO. Comparison of VOC concentrations was not possible since they were not continuously measured. Table 7.7 shows the average concentrations of O₃ and NO₂ measured using passive sampling and continuous monitoring as well as the respective absolute and relative differences calculated for both sites and periods.

For O₃, the comparison of both methods showed a maximum absolute difference of +4.10 µg m⁻³ and relative differences less than -8.8%. The maximum absolute difference for NO₂ was +5.2 µg m⁻³ and the relative differences were greater than 12% only for very low concentrations (2-3 µg m⁻³). These results indicated satisfactory reproducibility and precision of the measurements made using passive samplers.

Table 7.7 O₃ average concentrations measured with passive sampling and continuous monitoring and the respective absolute and relative differences calculated for both sites and periods.

Pollutant	Period	Site	Passive Sampling ($\mu\text{g m}^{-3}$)	Continuous Monitoring ($\mu\text{g m}^{-3}$)	Absolute Differences ($\mu\text{g m}^{-3}$)	Relative Differences (%)
O ₃	1 st	TF ₂	51.04	54.00	-2.96	-5.5
		LO	87.09	89.52	-2.43	-2.7
	2 nd	TF ₂	40.90	44.83	-3.93	-8.8
		LO	113.21	109.11	+4.10	+3.8
NO ₂	1 st	TF ₂	39.13	38.24	+0.89	+2.3
		LO	3.22	2.44	+0.78	+31.8
	2 nd	TF ₂	50.94	45.67	+5.27	+11.6
		LO	2.83	3.38	-0.55	-16.2

Comparison of Ozone Concentrations at Remote and Urban Areas

The O₃ concentrations measured at all sites, for both 1st and 2nd periods of passive sampling are shown in Figure 7.6.

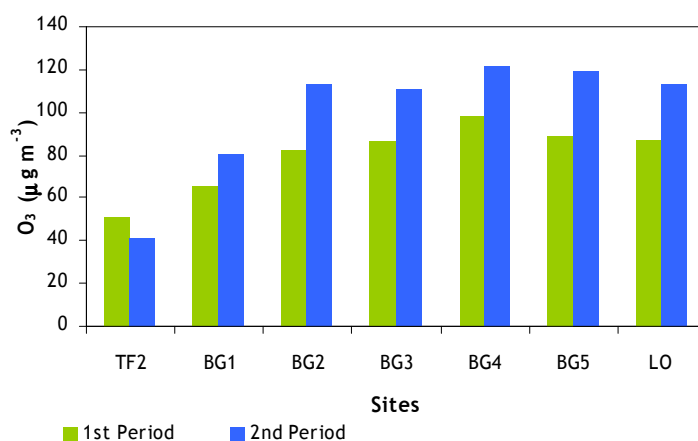


Figure 7.6 O₃ concentrations measured at all sites, during both 1st (around 305 h) and 2nd (around 640h) periods of passive sampling.

The lowest concentrations were observed at the TF₂ site being 51.0 µg m⁻³ and 40.9 µg m⁻³, respectively, for the 1st and 2nd periods. From all remote sites analysed, BG₄ was the one with the highest concentrations during both periods (97.9 µg m⁻³ and 122.0 µg m⁻³, respectively). At remote areas O₃ concentrations during the 2nd period were greater than during the 1st period, due to the increase observed in surface temperatures.

A comparison between TF₂ and LO was performed considering the following standard values defined by EU (Tables 2.4 and 2.5): i) information threshold (IT) associated with health risks for short-time exposure of groups particularly sensitive; ii) alert threshold (AT) associated with health risks for short time exposure of the population in general; and iii) target value for the protection of human health (TVPHH) associated with the long-term effects on human health. It was generally observed that the highest concentrations were measured at the LO site. Indeed, at this site in 2006, the IT was exceeded 95 times (93 from May to September 2006) against 15 times at the TF₂ site (all from May to September 2006). Also, the TVPHH was exceeded 72 times at the LO site against 18 times at the TF₂ site from May to September 2006. During the period of passive sampling, results confirmed that in general the highest concentrations were observed at the LO site. The exceedances of IT, AT, and TVPHH, during the period of passive sampling were, respectively i) TF₂: 10, 1, and 11; and ii) LO: 49, 8 and 20. As expected, during this period the exceedances of IT, AT, and TVPHH were greater at the LO site than at the TF₂ site, being, approximately, 5, 8, and 2 times greater, respectively.

Using passive sampling, the average concentrations at the LO site during the 1st and 2nd periods were 87.1 µg m⁻³ and 113.2 µg m⁻³, respectively, while at the TF₂ site, and for the same periods, they were 51.0 µg m⁻³ and 40.9 µg m⁻³, respectively. Subsequently, as at the BG₄ site the O₃ concentrations were the highest observed, the number of exceedances of the standard values for human health protection was surely greater at the BG₄ site than at the LO site, suggesting that this area is adequate to perform further studies regarding O₃ impact on childhood asthma.

Influence of Nitrogen Oxides and VOC on Ozone Concentrations

The NO₂ concentrations measured at all sites for both 1st and 2nd periods of passive sampling are presented in Figure 7.7.

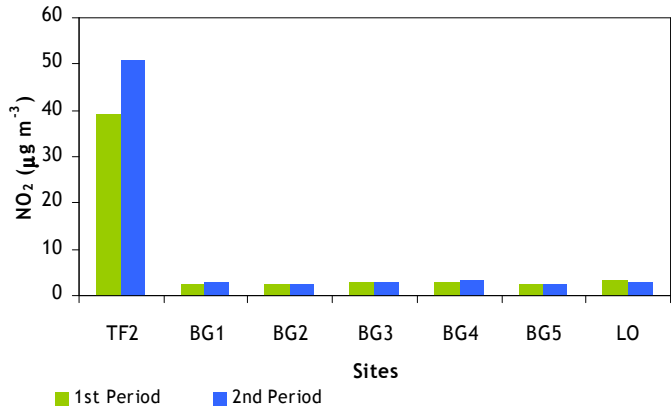
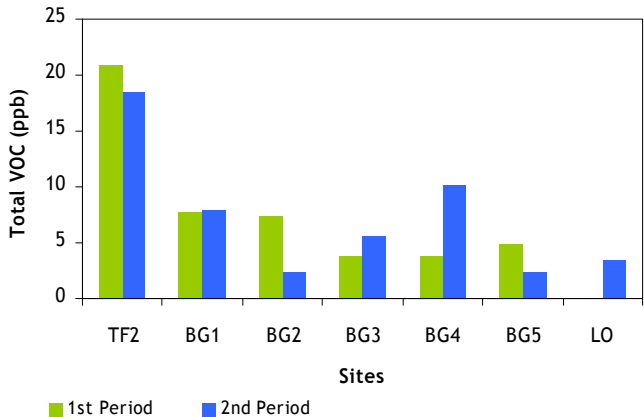


Figure 7.7 Concentrations of NO₂ measured at all sites during both 1st (around 305 h) and 2nd (around 640h) periods of passive sampling.

NO₂ concentrations at the TF₂ site were from 12 to 20 times greater than those at remote sites, due to the influence of traffic emissions. At remote sites, the concentrations were very low, being on average around 3 µg m⁻³.

The total VOC concentrations during the periods of passive sampling are shown in Figure 7.8. The VOC concentrations were also considerably high at the TF₂ site, being from 2 to 8 times greater than at remote sites, again confirming the traffic influence.

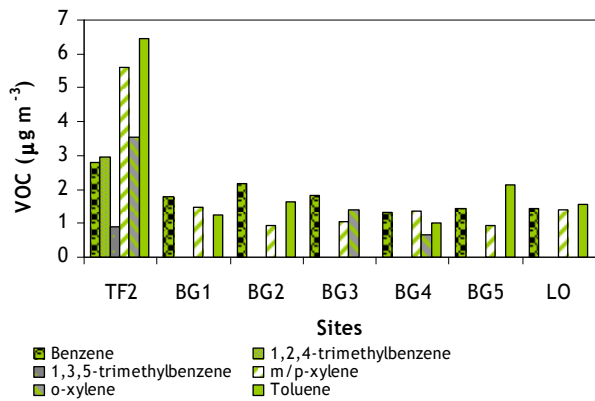


Data not available for 1st period at LO site

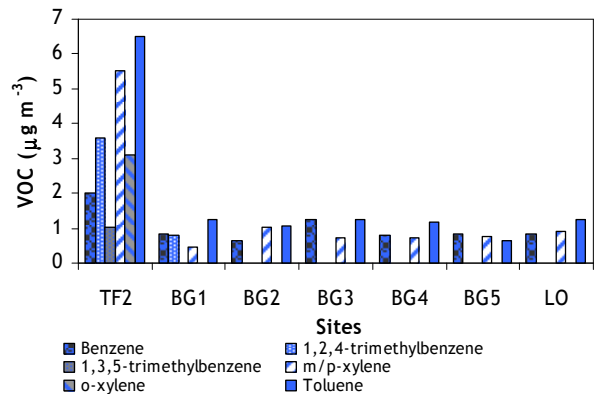
Figure 7.8 Concentrations of total VOC (C₅-C₁₂) measured at all sites during both 1st (around 305 h) and 2nd (around 640 h) periods of passive sampling.

The total VOC concentrations observed at remote sites were very low varying from 2.5 ppb to 10.1 ppb.

Shown in Figure 7.9 are the concentrations of benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene, and toluene, at all sites, when greater than the detection limit, during passive sampling: (a) 1st period; and (b) 2nd period.



(a)



(b)

Figure 7.9 Concentrations of benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene and toluene during passive sampling at all sites: (a) 1st period (around 305 h); and (b) 2nd period (around 640 h).

Once again the highest concentrations were observed at the TF₂ site, being m/p-xylene and toluene the pollutants with the highest concentrations during both periods. During the same periods the concentrations of these pollutants at remote sites were very low being always less than 3 $\mu\text{g m}^{-3}$.

As can be observed in Figures 7.7, 7.8, and 7.9, the concentrations of NO₂ and VOC were very low at remote sites, therefore confirming the absence of anthropogenic emission influence. However, it was simultaneously observed at these sites the highest concentrations of O₃, which can be explained through the competition between VOC and NO₂ for the OH radical. When [VOC]/[NO₂] is low, typical of urban areas, OH reacts predominantly with NO₂, retarding O₃ formation; thus, an increase of NO₂ concentrations leads to a decrease on O₃ concentrations. For greater [VOC]/[NO₂], typical of rural areas, OH reacts predominantly with VOC, accelerating O₃ formation: in this situation, an increase of NO₂ concentrations leads to an increase on O₃ concentrations (Seinfeld and Pandis, 1998).

Figure 7.10 shows daily profiles of 8-hour running averages at the TF₂ site for: (a) one day belonging to the period of passive sampling; and (b) the average values for all the period of passive sampling.

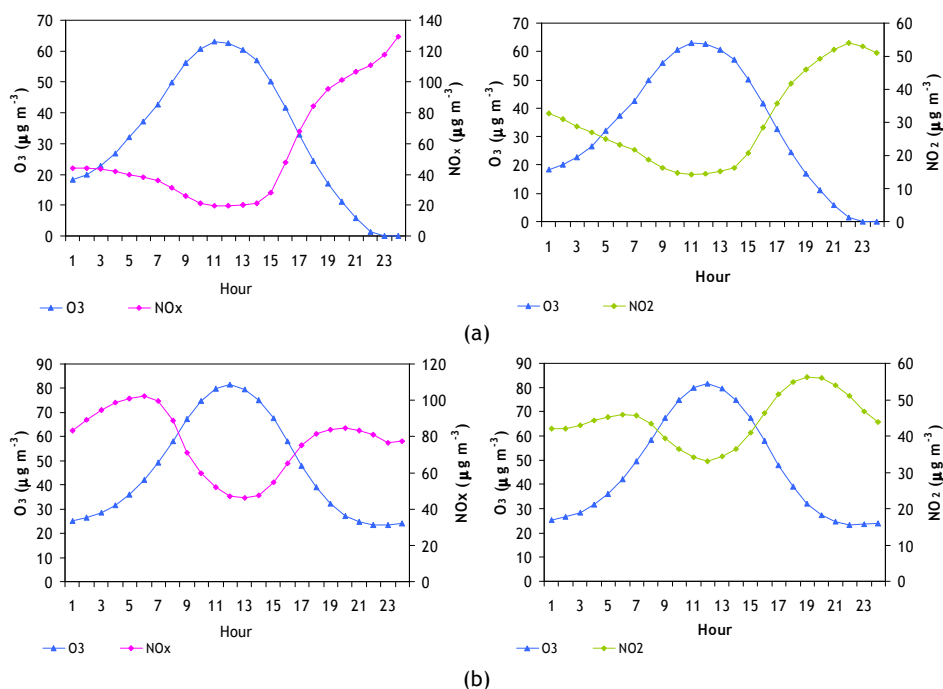


Figure 7.10 Daily profile of 8-hour running averages at the TF₂ site for: (a) one day belonging to the period of passive sampling; and (b) the average for all the period of passive sampling.

For the TF₂ site, a typical profile of an urban area was observed, where O₃ formation was controlled by concentrations of VOC, leading to a decrease on O₃ concentrations when NO_x concentrations increased.

Figure 7.11 shows daily profiles of 8-hour running averages at the LO site for: (a) one day belonging to the period of passive sampling; and (b) the average values for all the period of passive sampling.

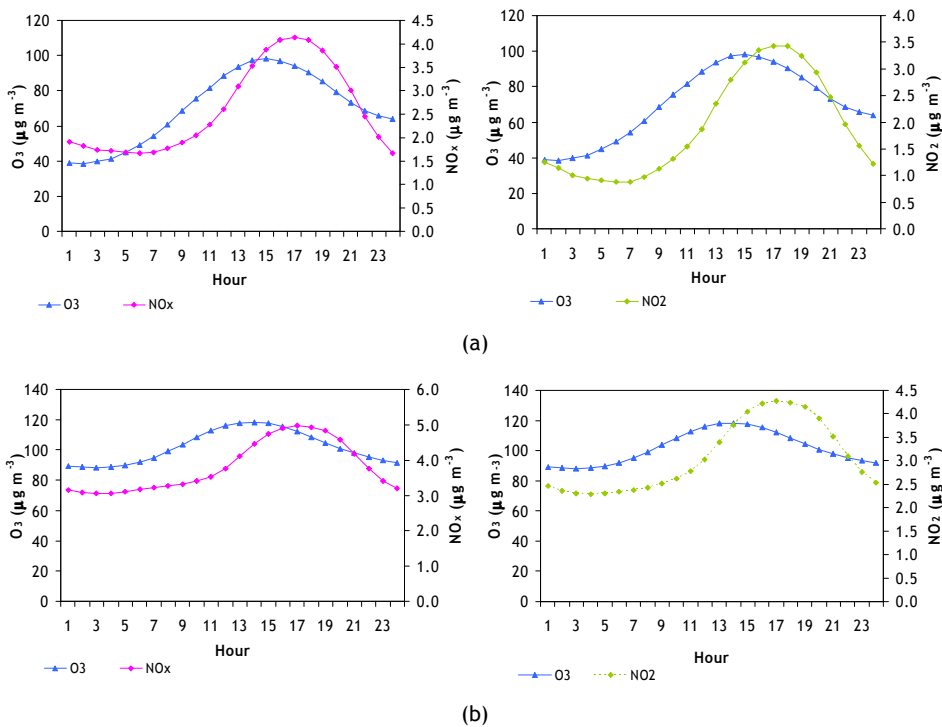


Figure 7.11 Daily profile of 8-hour running averages at the LO site for: (a) one day belonging to the period of passive sampling; and (b) the average for all the period of passive sampling.

For the LO site, a typical profile of a rural area was observed, where O₃ formation was controlled by NO_x concentrations and therefore a decrease on O₃ concentrations led to a decrease in NO_x concentrations. These results showed that [VOC]/[NO_x] were relatively high at the LO site because of the relatively quicker removal of NO_x from distant sources compared to that of VOC, coupled with the absence of NO_x local sources. Furthermore, in both sites the concentrations of NO₂ showed the same behaviour as those of NO_x.

Concluding, the absence of anthropogenic sources at remote areas, led to very low concentrations of NO_2 , that were responsible for the high concentrations of O_3 .

Selection of one Area to Perform the Study regarding Ozone Exposure Impact on Human Health

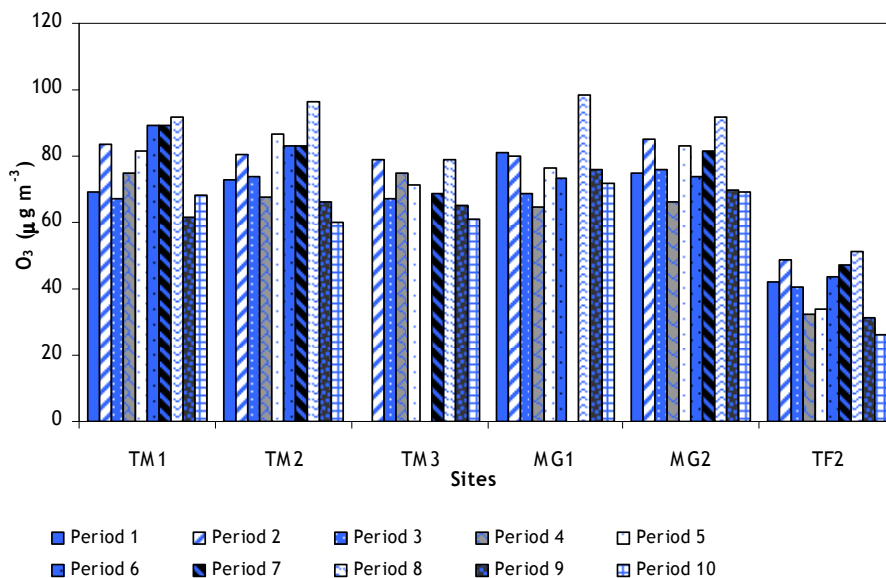
From all remote sites analysed, BG₄ was the one with the highest concentrations of O_3 during both 1st and 2nd periods of passive sampling (97.9 $\mu\text{g m}^{-3}$ and 122.0 $\mu\text{g m}^{-3}$, respectively) and the concentrations of NO_2 and VOC were significantly lower than at the TF₂ site. At the LO site the concentrations of O_3 were significantly lower than at BG₄ during both 1st and 2nd periods (87.1 $\mu\text{g m}^{-3}$ and 113.2 $\mu\text{g m}^{-3}$, respectively) being the IT exceeded 49 times, the AT exceeded 8 times and the TVPHH exceeded 20 times. Consequently, the number of exceedances at the BG₄ was surely greater, suggesting that this area is adequate to perform further studies regarding O_3 impact on childhood asthma. Another reason to select the BG₄ site was the greater population density of this area (84 inhab km^{-2}) in comparison with the other remote zones (between 5 and 22 inhab km^{-2}).

7.2.2.2 Second Phase

Assessment of Ozone, Nitrogen Dioxide and VOC Concentrations

From all remote sites analysed in the first phase (2006 summer), *Torre de Moncorvo* was the one with the highest O_3 concentrations (97.9 $\mu\text{g m}^{-3}$ and 122.0 $\mu\text{g m}^{-3}$, for each period studied). Therefore, for the second phase (2007 summer), *Torre de Moncorvo* was selected from all the remote areas previously studied, described in the previous chapter; the close area *Mogadouro* was added to this study aiming to guarantee a higher number of schoolchildren.

Figure 7.12 shows the O_3 concentrations measured at all sites and periods.

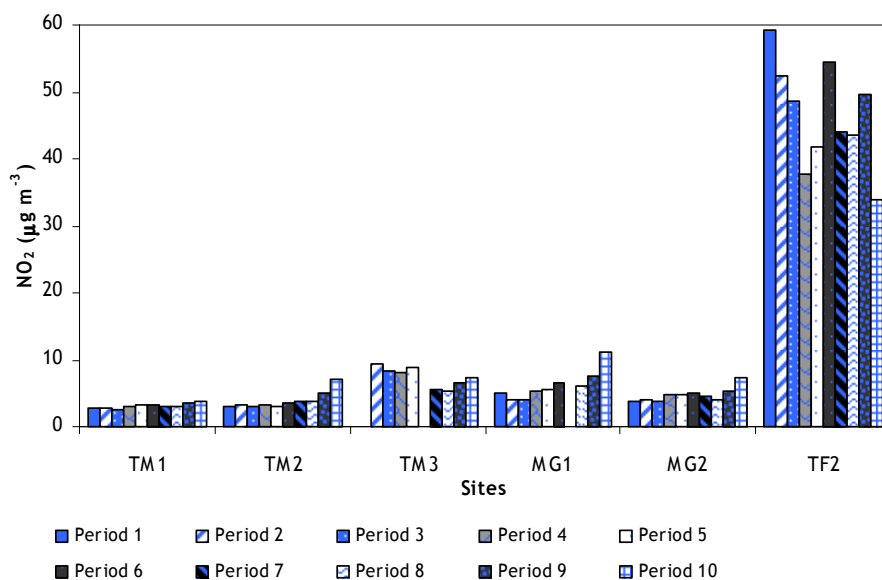


Data not available for: TM₃-Periods 1 and 6; MG₁-Period 7

Figure 7.12 Concentrations of O₃ measured at all sites during all the studied periods.

Remote sites had similar concentrations, between $60.0 \mu\text{g m}^{-3}$ (TM₂, P₁₀) and $98.7 \mu\text{g m}^{-3}$ (MG₁, P₈), being in average, $75.9 \mu\text{g m}^{-3}$. At TF₂, concentrations of O₃ varied between $26.3 \mu\text{g m}^{-3}$ (P₁₀) and $51.3 \mu\text{g m}^{-3}$ (P₈). Thus, concentrations were around 2 times higher at remote areas than at the urban site. The number of exceedances to the standard values set by the European Union (Directive 2002/3/EC) were higher at LO than at TF₂ during 2007: i) TVPHH was exceeded 44 times at the remote site against 3 times at the urban site; ii) IT was exceeded 25 times at the remote site against 5 times at the urban site; and iii) AT was only exceeded once at the remote site. The concentrations were higher during P₈ (average $91.5 \mu\text{g m}^{-3}$); accordingly, this was one of the periods with the highest temperatures (maximum average of 28°C) (IM, 2008). As it can be observed average concentrations of O₃ were lower because as temperatures were also lower for 2007 summer, the photochemical O₃ formation decreased. It should be referred that in Portugal O₃ levels during 2007 summer were among the lowest in the past decade. Accordingly, the number of exceedances in Europe was also lower than in any of the last ten summers (EEA, 2008).

NO₂ concentrations in 2007 summer were measured at all sites for all the periods and are shown in Figure 7.13.

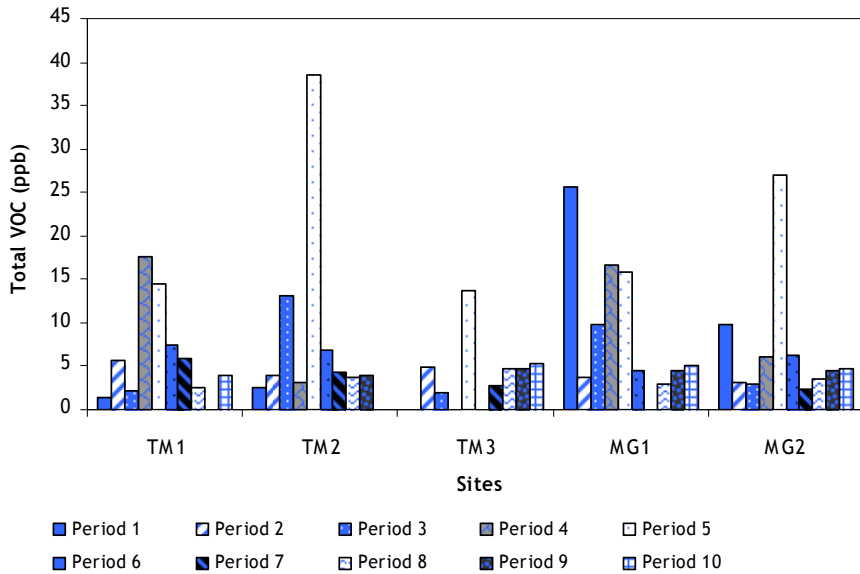


Data not available for: TM₃-Periods 1 and 6; MG₁-Period 7

Figure 7.13 Concentrations of NO₂ measured at all sites during all the studied periods.

The concentrations were very low, between 2.5 $\mu\text{g m}^{-3}$ (TM₁, P₃) and 11.3 $\mu\text{g m}^{-3}$ (MG₁, P₁₀), being in average, 5.0 $\mu\text{g m}^{-3}$. NO₂ concentrations at the urban site were between 34.0 $\mu\text{g m}^{-3}$ (P₁₀) and 59.2 $\mu\text{g m}^{-3}$, being in average 46.5 $\mu\text{g m}^{-3}$ (P₁), therefore significantly higher (9 times in average) than at *Torre de Moncorvo* and *Mogadouro*. The results indicated that remote sites had very low concentrations of NO₂, suggesting that they were not significantly influenced by traffic emissions.

The total VOC concentrations measured in 2007 summer are shown in Figures 7.14 and 7.15. Figure 7.14 shows the total C₅-C₁₂ VOC concentrations.



Data not available for: TM₁-Period 9; TM₂-Period 10; TM₃-Periods 1, 4 and 6; MG₁-Period 7

Figure 7.14 Concentrations of total VOC with boiling points between 50°C and 200°C (C₅-C₁₂) measured at all sites during all the studied periods.

The levels varied between 1.5 ppb (TM₁, P₁) and 38.6 ppb (TM₂, P₅), being in average, 7.6 ppb. P₅ was the period with the highest concentrations, being in average 21.9 ppb. The specific VOC analysed within this range were: benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene, and toluene; their concentrations are shown in Table 7.8.

Table 7.8 Concentrations of benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene, and toluene measured at all sites during all the studied periods ($\mu\text{g m}^{-3}$).

	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀
Benzene										
TM ₁	BDL	0.82	0.66	1.16	1.55	1.24	BDL	BDL	NA	0.48
TM ₂	0.68	0.73	3.44	1.20	6.72	1.66	0.40	0.57	0.50	NA
TM ₃	NA	1.01	0.58	NA	1.44	NA	BDL	0.68	0.49	0.67
MG ₁	1.83	0.61	0.91	1.18	2.15	1.28	NA	0.43	0.49	0.777
MG ₂	1.08	0.65	1.04	1.15	1.26	1.42	0.5	BDL	BDL	0.82
Toluene										
TM ₁	0.55	0.70	0.98	0.67	2.20	1.03	0.5	0.66	NA	0.53
TM ₂	12.4	0.96	4.57	1.10	14.27	1.48	0.88	1.43	0.89	NA
TM ₃	NA	1.66	1.35	NA	2.26	NA	1.02	1.78	1.09	1.39
MG ₁	0.67	1.26	1.11	1.19	3.75	2.25	NA	1.47	1.27	1.49
MG ₂	2.56	0.91	1.08	1.10	3.40	1.27	1.02	3.53	1.30	1.65
m/p-xylene										
TM ₁	BDL	1.64	BDL	0.25	0.54	2.06	BDL	BDL	NA	0.23
TM ₂	0.56	0.40	0.80	0.53	1.71	0.47	0.35	0.54	0.51	NA
TM ₃	NA	1.02	1.00	NA	2.55	NA	0.53	1.00	0.55	0.88
MG ₁	4.31	0.69	0.50	0.81	1.08	0.88	NA	0.57	0.64	0.87
MG ₂	0.25	0.49	0.62	1.33	0.87	0.52	0.45	1.94	0.55	0.71
o-xylene										
TM ₁	BDL	0.3	BDL	BDL	0.20	0.29	0.17	0.18	NA	BDL
TM ₂	0.19	0.15	0.23	BDL	0.54	BDL	0.11	0.18	0.15	NA
TM ₃	NA	0.37	0.37	NA	0.56	NA	0.19	0.32	0.20	0.27
MG ₁	1.17	1.73	0.20	0.29	0.39	0.28	NA	0.55	0.18	0.29
MG ₂	0.23	0.19	0.18	0.43	0.30	BDL	0.14	0.50	0.15	0.23

NA: Not Available

BDL: Below Detection Limit

Table 7.8 (cont) Concentrations of benzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m/p-xylene, o-xylene, and toluene measured at all sites during all the studied periods ($\mu\text{g m}^{-3}$).

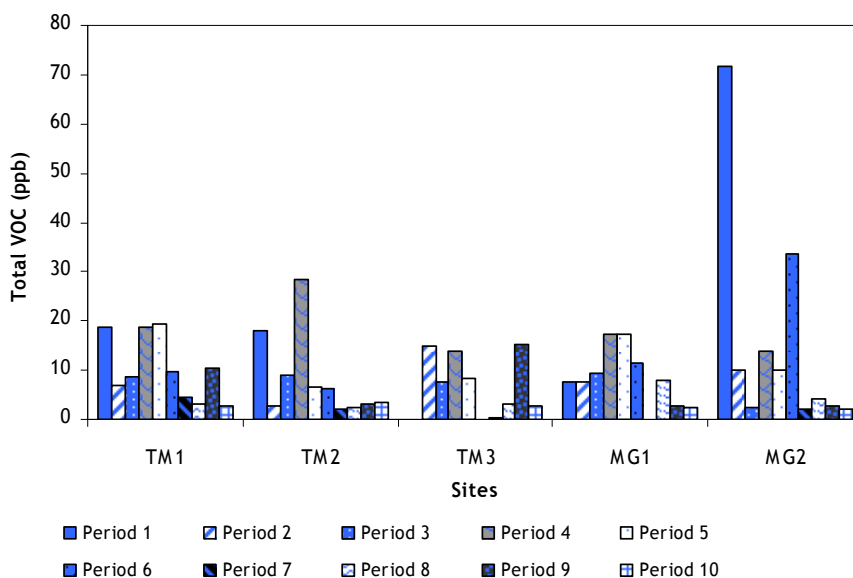
	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀
1,2,4-trimethylbenzene										
TM ₁	BDL	1.98	BDL	BDL	BDL	BDL	BDL	BDL	NA	BDL
TM ₂	0.85	BDL	BDL	BDL	1.39	BDL	BDL	BDL	0.42	NA
TM ₃	NA	BDL	1.11	NA	2.09	NA	BDL	0.31	0.49	0.77
MG ₁	1.68	0.61	BDL	1.16	BDL	BDL	NA	BDL	0.53	0.63
MG ₂	BDL	1.11	BDL	0.98	BDL	BDL	BDL	BDL	0.36	0.73
1,3,5-trimethylbenzene										
TM ₁	BDL	0.67	BDL	BDL	BDL	BDL	0.51	BDL	NA	BDL
TM ₂	BDL	BDL	BDL	BDL	0.43	BDL	0.76	0.71	BDL	NA
TM ₃	NA	0.51	0.36	NA	0.59	NA	BDL	BDL	BDL	0.36
MG ₁	0.54	BDL	BDL	BDL	0.51	BDL	NA	0.89	BDL	0.29
MG ₂	BDL	BDL	BDL	0.37	0.39	BDL	BDL	0.40	BDL	0.35

NA: Not Available

BDL: Below Detection Limit

These are compounds mainly associated with traffic emissions and toluene is also associated with the use of solvents (Fillella and Peñuelas, 2006). The average concentrations of benzene for each site were always lower than $3 \mu\text{g m}^{-3}$, with exception of TM₁ in P₅ ($6.7 \mu\text{g m}^{-3}$). According to Directive 2000/69/EC benzene should not exceed $5 \mu\text{g m}^{-3}$ averaged over a year. Toluene attended WHO guideline of $260 \mu\text{g m}^{-3}$ averaged over 1 week (WHO, 2000), being between $0.5 \mu\text{g m}^{-3}$ and $12.4 \mu\text{g m}^{-3}$; the concentrations of m/p-xylene, o-xylene, 1,2,4-trimethylbenzene and 1,3,5- trimethylbenzene were in average, respectively, lower than, $1.2 \mu\text{g m}^{-3}$, $0.6 \mu\text{g m}^{-3}$, $2.7 \mu\text{g m}^{-3}$ and $1.2 \mu\text{g m}^{-3}$. The low concentrations of these compounds showed, once more, that at these sites traffic emissions were very low.

Shown in Figure 7.15 are the C₇-C₂₈ VOC concentrations.



Data not available for: TM₃- Periods 1 and 6; MG₁- Period 7

Figure 7.15 Concentrations of total VOC with boiling points up to 280°C (C₇-C₂₈) measured at all sites during all the studied periods.

These compounds had in general low concentrations for all the sites studied, with exception of a sporadic peak value in MG₂, P₁. Concentrations varied between 0.36 ppb and 33.6 ppb, without considering the peak value (72 ppb), being in average, 10.7 ppb. The periods with higher concentrations were P₄, P₅ and P₆, when the temperatures were also higher, being in average from 12.2 ppb to 15.3 ppb (in P₁ average was higher because of the peak value above referred), against 2.3 ppb to 8.5 ppb in the other periods. Within the VOC analysed in this range, β -pinene and 3-carene were always below the detection limit (1.5 ng); α -pinene was higher at TM₁ and MG₂, being around 0.13 $\mu\text{g m}^{-3}$ and 0.4 $\mu\text{g m}^{-3}$; and the concentrations of limonene were, generally higher than the detection limit (1.5 ng) for P₄, P₅ and P₆, being between 0.25 $\mu\text{g m}^{-3}$ and 3.10 $\mu\text{g m}^{-3}$ (Table 7.9). Cerqueira et al. (2003), who studied the presence of VOC in two rural areas in Portugal, also found concentrations in the same range for α -pinene, but quite lower for limonene (between 0.03 $\mu\text{g m}^{-3}$ and 0.07 $\mu\text{g m}^{-3}$).

Table 7.9 Concentrations of α -pinene and limonene measured at all sites during all the studied periods ($\mu\text{g m}^{-3}$).

	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆	P ₇	P ₈	P ₉	P ₁₀
α-pinene										
TM ₁	1.39	0.88	0.63	0.92	0.72	0.91	0.44	0.48	0.38	0.17
TM ₂	BDL	BDL	BDL	BDL	0.23	0.30	BDL	BDL	BDL	BDL
TM ₃	NA	0.30	BDL	0.33	0.22	NA	BDL	BDL	BDL	BDL
MG ₁	BDL	BDL	BDL	0.27	BDL	0.34	NA	BDL	BDL	BDL
MG ₂	0.50	0.50	BDL	0.46	0.32	0.58	BDL	0.23	0.19	BDL
Limonene										
TM ₁	BDL	BDL	BDL	0.63	15.5	13.4	BDL	BDL	BDL	BDL
TM ₂	BDL	BDL	0.23	1.97	7.79	11.0	BDL	BDL	BDL	BDL
TM ₃	NA	0.62	BDL	2.81	11.7	NA	BDL	BDL	BDL	BDL
MG ₁	BDL	BDL	0.32	0.95	9.24	22.3	NA	BDL	BDL	BDL
MG ₂	0.57	BDL	BDL	0.46	11.2	20.7	BDL	BDL	BDL	BDL

NA: Not Available

BDL: Below Detection Limit

The concentrations of ethene, isoprene and 2-methyl-1-butene were always below the respective detection limits (10 ng and 1 ng for the last two). Propene and 2-methylbutane were in general below the detection limit (Table 7.10). Iso-butene showed concentrations between $0.04 \mu\text{g m}^{-3}$ and $0.35 \mu\text{g m}^{-3}$ (Table 7.10).

Isoprene and monoterpenes are highly reactive biogenic VOC present in the lower atmosphere emitted by terrestrial vegetation, thus are considered to have influence on O₃ production (So and Wang, 2004). In the present study, isoprene had very low concentrations in comparison to other studies performed at semiurban and rural sites (Qin et al., 2007; Filella and Peñuelas, 2006; Cerqueira et al., 2003).

Table 7.10 Concentrations of propene, iso-butene and 2-methylbutane measured at all sites during all the studied periods ($\mu\text{g m}^{-3}$).

	P1	P2	P3
Propene			
TM ₁	BDL	BDL	BDL
TM ₂	NA	BDL	BDL
TM ₃	NA	BDL	0.18
MG ₁	BDL	BDL	BDL
MG ₂	0.14	BDL	BDL
Iso-butene			
TM ₁	BDL	0.09	BDL
TM ₂	NA	0.04	0.25
TM ₃	NA	BDL	0.16
MG ₁	0.27	0.05	0.35
MG ₂	0.26	0.05	0.15
2-methylbutane			
TM ₁	BDL	BDL	BDL
TM ₂	NA	BDL	0.08
TM ₃	NA	BDL	0.20
MG ₁	0.06	BDL	0.65
MG ₂	BDL	BDL	BDL

NA: Not Available

BDL: Below Detection Limit

The study performed in the first phase (2006 summer) showed that lower concentrations of O₃ were observed at the urban site ($51.0 \mu\text{g m}^{-3}$ and $40.9 \mu\text{g m}^{-3}$, for each period studied), thus similarly to what happened in the second phase (2007 summer). The number of exceedances of the standard values defined by the European Union was also greater at the

remote site in 2006. During 2006 summer NO_2 concentrations were 12 to 20 times higher at an urban site than at remote sites and the concentrations of VOC during 2006 summer were from 2 to 8 times higher at urban sites than at remote sites; thus, the results obtained in 2007 summer confirmed those obtained in 2006 summer, showing that as industrial and traffic emissions were not significant at *Torre de Moncorvo* and *Mogadouro* they had high levels of O_3 and low levels of NO_2 and VOC.

7.2.3 Conclusions

The results obtained allowed concluding that:

- 1) Satisfactory reproducibility and precision was obtained from the measurements with passive samplers (the maximum absolute difference between passive sampling and continuous monitoring measurements was $5 \mu\text{g m}^{-3}$ and the relative differences were greater than 12% only for concentrations about $2\text{--}3 \mu\text{g m}^{-3}$);
- 2) In the first phase, the lowest concentrations of O_3 were observed at the urban site ($51.0 \mu\text{g m}^{-3}$ and $40.9 \mu\text{g m}^{-3}$). From all remote sites analysed, the one with the highest O_3 concentrations ($97.9 \mu\text{g m}^{-3}$ and $122.0 \mu\text{g m}^{-3}$) was located in the *Bragança* district. Nitrogen dioxide concentrations were from 12 to 20 times greater at the urban site than in remote sites and volatile organic compound concentrations were from 2 to 8 times greater, due to the influence of traffic emissions;
- 3) At the urban site, O_3 formation was controlled by volatile organic compound concentrations, leading to a decrease in O_3 concentrations when nitrogen oxides concentration increased. At the remote sites O_3 formation was controlled by nitrogen oxides concentration, due to its very low level. Accordingly, a decrease on O_3 concentrations was observed when nitrogen dioxide concentrations decreased. The low levels of nitrogen dioxide (due to the quicker removal of nitrogen oxides from distant sources compared to that of volatile organic compounds, coupled with the absence of anthropogenic sources at remote areas) were responsible for the high concentrations of O_3 at the remote areas;
- 4) The number of exceedances of the standard values for human health protection was greater at remote sites than at the urban site. The selected zone to perform further studies regarding O_3 exposure impact on health was *Torre de Moncorvo*, a remote site in the *Bragança* district. This area showed the highest O_3 concentrations, the lowest

concentrations of nitrogen dioxide and volatile organic compounds, as well as the greater number of exceedances of the standard values for human health protection, and the highest population density from all the remote zones studied.

5) The results obtained in the second phase confirmed those obtained in the first one, showing that as industrial and traffic emissions were not significant at *Torre de Moncorvo* and *Mogadouro* they had high levels of O_3 (between 60.0-98.7 $\mu g\ m^{-3}$) and low levels of NO_2 and VOC (between 2.5-11.3 $\mu g\ m^{-3}$ and 1.5-38.6 ppb, respectively).

Chapter 8

Prevalence of Childhood Asthma: Influence of Exposure to Ozone*

The work presented in this section was performed in the previously referred selected areas (*Torre de Moncorvo* and *Mogadouro*) and aimed to evaluate the specific impact of O₃ on childhood asthma (without the confounding effects of other pollutants), by comparing prevalence rates of asthma in children living at the selected remote areas with high ozone concentrations, with those living at an area with low concentrations of O₃ and of other pollutants (unexposed area), being the main difference between the areas related with O₃ concentrations. Also this part of the study was performed in two phases; in a first phase the asthma prevalence in children aged 6 to 13 years old was assessed through questionnaires and in a second phase that prevalence was validated through lung function tests.

* adapted from: Sousa SIV, Alvim-Ferraz MCM, Martins FG, Pereira MC, 2009. Ozone exposure and its influence on the worsening of childhood asthma. *Allergy*, 64:1046-1055 and from Sousa SIV, Ferraz C, Alvim-Ferraz MCM, Martins FG, Vaz LG, Pereira MC, 2009. Prevalence of childhood asthma: influence of exposure to high ozone levels. *Submitted*.

8.1. Methodology

8.1.1 First Phase

A total of 698 questionnaires were distributed in the schools, from which 68.5% were entirely answered (uncompleted questionnaires were excluded) by the children parents or guardians. Thus, the studied population was composed by 478 (out of 698) children aged 6 to 13 years old enrolled in 2 schools of *Torre de Moncorvo* and 2 schools of *Mogadouro* (coincident with the locations of the monitoring sites referred in Section 7.2.1.2). Data concerning asthma prevalence were collected through questionnaires, using the same questions as those used in ISAAC regarding asthma (Appendix B). The questionnaire included questions concerning sex, age, distance from home to school, social economic status, tobacco smoke habits and health symptoms related to asthma prevalence: asthma previously diagnosed, wheezing, dyspnoea, and their severity evaluated through asthma attacks (number in the previous year, speech -limiting, during night and induced by exercise) (Asher et al., 1995). The questionnaires were distributed to the children, with consented participation (Appendix C) of their parents or guardians who completed the questionnaires. In order to increase the number of answers, parents or guardians were contacted directly by the teachers of the children motivating participation in the study, but not interfering in the questionnaire answers. Also, a handout was delivered with the questionnaires to allow a full understanding of the study purposes by both children and parents or guardians (Appendix D). Questionnaires and their evaluation were validated by medical doctors. According to the questionnaire answers, asthmatic children were identified when wheezing and dyspnoea were simultaneously mentioned in the absence of upper respiratory infections (Alvim-Ferraz et al., 2005; Barros et al., 1999). To compare the prevalence of childhood asthma, an unexposed area (with low concentrations of O₃, NO₂ and VOC) needed to be identified. As O₃ concentrations are strongly increasing in Portugal, it was impossible in 2007 to find such a place. Therefore, previous studies carried out at *Espiunca*, a Portuguese remote rural area were considered for comparison, because at that time O₃ and other pollutant concentrations were there very low. Studies were performed there in 1999 and 2002 (Alvim-Ferraz et al., 2005). The concentrations of PM₁₀, SO₂, NO₂ and O₃ were evaluated. The concentrations of PM₁₀, SO₂ and NO₂ (2-5 µg m⁻³), were very low; O₃ concentrations were also low never exceeding the IT, AT and TVPHH for the periods studied (Alvim-Ferraz et al., 2005). Furthermore, this area was similar to the exposed ones in terms of geography and meteorology.

At the referred unexposed area (*Espiunca*) the prevalence of asthma in children from 6-12 years old was estimated for 1999 and 2002; the number of children involved was 720 and 956, respectively. Questionnaires used had the same questions related to asthma as those used in this study and children had also similar age (6-12 years old), indoor environmental exposure, diet, lifestyle and socio economic status. The criterium used for identification of asthmatic children was the same as the one used in this study: dyspnoea and wheezing in the absence of upper respiratory infections.

Therefore, considering that the main difference between the exposed area (*Torre de Moncorvo* and *Mogadouro*, with high levels of O₃ and low levels of other pollutants) and the unexposed one (*Espiunca*, with low levels of O₃ and of other pollutants) was related with O₃ concentrations, the comparison of asthma prevalence in children living at the exposed area with that of children living at the unexposed one, allowed evaluating the specific impact of O₃ on childhood asthma.

Logistic regression models were used to calculate OR. The level of statistical significance was set at 0.05. The analyses were performed using the statistical software SPSS 16.0 (SPSS Inc.).

8.1.2 Second Phase

From the cohort of 478 children included in the first phase of the study, a subgroup of 106 children that mentioned at least one of the asthma symptoms (wheeze, dyspnoea and cough), was selected to perform lung function tests; as 11 children were transferred to other schools, these tests were performed on 95 children (89.6%).

Data on lung function of the children were obtained by spirometric tests pre and post bronchodilator administration, being salbutamol the administered medication; the protocol of the study was approved by the Ethical Committee of *Hospital de São João*. Children were instructed how to do the tests, repeating them at least three times and until reproducibility was reached (Figure 8.1); tests were performed with Vitalograph Compact Spirometer (Vitalograph Ltd., Buckingham, England) according to the American Thoracic Society standards and the European Respiratory Society (ATS, 1994). The lung function indexes evaluated were FEV₁, FVC and FEF_{25%-75%}. All the tests were performed at one specific room of each school, to where medical doctors brought all the material needed; the specific indoor environment chosen to carry out the tests allowed to avoid confounding effects

related to weather conditions. Based on the spirometry results, children were considered asthmatic when: i) the percentage of FEV_1/FVC was less than 80%; or ii) the change in FEV_1 pre and post medication was equal or higher than 12%; or iii) the change in $FEF_{25\%-75\%}$ pre and post medication was equal or higher than 35% (ATS, 2007; Pellegrino et al., 2005).

Also for the study on this phase logistic regression models were used to calculate RR and OR. The level of statistical significance was set at 0.05 and the analyses were performed using the statistical software SPSS 16.0 (SPSS Inc.), as well.

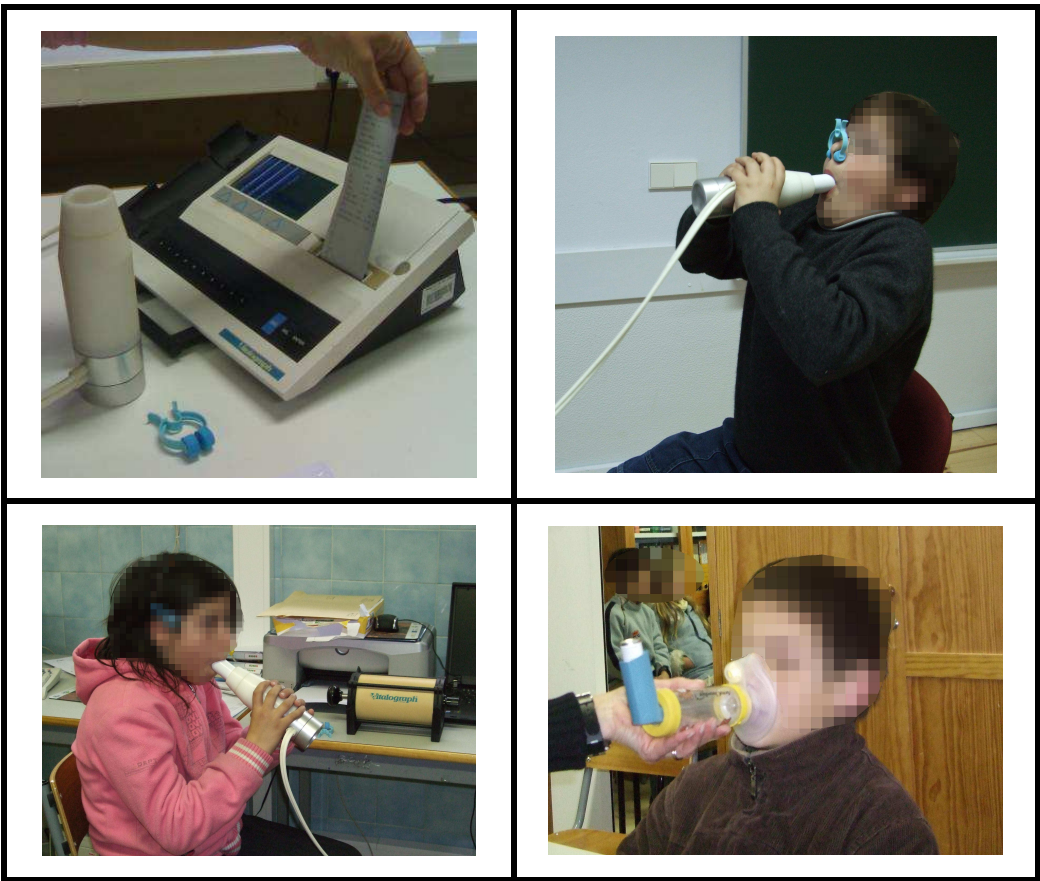


Figure 8.1 Spirometric tests.

8.2. Results and Discussion

8.2.1 First Phase

Assessment of Asthma Prevalence through Questionnaires

The population who answered the questionnaire is characterized in Table 8.1.

Around 23% of the studied children presented at least one of the respiratory symptoms investigated (wheeze, dyspnoea and cough) in the absence of upper respiratory infections. The prevalence of wheezing for lifetime period and in the past year was 15.9% and 6.3%, respectively. According to the questionnaire answers the lifetime prevalence of asthma at these remote areas was 7.1%.

The reported prevalence rates of asthma at the unexposed area *Espiunca* were 3.5 % and 3.2 % for 1999 and 2002, respectively, thus significantly lower than the prevalence rate obtained in the present study through questionnaires (7.1%).

Martinez and Weiss (2006) reported a study on the asthma prevalence during 1990-1999 in rural Alaska natives. Medical records of 1200 children, aged 0-10 years old were reviewed. No monitoring of air pollutants was performed in the area during the period of study. Results showed that the prevalence was 2.0% in 1990 and 3.0% in 1990-1994 and in 1995-1999, thus concluding that in a population of children not exposed to urban industrial, or rural agricultural pollutants, there was no significant change in the prevalence of wheezing or asthma, supporting the idea that environmental pollution contributes for the increase of asthma prevalence. This study did not consider standard epidemiological criteria for the diagnosis of asthma, neither smoking habits nor air pollution monitoring; the range of children ages was different from the present study and the population had a subsistence lifestyle, thus different from the one of the present study. Despite of the differences, it should be remarked that the estimated rates were significantly lower than those obtained in the present study through questionnaires, which might be due to environmental pollution contribution.

Table 8.1 Characterization of the children answering to questionnaire (1st phase).

	(%)	95% CI*
Sex		
Female	50.2	45.7-54.7
Male	49.8	45.3-54.3
Distance home-school		
0-10 km	63.0	58.6-67.3
10-20 km	17.8	14.4-21.2
≥ 20 km	5.4	3.4-7.5
Lifetime prevalence		
Wheeze	15.9	12.6-19.2
Dyspnoea	13.4	10.3-16.5
Asthma (previously diagnosed)	4.2	2.4-6.0
Prevalence in the past year		
Wheeze		
Spontaneous	6.3	4.1-8.5
Attacks number		
None	0.6	0.0-1.3
1 to 3	5.0	3.0-7.0
4 to 12	0.8	0.0-1.6
≥ 12	0.6	0.0-1.3
Nocturnal attacks number		
None	2.7	1.2-4.2
<1 night/week	2.9	1.4-4.4
≥ 1 night/week	1.5	0.4-2.6
Exercise-induced	2.9	1.4-4.4
Speech-limiting attacks	0.8	0.0-1.6
Dyspnoea		
Attacks number		
None	4.8	2.9-6.7
1 to 3	6.9	4.6-9.2
4 to 12	1.7	0.5-2.9
≥ 12	0.8	0.0-1.6
Nocturnal attacks number		
None	8.4	5.9-10.9
<1 night/week	3.6	1.9-5.3
≥ 1 night/week	1.3	0.3-2.3
Nocturnal cough (without infection)	29.7	25.6-33.8

* CI (95%) - 95% Confidence Interval

Priftis et al. (2007) studied 8 to 10 years old children from urban and rural areas in Greece, where the concentrations of all pollutants were lower in rural areas but those of O₃ were similar; the prevalence of wheezing was assessed by questionnaires, as in the present study. Lifetime and past year wheezing prevalence were, respectively, 18.4% and 7.7% (urban) and 17.3% and 6.1% (rural), thus similar in both areas. The range of ages was similar to the present study and considerations were made on environmental tobacco smoke, history of allergies and others. The prevalence of wheezing was similar to the prevalence assessed in the present study (15.9% and 6.3% for lifetime and past year, respectively), meaning that remote areas with high O₃ concentrations had similar prevalence of wheezing to the observed in urban ones affected by O₃ and other pollutants.

In the ISAAC study performed at the region of Great Lisbon, Portugal, results showed a last year prevalence of asthma of 12.8% for 1994/1995 and of 15.7% for 2000/2001, higher than the one obtained in the present study through questionnaires (Araújo, 2007). Nevertheless, at a smaller urban area (*Portimão, Algarve* in the south of Portugal) the ISAAC study performed by Nunes and Ladeira (2005) identified a lifetime prevalence of asthma in children from 6-7 years old of 6.2% and 4.9%, respectively for 1994 and 2002. This prevalence was assessed through questionnaires answered by the children parents, considering the influence of environmental tobacco smoke and the presence of animals at home; the study did not consider the influence of environmental pollution neither the ages of the studied population were the same as in the present study. Nevertheless, the prevalence was, in both years, lower than the obtained in the remote areas analysed in this study through questionnaires, even considering that urban pollution was present in *Portimão*. This probably means that O₃ present in the remote areas analysed had influence on the prevalence of childhood asthma.

Barros et al. (1999) performed a study to estimate lifetime and last year prevalence of asthma in 3022 children aged 6-9 years living in *Porto* and *Viseu* (Portugal). Like in the present study, data were obtained through questionnaires answered by the children parents and asthma was considered when dyspnoea and wheezing were present in the absence of upper respiratory infection. Results showed a lifetime prevalence of asthma of 13.2 % and 9.8 %, for *Porto* and *Viseu*, respectively. In both cities it was verified a tendency for prevalence to be higher with age, humidity at home, smoking mothers in pregnancy, environmental tobacco smoke and lower weight in children birth. As *Porto* is an urban region with higher traffic influence than *Viseu*, difference in prevalence might be due to environmental pollution. Asthma prevalence rates were higher than those obtained in the

present study through questionnaires, however, *Porto* and *Viseu* are urban sites strongly influenced by traffic emissions and even though, the prevalence at *Viseu* was not so different than the one obtained in the present study through questionnaires.

As already mentioned, the comparison with other previous studies was difficult because, the parameters for analysis are not conveniently standardized; therefore, the different previous studies considered different parameters, namely concerning the criteria for asthma identification, the presence of environmental tobacco smoke, the presence of other pollutants, the range of children age, and others like and the study power. Nevertheless, as it could be observed by the discussion above the prevalence obtained in the present study was quite high probably due to the influence of high O₃ concentrations.

Table 8.2 shows the distribution of asthma risk factors calculated for the children studied considering the socio-demographic characteristics, determined using univariate logistic regression analysis; OR and respective 95% CI are presented.

Table 8.2 Distribution of asthma risk factors calculated for the children answering to the questionnaire, considering the socio-demographic characteristics and respective odds ratio (OR) and 95% confidence interval (95% CI) (1st phase).

Variables	Asthma (%)	OR	95% CI
Sex			
Female	2.73	1	
Male	4.71	1.77	(0.82-3.83)
Age (years)			
6-7	1.74	1	
8-10	4.22	1.931	(0.78-4.80)
11-13	1.49	1.509	(0.49-4.65)
Distance home-school (km)			
0-10	5.21	1	
10-20	1.74	1.18	(0.48-2.88)
≥ 20	0.50	1.13	(0.25-5.13)
Social economic status			
Low	3.97	1	
Medium	2.48	1.02	(0.45-2.32)
High	1	0.90	(0.29-2.79)

For this analysis 75 questionnaires were excluded because they were incomplete concerning answers related with distance home-school and social economic status. Thus, for the 403 children answering to the questionnaire, the risk was higher for boys with a slight tendency to be higher with age, such as in other studies (Nunes and Ladeira, 2005; Barros et al., 1999). Nevertheless, it should be remarked that in a study performed in Taiwan on 11-16 years old adolescent, results showed that asthma prevalence decreased with age (Wang et al., 1999). Distance from home to school, social economic status and environmental tobacco smoke had no influence under the circumstances analysed. Therefore, for the children answering the questionnaire these factors did not present high risk, meaning that other factors, such as atmospheric pollution, might presented greater risk, which is in accordance to other authors (Ho et al., 2007).

8.2.2 Second Phase

Assessment of Asthma Prevalence trough Lung Function Tests

Aiming to validate the results obtained through questionnaires, spirometric tests were performed one year after the questionnaires, but the observed symptomatology at the time of the tests was similar to that identified through the questionnaires. The subpopulation of 95 children who performed the spirometric tests is characterized in Table 8.3, according to questionnaire answers of the first phase.

Asthma was diagnosed to 44 children (46.3% of this subgroup). It is important to emphasize that only around 18% of the children of this subgroup referred in the questionnaire to have previously diagnosed asthma.

Table 8.4 shows the distribution of asthma risk factors calculated for the subgroup of children who performed spirometric tests considering the socio-demographic characteristics, determined using univariate logistic regression analysis; odds ratio (OR) and the respective 95% confidence interval (95% CI) are also presented.

Table 8.3 Characterization of the children who performed spirometric tests (2nd phase).

	(%)	95% CI*
Sex		
Female	40.0	30.1-49.9
Male	60.0	50.1-69.9
Distance home-school		
0-10 km	64.2	54.6-73.9
10-20 km	14.7	7.6-21.9
≥ 20 km	6.3	1.4-11.2
Lifetime prevalence		
Wheeze	73.7	64.8-82.5
Dyspnoea	56.8	46.9-66.8
Asthma (previously diagnosed)	17.9	10.2-25.6
Prevalence in the past year		
Wheeze		
Spontaneous	29.5	20.3-38.6
Attacks number		
None	-	-
1 to 3	23.2	14.7-31.6
4 to 12	3.2	0.0-6.7
≥ 12	2.1	0.0-5.0
Nocturnal attacks number		
None	10.5	4.4-16.7
<1 night/week	10.5	4.4-16.7
≥ 1 night/week	7.4	2.1-12.6
Exercise-induced	13.7	6.8-20.6
Speech-limiting attacks	4.2	0.2-8.2
Dyspnoea		
Attacks number		
None	15.8	8.5-23.1
1 to 3	28.4	19.4-37.5
4 to 12	7.4	2.1-12.6
≥ 12	4.2	0.2-8.2
Nocturnal attacks number		
None	33.7	24.2-43.2
<1 night/week	13.7	6.8-20.6
≥ 1 night/week	6.3	1.4-11.2
Nocturnal cough (without infection)	60.0	50.1-69.9

* CI (95%) - 95% Confidence Interval

Table 8.4 Distribution of asthma risk factors calculated for the children who performed spirometric tests considering socio-demographic characteristics and respective odds ratio (OR) and 95% confidence interval (95% CI).

Variables	Asthma (%)	OR	95% CI
Sex			
Female	52.6	1	
Male	42.1	0.655	(0.29-1.50)
Age (years)			
8-10	52.1	1	
11-15	40.4	0.624	(0.28-1.41)
Distance home-school (km)			
0-10	46.7	1	
10-20	57.1	1.52	(0.48-4.82)
≥ 20	16.7	0.23	(0.025-2.05)
Social economic status			
Low	52.3	1	
Medium	42.1	0.644	(0.285-1.60)
High	38.5	0.571	(0.16-2.02)

For the 95 children who performed spirometry the risk was higher for girls with a tendency to be higher from 8 to 10 years old. A distance from home to school between 10 and 20 km represented a higher risk as well as low social economic status. Nevertheless, OR were not significantly different within the classes, meaning that other factors may present higher risk, such as atmospheric pollution, several times referred by other authors (Ho et al., 2007; Salvi, 2007; D'Amato et al., 2005). Differences can be observed when comparing to the risk factors obtained in the first phase, referring higher risk for boys, with a slight tendency to be higher with age and no influence from distance from home to school or social economic status. Thus, it should be remarked that results may not be significant to be extrapolate for the population in general.

Table 8.5 shows the mean, median and inter-quartile range of the predicted and measured values of lung function indexes FEV₁, FEV₁/FVC and FEF_{25%-75%} obtained pre and post bronchodilator administration (spirometric tests).

Table 8.5 Mean, median and inter-quartile range (IQR) of the predicted and measured lung function indexes FEV₁, FEV₁/FVC and FEF_{25%-75%} (%) pre and post bronchodilator administration.

Lung function indexes (%)	Pre			Post		
	Mean	Median	IQR	Mean	Median	IQR
FEV ₁	97.9	94.0	20.5	102.1	100.0	20.5
FEV ₁ /FVC (% predicted)	92.5	92.0	3.0	-	-	-
FEV ₁ /FVC (% measured)	83.7	86.0	8.0	-	-	-
FEF _{25%-75%}	98.6	95.0	39.0	105.9	103.0	31.0

Considering the total cohort of 478 children and according to the considerations described above, the lifetime prevalence of asthma at these areas with high O₃ concentrations was 9.2% with 82% of power ($p < 0.05$), prevalence even higher than the estimated through the questionnaires (7.1%); the difference observed on the prevalence rates may be related with the restrictiveness of the criterium used to estimate asthma prevalence through questionnaires (mentioning simultaneously wheezing and dyspnoea in the absence of upper respiratory infections). At the exposed area, with high O₃ concentrations and low of other pollutants, the asthma prevalence rate was considerably higher than at an unexposed area with low concentrations of O₃ and of other pollutants (3.2-3.5%). These results are in accordance with those achieved by Priftis et al. (26), who concluded that children living in an urban area with high levels of pollution had similar asthma prevalence as those living in a rural area with similar ozone concentrations and lower of other pollutants.

The prevalence rates achieved in both exposed and unexposed areas were compared, by calculating the RR and the OR of asthma. Results showed that children living at the exposed areas had a probability 3 times higher of having asthma than children living at the unexposed area: RR of 2.84 (95% CI: 1.82-4.43) and OR of 3.02 (95% CI: 1.88-4.86).

Considering the recognized effects of pollen and fungal spores on asthma, synergistic effects of high O₃ concentrations with pollen and fungal spores have to be taken in consideration. However, no correlation was found between O₃ and pollen and fungal spore concentrations (Section 7.1), thus meaning that the high O₃ concentrations observed in the exposed areas do not modify pollen and fungal spore concentrations. Considering this and that vegetation is similar in both exposed and unexposed areas, similar pollen and fungal spore concentrations are expected. Therefore, considering that exposed and unexposed areas were similar concerning geography, meteorology, as well as children lifestyle, diet, socio

economic status and exposure to indoor pollutants, the main difference between both areas was related with O₃ concentrations (Sections 7.2 and 8.2.1). Thus, it can be admitted that O₃ pollution increased the asthma prevalence. Nevertheless, it should be remarked that further studies with larger groups of children and also toxicological and clinical studies, should be done to confirm these results and prove causality.

8.3. Conclusion

According to the answers to questionnaires, around 40% of the studied children presented at least one of the investigated respiratory symptoms (wheeze, dyspnoea and cough) in the absence of upper respiratory infections. The prevalence of wheeze for lifetime period and in the past year was 15.9% and 6.3%, respectively. Asthmatic children were identified through the questionnaire when dyspnoea and wheezing were simultaneously mentioned in the absence of upper respiratory infections. Therefore, the lifetime prevalence of asthma among the 478 cohort included in the first phase was 7.1% against 3.2-3.5% in the region without O₃ influence. The comparison with other previous studies that assessed asthma prevalence with questionnaires was difficult because, the parameters for analysis are not conveniently standardized; therefore, the different previous studies considered different parameters, namely concerning the criteria for asthma identification, the presence of environmental tobacco smoke, the presence of other pollutants, the range of children age, and others like and the study power.

From the 478 children included in the study first phase, 95 children (who mentioned at least one of the asthma symptoms: wheeze, dyspnoea and cough) performed spirometric tests. For the subgroup studied, the risk was higher for girls, with a tendency to be higher from 8 to 10 years old; a distance from home to school between 10-20 km represented a higher risk, as well as low social economic status. Nevertheless, differences were observed when comparing to the risk factors obtained in the first phase, referring higher risks for boys, with a slight tendency to be higher with age and no influence from distance from home to school or social economic status. Therefore, it should be enhanced that these conclusions may not be significant to be extrapolated for the population in general.

The lifetime prevalence of asthma at these areas with high O₃ concentrations, calculated by assessing lung function through spirometric tests was 9.2%, with 82% of power ($p < 0.05$), prevalence even higher than the estimated through questionnaires; at the unexposed area the prevalence rate was considerably lower (3.2-3.5%).

It was concluded that children living at the exposed area had a 3 times higher risk (RR of 2.84; OR 3.02) of having asthma than those living at the unexposed area.

Considering that exposed and unexposed areas were similar concerning geography, meteorology, vegetation, pollen and fungal spore concentrations, as well as children lifestyle, diet, socio economic status and exposure to indoor pollutants, the main difference between both areas was related with O₃ concentrations. Thus, it can be admitted that O₃ pollution increased the asthma prevalence. Nevertheless, it should be remarked that further studies should be done to confirm these results and prove causality.

PART V
CONCLUSIONS AND PROSPECTIVE WORK

Chapter 9

Main Conclusions and Suggestions of Future Work

The study on the evolution of ozone concentrations in northern Portugal since the pre-industrial era showed that:

- In the nineteenth century, ozone in the atmosphere was not of photochemical origin, thus being possible to consider the respective concentrations as reference values. At that time, no periodic cycle that could be associated with anthropogenic activities was identified and the slight seasonal increase of ozone concentration in spring was explained by the more efficient transport of ozone from the stratosphere (the main ozone source) in this season.
- Nowadays, ozone concentrations have a clear seasonal variation, with minimum values during winter and higher ones during spring and summer. Relative to the nineteenth century, the current concentrations were, for the studied period, in average 147% higher (252% higher in May) due to the increased photochemical production associated with the increased anthropogenic emissions.

Concerning the development of models to predict ozone concentrations, comparisons were performed between i) time-series (TS), multiple linear regression (MLR) and feedforward

artificial neural networks (FANN); ii) MLR and FANN based on principal components (PC) and iii) MLR and quantile regression (QR). Results allowed concluding that:

- TS models presented the worst results in the prediction of ozone concentrations, both in training and validation steps, which may be the result of the absence of the variables used in the other models.
- FANN model allowed more accurate results than linear models (MLR and PCR), due to the account of non-linearities.
- The application of PC to FANN was considered better than using the original data, because it reduced the number of inputs and therefore decreased the model complexity, although the performance indexes were similar using both approaches. Thus, PC based neural networks improved the prediction of ozone concentrations, due to the elimination of collinearity problems and reduction of the number of predictor variables.
- The prediction of ozone concentrations using QR model led to an improvement when compared with MLR. QR was more efficient than MLR to predict both high and low extreme values. Nevertheless, for the validation step, the root mean squared error values were similar, as opposed to the ones obtained in the training step, meaning that the procedure used to infer which QR model equation would be the appropriate to predict ozone was not the most adequate. Even though, QR has proven to be useful to predict ozone concentrations, because it allowed more efficient previsions of extreme values.

Globally, PC application on FANN was the better approach, however with PCR showing similar performance indexes in the validation step. Additionally, the application of QR was also efficient especially in the prediction of extreme values which is useful to preview ozone episodes. These models are valuable tools for public health protection because they can help to develop efficient strategies to protect the public health, namely providing early warnings to the population.

Concerning the evaluation of the specific impact of ozone concentrations on the prevalence of childhood asthma without the confounding effects of other pollutants, results allowed to conclude that:

- Statistically significant correlations, calculated using correlation coefficients and MLR, were observed randomly between ozone and PM_{10} and biological pollutants. The parameters

that influenced each pollen and fungal spore, depended on the analysed period, which meant that the correlations identified as statistically significant could be inconsistent.

- The concentrations of ozone and PM₁₀ do not influence most of the airborne pollen and fungal spore concentrations. Nevertheless, in spite of the inconsistent trends between air pollutants and pollen and fungal spores, further research should be made concerning their synergistic effects on health.
- Torre de Moncorvo and Mogadouro (Bragança district) had the highest ozone concentrations, the lowest concentrations of nitrogen dioxide and volatile organic compounds, as well as the greater number of exceedances of the standard values for human health protection, and the highest population density from all the remote areas studied, thus being the selected as exposed area to perform the study of ozone impact on the prevalence of childhood asthma.
- According to questionnaires, the prevalence of wheeze for lifetime period and in the past year was, respectively, 15.9% and 6.3%. The lifetime prevalence of asthma among the exposed group was 7.1% against 3-3.5% for the unexposed group (asthmatic children were identified when dyspnoea and wheezing were simultaneously mentioned in the absence of upper respiratory infections). Consequently, at the unexposed area with low concentrations of ozone and other pollutants, the asthma prevalence was considerably lower than at the exposed remote areas, with high concentrations of ozone and low of other pollutants.
- Asthma was diagnosed, in a second phase, through spirometric tests to 46.3% of the subgroup (95 out of 478 children who mentioned at least one of the asthma symptoms).
- The distribution of asthma risk factors, for children answering to questionnaires, considering the socio-demographic characteristics showed higher risks for boys, with a slight tendency to be higher with age and no influence from distance from home to school or social economic status. Nevertheless, differences were observed when comparing to the risk factors obtained in the second phase, showing higher risk for girls with a tendency to be higher from 8 to 10 years old. A distance from home to school between 10 and 20 km represented a higher risk and also low social economic status. Therefore, it should be enhanced that these conclusions may not be significant to be extrapolated for the population in general.

- The lifetime prevalence of asthma at the exposed area with high ozone concentrations, calculated by assessing lung function through spirometric tests was 9.2%, even higher than the one achieved through questionnaires (7.1%).

It was concluded that children living at the area mainly polluted by ozone had a 3 times higher risk (relative risk 2.84; odds ratio 3.02) of having asthma than those living at the area without ozone influence. Considering that exposed and unexposed areas were similar concerning geography, meteorology, vegetation pollen and fungal spore concentrations, as well as children lifestyle, diet, socio economic status and exposure to indoor pollutants, the main difference between both areas was related with ozone concentrations. Thus, it can be admitted that ozone pollution increased the asthma prevalence.

Considering the results achieved strategies should be defined to reduce ozone concentrations and consequently protect public health even in remote areas such as *Torre de Moncorvo* and *Mogadouro*. Early warnings should be emitted whenever ozone concentrations are predicted to be high, so that exposure can be prevented.

Suggestions of Future Work

Concerning the evaluation and interpretation of ground-level ozone concentrations, deeper studies could be carried out to analyse vertical and horizontal transport and interpret how these could affect the concentrations.

With respect to the development of models, studies could be performed to evaluate the effects of exposure to pollution, by including the contribution of pollutant mixtures, due to the difficulty of finding nowadays an area without exposure to O₃.

Concerning the impact of ozone on childhood asthma, epidemiological studies could be done to confirm the results achieved, by using similar conditions but including more children in the group of study. Data provided by a hospital concerning the history of each child and of the occurrence of asthma episodes could be also included. The necessity to support causality could be also fulfilled by performing clinical studies in co-operation with medical doctors. Furthermore, depending on the daily lifestyle of children, indoor air quality should also be a subject of focus.

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APPENDICES

Appendix A - Linear correlation coefficients

A1. Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the concentrations of pollen (2003)

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
Aceraceae	0.609 (26)	0.132 (26)	0.477 (26)	-0.826 (26)	-0.298 (26)	0.116 (26)
<i>Alnus spp.</i>	-0.517 (36)	0.406 (36)	0.230 (36)	-0.169 (36)	-0.389 (36)	-0.421 (38)
Asteraceae	-0.122 (95)	0.159 (100)	0.213 (100)	0.101 (100)	-0.156 (100)	-0.200 (100)
Betulaceae	0.012 (67)	0.181 (67)	-0.092 (67)	-0.168 (67)	-0.007 (67)	0.094 (67)
Caryophyllaceae	0.526 (44)	0.137 (44)	0.273 (44)	-0.610 (44)	-0.238 (44)	0.281 (44)
<i>Castanea spp</i>	0.349 (38)	0.172 (38)	0.646 (38)	-0.360 (38)	-0.228 (38)	0.211 (38)
Chen/Amar	0.256 (145)	0.102 (150)	0.151 (150)	-0.113 (150)	-0.088 (150)	-0.018 (150)
<i>Corylus spp</i>	0.034 (63)	0.321 (64)	0.217 (64)	-0.119 (64)	-0.213 (64)	-0.062 (84)
Cupressaceae	-0.220 (42)	0.026 (42)	0.368 (42)	-0.081 (42)	-0.260 (42)	-0.115 (42)
Ericaceae	0.269 (106)	0.134 (111)	0.365 (111)	-0.400 (111)	-0.159 (111)	0.056 (111)
<i>Fraxinus spp</i>	-0.147 (32)	0.035 (32)	-0.052 (32)	-0.145 (32)	-0.239 (32)	-0.207 (32)
Myrtaceae	0.225 (28)	-0.114 (31)	0.083 (31)	-0.312 (31)	-0.084 (31)	0.244 (31)
<i>Olea europea</i>	0.224 (12)	0.838 (12)	0.598 (12)	-0.464 (12)	-0.540 (12)	-0.326 (12)
Pinaceae	0.394 (39)	0.534 (39)	0.586 (39)	-0.713 (39)	-0.271 (39)	-0.205 (39)
<i>Plantago spp</i>	0.410 (101)	0.097 (106)	0.537 (106)	-0.317 (106)	-0.122 (106)	-0.003 (106)
Platanaceae	0.029 (38)	0.066 (43)	0.150 (43)	0.166 (43)	-0.010 (43)	-0.255 (43)
Poaceae	0.240 (82)	0.470 (87)	0.689 (87)	-0.466 (87)	-0.280 (87)	-0.053 (87)
<i>Quercus spp</i>	0.143 (62)	0.089 (67)	0.432 (67)	-0.415 (67)	-0.190 (67)	-0.044 (67)
<i>Rumex spp</i>	0.205 (77)	-0.067 (82)	0.335 (82)	-0.084 (82)	-0.099 (82)	0.086 (82)
<i>Salix spp</i>	-0.096 (41)	0.519 (41)	0.109 (41)	-0.242 (41)	-0.273 (41)	-0.147 (41)
<i>Ulmus spp</i>	0.339 (39)	0.279 (39)	0.187 (39)	-0.382 (39)	-0.082 (39)	0.012 (39)
Urticaceae	0.340 (107)	0.141 (112)	0.637 (112)	-0.254 (112)	-0.124 (112)	0.077 (112)

Note: R>R_{crit} in bold; (data number)

A2. Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the concentrations of pollen (2004)

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
Aceraceae	0.478 (29)	0.155 (29)	0.484 (29)	-0.127 (29)	0.007 (29)	0.257 (29)
<i>Alnus spp.</i>	0.019 (21)	0.088 (18)	-0.413 (21)	-0.549 (21)	-0.226 (21)	-0.082 (21)
Asteraceae	0.038 (208)	-0.025 (200)	0.048 (210)	-0.152 (210)	-0.062 (210)	0.027 (210)
Betulaceae	-0.042 (31)	0.625 (31)	0.379 (31)	-0.088 (31)	-0.157 (31)	0.001 (31)
Caryophyllaceae	0.178 (42)	0.393 (42)	0.277 (42)	-0.361 (42)	-0.241 (42)	0.124 (42)
<i>Castanea spp</i>	-0.141 (33)	-0.073 (33)	-0.078 (33)	-0.077 (33)	-0.147 (33)	0.133 (33)
Chen/Amar	0.035 (100)	0.207 (100)	0.159 (100)	-0.410 (100)	-0.134 (100)	0.115 (100)
<i>Corylus spp</i>	0.060 (37)	0.010 (37)	0.386 (37)	-0.098 (37)	-0.129 (37)	-0.047 (37)
Cupressaceae	-0.059 (47)	0.277 (44)	0.232 (47)	-0.239 (47)	-0.347 (47)	-0.071 (47)
Ericaceae	0.074 (82)	0.270 (74)	0.307 (82)	-0.041 (82)	0.004 (82)	-0.153 (82)
<i>Fraxinus spp</i>	0.154 (18)	-0.058 (18)	-0.248 (18)	-0.383 (18)	-0.294 (18)	-0.053 (18)
Myrtaceae	-0.148 (125)	0.119 (114)	-0.095 (125)	0.011 (125)	-0.120 (125)	-0.114 (125)
<i>Olea europea</i>	0.350 (12)	-0.143 (12)	-0.559 (12)	0.514 (12)	0.333 (12)	0.162 (12)
Pinaceae	0.568 (51)	-0.180 (51)	0.435 (51)	-0.274 (51)	0.153 (51)	0.327 (51)
<i>Plantago spp</i>	-0.090 (140)	0.303 (132)	0.317 (142)	-0.075 (142)	-0.106 (142)	-0.089 (142)
Platanaceae	0.334 (30)	0.362 (30)	0.541 (30)	-0.221 (30)	-0.160 (30)	0.187 (30)
Poaceae	-0.559 (44)	0.095 (44)	0.423 (46)	0.037 (47)	-0.250 (46)	-0.374 (46)
<i>Quercus spp</i>	0.053 (61)	0.324 (53)	0.432 (61)	-0.046 (61)	-0.088 (61)	0.048 (61)
<i>Rumex spp</i>	-0.085 (72)	0.388 (64)	0.419 (74)	-0.062 (74)	-0.101 (74)	-0.147 (74)
<i>Salix spp</i>	-0.124 (48)	0.384 (45)	0.203 (48)	-0.028 (48)	-0.262 (48)	-0.092 (48)
<i>Ulmus spp</i>	0.167 (29)	0.490 (26)	-0.206 (29)	-0.443 (29)	-0.409 (29)	0.092 (29)
Urticaceae	0.188 (112)	0.417 (101)	0.317 (112)	-0.125 (112)	-0.020 (112)	-0.030 (112)

Note: R>R_{crit} in bold; (data number)

A3. Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the concentrations of pollen (2005)

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
<i>Aceraceae</i>	0.025 (20)	-0.010 (20)	0.784 (20)	0.518 (20)	0.503 (20)	0.326 (20)
<i>Alnus spp.</i>	0.018 (29)	0.194 (29)	-0.177 (29)	-0.067 (29)	-0.432 (29)	0.201 (29)
<i>Asteraceae</i>	-0.095 (75)	0.205 (75)	0.160 (75)	0.010 (75)	-0.084 (75)	-0.120 (75)
<i>Betulaceae</i>	0.220 (32)	-0.160 (32)	-0.355 (32)	-0.478 (32)	-0.290 (32)	0.030 (32)
<i>Caryophyllaceae</i>	0.110 (33)	-0.206 (33)	0.351 (33)	-0.067 (33)	0.154 (33)	0.018 (33)
<i>Castanea spp</i>	-0.032 (45)	0.455 (45)	0.591 (45)	-0.261 (45)	-0.229 (45)	-0.148 (45)
Chen/Amar	0.176 (158)	0.037 (158)	0.235 (158)	-0.105 (158)	-0.106 (158)	-0.011 (158)
<i>Corylus spp</i>	0.188 (56)	-0.171 (56)	-0.006 (56)	-0.066 (56)	-0.075 (56)	0.011 (56)
<i>Cupressaceae</i>	0.039 (38)	0.311 (38)	-0.160 (38)	-0.024 (38)	-0.439 (38)	-0.221 (38)
<i>Ericaceae</i>	0.001 874)	0.029 (74)	0.248 (74)	0.014 (74)	-0.100 (74)	-0.057 (74)
<i>Fraxinus spp</i>	-0.086 (30)	0.474 (30)	-0.068 (30)	-0.106 (30)	-0.208 (30)	-0.047 (30)
<i>Myrtaceae</i>	0.298 (69)	-0.102 (69)	0.181 (69)	-0.174 (69)	-0.008 (69)	0.251 (69)
<i>Olea europea</i>	0.203 (44)	-0.047 (44)	0.158 (44)	0.039 (44)	0.044 (44)	-0.174 (44)
<i>Pinaceae</i>	0.189 (52)	-0.244 (52)	0.682 (52)	0.294 (52)	0.197 (52)	0.023 (52)
<i>Plantago spp</i>	0.157 (76)	0.309 (76)	0.279 (76)	-0.163 (76)	-0.140 (76)	-0.097 (76)
<i>Platanaceae</i>	0.735 (11)	-0.624 (11)	0.001 (11)	0.235 (11)	0.532 (11)	0.734 (11)
<i>Poaceae</i>	0.191 (82)	0.603 (82)	0.585 (82)	-0.428 (82)	-0.236 (82)	0.053 (82)
<i>Quercus spp</i>	0.184 (52)	-0.230 (52)	0.266 (52)	0.016 (52)	-0.003 (52)	0.037 (52)
<i>Rumex spp</i>	0.042 (74)	-0.021 (74)	0.270 (74)	0.018 (74)	-0.164 (74)	-0.070 (74)
<i>Salix spp</i>	0.123 (43)	0.233 (43)	0.387 (43)	-0.085 (43)	-0.098 (43)	0.128 (43)
<i>Ulmus spp</i>	0.153 (26)	-0.076 (26)	-0.014 (26)	-0.226 (26)	0.095 (26)	0.383 (26)
<i>Urticaceae</i>	0.026 (69)	0.188 (69)	0.726 (69)	0.337 (69)	0.009 (69)	-0.001 (69)

Note: R>R_{crit} in bold; (data number)

A4. Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the concentrations of fungal spores (2003).

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
<i>Alternaria spp</i>	0.210 (351)	0.181 (362)	0.645 (365)	-0.243 (365)	-0.243 (365)	-0.195 (365)
<i>Aspergillaceae</i>	-0.027 (351)	-0.040 (362)	0.084 (365)	-0.050 (365)	-0.041 (365)	-0.034 (365)
<i>Botrytis spp</i>	-0.084 (351)	-0.157 (362)	0.234 (365)	-0.020 (365)	-0.070 (365)	-0.142 (365)
<i>Cladosporium spp</i>	0.178 (351)	0.074 (362)	0.645 (365)	-0.213 (365)	-0.210 (365)	-0.189 (365)
<i>Coprinus spp</i>	0.023 (351)	-0.054 (362)	0.205 (365)	0.020 (365)	-0.183 (365)	-0.202 (365)
<i>Corynespora spp</i>	-0.009 (351)	0.054 (362)	-0.025 (365)	-0.055 (365)	-0.015 (365)	0.045 (365)
<i>Didymella spp</i>	-0.124 (351)	-0.007 (362)	-0.167 (365)	-0.069 (365)	-0.032 (365)	0.030 (365)
<i>Drechslera spp</i>	0.227 (351)	0.110 (362)	0.347 (365)	-0.133 (365)	-0.122 (365)	-0.073 (365)
<i>Epicoecum spp</i>	0.066 (351)	0.122 (362)	0.465 (365)	-0.143 (365)	-0.152 (365)	-0.197 (365)
Rusts	-0.060 (351)	-0.223 (362)	-0.152 (365)	0.209 (365)	0.252 (365)	0.097 (365)
Fusarium	0.027 (351)	-0.026 (362)	0.541 (365)	-0.005 (365)	-0.168 (365)	-0.328 (365)
Ganoderma	-0.122 (351)	-0.111 (362)	-0.204 (365)	0.156 (365)	0.017 (365)	-0.035 (365)
Leptosphaeria	0.158 (351)	0.037 (362)	0.060 (365)	-0.155 (365)	-0.008 (365)	0.078 (365)
Oidium	0.017 (351)	-0.069 (362)	-0.060 (365)	0.062 (365)	-0.009 (365)	0.077 (365)
Periconia	0.144 (351)	0.129 (362)	0.389 (365)	-0.051 (365)	-0.072 (365)	-0.094 (365)
Pithomyces	-0.141 (351)	-0.137 (362)	-0.032 (365)	0.250 (365)	0.249 (365)	-0.053 (365)
Pleospora	0.074 (351)	-0.017 (362)	0.142 (365)	-0.018 (365)	-0.051 (365)	-0.088 (365)
Polythrincium	0.043 (351)	0.216 (362)	0.201 (365)	-0.100 (365)	-0.104 (365)	-0.149 (365)
Rhizopus	-0.007 (351)	0.096 (362)	0.136 (365)	-0.042 (365)	-0.006 (365)	-0.049 (365)
Torula	0.077 (351)	0.111 (362)	-0.052 (365)	-0.171 (365)	-0.106 (365)	0.070 (365)
Ustilago	-0.041 (351)	0.184 (362)	-0.172 (365)	-0.085 (365)	0.039 (365)	-0.153 (365)
Total fungi	-0.013 (351)	-0.013 (362)	0.376 (365)	0.035 (365)	-0.133 (365)	-0.180 (365)

Note: R>R_{crit} in bold; (data number)

A5. Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the concentrations of fungal spores (2004)

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
<i>Alternaria spp</i>	-0.011 (364)	0.123 (353)	0.366 (366)	-0.058 (366)	-0.136 (366)	-0.056 (366)
Aspergillaceae	-0.092 (364)	0.020 (353)	-0.119 (366)	0.032 (366)	0.067 (366)	0.028 (366)
<i>Botrytis spp</i>	0.002 (364)	0.091 (353)	0.036 (366)	-0.084 (366)	0.021 (366)	0.106 (366)
<i>Cladosporium spp</i>	-0.093 (364)	0.030 (353)	0.096 (366)	-0.012 (366)	-0.010 (366)	0.018 (366)
<i>Coprinus spp</i>	-0.052 (364)	-0.091 (353)	-0.119 (366)	0.024 (366)	0.072 (366)	0.018 (366)
<i>Corynespora spp</i>	-0.003 (364)	0.052 (353)	0.247 (366)	-0.087 (366)	-0.069 (366)	-0.050 (366)
<i>Didymella spp</i>	-0.202 (364)	-0.106 (353)	-0.140 (366)	0.237 (366)	0.103 (366)	-0.115 (366)
<i>Drechslera spp</i>	-0.063 (364)	0.092 (353)	0.007 (366)	-0.012 (366)	-0.053 (366)	-0.080 (366)
<i>Epicoccum spp</i>	0.050 (364)	-0.018 (353)	0.378 (366)	-0.067 (366)	-0.074 (366)	-0.029 (366)
Rusts	-0.068 (364)	-0.092 (353)	-0.005 (366)	0.147 (366)	0.029 (366)	-0.034 (366)
Fusarium	-0.037 (364)	0.109 (353)	0.334 (366)	0.021 (366)	-0.049 (366)	-0.119 (366)
Ganoderma	-0.007 (364)	0.154 (353)	-0.056 (366)	-0.066 (366)	0.033 (366)	-0.026 (366)
Leptosphaeria	0.053 (364)	0.058 (353)	0.100 (366)	0.003 (366)	-0.044 (366)	0.053 (366)
Oidium	-0.080 (364)	-0.024 (353)	0.013 (366)	0.021 (366)	-0.027 (366)	0.001 (366)
Periconia	0.003 (364)	-0.054 (353)	0.228 (366)	-0.017 (366)	0.007 (366)	-0.007 (366)
Pithomyces	-0.085 (364)	-0.060 (353)	-0.329 (366)	0.125 (366)	0.115 (366)	0.005 (366)
Pleospora	0.002 (364)	0.175 (353)	0.076 (366)	-0.068 (366)	-0.004 (366)	-0.011 (366)
Polythrincium	-0.045 (364)	0.080 (353)	0.137 (366)	-0.070 (366)	-0.100 (366)	-0.019 (366)
Rhizopus	-0.137 (364)	-0.043 (353)	0.125 (366)	-0.030 (366)	0.099 (366)	0.042 (366)
Torula	0.018 (364)	0.124 (353)	-0.105 (366)	-0.144 (366)	-0.054 (366)	0.075 (366)
Ustilago	0.143 (364)	0.044 (353)	0.067 (366)	-0.232 (366)	-0.085 (366)	0.036 (366)
Total fungi	-0.232 (364)	-0.071 (353)	-0.100 (366)	0.096 (366)	0.034 (366)	-0.044 (366)

Note: R>R_{crit} in bold; (data number)

A6. Linear correlation coefficients between O₃ and PM₁₀ concentrations, T, RH, PP WV, and the concentrations of fungal spores (2005)

Parameter	O ₃	PM ₁₀	T	RH	PP	WV
<i>Alternaria spp</i>	0.175 (364)	0.207 (364)	0.556 (365)	-0.199 (365)	-0.115 (365)	0.004 (365)
Aspergillaceae	0.022 (364)	-0.046 (364)	0.047 (365)	-0.088 (365)	0.013 (365)	0.181 (365)
<i>Botrytis spp</i>	-0.094 (364)	-0.079 (364)	-0.106 (365)	0.050 (365)	0.008 (365)	0.017 (365)
<i>Cladosporium spp</i>	0.067 (364)	0.040 (364)	0.262 (365)	-0.077 (365)	-0.018 (365)	0.043 (365)
<i>Coprinus spp</i>	-0.228 (364)	-0.215 (364)	-0.222 (365)	0.326 (365)	0.114 (365)	-0.034 (365)
<i>Corynespora spp</i>	-0.173 (364)	0.018 (364)	-0.101 (365)	0.049 (365)	-0.073 (365)	-0.093 (365)
<i>Didymella spp</i>	0.023 (364)	-0.209 (364)	-0.107 (365)	0.268 (365)	0.462 (365)	0.125 (365)
<i>Drechslera spp</i>	0.071 (364)	-0.024 (364)	0.171 (365)	0.006 (365)	-0.001 (365)	0.018 (365)
<i>Epicoecum spp</i>	0.083 (364)	0.121 (364)	0.337 (365)	-0.077 (365)	-0.130 (365)	0.049 (365)
Rusts	-0.002 (364)	0.098 (364)	-0.028 (365)	0.138 (365)	0.169 (365)	0.061 (365)
Fusarium	0.114 (364)	0.054 (364)	0.460 (365)	0.283 (365)	0.019 (365)	-0.185 (365)
Ganoderma	0.014 (364)	-0.218 (364)	-0.048 (365)	0.268 (365)	0.337 (365)	0.158 (365)
Leptosphaeria	0.080 (364)	-0.003 (364)	0.054 (365)	0.055 (365)	0.028 (365)	-0.008 (365)
Oidium	-0.029 (364)	0.065 (364)	0.139 (365)	0.073 (365)	-0.001 (365)	-0.019 (365)
Periconia	0.066 (364)	0.043 (364)	0.230 (365)	0.006 (365)	-0.004 (365)	-0.030 (365)
Pithomyces	-0.022 (364)	-0.185 (364)	-0.164 (365)	0.238 (365)	0.289 (365)	0.047 (365)
Pleospora	0.079 (364)	0.043 (364)	0.156 (365)	0.020 (365)	-0.075 (365)	-0.076 (365)
Polythrincium	0.051 (364)	0.308 (364)	0.131 (365)	-0.232 (365)	-0.171 (365)	-0.078 (365)
Rhizopus	-0.189 (364)	-0.155 (364)	-0.269 (365)	-0.011 (365)	0.197 (365)	0.143 (365)
Torula	0.118 (364)	0.061 (364)	-0.068 (365)	-0.187 (365)	-0.095 (365)	-0.013 (365)
Ustilago	0.043 (364)	0.243 (364)	0.058 (365)	-0.189 (365)	-0.174 (365)	-0.035 (365)
Total fungi	-0.048 (364)	-0.063 (364)	0.109 (365)	0.075 (365)	0.087 (365)	0.041 (365)

Note: R>R_{crit} in bold; (data number)

Appendix B - Questionnaire to collect asthmatic symptoms

QUESTIONÁRIO

Este questionário deve ser respondido pelos Encarregados de Educação que autorizaram os seus educandos a participar no estudo "Efeitos do Ozono no Agravamento da Asma Infantil".

A primeira folha é para a identificação do aluno. Por favor, escreva as respectivas respostas no espaço para o efeito.

Nas folhas seguintes são colocadas questões em que apenas é necessário marcar com um X o quadrado correspondente à resposta correcta. Caso se engane, risque o quadrado e marque novamente um X na resposta correcta.

OBRIGADO PELA SUA COLABORAÇÃO!

DATA ____/____/____

DADOS RELATIVOS À CRIANÇA

ESCOLA _____

ANO _____ TURMA _____

NOME _____

DATA DE NASCIMENTO ____/____/____

SEXO

☐ FEMININO

☐ MASCULINO

PROFISSÃO DA MÃE _____

PROFISSÃO DO PAI _____

DISTÂNCIA APROXIMADA DA HABITAÇÃO À ESCOLA _____

1. O seu educando vive com algum fumador?

☐ Sim

☐ Não

2. O seu educando teve ou tem asma?

☐ Sim

☐ Não

3. O seu educando alguma vez teve pieira (assobios) no peito?

☐ Sim

☐ Não

SE RESPONDEU "NÃO" POR FAVOR PASSE À QUESTÃO 9

4. Nos últimos 12 meses o seu educando teve pieira?

☐ Sim

☐ Não

SE RESPONDEU "NÃO" POR FAVOR PASSE À QUESTÃO 9

5. Nos últimos 12 meses quantos ataques de pieira o seu educando teve?

☐ Nenhum

☐ 1 a 3

☐ 4 a 12

☐ Mais de 12

6. Nos últimos 12 meses, em média, quantas vezes o seu educando acordou devido à pieira?

☐ Nunca acordou com pieira

☐ Menos de uma noite por semana

☐ Uma ou mais noites por semana

7. Nos últimos 12 meses a pieira foi suficientemente forte para limitar a conversa do seu educando a apenas uma ou duas palavras entre respirações?

☐ Sim

☐ Não

8. Nos últimos 12 meses o seu educando alguma vez sentiu pieira durante ou depois de fazer exercício?

☐ Sim

☐ Não

9. O seu educando alguma vez sentiu falta de ar?

☐ Sim

☐ Não

SE RESPONDEU "NÃO" POR FAVOR PASSE À QUESTÃO 12

10. Nos últimos 12 meses, quantas vezes o seu educando sentiu falta de ar?

☐ Nenhuma

☐ 1 a 3

☐ 4 a 12

☐ Mais de 12

11. Nos últimos 12 meses, em média, quantas vezes o seu educando acordou devido à falta de ar?

☐ Nunca acordou com falta de ar

☐ Menos de uma noite por semana

☐ Uma ou mais noites por semana

12. Nos últimos 12 meses o seu educando alguma vez teve tosse seca à noite sem estar constipado ou com infecção respiratória?

☐ Sim

☐ Não

Appendix C - Authorization to enrol in the study



Ex^{ma} Sr. Encarregado de Educação

No âmbito do projecto "Efeitos do Ozono no Agravamento da Asma Infantil", vimos propor, com vossa autorização, a participação do seu educando num estudo sobre qualidade do ar e seus efeitos na saúde. Tal participação consistirá no preenchimento de um questionário pelos encarregados de educação para detectar possíveis sintomas asmáticos. Nas crianças em que estes sintomas estejam presentes serão posteriormente realizados testes médicos de confirmação. Os testes médicos a realizar são:

1. Testes respiratórios para avaliar os débitos expiratórios forçados;
2. Testes cutâneos de confirmação da sintomatologia asmática;
3. Testes cutâneos para pesquisa de alergias.

Pedimos o favor da sua atenção para o folheto anexo e de destacar a autorização abaixo escrita que deve ser devolvida ao/à professor/a juntamente com o questionário até ao dia 20/06/2007.

Com os nossos melhores cumprimentos,

Sofia Isabel Vieira de Sousa



Autorizo o meu educando _____ (nome),
do _____ (ano e turma), escola _____ a
participar no Projecto "Efeitos do Ozono no Agravamento da Asma Infantil"
coordenado pela Faculdade de Engenharia da Universidade do Porto.

O Encarregado de Educação

(assinatura legível)

SOPA DE LETRAS

Descobre as palavras!!!

S	C	R	I	Ú	D	J	M	E	P
M	O	N	C	O	R	V	O	U	O
P	N	L	N	Z	M	U	G	Ç	L
A	C	O	A	O	E	O	A	A	U
L	E	E	S	N	B	K	D	N	I
U	N	Ú	A	O	Á	C	O	A	Ç
T	T	D	P	O	L	Á	U	R	Á
E	R	B	R	S	A	S	R	I	O
A	A	S	M	A	L	R	O	C	O
E	Ç	Ã	O	Ú	V	O	R	O	M
R	Ã	E	S	D	E	C	A	N	Ç
I	O	A	S	E	S	C	O	L	A
P	O	L	U	E	N	T	E	O	S
A	L	U	I	Á	N	O	S	E	M
N	O	O	A	M	Ú	L	E	D	M
S	A	C	C	R	I	A	N	Ç	A

Lista das palavras:

Ozono	Poluente
Polição	Concentração
Asma	Saúde
Mogadouro	Escola
Moncorvo	Criança

EFEITOS DO OZONO NO AGRAVAMENTO DA ASMA INFANTIL

Torre de Moncorvo Mogadouro

Sofia Isabel Vieira de Sousa
LEPAE - Laboratório de Engenharia de Processos, Ambiente e Energia
Departamento de Engenharia Química
Faculdade de Engenharia
Universidade do Porto
Telefone: 22 508 1976
E-mail:sofia.sousa@feup.pt

Em colaboração com:

- Comissão de Coordenação e Desenvolvimento Regional – Norte
- Climat Municipal de Torre de Moncorvo
- Climat Municipal de Mogadouro
- Hospital de São João, EPE
- Hospital Distrital de Bragança, S.A.
- Escola EB1 de Torre de Moncorvo
- Escola EB2,3 Visconde de Vila Maior
- Escola EB1 de Mogadouro
- Escola EB2 de Mogadouro

Efeitos do Ozono no Aggravamento da Asma Infantil

Universidade do Porto
Faculdade de Engenharia
FEUP

Efeitos do Ozono no Agravamento da Asma Infantil

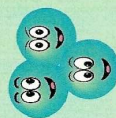
O que é a poluição atmosférica?

A poluição atmosférica é a presença no ar de substâncias que podem afectar negativamente a saúde e o ambiente. Algumas dessas substâncias (os poluentes) são o dióxido de carbono (CO_2), o dióxido de enxofre (SO_2), as partículas (PM), os óxidos de azoto (NO_x) e o ozono (O_3).



O que é o ozono?

O ozono pode existir na atmosfera em duas camadas diferentes: na estratosfera, onde circulam os aviões, e na troposfera, onde está o ar que nós respiramos. As moléculas de ozono são constituídas por átomos de oxigénio.



A camada de ozono da estratosfera protege-nos das radiações solares, sendo por isso benéfica para a nossa saúde. Este é o "Ozono Bom".



Na troposfera, o ozono pode afectar a nossa saúde com gravidade, sendo por isso de evitar a exposição em dias em que as concentrações sejam elevadas. Isto acontece mais no Verão. Este é o "Ozono Mau".



Quais são os efeitos do ozono na saúde?

O ozono pode causar danos no aparelho respiratório especialmente em grupos sensíveis, como os idosos, as crianças e as pessoas com problemas respiratórios e cardiovasculares. Os asmáticos podem sofrer mais com a presença do ozono. Pode ainda causar danos a nível do globo ocular.



Como pode este projecto ajudar?

O principal objectivo do projecto é avaliar se as crianças com problemas de asma ficam piores quando as concentrações de ozono são mais elevadas.

Para fazer esta avaliação foram seleccionados locais em que as concentrações de ozono são muito elevadas e as dos outros poluentes são muito baixas: Torre de Moncorvo e Mogadouro. Para comparação foi também



seleccionado um local com concentrações muito baixas de todos os poluentes.

Foi então escolhidas as escolas primárias e preparatórias desses locais para colocar os equipamentos de medição de poluentes para determinar as concentrações no ar exterior.



A participação das crianças destas escolas é muito importante, porque através de um questionário que será distribuído aos pais, será possível saber se nestes locais há mais crianças com asma.



Numa fase posterior, as crianças com sintomas asmáticos serão melhor estudadas por equipas médicas, através dos seguintes exames: 1) capacidade respiratória; 2) confirmação de asma; e 3) pesquisa de alergias.

