UNIVERSIDAD POLITÉCNICA DE MADRID

ESCUELA TÉCNICA SUPERIOR DE INGENIEROS DE MONTES, FORESTAL Y DEL MEDIO NATURAL

Urban trees and atmospheric pollutants in big cities: Effects in Madrid

Tesis Doctoral

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2014

DEPARTAMENTO DE SISTEMAS Y RECURSOS NATURALES

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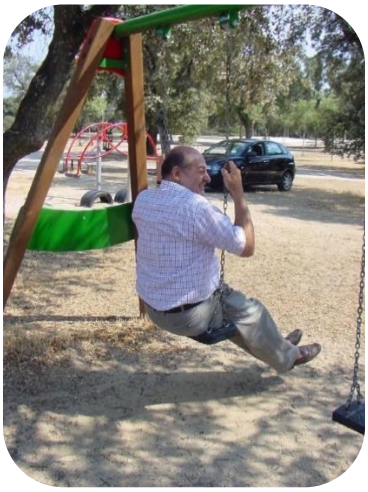

J.A. Rodríguez Barreal (1944-2007)

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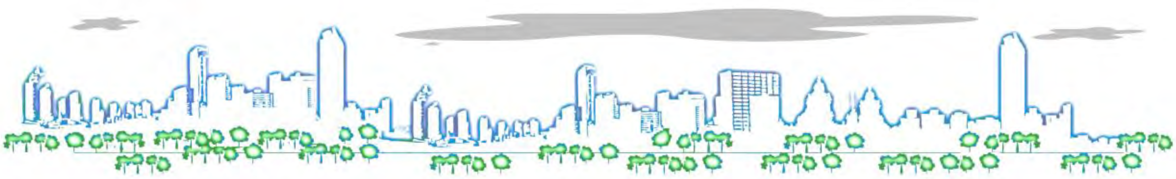
to my mother

to my son



Abstract

Research about air pollution mitigation by urban trees was conducted in Madrid (Spain), a southern European city with almost 4 M inhabitants, 2.8 M daily vehicles and 3 M trees under public maintenance. Most trees were located in two urban forests, while 650'000 trees along urban streets and in parks. The urban taxa included Platanus orientalis (97'205 trees), Ulmus sp. (70’557), Pinus pinea (49'038), Aesculus hippocastanum (22’266), Cedrus sp. (13'678 and Quercus ilex (1'650) along streets and parks. Leave samples were analysed sequentially in different seasons, PM10 data from 28 air monitoring stations during 30 years and traffic density estimated from 2’660 streets.

Heavy metal (HM) accumulation on the leaf surface and within leaves was estimated per tree related to air and soil pollution, and traffic intensity. Mean concentration of Ba, Cd, Cr, Cu, Mn, Ni, Pb and Zn in topsoil samples (dry mass) amounted in Madrid: 489.5, 0.7, 49.4, 60.9, 460.9, 12.8, 155.9 and 190.3 mg kg-1 respectively. Urban trees, particularly conifers (due to higher pollution in winter) contributed significantly to alleviate air pollution especially near to high ADT roads. The capacity of the six urban street trees species to capture air-born dust on the foliage surface as related to traffic intensity was estimated to 16.8 kg of noxious metals from exhausts per year. Pb and Zn pointed to be tracers of anthropic activity in the city with vehicle traffic as the main source of diffuse pollution on trees and soils. Tree species differed by their capacity to capture air-borne dust (by different leaf surface properties) and to allocate HM from soils. Pb and Zn concentrations in the foliage were above limits in different urban sites and microscopic Zn revelation showed translocation in xylem and phloem tissue. Punctual contamination in soils by Cu and Cr was identified in former industrial areas and spatial trace element mapping showed for central Retiro Park certain high values of [Pb] in soils even related to a Royal pottery 200 years ago. Different areas in the city centre also reached high levels [Pb] in soils. According to the results, a combination of Pinus pinea with understorey Ulmus sp. and Cedrus sp. layers can be recommended for the best air filter efficiency.

The effects of ozone (O_3) on trees in different areas of Madrid were also part of this study. Despite abatement programs of precursors implemented in many industrialized countries, ozone remained the main air pollutant throughout the northern hemisphere with background [O_3] increasing. Some of the highest ozone concentrations were measured in regions with a Mediterranean climate but the effect on the natural vegetation is alleviated by low stomatal uptake and frequent leaf xeromorphy in response to summer drought episodes characteristic of this climate. During a bioindication survey, abiotic O_3-like injury was identified in foliage. Trees were growing on an irrigated lawn strip in the centre of Madrid. Given the little structural evidence available for O_3 symptoms in broadleaved evergreen species, a study was undertaken in 2007 with the following objectives 1) confirm the diagnosis, 2) investigate the extent of symptoms in holm oaks growing in Madrid and 3) analyse the environmental factors contributing to O_3 injury, particularly, the site water supply. Therefore, macro- and micromorphological markers of O_3 stress were analysed, using the aforementioned lawn strip as an intensive study site. Symptoms consisted of adaxial and intercostal stippling increasing with leaf age. Underlying stippling, cells in the upper mesophyll showed HR-like reactions typical of ozone stress. The surrounding cells showed further oxidative stress markers. These morphological and micromorphological markers of ozone stress were similar to those recorded in deciduous broadleaved species. However, stippling became obvious already at an AOT40 of 21 ppm•h and was primarily found at irrigated sites. Subsequent analyses showed that irrigated trees had their stomatal conductance increased and leaf life-span reduced whereas their leaf xeromorphy remained unchanged. These findings suggest a central role of water availability versus leaf xeromorphy for ozone symptom expression by cell injury in holm oak.

KEY WORDS: urban areas; green spaces, trees, vegetation, atmospheric pollutants; trace elements; biomonitoring; mapping; GIS; soil contamination, PM_{10}, ozone, irrigation, xeromorphic characteristics.

Resumen

Una investigación sobre la mejora de la contaminación del aire (CA) por medio de arbolado urbano se realizó en Madrid, una ciudad con casi 4 M de habitantes, 2,8 M de vehículos y casi 3 M de árboles de mantenimiento público. La mayoría de los árboles estaban en dos bosques periurbanos. Los 650.000 restantes era pies de alineación y parques. Los taxones estudiados fueron *Platanus orientalis* (97.205 árboles), *Ulmus* sp. (70.557), *Pinus pinea* (49.038), *Aesculus hippocastanum* (22.266), *Cedrus* sp. (13.678) y *Quercus ilex* (1.650), de calles y parques. Muestras foliares se analizaron en diferentes épocas del año, así como datos de contaminación por PM_{10} de 28 estaciones de medición de la contaminación durante 30 años, y también la intensidad del tráfico (IMD) en 2.660 calles.

La acumulación de metales pesados (MP) sobre hojas y dentro de estas se estimó en relación con la CA y del suelo y la IMD del tráfico. La concentración media de Ba, Cd, Cr, Cu, Mn, Ni, Pb y Zn en suelo (materia seca) alcanzó: 489,5, 0,7, 49,4, 60,9, 460,9, 12,8, 155,9 y 190,3 mg kg^{-1} respectivamente. Los árboles urbanos, particularmente coníferas (debido a la mayor CA en invierno) contribuyen significativamente a mejorar la CA sobre todo en calles con alta IMD. La capacidad de las seis sp. para capturar partículas de polvo en su superficies foliares está relacionada con la IMD del tráfico y se estimó en 16,8 kg/año de MP tóxicos. Pb y Zn resultaron ser buenos marcadores antrópicos en la ciudad en relación con el tráfico, que fue la principal fuente de contaminación en los árboles y suelos de Madrid. Las especies de árboles variaron en función de su capacidad para capturar partículas (dependiendo de las propiedades de sus superficies foliares) y acumular los MP absorbidos de los suelos. Las concentraciones foliares de Pb y Zn estuvieron por encima de los límites establecidos en diferentes sitios de la ciudad. La microlocalización de Zn mediante microscópico mostró la translocación al xilema y floema. Se detectaron puntos de contaminación puntual de Cu and Cr en antiguos polígonos industriales y la distribución espacial de los MP en los suelos de Madrid mostró que en incluso en zonas interiores del El Retiro había ciertos niveles elevados de [Pb] en suelo, tal vez por el emplazamiento la Real Fábrica de Porcelana en la misma zona hace 200 años. Distintas áreas del centro de la ciudad también alcanzaron niveles altos de [Pb] en suelo. Según los resultados, el empleo de una combinación de *Pinus pinea* con un estrato intermedio de *Ulmus* sp. y *Cedrus* sp. puede ser la mejor recomendación como filtro verde eficiente.

El efecto del ozono (O_3) sobre el arbolado en Madrid fue también objeto de este estudio. A pesar de la reducción de precursores aplicada en muchos países industrializados, O_3 sigue siendo la principal causa de CA en el hemisferio norte, con el aumento de [O_3] de fondo. Las mayores [O_3] se alcanzaron en regiones mediterráneas, donde el efecto sobre la vegetación natural es compensado por el xeromorfismo y la baja conductancia estomática en respuesta los episodios de sequía estival característicos de este clima.

Durante una campaña de monitoreo, se identificaron daños abióticos en hojas de encina parecidos a los de O_3 que estaban plantadas en una franja de césped con riego del centro de Madrid. Dada la poca evidencia disponible de los síntomas de O_3 en frondosas perennifolias, se hizo un estudio que trató de 1) confirman el diagnóstico de daño de O_3, 2) investigar el grado de los síntomas en encinas y 3) analizar los factores ambientales que contribuyeron a los daños por O_3, en particular en lo relacionado con el riego. Se analizaron los marcadores macro y micromorfológicos de estrés por O_3, utilizando las mencionadas encinas a modo de parcela experimental. Los síntomas consistieron en punteado intercostal del haz, que aumentó con la edad. Además de un punteado subyacente, donde las células superiores del mesófilo mostraron reacciones características de daños por O_3. Las células próximas a las zonas dañadas, presentaron marcadores adicionales de estrés oxidativo. Estos marcadores morfológicos y micromorfológicos de estrés por O_3 fueron similares a otras frondosas

caducifolias con daños por O_3. Sin embargo, en nuestro caso el punteado fue evidente con AOT40 de 21 ppm·h, asociada a riego. Análisis posteriores mostraron que los árboles con riego aumentaron su conductancia estomática, con aumento de senescencia, manteniéndose sin cambios sus características xeromórficas foliares. Estos hallazgos ponen de relieve el papel primordial de la disponibilidad de agua frente a las características xeromórficas a la hora de manifestarse los síntomas en las células por daños de O_3 en encina.

PALABRAS CLAVE: zonas urbanas; zonas verdes, arbolado, vegetación, contaminantes atmosféricos; elementos traza; biomonitoreo; Cartografía; SIG; contaminación del suelo, PM_{10}, ozono, riego, características xeromórficas

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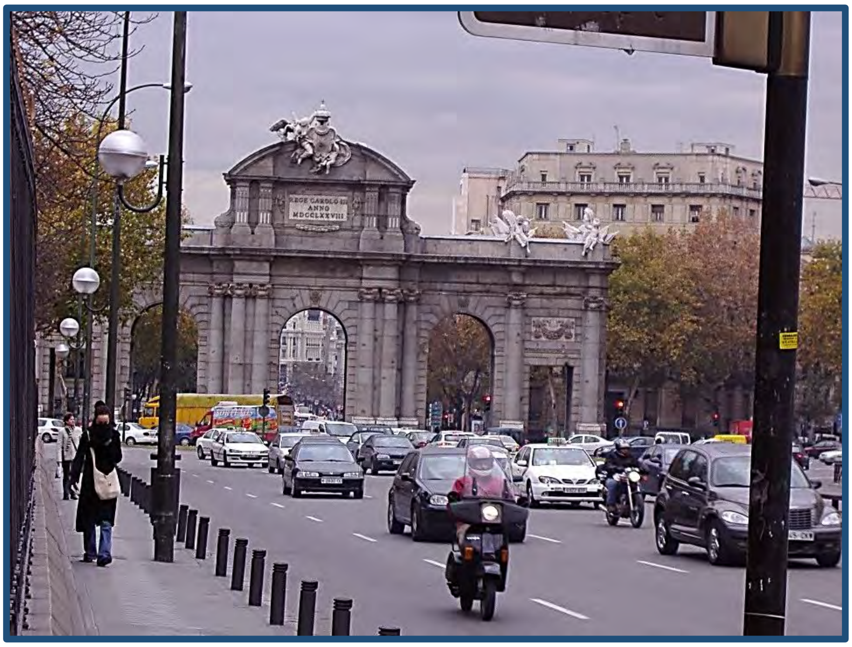
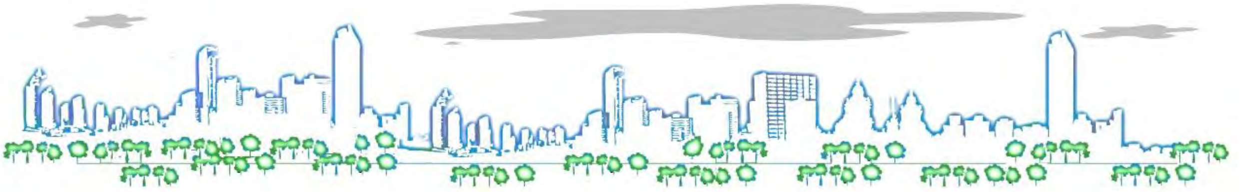


POPULATION IN THE CITIES, AIR POLLUTION AND THE ROLE OF GREEN SPACES AND URBAN TREES

Chapter 1

POPULATION IN THE CITIES, AIR POLLUTION AND THE ROLE OF GREEN SPACES AND URBAN TREES



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1. Significance and thesis structure

1.1 Significance of the thesis

One of the earliest childhood memories arise at the beginning of the summer holidays in 1975, when a 5-year kid was on the bus with his parents on the way to the intercity bus station *Palos de Moguer* in Madrid. In the middle of the traffic jam, as always, he used to look through the window of the bus at the branches of the street trees along *Reina Victoria* Avenue and *Cuatro Caminos* square that sometimes hit the bus' windows. The stunted pines, with very dark, almost black needles because of the pollution, had no cones and were barely higher than the bus. When we had arrived at the bus station, more than 200 buses were with the engines running in the underground basements. The air was almost unbreathable. It was common to see people with a handkerchief in his mouth, watery eyes, coughing and headache.

Many of those pines in *Reina Victoria* Avenue died a few years later and were replaced by privets (*Ligustrum lucidum*), which still are along the street. Maybe, those memories of pines and pollution remained in the subconscious over the years until the development of this thesis.

Nowadays, air pollution is still a major risk for environment and human health affecting worldwide developed and developing countries alike. The 2005 "WHO Air quality guidelines" indicated that by reducing particulate matter (PM_{10}) pollution from 70 to 20 micrograms per cubic metre (µg/m), air pollution-related deaths could be reduced by around 15%, which means millions of lives. This problem is more acute in the big cities, where the management of urban areas has become one of the most important development challenges of the 21st century.

All strategies to reduce air pollution must be considered. Aside the needed reduction in emission, one of the strategies may involve the ability of vegetation to remove air pollutants from the atmosphere. Urban trees could play an important role in the purpose of using vegetation as a sink for air pollutants.

The aim of this thesis is to study how public space urban park can be best designed to satisfy human needs and expectations regarding air pollution. This study is particularly focused on green space covered by urban trees and the role of these woody plants on the filtering and sorption effects of vegetation on air pollution. Another focus were the damage that air pollutants cause in urban trees and the fact, that certain plant species are more sensitive to air pollution and thus act as indicators of air pollution.

1.2 Structure

- **Chapter-1** consists of an analysis of the three main urban elements in this thesis: population, pollution and trees from the world level to the city level exemplified in Madrid. This exploration will follow the evolution of the components by comparison of the former and current situation of the urban population. A review of literature of the main pollutants and the pollution impact on vegetation and human health will be developed. The chapter finishes with the importance of plants in urban area. In particular, it will be investigated the role of urban trees in big cities to ameliorate the pollution, as well as the effects of air pollution and the city infrastructure on trees.

- **Chapter-2** is focused on the effects of one of the most important air pollutants (O_3) and its effects on plants. Symptoms in woody plants, as well as its effects on photosynthesis and growth rate are reviewed, based in the sensitivity and the defence mechanisms of the plants.

- **Chapter-3** presents an example of the effects of air pollution on current urban trees. The irrigated Holm oaks in green spaces of the city of Madrid are an evidence how air pollution affects tree species that initially could be classified as ozone-resistant because of its sclerosity, but microscopic and visible foliar symptoms could be observed due to long-term pollution linked to irrigation effects, which increase ozone uptaken in Holm oak foliage.

- **Chapter-4** shows results of urban tree inventories, spatial distribution of main air pollutants, the number of exceedances over the threshold, traffic intensity in main streets, spatial distribution of some heavy metals, the dust accumulation and the trapping efficiency of the six different species. It includes the microlocalization of the Zn heavy metals particles in foliar tissue. It also discusses the reasons behind the changes that occurred in polluted and non-polluted area, regarding the traffic intensity and the distance to the trees.

- **Chapter-5** Summarizes the results of the different studies regarding trees and pollution in the city.

- **Chapter-6** gives the resulting conclusions.

- The **annexes** contain the publications and works performed during the development of this thesis. Although they are not SCI publications, they are reports or peer reviewed communications that provide additional data regarding the urban trees and the green spaces in Madrid. They also give an evidence of the efforts to spread and to divulgate the main objectives proposed in this thesis.
  They contain the first results and discussions of Chapter 3 and 4 presented in the IUFRO conference for specialists (Annexes 1 and 2). They are followed by the communications submitted to the XIII World Forestry Congress (Argentina 2009) [annexe III], the Fifth Spanish Forestry Congress and the Flora Urbana Exhibition, where both were accepted as an oral communication (Annexe V and XI).
  The evolution of the green spaces in 19th and 20th century was studied in annexe X, while two examples of the phytopathological inventories developed in Madrid were shown in annexes VII and IX. The particulate matter deposited on leaves was analysed by electron microscope in Annexe VI and the variation in chlorophyll content in polluted green urban spaces was analysed in Annexe VIII.
  The effects of air pollution on trees was studied not only in Madrid City. The methodology was also applied in satellite cities near Madrid such as Pozuelo de Alarcón (annexes XII and XIV), as well as the beneficial effect of green corridors between green spaces in the city (annexe XIII). CO2 up-take by urban trees was studied in Madrid (Annexe XVI), as well as the [Cu] spatial distribution in soils in Madrid (Annexe XIX).
  The denial letters about the requested information regarding the analytical recycled irrigation water, as well as sketches of the location of the Royal porcelain factory inside the Retiro Park in Annexes XVIII and XX, respectively were also included.

- Last sections of each chapter includes bibliography

2. Background

The proximity of people, businesses and services linked in big settlements is essential in the concept of the modern life. The contemporary idea of the idyllic "**quality of life**" relies on a range of terms linked to the urban life, such as income and housing, proximity to social facilities for education and health care, a wide range of opportunities in social relations and job creation, at least one or two vehicles per family unit, and overall, a **healthy environment** to live with the relatives and friends. Therefore, the most important function of cities is to provide the meeting point for people to communicate, trade, produce and enjoy the day to day. Unfortunately, the impact and side effects in the intensive use of resources that demand the aforementioned activities imply certain environmental costs to the urban ecosystem, such as the high demand of transportation, power, water, etc. The consequences of these demands are paid in terms of pollution.

A survey carried out in 75 European cities in 2009 showed that there was a strong correlation between the perceived levels of air pollution and perceptions about whether a city was healthy to live in or not (Directorate-General Regional Policy European Commission, 2010). Thus, one of the most important challenges in the present time for the society and decision makers is how to provide a friendly urban environment to live to the increasing urban population, while minimizing or balancing negative the important side effects on the environment of the big cities.

The answer to these global demands regarding the environmental elements associated to the quality of life should include air quality, low noise levels, enough and good quality of water. Therefore, decision makers should establish the bases for an adequate urban design with necessary and high-quality **public green spaces for leisure, amelioration of air pollution and adaption to climate change**. At the same time, the solutions to the current environmental hazards facing the big cities and the later supervision of the achievements would require the accurate determination of the causes of environmental degradation, their possible origins and the supervision of these values. Once achievements and maintenance of quality levels have been obtained, it would be necessary to keep them updated, sustained and regulated by a series of acts, directives and recommendations from local and international legislation to stablish the setting and targets for air quality, water quality and maximum noise levels for a healthy urban environment. In this context, the **biomonitoring** should be an important tool to evaluate and control of these environmental elements associated to the quality of life in big cities.

This biomonitoring task could be performed by urban trees. They play an important role in monitoring and maintaining of the ecological balance in the cycle of nutrients and gases such as carbon dioxide (CO_2) and ozone (O_3).They also provide a huge leaf area valid for absorption and accumulation of air pollutants that could reduce the pollution levels in the urban environment (Escobedo *et al.*, 2008). These qualities are very important to humans in large cities. In the absence of urban trees, pollution would be absorbed by citizens, affecting directly the health of the population. Furthermore, the **trees also suffer from the effects of pollution**. In most cases, trees can mitigate the level of contamination, but long term pollution may cause a general weakening that associated with other harsh environmental factors could lead to the tree's death.

This study has investigated some of the current environmental hazards in a big city. It applied the monitoring on urban trees in the City of Madrid (Spain). It is an example of a helpful instrument to illustrate the pollution at a city level and the important role of the urban trees that sometimes has been underestimated. The first chapter will review the main three elements mentioned in thesis title: 1) population in the cities, 2) sources of pollution in the city affecting human health and vegetation and 3) the role of green spaces and urban trees.

2.1. Urban areas and population

As well as today's cities have little in common with their 18th and 19th century predecessors, the meaning of "urban" and the definition of urban areas and metropolitan area have changed during all this time too. Both terms are important keywords to establish the limits to this study. The meaning of urban will help us to delimitate the area of activity on this work versus the "rural" category, while urban area will be very helpful to understand the heterogeneity of the urban environment and to quantify the population by the demand of green spaces that could be directly affected by air pollution. However, in the following pages we will find that rural population is also affected by the pollution generated in the urban areas, including trans-boundary levels.

The mentioned terms have created a serious discussion over the years. Their definitions involve the complexity to define somewhat vague concepts, in addition to the lack of an agreement on a real and uniform criterion to identify this type of settlements. For example, the Census Bureau of the United Stated has been modifying and updating the definition of ''*urban*'' for more than a century. They defined **urban** as "*any population, housing, and territory located within incorporated places with a population of 2,500 or more*" (Bureau of the Census. Department of Commerce. USA, 2011), while the OECD classifies these "*local units*" as rural if their population density is below 150 inhabitants per square kilometre (OECD. Directorate for Public Governance and Territorial Development, 2011). In Spain, the limit between rural and urban settlements is set in 10,000 inhabitants.

Urban areas in the United States are defined by the U.S. Census Bureau as settlements with a population density of at least 1,000 inhabitants per square mile (about 400 per square km). Therefore, these agglomerations are delineated without regard to political boundaries. When the urban areas reaches a population of at least 50,000, they would be considered as the core of a metropolitan statistical area. Nowadays, the urban areas are among the most accurate measure of a city's true size, because they are all measured from the same criteria. This fact does not indicate that their limits are immovable. In fact, other experts define urban areas (or urban agglomerations) as areas of continuous urban development within a metropolitan area. The metropolitan areas represent the economic or functional form of a city. Consequently, a **metropolitan area** will be the combination of the urban area(s) and rural areas, which together comprise the economic region or labour market (Fig .1).

2.1.1 The big city: structure and role

The general structure of the current cities is composed of a historic centre that uses to be greatly modified since its origins by new constructions, such as business, services and trading buildings (Fig. 1). The old town is surrounded by a periphery of districts composed of commercial areas, residential areas and high-rise dormitories. The suburban is organized in a certain number of settlements, as nucleolus-like, linked by a network of motorways and railways, which allow constant movement of people and goods between the inner city and the outer of the urban area. As an example, only in Madrid downtown, the number of daily journeys was 4.2 million by 2.2 million vehicles in 2013 (Ayuntamiento de Madrid, 2013b).

This role of the city centre in the urban areas as epicentres for tertiary activities is being accentuated in the last decades. The urban growth results from a combination of economic, social and cultural factors (Mumford, 1961), where the benefit of the proximity promotes the multiple contacts and activities as a kind of information hub and creative multicultural centre (Fig. 2).

Figure 1: *View of the structure of the City of Toronto from CN tower (Canada).The City of Toronto is an example of a big city accounting 2,615,060 inhabitants, while the metropolitan area reached near to 6 million in 2013. Photo source: [Calderon Guerrero, C. (2002)]*

Moreover, the own economic activity is also often reinforcing the pressure on city centre infrastructures, such as the office construction, reduction of green areas and increment of traffic nuisance, which is affecting the quality of life and pushing the exodus to the suburbs, specially by youth. The outstanding dwellings use to be occupied by low-medium working class and migrants; remaining a few enclaves for the rich classes in the best districts.

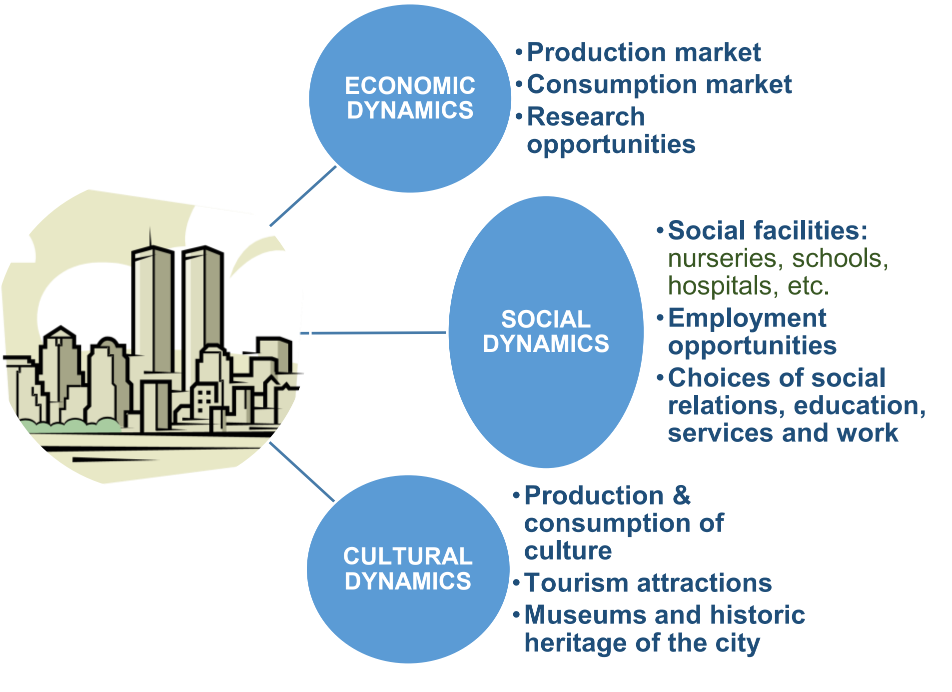


Figure 2: *The city as an information hub and creative centre*

2.1.2 Distribution and growth of the urban population in the world

The spatial extent of urbanization by the human being on Earth is appreciated from satellite-generated city lights maps (Fig. 3). This could be only an example of light pollution, but is also helpful to detect the human agglomerations in the world. This way, the brightest areas of the Earth are the most urbanized, although not necessarily the most populated. For example, Western Europe is brighter than China and India, although the population is quite lower. Some regions remain dark and uninhabited, such as Antarctica, deserts in Africa, Arabia, Australia, Mongolia and the great mountains of the Himalaya. Most of the jungles of Africa and South America are dark too, but lights are beginning to appear in the Amazonas region because of the human pressure on environment.

Figure 3. *A global image of earth's city lights captures by a network of satellites' sensors. Source: [Data courtesy Marc Imhoff of NASA GSFC and Christopher Elvidge of NOAA NGDC]. Image by [Craig Mayhew and Robert Simmon (NASA GSFC, 2006)]*

Returning from the satellite view to a situation at ground level, the forthcoming demographic changes are not good omens for the health of the global environment. During the last century, **rural populations** were decreasing as **urban populations** were growing. This tendency will be important for the demography in Africa and Asia for the next decades.

- The **urban population** of the world has grown rapidly from 746 million in 1950 to 3.9 billion in 2014. Nowadays, 54 % of the world's population lives in urban areas. United Nations expects that the percentage will reach the 66% by 2050, which would be an increment of 2.5 billion people to urban populations, mainly located in India (404 million), China (292 million) and Nigeria (212 million) (United Nations. Department of Economic and Social Affairs. Population Division, 2014b). Therefore, urban growth will take place in countries of the developing regions; where it still is lower than 50 %. In particular, Africa will be a key component of this new increment in the next decades (light green colours in Fig. 4).
- Nowadays, the global **rural population** is now close to 3.4 billion and India tops UN's ranking (857 million) followed by China (635 million).

The spatial transformation could be enormous, with people moving out of agriculture into urban settings, in particular, to big cities. This forecast is not surprising since urban growth in African big cities was 6.5 % per year during 1990-2010 versus 2.4 % in the smaller towns (Dorosh & Thurlow, 2013).

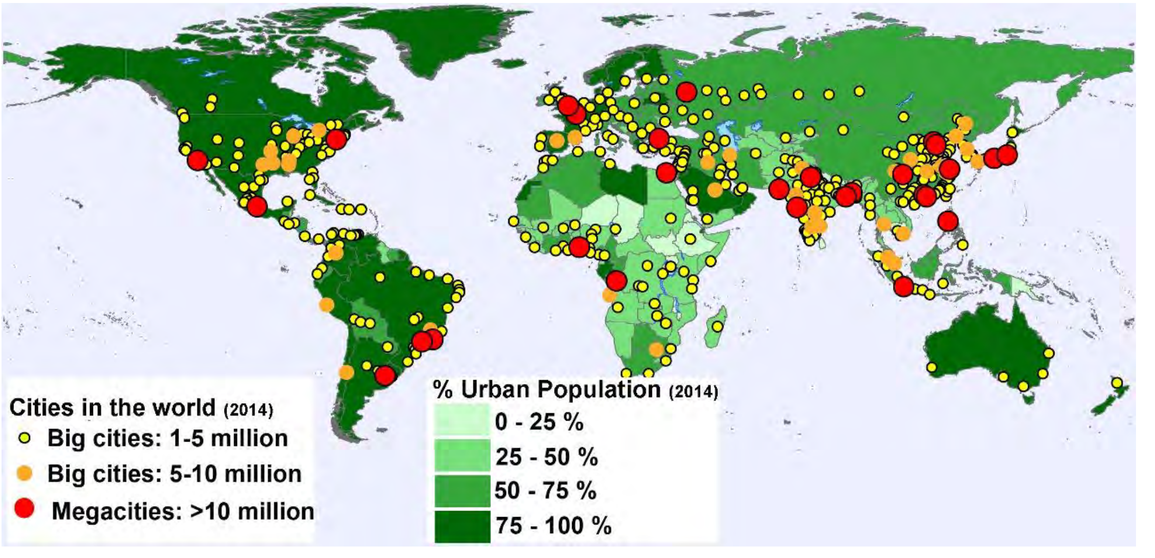


Figure 4: *Location of the bigger cities in the world and percentage of urban population per country in 2014. Source: [Data sheet obtained from available data in United Nations. Department of Economic and Social Affairs. Population Division (2014a)]*

It is interesting to find that the highest increment will be not only associated to megacities. In particular, the group of medium and big cities will be reaching the fastest growing in the world (Dorosh & Thurlow, 2012). Therefore, the largest rural population that was located mostly in those developing countries could experience a dramatic change for the global environment and especially, the urban environment in terms of pollution (Mage *et al.*, 1996).

2.1.3 The largest urban agglomerations: medium cities, big cities and megacities of the world

If the previous concepts: "urban" and "urban areas" involved certain complexity to define them, the classification of the cities according to their different sizes is difficult to establish too. Frequently many of these settlements are called cities, associated to the positive status of "living in a city", but experts use to categorize them according to the number of inhabitants and the density. This classification use to be different depending on the country. In Spain, for example, the small and medium size cities are in the range of population of 10,001-50,000 and 50,001-100,000 respectively, meanwhile OECD-EC (Table 1) and the United Nation use other ranges currently that will be explained below.

Size	Population	Size	Population
S	between 50,000 and 100,000	XL	between 500,000 and 1,000,000
M	between 100,000 and 250,000	XXL	between 1,000,000 and 5,000,000
L	between 250,000 and 500,000	Global city	of more than 5,000,000

Table 1: *Urban centre sizes in population according to new OECD-EC definition (Dijkstra & Poelman, 2012)*

2.1.3.1 Intermediate or medium cities

The intermediate or medium city is a concept sometimes forgotten when talking about urban populations. These cities are in the range 20,000 to 1,000,000 inhabitants, although they have a relative importance in relation to the environment and pollution, as they are the largest and most diverse group of cities, being scattered around the world. According to United Nation, 62% of the world's urban population lived in cities of less than 1 million inhabitants in 2001 (United Nations Population Division, 2002).

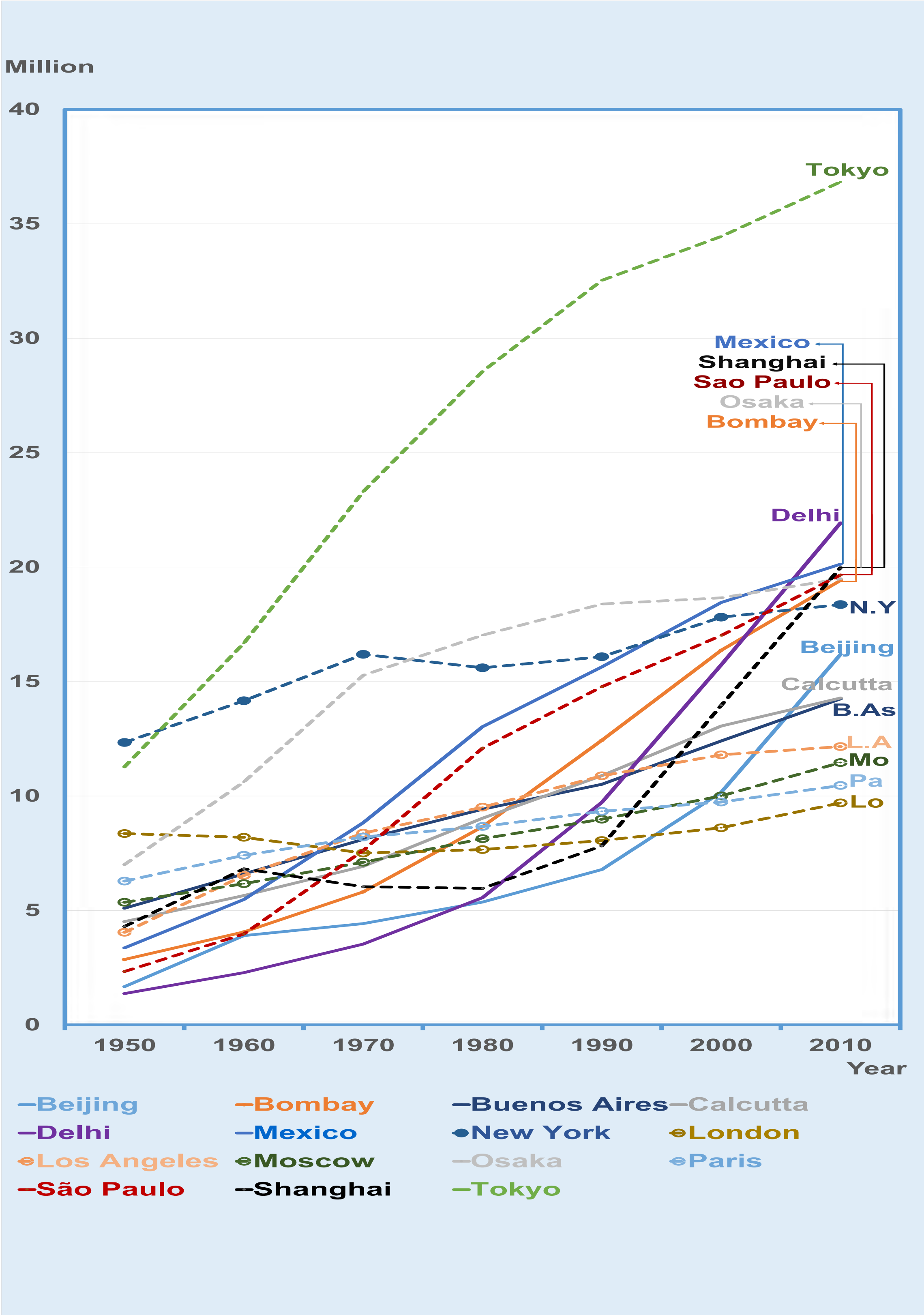


Figure 5: *Variation of the population in the most representative largest urban agglomerations ranked by number of inhabitants at each point in time, 1950-2010. Source: [Data sheet obtained from United Nations. Department of Economic and Social Affairs. Population Division (2014a)]*

2.1.3.2 Big cities

The next group consists of the cities between one and 10 million inhabitants, so called big cities properly. This group use to appear split into two subgroups: 1) big cities in the range of one to 5 million and 2) big cities from five to 10 million. These subgroups are displayed in Fig. 4 in yellow and orange circles, representing the most important populations in the world, such as capitals and main financial centres.

2.1.3.3 Megacities

The last group is formed by the megacities (cities accounting more than 10 million people) and displayed in Fig. 4 as red circles. The group has increased in the last decades from 10 megacities in 1990 and 153 million inhabitants, to 28 mega-cities worldwide, home to 453 million people (12% of the world's urban dwellers) in 2014.

Nowadays, Tokyo keeps on topping UN's ranking of most populous cities (36.8 million people) [light green line in fig. 5], followed by Delhi (21.9 million), Mexico City (20.1 million), Shanghai (20 million), São Paulo (19.7 million), Osaka (19.5 million), Bombay (19.4 million) and New York-Newark area (18.4 million). The withdrawn lines as New York, Los Angeles, Moscow, Paris and London belong to cities that population is growing slowly or stable in the last years.

Sixteen megacities are located in Asia, 4 in Latin America, 3 each in Africa and Europe, and 2 in Northern America.

Figure 6: *Europe's urban areas, which accommodate more than three-quarters of the region's population. Source: [EEA, 2014]*

The forecast for next decades suggests that megacities in developing countries (México, Sao Paolo and Bombay's trend in Fig. 5) will become more prominent, while consolidated urban areas such as New York-Newark, Los Angeles or Osaka would fall in rank.

In the past decades, most of the European megacities have stopped growing (i.e. Paris, London or Moscow in Fig. 5), as well as other intermediate cities which scarcely taken part in the industrialization of the 19th and 20th century, and those specialized in industries which are nowadays of declining importance. However, the rural and international migration have increased the population in the first years of the 21th century in agglomerations such as Berlin or Southern European cities. These migrations and the political and economic characteristics of the regions has configured a map of European urban areas (Fig. 6) which displays a higher concentration of urban areas in the Central and Northern part of Europe. In total, these areas accommodate more than three-quarters of the region's population.

To finish this point is important to mention that although the title of this thesis dissertation is referred to big cities. The most accurate sentence in the title should be "medium cities, big cities and megacities of the world", but was shortened to the general concept of "big city".

2.1.3.4 Megacities and their environmental challenges

Nowadays, most of the megacities and big cities are fighting different environmental challenges. Each city has particular geographical and climatological conditions that influences the environment, but the common factors in all megacities are the multiple air pollutants that affects the air quality of the agglomeration (Mayer, 1999). Every city faces different problems concerning air pollution. In cities like Rio de Janeiro, Beijing, Calcutta or Cairo, the major problem regarding air pollution is the high particulate matter levels reached every year. In others megacities like Los Angeles, the high concentrations of ozone and nitrogen dioxide are the problem to face. Meanwhile, in Mexico City the problem includes all previous pollutants (PM, NO_x and O_3). In general, air pollution levels are higher in big cities in developing countries such as Karachi, Bombay and Lagos, than in highly developed industrialized countries. The metropolitan area of Madrid has the typical characteristics of large urban settlements (Sukopp & Werner, 1989), being particularly noteworthy for the strong heat island effect (Ilera & García, 1995).

2.2 Air pollutants and the impacts of the urban activity on the environment

The words pollution and contamination have been taken from the Latin words *pollutio* and *contaminatio* respectively (Arora, 1999). The air pollution is a phenomenon of atypical increase in trace contaminant levels of the atmosphere, because of indoor and outdoor activities of man or extraordinary natural events such as volcanic eruptions, dust storms, or fires. Acute effects (high-dosage) of air pollutants are generally associated with roadways, industrial facilities or urban areas. This general term comprises different types of contamination concerning the different environmental conditions. The most important concepts associated to the outdoor environments are summarized in the following definitions:

- According to the World Health Organization (WHO, 1972), the term **air pollution** *"is limited to the situations in which the outdoor ambient atmosphere contains materials in concentrations which are harmful to man or to his environment"*. Normally the substances that are released into the air provide from human activities. Although outdoor pollution is the objective of this study, it is important to mention that indoor smoke is also a serious health risk for 3 billion people who cook and heat their homes with biomass fuels and coal every day (WHO, 2014).
- As a complement for indoor pollution, **ambient air pollution** is a broader term used to describe air pollution in outdoor environments. Poor ambient air quality occurs when pollutants reach high enough concentrations to affect the environment and/or human health. **Urban outdoor air pollution** is a more specific term referring to the ambient air pollution experienced by populations living in urban areas, typically in or around cities.

2.2.1 Past and current situation of air pollutants in the world

Air pollution is not a recent problem. In the early episodes, the firewood and coal combustion was the main source of pollution instead of traffic emissions, which is more recent. The origin of air pollution on the Earth can be traced from the early times when man started using firewood for cooking and heating in caverns. It became to be an important issue since the 18th and 19th century. The Industrial Revolution was based on the use of coal. Industries were often located in towns, and together with the burning of coal in homes for domestic heat, urban air pollution levels often reached very high levels. There were infamous episodes in the history, but the serious ones were recorded in the mid-twentieth century, when different cities in the United States and Europe registered a large number of hospital admissions that resulted in deaths (*London Fog* triggered by SO_2 emissions caused the death of 5000 people in London in 1952). These recurrent winter smog's episodes were associated to coal combustion and their emissions of sulphurous compounds and black particles in the atmosphere. These events were the most common problems in big cities in the Northern hemisphere during the 1960s, 1970s, and early 1980s. Still in our days, these circumstances are addressed in cities of developing countries.

The problems concerning air pollution by coal combustion have been ameliorated in most developed cities, despite urban air pollution is still a serious problem mainly due to current traffic emissions instead of coal combustion. In the last decades, experts have focused the attention in other air pollutants such as the particulate matter (PM_{10} and $PM_{2.5}$), secondary pollutants such as oxides of nitrogen (NO_x) and ozone (O_3) and new harmful organic pollutants, practically found in all urban areas around the world (Fenger, 1999). The current legislation has established a series of threshold values for each pollutant, which allows a single comparison for each pollutant in a group of cities, as shown in Fig. 7, which compares annual mean concentrations of PM_{10} recorded in the same 15 representative urban areas cited in Fig. 5 [2.1.3.3], as the most representative largest urban agglomerations. In Fig. 7, the concentrations vary by more than a factor of 11, if we compare the top value reached in Delhi (PM_{10}= 225 µm/m^3) with Paris, the lower annual value. This settlement is the only megacity with the recommended limit value (PM_{10}=20 µm/m^3 annual mean) suggested by WHO air quality guidelines (WHO, 2006). The most recent suggestion to compare and monitoring air quality changes in big cities over the time are the implementation of a multi-pollutant index that evaluates and ranks megacities in terms of their ambient air quality (Gurjar *et al.*, 2008). This index considers the combined concentrations of PM_{10}, SO_2 and NO_2.

Different measures have been adopted to control the exceedances in developed countries (mainly in USA and in Western European cities). Therefore, the problem of pollution suffered by industrialized cities a few decades ago, as they had factories and nearby industries was gradually moving to rural areas surrounding them due to the implementation of more stringent environmental regulations and construction of taller chimneys, whose plume can disperse pollutants over long distances. Nevertheless, urban air pollution in developing countries has been worsening because of the rapidly increment of traffic on roads, growing energy consumption and the lack of environmental regulations. The classical rural distribution of population in Asia, Africa and Latin America has moved rapidly to big urban areas in the last decades. This new megacities are experiencing even worse air pollution levels than those of industrialized cities of the last century. For example, in Shanghai (megacity of more than 24 million people in China), the red alert pollution (most on a scale of four colours) was declared for the first time in December 2013 and numerous airline flights to arrive in the economic capital of China were rejected because of the lack of visibility due to heavy pollution. The air concentration of particles with a diameter less than 2.5 microns ($PM_{2.5}$) reached peaks of 600 micrograms per cubic meter in several areas of the city. Those were extremely dangerous levels, as the World Health Organization recommends a concentration below 25 µg/m^3 24-hour mean. Levels above 500 µg/m^3 24-hour mean is considered as 'outside of the parameters'. In others big cities, such as Beijing, $PM_{2.5}$ >1,000 micrograms were reported in the past too. Given that situation, schools were closed, students were required not to leave home, some factories, particularly polluting, had to reduce the rate of production and public outdoor activities were cancelled. The final solution that Shanghai authorities adopted was to raise from 75 micrograms per cubic meter to 115 the threshold considered for acceptable air, thus alerts decreased.

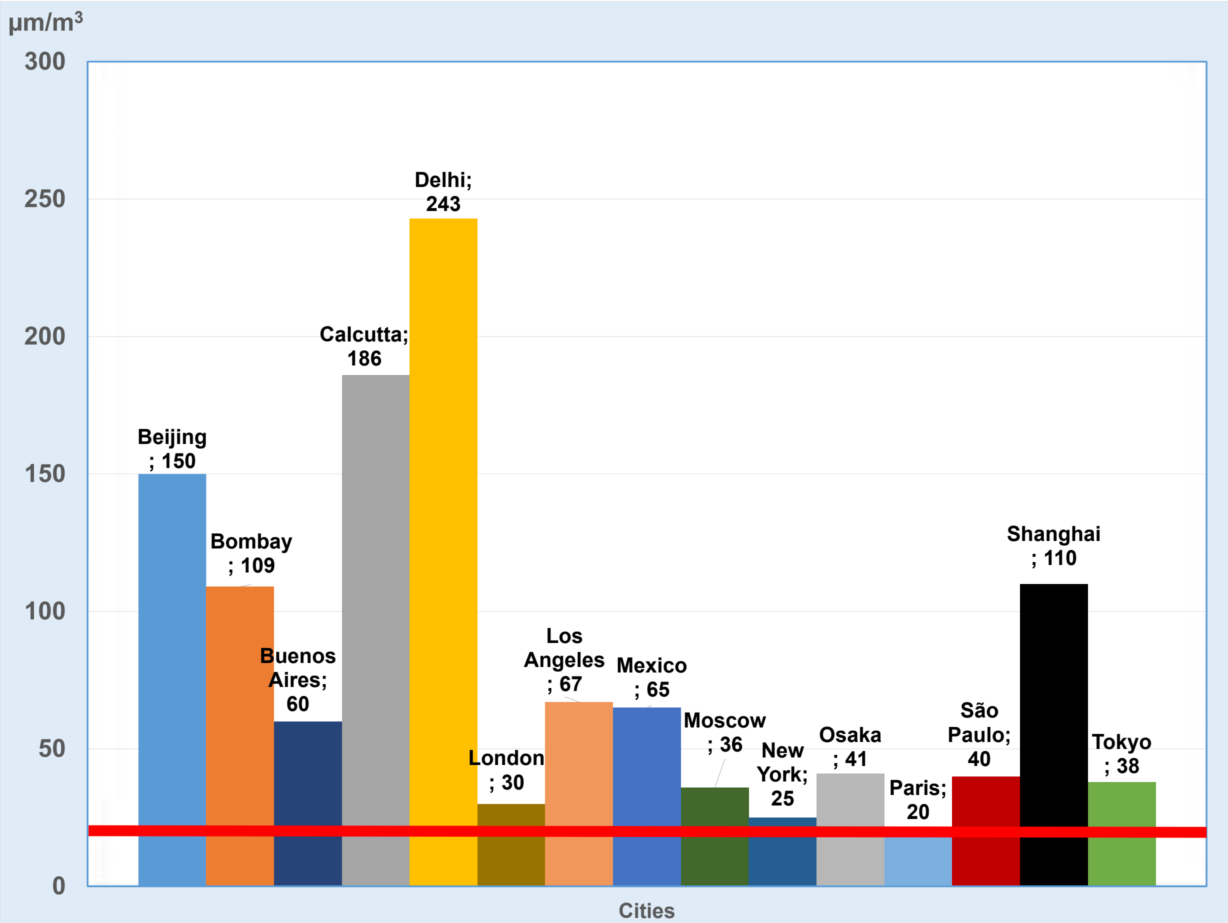


Figure 7: *Annual mean concentrations of PM_{10} recorded in same representative megacities as Fig. 5 in 2000-2005 (same colour for each city as Fig. 5). Data obtained from: [(WHO, 2006; WMO/IGAC, 2012)]*

2.2.2 Air pollution and impacts on human health

- **Worldwide situation**

Both ambient (outdoor) and household (indoor) air pollution cause respiratory and other diseases, which can be fatal. Outdoor air pollution is a major environmental risk to health and environment affecting everyone in developed and developing countries alike. 88% of such premature deaths occurred in low- and middle-income countries, and the greatest number in the Western Pacific and South-East Asia regions (WHO, 2011). Pollutants of major environmental and public health concern include particulate matter, carbon monoxide, ozone, nitrogen dioxide and sulphur dioxide.

The recent annual reports provided by the World Health Organization (WHO) and the United Nations Environmental Programme (UNEP) about air pollution estimated to cause 3.7 million premature deaths worldwide per year by ambient exposure (outdoor air pollution) in both cities and rural areas. They concluded that outdoor and indoor air pollution was the world's largest single environmental health risk accounting 7 million deaths (WHO, 2011). Furthermore, 1.628 cities worldwide (91 countries) were reporting exceedances in air pollution levels (WHO, 2014). Their data revealed a stronger link between air pollution exposure and the development of respiratory diseases, cardiovascular diseases and cancer, due to exposure to small particulate matter of 10 microns or less in diameter (PM_{10}).

➢ Situation in Europe

The percentage of the urban population exposed to air pollutant concentrations above the EU and WHO reference levels for 2009-2011 period reflect the magnitude of the problem (Fig. 8). A 2013 assessment by WHO's International Agency for Research on Cancer (IARC) concluded that outdoor air pollution is carcinogenic to humans, with the particulate matter component of air pollution most closely associated with increased cancer incidence, especially cancer of the lung (IARC, 2013). Ambient air pollution, notably particulate matter and O_3, has been associated with increases in morbidity and mortality in many European urban studies (Barrett *et al.*, 2008; de Leeuw & Horalek, 2009).

➢ Cause/effect relationship between the pollutants and human health

In general, it could be accepted that the lower the levels of air pollution, the better the cardiovascular and respiratory health of the population will be, in both long- and short-term. However, the last studies suggest that there is not a threshold level to cause health damages. Even the lower level of pollution could influence the mortality rate of the population (Alas Brun, 2003). The statistical analyses of the latter case-study carried out in different cities show a relationship between increases in the concentration of suspended particles and the short-term increase in deaths, in particular cardiac causes and respiratory causes. All people are potentially exposed to air pollution, but specifically people with respiratory diseases or heart conditions, older adults and individuals performing activities that lead to increased breathing rate, suffer from air pollutants.

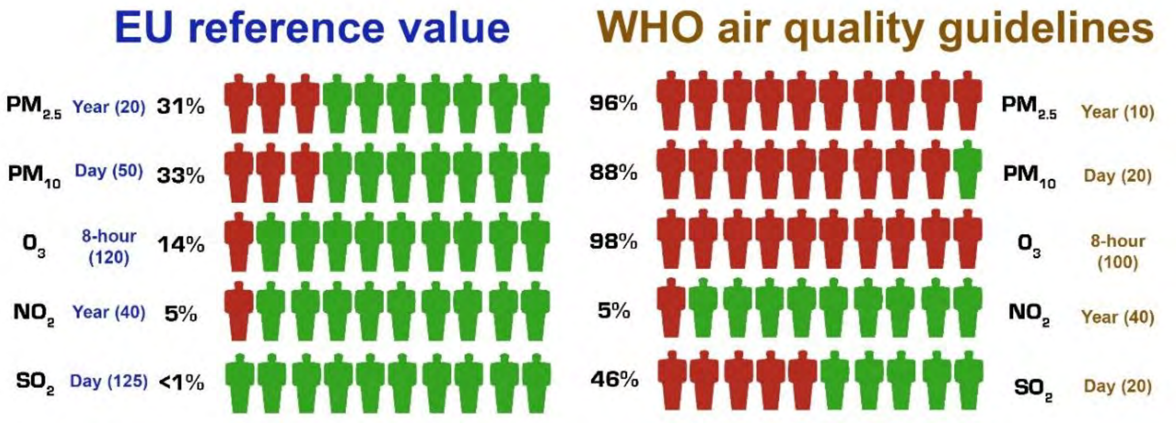


Figure 8: *Percentage of the urban population in the EU exposed to air pollutant concentrations above the EU and WHO reference levels (2009–2011). The reference levels (in µg/m³) include EU limit or target levels (blue) and WHO air quality guidelines (brown). Data source: [(EEA, 2013b, 2014)]*

The 2005 "WHO Air quality guidelines" indicated that by reducing particulate matter (PM_{10}) pollution from 70 to 20 micrograms per cubic metre (µg/m), air pollution-related deaths could be reduced by around 15%. This way, by reducing air pollution levels, countries can reduce the burden of disease from stroke, heart disease, lung cancer, and both chronic and acute respiratory diseases, including asthma. Based on the last paragraphs, we believe that urban trees could play an important role and could ameliorate the burden of diseases for the urban and rural inhabitants.

2.2.3 Air pollution and impacts on vegetation

Apart from changes in the nature of pollutants in urban air in comparison to the atmosphere of a century ago, in the last few decades pollutants have become more widely distributed. E.g., the effects of ozone are visible in sensitive plants in remote areas far away from the emission source. These changes imply a wide area of influence on vegetation.

2.2.3.1 Past and current situation

At the same time that smog episodes in the 19th century began to be serious, the first experiments on the effects of air pollutants on plants were investigated. This smog could be probably associated to the early experiments by Cohen and Ruston (1912) about the effects of air pollution on the growth of lettuces from the city centre in comparison to the outskirts of the conurbation showed a remarkably good correlation between the growth and the estimated annual deposition of SO_3. This way, the fresh weight increased three to four times by the distance to the city centre of Leeds, as well as the fresh weight decreased four times by the increment of the annual deposition (kg) of SO_3 per hectare.

In the 1950s, 1960s and 1970s the main studies performed on the effects of air pollution on vegetation concerned herbaceous plants and cropsy (Middleton, 1950), meanwhile in the 1980s the interest shifted to conifers from North America and Europe of economic importance such as spruce and fir (Godbold & Hüttermann, 1994; Johnson & Siccama, 1983).

In the last years, the studies are focused in the establishment of critical levels for each pollutant and vegetation category and their validation under experimental fumigations, as reported bellow.

2.2.3.2 Critical loads and critical levels for the protection of crops, trees and natural vegetation

The United Nations Economic Commission for Europe (UNECE) has provided a basis for air quality control standards for the protection of crops, forests and both natural and managed ecosystems with the aim of protecting the most sensitive elements of any ecosystem from long-term damage. These basic terms are defined as:

- **Critical load for ecosystems**: *"a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur according to present knowledge".* The term of critical loads could be applied to any toxic factor affecting any component of the biosphere, as it could be the total deposition of a particular pollutant or of their derivatives.
- **Critical levels**, or threshold gaseous concentration exposures, are "*the concentrations in the atmosphere above which* ***direct adverse effects*** *on receptors such as plants, ecosystems or materials, may occur according to present knowledge*".

Information and critical load values for different types of vegetation has been given by Sanders *et al.* (1995). The establishment of critical levels for each pollutant and vegetation category can only be validated by experimental exposure in experiments under fumigation conditions, normally in chambers. It is important to remind that different subspecies or genotypes of the same species may differ in their sensitivity to pollutants and the kind of symptoms or physiological response.

Critical loads and levels are often displayed on maps, representing values that may affect the sensitivity of vegetation or any organisms to be taken into account. Related examples of this kind of information about pollutants distribution or deposition loads are given in Figs. 13 and 14 regarding critical load or level exceedance maps for O_3 in Europe.

2.2.3.3 Main effects of urban air pollutants on the vegetation

In contrast to animals, plants remain static at their habitat when conditions are not optimal. Consequently, they are the first “sufferers”, being continuously exposed to different levels of air pollutants from diverse sources in the city (Mandal & Mukherji, 2000). Pollutants can directly affect vegetation via leaves or indirectly via soil. If they are exposed constantly to airborne pollutants, most plants develop physiological alterations before showing foliar visible symptoms (Liu & Ding, 2008).

Air pollution injury to plants is often classified as **chronic** or **acute** (Kardel, Karen, & Roeland, 2010)**:** 1) **Chronic symptoms** often result from exposure of a plant to low levels of pollution for a long time, or occur when a plant is fairly resistant to a pollutant. 2) **Acute injury** occurs after a short-term high level of pollution, or to very sensitive plants. Chronic symptoms usually imply tissue injury but not death, while acute injury normally implies tissue death.

When vegetation suffers a significant alteration, the symptoms of the plant response could be related to two types of changes regarding morphologic and physiologic alterations.

1) **Morphological changes**: Injury in cells and tissues in most cases appear in the foliage after hours to weeks when pollutiants exceed the threshold. However, plant morphology can also be altered by chronic exposition and particularly by pollution stress during formation (smaller leaves, xeromorphic features, smaller year rings, changed root systems, etcetera).
2) **Physiological changes:** Pollutants influence plant physiology immediately. Stomatal regulation is changed, plant biochemistry is influenced, but these effects involve also defense reactions and can be to a certain extent transitional.

The main damages of air pollutants in plants could be categorised as direct and indirect damages (table 2):

Direct damage	Indirect damage
Foliar necrosis	Increased fungal attack
Foliar discolouration	Increased insect attack
Imbalances in the regulation of stomatal opening and closing	Nutritional imbalances by changes in soil biochemistry
Changes or reduction of plant growth	
Defense overflow and reduced stress tolerance	Increased sensitivity to the effects of frost, drought, etc.
Weakening of the vegetative vigour of the plant.	
Alteration of the number of flowers and fruits.	

Table 2: *Overall injury caused by air pollution in vegetation*

The response to various air pollutants varied according to the level of exposure and the characteristics of the plant. The sensitivity of the vegetation to pollutants developed injury in foliar structures and impaired plant growth (Ulrich, 1984). Furthermore, Davison and Blakemore (1976) observed that the common effects in affected plants were chlorosis, necrosis, inhibition in photosynthesis and decreasing plant growth. In other plants, the effects of pollutants were reported as stomatal damage, disturbed membrane permeability and premature senescence, as well as the decrease of the leaf photosynthetic activity and production rate (Tiwari, Agrawal, & Marshall, 2006). If the level of pollution was low, certain plants responded with an increase in the uptake of elements (Abbasi *et al.*, 1992), however, in other plants, the excessive presence of some elements produced inhibitory effects by blocking the uptake of other elements (Altaf, 1997). If leaves and needles suffered a chronic exposure to various air pollutants, a fragility of the epicuticular wax layer and a reduced defense capacity allowed increased attack by diseases, pests, drought or frost.

2.2.3.4 Air pollution impact on urban areas

The main damages caused by air pollutants on vegetation in urban green areas usually occur next to emission sources (traffic, heating and industries). Their effects are particularly present on the leaf systems of trees situated in the edge of the masses or alignments, where PM, NOx and photochemical pollutants (O_3 and PAN) has the highest incidence. Some of the organs where air pollution in cities is most evident is in the stomata of the leaves of woody plants. Gaseous pollutants affect opening and closing of the guard cells, resulting in chemical reactions that either directly cause the necrosis of stomatal cells or indirectly through the blockage by particulate matter. These particles could be chemically phytotoxic in combination with other substances, but also the physic barrier of the particulates in stomata or on leaf surface could reduce the photosynthesis. The effects of pollutants on stomatal behaviour has been studied in different species and conditions (Robinson, Heath, & Mansfield, 1998). We will study this issue in Chapter 3, which is focused in *Quercus ilex L.*, as an example of these interactions between ozone effects, irrigation and the intrinsic plant strategy to avoid drought stress in non-irrigated trees. There is a reduction in transpiration by decreasing the stomatal conductance and its rate of water loss.

Deciduous trees typically do not show great damages, as normally the highest injury occurs on soft tissues from newly sprouted leaves or opened buds and often coincides with a quantitative decrease in the emission of pollutants to the atmosphere in urban areas (spring in Northern Hemisphere). The highest levels of pollution are reached in autumn and winter, when traffic intensity is higher and fuels use for heating is demanded, it is when leaves senescent or shed. In **evergreen plants**, pollution often leads to chronic damage, due to a longer lifespan of their leaves and the length of the synergistic effect of several agents.

Difficulties in urban experiments

The studies on urban trees imply more difficulties than other studies on plants because the increments in factors conditioning the results. Nowadays, it is possible to identify some effects of individual pollutants, such as ozone or heavy metals and the current knowledge of the mechanism of action of some major air pollutants is well known. However, more studies are required on the interactions between pairs or groups of pollutants and between stress factors and pollutants, which are the most common situations in nature and in urban conditions.

The most important problems regarding the study of urban trees and air pollution in the city are linked by the variability of factors:

- The first important problem on urban trees is the lack of information that exists regarding "field work" on urban trees species. Most of the studies for validation of visible symptoms to pollutants exposure consists in controlled essays in the laboratory or in open top chambers (OTC), where fumigation is controlled. However, experiments in the city are scarce and it is difficult to proceed with the same procedures in order to compare results in different cities. One of the complexities surrounding the response of individual trees is the extrapolation of a few samples in a single tree in order to estimate the entire tree or a group of trees. Urban trees are exposed to several factors such as soil restriction, interactions with buildings (shadow), poor soil quality, leaf position in the canopy, etc. therefore, the variability within the tree is very high.

- The second important problem (our point of view) is the lack of information in the accumulative effects of the pollutants in the long-term exposure. There is an ongoing debate since the 1980s about the role of the air pollutants in causing deterioration in the health of the forest and urban trees. Most of the evidences that have been studied in papers are focused in the qualitative or quantitative effect at the morphological or physiological tree level to short-term exposures and frequently on young trees (sometimes even in seedlings). The results are interesting, but show severe limitations to our understanding regarding the feasibility of those results for the long-term and the accumulative effects on mature trees in the city or in the forest.

- Other problems are the difficulties to maintain an essay in public areas where stationary devices are exposed to vandalism. Moreover, the continuous road traffic, constructions, urban remodelations, etc. complicate the long-term tracing of the experiment in dentical conditions. Sometimes the lack of information come from the negative response of administration to give environmental data, fearing that it could be problematic for them.

2.2.4 Main air pollutants. Classifications and sources

Industry (steel and chemical industries, power plants), agriculture, waste incineration, combustion of fossil fuels and road traffic are the most important local sources (Çelik *et al.*, 2005). Among the most common and virulent air pollutants are ozone (O_3), suspended particulate matter (PM), nitrogen oxides (NOx) and organic compounds. The last ones are becoming to be studied in the last decades, while the others are well-known (Fenger, 2009). The different classifications of air pollutants are the following:

A) By the physical state of pollutants

According to the physical state of pollutants in the atmosphere, they are **A.1) gaseous** air pollutants, when they are small molecules present as gases or vapours. The most significant gaseous contaminants of urban atmospheres are the oxides of nitrogen, sulphur and carbon, hydrocarbons and ozone, due to their abundance, human and vegetative health consequences and ability to deteriorate materials. **A.2) particulate matter**, that are suspended in the atmosphere in solid or liquid phase, covering a wide range of sizes, provenance and chemical compositions (Stern, 1977).

B) By the origin of the sources

There are different ways of categorizing the sources of emissions that produce air pollutants. The most common categorization is between B.1) **stationary sources** (industrial and household emissions, etc.), B.2) **mobile sources** (road vehicles, airplanes, railway trains, etc.) and B.3) **natural sources**

B.1) Stationary combustion sources

This is one of the major sources of pollutants emissions in many industrialized countries and in developing countries, as well as emissions from domestic heating and cooking. They are the main source for NO_x, volatile organic compounds (VOC) and SO_2 (if sulphur were present in the fuel). It is not an important source in cities like Madrid (there is only a stationary combustion plant), but it could be an important source in remote place were power is produced for power supply to the city. These are responsible for 3.7 million deaths per year according to the ultimate data (WHO, 2014)

B.2) Mobile sources. Road transport

Traffic is the most important source of pollution in most of the big cities and is responsible for 60 to 70% of the pollution found in an urban environment (Singh *et al.*, 1995). For example in Madrid, road transport provide the 85% of NO_x and 87% of PM_{10} (Ayuntamiento de Madrid, 2004). The exhaust gases produced by the combustion of petrol and diesel fuel include carbon monoxide (CO), NO_x, O_3, VOCs and PM (Costa, 2001), but they are not the only pollutants provided by the traffic. There are other non-exhaust emissions of PM such as the wear of brake components and the abrasion of tyres and asphalt. Oil additives for engines or paintings on the road contain heavy metals too (Korenromp & Hollander, 1999; Nadkarni, 1991; Ozaki, Watanabe, & Kuno, 2004; Sörme & Lagerkvist, 2002).

Apart of the geometry of the mobility of the sources, the emission area could give us an important information about the effect of the pollutants spread to the atmosphere. The most important types are: 1) **point sources**, such as individual industrial sites, even with several chimneys in a factory, but considered as an individual point source because of the focused emission point, 2) **line sources**, such as road vehicles and railway trains, where vehicles travel along defined routes. The emissions could be considered as a line with similar values, except in the junctions, where the value is increased by the addition of the individual road values at that point. 3) **Areal sources.** The sources of emission are diffuse and considered as a uniform, due to pollutants are spread over a considerable area, for example over a big city.

B.3) Natural sources

The natural emission of gases and particles within the atmosphere should be considered as another source. It could be local, such as sea spray, or even trans-boundary, when the wind-blown soil and dust is translated to other countries, as it happens with massive increases in PM concentrations in Southern European countries because of Saharan dust storms episodes (Fig. 9). This kind of dust outbreaks in Europe are occasional every year. The example in Fig. 9 happened between the 5th and 9th of April 2011. The Iberian Peninsula was affected by thick dust clouds that were generated by a dust outbreak resulting from strong winds over northern Africa. In fact, the dust clouds continued moving northward over the Atlantic Ocean reaching the British Islands after 7 April, which even pushed the dust cloud over Scandinavia after 9 April.

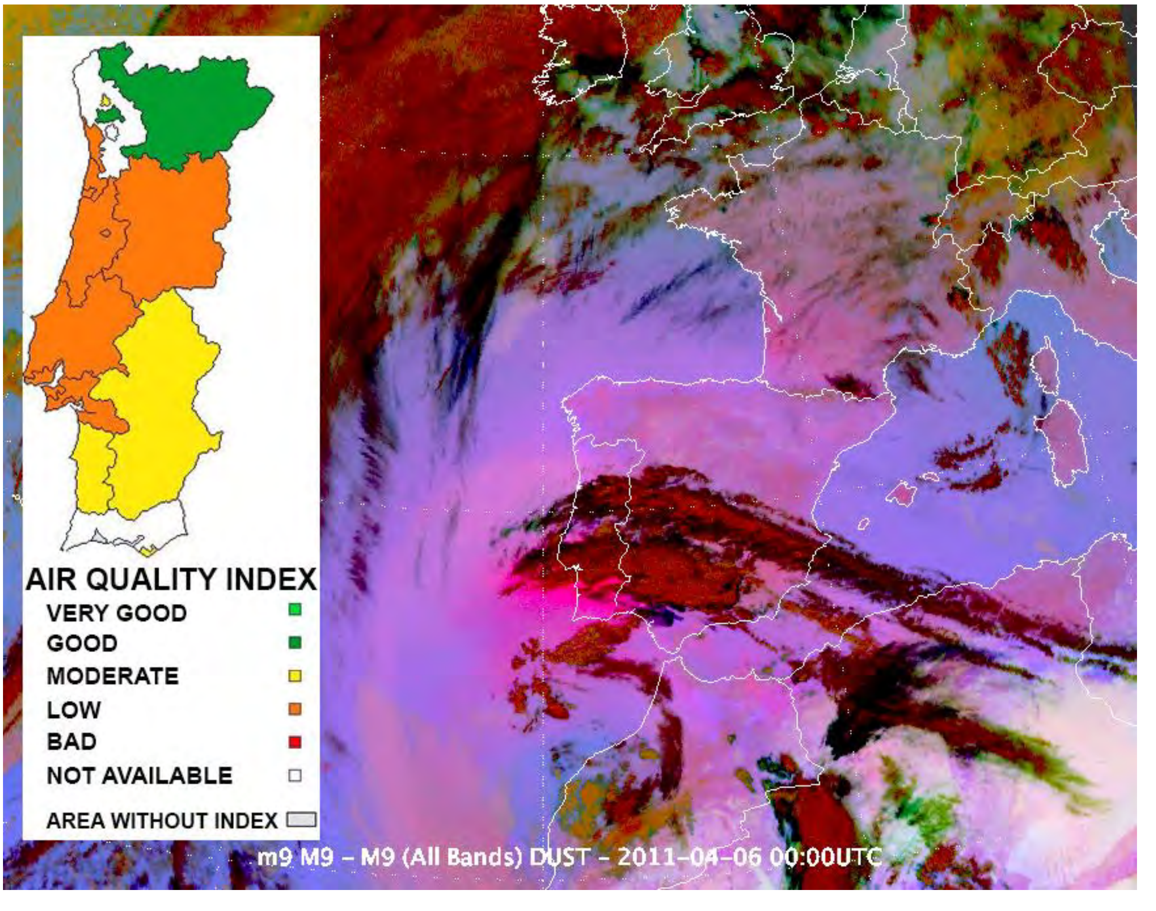


Figure 9: *Natural sources: METEOSAT satellite image of a dust outbreak (pink-magenta colour) over the Iberian Peninsula resulting from strong winds from Sahara desert and the effect in the air quality index in Portugal on 7th April 2011 with poor quality in many parts of the country, in a scale that ranges from light green (very good quality) to red (bad quality). There was a sharp increase of $PM_{2.5}$ and PM_{10}.*
Source: [Figure composed of data and image from two different sources. Image from EUMETSAT. Satellite: METEOSAT-9]. Type of image: Dust RGB Composite IR12.0–IR10.8, IR10.8–IR8.7, IR10.8. Date and time: 6 April 2011, 00:00 UTC. Air quality index data obtained from [*Portuguese Environmental Agency/ Instituto Português do Mar e da Atmosfera* (IPMA)].

The emission of isoprene, terpenes and other constituents by vegetation is another key factor on the release of biogenic VOC that contribute to the production of tropospheric ozone.

C) **Composition of the main pollutants** (Table 3):

SULPHUR DERIVATIVES:

- SH_2
- SO_2
- Other chemical derivatives:
  - Sulphuric acid mist
  - Hydrogen sulphide
  - Carbon bisulfide
  - Sulphur chlorides

CARBON DERIVATIVES:

- CO_2
- CO
- Hydrocarbons
- Other derivatives:
  - Acetylene
  - Aldehydes
  - maleic acid or anhydride
  - Acetic acid and anhydride
  - Phthalic acid and anhydride
  - Fumaric acid

HALOGEN AND DERIVATIVES:

- F
- Cl
- Other halogen derivatives
  - Brome
  - Iodine
  - Hydrofluoric acid
  - Hydrochloric acid
  - Hydrobromic acid
  - Hydroiodic acid
  - Fluosilicic acid
  - Fluorides
  - Carbon oxychlorides

AEROSOLS
SOLID PARTICLES
OZONE
NITROGEN DERIVATIVES:

- NO
- NO_2
- N_2O
- NO_3
- PAN
- PPN
- PBN
- NH_3
- Amines
- Other derivatives:
  - Hydrogen cyanide
  - Cyanides
  - Cyanogen

SOLID PARTICLES:

- Heavy Metals
  - Pb
  - Cd
  - Zn
  - Cu
  - Co
  - Hg
  - Al
  - Fe
  - Mn
  - Cr
  - Mo
  - W
  - Ti
  - V
- Light Metals
- Non metals
- Natural particles (organics & inorganics)
- Other urban particles from vehicles and construction
- Asbestos
- Arsenic and its derivatives
- Cyanides
- Talc
- Fiberglass

VOLATILE ORGANIC COMPOUNDS:

- Hydrocarbons
- Solvents
- intermediate chemicals as vinyl chloride
- VOCs of sulphur (mercaptans, etc.)

OTHER

Solid particles
Aerosols
Other inorganic compounds

***Table 3:** Classification of the main pollutants according to their composition.*

D) Way of emission into the atmosphere

Air pollutants could be sorted by the way that they are emitted into the atmosphere as D.1) **primary air pollutants** or formed within the atmosphere itself D.2) **secondary air pollutants**.

D.1) Today, the most common **primary air pollutants** are sulphur dioxide (SO_2), oxides of nitrogen (NO_x), carbon monoxide (CO), volatile organic compounds (VOC), and carbonaceous and noncarbonaceous primary particles. They are emitted into the atmosphere from specific sources such as a factory chimney or vehicle exhaust pipe. However, there are diffuse sources such as wind-blown dusts (Fig. 9) that produce the suspension of contaminated dusts by the wind and it is more difficult to estimate their provenance.

2.2.4.1 Primary air pollutants

D.1.1 Sulphur dioxide (SO_2)

- **Definition and principal sources**

It is a highly reactive colourless gas with a sharp odour. The main anthropogenic source of SO_2 is the burning of sulphur-containing fossil fuels for domestic heating, power generation and motor vehicles. Fossil fuels, like coal and oil, use to contain around 1-7% of sulphur. Despite SO_2 has been reduced in most developed countries by the use of other fuels and refining processes, in the less developed countries the burning of coal and the use of fuel oils with a higher sulphur content are still the major sources of SO_2.

The WHO's guideline values for SO_2 suggested by the 2005 revision are:

Limit	Duration
20 µg/m³	24-hour mean
500 µg/m³	10-minute mean

Table 4. *Guideline values for SO_2 suggested by WHO (2006)*

The current EU-limit value for sulphur dioxide is 125 microgram SO_2/m^3 as a daily average, not to be exceeded more than three times a calendar year.

- **Health effects**

SO_2 affects the respiratory system. It causes irritation of the eyes and inflammation of the respiratory tract (coughing, mucus secretion, asthma and chronic bronchitis)

- **Effects on vegetation**

When SO_2 is oxidized to sulphur trioxide and combined with water vapour, it forms sulphuric acid aerosol, which is the main component of the deforestation by acid rain.

D.1.2 Oxides of nitrogen (NO_2)

- **Definition and principal sources**

It is a toxic gas, which is highly reactive, oxidant and corrosive. The main sources of anthropogenic emissions of NO_2 are combustion processes (heating, power generation, gas stoves and engines in vehicles, airplanes and ships). In all high-temperature combustion processes, the nitrogen is converted to oxides of nitrogen, as it occurs in the vehicles engines in road traffic. Most of the nitrogen oxides produced during this process are nitric oxide and the major proportion of atmospheric nitrogen dioxide (95%) is a secondary air pollutant. NO_2 is the main source of nitrate aerosols (See Fig. 11), which form an important fraction of $PM_{2.5}$ and, in the presence of ultraviolet light, promote the formation of ozone, as secondary air pollutant.

The guideline values for NO_2 suggested by the WHO's 2005 revision are:

Limit	Duration
40 µg/m^3	annual mean
200 µg/m^3	1-hour mean

Table 5. *Guideline values for NO_2 suggested by WHO (2006)*

The current EU-annual mean limit value for nitrogen dioxide is 40 microgram NO_2/m^3.

➢ **Health effects**

At short-term concentrations exceeding 200 µg/m3, it is a toxic gas, which causes significant inflammation of the respiratory tract (bronchitis). At concentrations currently registered in cities of Europe and North America, it could decrease lung function and may increase the risk of respiratory infections (EPA, 2014)

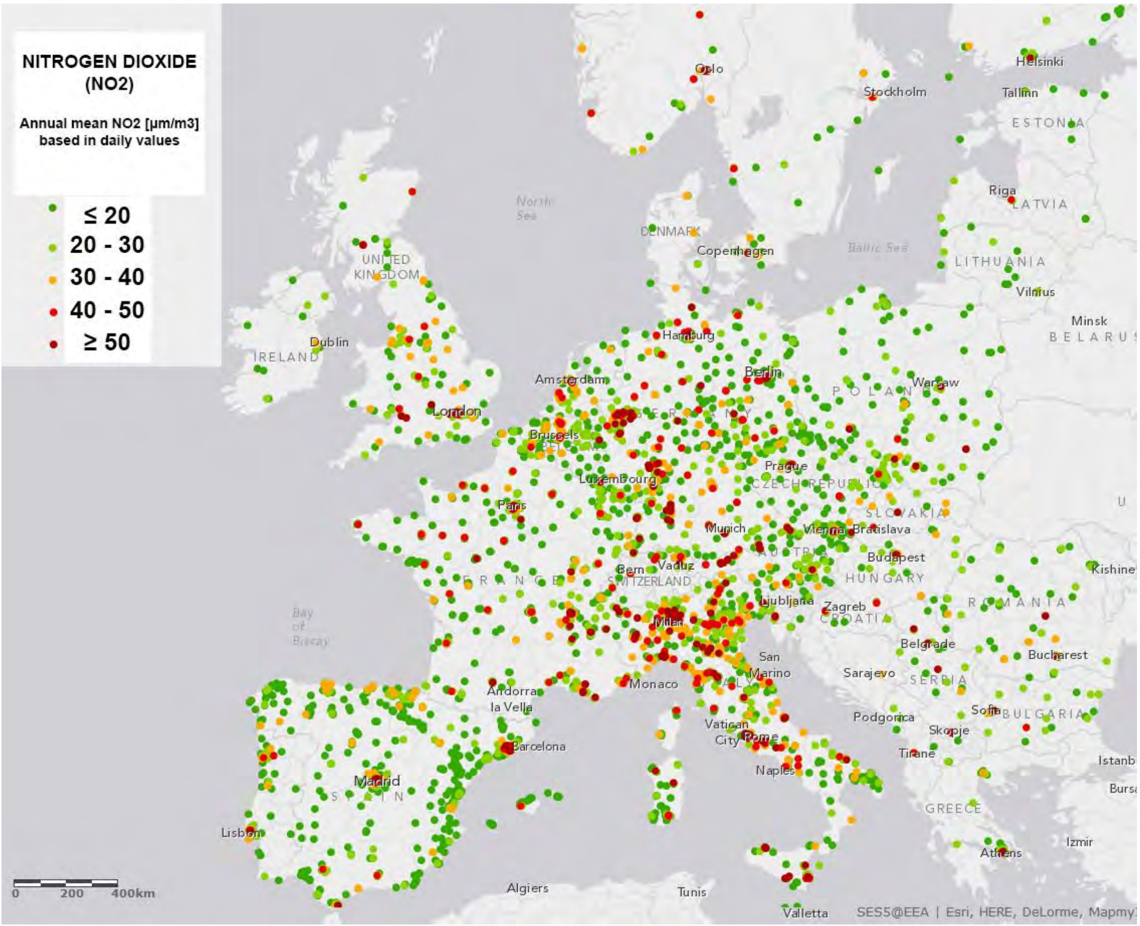


Figure 10: *Annual mean nitrogen dioxide (NO_2) concentrations in Europe (2010-2011) based on daily averages with at least 75% of valid measurements, in µg/m3 ((40 µg/m3, limit value for human health as set out in the Air Quality Directive, 2008/50/EC, as well as the WHO's limit value for the annual mean).* Source: [EEA-AirBase v.8 (EEA, 2014)]

D.1.3 Particulate matter (PM)

➢ Definition and principal sources

Particulate matter (PM) is the term employed for a complex mixture of extremely small solid and liquid trace elements. They may be organic and inorganic particles of different diameters suspended in the air (Fig. 11). The organic fractions may contain aliphatic and aromatics hydrocarbons, aldehydes, ketones and acids. The inorganic fraction usually contains metallic elements such as calcium, aluminium, iron and silicon. Other particles are pollen grains, fungal spores and bacterial cells. The action of the wind can suspend particles of soil from land surfaces into the atmosphere. PM also can be dust, dirt, soot, smoke or liquid droplets, although their characteristics are mainly influenced by the nature of the main source of particulate matter in the urban environment: the combustion of fuels. In particular, PM are emitted by diesel vehicles, or by coal-fired power plants in industrial areas. Urban areas generally have higher particulate loads in the winter than in the summer (Spirtas & Levin, 1971). The major components of PM are sulphate, nitrates, ammonia, sodium chloride, black carbon, mineral dust and water. Therefore, they comprise a wide range of compounds of different origins that could be roughly sorted by **carbonaceous particles**, as the particles emitted from burning fossil fuels (diesel and petrol engines) and biomass, or **non-carbonaceous primary particles**, as fly ash or small fragments of rock from quarrying/construction/demolition.

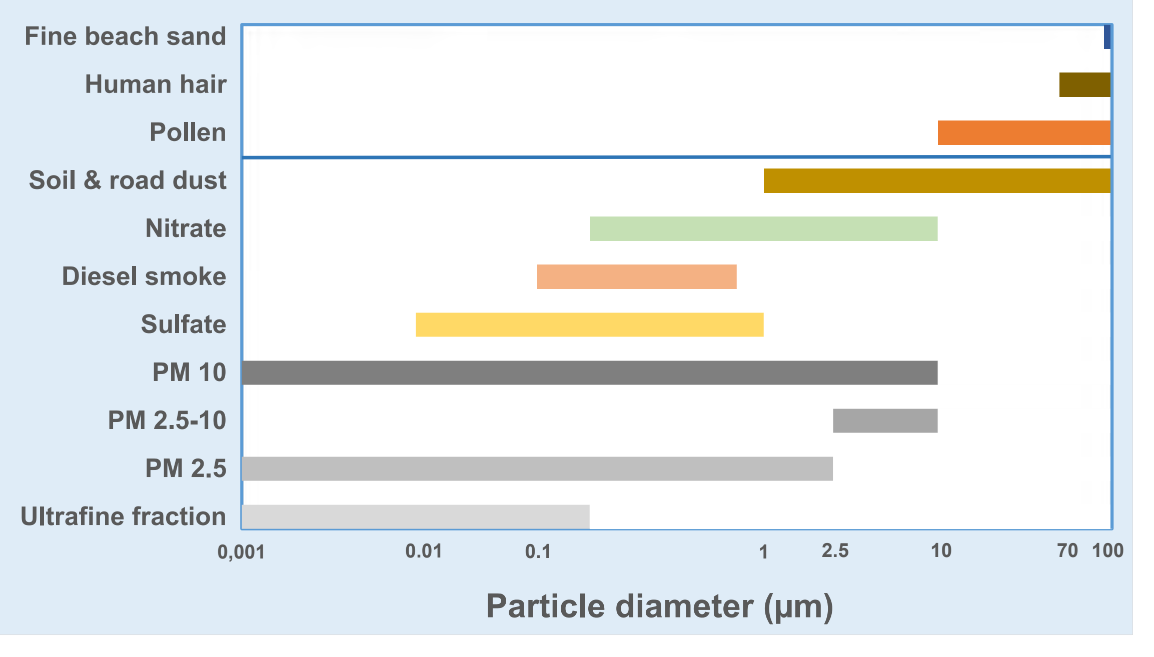


Figure 11: *Average particle diameter of the most common particulate matter that could be found in the air. Particulates may range in size from approximately 0.001 to 100-500 µm in diameter.*

The small particles of PM are measured in microns and could be sorted out by a size range due to the variations because of the interaction with water and gases. The size of particles is directly linked to their potential to causing health problems. The smaller these particles are (Fig. 11), the more hazardous they can be in respiratory diseases. Regarding their aerodynamic diameter, particulate matter can be grouped into two categories:

- **PM_{10}**. Particles less than 10 micrometres in diameter (≤ PM10), which can be inhaled into, penetrate and lodge inside the throat, trachea and lungs. PM10 consists of fine particles with diameters smaller than 2.5 microns (PM2.5) and coarse particles of between 2.5 and 10 microns. Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases, as well as of lung cancer.

- **$PM_{2.5}$**. Particles less than 2.5 micrometres in diameter. They are more hazardous that PM_{10} because particles of this size or smaller may induce effects to the respiratory and cardiovascular system due to the risk to lodge deeply into the lungs. In particular, if PM size is smaller than 1 micrometre, they could reach alveoli (Fig. 11).

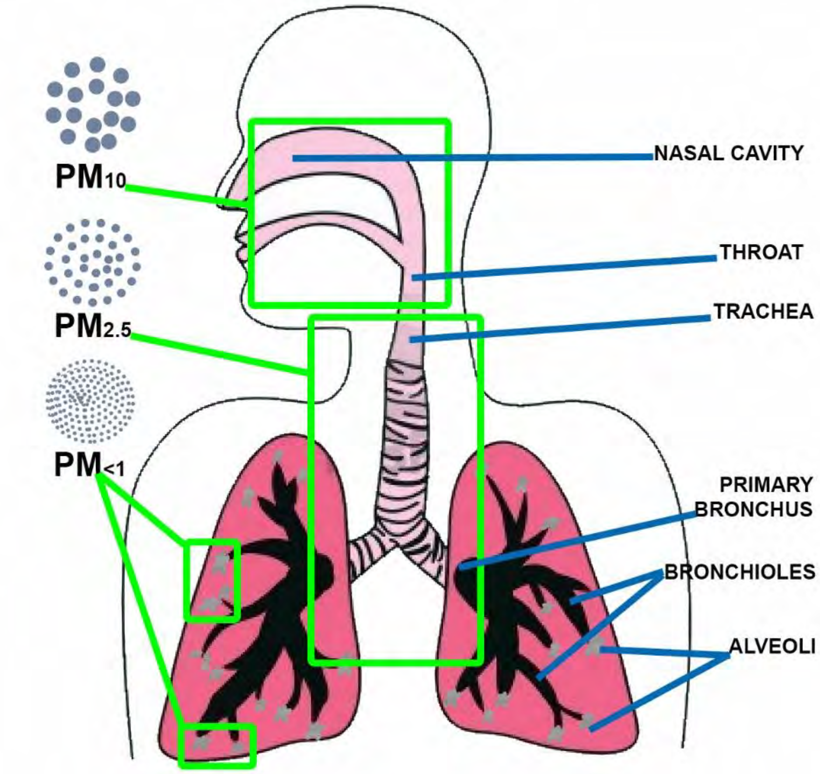


Figure 12: *The size of particles is directly linked to their potential for causing respiratory health problems*

The guideline values for PM_{10} and $PM_{2.5}$ suggested by the WHO's 2005 revision are:

PM_{10}	
Limit	**Duration**
20 µg/m³	annual mean
50 µg/m³	24-hour mean

$PM_{2.5}$	
Limit	**Duration**
10 µg/m³	annual mean
25 µg/m³	24-hour mean

Table 6. *Guideline values for PM_{10} and $PM_{2.5}$ suggested by WHO (2006)*

Air quality measurements are typically reported in terms of daily or annual mean concentrations of PM_{10} particles in terms of micrograms per cubic meter (µg/m³). When sufficiently sensitive measurement tools are available, concentrations of fine particles ($PM_{2.5}$ or smaller) are also reported. The new EU legislation include its correspondent measurement and control. The current EU-limit value for PM_{10} is 50 microgram/m³ (24-hour average, i.e. daily), not to be exceeded more than 35 times a calendar year.

- **Health effects**

The effects of PM on health is commonly extended to all population in the world, due to their effects occur at levels of exposure currently being experienced by people living both in urban and rural areas and in developed and developing countries. However concentration and doses are different, because exposures in many fast-developing cities today are often far higher than in developed cities of comparable size, as we have observed in Fig. 7 in megacities such as Delhi, Bombay, Beijing or Calcutta *versus* New York, London, Tokyo or Paris.
Small particulate pollution have health impacts even at very low concentrations (WHO, 2011). This is the reason why the proposed level of $PM_{2.5}$ particles in table 6 proposed by WHO are so low. According to the criteria proposed by WHO, the average of up to 10 micrograms per cubic meter would be breached by 37 out of 46 Spanish cities studied in the period 2008-2012. In a worldwide evaluation of air quality in 1,600 cities in 91 countries, only 12% of the people living in cities comply with WHO air quality guideline levels for $PM_{2.5}$ and PM_{10} levels (WHO, 2014). According to this ranking, the most polluted cities in the world are New Delhi, Dhaka, Ulan-Bator, Beijing and Karachi in Asia; Abu Dhabi, Doha, and Cairo in the Middle East; Dakar and Accra in Africa; Sofia and Ankara in Europe. In Latin America, the city with the worst levels is Lima.

- **Effects on vegetation**

The particles that air contains are deposited on plant surfaces. This particulate matter can clog stomatal openings of plants and interfere with photosynthesis functions (Hogan, 2010) or even could lead to growth stunting or mortality in some plant species, if the concentration of PM would be high enough.

Apart of the physic interaction, in the chemical point of view, the toxic effects of different types of particles are due to the presence of substances such as lead, cadmium, copper, zinc or fluorine that can be taken up by the plant via soil/roots after the deposition.

D.1.4 Carbon monoxide

- **Definition and principal sources**

This is another important air pollutant emitted by road traffic. The origin of this pollutant is the incomplete combustion of carbon in fuels, as it occurs with the combustion of petrol in vehicles engines.

D.1.5 Volatile organic compounds (VOCs)

- **Definition and main sources**

This group of pollutants include a heterogeneous variety of hydrocarbons, oxygenates, halogenates and other carbon compounds. Basically, they are solvents that contain carbon and evaporate easily at 20 ºC, such as inks, adhesives and all kind of organic solvents used in painting, adhesives or printing. The sources are diverse, although many of them are directly related to road vehicles because of the combustion of fossil fuels and the exhaust pipe or indirectly associated because of the evaporation of liquid fuels such as benzene from the fuel tank of the vehicles or from the petrol stations. Traffic road generated more than 50% of VOC emissions (Watson, Chow, & Fujita, 2001). The incineration processes and the leakage from pressurized systems, such natural gas, are another important source of VOCs.

- **Health effects**

VOC include carcinogens, mutagens and other products toxic for humans' reproduction (Council of the European Union, 1999)

2.2.4.2 Secondary air pollutants

These pollutants are obtained from chemical reactions of primary pollutants and natural elements, such as oxygen and vapour water in the atmosphere. Nowadays, the most important secondary pollutants in the air are **ozone (O_3)**, oxides of nitrogen (NO_x) and secondary PM.

The oxides of nitrogen/ozone system in troposphere is ruled by an equilibrium between groups of chemical reactions that control the nitrogen dioxide concentrations. Each reaction is activated depending on the situation, but always keeping the photostationary state. The three reactions that rule the equilibrium are as follows (Harrison, 2001; Monks, 2003):

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2} \qquad \mathbf{(1)}$$

$$\mathbf{NO_2 + UV}\ \text{(sunlight)} \rightarrow \mathbf{NO + O} \qquad \mathbf{(2)}$$

$$\mathbf{O + O_2 \rightarrow O_3} \qquad \mathbf{(3)}$$

Reaction 1 acts in presence of enough ozone to convert all nitric oxide to nitrogen dioxide Reaction 2 only is effective on sunshine and the nitrogen dioxide breaks down as a result of absorption of sunlight to form nitric oxide (NO) and an oxygen atom (O), which reacts with an oxygen molecule (O_2) to re-form ozone (O_3) in reaction 3.

This photostationary state could be altered in presence of bright sunshine and chemically reactive hydrocarbons. In polluted big cities, there is an abundance of more reactive hydrocarbons arising from anthropogenic emissions. This situation is common in more polluted atmospheres outside big cities, as Los Angeles, Mexico city or conurbations of Western Europe, in which ozone forms and is transported over long distances. In this situation, oxidation of the hydrocarbons can lead to the formation of highly reactive peroxy radicals that allow the reaction as follows:

$$\mathbf{NO + RO_2}\ \text{(alkyl peroxide)} \rightarrow \mathbf{NO_2 + RO} \qquad \mathbf{(4)}$$

In reaction 4, peroxy radicals react with nitric oxide and oxidize it to nitrogen dioxide. This is an important fact, because the nitric oxide could be converted to nitrogen dioxide without consuming an ozone molecule. Therefore, the equilibrium of the photostationary state is altered when reaction 4 is added to reactions 1−3, as mentioned above, and high concentrations of ozone can be reached as long as peroxy radicals are present in bright sunshine conditions.

D.2.1 Ozone (O3)

- **Definition and principal sources**

Ozone is a colourless gas with a pungent smell. It is a natural component of our air, existing in the upper atmosphere, where it filters out dangerous ultraviolet radiation. Tropospheric ozone should not be confused with the ozone layer in the upper atmosphere. This air pollutant can affect human health and damage the environment.

Tropospheric ozone is formed by the reaction with sunlight (photochemical reaction) of pollutants such as NO_x from vehicle and industry emissions, and VOCs emitted into the atmosphere from automotive exhaust, solvents and industry. These compounds undergo photochemical reactions in the presence of sunlight, producing ozone along with a variety of other compounds (reactions 1−4). Ozone formed in this manner travels long distances and causes plant injury, especially in the summer season, when the highest levels of ozone pollution occur during periods of hot and sunny weather. Because of the formation time of O_3 from NO_2

and translocation, ozone concentrations are higher in suburban and rural areas as compared to the urban areas (Tiwari, Agrawal, & Marshall, 2006).

The WHO's guideline values for O_3 suggested by the 2005 revision are:

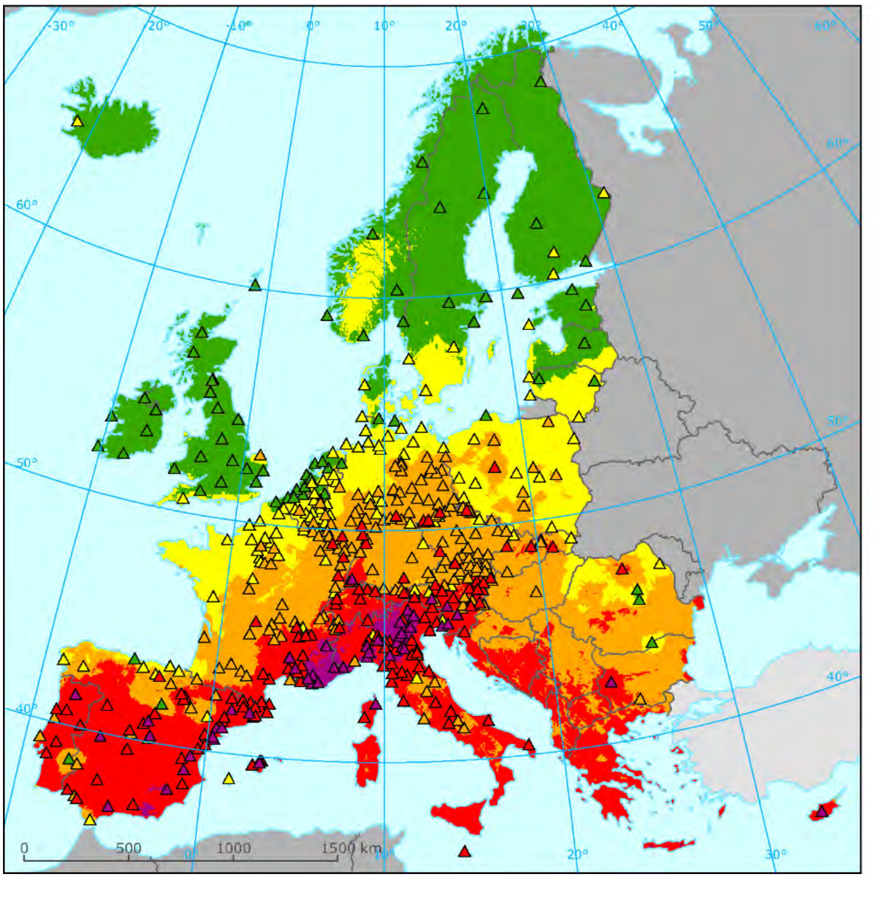
Limit	Duration
100 µg/m^3	8-hour mean

Table 7. *Guideline values for O_3 suggested by WHO (2006)*

The current EU-target value for ozone is 120 microgram O_3/m^3 as daily maximum of 8-hour mean, not to be exceeded more than 25 days per calendar year, averaged over three years and to be achieved where possible by 2010.

➢ Health effects

It is currently one of the air pollutants of most concern in Europe and North America. The pollutant produces breathing problems, trigger asthma and cause lung diseases. Different studies have reported that the daily mortality rises by 0.3% and that for heart diseases by 0.4%, per 10 µg/m^3 increase in ozone exposure (HEI, 2010).



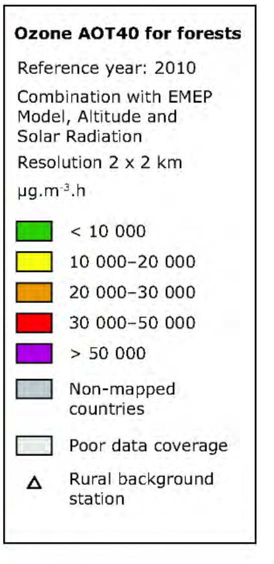


Figure 13: *Ozone AOT40 for forest in Europe (2010) Source: [EEA-AirBase v.8 (EEA, 2014)]*

➢ Effects on vegetation

Its effect on plants was first observed in the Los Angeles area in 1944 (Heather, 2003).Ozone symptoms on broadleaved species appear as small flecks or stipples of yellowish/ brownish coloured or reddish tissue on the adaxial surface. Injury is not produced on the abaxial surface. Acute ozone injury to conifers often results in death of small areas of needle tissue, or in severe episodes, death of the entire needle. The less severe episodes are associated to chlorotic mottling with small patches of yellow or brown injured tissue alternate with green healthy patches of tissue (Günthardt-Goerg & Vollenweider, 2007). As with most pollutants, ozone may induce premature defoliation of older needles.

A detailed description of ozone and its effect on forest and vegetation is reported in the next chapter (Chapter 2). At this point, we are only going to mention the **target value** and **long-term objective value** for ozone (O_3) for the protection of vegetation that EU has set in the air quality directive (2008/EC/50). Both terms are based in the Ozone AOT40 values (also descripted in Chapter 3). The most recent values for ozone AOT40 for forest in Europe (2010) are displayed in Fig. 13.

The definitions for the AOT40, target value and long term objective value for ozone (O_3) are:

- **AOT40** (expressed in ($\mu g/m^3$) · hours) means the sum of the difference between hourly concentrations greater than 80 $\mu g/m^3$ (= 40 parts per billion) and 80 $\mu g/m^3$ over a given period using only the one-hour values measured between 8.00 and 20.00 Central European Time (CET) each day.
- **Target value:** the AOT40 should not exceed 18000 ($\mu g/m^3$) per hour in the period from 1 May to 31 July averaged over five years.
- **Long-term objective value:** the AOT40 should not exceed 6000 ($\mu g/m^3$) per hour in the period from 1 May to 31 July within a calendar year.

More information is provided in Annex VII of directive (2008/EC/50).

The map of the target value for the protection of vegetation in 2011 (Fig. 14) reflects that the impacts of the pollution in big cities are not only suffered by the citizen of the urban areas. These effects are also felt in remote areas. Rural settlements supply the cities in the demand of energy and resources such as water and food. On the other hand, they suffer from air pollution and wastewater emitted by the city. Some of these pollutants, such as the tropospheric ozone, have transboundary effects.

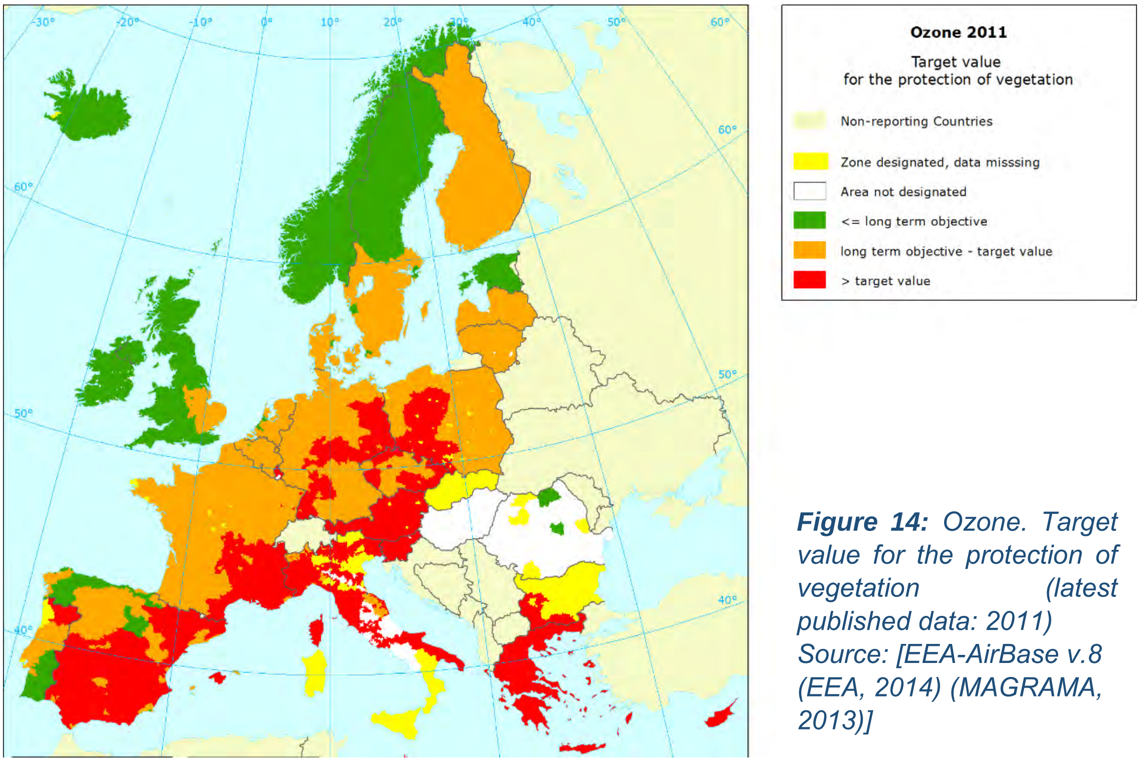


__Figure 14:__ Ozone. Target value for the protection of vegetation (latest published data: 2011) Source: [EEA-AirBase v.8 (EEA, 2014) (MAGRAMA, 2013)]

2.2.5 Air quality in Europe

The air quality has improved for some pollutants in Europe in the last years. The reduction has been successful for sulphur dioxide (SO_2) and carbon monoxide (CO) in the air environment as well as a slight reduction of NO_X. In addition, lead concentrations have decreased significantly with the introduction of unleaded petrol. However, exposure to particulate matter (PM) and ozone (O_3) remains as one of the most important environmental problems.

In Europe, around 75 % of the population lives in urban areas and this is projected to increase to about 80 % by 2020 (EEA, 2006). Thus, a significant proportion of Europe's urban population is exposed to air pollution concentrations exceeding the EU air-quality limits. Over the period 2001 to 2011, 13 to 63 % of the European population may have been exposed to concentrations of particulate matter (PM_{10}), ozone (O_3) or nitrogen dioxide (NO_2) above the EU air-quality limits or targets. This percentage is substantially lower in comparison with the World Health Organization's guidelines that are more stringent (Fig. 15). The proportion of population affected varies from year to year because of variability in emissions, pollution build-up and dispersion/deposition conditions, which depend mainly on weather processes.

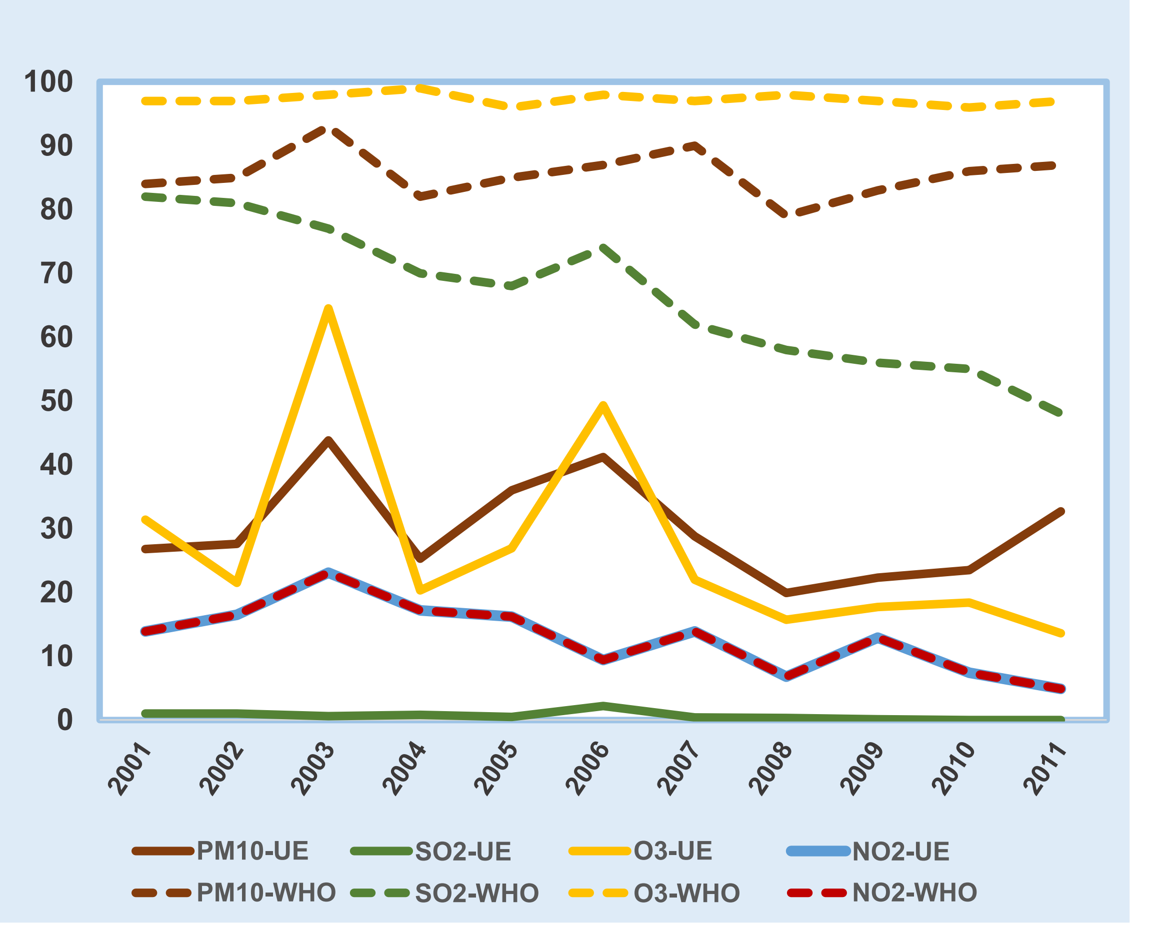


Figure 15: *Evolution of the percentage of the EU urban population exposed to air pollution exceeding EU limit/target values in comparison to WHO air quality guidelines during 2002-2011.*
Source: [(EEA, 2014; WHO, 2006)]

The spatial distribution of ozone exceedances throughout Europe is an important issue for the air quality. The locations of the exceedance is generally similar from year to year. The highest ozone levels are found in northern Italy and southern France and also in several locations around the Mediterranean area, such as Spain and Greece, but also in isolated locations in central and eastern Europe (Fig 13 and 14). Northern and north Western Europe are almost not affected. Thus, the fewest exceedances of the LTO use to be reported from Scandinavia, United Kingdom, Ireland and the Baltic states. The distribution of ozone exceedances can be illustrated by number of days with long-term objective (LTO) exceedance for the protection of human health during summer 2012 (Fig. 16). The values displayed are the number of calendar days on which at least one exceedance was observed by EU country.

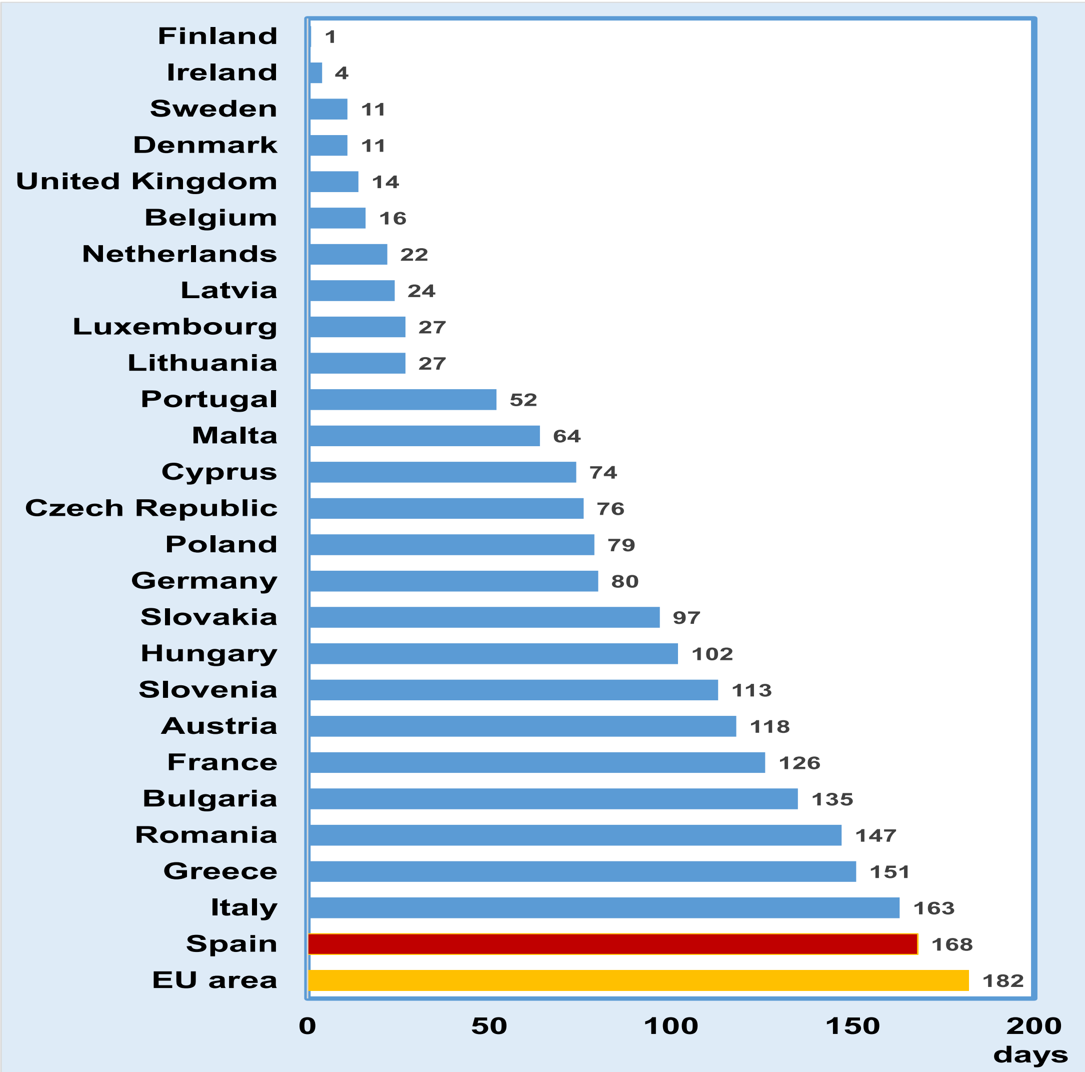


Figure 16: Number of days with long-term objective (LTO) exceedance for the protection of human health during summer 2012. The values are the number of calendar days on which at least one exceedance was observed by EU country. Source: [(EEA, 2013a)]

The reason that Spain tops the ranking in Fig. 16 could be attributed to a wider spatial area where the exceedances could occur and due to a higher number of stations measuring ozone levels (Spain:401; Italy: 287; France: 375; Greece:20: Bulgaria: 18; Romania: 89).

It is not surprising that there was only one single day without an LTO exceedance in European cities in summer 2012. According to EEA (2013a), with the exception of 2008, there have been exceedances of the LTO threshold every day of every summer since 2001, which it gives an idea of the magnitude of the ozone problem in Europe.

The annual average concentrations of PM_{10} in the European urban environment has not changed significantly over the last decade. The main source was road traffic, which in a second stage was followed by industrial activities and the use of fossil fuels for heating and power production. Regarding the spatial distribution of PM, the situation is worse, especially in the Mediterranean cities. Solar radiation, low rainfall, the design of cities (large buildings and narrow streets) or the lack of vegetation and greenery area are factors that contribute to a higher concentration of PM in those countries.

If the number days with exceedances of the three main air pollutants are shown for the largest cities of Europe, the number obtained give us evidences of the state of the air quality in each city (Table 8).

1	SOFIA	320	**34**	ANTWERP	81	**67**	HELSINKI	34
2	MILAN	272	**35**	LEIBNITZ	78	**68**	GLASGOW	33
3	KRAKOW	210	**36**	BYDGOSZCZ	69	**69**	MURCIA	33
4	MARSEILLE	200	**37**	SZCZECIN	68	**70**	BIELEFELD	32
5	PLOVDIV	189	**38**	TIMISOARA	64	**71**	NUREMBERG	30
6	**MADRID**	**188**	**39**	LUBLIN	63	**72**	GOTHENBURG	29
7	TURIN	174	**40**	STUTTGART	63	**73**	MALMO	28
8	WROCLAW	166	**41**	BREMEN	61	**74**	CORDOBA	27
9	ROME	157	**42**	STOCKHOLM	61	**75**	ZARAGOZA	27
10	WARSAW	152	**43**	HAMBURG	60	**76**	LEEDS	26
11	LONDON	150	**44**	LYON	60	**77**	ROTTERDAM	25
12	VARNA	150	**45**	BILBAO	59	**78**	BIRMINGHAM	24
13	BOLOGNA	141	**46**	BARCELONA	57	**79**	VALENCIA	24
14	PARIS	139	**47**	GENES	54	**80**	SHEFFIELD	20
15	NAPLES	137	**48**	AMSTERDAM	52	**81**	FÜRTH	19
16	KATOWICE	134	**49**	COPENHAGEN	52	**82**	DUBLIN	18
17	VIENNA	129	**50**	MUNICH	52	**83**	MALAGA	18
18	PALERMO	125	**51**	TOULOUSE	51	**84**	LAS PALMAS	18
19	BRATISLAVA	121	**52**	DUISBURG	50	**85**	VALLADOLID	17
20	LÓDZ	120	**53**	BARI	49	**86**	BRISTOL	15
21	THESSALONIKI	120	**54**	RIGA	49	**87**	BONN	14
22	BUDAPEST	115	**55**	THE HAGUE	44	**88**	UTRECHT	14
23	BRNO	114	**56**	KAUNAS	44	**89**	PALMA DE	13
24	FLORENCE	112	**57**	COLOGNE	43	**90**	LIVERPOOL	12
25	POZNAN	110	**58**	DORTMUND	42	**91**	LEICESTER	9
26	PRAGUE	96	**59**	DUSSELDORF	42	**92**	TALLINN	7
27	LISBON	92	**60**	DRESDEN	39	**93**	CARDIFF	4
28	ATHENS	90	**61**	ESSEN	39	**94**	MANCHESTER	4
29	NICE	90	**62**	VILNIUS	37	**95**	COVENTRY	3
30	SEVILLE	88	**63**	ALICANTE	35	**96**	CLUJ-NAPOCA	0
31	ZAGREB	87	**64**	AARHUS	35	**97**	EDINBURGH	0
32	BUCHAREST	86	**65**	FRANKFURT	35	**98**	BRADFORD	NC
33	BERLIN	83	**66**	GDANSK	35	**99**	HANOVER	NC
						100	BOCHUM	NC

Table 8: *Classification of largest cities of Europe in terms of number day with air quality exceedances of thresholds (PM_{10}), and/or nitrogen dioxide (NO_2) and/or ozone (O_3) in 2011. Source: [(EEA, 2014)]*

As in Fig. 16, it is important to remind that data measurements were analysed from a limited number of stations. According to the population of each city, there is a minimum number of monitoring stations as EU-legislation indicates. Thus, data give us an approximation of the air quality, but the number of stations could be not enough consistent for comparison. For example, Cluj-Napoca (Romania), the country's third largest city with 304,500 people, appears with no exceedances, but has only two stations for measuring air pollution, while Berlin has 48 stations. Berlin is ranked 65th with 83 days a year of exceeding levels for air pollution.

2.2.6 Air quality in Madrid

The situation to the end of 20th century and the first years of 21th century is summarized by daily clogged roads and traffic jams that increased the air pollution in the city, as in other European cities (Fig. 17).

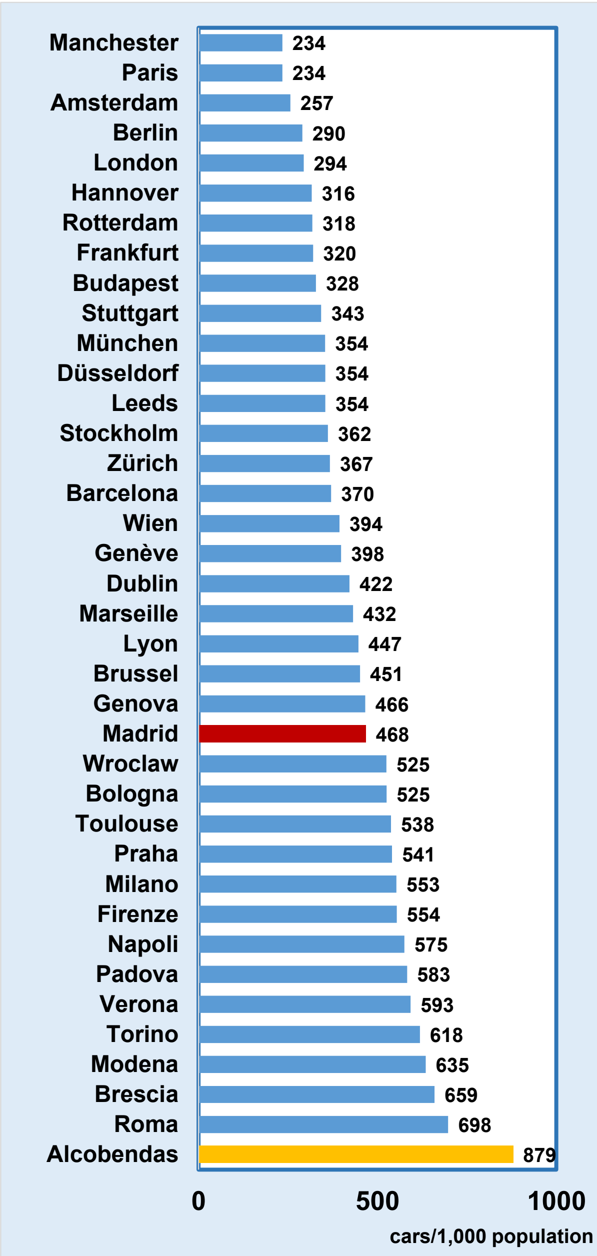


Figure 17: *Number of registered cars per 1,000 population in representative European cities. The Italian cities are topping Eurostat Motorisation Ranking in 2012. Madrid registered a medium/high rate. Although satellite cities such as Alcobendas are on the top of the list. Source of data: [Eurostat (EU, 2014)].*

Because of the crisis, traffic fell 15 percent between 2004 and 2012 and the 2.1 million vehicles in Madrid, decreased to 1.7 million vehicles. Of these, 80 percent were private cars. This pool has barely grown since 2005, because of the crisis and the ageing population. Young people and economic activity has been moving to the outskirts, easing up traffic downtown but clogging up the roads beyond the M-30 beltway. On any given working day, there are over 2.5 million commutes in Madrid, and seven out of 10 either start or end in the suburbs. It is also worth noting that while Madrid has 3,000 kilometres of streets, 85 percent of traffic is concentrated on one-third of them. As we mentioned in previous pages, all these pollutants also have a clear detrimental effect not only on vegetation, but also on the health of the population of Madrid. They can cause disturbances and respiratory irritation, if the effect is low or medium, while in the long-term, they can drive to hospital admissions or deaths in susceptible groups such as elderly or patients suffering respiratory difficulties (Linares & Díaz, 2010).

The basic elements to define the situation of the air quality in a given city, as far as air pollution is concerned, are: 1) the amount of pollutant emissions, 2) immission levels and 3) the measures adopted. Consequently, the air quality in Madrid during the studied period will be presented in three different sections: 1) Emissions of pollutants in the municipality of Madrid. 2) Levels of pollution in the atmosphere of Madrid and 3) Strategy adopted by mobility and action plans.

2.2.6.1 Emissions of pollutants in the municipality of Madrid

Madrid as well as other cities around the world are emitting into the atmosphere each year thousands of tons of pollutants. These emissions of pollutants could be estimated by an emission inventory of the municipality of Madrid (table 9). The basic objective of this catalogue was to provide complete information regarding coverage and polluting activities, consistent over time, as the transparent estimation procedure and the accurate comparison to the estimated values in the future. The list of investigated emission activities that potentially were emitting air pollutants corresponds to the SNAP nomenclature, which was harmonized by the Intergovernmental Panel Climate and the Organization for Economic Cooperation and Development (IPCC/OECD). Total emissions of main pollutants are shown in Fig.18.

Among all the activities performed in the city, the two largest contributors to increase the concentration of particulate pollutants are the combustion of petrol and diesel fuels by vehicles, along with the combustion of fossil fuels for heating in winter. The percentage of total energy consumption by the industry sector in Madrid region at the beginning of the twentyfirst century was only 20% of the total, while most of the energy consumed came from petroleum and derivative (more than 50%), especially gasoline, diesel and gas used for transportation and heating (Ayuntamiento de Madrid, 2004). The remaining percentage of consumed energy was related to the power consumption (electricity), which in turn has an additional percentage of consumption of fossil fuel by combustion to produce electric power.

The NO_x emissions were dominated clearly by the contribution of road transport, which shared around 77% of total emissions of this gas. As for SO_2, emissions were dominated by the non-industrial combustion (residential, commercial and institutional) with 68.5% of total emissions. The traffic road sector was still important by a 17.2% and the industrial combustion plants sector with 7.4%. As for NMVOC emissions, the main contributor was the use of solvents and other products with 52.9%, followed by road transport with 33.6%. With a contribution of between 2% and 5% non-combustion industrial processes, “Other sources and sinks (Nature)” and the processes of extraction and distribution of fossil fuels were located. The distribution of CH_4 emissions absolutely dominated the field of waste treatment and disposal of waste with 89.8% of the emissions of this pollutant. As for CO, the majority sector was the road transport with

91.4% of emissions, followed by non-industrial combustion with 5.4%. The main contributors for emissions of CO_2 were the road transport sector by 50.9% and non-industrial combustion by 33%. Emissions of N_2O were attributed to the traffic road sector with 45.9%, followed by non-industrial combustion with 26.5%. Finally, the distribution of NH_3 emissions were dominated by the sector of treatment and disposal of waste with 65.4% of emissions followed by road transport 21.1% and 2% to 8% by “Other sectors sources and sinks (Nature)”, Agriculture and the use of solvents.

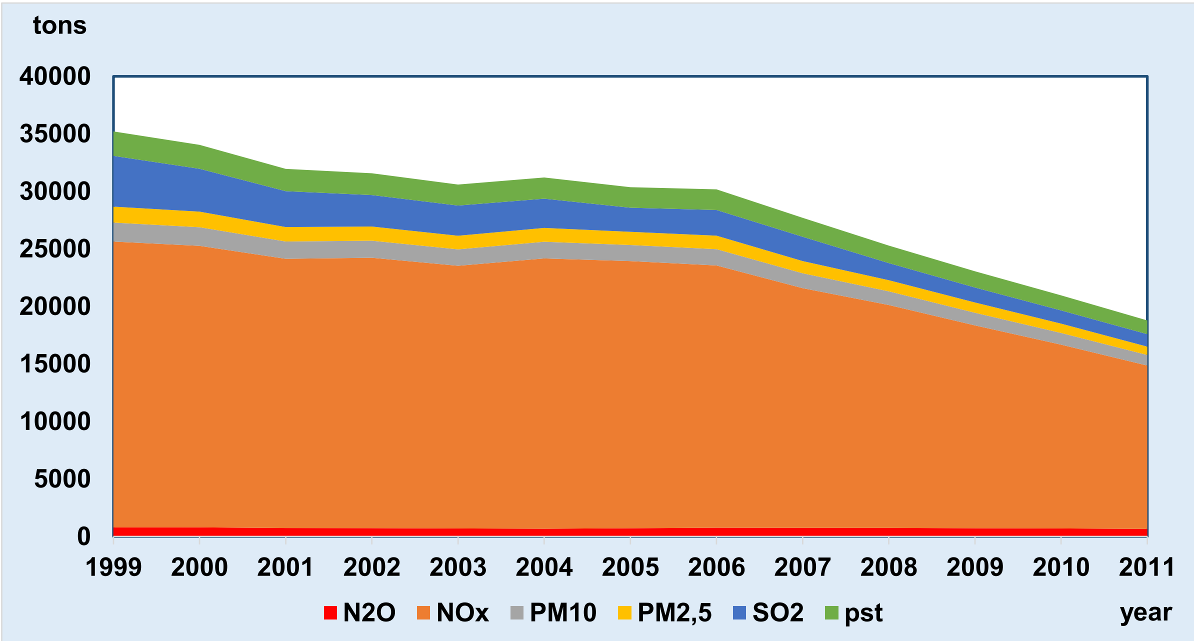


Figure 18: *Total emissions by main pollutant in Madrid during 1999-2011. Source: [(Ayuntamiento de Madrid, 2013a)]. Pst = Total solid particles*

Sectors at group level	Acidifiers, precursors of ozone and other greenhouse gases											Heavy metals									Particles		
	SO_x (t)	NO_x (t)	COVNM (t)	CH_4 (t)	CO (t)	CO_2 (kt)	N_2O (t)	NH_3 (t)	SF_6 (kg)	HFC (kg)	PFC (kg)	As (kg)	Cd (kg)	Cr (kg)	Cu (kg)	Hg (kg)	Ni (kg)	Pb (kg)	Se (kg)	Zn (kg)	$PM_{2.5}$ (t)	PM_{10} (t)	PST (t)
01 Combustion in energy production and conversion																							
02 Non-industrial combustion plants	2.164	1.910	204	1.100	5.066	2.766	242					85	11	64	85	24	128	178	11	71	159	289	645
03 Industrial combustion plants	234	1.662	165	46	160	587	45					2	2	4	2	2	103	4	2	(<)	11	14	17
04 Industrial processes without combustion	48	74	2.792	1	743	19						6	111	56	149	63	19	2.117		8.170	79	158	186
05 Extraction of fossil fuels and geothermal energy			1.469	3.190		(<)																	
06 Use of solvents and other products			29.780				132	52	567	84.942	564		134	525	6.295		539	2.614	13	57.493	1.376	1.591	5.895
07 Road Transport	545	22.585	18.908	653	86.198	4.268	420	421					2	8	277		11		2	163	58	60	63
08 Other modes of transport and mobile machinery	158	2.083	513	49	2.027	515	19	(<)				4	(<)	8	30	4	14	25	4	4.702	15	15	15
09 Treatment and elimination of waste	10	947	18	48.688	78	226	34	1.302															
10 Agriculture	(<)	2	45	150	18		23	71															
11 Other sources and sinks (nature)	(<)	58	2.390	326	1	-36	(<)	144															
TOTAL SECTORS	**3.160**	**29.321**	**56.283**	**54.203**	**94.291**	**8.343**	**914**	**1.990**	**567**	**84.942**	**564**	**97**	**260**	**665**	**6.838**	**92**	**814**	**4.938**	**31**	**70.599**	**1.697**	**2.127**	**6.822**

(<) Emission less than 0.5 tons or 500 tons emission in the case of CO_2

***Table 9**. Emissions inventory (absolute values) in 2002. Ayuntamiento de Madrid (2004). COVNM = non metallic volatile organic compounds.*

2.2.6.2 Levels of pollution in the atmosphere of Madrid

2.2.6.2.1 The air quality-monitoring network

The Madrid City Council had a stable Air Quality Monitoring Network during the period 1986-2009 that comprised up to 28 monitoring stations, which were the base to obtain the mean value of concentrations of air pollutants in the city.

	LOCATION	DISTRICT	LONGITUDE	LATITUDE	ALTITUDE (metres)
01	PASEO DE RECOLETOS	CENTRO	3°41'31,00"	40°25'21,36"	648
03	PL. DEL CARMEN	CENTRO	3°42'11,42"	40°25'09,15"	657
04	PL. DE ESPAÑA	MONCLOA	3°42'44,40"	40°25'26,37"	637
05	BARRIO DEL PILAR	FUENCARRAL	3°42'41,55"	40°28'41,62"	673
06	PL. DR. MARAÑÓN	CHAMBERÍ	3°41'27,00"	40°26'15,39"	669
07	PL. M. SALAMANCA	SALAMANCA	3°40'49,19"	40°25'47,81"	679
08	ESCUELAS AGUIRRE	SALAMANCA	3°40'56,35"	40°25'17,63"	672
09	PL. LUCA DE TENA	ARGANZUELA	3°41'36,35"	40°24'07,68"	605
10	CUATRO CAMINOS	CHAMBERÍ	3°42'25,66"	40°26'43,95"	699
11	AV. RAMÓN Y CAJAL	CHAMARTÍN	3°40'38,47"	40°27'05,30"	708
12	PL. MANUEL BECERRA	SALAMANCA	3°40'06,71"	40°25'43,70"	678
13	VALLECAS	PUENTE VALLECAS	3°39'05,48"	40°23'17,34"	600
14	PL. FDEZ. LADREDA	USERA	3°42'59,71"	40°23'06,28"	605
15	PLAZA DE CASTILLA	TETUÁN-CHAMARTÍN	3°41'19,29"	40°28'05,73"	729
16	ARTURO SORIA	CIUDAD LINEAL	3°38'21,24"	40°26'24,17"	698
18	GENERAL RICARDOS	CARABANCHEL	3°43'54,60"	40°23'41,20"	625
19	ALTO EXTREMADURA	LATINA	3°44'30,83"	40°24'28,29"	635
20	AV. DE MORATALAZ	MORATALAZ	3°38'43,03"	40°24'28,64"	685
21	ISAAC PERAL	MONCLOA	3°43'04,54"	40°26'24,51"	655
22	PASEO PONTONES	ARGANZUELA	3°42'46,56"	40°24'22,95"	625
23	C/ ALCALÁ (Final)	SAN BLAS	3°36'34,62"	40°26'55,44"	637
24	CASA DE CAMPO	MONCLOA	3°44'50,44"	40°25'09,68"	645
25	SANTA EUGENIA	VILLA VALLECAS	3°36'09,18"	40°22'44,48"	652
26	URB. EMBAJADA	BARAJAS	3°34'48,42"	40°27'33,56"	620
27	BARAJAS PUEBLO	BARAJAS	3°34'48,10"	40°28'36,94"	631
28	RETIRO	SALAMANCA	3°40'57,38"	40°24'52,68"	665

Table 10: *Location, district and altitude of the 28 remote air quality monitoring station. Source: [(Ayuntamiento de Madrid, 2009)]*

The quality of the air breathed in Madrid was, as in other cities, the result of pollutant emissions that reached the atmosphere and their diffusion according to atmospheric conditions. Both emissions and atmospheric conditions were not constant and, therefore, air pollution levels varied over time. The monitoring of these levels was performed by the municipality in real-time via remote control stations that configured the "air quality monitoring network". The host computers registered the data provided by the remote stations of the emission levels of a wide range of contaminants. Then, once these emission levels were logged, the values were evaluated by comparison with the limits established by law or with the target levels planned. Once the assessment of pollution levels were finished, they was evaluated regarding the possible sources of emission and the emitters of pollutants, according to the emission inventory [2.2.6.2] for any type of action to be truly effective.

The City of Madrid started the monitoring and control of air pollution in 1968. Since that date, the conditions that determined the quality of the city air have varied substantially. This reason led to changes in both, the consideration of the most important pollutants that concerned to the population, as well as the introduction of measures to address the problems raised in that period. Certainly, the continuous action plans, adaptation and measures of response undertaken by the city in the last decades produced significant improvements in air quality. Though the values reached in certain pollutants were extremely high in determined areas.

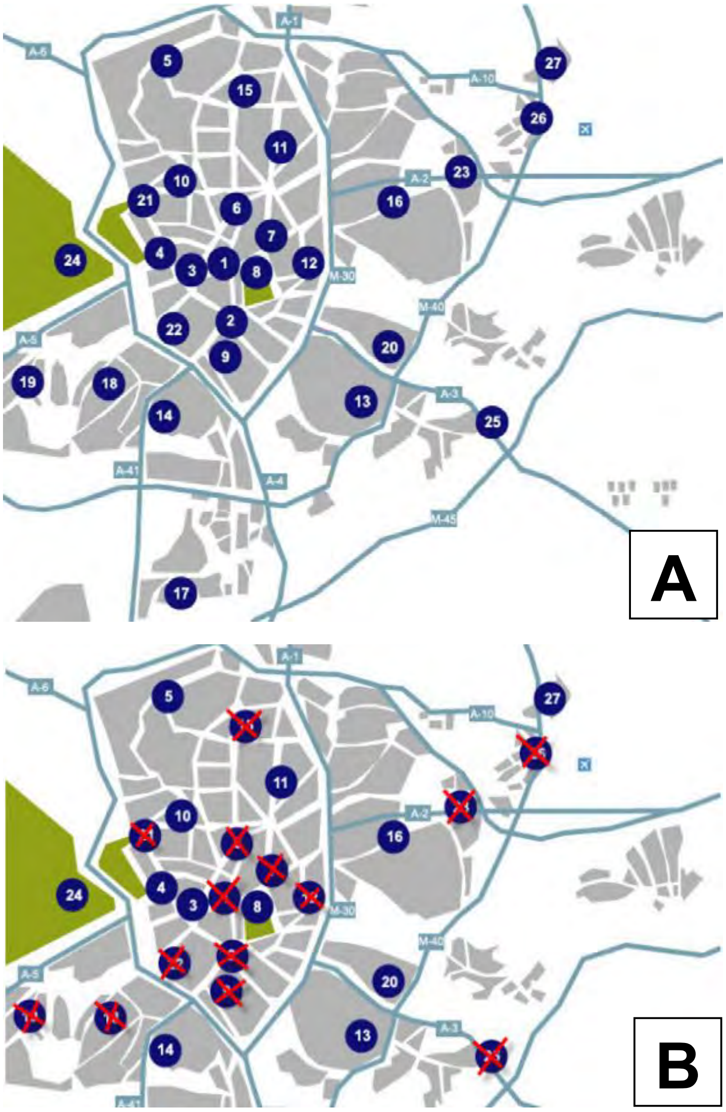


__Figure 19:__ A) Spatial distribution of air quality monitoring stations in Madrid until 2009. B) Stations affected in location or changes in the measurement of pollutants by the remodelling of the network in late 2009. Source: [(Ayuntamiento de Madrid, 2009, 2010)]

During 2009 actions were carried out on the adaptation of the monitoring network to the new European Directive 2008/50/EC on the air quality and cleaner air for Europe, which is the latest European standard regulation for the assessment of air quality. The Directive established the pollutants levels of those that were most relevant for their effects on human health and incorporated new parameters, such as $PM_{2.5}$ particles. The remodelling of the network began in late 2009 until early 2010 (Fig 19).

According to the Municipality, the new air quality monitoring network was "*an optimization of the resources available, a better representation of the population exposure to air pollution Madrid and facilitated the comparability with other European cities"*. They reported that the number and distribution of sampling points of the different parameters was consistent with the spatial variation and contribution of each to the problems of pollution. To design the new network several factors were taken into account: 1) population growth, 2) population distribution, 3) exposition to pollution, 4) new methodologies for evaluating existing and new pollutant parameters such as more fine particulate matter ($PM_{2.5}$) and 5) the need to balance the ratio of number of stations of different types: traffic, urban and suburban background, adjusting the ratios set by the directive (Ayuntamiento de Madrid, 2009, 2010).

In contrast, NGOs and ecological associations suggested that the reorganization was an excellent opportunity to disguise the continued disproportionate exceedances of ozone (O_3), nitrogen oxides (NO_x) and particulate matter (PM_{10}) above the air quality limits that have been exceeded for years (Fig. 20). In any case, the unchanged stations were not enough to be compared to the data of the previous years or carry out any kind of spatial interpolation. The remotion of the most significant pollution stations (those that had reported the highest peaks of NO_2 and PM_{10} in the last years) or the new configuration of the remaining stations to analyse others air pollutants, were the main reasons to our analyses in 2009. Moreover, significant stations situated near to heavy traffic roads (Stations 1 and 6) were maintained, but in different plots, a few hundred meters away from the original location (Fig. 19-B), suffering slightly less traffic intensity. Thus, the period of data that we have analysed in this study ended in late 2009, although specific comparisons, data from 2010 or 2011 were included to analyse decreasing of the pollutant concentrations.

2.2.6.2.2 Levels of pollution in the atmosphere of Madrid

Pollution is a direct result of gaseouss and particulate material emissions into the air derived from the anthropogenic activity (social and economic) in Madrid. Among air pollutants with different impact on the atmosphere and hence on the quality of life and madrilian ecosystems, are sulphur dioxide (SO_2), nitrogen oxides (NO_2, NOx), carbon monoxide (CO), ozone (O_3), the particulate material (including metals, inorganics side and a large amount of organic compounds) and a large number of volatile organic compounds (VOCs) the most important in Madrid. Special mention deserves the carbon dioxide (CO_2), as its effects are not related to the contamination of the air quality, but to the climate for their contribution to the greenhouse effect. Pollution levels in the city of Madrid are similar and even lower in some parameters, such as sulphur dioxide, carbon monoxide and lead concentrations (current concentrations below those of established regulations), to other large European cities. . Despite of these positive data, as in most Southern European cities with heavy traffic, serious problems persist in relation to nitrogen dioxide, particulate matter and tropospheric ozone, as shown previously in table 8 and Fig.20.

Tropospheric ozone increased its levels, especially in suburban of the city during the studied period, due to the high insolation levels and maintained emissions of its precursors (NOx and VOCs). Regarding the number of exceedance, the number of areas that exceed the target for health protection value was important. These exceedances and the spatial ozone distribution could be displayed in on-line geo-processed maps of the Iberian Peninsula (Fig. 21). In both images, the emission sources proceeded from the main cities (Madrid, Barcelona, Seville, Bilbao, Valencia, Malaga, Lisbon and Porto). In Fig 21-A, the ozone precursors generated the pollutant in Barcelona and Madrid suburban areas. The Northern winds in Madrid area and the Southeast wind in Barcelona area diffused the ozone in those directions. In Fig 21-B, the wind streams moved the pollutant to the South of Madrid region and to the North-west of Barcelona region. The reddish and yellowish colours show the magnitude of the dispersion. These kind of episodes are usual in the Mediterranean, Central and South European countries in summer.

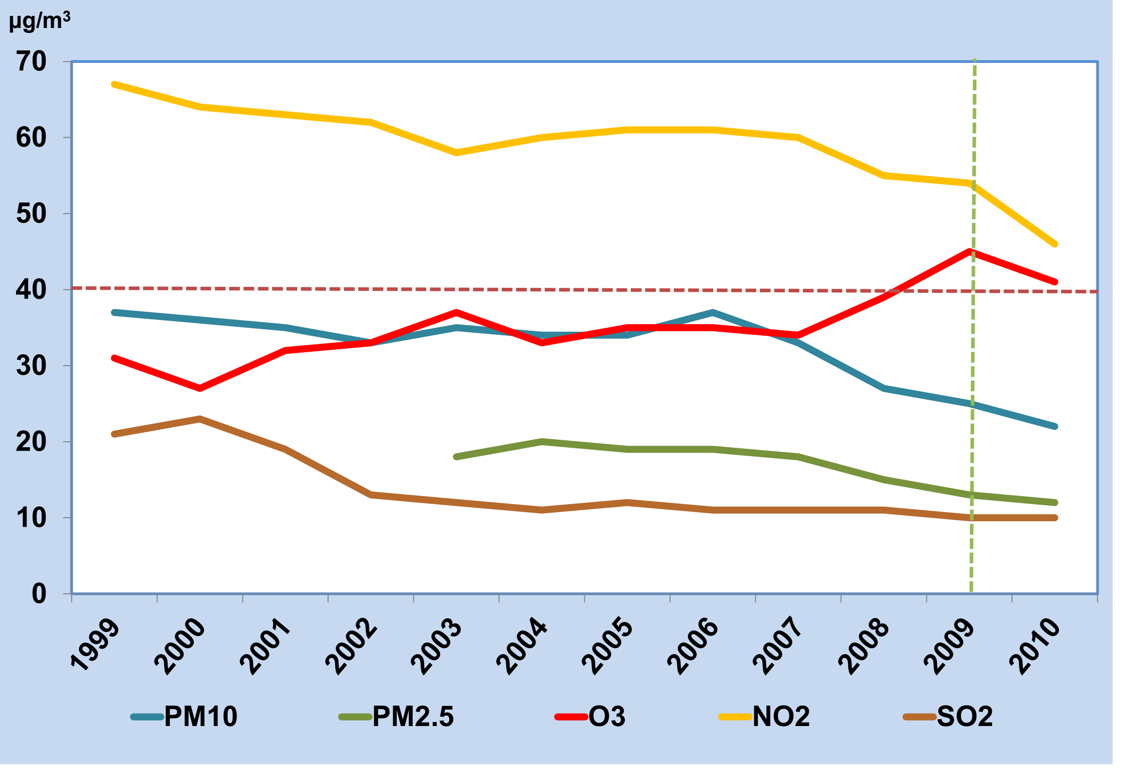


Figure 20: *Evolution of the most important air pollutants in the city of Madrid during 1999-2010. Red dot line= limit for annual PM_{10} and O_3 concentration (40 µm/m³). Green dot line= end of data recorded by the former network.*
Source: [(Ayuntamiento de Madrid, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011)]

The annual reports, as well as analyses, evaluations and conclusions regarding air quality in Madrid, varied according to the institution that had written the report (annual reports by local authorities or by NGOs and ecological associations). Official reports over the years tend to highlight the downward trend in **annual** pollution levels and satisfactory levels of quality of air that citizen breathe in Madrid. The opposite point of view, generally, comes from journalists, NGOs and environmental association that often emphasize **daily** exceedances of the thresholds by specif atmospheric pollutants that systematically are exceeded regarding current legislation. Besides, NGOs often complain about the methodology used in the location and measurement of pollutants by the municipality monitoring network. In particular, the labours of maintenance of the monitoring stations, generally during the days that network is experiencing the highest peaks of pollutants.

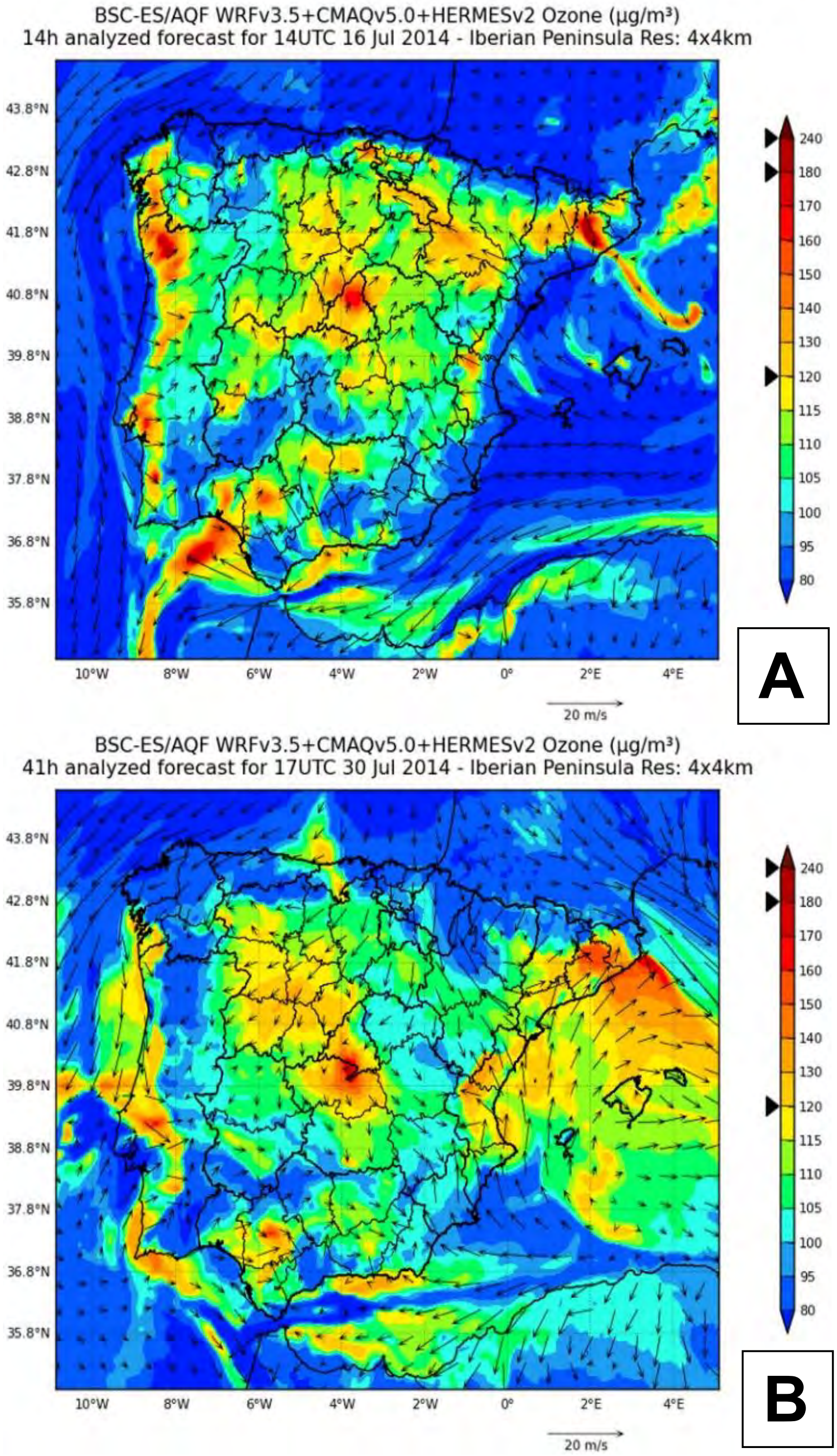


Figure 21 (a and b): *Images captured from on-line geo-processed maps of the ozone distribution in the Iberian Peninsula (resolution 4x4km) for two different episodes on 16 and 30 of July 2014). The maps are built in high spatial and temporal resolutions using a set of models: the HERMES emission model, WRF-ARW meteorological model, BSC-DREAM8b model, and CMAQ chemical transport model. Images CALIOPE model are operated by the Barcelona Supercomputing Centre (http://www.bsc.es/caliope/). Legend indicated the threshold limits for O_3.*
Source: [Images captures were obtained from the air quality forecast system for Spain (CALIOPE), developed at Earth Sciences Department of the Barcelona Supercomputing Centre - National Supercomputing Centre (BSC-CNS)].

2.2.6.2.3 Air pollution and climatological factors in Madrid

Air pollution problems in urban areas as Madrid are often aggravated by combinations of climatic and geographic factors, which act to concentrate pollutants in the city and prevent their dispersion and dilution into the atmosphere.

Madrid is occasionally affected by two climatic factors: 1) the temperature inversion and 2) the dust from Sahara Desert.

Figure 22: *Temperature inversion in Madrid*

1) **Temperature inversion**

Madrid is on a plain area, which is surrounded by mountain chains to the North-West of the region, which makes an inversion and trap the air in the city. Under normal conditions, the pollutants emitted as hot gases rise higher the more they come into contact with colder air masses (normal diffusion situation). In certain circumstances (e.g. a winter anticyclone in the evening), the temperature at an altitude of a few hundred metres is higher than the ground-level temperature. The temperature inversion stops atmospheric convection (which is normally present) and the upward movement of the pollutants is then arrested (Fig. 22), which can lead to the air becoming quieter and cloudy from the collection of dust and pollutants that are no longer able to be lifted from the surface. If the situation persists for two or three days without winds, the pollutants increase considerably and form a brownish haze (smog) that can cause respiratory problem.

A problem arises in Madrid, especially in autumn or winter when the traffic intensity is high and the anticyclone remains in the weather conditions. This kind of inversion effects occur frequently in other big cities with similar climatic and geographic factors such as Los Angeles, Milan, Mexico City, Bombay or Santiago de Chile. The Great Smog of 1952 in London, England, is one of the most serious examples of such an inversion. It was blamed for an estimated 11,000 to 12,000 deaths.

2) Dust outbreaks from Saharan dust storms episodes

These natural sources of dust were discussed previously in chapter [2.2.4 (b-3)] and Fig. 9.

They are common in southern Europe countries, due to the characteristic climatology and the lower percentage of vegetation cover. The increment of PM_{10} concentration in the air by dust has been considered by the current air quality legislation and those values are not included for calculations and European statistics.

3) Precipitation, temperature and wind

The Mediterranean weather with some continental influences gives a particular climatology to Madrid (Critchfield, 1983). The climate is characterized by drought and an increase of extreme temperatures. The atmospheric general circulation promotes clear differences between winter and summer seasons. Winters are cold and characterized by high air pressures. There is a moderate number of frost days and persistent temperature inversion situations are relatively common. When high pressures move to the South, they allow the entry of Atlantic depressions that are accompanied by rains. However, the usual influence of a thermal anticyclone in the Azores Island causes cold, dry weather and can extend its action to the Iberian Peninsula, consequently avoiding the possibility of rain. Summer is hot with temperatures in the lower areas of the basin above 35 °C for over a month. Weather is characterized by areas of high pressure and very low precipitation providing a warm and dry weather. However, low pressure in mountain areas of the Peninsula can lead to the development of storms (Cuadrat & Pita, 1997). The climate conditions provide a marked seasonality in the behaviour of precipitation, which usually occur in spring and autumn with stormy origin.

The main components of the prevailing winds in the region are the SW and NE component. During the day the SW winds are more frequent, while NE winds prevails by night. The corresponding SW winds average speed is higher than the NE winds. Therefore, SW winds facilitates the air circulation and air pollution disperse. The lower value of average wind speed in November and December (mean= 7 km/h) (Higueras, 1997) is characteristic. If these circumstances occur frequently in the region during the influence of the anticyclone, the poor ventilation in the atmosphere leads to temperature inversions and consequently to the accumulation of pollutants in the area and the development of air pollution episodes.

The wind speed at the street-level and the concentration of pollutants is affected by the urban design of the streets. Georgii (1970) studied the CO concentration as a function of wind speed and height above the streets. The higher the height of the buildings, the greater was the wind speed and the ventilation of this pollutant (Georgii, 1970).

Contrary to what than one might think, wind speed near ground level in front of high-rise buildings, placed among lower buildings can be increased by up to 300 percent, helping in diluting street-level air pollutants by the mixing of the air flowing above the buildings with polluted air at the ground level.

2.2.6.2.4 Air quality legislation

The analyses presented in this study regarding the data recorded in the air quality-monitoring network, took into account the legislation that currently was applied for each period:

- **Royal Decree 717/1987** of May, 27th, marks the annual limit value for nitrogen dioxide for the protection of human health (**in force until 1 January 2010**)
- **Royal Decree 1073/2002** of October 18th. Set limit values and, in some cases, alert for pollutants: sulphur dioxide (SO_2), particulate matter (PM_{10}), nitrogen dioxide and oxides (NO_x, NO_2), carbon monoxide (CO), benzene (C_6H_6) and lead (Pb).
- **Royal Decree 1796/2003** of December 26th. Set target values, information thresholds and alert for ozone.
- **Royal Decree 812/2007,** June 22th on the evaluation and management of ambient air quality in relation to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons
- **Directive 2008/50/EC** of the European Parliament and Council of 21th of May 2008 on ambient air quality and cleaner air for Europe.

- The Directive 2008/50/EC, together with the so-called fourth daughter directive was transposed into Spanish law by **Royal Decree 102/2011** only on the improvement of air quality.

2.2.6.2.5 Pollen and pollution synergy

In the next pages, we will talk about the advantages of urban trees and their role of air pollution amelioration, but for a part of the emission of VOCs vegetation is also a source of air quality problems, regarding the pollen.

Air pollution has a double effect on respiratory problems. Aside to the worsening of breathing symptoms due to contaminating particles, several studies have shown an increased aggressivity of pollen. Thus, allergic reactions are exacerbated by air pollution (Behrendt *et al.*, 1997; Knox *et al.*, 1997). Ozone, for example, can damage the mucosa of the respiratory system directly and alter their permeability, such that pollen proteins induce more damage (Fauroux *et al.*, 2000). It also happens with the particles of diesel to increase inflammation allergic disease.

Air pollution also explains more allergy prevalence in urban areas, where pollens become more aggressive. Pollutants modify the way that proteins of pollen genes are expressed, intensify their action, and make them more aggressive. This reason also explains the increase of asthma and allergic diseases that has occurred in recent years. The last reports show how the most polluted regions are associated to pollen that are more aggressive. Respiratory allergies have doubled in the last 20 years in industrialized countries (ANSES, 2014).

Air pollutants can also affect pollen grains and leverage the potential allergenicity. Studies have detected traces of pollen particles emitted by motor transport. By entering into contact with a chemical pollutant, the wall of the pollen grain deforms and eventually rupture, releasing tiny fragments called pollen allergens, which is then discharged into the air. Or allergens have a size that allows them to enter the respiratory system more deeply than pollen grains (ANSES, 2014).

Air pollutants that promote climate change indirectly influence the production of pollen. The starting date of pollination of many plant species is earlier, resulting in a lengthening of the average pollination of a fortnight.

2.2.6.3 Strategy, action plans and mobility plans adopted by the Municipality. Current situation

The results obtained from the air monitoring of air pollution in Madrid over the last 45 years allowed to perform actions that sought to reduce the progressive deterioration in the air quality and in the urban environment. The actions performed did not produce an abrupt and substantial decrease in the concentrations of pollutants in the air of Madrid, but, at least, helped to ameliorate the growing trend of emissions and consequently, avoid the effects of the most harmful pollutants.

These measures were diverse, according to the detection and information of atmospheric alert situations and the incorporation of environmental considerations in urban planning, to avoid the problems caused by improper location of activities and infrastructures that in the long term might condition the quality of life of millions of inhabitants in Madrid.

Examples of the most important actions were the ***First and Second Atmospheric Plans (1982-89) and (1990-2002)***:

Over the 1970s, the average air pollution levels in Madrid were reduced substantially and usually the number of the exceedances of air quality limits were acceptable to the first limits established by the Spanish legislation in those days (Decree 833/1975). However, high pollution episodes were registered under certain weather conditions, such as the temperature inversions that could lead to undesirable periods of short duration, but with quite high pollution. In order to limit those occasional situations, it was necessary to act continuously and systematically. In order to structure the actions to this aim, the ***first air quality plan for the improvement of pollution*** was developed during 1982-1989.

The plan included the preparation of a first inventory of emissions, campaigns of quality control of solid fuel sulphur content, an update of the municipal ordinances regarding to environmental issues (Ordinance for the General Protection of the Urban Environment) and campaigns for periodical revisions of diesel engines. The most effective actions during this plan were the campaign to control the conditions and operation of heat generators for domestic central heating. The first results of this campaign showed a very poor maintenance and low performance of these installations, which drove to launch a voluntarily plan to renew central heating, that consisted in a series of economic contributions by the municipality for the transformation of coal heating generators to other cleaner and environmental friendly fuels (Fig. 23).

Figure 23: *Old posters from 1980s advertising the Air quality plans and the change into environmental friendly central heating boilers. Source: [Ayuntamiento de Madrid].*

The results of these measures were visible in the 1980s, by the decrease achieved in the annual mean levels of pollutants like sulphur dioxide, which years ago had been the most serious problem. However, these levels become to exceed the limits established by the new current legislation in those days (Royal Decree 1613/1985). In particular, when weather conditions in the winter favoured the high concentrations of pollutants and were trapped to ground level by temperature inversions. Therefore, a **second plan** was developed to avoid this situation. The *Second Plan* (between 1990 and 2002) consisted in a grant programme to facilitate and incentivize the voluntary transformation of these old, inefficient and highly polluting generators for heating and hot water in new ones which were incorporating cleaner forms of energy. The plan included the collaboration of the producers or suppliers of energy devices by agreements signed between the companies and the Municipality.

Under these municipal grants, 5,783 existing coal facilities were renewed from 1990 to 2002. The quantification of the variations in fuel consumption (1990-2002) by replacing coal boilers was -204.869 tons of coal, meanwhile the SO_2 emissions decreased in -3,036 tons during that period (Ayuntamiento de Madrid, 2004).

2.2.6.4.1 Target for the next years

After the previous plans, there were other plans, such as “Plan of the City of Madrid 2006-2010”, “Blue Plan for the Region of Madrid 2006-2012” and, the last one, which was adopted on April 26, 2012 by the Municipality of Madrid: the “Air Quality Plan of the City of Madrid 2011-2015”.

The last mentioned plans have provided poor results according to the Decision of the EU Commission to the Kingdom of Spain and caused the rejection of the extension of the deadline to reach the annual limit value for NO_2 and daily exceedances. The EU committee put in doubt the achievements of the pollution limits for the next years and told to include relevant measures to reduce pollution in the most stringent air quality plans in Madrid. It therefore denied the extension request submitted by the city of Madrid (Comisión Europea, 2013), after the continuous exceedances since 2004. The Commission could take the case to the Court of Justice of the European Union. This process should lead to the imposition of a fine on the Spanish State and may impose a penalty for each year of noncompliance with the laws of air quality since the first year that fulfilling of NO_2 limit value is mandatory (2010).

Under this situation, the new “Air Quality Plan of the City of Madrid 2011-2015” propose a series of environmental targets for the Municipality of Madrid that aim to reduce the current 29 percent of commutes in private vehicles to 22 percent over the next five years by encouraging people to use public transport and bicycles and to travel on foot. Another target is to comply with the European Union’s pollution limits that as we have seen, were not fulfilled.

Authorities try to push gradually cars out of the city centre, favouring pedestrians, bicycles and public transport. These measures should be supported by the use of public transport. The city’s public transport system carries three million passengers a day, 40 percent of whom ride buses. Since 2004, however, there has been a nine percent drop in passengers, mostly because of the crisis. The high increment of fares has contributed too. Thus, the number of user have decreased in the last years by -5.5%, -7.2% and -3.1% in 2012, 2013 and 2014 respectively, according to metropolitan public transportation data of the Passenger Transport Statistics (INE, 2014).

The current measures in Madrid are proposed to deter drivers by the creation of new restricted-access areas where only residents are allowed to enter with their cars or to increase pedestrian-only areas by 25 percent.

2.2.7 Air pollution and the impact on water and soil in Madrid

One of the direct consequences of the air pollution in the air is the deposition of some of these harmful particles. Deposition in the city occurs mainly on plants, buildings and the soils surface. The mechanics of deposition of particles on natural surfaces is associated to three processes: sedimentation under the influence of gravity, impaction under the influence of eddy currents, and deposition under the influence of precipitation.

Soils are a source of dust but the major absorbent of siliceous particulate matter in air too. Heavy metal and other pollutant aerosols are absorbed and rapidly rendered unavailable to plants in the upper soil layer. This best plant availability depends on the soil pH and is for Pb in the range of pH = 3 to 4, for Cu of 5 and for Zn = Cd of pH 6 (Kabata-Pendias, 2010). Roots can absorb a variable percentage of metals, depending on the metal binding to soil clay and organic matter, soil pH and roots assimilation properties.

The continuous deposition and other applications such fertilizer, recycled water or compost, may lead to toxic concentrations for urban trees. In general, the pollution of urban soils is due to the presence of heavy metals, while pesticide residues are found in high concentrations in the parks - the level of pesticides may be even higher in cities than in rural areas (Carey, 1979). Therefore, urban soils are the pool where a considerable percentage of the pollutants end. They are be an excellent indicator of accumulated pollution in the city over the time.

Soil pollution will be further detailed in Chapter IV, where the study case of the soils in Madrid will be analysed.

The quality of the water in the city is also affected. The rain wash part of the dry deposition from tree leaves and together with the wet deposition it is accumulated in the rainwater. Part of the pollutants can be washed away, channelled through a general system of drainage, and redistributed by the sewerage treatment stations to the plants. Part of this water is ameliorated by the primary and secondary treatment in recycling stations. Not always, a tertiary treatment is done due to costly conventional methods of removing heavy metal ions from wastewater. Moreover, in times of high rainfall the locks are just open, whereby rainwater and wastewater meet and pass directly into rivers without having been subjected to any treatment. The result of this procedure is reflected in certain areas of the rivers. Heavy metals in Spanish rivers (Ramos *et al.*, 1999) as well as other anthropogenic related pollutants such psychoactive pharmaceuticals were found in the discharge of sewage treatment plants in Madrid's metropolitan area and Madrid basin rivers (González Alonso *et al.*, 2010).

Nowadays the problem of the direct discharges due to heavy rain episodes is solved by the construction of “detention ponds” to store the water meanwhile the sewage treatment plants are busy. This recycled water is usually reused for cleaning the streets or for irrigation of parks and gardens, while the solid residues may be employed for the use of compost, provided with the corresponding analysis of maximum concentrations of heavy metals admitted.

The present study sought to analyse the quality of water used for irrigation of public parks in the case of recycled water would be employed. Unfortunately, despite the Arhus Convention obliges public authorities to give a full environmental information, it was impossible to have direct data on the quality of irrigation water for parks and gardens in Madrid. On the one hand, heavy metals are no variables in the analyses of irrigation water in parks according to the Spanish legislation, which is only limited to the concentration of oxygen dissolved in water and the presence of bacteria in the water. On the other hand, the concentration of heavy metals in recycled water is analysed periodically by companies that manage regenerated water in Madrid and made available this information to the public agency that manages the distribution and treatment of water in Madrid: the *Canal de Isabel II*. Unfortunately, this information was denied by this Agency directly (see responding letter to the request by the University). Similar requests were made to the City of Madrid and Government of the Community of Madrid. The results of these requests were not satisfactory. Some reports have been performed to study the influence of recycled water on the health of urban trees (C. Calderón Guerrero, Saiz de Omeñaca, & Aznar López, 2013), but the information is scarce.

Regarding the public information of urban soils in Madrid, the results were not different. In the 90s the contents of organic matter and 48 metal elements were analysed in about 1'800 sampling points on a regular grid covering the entire municipality of Madrid, with the exception of Monte del Pardo and Soto de Viñuelas. The objective was to know the real situation of soil pollution and serve as a basis for the developments of following monitories. To our knowledge, the results were never made public and their scientific dissemination was prevented, so it has not been possible to compare the previously existing results with those obtained in this study in Chapter IV.

Numerous studies have been developed over the years to compare the high degree of degradation of contaminated soil next to streets with high traffic intensity versus soils of urban parks concerning environmental pollution. This has been the classic way to describe the anthropic impact on the soils in the big city (Zukowska-Wieszczek, 1980).

Lead (Pb) has been the most common HM in air and soil in the last century, due to important Pb emissions registered by road traffic in the second half of the century. Other sources that contain Pb are paints and manufacturing industry (see chapter 4 for more details). As other HM, Pb could be found on leaves surface. After washing off, Pb is accumulated in soils and can induce injury in tree roots. Zinc (Zn), cadmium (Cd) or copper (Cu) have been commonly mentioned in the literature. At toxic concentration, they lead to chlorosis and necrosis along the leaf veins and the leaf rim. Other metals, e.g. Mercury (Hg) (Kabata-Pendias & Pendias, 1992) are extremely harmful.

Many studies have been performed for different heavy metals to determine the proportion stored in roots or translocated upward to leaves and fruits, but still the information of their effects on most common urban trees is scarce. The information that a small portion of heavy metals could be absorbed by leaves requires more investigation. **Biomonitoring** could be an interesting tool to increase this information about the percentage of heavy metals that is located on/in different plant parts.

2.3 Biomonitoring

Plant species which are more sensitive act as biological indicators of air pollution such as lichens (Cox, 2003).Trees can be used as both passive biomonitors and biomitigators in the urban environment to indicate the environmental quality and to attenuate the pollution level in a determinate site (Beckett, Freer-Smith, & Taylor, 1998).
Biomonitoring uses a combination of physical and chemical procedures to determie the presence of heavy metals in surface particles by washing off from harvested leaves. The collection of dried particulates after washing is facilitated by evaporation of washing solvents. These particles can be directly weighted or used for chemical analyses by different technics of spectrophotometry, X-ray fluorescence, etc.
The variability of the effectivity to remove the wax and particulates from leaf surface depending on the detergent and deionized water mixture employed is one of the objections for this method.

2.3.1 Diagnosis of air pollutant injury in plants

As we have seen in [2.2.2], the effects caused by air pollution in vegetation are varied. The knowledge of expected injuries and effects of air pollution on urban trees according to bibliography could be very helpful for biomonitoring and rough evaluation of air pollution on urban vegetation, but is not enough to provide scientifically ascertained diagnoses of a specific pollutant and its incidence on tree species. The symptoms could be different depending of the duration of the effect, the susceptibility of the species and subspecies or the environmental factor that could moderate or exacerbate the symptoms. Thus, this is a time-demanding task that requires of experience in different fields such as tree physiology and nutrition, ecology, entomology, phytopathology, urban silviculture, arboriculture, chemical analysis, GIS and climatology. Sometimes, the luck or coincidence are also important in fieldwork. The ozone visible symptoms observed in Chapter III were found, while analysing gas exchange in Holm oak leaves with an Infrared Gas exchange analyser.
Except for specialists, the list of candidates for the origin of symptoms in urban trees that could resemble those caused by air pollutants is large. They could be biotic agents such as mites, insects, fungi or bacteria/viruses, or they could be abiotic factors such as local winds,

temperature, light, water, nutrients, pesticides, etc. The cause of the symptom may be blamed on an individual agent, but sometimes the reason could be the combination of different factors. The investigation of the causes would need a complete compilation of geographical information such as pollutant sources, winds patterns and topography, associated to a report of the phytopathological and nutritional status, as well as the inventory and location of trees.

The whole information compiled would help to evaluate the results of the samples harvested during the biomonitoring and posteriorly processed and analysed in laboratory.

2.3.2 Biomonitoring airborne heavy metals and dust

In addition to potential phyto-toxicity of air pollutants, such as O_3, NO_x or PAN, urban trees are constantly exposed to airborne particles. They include inert dust from rocks in natural conditions or heavy metals, such as cadmium (Cd), copper (Cu), chrome (Cr), iron (Fe), lead (Pb), mercury (Hg), nickel (Ni) and Zinc (Zn), which are more related to anthropogenic activities. The particulates that urban trees capture can remain on their leaves and bark, be blown off or washed away from the leaves to the bark and finally accumulated in soils. A small percentage may enter leaves through stomata or by injuring the epidermal cells. This capability to collect airborne particles by trees has been employed for biomonitoring airborne heavy metals and dust (Manning & Feder, 1980).
Other plants such as mosses and lichens have been used frequently to biomonitor air pollutants. These lower plants are more accurate to estimate the content of heavy metals due to lack of roots to absorb heavy metals apart of air and precipitation. Unlike mosses and liquens, urban trees adsorb heavy metals from air as well as by roots from urban soils, which are a serious source of pollutants. Therefore, results have to be interpreted with care. On the other hand, urban trees are helpful to study air pollution without other environmental restrictions, which bias studies on liquens and mosses. Air pollutants could be monitored in a huge area of big cities and for long-term studies using urban trees.

2.3.3 Biomonitoring in the city

Biomonitoring in ambient conditions is a complex task due to the concurrence of multiple factors interacting between trees, pollutants and the surrounding environment. The combinations of all these factors could modify the tree response to specific pollutants. The main factors affecting the tree response to pollutants are:

1) Tree age and the maturity of the studied part of the tree (e.g. leaf generations)
2) Ambient conditions, such as air temperature, air relative humidity, soil moisture, soil characteristics, nutrients level, light and cloud cover, wind speed and direction, etc.
3) Exposure period and concentration of the pollutant. Unlike other pollutants sources produce acute exposure in certain situations. The urban environment uses to be characterized by a low/medium pollutant concentrations for long exposure periods that is exacerbated by repeated short acute episodes during the year, leading to chronic exposure for citizens, plants and buildings.
4) The genetic predisposition or resistance in certain species, which determines morphological and/or physiological responses after exceeding the pollutant concentration threshold during an exposure period

Figure 25: *Tree sampling of Horse chestnut leaves (Aesculus hippocastanum) in Retiro Park during summer.*

Figure 24: *Storage of cedar needles (Cedrus atlantica) in plastic bags during the biomonitoring at Plaza de España sampling site.*

2.4 Green spaces and urban trees

The accelerated urban expansion around the world is breaking down the boundaries between suburban and rural areas. The former farmlands are gradually integrating into the new spaces within the city. In this anthropic environment, green spaces and mainly urban trees, are often the only link of the population with nature. These urban habitats are also the only ones available for wildlife in cities.

Warren (1973) defined a **green space** as the land covered with some form of vegetation - grass, shrubs, or trees. The green spaces and urban trees in a large city have a number of specific features, but perhaps the most determinant of all is precisely their status of "urban", which is clearly influenced by the urban environment and the needs of the population. The former natural ecosystem is modified and most often replaced by dense centres created by and for human being (Rublowsky, 1967), creating an urban ecosystem in which trees play a fundamental role.

An **urban tree** has a series of characteristics that differ from those in a forest stand. Under natural conditions, the limitations are defined by the characteristics of the forest site and the intraspecific competition for the nutrients, light and water. In the city, the problem is properly the site itself where the tree is planted. The presence of architectural barriers, as well as other elements of the city infrastructure such as walls, lights, distance to the road, pipes, etc. constrain the roots and stem development. Therefore, the typical tree parameters are modified in order to be adapted to the city conditions. These constraints cause injuries that make trees prone to disease and ultimately produce premature death of the urban tree.

Figure 26: View of a Japanese pagoda tree before pruning/felling. Photo source: [Martín Lorenzo & Calderón Guerrero]

Figure 27: View of a Japanese pagoda tree during pruning/felling. Photo source: [Martín Lorenzo & Calderón Guerrero]

2.4.1 Past and current situation of urban green spaces

2.4.1.1 Origins of the European public green areas

The presence of gardens and parks is linked to the history of man since biblical times. The Book of Genesis mentions Tigris and Euphrates as two of the four rivers bounding the Garden of Eden. Since those times, many civilizations have used the garden over the history, although the idea of parks and gardens as we know today could be linked to the earliest public park in the world: *La Alameda de Hércules* in Seville (Spain) that was built in 1574 (Albardonedo Freire, 2002). A few decades later, the first urban parks in French or English style were developed in major cities during the seventeenth and eighteenth century. A few examples could be:

- The *Jardin des Plantes,* the oldest garden in Paris created in 1626 as a royal botanical garden meant to cultivate herbs for medical purposes, which was designed and planted by Guy de La Brosse, the physician of Louis XIII. It was not open to the public until 1650.
- The *Englischer Garten* in Munich. This urban park was opened by the monarchy for public recreational use (Hannwacker, 1992)
- The *City Park* in Budapest. The park was property of the *Batthyány* family and become open to the public in the first decades of the 19th century.

From the mid-17th century, some royal gardens were opened for public use in Europe, at least for the high and mid-level society (Szilágyi, 2011). This necessity of green spaces was increasing in the urban population of the 18th and 19th centuries under the serious social conditions of urban expansion, increasing population and environmental pollution. The urban and industrial development during the eighteenth century concentrated the urban population in huge conglomerations that required of more open spaces in the urban environment. During this time, royal gardens and parks were opened and given as urban recreational open-air areas to the public society of the large industrialized and urbanised cities. Meanwhile, other parks such as Hyde Park, in London, were designed since the beginnings as a free and open to the public city park. After the 1930s, the original royal gardens could not meet the needs of the public; therefore, many cities constructed a number of new parks in the cities. In the last decades of 20th century, the necessity of green areas in big cities to find a direct contact with nature was a matter of vital importance. According to Sukopp and Werner (1989), more than 70% of the leisure time was spent on areas near the own residence. This need has developed a movement of people from the big cities to the suburbs to find a quieter environment with large open spaces. This change has led to the decline or stabilization of population in some big cities in West Europe and the United States. In spite of this, nowadays there is a lack of the green spaces in developed countries, which is hard to solve due to the difficulties to find available sites for new green spaces.

2.4.1.2 Current percentage of green spaces in Europe and the possibility of enlargement in core cities

In large cities where the urban development pressure is high, such as Madrid, it is difficult to create new small green spaces, because available surfaces usually tend to end up being built, unless is prevented by existing planning guidelines or legislation. In these situations, it would be mandatory at least to establish new green areas near the new urbanized areas. Thus, another important issue in the last decades has been the percentage of green spaces that should exist in a big city. As expected, the existing percentage is very poor in densely populated cities in Europe. This percentage was set according to the rules and development plans of each city. The current percentages are variable depending on the country (Fig. 28). The highest percentages of urban green areas are located in Central Europe, where values are exceeding 50% of green surface. Those countries such as Germany considered years ago by legislation that 50% of the surface should be the critical values of buildable area. Unfortunately, the current average percentage in the rest of Europe ranges between 10% and 30% of green space, displaying a clear predominance of red and orange circles in Southern and Western Europe.

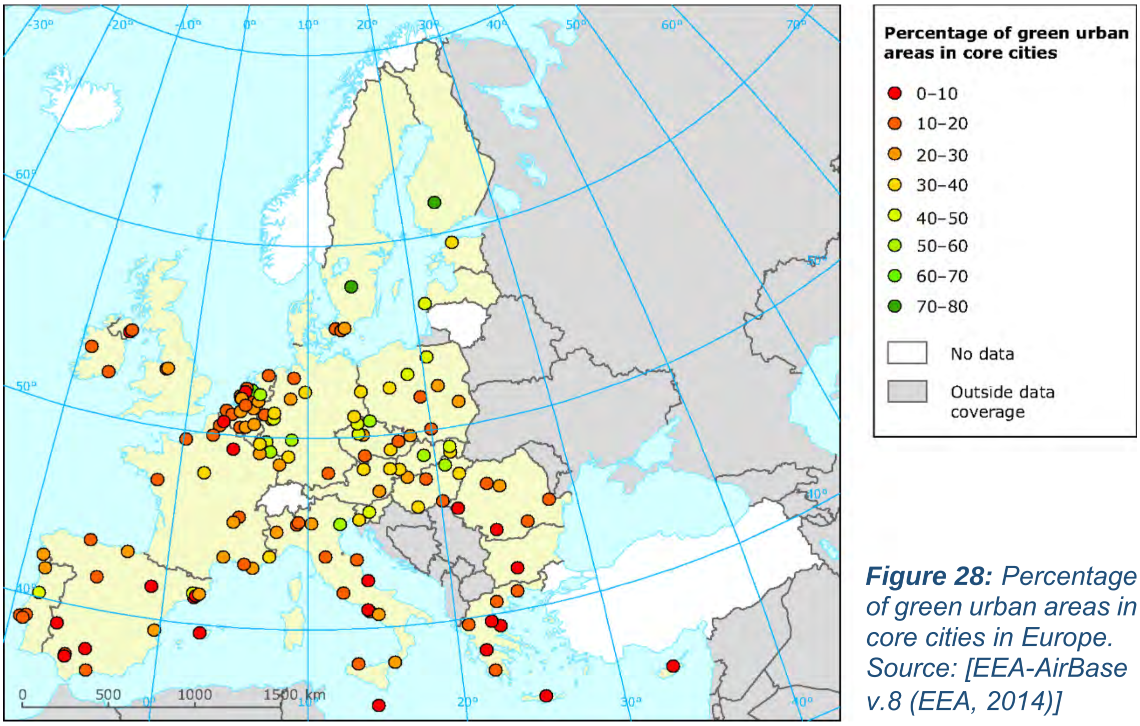


Figure 28: Percentage of green urban areas in core cities in Europe. Source: [EEA-AirBase v.8 (EEA, 2014)]

2.4.1.3 The anthropic pressure on peri-urban forests

Among the green spaces in large cities (street trees, peri-urban forests, parks and gardens), normally the forest parks are the ones in better conditions and usually offering the richest flora and fauna. Typically the environment is less modified, featuring better soils and drainage than those surrounded by streets and buildings (Sukopp, Blume, & Kunick, 1979). These better conditions could be affected in the forest edge areas next to roads or passageways areas, as is happens in the busiest areas of the peri-urban forest of *Casa de Campo* (Madrid). The air quality station located in the inner area of this urban forest reached the highest values of NO_2 concentration in the city of Madrid in certain hours of the night on weekends due to the nocturnal activities carried out and the traffic that it involved. Besides this nocturnal disturbance, high recreational use by pedestrians and families on weekends also affected natural regeneration of species and soil compaction (C. Calderón Guerrero & Rodriguez Barreal, 2007) (annexe IX). Several authors highlighted the importance to establish criteria to determine intensities of use and define greater protection areas. If possible, it is recommended to develop green corridors that would allow the interconnection of different green spaces, previously isolated (Palao Núñez & Calderón Guerrero, 2010) (annexe XIII).

2.4.2 Main characteristics of green spaces and urban trees in the city

After explaining the various relationships between the vegetation and other factors, both biotic (human, wildlife, etc.) and abiotic (air pollution), it is necessary to determine certain intrinsic characteristics of the trees themselves that are living in the cities to understand and to distinguish the possible effects of air pollution on urban trees.

2.4.2.1 Factors that may influence the selection of appropriate tree species

The health and development of urban species are conditioned by a series of factors regarding the maintenance, tree selection and environmental conditions that can be summarized as:

A) Maintenance:

- The species should be easy to maintain (low a labour-intensive maintenance).
- They should be low nutrient demanding and soil resistant species, due to the alteration of soil and vegetation cover by using compost and mulches, along with the elimination of spontaneous vegetation and the removal of litter, plant debris or pruning.
- The shrub species should assure an easy maintenance and facilitate mechanized tasks.

B) Species selection:

- There is a high percentage of exotic species that are chosen for their shape, flowering or appearance. The candidate species should comply with some of the above requirements.
- Trees are usually arranged in alignment, under squared disposition and should support pruning. Candidate species should be adapted to these conditions.
- The ornamental well-watered grass and the seasonal flower plants understorey in many parks and gardens will limit the number of species that do not support excessive watering.

C) Environmental conditions:

- The species should tolerate the excessive pressure that may be submitted by diverse circumstances (environmental and physiological stress, traumatic pruning, transplanting, compaction, paving and frequently works, construction, etc.).
- Generally, the percentage of built and paved surface increase, while the surface of the green areas is reduced as we move into the city. Oppositely, the isolation of these green areas in comparison to outer green areas is increased. Therefore, the pressure suffered by species of green areas in the city centre will be higher than for species in suburban green spaces.
- They may suffer high emission of pollutants from traffic (Fig. 31).

In general, the maintenance is focused on the aesthetics and mechanized tasks of the maintenance companies, which are often the same companies that have selected the species from their own nurseries. This type of design of parks and gardens is the usual trend since the second half of the twentieth century, where green areas with abundant grass and ornamental variety of exotic species dominated, eliminating in most cases the native species regrowth. Likewise, urbanization decreases both qualitatively and quantitatively native species and promotes their movement outside the urban area. In particular, it will affect the species that have special requirement (light, water, etc.). These conditions may favour a number of invasive species such as *Ailanthus altissima* and *Cupressus arizonica* that tend to spread successfully in competition with native species that are more sensitive to the pressure of the anthropic conditions.

It is recommended to select a group of candidate species for each stressful situation, such as the exposure to pollutants, pesticides or salts thrown in winter when it snows. On the other hand, if trees suffer a disease spread by pruning tools, it is expected that species with greater genetic variability would survive better than those propagated by vegetative reproduction.

The following characteristics should be verified with regard to the most appropriate species in the city:

- **Tree risk:** the fragility of the wood and the vulnerability to breakage in certain urban tree species could affect the stability of the stem and the branches. Consequently, this is a risk for pedestrians and vehicles.
- **Longevity**: the life expectancy of determinate urban tree species is shorter than others. I will be necessary to study of the costs of maintenance and renovation for the species selected.
- **Growth rate:** the fast-growing species are often more vulnerable to breakage. The presence of this kind of species in narrow streets ensure successive pruning operations to prevent branches intercept with buildings and vehicles, which will end up in shortening the life of the tree.
- **Resistance to pests and diseases**: The high-sensitive species to these agents should be discarded and the maintenance costs to infectious agents in vulnerable species considered.
- **Final size adult trees**: it is important to know the size of the aerial part and the root system, as well as the foliage and its adaptation to the conditions of physical space (Fig. 29).
- **Foliage Persistence**: the design of urban green spaces should consider aspects like the shadow and the radiation, which it could be beneficial in particular periods
- **Allergenic species**: it is a key consideration in the selection criteria of species for urban trees. The allergenic nature of many of them should be reviewed to avoid respiratory problems with species such as plane tree (Gutiérrez, Sabariego, & Cervigón, 2008)

***Figure 29**: London plane tree shaped and pruned to allow traffic of double-decker buses in London. Photo Source: [Calderón Guerrero]*

In addition to technical considerations about the characteristics of the most favourable urban tree species for each site, educational campaigns are needed to integrate population and tree benefits

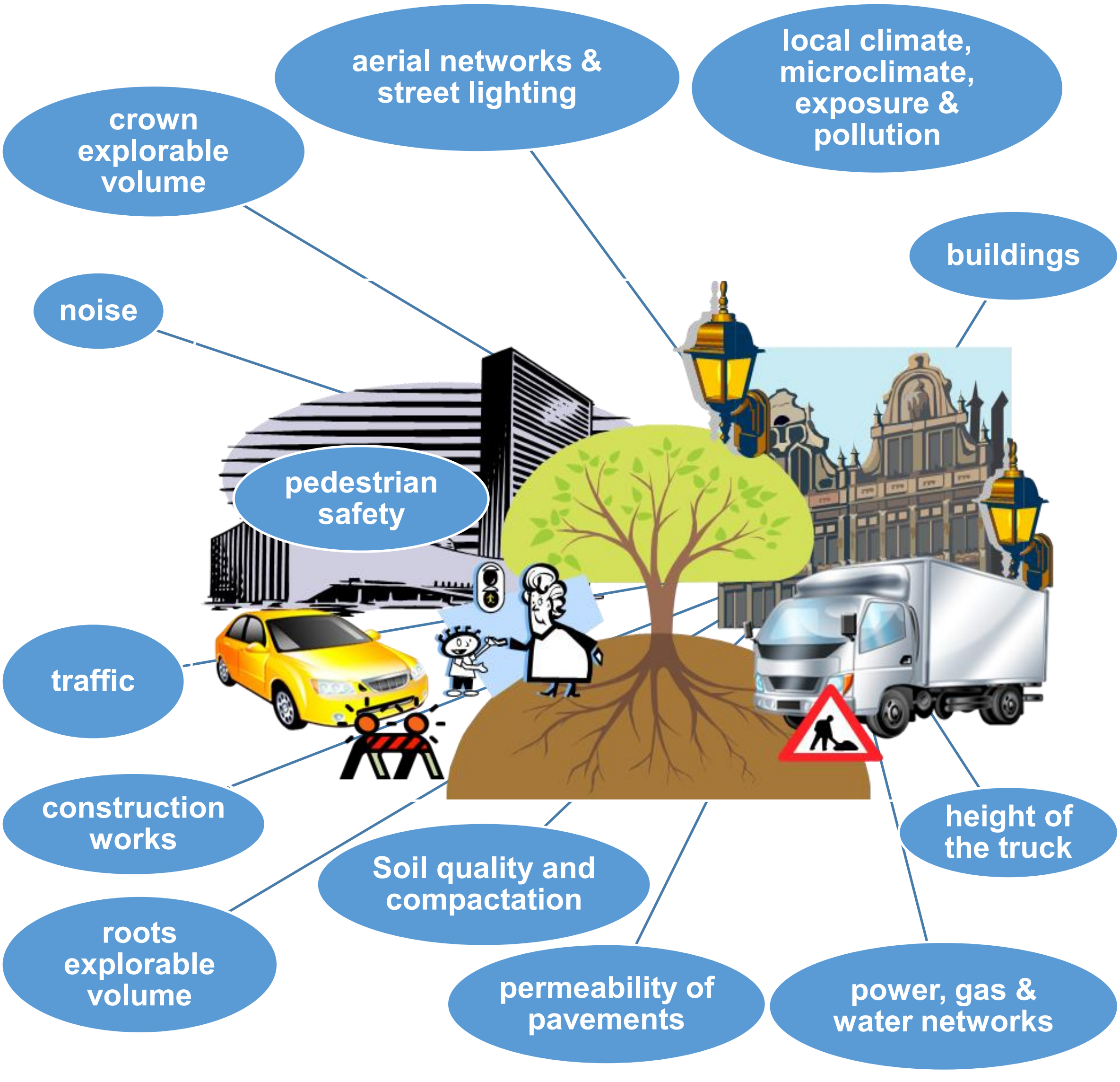


Figure 30: *Problems faced by urban trees in big cities*

2.4.2.2 Problems faced by urban trees in the big city

The collection of problems faced by the urban tree could be summarized in the Fig. 30 and in the followings points:

- The powder adheres and deposited on the leave surface of plants could produce a lower efficiency of the photosynthetic activity.
- Gaseous pollutants such as NO_2, SO_2, O_3 or PAN may be up taken into the leaf through the stomata, also affecting the physiology of the plant.
- The soil compaction and the numerous obstacles in the rm of underground pipelines, ditches or underground constructions decrease the concentration of oxygen available in the soil.

- The development and growth of the roots will be also affected by the small space available (especially in street trees)
- The presence of mycorrhizae may be lower than usual in forest areas.
- The increased presence of anti-icing salts in the soils of the edges of roads prevent the proper absorption of nutrients by the urban trees.
- Nutrient deficiency.
- Drought.
- Removal of leaves after senescence and other debris from vegetation, such as branches or fruits, decrease the concentration of nutrient available in the soil for the plants and harm the detritivorous fauna
- The excessive use of fertilizers and pesticides affect the balance of nutrients and natural pest control.
- Mechanical damage by road traffic, construction and vandalism.
- The lack of diversity in the urban tree species.

Figure 31: *Smog over Casa de Campo urban forest during a temperature inversion in winter in Madrid.*

Variability and exotic species

Despite the increase of diversity regarding tree species in the last years, the lack of species variability is a weakness against diseases, due to the fact that most of the urban trees belong to a few species (in the case of Madrid, *Platanus orientalis var. acerifolia* and *Ulmus pumila* represent more than 50% of urban trees in Madrid). On the other hand, the lack of variability simplifies maintenance. The urban tree species selection should be proposed for each area of the city. Species should be selected with the criteria of representativeness of the native flora. At a first glance, these species should be better adapted to the natural environmental conditions.

The flora of the parks and gardens of large cities is characterized by the high percentage of exotic species. These species are chosen according ornamental criteria (shape, colour, etc.), without taking into account other criteria. Consequently, the number of species selected when designing a park is reduced to a number of exotic species, without taking into account most of the time the use of native species.

The urban forest maintain the native vegetation generally, but sometimes the species that are easier to handle and care are favoured.

2.4.3 Green spaces in Madrid

Madrid is a large city with a significant number of trees. This large arboreal heritage has not only aesthetic purposes, but also a valuable contribution to the fight against air pollution by acting as green lung of the city. As we will see in [1.4.4], the madrilian green spaces produce many benefits to the urban environment. The vegetation acts as a buffer for noise and air pollution from traffic, absorbs CO_2, creates a special microclimate around the site due to evaporation of the water previously extracted from the soil, provides oxygen, brings variety and colour to the city, and is a refuge for many animal species. Trees also restore the mental balance of the citizens and improve emotional health from stress, which is very important in the day-to-day life in cities like Madrid.

The green spaces of public maintenance in Madrid could be categorised by three main groups:

- Street trees [2.4.3.3]
- Public parks and gardens [2.4.3.4]
- Urban and peri-urban forests [2.4.3.4]

The maintenance [2.4.3.2] corresponds to the Park service of the municipality of Madrid and the *National Heritage* service; both entities are in charge of official public maintenance, although the municipal maintenance is carried out by private companies by appointment of the Council. An adequate management of urban trees would require of the most detailed information from inventories [2.4.3.1] and a good coordination between the respective departments.

2.4.3.1 Urban tree data and inventories

Historically, it has always been said in the media that "Madrid is the second city in the world with more trees after Tokyo" (this sentence [in Spanish] could be found 44 times by Google search), but this information has been contrasted barely. Even today, there is not a precise number of trees in Casa de Campo urban forest. In the same way, the tree inventory for some city parks, such as *Fuente del Berro* Park still was missing a few year ago. Thus, it was difficult to specify the total amount of urban trees by the media a few years ago, when information was still scarce and there was a lack of exact data. The precise number of total public trees in the city of Madrid will be given in Chapter IV and annexes. Moreover, the exact location of each tree was necessary for the GIS (Geographic Information Systems) calculations, which resulted a very helpful tool for this study.

At the beginning of the 21th, the use of new tools for tree inventories, such as the GIS has facilitates the configuration of tree databases containing the main details of each tree towards their maintenance and management (Fig. 32). However, the official information from the Municipality office was not yet completed during the development of this study and required an *ad hoc* solution to solve the lack of information.

During this study, it was not possible to access to the information of the tree inventories of important historical parks such as *Parque de El Retiro* or *Parque Juan Carlos I*. The local heads of these historical park services (each historic park has its respective head) rejected to provide such information, despite of being available and provided to private companies that required it at the same time. Thus, an inventory of tree by tree for 5 months during 2005-06 was carried out in order to get the exact position and characteristics of each tree in Retiro and Juan Carlos I Parks. This information was essential to calculate the short distance to the closest traffic road for each tree (See Chapter IV).

Figure 32: Detail of the spatial location by GIS of each individual position of all urban trees (street trees of Moncloa district and in Parque del Oeste Public Park) in Madrid. Position of urban trees (green, orange and red colours). Data: [Calderón Guerrero]

The rest of inventories (except the aforementioned inventories of the two historic parks and the Casa de Campo urban forest) were graciously provided by the General Directorate of the Environmental Heritage at Madrid City Council (*Dirección General de Patrimonio Verde del Ayuntamiento de Madrid*) and the Spanish Royal Heritage (*Patrimonio Nacional*). The municipal inventories of city parks and gardens (except historic parks), as well as street trees inventories were performed by the private maintenance companies in charge of each of the management units [1.4.3.2], in which Madrid was divided. These inventories were performed during the progress of this thesis and we had full information to these inventories, once that they were finished in 2008-2010. Currently the best information about Madrid's urban trees is available at *"Un alcorque, un arbol"* web site [http://unalcorqueunarbol.cloudapp.net/]) supported by the General Directorate of the Environmental Heritage. Unfortunately, the web site only provide information for individual street trees (alignment), but trees in parks, gardens and urban forest are missing.

Currently the Municipality says in the media that there is 300,000 street trees, while stating that the number of urban trees under Municipality maintenance raise to the total account of 2 million trees, without going into details.

2.4.3.2 Urban tree management, maintenance and new treatments

A) Urban tree management

The management of parks, gardens, street trees and urban forests has been established in a general way without differentiating between the different green spaces during 19th century and most of the 20th century. But since 2001, the first group integrated parks and gardens. Street trees were assigned to the second group. This measure was caused by the large number of trees that existed along the roadsides. It was better to treat them as independent components, due to the very distinct characteristics (see shape in Figs. 26, 27 and 29). This way, it was possible to manage each group taking into account their needs, and being able to specialize the work for better management.

Thus, the management of the city is organized in different components: 1) street trees units, that cover all metropolitan area and 2) parks and gardens that were splitted in four units (Fig. 33) with a balanced percentage of green spaces in each unit.

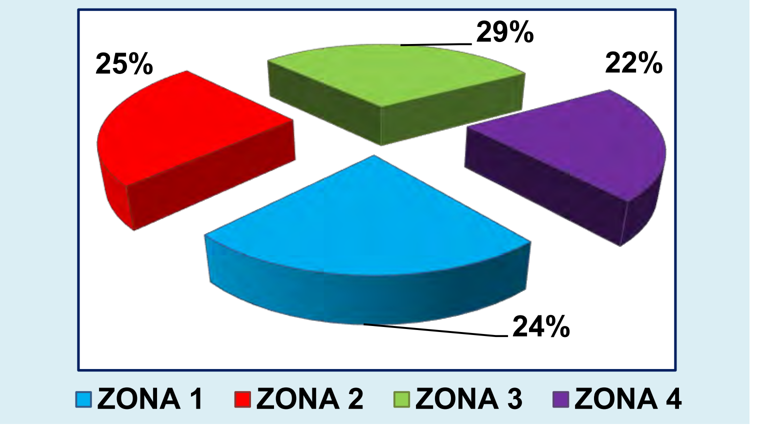


Figure 33: *Distribution of green spaces by management units ("zona" 1 to 4)*

DISTRICTS	TOTAL SURFACE BY DISTRICT (ha)	DENSITY Tree/ha
CENTRO	524	15
TETUAN	537	11
CHAMBERI	469	26
FUENCARRAL	24345	1
MONCLOA	4493	3
CHAMARTIN	920	17
CIUDAD LINEAL	1136	11
HORTALEZA	2801	4
SAN BLAS	2181	6
BARAJAS	4267	2
RETIRO	538	13
SALAMANCA	541	23
PUENTE DE VALLECAS	1489	13
MORATALAZ	634	12
VILLA DE VALLECAS	5156	3
VICALVARO	3271	3
ARGANZUELA	655	16
LATINA	2543	4
CARABANCHEL	1409	10
USERA	770	10
VILLAVERDE	2029	6

Table 11: *Total surface of green spaces and tree density by management units (same colours as Fig. 33) and districts in Madrid. These units may change in the last year due to cost reductions in maintenance.*

Each unit (*Zona1, Zona 2, Zona 3 and Zona 4*) was composed by a group of districts (see the colours correspondence between Fig. 33 and table 11. The location of districts is available in Fig. 34).

The districts assignation followed a spatial criterion, taking into account the balance of surface between units; despite the tree density was unbalanced, as it is shown in Table 11.

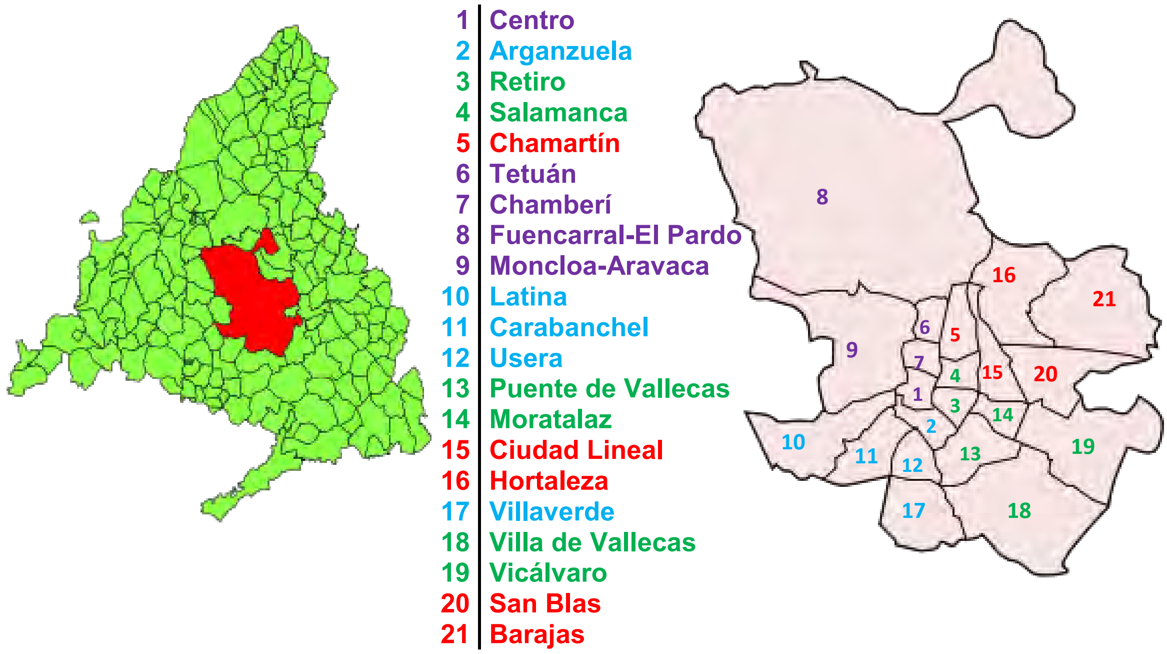


Figure 34: *Madrid region (green) and city of Madrid (red) (map on the left). Summary map of the City of Madrid (map on the right) and division into districts (centre)*

B) Maintenance

Usually, the living conditions of a street tree are not the best for a healthy development. They are not in their natural environment and capabilities are much depleted. Thus, they are more sensitive to any significant alteration and attack. The adverse conditions, in which they develop, require more attention to keep these trees healthy and safe for pedestrians. Throughout the year, the work to improve their environment consist of different tasks. They are watered, digged, treated against pathogens that attack them; and pruned to avoid conflicts generated by growth into windows, traffic lights, street lights, pedestrian area, vehicles, etc. The budget assigned by the Madrid City Council through the General Directorate of Environmental Heritage for the management of urban street trees was 15,334,099.49 € in 2006 (Morcillo San Juan, 2007). This budget for street trees is a 15% of the total budget for green spaces. About 78% goes to the green areas (parks and gardens) of the 21 districts in the city and the 7% remaining is assigned to parks and gardens of special protection (DIARIOMADRID, 2009).

Unlike to the few or no treatments that receives a tree in natural conditions, urban trees must be maintained to avoid problems for pedestrians and traffic. Thus, it begins a cycle of pruning to avoid unwanted accidents by falling branches. Others trees are modified by pruning in order to alter their growing in inconvenient directions that intercept buildings or vehicles. These pruning should not be excessive or aggressive. Pruning is not aesthetically recommended and can be a source of diseases and pests.

Maintenance of green spaces in Madrid implies certain controversy. Opinions are quite discordant depending on the group that react. The overall maintenance and conservation of the urban trees 35 years ago was often not the one desired according to the Spanish Association of Arboriculture in newspapers (Martínez Sarandeses & Moreno Soriano, 1999).

In the last 10-15 years a considerable improvement in maintenance and management has been developed. However, it was a hard task to maintain trees, featuring serious consequences of previous pruning and poor living conditions. Unfortunately, the urban trees of Madrid have made headlines in the summer of 2014 due to the numerous incidents with trees. In two months there were a total of 25 reports of incidents of trees in Madrid, which left two dead and six injured by falling branches and trees in poor condition in public places. The problem led the City Council to establish a group of experts to reduce risks (Agencia EFE, 2014).

In order to avoid inconvency with pest and disease, the pruning campaign is executed from November to February, which involves 10 to 15 units per brigade and day. Another important work is the campaign that performs the arboriculture pruning throughout the year, which also involves 15 to 20 units per day and brigade (Morcillo San Juan, 2007). Therefore, the total pruning activity in both tasks implies that 4% of the street trees are submitted to pruning each year.

C) New treatments

- The installation of automatic irrigation systems by recycled water supply has been implanted in new green spaces, as well as renewal of existing water conductions in the last 10 years. At a first glance, it allows significant savings in water consumption and a way to employ the recycled water obtained from the sewerage treatment stations. However, long-term effects in soils and trees by contribution of substances that could be harmful (annexe XV) are not clear.

- The pruning program originated 4800 tons per year of plant debris, which were taken to the composting plant of *Migascalientes* (10%) with a processing capacity of 20,000 tons of plant debris, and annually produces 2,300 t compost. The product is used as fertilizer in the parks and gardens of the city (FIDA, 2010).The main percentage of debris is stored in Valdemingomez technology Park (90%), where since 2010 itis crushed and stored. The amount of 10% of the waste from the municipal parks is certainly an improvement in waste management, but will require of an analysis of the effects of the contribution of this kind of residues on certain green areas, due to the heavy metals deposition.

2.4.3.3 Street trees

As it will be discussed in Chapter IV, Madrid is one of the cities with most trees along their streets. Over 55% of the streets are tree-lined with more than 200,000 street trees and a large variety of species, although Plane tree (*Platanus orientalis var. acerifolia*) still is the predominant shade tree. Their physiological conditions and resistance to pest and diseases allow them to survive in the hostility of the urban environment.

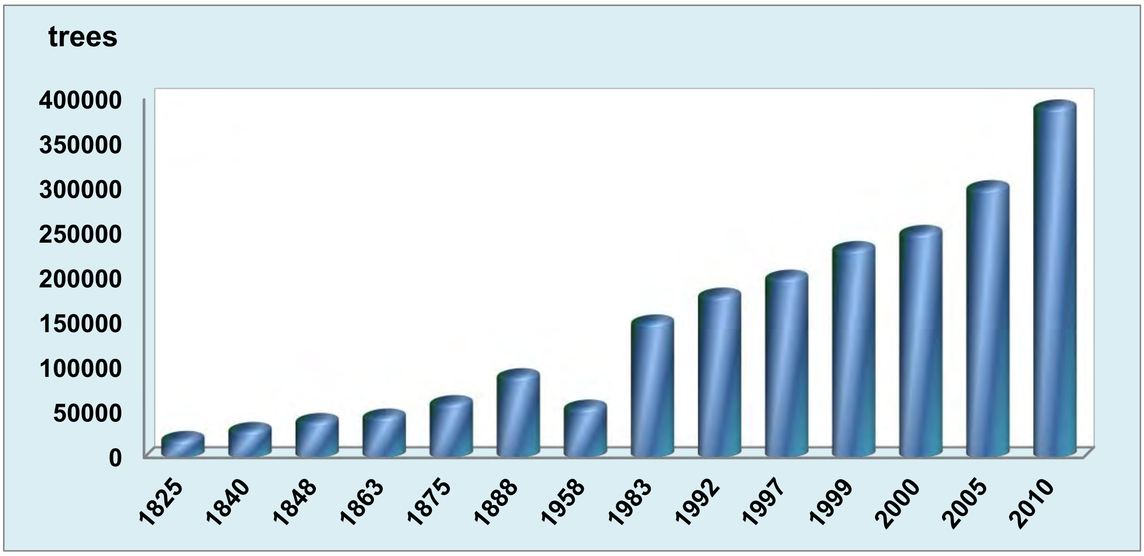


Figure 35: *Evolution of the number of urban street trees existing in Madrid [(Ayuntamiento de Madrid, 1929; C. Calderón Guerrero, Saiz de Omeñaca González, & Günthardt-Goerg, 2009; de Tornos, 1849, 1855; Gómez Mendoza, 1995; Madoz, 1848; Rodrigáñez, 1888; SUFISA, 2004)].*

A) Origins of the madrilian street trees

In Madrid, as in other European cities in the 18th and 19th century, new street trees plantations were primarily made in the outskirts of the city, while downtown remained with its narrow streets with a poor presence of public green elements, except in certain boulevards in major roads. The aspect that the city showed in the first part of the 19th century, after Napoleon's occupation from 1808 to 1814, was an absolute lack of urban trees within the town centre. The only emblematic tree that survived, was the oldest tree in Madrid in the Parterre of the Retiro Garden, the *Ahuehuete* (*Taxodium mucronatum*), which was planted in 1632 (Gayà, 2007). This tree was the only one saved from the destruction by the Independence War because the French troops used the branches of the tree to place on it the artillery.

Several plantations were done in the second part of the 19th century to fill this gap of empty spaces in the city (Fig. 35). During those years, the most employed urban trees were elms, poplars and several varieties of acacias, such as the pagoda tree and the honey locust. As well as hackberry and mulberry trees, maples and even introduced treed such as ailanthus (de Tornos, 1849, 1853, 1855; Dictamen, 1872; Madoz, 1848; Rodrigáñez, 1888). The percentage of urban trees species in Madrid during the second half of 19th century was led by four species: elms (34 %), black locust (26 %), honey locust (16 %) and pagoda trees (10 %). Forty year later, the elm had decreased to 10% due to the lack of irrigation and the elm disease caused scolytids (*grafiosis*) (Gómez Mendoza, 1995; Rodrigáñez, 1888). As soon as elm was disappearing, the notoriety of the Plane tree as urban tree increased, which had already come into use in the late eighteenth century near the court.

In the next century, because of the Spanish Civil War (1936-1939), the urban trees of the capital were heavily deteriorated again. It was necessary to remove a high amount of dead or seriously affected trees. That is the reason of the sharp decline before 1958 in Fig. 35. During the second part of the 20th century, a progressive increase remained until the present days. A larger variety of trees such as maples, redbud, cherry trees, privet, madrones, horse chestnuts, etc., has been planted alongside traditional plane trees, Siberian elms and acacias.

B) Main urban street tree species in Madrid

In 2006 for Madrid more than 279,170 street trees along 4,146 streets, a ratio of 1 tree/14 inhabitants were reported, but the diversity of street trees species was low. The sum of only six of them reaches almost 75% of the street trees: *Platanus orientalis* L. var. *acerifolia* Aiton (Plane tree) (65,544 trees), *Sophora japonica L. (Japanese pagoda tree) (35,010 trees), Ulmus pumila L. (Siberian elm) (32*,158 trees), *Robinia pseudoacacia* L. (black locust) (25,454 trees), *Acer negundo* L. (American maple) (15.186 trees), *Ligustrum lucidum* W.T.Aiton (Japanese privet) (14,602 trees), (Sepulveda González, 2006) (Fig. 36).

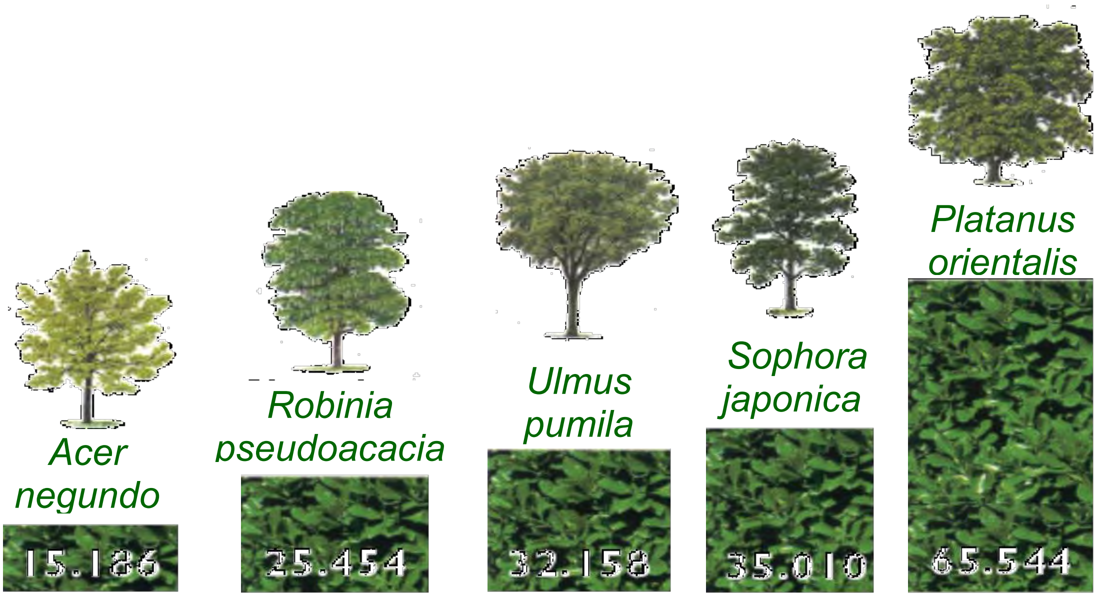


Figure 36: Main urban street trees species in Madrid in 2004 (Sepulveda González, 2006)

2.4.3.4 Urban forests, parks and gardens in Madrid

A) Surface of public green spaces in Madrid

Beyond the fact or legend that Madrid could be considered the second city in the world for green areas (some people say that after Guayaquil and other after Tokyo), the exact position in the ranking will be discussed in Chapter IV. The data of green surface were more exhaustive. The green spaces represented about 33% of the total area of the municipality (22,000 ha) and there were 150 parks, 925 gardens and 250 areas of protection in 2004 (SUFISA, 2004). Currently, the surface occupied by public green spaces in the municipality of Madrid included:

- Green spaces of municipal conservation, such as parks and gardens (about 5,000 ha excluding cemeteries) as shown in Fig. 3 in Chapter 4.
- Green spaces maintained by National Trust, which are open to the public in *El Pardo Forest* and *Campo del Moro Park*, which are about 18,600 ha)
- The Royal Botanic Garden (about eight ha) that belongs to the *Higher Council for Scientific Research* (CSIC).

Out of 4800 hectares under municipal conservation, the urban green areas (parks and gardens) represents 41% (1,900 hectares), while peri-urban and urban forests accounts 59% of total (2,700 hectares). The main species in forest parks and peri-urban parks are *Quercus ilex* and *Pinus pinea,* details will be shown in Chapter IV.

B) Origins of madrilian public parks

The origins of the first Madrilian public **urban parks**, as mentioned in [1.4.1] for European parks, are a consequences of the Industrial Revolution. During those years, there was a huge migration of population from rural settlements to main cities. The creation of public green spaces improved the quality of life of the working class that was living in the worst conditions. The first park that was created in Madrid for this purpose was the *Parque del Oeste*. It was built in the very late nineteenth century and the beginning of the next century (see annexe X). Previously, the Buen Retiro Park had been opened to the public, because of the expulsion of Isabel II of the Spanish throne. Years later in the 20th century, Madrid had a public urban forest: the *Casa de Campo*. The forest park ceased to belong to the Crown after the proclamation of the Second Republic and completed the great northwest green mass along with El Pardo peri-urban forest and the University Campus during the reign of King Alfonso XIII (Gómez Mendoza, 1995). After the destruction of most of the parks during the Spanish Civil War, the City Council acquired two former private possessions and created two new public parks: *Eva Duarte de Peron* and *Fuente del Berro* in the 1950s. In the last 50 years, the increase in urban gardening has been progressive and numerous green spaces, plazas, gardens, and a large number of parks have been created or restored.

The average values observed in Fig. 37 indicate that the percentage of green spaces corresponding to each inhabitant has increased gradually. The assignation of green surface expressed in m^2 per inhabitant, rose from 4.5 to 9, 13 and 17 m^2/inhabitant in 1985, 1988, 1991 and 1999, respectively. Madrid reached one of the first positions in the ranking of European cities with more public green surface per inhabitant. The General Plan for Madrid of 1997 aimed to increase that surface in 2,500 hectares and increase the average surface of urban green spaces from 14 m^2 /inhabitant to 24 m^2 /inhabitant. This is an important percentage when compared with other worldwide cities. The *Monte de El Pardo* peri-urban forest and the *Campo del Moro Park* (under the National Trust maintenance) are not included on these calculations. If this surface would be included, we should add 3.2 m^2/inhabitant. Thus, each madrilian disposed of about 20 m^2 of public green area approximately in 1999 (SUFISA, 2004)

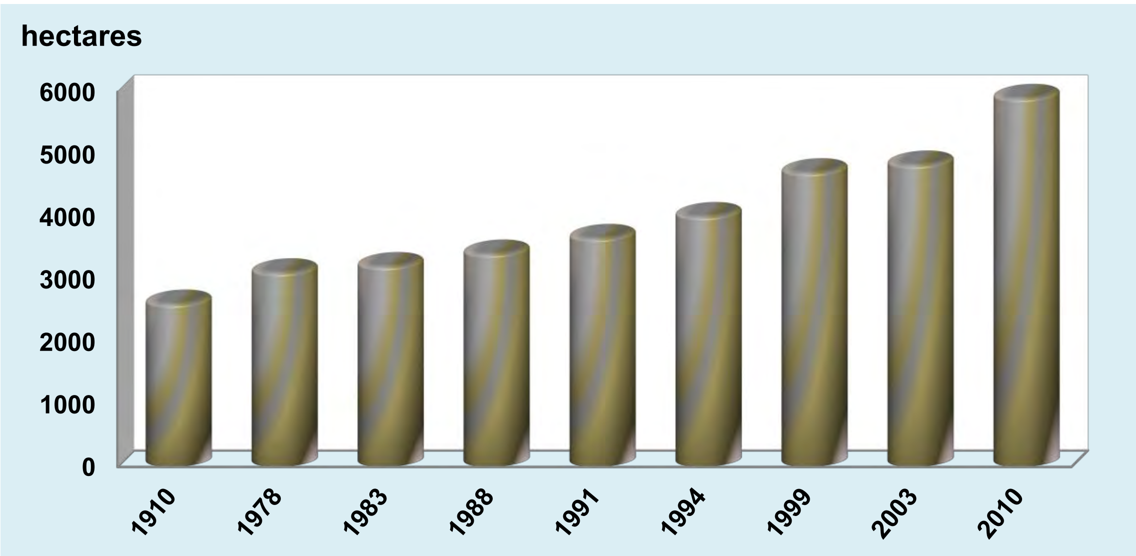


Figure 37: *Evolution of the public green spaces surface (ha) in Madrid (Ayuntamiento de Madrid, 1929; C. Calderón Guerrero, Saiz de Omeñaca González, & Günthardt-Goerg, 2009; Gómez Mendoza, 1995; SUFISA, 2004).*

C) Catalogue and classification of green spaces

The Madrid's urban trees catalogue is composed by more than two hundred different species. Unlike what happened with the road trees, trees in parks and gardens have a current high tree diversity that has been reached after many years of change, after the historical tradition of selection of trees species focused in a small group of common species (plane trees, elms, acacias and pines). The high heterogeneity favours aesthetic values and the attractiveness of parks, streets, squares and avenues.

The most important green spaces in the city of Madrid are listed below, according to the classic organization of the municipal park service:

C-1) National Heritage green spaces

The National Heritage Green spaces are compounded by:

National Heritage Green spaces	
Campo del Moro Park at Royal Palace	*Gardens of El Pardo Palace*
La Quinta	*Casita del Príncipe*
Free and reserved areas of El Monte de El Pardo peri-urban forest.	

Table 12: *National Heritage Green spaces*

C-2) Urban forest parks

Forest parks in the past were former royal hunting areas that become to be public. They form a green mantle into the urban fabric, bonded through green corridors. The most representative are:

Forest parks and nurseries (2,106 hectares)	
Casa de Campo forest park	*Cuña Verde de O´Donnell and Fuente Carrantona*
Tres Cantos Forest area	*Valdebebas forest park*
Municipal Rose Gardens and Nurseries (including Estufas del Retiro, Casa de Campo Nursery, Migas Calientes Nursery, Laboratory for in vitro culture, Rosaleda de Madrid at Parque del Oeste, Talleres de Estufas del Retiro)	

Table 13: *Forest parks and nurseries in Madrid*

C-3) Singular and historic parks:

In the category of public parks and gardens, there is a special type of green spaces the *singular and historical parks*. Most of these historic gardens belonged to the aristocracy or the Crown until the early twentieth century. For example, the *Casa de Campo* urban forest was transferred to Madrid in the Second Republic, while El Retiro Park was a full public green space earlier in the First Republic. Other parks were the result of purchases of lands by the municipality. Currently they are defined and protected by various laws of European, national and regional range (Law 16/85 of the Spanish Historical Heritage / Law 10/1998 of 9 July, Historical Heritage of the Community of Madrid. BOCM BOE of 16/07/1998 and 28/09/1998. / Law 16/1985 of

Spanish Historical Heritage and Royal Decree 111/1986 of partial development of the previous Law). The main singular and historical parks are:

Historic and special protection parks (303 hectares)	
Jardines de El Buen Retiro	*Parque Quinta de los Molinos*
Parque del Oeste	*Quinta de la Fuente del Berro*
Jardín Histórico El Capricho de la Alameda Osuna	*Parque de la Dehesa de la Villa (50% park, 50% urban forest)*
Jardines de Sabatini	*Jardines de la plaza de Oriente*
Parque del Oeste (including: Jardines del Templo de Debod, Príncipe Pío and Jardines de Ferraz)	

Table 14: *Historic and special protection parks in Madrid*

Singular parks (318 hectares)	
Palacio de Cristal de la Arganzuela	*Parque Madrid-Río*
Parque Lineal del Manzanares	*Parque Juan Carlos I*
Árboles de aire del Bulevar Bioclimático (Villa de Vallecas)	*Parque Juan Pablo II*
Singular Green spaces Las Tablas distrit	

Table 15: *Singular parks in Madrid*

C-4 Parks and gardens

The parks and gardens of the city of Madrid are the big green spaces and green heritage of the city. They stretch out like a mosaic between the streets and buildings of the big city and are small green oasis of the day-to-day life in the big city. The most representative parks and gardens (190 green areas in 2014) are listed below:

Public parks and gardens in Madrid (190)

- Estufa Fría del Parque Juan Carlos I
- Jardines calles Raimundo Fernández Villaverde, Ponzano y Maudes
- Jardines de El Buen Retiro
- Jardines de la Basílica
- Jardines de la calle Teresita González Quevedo
- Jardines de la Organización Mundial del Turismo
- Jardines de la Plaza Conde del Valle de Suchil
- Jardines de la Plaza de Chamberí
- Jardines de la Plaza de la Villa de París
- Jardines de la Plaza de Olavide
- Jardines de la Plaza de Oriente, Lepanto y Cabo Noval
- Jardines de las Vistillas
- Jardines de Perón
- Jardines de Sabatini
- Jardines de San Fernando
- Jardines del Arquitecto Ribera
- Jardines del Campo del Moro
- Jardines del Descubrimiento
- Jardines del Doctor Fleming
- Jardines del Mundial. Castellana
- Jardines del Príncipe de Anglona
- Jardines Gregorio Ordóñez
- Jardín Concejal Alejandro Muñoz Revenga
- Jardín de Embajadores M-30 (Madroños)
- Jardín de la Colonia Congosto
- Jardín de Larra
- Jardín de las Bellas Artes
- Jardín del Bulevar de Peña Gorbea
- Jardín del Maestro Padilla
- Jardín del paseo Federico García Lorca
- Jardín del Templo de Debod
- Jardín Dionisio Ridruejo
- Jardín Doña Concha Piquer
- Jardín el Torero
- Jardín Fachada Pirámides I
- Jardín Glorieta de Azorín
- Jardín Histórico El Capricho de la Alameda Osuna
- Jardín Jazmín – Parque de la Cornisa
- Jardín Palacio O'Reilly
- Palacio de Cristal de la Arganzuela (Invernadero)
- Parque Agustín Rodríguez Sahagún
- Parque Alcampo
- Parque Almansa
- Parque Aluche - Poblados
- Parque Alzola
- Parque Antonio Pirala
- Parque Anunciación
- Parque Arquitecto Antonio Palacios
- Parque Arroyo de los Pinos
- Parque Arroyo Fontarrón
- Parque Arroyo Fresno
- Parque Avenida de Portugal
- Parque Azorín
- Parque Barrio Las Musas
- Parque Begoña
- Parque Biosaludable
- Parque Campo de la Paloma
- Parque Caramuel
- Parque Carlos Arias Navarro
- Parque Cerro Almodóvar
- Parque Cerro del Tío Pío
- Parque Cerro Peñabel
- Parque Cerro Águila
- Parque Ciudad de los Ángeles
- Parque Cuesta del Galbán
- Parque Cuña Verde de Vicálvaro. Zona A
- Parque Cuña Verde de Vicálvaro. Zona B
- Parque Dalieda de San Francisco
- Parque de Alfonso XIII
- Parque de Amos Acero
- Parque de Ana Tutor
- Parque de Arriaga
- Parque de Atenas
- Parque de Canillejas
- Parque de Comillas
- Parque de Darwin
- Parque de Enrique Herreros
- Parque de Francos Rodríguez
- Parque de Fuencarral
- Parque de Fuentechica
- Parque de Fuentelarreina
- Parque de Gabriela Mistral
- Parque de Isabel Clara Eugenia
- Parque de Juan XXIII
- Parque de la Alcazaba
- Parque de la Almudena
- Parque de la Amistad
- Parque de la Bombilla
- Parque de la Casa de Campo
- Parque de la Cuesta de la Vega
- Parque de la Cuña Verde de Latina
- Parque de la Cuña Verde de O´Donnell
- Parque de la Dehesa Boyal
- Parque de la Maceta
- Parque de la Peseta
- Parque de la Supermanzana
- Parque de la Ventilla
- Parque de la Vicalvarada
- Parque de las Avenidas
- Parque de Las Cruces

- Parque de las Delicias
- Parque de los Llanos
- Parque de los Tilos Fase I
- Parque de Malmoe
- Parque de Manoteras
- Parque de Moratalaz
- Parque de Pan Bendito
- Parque de Peñagrande
- Parque de Pinar de Barajas
- Parque de Plata y Castañar
- Parque de Pradolongo
- Parque de Rafael Finat
- Parque de San Isidro
- Parque de Santa Ana
- Parque de Villarosa
- Parque Dehesa de la Villa
- Parque del Bronce
- Parque del Espinillo
- Parque del Museo del Prado
- Parque del Norte
- Parque del Oeste
- Parque del Pueblo del Pardo
- Parque Duque de Ahumada
- Parque El Calero
- Parque El Cedral
- Parque El Cruce
- Parque Emir Mohamed I
- Parque Emperatriz María de Austria
- Parque Enrique Tierno Galván
- Parque Entrevías Forestal
- Parque Entrevías Urbano
- Parque Este de Valdebernardo
- Parque Eugenia de Montijo
- Parque Eva Duarte
- Parque Forestal de Vicálvaro
- Parque Félix Rodríguez de la Fuente
- Parque General Fanjul - Santa Margarita
- Parque Hortaleza
- Parque Huerta del Obispo (Tetuán)
- Parque Huerta del Obispo (Villaverde)
- Parque Juan Carlos I
- Parque Juan Pablo II
- Parque La Rinconada
- Parque La Viña
- Parque Ladera de los Almendros
- Parque Lineal de Palomeras
- Parque Lineal del Manzanares (Usera)
- Parque Martin Luther King
- Parque Meseta de Orcasitas
- Parque Mirador de las Cárcavas
- Parque Mirador de Tierno Galván
- Parque Nudo Norte de Begoña
- Parque Olof Palme
- Parque Paseo Muñoz Grandes
- Parque Payaso Fofó
- Parque Peñuelas
- Parque Pinar de la Elipa
- Parque Pinar del Rey
- Parque Plaza Chozas de Canales
- Parque Plaza Colonia Oroquieta
- Parque Plaza de España
- Parque Quinta de los Molinos
- Parque Roma
- Parque Salvador de Madariaga
- Parque San Blas. El Paraíso
- Parque San José de Calasanz
- Parque San Juan Bautista
- Parque Sancho Dávila
- Parque Santa Eugenia
- Parque Santa Rita
- Parque Segura
- Parque Soto de Entrevías
- Parque Urpisa
- Parque Valdebernardo Este
- Parque Valdebernardo M - 40
- Parque Valle de Enmedio
- Parque Vallecas Villa
- Parque Vandel
- Parque Virgen de la Esperanza
- Pinar Santa Eugenia
- Pirámide del Parque Juan Carlos I
- Quinta de la Fuente del Berro
- Rosaleda de los Jardines de El Buen Retiro
- Rosaleda de Ramón Ortiz.
- Rosaleda del Parque del Oeste
- Vivero de la Casa de Campo
- Vivero Estufas del Retiro
- Vivero municipal de Migas Calientes
- Zona verde C/ Fresnedillas
- Área Forestal de Tres Cantos

Table 16: *Public parks and gardens in Madrid*

2.4.3.5 Phytopathological situation of major parks and gardens in Madrid

The vegetation is usually subjected to a number of factors and agents that interact with the plant (environment and pathogens), conditioning its evolution and survival. Among these factors, we must not forget the great impact that population represents to the urban vegetation by the alteration of soil quality, humidity, water availability, air quality status, etc. In addition to these human effects, the fact is that most of the vegetation in large cities is exotic or normally is not the climax vegetation for those environmental conditions. Usually these circumstances represent more vulnerability to attacks by different agents. The urban environment is very aggressive to the vegetation, due to the conjunction of ideal environmental conditions that concentrate various biotic and abiotic agents, which usually are greatly influenced by urban population.

The vegetation damaging agents are classified into two groups, which are the **biotic** and **abiotic** agents. Among the various biotic agents that cause the vegetation deterioration, the **diseases** and **pests** are the most important agents.

- **Pests** are usually caused by invertebrates and are characterized by the number of individuals, the moment of the attack and the parts affected in the plant.
- The **disease**-causing agents are distinguished by their nature:

1) Biotic agents

i. Virus and viroid
ii. Bacteria
iii. Parasitic phanerogams
iv. Producing fungi diseases
v. Fungi producing alterations (chromogenic or rot)

2) Abiotic agents

a. Natural origin:

i. Nutritional deficiencies
ii. Lack or excess of water in the soil
iii. Inadequate temperatures
iv. Other meteorological agents (wind, snow, lightning, etc.)

b. Human origin:

i. Fire
ii. Causing mechanical damage (inadequate pruning, breaks, etc.)
iii. Chemicals
iv. Misapplied pesticides or fertilizers or inadequate doses
v. Anthropogenic air pollutants

The highest damages to vegetation are caused by fungi (biotic agent) and pollutants released into the atmosphere by human activity (abiotic agent) respectively. Once pollutants are emitted into the atmosphere, they produce direct damage to the plant (usually on/in leaves) or indirect damage by the deposition in the soil and subsequently affect to the root systems.

Special attention deserves the negative human actions, such as vandalism and inadequate pruning maintenance practices.

Figure 38: *Four street trees poplars in Los Molinos (Madrid) after the pruning of all branches and half of the stems. This kind of pruning is not allow by law. Photo source: [Calderon Guerrero, C. (2008)]*

Figure 39: *Pruning of "half of the tree" of two conifers (Sequoiadendron giganteum and Cedrus deodara) in a garden in Cercedilla (Madrid). Photo source: [Calderon Guerrero, C. (2008)]*

Among other reasons, these problems of maintenance are consequence of:

- Excessive pruning pressure on branches above 15 or 20 cm in diameter. Certain pruning practices should be punished as in Figs. 38 and 39.
- The practice of "terciado" (pruning of a third of the branches length) is quite common in urban street trees in Spain, but sometimes misinterpreted as the "terciado" means removing a third of the branch (the top section), while in many cases, what is done is to leave only one third of branch, a procedure, which should not be not allowed by the weakening the tree that it produces.
- Paving or renovation of pipes in the ground. This works cause soil compaction and root mutilation.
- Vandalism causes mechanical damage that result in injuries that are potential sources of disease in the affected tree.

This type of abusive practices regarding pruning is not a new issue in Madrid. Excessive pruning of shade trees were denounced by de Tornos (1853) as unnatural practice and there are quotes from a protest by pruning of the trees along Prado St. in 1927 (Winthuysen, 1927)

Unfortunately vandalism is still present in the maintenance of trees, although environmental education of citizens is growing. The combination of good procedures in maintenance and cleaning of the green area decrease the deterioration by vandalism (Corraliza, 2001).

2.4.4 Benefits of urban trees

Social demanding of green spaces in the city justified by the scientific research ensure the economic, psychological and physical benefits of green spaces for urban population. These benefits include the high value and social impact of green areas in the commerce and economy of the city (E. G. McPherson, 1992). The beneficial effect can be translated into various factors to consider (Fig. 40):

a) Air quality improvement

The action of the green spaces as a whole and particularly of woody vegetation in this aspect can be considered under different aspects:

- The urban trees uptake of a large amount of CO_2 produced in cities, both in the respiratory processes of the biocenosis, and the combustion of fossil products (fuels), because of the incomplete combustion of fossil fuels (see annexe XII).
- The CO_2 absorbed by the vegetation is processed by its photosynthetic function and subsequently, O_2 is released into the atmosphere.
- The leaf stomata can uptake SO_2 in small amounts. According to some studies by (W. Smith, 1981) an atmosphere containing 100 µg/m^3 of SO_2 is clean by the action of crossing one hectare of broadleaves forest. Freer-Smith and Broadmeadow (1996) suggested that the air improving properties of urban trees could up-take significant amounts of both O_3 and SO_2 (up to 21 and 20% of exposure concentrations during episodes of O_3 and SO_2 respectively)
- They act as efficient filters of airborne particles by removing a large amount of atmospheric dust due to their large size, high surface to volume ratio of foliage, frequently hairy or rough leaf) and bark surfaces (Chakre, 2006). E. McPherson, Nowak, and Rowntree (1994) estimated that the trees of Chicago removed approximately 234 tons of PM_{10},17 tons of CO, 93 tons of SO_2, 98 tons of NO_2, and 210 tons of O_3 in 1991.

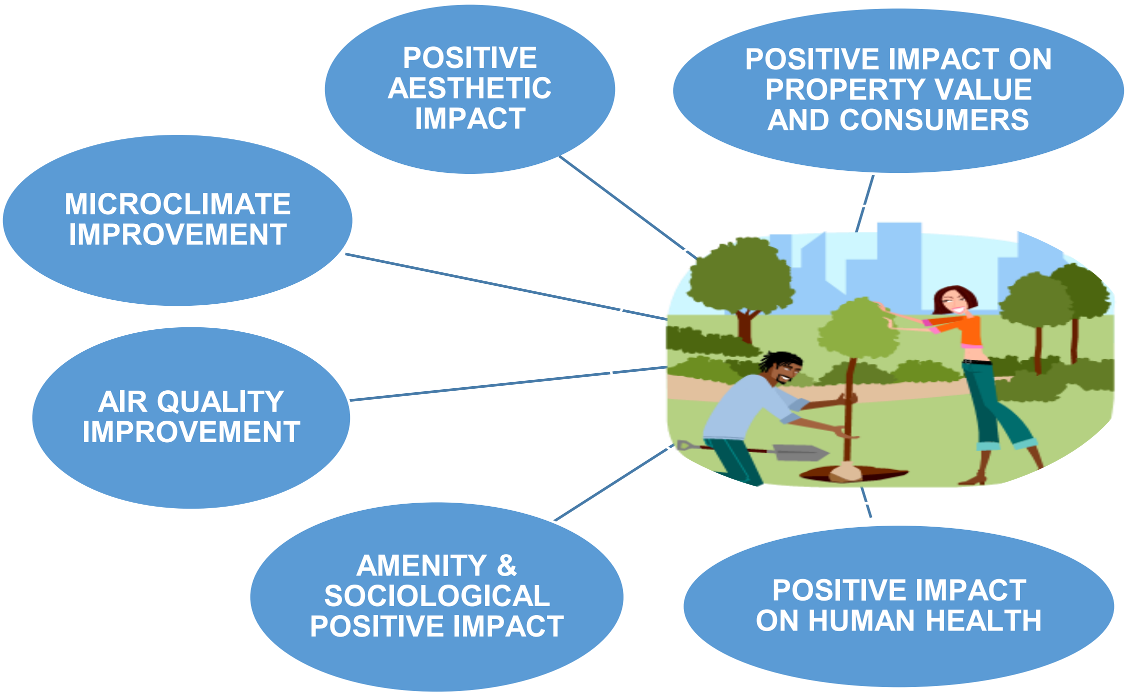


Figure 40: *Benefits of urban trees*

b) Microclimate improvement

The benefits in the microclimate are observed in the following factors:

- Temperature. Tree species can reduce ambient air temperature. This ability varies due to a number of factors, such as tree size, tree canopy characteristics or may specific urban topography (E.g. street orientation), which affect the penetration of solar radiation. In general, there is an improvement of the thermal conditions in areas with abundant green spaces compared to the temperature in areas of the city where buildings built with brick and paved roads predominate. In these latter areas, a large accumulation of heat occurs. This could be the reason that average temperature was higher in districts of Madrid, where the green cover was lower (Fig. 41-a). The difference of the annual average temperature between districts ranged between 0.5º C and 2.1º C. (C Calderón

Guerrero, 2005). Other authors cited an increase of 5° C in cities like Tokyo (Numata, 1977). In general, the average on the cooling effect of parks with data from several parks around the world was 0.94 °C cooler during the day (Bowler *et al.*, 2010). The presence of trees in parking lots can affect evaporative emissions from vehicles. Scott, Simpson, and McPherson (1999) estimated that the increase of parking lot tree cover from 8% to 50% could reduce VOC evaporative emission rates by 2% and nitrogen oxide start emissions by less than 1%. Temperature is also reduced by the evaporation effect of leaf surfaces.

- Precipitation. In some cities, the precipitation is associated with higher green cover. In Madrid, the higher rainfall recorded by the air pollution station network in certain areas of the city could suggested an increase of precipitation in districts showing dense green spaces. The average annual precipitation increased by 8% in some areas with the highest percentage of green space (Fig. 41-b), although the difference was not proportional to the density of trees. Moreover, the evapotranspiration causes an increase of the relative humidity in the ambient and releases an important amount of water vapour into the atmosphere.

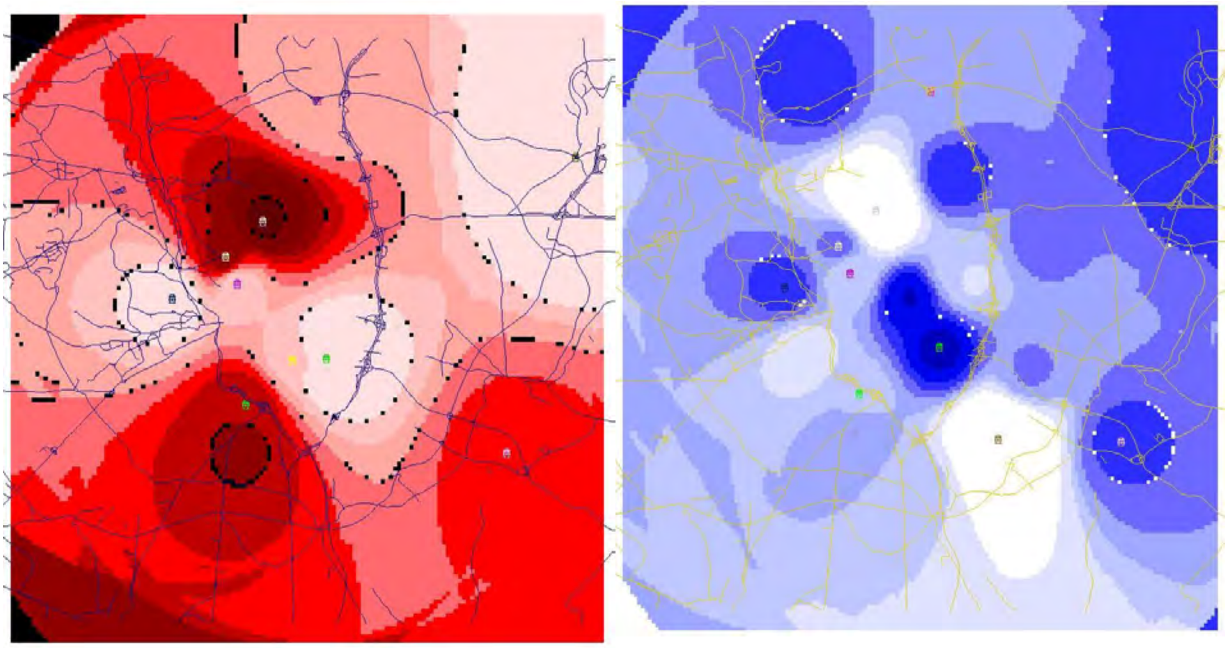


Figure 41 (a and b): *a) annual average temperature (each reddish colour category is equal to an increase of 0.2ºC) and b) annual average precipitation in the city of Madrid in 1999 (each blueish category is equal to an increase of 5 mm/year). The almond shape of Madrid is in the centre. (C Calderón Guerrero, 2005).*

c) Positive impact on human health

The health-environment interaction is a fact already verified time ago (Lee & Maheswaran, 2011). Is is taking a special dimension in the case of large cities, where human stress and environmental pollution (smoke, noise, etc.) come together, producing an increase in adverse effects on physical and mental health of citizens. Against this negative situation, urban green spaces represent an "oasis" of leisure and mental relaxation in the city, and at the same time involve a number of advantages for physical health of citizens, among which may be mentioned:

- Pregnancy. The presence of green spaces is beneficial for expectant mothers and the correct course of pregnancy (Dadvand *et al.*, 2012).

- Infancy. Large urban forests are very important for young children, assuming an ideal place for proper early development and physical activities in general (Taylor *et al.*, 1998)
- Different medical conditions. The urban green spaces act positively in different clinical specialties:
  - **Cardiology**. In general, staying in green spaces works as a therapeutic measure.
  - **Endocrinology** and all types of hormonal disorders, such as obesity or diabetes, require the exercise (in green spaces), as well as medicines (Lachowycz & Jones, 2011).
  - **Traumatology, neurology and movement disorders**. Exercise is important to boost the damaged muscles in addition to the medication. Staying in green space could be a suitable place to prevent these diseases (Hartig, 2008).
  - **Pneumology**. The clean or less polluted atmosphere positively affects all types of respiratory disorders such as: asthma, bronchitis, etc., except those cases of allergy to certain elements of the vegetation (pollen, resins, etc.).
  - **Psychiatry and geriatry-related diseases** also need leisure and recreation areas because of the sedative effect of exercise in the mind of patients. Green spaces also provide areas of distraction for the elderly persons, as well as meeting points and tranquillity (Rosso, Auchincloss, & Michael, 2011).

d) Amenity and sociological impact

The urban forest provides isolation of the disturbances involving city traffic (Van den Berg *et al.*, 2010). Green spaces have assumed various social functions formerly performed in the typical squares and boulevards of small populations. Today urban parks and gardens are considered usual places of meeting of young people, play areas for children, walking areas and relaxation for adults and seniors, practice sites for maintenance of people of different ages and social status, etc.

e) Impact of aesthetics

Urban trees beautify the environment, soften the forms, streamline the monotonous spaces, provide variety of forms, volumes and colours throughout the year, hiding undesirable views, etc. (Price, 2003). The use of urban trees to enhance certain elements of buildings and monuments is commonly used in architecture, helping to focus attention on the elements that should be highlighted (Smardon, 1988). For the aesthetic values of trees, it is appropriate to differentiate between trees in road alignment and squares, where it is important to consider the aesthetic values of the species employed. On the other hand, aesthetic purposes never should prevail in tree selection in large green spaces, where functional purposes should be prioritized.

f) Positive impact on residential property value and consumers

Urban trees also have a positive effect on business activity. According to Tyrväinen and Miettinen (2000), a 1 km-increase in the distance to the nearest forested area in the district of Salo in Finland leaded to an average 5.9 % decrease in the market price of the dwelling. Meanwhile properties with a view to forests were on average 4.9 % more expensive than dwellings with otherwise similar characteristics. Similar results (6 %) were found by (Morales, 1980) to the property value of the homes observed in the United States.

Urban trees may influence other consumer responses and behaviours in business districts in the sense of positive district perceptions, patronage behaviour, and product pricing (Wolf, 2005).

2.4.5 Trees as a sink of air pollutants

Trees in urban environments have considerable potential to remove both particulate and gaseous pollutants from the atmosphere (E. McPherson, Nowak, & Rowntree, 1994). Somehow, they could be considered as sink. Warren (1973) Defined "*sinks*" as the components of ecosystems that remove contaminants from the atmosphere and store, metabolize, or transfer them. When the plant tolerance to certain pollution loads is great enough, they could be a suitable sink for those anthropogenic pollutants in the urban environment (Lamanna, 1970).

2.4.5.1 Particulate collection by vegetation

Vegetation in large cities have the function of reducing environmental pollution. They do this by a passive process, as plants intercept pollutants particles, staying deposited on their surface.

Figure 42: *Resuspended particles deposited on Aesculus hippocastanum leaves in Retiro Park in August 2005 during the first samplings of this study. The cause of particulate resuspension were the police cars and park service vehicles moving along limestone gravel roads (See Annexe VI). Photo source: [Calderón Guerrero].*

Figure 43: *Dust deposited on Cedrus deodara in Retiro Park during the sampling procedure in winter 2006 in one of the higher polluted sites in the park. Photo source: [Calderón Guerrero].*

The particulate matter interception has been studied in rural, suburban, and urban road-side environments since the second half of 20th century. Early studies experimented with particles in nonurban environments with objectives unrelated to air pollution. These particles were larger than most that are present in urban atmospheres, such as pollen grains. Raynor *et al.* (1966) suggested that the concentration of pollen particles carried by the wind through a woodland decreased rapidly from the edge. In the urban environment, W. H. Smith (1974) estimated that the current twigs of a 30-cm diameter urban sugar maple removed from the atmosphere 60, 140, 5,800, and 820 mg of cadmium, chromium, lead, and nickel respectively during the growing season. Thus, this role could be developed by urban trees in the polluted atmosphere of the main cities. The green spaces also could prevent that particles deposited on the ground would be resuspended again by wind action

Physicals characteristics of the particulate capture:

The estimation for the removal capacity of an urban tree differs according to several factors such as location, species, size and morphology of the leaves, etc. Chamberlain (1967) indicated that impaction is the main way of capture particles under suitable conditions. The average ranges for the variables is:

- Particle size is near to 10 microns or greater.
- Obstacle size is on the range of a few centimetres or less
- Approach velocity is on the range of meters per second or more
- The collecting surface is wet, sticky, hairy, or otherwise retentive.

The characteristics of the leaves surface are important on particulate retention. Deposition on rough pubescent leaves could be 10 times greater than on smooth, waxy leaves. As (Wedding *et al.* (1975)) reported during the examination of deposition of lead aerosols on leaf surfaces of sunflower in comparison to yellow-poplar leaves under controlled wind tunnel and aerosol generator conditions.

At the end of this process, most of the particles are deposited in the soil. This is particularly important with regard to heavy metals fate. Precipitation washes or leaches these particles from the foliar surface to contaminate the soil below. It is important to trace the fate of the leaf-disposal methods. If, for example, leaves are collected and stored for compost production, as it happens in Madrid at Migascalientes compost station, control measures to trace the compost should be scheduled. If leaves are burned, the particulates could be reintroduced to the atmosphere.

2.4.5.2 Mechanisms of gaseous pollutants removal

As well as vegetation intercepts pollutants particles, the urban green spaces also removes gases from the atmosphere in different ways. Much of the evidence comes from controlled environmental studies in laboratory or from models obtained from computer estimations. Iit is clear that the main way is by **uptake through the stomata**, because of the plants gases exchange with the ambient atmosphere through leaves and branches for the processes of transpiration and photosynthesis.

The gases absorbed by the plant from the atmosphere are metabolized and translocated to different parts of the plant. Gases with a nutritional (NO_2) effect contrast those, which decay at the leaf surface (O_3) inducing harmful oxygen radicals (Chapter II and III).

3. Objectives

Due to the complexity and factors involved in the processes of air pollutants and their deposition/ uptake by urban trees, the estimation of pollutants accumulated in plants and soils, as well as the visible and microscopic symptoms, resulted in an exhaustive work not free of uncertainties that implicate the spatial and temporal variables in the urban environment scenary.

Within this framework, the **general objective** of the present thesis is to analyse and to evaluate the role of the urban trees as a sink of air pollutants to alleviate the effects of pollution on human health and the environment, as well as the side effects that this task produces in the exposed urban trees to this pollution.

The main objectives to be achieved in this thesis were:

A) To review the former and current situation regarding population, pollutants and green spaces.

B) To study some of the **effects that air pollution produced on trees**, such as:

- **Foliar visible symptoms produced by ozone** on *Quercus ilex*. (for the first time reported)
- Detection of **heavy metals concentration exceedances in soils and plants** (in tissues or on the surface) using techniques of atomic absorption spectrophotometry.
- The **heavy metal microlocalization** of Zn in the foliar tissue of the studied species.

C) To estimate the contribution in terms of **reduction of the levels of pollution by a group of deciduous species** (*Platanus sp., Ulmus sp.* and *Aesculus hippocastanum*), as well as **evergreen species**, such as *Quercus ilex, Pinus pinea* and *Cedrus* sp. by annual quantities of traffic-related heavy metals (Pb, Zn, Cr, Cu) captured by these trees.

D) To represent the spatial distribution of some air pollutants in Madrid using GIS to an entire city level

- Concentration of main heavy metals in the soil
- Number of exceedances of PM_{10} in the last 10 and 30 years
- Levels of exposition to particulate matter that each individual tree is exposed to regarding the traffic intensity

E) To contribute to a better understanding of the quantification of the number of urban trees in Madrid categorized by species, type of green spaces and the total amount of urban trees by the aggregation of existing and ad-hoc inventories.

F) Proposal of the most efficient and suitable species that could be recommended in the urban environment, based on dust capture, sensitivity to pollutants and arboriculture criteria.

G) To promote respect and compliance for the urban trees among the society

4. General methodology and study areas

4.1 General methodology

The development of this study involved the combination of different methodologies and procedures in response to the diverse situations evaluated, including several field studies, field work methodology, laboratory analytical techniques and the use of statistical tools as well as GIS and CAD tools for spatial data analysis.

4.1.1 Experimental design of the field studies

The investigation work developed in the present study is based on field studies in combination to air pollution data provided by the municipal authorities. In order to achieve the specific objectives for each study, different experimental approaches were established, which included the selection of the sampling sites, the environmental parameters to measure and the type of sample to be studied throughout the investigation, the most adequate techniques for the fieldwork, the sampling/measurements frequency and the duration of the studies. The collection of samples required of a previous study of the procedure and the type of collecting device that should be designed and built to collect the leaves avoiding the dust loss by impact after the cutting and removal of the branches.

Other studied variables of interest were the gas exchange (stomatal conductance and respiration rate) that were obtained by an IRGA (infrared gas analyser), the chlorophyll contents that were analysed by spectrophotometry, the dasometric variables (diameter at breast height, crown and total height), as well as age, dry biomass and fraction canopy cover. Finally, the health status (biotic and abiotic agents) was monitored for all those trees that required it.

4.1.1.1 Selection of species

The species (*Platanus* sp., *Ulmus* sp., *Aesculus hippocastanum*, *Quercus ilex*, *Pinus pinea* and *Cedrus* sp.) were selected in terms of representativity by the percentage of urban trees in green spaces of Madrid, as well the deciduous/evergreen condition and the morphological characteristics to capture particulate matter.

4.1.1.2 Spatial and temporal sampling

All investigated trees were obtained randomly from the tree inventories. Once the tree was selected, the following considerations about the **spatial location** of the sampling sites were taken into account:

- Orientation and exposure of the leaves in the tree in relation to the prevailing wind direction, the light exposition and the source of pollutants.
- Determination of the barrier/filter particulate matter effect by spatial comparison between the trees within the inner areas of the parks and the trees in the perimeter (edge effect).

The sampling was performed periodically in different season of the years. This way, the samples were exposed to different levels of higher and lower concentration of pollutants in the air. Trees were sampled from summer 2005 to spring 2007 in the first phase in the vicinity of air pollution monitoring stations of the City of Madrid and in remote sites outside of the city influence. In a second phase from 2008 to 2012, the samples and gas exchange measures were obtained only for trees and variables that were required for a greater precision in the estimations.

4.1.2 Laboratory analytical techniques

The concentration of heavy metals in leaves, dust residue and soils were obtained through analysis techniques such as absorption spectrometry and atomic emission applied to the quantification of major components and heavy metals (Pb, Ba, Cd, Cu, Fe, Cd, Cr, Al, Mn, Li, Ni, Zn). Initially, the analysis of heavy metal concentrations were planned in foliar, soil and bark samples, which could be completed by the official data of the concentration of heavy metals in the recycled water for tree irrigation in parks. Unfortunately, we were not allowed by the head of the *Canal of Isabel II* to receive the data of concentration of pollutants in the water. The bark analyses were performed, but the results finally not displayed in this thesis. All samples were previously conditioned to the laboratory prerequisites.

4.1.3 Data base management

Analysis of time series required of a previous process of compilation of data in *Microsoft Access* and *Excell* (*Microsoft Office* 2007, 2010 and 2013. *Microsoft Corp. ©.* Redmond, Washington, USA). The early files were exported from Excell 2007 to Excell 2010 in a first step due to the limitation to 68'000 rows of the 2007 version, which limited the browses of the full inventory of trees in parks and along the streets (in the range of million trees). Once the data and inventories were processed, the development of mapping of the spatial distribution was performed by Geographic Information System (GIS) software and geodatabase management applications GIS (*ARCGIS* 9 and 10 by *Esri* ©. Redlands, California, USA) and by assisted design (*AutoCAD*.2007 and 2012 by *AutoDesk* © San Rafael, California, USA) of:

1) Concentrations of air pollutants in the municipality of Madrid. (Period: 1980-2010)
2) Meteorological data series of Madrid. (Period: 1980-2010)
3) Urban tree inventories

4.1.4 Statistical analysis

Different statistical tools were used for the analysis of parametric and non-parametric variables, according to the kind of data set and the objectives of each study. The analyses comprised t-test, analysis of variance, correlations and multiple linear regression models. All statistical analysis were performed using the *SPSS* (Version 22.0. IBM Corp. ©. Armonk, NY, USA) software package.

4.2 Study areas

The sampling sites used in this research work are located around the city of Madrid (Fig. 1 in Chapter 3 and Fig. 3 in Chapter 4). Although the entire city of Madrid could be considered, each street tree position was employed to calculate the minimum distance to the nearest traffic road. In chapter 4, additional remote sites were located in the forests of Cercedilla (Madrid). Initially, the study area for this thesis was the Retiro Park in the centre of Madrid, due to parallel projects developed during the early tree inventory in Retiro Park that consisted in phytopathological assessments of the urban street trees; these trees were included in the thesis. Additional, phytopathological reports developed in the main parks and gardens, as well the Casa de Campo forest Park, concluded to include all urban trees in Madrid, to complete the request of the National Heritage to study the trees that were under their public maintenance. Thus, the entire urban trees under public maintenance in Madrid were included in the research work. In the study conducted in the chapter 4, the chemical properties of the soils were characterized in several urban sites.

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6. List of abbreviations, symbols and acronyms

- % - percent
- Carbon monoxide (CO),
- cm – centimetre
- cm^2 - centimetre square
- CO - carbon monoxide
- CO_2 – carbon dioxide
- CO_2 carbon dioxide
- CSIC. Higher Council for Scientific Research (Spain)
- OECD. Directorate for Public Governance and Territorial Development
- FIDA: Fundación para la Investigación y el Desarrollo Ambiental (Spain)
- g – gram
- GIS. Geographic Information Systems
- H_2SO_4 - Sulphuric acid
- hr – hour
- km - kilometre
- km^2 – square kilometre
- m – meter
- mm – millimetre
- NMVOCs. Non-methane volatile organic compounds
- NO_2 – nitrogen dioxide
- NO_x - nitrogen oxides
- O_3 - ozone
- ºC – Celsius degree
- OECD Organisation for Economic Cooperation and Development
- Oxides of nitrogen (NO_x),
- PAN – peroxyacyl nitrates
- Pb – lead
- PM - particulate matter
- PM_{10}. Particulate matter of 10 microns or less in diameter
- PM_{10}. Particulate matter of 2.5 microns or less in diameter
- ppm - parts/million
- SO_2 – sulphur dioxide
- SO_x - sulphur oxides
- sq. - square
- STS. Sewerage treatment stations
- Sulphur dioxide (SO_2),
- UNECE: United Nations Economic Commission for Europe
- UNEP: United Nations Environmental Programme
- VOC – volatile organic compound
- w - weight
- WHO: World Health Organization
- WSL: Swiss Federal Institute for Forest, Snow and Landscape Research (Switzerland)

Chapter 2

OZONE EFFECTS ON FORESTS

Chapter 2

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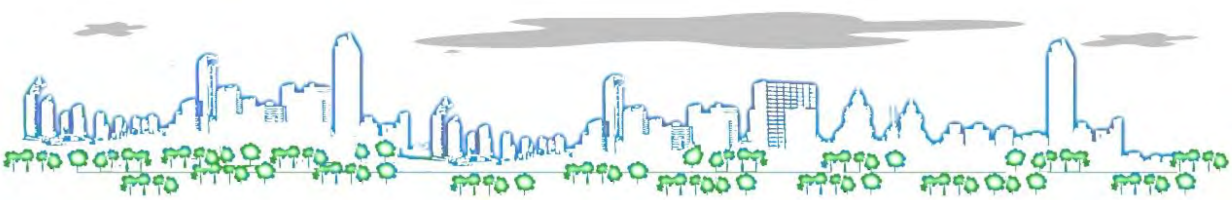

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Review

Ozone effects on forests

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Tropospheric ozone concentration has been rising in the last decades, due to industrial and other human activities. For plants, ozone constitutes one of the most damaging air pollutants. Main effects of ozone on forest species are reviewed: visible symptoms caused by acute exposure at the anatomical, structural and metabolic level, and the long run effects on growth and development derived from chronic exposure. Particular attention is given to photosynthesis and the effects on stomatal functioning, as major ozone injuries are inflicted to the plant after entering through the stomata. Plant detoxification capacity, carbohydrate allocation, growth and development are also revised, as well as the effects at the ecosystem level, defence mechanisms of plants against ozone, and their sensitivity and tolerance. The rising problem of tropospheric ozone contamination should awaken the international awareness and measures should be taken to control ozone atmospheric levels considering their transnational implications.

Key words: Abiotic stress, atmospheric pollution, climatic change, environmental pollution, forest decay, forest ecosystems, forest species, ozone, reactive oxygen species, tropospheric ozone.

INTRODUCTION

The ozone (O_3) layer that is formed in the stratosphere by ionisation of oxygen absorbs most ultraviolet radiation coming from the sun, thus protecting life from an excess of high energy radiation harmful to living organisms. Thinning of this stratospheric layer (between 20 and 30 km altitude) is the cause of more ultraviolet radiation passing through and producing tropospheric ozone. Most atmospheric ozone (ca. 90%) is stratospheric, while the tropospheric ozone concentration is usually small, in the order of a few ppb (Seinfeld and Pandis, 2006).

The increment of tropospheric ozone concentration, dispersion and effects have been related the industrial activities (Borell et al., 1997; Martin et al., 1991; Millán et al., 2000). The reaction of nitrogen oxides (NOx) with ultraviolet light, oxygen and exhaust gases generates O_3, which adds to that brought down from the stratosphere by vertical winds produced during electrical storms. Ozone concentration is minimal by night but builds up to phytotoxic levels in the atmosphere during calm, warm, sunny weather when pollutants accumulate in stagnant air. This situation is typical of spring and summer days. Accumulation also occurs during atmospheric inversions in valleys and basins. The combination of these processes contributes to maintain a basal concentration of about 20 to 45 ppb (nmol/mol) in intermediate latitudes of the northern hemisphere. The concentration of O_3 has been registered since the end of the XIX century, indicating an increment at a rate between 1 and 2.5% annually (Jonson et al., 2006).

In Japan, concentrations above 100 ppb have been recorded in both urban and mountainous areas (Watanabe et al., 2012). In a polluted atmosphere in which emissions of NOx and volatile organic compounds feed the photochemical reactions, O_3 concentration may reach levels as high as 200 to 400 ppb (Emberson et al., 2003; Fiala et al., 2003). It has been stated that ozone is the most damaging air pollutant to plants (Gimeno et al., 1995; Peñuelas et al., 1999), cultivated crops as well as

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forest vegetation (Treshow and Stewart, 1973) and numerous shrub species (Findley et al., 1997a). Nowadays, susceptibility to ozone is a criterion to choose a plant crop, especially for ornamental woody plants (Sacramento Tree Foundation, 2010).

The aim of this review was to emphasize the importance of tropospheric ozone contamination, underlining its effects on forests and natural ecosystems. Until recently, most research on ozone damage was focused on commercial crops, and the effects on forests were not considered as important as those caused by pests and diseases. We try to give a global scope of ozone damage on plant growth and development, from the physiological to the ecosystem level. In a context of global climate change, the interaction of ozone with increasing CO_2 concentrations and with the water balance of plants should increase public awareness of the problem.

SYMPTOMS OF OZONE-DERIVED TOXICITY IN WOODY PLANTS

Symptoms of ozone damage may be visible symptoms such as brown or red-brown punctures or chlorotic bands in the leaves, caused by acute, high ozone concentrations during short periods, or premature leaf senescence and reduced growth and productivity, usually caused by moderate, chronic concentrations during long periods. Morpho-anatomical symptoms include tissue collapse, interveinal necrosis, and markings on the upper surface of leaves known as stipple (numerous tiny spots of different pigmentations), flecking (silver or bleached straw white spots), mottling (irregular blotches of green, light green, and yellow), yellowing, bronzing, or bleaching. Ozone-affected leaves may show the most severe injuries within the palisade tissue (Paoletti et al., 2009). The main way of O_3 entrance into the plant is the stomata. Certain species are sensitive to very low levels (0.05 ppm). Furthermore, ozone produces other toxic compounds, such as hydrogen peroxide (H_2O_2), superoxide (O_2^-), atomic oxygen (O), and hydroxyl radical (·OH). Some visible symptoms frequently attributed to O_3 are black, reddish or brownish spots in the limb (Fumagalli et al., 2001; Hayes et al., 2007). In a more advanced stage, old leaves appear brilliant white mottled. Conifers frequently show a yellow to brown mottling and tipburn, pink spots or a yellow to brown or orange-red flecking and banding of the needles (Anttonen and Kärenlampi, 1996; Baker and Allen, 1996; Vollenweider et al., 2003).

On the other hand, many toxic effects caused by ozone to some woody plants, including premature aging, may occur in the absence of visible symptoms (Günthardt-Goerg, 1996; Günthardt-Goerg et al., 1996; 1997; Vollenweider et al., 2003). Foliar damage attributed to tropospheric ozone was first observed to be phytotoxic to *Vitis vinifera* in southern California in the 1950s (Richards et al., 1958) and in the 1960s, "X" disease of ponderosa pines within the San Bernardino Mountains was likewise determined to be due to O_3 (Karnosky et al., 2007). Foliar O_3 symptoms have been verified for seedlings under controlled chamber conditions, but due to complex interactions within forest stands, evidence of similar losses within mature tree canopies remains difficult to find. Investigations on tree growth, O_3 flux, and stand productivity are being conducted along natural O_3 gradients and in open-air exposure systems to better understand O_3 effects on forest ecosystems (Karnosky et al., 2007).

In ozone affected plants, stomata lose turgor and close. Toxic radicals alter the membrane permeability, chloroplasts disaggregate and the whole metabolism is affected. Some species, e.g. poplars, are especially susceptible, and in ash, although no visual symptoms are obvious, the epidermis may collapse and chloroplasts may start to degenerate. Ozone toxicity is determined by its absorption process through the stomata and the plant mechanisms of detoxification and reparation (Massman, 2004; Wieser and Matyssek, 2007). In addition to the external O_3 concentration, the uptake of O_3 by plants is primarily influenced by stomatal conductance (g_s), which is strongly dependent on climatic conditions, varying between species and site characteristics (Manzanera and Martinez-Chacon, 2007), the position of leaves within the canopy as well as leaf and plant age (Matyssek et al., 2004). However, ozone concentration in the intercellular space is very low, probably because it is decomposed after uptake (Laisk et al., 1989).

OZONE EFFECTS ON PHOTOSYNTHESIS

Ozone has a marked effect on photosynthesis, limiting the net assimilation rate and the chlorophyll content. However, the major alterations take place in the electron transport chain and in the carbon fixation role of ribulose-1, 5-bisphosphate carboxylase oxygenase (Rubisco). In ponderosa pine needles following exposure to ozone, an observed broadening of the chlorophyll absorption band has been interpreted as a consequence of chloroplast disorder and granulation of the thylakoid membranes (Ustin et al., 2009). Indirectly, stomatal guard cell function is impaired by ozone. Photosynthesis as a whole is variably affected by limiting the net assimilation rate, the chlorophyll content, the electron transport chain, the carbon fixation role of Rubisco and the stomatal guard cell function. These effects also depend on the genotype and the stage of development. Furthermore, defence mechanisms are weakened and ozone-killed tissues are readily infected by certain fungi, decreasing the detoxification capacity of the plant and consequently, increasing damage (that is, Massman, 2004). Greitner and Winner (1989) demonstrated that ozone reduced the photosynthetic rate in *Alnus frangula* and observed that the plant cells of the root nodules were damaged, but not those of the *Frankia* symbiont. Alterations of photosynthesis vary depending on the species, clone or ecotype and developmental stage.

Normally, woody perennials are more tolerant than deciduous broadleaved species (Calatayud et al., 2010). Another general rule is that more tolerant species to other types of stress, for example hydric stress, are also more tolerant to ozone. This occurs in mediterranean schlerophylous species, such as *Quercus ilex* (Calatayud et al., 2010) and *Pinus halepensis* (Alonso et al., 2001). Other cases of intraspecific diversity in the capacity of response to ozone absorption have been tested in long run Open Top Chamber (OTC) experiments with two ecotypes of *Quercus coccifera* (Elvira et al., 2004), where one-year old plants of ecotype *garriga* show a decrease in net assimilation and g_s for two years, as compared to plants of other ecotype. Also, younger leaves show less damage and less chlorophyll destruction than mature leaves (Broadmeadow and Jackson, 2000) and a greater capacity of detoxification (Alonso et al., 2001; Massman, 2004).

EFFECTS ON GROWTH AND DEVELOPMENT

Plant growth is often stunted (Leisner and Ainsworth, 2012). Findley et al. (1997b) demonstrated that ozone concentrations below the sensitivity threshold to cause visible foliar symptoms nevertheless cause growth and flowering drop in *Buddleia davidii*. Diameter growth and size-growth relationships are also affected in spruce and beech (Pretzsch and Dieler, 2011). Root development is inhibited by ozone (Bassirirad, 2000) and it has been postulated that ozone may cause greater and earlier disruption of below-ground growth with long-term consequences for productivity. As a result the hydraulic capacity to provide the transpiring shoots with water is reduced. This reduction in root capacity could reduce photosynthesis and plant water use. Total root biomass is reduced, the fraction of plant biomass in root tissues declines, and the number and branching patterns of roots is altered by ozone. Root dry weight show a tendency towards reduction in *Q. pyrenaica* plants fumigated with 30 ppb ozone (−45%, $p < 0.1$), and biomass partitioning was significantly altered in this species: reduction in root growth was stronger than reduction in above-ground biomass (13%); thus, above-ground biomass/below-ground biomass ratio increased significantly in this species (50%), but other oak species were not so sensitive (Calatayud et al., 2011).

Ozone effects on roots or on the above-mentioned ratio have been reported as a consequence of reduction in CO_2 assimilation but also of photo-assimilate allocation from source tissues of the leaves to sink tissues in the roots (Andersen, 2003). Under natural conditions, root reduction and changes in biomass partitioning in tree species may reduce resistance to wind throw (Broadmeadow and Jackson, 2000). In many species, it is expected that ozone-driven severe symptoms and strong effects on photosynthesis are parallel to the highest biomass reductions. However, effects at leaf-level, and especially visible injury, are frequently uncoupled with growth or biomass reductions: the latter effects can be limited if, for example, leaves become affected toward the end of the growing season, when growth has already stopped or is reduced (Novak et al., 2007), or by compensatory responses of younger or non-affected leaves.

Present tropospheric ozone concentrations and those projected for later this century are toxic to trees and have the potential to reduce the carbon sink strength of these forests (Wittig et al., 2009). Current ambient O_3 (40 ppb on average) significantly reduced the total biomass of trees by 7% compared with trees grown in charcoal-filtered controls, which approximate preindustrial ozone concentration in the atmosphere. Above and belowground productivity were equally affected by ambient levels in these studies. Elevated concentrations of 64 ppb reduced total biomass by 11% compared with trees grown at ambient levels, while an elevated O_3 concentration of 97 ppb reduced total biomass of trees by 17% compared with charcoal-filtered controls. The root-to-shoot ratio was significantly reduced by elevated O_3 amounts, indicating a greater sensitivity of roots to this contaminant. At elevated O_3 concentrations, trees had significant reductions in leaf area, Rubisco content and chlorophyll content, which may underlie significant reductions in photosynthetic capacity. Trees also had lower transpiration rates, and were shorter in height and had reduced diameter when grown at elevated concentrations.

Further, at elevated tropospheric O_3, gymnosperms were significantly less sensitive than angiosperms. Taken together, these results demonstrate that the carbon-sink strength of northern hemisphere forests is likely reduced by current O_3 and will be further reduced in future if O_3 amount rises. This implies that a key carbon sink currently offsetting a significant portion of global fossil fuel CO_2 emissions could be diminished or lost in the future (Wittig et al., 2009). Radial growth and structure of five 5-year-old trembling aspen (*Populus tremuloides*) clones and the wood characteristics of paper birch (*Betula papyrifera*) were affected by the interaction of ozone in an atmosphere with elevated concentrations of CO_2 (Kostiainen et al., 2008). Material for the study was collected from the Aspen FACE (Free-Air CO_2 Enrichment) experiment in Rhinelander, WI, where the samples had been exposed to four treatments: control, elevated CO_2 concentration (560 ppm), elevated O_3 concentration (1.5 times ambient) and their combination for five growing seasons. Wood properties of both species were altered in response to exposure to the treatments. Ozone also may cause changes in flowering timing and less flower and fruit production (Hayes et al., 2012; Leisner and Ainsworth, 2012). Seed germination rate may be reduced, as well as pollen germination and growth, as it has been observed in *Pinus strobus* (Benoit et al., 1983), *Prunus, Malus* and *Pyrus* (Black et al., 2000; Hormaza et al., 1996).

EFFECTS AT THE ECOSYSTEM LEVEL

Ozone weakens forest plants, which become more susceptible to drought and diseases. In a climatic change context of CO_2-rich atmosphere, it is expected that stomatal regulation should difficult ozone absorption. However, experiments combining both gases show a high variability in response (Fiscus et al., 2005). After four years of experiments using an open-air exposure system, trying to assess the impact of elevated atmospheric CO_2 and O_3 on the O_3-sensitive species trembling aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*), as compared to the O_3-tolerant species sugar maple (*Acer saccharum*), the responses to these interacting greenhouse gases have been remarkably consistent in pure aspen stands and in mixed aspen/birch and aspen/maple stands, from leaf to ecosystem level, for O_3-tolerant as well as O_3-sensitive genotypes and across various trophic levels. These two gases act in opposing ways, and even at low concentrations (1.5 times ambient, with ambient averaging 34-36 ppb during the summer daylight hours), ozone offsets or moderates the responses induced by elevated CO_2. After three years of exposure to 560 µmol/mol CO_2, the above-ground volume of aspen stands was 40% above those grown at ambient CO_2, and there was no indication of a diminishing growth trend. In contrast, O_3 at 1.5 times ambient completely offset the growth enhancement by CO_2, both for O_3-sensitive and O_3-tolerant clones (Karnosky et al., 2003).

More recently, leaf biomass production was monitored in the same aspen, birch and maple stands for seven years, concluding that the overall effect of elevated ozone was to decrease leaf mass by 13%. Interactions with CO_2 concentration, forest community composition and stand development process were observed. Ozone also retarded nitrogen cycling (Talhelm et al., 2012). Another good example of ozone effects at ecosystem level is the San Bernardino Mountains forest, California, formerly covered by *Pinus ponderosa* and *P. jeffreyi* (Arbaugh et al., 1998). Those pines lose foliage and vigour, and were attacked by bark beetles, due to drought and ozone-driven weakening. Other ozone-tolerant species outcompeted both pines and the species composition changed. Mediterranean plants are often adapted to different oxidative stress factors (e.g., high temperature, strong sun-light and drought) that can make them more tolerant to ozone stress, as molecular responses to all these stresses may be convergent (Bussotti, 2008; Calatayud et al., 2010; Pell et al., 1997). Overall, the results recorded until now are consistent with previous studies comparing related evergreen and deciduous species, which showed a much higher tolerance in evergreen species (Calatayud et al., 2010).

Ozone may influence chemical processes of litter and organic matter decomposition with impact on soil microorganisms and roots, as observed in ponderosa pine (Olszyk et al., 2001). Furthermore, some species show natural selection responses in sensitivity to ozone (Berrang et al., 1991). Interspecific competence may also be altered, as leguminous plants in general are more sensitive to ozone. This has a potentially negative effect on nitrogen fixation (Andersen, 2003).

DEFENCE MECHANISMS OF PLANTS AGAINST OZONE

Reactive oxygen species formation takes place in normal plant metabolism by partial reduction of molecular oxygen. When O_2 accepts one or two electrons, produces superoxide (O_2^-) or peroxide (O_2^{2-}) anions, or the hydroxyl radical ($^{\cdot}OH$), which are dangerously reactive, oxidizing proteins and causing DNA mutations. Also, singlet oxygen can be produced from the photosynthetic light-harvesting chlorophyll molecules and is highly reactive. To avoid those dangerous free radicals and reactive oxygen species, plants possess different protection systems. In fact, there is formation/destruction equilibrium of those toxic radicals but this equilibrium may be affected by several factors, such as drought, solar radiation, high temperature or ozone contamination, among others. Several enzymes delete those radicals. Ascorbate peroxidase plays this protective role in chloroplasts, cytoplasm and mitochondria, using ascorbate as a substrate to reduce peroxide. In fact, ascorbic acid and apoplastic ascorbate are antioxidants that react with free radicals in plant cells. Other antioxidant cell protectants, such as glutathione, react with singlet oxygen. For instance in spruce (*Picea abies*), superoxide dismutase activity declined under ozone stress, while the redox states of the ascorbate and the glutathione pools were not affected by any treatment, suggesting that spruce needles seem to be able to acclimate to ozone stress by increasing their ascorbate pools and protecting pigments (Kronfuss et al., 1998). Alonso et al. (2001) exposed two year old Aleppo pine (*Pinus halepensis*) plants to high ozone concentrations. These authors observed that the pines activated protection mechanisms against oxidative stress in the newest needles, as opposed to older needles, which were damaged. Younger needles show higher detoxification capacity thanks to the induction of antioxidant enzyme activity. Those detoxification mechanisms decrease ozone impact but at a high photoasimilate expense, thus depending on environmental and ecophysiological conditions, such as hydric stress. Plant responses to ozone are therefore expressed as phenologic and physiological changes, indicating that plants activate their protection systems in increasing ozone atmospheres (Alonso et al., 2001).

SENSITIVITY AND TOLERANCE

Identification and classification of ozone-sensitive species has been difficult and controversial. For instance, holm oak (*Quercus ilex ssp. ilex*) show stippling symptoms and was more sensitive to ozone than *Q. ilex ssp. ballota, Olea europaea cv. vulgaris* and *Ceratonia siliqua*, in a two year long OTC experiment of exposition to ozone (Ribas et al., 2005). However, other authors have not recently included holm oak as a sensitive species (Calatayud et al., 2010; 2011). Differences in O_3 sensitivity between pioneer and climax forest tree species has been reviewed by Matyssek et al. (2010), based on recent evidence from novel phytotron and free-air ozone fumigation experiments in Europe and America. As previously mentioned, O_3 counteracts some effects of elevated CO_2 on plant growth, the response being governed by genotype, competitors, and ontogeny rather than by the species. Complexity in O_3 responsiveness increased under the influence of pathogens and herbivores (Matyssek et al., 2010). Gerosa and Ballarin-Dente (2003) identified risk areas for trees and shrubs in Lombardy, Northern Italy, by combining distribution maps of sensitive species and ozone concentration maps with critic levels. In the particular case of shrub species, a methodology of damage monitoring based on symptomatology has been developed both in Europe and USA (Bussotti et al., 2006; 2009; Ferretti et al., 2008). Mills et al. (2011) collected a database with 644 cases of ozone pollution and their effects in 18 European countries. 22.9 % of the cases referred to shrubs, 39% were for crops (27 species), and 38.1% were for (semi-) natural vegetation (95 species). The effects of ozone could be generalized, fitting better with the modelled accumulated stomatal flux over a threshold 3 nmol/m^2/s than with the Accumulated Ozone concentrations over a Threshold of 40 µg/m^3 h (AOT40) index. In the mid 90's, the AOT40 index was adopted for defining O_3 exposure instead of one, 10, 12 or 24 h average concentrations, recognizing the importance of cumulative exposure approaches (Kärenlampi and Skärby, 1996). However, a consensus has recently evolved that O_3 phytotoxic effects are more closely related to the amount of pollutant entering the plant through the stomatal pores and reaching the sites of damage within the leaves (Musselman et al., 2006).

Ozone sensitivity has shown to be a genetic trait in black cherry, where families differed significantly in their response to ozone treatments in severity of adaxial stipple, but not in leaf senescence or growth. Family heritability estimates for foliar injury, calculated by treatment and week of measurement, were generally above 0.5 under 90 and 120 ppb ozone treatments. The relative ozone sensitivity of these cherry families in Continuously Stirred Tank Reactor (CSTR) chambers corresponded well with susceptibility rankings of their 27-year-old parents, replicated in a clonal seed orchard, and growing under ambient ozone exposures. The existence of localized, heritable variation in ozone sensitivity in wild populations has obvious implications for the use of bioindicators in forest health monitoring (Lee et al., 2002). The ozone sensitivity in oak species, namely *Quercus ilex, Q. faginea, Q. pyrenaica* and *Q. robur* is the result of the interaction between ozone uptake and species-specific leaf characteristics, e.g., leaf habit, thickness, stomatal density (Calatayud et al., 2011). Leaf Mass per Area (LMA), has been used to distinguish between ozone-tolerant and ozone-sensitive species. This index is also considered an index of sclerophylly, with the threshold at 7.5 mg/cm^2 (Bussotti, 2008), reaching 9.7 mg/cm^2 in *Q. faginea* and 15.2 in *Q. ilex*. Sclerophyllous adaptations include the development of cells with thick walls and more supportive tissue that can affect gas diffusion inside the leaves.

Thick leaves are considered to be more ozone-tolerant than thinner leaves (Bennet et al. 1992; Karlsson et al. 2004; Lyons et al. 2000; Pääkkönen et al., 1995a; 1995b), in part because of differences in the gas-phase diffusion pathways (Chappelka and Samuelson, 1998). The presence of cells with thick walls strongly influences the length of the diffusion pathway for ozone and modifies the interaction with oxidative constituents of the apoplast. The density of the cell wall (degree of cross-linking, suberification or lignification) would also be expected to influence the tortuosity of the diffusion pathways for ozone (Lyons et al., 2000). The dense trichoma layer presents in the lower leaf surface of *Q. ilex* increases boundary layer resistance, and eventually may increase the surface of reaction with ozone, contributing to its depletion. In addition to these processes, leaves with higher LMA values have been correlated with higher antioxidant capacity levels (Matyssek et al., 2007) and a high tissue density is considered to be able to better feed detoxification processes (Bussotti, 2008).

CONCLUSION

Public opinion is increasingly aware of the risks of ozone to human health, the environment and forests in particular. Efforts to limit tropospheric ozone have been undertaken by industrialised countries of the northern hemisphere, and expectedly will extent all around the world. We have tried to underline the damage on forests and natural ecosystems. We have revised ozone damage on photosynthesis, plant growth and development, from the individual to the ecosystem level. Implications of tropospheric ozone contamination should be considered at three levels: coordinated efforts among countries to reduce ozone pollution; adoption of measures of environmental management to mitigate ozone effects; and search for species or ecotypes with greater tolerance to ozone and more capacity of detoxification, taking into account the genetic diversity and phenotypic plasticity of plant species.

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Chapter 3

FOLIAR SYMPTOMS TRIGGERED BY OZONE STRESS IN IRRIGATED HOLM OAKS FROM THE CITY OF MADRID, SPAIN

Chapter 3

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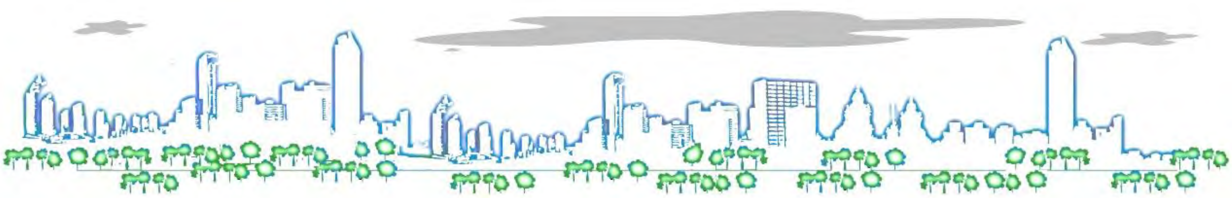

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Foliar Symptoms Triggered by Ozone Stress in Irrigated Holm Oaks from the City of Madrid, Spain

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Abstract

Background: Despite abatement programs of precursors implemented in many industrialized countries, ozone remains the principal air pollutant throughout the northern hemisphere with background concentrations increasing as a consequence of economic development in former or still emerging countries and present climate change. Some of the highest ozone concentrations are measured in regions with a Mediterranean climate but the effect on the natural vegetation is alleviated by low stomatal uptake and frequent leaf xeromorphy in response to summer drought episodes characteristic of this climate. However, there is a lack of understanding of the respective role of the foliage physiology and leaf xeromorphy on the mechanistic effects of ozone in Mediterranean species. Particularly, evidence about morphological and structural changes in evergreens in response to ozone stress is missing.

Results: Our study was started after observing ozone -like injury in foliage of holm oak during the assessment of air pollution mitigation by urban trees throughout the Madrid conurbation. Our objectives were to confirm the diagnosis, investigate the extent of symptoms and analyze the ecological factors contributing to ozone injury, particularly, the site water supply. Symptoms consisted of adaxial and intercostal stippling increasing with leaf age. Underlying stippling, cells in the upper mesophyll showed HR-like reactions typical of ozone stress. The surrounding cells showed further oxidative stress markers. These morphological and micromorphological markers of ozone stress were similar to those recorded in deciduous broadleaved species. However, stippling became obvious already at an AOT40 of 21 ppm•h and was primarily found at irrigated sites. Subsequent analyses showed that irrigated trees had their stomatal conductance increased and leaf life -span reduced whereas the leaf xeromorphy remained unchanged. These findings suggest a central role of water availability *versus* leaf xeromorphy for ozone symptom expression by cell injury in holm oak.

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Introduction

Southern Europe is affected by high tropospheric ozone (O3) concentrations [1]. With 6.4 million inhabitants and 4.4 million motor vehicles, the Madrid conurbation acts as a large source of O3 precursors leading to substantial O3 pollution - especially in the Madrid outskirts [2], [3], [4], [5], [6], [7]. During the summer months on the central plateaus, the polluted air masses are re-circulated inside convective cells remaining stable for many days or even months [8], [9] making Madrid one of the regions with the highest O3 pollution in the Iberian Peninsula [3], [4], [5], [6], [7] during 2003–2008.

For several decades, visible foliar injury caused by O3 stress has been investigated in more than 75 European and 66 North American plant species and partly validated by controlled exposure experiments and microscopic analysis [6]. [11], [12], [13]. Despite a high variability, macro and micro-morphological markers of O3 stress share common structural and distribution features which can be used for identifying an O3 stress signature [14], [15], [16], [17]. These features are indicative of outbalances within the antioxidant detoxification system as a consequence of reactive oxygen species (ROS) produced in cascade after O3 uptake and synergies between O3 and photooxidative stress [18], [19], [20]. The elicited plant response and its associated structural changes in foliage can vary according to the O3 dose and levels of photooxidative stress thus leading to more than one pattern of O3 symptom expression within the same species [21]. However, O3 symptoms in broadleaved Mediterranean evergreen trees have so far seldom been documented and, to our knowledge, only one study has shown evidence of microscopic injury [22]. Holm oak (*Quercus ilex* L.) is the main tree species in many Mediterranean sclerophyll evergreen forests. Its deep rooting system, xeromorphic leaf structure and efficient stomatal control ensure tolerance to yearly summer droughts [23], [24], [25]. Compared to other sclerophylls however, it prefers rather mesic and slightly moist sites [26], [27]. In the Madrid region, holm oak is a dominant climacic species in the forest belt surrounding the city [28] and is valued as an ornamental tree in Madrid parks and streets.

The O3 sensitivity of holm oak is still controversial. In a general way and similar to other sclerophylls, this species appears to be rather O3-tolerant [1], [29], partly as a consequence of the xeromorphic traits to be found in the foliage and which are regarded as being an efficient morphological protection against O3 stress [30]. However, some of the most extreme stress reactions to O3 exposure among all sclerophyll evergreen trees so far tested were found in experiments with this species [31], [32]. Depending on the peak O3 concentration, daily irrigated holm oak seedlings thus showed photosynthesis, biomass or chlorophyll content reduction and an increase in some detoxifying enzyme activity in response to O3 exposures as low as 3.6 and 11.7 ppm•h [30], [32]. Visible leaf injury in the form of "slight stippling" [28] or "dark pigmented stipples" [31] has been observed in response to O3 exposure (AOT 40) of 59.27 ppm•h in 6 months and 79.8 ppm•h in 11 months respectively.

The present study is part of an investigation about air pollution mitigation by urban trees. During a bioindication survey, abiotic O3-like injury was identified in foliage of the holm oaks growing on an irrigated lawn strip in the center of Madrid. Given the little structural evidence available for O3 symptoms in broadleaved evergreen species, a study was undertaken in 2007 with the following objectives 1) confirm the diagnosis, 2) investigate the extent of symptoms in holm oaks growing in Madrid and 3) analyze the environmental factors contributing to O3 injury. Therefore, macro- and micromorphological markers of O3 stress were analyzed, using the aforementioned lawn strip as an intensive study site, (objective 1), 65 other urban sites with holm oaks were surveyed for similar type of leaf injury (objective 2) and data on the possible abiotic contributors, i.e. the Madrid climate, lawn strip irrigation and air pollution, were collected and analyzed (objective 3). Given the generally higher O3 sensitivity of trees growing at moist sites [33], [34] and the relative insensitivity of sclerophylls [1], [29], higher rates of stomatal conductance (first hypothesis) and reduced xeromorphic traits (second hypothesis) were hypothesized to be the principal factors determining the development of O3 injury observed at irrigated sites. Their contribution was verified by measuring gas exchanges and assessing the leaf biomass during a subsequent vegetation season (2011) at the irrigated *versus* another comparable but non-irrigated urban intensive site nearby.

Materials and Methods

All necessary permits were obtained for the described field studies at these sites and for the symptoms survey (paragraph 2.4.) by the Madrid park service (Dirección General de Patrimonio Verde del Ayuntamiento de Madrid, signed by Mr. Santigo Soria Carrera, vice-director of green spaces and urban trees) and by the municipal authority (Departamento de Calidad del Aire del Ayuntamiento de Madrid, provided by Mr. Francisco Moya, head of the air quality department).

Intensive Study Sites

The irrigated site was situated in the center of Madrid near the train station of Atocha (Fig. 1; Fig. 2B). It consisted of a green lawn strip irrigated by tap water sprayers and planted with *Quercus ilex* ssp. Ilex (a holm oak sub-species showing minor differences with the *Quercus ilex* spp. ballota native to the Madrid area) and with wide spaces between the trees. Escalonilla, the non-irrigated site, was situated 4 km west of Atocha along a paved street lined with similarly and regularly spaced trees planted on a 0.8 m2 grate and surrounded by a concrete pavement (Fig. 1; Fig. 2A). The holm oak subspecies at Escalonilla was the same as in Atocha.

Climate and Air Pollution in the Madrid Conurbation

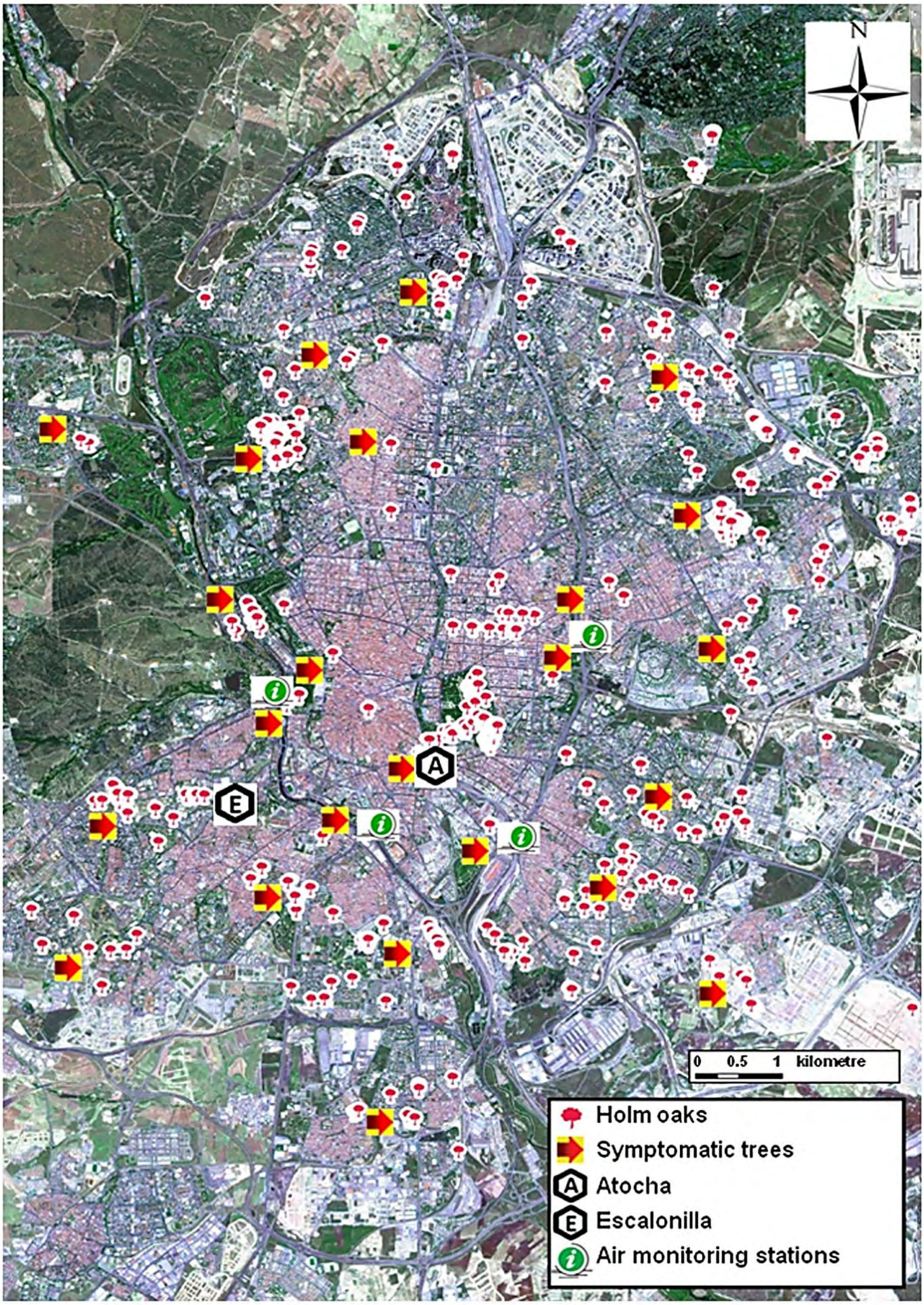
Climate conditions and air pollution of Madrid were characterized on the basis of the 1971–2007 daily records of temperature and precipitation and the 2003–2007 hourly O3 and other air pollutant concentrations from four air quality monitoring stations (Fig. 1). The closest air monitoring station was 900 m away from Atocha at a similar elevation (650 m a.s.l.). AOT40 exposure index, expressed on a daily or yearly basis, was calculated as a cumulative dose of O3 concentrations over a threshold of 40 ppb, using the April to September hourly average data measured during daylight hours and for solar radiation above 500 W/m2 [35].

SO_2 concentrations were low over the reported period (yearly mean = 11 μg/m^3). NO_2 concentrations (yearly mean = 60 μg/m^3) do not induce visible leaf injury [13,36]. Climate, air pollution and site irrigation data was provided by the national meteorological agency (Agencia Estatal de Meteorología - AEMET), the municipal authority (Departamento de Calidad del Aire del Ayuntamiento de Madrid) and the Madrid park service (Dirección General de Patrimonio Verde del Ayuntamiento de Madrid), respectively. Irrigation data was converted to mm of precipitation per month and added to the natural precipitation to calculate the total water supply.

Macro- and Micromorphological Observations

At Atocha, three 8 m high trees with a diameter at breast height (1.3 m, dbh) of 20±2.5 cm and with up to four leaf generations (current: C+0, 1-year: C+1, 2-year: C+2, 3-year: C+3 formed in 2007, 2006, 2005 and 2004, respectively), were selected. In June 2007, four sun-exposed branches per tree were sampled at the mid crown position, assessed for abiotic visible injury using a hand lens and dried in a herbarium after excision of leaf material for microscopy (see below). In the laboratory and to determine the percentage of stippling per leaf area, individual leaves were photographed using a macro-objective, natural light and a dark background. Digital images were analyzed by means of an image analysis system (Scion Image, Scion Corporation, Frederick, Maryland, USA) [37].

For microscopic analysis, the aforementioned sample collection harvested in June was completed in October of the same year using the same trees and mid crown branches at Atocha. Disks, 1 cm in diameter, were excised from asymptomatic and symptomatic C+0, C+1 and C+2 leaves. The leaf disks were immediately fixed either in methanol or in 2.5% glutaraldehyde buffered at pH 7.0 with 0.067 M Sorensen's phosphate buffer. They were entirely infiltrated with the solution by evacuation before storage at 4°C until further processing. Histological, cytological and histochemical observations were performed using 2 μm semi-thin or 50 μm hand-microtomed cuttings. Semi-thin sections were obtained after dehydrating the fixed material with 2-methoxyethanol (three changes), ethanol, n-propanol, n- butanol [38], embedding in Technovit 7100 (Kulzer HistoTechnik) and cutting using a Supercut Reichert 2050 microtome. Sections were stained with different methods including toluidine blue O, *p*-phenylenediamine and acid-vanillin and subsequently mounted in inclusion medium [17], [21]. All sections were observed using a Leica microscope Leitz DM/RB, 5× to 100× objectives and diascopic light illumination. Micrographs were taken using the digital Leica DC 500 camera interfaced by the Leica DC500 TWAIN software under control of the Image Access Enterprise 5 (Imagic, Glattbrugg, Switzerland) image management system.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0 0.5 1 kilometre
Holm oaks
Symptomatic trees
Atocha
Escalonilla
Air monitoring stations
A
E

Figure 1. Localization of holm oak sites and air monitoring stations in Madrid. The Atocha (A) and Escalonilla (E) intensive study sites were located in the city centre. Sites with at least one symptomatic tree are indicated by red arrows.
doi:10.1371/journal.pone.0069171.g001

Symptomatic Tree Survey

In October 2007, once all current foliage had completed its development, the extent of visible O_3 injury in Madrid's holm oaks was investigated by surveying 65 public park and street sites inventoried during a preceding tree survey [39]. 257 out of 2314 holm oaks with growth and age similar to trees at Atocha were selected on the basis of their dbh. Examining all leaf generations, the presence/absence of visible O_3 injury in foliage accessible from the ground was assessed and the proportion of trees showing symptoms per site calculated. Already in the field, it quickly became apparent that symptomatic sites had been irrigated and that the mode of water supply should be recorded.

Gas Exchange and Biomass Measurements

From February to October 2011, gas exchange and biomass measurements were carried out at the irrigated (Atocha) and non-irrigated (Escalonilla) intensive study sites using the same trees as in 2007 in Atocha and selecting trees of comparable age (40–50 years), height (8–10 m), and dbh (17.5–22.5 cm) at Escalonilla. The Atocha trees showed visible O3 injury similar to findings in 2007 with regard to the injury distribution and intensity whereas the Escalonilla holm oaks were asymptomatic. New foliage sprouted twice a year at Atocha (end of April and occasionally September, average air temperature reaching 22 and 25°C, respectively) *versus* only once at Escalonilla (end of May, average air temperature reaching 22.5°C); the leaves being completely developed by the onset of the summer drought (June, Fig. 3). Once a month, 5 leaves per leaf generation in 3 randomly selected branches (10–15 leaves per branch) from the mid part of the sun crown of each tree were measured (10 repetitions per leaf). Stomatal conductance (gs) photosynthetic active radiation (PAR) at leaf surface and leaf temperature (Tleaf) were measured in situ under ambient conditions between 09:00 and 15:00 (CET) using a portable infrared gas analyzer (IRGA model ADC-LCA4) equipped with a 6.25 cm2 chamber for broadleaf plants (PLC4, ADC Inc., Hoddesdon, Hertfordshire, UK). During measurements, the leaf and air temperature remained within a ± 2°C range and leaf natural orientation was maintained. Daily course of gs, PAR and Tleaf was measured from dawn to dusk during two subsequent and clear days with similar weather conditions (Fig. 4), using C+1 leaves (formed in 2010).

Following measurements, the selected branches were harvested with a view to leaf area and biomass determination. Individual leaf area was ascertained using an Epson GT5000 scanner and images were analyzed using the aforementioned image analysis system. Leaves were then dried (85°C until constant weight), weighed and the leaf mass per area (LMA) determined.

Statistical Analysis

In the case of the amount of stippling assessed at the irrigated intensive study site in 2007, an estimate for a given leaf generation was calculated by averaging measurements from three leaves per branch and four branches per tree the statistical unit being the branch (n = 4). Hence, the experiment was a split-plot design with the whole plot factor *tree* and the split-plot factor *leaf generation*. Effects of these factors on the stippling intensity were tested by means of ANOVA (with post hoc pairwise Tukey's studentized range (HSD) test) using the SAS software package (SAS Institute, Inc, Cary NC). Given the incomplete randomization of whole plot factors in a split-plot design, the factor *tree* was tested against its interaction with the *leaf generation* factor and the *leaf generation* against the residual error.

In 2011, gs and LMA estimates per leaf generation at the irrigated *versus* non-irrigated intensive study site were calculated by averaging five leaves per branch and three branches per tree but the statistical unit in this case was the tree (n = 3). The experiment was also a split-plot design with the whole plot factor *irrigation* and the split-plot factor *leaf generation* and *month*. Effects of these factors on gs and LMA were also tested by means of ANOVA followed by post hoc tests with the factor *irrigation* and *leaf generation* tested against their interaction and the *month* against the residual error.

Results

Site Conditions

The climate of Madrid (Fig. 3) is Mediterranean and continental with hot summers (on average 23.2°C), cold winters (on average 8.1°C) and little annual precipitation (436 mm), especially during the summer (precipitation minimum in August). Therefore to alleviate the summer drought many places throughout the city of Madrid are irrigated either manually or automatically, as can be seen at Atocha. At this site, artificial irrigation is supplied by sprinklers at varying levels between March and November, peaking in June, July and August and reaching overall 1027 mm per year (Fig. 3).

Ozone Pollution

The concentration and yearly course of O3 recorded at the Madrid air monitoring stations between April and September (2003–2007) was typical for an urban site. On average, and as a consequence of precursor accumulation and O3 production by road traffic and solar radiation, O3 concentration increased during the day and reached 48 ppb at 17:00 CET. In the evening and during the night, O3 concentration dropped to a minimum of 14 ppb at 09:00 CET (Fig. 5). The daily average, calculated on an hourly basis, reached 31 ppb with values ranging from 0 to 99 ppb. The exceedance of O3 threshold values (one-hour O3 concentration >180 µg/m3/92 ppb; [36]) amounted to 10 hours over 7 days in 2007, 13 hours over 8 days in 2006, 113 hours over 29 days in 2005, 74 hours over 22 days in 2004, and 165 hours over 36 days in 2003.

Regarding O3 exposure, yearly AOT40 (April to September) amounted to 15/11/9/13/8 ppm•h in 2003/2004/2005/2006/2007 and an average of 11 ppm•h for the whole period (Fig. 6). The highest daily AOT40 were recorded in 2003 and 2006 whereas rainy and cloudy weather, especially in 2007, reduced O3 exposure sizably. The cumulated O3 dose experienced by C+3 foliage, formed in 2004, amounted to 41 ppm•h.

Visible Injury

Visible O3-like injury in foliage of holm oak appeared as depressed, tiny, necrotic and intercostal stipples amid still green leaf tissue (Fig. 2I, Fig. 2J, Fig. 2K). Their small size and high frequency let the leaf appear homogeneously discoloured unless the stipples were resolved using a hand lens (Fig. 2D, Fig. 2E *versus* Fig. 2I, Fig. 2K). Stipples developed on the upper leaf side of non-shaded foliage exposed to full sun light. Leaf parts shaded by other leaves or twigs showed reduced stippling (Fig. 2F, Fig. 2G). The recently flushed foliage (C+0; Fig. 2D, Fig. 2H) was predominantly

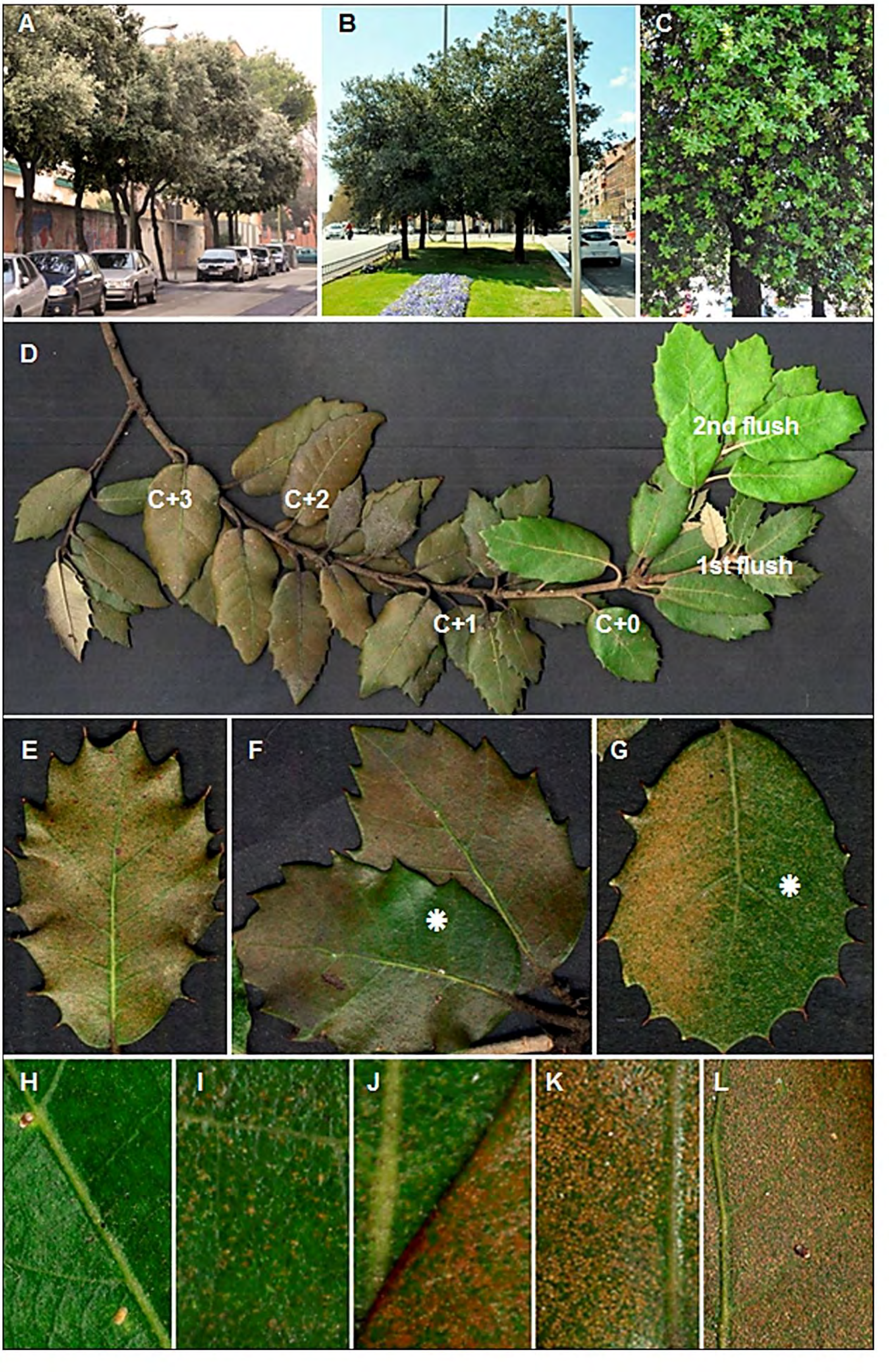
A
B
C
D
2nd flush
C+3
C+2
1st flush
C+1
C+0
E
F
G
H
I
J
K
L

Figure 2. Visible injury caused by ozone stress in urban holm oaks from Madrid. A the non-irrigated intensive study site at Escalonilla. Trees were asymptomatic. **B, C** the irrigated intensive study site at Atocha. At tree level, the older and symptomatic foliage showed dark brownish tones whilst the newly flushed leaves were green (**C**). **D–L** visible injury in holm oak at Atocha in 2007. **D** at branch level, the symptomatic foliage showed a bronze discoloration that increased with leaf age. **E–L** at leaf level, symptoms were characterized by, tiny, slightly depressed, intercostal and necrotic adaxial stippling surrounded by still green leaf parts. The high stippling frequency gave an overall bronze appearance to the injured leaf (**E, L**). Shaded leaf parts (*) showed less injury (**F–G**). The stippling frequency increased with leaf age (asymptomatic: **H:** C+0; symptomatic: **I:** C+0, **J:** C+1, **K:** C+2, **L:** C+3; leaf formation: C+0:2007, C+1:2006, C+2:2005, C+3:2004).
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asymptomatic whereas stipples generally developed in C+1 and C+2 leaves (Fig. 2J, Fig. 2K). Stippling intensity increased with leaf age (Fig. 2D) to such an extent as to give the older foliage an overall bronzed appearance (Fig. 2B, Fig. 2C, Fig. 2E, Fig. 2L). The stippling rates varied significantly between trees and increased with leaf age ($P<0.02$, Fig. 7). Holm oak subspecies showed similar type of visible injury (Fig. not shown).

Other visible symptoms occasionally observed and unrelated to the aforementioned stippling include 1) aphid exuviae and honeydew traces on C+0 leaves, 2) accumulation of soot and dust particles primarily trapped by hairs on the lower leaf side and nesting epiphytic communities in older foliage and 3) discretely distributed fungal infections (Fig. not shown).

Microscopic Symptoms

The leaf blade structure of the investigated holm oak leaves showed xeromorphic traits typical of a Mediterranean evergreen tree and which include a thick leaf lamina, thick-walled and lignified epidermis, thick cuticle and lower leaf side stomata protected by a thick and dense layer of hair (Fig. 8). In leaf parts with stipples, discretely distributed groups of necrotic cells were observed in the mesophyll (Fig. 8C, D *versus* 8A, B). Necrosis developed in the upper palisade cells and often extended into the lower assimilative layers. Stipples showed characteristic hypersensitive response-like (HR-like, [41], [42]) traits including 1) distribution of dead cells in discrete intercostal groups 2) cell collapse 3) cell content disruption and 4) cell remnant condensation (Fig. 8D *versus* Fig. 8B). Similar to stipples in fumigated foliage of *Fraxinus ornus* [21], folds and cracks in cell walls together with cell fragments leaking into the intercellular space were observed. Stipples were surrounded by degenerating cells as shown by cell wall thickening, chloroplast condensation and vacuolar accumulation of phenolics (Fig. 8C). Interestingly, the latter two markers were also observed within dead cells belonging to stipples (Fig. 8D). In contrast to the tissue level, cell-level gradients of injury caused by varying light exposure were missing. Droplets of cell wall material protruding into the inter-cellular space were often observed in the lower leaf blade - mostly within the spongy parenchyma layers (Fig. 8F *versus* 8E). Elevated levels of oxidative stress were indicated by the accumulation of oligo-proanthocyanidins (OPC) inside and surrounding recently formed stipples (Fig. 8H *versus* Fig. 8G). In C+1 *versus* C+0 leaves, an increase in oxidation of the cellular material was shown by the lower OPC signal and brownish unspecific staining of stipples (Fig. 8I *versus* Fig. 8H).

Structural changes by fungi and bacteria or insects were detected but they were spatially distinct and causally unrelated to stipples. They included 1) cell wall thickening in cells of hairs covering the lower leaf side and trapping dust particles or 2) cell collapse, cell wall thickening and cell content degeneration in vein phloem and nearby lower leaf blade tissues as a consequence of aphid feeding (Fig. not shown).

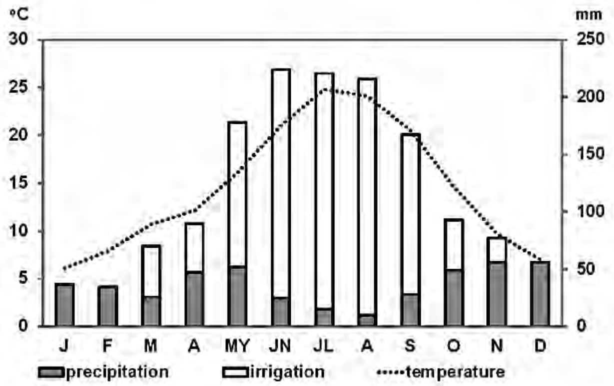

Figure 3. Climate diagram. Climatic conditions in Madrid and monthly irrigation totals at the Atocha intensive study site. Reference period for the climatic data: 1971–2007, average summer/winter temperature: 23.2°C/8.1°C, annual rainfall: 436 mm, annual irrigation: 1'027 mm.
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O3 Symptoms Survey

Out of the 65 sites surveyed in the Madrid conurbation in 2007, 24 (37%) including Atocha, were symptomatic with foliage of holm oaks showing varying levels of O3 injury (Fig. 1). With the exception of one site next to a stream, all symptomatic sites had supplementary water supplied by an automated irrigation system. On average, the proportion of symptomatic trees per site amounted to 25% ±5.3 (SE; range: 11–100%). Out of the 41 asymptomatic sites, only 12 (30%) were irrigated with water supplied by drip (19%) or manual (11%) once a month, presumably with lower amounts than at symptomatic sites. Variation in the plot size, water supply, site conditions or holm oak sub-species prevented further quantification of the stippling frequency.

Stomatal Conductance

On average, during a typical summer day in 2011, and from dawn to dusk, the C+1 holm oak foliage showed higher gs at Atocha than Escalonilla ($P<0.001$) with values 55.5% larger at the irrigated *versus* non-irrigated intensive study site (Fig. 4). At both sites, gs was highest in the morning topping at 9:00/7:30 CET in Atocha/Escalonilla. Gs experienced a slight midday depression increasing moderately again from 16:00 to17:00 CET, prior to a further drop in the evening. Hence, at Atocha, besides increasing gs, irrigation delayed the midday depression by a few hours, as shown by significant differences ($P=0.05$) between the sites from 9:00 to 12:00 am (Fig. 4).

The stomatal conductance varied as a function of the irrigation, leaf age and month (Table 1; Fig. 9). Particularly current year leaves C+0 followed the irrigation curve (Fig. 9 compared to Fig. 3, Pearson correlation coefficient for C+0 and irrigation = 0.88), whereas C+1 was correlated to C+2 (0.86). The site irrigation caused a significant increase in gs from May to October. During the peak irrigation period (May to September), gs values in C+0/C+1 leaves were 54%/31% higher on average at Atocha *versus*

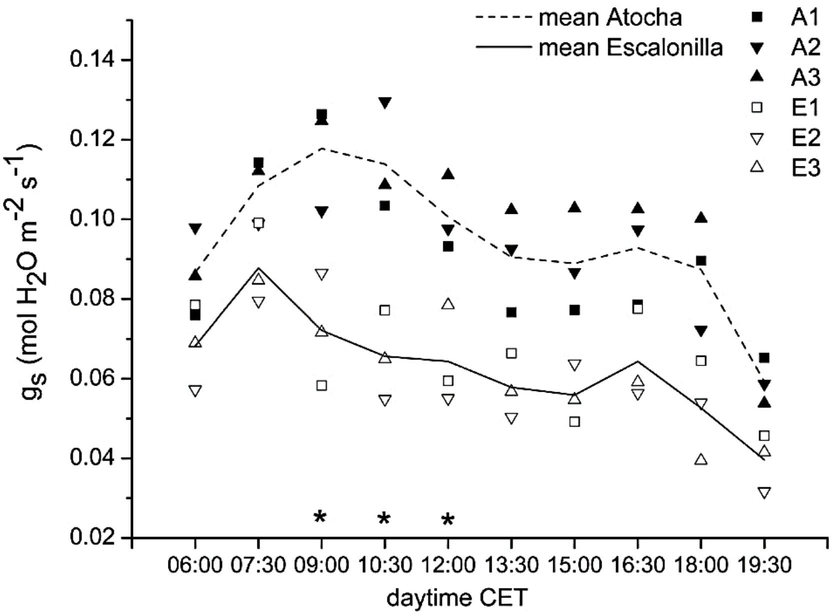

Figure 4. Daily time-course of stomatal conductance (gs). C+1 leaves (leaf formation: 2010) during a typical early summer day at the irrigated (A) Atocha (10[th] of June 2011; $T_{min} = 16.1°C$, $T_{med} = 20.1°C$, $T_{max} = 25.5°C$) and non-irrigated (E) Escalonilla (11th of June 2011; $T_{min} = 16.4°C$, $T_{med} = 20.5°C$, $T_{max} = 26°C$) intensive study site (means ± SE, n = 3 trees). The factors site (p>0.0001) and daytime (P<0.003) were significant. Stars indicate a significant difference between the site means (*p*<0.05) from 9:00 to 12:00 am.
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Escalonilla. Leaf age caused a significant decrease in stomatal conductance and younger leaves were more responsive to higher water availability (significant irrigation*leaf age interaction from May to October, Table 1). The C+1 and C+2 leaves showed a decrease in gs after the new C+0 foliage had sprouted. During the vegetation season (February to October), stomatal conductance varied between months, especially regarding younger leaves (significant leaf age*month interaction from May to October).

Leaf Biomass Partition and LMA

At both intensive study sites, the youngest leaf generation formed the highest biomass fraction in the analyzed branches (Fig. 10). However, there were differences between sites and, prior to and after the development of new C+0 leaves, older foliage made up a larger proportion of the total foliage biomass at Escalonilla than at Atocha. Hence from June to October 2011, during the highest irrigation and most O3-polluted period, the C+0 and older foliage biomass fraction amounted to 56% and 44% at Escalonilla *versus* 80% and 20% at Atocha. Finally at each site in October, the C+0 foliage's contribution to the total foliage biomass amounted to 61% and 86%, respectively.

As indicated by LMA and irrespective of the leaf generation, holm oak foliage showed a similar leaf xeromorphy at both sites (Table 2). During the 2011 vegetation season, monthly LMA

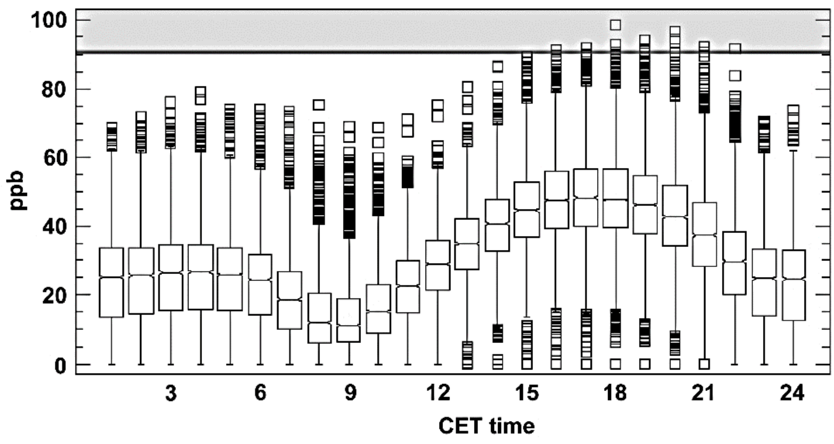

Figure 5. Boxplot of the average hourly (CET) O3 concentrations during the vegetation season. Data from April to September in Atocha for the years 2003–2007. The grey zone outlines the range of values exceeding the population warning threshold (box: interquartile range; whiskers: lower and upper quartiles; median horizontal line of boxes: median; white squares: maxima and minima).
doi:10.1371/journal.pone.0069171.g005

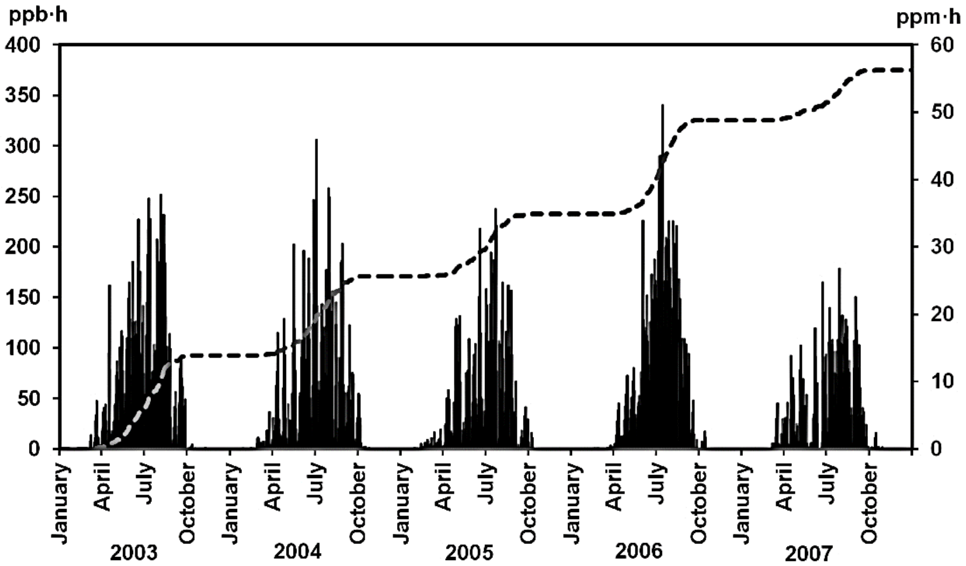

Figure 6. Daily (ppb·h, black spikes) and cumulated (ppm·h, grey line) AOT40 in Atocha from 2003 to 2007. Yearly AOT40 (April to September) in 2003/2004/2005/2006/2007 amounted to 14.55/11.26/9.0/13.45/7.55 ppm·h.
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estimates for C+1 and C+2 leaves at Atocha *versus* Escalonilla were not significantly different except during new foliage development (April and May). Regarding the C+0 leaves, it took three months at Atocha *versus* four at Escalonilla (Fig. 10) until adult and comparable leaf LMA values could be achieved (75±10.5 to 162±5.3 mg/cm2 from April to June *versus* 74±1.3 to 164±3.6 mg/cm2 from May to July).

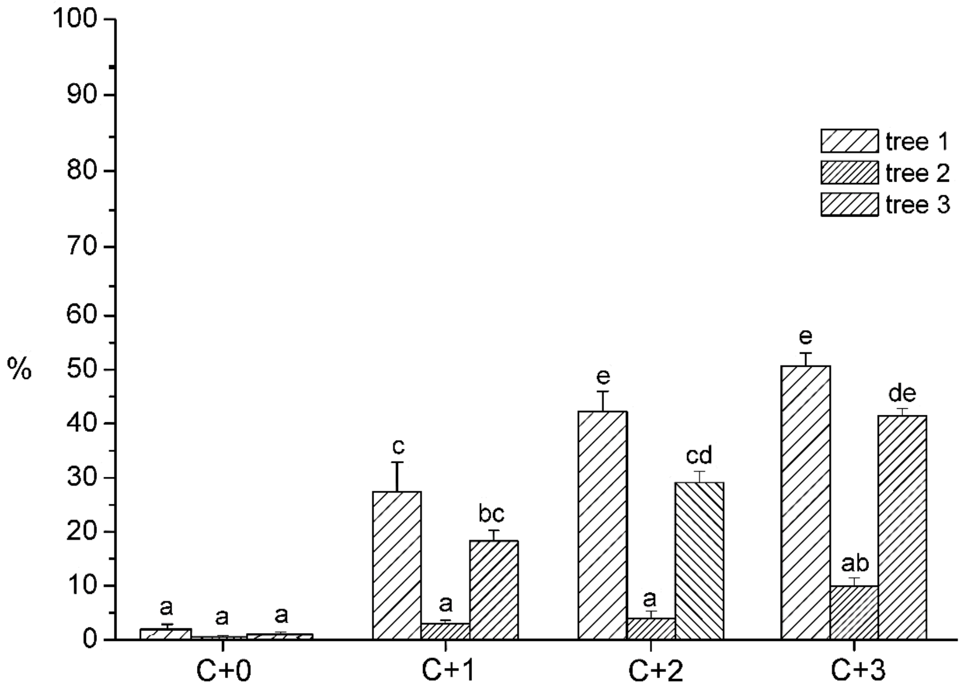

Figure 7. Mean percentage ± SE of leaf area showing adaxial stippling in holm oaks. Samples from Atocha in June 2007 (n = 4 branches per tree each with leaf age C+0, C+1, C+2, C+3). Different letters indicate significantly different percentages of symptomatic leaf area ($p \leq 0.05$).
doi:10.1371/journal.pone.0069171.g007

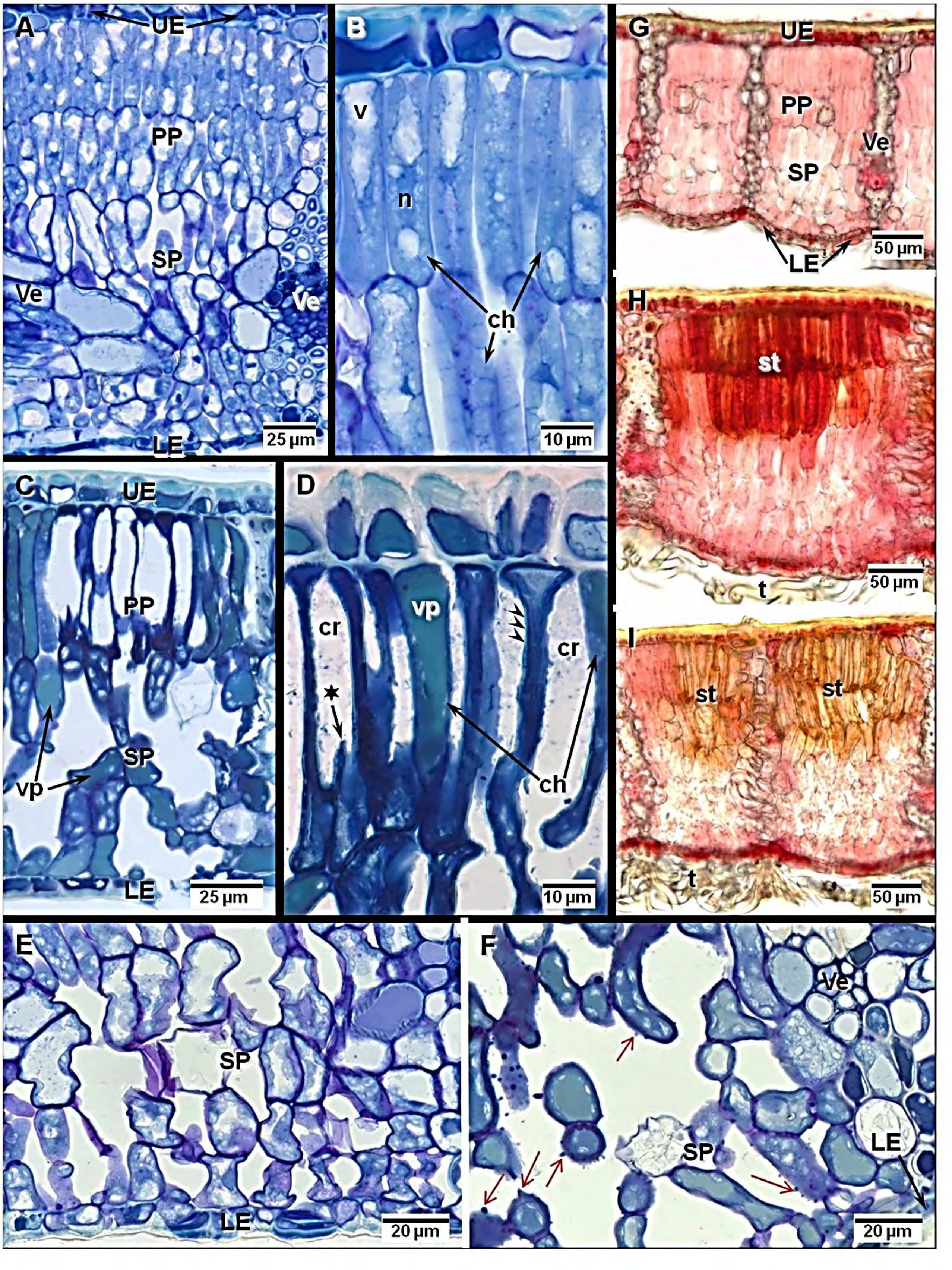
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Figure 8. Structural and histochemical changes in the leaf blade. Leaf age/formation C+0/2007, (**G**, **H**) and C+1/2006 (**A**–**F**, **I**). Symptomatic (**C**, **D**, **F**, **H**, **I**) *versus* asymptomatic (**A**, **B**, **E**, **G**) foliar samples. Leaf parts with stipples in symptomatic *versus* asymptomatic (**C** *versus* **A**) material showed discrete groups of necrotic and collapsed palisade parenchyma (PP) cells surrounded by degenerating mesophyll tissue. At cell level (**D** *versus* **B**), necrotic cells showed cell wall thickening (arrowheads), cracking (*) and folding and a disrupted cell content. The intercellular space contained cellular remains (cr). Degenerating cells showed thickened cell walls, enlarged vacuoles (v) filled with phenolics (vp) and smaller and condensed chloroplasts (ch). Within the spongy parenchyma, cell wall protrusions (red arrows), the frequency of which increased in symptomatic versus asymptomatic material (**F** *versus* **E**), were indicative of oxidative stress in the apoplast. **G**–**I** Photo-oxidative stress in stipples (st) of symptomatic (**H**, **I**) *versus* asymptomatic (**G**) samples was shown by gradients of condensed tannin reacting with acid-vanillin (red staining) between the upper (stronger staining) and lower (weaker staining) mesophyll cell layers. In older samples (C+1, **I**) and in contrast to younger symptomatic samples (C+0, **H**), stronger oxidation of proanthocyanidins in stipples was shown by the weak reaction of condensed tannins to acid-vanillin. UE, LE upper and lower epidermis; Ve: veins; n: nucleus; t: trichomes.
doi:10.1371/journal.pone.0069171.g008

Discussion

Stipples as Structural Injury Due to Ozone Stress

Within the analyzed holm oak leaves, the stipple morphology and the changes observed at cell level were typical of those associated with acute O3 stress as described for deciduous broadleaved species [13], [43]. Apparently, the thick leaf blade, a xeromorphic trait in *Q. ilex* [44], [45], did not modify the development of stipples although the distance between the O3-absorbing stomata and necrotic upper palisade parenchyma was larger than in deciduous foliage. In comparison to *Pistacia lentiscus* [22], not only degenerative changes but also necrotic stipples indicative of HR-like and resulting from defensive programmed cell death (PCD, [13], [46]) were found. Cracks in cell walls and cell content leakage similar to HR-like injuries reported for fumigated Manna ash seedlings [21] indicated a large production of and severe injury by ROS [47]. Differing from the latter species, necrotic cells in the present study showed phenolic accumulation and cell content disruption suggesting that PCD was preceded by a degenerative phase lasting more than a year according to morphological observations about stippling emergence. Indeed, PCD is ROS- concentration dependent [48] and an oxidative stress threshold thus needs to be exceeded prior to activating a PCD-program. Other oxidative and O3 stress markers in the studied holm oaks included 1) the wart-like droplets in lower mesophyll [49], [14], [16], 2) the positive reaction with acid-vanillin in and around young stipples [50] and 3) the impediment of the acid-vanillin reaction within older leaf material due to the oxidation of necrotic cell remnants [17]. The interaction between O3 and photo-oxidative stress [21] was indicated by the gradient of injury and OPC between lower and upper mesophyll in leaf parts with stipples.

Table 1. Significance (P-values) of two-way analysis of variance.

Factor	d.f.	g_s February to April	g_s May to October
Irrigation	1	ns	<0.001
Leaf age	3	0.001	<0.001
Month	2 or 5	0.011	ns
Irrigation * leaf age	2	ns	0.003
Irrigation * month	2	ns	ns
Leaf age * month	4 or 10	ns	0.006

Effects of the factors: irrigation (Atocha *versus* Escalonilla), leaf age/formation (C+0/2011, C+1/2010, C+2/2009, C+3/2008) and month on stomatal conductance (gs) and their interactions during spring with little irrigation (February to April) and summer with irrigation (May to October), ns not significant p≥0.05.
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The visible stippling morphology and distribution, together with the observed shading effects, were typical for O3 stress [10]. The homogeneous and intercostal distribution of stipples in foliage of the sun-exposed crown, their frequency increasing with leaf age and their occurrence within large tree crown portions of several trees per site at the many sites further confirmed the diagnosis [51]. Regarding the role of other stress factors, as potential causes for the observed leaf injury, besides ozone, a contribution can be excluded based on: 1) other phytotoxic components of photochemical smog, such as peroxyacetyl nitrate (PAN), do not cause HR-like reaction leading to stippling symptoms [13], [52], 2) the concentration of other gaseous air pollutants, such as the aforementioned SO_2 and NO_2, were too low or not phytotoxic, 3) the detected biotic injury was spatially and causally not related to the analyzed stippling, 4) eventual nutrient deficiencies or imbalances cause specific patterns of visible injury different from those caused by ozone stress [43] and 5) eventual soil contamination with metals lead to microscopic changes primarily along the water pathway through the leaf and these microscopic symptoms are clearly different from those induced by ozone stress [13], [51].

Ozone-triggered stippling has already been observed in fumigated holm oak seedlings [31], [32] and similar visible leaf injury has been documented in other deciduous and partly evergreen Spanish oak species (*Q. faginea, Q. pyrenaica*) exposed to O3 under controlled conditions [53]. To our knowledge however, the findings presented here are the first to show the structural changes associated with O3-triggered stippling in leaves of holm oak.

Ozone Stress in the Holm Oaks of Madrid

In the center of Madrid, the 2003–2007 AOT40 average (11 ppm•h) was above both the former (10 ppm•h) and present (5 ppm•h) concentration-based critical level for European forest trees [54], [55]. Compared to other South-Western European sites, it was slightly inferior to the 2000–2002 AOT40 range (13–19 ppm•h), whereas the warmer 2003 and 2006 years fitted into the lower part of the range [56]. Gradients of O3 concentration, increasing between the Madrid center and suburbs and varying according to micro-climatic conditions [2], may relate to the higher frequency of symptomatic sites at the city's periphery. Between 2003 and 2007, Madrid experienced exceedances over the 180 µg/m3 alert threshold more often than on average in the Iberian Peninsula but less frequently than in South-Eastern France and Italy (for example [3], [4], [5], [6], [7], 2003–2008). The 21 ppm•h O3 exposure required for the appearance of visible injury in holm oak at Atocha (sum of 2007 and 2006 AOT40) was lower than that indicated for the fumigated holm oak seedlings mentioned previously [31], [32]. However, it was still largely higher than that which causes symptoms in most young deciduous broadleaved trees so far tested [57], [58], [59] or promoting functional alterations in holm oak foliage fumigated experimentally (3 ppm•h, [32]). The O3 exposure needed for the develop-

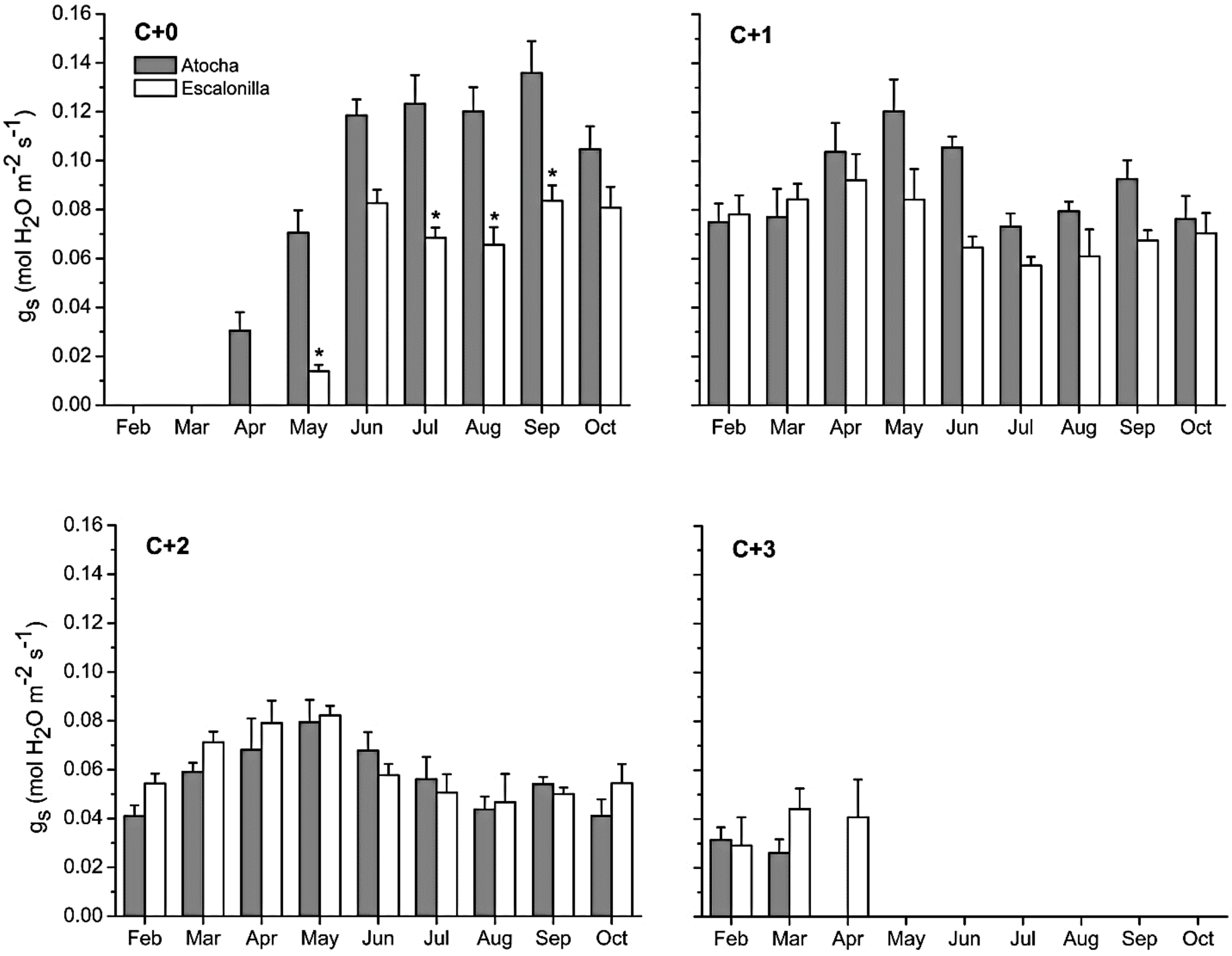

Figure 9. Seasonal variation of stomatal conductance (gs). C+0, C+1, C+2 and C+3 foliage (leaf formation: 2011, 2010, 2009, 2008, respectively) at the irrigated (Atocha, grey bars) *versus* non- irrigated (Escalonilla, white bars) intensive study site in 2011 (means ± SE, n = 3 trees). The monthly irrigation supply at Atocha is shown in Figure 2, the significance of influencing factors in Table 2.
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ment of leaf injury may also change according to the years and experimental settings as shown for *Pistacia lentiscus*, another evergreen xerophyte, with injury threshold varying from 9 to 74 ppm•h [22]. Hence, the O3 exposure recorded at Atocha was considerable with respect to the Iberian average but remained, with regard to structural injury in holm oak, within the lower range of values expected to cause symptoms in a sclerophyll evergreen tree relatively insensitive to O3 stress [1], [60].

Table 2. Mean leaf mass per area.

Leaf age/ formation	C+0/2011	C+1/2010	C+2/2009	C+3/2008
Atocha	16.5±0.1	16.9±0.3	17.3±0.1	17.2±0.3
Escalonilla	16.5±0.1	16.7±0.3	17.1±0.2	17.1±0.3

LMA (mg/cm2) ± SE per leaf generation at the irrigated (Atocha) and non-irrigated (Escalonilla) site in October (C+0, C+1, C+2) and March (C+3) 2011. Differences between sites and leaf generations were not significant (p>0.05; N = 3 trees).
doi:10.1371/journal.pone.0069171.t002

Increased Ozone Uptake in Holm Oak Foliage as a Trade-off for Site Irrigation

By raising gs in Atocha *versus* Escalonilla, irrigation was confirmed to increase O3 uptake during the whole day and alleviate the midday gas exchange reduction during peak O3 hours. Other studies have also documented the responsiveness of holm oak to higher soil moisture availability [61], [62] with enhanced O3 stomatal uptake at O3 polluted sites as a trade-off for an elevated water supply [63], similar to findings on other species [33]. In Madrid, findings from the leaf injury survey suggest that O3 symptoms were even conditioned to site irrigation and higher water availability. At Atocha, the highest levels of O3 exposure, site irrigation and leaf gs were recorded during the summer and these factors could synergistically contribute to an increased O3 uptake in irrigated *versus* non-irrigated holm oak. Interestingly, only the younger C+0 and C+1 leaf generations were responsive to elevated water availability. Besides shading by new foliage and lower gs with increasing leaf age [64], leaf injury might further reduce gs in older holm oak foliage as suggested by the concomitant development of stippling and reduction of gs in C+1 leaves recorded during the summer. Overall, the gs values

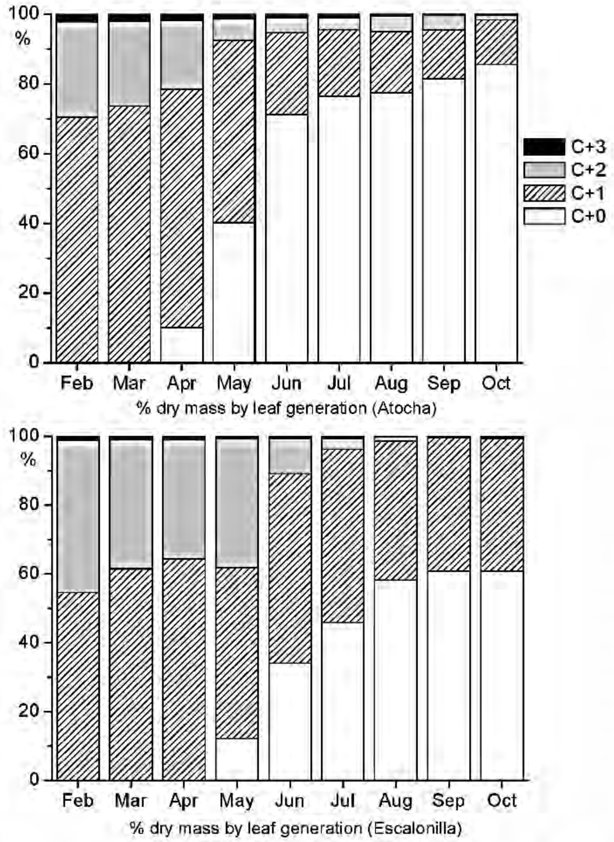

Figure 10. Monthly changes in the foliage biomass fraction (expressed in %) of each leaf generation. Leaf age/formation C+0/2011, C+1/2010, C+2/2009, C+3/2008 within holm oaks from the irrigated (Atocha) and non-irrigated (Escalonilla) intensive study site in 2011 (mean values of 3 trees).
doi:10.1371/journal.pone.0069171.g010

measured in Madrid were in the range of those published for Mediterranean forests subjected to summer drought [65], [66], the highest gs rates for C+0 leaves were in line with findings by [62]. The C+0 and C+1 leaf generations with the highest gs were also those least symptomatic. This paradox probably related to the aforementioned exceedance of an oxidative stress threshold needed for triggering a PCD-program and causing visible stippling, as a consequence.

Leaf Life Span of Irrigated Foliage

Compared to Escalonilla, the leaf turn-over in Atocha's holm oak foliage was accelerated. Generally, foliage showing higher stomatal conductance, as in Atocha, is also shed earlier [67]. Furthermore, water-restricted versus water unrestricted evergreen trees tend to keep their older foliage a longer time and use it more intensively [68]. Competition between older and younger leaves might also contribute to leaf turn-over, as suggested by leaf-drop primarily after new leaf flushing instead of throughout the spring and after the summer drought period, as usual. Besides leaf physiology and competition factors, O3 accelerates leaf senescence [69], [70] which can lead to a reduction in the amount of leaf generations in evergreen trees [71]. Here, this effect is suggested by the concomitant decrease of gs and development of stippling. Hence and synergistically with other causes, O3 might contribute to reduced leaf life span in the irrigated and symptomatic holm oaks.

Leaf Xeromorphy and Irrigation

Whatever the leaf generation, the leaf xeromorphy was not affected by irrigation, as indicated by similar LMA at both study sites. With reference to [72], these findings were unexpected. The values found in Madrid were similar to those indicated for holm oak in other urban conditions [73] on rather mesic Italian sites [74] or under similar precipitation and temperature regimes in Catalonia, Spain [75]. As found by [45], the LMA of mature leaves did not change significantly through time. Consequently, the development of O_3 injury proceeded independent of the leaf xeromorphy and primarily related to enhanced gs and higher O_3 uptake.

Conclusions

In synthesis, the initial O3 symptom diagnosis was confirmed on the basis of the macro- and micro-morphological changes found in irrigated holm oak foliage (objective 1). Ozone injury similar to that detected at the intensive study site of Atocha was found throughout Madrid but predominantly at sites with automated irrigation (objective 2). O3 exposure up to a harmful level for the natural vegetation was recorded in air monitoring stations close to our intensive study sites but at levels apparently too low to cause visible injury in an evergreen tree rather insensitive to O3 stress (objective 3). On the basis of subsequent gas exchange and biomass/LMA measurements, higher rates of stomatal O3 uptake in irrigated and symptomatic trees were corroborated (first hypothesis) whereas no difference in the leaf xeromorphy between the irrigated and non- irrigated site was found and therefore the second hypothesis was rejected. Given the concomitant maximum irrigation and peak O3 pollution, the O3 tolerance of irrigated holm oaks appeared to be lowered to levels similar to those recorded for other broadleaved trees. This particular case of leaf injury by O3 stress because of the irrigation gives insight into mechanisms driving O3 symptom expression in sclerophyll evergreen trees. In holm oak at least, they suggest that stomatal closure, particularly during peak O3 pollution, can be more effective than leaf xeromorphy to reduce stomatal O3 uptake and outlines the driving contribution of soil moisture availability for O3 symptom expression in dry climates.

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Author Contributions

Conceived and designed the experiments: CCG PV MGG. Performed the experiments: CCG. Analyzed the data: CCG PV MGG. Contributed reagents/materials/analysis tools: CCG PV. Wrote the paper: CCG PV MGG.

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Chapter 4

URBAN TREES AS AFFECTED BY AIR AND SOIL POLLUTION IN BIG CITIES – THE EXAMPLE OF MADRID

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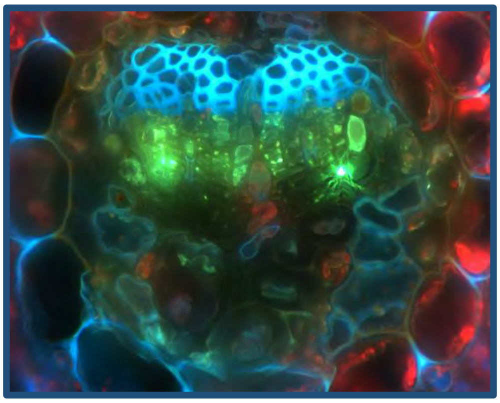

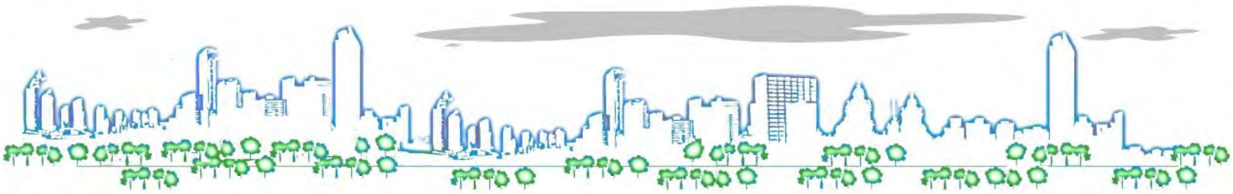

Chapter 4 URBAN TREES AS AFFECTED BY AIR AND SOIL POLLUTION IN BIG CITIES – THE EXAMPLE OF MADRID

Chapter 4 URBAN TREES AS AFFECTED BY AIR AND SOIL POLLUTION IN BIG CITIES – THE EXAMPLE OF MADRID

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Abstract

Urban pollution and urban trees have been studied in Madrid, a southern European city with almost 4 M inhabitants, 2.8 M daily vehicles and 3 M trees under public maintenance, during the last decade. Most trees are located in the two peri-urbans forests, 650'000 trees along urban streets and in parks. The urban taxa included *Platanus orientalis* (97'205 trees), *Ulmus* sp. (70’557), *Pinus pinea* (49'038), *Aesculus hippocastanum* (22’266), *Cedrus* sp. (13'678 and *Quercus ilex* (1'650) along streets and parks. Leaf samples were analysed sequentially in different seasons, PM_{10} data from 28 air pollution stations during 30 years, traffic density estimated from 2’660 streets.
Metal accumulation on the leaf surface and within the leaves was estimated per tree related to air pollutants, traffic intensity and soil contamination. Mean concentration of Ba, Cd, Cr, Cu, Mn, Ni, Pb and Zn were measured on topsoil samples collected nearby the sampled trees amounting: 489.5, 0.7, 49.4, 60.9, 460.9, 12.8, 155.9 and 190.3 mg kg^{-1} respectively. Pb and Zn pointed to be tracers of anthropic activity in differenced areas of the city regarding vehicle traffic as the main source of diffuse pollution on trees and soils. The tree species differed by their capacity to capture air-borne dust and to allocate trace elements from contaminated soil. Pb and Zn concentrations in the foliage were above the limits in different sites and microscopic Zn revelation showed translocation of Zn in xylem and phloem tissue. Spatial trace element mapping showed for central *Retiro* Park certain high lead concentrations in the soil related to a Royal pottery 200 years ago. According to results, the use of a combination of *Pinus pinea* with an understorey *Ulmus* and *Cedrus* sp. layer could be recommended for best air filter efficiency.

Keywords: Air pollution, trace elements, biomonitoring, mapping, soil metal contamination, PM_{10}

1. Introduction

1.1 Urban air pollution

The urban environment in the next decades will be of increasing importance regarding four main issues: 1) population, 2) energy consumption; and as a consequence, 3) urban pollution and 4) human health. According to UNEP (2011), world’s cities accounted for 60-80% of the energy consumption and 75% CO_2 emission in only 2% planet’s surface, associated to more than 20 world mega-cities (>10 M inhabitants) and a number of intermediate-size big cities (1-10 M inhabitants) that has increased from 270 to 486 in the last 20 years. The proportion of urban population in more developed regions in the world have reached 77.7% of the total world population (6’916 M) on average in 2011, accounting 35.6 M in Spain (United Nations, 2011). In Madrid, Spain, (example of an intermediate-size big city with almost 4 M inhabitants) road traffic is generated by 2.8 M vehicles, being the main contributor to air pollution with 87.35% of PM_{10} (particulate matter having an aerodynamic diameter <10μm) and 84.13% of NO_x vs. 9.46 % and 6.51% by heating systems and 2.97% and 5.92% by industrial activities, respectively (Ayuntamiento de Madrid, 2002). Consequently, pollutants released from industry, energy providing and, mainly, vehicular activities will be a serious problem to face.

Although urban air quality in the more developed countries has generally improved over the last 20 years by controlling emissions from stationary and mobile sources, urban air pollution is still a serious problem for human health. In particular, PM_{10} particles enhance respiratory diseases (Brunekreef & Forsberg, 2005). According to Ministry of Environment, 20'000 persons die each year as a consequence of air pollution in Spain, 400'000 in Europe (Comunidad de Madrid, 2012) and early death of more than 2 M every year in the world is estimated (WHO, 2011). Cities that have reduced PM_{10} levels of 20 µg/m^3 have a 10% lower mortality rate than those with levels of 150 µg/m^3 (Dora, 2007).

1.2 Traffic

Diesel engines were among the most important sources of PM_{10}, accounting 207 M of passenger cars in the world in 2010 (CCFA, 2011), besides commercial vehicles, heavy trucks, coaches and old buses fleet. In the EU countries, diesel-engine vehicles represented 35% of the total number of engines on average. This percentage of registered diesel-engine vehicles was even higher in Austria, Belgium, Spain, France and Luxembourg, exceeding 50%. In Spain, the percentage of diesel vehicles increased from 14% to 53% and 70% in 1990, 2000 and 2010 respectively. Diesel fuels used by diesel-driven motor vehicles accounted for 79% of total petrol consumption in Spain (CEPSA, 2009). Beside, traffic jams affected nearly 1M users that led to lose 329'000 working hours a day with an estimated cost of 3.4 M € each day (RACC, 2009).

The pollution forecast for the next years suggests that the 50 µg/m^3 daily PM_{10} threshold, which has been reduced to 7 days per year since 2010, will be exceeded in the next decade due to high Average Daily Traffic (ADT) in different areas in Madrid, as well as other European cities such as Paris or Rome. Some restrictions as speed limits or the number of allowed vehicles are common measures applied to reduce the pollution during the highest pollution episodes (Invernizzi *et al.*, 2011). Apart of high ADT, which only has decreased in the last years because of the crisis, road network has been growing. Out the 60'709 hectares of Madrid Municipality total area, 5'100 hectares (8.4% of total) corresponded to the road network of sidewalks (1/3) and driveways (3/4), which have increased from 2'500 to 4'500 km in the last decade due to the new PAU developments (Program of City-planning Action). Thus, traffic will be a serious problem regarding to pollution in the cities.

1.3 Trace element emissions by traffic

Vehicles are the main source of emission of the most common urban trace elements: Ba, Cd, Cr, Cu, Mn, Ni, Pb and Zn (so-called heavy metals (HM)). Directly by: 1) emission from the combustion of gasoline and diesel [Ba is included in gasoline such as a substitutive of Pb and Mn is a fuel additive,(Monaci & Bargagli, 1997; Monaci *et al.*, 2000)]; or indirectly from traffic-related sources: 2) corrosion of component wear such as brakes and radiators (Cu), 3) degradation of asphalt pavement (Zn, Pb, and Cu depending on the components of asphalt), 4) abrasion of tyre rubber [Cd, Zn and Pb, (Sörme & Lagerkvist, 2002)], 5) road marking paints [Cd, Pb, Cr, (Ozaki, Watanabe, & Kuno, 2004)], 6) anticorrosive and galvanized protections [Zn, (Korenromp & Hollander, 1999)] and 7) additive materials in oil lubricants [Ba, Cd, Cr, Ni, Pb and Zn, (Nadkarni, 1991)]. These metals remain in soils for years. Thus, they can indicate the deposition of atmospheric particles by road traffic in urban areas (Sutherland, 2000), even from the past.

1.4 Trace elements in urban soils

Generally, urban soils have a poor structure and a variable concentration in trace elements that can reach high values compared to natural background levels (Kabata-Pendias & Pendias, 1992). Soil monitoring in cities is compromised by the sources variability and mobility in time and space (e.g. civil constructions, water recycling irrigation and sewage sludge from municipal wastewater treatments), but also by accessibility of soil sampling in the city, restricted to open spaces such as parks, gardens, peri-urban forests, road embankments, landfill or recreational area. Despite the spatial restrictions, urban soils provide valuable information about toxic effects on humans and groundwater contamination (De Miguel *et al.*, 2007). Different sampling techniques, conditioning, preparation, chemical analytic procedures and changes in legislation increase the difficulties to compare with previous studies. The needed reference background levels are often missing or obsolete with current levels. In the last 15 years, effort has continued and more than 160 urban soils studies have been carried out (Biasioli, Barberis, & Ajmone-Marsan, 2006); some of them in Spanish cities such as Seville (Madrid, Díaz-Barrientos, & Madrid, 2002) or Madrid (De Miguel, Jiménez de Grado, Llamas, Martın-Dorado*, et al.*, 1998). Unfortunately their restricted areas or the scarce amount of selected sites do not allow an overview on big city's soil pollution. The use of Geographic Information Systems (GIS) in polluted soils and trees have been addressed in some studies (Jensen *et al.*, 2004; Manta *et al.*, 2002), including Barcelona (Spain) (Viladevall *et al.*, 2013) in some districts of Barcelona, while concentrations of HM geographically generated in an entire city in Spain remain poorly documented and, to our knowledge, no-one has compared the number of tree species for a soil-trees-traffic-air pollution situation to this scale.

Most historic parks in the cities have remained in the same location for centuries and could be used as biomonitors or markers of the pollution in the past (Calace *et al.*, 2012). *Retiro* Park is one of the main green areas in the centre of Madrid. The park belonged to the monarchy since the 15th century and was an isolated place for private use (hunting and leisure). Therefore, it was supposed that lowest soil contamination would be found in the centre of the park, while the perimeter would be affected by the influence of atmospheric particulates from the dense traffic road, as in Athens (Chronopoulos *et al.*, 1997).

1.5 Urban pollution and trees. Monitoring, effects and air pollution amelioration.

For a comprehensive study of the effects of urban pollution on trees and air pollution amelioration by urban trees, HM concentration in soils and atmospheric deposition values were required. The uptake, deposition and accumulation was addressed by two different ways of capture/uptake: 1) foliar surface and 2) root system (Alfani *et al.*, 1996). In the last decades, the use of mosses or lichens as biomonitors has been widely spread (Aboal *et al.*, 2006; Zechmeister *et al.*, 2005), as well as algae (Pinto *et al.*, 2003) and higher plants (Weiss *et al.*, 2003). Manning and Feder (1980) highlighted that tree canopies in forests captured pollutant particles more efficiently than any other type of vegetation. Air-borne particles were retained on the leaf surface (Beckett, Freer Smith, & Taylor, 2000), acting as "green lungs" by filtering air pollution (TEEB, 2010). Thus, urban trees may show HM introduced by deposition of traffic emissions. Meanwhile, the effects of air and soil pollution on urban trees have been studied in different urban and rural environments (Bargagli, 1993). Therefore, urban trees may be a reliable alternative in big cities.

Computational models to estimate the quantity of air pollutants (SO_2, CO_2, O_3 and NO_2) removed by green vegetation were developed in different cities in the USA (McPherson, Nowak, & Rowntree, 1994), whereas empirical studies of HM accumulation or airborne captured by urban trees surfaces, associated with soil contamination in a big city scale have remained poorly documented.

1.6 Aims of the study

In our point of view, the aforementioned soil-trees-traffic-air pollution system and their interactions required of a progressive interpretation, from the cell's tissues to the tree level (Günthardt-Goerg *et al.*, 2008) and finally to a city scale overview. The present study aims: (1) to distinguish the air-born from soil-born trace metal uptake in the trees species, (2) to map each single urban trees position related to ADT on streets, as well as, the quality of the air and soil pollution of a big city like Madrid and (3) to obtain the different urban trees capacity to capture air-born dust on the foliage surface as related to traffic intensity. In this sense, we aim to suggest adequate tree species and, finally, to enhance an often undervalued role of urban trees in big cities.

2. Material and methods

2.1. Air pollution. PM_{10}

Air quality was monitored by analysers integrated in a network of air monitoring stations and operating continuously by recording an average value every 5". 20 stations were operating in the early 80's, four more were added since 1990 (Ayuntamiento de Madrid, 2002). The network reached 28 monitoring stations in 2007 (Fig. 3 & Figs. 5-7). Data of particulate matter (PM_{10}) in Madrid were provided by the Air Quality Municipality Department and processed to daily average for each monitoring stations during 1980-2010 (Figs. 5 & 6). The collection of data was regulated under the 80/779/CE Directive, amended by 89/427/CE, when particles were measured by the gravimetric method. The number of days with exceeding values were calculated for each station and year. From 2001 to 2005, the annual limits were set gradually to decrease from 75 to 50 µg/m^3 by a restriction of 35 exceeding days, maintaining this limit, but reducing the restriction of the exceedance to only 7 days after 2010. In the absence of clear criteria for PM_{10} exceedance from 1980 to 1999, we applied the daily limit of 75 µg/m^3 for 35 days, established in 2000, also for previous years. Punctual missing values were completed by the average of the network station for a specific date and estimated by proportionality to the whole period. The studied period finished in 2010 due to reorganization of the air quality network in Madrid.

2.2. Traffic

The continuous data collection for the traffic density estimation were provided by 60 permanent automatic stations plus a large number of automatic gauging for weekly and daily traffic at intersections These values were given by the municipality of Madrid and displayed spatially by their coordinates as the average for the 2003-2008 period for each of 2'660 street sections in 2'314 main streets (Fig. 7). ADT is the number of vehicles passing through a road distance for 24 hours in both directions on a working day. AADT is the average ADT per year. During the period 2004-2007 ADT in Madrid Southeast were affected by works for the M-30 1st ring tunnel construction between the A-4 and A-5 highways (Fig. 7 between * and **). Individual quantitative estimation of the PM_{10} deposition on trees by mobile sources was calculated by the average value of the daily traffic density (ADT) on every street and the distance to the trees.

2.3. Soils

Soil and foliage samples were simultaneously randomly collected (n=196) to represent the city area. The sites were situated mainly in green areas of the central almond of the city surrounded by the M-30 (1st ring) motorway, as well as in peri-urban forests and districts inside the M-40 (2nd ring) motorway, except El Pardo forest, which was excluded due to access restrictions. 14% of the samples were collected on tree grates at paved major road intersections. Seven soil samples from *Cedrus* and *Aesculus* forest, in an undisturbed environment, 78 km away from Madrid were collected to set background level. Soils samples in *Retiro* Park were double-checked to confirm lead concentrations. HM concentration was also compared to regulations. In particular to Order 761/2007 and 2770/2006 of the Ministry of Environment and Spatial Planning on generic reference levels for protection of human health from heavy metals and other trace elements in soils of the Community of Madrid.

Soils samples were collected by auger in 20 cm topsoil without litter, stones and unexpected objects. Four subsamples (2 kg) within the range of the tree crown projection were pooled, mixed and sealed in plastic bags. After homogenization and air drying, 1 kg was oven-dried at 105°C for 72 hours, passed through a 2 mm plastic-mesh sieve and crushed to a particle size (<100µm). An aliquot of 0.5 g dried and pulverized sample was digested with 5 ml HNO_3 in a microwave oven (Milestone model Ethos Plus2). The total contents of Pb, Ba, Cr, Cu, Mn, Ni, Cd and Zn were measured using a plasma emission spectrophotometer THERMO-OPTEK (Model: Iris Advantage Duo Ers).

2.4. Trees and foliage sampling

The six selected tree species were three deciduous (*Platanus* sp., *Ulmus* sp., *Aesculus hippocastanum*) and three evergreen tree taxa (*Quercus ilex* L., *Pinus pinea* L. and *Cedrus* sp.) which accounted 80% of Madrid's urban trees. Sampled trees were randomly selected from the inventory data provided by: 1) environmental authority at Madrid Council, 2) National Heritage and 3) *ad-hoc* data from own inventories at: 3.a) *Retiro Park* (carried out in 2005/2006) and 3.b) *Casa de Campo* peri-urban forest, obtained from transects for phytopathological assessments (2002-2007) (Calderón Guerrero & Rodriguez Barreal, 2007). For each tree species, X,Y-coordinates, diameter at 1.3 m tree height (DBH), total height, crown height, crown diameter, tree age and type of irrigation were measured and mapped (Fig. 3).

Selected trees (DBH≥15 cm) were assigned to one of the surrounding areas of the 28 Municipality Air Quality Monitoring Stations, including trees in the 120-hectares *Retiro* Park and organized in sampling sites. Foliage was sampled from summer 2005 to spring 2007. Branches from mature and healthy trees (mean DBH: 35 cm; mean height: 13 m) were selected and cut using a 4-meter adjustable telescopic pruning lopper with pulley system (picture page 125) and a collecting basket (ø=60 cm; h=100 cm), set at cutting height in order to avoid loss of dust from the leaf surface. 20 branches about 50-100 cm in length were cut equally in all directions around the edge of the crown. Leaves ≥ 2 kg fresh weight were removed (wearing polyethylene gloves) immediately from the middle of the main shoots and stored in a set of re-closable plastic bags in portable freezers. The harvesting of samples was performed ≥5 days after precipitation in order to avoid wash-off or leaching immediately before the collection.

In the lab, 50-100 leaves or 500 needles from samples were randomly selected to determine fresh weight, leaf area (EPSON scanner, image analysis system, Scion Image, Scion Corporation, Frederick, Maryland, USA) and dry mass (broadleaves 80ºC, needles 105ºC, 48 hours in a ventilated oven). Needle projected area was corrected with factor 2.74, which was deduced from *P. pinea* and *Cedrus* sp. needle geometry. Elemental analyses were carried out as for soil samples. Complete foliar biomass values for the studied species were obtained from trees felled after storms or because of their potential risk for pedestrian during the studied period. The total weight of the individual trees was obtained by truck weight (loaded and unloaded). Trees were separated in foliage, branches (Ø> 3 cm), twigs (Ø≤ 3 cm) and stems, ratios were calculated, as explained in (Martín Lorenzo, 2010). The biomass measurements were part of the results of the bachelor thesis with the collaboration of the author of this thesis dissertation, who also was the bachelor thesis supervisor.

Extracellular epicuticular wax with trapped fine dust particles from representative foliage per tree crown (harvested branches included several leaf generations in evergreens) was obtained after washing 150 g of fresh foliage with a mixture of ultrapure water and CH_2Cl_2. When water was employed, a certain percentage of the dust particles remained trapped in the epicuticular wax after washing (Fernández Espinosa *et al.*, 2002; Voutsa & Samara, 2002). When organic solvents were used, extracted epicuticular wax may contain also leaf-internal trace elements and nutrients. After different test concentrations for each species and leaf surface checked by incident light and scanning electron microscopy (Calderón Guerrero, 2006), the following mixtures were used for a 5 minutes extraction by shaking: *Cedrus* sp. and *Pinus pinea* (100:100ml H_2O:Cl_2CH_2), *Quercus ilex* (100:200), *Aesculus hippocastanum, Platanus orientalis* and *Ulmus* sp. (400:100) (table 6). The leaf samples were rinsed with water and their area and dry mass determined. Ultrapure water was estabilished by a Milli-Q plus system (Resistivity ≤ 18.2 MΩ•cm^{-1} at 25 ºC, Millipore, Bedford, USA).

Subsamples of entire leaves before extraction, surface (wax+dust) and leaf-internal (washed leaves) material were prepared for analyses of Ba, Cr (detection limit 0.6 mg·kg^{-1}), Cu (3.6), Ni (0.9), Pb (3) and Zn, the same as the soil samples. Analyses were carried out by ICP-AES in the central laboratory of WSL.

2.5. GIS

Data were processed for statistical analysis using *Statgraphic* 2010. ADT map was produced in *AutoCAD* Civil 2012 by *Autodesk*. These data, as well as trace elements and PM_{10}, were processed in *ArcMap* 10.3 (*ESRI* Inc., California, USA) and georeferenced to WGS European 1984 for spatial distribution maps and layouts. For all GPS-based trees (>650'000 on street, parks and gardens), the short distance from each single position (X,Y) to the closest principal adjacent road or main junctions (when traffic density from various streets increased the emission values) were automatically calculated by *ArcMap* tools to investigate the effect of the tree's distant to the mobile sources.

Distribution patterns of the main anthropogenic HM in soils were displayed by a set of single element concentration maps and a graphical analysis was performed to obtain layers, covering the studied area by the spatial analyst visualization tool. Two different spatial interpolation techniques: (1) inverse distance weighting (IDW) and (2) Kriging were applied. High-resolution raster layers were reclassified into 8-10 intervals. The criteria for the spatial modelling regarding categories, classification and thresholds of the values followed the literature about phytotoxicity thresholds for different soils in the world (Alloway, 2013; EPA, 2003; Kabata-Pendias & Pendias, 1992; Pais & Jones, 2000; Siegel, 1975), as well as international (CCME, 2012), European (Ministério do Ambiente, 2006; Ministero dell'Ambiente, 2006; Ross SM *et al.*, 2007; SEPA, 2002) and national/regional standards (9/2005 law and 2770/2006 act amended by 761/2006 act) according to the most suitable situation. This approach based in geostatistic techniques should be considered under the assumptions of continuity of concentration values in soils. Despite discontinuity caused by human activities and structures, it could contribute for a general overview of big city's soil pollution. Spatial interpolations were cropped by the city-limit extension of the individual urban trees positions studied.

2.6. Macroscopic and microscopic observation. Histochemical revelation of Zn

20 randomly selected leaf samples from 3 *Cedrus* and 3 *Aesculus hippocastanum* from *Retiro Park* were prepared for Scanning Electron Microscopy (SEM) for both adaxial and abaxial leaf surfaces using a *Philips XL30* apparatus. Discs of 10 mm diameter were cut from unwashed leaves. Ten photomicrographs were randomly taken of each 0.03 mm^2 area at a 624-fold magnification. Five randomly selected leaf samples from six different tree species were prepared for binocular observation. A disc of 20 mm diameter was cut from each unwashed leaf. For histochemical revelation of Zn, sub-samples of fresh current-year leaves/needles from the middle crown were harvested in September 2006 at sites with different soil Zn concentrations (34.5 to 470 mg kg^{-1}). Middle parts of leaves and needles were excised and further proceeded as reported by (Vollenweider *et al.*, 2011).

3. Results

3.1 Tree inventories

Data from National Heritage and municipal inventories (completed by own inventories when needed) were joint in the same format from the different data bases to include all major tree species in Madrid (Fig.1), each tree being located by GIS (except trees of two major suburban parks) (Fig.3). Madrid counted 2'980'583 trees under public maintenance during 2005-2010. 674'197 trees, including those managed by the National Heritage, were street trees or located in public parks/garden. 2.3 M were in peri-urban forests around the city such as the *Casa de Campo* (0.7 M) and *El Monte de El Pardo* forests (1.6 M). The comparison between street trees and the greenest cities in the world is provided in Table 1.

The six studied taxa accounted 2.3 out 3 M trees in the municipality of Madrid (78.5% of total inventory) (Table 2). The two predominant species: *Q.ilex* and *P.pinea* were common in peri-urban parks, while the most common tree species in alignment and parks were *Platanus* sp. and *Ulmus* sp. (Fig. 2). The ad hoc inventory carried out in *Retiro* Park in 2005/06 indicated that *Aesculus hippocastanum* was the main species, 6'725 out of 20'589 trees, followed by *Platanus* (1'198) in the broadleaves group, while *Pinus* sp. (1'027) and *Cedrus* sp. (654) were the most frequent conifers. The average dasometric characterization for the studied species is summarized in Table 3. Those values showed the average data obtained for dasometriy for a representative adult tree and used in the calculation of biomass and specific leaf area (SLA) as explained in the methodology section. The values of SLA [m^2 kg^{-1}] obtained were: *Platanus* sp.= 15.14, *Ulmus* sp.= 12.77; *Quercus ilex*= 5.68; *Pinus pinea*= 4.21; *Cedrus* sp.= 5.71 and *Aesculus* sp.= 17.36.

3.2 Spatial distribution of the particulate matter in the city

The yearly average of PM_{10} particles concentration was below the standard but daily limits exceedances were frequent, due to daily values exceeding the 50 µg/m^3 threshold on more than 35 days every year at several air pollution stations during the studied period (Fig.4). In order to corroborate the evolution of PM_{10} values and the general air pollution levels in Madrid, NO_2 concentrations were included. NO_2 concentration exceeded clearly the limits every year, reaching the highest value in 1989 (Fig.4).

The sum of days exceeding the PM_{10} threshold values from 1980 to 2010 (Fig. 5) showed that most of the Madrid air monitoring stations had exceeded the theorical limit of 1'085 exceedances (35 exceedances x 31 years). Only the bluish areas (Fig. 5) between the 1st and 2nd ring motor highways at Eastside downtown were below that limit. In the city Westside, the adjacent *Casa de Campo* periurban forest influenced the registered 1'067 exceedances over the threshold in respect to the limit of 1'085. Investigating the PM_{10} exceedances in the last 10 years (2000-2010; >350, Fig.6), the less polluted areas followed a similar pattern to Fig. 5 in a preliminary analysis. However, more details can be detected without the influence of the peak values in the early years of the 3-decades series. The decrease of PM_{10} levels in Station 8 (Fig. 5 vs. Fig. 6) was related to the tunnel built under this station with an ADT decrease from 80'000 to 30'000 vehicles/day, due to traffic jams elimination. Station 9 (Fig. 6) registered one of the higher levels of exceedances, due to gathering all traffic from the Southside suburbs in a sloped 5-traffic lanes canyon-like avenue with several junctions controlled by traffic lights which required of continuous accelerations/decelerations and moving off. Station 6 (Fig. 6) was located in an important junction and a city crossing point from all directions with more than 180'000 vehicles per day. Other sites accounting high exceedances were station 14 (Fig. 6), situated in a junction, displaying heavy traffic from Toledo highway (N-42) and station 5 near to the shopping centres and the M-30 ring.

3.3 ADT in the city

During the studied period, ADT (Fig.7) showed heavy traffic in 1) downtown (blue (ADT=50'001-70'000) and red (ADT= 70'001-90'000) wide lines in central almond), 2) The main axis (*Castellana* Rd.) from North to South, reaching dark red (ADT=90'001-125'000) and black (ADT=125'001-180'000) lines in certain sites, 3) The 1st and 2nd rings (black (ADT=125'001-180'000) lines), except the Westbound of M-30 which was affected by the mentioned tunnel constructions and 4) the radial motorways, exceeding an ADT of 90'000 vehicles/day. The great increase of the traffic in Madrid in the last decades was inferred by the 602'878 vehicles/day on the streets in 1990 to 2'798'829 vehicles/day ten years later (464% of increment) with a following slight decrease (Fig.4).

3.4 Heavy metals in soils

Results of main descriptive statistics on concentration (median values, standard deviations and variability ranges) of trace elements: Ba, Cd, Cr, Cu, Mn, Ni, Pb and Zn in urban soils of Madrid *versus* reference values in remote natural forest soils in Madrid region are listed on Table 4, as well as reference levels for heavy metals in soils (Table 5).

The average pH value in water was 7.04. The pH values of soils ranged from 5.5 to 7.8, depending on their composition. The highest levels corresponded to clay materials and the lowest levels to the sandy detrital. HM concentrations were not correlated with pH. However, a possibly reduced HM translocation may be present at specific areas with higher pH. When comparing the HM concentrations for the elements Ba, Cd, Cr, Cu, Mn, Ni, Pb and Zn to the threshold values established by regulations, certain areas exceeded those thresholds. Because pH was slightly higher than 7.0 in some sites, along with a higher or lower content of organic matter, mobility of these elements could be somewhat reduced.

The results obtained in the [Pb] distribution in soil modelled by IDW (Fig. 8), identified four areas in which higher concentration reached over 200 mg kg^{-1}. 1) The central area on the old inner city. 2) The high traffic density along the central axis way (*Castellana* Rd.) that divided the city in two parts that showed the main junctions with highest ADT (Fig. 7). 3) The 1st ring and, particularly, the way-out from the 1st ring to the main highways (A-1 to A-6) (Fig. 7). They appeared like small nucleus in the most important junctions of the M-30 and M-40 rings motorways and the radial motorways that had their common origin in the centre of Madrid. 4) Some distant areas near to these highways that could be related to traffic jumps or any other former anthropologic activity. The area with low-level pollution regarding lead are close to the big peri-urban forests and in areas with more parks and less traffic, except the high values found in the centre of the *Retiro* Park.

Mean values of Pb and Zn were not exactly correlated, although their concentrations showed similar spatial distribution in certain areas of the city, such as (i) crossing and major junctions with high AADT traffic road (1st and 2nd ring highways and main traffic axes) indicating a substantial role of traffic on those elements concentration and (ii) historic downtown (Figs. 8 & 9).

3.5 Deposition on leaf surface and heavy metal concentrations in washed and unwashed leaves

Fine dust dry weight trapped on leaf surface (including extracellular epicuticular wax) is shown in Fig. 10. The amount of dust and epicuticular wax varied depending on the capability to capture and retain particles for each tree and the characteristics of wax layer. *Aesculus* sp. was the species that accounted the lowerst weight (1.385 g). *Platanus* sp., *Quercus ilex*, *Ulmus* sp, *Pinus pinea* and *Cedrus* sp. amounted 1.3, 3.6, 4.2, 5.9 and 8.4-times higher values than *Aesculus hippocastanum* respectively. The leaf life span of the different tree species varied from 8-months life in *Aesculus hippocastanum*, *Platanus* sp. and *Ulmus* sp. (middle of April to the end of November), to the range of 24-36 months (depending of environmental conditions) in evergreen *Quercus ilex*, *Pinus pinea* and *Cedrus* sp. (Fig.11).

Results of the **HM concentrations in the dust residue** on leaf surface are presented in table 7. The most efficient species on particles capture by leaves were *Quercus ilex* within the perennial group and *Aesculus hippocastanum* within the deciduous group. The species that showed lowerst HM concentration in the dust residue was in *Ulmus* sp. The comparison of HM concentrations for each species relative to the concentration in *Ulmus* sp. indicated that [Pb] in dust residue of *Quercus ilex*, *Cedrus* sp., *Aesculus* sp., *Platanus* sp. and *Pinus pinea* were 2.4, 2.3, 2.2, 1.7 and 1.2-fold higher than *Ulmus* sp., whereas [Zn] in dust residue of *Aesculus* sp. and *Platanus* sp., were 2 and 1.7-fold higher in comparison to *Ulmus* sp. The species that resulted more effective for the rest of the HM (apart of *Quercus ilex* and *Aesculus hippocastanum*) were *Cedrus* sp. and *Platanus* sp. The less effective species were *Pinus pinea* and *Ulmus pumila*. The [Pb] in dust residue in the six urban trees species in Madrid ranged between 3.19 and 125.99 mg kg^{-1}. Both extremes belonged to cedar trees in the *Retiro* Park. The minimum [Pb] corresponded to a *Cedrus deodara* tree in the centre of the 120 hectares *Retiro* Park, 1 km far away from traffic roads. Reference [Pb] of 2.08 mg kg^{-1} was found in *Cedrus* sp. at the remote control site in Cercedilla forest. Average [Pb] in residue powder in cedars was slightly higher in summer, although the highest values of [Pb] were reached both in January [125.99 mg·kg^{-1}] on a cedar tree in the perimeter of *Retiro* Park (ADT= 90'001-125'000) and in July [107.59 mg·kg^{-1}] on a cedar tree in Gregorio Marañón Sq. (ADT= 125'001-180'000). The highest [Zn] (823.94 mg·kg^{-1}) was also reached in a Horse chestnut tree at the same location as maximum [Pb] in *Retiro* Park (at Puerta de Alcala corner), while maximum [Ba] (626.72 mg·kg^{-1}) was also obtained in another cedar tree in the *Retiro* Park border, next to Alcala St. The lowest [Ba] in the city was also detected in the centre of *Retiro* Park (71.2 mg kg^{-1}) that was the most distant point to the border of the *Retiro* Park site.

The **HM concentration in the unwashed leaves** followed a different trend. They were influenced by the soil concentration, additional to air pollution. Generally, the perennial species reached higher concentrations than the deciduous species (table 8), due to the longer leaf life span exposition. [Pb], [Zn], [Cd] in unwashed leaves were 23.67, 55.52 and 0.32 mg·kg^{-1} in *Cedrus* needles *vs.* 3.14, 32.25 and 0.05 mg·kg^{-1} in *Aesculus* leaves respectively (table 8). The HM concentration variation between August and November was less pronounced in *Aesculus than* in *Cedrus* leaves.

Heavy metals concentrations in washed leaves (without leaf surface contamination) indicated that [Pb] in summer were below the detection limit for Pb (<3 mg·kg^{-1}) for all species except *Quercus ilex* (4.24 mg·kg^{-1}). In winter, [Pb] in washed leaves of *Platanus*, *Aesculus*, *Cedrus* and *Ulmus* were 10.56; 3; 18.15 and 3.64 mg·kg^{-1} respectively. [Zn] in *Q. ilex*, *Platanus* sp., *Aesculus*, *Cedrus* and *P. pinea* washed leaves increased from summer to winter 76.5 %; 37.6 %; 44.6 %; 59.8 % and 88,6 % respectively, except in *Ulmus* that decreased barely. Maximum concentrations in washed leaves were reached within the areas of highest concentration of Zn in soils (Fig. 9).

The estimation of the trace elements related to traffic emissions deposited per adult tree and year was obtained from the average HM concentration in mg·kg^{-1}, the foliar surface and biomass for a single tree of the six studied species (Fig. 12). Estimates at tree level biomass (dry weight) was determined in trees felled throughout Madrid (Martín Lorenzo, 2010) and associated to the aforementioned SLA results calculated from the foliar samples collected [3.1]. The HM concentration of perennial species were normalized to 1-year accumulation to compare to the deciduous species. The capability to accumulate HM by individual trees suggests other species than the aforementioned as the best tree capturer. The leaf surface of *Aesculus* and *Quercus ilex* had good characteristics to accumulate particles on their surfaces, but the total leaf surface of a single tree of both species had lower foliar surface than other species such as *Cedrus* sp., *Pinus pinea* or *Ulmus pumila*. The 254.394 street trees of the six species accounted 2'857'399 kg of dry biomass, as described in Table 10. Total of metals trapped by the six analysed species amounted to 16.8 kg/year (Fig. 13)

GPS-based location of more than 650'000 trees on street, parks and gardens was employed to display a map of trees as affected by particulate matter contamination by road traffic. The amount of dust trapped on leaf surface (mg dust residue/g leaf dry weight) per adult tree for each species was correlated to the ratio between AADT and the shortest distance from each single tree position (X,Y) to the closest principal adjacent road or main junctions to investigate the effect of the tree's distance to the mobile sources (Fig. 16). The resulting values were categorized in 4 classes regarding the potential pollution by traffic emissions (low, medium, high and very high).

3.6 SEM and binocular evaluation

Atmospheric particles were observed on leaf surfaces using SEM as presented in Fig. (14). Fine particles were often found in areas around and over the stomata (Figs. 14 B, C, D). The morphological composition suggested that the most abundant particles were carbonaceous soot, quartz and soil mixed aggregates (Fig. 14-E) that were also corroborated by binocular in trichoma of *Quercus ilex* and on needle surfaces (15A, 15-B). The X-ray spectrum of fine particles displayed that C, K, Ca, Si, Mg and Al were the elements most represented as expected (Fig. 14-A). The presence of HM related to anthropogenic activities such as Pb, Cu, Zn and Cd as minor constituents were also identified. According to photomicrograph (Fig. 14-E) and X-ray spectrum of fine particles, silicon seems to be the most abundant element on the leaf surfaces, which is usually known as a marker of soil particle origin. Other significant peaks corresponded to Ca. In *Retiro* Park it was very common to cover the pedestrian road pavement by limestone which was removed by the transit of vehicles of the park and easily deposited on the leaf surface.

3.7 Zn microlocalization/revelation

Inside the leaf blade of *Platanus* and the needles of *Pinus pinea* and *Cedrus*, Zn allocation inside the veins, the living xylem cells and mainly in phloem, evidenced a translocation from leaf to root and other locations (and vice versa), which was present in the 3 species displayed in Fig. 15 C-N. Zn was detected in *Ulmus* sp. using 8-hydroxyquinoline (HQ) too (image not shown), whereas allocation in *Quercus ilex* and *Aesculus hippocastanum* was not significant.

4 Discussion

4.1 The urban tree presence in the city

The maintenance and management of urban trees in the 20th century frequently was considered a minor issue and often did not received the value that they deserved. Their management was also associated to departments in charge of cleaning and waste collection in the city and were headed by politicians, who in most cases had little knowledge about of urban trees and green areas management. Meanwhile, the most important decisions were decided in the Department of planning, regardless of the opinions of experts in arboriculture and urban forestry. That situation caused the lack of clear management criteria, exemplified in the deficiency information about the number and species in urban green spaces in Madrid. In our opinion, there was not a detailed study of the exact amount of urban trees to be managed in Madrid over the past decades of the 20th century. Local media and authorities expanded the rumour that Madrid was the second city in the world ranking of cities accounting the highest number of urban trees, behind Tokyo, although many green areas lacked an inventory of species. In order to avoid the heterogeneity of the data provided by different administrations (trees per thousand of inhabitants, trees accounted in urban forest or only trees in alignment), the world-comparison (Table 1) referred only to street trees units (Pauleit *et al.*, 2002). Here Madrid reached the fourth position after New York, Berlin and Tokyo. The management of the green spaces and the resources of information has been improved considerably in the last decade and nowadays the management is totally organized. Currently the best information about Madrid's urban trees is available on-line (Ayuntamiento de Madrid, 2014). Unfortunately, it only provides information about single street trees, but detailed urban tree information in parks, gardens and urban forest is missing. The help of computer-aided tools have produced an improvement in the inventories that has allowed the calculation of more complex variables, such as the dasometric and biomass mensuration. The inventories and the information about the tree dimensions associated to the measurement of the biomass and leaf surface also allowed to estimate the total leaf surface by tree and species, and consequently the amount of HM in/on leaves could be calculated.

The comparison of data has allowed to compare urban data with respect to published literature in forestry, which shows that the species present in the urban environment suffer more restrictions for space than in natural condition. Typical street trees species in alignment, as *Platanus* sp., are affected in average DBH or height by the effect of soils restriction in grids or pruning to avoid inconveniences to vehicles and buildings (Chapter 1, Figs. 26 & 27). However, in other locations, such as *Casa de Campo* or *Monte de El Pardo* peri-urban forests, *Quercus ilex* and *Pinus pinea* maintained a biomass similar to natural conditions, as compared to those data reported by Montero, Ruiz-Peinado, and Muñoz (2005) from the Spanish forests inventory.

4.2 PM_{10} exacerbated by traffic and modified by climatology and vegetation

In Madrid, as in most European cities, air pollution standards for O_3, NO_X and PM_{10} (Fig.4) have been exceeded in the last decades. Average yearly values in Madrid reached one of the worst PM_{10} levels in 2002-2003 compared to other big European cities due to extremely dry weather during that period, which registered several dust storms from Sahara (EUMETSAT, 2014). At a wide-scale, some of the exceedances have their origin in the continental weather that produces temperature inversions during winter or dust intrusions from remote areas without vegetative cover. To a local level, range of 4-5 ºC between monitoring sites in a single day has been reported because of the urban head-island effects, and even precipitation was significantly higher, especially in green areas of the city (López Gómez *et al.*, 1993). These different local weather conditions between monitoring sites could affect the removal of particles by the wind and the precipitation wash-off. Luca de Tena site (station 9) reached the maximum PM_{10} levels (Figs. 5 & 6) over the years until the station has been removed from the network. This site was surrounded by buildings in narrow streets and courtyards under heavy traffic load, which resulted in poor ventilation and dilution of atmospheric constituents. These factors were reflected in the PM_{10} exceedances. Most of the Madrid air monitoring stations had exceeded the limits over the years. Air pollution by particulate matter seems to be a recurrent problem affected by traffic and/or climatology. As a result, the continuous low/medium pollutants' level in Madrid's environment for years, led (more than sporadic acute levels) to chronic damage by continuous inputs of heavy metals and other air pollutants.

The effects of longer series of years (Fig. 5) may soften those values reached in a spatial representation between districts in Madrid. The sum of daily exceedances of the PM_{10} threshold values from 2000 to 2010 in Fig. 6 allowed to observe more accurately the differences between areas of the city. Within the central almond of Madrid surrounded by the M-30 1st ring highway, only station 99 in the *Retiro* Park showed its beneficial green influence. Additional low levels were found in stations 3, 7 and 21, situated in low AADT areas. Station 27, in the Eastern limit of the city showed high exceedances, despite rather low AADT. The proximity (2 km) to the international Barajas airport, which ranked the eleventh busiest globally and fourth in Europe during that period could be the reason. During the complete studied period, the slow decrease of PM_{10}, as well as NO_2, could be attributed to the control of diesel emissions by new fuels and new technologies, despite the intense increase of AADT in 1993-1997 period, ranging from 38.2 in 1998 to 33.0 μg/m^3 in 2007 (Ayuntamiento de Madrid, 2011) (Fig. 4). The difference in the concentration and the type of pollutants in the emissions could be also inferred to the effect of the dieselization of the Madrid car fleet during 2000-2009 (CEPSA, 2009), which caused a deeper negative slope in the trend of NO_x values in comparison to PM_{10} in the last 4 years of the studied period. Both decreases in PM_{10} and NO_2 values could be attributed to the effects of the economic crisis on ATD, besides the reorganization of the air-monitoring network. During the study period, different constructions (tunnel construction of M-30 ring motorway), as well as the exceptional high rate of building construction could be additional sources of pollution, among by street dust resuspension. In normal weather condition, 50% of deposited particles intercepted by the trees are resuspended (McPherson, Nowak, & Rowntree, 1994). Thus, most of the particles will be accumulated in the soil by wet deposition (rainfall) or by dry deposition (directly or indirectly by the leaf fall or compost sewage) and then taken up again by the trees and translocated to different organs of the plant depending on the heavy metal mobility of the elements.

The period of exposition of trees to urban pollution and the local climatology influenced the capture and accumulation of particulate matter on leaves. This effect was more evident in evergreens than in deciduous leaves in winter due to the presence of perennials during this period when traffic and heating systems reach maximum levels of emission in the absence of deciduous leaves.

4.3 Spatial distribution of HM in urban soils and likely sources of contamination

The spatial distribution of the Pb, Zn and Cu concentrations in soil samples revealed remarkable changes in their spatial patterns around the city that suggested the deposition of air-borne particles according to a trend of decreasing concentration with the distance from the mobile sources to the urban trees. This result agreeed with Calace *et al.* (2012) who reported similar decreasing in HM concentrations with distance to roads in soils samples in Rome parks. The inverse proportionality of HM concentration with distance was not so evident in remote samples from roads, that it could be attributed to the diffusion of particles over a wide area of influence (>30 km), as suggested by Llamas, Chacón, and De Miguel (1993). However, Biasioli, Barberis, and Ajmone-Marsan (2006) restricted the buffer area to 1-km strip around the source. In our study, [Pb] in soils matched with this suggestion near to mayor roads featuring high ADT, as displayed in Fig. 8. European Commission set 2000 as deadline for the removal of Pb and Mn from fuel market, although Spain, Italy and Greece obtained a moratorium until 2002. Since that date lead was no longer a component of petrol in Western Europe. Thus, spatial distribution of [Pb] in soils seemed to be associated with former traffic emissions. Zinc (Fig. 9) and Cu (image not shown) followed a similar pattern, although the remarkable differences could be related to additional sources as mentioned previously in literature (asphalt, tyres, lubricants and anticorrosive protections). For Ba, Cd, Cr, Mn and Ni, spatial variations in soils regarding decreasing concentration with the distance from the mobile sources were less evident, reflecting other sources of anthropogenic contribution. Several sources may be associated with urban activities on soils, due to the most common use of fossil fuels in transport or energy, to all sorts of industries, commercial and domestic activities, as well as some uncontrolled waste disposal. Closer examination of the origin of the heavy metals in the soil in relation to their spatial distribution suggested the existence of the following sources:

A.- Traffic. The Madrid's AADT map (Fig. 7) corroborated that the atmospheric deposition of particles generated by vehicles was the main source and secondarily the heating systems in winter (Ayuntamiento de Madrid, 2002). In particular, Pb and Zn seemed to be associated with traffic (Fig. 8 & 9), despite the disappearance of leaded fuels previously. Higher concentrations of Pb seemed associated with important junctions or intersections of the main streets, but the trend of increasing concentration with the increase of AADT was not correlated (Fig. 8 *vs*. Fig. 16). The reason could be attributed to modifications of old busy road or changes in road layouts, roundabouts or newly built residential areas that may not reflect the accumulative concentration in soils for years.

B.- Industry. Currently, the industrial emissions have a relatively low importance in the city of Madrid. They were established in the Southern suburban in the middle of the last century and it could be an explanation to unusual punctual non-traffic-related high HM concentration in certain areas in Fig. 9. Additional sources for the rest of the studied elements could be found in some areas in the SW of Madrid where the presence of Cr, Cu, Ni and Zn could be associated with chrome and nickel industries that existed in this area in the 20th century. Moreover, in suburban parks such as *Casa de Campo,* the presence of Cd, Zn and Cu [Annexe XIX] in some cases, may be associated with the application of pesticides in forest areas in former decades, as these elements were common in the composition of such products. Trace elements were also found in elevated concentration near the former military camp areas, perhaps related to military activities. High concentrations of Zn and Cu were found near Madrid-Barajas airport too. Other complementary sources can be attributed to paintings, cables or pipes and the day-to-day corrosion of many structures and vehicles, that may cause the release of heavy metals such as Zn, Fe, Cu, and Pb.

C.- Natural sources. Most of the elements analysed, except Mn and Cd, are considered "anthropic" elements, because they are provided typically by human activity. At certain sites however, the presence of Ni and Cr is derived from the natural alteration of rocks, which renders the source uncertain (De Miguel *et al.*, 2002).

D.- Anthropogenic sources. Apart of the air pollution influence, the average concentration of elements in some parks can be augmented by others anthropogenic sources:

d.1) Landfills. The poor soil site quality in some parks has caused tree decline in many urban trees (Calderón Guerrero, Saiz de Omeñaca, & Aznar López, 2013) (Annexe XVII)**,** due to current fact that large parks were landfills in the suburb years ago. For example, debris were accumulated in the Madrid outskirts after the Spanish Civil War (1939) (González-Ruibal & Marín Suárez, 2010). Some of these areas were paved with reconstructions, others used for green spaces, as *Parque del Oeste*. In the last decade, abandoned rubbish dumps have been recovered as green areas too (Ayuntamiento de Madrid, 2005). The group of elements: Al, Fe, Mg and Ca are often associated with areas of old tailings.

d.2) Sewage sludge and compost applications could be another important source to enhance heavy metals concentration in urban soils. According to the Department of Parks and Gardens of the Madrid City Council, the compost used for the green areas came from their own production at the Municipal dependencies of Viveros and they have not employed any composted sewage sludge as a fertilizer from "La China" or any other waste-water treatment plant in Madrid. However, the use of this kind of substrate in the green urban areas under municipality maintenance more than 25 years ago was reported in De Miguel, Jiménez de Grado, Llamas, Martín-Dorado*, et al.* (1998). Thus, sludge compost addition could be another important source to evaluate the sources of trace elements in urban soils in Madrid. In particular, regarding elevated contents of Pb, Cr, Ni, Zn and Cu in parks and gardens.

d.3) Irrigation. Another possible source of trace elements in soils is provided to plants by irrigation using water recycled from the waste-water treatment. We cannot evaluate this source due to the lack of data because of authorities' reluctance to provide such information (Annexe XVIII).

d.4) Historic sources. *Retiro* Park. The cumulated effect of pollution in soils can be masked during decades, or even centuries. Heavy metals remain in the soil although the source of emission has disappeared decades ago (Stigliani, 1988). Buffering capacity of soils plays an important role in heavy metal immobilization and its sorption capacity remains until soil acidifications is exceeded. Despite the expected role of *Retiro* Park vegetation as a barrier for atmospheric particulates from the dense traffic road, like parks in Athens (Chronopoulos *et al.*, 1997), the high values of soil contamination obtained in the centre of the park could be attributable to the use of Pb, Mg, B and Ba in the Royal porcelain and glass factory during the period 1784-1812. According to PASEO (1815), the building was located in the park where nowadays the monument to the Fallen Angel (Fernando Sáez, 2006)(annexe XX) is situated and the deposits were in the same area where the highest concentration of lead samples were found (Fig. 8). Fragments of this porcelain and glasses found in *Retiro* Park were analysed. PbO concentration reached up to 27.2%, while B_2O_3 3.1% and glasses contained high percentage of $BaSO_4$. (Mañueco *et al.*, 2001). Thus, Pb was a major component in their composition for paintings and stain. The Royal factory and the deposits where the primary goods were stored was exploited and destroyed by the British army at the end of the Spanish Independence War in 19th century. Although 200 years have passed, it gives an explanation for the high levels of Pb found in soils exactly in the same location. Any other sources, like compost addition would be spread to same levels all around the park and not in this particular zone where without significant compost adding. Furthermore, compost in contrast use to contain traces of Au and Pt. A similar situation is described by (Calace *et al.*, 2012) in an archaeological park in the centre of Rome.

4.4 Comparison of HM concentration in soils to reference levels

The diffuse pollution in Madrid could be observed in soils by the fact that even the minimum values of urban soil samples were higher than the mean values of the natural/rural soil, as it was reported also for Rome (Biasioli, Barberis, & Ajmone-Marsan, 2006). It was observed similarly in the main periurban forest where generally there is a gradation of the pollutant's concentration in soils to the inner area of the urban forest (Smith, 1981). The city's influence in soil contamination usually is estimated by comparison to the background values from natural areas or to the regional legislative limits. There is a wide range in HM limits. According to the legislation in each region/country and the reference values that can be considered, the soil values could be below or exceeding the thresholds. In Madrid, these limits were slightly higher than other regulations (table 5). We also compared the HM concentrations with soil samples in remote areas. The only soils in the Madrid region that apparently had not been altered anthropogenically could be found in remote areas. According to Llamas, Chacón, and De Miguel (1993), the concentration of Pb, Cu and Zn in urban soils of Madrid decreased significantly to a distance up to 15 km from the city centre. That is the reason for selecting a nature site for soil sampling in a forest area at 78 km from Madrid with at least 10 km far away from highways. Even there, the soil concentration was affected slightly, as in our samples in Cercedilla Forest.

In our samples, high mean and standard deviation values of HM concentrations suggested anthropogenic sources for Pb and Zn (table 4). A significant degree of soil pollution regarding Pb, Zn and Cu existed in some sites of the city. These results were corroborated by the comparison between the soil in rural settings and the urban soils, influenced by the increment of pollution produced by a higher concentration of anthropogenic activities. The average urban soil were 13.0 and 10.9 fold higher (Table 4) than the control (natural area) concentration in Madrid. In a second level of importance, Cu, Cr, Mn, Ba and Ni were 3.2, 1.6, 1.6, 1.8, and 2.1-fold higher respectively. The high range of values in some elements related to traffic and anthropic activities (up to maxima of: Pb (784), Ba (949) or Zn (470) confirmed the considerable fluctuation in different areas of the city, especially between green low emission areas and others with high traffic density. These variations were spatially distributed along different districts of the city. In certain elements, the minimum values in the city were slightly below the minimum values in the control area, that could be attributed to diffused pollution even in remote sites and the high alteration in city's soil, where the upper layer could be replaced whenthe soil's quality was very low (table 4). The median values for the anthropogenic elements Cu, Pb and Zn were similar to those reported in most common West-European cities (Calace *et al.*, 2012) and in the range of the mean values found in Italian cities such as Torino (Pb=149; Zn=183; Cu=90 $mg \cdot kg^{-1}$), but lower than those measured from soil samples from Chinese cities (Wei & Yang, 2010). Cu, Cr, Mn, Ni and Ba concentrations were mostly similar to those reported for other European cities. Concentration values agreed with the average values shown in other big Spanish cities such as Seville or Madrid in the nineties (Madrid, Díaz-Barrientos, & Madrid, 2002). In particular, mean concentrations in Madrid were in the same range in comparison with the average provided by (De Miguel, Jiménez de Grado, Llamas, Martın-Dorado, *et al.*, 1998), However, we could not compare the sites more detailed because only average values were provided without information to areas below the districts.

4.5 Potential phytotoxicity thresholds in soil samples for urban trees

In this study atmospheric deposition of certain elements was monitored in the HM concentration of soils. The levels of the elements studied are in the line of other European high ADT cities, but the established limits are different. The Pb limit of a polluted soil varied depending on the countries or even their regions. In Spain, Catalonia region proposed for the protection of the human health, a generic reference level of 55 mg·kg^{-1} for urban use, while for the protection of ecosystems it was decreased to 22 mg·kg^{-1} (background: 21.8 mg·kg^{-1}). Madrid region provided the generic reference level of 270 mg/kg for urban use (VR90: 30 mg·kg^{-1}) to human health protection, while in the Basque country, indicative values for human health were 120 mg·kg^{-1} for children's playground areas, 150 mg·kg^{-1} for residential areas and 450 mg·kg^{-1} for public parks. Usual lead concentration in current soils in the world varies between 10 and 67 mg·kg^{-1}, with an average value around 30 mg·kg^{-1} (Pais & Jones, 2000). Phytotoxicity thresholds listed in the literature for different soils in the world ranged between 110 mg·kg^{-1} (EPA, 2003) and 100-400 mg·kg^{-1} (Kabata-Pendias & Pendias, 1992). The 9.8% of the urban soils in Madrid was above the “contaminated soils” Pb limit, according to current Madrid regulations, and 98.4% was above the suggested VR90 value for Pb, ranging from 9 to 793.6 mg·kg^{-1}, reflecting a very strong anthropogenic activity in the city. The VR90 value was never reached in the baseline samples at Cercedilla (Table 4). Lead presence was mainly anthropogenic and linked to the urban traffic until 10-15 years ago in most West-European countries, due to the use of leaded gasoline during decades. The mobility of lead is reduced. Thus, Pb concentrations remain in urban soils. The concentration in certain spots may be controlled and monitored in the future, according to the trend of forthcoming regulation limits.

The average content of Zn in the world varies depending on the nature of the soils: 100, 40 and 20 mg·kg^{-1} in basic rock, granitic rocks and sedimentary materials (sandstones , limestone and dolomites) respectively .Phytotoxicity is reached at 50 (EPA, 1996) and 70-400 mg·kg^{-1} of Zn in soils (Kabata-Pendias & Pendias, 1992). Its solubility rises as the pH decreases. As lead, Zn limit for polluted soil varies depending on the Spanish regions: 640 and 11’700 mg·kg^{-1} for urban use in Catalonia and Madrid respectively. The protection of ecosystems is set to 73 mg·kg^{-1} (background: 56 mg·kg^{-1}). All urban soils were below the Zn limit for “contaminated soils”, according to Madrid regulations (11’700 mg·kg^{-1}), although 91.9% was above the suggested VR90 value for Zn (73 mg·kg^{-1}), ranging from 34.54 to 470 mg·kg^{-1} and reflecting a moderate anthropogenic activity in the city. The VR90 value was only reached in the baseline samples at Cercedilla and in only one sample (76 mg·kg^{-1}) (Table 1). The sources of risks of contamination of this element vary. Apart of traffic in Madrid, they are mainly related to the management of municipal waste rich in this element, Zn metallurgy, galvanization and paintings. Thus, although Zn is a pant micro-nutrientelement, athropogenic Zn can affect the urban trees in various ways, including locally pesticides.

All urban soils were below the “contaminated soils” Cu limit, according to Madrid regulations (800 mg•kg-1), although 89.1% was above the suggested VR90 value for Cu (20 mg•kg^{-1}, this element ranging from 6 to 170 mg·kg^{-1}). The VR90 value was never reached in the baseline samples at Cercedilla (Table 4). Phytotoxicity thresholds listed in the literature for different soils in the world ranged between 100 mg·kg^{-1} (EPA, 2003) and 60-100 mg·kg^{-1} (Kabata-Pendias & Pendias, 1992). Other trace elements as Ni had a low variation, except in certain areas associated to activities that accumulated this element in the soil over the years. All urban soils were below the “contaminated soils” Ni limit, according to Madrid regulations (1’560 mg•kg^{-1}), although 8.2% was above the suggested VR90 value for Ni (21 mg•kg^{-1}, this element ranging from 2.9 to 25 mg·kg^{-1}). The VR90 value was never reached in the baseline samples at Cercedilla (Table 4). Phytotoxicity thresholds listed in the literature for different soils in the world ranged between 100 mg·kg^{-1} (EPA, 2003) and 30 mg·kg^{-1} (Kabata-Pendias & Pendias, 1992). Due to most of the concentration of Cd were under the detection limit (1ppm), results and map of distribution was not included.

4.6 Presence of HM on/in foliar samples

The atmospheric HM deposition on urban trees has been evidenced by the difference between the concentrations in washed and unwashed leaves, as well as the comparison of their weight in the dust residue. As also pointed out by some authors (Wyttenbach & Tobler, 1998), there has been a significant difference between the concentrations in washed and unwashed leaves.

Urban trees appeared to have different pollutant capturing efficiency. The waxy residue on leaves reflected these differences, as well as the variation of heavy metals concentration, in particular, those traffic-related elements such as Pb, Zn, Ba, Cu, Cr and Ni. The combined washing solution that was employed to wash the leaves/needles assured a representative measure of HM on leaves, as different mixtures and concentrations were tested previously. The heavy metal concentration in washed needles varied slightly during the year in comparison to the concentration of HM in residue powder, as previously reported by (Tomašević *et al.*, 2004). The quantity and composition of the residue was affected by the precipitation during the year and especially by storms in summer. The Mediterranean weather is characterized by two dry periods in winter and summer, which could be interrupted by storms in summer. Due to this reason, sampling was delayed 5 days after the last heavy rain in order to avoid a considerable loss of residue on leaf surface by wash-off.

Dust was trapped on the leaf surfaces particularly between hairs and trichoma of *Q. ilex* (Fig. 15-A) and *Platanus*, while the rough foliar surface in *Aesculus* helped to retain them. In conifer species, long shoots, with needles arranged singly on the twig and short shoots with many needles in a cluster were also able to trap dust particles (Fig. 15-B). Cedrus and Pinus were the species that amounted higher residue powder, due to their epicuticular wax layer and dust deposition. Their needles, as well as *Quercus ilex* leaves may remain in the tree for three years, as shown in Fig. 11. Thus, they can accumulate dust over the whole period in comparison to the shorter deciduous lifetime. The leaf xeromorphy and the thicker wax layer also explained the higher weight regarding to other species, namely *Platanus orientalis* or *Aesculus hippocastanum*. *Ulmus* sp. was the species that accumulated the highest amount of wax and dust residue among the deciduous species. Average HM concentrations in dust residue decreased from summer to winter. The average decrease by species was: *Pinus pinea* (-40.1 %); *Ulmus* (-21.2 %); *Aesculus* (-19.9 %); *Platanus* (-15.8 %) *Cedrus* (-14.1 %) and *Quercus ilex* (-11.7%), mainly as a consequence of the wash-off and wind street dust resuspension action, as suggested by Beckett, Freer-Smith, and Taylor (1998). Despite the decrease, a considerable load remained adhered to leaves at the end of the vegetation period. These factors may evidence that the waxy, elastic and movable *Pinus pinea* needles can capture a high amount of fine particles (Fig. 15-B). Nevertheless particles are removed by the wind and water easier thanfrom the smaller but complex structured cedar's needles. In the same way *Ulmus pumila* petiole allows the free movement of the leaf by the action of the wind and its leaf surface is softer that the abaxial tomentose leaf surface of *Quercus ilex* (Fig. 15-A). The rougher surface of *Aesculus hippocastanum* leaves also contributed to the higher level of particle trapping as displayed in SEM micrographs (Fig. 14-B). According to these SEM micrographs (Fig. 14) and images captured by cam on binocular (Fig. 15-A and 15-B), coarser particles as well as crystals were captured in a higher proportion by *Cedrus* and *Pinus* needles, perhaps due to their sticky surfaces and whorls, while a higher proportion of finer particles appeared on the surface of the rougher leaves of *Aesculus hippocastanum* and in *Quercus ilex* trichoma. This could be a point in favour of broadleaves because of the higher deleterious effect of fine particles for health.

Heavy metal concentrations in unwashed leaves (Table 8) were in the range of the reference values (Markert (1992); Prasad, 2004) for most of the trace element concentrations or slightly above the thresholds in most of the leaf samples. However, *Cedrus* needles exceeded in [Pb] 2 to 3-fold times the critical concentration (Kabata-Pendias & Pendias, 1992; Markert, 1993) (Table 9) in some areas during the high level of pollution, especially in those positioned at the edge of the park and very close to the *Independencia* Sq. junction. These exceedances were located mainly in trees near high AATD roads or in soil over the threshold values. The lowest pollution level were observed in cedars' needles sampled in the inner area of the *Retiro* Park (Fig. 16). Despite the fact, that they reached the lower concentrations of heavy metals in the city, they were higher than those reached at the remote site.

Heavy metals concentration in some washed leaves from city parks showed the accumulation of Zn (and Pb to a lesser degree), indicating certain soil contamination (as shown in Fig. 8 &

9). The Zn toxic levels were found in 3-year needles and holm oak leaves. Leaf/needle and soil concentration of Zn ranged 13.9-314.2 and 34,5-470 mg·kg^{-1} respectively, which in certain areas reached the 'excessive or toxic' limit of 100-400 mg·kg^{-1} for polluted plants and 70-400 mg·kg^{-1} toxic limit for soils (Kabata-Pendias, 2010); but [Zn] was usually below this level. The capacity of translocation of Zn from root to leaf level compared to other elements such as lead is known (Vollenweider *et al.*, 2011), but bioavailability is strongly influenced by the pH value in soils, being more mobile in acid soils than in neutral and alkaline (Prüeß, 1997). The pH in soils from city parks ranged from 5.5 to 7.8, consequently [Zn] in leaves varied depending on tree species, leaf age and pH. These different levels of [Zn] in soil and foliage according to environmental pollution in areas of Madrid were reflected also by revealing a Zn signal using HQ in the main leaf veins and especially in phloem that could act as a transport way and sink of Zn. Our foliage samples from different contaminated levels of Zn (Figs. 15 C-N) showed accumulation patterns of Zn in phloem in a different intensity and presence in both conifers species as compared to poplar (Vollenweider, Menard, & Günthardt-Goerg, 2011).

The information provided by ADT on every street and the individual location of each urban tree, as well as the dust residue measured on foliar samples, was used to calculate the shortest distance of each tree to the next emitting road and estimated the amount of dust that could be captured according to the previous foliar analyses. Results are displayed in a map of the entire city about the potential particulate matter pollution effects in trees (Fig. 16). The filter effect could be perfectly observed in the gradual diminution of pollution from the border of the park (red level) to the inner area of the park (green level). It can be observed by comparison of Fig. 6 and Fig. 16, how the usual low presence of trees in the Southern surrounding areas of Madrid matched with the places where higher PM_{10} concentrations were reached (air pollution stations 17 and 25 in Fig. 6). Fortunately, this problem has become to be corrected in Madrid in the last decade by the new green areas establishment in "*Parque Sur*" and recent Southern green areas known as "*Compensatorias*" (Southeast of Madrid in Fig. 16).

4.7 Effective tree species to ameliorate particulate air pollution

The presence of airborne particles may lead to a poor quality of air. The influence of traffic is the most determining factor in the vicinity of major communication routes. A certain amount of dust is captured by vegetation, which helps to reduce PM_{10} level in the city and consequently respiratory problems.

There are diverse factors to explain the different load of particles on the leaf surface: coarse surfaces and pubescent leaves in broadleaves, sticky surfaces and whorls in conifers, or the entire structure of the tree that could be more or less sensitive to turbulences (Beckett, Freer-Smith, & Taylor, 1998). Deposition on leaf surface is increased with the development of leaves structures (hairs or trichoma) and roughness. This could be the strategy in species like elms, holm oaks or plane trees. Conifers, such as pines or cedars are more oriented to the capture of particles due to their complex foliar structure. The type of particles between species showed that deposition was conditionated by the presence of rougher surfaces in deciduous broadleaves, while the duration of the exposition was more effective in evergreen species.

This work confirms that coniferous species are more effective than broadleaves capturing PM_{10} particles (Fig. 12), while the species with leathery or smooth leaves have a lower efficiency in capture particles. *Cedrus* sp., *Ulmus* sp. and *Pinus pinea* resulted appropriate for a green filter barrier. As we have seen before, more than effective surfaces to capture fine particles, the surface/dry weight ratio allowed them to have larger foliar surfaces. Cedrus' shape assured a good interception in the lower stratus for particulate matter trapping, as well as noise reduction (Fan *et al.*, 2010). Especially, the morphological disposition of their fasciculate needles is a good instrument to trap the dust between their intricate needle positions. *Ulmus* sp. has a good interception capacity according to values obtained, and the umbrella shape of *Pinus pinea* may provide cover in the higher stratus. Elm genus presents different foliar characteristics depending on the species (*Ulmus glabra* provides the roughest surface, followed by *Ulmus minor* and their hairs and medium-rough surface). Unfortunately, its presence is scarce currently in the city, due to serious diseases. The most frequent elm tree is *Ulmus pumila*, which features a reduced ability to capture particles due to smoother surface. In the case of *Cedrus* and *Pinus*, the stickiness of the leaf surface and the complexity of the different needle orientations could be an explanation for the high load. In particular *Cedrus* use also to suffer the attack of many aphids that produce a honey-dew sticky substance that increases the retaining capacity.

The distribution of the trees along the street is another important issue. The aforementioned combination of Cedrus in the lower stratus, Ulmus in the intermediate and Pinus pinea in the upper level would provide an efficient belt barrier. An example of the effective role of urban trees in Madrid to ameliorate the air pollution could be found in the urban trees near to Prado Museum. The plane trees boulevard along *Prado* Rd. (AATD= 125'000-180'000 vehicles/day) (see station 1 in Fig. 3) could be an excellent example of effective filter by creating a continuity between discrete green areas as a buffer around this high polluted traffic road. However, there is a lack of green belt barrier in other high AATD central areas featuring several traffic congestions. These areas should be the most suitable places where urban trees will be urgently needed. As a first measure, urban trees would be helpful as belt barrier in areas lacking in urban greenery in order to protect from the recirculation of particulate matter.

The capacity of the six urban street trees species investigated (254'394 trees) to capture air-born dust on the foliage surface as related to traffic intensity was estimated in 16.8 kg of noxious metals from exhausts per year. According to this value, trees planted along large road axes can directly trap sizable amounts of dust (Fig. 13). Empirical information is scarce. Broadmeadow et al. (1998) reported a potential capacity to remove pollutant particles near to 18 kg/hectares in a growing season. Obviously the load of trace elements obtained in our results was somewhat lower than expected due to wash-off or leaching by rain or wind street dust resuspension.

According to our point of view, the strategies for reductions of air and soil pollution in big cities should be focused on the improvement of air quality by traffic restrictions, control of heating systems and industrial activities emissions, but also the role of the urban trees by capturing particulate matter should be highlighted. The plantation's increment of optimal species for this purpose would increase the benefit in terms of air quality improving, cost savings or health benefit. Programs regarding urban trees' benefits would be specially indicated in developing countries' megacities where pollution is a serious problem.

5 Conclusions

The diffuse pollution in big cities is usually widespread to surrounding urban trees and soils kilometres away. Thus, the current soils concentrations are always increased over the natural lithological content. The spatial representation of HM concentrations in soils, PM_{10} distribution and AADT on streets on thematic maps and database by GIS software corroborated that vehicle traffic represented the most important pollutant source in Madrid. These maps also suggested the partial influence of a diffuse pollution by deposition of atmospheric particles in areas of the city where mobile sources seem remote. They further pointed to other anthropic activities by comparing the spatial Pb, Cu, Ni, Cr and Zn mean concentrations obtained in soils to the PM_{10} values in the map (e.g. former industrial activities, even those developed centuries ago such as the former Royal pottery at *Retiro* Park).

Anthropogenic HM concentrations in Madrid urban soils and urban trees could be used as a good tracer for monitoring air pollution in comparison to background levels. Soils reflected pollution in the past, while urban trees leaves proved to be a good monitoring source for current pollution (leaves). Average Pb, Zn and Cu **concentration in soils** were higher than in natural soils and similar to the pollution levels of other big cities. A punctual contamination in soils by Cu and Cr was identified in former industrial areas. Pb contamination in soils appeared to be the most prominent in the city of Madrid, as well as other EU cities at the beginnings of this century, despite the change into unleaded fuel since 2002, attributed to the low mobility of this HM in soil and soil amendments. The capacity of the six urban street trees species to capture air-born dust on the foliage surface as related to traffic intensity was estimated in 16.8 kg of noxious metals from exhausts per year. According to this value, trees planted along large road axes directly traped sizable amounts of dust. The effectiveness of particulate matter interception by trees was increased by rough surfaces, spatial geometry or by sticky needles, or any other complex structures that facilitate interception and capture. Due to higher pollution in winter perennial species, in particular Cedar, showed an increased dust trapping facility.

If possible, a mosaic of these species (or any other indigenous species with similar morphological attributes) at different age classes is recommended to intercept PM_{10}, beside the encouragement of greater species richness and biodiversity in the city. The vertical and horizontal distribution should assure the interception of particulate matter at understory, middle crown and canopy level, together with establishing a continuity between discrete green areas. Regarding the studied species, a combination of *Cedrus/Ulmus/Pinus pinea* resulted in an effective barrier, to filter dust of the urban air in a spatial and temporal aspect. These spacies can be recommended for Mediterranean big cities urban areas. Therefore urban trees can contribute significantly to alleviate air pollution especially near to high ADT roads.

The necessity of an appropriate design, selection of urban trees species and proper location to ameliorate the air quality levels under serious episodes of PM_{10} pollution should be an important criteria among others such landscaping, adaptive capacity or ornamental selection in big cities strategy to ameliorate pollution. These aptitudes would validate a sometimes undervalued role of urban trees in big cities.

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Tables:

Table 1. Street trees (only alignments) of the world's major cities as reported by authorities or cited in literature. [*= data obtained from Pauleit et al., (2002)].

Table 2: Number of urban trees corresponding to the six studied species under public management in Madrid. (a+b+c+d) trees in peri-urban forests, trees along the street and parks. Map is a combination of all tree inventories**.**

Table 3. Main results from inventory regarding average tree dimensions. All values in metres except DBH in centimetres.

Table 4. Descriptive statistics of HM in soils (n=196) (average, median, standard deviation, standard error of the mean, minimum and maximum values) vs. reference values in natural soils covered by same species in restricted mountain areas of *Cercedilla*, 78 km from Madrid (n=7) (average).

Table 5. Reference levels for heavy metals in soils in the Community of Madrid (mg kg^{-1}) according to land use. VR90 = reference value for percentile 90 (Orders 741/2007 and 2720/2006 of the Community of Madrid) and other international reference levels (all units in mg kg-1, except USA in kg ha^{-1}).

Table 6. Solvent proportion of ultrapure water and CH_2Cl_2 used for washing dust residue.

Table 7. Heavy metal concentration (mg kg^{-1}) in residue powder (average and standard deviation)

Table 8. Heavy metal concentration (mg kg^{-1}) in unwashed leaf samples of *Cedrus* sp. and *Aesculus hippocastanum* (average and standard deviation) in urban trees in Madrid.

Table 9. Average HM concentration in reference plants levels according to: (a) Markert (1992); (b) Prasad (2004). Critical of levels (toxic) HM in plants. (c) Markert (1993) (d) (Kabata-Pendias and Pendias (1992)) (ppm DW).

Table 10. Dry biomass (kg) of the trees along the streets and parks by species (biomass from trees in peri-urban forest is excluded).

City	Street trees	City	Street trees
New York	592'000	Barcelona	188'000 *
Berlin	416'000	San Francisco	100'000
Tokyo	400'000	Paris	88'000 *
Madrid	239'000	Munich	77'000 *
Bangkok	200'000		

Table 1

	Total trees	*Q. ilex*	*Platanus*	*Aesculus*	*Cedrus*	*Ulmus*	*P. pinea*
a) El Pardo	1'605'679	1'414'770	0	0	0	0	135'613
b) Casa Campo	700'707	142'633	20'402	9'783	4'189	34'253	325'181
c) Municipality trees along the streets	235'062	195	55'300	4'399	172	27'058	2'957
d) Municipality trees in parks	439'135	1'455	41'905	17'867	13'506	43'499	46'081
e) Total Municipality trees (c+d)	674'197	1'650	97'205	22'266	13'678	70'557	49'038
f) Total trees of studied species		**1'559'053**	**117'607**	**32'049**	**17'867**	**104'810**	**509'832**
Total public trees in Madrid (a+b+c+d)	**2'980'583**						
Dry leaf biomass (kg)		**21'175'666**	**975'403**	**223'099**	**307'734**	**1'139'346**	**10'636'244**

Table 2

	Stem height	Crown height	Total height	DBH	Crown width
Platanus sp.	3.4	6.7	10.4	25.3	6.2
Ulmus sp	3.4	6.6	10.6	27.3	6.2
Quercus ilex	3.0	6.1	7.3	18.4	5.4
Pinus pinea	4.6	6.5	8.2	29.9	5.8
Cedrus sp.	0.8	11.0	11.5	30.7	6.2
Aesculus sp.	3.7	6.3	9.2	20.3	5.4

Table 3

	Mean	Median	Std. dev.	Std. err.	Min.	Max.	Ref. Mean	Ref. Median	Ref. Std. dev.	Ref. Std. error	Ref. Min.	Ref. Max.
Ba	489.5	483.4	122.3	9.1	294.0	949.3	266.7	263.0	12.9	7.4	256.0	281.0
Cd	0.7	0.5	0.6	0.0	0.0	4.5	0.5	0.5	0.0	0.0	0.5	0.5
Cr	49.4	34.0	50.0	3.7	0.5	420.1	30.0	29.0	7.5	4.4	23.0	38.0
Cu	60.9	54.0	34.8	2.6	6.0	170.0	4.7	4.0	1.2	0.7	4.0	6.0
Mn	460.9	435.9	133.3	10.0	76.5	994.7	285.0	284.0	32.5	18.8	253.0	318.0
Ni	12.8	12.7	5.1	0.4	2.9	25.0	6.0	5.0	2.6	1.5	4.0	9.0
Pb	155.9	140.7	99.7	7.4	9.0	793.6	14.3	15.0	2.1	1.2	12.0	16.0
Zn	190.3	186.1	91.2	6.7	34.5	470.0	60.3	56.0	14.0	8.1	49.0	76.0

Table 4

	Industrial	Urban	Other use	VR90	USA 2000 kg/ha	UK 2002	Nederland 1999	Germany 1999	Taiwan 2000	Canada 2001	Italy 1999	Sweden 1999
Ba	100.000	15.200	4.200	138								
Cd	300	30	3	0,22	39	2	12	10/20/50	5			
Cu	8.000	800	80	20	1500		36/190		200	63	120	100
Cr	2.300	230	90	32		130	100/380	200/400/1000	250	64	150	120
Mn	33.900	3.90	690	690								
Ni	15.600	1.560	405	21	420	50	35/210	70/140/350	200	50	120	35
Pb	2.700	270	75	30	300	450	85/530	200/400/1000	500	140	100	80
Zn	100.000	11.700	1.170	73	2800		140/720		600	200	150	350

Table 5

	H_2O	Cl_2 CH_2
Cedrus sp. *and Pinus pinea*	100 ml	100 ml
Quercus ilex	100 ml	200 ml
Aesculus hippocastanum *Platanus orientalis* *Ulmus* sp.	400 ml	100 ml

Table 6

		Cedrus			Pinus pinea		
		Average	Summer	Aut/Win	Average	Summer	Aut/Win
Pb	Media	58,65	60,52	56,67	31,09	39,03	23,14
	SD	32,10	29,62	35,42	9,74	5,43	1,69
Zn	Media	212,36	237,35	185,81	177,81	195,61	160,02
	SD	90,02	86,51	88,57	26,65	27,77	9,61
Cu	Media	203,78	241,77	163,40	141,87	174,66	109,08
	SD	144,24	173,91	93,53	45,82	44,27	6,12
Ba	Media	181,19	187,60	174,39	111,16	149,03	73,28
	SD	119,66	142,46	93,80	45,76	22,21	7,10
Cr	Media	31,83	32,88	30,71	28,88	37,46	20,30
	SD	21,74	26,12	16,67	9,95	0,29	1,62
Ni	Media	9,01	9,49	8,50	7,55	9,92	5,18
	SD	4,50	5,17	3,77	2,83	1,06	0,65
		Quercus ilex			**Aesculus**		
		Average	Summer	Aut/Win	Average	Summer	Aut/Win
Pb	Media	60,90	47,88	73,93	56,18	58,25	49,12
	SD	38,20	17,89	58,12	16,02	17,53	6,05
Zn	Media	299,23	324,07	274,39	562,78	581,99	497,47
	SD	65,63	29,49	97,91	146,42	161,75	31,60
Cu	Media	235,20	309,45	160,95	269,38	273,30	256,07
	SD	97,28	35,52	71,27	97,55	111,08	17,71
Ba	Media	187,31	207,72	166,90	234,09	244,34	199,21
	SD	24,33	7,62	7,19	70,05	76,40	21,02
Cr	Media	40,02	46,37	33,66	44,26	46,03	38,23
	SD	9,05	1,47	9,07	12,69	13,80	4,99
Ni	Media	11,17	12,01	10,33	19,44	21,80	11,41
	SD	1,95	2,32	1,79	7,47	6,48	4,48
		Platanus			**Ulmus**		
		Average	Summer	Aut/Win	Average	Summer	Aut/Win
Pb	Media	43,89	48,31	40,31	25,40	30,98	18,88
	SD	10,15	11,29	4,89	11,03	9,58	6,47
Zn	Media	466,48	487,13	443,29	279,43	286,22	273,36
	SD	80,07	101,15	45,78	100,00	140,03	11,45
Cu	Media	248,78	265,32	228,77	203,83	207,04	199,64
	SD	70,00	94,35	17,43	58,80	76,77	15,89
Ba	Media	213,82	227,17	199,95	140,13	151,32	124,43
	SD	39,39	48,75	19,71	41,00	50,17	11,65
Cr	Media	44,01	45,21	41,83	30,65	34,59	24,57
	SD	21,18	29,01	7,93	19,50	24,61	5,72
Ni	Media	17,77	20,57	13,13	13,88	16,07	10,70
	SD	11,75	15,29	3,24	10,34	13,05	2,60

Table 7

		Cedrus			Aesculus		
		Average	August	November	Average	August	November
Pb	Average	23,67	15,86	30,70	3,14	3,24	2,98
	SD	25,93	15,09	31,33	0,86	0,99	0,59
Zn	Average	55,52	47,66	62,61	32,25	34,13	29,28
	SD	22,16	16,96	24,04	7,37	8,18	4,62
Cu	Average	31,17	24,48	37,19	17,51	14,65	22,04
	SD	21,57	27,86	23,91	16,12	7,11	23,94
Ba	Average	26,13	20,27	31,39	15,30	14,80	16,09
	SD	18,47	11,97	21,63	4,22	3,65	4,98
Cd	Average	0,32	0,56	0,10	0,05	0,07	0,03
	SD	1,97	2,86	0,04	0,09	0,11	0,01
Ni	Average	2,17	2,79	1,61	3,62	3,97	3,08
	SD	3,77	5,37	0,90	6,65	8,44	1,41

Table 8

	Zn	Pb	Cu	Ni	Cr	Cd	Ba	Mn
Average HM	50 (a); 8-100 (b)	1 (a); 1 -13 (b)	10 (a); 4 -15 (b)	1.5 (a); 1 (b)	1.5 (a); 0.2 - 1 (b)	9 (a); 1 -13 (b)	40 (a)	200 (a); 15 -100 (b)
Critical HM	>200 (c); 150-200; 100-500 (d)	3–20 (c)	>20; 15-20; 10-30 (d)	20-30; 10-30 (d)	1-2; 1-10 (d)	5-10; 10-20 (d)		

Table 9

	Q.ilex	*Platanus*	*Aesculus*	*Cedrus*	*Ulmus*	*P. pinea*
Number of trees	1650	97205	22266	13678	70557	49038
Dry biomass	14’073	806’194	154’992	237’182	472’860	1’172’098

Table 10

Figure captions

Fig. 1: Number of trees per species in parks and gardens (red) and along the streets (blue) in Madrid
Fig. 2: Number of urban trees of the six studied taxa classified by their presence in urban & peri-urban forests, parks and gardens and street trees (logarithmic scale)
Fig. 3: Trees under public maintenance in Madrid. Each single tree position (street trees in orange and trees in green spaces in green points) is located by GIS in the map (precision less than 10 cm). Exception: trees in two major peri-urban parks, where only forest area is represented without tree geoposition. Air pollution stations and soil sampling sites are also displayed.
Fig. 4: Yearly average of PM_{10} and NO_2 concentrations. Traffic intensity was measured in permanent gauging stations of the city, accounting 10 stations from 1988 to 1993, 20 stations from 1995 to 1996 and 45 stations from 1997 onwards. AADT source: *Government Department of Safety and Community Services. Directorate General for Mobility*.
Fig. 5: The sum of days exceeding the PM10 threshold values from 1980 to 2010 (limit=1'085 exceedances)
Fig. 6: The sum of days exceeding the PM10 threshold values from 2000 to 2010 (limit= 350 exceedances)
Fig. 7: Average daily traffic for the 2003-2008 period in 2'660 street sections. During the period 2004-2007 ADT in Madrid Southeast was affected by works for the M-30 1st ring tunnel construction between the A-4 and A-5 highways (between * and ** in upper grey map).
Fig. 8: Pb spatial distribution in soils in Madrid
Fig. 9: Zn spatial distribution in soils in Madrid
Fig. 10 Epicuticular wax layer and dust deposition during summer
Fig. 11: Attached foliage dry mass in *Cedrus* sp. (percentage of different needle ages)
Fig. 12: Estimation of trace elements related to traffic emissions deposited per adult tree and year. The amount of dust trapped by foliage varied for the 6 species. Evergreen needles of *Cedrus* and *Pinus* collected more particulate matter from road traffic emissions during peak winter period.
Fig. 13: Total of heavy metals collected by the six analysed species each year in Madrid (16.8 kg).
Fig. 14: Scanning electron micrographs (*SEM):* **(14-A)**: X-ray spectrum of fine particles covering the stomatal opening in a cedar's needle (see 14-E). It displayed a different chemical elements such as Si, Al, K, Ca, Fe and Mg that possibly came from construction works and the dust of the pedestrian road (limestone gravel layer covers the tracks in the park), as well as other minor HM from road traffic. **(14-B & C)**: Scanning electron micrographs of two stomatal areas of unwashed abaxial leaf surface of *A. hippocastanum*. **(14-B)** Detail of stomata and cuticular ridges in areas of low pollution in the centre of *Retiro* Park. **(14-C)**: Air pollution caused a distortion of the outer epidermal cell walls folds, followed by a smaller size and poor aspect of stomatal guard cells. **14-D & E:** Cedar's needles from the centre of *Retiro* Park **(14-D)** and from the border of the park **(14-E)**; It may be suggested that the particles deposited on 14-E mostly originated from the traffic, or from the resuspended particulate matter.
Fig. 15. (15-A) Binocular picture of particles deposited on *Quercus ilex* trichoma; **(15-B)** Binocular picture of aggregate form as agglomerates of similar-sized particles and individual large particles carying several smaller attached particles on *Pinus pinea* needle surface. The leaves/needles were situated at 300 m from civil constructions activities and at 10 m height from medium/high duty traffic (ADT=70'000 to 90'000 vehicles/day) in *Castellana* St.; **(15 C-N).** Zn revelation in *Pinus*, *Platanus* and *Cedrus*. Examples of microlocalization of Zn after 8-hydroxyquinoline (HQ) revelation in *Pinus pinea* **(C-F)**, *Platanus orientalis* **(G-J)** and *Cedrus atlantica* **(K-N)** in the form of massive crystals showing greenish fluorescence. They were found mostly in the conductive tissues in the leaf/needle vein, especially in phloem **(p)** in (D,F, J, L N) and less in not-living cells of the xylem **(x)** and sclerenchyma **(s)**. The signal in trees found in low Zn soils concentration were scarcer in (C, D, G, H, K, L) [Zn] = 108 and 129 mg kg-1 in *P.pinea* at *Dehesa de la Villa* urban forest (C) and *C. atlantica* at *Retiro* Park (K) than (E, **I**, M). [Zn = 314, 245 and 277 mg kg-1 (E: *Castilla* Sq., **I**: *España* Sq. and M: *Recoletos* Rd.). No signal was detected in *Pl. orientalis* at G: *Casa de Campo urban* forest accounting low Zn concentration.
Fig. 16: Map of the potential particulate matter pollution in function of the AADT, the dust residue measured in samples and the shortest distance of the tree to the next emitting road

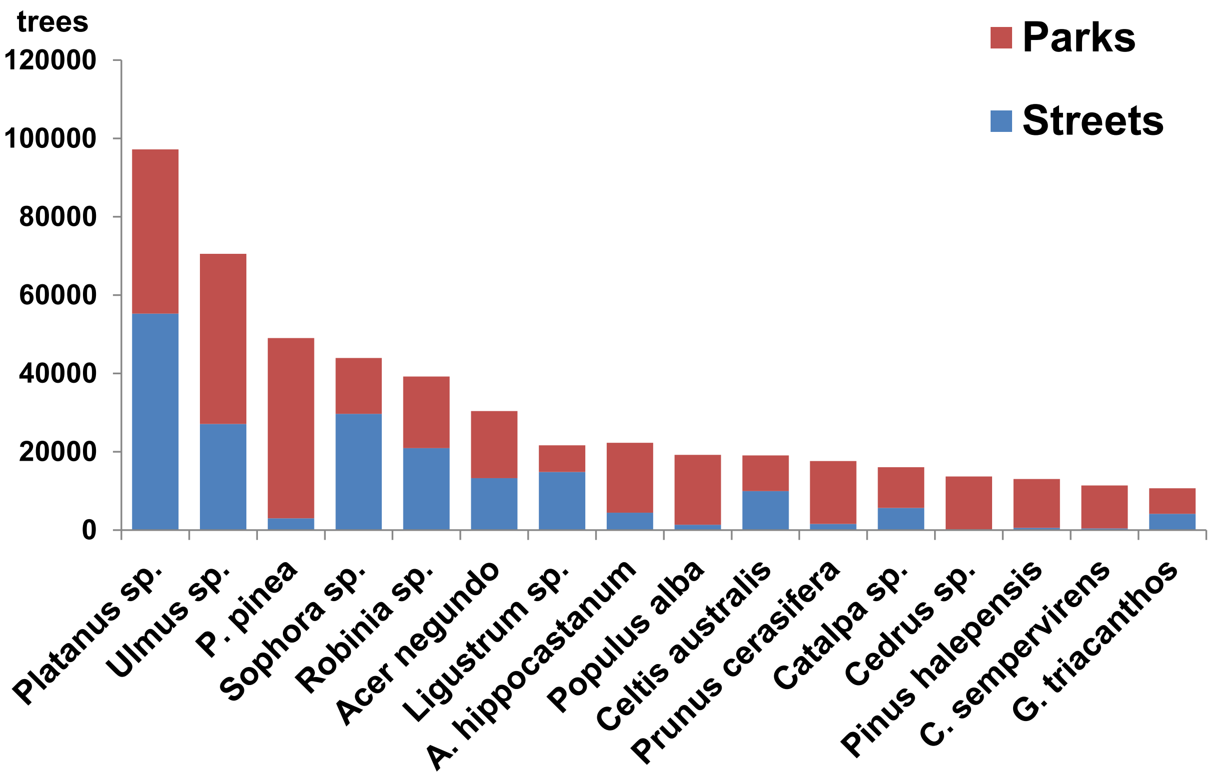

trees
120000
100000
80000
60000
40000
20000
0
Parks
Streets
Platanus sp.
Ulmus sp.
P. pinea
Sophora sp.
Robinia sp.
Acer negundo
Ligustrum sp.
A. hippocastanum
Populus alba
Celtis australis
Prunus cerasifera
Catalpa sp.
Cedrus sp.
Pinus halepensis
C. sempervirens
G. triacanthos

Fig. 1

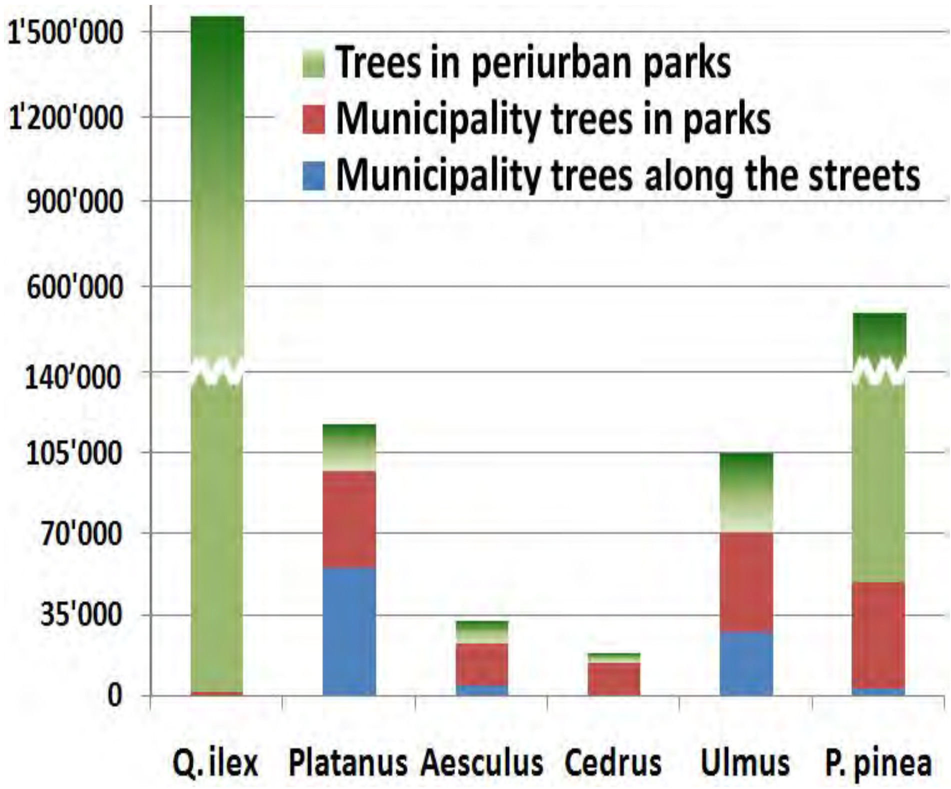
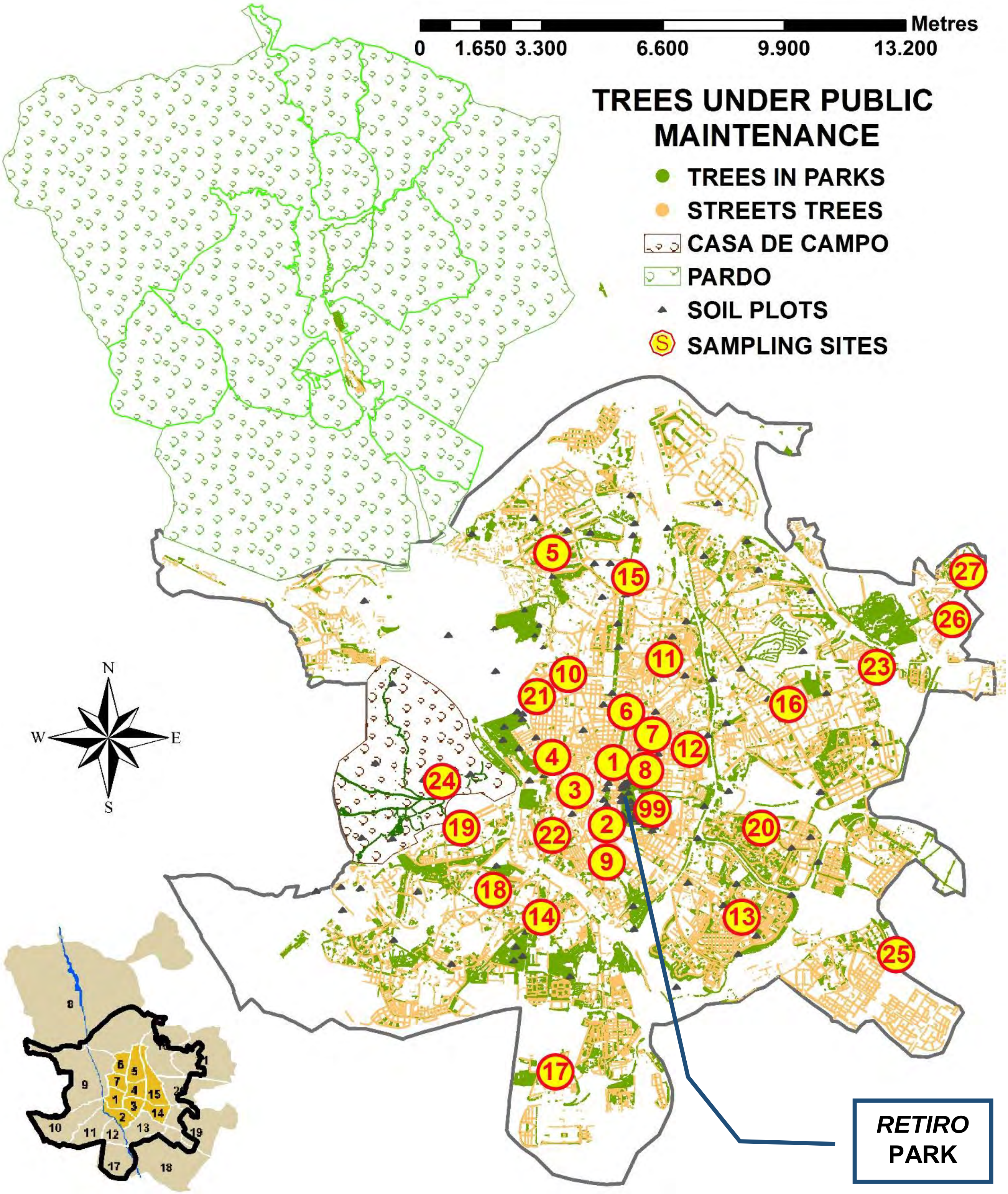

1'500'000
1'200'000
900'000
600'000
140'000
105'000
70'000
35'000
0
Trees in periurban parks
Municipality trees in parks
Municipality trees along the streets
Q. ilex
Platanus
Aesculus
Cedrus
Ulmus
P. pinea

Fig. 2.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TREES UNDER PUBLIC MAINTENANCE
TREES IN PARKS
STREETS TREES
CASA DE CAMPO
PARDO
SOIL PLOTS
SAMPLING SITES
N
W
E
S
RETIRO PARK

Fig. 3

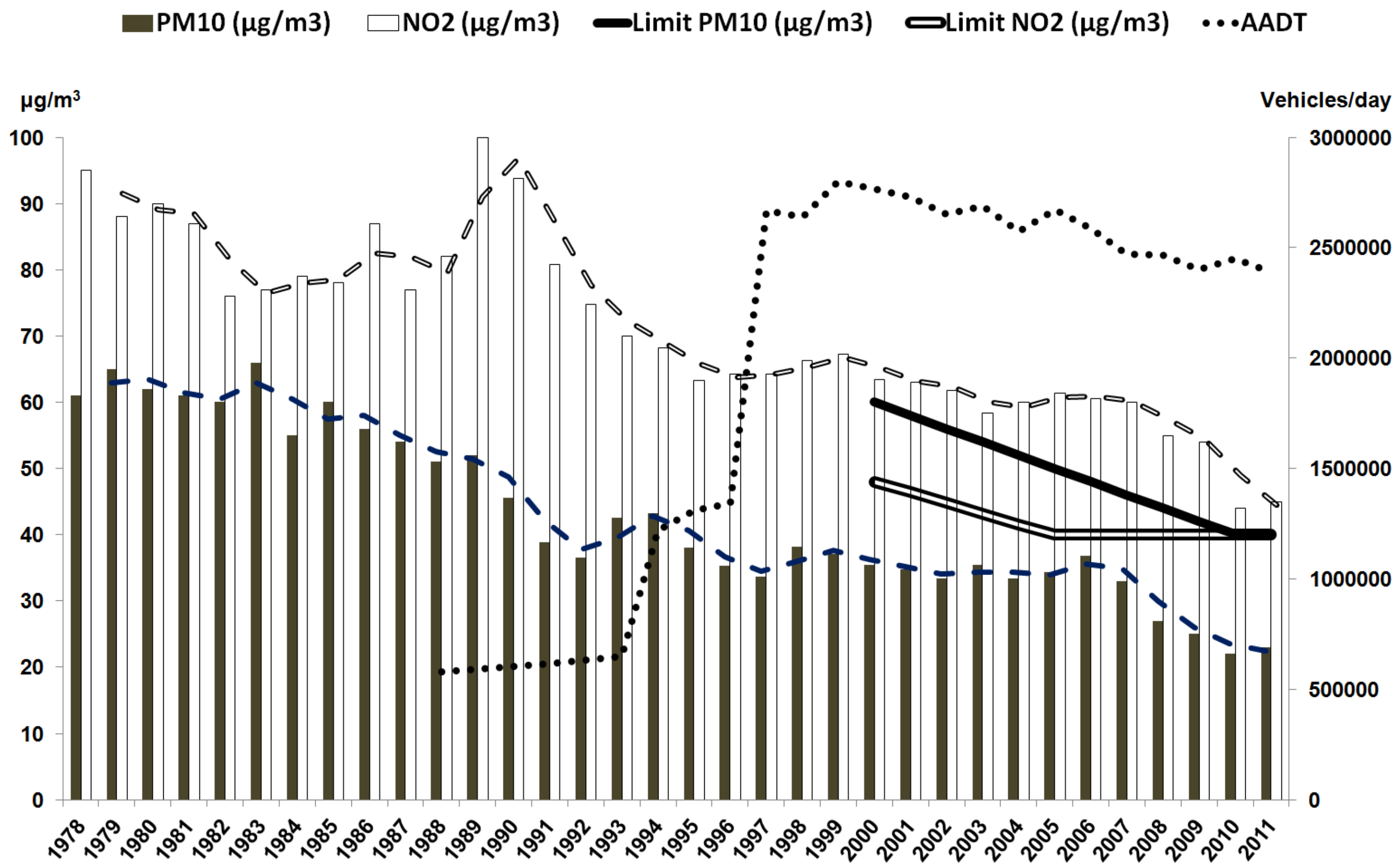

PM10 (µg/m3)
NO2 (µg/m3)
Limit PM10 (µg/m3)
Limit NO2 (µg/m3)
AADT
µg/m3
Vehicles/day
100
90
80
70
60
50
40
30
20
10
0
3000000
2500000
2000000
1500000
1000000
500000
0
1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011

Fig. 4

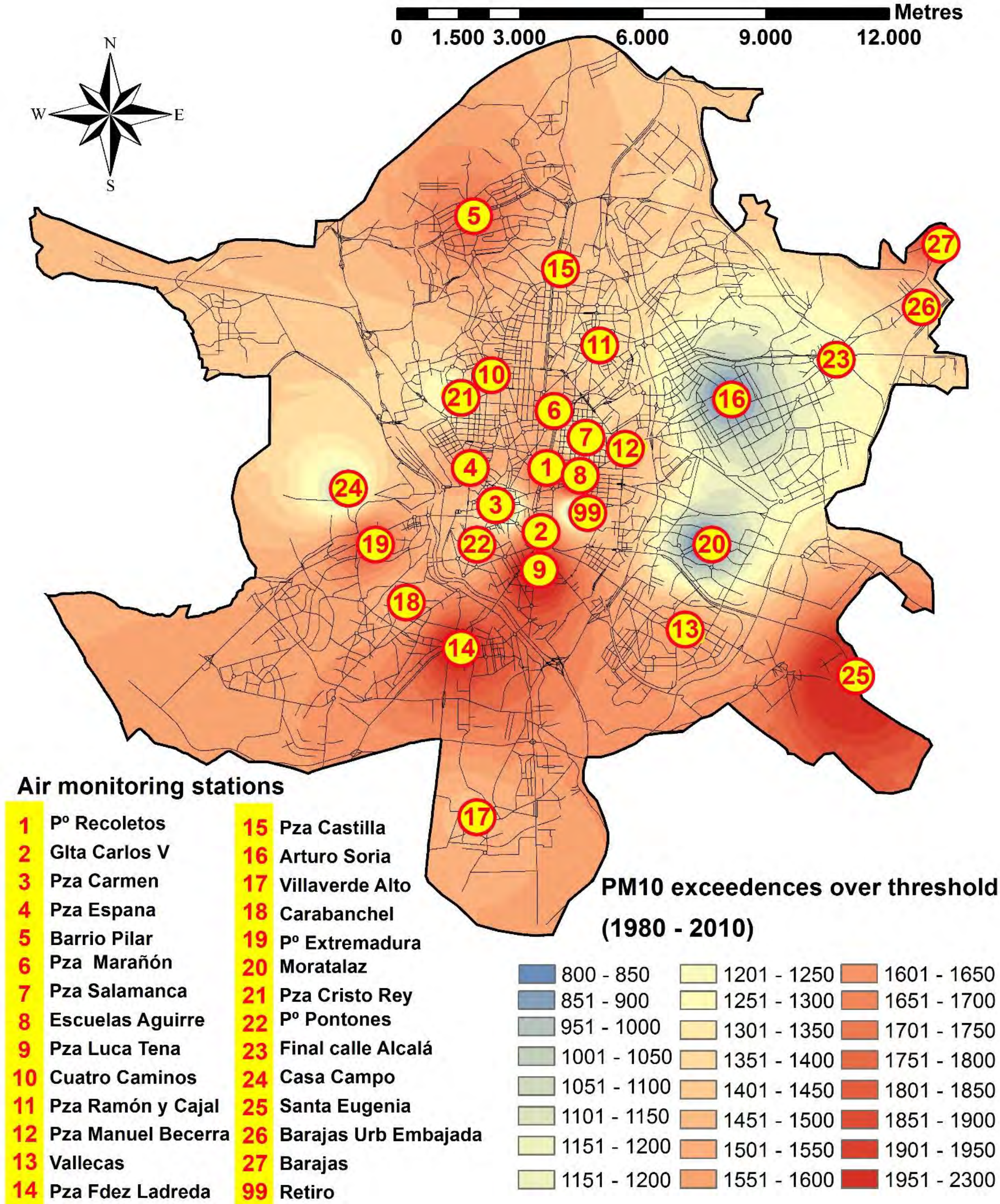
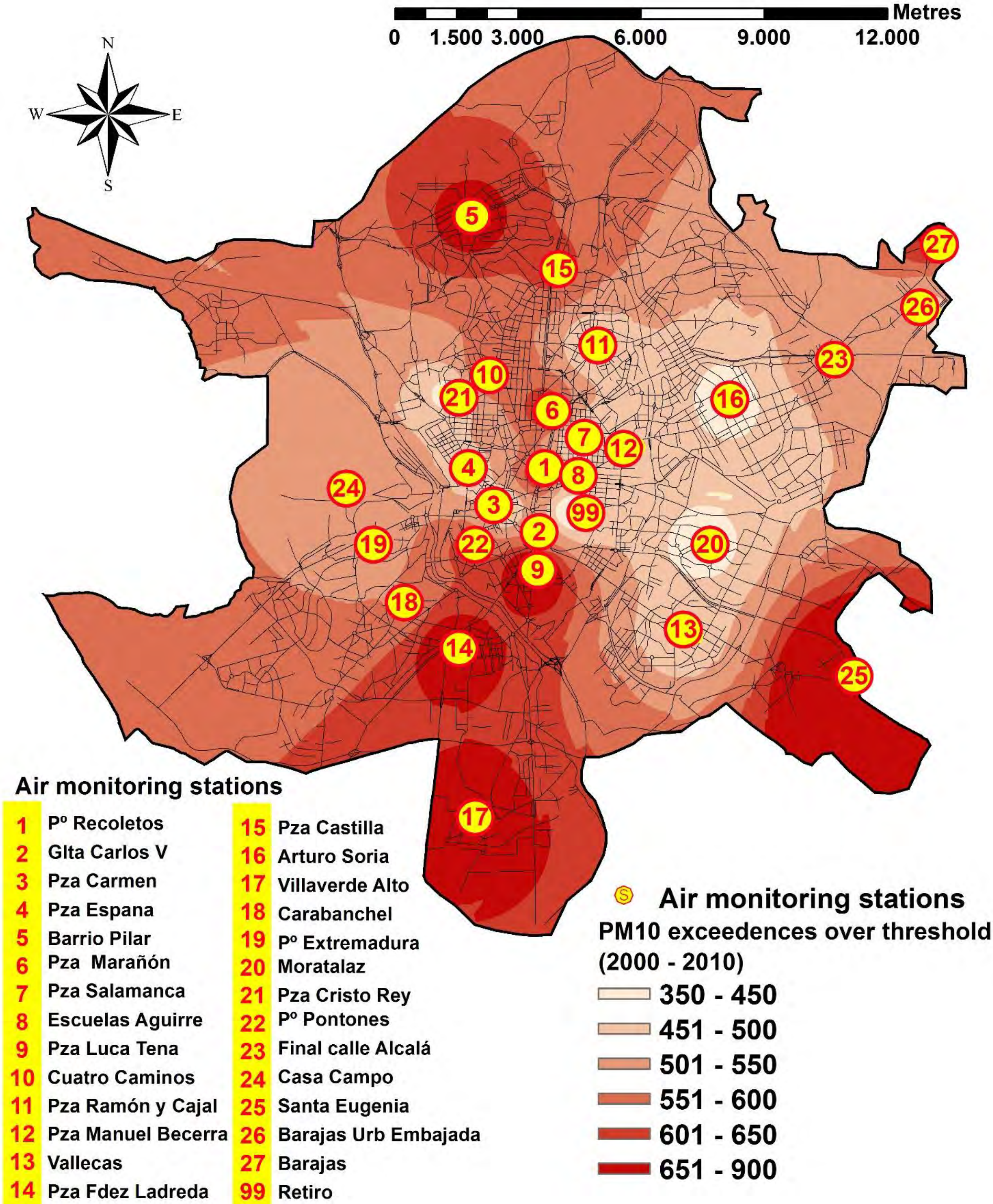

Metres
0 1.500 3.000 6.000 9.000 12.000
N
W
E
S
Air monitoring stations
1 Pº Recoletos
2 Glta Carlos V
3 Pza Carmen
4 Pza Espana
5 Barrio Pilar
6 Pza Marañón
7 Pza Salamanca
8 Escuelas Aguirre
9 Pza Luca Tena
10 Cuatro Caminos
11 Pza Ramón y Cajal
12 Pza Manuel Becerra
13 Vallecas
14 Pza Fdez Ladreda
15 Pza Castilla
16 Arturo Soria
17 Villaverde Alto
18 Carabanchel
19 Pº Extremadura
20 Moratalaz
21 Pza Cristo Rey
22 Pº Pontones
23 Final calle Alcalá
24 Casa Campo
25 Santa Eugenia
26 Barajas Urb Embajada
27 Barajas
99 Retiro
PM10 exceedences over threshold
(1980 - 2010)
800 - 850
851 - 900
951 - 1000
1001 - 1050
1051 - 1100
1101 - 1150
1151 - 1200
1151 - 1200
1201 - 1250
1251 - 1300
1301 - 1350
1351 - 1400
1401 - 1450
1451 - 1500
1501 - 1550
1551 - 1600
1601 - 1650
1651 - 1700
1701 - 1750
1751 - 1800
1801 - 1850
1851 - 1900
1901 - 1950
1951 - 2300

Fig. 5


Metres
0 1.500 3.000 6.000 9.000 12.000
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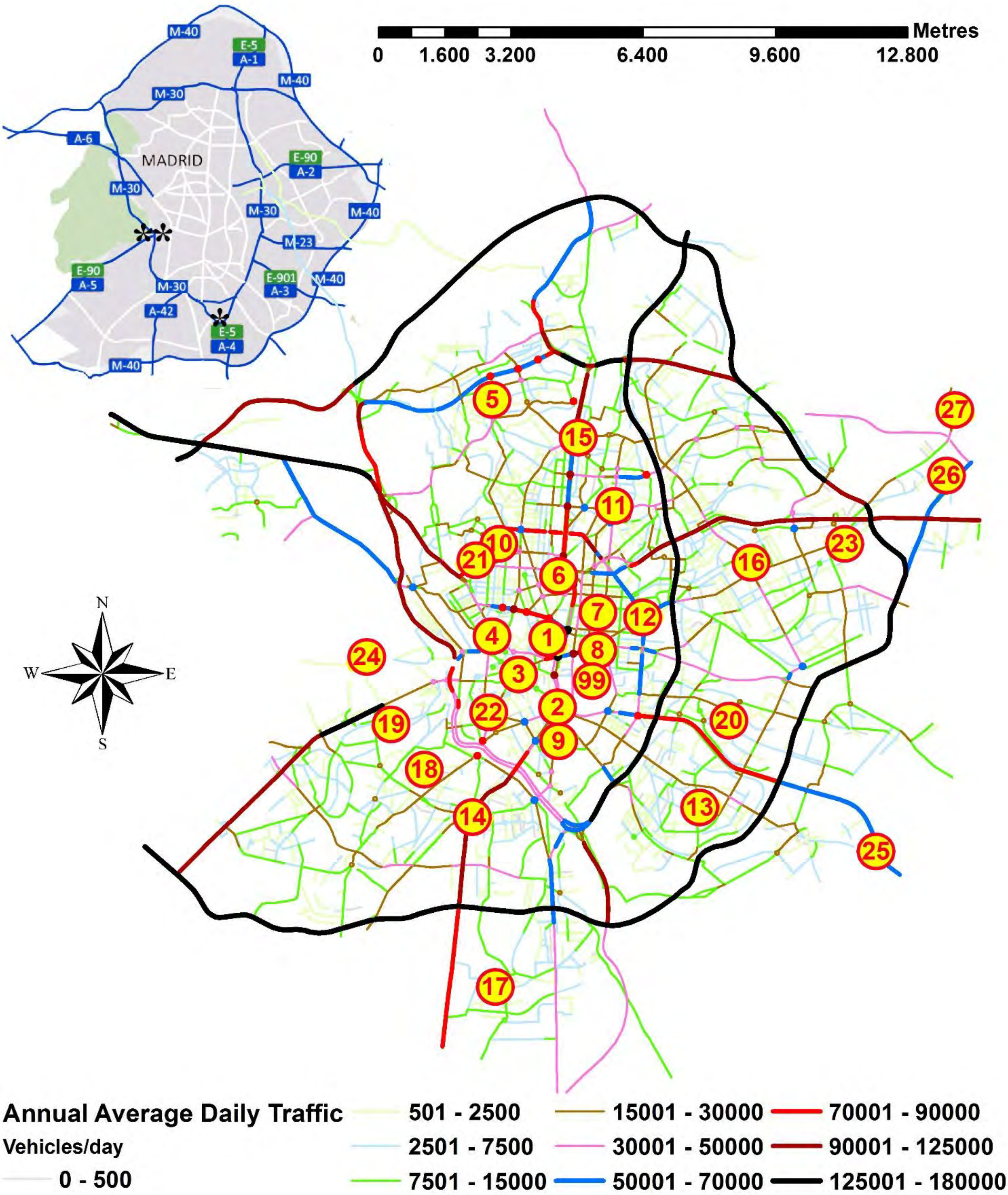
W
E
S
Air monitoring stations
1 Pº Recoletos
2 Glta Carlos V
3 Pza Carmen
4 Pza Espana
5 Barrio Pilar
6 Pza Marañón
7 Pza Salamanca
8 Escuelas Aguirre
9 Pza Luca Tena
10 Cuatro Caminos
11 Pza Ramón y Cajal
12 Pza Manuel Becerra
13 Vallecas
14 Pza Fdez Ladreda
15 Pza Castilla
16 Arturo Soria
17 Villaverde Alto
18 Carabanchel
19 Pº Extremadura
20 Moratalaz
21 Pza Cristo Rey
22 Pº Pontones
23 Final calle Alcalá
24 Casa Campo
25 Santa Eugenia
26 Barajas Urb Embajada
27 Barajas
99 Retiro
Air monitoring stations
PM10 exceedences over threshold
(2000 - 2010)
350 - 450
451 - 500
501 - 550
551 - 600
601 - 650
651 - 900

Fig. 6.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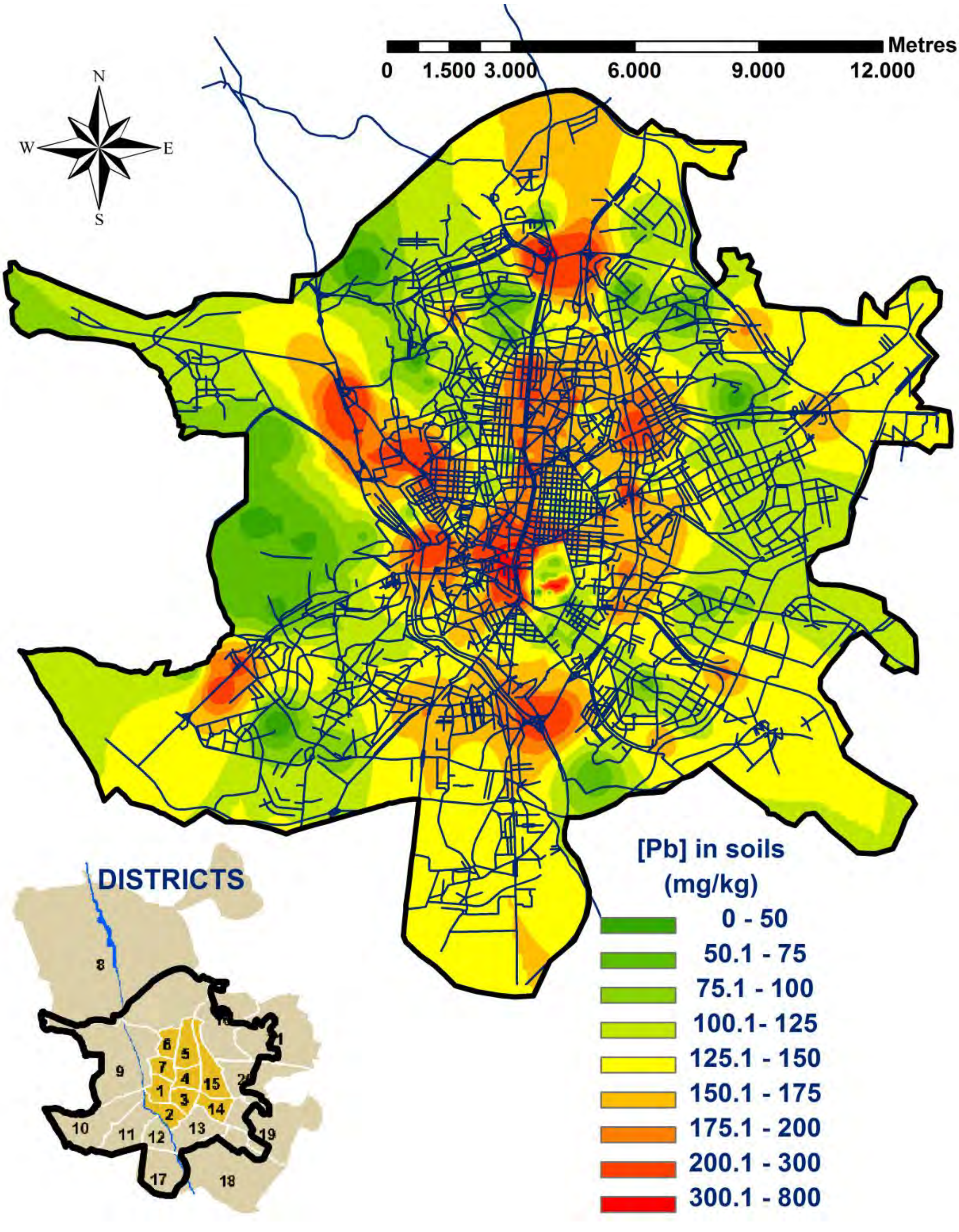
6.400
9.600
12.800
M-40
E-5
A-1
M-30
A-6
MADRID
E-90
A-2
M-23
E-901
A-3
E-90
A-5
A-42
E-5
A-4
N
S
W
E
Annual Average Daily Traffic
Vehicles/day
0 - 500
501 - 2500
2501 - 7500
7501 - 15000
15001 - 30000
30001 - 50000
50001 - 70000
70001 - 90000
90001 - 125000
125001 - 180000

Fig. 7.


Metres
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N
W
E
S
DISTRICTS
[Pb] in soils
(mg/kg)
0 - 50
50.1 - 75
75.1 - 100
100.1- 125
125.1 - 150
150.1 - 175
175.1 - 200
200.1 - 300
300.1 - 800

Fig. 8.

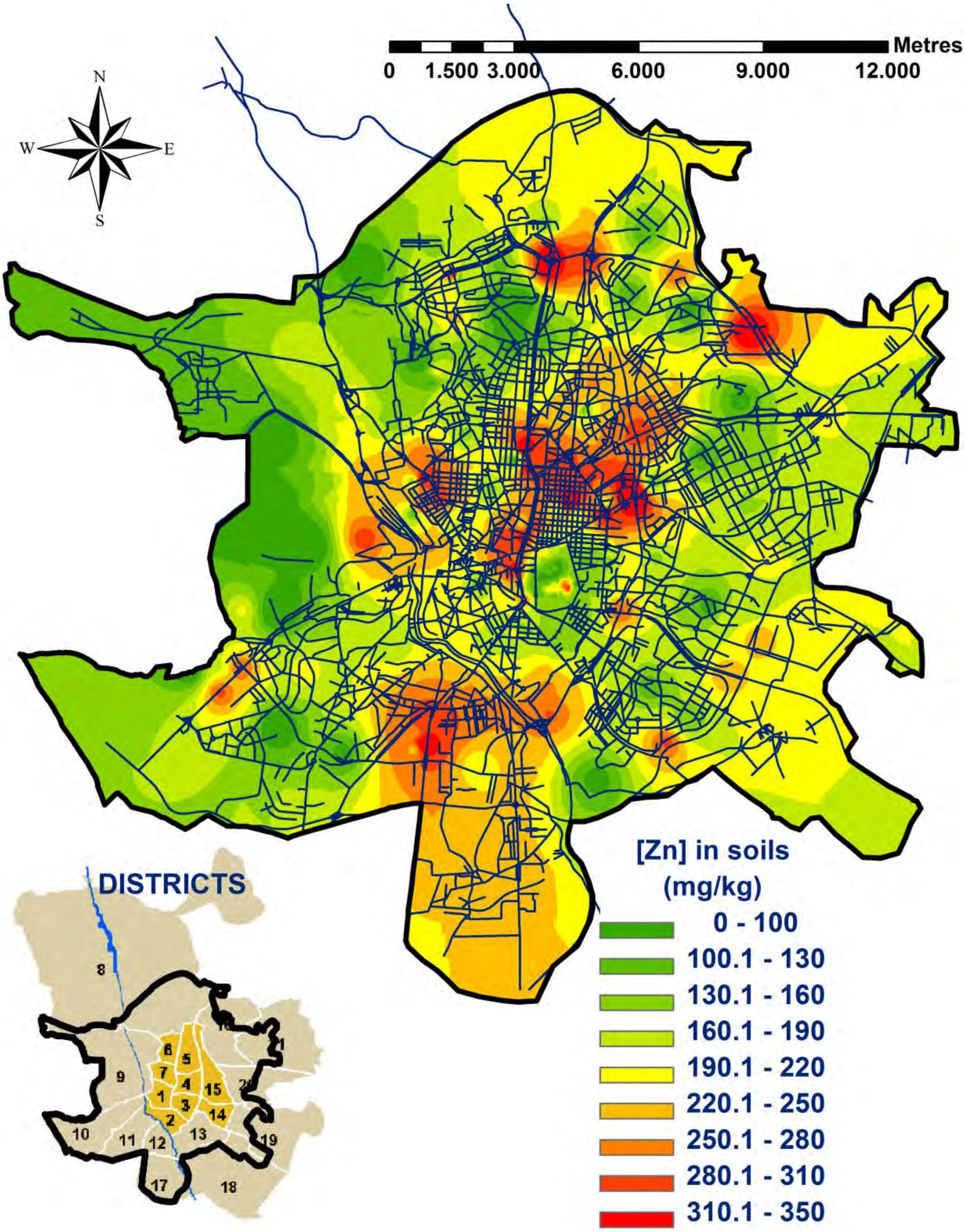

N
W
E
S
Metres
0 1.500 3.000 6.000 9.000 12.000
[Zn] in soils
(mg/kg)
0 - 100
100.1 - 130
130.1 - 160
160.1 - 190
190.1 - 220
220.1 - 250
250.1 - 280
280.1 - 310
310.1 - 350
DISTRICTS
8
9
6
5
7
4
15
1
3
14
2
10
11
12
13
19
17
18

Fig.9.

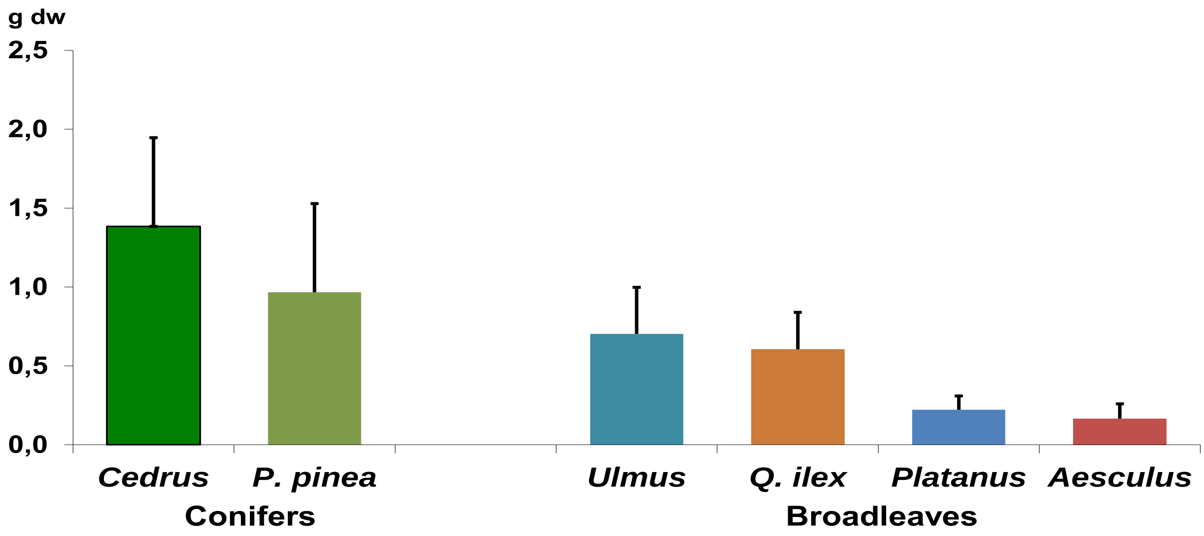


Fig. 10

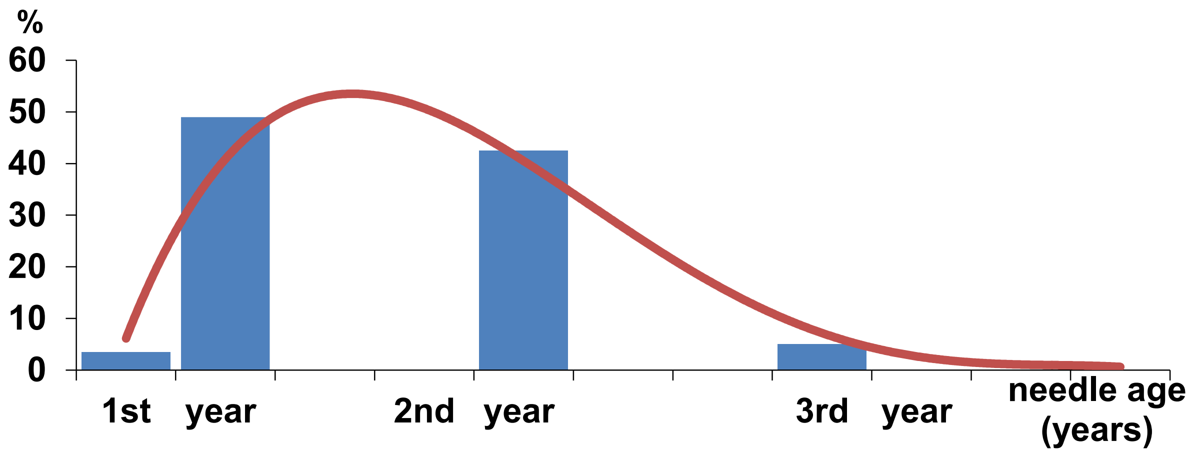


Fig. 11

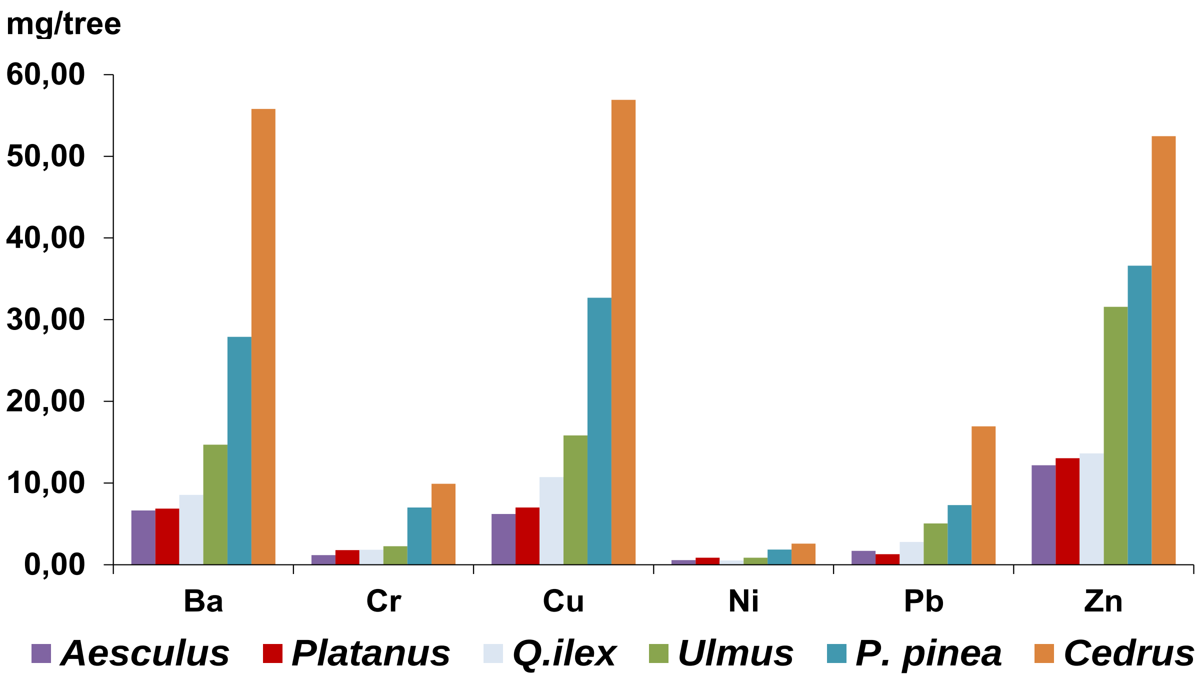


Fig.12

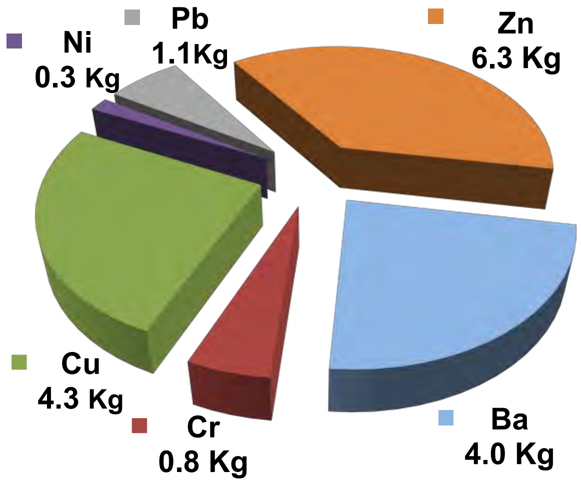

Ni
0.3 Kg
Pb
1.1Kg
Zn
6.3 Kg
Cu
4.3 Kg
Cr
0.8 Kg
Ba
4.0 Kg

Fig.13

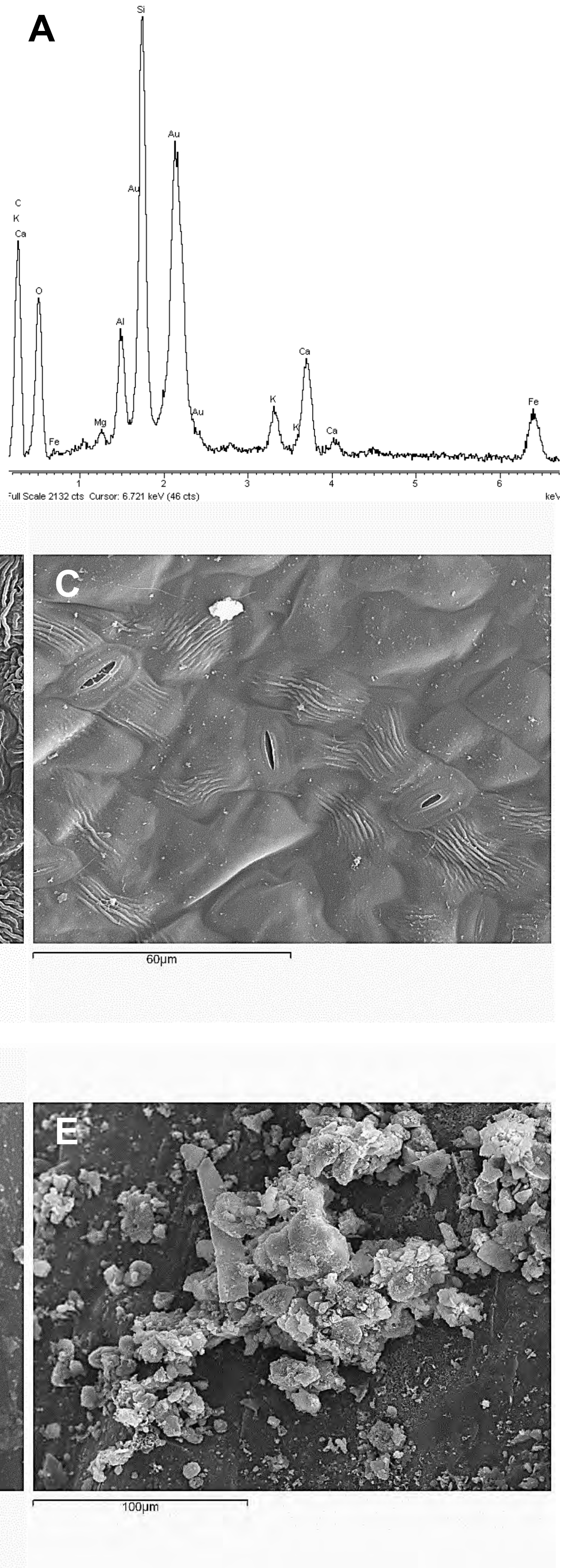

A
Si
Au
Au
C
K
Ca
O
Al
Mg
Fe
Au
K
Ca
K
Ca
Fe
1
2
3
4
5
6
keV
Full Scale 2132 cts Cursor: 6.721 keV (46 cts)
B
40µm
C
60µm
D
100µm
E
100µm

Fig.14

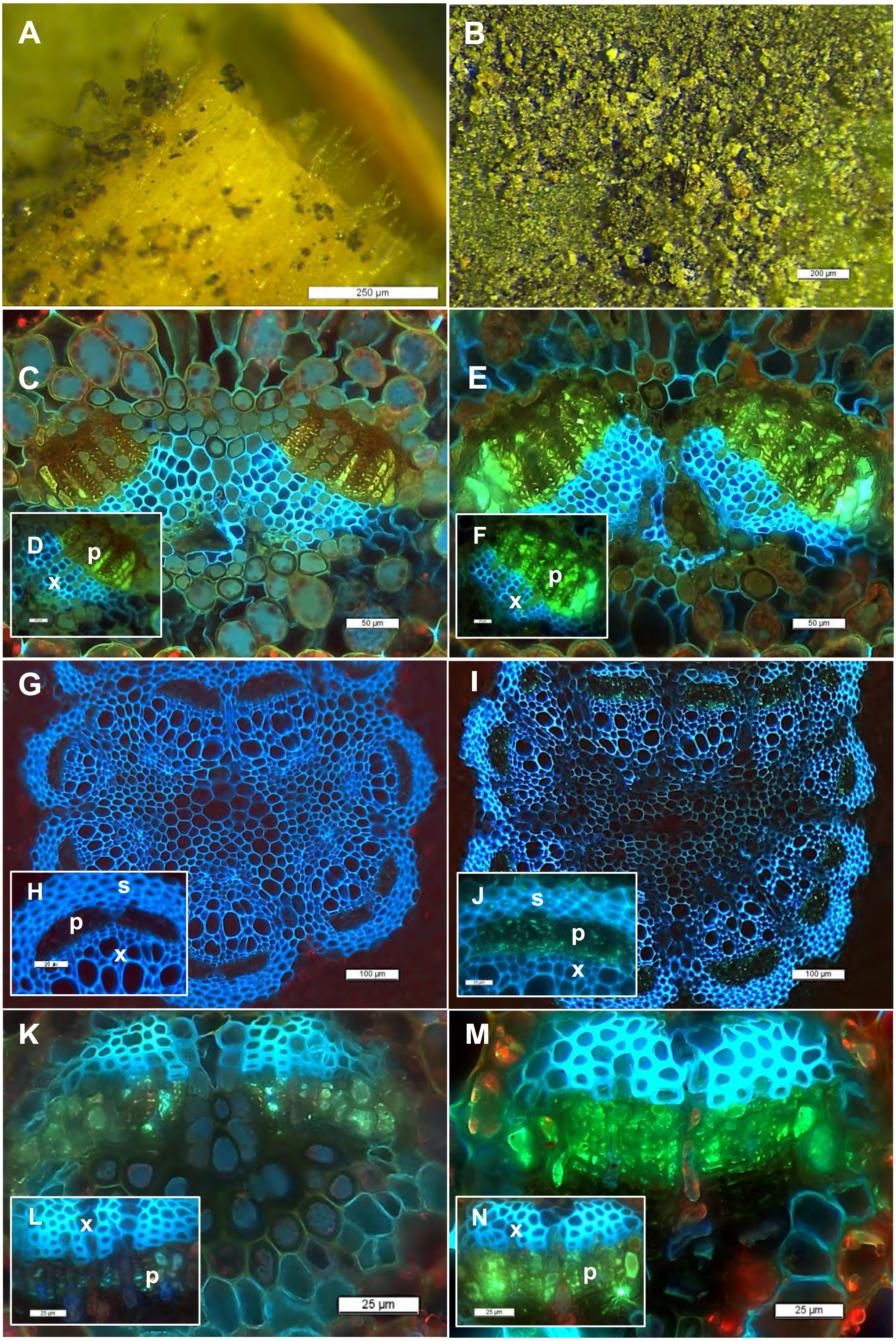

A
250 µm
B
200 µm
C
D
p
x
50 µm
E
F
p
x
50 µm
G
H
s
p
x
100 µm
I
J
s
p
x
100 µm
K
L
x
p
25 µm
M
N
x
p
25 µm

Fig.15

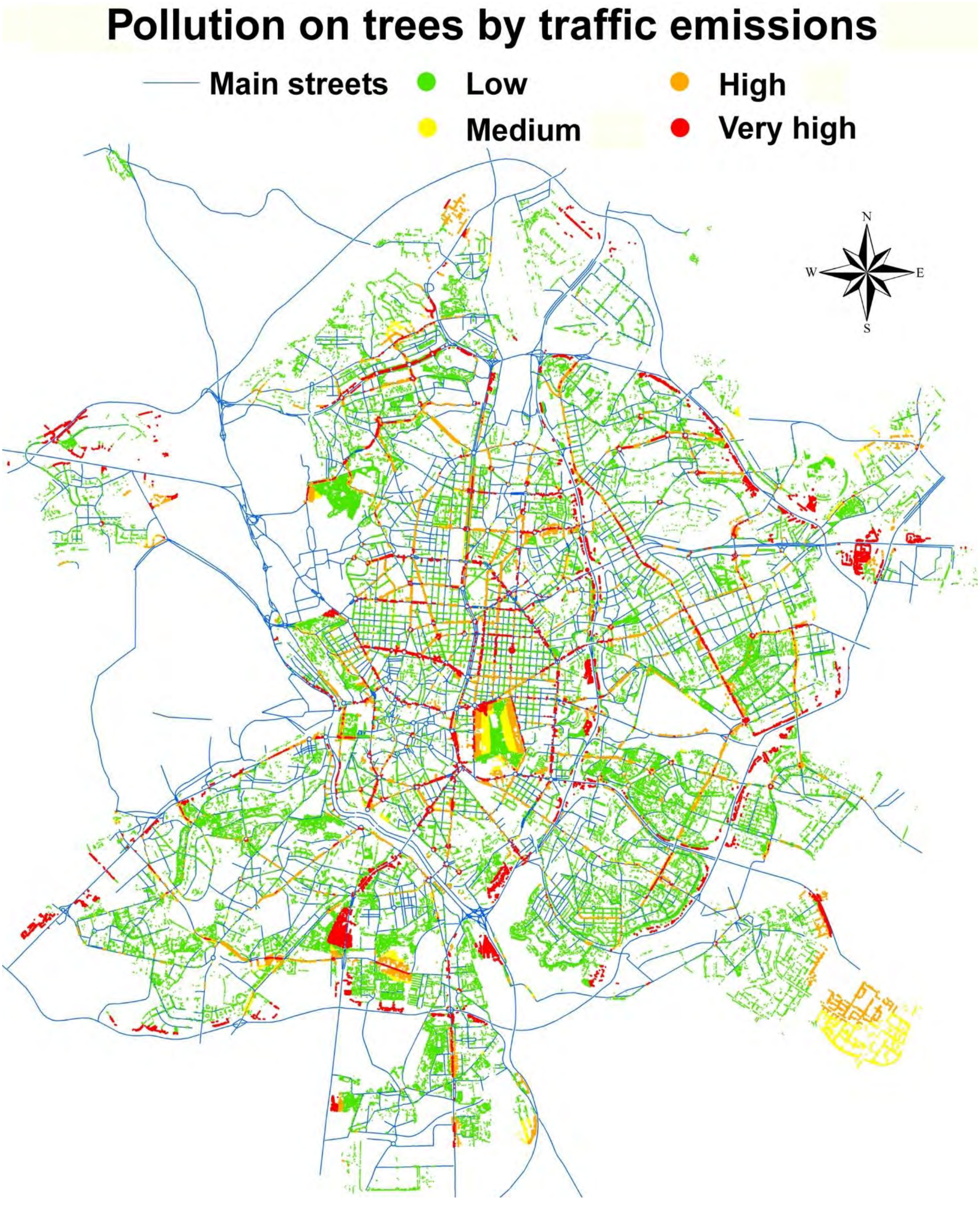

Pollution on trees by traffic emissions
Main streets
Low
High
Medium
Very high
N
W
E
S

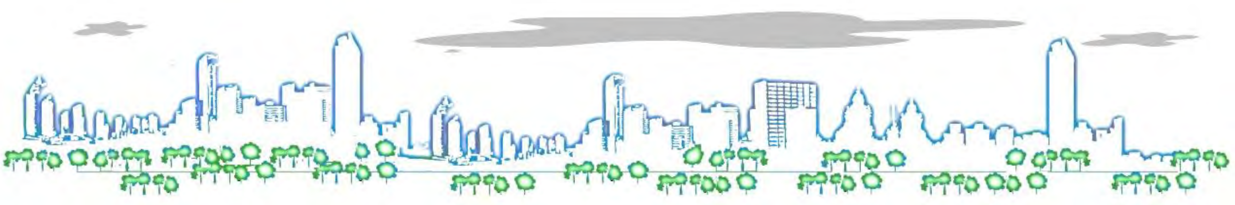
Fig.16

Chapter 5

GENERAL DISCUSSION

Chapter 5

GENERAL DISCUSSION



Chapter 5 GENERAL DISCUSSION

5. General discussion

In this chapter, the discussion addressed the aims of the thesis and the outcome, particularly by discussing the link between the different chapters in a common, general view.

The three main topics introduced in Chapter 1 were: 1) urban areas and population, 2) air pollutants and the impacts of the urban activity on the environment, 3) biomonitoring and 4) green spaces and urban trees. These topics will be discussed here and their relation in the different chapters according to the objectives [Chapter 1, 3.]. Thus, main discussion regarding air pollution and urban trees were the two sides of the same coin: pollution that affects urban trees [Chapter 5, 5.2] in relation to objective B; and trees that ameliorated the air pollution and urban environment [chapter 5, 5.3] in relation to objectives C, D, E & F. In chapter 1, objective A was achieved, while objective G was achieved in Annexes and in the attendance to workshops and even appearances in media (ATRESMEDIA, 2014) during TV news.

5.1 Urban environment

The city of Madrid, like other big cities in the world, has a number of distinctive socio-economic characteristics:

1) High population density

2) Income per capita above the Spanish and European average

3) Strong economic activity to the detriment of rural activity

Thus, urban environment created in Madrid was the consequence of a complex and interrelated flux of relationships between the urban development and the urban environmental system, where the solution to one problem was often the cause of another. As shown in chapter 1, the type of production developed in the large cities and their urban planning model required a high demand on resources (electricity, fuel, building materials, food, water and roads), to generate a huge amount of waste (garbage, toxic waste, air pollution and contaminated water), not only in the area occupied by the city (150 km^2), but even in remote areas, as e.g. ozone pollution in Mediterranean coast (350 km^2 away), where one of the main sources was the traffic in Madrid (Sanz, Calatayud, & Calvo, 2000). In a number of Southern European cities, such as Athens and Naples, there has been a significant increase in most air pollutants and a corresponding reduction in air quality. This can be traced to the major growth in population of these cities, due to an exodus from the rural areas of Southern Europe. The growth of urban industry and vehicle emissions in Athens, for example, forced the authorities to introduce a system whereby vehicles are only permitted to enter the city centre on alternate days. These measures have only succeeded in preventing the situation from worsening. They cannot be considered as long-term solutions. Madrid city council is planning these kind of traffic restrictions in 2015, according to the Air Quality Plan of the City of Madrid 2011-2015.

Regarding the trend of the current population in Madrid, Madrid would be a XXL city, according to the urban centre sizes classification in table 1 (Dijkstra & Poelman, 2012). Despite to the decrease of population in last two years (INE, 2014a), the trend tends to maintain the XXL category in the next decade.

The number of registered cars per 1,000 population in representative European cities situated Madrid as a city still heavily motorized, reaching 468 car per 1’000 inhabitants (EU, 2014), while satellite cities such as Alcobendas (15 km to the North of Madrid) are on the top of the list. The outlook for the coming years is a decreasing on the rate of diesel vehicles due to the disadvantages facing the parking fares and taxes, but still the price of diesel fuel is slightly cheaper than gasoline. The inventory of total emissions of the main pollutant in Madrid tends to decrease too (Ayuntamiento de Madrid, 2013) since 2006. Under this suitable scenario, the Municipality of Madrid aims to reduce the percentage of private commutes by encouraging people to use public transport. Despite of these efforts, Madrid still does not comply with the European Union's pollution limits that, as we have seen, were not fulfilled (Annexe XV). Artınano *et al.* (2004) warned of the difficulty of compliance with new European directives regarding PM_{10} exceedances. The current measures in Madrid are proposed to deter drivers by the creation of new restricted-access areas in 2015 in downtown, a part of the aforementioned temporary actions during limit exceedance episodes.

Paradoxically, although air quality in developed countries has improved over the last decades, the results in health are adverse due to the effects of particulate matter, even at relatively low levels and particularly, $PM_{2.5}$ particles that penetrate deep into lung. A recent study involving 312,944 people in 17 European countries revealed that there was no safe level of particulate matter, as mentioned in chapter 1 by Alas Brun (2003). Each increase of 10 μg/m^3 in PM_{10} or $PM_{2.5}$ imply to rise a 22% or 36% the rate of lung cancer respectively (Raaschou-Nielsen *et al.*, 2013). WHO estimates that 12.7% of deaths could be averted by improving air quality worldwide. Lower levels of air pollution will reduce the burden of respiratory and cardiovascular disease-related illnesses, health-care costs, and lost worker productivity due to illness, as well as increasing life expectancy among local populations. All these reasons about the adverse effects of particulate matter in health, highlight the capability of vegetation to capture and retain these particles on leaf surfaces [Chapter 4]. As it has been mentioned in chapter 1, a reduction of 10 μg/m^3 in the concentration of the particulate matter in the atmosphere, means a great percentage of human lives.

5.2 Urban trees affected by air pollution in the city

The most important air pollutants that affects vegetation in urban green spaces were PM and O_3, as mentioned in Chapter 1 [2.2]. In particular, PM_{10} showed the highest incidence on foliar systems of trees situated in the edge of the masses or alignment. Indirectly, the deposition of particulate matter may increase the concentration of heavy metals in the soils.

5.2.1 Ozone effects on urban trees

The harmful effect of O_3 on plants was described 60 year ago. Currently, O_3 is considered as one of the most noxious air pollutants on vegetation in forest (MR. Ashmore, 2005). Among others, effects of O_3 on plants included reductions in photosynthesis, visible leaf injury and growth limitation (Matyssek & Sandermann Jr, 2003). Thus, chapter 2 and 3 was completely dedicated to the effects of O_3, as well as Annexe I and IV. Chapter 2 and Annexe IV gave a general review of the effects on photosynthesis, plant growth and development, from the individual to the ecosystem level. Therefore, they were more focused into a physiological approach to these effects. Meanwhile, chapter 3 exemplified the effects of O_3 in *Quercus ilex* in urban and periurban areas in Madrid and added an anatomical and histochemical approach to chapter 2.

There were previous reviews about the effects of ozone in vegetation (Davison & Barnes, 1998; Krupa & Manning, 1988; Rich, 1964; Sandermann Jr, 1996; Skärby *et al.*, 1998), and recently in the Mediterranean forest (Paoletti, 2006). As well as new studies of free-air exposure techniques under field conditions in forests (M. Ashmore, 2015), but we wanted to approach these effects to the current problems that urban trees could face in the city. These effects were not only characteristics of the urban environments, although they were the most frequent. In particular, the effects on photosynthesis and the stomatal functioning were reviewed as the major ozone injuries that were inflicted to the plant after entering through the stomata. Plant detoxification capacity, carbohydrate allocation, growth and development were also revised, as well as the effects at the ecosystem level, defence mechanisms of plants against ozone, and their sensitivity and tolerance. The review annexe IV focused on the ozone effects on photosynthesis, in particular, on the alterations in the electron chain, the activity of rubisco and the variation in the content of chlorophyll, as well as the effects on carbohydrate distribution and the changes in the capacity of detoxification and the stomatal function.

Chapter 3 consisted in a study of the visible symptoms that O_3 caused in Holm oak. In contrast to fumigation experiments, it was conducted for four years in urban ambient conditions. There were few gas exchange measurements in adult trees in polluted sites of the city in literature (L. Gratani, Crescente, & Petruzzi, 2000), whereas controlled fumigation experiments on seedlings were commonly carried out (Inclán *et al.*, 1999), due to a better monitoring of the ambient factors and O_3 exposure in open-top chambers (OTC) (Elvira *et al.*, 1995). In the last years, the O_3 experiments have become more complex regarding stress interactions with other abiotic and biotic factors (Matyssek *et al.*, 2014). The development of free-air exposure techniques on trees and young forests under field conditions (Karnosky *et al.*, 2007) have allowed to differentiate the physiological differences between juvenile and adult trees.

The controversial on the O_3 sensitivity of sclerophyll evergreen species have been discussed in several manuscripts (Calatayud *et al.*, 2010). In particular, Holm oak appeared to be rather O_3-tolerant, being the less sensitive species of the *Quercus* genus in Spain according to (Calatayud *et al.*, 2011). In contrast, *Quercus ilex* was reported for the most extreme stress reactions to O_3 exposure among other sclerophyll evergreen trees investigated (Ribas *et al.*, 2005). Despite the preliminary idea of the relative insensitivity of sclerophylls to O_3 suggested by some authors, it was proved that the principal factors that determinate the development of O_3 injury observed at irrigated sites were the higher rates of stomatal conductance and reduced xeromorphic traits. The comparison of the repeated measurement of gas exchanges and the harvesting of leaf biomass during the 2011 vegetation season provided the information at two comparable sites (irrigated *versus* non-irrigated urban sites). The foliar samples of Holm oak were examined for visible O_3-like injury and microscopic symptoms at the WSL (Swiss Federal Institute for Forest, Snow and Landscape Research) laboratories. The results underlined the characteristic O_3 oxidative stress based in the presence of a visible, homogeneous and intercostal distribution of stipples in foliage that increased with leaf age, which agreed with Vollenweider and Günthardt-Goerg (2005), as well as observed shading effects, which is typical for O_3 stress. The microscopic modifications induced by O_3 were consistent with previously reported microscopic observations on Mediterranean evergreen species (Reig-Armiñana *et al.*, 2004).

The O_3 symptom diagnosis was confirmed on the basis of the macro- and micro-morphological changes found in irrigated holm oak foliage. The responsiveness of holm oak to higher soil moisture availability enhanced O_3 stomatal uptake at O_3 polluted sites, as also reported by Schaub *et al.* (2003) in other deciduous tree species, and enhanced leaf injury by O_3 stress on these sclerophyll evergreen trees. Recently Moura, de Souza, and Alves (2014) and (Moura *et al.*, 2014) reported also native tropical tree species sensitivity to O_3 oxidative stress.

5.2.2 Effect of air pollution on chlorophylls content

Few knowledge on chlorophyll analysis in foligage from the urban environment has been published. A difference from year to year in the average chlorophyll content (higher in leaves from 2007 samples than those from 2006) was found (Annexe VIII) in samples at the control sites, while in contaminated areas total chlorophyll content was a sign of phytotoxicity in *Cedrus* and *Pinus pinea* sp. needles. The weather in 2007 was cooler than 2006. The higher average chlorophyll content in 2007 samples agreed with the comparison of average temperatures in *Retiro Park* central weather station (AEMET), namely 15.9º C in 2006 and 14.6º C in 2007 (INE, 2014b). The AOT40 levels in Madrid in 2006 *vs.* 2007 (Fig. 6 in Chapter 3) corroborated this idea, because O_3 increases with high temperatures. The chlorophyll content of both young and adult needles was decreasing in polluted areas in comparison to peri-urban forests, particularly in older needles and those more exposed to traffic. These polluted areas were also the sites where [Pb] and [Zn] in needles and soil were agmented (Chapter 4). A decrease in pigments therefore also suggested the idea that chlorophyll biosynthesis may be inhibited by the stress caused by heavy metals. This idea was reported by Chettri *et al.* (1998) for lichens. Similar results were reported in needles of *Pinus pinea* and *Picea abies* as a consequence of high concentrations of heavy metals (Bayçu *et al.*, 1999) or dust pollution (Mandre & Tuulmets, 1997). Therefore, contents of chlorophyll may be a suitable integrating indicator for pollution stress in cities. The visible leaf symptoms, and the location of the discolouration within the leaves (along veins for HM stress, but between veins for O_3) indicates which stress was prevailing (Günthardt and Vollenweider 2007).

5.2.3 Soils

The presence of heavy metals in the trees depend on the topsoil HM concentration, pH and clay and organic matter content. Trace elements have different mobility in soil. In alkaline conditions, Zn and Cd mobility is reduced, that of Cu depends on the (soluble) organic matter. Mobility of Hg and Pb is very low (Kabata-Pendias, 2010). Since the average pH of the sampled soil in Madrid was 7.04 and ranged from 5.5 to 7.8, the mobility of HM depended on the individual sample soil HM concentration, with a small influence of the soil pH.

5.2.3.1. Problems faced by urban trees in Madrid City soils

According to the results of HM in soils (table 4, chapter 4) and the visual inspections during the sampling campaign, trees were usually planted in soils that were poorly suitable due to their physical and chemical limitations for tree establishment and development. Urban trees grew in environments determined by human activity, but the poor soil volume dedicated for the trees in certain locations, as well as the HM concentration and the soil compaction may be the reasons of the current weakening of some species, such as cedars (Annexe XVII).

Soils, and therefore trees, were are subjected to the action of pollutants. The most common anthropic activities found in the soils of Madrid during our study were traffic, fuel combustion, and waste disposal, to a minor extent also industry that often resulted in soil pollution with organic and inorganic pollutants. Our study therefore was restricted to the most common traffic-related HM due to economic restrictions, although other pollutants, such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins, and metalloids have been analysed in other cities (Prasse *et al.*, 2012).

As mentioned above, a common problem in the soils of green areas in Madrid was the compaction of the surface layer and the lack of aeration of the lower strata that probably caused imbalances in the biological activity of the root and microorganisms as well as interactions with other anthropogenic materials, as mentioned by De Kimpe and Morel (2000). In urban soils vegetation debris such as leaves and twigs are removed as waste and with this activity the nutrient cycle is broken. This fact could be the reason that some soils samples showed elemental concentraions below the average of HM and other macronutrient contents (see also next paragraph).

5.2.3.2. Difficulties of sampling soils in Madrid:

Sampling of foliar or soil samples in Madrid, as in other large cities, were subjected to a number of difficulties to perform the monitoring as a consequence of the intensive use of the territory, restrictions, and the rapid land use changes. Thus, the sampling coverage was slightly different to that planned initially and limited by the restrictions of plots in the sampling sites that had to be relocated. Whereas foliage could be sampled in the previously selected trees, certain soils became sealed or inaccessible.

Some HM concentrations in soils of Madrid showed unexpected values in comparison to reference values or in relation to the current traffic AADT (table 4, chapter 4). These unusual values can be explained by different processes that frequently occured in the built environment of Madrid, such as excavations, redistribution, mixing of the soil matrix and addition of extraneous materials, as it occurs in all large cities (Morel *et al.*, 2005). The high variability showed in the spatial distribution of [Pb], [Zn], as well as [Cu] in Annexe XIX, could be explained by the fragmented distribution of available soils as mentioned in chapter 4 [1.2]. Out of the 60’709 hectares of Madrid Municipality total area, 5’100 hectares (8.4% of total) corresponded to the road network and a large portion of the surface of an urban area is sealed by constructions. The high spatial variability of chemical, physical, and biological properties was also reported by Madrid *et al.* (2006) in six other European cities.

Average [Pb] and [Zn] in soils of Madrid [Figs.8 & 9, chapter 4] were in the range of many other cities (Yang *et al.*, 2006) and their values were grouped in the map according to the common limits for the evaluation of soil Pb and Zn concentrations in Europe (Environment Agency, 2002). The changes from greenish to reddish colours were established in 110 mg kg^{-1} for [Pb] according to Davies (1983) and 140 mg kg^{-1}, according to (VROM-The Ministry of Housing, 2000), which was world-wide employed in the 2000s. Average [Pb] in soils (155.9 mg kg^{-1}) was in the range of other medium-large sized cities in the world and bellow the [Pb] average of 200 mg kg^{-1} featured in cities such as Chicago or Rome (Finster, Gray, & Binns, 2004).

The differences among diverse studies about the HM concentrations are frequent in literature, due to the sampling strategies and analytical procedures employed, which itself increases the already high variability of urban soils (Ajmone-Marsan & Biasioli, 2010) and specially when comparing to studies in developing countries (Wei & Yang, 2010).

5.2.3.3. HM pollution and traffic

The relation between HM concentration in soil and the traffic intensity in Madrid was studied in Chapter 4 [Figs. 8 & 9]. The relationship between AADT and [Pb] and [Zn] in soils was clear in certain areas that reported high AADT, as aforementioned. However, over all sites the correlation between [Pb] and the corresponding ADT was minor, which may be explained as a consequence of the changes of use and modifications in soils (excavations, landfills, etc.), as well as changes in the traffic configuration (detours, blocked roads, bypass roads, etc.). Despite these inconveniences, Arslan (2001) reported a good correlation between the ADT and the metal content found, although these samples were “soil dust” at 10-15 m apart from the road, instead of our 20 cm topsoil samples.

5.2.4 Effect of air pollution on the leaf epidermis

To our understanding, there is no previous study reporting cedar needle surface by SEM and also information on *Aesculus* is scarce. The small folds on ab- and adaxial leaf surface (cuticular ridges) of *Aesculus* were apparent and clearly shaped insamples from control sites, while in polluted areas, these folds were missing, diffused, or distorted (Figs.14-B *vs.* 14-C in Chapter 4). These symptoms and the damage of the stomata were similar to those reported by (Godzik & Sassen, 1978). However, also the contrary reaction has been reported (Garg and Varshney

(1980). A problem may be that the collected leaves were entirely comparable in particular concerning leaf age and position within a tree. Cedar's needle and horse chestnut leaf surfaces in polluted areas presented an increasing number of dust particles. In these polluted areas the epidermal cells were more rigid than in the unpolluted areas. Obviously stomata were occluded by dust also when present at the abaxial leaf surface as in chestnut.

5.2.5 Cytochemical detection of zinc

The traces of Zn were observed in leaf samples of *Pinus pinea*, *Platanus* sp. and *Cedrus* sp. Zinc was micro-localized in vein tissues noteworthy the phloem. Similar experiences were conducted previously by (André, Vollenweider, & Günthardt-Goerg, 2006).

5.3 Pollution and quality of life ameliorated by urban trees

As shown in Chapter 1 and 4, the green spaces of public maintenance in Madrid could be categorised by three main groups: street trees, public parks and gardens and urban and peri-urban forests. Like trees along streets and in parks and gardens, city forests are one element of the wider term "urban forest" to refer to the planning and management of all tree-dominated green resources (Konijnendijk, 2008).The last group represents in Madrid the main source of biomass due to accounting more than 2 M trees.

One of the main problems that tree management suffers in the city, is the species selection. Still nowadays, when trees are selected in the city planning, usually greater emphasis is placed on the aesthetic aspect than in their eligibility to survive in the urban environment. The micro-environments where trees are living in some street sections in the city are markedly different from each other and often very contrasting with the natural environment, in which selected trees are living in nature. Due to the large number of constraints of urban trees in the city, these trees usually grow slowly or are stunted, but in good conditions they could live as long as those in nature. This situation was present in chapter 3, regarding the irrigation of Holm oak in contrast to other sites without irrigation.

5.3.1 Inventories

The measurement of city tree cover by the inventory of urban trees can aid in urban greening management by providing characteristics of trees across the city. The inventory should comprise a number of characteristics that allow to diagnose the tree: species identification, age, size (basal diameter, total height, crown height, etc.), the site conditions (type of irrigation, dimensions of the tree pit, slope, etc.) and the phytopathological assessment and tree risk. These data and measurement where especially important on the development of the study in Chapter 3. Although the irrigation data and the site exposition were not really relevant during the inventories of the sites where data available by the municipality were missed, they resulted significant years later during the study of O_3 visible and microscopic symptoms in Holm oak. The crown diameter and height were also very helpful for the biomass estimation in Chapter 4. The classic tree inventories could be substituted in other studies that analysed the tree cover in the city. This procedure has been widely extended in America since the first estimation by McPherson and Nowak. There is a wide variation regarding urban tree cover based on each individual city characteristics. Nowak *et al.* (1996) indicated that this variation in the USA ranged from 0.4 to 55%. Unfortunately, these calculation are difficult to compare with our results.

5.3.2 Benefits

Urban trees provide environmental and social benefits to the urban environment and society. As mentioned by Nilsson, Sangster, and Konijnendijk (2011), the incidence of different forms of poor health related to modern lifestyles has increased by the sedentary population and the levels of psychological stress of contemporary work practices. In this context, the urban trees ply an important role. The following improvements have been corroborated as environmental benefits in the City of Madrid during this study: 1) Trees helped by absorbing particulate matter as reported in Chapter 4. This benefit was previously described for xy (?) and Naples NY (Beckett, Freer-Smith, & Taylor, 1998; Beckett, Freer Smith, & Taylor, 2000; Luley & Bond, 2002) too. 2) CO_2 uptake was estimated in Madrid in Annexe XVI and gas exchange for Holm oak was analysed in Chapter 3. General estimations about CO_2 uptake and carbon dioxide sequestration were also provided by Nowak and Crane (2002) and other species have been studied in the urban environment (Loretta Gratani & Varone, 2006); 3) Microclimate and the variation of temperature and precipitation in Madrid area was analysed during DEA (Advanced Studies Diploma) at the beginnings of this PhD study (Calderón Guerrero, 2005) (Fig 44 in Chapter 1 [1.4.4]). The influence of urban trees in the urban microclimate also was reflected in studies of parking lot shade (McPherson, Simpson, & Scott, 2002) or cooling the home in summer and warming in winter (Dwyer *et al.*, 1992; McPherson, 1996). There are other benefits that have not been tested in this work such as the controlling and cleaning storm water runoff (Xiao *et al.*, 1998) and the control of erosion (Miller, 1988) by green spaces in the city. There is an ongoing work about the correlation between the PM_{10} and O_3 air pollution episodes in Madrid and the hospital emergency room visits and hospital admissions from chronic respiratory diseases regarding the green cover in the patients' neighbourhood that will be finished after this PhD dissertation by the author. Another study about the presence of the green spaces and decrease of violence in those districts were the tree cover is higher in Madrid It has been developed. According to our understanding, there is a lack of investigation about the health and social benefits of urban trees in big cities including Madrid. The following topics could be future research avenues: 1) the decrease of road rage (Cackowski & Nasar, 2003); 2) the recovery on healing (Ulrich, 1984); 3) the impact on mood of brief visits to urban parks (Hull, 1992); 4) worker productivity (Kaplan, 1993) and stress (Sop Shin, 2007); 5) real estate values (Conway *et al.*, 2010; Donovan & Butry, 2011), 6) business (Wolf, 2003); 7) perceptions of safety and decreasing of violence (Kuo & Sullivan, 2001a, 2001b).

To our understanding, there was no approach done in Madrid to quantify the benefits and costs of urban trees. Several studies have been developed in different cities of the United Stated (McPherson *et al.*, 2005), as well as in small communities (Maco & McPherson, 2003) with an average benefit-cost ratio of 1.37:1 to 3.09:1 in big cities and 3.8:1 in smaller settlements. Only real estate agencies gave an estimate of the property value (600 € per square meter) when the properties had views to Retiro Park (Salido Cobo, 2014).

5.3.3 Biomonitoring

The estimation of air pollution toxicity levels in the city is difficult due to the complexity of the urban environment, which depends on several factors such as morphologic characteristics of plant species, physiological status, metal availability for plants and heavy metal concentrations in air and in soil, but also is influenced by local city microclimate, type of irrigation and the duration of the exposition to pollution sources. All these variables have been widely discussed in Chapter 3 regarding the biomonitoring of O_3 symptoms or in chapter 4 in relation to the HM deposition and accumulation.

As in the soil sampling, the monitoring and analytic procedure in foliage presented different inaccuracies. Previous studies reported on urban trees showed the common inconveniency of different procedures regarding to monitoring, sampling and analytical methods (such as type, concentration and duration of washing solution and rinses repetitions on leaves surface). In these circumstances, the heterogeneous environment and the changing city use are additional inconvenient to compare big cities' tree health. The HM concentration in washed and unwashed leaves was in the same range as to those reported for other species in urban environments (Tomašević *et al.*, 2011).

The employment of trees for biomonitoring has been carried on by different authors in the urban environment (Piczak, Leśniewicz, & Żyrnicki, 2003). They were found to be useful biomonitors of determinate heavy metals. Other authors preferred mosses because of the limited efficiency of tree species as bioaccumulators and in reflecting atmospheric contamination in clean areas. Aboal, Fernández, and Carballeira (2004) reported that oak (*Quercus robur*) leaves and pine (*Pinus pinaster*) needles had a low capacity for monitoring air quality in forest areas of the NW of Spain. They pointed to a limited efficiency as bioaccumulators of heavy metals in comparison to pine–moss and oak–moss. However they underlined trees as a large reserve of HM in the ecosystem, given the large biomass that they represent compared to mosses. As in our study in chapter 4, [Pb], [Zn] and [Cu] in the soils and plant tissue were also found to be higher in the areas of high AADT and air pollution by (Sgardelis *et al.*, 1994).

In Turkey, the [Pb] and [Zn] in washed and unwashed leaves for *Fraxinus excelsior, Pyracantha coccinea, Elaeagnus angustifolia Neriun oleander* in urban roadside resulted in slightly higher HM concentration than in our washed and unwashed samples (Akguc, Ozyigit, & Yarci, 2008; Aksoy & Demirezen, 2006; Aksoy & Öztürk, 1997; Aksoy & Sahin, 1999; Aksoy, Şahİn, & Duman, 2000). [Pb] in unwashed Holm oak leaves in Naples (Italy) also were in line wiht our results, although they reported a considerable decrease in [Pb] in a 7-year time-lapse.

The concentration of heavy metals in our washed leaf samples showed a seasonal effect. [Pb] and [Zn] tended to increase in the autumn and winter, as also reported (Kim & Fergusson, 1994) in *Aesculus hippocastanum.* In unwashed leaved, Baycu *et al.* (2006) indicated a decrease in [Zn] from spring to autumn in *Aesculus* as we found in our samples. However, the values that they reported for [Zn] in *Aesculus* were quite lower: 40.36 and 33.82 mg kg^{-1} in spring and autumn respectively, in comparison to our results.

According to our results, it can be generally stated that the areas within the vicinity of heavy urban traffic are affected by the exhaust emissions according to their load of heavy metals. In most of the urban sites, there were medium [Pb] concentrations probably indicated a former pollution that came from the usage of leaded oil in previous years and the resuspension of remaining particles. However, [Pb] in washed leaves of the examined trees was below toxicity range in most of the samples. The reason may be the low bioavailability, allowing the accumulation mostly in roots.

Regarding the relation that could be established between O_3 symptoms in Holm oak [chapter 3] and HM deposition on leaves [Chapter 4], as a potential cause for the observed leaf injury, besides ozone, a strong contribution can be excluded based on the aforementioned [Pb] in washed leaves of the studied trees that was below toxicity range. Once studied the visible symptoms on foliar samples, it was corroborated that HM do not cause HR-like reaction leading to stippling symptoms that were observed in our samples. Moreover, eventual high concentrations of HM in soils lead to microscopic changes primarily along the water pathway through the leaf and these microscopic symptoms are clearly different from those observed in our symptomatic leaf samples that were induced by ozone stress as reported by Günthardt-Goerg and Vollenweider (2007).

5.3.4 Particulate capturing

The quantification of the dust deposition on the leaf surfaces in our samples was obtained by the weight of the dust residue in our six studied species that included the epicuticular wax layer that could be removed by the CH_2Cl_2.washing procedure. Our results [Chapter 4, Fig. 10] suggested that conifers may be the best choice for pollution-control plantings, as well as those broadleaved species featuring rough or hairy leaf surfaces, which agrees with Beckett, Freer Smith, and Taylor (2000). Several estimations by mathematical models have been proposed in literature in the last 20 years to quantify the interception of particles by vegetation. Most of these studies were conducted in different cities of the USA, such as Philadelphia or Chicago (McPherson, Nowak, & Rowntree, 1994). Our estimations of the six trace elements captured on the leaf surfaces regarding all studied tree species were difficult to compare to the estimation provided in Chicago, due to different measurements (weight of particulate matter *versus* HM concentrations) [Chapter 4, Figs 12 & 13]. In addition, many of those experiments utilized purified water for the leaf washing. That procedure ensured no removal of epicuticular wax, but a certain percentage of dust could remain attached to the leaf surface wax after the washing, particularly in conifers. In our case, the washing dilution removed part of the epicuticular wax layer, but we ensured a better removal of all dust residue. This is the reason why we cannot provide the weight of PM_{10} as given by other authors, although we believe that our HM estimation would be more accurate because of the antagonist nature of the two washing solutions employed that allow to remove particles that otherwise could not be removed by water wash-off alone.

The differences in weight of dust residue in our samples varied for each species because of the wax weight differs by species. However, the variations of the HM concentration were most likely due to **site specific variables** that may be related to ADT and the PM_{10} distribution in the city [Chapter 4; Figs. 5 to 7], as well as the weather conditions, in particular on local wind speed. The combination of these circumstances underlined the highly complex pattern of the capture of particulate pollutants in urban areas. The street width to building height ratio may contribute to the results obtained too, as mentioned in chapter 1. These suggestions agree with Croxford, Penn, and Hillier (1996) at the scale of the street segment in the city and the effects of the urban heat island (Gago *et al.*, 2013).

5.3.5 Trees suitable for air pollution

Madders and Lawrence (1982) suggested that the most effective use of trees as particulate filter was achieved when trees were planted as close as possible to the emission source, due to the buffer effect around the emission. This is the reason why we recommended to employ trees along the streets in boulevards (such as green tunnels) in order to capture the particulate matter from duty traffic roads. Apart of the studied species, other recommended species for particulate capturing in Madrid could be nettle tree (*Celtis australis*) because of its rough leaf surface, as well as silver berry (*Eleagnus angustifolia)* or whitebean (*Sorbus aria*) because of its rough adaxial leaf and pubescent abaxial leaf surface. whitebean was also suggested by Beckett, Freer Smith, and Taylor (2000), although this species would be only suggested for sites with good soils, irrigation and shade. We should try to skip certain species featuring small leaf surface and low capacity to capture and retain particles (e.g. large petiole).

5.3.6 HM estimation and the spatial distribution of the deposition in urban trees

To our understanding, the present is the first estimation of HM deposition on trees to an entire extension of a big city in Europe. The aforementioned experiment by Beckett, Freer Smith, and Taylor in UK could be the most similar to our results, but their investigations were restricted to a few rows of urban trees in different cities and urban environments, without a quantification of traffic-related HM (only PM_{10}). The estimations by Nowak *et al.* (1996) in the USA also allow the calculation of PM_{10} to a city level regarding the tree cover percentage. However, the tree characteristics and the different climatology should be considered. Thus they could not be comparable to our data. We did not find other studies that compared a high amount of urban trees in a GIS-based application regarding particulate pollution (HM) and traffic intensity on each street to a city scale with the precision of an individual tree level.

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Chapter 6

GENERAL CONCLUSIONS

CONCLUSIONS

Urban trees provide environmental and social benefits to the urban environment and society. Urban population is increasing as well as the necessity of resources, goods and leisure, which is highly demanded in large cities. In this context, green spaces play an important role that has been examined in this study from the point of view of the air pollution. The general conclusion to this study are:

- Madrid keeps an important green heritage due to its development near to naturally forested areas, such as the Casa de Campo or Monte del Pardo Forests. A complete inventory of trees gave an overall diagnosis of the state of the urban trees in Madrid. First we determined the total number of trees in Madrid. Madrid counted 2'980'583 trees under public management and maintenance during 2005-2010. 674'197 trees, including those managed by the *National Heritage*, were trees along the streets and in public parks/garden. 2.3 M were in peri-urban forests around the city such as the *Casa de Campo* (0.7 M) and *El Monte de El Pardo* forests (1.6 M). The six studied taxa accounted 2.3 out 3 M trees in the municipality of Madrid (78.5% of total inventory).

- According to the air pollution measurement Madrid does not suffer sporadic acute levels of air pollutants. However, low/medium concentration lead to chronic injuy by continuous inputs of air pollutants, which are affecting the urban environment and human dayly life.

- We have two sides of the same coin: air pollution that affects urban trees and trees that ameliorate the air pollution and the quality of life in the city. Trees take up harmful gases and capture particulate matter from the air that otherwise will affect human health. Thus, **urban trees contribute significantly to alleviate air pollution.**

- Unlike animals, urban trees are the first sufferers of air pollution due to their inability to move when the environment is hostile. Nowadays, the most serious air pollutant is ozone. The effects of O_3 have been studied for the first time in Madrid's Holm oak. The findings presented in Chapter 3 show **the structural changes associated with O_3-triggered stippling in leaves of Holm oak.**

- Significant amount of heavy metals were removed from the atmosphere by the six analysed tree species along the streets (254'394 trees) throughout Madrid, accounting **16.8 kg of six heavy metals (Ba, Cr, Cu, Ni, Pb and Zn) each year. When** the significant removal of particles by wind or by washing off from leaf surfaces during heavy or prolonged periods of rainfall (leading to deposition in the soil) could be considered, this amount would be even much larger. .

- The presence of atmospheric deposition was especially evident in samples near to high ADT roads. The heavy metal concentrations in/on tree leaves and soils from urban trees in Madrid showed the accumulation of Cu, Pb, and Zn, reflecting atmospheric deposition by traffic and a sizable soil contamination in some samples, mostly as a consequence of wet and dry atmospheric deposition. Other anthropogenic sources were involved punctually.

- The six tree species constituted **good biomonitors of air pollution in the city** and the amount of particles and HM were sizable, given the large biomass and foliar surface of the urban trees.

- The rate of capture of particles varied between species and they were most likely due to **site specific variables** and **leaf's characteristics**. All these factors underlined the highly complex pattern of pollutant concentrations in urban areas

- **Site specific variables** may be related to **ADT**, **PM_{10} distribution**, **weather conditions** and particular circumstances such as **canyon-like streets**.

- **Leaf capture efficiency of particulate matters** may contribute to increase particle retaining efficiency. High loads of particles on **broadleaved species** could be explained by the relative abundance of leaf roughening structures (**veins, hairs, trichomes, etc.).** C**onifers** featured a higher **structural complexity (whorls)** that facilitated the interception and capture. The **stickiness of the surfaces** by "honey-dew", fungi or resins added the efficieny in both groups of species.

- Perennial *versus* deciduous species had the additional advantage of retaining their foliage during winter, when particulate matter concentrations werehigher. Species featuring leathery or smooth leaves (*Platanus* sp.) had a lower efficiency in particles capturing that could be balanced by a higher foliar surface in individual trees.

- A **combination of *Cedrus/Ulmus/Pinus pinea* resulted an effective barrier to filter dust** of the air in a spatial and temporal aspect for Mediterranean urban areas, where they are common urban tree species. Fasciculate cedar needles assured a good interception in the lower stratus. *Ulmus* sp. had a good interception capacity and was suitable for the intermediate stratus, and the umbrella shape of *Pinus pinea* may provide cover and interception in the higher stratus. The vertical and horizontal distribution should assure the interception of particulate matter at understory, middle crown and canopy level, besides establishing continuity between discrete green areas.

- The **spatial disposition matters. Therefore,** if possible, a mosaic of the latter species at different age classes is recommended to intercept PM_{10}.

  Different technics and procedures allowed to examine the presence of particles on leaf surfaceat a microscopic level (SEM), as well as the cytochemical detection of HM in leaves at polluted sites, namely the micro-localization in vein tissues. Chlorophyll contents in leaves were also correlated to pollution and thus proved to be a biomonitoring tool. GIS was very helpful to detect exceedances at each air quality monitoring station. GIS further allowed to investigate the effect of the tree distance to mobile sources and the amount of dust trapped on leaf surfaces. A map underlined the presence of particulate pollution throughout the city. It was generated to display each GPS-based location of 674'197 trees of the six studied species along the streets, in parks and gardens as related to the potential particulate matter contamination by road traffic during the 2003-2008 period in 2'660 street sections.

- The strategies for reduction of air pollution regarding the traffic access in the big cities *versus* the health of the citizens will be a serious issue in the future. Countries that are major world manufacturers of vehicles, such as Spain or Italy, may look askance any action that may affect their economy in terms of production and internal trade in these times of severe economic crisis. The future actions of the city council to restrict traffic in the neighbourhoods of downtown would only move the pollution out of those districts that would increase in the periphery, where high levels of particulate pollution were also displayed in the map.

- Therefore to our point of view, the strategies for reduction of air pollution should also highlight the role of the urban trees by capturing particulate matter. The plantation's increment of optimal species for this purpose would increase the benefit in terms of air quality improving, cost savings or health benefit. Programs regarding urban trees' benefits would be specially indicated in developing countries' megacities where pollution is a serious problem.

- The necessity of an appropriate design and selection of urban trees species and proper location to ameliorate the air quality levels under serious episodes of PM_{10} pollution should be an important criteria among others such as landscaping, adaptive capacity or ornamental selection in big cities strategy to ameliorate pollution. These aptitudes would **recognize a sometimes-undervalued role of urban trees in big cities**.