Source areas and atmospheric transport processes of chemical compounds and pollen in the NE Iberian Peninsula and the Canary Islands

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Memòria presentada per

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per optar al grau de Doctora

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A la meva família

Chapter 1

General introduction

Atmospheric deposition

The atmosphere is a major component of the Biosphere, as well as a medium through which substances can be mobilized among ecosystems. The Earth's atmosphere is characterized by variations in temperature and pressure with altitude. Therefore, the atmosphere can be conceptually divided into several layers, according to its thermal and ionization structure. The lowest layer is named troposphere. The troposphere can be divided into two parts: the planetary boundary layer (PBL), which extends upward from the surface to about 1Km, and above it is the free troposphere (FT). In spite of its apparent unchanging nature, the atmosphere is in fact a dynamic system with its gaseous components being continuously exchanged, reacting between them and with the vegetation, the oceans, and the biological organisms. A complex mixture of solid and / or liquid substances is suspended in the atmosphere and constitutes what is called atmospheric particulate matter (PM) or simply atmospheric aerosol.

Atmospheric deposition contributes to the chemistry of plants, soils, and surface water, and to the cycling of nutrients in ecosystems (Richter and Lindberg, 1988). Wet and dry deposition are efficient pathways for removing soluble gases and particles from the atmosphere and furthermore, deposition has an important role in inter-reservoir transfer mechanisms. The term wet deposition encompasses all processes by which airborne species are transferred to the Earth's surface in aqueous form (e.g. rain, snow or fog). The main transfer mechanisms are: (1) dissolution of atmospheric gases in airborne droplets; (2) atmospheric particles that serve as nuclei for the condensation of atmospheric water to form a cloud or fog droplet and are subsequently incorporated in the droplet; and (3) removal of atmospheric particles when the particle collides with a droplet both within and below clouds (Seinfeld and Pandis, 2006). Dry deposition denotes the direct transfer of species, both gaseous and particulate, to the Earth's surface and proceeds without the aid of precipitation (Seinfeld and Pandis, 2006). Measuring the atmospheric deposition is essential for understanding regional variations of the precipitation chemistry, temporal trends and for determining critical load exceedances (Balestrini et al. 2000).

The concentrations of the chemical species in precipitation vary widely and mostly depend on the type and distribution of aerosols, the length of atmospheric transport, the particular chemical species and the scavenging processes (Celle-Jeanton et al. 2009). However, it has been recognized since long ago that the method used for the collection of precipitation samples for chemical analysis can have a significant effect on the results (Galloway and Likens, 1978; Sisterson et al. 1985; Dämmgen et al. 2005; Cape et al. 2009; Kelly et al. 2012). Wet deposition is measured by using a collector which has a removable lid that covers a collecting bucket or funnel to exclude dry deposition during the dry periods and opens whenever precipitation is detected by means of a precipitation sensor (Plaisance et al. 1998; Dämmgen et al. 2005; Staelens et al. 2005). However, in many ecological studies precipitation often is collected by a bulk collector which consists of an open funnel (glass or plastic) connected to a sampling bottle (Erisman et al. 2003). Bulk deposition is the operational term for a mixture of wet and dry

deposition as measured by means of continuously exposed sampling devices. With such open collectors only deposition of coarse particles by gravitational settling is effective while gases and fine particles are heavily underestimated by bulk sampling (Galloway and Likens, 1976; Fowler and Cape, 1984; Draaijers et al. 1998; Akkoyunlu and Tayanc, 2003; Anatolaki and Tsitouridou, 2007). By contrast, this sampling method does not require a power supply to activate movable lids and thus it allows for an efficient operation in large networks where electricity supply may not always be available (Cape et al. 2009).

The measurement of dry deposition is not as straightforward as the measurement of wet deposition because it involves an understanding of several influential variables including the atmospheric characteristics, the nature of the surface and the properties of the depositing species itself (Davidson and Wu, 1990). Indeed, there is not a standard method for the measurement of the dry deposition. Dry deposition has been often inferred from the product of the measured species in ambient concentrations and its dry deposition velocity (Duce et al. 1991; Erisman et al. 1998; Guerzoni et al. 1999; Migon et al. 2001; Anatolaki and Tsitouridou, 2007), by means of statistical models (Dulac et al. 1989; Erisman et al. 1994; Brook et al. 1997; Yi et al. 1997; Staelens et al. 2008) or through micrometeorological approaches (Erisman and Draaijers, 1995). Still, a routine direct measurement technique is required for validating these estimates (Sakata et al. 2008). Direct measurements have included: 1) collection on dry-only collectors (Prakasa Rao et al. 1992; Morales-Baquero et al. 2006; Pulido-Villena et al. 2008; Al-Momani et al. 2008), 2) collection on surrogate vegetation surfaces (Ferm and Hultberg, 1999; Sanz et al. 2002; Moumen et al. 2004; Inomata et al. 2009), and 3) collection of throughfall (Parker, 1983). To better mimic the transport to waterbodies and moist landscapes, in some studies the surface of the sampler is wetted (Shahin et al.1999; Balestrini et al. 2000; Azimi et al. 2003; Raymond et al. 2004; Anderson and Downing, 2006; Sakata et al. 2008). Also, measurements by electron microscope counting, wind-tunnel studies and chamber studies have been used to estimate dry deposition (Erisman et al. 1994). Despite the difficulties associated with dry deposition measurements, these different methods have provided data for an accurate characterization of total atmospheric deposition.

Long-range atmospheric transport of chemical compounds over the western Mediterranean area

Long-range pollutant transport

Atmospheric fluxes are an important component of the global cycle of a number of elements. The residence time of substances that, by natural or anthropogenic causes, are introduced into the atmosphere can be very variable, but it is generally long enough (more than one day) for them to be transported away from sources of emission and settle thousands of km away over land and oceans. Four rough spatial categories have proved convenient to classify atmospheric scales of motion: microscale (0-100m), mesoscale (100m-100Km), synoptic scale (100-1000Km)

and global scale (>1000Km) (Seinfeld and Pandis, 2006). Despite the complexity of the interactions among different scales, for simplicity we can distinguish between the small scale transport (in which a significant portion of the substances will settle near the sources, for example within a horizontal distance of 100 km) and the large-scale transport. The first one occurs in the PBL under the prevailing influence of local circulations (such as breezes) and topographic features. Long-range transport occurs in the FT and is determined by global circulation patterns and synoptic scale systems.

The climate and geographic characteristics of the Mediterranean region produce air-quality patterns with remarkable spatial and temporal variability (Kallos et al. 2007). The Mediterranean region lies in a transition zone between the arid climate of North Africa and the temperate and much wetter climate of central Europe and is affected by the interaction between mid-latitude and tropical atmospheric processes. Because of these features, even relatively minor modifications of the general circulation can lead to substantial precipitation and temperature changes in the Mediterranean area (Giorgi and Lionello, 2008). In this context, the atmospheric dynamics in the West Mediterranean Basin (WMB) is conditioned by complex interactions of climatic and topographic effects that include the Azores high-pressure system, the continental thermal lows over the Iberian Peninsula and the Sahara, the orographic effects of the coastal ranges surrounding the Mediterranean coast, and the arrival of frequent African dust intrusions (e.g. Millán et al. 1997; Soriano et al. 2001; Rodríguez et al. 2003; Escudero et al. 2005; Pérez et al. 2008), which produce marked seasonal variations in temperature, humidity and rainfall. Moreover, modifications in the wind circulation and precipitation patterns have been predicted for the Mediterranean region linked to climate change. Specifically, the climate change projections show a pronounced decrease in precipitation, especially in the warm season, due to increased anticyclonic circulation that yields increasingly stable conditions and is associated with a northward shift of the Atlantic storm track (Giorgi and Lionello, 2008). In addition, some studies have reported an increase of the arrival of African air masses over South Europe since 1970s (De Angelis and Gaudichet, 1991; Wagenbach et al. 1996). Other studies found a good correlation between atmospheric African dust and the North Atlantic Oscillation (NAO) index, with an upward trend for both (Moulin et al. 1997). However, longer time sequences are necessary to confirm this finding.

Many studies have focused on the importance of long-range transport patterns. Atmospheric fluxes from long-range transport from distant source areas may acquire biogeochemical relevance in many terrestrial and aquatic ecosystems (Schlesinger et al. 1982; Okin et al. 2004; Morales-Baquero et al. 2006; Pulido-Villena et al. 2006) and this recognition has been the core for the onset of international agreements for the reduction of emissions in Europe and North America.

Air pollution can be defined as: ‘‘when gases or aerosol particles emitted anthropogenically, build up in concentrations sufficiently high to cause direct or indirect damage to plants, animals,

other life forms, ecosystems, structures, or works of art'' (Jacobson, 2002). There is a growing public concern about atmospheric pollution, which has led to an increasing interest in the study of the atmosphere as a carrier of pollutants (Fraile et al. 2006). Deposition of acidifying pollutants, known to be a factor of forest damage and extinction of aquatic life populations in lakes and streams, is attributed to long-range transport of sulphur and nitrogen compounds which originate mainly from anthropogenic emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) (Dambrine et al. 1995; Probst et al. 1995). During its transport in the atmosphere, SO_2 and NO_x are partially oxidized into sulphuric acid (H_2SO_4) and nitric acid (HNO_3) before being transferred to the soil by wet or dry deposition. As a consequence of the long-range transport of acidic pollutants, low pH values have been recorded in precipitations collected in remote areas of the world (Galloway et al. 1982). Systematic investigation of the rainwater chemical composition and an assessment of the different emission sources that influence it are a prerequisite knowledge to reduce the consequences of pollution on ecosystems (Arsene et al. 2007).

In Europe, the Convention on Long Range Transboundary Air Pollution (CLRTAP) has launched several protocols to reduce sulphur and nitrogen emissions (besides O_3, VOCs and trace metals) to the atmosphere starting in the early 1970s when the problem of acidification at a continental scale and its effects on ecosystems was formally recognized internationally. As a result of the implementation of abatement measures, sulphur deposition has steadily decreased throughout Europe in the last 30 years (e.g. Stoddard et al. 1999; Skjelkvale et al. 2005; Àvila and Rodà, 2012). However, success has been more limited for nitrogen compounds (Gundersen et al. 2006). Indeed, the large reduction in SO_2 emissions regimes in Europe over the last decades (~73% from 1990 to 2009; EMEP, 2011) has played an important role on nitrate aerosol concentrations. Because less gaseous ammonia (NH_3) is being converted to sulphate aerosols (e.g. NH_4HSO_4, $(NH_4)_2SO_4$), ammonia in excess can combine with nitrate to produce ammonium nitrate aerosols (NH_4NO_3). Since atmospheric ammonia is first used to neutralize sulphate to form ammonium sulphate aerosol, particulate nitrate can only be formed if excess ammonia is available, a condition which is met in areas with abundant use of fertilizers for the agriculture and intensive farming practices.

Concerning NO_x emissions, not all European countries have equally succeeded in their abatement. Such is the case of some of Southern European countries. Specifically, Portugal, Spain and Greece have increased their emissions (Fagerli and Aas, 2008). Furthermore, despite the fact that European emissions on land are progressively controlled, marine sources are reported to increase their contribution to air pollution. This is the case of commercial shipping, which is estimated to contribute 5-8% of global anthropogenic SO_2 emissions and 15-30% of global fossil fuel NO_x emissions (Eyring et al. 2005). Estimations of emissions of SO_2 and NO_x from international shipping suggest an annual increase of 2.5% caused by an increase in traffic and the lack of emission controls (Endresen et al. 2003).

Nitrogen deposition can affect ecosystems by promoting acidification of the soil and waters (Schindler, 1988), nitrogen enrichment and nutrient imbalances in terrestrial and aquatic ecosystems (Matson et al. 2002; Rabalais, 2002), and eutrophication of water bodies (Paerl and Whitall, 1999). Therefore, the study of temporal trends of N deposition is necessary to understand the causal relationships between changes in land-based emissions sources and perturbations or evolutions in biogeochemistry either in terrestrial or marine ecosystems.

Long-range mineral dust transport

High atmospheric concentrations or fluxes in deposition are not always the result of human activities. For instance, mineral dust or biogenic aerosols are atmospheric aerosols of natural origin which entrained massively into the atmosphere can have broad environmental impacts (Dentener et al. 1996). The term “aeolian dust” is typically used to refer to mineral particulate matter originating from the wind erosion of soils (Lawrence and Neff, 2009). The global emission, chemical characteristics and transport pathways from desert areas is subject to increasing scientific attention owing to the climatic and biogeochemical effects of crustal aerosols. Mineral dust is known to affect the climate system by changing the energy balance and thermal radiation, although the magnitude of the radiative forcing is still uncertain (Tegen et al.1997; Haywood and Boucher, 2000; Harrison et al. 2001; Sokolik et al. 2001; Arimoto 2001; IPCC, 2007). The presence of dust can favor atmospheric heating by modifying the surface temperature (Miller et al. 2004). Interactions with other pollutants can modify the dust chemical and physical properties, such as its chemical composition, morphology or hygroscopicity (Semeniuk et al. 2007; Matsuki et al. 2005; Falkovich et al. 2004; Levin et al. 1996). It is also known that some species, such as organic acids, ozone, sulphates or chlorine, can be adsorbed onto mineral dust during the transport process (Sullivan et al. 2007; Falkovich et al. 2004; Mamane et al. 1980). Dust is also a transport vehicle for microorganisms which are potential pathogens and the influence of these organisms on ecosystems or human health is not yet well known (Shinn et al. 2003; Kellog and Griffin, 2006; Griffin et al. 2007).

Mineral dust has some positive effects. For example Saharan dust rich in carbonates has been shown to counterbrace acidic rain (e.g. Löye-Pilot et al. 1986; Rodà et al. 1993; Hedin and Likens, 1996) and acidity in mountain lakes (Rogora et al. 2004; Pulido-Villena et al. 2006). Over long timescales dust can also be an important factor in the formation and development of soils (Yaalon and Ganor, 1973; Simonson, 1995; Fiol et al. 2005; Muhs et al. 2010). Dust accumulation in soils can influence texture, element composition, acidic neutralizing capacity (Miller et al. 1993; Larsen and Carmichael, 2000; Muhs and Benedict, 2006) and may influence soils weathering fluxes (Porder et al. 2007). Moreover, it acts as a fertilizer, adding important nutrients that stimulate forest productivity (Reichholf, 1986; Swap et al. 1992; Kennedy et al. 1998; Chadwick et al. 1999; Griffin, 2005; Koren et al. 2006; Okin et al. 2004), and phytoplankton productivity in the oceans (Jickells et al. 2005; Krishnamurthy et al. 2007, 2009, 2010; Duce et al. 2008; Mahowald et al. 2009; Okin et al. 2011).

Dust can be transported over thousands of kilometres and is deposited downwind of arid sources; its deposition amount generally depending on the distance to the source (O'Hara et al. 2006). The Sahara-Sahel dust corridor in Africa is the most productive source (Prospero, 1996; Goudie and Middlenton, 2006): estimates of its dust production range from 170 to 760 10^6 t $year^{-1}$ dust (Goudie and Middlenton, 2001). All year long, massive airborne plumes of desert dust from the Sahara and surrounding regions are exported to the Western Atlantic (e.g. Carlson and Prospero, 1972; Prospero, 1999) and the Mediterranean and Central Europe (e.g. Bergametti et al. 1989; Chester et al. 1993; Molinaroli et al. 1993; Chiapello et al. 1995; Guerzoni and Chester, 1996; Àvila et al. 1997; Kallos et al. 1997). Specifically, the mean annual deposition mass fluxes of mineral dust were calculated in *circa* 8, 12 and 35 g m^{-2} $year^{-1}$ for the western, the central and eastern Mediterranean basin respectively (Guerzoni and Molinaroli, 2005); these values were used to estimate the total annual atmospheric dust flux, which turned out to be approximately 41 10^6 t $year^{-1}$ for the whole Mediterranean basin (Guerzoni and Molinaroli, 2005).

According to Escudero et al. (2005), four meteorological scenarios originate the transport of African dust air masses towards the Western Mediterranean Basin: (1) the *North Africa High Located at Surface Level* (NAH-S). This scenario is characterised by an anticyclone located over southern Iberia, the western Mediterranean or off the Atlantic coast without the presence of the quasi-permanent Azores high which causes a transport plume from the western Sahara and Sahel to the north Atlantic in an arc-like pattern; (2) the *Atlantic Depression* (AD). This scenario occurs when a relatively deep low is located off the SW Portuguese coast and is associated with a high or ridge over the central Mediterranean Sea producing dust transport in all altitude levels from Mauritania, Mali and Morocco toward eastern Iberia; (3) the *North African Depression* (NAD). This scenario emerges when the Azores high is slightly shifted to the east of its normal position, and a ground level low is centred over Morocco, Algeria, Tunisia, or even over the western Mediterranean, and a trough is observed over the Iberian Peninsula. As a result dust is transported from Algeria, Tunisia, Libya and Chad at lower layers; and (4) the *North African High Located at Upper Levels* (NAH-A). This scenario is produced by the intense heating of the Sahara and the consequent development of the North African thermal low and the considerable vertical growth of the boundary layer. This convective system injects dust into the upper atmospheric levels which may be transported toward the Iberian Peninsula by the eastern branch of the high present over North Africa, forming a wide plume of dust.

The mineralogical signature may be used as an indicator of the dust source (Àvila et al. 1997). Mineral dust mainly consists of a mixture of silicates (clay minerals, feldspar, quartz) associated with carbonates (Guerzoni and Molinaroli, 2005). During transport, dust particles are continuously removed from the atmosphere by processes of dry and /or wet deposition. The relative importance of these different mechanisms varies both temporally (Guerzoni et al. 1997) and spatially (Ginoux et al. 2004) and several factors can influence the dominating mechanism of dust deposition. These factors include the seasonal timing of dust storms (Tegen et al. 2002),

the particle size distributions of the transported dust (Tegen and Fung, 1994), and local climate conditions. Dry deposition is the dominant mechanism removing sand and large silt-size particles, while wet deposition is the dominant mechanism removing clay-size particles (Tegen and Fung, 1994). In addition, dust plumes are very often mixed with the anthropogenic aerosol emissions from vehicle traffic, and industrial and domestic activities (Migon and Sandroni, 1999), including biomass burning mostly produced in Southern Europe (Guieu et al. 2005). Therefore, dust episodes may contain a mixing signature of natural and anthropogenic aerosols (e.g. Löye-Pilot et al.1986; Gaudichet et al. 1995; Mahowald et al. 2005; Shen et al. 2007; Erel et al. 2006; Heimbürger et al. 2010).

Dust-derived element fluxes have been found to influence terrestrial and marine ecosystems of the western Mediterranean area. Atmospheric dust deposition may provide significant amounts of nutrients to European forest systems and it may significantly impact the nutrient budgets. Three facts support the hypothesis of a quick nutrient release from aeolian dust: (1) aeolian dust contains labile and nutrient-rich minerals (up to 30% carbonates), but also more weathering-resistant minerals are present, (2) dissolution rate increases with increasing mineral specific surface, thus rapid dissolution occurs in the finer segment of the particles distribution, and (3) conditions in the litter layer such as low pH and high biologic activity would enhance the release of nutrients from dust to the soil solution (Lequy et al. 2012). However, to better constrain the role of dust for sustaining plant productivity many other factors must be considered including the endogenous supplies of nutrients from soil and bedrock weathering, the internal cycling of nutrients, or annual losses from the system (Lawrence and Neff, 2009). Atmospheric dust deposition over European forests was found to range between 4 and 159 kg ha^{-1} $year^{-1}$, leading to maximum nutrient fluxes of 3.3, 1.8, 2.0 and 0.8 kg ha^{-1} $year^{-1}$ of calcium (Ca), magnesium (Mg), potassium (K) and phosphorous (P), respectively (Lequy et al. 2012). The delivery of P from aeolian dust is ecologically important because P is often a limiting or co-limiting nutrient for biologic processes in many different ecosystems (e.g. Schindler, 1977; Peterson et al. 1993; Cleveland et al. 2002). Further research is needed to better understand the contribution of dust deposition to nutrient fluxes to the soil and to refine nutrient forest balances. Specifically, more detailed analysis of dust P chemistry are warranted to better determine P availability once it is deposited, since the rate of P input at site is likely to be a key determinant of whether the ecosystem is sustainable in the long-term (Newman, 1995).

The deposition of dust may represent also an essential source of nutrients to the Mediterranean marine ecosystems. The Mediterranean Sea is an oligotrophic semi-enclosed basin subject to significant seasonal variations of its trophic state linked to a depletion of nutrients during stratification periods. Winter (November-May) conditions are characterized by the formation of deep water, which leads to intense vertical mixing and brings nutrients to the surface waters. With these conditions, hydrological and riverine sources of nutrients predominate over the inputs from the atmosphere (Béthoux et al. 1998). In contrast, during summer (June-October) the biological production in Mediterranean Sea is limited by the lack of nutrient supply from

deep waters due to stratification. In these conditions, the atmosphere becomes the main external source of nutrients for phyto and bacterioplankton in the surface layer (Guieu et al. 2010). It has been shown that anthropogenic and natural atmospheric inputs clearly impact marine cycles and budgets of elements in the Mediterranean Sea either depositing pollutant metals (Elbaz-Poulichet et al. 2001; Sato et al. 1998), macronutrients such as nitrogen and phosphorous (Löye-Pilot et al. 1990; Bergametti et al. 1992; Herut et al. 1999; Kouvarakis et al. 2001; Markaki et al. 2003; Krom et al. 2004) or micronutrients such as iron (Bonnet and Guieu, 2006). These atmospheric inputs can impact on the heterotrophic (Thingstad et al. 1998, Pulido-Villena et al. 2008) and autotrophic production (Klein et al. 1997; Bonnet et al. 2005; Guieu et al. 2010; Ternon et al. 2010) of the Mediterranean Sea. Specifically, in the oligotrophic Mediterranean both bacteria and phytoplankton are phosphorus-limited (Thingstad et al. 1998). Thus biological production depends in part on atmospheric inputs. Therefore, to better understand the effects of atmospheric deposition on the western Mediterranean Sea it is important to determine the main processes of deposition.

The influence of dust deposition on biogeochemical cycling of elements is in some ways controlled by the relative availability for uptake by biological organisms of each element of interest. Within the dust, many elements occur in multiple geochemical forms, which vary in their biological availability. Elements that are soluble and /or exchangeable may quickly become available for biological uptake, chemical reactions, or export. Conversely, weathering resistant portions of dust are less readily available for biological uptake or export and are more likely to accumulate in soils or sediments. In the Mediterranean region, several studies have provided contrasting estimates on the relative role of dry *vs.* wet deposition (Markaki et al. 2003; Morales-Baquero et al. 2006; Guieu et al. 2010). Particularly for P, wet deposition has been reported as the main source of dissolved P to the western Mediterranean (Ridame and Guieu, 2002; Ternon et al. 2010), though other studies have shown that phosphate is readily leached from dry fallout (Migon et al. 2001; Herut et al. 2002, 2005; Carbo et al. 2005). Differences in the contribution wet /dry are likely due to the type of pollutant (anthropogenic *vs.* mineral dust) and to the local weather regime (annual rainfall and the frequency and magnitude of African outbreaks), but more research is needed for a deeper understanding of such depositional processes in this system. Indeed, recent research suggested that variations in acid gas emissions by natural and anthropogenic sources may play and important role in regulating marine primary productivity and autotroph nutrient limitation through their effect as enhancing dissolution of P in mineral aerosols (Nenes et al. 2011).

Air mass trajectory statistical analysis methods

Several studies across the globe typically assess the geographical source contributions to atmospheric deposition by using individual chemical concentrations. This approach can often complicate the attempts to understand the behaviour of a particular species when multiple sources with varying strengths contribute to its concentration (Treolar 1993). In an attempt to overcome this difficulty, in the last couple of decades several studies have adopted analytical methodologies that exploit the statistical association between groups of chemical species identified by their origin. Such methods include multiple linear regression, principal component analysis, cluster analysis, positive matrix factorization (PMF), and other factor analytic approaches (e.g. Eder, 1989 and cites cited therein; Hooper and Peters, 1989; Kessler et al. 1992; Treolar, 1993; Antilla et al. 1995).

A common and simple method for tracing the origin of the observed aerosols is the calculation of back-trajectories using Lagrangian trajectory models (the Lagrangian trajectory approach). With this method, a few trajectories directed backwards in time are started from the monitoring location and evaluated a few hours or days back in time. The resulting trajectories roughly show the direction from where the air masses arrived at the observation site during the observation time period. For many years, trajectories have frequently been used for the interpretation of individual flow situations. However, more recently statistical methods for large sets of trajectories have been developed and implemented. Over the last several decades, Trajectory Statistical analysis Methods (TSMs) have been used to examine transport patterns and dynamical processes of the air masses (Stohl, 1998; Dvorská et al. 2009). It has been demonstrated that clusters of back trajectories arriving at a specific location can serve as a surrogate of different synoptic circulation patterns, hence many researchers have applied cluster analysis techniques to categorize back trajectories (e.g. Moody and Galloway, 1988, Dorling et al. 1992; Dorling and Davies, 1995; Jorba et al. 2004; Markou and Kassomenos, 2010). These statistical clustering techniques have also been used to identify synoptic weather regimes and long-range transport patterns that may affect air pollution (e.g. Moody and Samson, 1989; Cape et al. 2000; Abdalmogith and Harrison, 2005; Àvila and Alarcón, 1999; Riccio et al. 2007; Salvador et al. 2007, 2010; Kassomenos et al. 2010).

Cluster analysis can be used to classify the origin of air masses that arrive at site, but this method does not provide information on the geographical location of potential source regions (Salvador et al. 2010). The identification of the probable sources of atmospheric pollutants is very frequently resolved with the use of TSMs. Several works have tried to validate various TSMs, mostly through direct comparison of trajectory patterns with known sources (e.g. Stohl, 1996; Wotawa and Kröger, 1999; Begum et al. 2005; Lee and Ashbaugh, 2007). In a more quantitative approach three TSMs (Potential Source Contribution Function, (PSCF), concentration field method (CF), and redistributed concentration field method (RCF)) were subjected to two validation approaches: 1) the validation with virtual and real sources under

idealised conditions, where the effects of dispersion and removal of the trace substances are excluded, and 2) the comparison with EMEP SO_2 inventory under realistic conditions (Scheifinger and Kaiser, 2007). More recently, PSCF, CF and concentration weighted trajectory (CWT) methods were tested using known sources and artificially generated data sets to determine the ability of TSMs to reproduce spatial distribution of the sources (Kabashnikov et al. 2011). All these studies have concluded that methods of trajectory statistics are computationally fast procedures which deliver first hints on potential source areas. These works also agree that TSMs provide a helpful tool in estimating the spatial distribution of emissions of air pollutants from measurements. Between TSMs, the Seibert's methodology based on concentration fields (Seibert et al. 1994) and the method based on the conditional probability fields (PSCF) have been profusely used for the interpretation of air pollutant transport (e.g. Gao et al. 1993; Polissar et al. 2001; Hoh and Hites, 2004; Salvador et al. 2004; Xie and Berkowitz, 2007; Wang et al. 2009; Brereton and Johnson, 2012). While most TSMs applications have dealt with the chemical components of the atmosphere, much less work has been done on the biological aerial component for which this methodology is equally adequate since biological material may be transported across great distances by the same mechanisms that move gases and chemical particles. Therefore, the atmospheric behaviour of biological material is liable to be treated with the same methods as those used with chemical compounds. In fact, some authors have recently used TSMs and transport models to explain the movement of the pollen at a large scale (Belmonte et al. 2000, 2008; Sofiev et al. 2006; Skjøth et al. 2007; Siljamo et al. 2008). Back-trajectories and source-receptor models have been also used to explain long-distance movements of butterflies (French, 1969; Stefanescu et al. 2007; Dantart et al. 2009; Schaffers, 2009). However, until now very few works have used source-receptor models to describe the source areas of biological organisms.

Long-range pollen transport

Many organisms can significantly increase the efficiency of their movements by taking advantage of air currents (Isard et al. 2005). Biota that flow in the atmosphere range from very small (viruses, bacteria, pollen and spores) to quite large (seeds, aphids, odonates, butterflies and moths, songbirds, and waterfowl among others) (Gage et al. 1999). The link between their life cycles and the atmosphere is crucial to understand their population dynamics and the diseases spread by aerobiota. Emphasis is placed on identifying biologically-relevant temporal and spatial scales of atmospheric motion (microscale, mesoscale and macroscale) and other atmospheric variables which help understand the abundance and dispersal of airborne biota, specifically insects, spores, pollen, fungi, and plant pathogens (Westbrook and Isard, 1999).

The most studied biogenic aerosol is the pollen grain. Pollen transfers the male gametophyte to the female reproductive organs, in a process termed as pollination. Pollen records from aerobiological monitoring sites have traditionally been interpreted as if pollen was originated from the local environment. Consequently, pollen forecasting tools have been designed by

taking into account only local meteorological variables and phenological observations in the neighbourhood. This view has been recently changed to acknowledge much broader bioaerosol movements, based on increasing evidences of pollen and spore transport at much greater distances, implying continental (Belmonte et al. 2000; Sofiev et al. 2006; Siljamo et al. 2007, 2008; Belmonte et al. 2008; Skjøth et al. 2009) or intercontinental scales (Prospero et al. 2005; Kellogg and Griffin, 2006).

This long-range transport of bioaerosols is a cause of concern because of its potential to distribute pathogens and allergens which can affect the human health or human interests such as agriculture and farming (Griffin et al. 2001; Taylor, 2002; Brown and Hovmoller, 2002; Shinn et al. 2003; Garrison et al. 2003; Kellog et al. 2004; Griffin 2007; Paz and Broza, 2007). This transport can also have an impact on the structure of populations, since pollen is responsible for gene flow (Ellstrand, 1992; Ennos, 1994; Burczyk et al. 2004, Belmonte et al. 2008), and it contributes to determine the spatial distribution of plant species (Ellstrand, 1992; Smouse et al. 2001; Sharma and Kanduri, 2007; Schmidt-Lebuhn et al. 2007; Belmonte et al. 2008). Therefore, the study of pollen gene dispersal is instrumental for the interpretation of the biogeographic range of some plants and for plant conservation issues.

Extra-regional transport of pollen at distances greater than a few hundreds of kilometres has recently been studied by several authors, some of which are briefly commented here. Van Campo and Quet (1982) identified several pollen types that had been transported from North Africa to Montpellier (France) together with mineral desert dust. Similarly, Franzen and Hjelmroos (1988) had observed pollen transport from Germany, Holland and England to the Swedish coast and Franzen (1989) and Franzen et al. (1994) documented the arrival of pollen grains to Fennoscandia from the Mediterranean. Also, *Cannabis sativa* (marihuana) pollen originating in Morocco was detected in Malaga, southern Spain (Cabezudo et al. 1997) and *Cannabis, Cupressus, Pinus, Platanus* and *Sambucus* pollen were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al. 2004). Transport of pollen to western Europe has also been reported. This is the case of the arrival of *Betula* pollen to Denmark coming from Eastern Europe, Germany, Scandinavia and British Isles (Skjøth et al. 2007; Mahura et al. 2007), to Finland coming from Russia (Siljamo et al. 2008) and to Lithuania from Latvia, Sweden, Denmark, Belarus, Ukraine, Moldava, Germany and Poland (Veriankaité et al. 2010). Also, *Ambrosia* pollen originated in the Czech Republic, Slovakia, Hungary, Ukraine, Serbia and South-Southeastern Russia was found in Poland, Balkans and Italy (Saar et al. 2000; Cecchi et al. 2006, 2007; Stach et al. 2007; Kasprzyk, 2008; Smith et al. 2008; Sikoparija et al. 2009; Kasprzyk et al. 2011). In contrast, *Ambrosia* pollen was transported following the opposite direction from France, Italy and Croatia to Hungary (Makra and Palfi, 2007), as well as from France to Switzerland (Clot et al. 2002). Furthermore, an increasing risk of long-distance *Ambrosia* pollen arrival was detected in Scandinavia due to the rapidly ragweed spreading in North-Northeastern Europe (Dahl et al. 1999). Transport from northern latitudes has been described in Spain: *Ambrosia* pollen was recorded in Catalonia (North-

Eastern Spain) coming from France, Italy, Hungary and Serbia (Belmonte et al. 2000; Fernández-Llamazares et al. 2012) and beech pollen reaching Catalonia was traced back to central Europe (Belmonte et al. 2008). Greece, Hungary, Germany and Italy were also affected by long range transport of several pollen types coming from other European regions (Rizzi and Pizzulin, 2010, Markra et al. 2010). In North America, Raynor et al. (1983) tested a version of the Air Resources Laboratories Atmospheric Transport and Dispersion Model (ARL-ATAD) on cases of pollen wet deposition in Albany (New York,) after long-distance transport from source areas located in the South-Southwestern. The arrival to Tulsa of *Juniperus ashei* pollen released in southern Oklahoma and Texas has been reported (Rogers and Levetin, 1998; Van de Water et al. 2003). In South America, extra-regional pollen of *Celtis* coming from the Northeast and of *Nothofagus* from the Southwest has been found to contribute to Mar de Plata City (Argentina) pollen records (Gassmann and Pérez, 2006). In northwest India, bioaerosols collected during dust storms sporadically contained pollen from Himalayan species (Yadav et al. 2007). The presence of pollen grains from trees forming forests at much lower latitudes has been evidenced in the Arctic environment (Bourgeois, 2000; Savelieva et al. 2002; Rousseau et al. 2003, 2004, 2005, 2006, 2008). Extra-regional pollen transport has also been found in the Antarctic (Wynn-Williams 1991), the Arctic (Campbell et al. 1999), Australia (Salas, 1983; Hart et al. 2007) and New Zeland (Moar, 1969).

Finally, the study of aerobiological the long range transport has stimulated a new research line about the viability of pollen (Bohrerova et al. 2009), bacteria (Hervàs et al. 2009) and fungi (Gorbushina et al. 2007) after the long distance dispersion. Also a field of research has recently been opened on the implications of the biological component associated to both mineral dust and anthropogenic pollutants, since the interactions of pollen with fine aerosols of anthropogenic origin is confirmed by observations indicating that small carbon particles stick to the surface of pollen grains (Behrendt and Becker, 2001) and air pollution levels were associated with an increased risk of asthma symptoms in pollen-allergic asthmatic patients (Feo Brito et al. 2007).

Thesis objectives and outline

The main objective of the thesis is to study atmospheric deposition and transport processes of chemical species and pollen taxa in the western Mediterranean area and in the Canary Islands, and to evaluate the possible impacts that may produce over ecosystems. It is organised as:

Chapter 2. Comparison of collection methods to determine atmospheric deposition in a rural Mediterranean site (NE Spain)

The objective of this chapter is to evaluate the methodologies currently used to determine dry and wet deposition. This is done by carrying out parallel measurements of atmospheric deposition with wet-only, dry-only, bulk and the recovery of sedimentation over funnel collectors at a rural area in the Montseny mountains (NE Spain).

Chapter 3. Atmospheric transport patterns and trends in precipitation chemistry using trajectory statistical methods at a rural site in NE Spain, 1984-2009.

The aim of this chapter is to characterize the synoptic climatology and long-range transport of air pollutants to a rural area in the Montseny mountains (NE Spain) in order to examine and interpret the variation of precipitation chemistry during the last 25 years. To this aim, we have used a robust methodology that combines back-trajectory calculation, cluster analysis and source-receptor models. To evaluate the changes in precipitation chemistry in the last decades, we examine the main transport routes and source areas for an early monitoring period (1984-1993) which is compared to a more recent one (1998-2009).

Chapter 4. Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its role in marine productivity.

The goal of this study is to add to existing knowledge on phosphorous deposition to the western Mediterranean Sea by better constraining the sources, magnitude and modes of atmospheric inputs. This has been accomplished by analysing aerosol concentrations and wet and dry deposition fluxes from 2002- 2003 in a rural area in the Montseny mountains (NE Spain) close to the coast. Because of the important contribution of African sources and the well known interannual variability of African outbreaks, a long term record (1996-2008) of Saharan rain events was also analyzed to determine the potential impact of high phosphorous deposition during African events on the biogeochemistry of the western Mediterranean Sea.

Chapter 5. Source areas and long-range transport of pollen from continental land to Tenerife (Canary Islands).

The Canary Islands constitute an adequate site for the study of long-range pollen transport from the surrounding land masses. In this study we have analyzed the airborne pollen diversity and concentration at two sites: Santa Cruz de Tenerife (sea level corresponding to the marine

boundary layer) and Izaña (2367 m asl corresponding to the free troposphere) for the years 2006 and 2007. To describe the pollen transport we have used three approaches: an ANOVA classification of provenances, the study of special events of high pollen concentrations and their associated meteorology, and a source-receptor model applied to a selection of the pollen taxa to determine potential pollen source areas.

Chapter 6. Conclusions

Note:

The four central chapters are presented in scientific paper format, which entails some redundancy in the introduction and methods' information of the different chapters.

Sampling methods

Sampling methods used in this thesis are here briefly addressed, though the corresponding methods are described in more detail in the chapters.

The atmospheric deposition of chemical compounds was weekly sampled at La Castanya station (LC, 41º46'N, 2º21'E, 700m above sea level (m asl)). The weekly amount of precipitation was recorded by means of a Hellman rain gauge (Fig. 1a) and the daily precipitation by a rain gauge (Campbell Scientific Ltd.) connected to a data logger (Fig. 1b). For the collection of atmospheric deposition samples two collector systems were used: wet/dry deposition collector (ESM Andersen instruments, G78-1001; Fig. 1c) and 2 open bulk deposition collectors (Fig. 1d). Data obtained by means of these sampling methods were used in chapters 2, 3 and 4.

Figure 1. Atmospheric deposition sampling and precipitation measurement at LC: a) Hellman rain gauge; b) Campbell rain gauge connected to a data logger; c) Andersen wet/dry sampler (ESM Andersen instruments, G78-1001) and d) open bulk deposition collectors.

Total suspended particles (TSP) were collected at LC with a high volume sampler (DIGITEL DHA-80, Fig. 2) at air flow rate of 30 m^3 h^{-1}. Two consecutive daily filters (quartz fiber, QF20 Schleicher and Schuell) were obtained each week. Aerosol data were utilized in chapter 4.

Figure 2. TSP collector - DIGITEL DHA-80

Pollen was sampled at two monitoring stations: Santa Cruz de Tenerife (SCO; 16º14'51" W; 28º28'21" N; 52m asl) and Izaña Atmospheric Observatory (IZO; 16º29'58" W; 28º18'32" N; 2367m asl). Pollen samples were collected using samplers (Lanzoni VPPS 2000, Bologna, Italy) based on the Hirst method (Hirst, 1952) and analysed following the standardised Spanish methods (Galán et al. 2007). Aerobiological data were utilized in chapter 5.

Figure 3. Hirst pollen sampler (Lanzoni VPPS 2000, Bologna, Italy) at SCO station

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Chapter 2

Comparison of collection methods to determine atmospheric deposition in a rural Mediterranean site (NE Spain)

Izquierdo R. and Àvila A. 2012. Comparison of collection methods to determine atmospheric deposition in a rural Mediterranean site (NE Spain). Environmental and Assessment Monitoring, *under review*

Abstract

Parallel measurements of atmospheric deposition were conducted in a rural site in North-eastern Spain to study wet, dry and bulk deposition fluxes. Wet-only, dry-only, bulk deposition and sedimentary particles deposited after the last rain (DSP) were collected weekly at La Castanya station in the Montseny mountains (NE Spain, 41º46'N, 2º21'E) from February 2009 to July 2010. These samples were analysed for pH, alkalinity, and the concentrations of major anions (Cl^-, NO_3^-, SO_4^{2-},) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+). Significant differences were observed between bulk and wet-only precipitation, with an enrichment of ions associated to coarse particles in bulk deposition. The comparison between wet and dry fluxes revealed that the removal of compounds at Montseny occurred mainly by wet deposition, which accounted for 74% of total deposition. The dry flux was characterised by the predominance of K^+, Ca^{2+} and Mg^{2+}. Bulk deposition at Montseny was considered representative of total atmospheric deposition, since bulk deposition plus the recovery of deposited particles after the last rain (DSP) accounted for 97% of total deposition (wet+dry).

Introduction

Atmospheric deposition contributes to the chemistry of plants, soils, and surface water, and to the cycling of nutrients in ecosystems (Richter and Lindberg, 1988). Wet and dry deposition are efficient pathways for removing soluble gases and particles from the atmosphere. Wet deposition is defined as the process by which gases and aerosols are incorporated into cloud droplets or form cloud condensation nuclei and are deposited back to the earth's surface in the form of rain, snow and mist (Chantara and Chunsuk, 2008). Dry deposition of particles occurs by direct impact and gravitational settling on land and over water surfaces (Azimi et al. 2003). Several studies consider wet precipitation as the most effective scavenging factor for removing particulate and organic and inorganic gaseous pollutants from the atmosphere (Al-Khashman 2009; Arsene et al. 2007; Prathibha et al. 2010). However, recent investigations indicate that dry deposition may have a higher contribution in arid environments (Dolske and Gatz, 1985; Guerzoni et al. 1999; Aas et al. 2009), and therefore the effect of dry deposition on this type of ecosystems may be substantial (Raymond et al. 2004).

The concentrations of chemical species in precipitation vary widely in relation to different factors: type and distribution of aerosol sources, transport, chemical species and scavenging processes (Celle-Jeaton et al. 2009). However, it has long been recognized that the method used for the collection of precipitation samples for chemical analysis can have a significant effect on the results (Galloway and Likens, 1978; Sisterson et al. 1985; Dämmgen et al. 2005; Cape et al. 2009; Kelly et al. 2012). Wet deposition is measured by using a collector which has a removable lid that covers a collecting bucket or funnel to exclude dry deposition during the dry periods and opens whenever precipitation is detected by means of a precipitation sensor (Plaisance et al. 1998; Dämmgen et al. 2005; Staelens et al. 2005). However, in many ecological studies precipitation often is collected by a bulk collector which consists of an open funnel (glass or plastic) connected to a sampling bottle (Erisman et al. 2003). This sampling method does not require a power supply to activate movable lids and thus it allows for an efficient operation in large networks (Cape et al. 2009).

Chemical differences have been reported between the sampling methods described: in most cases, the deposition of material to the bulk collectors is significantly greater than to the wet-only collectors with exception of free acidity (H^+) and ammonium (NH_4^+) (Staelens et al. 2005; Cape et al. 2009). On one hand, the physical properties of the samplers, such as differences in flow distortion or a high evaporation rate from the sampling funnel (Dämmgen et al. 2005), are likely to play an important role. However, differences between bulk and wet-only deposition are mainly attributed to the contribution of the dry deposition flux (Galloway and Likens, 1976; Fowler and Cape, 1984; Draaijers et al. 1998; Akkoyunlu and Tayanc, 2003; Anatolaki and Tsitouridou, 2007).

The accurate estimation of dry deposition involves an understanding of several influential variables including the atmospheric characteristics, the nature of the surface and the properties

of the depositing species itself (Davidson and Wu, 1990). Indeed, there is not a standard method for the measurements of dry deposition. Dry deposition has been often inferred from the product of the measured species in ambient concentrations and its dry deposition velocity (Duce et al. 1991; Erisman et al. 1998; Guerzoni et al. 1999; Migon et al. 2001; Anatolaki and Tsitouridou, 2007), by means of statistical models (Dulac et al. 1989; Erisman et al. 1994; Brook et al. 1997; Yi et al. 1997; Staelens et al. 2008) or through micrometeorological approaches (Erisman and Draaijers, 1995). Still, a routine direct measurement technique is required for validating these estimates (Sakata et al. 2008). Direct measurements have included: 1) collection on dry-only collectors (Prakasa Rao et al. 1992; Morales-Baquero et al. 2006; Pulido-Villena et al. 2008; Al-Momani et al. 2008), 2) collection on surrogate plant surfaces (Ferm and Hultberg, 1999; Sanz et al. 2002; Moumen et al. 2004; Inomata et al. 2009) and 3) throughfall (Parker 1983). To better mimic the transport to waterbodies and moist landscapes, in some studies the surface of sampler is wetted (Shahin et al.1999; Balestrini et al. 2000; Azimi et al. 2003; Raymond et al. 2004; Anderson and Downing, 2006; Sakata et al. 2008). Also, measurements by electron microscope counting, wind-tunnel studies and chamber studies have been used to estimate dry deposition (Erisman et al. 1994). Despite the difficulties associated with dry deposition measurement, these different methods have provided data for an accurate characterization of total atmospheric deposition.

Qualitative and quantitative assessment of atmospheric deposition is essential for understanding regional variations of the precipitation chemistry, temporal trends of atmospheric deposition and for determining critical load exceedances (Balestrini et al. 2000). In the western Mediterranean basin the contribution of dry deposition to the total deposition flux has received little attention, despite important factors such as the frequent impact of African dust outbreaks contributing to the build up of particles and pollutants in the atmosphere (Querol et al. 1998; Rodríguez et al. 2001; Escudero et al. 2005), stagnant summer air producing an accumulation of pollutants (Millán et al. 1997, Rodríguez et al. 2002) and long spells of dry weather in summer (and sometimes also in winter), all suggesting that dry deposition may have an important role in this region.

In this context, the objective of this study has been to carry out parallel measurements of atmospheric deposition with wet-only, dry-only, bulk and recovery of sedimentation collection methods to examine their performance to describe total deposition at a rural area in the Montseny mountains (NE Spain),

Material and methods

Study site

Weekly deposition sampling was conducted at La Castanya station (LC, 41º46'N, 2º21'E, 700 m above sea level (MASL)), located in the Montseny mountains of the Pre-litoral Catalan Range (Fig.1). Since 2002 this location has been outfitted with instruments as a background regional air quality site (Pérez et al. 2008, Pey et al. 2009). The air quality station is amidst extensive holm oak (*Quercus ilex* L.) forests in the Montseny Natural Park, 40 km to the N-NE from Barcelona and 25 km from the Mediterranean coast (Fig. 1), and since the late 70s it provides deposition data for long-term biogeochemical studies that have been undertaken in a close holm oak forest plot (Rodà et al. 1999). Agricultural and sylvo-pastoral activities extend into the site surroundings. The lithology of Montseny is mainly composed of schists and granodiorites.

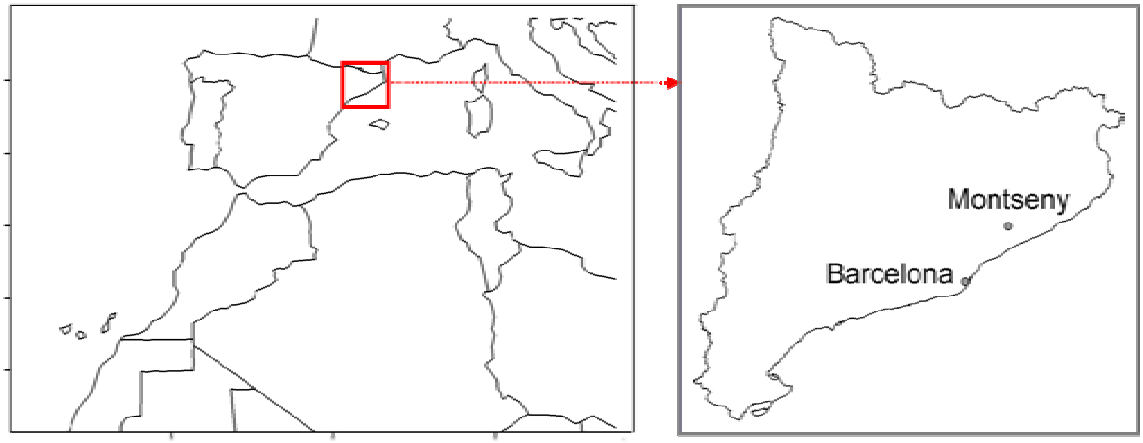

Figure 1. Map of Montseny study site, northeastern Spain.

The climate in Montseny is meso-Mediterranean sub-humid, with high interannual variability in precipitation, ranging from 503 to 1638 mm y^{-1} (mean: 840 mm y^{-1} at LC) from 1983 to 2009. Summer droughts are common, though often attenuated by frequent orographic storms in August and September. Mean air temperature at LC was 9ºC during the period 1983-2000. During the coldest season, the LC station is usually outside the mixing layer and is therefore less affected by regional anthropogenic pollution, however, during specific anticyclonic conditions which are common in summer and winter, highly polluted air masses from the coast and valleys are transported towards LC by mountain/sea breezes (Pérez et al. 2008).

Sampling and chemical analysis

From February 2009 to July 2010 two different collector systems typically used in monitoring programs and ecological studies were weekly sampled in parallel: bulk deposition and dry/wet Andersen sampler (dry-only from April 2009 on). A Hellmann sampler, which is considered to be the standard rain gauge for much of Europe (Sevruk and Klemm, 1989), was used to measure the reference precipitation.

Precipitation was collected in 2 open bulk deposition collectors placed at 1.5m above the ground. The collectors were designed as in Likens et al. (1977), and consisted of a polyethylene funnel of 19cm diameter connected by a tygon looping tube to a 10-L polyethylene bottle, with a nylon sieve stopper in the neck of the funnel to prevent contamination from insects and plant debris. In addition, the sedimentary particles deposited after the last precipitation (DSP) were collected by rinsing the funnel walls with 250ml of deionized distilled water. At each sampling date, the bulk deposition collectors were retrieved and replaced by a clean sampling kit. Cleaning procedures for funnels, tubes and buckets included repeated washes in the laboratory of all the material with deionized distilled water until electrical conductivity of the rinse was ~ 1 $\mu S\ cm^{-1}$.

For wet-only and dry-only collection, an Andersen sampler (ESM Andersen instruments, G78-1001) was used. The collector was equipped with two polyethylene buckets (29cm inner diameter) and a shutting lid, which was controlled and moved by a rain sensor at the beginning and the end of each rain event. The weekly rain samples were transferred into clean 250ml bottles and transported to the laboratory. The dry bucket was open during dry periods and closed during rain events. The weekly dry samples were recovered by rinsing the collection bucket with 250ml deionized water which was transferred to a clean polyethylene bottle. Cleaning procedures of wet/dry buckets by repeated washes with deionized water were carried out in the field. Visual observation of any detectable contamination (e.g. bird droppings, plant debris) was made and samples containing these contaminants were rejected. Samples were taken to the laboratory where they were processed according to previously described protocols (Àvila, 1996; Àvila and Rodà, 2002). The following parameters were determined for each sample: pH, alkalinity, and the concentrations Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}. Alkalinity and pH were measured in unfiltered samples within 48h of sampling. Samples were filtered through 0.45μm size pore membrane filter and stored for analysis. Ion chromatography was used for Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+ with a CS12A Dionex cation column on a Dionex ICS-1100 Ion Chromatograph (Dionex, Sunnyvale, USA) and for Cl^-, NO_3^- and SO_4^{2-} with a AS4A-SC Dionex anion column on a Dionex DX-100 Ion Chromatograph (Dionex, Sunnyvale, USA). Data quality was evaluated by (1) the use of control solutions during all analytical runs, and (2) an ionic ratio (cation sum/anion sum) accepting a 20% variation about the central value (= 1.00). For DSP and dry-only samples a 30% allowance was accepted because of the very low concentrations in these solutions. Results of the quality indexes are shown in Table 1.

Table 1. Data quality: Results of reference sample replication and average of the quality control index (cation sum/anion sum) calculated for type of measurement. DSP= rinse of the bulk collector walls after the last precipitation.

	n	Reference solution (μeq/L)	Analysed value Mean ± s.e (μeq/L)
Na^+	9	50	55.3 ± 1.36
K^+	9	10	11.0 ± 0.34
Ca^{2+}	9	100	107 ± 2.47
Mg^{2+}	4	32	33.8 ± 1.57
Mg^{2+}	5	25	25.8 ± 1.27
NH_4^+	4	40	43.2 ± 2.39
NH_4^+	5	50	52.5 ± 4.43
NO_3^-	15	18	18.4 ± 0.48
SO_4^{2-}	15	40	40.3 ± 0.68
Cl^-	15	20	21.1 ± 0.52
Index Σcations/Σanions	n	Theoretical value	Mean ± Standard Error
Bulk	47	1,00	1.10 ± 0.02
Wet-only	47	1,00	1.15 ± 0.01
Dry-only	40	1,00	1.10 ± 0.02
DSP	43	1,00	1.14 ± 0.03

The Hellmann rain gauge was used to calculate volume weighted mean (VWM) concentrations. Deposition fluxes were obtained as the product of VWM concentrations by precipitation volume collected during the study period. Dry and DSP deposition collected rinsing both sampling devices was calculated multiplying the arithmetic mean concentrations by the volume of washing solution (250ml). Wet-only, dry-only, bulk and DSP deposition fluxes for our study period were recalculated to obtain annual deposition values.

Total deposition is defined as the sum of wet and dry deposition. However, we have to keep in mind that in this study this term was applied to the wet deposition plus the gravitatory settling fraction of dry deposition, since particles, especially in the sub-micron to micron range, are subject to Brownian, wind, and turbulent eddy motion, and may be blown over and around the bucket or funnel walls rather than deposited into it (Azimi et al. 2003). Here, the total deposition was estimated using measures from two different sampling methods: 1) the sum of separate dry-only and wet-only measures, and 2) the sum of bulk deposition plus DSP. Thus, four weekly sample types were necessary to compare both estimations of total deposition.

Statistical analyses

Wilcoxon tests, linear regressions and Pearson correlations were computed with Statistica™. The coefficient of determination (r^2) has been used to compare the different sampling methods Pearson correlation (r) has been used to describe the relationships between ions within each type of sampling method. To give an indication of the range of variability observed in the samples, arithmetic means were accompanied by ± standard deviation (S.D.). Samples containing observable contamination (2% for bulk and wet-only samples and 14% for dry-only samples) were excluded from the calculations.

Results

Amount of precipitation

In the study period (February 2009 to July 2010), 98% of the samples corresponded to rain, the rest corresponding to mixed rain and snow. Weekly precipitation volume collected with the Hellmann rain gauge ranged from 2.4 to 149.4 mm during this period, with a mean of 29.4 ± 28.6 mm. Hellmann weekly amounts were 6% and 9% higher than bulk and wet-only collectors respectively (p<0.01). A good correlation was observed between the Hellmann rain gauge and the other sampling devices (r^2=0.99, Fig.2).

Precipitation amount collected in bulk and wet-only collectors also showed significant differences in the Wilcoxon test (p<0.01, Table 2). Bulk collection efficiency was 3.2% higher than wet-only. Also, a high correlation (r^2=0.996; Table 2) between the both collector types was found.

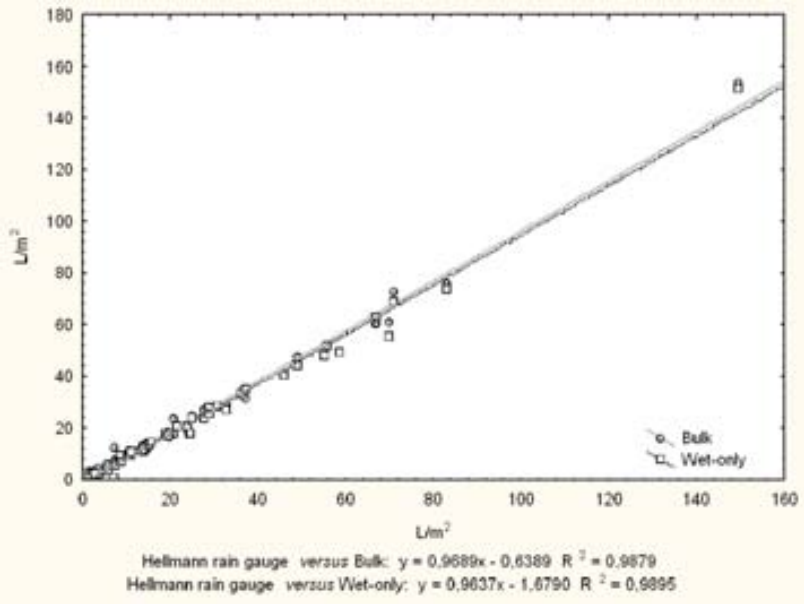

Figure 2. Regression analysis between precipitation amount (mm) collected by the Hellmann rain gauge *versus* bulk and wet-only collectors.

Table 2. Descriptors (range, median and arithmetic mean) of the chemical composition of bulk and wet-only samples at La Castanya (Montseny) for the period February 2009-July 2010. Significance level of the differences according to the Wilcoxon signed-rank test and R^2 for linear regressions between bulk and wet measurements are also given.

		Bulk					Wet-only					Wilcoxon	Linear
	n	Min.	Max.	Median	A.mean	S.D	Min.	Max.	Median	A.mean	S.D	*p*-value	R^2
Rain (mm)	41	2.24	154.1	18.3	27.6	28.0	1.89	151.4	17.8	26.8	27.6	<0.01	0.996***
Alkalinity (μeq L^{-1})	47	-8.33	236.5	23.9	32.4	42.0	-20.6	559.0	19.2	35.3	83.7	0.362	0.77***
pH	47	5.05	7.15	5.93	5.96	0.50	4.68	7.39	6.05	5.96	0.57	0.772	0.64***
Na^+ (μeq L^{-1})	47	2.99	89.4	9.00	14.7	15.2	1.80	78.7	6.77	11.0	12.5	<0.01	0.91***
K^+ (μeq L^{-1})	47	0.66	17.7	2.91	4.14	3.29	0.50	14.6	2.56	3.27	2.83	<0.05	0.39***
Ca^{2+} (μeq L^{-1})	47	5.39	609.0	49.6	71.7	97.3	5.05	723.0	27.8	56.6	110.9	<0.01	0.93***
Mg^{2+} (μeq L^{-1})	47	0.84	61.3	7.50	10.1	10.7	0.93	63.0	5.10	7.22	9.34	<0.01	0.82***
NH_4^+ (μeq L^{-1})	47	1.62	129.3	17.9	27.8	26.7	3.44	126.0	40.0	40.2	27.5	<0.01	0.64***
NO_3^- (μeq L^{-1})	47	5.29	167.5	25.0	35.5	31.0	3.49	160.8	25.5	33.5	30.7	<0.05	0.76***
SO_4^{2-} (μeq L^{-1})	47	6.10	137.7	21.5	27.7	21.3	4.40	150.6	20.7	26.1	23.4	<0.05	0.86***
Cl^- (μeq L^{-1})	47	3.64	103.2	11.4	16.3	17.5	2.20	78.2	6.46	10.8	12.8	<0.01	0.91***

***p<0.001

Wet-only and bulk deposition concentrations

The chemical composition of 47 wet-only and bulk precipitation samples obtained from February 2009 to July 2010 was used in this comparison (Table 2). For all chemical components (except for pH) the median values were lower than the arithmetic means (Table 2) indicating strongly skewed distributions to the left in both the bulk and wet only samples.

The Wilcoxon signed-rank test showed weekly bulk concentrations to be significantly (p<0.05) higher than wet-only concentrations for Na^+, Ca^{2+}, Mg^{2+}, Cl^- ,NO_3^- and SO_4^{2-}, while the reverse was true for NH_4^+ (Table 2). No significant differences were found for alkalinity and pH.

Regression analysis for the chemical constituents in bulk *versus* wet-only samples indicated high coefficients of determination (r^2 >0.75) ordered by this rank: Ca^{2+} > Na^+ > Cl^- > SO_4^{2-} > Mg^{2+} > alkalinity > NO_3^-. Ammonium and pH showed moderate coefficients of determination (r^2 =0.64), and for K^+ it was low (r^2 =0.39), but still significant (p<0.001).

It should be noticed that VWM concentrations (Table 3) were lower than the arithmetic mean concentrations (Table 2) indicating that higher concentrations are associated with lower rainfalls. This is due to the scavenging of the below-cloud atmosphere by the first drops of rainfall that present the highest concentrations with low precipitation amount and the exhaustion of pollutants as precipitation proceeds (Colin et al. 1989; Beverland et al. 1998; Prado-Fiedler, 1990; Kelly et al.2012).

Table 3. Volume-weighted mean (VWM) concentrations for the analysed chemical species (units in μeq L^{-1}) and ratio of the VWM bulk and wet concentrations.

	Bulk	Wet-only	Ratio (bulk/wet-only)
Alkalinity	17.7	17.1	1.03
pH	6.45	6.43	1.00
Na^+	13.1	9.89	1.33
K^+	3.27	2.38	1.37
Ca^{2+}	38.2	27.2	1.41
Mg^{2+}	6.36	4.69	1.36
NH_4^+	22.3	30.2	0.74
NO_3^-	22.7	20.3	1.11
SO_4^{2-}	19.8	18.0	1.10
Cl^-	15.6	10.8	1.44

The pH of weekly samples of wet-only and bulk precipitation ranged between 4.7 and 7.4 (the maximum range was for wet-only deposition, Table 2). Such co-occurrence of acidic and alkaline rains within the averaging period precludes the use of the conventional method of computing VWM precipitation pH from VWM H^+, because H^+ is not conservative (Escarré et al.

1999). Instead alkalinity is the conservative property to average: assuming that bicarbonate accounts for most of the alkalinity and using the constants of the carbonate-bicarbonate equilibrium, the average pH can be calculated (Liljestrand 1985; Young et al. 1988). The resultant VWM pH was 6.4 for both sample types (Table 3).

Based on the VWM, the predominant anions were NO_3^- and SO_4^{2-} with mean concentrations of 20-23 μeq L^{-1} and 18-20 μeq L^{-1} in wet and bulk deposition, respectively (Table 3). The predominant cations were Ca^{2+} and NH_4^+ which constituted about 73-80% of the sum of cations in wet-only and bulk samples (VWM concentrations 27-38 μeq L^{-1} and 22-30 μeq L^{-1}, respectively; Table 3).

Pearson correlations between measured ions in bulk (Fig. 3a) and wet-only (Fig. 3b) deposition have been computed in order to understand their sources and shed light on the differential processes affecting them. Both sample types showed similar patterns characterized by close correlations between constituents of coarse particles (r>0.70 for Na^+, Mg^{2+}, Ca^{2+}, Cl^- and partially SO_4^{2-}) and low correlation coefficients between those components which usually constitute fine particles (r<0.70 for NO_3^-, NH_4^+ and partially SO_4^{2-}). In wet-only samples the correlation between NO_3^--SO_4^{2-} (r=0.78) and K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} (r≈0.6) was higher than in bulk samples (r<0.6).

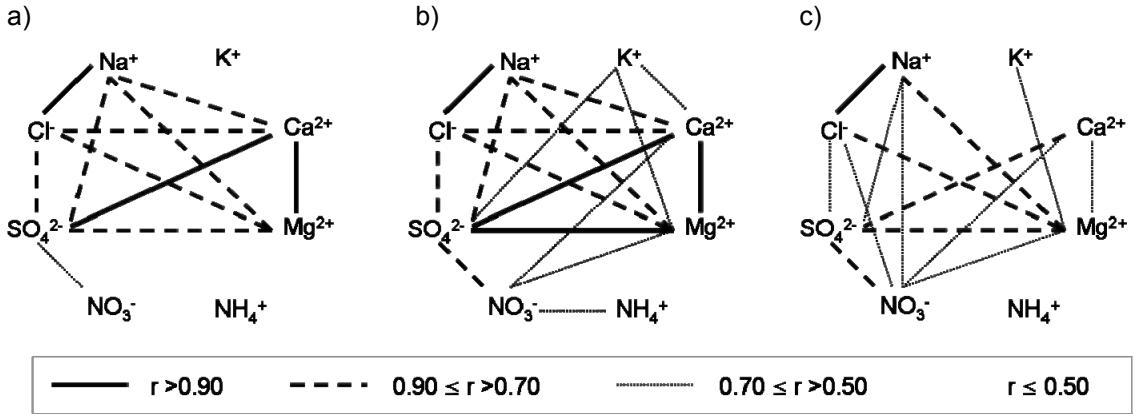

Figure 3. Pearson correlations (r) between the analyzed ions in: a) bulk, b) wet, and c) dry deposition.

Dry-only deposition concentrations

The arithmetic means for alkalinity, pH and ion concentrations in dry deposition are shown in Table 4. The mean pH was 6.50 ± 0.72 and mean alkalinity was 74.0 ± 45.9 μeq L^{-1}. The highest ion concentration was Ca^{2+} with 126.1 ± 70.8 μeq L^{-1}. In descending order the ion concentrations means were Ca^{2+} > alkalinity > NO_3^- > SO_4^{2-} > Na^+ > Cl^- > Mg^{2+} > K^+ > NH_4^+.

Pearson correlations in dry-only deposition samples (Fig. 3c) were different from those observed in wet-only deposition samples (Fig. 3b). The relationship between crustal compounds (Mg^{2+}, Ca^{2+} and partially SO_4^{2-}) and between Ca^{2+} and SO_4^{2-} *versus* sea-salt ions decreased in dry-only samples. Conversely correlations between NO_3^- and marine compounds were higher. Only K^+ was correlated with Mg^{2+} (r=0.60) while non significant correlations were observed for NH_4^+.

Table 4. Descriptors (range, median, arithmetic mean and standard deviation) of the chemical composition of dry-only samples at La Castanya (Montseny) for the period April 2009-July 2010. Concentrations in μeq L^{-1}.

Dry-only	n	Min.	Max.	Median	A.mean	S.D
Alkalinity	43	12.9	172	66.5	74.0	45.9
pH	43	5.40	8.32	6.35	6.50	0.72
Na^+	43	2.77	134	11.6	21.7	26.1
K^+	43	1.50	56.2	8.41	15.0	15.5
Ca^{2+}	43	29.3	325	109	126	70.8
Mg^{2+}	43	4.93	44.7	15.0	17.0	9.87
NH_4^+	43	0.70	89.7	5.00	10.2	17.1
NO_3^-	43	0.71	107	28.5	34.6	25.8
SO_4^{2-}	43	6.07	98.9	20.2	26.4	18.9
Cl^-	43	3.27	142	12.4	22.9	28.3

Total deposition fluxes

Co-located bulk and wet/dry samplers allowed the calculation of deposition fluxes in both collector types and to compare their collection efficiency. For bulk deposition fluxes, DSP was also collected and added. We considered that wet+dry should be equivalent to bulk+DSP fluxes and this equivalence is shown in Fig. 4 and Table 5. Indeed, the total bulk+DSP flux accounted the 97% of wet+dry flux (27.04 *vs.* 27.81 kg ha^{-1} yr^{-1}). Differences between both methodologies were <7% referred to wet+dry deposition for Ca^{2+}, Mg^{2+}, N-NO_3^-, S-SO_4^{2-} and Na^+, while for N-NH_4^+, K^+ and Cl^- they were >15% (Fig. 4). The N-NH_4^+ wet+dry deposition flux was 3.90 kg ha^{-1} yr^{-1} compared to 2.71 kg ha^{-1} yr^{-1} for bulk+DSP. For K^+ the wet+dry flux was 18% higher than the bulk+DSP flux (1.63 and 1.33 kg ha^{-1} yr^{-1} respectively). Conversely, for the marine ions the wet+dry flux was lower than the bulk+DSP: 15% for Cl^- (4.57 *vs.* 5.26 kg ha^{-1} yr^{-1}) and 7% for Na (2.71 *vs.* 2.90 kg ha^{-1} yr^{-1}). The linear regressions between both deposition estimations (sum wet+dry and bulk+DSP) showed significantly good correlations ($r^2 \geq 0.65$, $p<0.001$) for all ions, except for K^+ (r^2=0.42, p=0.003).

Table 5. Annual deposition (in kg ha^{-1} yr^{-1}) for the different considered fluxes from April 2009 to July 2010. Percentages relative to total (wet+dry) are also indicated.

Annual deposition	Bulk	DSP	Bulk+DSP	Wet-only	Dry-only	Total (wet+dry)
Na^+	2.73 (101%)	0.16 (6%)	2.90 (107%)	2.07 (76%)	0.64 (24%)	2.71
K^+	1.13 (69%)	0.20 (12%)	1.33 (82%)	0.87 (54%)	0.76 (46%)	1.63
Ca^{2+}	7.06 (86%)	1.10 (13%)	8.16 (100%)	4.92 (60%)	3.26 (40%)	8.18
Mg^{2+}	0.70 (92%)	0.09 (11%)	0.78 (104%)	0.49 (65%)	0.27 (35%)	0.76
$N\text{-}NH_4^+$	2.64 (68%)	0.08 (2%)	2.71 (70%)	3.71 (95%)	0.18 (5%)	3.90
$N\text{-}NO_3^-$	2.78 (91%)	0.14 (4%)	2.92 (96%)	2.42 (79%)	0.62 (21%)	3.04
$S\text{-}SO_4^{2-}$	2.82 (93%)	0.16 (5%)	2.98 (98%)	2.48 (82%)	0.55 (18%)	3.03
Cl^-	4.98 (109%)	0.28 (6%)	5.26 (115%)	3.52 (77%)	1.05 (23%)	4.57
Total	24.83 (89%)	2.21 (8%)	27.04 (97%)	20.48 (74%)	7.33 (26%)	27.81

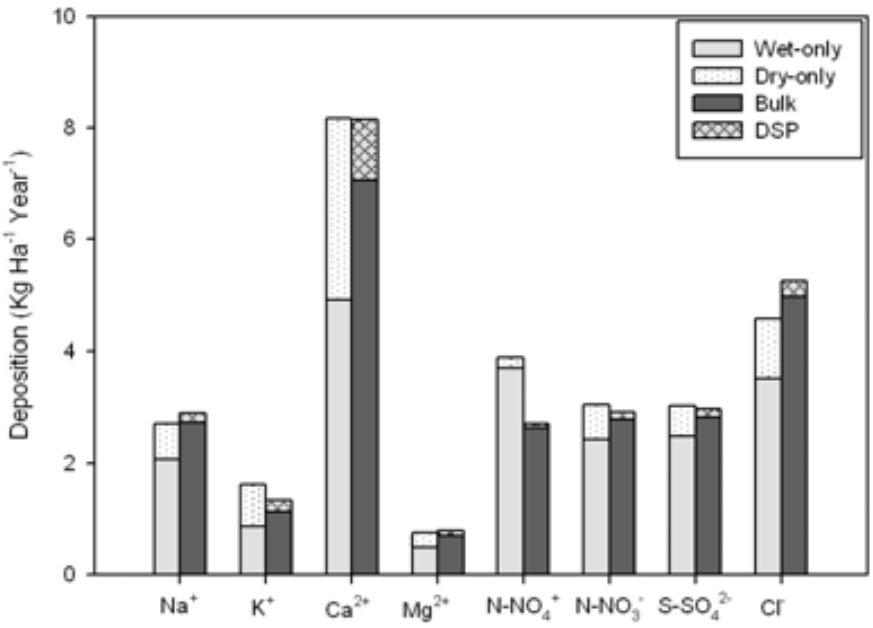

Figure 4. Comparison of wet+dry and bulk+DSP deposition (in kg ha^{-1} yr^{-1}) for each chemical species in Montseny.

The bulk annual deposition accounted for 89% (24.83 kg ha^{-1} yr^{-1}) of wet+dry flux and more than 80% of all chemical species, except for K^+ and N-NH_4^+ which represented ~70% (Table 5). On the other hand, the total DSP annual deposition was 8% (2.21 kg ha^{-1} yr^{-1}) of wet+dry flux. For individual ions, DSP percentages ranged between 6-13% for ions associated with coarse particles (Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+) and 2-5% for fine particles (N-NH_4^+, N-NO_3^-, S-SO_4^{2-}, Table 5)

Wet deposition contributed 74% of total in the study period. Even if dry deposition only accounted for 26% of wet+dry deposition, it was relatively more important for K^+, Ca^{2+} and Mg^{2+} with ~45% (0.76 kg ha^{-1} yr^{-1}), ~40% (3.26 kg ha^{-1} yr^{-1}) and ~35% (0.27 kg ha^{-1} yr^{-1}) of the wet+dry flux. Conversely, N-NH_4^+ dry deposition only represented 5% (0.18 kg ha^{-1} yr^{-1}) of total N-NH_4^+ deposition (Table 5).

Discussion

Amount of precipitation

Bulk and wet deposition are calculated as the product of representative concentrations (usually VW means) and the amount of precipitation. Precipitation amount should be measured with standard rain gauges because the collection efficiency of precipitation samplers is influenced by disturbance of the airflow over and around a collector, height above the ground, evaporation of collected rainwater and, in the case of wet-only collectors, the efficiency of rain sensors (Stedman et al. 1990). The Hellman sampler is considered as a standard rain gauge for the measurement of precipitation (Sevruk and Klemm, 1989) with an error of 7% (German standard DIN 58666, 1966). Figure 2 indicates that bulk and wet-only deposition samplers showed good agreement with the Hellmann rain gauge in this study. However, the Hellman gauge collected higher amounts than bulk and wet-only collectors (6% and 9% respectively). A similar pattern was observed in Thailand, where bulk and wet-only deposition collectors collected 2.0% and 0.3% less than the standard rain gauge, respectively (Chantara and Chunsuk, 2008). For 20 countries participating in a European study, significant differences were reported between the rain gauge value and the best estimate of bulk deposition and wet-only deposition (Erisman et al. 2003). Unlike our results, the precipitation volumes collected in their study were systematically higher in bulk and wet-only samplers compared to the Hellmann rain gauge (15 and 5% respectively, Erisman et al. 2003).

The rain amount collected with bulk and wet-only deposition devices in our study followed the same trend reported by other authors (Stedman et al. 1990; Thimonier, 1998, Balestrini et al. 2000; Erisman et al. 2003; Cape et al. 2009) in that the precipitation volume collected by bulk deposition samplers was significantly higher than by wet-only (Table 2). This difference is attributed to differences in device structure (Draaijers et al. 1998) and to the delayed opening of the lid at the onset precipitation (Stedman et al. 1990; Erisman et al. 2003, Kelly et al. 2012)

Wet-only and bulk deposition concentrations

Accepting that the collectors all undercatch to differing degrees, it is important to investigate how chemically representative the collected samples are. For bulk and wet deposition, VWM mean concentrations are best representative of mean concentrations, since these fluxes are dependent upon the precipitation amount. Bulk precipitation chemistry at Montseny was characterized by a positive alkalinity with most of the potential acidity of strong acids being neutralized by Ca^{2+} and NH_4^+ (Table 3). Since bulk deposition includes both wet and some dry deposition, the concentration of chemical components in bulk deposition was higher than the concentrations in wet-only samplers, as also found in other studies (Akkoyunlu and Tayanç, 2003). All ion concentrations, except NH_4^+, were significantly higher in bulk than wet-only precipitation (Table 2, Wilcoxon signed-rank test). A greater enhancement in bulk deposition of soil-derived ions from large wind-blown particles such as Ca^{2+}, Mg^{2+}, K^+, sometimes SO_4^{2-} and sea-salt ions (Na^+, Mg^{2+}, Cl^-) is observed, which is akin to results of other studies (Thimonier, 1998; Erisman et al. 2003; Akkoyunlu and Tayanc, 2003; Staelens et al. 2005; Pelicho et al. 2006; Cape et al. 2009). Although NH_4^+ belongs to the group of ions derived from gases or sub-micron particles, the concentrations in the wet-only samples were noticeably higher than in the bulk samples (ratio bulk/wet-only = 0.74, Table 3). Wet deposition of nitrate and ammonium is determined primarily by the precipitation amount and to a much lesser extent by its concentration in precipitation (Prado-Fiedler, 1990). Here, the precipitation amount was 3% lower in wet than bulk collectors (Table 2) so that other factors must account for such a difference. N-species are in general unstable and decompose under high temperatures during sampling, therefore losses of nitrates and/or ammonium are likely to take place (Anatolaki and Tsitouridou, 2007). As the highest dry deposition rates of NH_3 (Cape and Leith, 2002) and particles (Ruijgrok et al. 1997) are obtained for wet surfaces, a delayed opening time may contribute with higher dry deposition of NH_3 and NH_4^+ particles onto the wet-only collector after rain events. Additionally, it is possible that any dry-deposited NH_3 or NH_4^+ was more susceptible to biological degradation in a continuously-open sampler than in a lidded wet-only sampler (Cape et al. 2009), since algae use N for their growth and bacteria present in the sampling bottles may cause nitrification through which part of the NH_4^+ is transformed to NO_3^- and H^+ (Draaijers et al. 1998).

Ions associated with coarse particles (soil-derived and sea salt ions, except K^+) showed the best linear relationships between bulk and wet-only samples (Table 3). The close relationships observed in regression analysis suggest that bulk and wet-only samples were collecting ions from the same source and in the same chemical form. The different behaviour of K^+ could be ascribed to the contribution of particulates of biological origin, such as pollen, small vegetation fragments or ash from biomass burning, deposited on the bulk surface at certain times of year (Likens et al. 1994; Balestrini et al. 2007; Praveen et al. 2007)

Pearson correlations between ion concentrations (Fig. 3a,b) provided some information on the sources of ions collected in bulk and wet-only samples separately. Both sample types showed

high correlations between coarse particles: the Na^+ and Cl^- correlation indicated the marine influence received at LC which is located at 25 Km from the Mediterranean coast; Ca^{2+}, Mg^{2+} and SO_4^{2-} correlations can be in part attributed to the dissolution of African mineral dust due to the usual occurrence of mineral dust plumes from Africa over the Iberian Peninsula (Rodríguez et al. 2001; Escudero et al. 2005; Moreno et al. 2005). Correlations between marine and crustal compounds may indicate the incorporation of marine aerosols into clouds as the air mass trajectory crosses over the Mediterranean Sea from North Africa to NE Spain. Accordingly, previous studies at Montseny have found very high concentrations of marine and crustal components in African rains compared to rains of other provenances (Àvila et al. 1997). Correlations between NH_4^+, NO_3^- and SO_4^{2-} are usually related with anthropogenic emissions and high pollution levels (Saxena et al. 1997; Tanner, 1999; Praveen et al. 2007). Additionally, the good correlation observed among NO_3^- *versus* Na^+ and Ca^{+2} can be associated with the formation of secondary coarse $NaNO_3$ and $Ca(NO_3)_2$ aerosols originating from the interaction of HNO_3 and sea salts and calcite ($CaCO_3$) during warm periods when NH_4NO_3 is thermically unstable (Harrison and Pio, 1983, Pakkanen 1996, Querol et al. 1998). The lack of correlation between K^+ and crustal ions (Ca^{2+} and Mg^{2+}) suggests that a biological origin was predominant for K^+ (Balestrini et al. 2007).

Dry-only deposition concentrations

The chemistry of dry deposition samples at La Castanya (Table 4) was dominated by Ca^{2+} concentrations. The relatively high concentrations of the other base cations (K^+, Na^+, Mg^{2+}) indicated that alkaline and alkaline-earth metals provided high alkalinity (74.01 $\pm$ 45.9 μeq L^{-1}) and were responsible for the high pH (6.50 $\pm$ 0.72) of these samples. In dry deposition, NO_3^- (34.6µeq L^{-1}) predominated over NH_4^+ (10.2µeq L^{-1}); this could be attributed to several mechanisms, such as NH_4^+ volatilization, biological NH_4^+ consuming process as mentioned for the bulk samples, or to fine NH_4^+ containing aerosols not being dry deposited by sedimentation. These results were within the range of ion concentrations in dry deposition observed in Italy (Balestrini et al. 2000) though in this study NH_4^+ concentrations (6-76µeq L^{-1}) were however higher than NO_3^- (9-46 µeq L^{-1}).

A close correlation was observed between marine components$^-$ (Na-Cl r=99; p>0.001; Mg^{2+}-Na^+ and Cl^-, 0.90 < r > 0.70) for all deposition types, confirming the sea salt influence in wet and dry deposition (Fig 3). However, for other components, correlations differed between deposition types: e.g. Na^+ and NO_3^- showed high correlations only in dry deposition. Taking into account that dry deposition is size dependent (Koçak et al. 2010) this suggests dry deposition of coarse $NaNO_3$ onto dry collectors. Sulphate showed stronger correlations with Ca^{+2} and Mg^{2+} in wet than in dry or bulk deposition, suggesting that other sources of Ca^{+2} and Mg^{2+} (Ca and Mg carbonates) have a higher contribution to dry than to wet deposition.

Total deposition fluxes

The effect of deposition on terrestrial ecosystems depends on total deposition. This study demonstrated that the bulk+DSP flux accounted for 97% of wet+dry flux (Table 5). Differences between both methodologies for Ca^{2+}, Mg^{2+}, $N\text{-}NO_3^-$, $S\text{-}SO_4^{2-}$ and Na^+ were <7% referred to wet+dry deposition (Fig. 4; Table 5). Furthermore, a good correlation between bulk and wet collecting method was found for all chemical species, except for K^+(Table 2). Small observed differences can be attributed to the uncertainty associated to collection catch. The lower NH_4^+ and K^+ values in bulk deposition (30% and 18%, respectively) probably result from biological interactions such as NH_4^+ consumption from microorganisms in bulk samplers, and contamination with biological particles in dry deposition samplers.

Bulk deposition accounted the 89% of total deposition (wet+dry) and more than 80% of all chemical species, except for K^+ and $N\text{-}NH_4^+$ which represented ~70% (Table 5). For K^+ and NH_4^+ our results concur with many other studies to indicate that deposition estimates should be interpreted with caution since biological interactions may occur (Draaijers et al. 1998; Balestrini et al. 2002; Cape et al. 2009). DSP accounted for only 8% of annual wet+dry flux and was higher for components of coarse particles (6-13%) than those of fine particles (2-5%; Table 5). The bulk flux+DSP flux at Montseny accounted 97% of total deposition (wet+dry); thus it can be taken as representative of atmospheric deposition. Given the advantages this method has for remote sites, and taking into account that NH_4^+ and K^+ measurements may have a greater uncertainty, it can be recommended for extensive low cost sampling in comparable environments in the Mediterranean.

Wet deposition was the most effective removal mechanism from the atmosphere at Montseny, since the wet deposition flux contributed 74% of total annual deposition and more than 50% for all chemical species in 2009-2010 period (Table 5). Surprisingly, the relative contribution of wet and dry deposition fluxes to the total annual deposition was similar to registered at Montseny in 2002-2003 period, despite the differences in the amount of material deposited during the two compared periods, in the total amount as well as individually for each chemical compound (Castillo et al. 2006).

Dry deposition was dominated by Ca^{+2}, Mg^{+2} and K^+ which accounted for 40, 35 and 45% of the total deposition. These values were close to percentages observed in other locations of the Mediterranean such as northern Italy (Balestrini et al. 2000; 41-60, 35-64 and 57-67%, respectively) or southern France (Celle-Jeanton et al. 2009; 36, 24 and 46% respectively), but lower than at Sierra Nevada (South Spain) where Ca^{+2} dry deposition was 64% of total deposition (Morales-Baquero et al. 2006). The higher influence of Saharan dust inputs and the lower rainfall amount in southern Spain may explain higher Ca^{2+} dry deposition in Sierra Nevada (Morales-Baquero et al. 2006).

On the other hand, at Montseny dry deposition of acidifying compounds accounted for ~17% for SO_4^{2-}, ~20% for N-NO_3^- and 5-18% for N-NH_4^+. These results are in accordance with the range of percentages recorded in Italy and France (14-50% for SO_4^{2-}; 15-31% for N-NO_3^-; 1-37% N-NH_4^+; Possanzini et al. 1988; Balestrini et al. 2000, 2002; Celle-Jeanton et al. 2009). In dryer climates such as Greece and the Eastern Mediterranean, dry deposition was the main source of N-NO_3^- (75-90%; Anatolaki and Tsiuridou, 2007; Al-Momani et al. 2008; Koçaç et al. 2010) and S-SO_4^{2-} (55-63%; Anatolaki and Tsiuridou, 2007; Al-Momani et al. 2008).

Conclusions

At Montseny (NE Spain) total deposition estimated by wet+dry and bulk+DSP was generally equivalent, except for K^+ and NH_4^+. Data for ammonium highlight the difficulties of studying biologically labile species. Results for K^+ suggest that deposition of biological components of local origin, such as pollen, ash, and small plant debris may have an influence when sampling at a weekly schedule.

The removal of atmospheric compounds occurred mainly by wet deposition, which contributed 74% of total wet+dry deposition. Dry deposition was characterized by the predominance of crustal ions such as Ca^{2+} and Mg^{2+} or crustal-biological such as K^+. Although the recovery of deposited particles after the last rain (DSP) only contributed 8% to total deposition (wet+dry), this is an important measurement to include, since bulk deposition plus DSP accounted for 97% of total deposition (wet+dry). Thus, in Mediterranean rural environments, when field conditions do not favor the installation of wet-only/dry-only devices, bulk plus DSP measurements can be implemented because, as shown in this work, they mostly accounted for the sum of wet and dry deposition.

Acknowledgements

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Chapter 3

Atmospheric transport patterns and trends in precipitation chemistry using trajectory statistical methods at a rural site in NE Spain, 1984-2009

Izquierdo R., Àvila A. and Alarcón M. Atmospheric transport patterns and trends in precipitation chemistry using trajectory statistical methods at a rural site in NE Spain, 1984-2009. Atmospheric Environment, *under review*

Abstract

The aim of this study is to characterize the synoptic climatology and long-range transport of air pollutants to Montseny (NE Spain) in order to interpret the variation of precipitation chemistry during the last 25 years. Trajectory cluster analysis and source-receptor models were applied to an early monitoring period (1984-1993) which was compared to a recent one (1998-2009). A decrease of Atlantic advections and increase of African and European air flows over NE Spain was found. Cluster analysis and source-receptor approaches showed that this region is under the influence of natural and anthropogenic sources from the local scale and long-range transport processes. In the initial period (1984-1993) anthropogenic pollutants (SO_4^{2-}, H^+ and NO_3^-) were mostly originated in central and Eastern Europe. Stricter environmental policies for the abatement of sulphur emissions over central Europe resulted in a significant temporal decrease of SO_4^{2-} and H^+ in precipitation collected at Montseny. The increase of emissions from ships and the industrialisation of countries in Eastern Europe and North Africa explained the location of the pollutants main source areas (North Sea, Eastern Europe and North Africa) in the more recent period (1998-2009).

Introduction

The atmospheric dynamics in the West Mediterranean Basin (WMB) is conditioned by complex interactions of climatic and topographic effects that include the Azores high-pressure system, continental thermal lows over the Iberian Peninsula (IP thereafter) and the Sahara, orographic effects of the coastal ranges surrounding the Mediterranean coast, marked seasonal variations in temperature, humidity and rainfall and the arrival of frequent African dust intrusions (Millán et al. 1997; Rodríguez et al. 2003). Modifications in the wind circulation and precipitation patterns have been predicted for the Mediterranean region linked to climate change: climate change projections show a pronounced decrease in precipitation, especially in the warm season, due to increased anticyclonic circulation that yields increasingly stable conditions and is associated with a northward shift of the Atlantic storm track (Giorgi and Lionello, 2008). An increase of African Air masses over Southern Europe has been suggested (Moulin et al. 1997) but this is still subject of debate. A systematic investigation on the emission sources and the rainwater chemical composition is necessary to understand the consequences of pollution on ecosystems (Arsene et al. 2007). In Europe, the Convention on Long Range Transboundary Air Pollution (CLRTAP) has launched several protocols to reduce sulphur and nitrogen emissions to the atmosphere since the early 1970s. As a result, sulphur deposition steadily decreased throughout Europe in the last 30 years (Stoddard et al. 1999; Skjelkvale et al. 2005), but success has been more limited for nitrogen compounds (Gundersen et al. 2006). Nitrogen deposition can affect ecosystems by promoting acidification of soil and water (Schindler, 1988), nitrogen enrichment and nutrient imbalances in terrestrial and aquatic ecosystems (Matson et al. 2002; Rabalais, 2002), and eutrophication of water bodies (Paerl and Whitall, 1999).

Meteorological classification refers to the identification of distinct patterns that influence climate/weather-related variables (Riccio et al. 2007). Over the last several decades, Trajectory Statistical analysis Methods (TSMs) have been used to examine transport patterns and dynamical processes of the air masses (Stohl, 1998). Cluster analysis has been widely used to categorize back trajectories (Dorling and Davies, 1995; Jorba et al. 2004) and to identify synoptic weather regimes and long-range transport patterns that affect air pollution (Cape et al. 2000; Salvador et al. 2007). Cluster analysis can be used to classify air mass origin arriving at a site but do not provide further information on the geographical location of potential source regions (Salvador et al. 2010). This is frequently resolved with TSMs which are helpful for estimating the spatial distribution of emissions based on measurements at a receptor site (Stohl, 1996; Begum et al. 2005). Between the currently available TSMs, the Seibert's methodology based on concentration fields (Seibert et al. 1994) and the method based on the potential source contribution function (PSCF) have been profusely used for the interpretation of source areas (Polissar et al. 2001; Hoh and Hites, 2004; Salvador et al. 2004).

The aim of this study is to characterize the synoptic climatology and long-range transport of air pollutants arriving in Montseny (NE Spain) in order to interpret the variation of precipitation

chemistry during the last 25 years. To this end, we have used back-trajectories, cluster analysis and source-receptor models for an early monitoring period (1984-1993) which are compared to a more recent one (1998-2009).

Material and Methods

Study site

La Castanya station (LC, 41º46'N, 2º21'E, 700 m is located in the Montseny mountains of the Pre-litoral Catalan Range (Fig.1). The study site is amidst extensive holm-oak (*Quercus ilex* L.) forests in the Montseny Natural Park, 40 km to the N-NE from Barcelona and 25 km from the Mediterranean coast (Fig.1). Long-term biogeochemical studies have been undertaken since the late 1970 in a forest plot close to the atmospheric sampling site (Rodà et al. 1999).

The climate in Montseny is meso-Mediterranean sub-humid, with high interannual variability in precipitation (range: 503-1638 mmy^{-1}, mean: 840 mmy^{-1} at LC, from 1983-2009). Summer droughts are common and snow is sporadic. Mean air temperature at LC was 9ºC during the period 1983-2000.

Figure 1. Map of La Castanya study site (LC), NE Spain.

Sampling and chemical analysis

Precipitation was collected weekly at LC from August 1983 to July 2010 (no data from September 2000 to March 2002). Two different collector systems were used: bulk deposition and dry/wet Andersen sampler (ESM Andersen instruments, G78-1001).

Precipitation was collected with 2 open bulk deposition collectors from January 1984-September 2000 and March 2007-July 2010, and with wet/dry collectors from April 2002-July 2004, February 2005-March 2007, and February 2009-July 2010. In the last period, bulk and wet-only deposition were sampled in parallel. Only data from the wet-only collector are considered. Any detectable contamination (e.g. bird droppings) was annotated and discarded.

Samples were taken to the CREAF laboratory where they were processed according to previously described protocols (Àvila, 1996; Àvila and Rodà, 2002). Conductivity, alkalinity and pH were measured in unfiltered samples within 48h of sampling. Samples were filtered through 0.45μm membrane filters and stored at -20ºC. Ion chromatography was used to determine the concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}. Data quality was evaluated by:

(1) control solutions within analytical runs, and (2) an ionic ratio (cation sum/anion sum) accepting a 20% variation about the central value (= 1.00).

Regression analysis was performed between wet-only and bulk-deposition data for the parallel sampling for each chemical compound and good correlations were obtained ($R>0.8$, $p<0.001$). Then, regressions between wet and bulk concentrations were used for each analyte to obtain a complete bulk-deposition database from 1984 to 2009. Years 2001, 2004 (for base cations) and 2005 were not included due to fragmentary sampling.

Cluster analysis

A daily meteorological analysis was undertaken based on 96-h isosigma back-trajectories at 12:00h UTM and 1500m asl by using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) 4.0 dispersion model from the Air Resources Laboratory (ARL, available at http://www.arl.noaa.gov/ready/hysplit4.html, Draxler and Rolph, 2003). This height can be taken as representative of the mean transport wind at a synoptic scale within the upper boundary layer. The meteorological input was obtained from the ARL (Air Resources Laboratory) reanalysis database for the early 10-years monitoring period (1984-1993), and from FNL (1998-2004) and GDAS (Global Data Assimilation System) (2005-2009) from the NCEP (National Center for Environmental Prediction) for the most recent period (1998-2009).

Cluster analysis statistically aggregate observations into clusters such that each of them is as homogeneous as possible with respect to the clustering variables (Sharma, 1996). This clustering methodology was applied to daily trajectories for an early (1984-1993) and recent (1998-2009) period.

Our rain chemistry data base consisted on weekly observations but trajectories were obtained daily. We estimated a daily chemical concentration for the days with precipitation by proportionally correcting weekly chemical concentrations by the precipitation contribution of the rainy days to the weekly amount. The rainy days within each week and their precipitation amount were obtained from records at LC, and from the AEMET stations (Spanish Meteorological Service) of Turó de l'Home and Tagamanent which are 6.9 and 7.9 Km distant from LC, respectively. Precipitation events <3 mm were not included, and only the days with rainfall amount >0.02 mm were considered for the determination of rain days within a week.

The interpretation of the back trajectories was complemented with meteorological synoptic maps and the DREAM dust forecast model (http://www.bsc.es/projects/earthscience/DREAM).

Source-receptor model

Source-receptor methodologies establish relationships between a receptor point and the probable source areas by associating each chemical concentration value with its corresponding back-trajectory. Daily 00:00h and 12:00h UTC 72-h back-trajectories at 1500 m asl were

computed for rainy days in both study periods. A grid with 2601 cells of 1º x 1º latitude and longitude was superimposed on the integration trajectory field to map contributing areas.

The Seibert methodology (Seibert et al. 1994), whereby a logarithmic mean chemical concentration is computed for each grid cell based on the residence time of the trajectories in the cells, was used:

$$\log C_{ij} = \frac{\sum_{l} n_{ijl} \log C_l}{\sum_{l} n_{ijl}}$$

where Cij is the concentration in the cell (i,j), l is the index of the trajectory, n_{ijl} is the number of time steps of the trajectory l in the cell (i,j), and C_l is the chemical concentration measured at the receptor point corresponding to the trajectory l. To minimize the uncertainty of the trajectories, a smoothing was applied and the value of each cell was replaced by the average between the cell and its eight neighbouring cells. A final filter excluded cells with less than five end points. The abundance field map thus obtained reflects each cell contribution to the chemical rain concentration at the receptor point.

The Seibert's methodology and the PSCF were both computed and a sensitivity analysis to different factors was applied. Although the models were sensitive to all factors, the source areas obtained with both methods did not vary significantly and the Seibert's model was chosen for its wide use.

Results

General air flow transport patterns

Cluster analysis established 8 trajectory groups for both study periods (Fig 2; Table 1), which represented the general air flow pathways arriving at LC in terms of direction and wind speed at 1500m asl. Predominant transport regimes were similar in both study periods, and were classified in northern flows (cluster 1), north-western (cluster 2), western (clusters 3, 4), south-western (cluster 5), south-eastern (cluster 6) and regional recirculation (cluster 7). Exceptions were the fast-moving NW trajectories in 1984-1993 (cluster 8*a*) and north-eastern flows from central Europe in 1998-2009 (cluster 8*b*).

From Fig. 2 it can be seen that fast W flows contributed 7% in both periods, slow W flows decreased from 16% to 7%, whereas fast and moderate NW flows were about constant between study periods (16%-17%). The sum of Atlantic flows accounted for 39% and 31% of data in the early and recent period, respectively. North African transport increased slightly, due to the increase of SW flows (from 9% to 13%). Flows from Europe increased from 13% to 18%, this being related to a central Europe contribution (12% of data) which was absent in the earlier period. Regional recirculation contributed between 25-27% (Fig. 2).

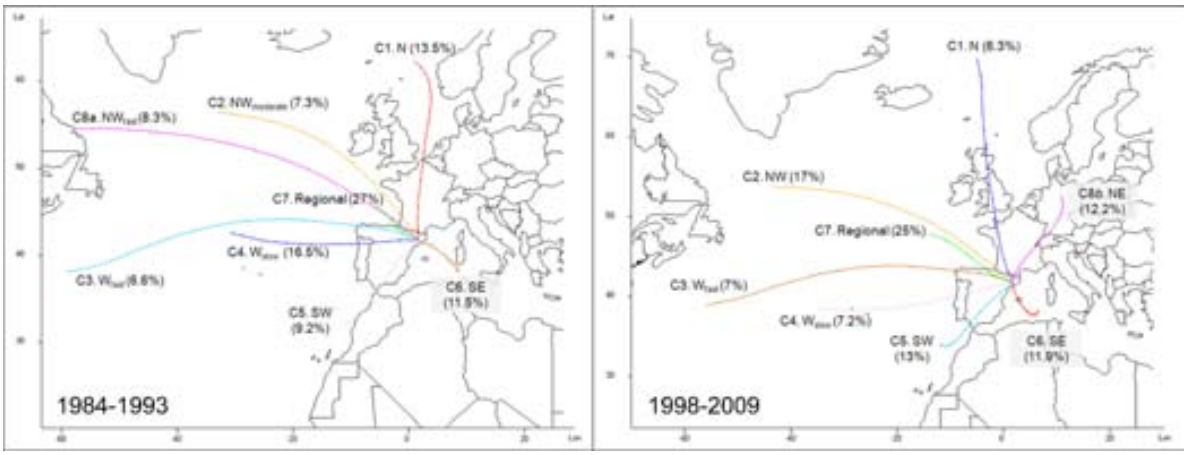


Figure 2. Cluster centroids and frequency of back-trajectories associated to each cluster at LC station for both study periods at 1500m asl.

Table 1. Seasonality of atmospheric transport regimes for early 10-years monitoring period (1984-1993) and the more recent one (1998-2009): frequency of back-trajectories associated to each cluster and frequency of clusters associated to each provenance (%). Winter: December-February, spring: March-May, summer: June-August and autumn: September-November.

Period 1984-1993						**Period 1998-2009**					
Cluster classification	N	Winter	Spring	Summer	Autumn	Cluster classification	N	Winter	Spring	Summer	Autumn
C1. N	492	16.5	16.0	10.7	10.8	C1. N	275	9.0	7.3	2.1	6.9
C2. NW_{fast}	303	12.5	8.8	4.7	7.3	C2. NW_{fast}	742	20.8	16.7	12.4	18.2
C3. W_{fast}	240	12.5	5.3	2.2	6.4	C3. W_{fast}	313	12.4	8.8	2.1	5.4
C4. W_{slow}	602	15.5	16.1	17.5	16.8	C4. W_{slow}	307	7.7	8.4	5.4	6.7
C5. SW	344	7.2	6.8	11.6	12.0	C5. SW	569	7.7	11.3	18.9	14.2
C6. SE	421	14.2	11.6	6.5	13.8	C6. SE	521	9.7	10.5	15.8	11.8
C7. Regional recirculation	985	17.1	26.1	38.6	25.9	C7. Regional recirculation	1106	17.2	23.1	35.4	25.6
C8*a*. $NW_{moderate}$	266	4.5	9.2	8.3	7.0	C8*b*. NE	532	15.5	14.0	8.0	11.3
Provenances						Provenances					
Atlantic (NW+W)	1411	45.1	39.5	32.6	37.5	Atlantic (NW+W)	1362	40.9	33.9	19.8	30.3
Europe (N)	492	16.5	16.0	10.7	10.8	Europe (N+NE)	807	24.5	21.3	10.1	18.2
North Africa (SW+SE)	765	21.4	18.5	18.2	25.8	North Africa (SW+SE)	1090	17.4	21.7	34.7	25.9
Regional - Local	985	17.1	26.1	38.6	25.9	Regional - Local	1106	17.2	23.1	35.4	25.6

Cluster occurrence by season is detailed in Table 1. The 8 back-trajectory clusters were grouped in four main geographic provenances: Atlantic (NW plus W air flows), European (N and NE), North African (SW and SE) and Regional-local. The Atlantic provenance dominated in all seasons (30-45%) except in summer when Regional circulations predominated (Table 1). The seasonal patterns for Atlantic and regional provenances were similar for the two study periods but the Atlantic contribution decreased in the recent period. European and North African provenances showed differences, e.g. a higher frequency of European flows in winter-spring (21-25%) and autumn (18%) in the recent period. North African flows increased in spring-summer recently (22-35%, Table 1).

Air flow transport pathways for rainy days

Cluster analysis was applied to the subset of only rainy days, and with data base seven main groups were obtained (Fig. 3). Transport regimes for rainy days were: northern (cluster 1), north-western (clusters 2 and 3), western (cluster 4), south-western (cluster 5), south-eastern (cluster 6) and western recirculation (WR, cluster 7), with a similar grouping for both study periods. Recirculation transport was the most frequent situation for rainy days, but it decreased from 27% to 21% between periods (Fig. 3). $Western_{fast}$ and south-eastern flows slightly decreased between periods (13 to 10% and 15 to 12%, respectively). Northern, $North\text{-}western_{fast}$ and South-western flows increased from 14 to 17%, 4 to 9% and 16 to 19%, respectively and $NW_{moderate}$ remained constant about 10% (Fig. 3).

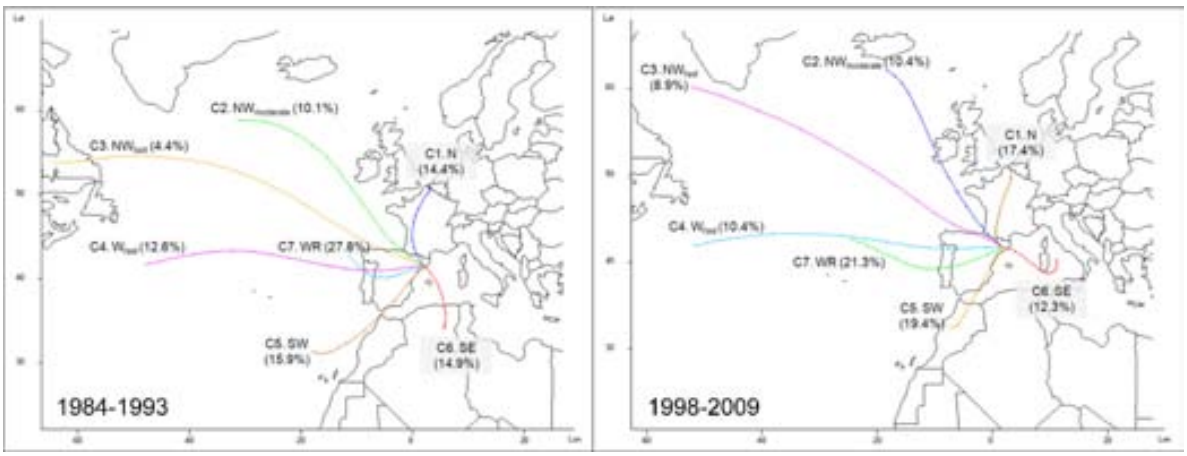


Figure 3. Cluster centroids and frequency of back-trajectories associated to each cluster for rainy days at LC station for both study periods at 1500m asl

Seasonal patterns for rain-day clusters are shown in Table 3, where a similar grouping for broad geographical areas as in the previous section has been applied. In agreement with the precipitation seasonal regime in the Mediterranean area, a higher occurrence of rainy days in spring and autumn was observed in the grand total, not changing between periods. Winter and spring precipitation originated predominantly from the Atlantic (30-36%), summer precipitation

from Europe (23-26%) and from regional recirculation (27-33%), and autumn precipitation was dominated by North African flows (38-49%).

Table 2. Seasonality of atmospheric transport regimes for rainy days in both study periods: frequency of back-trajectories associated to each cluster and frequency of clusters associated to each provenance (%). Winter: December-February, spring: March-May, summer: June-August and autumn: September-November.

Period 1984-1993						Period 1998-2009					
Cluster classification	N	Winter	Spring	Summer	Autumn	Cluster classification	N	Winter	Spring	Summer	Autumn
C1. N	101	9.8	22.5	25.9	11.4	C1. N	108	17.4	18.1	22.9	13.5
C2. $NW_{moderate}$	46	2.9	10.0	11.1	7.0	C2. $NW_{moderate}$	66	8.3	12.6	13.8	8.4
C3.NW_{fast}	25	6.9	6.0	2.8	1.9	C3.NW_{fast}	50	14.4	10.7	0.9	4.5
C4. W_{fast}	78	20.6	13.5	11.1	11.4	C4. W_{fast}	61	12.9	7.9	8.3	11.6
C5. SW	100	14.7	14.5	11.1	27.8	C5. SW	109	10.6	14.9	22.0	25.2
C6. SE	75	21.6	7.5	4.6	20.9	C6. SE	73	18.2	10.7	5.5	12.9
C7. WR	143	23.5	26.0	33.3	19.6	C7. WR	144	18.2	25.1	26.6	23.9
Provenances						Provenances					
Atlantic (NW+W)	149	30.4	29.5	25.0	20.3	Atlantic (NW+W)	177	35.6	31.2	22.9	24.5
Europe (N)	101	9.8	22.5	25.9	11.4	Europe (N+NE)	108	17.4	18.1	22.9	13.5
North Africa (SW+SE)	175	36.3	22.0	15.7	48.7	North Africa (SW+SE)	182	28.8	25.6	27.5	38.1
Regional - Local	143	23.5	26.0	33.3	19.6	Regional - Local	144	18.2	25.1	26.6	23.9
TOTAL	568	18.0	35.2	19.0	27.8	TOTAL	611	21.6	35.2	17.8	25.4

Association of rain chemical composition with transport pathways

The rain chemical composition that characterised each cluster for both study periods is presented in Table 3. The mean daily rain volume decreased from 14.8 mm in 1984-1993 to 10.0 mm in 1998-2009. The VWM concentrations were calculated as mean ion concentrations corrected for the precipitation amount (Table 3). The comparison of grand total VWMs for both study periods shows an increase of NO_3^- (22 to 31 μeqL^{-1}), NH_4^+ (23 to 29 μeqL^{-1}) and Ca^{2+} (60 to 65 μeqL^{-1}), and a decrease of SO_4^{2-} (47 to 33 μeqL^{-1}), H^+ (15 to 4.6 μeqL^{-1}) and Mg^{2+} (10 to 8.6 μeqL^{-1}) while Na^+ and Cl^- remained constant about 23 and 29 μeqL^{-1} respectively. The N and WR flows presented the highest H^+ in 1984-1993 (~20 μeqL^{-1}) while $NW_{moderate}$ the lowest (9.8 μeqL^{-1}). Notice that in the recent period the maximum H^+ concentrations per cluster (SE, 7.9 μeqL^{-1}) was lower than the lowest H^+ concentrations in the early period ($NW_{moderate}$, 9.7 μeqL^{-1}). Ammonium and NO_3^- showed maximum values in N-NW provenances for both periods. In the recent period concentrations from the SW were of similar magnitude. Sulphate also showed maximum concentrations for N flows and regional recirculations in the early period, but both decreased steeply (from 63 to 36, and 52 to 30 μeqL^{-1} respectively).

Table 3. The arithmetic mean of daily rain volume (mm) and volume-weighted mean (VWM) concentrations for the analysed chemical species (in μeq/L) and for each cluster in both study periods

1984-1993 period	Rain	N cations	N anions	H^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-
C1. N	8.9	101	101	20.0	15.4	60.0	10.1	37.8	32.0	63.5	20.8
C2. $NW_{moderate}$	10.9	46	46	9.7	19.1	46.8	8.5	23.5	21.5	41.6	23.9
C3*a*.NW_{fast}	9.0	25	25	13.1	21.5	80.7	11.3	30.7	23.3	53.5	25.9
C3*b.* NW_{fast} *modified*	9.4	22	22	13.5	19.4	49.7	9.6	32.3	22.9	47.8	23.4
C4. W_{fast}	12.9	78	78	14.9	18.8	49.5	9.2	24.5	20.5	45.9	24.4
C5. SW	16.9	100	100	11.0	29.3	87.3	11.8	18.6	20.8	46.6	36.1
C6. SE	26.2	75	75	12.2	27.4	58.5	10.1	14.7	15.1	36.6	34.3
C7. WR	14.9	143	143	20.4	20.2	46.2	9.9	27.0	25.5	51.8	26.0
Total	14.8	568	568	15.1	23.0	60.2	10.2	23.2	21.9	47.2	29.1
1998-2009 period											
C1. N	5.9	89	108	2.6	14.3	52.7	6.8	38.5	35.2	36.4	18.4
C2*a*. $NW_{moderate}$	5.6	55	66	2.4	46.1	119	16.0	34.4	44.2	46.9	54.2
C2*b*. $NW_{moderate}$ *modified*	4.4	43	54	3.7	21.6	55.2	8.7	41.3	42.3	37.5	25.1
C3. NW_{fast}	7.1	45	50	5.6	31.3	60.8	10.4	26.0	26.9	30.4	36.0
C4. W_{fast}	9.3	56	61	5.3	28.8	52.8	10.1	21.3	22.2	26.8	35.3
C5. SW	12.9	94	109	3.2	19.0	79.9	8.1	31.2	40.6	37.4	27.5
C6. SE	13.9	72	73	7.9	24.1	53.8	7.1	27.1	20.7	28.6	23.6
C7. WR	12.1	134	144	4.7	19.8	60.6	7.9	27.0	29.1	30.4	25.7
Total	10.0	545	611	4.6	22.9	65.9	8.6	29.0	31.1	33.0	28.3

Marine ions (Na^+, Cl^-, partly Mg^{2+}) presented high concentrations in southern and western flows, coming from the Mediterranean and Atlantic Ocean. Calcium presented high values in SW flows in both periods, but contrary to previous results at LC form Àvila and Alarcón (1999), also in NW_{fast} and $NW_{moderate}$. A closer look at those data showed that northern clusters were influenced by African mineral dust even if air flows were coming from the North Atlantic. For example, the episode sampled from 29/10/2008 to 5/11/2008 had a Ca^{2+} concentration of 176 μeqL^{-1} and a rain amount of 157mm. Three rainy days occurred within this sampling period (31st October and 1st and 2ndNovember) and back-trajectories for these rainy days were classified as NW and W, but these back-trajectories also crossed over Morocco and the southern IP (Fig. 4a). The synoptic meteorology from October 31st to November 2nd (Fig. 4b) shows that a low-pressure system was over the IP and a high-pressure system over the eastern Mediterranean triggering air masses from North Africa to South-eastern Spain and the Mediterranean. This is also seen in the DREAM dust model (Fig. 4b). If Ca^{2+} mean concentrations are recalculated for NW flows excluding the episodes with African influence, their values were about halved (Table 3, indicated as 'modified').

Long term trends in chemical composition of precipitation and source receptor model results

Regressions of annual precipitation and ion VWM concentrations against time at LC from 1983 to 2009 showed significant decreasing trends for H^+ and SO_4^{2-} ($p<0.01$) and an increasing trend for NO_3^- ($p<0.05$; Table 4), consistent with the comparison between periods outlined before. The rest of analyzed ions did not show significant trends.

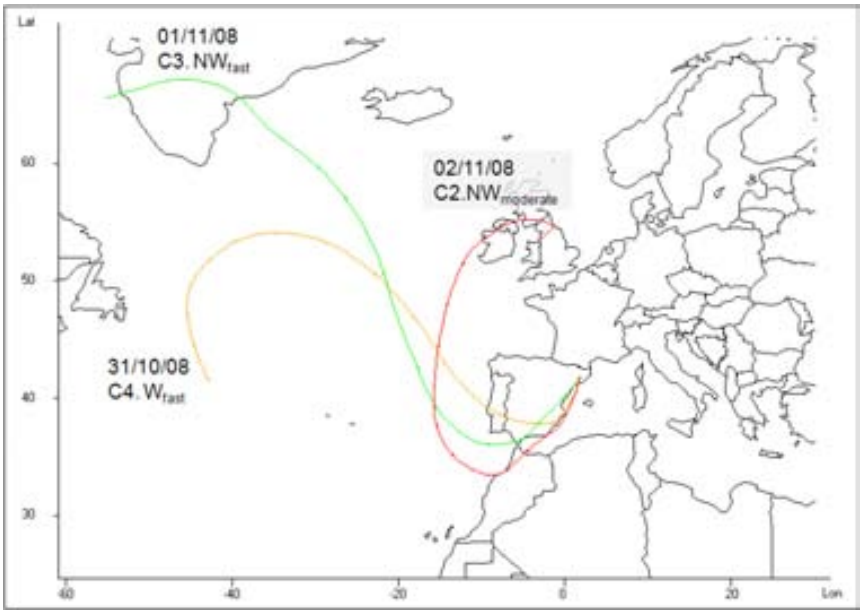
Table 4. Linear regressions (y=a+bx) of annual precipitation amount (mm) and annual VWM ion concentrations ($\mu eq\ L^{-1}$) in bulk precipitation samples at LC from 1983 to 2009 (no data from 2001, 2004 and 2005).

Linear regression	N	a	Std.Err.	b	Std.Err.	R^2	p
Precipitation	24	926	103	-5.68	6.94	0.029	0.42
H^+	24	17.8	1.50	-0.65	0.10	0.654	<0.01**
Na^+	24	20.4	2.44	0.13	0.16	0.029	0.43
Ca^{2+}	24	49.3	12.6	0.97	0.84	0.056	0.26
Mg^{2+}	24	9.5	1.00	-0.03	0.07	0.006	0.71
NH_4^+	24	22.3	3.22	0.24	0.22	0.052	0.28
NO_3^-	24	18.9	1.73	0.30	0.12	0.236	0.02*
SO_4^{2-}	24	52.1	2.61	-0.97	0.17	0.582	<0.01**
Cl^-	24	28.0	3.05	-0.03	0.20	0.001	0.88

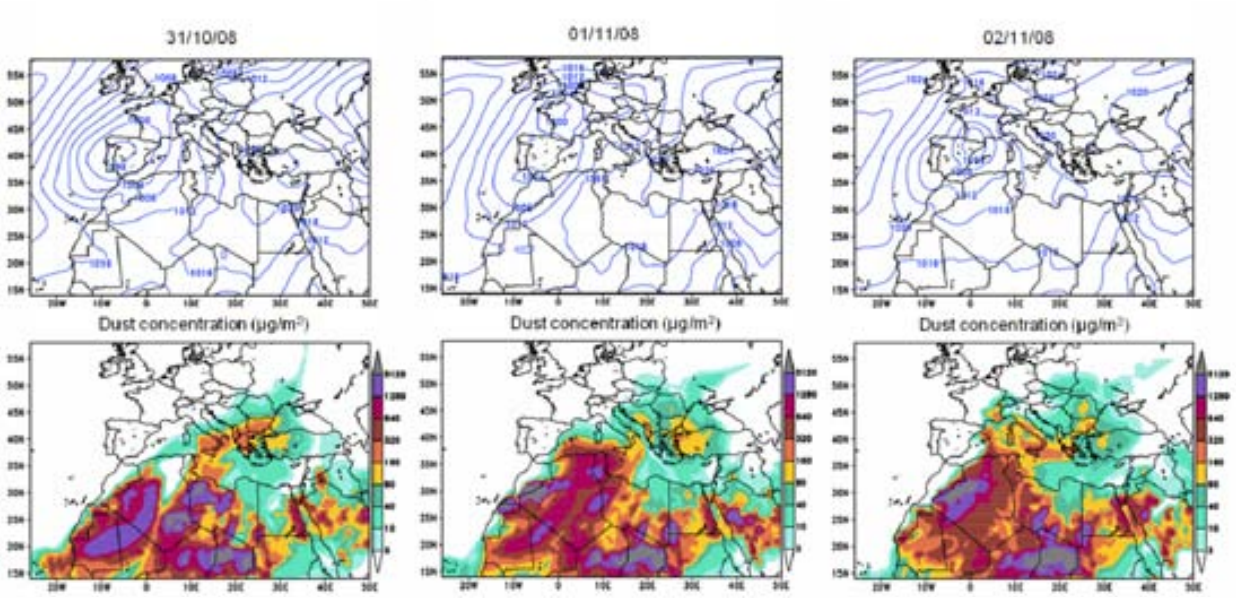
*p<0.05 **p<0.001

Figure 4. Study case of combined transport: episode from 29/10/2008 to 5/11/2008:

a) back-trajectories of rainy days and its cluster classification



b) synoptic and dream dust model maps for rainy days



A source receptor model was applied to the ions with significant trends (SO_4^{2-}, H^+ and NO_3^-). This model indicated that SO_4^{2-} and H^+ in the initial period were mostly originated in a broad area encompassing most central Europe (specifically NE France, Benelux, Germany and the North Sea; Fig. 5). For H^+, the same area plus an extension to western Poland, Switzerland and northern Italy was identified. The reduction of SO_4^{2-} and H^+ concentrations in precipitation at LC for the last two decades was matched with a dramatic reduction of these European source areas (Fig. 5). For NO_3^-, source areas in central Europe in the early period increased strikingly extending to the North Sea, northern France, eastern Germany, southern Poland, Austria and northern Italy (Fig. 5c).

Sulphate and nitrate, in addition to its European origin, also presented an African source which was mostly located in Western North Africa in the early period and in central Algeria in the recent one (Fig. 5a). The African source area of NO_3^- only appeared in the recent period and was situated in central Algeria (Fig. 5c).

Discussion

Atmospheric regimes and seasonal patterns

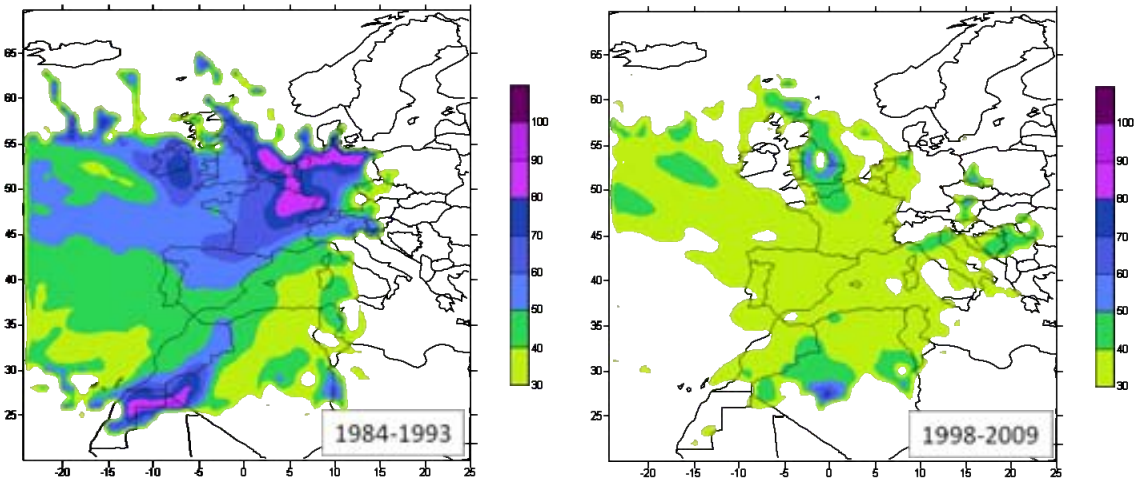
The fastest trajectories coming from the N, NW and W were more frequent in winter when the Azores high usually presents its lowest intensity and is frequently situated well to the West of its usual position to the South of the Azores, thus favouring the entry of Atlantic air masses to the Western Mediterranean. But in winter the Azores high can also move and reside for long periods of time closer to the IP resulting in the stagnation of air masses over the Peninsula (Millán et al. 1997). This may account for the 17% occurrence of regional recirculation in winter observed in this study.

In summer, the Azores high undergoes its highest intensity and is located to the East and North of its usual position, whereas thermal lows are developed over the IP and the Sahara (Millán et al. 1997). This accounts for the observed short trajectories with recirculation in the study region and African fluxes. Our results matched similar trajectory cluster analysis for aerosol transport in the IP (Jorba et al. 2004; Borge et al. 2007; Salvador et al. 2008) and more specifically with results at LC (Pérez et al. 2008, Pey et al. 2009).

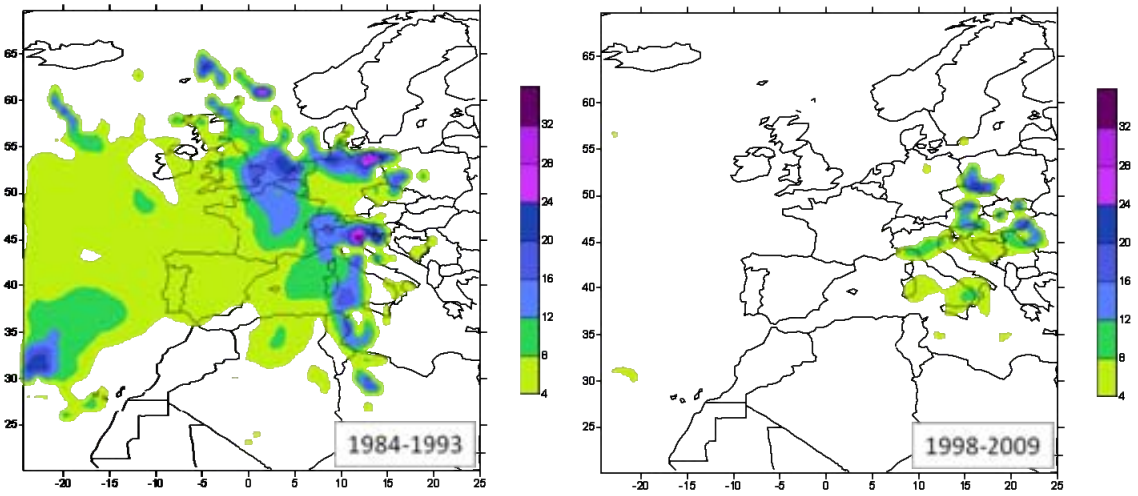
The seasonal analysis for rainy days indicated that precipitation in winter and spring originated mostly from the Atlantic, in autumn from North Africa and in summer, from Europe and the regional recirculation (Table 2). This was similar to previous classifications at LC based on meteorological synoptic maps and trajectory analysis (Àvila and Alarcón, 1999).

Figure 5. Source receptor concentrations maps (μeq L^{-1})

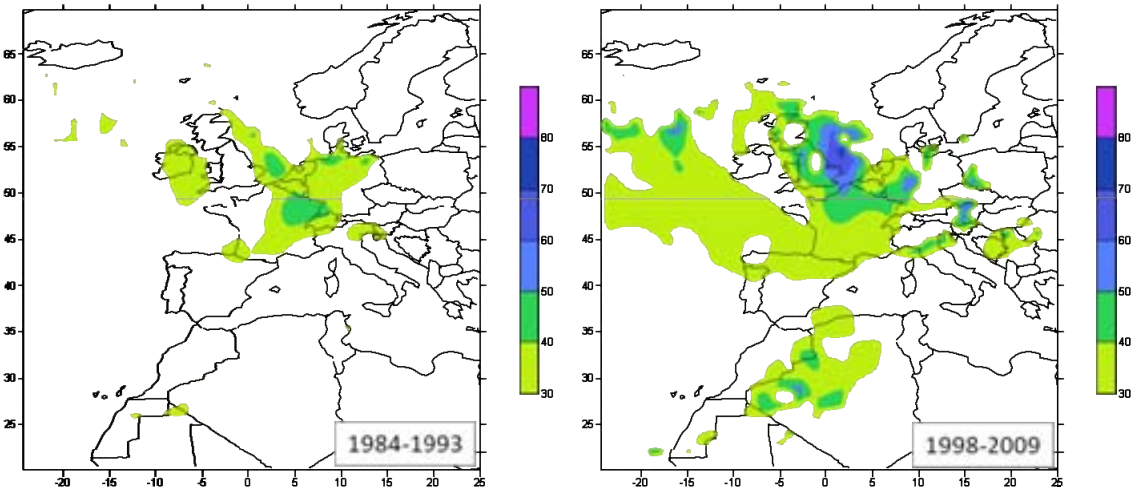
a) Sulphate (SO_4^{2-})



b) Hydrogen ion (H^+)



c) Nitrate (NO_3^-)



Decadal trends, air mass transport and potential source areas of precipitation chemical compounds

The simultaneous decline of SO_4^{2-} and H^+ concentrations observed from 1983 to 2009 at LC (Table 3) is an indication that acidic aerosols of sulphate (H_2SO_4, NH_4HSO_4) contributed to bulk deposition over NE Spain during the 1980s and 1990s (Àvila, 1996). This decline can be related with the general decrease of SO_2 emissions throughout Europe (~73%, from 1990-2009, EMEP, 2011) because northern fluxes coming from Europe showed an important decrease (from 63 to 36 μeqL^{-1}, Table 3). Previous classification for provenance at LC also showed the highest SO_4^{2-} and H^+ mean concentrations for European rains (103 and 41 μeqL^{-1}, respectively; Àvila and Alarcón, 1999). Concentration maps from the source-receptor model in the period 1984-1993 attributed SO_4^{2-} source areas to north-eastern France, Benelux, Germany and the North Sea (Fig. 5a), and almost the same area plus Poland, Austria, Switzerland, Slovenia and northern Italy for H^+ (Fig. 5b). These results partially agree with the flux maps from the EMEP database in 1989 that locate large SO_4^{2-} deposition fluxes (500-2000mol ha^{-1} yr^{-1}) in the Black Triangle (the area between Germany-Czeck Republic-Poland), Ukraine and former Yugoslavia (Van Leeuwen et al. 1996). Trajectories with low pH (<5.2) from this region also contained high SO_4^{2-} rain concentrations at several sites in France in the period 1992-1995 (Charron et al. 2000).

Our study, indicating the highest H^+ concentrations in SE flows (7.9 μeqL^{-1}) in the recent period along with source-model results, suggests that a shift has been produced in the transport of acidity from the north-central European area to eastern Europe and that concomitantly acidity transport has been drastically reduced.

However, and despite of European emissions on land being progressively abated, marine sources are increasing. The commercial shipping contribution has been estimated at 5-8% of global anthropogenic SO_2 emissions and 15-30% of global fossil fuel sourced NO_x emissions (Eyring et al. 2005). Estimates of SO_2 and NO_x emissions from international shipping suggest a 2.5% annual increase related to increased maritime traffic and lower restrictions on ship fuels (Endresen et al. 2003). In the Mediterranean, ship exhausts have been reported to generate high levels of SO_4^{2-} aerosols (Salvador et al. 2010) and it has also been shown that 54% of total SO_4^{2-} column burden in summer was originated from ship emissions (Marmer and Langmann, 2005). In the North Sea, the area around Rotterdam and Hamburg is one of the highest ship traffic in the world. Consequently, northern Germany and Denmark in summer, when NO_2 and SO_2 is more efficiently oxidized by the increase of photochemical activity, suffer a 50% increase of SO_4^{2-}, NO_3^- and NH_4^+ aerosol concentrations due to ship emissions (Matthias et al. 2010). The implementation of a sulphur emission control area (SECA) in the North Sea at the end of 2007 showed directly results in reduced SO_2 and SO_4^{2-} aerosol concentrations while NO_3^- concentrations slightly increased in the North Sea coastal areas (Matthias et al. 2010). In our study, the high SO_4^{2-} concentrations from N and $NW_{moderate}$ clusters and the SO_4^{2-} source area over the North Sea may be related with SO_2 emissions from shipping.

The significant increase of NO_3^- concentrations in bulk precipitation at LC (Table 4) has also been observed at other sites in NE Spain (Àvila et al. 2010) and was linked to a general increase of Spanish NO_x emissions, and to site-specific changes such as increase in local population and industrial activity. However, long-range transport from Europe also affected LC NO_3^- rain concentrations, as shown by Àvila and Alarcón (1999). Aerosol NO_3^- from local scale and long-range transport from central and Eastern Europe was also identified in NW Spain (Salvador et al. 2007). Our study was consistent in that the highest NO_3^- rain concentrations were found in northern and regional air flows (Table 3), which corresponded with European and local origins. The source-receptor model indicated NO_3^- long-range transport from North-France, West-Germany and Switzerland in the early period (Fig. 5c). Other studies have also reported large NO_3^- fluxes from Central Europe: e.g. the highest NO_3^- rain concentrations observed at France resulted from air masses which had crossed a region comprising northern France, Belgium, The Netherlands and northern Germany (Charron et al. 2000). In the recent period, high NO_3^- concentrations were found in N (35 μeqL^{-1}) and $NW_{moderate}$ (cluster 2*b*; 42 μeqL^{-1}) air flows and the source map indicated an expansion of source areas to the North Sea, British Islands, northern France, eastern Germany, southern Poland, Austria and northern Italy (Fig. 5c). These continental source areas corresponded quite well with the main European NO_x emission sources according to satellite measurements and the EMEP emission inventory (WMO, 2004). However, NO_3^- source areas located on the North Sea and central Europe can also be related to NO_3^- emissions from maritime traffic as explained above.

On the other hand, large recent SO_2 emission reductions in Europe have played an important role in modifying nitrate aerosol concentrations through a relatively larger formation of NH_4NO_3 aerosols as less gaseous NH_3 is being converted to sulphate aerosols (NH_4HSO_4, $(NH_4)_2SO_4$). Since atmospheric ammonia is first used to neutralize sulphate to form ammonium sulphate aerosol, particulate nitrate can only be formed if excess ammonia is available. As a result, over large parts of Europe, nitrate aerosol concentrations are predicted to be more than 25% higher than they would have been if SO_2 emissions had not been reduced. This effect has been especially large in Central and East Europe (Fagerli and Aas, 2008). Ammonium aerosols resulting from NH_3 combination with sulphuric and nitric acids are transported over several thousand kilometres (Hov and Hjollo, 1994), therefore the increase of ammonium-nitrate aerosols concentrations in Europe, which are capable of being transported over long distances, could contribute to the increase of NO_3^- concentration in precipitation at LC.

North Africa is one of the largest sources of mineral dust in the world (Prospero 1996). Several studies have already shown that African dust pulses affect the rain chemical composition over the Mediterranean basin (e.g. Loÿe-Pilot et al. 1986; Rodà et al. 1993; Àvila and Alarcon, 1999). The so-called “red-rains” are characterised by very high pH values and calcium contents (Loÿe-Pilot et al. 1986; Àvila et al. 1997). In addition, Mg^{2+} and SO_4^{2-} can be partially attributed to the dissolution of dolomite (CaMgCO3) and calcium sulphate present in African mineral dust (Guerzoni et al. 1997). The meteorological scenarios of dust transport from North Africa to the

IP have been classified by Escudero et al. (2005) as: North Africa High Located at Surface Level (NAH-S), Atlantic Depression (AD), North African Depression (NAD) and North African High Located at Upper Levels (NAH-A). South-western air flows in our study could be associated to AD, NAD and NAH-A dust outbreak scenarios. By contrast, the NAH-S scenario could explain the episodes that have been defined as marine by the clustering technique but have African chemical characteristics (Fig. 4) such as high Ca^{2+}, Mg^{2+} and SO_4^{2-} (Table 3).

Source receptor maps show high SO_4^{2-} coming from North Africa (Fig.5a). Natural sources from North African gypsum soils and salt-lakes (Caquineau et al. 1998; Prospero et al. 2002) may account for this, but also an anthropogenic source cannot be ruled out since several studies indicate that dust readily reacts with and incorporate anthropogenic aerosols (Lelieveld et al. 2002; Guieu et al. 2002). Additionally, the formation of secondary coarse $NaNO_3$ and $Ca(NO_3)_2$ aerosols originating from the interaction of HNO_3 and sea salts and calcite ($CaCO_3$) during warm periods when NH_4NO_3 is thermically unstable (Pakkanen, 1996; Querol et al. 1998) may also contribute. Thus the SO_4^{2-} and NO_3^- source areas observed in North Africa (Fig. 5a, 5c) may be related to a mix of natural and anthropogenic sources, comprising emissions from the IP, North African countries and maritime traffic in the Mediterranean.

Conclusions

Back-trajectory clustering showed a decrease of Atlantic advections and an increase of African and European air flows. Precipitation in winter and spring was predominantly originated from the Atlantic, in autumn from North Africa and in summer, European and regional recirculation flows contributed similarly.

Back trajectory clusters and a source-receptor model indicated that NE Spain is under the influence of natural and anthropogenic sources from the local scale and long-range transport. A significant decrease of SO_4^{2-} and H^+ and an increase of NO_3^- over time was observed. The source-receptor model indicated that in the initial period (1984-1993) these pollutants were mostly originated in central and eastern Europe. The reduction of SO_4^{2-} and H^+ concentrations in precipitation at LC for the last two decades was matched with a dramatic reduction of these European source areas, as also from local emissions, and a shift towards Eastern Europe was observed. For NO_3^-, initial source areas in central Europe were extended towards the North Sea, northern France, eastern Germany, southern Poland, Austria and northern Italy in the recent one. European policies for the abatement of sulphur emissions have resulted in significant temporal decreases of SO_4^{2-} and H^+ in precipitation collected at Montseny. However, the increase of emissions from ships and the industrialisation of countries in Eastern Europe and North Africa probably explained the location of pollutants main source areas (North Sea, Eastern Europe and North Africa) in the recent period (1998-2009).

Acknowledgements

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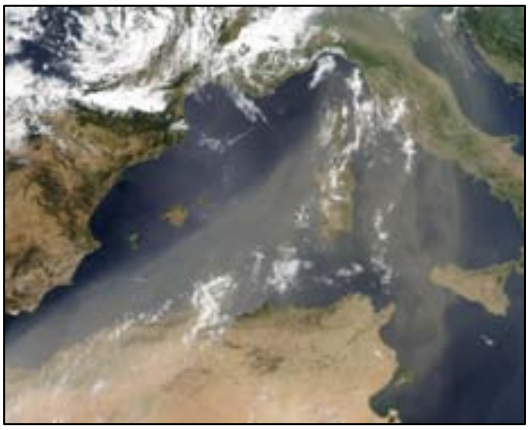
Chapter 4



Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its role in marine productivity

Izquierdo R., Benítez-Nelson C.R., Masqué P., Castillo S., Alastuey A. and Àvila A. 2012. Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its role in marine productivity. Atmospheric Environment 49, 361-370. Doi:Doi:10.1016/j.atmosenv.2011.11.007

Abstract

In this study, African red-rains were collected at Montseny (NE Spain) on a weekly basis and analyzed for total particulate phosphorus (TPP), total dissolved P (TDP) and soluble reactive P (SRP) for the period 1996-2008. Wet and dry weekly deposition of TPP was analyzed for all provenances in 2002-2003. In this period, African sources were found to contribute 66% of the 576 μmols m^{-2} y^{-1} of total particulate phosphorus (TPP) deposited in Montseny, split almost evenly between dry and wet deposition. Measurement of this dry deposition further allowed a direct determination of deposition velocity (V_d), which suggested significant depositional differences between African (V_d = 3.1 ± 0.80 cm s^{-1}) and non-African events (V_d = 1.07 ± 0.13 cm s^{-1}). Measurement of TDP concentrations during the African rains suggests a solubility of 11.2% TPP. SRP solubility was lower (2.2%), highlighting the importance of understanding the composition of the atmospherically derived P component. Samples were collected 25 km from the Mediterranean coast and were assumed to represent the atmospheric P input to coastal waters. On an annual basis, atmospheric-derived soluble P contributed < 1% of annual new primary production in the western Mediterranean. However, one strong African dust event (22-27 May, 2008) accounted for 24-33 % of the atmospheric P-induced annual new production. These results highlight the potential biogeochemical importance of seasonality, source, and composition of aerosols deposited in the Western Mediterranean Sea.

Introduction

Phosphorus (P) is a fundamental component of all living organisms and a limiting factor for primary production in both marine and terrestrial ecosystems (Schlesinger, 1997; Chadwick et al. 1999; Wu et al. 2000; Mills et al. 2004). Unlike the cycling of other biologically essential elements such as carbon (C) and nitrogen (N), P does not have a stable gaseous phase in oxygenated environments (Benitez-Nelson, 2000). As such, the only natural sources of new P to oceanic waters are via atmospheric deposition and riverine discharge (e.g. Benitez-Nelson, 2000; Mahowald et al. 2008).

The Mediterranean Sea is one of the most oligotrophic marine ecosystems in the world (Béthoux et al. 1998). During summer, both phytoplankton and bacterial production are P limited due to N/P ratios much higher than Redfield ratios and the lack of nutrient supply from deep waters due to stratification (Thingstad and Razzoulzadegan, 1995; Vaulot et al. 1996; Thingstad et al. 1998). Dissolution of atmospheric particles rich in P-containing minerals may therefore influence biological production, with dissolution rates affected by a range of factors, such as particle composition, grain size, and surrounding solution characteristics (Colin et al. 1990; Guieu et al. 1997; Ridame and Guieu, 2002). Several studies have shown episodic summer phytoplankton blooms in the Mediterranean in response to nutrient inputs (N, P) from the atmosphere (Migon and Sandroni, 1999; Herut et al. 1999, 2002; Ridame and Guieu, 2002).

The Mediterranean is strongly impacted by Saharan events loaded with mineral dust. This dust deposition averages around ~ 5-12 tons km^{-2} y^{-1} to the western Mediterranean Sea (Löye-Pilot and Martin, 1996; Àvila et al. 1997, 2007) which represents a P contribution of ~132-317 µmols m^{-2} y^{-1}, assuming a total P concentration in the Saharan end-member of 0.082% (Guieu et al. 2002). African dust intrusions further have a marked seasonality, with higher frequency between March and October (Guerzoni et al. 1997; Querol et al. 1998; Escudero et al. 2005; Pérez et al. 2008).

The Mediterranean basin is also strongly influenced by anthropogenic sources from vehicle traffic, and industrial and domestic activities (Migon and Sandroni, 1999), including biomass burning (Guieu et al. 2005). In the Western Mediterranean high atmospheric pressures in summer prevent air renewal and allow a regional accumulation of pollutants (Querol et al. 1998). Precipitation is also lower in summer leading to a higher buildup of locally or regionally resuspended particulate matter (PM) resulting from the dryness of soils.

Several studies have provided contrasting estimates on the relative role of dry *vs.* wet deposition in the Mediterranean region (Markaki et al. 2003; Morales-Baquero et al. 2006; Guieu et al. 2010). For P, wet deposition has been reported as the main source of dissolved P to the western Mediterranean (Ridame and Guieu, 2002; Ternon et al. 2010), though other studies have shown that phosphate is readily leached from dry fallout (Migon et al. 2001; Herut et al. 2002, 2005; Carbo et al. 2005). Differences in the contribution wet /dry are likely due to

the type of pollutant (anthropogenic *vs.* mineral dust) and to the local weather regime (annual rainfall and the frequency and magnitude of African outbreaks), but more research is needed for a deeper understanding of such depositional processes in this system.

Bioavailable forms of P (dissolved phosphate inputs) dominate in rainwater (Ridame and Guieu, 2002); therefore the wet deposition mode is often assumed to provide most of the readily available nutrients. This rainwater, however, includes both dissolved and particulate forms. Experimental dissolution of loess in seawater produced P dissolution rates of 8 to 11% of the total P in the sample (Lepple, 1975; quoted in Graham and Duce, 1979; Herut et al. 1999). In seawater-leached aerosol samples collected in Israel, P solubility was between 22-25 and 45-73% (Herut et al. 2002, 2005; Carbo et al. 2005). Ridame and Guieu (2002) found that the %P dissolved from Saharan dust was inversely related to particle concentration for equal water contact time. Rain pH may also influence the dissolution rate, with enhanced dissolution at low pH, generally occurring with polluted rains (Ridame and Guieu, 2002; Markaki et al. 2003). African rains are alkaline and particle-loaded, thus less soluble, but they may dominate as a source of bioavailable P due to their high dust loads.

In order to better understand the effects of P deposition on the western Mediterranean Sea, it is important to determine its deposition pathways (wet *vs.* dry). Direct measurements of the dry deposition flux are needed, since P dry fallout has often been obtained from the product of aerosol concentrations and a deposition velocity value from the literature instead of measuring the flux directly. Another point of interest in the western Mediterranean is to determine the relative contribution of African P deposition relative to non-African, background episodes. Previous studies have found that African wet episodes occurred only 3% of the time annually, while African dry episodes amounted to 15% (Escudero et al. 2005). For wet events, acidity was higher in non-African events (Àvila and Alarcón, 1999), so differential P dissolution depending on air mass trajectory is expected.

The goal of this study is to add to existing knowledge on P deposition to the western Mediterranean Sea by better constraining the sources, magnitude and modes of atmospheric inputs. This has been accomplished by analysing aerosol concentrations and wet and dry deposition fluxes from 2002-2003 in a site in NE Spain close to the coast. Because of the important contribution of African sources and the well known interannual variability of African outbreaks, a long term record (1996-2008) of Saharan bulk weekly samples was also analyzed to determine the potential impact of high P deposition events on the biogeochemistry of the western Mediterranean.

Material and methods

Study site

Atmospheric aerosol concentrations and wet and dry deposition were sampled weekly from March 2002 to December 2003. Sampling was conducted at La Castanya (LC, 41º46'N, 2º21'E, 700 m above sea level), a long-term biogeochemical study site located in the Montseny mountains of the Pre-litoral Catalan Range (Rodà et al. 1999). The site is amidst an extensive holm-oak (*Quercus ilex* L.) forest in Montseny Natural Park, 40 km to the N-NE of Barcelona and 25 km from the Mediterranean coast. Since 2002, this site has been instrumented as a background regional air quality site (EUSAAR network-European Supersites for Atmospheric Aerosol Research, http://www.eusaar.net).

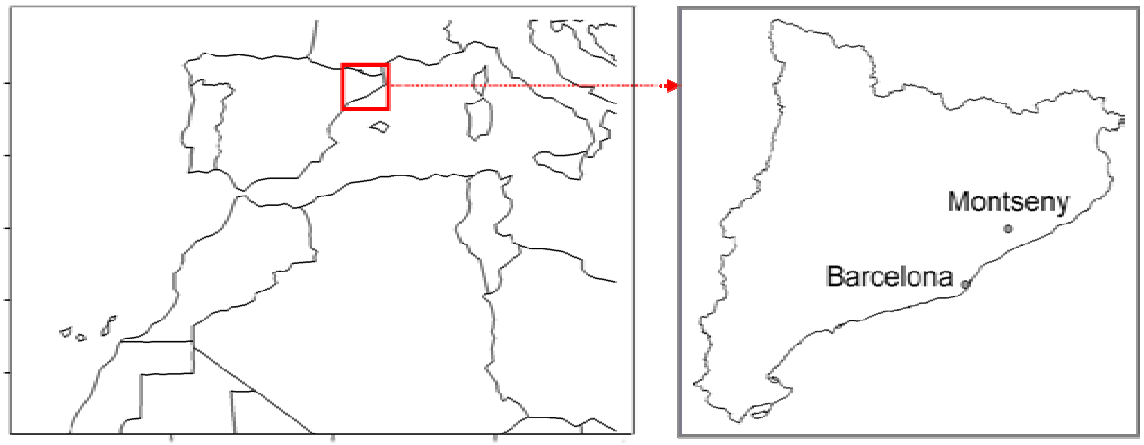


Figure 1. Map of Montseny study site, northeastern Spain.

The record from LC is taken to be broadly representative of deposition fluxes over the NW Mediterranean due to the large-scale of dust transport (scale of hundreds to thousands of km, Lawrance and Neff, 2009). This presumption is confirmed by the very close correspondence between the African dust events recorded at Montseny and Mallorca (Balearic Islands) from 1984 to 2003, with records of simultaneous African red-rains (rains containing a reddish silty residue from desert dust) in 71% of the cases (Fiol et al. 2005; Àvila et al. 2007). Moreover, it is generally accepted that elemental fluxes measured at a coastal site can be extended to regional open waters (Migon et al. 2001; Herut et al. 2002; Guieu et al. 2010; Koçak et al. 2010).

Sampling and definitions

Total suspended particles (TSP) were collected with a high volume sampler (DIGITEL DHA-80) at an air flow rate of 30 m^3 h^{-1}. Two consecutive daily filters (quartz fiber, QF20 Schleicher and Schuell) were obtained each week, resulting in a total of 151 filters collected between March 2002 and December 2003. From July 2002 to December 2003, weekly wet and dry deposition samples were collected at LC using a dry/wet deposition collector (ESM Andersen instruments,

G78-1001), consisting of two buckets (28cm-diameter; 30cm-depth) and a shifting lid which covers the wet collector during dry periods and the dry bucket as rain starts. A data logger keeps a record of the number and timing of the rain events. It should be noted that there is no well-established technique for dry deposition determination. Previous studies have shown that in some cases, dry dust deposition may in fact be the result of deposition conveyed by a few water droplets that are later evaporated, thus confounding the distinction between dry and the wet deposition modes (Löye-Pilot and Martin, 1996). In our study, we consider this effect to be small, as dry deposition weeks were cross checked with the rain record of a co-located rain gauge. However, a more careful study is needed to ascertain the importance of these very small rain events that may even remain unregistered in current rain gauges. In spite of these limitations, the instrumentation and procedures used herein has been widely used around the Mediterranean (Özsoy and Saydam, 2001; Ballestrini et al. 2002; Morales-Baquero et al. 2006).

From January 1996 to December 2008 (except 2002-2003), bulk deposition samples were also collected weekly at LC. From this record, only the weeks containing red rains (rains that left a reddish dusty residue on rainwater collectors) are considered. Rainfall was collected in 4 (1996-1997) or 2 (1998-2008) bulk deposition collectors placed 1.5 m above the ground, each consisting of a 19-cm diameter-polyethylene funnel with a nylon stopper in the neck connected by a Tygon looping tube to a 10-L polyethylene bottle. At each sampling date, bulk deposition collectors were replaced by a clean sampling kit. Cleaning procedures for funnels, tubes and buckets for bulk, wet and dry deposition included repeated washes of all the material with deionized distilled water until electrical conductivity of the rinse was ~ 1 μS cm^{-1}.

Dry deposition samples were recovered by washing the dry bucket with 250 ml of distilled deionized water and gently brushing the bucket walls with a clean plastic brush to free adhered particles. Prior to recovery, the sample bucket was carefully scrutinized for the presence of small vegetative debris or insects, and if present, they were removed with clean tweezers. All liquid samples (bulk deposition, wet and dry deposition) were taken to the CREAF laboratory and were subject of previously described protocols (Àvila, 1996; Àvila and Rodà, 2002). Within the lapse of 48h, samples were filtered through 0.45-μm pore size cellulose acetate Millipore filters to separate insoluble and soluble material. Prior to filtration, samples were stored at 4ºC in the dark; after filtration soluble samples were frozen (-20ºC) and filters were dried at 100ºC for one hour and later stored in a dessicator. Samples were agitated for 0.5 - 1 min before filtration such that soluble and insoluble (half filter) aliquots are considered to be representative of the entire sample. Particulate P retained on the 0.45-μm filters is here defined as TPP (total particulate P). The dissolved fraction has been analyzed for total dissolved P (TDP) and for soluble reactive P (SRP). For the period 1996 to 2008 TPP, TDP and SRP were analyzed for the main African rains (29 samples). For 2002-2003 only TPP was analyzed, for all wet (47) and dry (65) samples. Table 1 summarizes the variables and periods reported in this study.

Table 1. Measurements, sample provenances and variables studied at La Castanya (LC), Montseny (NE Spain) for the different sampling periods.

Sampling	Measurements	Provenances	Variable	N (weeks)
March 2002 - Dec.2003 July 2002 - Dec.2003 July 2002 - Dec.2003	Aerosol (TSP) Wet deposition Dry deposition	All	TPP	151 45 65
1996-2008	Bulk deposition	African	SRP TDP TPP	29

Analytical methodology

TSP filters and bulk, wet and dry deposition filters

TSP mass concentrations were determined by standard gravimetric procedures (Querol et al. 2001). For deposition, a known volume of bulk, wet or dry solutions was filtered on pre-weighed filters and re-weighed after drying at 100ºC for 1 hour (plus 30 min rest in a desiccator). All filters received the same treatment, with half of each filter digested in closed PFA reactors with HNO_3:$HClO_4$:HF at 90°C. The acidic solution was allowed to cool and was then dried on a hot plate at 200^{o}C. The dry residue was re-dissolved in 2 mL of HNO_3 and subsequently diluted to a volume of 25 mL. The contents of major elements and some trace, including P, were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectometry; IRIS Advantage TJA Solutions, THERMO) at the IDAEA-CSIC laboratory. During all analytical runs, blank values corresponding to blank Millipore filters (mean TPP concentration of blanks=0.0004 µmol L^{-1}; min=0.0002 µmol L^{-1} and max=0.0009 µmol L^{-1}; n=8) were subtracted from measured concentrations. Certified reference materials (1633b, and reference samples SO-1-dust, MAG-1-marine mud) were run throughout the different analytical runs. Accuracy was 8-10% of certified values which ranged between 0.23 and 1.0% P concentration. Repeated replicate analysis demonstrated precision within 10%.

Wet and dry soluble P

At the Radiobiogeochemistry Laboratory of the University of South Carolina, TDP and SRP were analyzed in 40 African rain samples representing 29 weeks of deposition, and including replicate field samples (from 2-4 replicated collectors) of 9 weekly rain samples. Rain samples from Montseny were introduced in 10 ml vials, packed in Styrofoam boxes with ice packs and sent frozen by express air-mail. SRP and TDP concentrations in filtered samples were determined using the methods described by Koroleff (1983) and Monaghan and Ruttenberg (1999), respectively. The latter method includes combustion at 500ºC to convert all the organic P into inorganic P prior to spectrophotometric analysis. Dissolved organic P (DOP) is subsequently determined by difference (TDP-SRP=DOP). SRP and DOP are operationally

defined terms, presumed to be dominated by inorganic (PO_4^{3-}) and organic P, respectively. Detection limits were 0.04 μmol L^{-1}, defined as three times the standard deviation of the blanks. Field replicate analyses agreed to within 5% of each other. When replicated samples differed by more than 0.2 μmol L^{-1}, only the lowest value was retained in the data set. For 9 events, replicate samples were analysed for TDP, with very good reproducibility (mean of s.d = 0.083 μmol L^{-1}). Through linear regression analysis of TDP with K^+ and NH_4^+ (used as indicators of biogenic contamination; Tsukuda et al. 2004) two samples were identified as contaminated and excluded.

Classification of provenances

Synoptic maps and HYSPLIT back trajectories from the Air Resources Laboratory (available at http://www.arl.noaa.gov/ready/hysplit4.html, Draxler and Rolph, 2003) were used to classify African *vs.* non-African provenances. Back trajectories were computed in the vertical velocity model (starting point at 12 UTC from LC coordinates run backwards for 144 h) at 750, 1500 and 2500 m asl Identification of African dust outbreaks was complemented by satellite images (SeaWifs) and dust forecast models (DREAM, http://www.bsc.es/projects/earthscience/DREAM; SKIRON, http://forecast.uoa.gr/) and satellite information (MODIS, http://rapidfire.sci.gsfc.nasa.gov/; TOMS AI Index, http://toms.gsfc.nasa.gov/). To classify a weekly sample as being from an African provenance, the day (or days) of precipitation within the weekly bulk or wet deposition sample were identified and back trajectories, satellite images, dust models and atmospheric synoptic patterns were screened for the rain days. The week was considered “African” when all of the combined evidence suggested an African outbreak. For dry deposition, different air mass provenances may contribute to the particulates deposited within a week, and here it is more probable that some mixing occurred. These weeks were classified as African if at least one African intrusion lasting for 2-4 days determined by back trajectories, satellite images, dust models and synoptic patterns occurred within the week long period. Synoptic patterns associated with African intrusions were identified as described in Escudero et al. (2005).

Statistical analyses

Linear regression and correlation analysis, and ANOVA (pair-wise post-hoc comparisons with the Tukey test) were computed with Statistica™. ANOVA analysis is used to show the effect of an independent variable or factor (here, season) on a continuous dependent variable (here, deposition fluxes) when independent variables are nominal. Post-hoc testing is specifically designed to make many comparisons among the groups of means determined by the factor of interest.

To give an indication of the uncertainty of the mean, arithmetic means are accompanied by ± standard error.

Temporal aerosol concentrations and deposition values revealed a seasonal trend which was modelled as:

$$Y_i = a_0 + a\ B \cos (2 + \pi/365\ t + \phi) \qquad \text{(equation 1)}$$

where Y_i is the TPP concentration, a_0 is a constant, a is the coefficient of the periodic term, ϕ stands for its phase in radians and t is the number of days lapsed. This model has two components: one is a constant coefficient (a_0) that gives the mean aerosol concentration for the whole studied period, and the other is a cosine term with a period of 365 days which accounts for the seasonal variation observed in the data. The presence of the cosine term required the use of nonlinear regression techniques (Levenberg-Marquardt algorithm built-in STATISTICA^{TM}) to adjust the model to the observations.

Results

Aerosol composition and concentrations

Aerosol TPP concentrations were correlated with the mass of suspended particles (TPP=4.64+0.74TSP, r=0.67; *p*< 0.001, with TPP in nmols m^{-3} and TSP in mg m^{-3}). African events contained the highest TSP and TPP concentrations (Fig. 2). TSP in Montseny is mainly crustal-derived (27% of total mass) as shown by apportionment analysis (Pey et al. 2009).

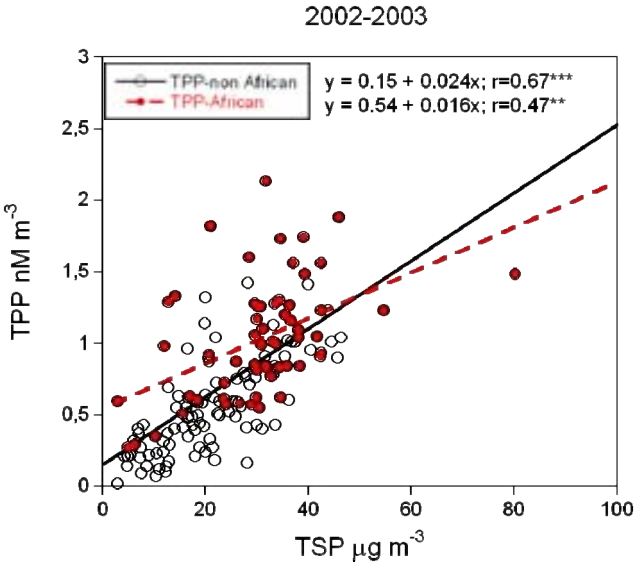


Figure 2. Aerosol total particulate phosphorus (TPP) plotted against Total Suspended Particles (TSP). Regression lines for African (filled dots) and non-African (white dots) are also shown.
*** indicates significance of regression p<0.001 and ** indicates p<0.01.

High correlations were found in TSP between P and Al, Ca, Mg and Fe (correlation coefficient between 0.71 and 0.74), consistent with the crustal P origin. High correlation was also found between P and organic carbon (OC, r=0.74) indicating also a biogenic/biomass burning source. Potassium, which represents a mixture of crustal and biogenic sources presented the highest correlation with P (r=0.83). This again suggests that atmospheric P is derived from a mixture of sources (crustal, biogenic and biomass burning).

Aluminium is often used as indicator of the crustal origin of aerosols, and for Saharan aerosols a P/Al ratio of 0.013 has been reported (Guieu et al. 2002). Excess P concentration relative to P/Al in the Saharan dust end-member is assumed to represent the fraction of P derived from anthropogenic activities. At Montseny, P was significantly correlated with Al. A considerable overlap was found between African and non-African sources so that the respective regressions were not significantly different (Fig. 3). This may indicate that African dust interacts with anthropogenic derived pollutants, producing a mixing of mineral dust with industrial emissions and biomass burning. However, the mean P/Al ratio for non-African events was higher than for African (0.11±0.021 *vs.* 0.04±0.030) and the % anthropogenic contribution for non-African events (73.4±1.7) was significantly higher than for African (58.5±2.45; $p<0.05$). The anthropogenic contribution for all samples was inversely related to TSP levels (r= -0.40; $p<0.01$).

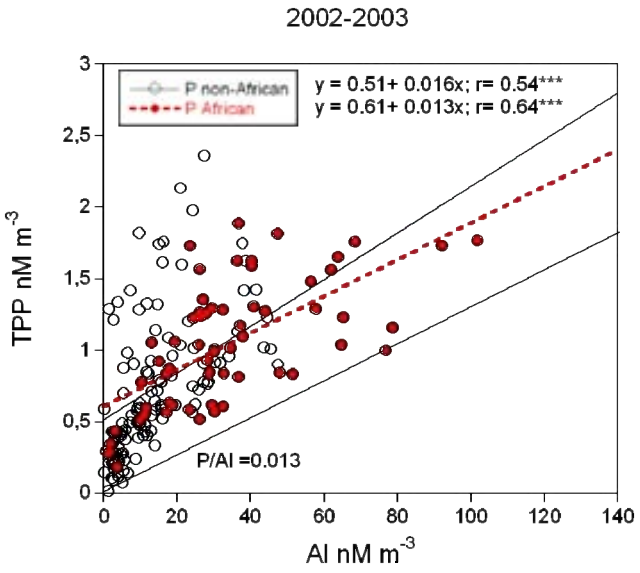


Figure 3. Aerosol total particulate phosphorus (TPP) concentrations plotted against Al concentrations (in nM m^{-3}).

Mean TSP levels at Montseny in the period March 2002 – December 2003 were 24.7±0.99 µg m^{-3}, ranging from 3 to 80 µg m^{-3} (Table 2). Mean TPP concentration in TSP-aerosols was 0.74±0.035 nmols m^{-3} (range: 0.016-2.13 nmols m^{-3}, Table 2). There was a marked seasonal pattern for the particulates and their TPP content, with minimum concentrations in winter and higher values in summer (Fig. 4). Spring and early summer of year 2003 were highly affected by African intrusions; this seasonality is usual, but year 2003 was specially affected. The summer

of 2003 was affected by high pressures over Europe, which induced a heat wave in Western Europe from June to August. This may have influenced the aerosol load (with a local and regional contribution besides African transport) over Montseny. Back trajectory analysis shows that most of the African intrusions occurred during 2003 summer. Since TPP concentrations in aerosols were higher in the African episodes compared to non-African ones (0.99 nmols m^{-3} *vs*. 0.58 nmols m^{-3}, $p<0.05$), this suggests that African influence determined the cycle. However, the seasonal model (equation 1) showed the highest TPP correlation (r=0.74; 55% variance explained) with the seasonal trend of non-African episodes, while the inclusion of African events decreased the correlation (r=0.68; 46% variance explained), indicating a seasonal trend irrespective of the occurrence of African episodes.

Table 2. Statistics for total particulate phosphorus (TPP) concentrations in aerosols (total suspended particles, TSP) at La Castanya, Montseny (NE Spain) from March 2002 to December 2003.

	TSP μg m^{-3}	TPP in TSP (all samples) nmols m^{-3}	TPP in TSP (non-African) nmols m^{-3}	TPP in TSP (African) nmols m^{-3}
Arithmetic mean	24.7	0.74	0.58	0.99
Standard error	0.985	0.035	0.031	0.032
Median	24.0	0.63	0.50	0.95
Min.	3	0.016	0.016	0.27
Max	80	2.13	2.13	1.88
n	151	151	95	56

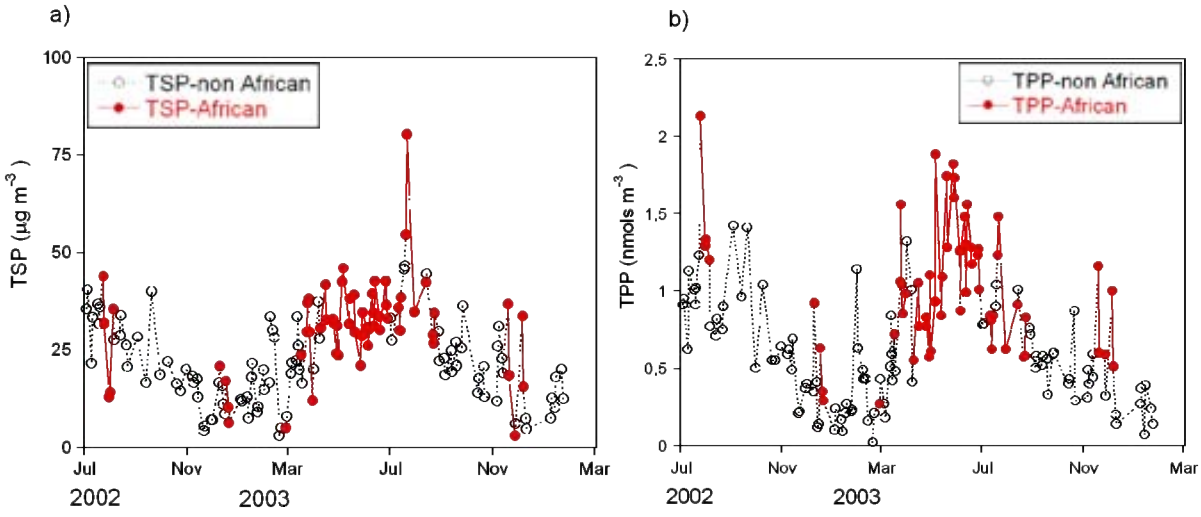


Figure 4.Temporal variation of: a) TSP (μg m^{-3}) and b) TPP concentrations (nmols m^{-3}) in aerosols at La Castanya (Montseny). Full dots indicate African events.

Dry / wet TPP deposition and African source partitioning

From July 2002 to December 2003, 65 dry deposition and 45 wet-only deposition samples were collected at LC and analysed for TPP. Dry deposition was collected every week, but since not all weeks had rainfall, fewer wet samples were obtained relative to dry samples.

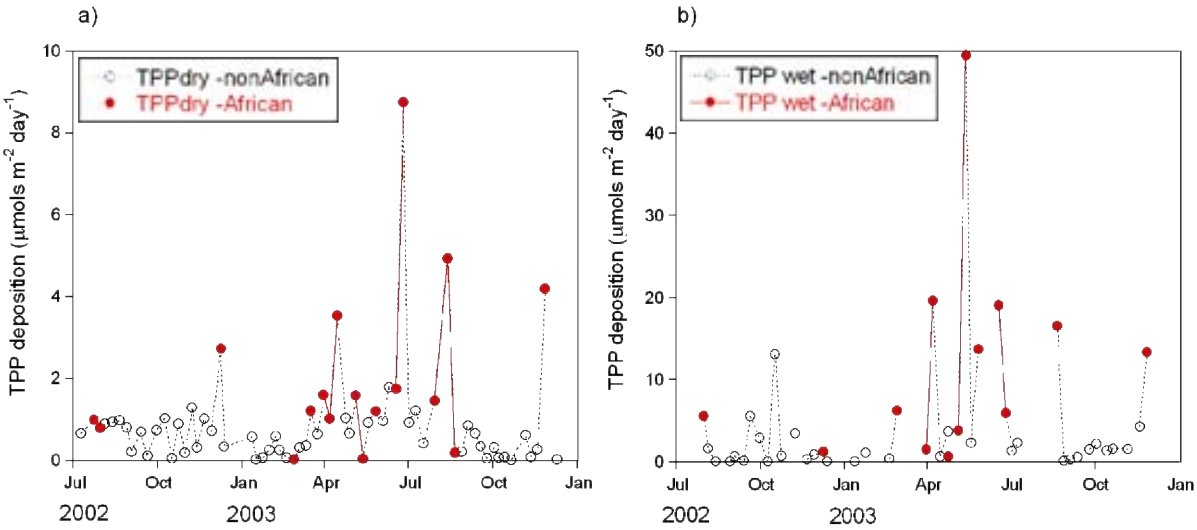


Figure 5. Temporal variation of TPP daily deposition (µmols m^{-2} d^{-1}) in: a) dry and b) wet deposition modes at La Castanya (Montseny). Full dots indicate African events.

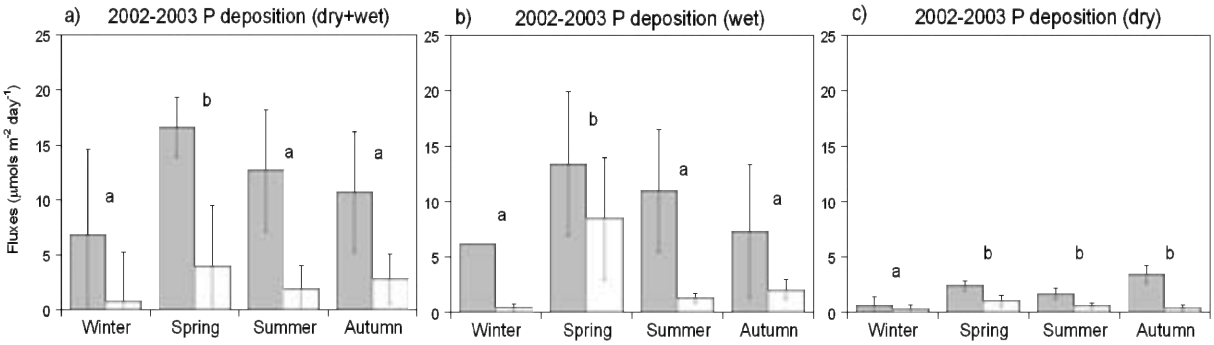


Figure 6. ANOVA analysis of TPP deposition with season and rain type by provenance for the period July 2002 – December 2003. Shaded bars= African events; white bars =non-African events. Different letters indicate significant statistical differences with post-hoc Tukey tests (p<0.05) for season. Winter= January, February, March; Spring= April, May, June; Summer= July, August, September; Winter= October, November, December. Differences between rain types (African *vs.* non-African) were always significant for wet and total deposition, but for dry deposition only significant differences were found in autumn.

The temporal evolution of wet and dry daily TPP deposition is shown in Fig. 5. On a daily basis, arithmetic mean wet deposition (4.86±1.28 μmols $m^{-2}d^{-1}$) was higher than mean dry deposition (0.95±0.17 μmols m^{-2} d^{-1}; p=0.0017). There was also higher variability in wet deposition, with maximum values up to 50 μmols m^{-2} d^{-1} compared to maxima of only 9 μmols m^{-2} d^{-1} for dry deposition. A seasonal pattern was evident in both deposition modes, with higher fluxes during spring-summer. Moreover, the highest deposition values usually corresponded to African events, either in the wet or dry deposition mode. ANOVA analysis of daily TPP deposition grouped by seasons and rain type showed African deposition to be higher, especially in the wet mode (Fig. 6).

The cosine seasonal model showed a remarkable seasonal variation for dry deposition (r=0.59, 34.4% variance explained), which was much lower for wet deposition either considering all events (r=0.38; 15% variance explained) or non-African events alone (r=0.39; 16% variance explained). Thus, dry deposition more closely followed the seasonal patterns observed for P aerosols.

For the period July 2002 to December 2003, annual TPP deposition at LC was 576 μmols P m^{-2} y^{-1} (Table 3), evenly distributed between wet (285 μmols P m^{-2} y^{-1}) and dry deposition (291 μmols P m^{-2} y^{-1}). Despite the abovementioned differences in daily mean deposition rates in dry and wet modes, the higher number of dry deposition days compared to wet deposition days resulted in similar total annual deposition in both modes. African weeks accounted for 380 μmols P $m^{-2}y^{-1}$ (66% of annual total, Table 3), with deposition partitioned into 212 μmols P $m^{-2}y^{-1}$ in the wet and 168 μmols P $m^{-2}y^{-1}$ in the dry modes. Therefore, dry deposition accounted for 44% of total TPP deposition in African events, while for non-African ones dry deposition predominated (63%, Table 3). Overall, the major contribution to TPP deposition was from wet African weeks (37% of total deposition) followed by dry African deposition (29%) and non-African dry deposition (21%). Wet deposition from non-African weeks only amounted to 13% of TPP deposition.

Table 3. African, non-African, and annual total particulate phosphorus (TPP) deposition (in μmols m^{-2} y^{-1}) and their dry percentage contribution to total wet plus dry deposition at La Castanya, Montseny (NE Spain) from July 2002 to December 2003.

	Wet	Dry	Total (Wet+Dry)	% Dry to Total
African	212.5	167.8	380.3	44.1
Non-African	72.9	123.2	196.1	62.8
Total Annual	285.4	291.0	576.4	50.5
% African to Annual	74.5	57.7	66.0	

African rain samples from 1996 to 2008

Given the importance of African TPP deposition, we examined these inputs more closely by analysing TDP and SRP for African red-rains from 1996-2008. The mean annual TPP deposition in red-rains in this period (29 samples corresponding to red rains between 1996 and 2008) was 217 μmols m^{-2} y^{-1}, a value that falls within the range of TPP African deposition that can be calculated from the P content in the African end member (0.08% Guieu et al. 2002) and the African deposition flux in the western Mediterranean (5-12 kg km^2 y^{-1}), which results in 132-317 μmols P m^{-2} y^{-1}. Because these measurements only refer to African wet weekly samples, we need to correct them for total annual deposition. For this correction, the percent wet African to total deposition for year 2002-03 (37%, Table 3) was applied to the 1996-2008 mean TPP red-rain deposition, producing an estimate of 588 μmols m^{-2} y^{-1} TPP for the period 1996-2008, which closely compares with the wet deposition obtained for the period 2002-2003 (576 μmols m^{-2} y^{-1}, Table 3). For African rainfall samples, there was a good correlation between TPP and TDP (r=0.65; p<0.0002) and TPP *vs.* SRP deposition (r=0.88; p<0.0001). On a weekly basis, TDP accounted for 11.2 % of TPP, while SRP was only 2.2% of TPP (Table 4).

Table 4. Statistics for weekly deposition (μmols m^{-2} $week^{-1}$) for TPP, TDP, SRP and DOP at La Castanya (Montseny, NE Spain) for red-rain weekly samples from 1996-2008. DOP estimated from TDP-SRP.

	TPP	TDP	SRP*	DOP
Arithmetic mean	78.2	8.82	1.70	4.82
Standard error	23.8	1.83	0.59	1.66
Min.	2.6	0.35	0.05	0.3
Max	661	33.9	8.03	22.1
n	29	27	13	13

*Calculated without values below detection limit

Discussion

Seasonality and provenances

TPP in aerosols and dry deposition during 2002-2003 was well correlated with a seasonal model (r=0.68 and 0.59, respectively), but wet deposition showed a more irregular seasonal pattern (r=0.38). TPP wet deposition was not correlated with precipitation (r= -0.021; p=0.89); rather, it was much more influenced by the sporadic occurrence of African events (Fig. 5), similarly to findings of Morales-Baquero et al. (2006) in Sierra Nevada, southern Spain, and Bergametti et al. (1992) in Corsica. Bergametti et al. (1992) found higher P concentrations in aerosols from North-Africa than from European trajectories (0.57 nmols m^{-3} *vs*. 0.33 nmols m^{-3}). At Crete and Turkey, TPP aerosol concentrations from the S and SW (corresponding to North Africa) were higher than from N-NE, NW and W (1.2-1.3 nmols m^{-3} and 0.6-0.7 nmols m^{-3} for Crete and Turkey, respectively; Markaki et al. 2003). In our study, aerosol TPP concentrations closely matched the findings for the Eastern Mediterranean: 0.99 nmols m^{-3} for African and 0.58 nmols m^{-3} for non-African provenances (Table 2).

Calculation of the P deposition velocity (V_d)

Many studies obtain dry deposition fluxes from the relationship between the deposition flux (F_d) and atmospheric concentrations (C_a) through the deposition velocity parameter (V_d):

$$F_d = C_a \cdot V_d \qquad \text{(equation 2)}$$

Estimates of V_d for P deposition are limited. One of the most widely used estimate is that obtained by Duce et al. (1991) for compounds in the coarse fraction (including P), which was established at 2 cm s^{-1}. Bergametti et al. (1992) in Corsica calculated a P V_d e of 2.7 cm s^{-1} from P aerosol measurements and P total deposition during the dry period. At Crete, using inorganic P measured in aerosols and dry inorganic P deposition, a mean V_d of 2.3 cm s^{-1} was estimated (Markaki et al. 2003).

Our data at Montseny provide another data set to add to these V_d estimations for particulate P. Aerosol concentrations and dry deposition showed similar seasonal trends, indicating strong linkages between them. Because dry deposition rates are size dependent and P is usually found within the coarse fraction of particles (diameters>1 μm; Duce et al. 1991; Prospero et al. 1996; Markaki et al. 2003), our measurements of dry deposition onto a dry bucket will contain most of the gravitational flux, the main deposition pathway for coarse particles. Using equation 2, an average V_d of 1.6±0.3 cm s^{-1} was obtained for all samples in 2002-2003. When accounting for air-mass provenance, a significantly lower V_d of 1.07±0.13 cm s^{-1} was found for non-African events (n = 45), compared to 3.1±0.80 cm s^{-1} for African weeks (n = 16; *p*=0.00025), indicating higher settling velocities for coarser desert dust particles. Indeed, a particle size mass distribution study for dust at Crete found that 85% of dissolved P was associated with particle diameters between 1-10 μm and showed a similar distribution to Ca, a tracer of crustal material (Markaki et al. 2003). Measurements of the grain size distribution (particle diameter measured with a Coulter LS100 counter) of 4 African rain samples collected at Montseny indicated a median particle diameter of 9.8 μm, which is similar to that obtained for the particulate phase of 7 Saharan rains collected at Corsica (median of 8 μm; Guieu et al. 2002), thus confirming large particle diameters for African aerosols.

Mean aerosol and deposition values

TPP mean concentration in aerosols (0.74±0.035 nmols m^{-3}) was similar to values in Corsica (0.33-0.63 nmols m^{-3}, Bergametti et al. 1992) and the Eastern Mediterranean (0.43-0.77 nmols m^{-3} at Crete and Turkey, respectively; Markaki et al. 2003), but lower than in southern France (1.65 nmols m^{-3}, in Cap Ferrat; Migon et al. 2001), though this later study was only for a one-month period. The mean daily TPP deposition fluxes were 4.64±1.28 μmols $m^{-2}d^{-1}$ and 0.95±0.17 μmols m^{-2} d^{-1}, for the wet and dry modes respectively. Migon et al. (2001) estimated lower dry deposition fluxes in the range of 0.15-0.7 μmols TPP $m^{-2}d^{-1}$, an estimate that was obtained from the product of aerosol concentrations and V_d values from the literature (0.1-0.5 cm s^{-1}; Duce et al. 1991) for the summer period in Cap Ferrat, southern France.

Ridame and Guieu (2002) reported deposition values in the range from 0.03 to 2.6 μmols $m^{-2} d^{-1}$ of DIP considering only African rain events at Villefranche sur Mer (south France). Taking into account that the partitioning of atmospheric P between soluble and insoluble forms for Saharan rains may vary between 8-15% of total P (Lepple, 1975; Herut et al. 1999, 2002; Ridame and Guieu, 2002), and using 10-15% as an indicative value for the percent dissolution, the above DIP figures would translate into 0.2 to 23 μmols TPP $m^{-2} d^{-1}$. Thus, our results are towards the lower range of previous estimates.

The annual TPP deposition flux at LC was 576-588 μmols $m^{-2} y^{-1}$ by the two estimation methods used. Deposition was similarly distributed between wet and dry deposition. The annual P fluxes at Montseny are towards the lower end of the TPP fluxes measured at various locations throughout the Mediterranean region (Table 5), but similar to those obtained in southern Spain (Sierra Nevada). Our results suggest that, in NE Spain, the major TPP deposition pathway is through African rains (37%), followed by African dry dust deposition (29%). However, dust input from African rains at Montseny (5 g $m^{-2} y^{-1}$) is lower than that measured in Corsica (12-14 g $m^{-2} y^{-1}$; Löye-Pilot et al. 1986; Bergametti et al. 1989) and much lower than in the eastern Mediterranean (20-40 g $m^{-2} y^{-1}$; Ganor and Mamane 1982). This is consistent with an increasing trend in mean annual PM10 levels from the western to the eastern Mediterranean Sea (Querol et al. 2009), which would account for the higher dry deposition in the eastern basin. These differences between geographic regions are most likely related to dissimilar wind and rain patterns and to the distance to the dust source, and may account for the variability in nutrient deposition amounts and the differences in preferential depositional pathways between basins (Guieu et al. 2010).

At Montseny, dry deposition represented 50% for all events and 44% of the African TPP deposition. This contrasts markedly with other studies in the western Mediterranean which have reported dry deposition of Saharan dust to be negligible (Löye-Pilot and Martin, 1996; Ridame and Guieu, 2002). On the other hand, in a study of P deposition in the eastern Mediterranean (Crete), DIP from dry deposition accounted for 65% of total deposition (Markaki et al. 2003), a result that is probably related to the previously mentioned higher impact of dust intrusions in the eastern basin. Our data provide a first estimate of the dry/wet partitioning for the western Mediterranean. The paucity of data regarding dry and wet fluxes and the fact that P solubility is different in wet and dry deposition modes (Herut et al. 1999, 2005), attests to the need of more studies for a better knowledge of the effect of P deposition on marine productivity in the western Mediterranean Sea.

Table 5. Annual deposition (μmols m^{-2} y^{-1}) for TPP, and TDP or DIP from references around the Mediterranean and from this study.

	Wet	Dry	Total (Wet+Dry)	Period	Reference
TPP					
Sierra Nevada (Spain)	144.4	368.5	512.9	2001-02	Morales-Baquero et al. (2006)
Corsica (France)			1295	1985-88	Bergametti et al. (1992)
Corsica (France)			1184	1985-87	Guieu et al. (2002)
Cap Ferrat (S.France)	70			1997-98	Migon and Sandroni, (1999)
Cap Ferrat (S.France)		60-250		June-July 1998	Migon et al. (2001)
Crete (Greece)	178			1999-00	Markaki et al. (2003)
Erdemli (Turkey)	250.2			1999-00	Markaki et al. (2003)
Israel	290.3		1000	1996-98	Herut et al. (1999)
Israel		800		2001-03	Carbo et al. (2005)
All Mediterranean (mean of 9 sites)			1064.5	2001-02	Guieu et al. (2010)
Montseny (NE Spain)	285.4	291.0	576.4	2002-03	This study
Montseny (NE Spain)	289*		588*	1996-08	This study
DIP or TDP					
Cap Ferrat (S.France)	95			1997-98	Migon and Sandroni (1999)
Western Med			464-608	2001-02	Markaki et al. (2010)
Central Med			355-371	2001-02	Markaki et al. (2010)
Eastern Med			243-480	2001-02	Markaki et al. (2010)
Crete (Greece)	68.4	125	193.4	1999-00	Markaki et al. (2003)
Erdemli (Turkey)	168			1999-00	Markaki et al. (2003)
Israel	280-290	400		1992-98	Herut et al. (1999, 2002)
Israel		500		2001-03	Carbo et al. (2005)
Villefranche s.Mer (S.France)	12-16			1999	Ridame and Guieu (2002)
Montseny (NE Spain)	46-60	56-80	102-140	2002-03	This study

* Mean TPP deposition for wet African events corrected from wet Africa percent to total annual, from Table 3.

Estimation of bioavailable P deposition to the NW Mediterranean

TPP and TDP concentrations averaged 3.5±0.96 μmols L^{-1} P and 0.27±0.03 μmols L^{-1} P (n=26) respectively in red-rains collected in the period 1996-2008. The good correlation between TPP and TDP concentrations (r=0.65; p<0.0002), suggests that TPP undergoes dissolution in rainwater. The average percent TDP dissolution respective of TPP in red-rains was 11.2%, close to the 8-11% values reported for P dissolution from dust (Herut et al. 1999; Lepple, 1975). Dissolution percentages were negatively correlated with rainwater pH (r=-0.52; p= 0.02). For rainwater with pH values between 5.6-7.0, P dissolution was 26.9% while for pH>7.0 it decreased to 7.5%. Our data refer to a population of dust-loaded rains of African provenance, but pure African events in the western Mediterranean are scarce, as the aerosol data in Montseny demonstrate (Fig. 3): some points classified as African lie well above the crustal line (P/Al=0.013) indicating that they also contain an anthropogenic P contribution. Most of these African rains have likely encountered polluted air masses on their way to the NE Iberian Peninsula and may have incorporated more soluble P species associated with anthropogenic pollution (biomass burning, incineration and other industrial processes). Alternatively, the dust air masses may have come upon aged recirculating air masses (Millán et al. 1997) containing acidic trace gases (HNO_3, SO_2) which can be absorbed onto the water coated dust particle and react to form sulphate and nitrate (Phadnis and Carmichael, 2000; Hanke et al. 2003). The carbonate content in the dust (Àvila et al. 1997, 2007; Löye-Pilot et al. 1986) will neutralize the acidity associated to sulphate and nitrate, but during this process, solubilisation of P-minerals would likely occur.

Several African red-rain samples were also measured for SRP, with much lower mean concentrations than those found in the TDP pool (0.068±0.007 μmols L^{-1} P, n=13). In fact, nearly half of the SRP analysed samples were below the detection limit. When encountering values below detection limits, one can either remove these values or use instead a very low figure representing the below detection value (some authors use the lowest detected value divided by two; others use the 3 x standard deviation of the blanks). However, either procedure induces a bias of the true correlations (Lyles et al. 2001). Because a complete analysis of this issue is beyond the scope of this paper, we have calculated the basic statistics and correlations with the two procedures, and found that differences were of degree but did not appreciably change interpretations: SRP-TPP correlations changed from r=0.65, n=13 p<0.05 when considering only detected pairs to r=0.88, n= 27, p<0.001 when including a value for undetected values (=0.02 μmol P), and the SRP averages decreased by 15% when including a value for the undetected values.

SRP concentrations measured in this study were ~50% lower than the concentrations measured by Markaki et al. (2010), but within the range obtained by Herut et al. (1999) using similar methods. DOP concentrations were similarly lower, only ~ 6 % as opposed to the 13–19 % measured in eastern Mediterranean (Carbo et al. 2005). We hypothesize that our lower %SRP and DOP are due to the strong influence of African dust, and is consistent with the solubility

results reported by Ridame and Guieu (2002). These differences between TDP, DOP, and SRP concentrations highlight the importance of determining the P source and speciation in establishing the P pools bioavailable for planktonic uptake following deposition.

TPP deposition values for the period 2002-2003 (for which the wet and dry partitioning in background and African weekly samples were measured) were converted to dissolved P fluxes using average solubility percentages for African (11.2%) and background events (30-50%, from literature references). This produced wet+dry soluble P fluxes of 43 μmols m^{-2} y^{-1} for African rain samples and 59-98 μmols m^{-2} y^{-1} for non-African ones, and thus a total deposition of ~100-140 μmols m^{-2} y^{-1} (Table 6). When splitting data into wet and dry deposition, TDP deposition was estimated as 46-60 μmols m^{-2} y^{-1} in the wet mode and 56-80 μmols m^{-2} y^{-1} in the dry mode (Table 6). Dry deposition from background polluted air masses, with higher solubility, explain the increased P contribution of the dry deposition mode. A compilation of data from the literature on soluble P deposition (measured predominantly as DIP) around the Mediterranean indicates that dissolved fluxes at Montseny are similar to those measured at Crete, but higher than those determined at a closer coastal site in southern France (Villefranche sur Mer;Table 5).

Table 6. Estimation of the dissolved P inputs (μmols m^{-2} y^{-1}) from the measured values of total particulate phosphorus (TPP) for wet, dry and total deposition split into African and non-African weekly samples at La Castanya (Montseny) for the period July 2002-December 2003.

		TPP input	% dissolution	Dissolved	Dissolved input range
Wet					
	African	212.5	11.2	23.7	
	Non-African	72.9	30	21.9	
			50	36.5	46 - 60
Dry					
	African	167.8	11.2	18.8	
	Non-African	123.2	30	37.0	
			50	61.6	56 - 80
Wet+Dry					
	African	380.3	11.2	42.6	
	Non-African	196.1	30	58.8	
			50	98.1	100-140

Recent studies have shown that P atmospheric deposition to the Mediterranean may significantly influence annual new production rates, considering Dugdale and Goering (1967) definition of new production as the annual primary production supported by externally supplied nutrients (e.g. nitrogen or phosphorus). Using the Redfield molar ratios C:P 106:1 (Redfield et al. 1963), atmospheric P-induced production in the eastern Mediterranean represents ~ 4-11% of new production (Herut et al. 2002; Carbo et al. 2005) and as high as 20-38% during the

stratified oligotrophic period (Markaki et al. 2003). This is in contrast with a negligible contribution in the western Mediterranean, where it has been evaluated as 0.1-0.2% of the annual new production (Ridame and Guieu, 2002). Considering soluble P inputs estimated at Montseny (100-140 μmol m^{-2} y^{-1}) as representative for inputs in the NW Mediterranean coastal waters and using the C:P Redfield ratio, new production due to atmospheric P is estimated between 0.13-0.18 g C m^{-2} y^{-1}. Compared to new production values for the western Mediterranean (35, 42 and 52 g C m^{-2} y^{-1}, from Béthoux (1989), Marty and Chiaverini (2002) and Morel & André (1991) respectively), this atmospheric P-induced production is ~ 0.3-0.5% of new production, thus confirming the findings by Ridame and Guieu (2002). Nevertheless, as also suggested by other authors in the Mediterranean, large episodic dust events may have a higher impact. For example, a high intensity dust event in 22-27 May 2008 delivering 3.7 g m^{-2} African dust provided a TDP input of 34 μmol P m^{-2} (0.32 μmol L^{-1} TDP; 106 mm precipitation). Using the assumptions above, such a deposition event would trigger a new production of 0.043g C m^{-2}, which represents 24 - 33% of annual values of the new production induced by atmospheric P.

Conclusions

The results of this study show that dry deposition accounted for ~50% of total annual particulate phosphorus deposition which amounts to 576 μmols P m^{-2} y^{-1}. This indicates that the dry deposition pathway needs to be considered when nutrient budgets for the Mediterranean are calculated. African events were very relevant in the annual budget (66% of TPP); in these African weeks wet deposition dominated over dry deposition. TPP deposition in north-eastern Spain lies toward the lower range of reported values for Corsica and the eastern Mediterranean, in agreement with an increasing impact of African dust from west to east in the Mediterranean.

This study corroborates the findings of other researches in the Western Mediterranean suggesting that African events, albeit undergoing lower TPP dissolution rates, may represent an important source of nutrients to surface waters, specially when they occur during the stratification period when nutrients are depleted at the surface.

Acknowledgements

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Chapter 5

Source areas and long-range transport of pollen from continental land to Tenerife (Canary Islands)

Izquierdo R., Belmonte J., Àvila A., Alarcón M., Cuevas E. and Alonso-Pérez S. 2011. Source areas and long-range transport of pollen from continental land to Tenerife (Canary Islands). International Journal of Biometeorology 55, 67–85. Doi:10.1007/s00484-010-0309-1

Abstract

The Canary Islands, due to its geographical position, constitute an adequate site for the study of long-range pollen transport from the surrounding land masses. In this study we have analyzed airborne pollen counts at two sites: Santa Cruz de Tenerife (SCO), at sea level corresponding to the marine boundary layer (MBL), and Izaña at 2367 m asl corresponding to the free troposphere (FT), for the years 2006 and 2007. To describe the pollen transport we have used three approaches: (1) a classification of provenances with an ANOVA test to describe pollen count differences between sectors, (2) the study of special events of high pollen concentrations with consideration of the corresponding meteorological synoptic pattern responsible for the transport and back trajectories, and (3) a source-receptor model applied to a selection of the pollen taxa to show pollen source areas.

Our results indicate several extra-regional pollen transport episodes to Tenerife. Main provenances were: (1) The Mediterranean region, especially from the southern Iberian Peninsula and Morocco through the trade winds in the MBL. These episodes were characterized by the presence of pollen from trees (*Casuarina, Olea, Quercus* perennial and deciduous types) mixed with pollen from herbs *(Artemisia,* Chenopodiaceae-Amaranthacea and Poaceae wild type*)*. (2) The Saharan sector, through transport at the MBL level carrying principally pollen from herbs (Chenopodiaceae-Amaranthaceae*,* Cyperaceae and Poaceae wild type) and, in one case, *Casuarina* pollen uplifted to the free troposphere. And (3) the Sahel, characterized by low pollen concentrations of Arecaceae, Chenopodiaceae-Amaranthaceae, Cyperaceae and Poaceae wild type in sporadic episodes.

This research shows that sporadic events of long-range pollen transport need to be taken into consideration in Tenerife for possible responsibility in respiratory allergy episodes. In particular, it is estimated that 89-97% of annual counts of the highly allergenic *Olea* pollen originates from extra-regional sources in southern Iberia and northern Africa.

Introduction

Pollen records from aerobiological monitoring sites have traditionally been interpreted as if pollen was originated from the local environment. Consequently, pollen forecasting tools have been designed by taking into account only local meteorological variables and phenological observations in the neighbourhood. This view is recently changing to acknowledge much broader bioaerosol movements, based on increasing evidences of pollen and spore transport at much greater distances, implying continental (Belmonte et al. 2000; Sofiev et al. 2006; Siljamo et al. 2007, 2008; Belmonte et al. 2008a; Skjøth et al. 2009) or intercontinental scales (Prospero et al. 2005; Kellogg and Griffin, 2006).

Despite its large size (5-50 times greater than aerosols; Nilsson and Praglowski, 1992), the behaviour of many pollen taxa in the atmosphere is similar to that of the conventional atmospheric aerosol due to the low density of the anemophylous pollen grains which reduces their gravitational deposition, along with other features such as aerodynamic contours and low ornamentation. The residence time of pollen grains in the atmosphere, 2-3 days, and their deposition velocity, estimated at about 1 cm/s (Sofiev et al. 2006), are comparable to those of atmospheric aerosol species, and implies that about a half of the emitted mass will be transported to distances $>10^3$ km (Aylor, 2002).

This long-range transport of bioaerosols is a cause of concern because of its potential to distribute pathogens and allergens which can affect the human health or human interests such as agriculture and farming (Belmonte et al. 2000; Griffin et al. 2001; Taylor, 2002; Brown and Hovmoller, 2002; Shinn et al. 2003; Garrison et al. 2003; Wu et al. 2004; Kellog et al. 2004: Griffin, 2007; Polymenakou et al. 2008). This transport can also have an impact on the structure of ecosystems, since pollen is responsible for gene flow (Ellstrand, 1992; Ennos, 1994; Burczyk et al. 2004), and it contributes to determine the spatial distribution of plant species (Ellstrand, 1992; Smouse et al. 2001; Sharma and Kanduri, 2007; Schmidt-Lebuhn et al. 2007). Therefore, the study of pollen gene dispersal is instrumental for the interpretation of the biogeographic range of some plants and for plant conservation issues.

Extra-regional transport of pollen at distances greater than a few hundreds of km has recently been studied by several authors, some of which are briefly commented here. Van Campo and Quet (1982) identified several pollen types that had been transported from North Africa to Montpellier (France) together with mineral desert dust. Similarly, Franzen and Hjelmroos (1988) had observed pollen transport from Germany, Holland and England to the Swedish coast and Franzen (1989) and Franzen et al. (1994) documented the arrival of pollen grains to Fennoscandia from the Mediterranean. Also, *Cannabis sativa* (marihuana) pollen originating in Morocco was detected in Malaga, South Spain (Cabezudo et al. 1997) and *Cannabis, Cupressus, Pinus, Platanus* and *Sambucus* pollen were observed in Cordoba (South Spain) exclusively during dust African events (Cariñanos et al. 2004). Transport of pollen to western Europe has also been reported. This is the case of the arrival of *Betula* pollen to Denmark

coming from Poland and Germany (Skjøth et al. 2007), and to Finland coming from Russia (Siljamo et al. 2008). Also, *Ambrosia* pollen originated in the Czech Republic, Slovakia, Hungary and Ukraine was found in Poland and Italy (Cecchi et al. 2006; Stach et al. 2007; Kasprzyk, 2008). Transport from northern latitudes has been described in Spain: *Ambrosia* pollen was recorded in Catalonia (North-Eastern Spain) coming from France (Belmonte et al. 2000) and *Fagus sylvatica* (beech) pollen reaching Catalonia was traced back to central Europe (Belmonte et al. 2008a). In North America, the arrival of *Juniperus ashei* pollen released in southern Oklahoma and Texas to Tulsa has been reported (Rogers and Levetin, 1998). In South America, extra-regional pollen of *Celtis* coming from the northeast and of *Nothofagus* from the southwest has been found to contribute to Mar de Plata City (Argentina) pollen records (Gassmann and Pérez, 2006). In northwest India, bioaerosols collected during dust storms sporadically contained pollen from Himalayan species (Yadav et al. 2007). The presence of pollen grains from trees forming forests at much lower latitudes has been evidenced in the Arctic environment (Bourgeois, 2000; Rousseau et al. 2003, 2006, 2008). Extra-regional pollen transport has also been found in the Antarctic (Wynn-Williams, 1991) and Australia (Hart et al. 2007).

A strong association of biological particles with desert dust has recently been suggested (Kellog and Griffin, 2006). Dust clouds generated by storm activity over arid land can result in viruses, fungi spores and pollen associated with mineral particles being raised to altitudes higher than 2 km which are then transported for thousands of km at a planetary scale. For example, viable microorganisms and fungi spores from Africa were sampled at Barbados after being transported by African dust plumes (Prospero et al. 2005). Intercontinental mineral dust transport has been the subject of much attention during the last decades (Guerzoni and Chester, 1995; Goudie and Middleton, 2001; Prospero et al. 1996; Zhang et al. 1997), but further research is needed on the biological component associated to the dust.

African dust is mobilized and transported through specific meteorological conditions involving convective vertical movements and zonal wind patterns. The African wind system is characterized by a strong seasonal component related to the annual oscillation of the Intertropical Convergence Zone (ITCZ): in summer (May - November) trade winds carry Saharan dust to the Caribbean and North America, whereas in winter (December - April) dust flow is shifted to South America. Throughout the year, episodic pulses of dust from North Africa derive into Europe associated with the movement of storms tracks from the Atlantic to the Mediterranean at the Iberian Peninsula latitude (Moulin et al. 1997; Escudero et al. 2006).

The island of Tenerife (Canary Islands) constitutes an ideal location to study air mass transport from Africa because of its geographical position in the northern edge of the African dust belt. The chemical and mineralogical properties of dust reaching Tenerife have been thoroughly described (Coudé-Gausen et al. 1987; Bergametti et al. 1989; Viana et al. 2002, 2006; Díaz et al. 2006; Alonso-Pérez et al. 2007; Rodríguez et al. 2007) but no studies regarding pollen transport have been undertaken in the Canary Islands until now.

The lower troposphere of Tenerife can be clearly divided into two layers, each affected by different air mass circulation. The lowest humid and relatively cold troposphere, or marine boundary layer (MBL), is affected by the north-easterly trade winds. Through this circulation pattern, Tenerife receives the influence of Mediterranean or south European air masses. The very dry free troposphere at Tenerife is separated from the MBL by the trade wind inversion layer (TIL) at an altitude that oscillates between 500 and 1600 m above sea level (m asl) (Torres et al. 2001; Rodríguez, 1999; Alonso-Pérez et al. 2007). The free troposphere (FT) is characterized by subsiding NW air masses, except in summertime when this normal flow is alternated with dust-loaded Saharan air mass outbreaks.

In this study we have analyzed the airborne pollen counts at two sites, one corresponding to the MBL (Santa Cruz de Tenerife Observatory, SCO, at 52m asl) and the other to the FT (Izaña Observatory, IZO, at 2367m asl). The aim of the study is to describe some episodes of long-range pollen transport to Tenerife and to identify the provenance areas at these two altitudes for some pollen taxa. Some debate exist on the distance needed to be considered as long-range transport because this definition depends on the subject of study, with lighter biological structures being able to be transported much afar distances (Nathan et al. 2003). In the case of our pollen study, we consider that extra-regional trajectories (from outside the Canary Islands) correspond to long-range transport, since they are always larger than 500 km.

To describe the pollen transport we have used three approaches: (1) a classification of provenances with an analysis of variance (ANOVA test) to describe pollen count differences between sectors, (2) the study of special events of high pollen concentrations with consideration of the corresponding meteorological synoptic pattern responsible for the transport and back trajectories, and (3) a source-receptor model applied to a selection of the pollen taxa to show their source areas.

Material and methods

Study area

The island of Tenerife (Canary archipelago) is located 350 km west of the Western Saharan coast and 1300 km south-west of the Iberian Peninsula. Its meteorology is highly influenced by the North Atlantic anticyclone, which varies in strength and position throughout the year, and by the quasi permanent action of the trade winds that circulate along the eastern side of the anticyclone approaching the island from the north-east. The predominance of trade winds in the MBL plays a key role in the atmospheric dynamics of Tenerife (Font, 1956; Cuevas, 1996; Viana et al. 2002; Rodríguez et al. 2004).

Sampling was performed at two sites: Santa Cruz de Tenerife (SCO; 16º14’51” W; 28º28’21” N; 52m asl) as representative of the MBL and Izaña Atmospheric Observatory (IZO; 16º29’58” W; 28º18’32” N; 2367m asl) as representative of the FT. Both sampling stations are managed by

the Izaña Atmospheric Research Center of the Agencia Estatal de Meteorologia (AEMET). Santa Cruz de Tenerife is a 220,000 inhabitant city located to the northeast of Tenerife by the Atlantic Ocean and close to the Macizo de Anaga ridge. The climate is mild (mean annual temperature: 21.2º C) and dry (214 mm mean annual rainfall). IZO station is located in the central mountain chain of Tenerife 15 Km north-east of the Teide volcano (3.718m asl). The climate is cold (mean annual temperature: 9.8º C) and more humid than the lowland (440 mm mean annual precipitation).

Vegetation

The vegetation of Tenerife is mostly arranged in concentric belts around the Teide peak, with the exception of a forested and humid area (laurel forest) only present at the North side of the island where rainfall and mists are frequent due to the trade winds. Following Rivas-Martínez (1987) and Arco Aguilar et al. (2006) the vegetation of Tenerife can be summarised as: Vegetation from rocky environments (above 3000m asl), "Retamares" (dominated by the endemic broom *Spartocytisus supranubius*), *Pinus canariensis* forests, Laurisylvae and "fayal-brezal" heaths at the more humid northern area (with *Laurus*, *Persea*, *Ocotea*, *Ilex*, *Myrica*, *Ilex*, *Erica*…), "Sabinares" (*Juniperus*) and thermophile forests and "Cardonales" (sub-desert scrub formations with *Euphorbia canariensis* and *E. balsamifera* as dominating species) as well as vegetation from saline and sandy environments in these very special areas (Fig. 1). Other vegetation types that have to be considered are the ornamental plants introduced in the urban and urbanized areas and the ruderal and nitrophilic plant communities growing close to human settlements. Every vegetation type mentioned has a particular list of species besides those that are cited as representative, most of which will constitute the atmospheric pollen spectra.

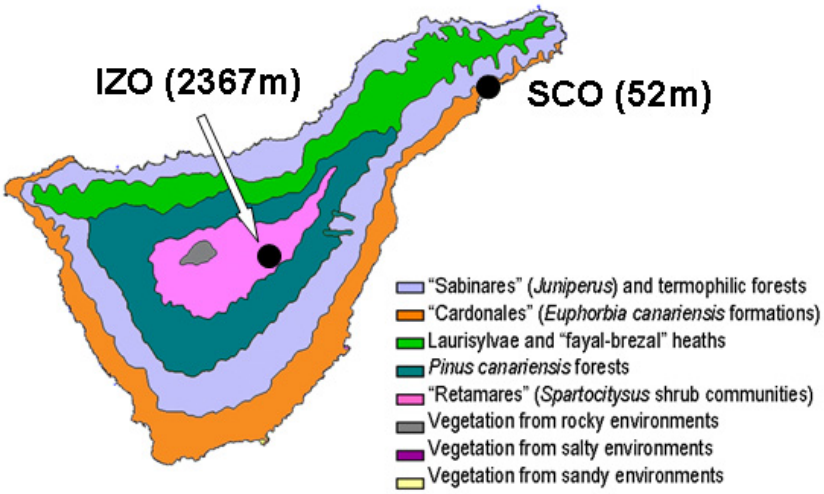


Figure 1. Tenerife vegetation map (Belmonte et al. 2008b).

Pollen data record

Pollen data were recorded at the two monitoring stations using samplers (Lanzoni VPPS 2000 trade mark) based on the Hirst method (Hirst 1952), the standard method accorded by the European aerobiological networks. The pollen counting followed the method of the Spanish Aerobiology Network (Red Española de Aerobiología, REA; Galán et al. 2007). The Hirst method performs a sequential and non interrupted sampling that has been proven useful in long-range transport research (Gassmann and Pérez, 2006; Belmonte et al. 2008a; Siljamo et al. 2008; Skjøth et al. 2009; Šikoparija et al. 2009).

Sampling was undertaken during the years 2006-2007. The sampling period at SCO was continuous during both years, whereas at IZO, samples were only collected from June 11th to November 11th in 2006 and from April 23rd to November 4th in 2007 because of adverse meteorology in the rest of the year.

Criteria to determine extra-regional transport

At a first approach we applied an ANOVA analysis to pollen counts distinguishing for provenance areas as this will give a hint of preferential geographical regions providing the pollen (Fig. 2).

Figure 2. Definition of sectors of back trajectory provenance. Map base from Basarsoft and Geocentre consulting, PPWK, Tele Atlas, MapLink/Tele Atlas, Europe Tecnologies 2008, available at http://maps.google.es.

Then, the temporal series of pollen counts were analysed. Most taxa showed low background concentrations during most of the time (hypothesized as coming from the local environment) which were broken by outstanding peak events. An example of the pollen daily variation showing the peak events is given for Poaceae in Fig. 3. Once identified, the meteorological situation for peak events was analysed in depth with the help of synoptic meteorological maps and meteorological and dust models. This provided information to unveil any coherent air mass movements from specific source areas.

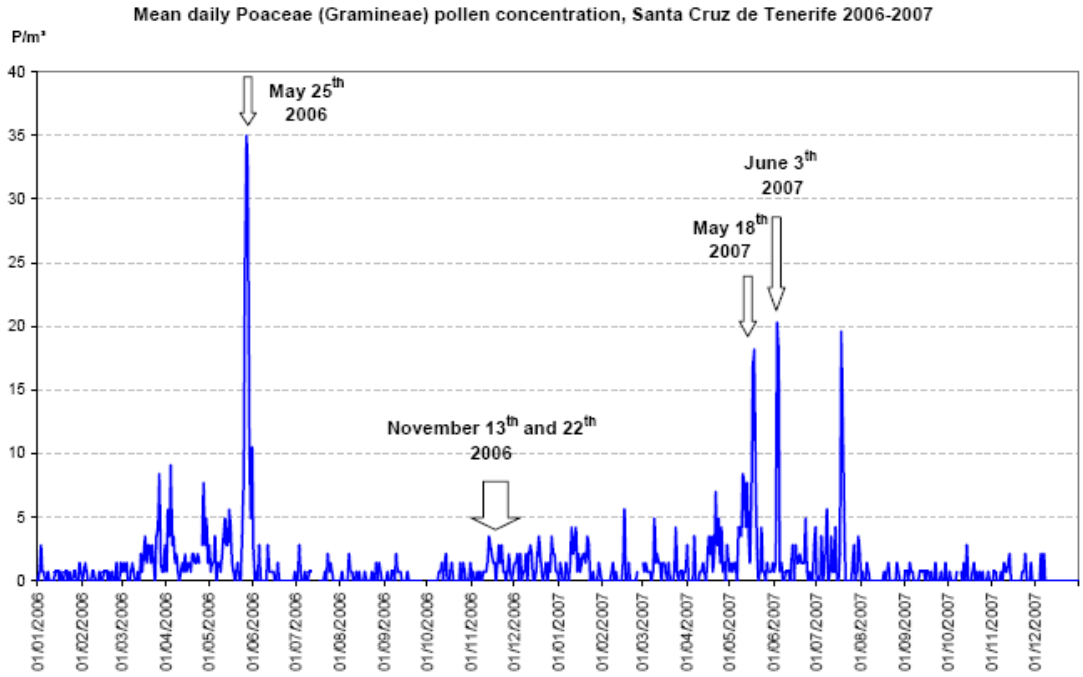


Figure 3. Sequence of mean daily pollen concentrations of Poaceae wild type pollen at Santa Cruz de Tenerife (SCO), from 1 January 2006 to 31 December 2007. *Arrows* illustrates the studied peak events.

Classification of provenances

The provenance of the air-masses was identified with HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) 4.0 dispersion model back-trajectories from the Air Resources Laboratory (ARL, available at http://www.arl.noaa.gov/ready/hysplit4.html, Draxler and Rolph, 2003), using the GDAS (Global Data Assimilation System) meteorological dataset from the NCEP (National Center for Environmental Prediction) and the vertical velocity model. The starting point was set at 12.00 UTC from the coordinates of each monitoring site and run backwards for 144h. Back-trajectories were calculated daily near the surface at both sampling stations and at a higher level (altitudes of 100 and 1500 m asl at SCO and 2500 and 3000 m asl at IZO). For classifying the provenances, only the back trajectories at height, indicating synoptic movements (1500m and 3000 at SCO and IZO respectively) were considered.

According to the area crossed by the back trajectories provenances of the air masses reaching the two Tenerife stations were classified into 6 predefined source geographic sectors (Fig. 2): (1) Sahel, Sudanese and Guinean Regions (SAHEL-SGR), (2) Sahara Desert (SAHARA), (3) Mediterranean- North Africa (MED-NAF), (4) Europe (EU), (5) Eastern Atlantic (EAST ATL) and (6) Atlantic (ATL). A seventh category was added because several trajectories were observed to cross south Europe, the Mediterranean and North Africa, combining categories 3 and 4 (EU+MED-NAF). The abovementioned sectors of the African continent (1 to 3) have been established considering the latitudinal distribution of vegetation belts in northwest Africa reported in White (1983).

To test whether differences existed in mean pollen counts of the studied taxa between the different provenances, we applied an ANOVA analysis to the normalized pollen data (logarithm of pollen concentrations). For pairwise post-hoc comparisons, the Tukey test was applied; significance was set at $p<0.05$ level.

Peak events

The daily pollen dynamics was screened to identify peak events by means of a Student t-test: for each taxon, concentrations at day *d* were compared to those of the previous day (*d-1*) with a one-tailed t-test. The null hypothesis states that the concentration differences in two consecutive days are not significantly different from zero (at $p<0.05$). Peak days were those that showed significant differences in consecutive days. For the significant peak events we calculated the corresponding Four-dayensemble back trajectories at 500 m asl for SCO (within the MBL) and 2500 m asl for IZO (in the FT). The starting point was set at 00.00 UTC from the coordinates of each monitoring site. The interpretation of the back trajectories was complemented with meteorological synoptic maps. Because dust and biological components are jointly uplifted to the atmosphere by the same convective air motions (Kellog and Griffin, 2006), and because dust images can help visualise the areas where both components were uprooted, dust forecast models such as DREAM (http://www.bsc.es/projects/earthscience/DREAM) and SKIRON (http://forecast.uoa.gr/) and satellite information such as MODIS (http://rapidfire.sci.gsfc.nasa.gov/) and TOMS AI Index, (http://toms.gsfc.nasa.gov/) were scrutinized for the peak periods. Four outstanding peak events were identified and are described in detail below.

Source-receptor model

Pollen taxa that presented significant differences between provenances (based in the ANOVA analysis) and that showed significant peak patterns (based in t-tests) were selected for further exploration of source areas by applying a source-receptor model. The selected taxa were: *Artemisia*, Chenopodiaceae/Amaranthaceae and Poaceae wild type at SCO and IZO, and Arecaceae, Cyperaceae and *Olea* only at SCO, due to lack of data at IZO.

The identification of the probable sources of atmospheric pollutants is very frequently resolved with the use of Trajectory Statistical analysis Methods (TSMs). Several works (Wotawa and Kröger, 1999; Stohl, 1996; Begum et al. 2005) have tried to validate various TSMs, mostly through direct comparison with known sources. More recently, a more quantitative approach (Schefinger and Kaiser, 2007) was applied to three TSMs using virtual and real sources as well as comparison with EMEP emission inventory. All these studies have concluded that methods of trajectory statistics are computationally fast procedures which deliver first hints on potential source areas. These works also agree that TSMs provide a helpful tool in estimating the spatial distribution of emissions of air pollutants from measurements. Between TSMs, methods involving air pollution data as the Seibert's methodology based on concentration fields (Seibert et al. 1994), is one of the most used, together with the method based on the conditional probability fields (Potential Source Contribution Function, PSCF). Both are still very much in use in the transport interpretation of inert air pollutants; for example, Apdula et al. (2003) used these approaches to the localization of source and sinks of carbon dioxide in high mountain areas in Europe; Polissar et al. (2001) applied the PSCF to the atmospheric aerosol at Barrow; Hoh and Hites (2004) to pesticides in USA; Salvador et al. (2004) to the PM10 in Spain, and Xie and Berkowitz (2007) to hydrocarbons in Texas. More recently, Wang et al. (2009), have implemented a GIS-based software that combines statistical analysis of air mass back trajectories with long-term air pollution measurements to identify potential sources. While most TSMs applications have dealt with the chemical components of the atmosphere, much less work has been done on the biological aerial component, though the methodology is equally adequate. In a recent research, Belmonte et al. (2008a) described the source area of *Fagus* pollen reaching Catalonia with the use of the Seibert source-receptor model.

Source-receptor methodologies establish relationships between a receptor point and the probable source areas. Daily 96-h back-trajectories were computed for the full sampling period and each back trajectory was associated to the corresponding daily pollen abundance. The back-trajectories considered were from 1500 m asl at SCO and 2500 m asl at IZO, with segment end points of 60-min time steps. A grid, in our case with 2601 cells of 1º x 1º latitude and longitude, was then superimposed on the integration region of the trajectories in order to map the contributing areas for selected pollen taxa.

The Seibert methodology (Seibert et al. 1994) was applied, where a logarithmic mean pollen concentration is computed for each grid cell based on the residence time of the trajectories in the cells:

$$\log C_{ij} = \frac{\sum_{l} n_{ijl} \log C_{l}}{\sum_{l} n_{ijl}}$$

where Cij is the pollen concentration in the (i,j) cell, l is the index of the trajectory, n_{ijl} is the number of time steps of the trajectory l in the cell (i,j), and C_l is the pollen concentration measured at the receptor point corresponding to the trajectory l. To minimise the uncertainty of the trajectories, a smoothing was applied and the value of each cell was replaced by the average between the cell and the eight neighbouring cells. A final filter excluded cells with less than five end points. The abundance field map obtained in this manner reflects the contribution of each cell to the pollen abundance at the receptor point.

Source-receptor sensitivity analysis

We initially applied both the Seibert's methodology and the PSCF to our data pollen. A sensitivity analysis to different factors such as the averaging in the smoothing procedure, the number of total time steps considered in the back trajectories (48, 72, 96, 120 and 144), the weighting function used to minimize the effect of the cells with low number of time steps, and the exceedance criterion values (average, percentile 80, percentile 90, and percentile 95) was done. In spite that the models are sensitive to all these factors, the source areas obtained did not vary significantly.

Results

ANOVA analysis

Seventy pollen types were identified at SCO during 2006-2007 (710 days of measures). Only six pollen types presented ANOVA significant differences between provenances: Arecaceae (palms)*, Casuarina,* Cyperaceae (sedges), Chenopodiaceae/Amaranthaceae*,* Moraceae and *Salix* (willows*)* (Table 1)*.* In this table, numbers with the same superscript letter are not statistically different. Conversely, numbers with different superscripts are significantly different at $p<0.05$. It can be seen that the SAHEL-SGR was the predominant provenance for Arecaceae and Cyperaceae pollen; the North African origin, especially the MED-NAF provenance, prevailed for *Casuarina* and Chenopodiaceae/Amaranthaceae. Moraceae and *Salix* didn't show a clear pattern, but in both cases EU was the predominant provenance.

Forty-six pollen types were identified at IZO during the study periods in 2006-2007 (341 days of measures). Six pollen types showed ANOVA significant differences between provenances: *Artemisia,* Boraginaceae, Chenopodiaceae/Amaranthaceae, Ericaceae*, Pinus* and *Quercus* deciduous type (Table 1)*.* MED-NAF was the predominant provenance for *Artemisia,* Boraginaceae, and Chenopodiaceae/Amaranthaceae, but the SAHEL-SGR provenance was also important for the two last pollen types. EU+MED-NAF was the most important origin for Ericaceae, *Pinus* and *Quercus* deciduous type.

Table 1. Mean daily airborne pollen concentration (p/m^3) for each provenance at both studied stations for the taxa that showed significant differences with an ANOVA analysis ($p<0.05$). Superscript letters indicate post-hoc Tukey test differences between provenances.

	SAHEL-GR	SAHARA	MED-NAF	EU	EU+MED-NAF	ATL	EAST ATL
SCO							
Arecaceae	5.72^{a}	3.03^{ab}	1.85^{b}	1.33^{b}	1.44^{b}	1.90^{b}	2.03^{b}
Casuarina	0.00^{ab}	0.13^{ab}	0.21^{a}	0.03^{b}	0.08^{ab}	0.03^{b}	0.06^{b}
Chenopodiaceae/ Amaranthaceae	0.47^{abc}	1.56^{bc}	1.78^{b}	0.37^{bc}	1.05^{bc}	0.36^{c}	0.44^{c}
Cyperaceae	0.58^{a}	0.09^{bc}	0.13^{b}	0.04^{bc}	0.08^{bc}	0.01^{c}	0.00^{c}
Moraceae	0.12^{ab}	0.21^{b}	0.30^{ab}	0.86^{a}	0.30^{b}	0.28^{b}	0.42^{a}
Salix	0.00^{ab}	0.08^{ab}	0.00^{ab}	0.09^{a}	0.03^{ab}	0.01^{b}	0.01^{b}
IZO							
Artemisia	0.06^{b}	0.08^{b}	1.20^{a}	0.11^{b}	0.08^{b}	0.17^{b}	0.19^{a}
Boraginaceae	0.04^{ab}	0.00^{b}	0.09^{a}	0.04^{ab}	0.00^{ab}	0.01^{b}	0.00^{ab}
Chenopodiaceae/ Amaranthaceae	0.78^{a}	0.39^{ab}	0.81^{a}	0.21^{ab}	0.25^{ab}	0.20^{b}	0.47^{ab}
Ericaceae	0.02^{b}	0.02^{b}	0.23^{b}	0.04^{b}	0.95^{a}	0.08^{b}	0.00^{b}
Pinus	0.26^{ab}	0.22^{b}	0.88^{ab}	0.63^{ab}	3.54^{a}	1.45^{ab}	0.19^{ab}
Quercus deciduous type	0.00^{ab}	0.03^{ab}	0.11^{ab}	0.00^{ab}	0.16^{a}	0.005^{b}	0.00^{ab}

Study cases

Episode on 25 to 29 May 2006 at SCO

From 25 to 29 May 2006, a significant increase in daily airborne pollen concentration (on the basis of t-tests) of *Olea* (olive trees*), Quercus* deciduous type (deciduous oaks and corks)*, Vitis* (grape vine) and Poaceae wild type (grasses) was observed at SCO (Fig. 4a). *Olea* pollen concentration on May 28th reached 112 pollen grains/m^3 (p/m^3). No data are presented for IZO because the instrument was not yet operative at these dates.

The synoptic meteorology on 28 May exemplifies the whole episode (Fig. 4b): a low-pressure system situated over the Atlantic coast of Morocco triggered a movement of air masses from North Africa and the Iberian Peninsula to the Canary Islands. This can be seen in the ensemble back trajectories (Fig. 4c). The pollen types identified during this episode (olive, grape vine and deciduous and cork oaks) correspond to typical taxa of the Mediterranean vegetation (although ubiquitous grasses were also found), a result wholly compatible with long-range transport from the Mediterranean region; more specifically, from southern Spain and northern Morocco and Algeria.

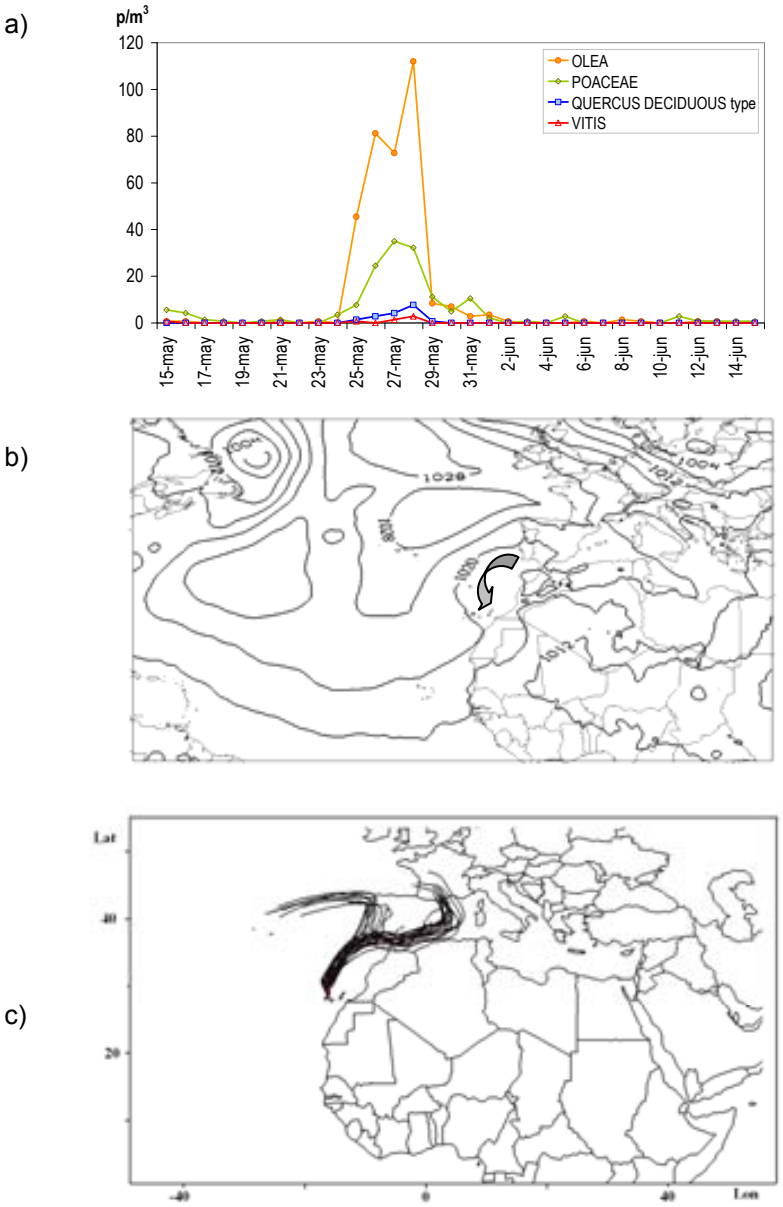


Figure 4. Episode from 25 to 29 May 2006 at SCO: a) mean daily pollen concentration; b) synoptic weather map showing sea level pressure (hPa) from ECMWF on 28 May 2006. *Arrow* Movement of the air mass; c) Four-day ensemble back trajectories calculated at 500 m asl altitude at 00:00 UTC from 28 May 2006.

Episodes during November 2006 at SCO

In November 2006, two episodes (10-15 and 19-22 November) of pollen peak concentrations of Chenopodiaceae/Amaranthaceae, accompanied with lower, though significant, peaks of Cyperaceae and Poaceae wild type, were recorded at SCO (Fig. 5a). As before, no data are presented for IZO because the sampler was not operating. The atmospheric situation was similar in both episodes. The Canary Islands were between two high-pressure systems: one located to the north of the Archipelago and centred in the island of Madeira and the other one over North Africa (Fig. 5b). High pressures over North Africa caused the transport of air masses

carrying edaphic dust and pollens from Mauritania and the Western Sahara to the Canary Islands. Four-day ensemble back trajectories for 10-11 November and 20-21 November originated mostly in a broad region around the borders of Argelia-Mali-Mauritania (See Fig. 5c for the episode on 20 November). Vegetation which showed significant pollen peaks in these episodes is present in this area as reported in the African Flowering Plants Database, version 3.1 (Conservatoire et Jardin botaniques de la Villle de Genève and South African National Biodiversity Institute, Pretoria, retrieved May 2009, from http://www.ville-ge.ch/musinfo/bd/cjb/africa/).

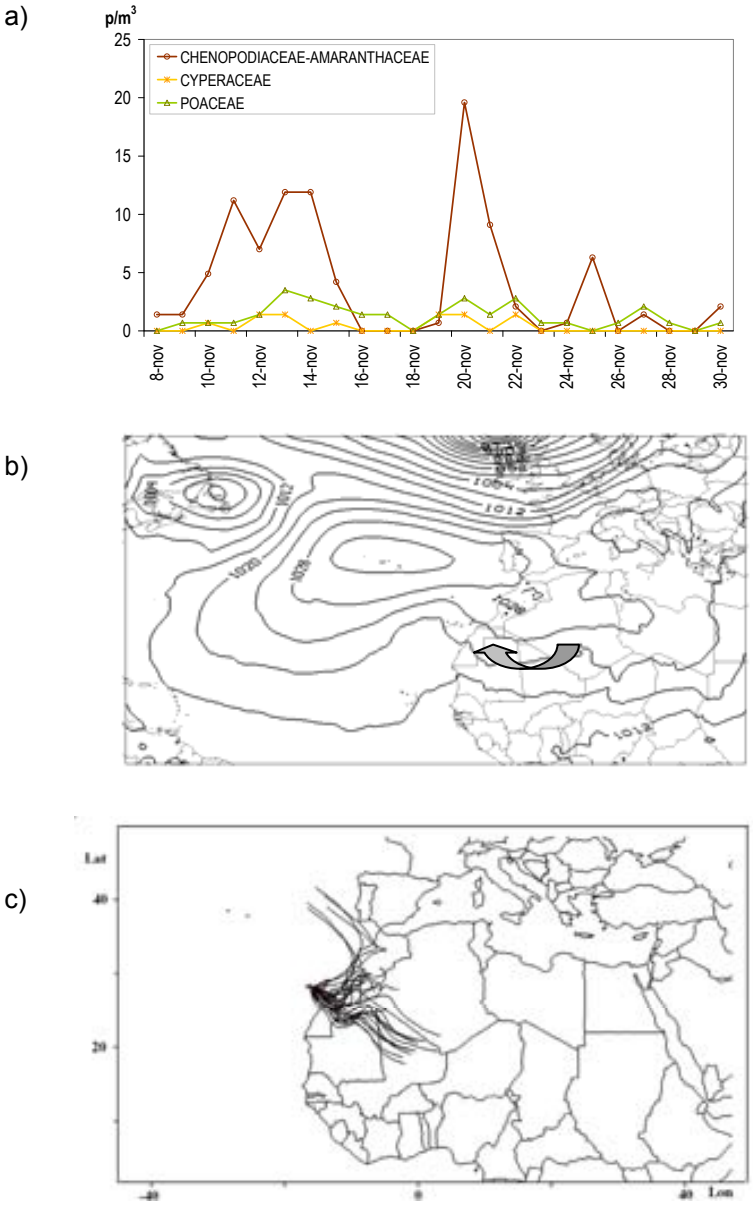


Figure 5. Episodes during November 2006 at SCO: a) mean daily pollen concentration, b) synoptic weather map showing sea level pressure (hPa) from ECMWF on 20 November 2006. *Arrow* Movement of the air mass; c) Four-dayensemble back trajectories calculated at 500 m asl altitude at 00:00 UTC for 20 November 2006.

Episodes during May 2007 at SCO and IZO

In May 2007, two pollen concentration peaks of *Olea* and *Quercus* perennial type were observed at SCO and IZO: the first was on 7-11 May and second, with higher concentrations, on 16-20 May. At SCO, the concentration peak was simultaneous for both pollen types on 18 May. Pollen concentrations at SCO were always higher than those at IZO (Fig. 6a).

The meteorological scenario during the first episode was characterized by the presence of a high-pressure system located to the west of the Iberian Peninsula (Fig. 6b). This had a heavy impact on surface winds and caused the trade winds to be replaced by air streams coming from North Africa. This is confirmed by the ensemble back trajectories at 500 and 2500 m asl for 8 May (Fig. 6c,e), and the SeaWifs images on 8 and 9 May which show a clear dust intrusion over the North Atlantic impacting over the Canary Islands (Fig. 6d).

Although both the MBL and the FT were affected by this atmospheric situation, the transport basically occurred at the lowest levels of the troposphere producing higher concentrations at SCO. On 9 May (not shown), back trajectories at 500 and 2500 m asl showed a Moroccan origin which crossed areas of distribution of *Olea* and *Quercus ilex* in northern Morocco (Charco, 1999).

In the second episode, besides the western Iberian Peninsula high-pressure system, a low-pressure system was located in the centre of the Sahara (not shown), reinforcing the air flow from the African Mediterranean region towards the Canary Islands. The second episode, from 16 to 20 May, corresponded to what we define as a combined transport. Combined transport would occur in two steps. Here, it began with an air movement produced by the depression over the Sahara which carried a cloud of dust and pollen over the Atlantic, and, from that point, an air flux from the eastern branch of the high situated in the west of the Iberian Peninsula would impinge on the dust cloud carrying the material to the Canary Islands (Fig. 6f).

Episode on 2-5 June 2007 at SCO and IZO

During the episode from 2 to 5 June 2007, a sudden increment of *Casuarina* daily concentrations at IZO, reaching values up to 221.9 p/m^3 was observed. Simultaneously *Olea,* also showed significant increases at IZO (Fig. 7a). At SCO, significant peaks were found for *Olea, Quercus* perennial type, Poaceae wild type and *Vitis.* Possible pollen transport to IZO from the lower parts of the island was unlikely since moderate synoptic winds (higher than 20 km/h) were recorded at IZO on 3 and 4 June, inhibiting the valley-to-mountain breeze in the morning. During the night a catabatic flow assures free-troposphere conditions at IZO. So, the remarkable high peak of *Casuarina* recorded at IZO, much higher than concentrations at SCO (non significant peak), must be due to long-range transport of pollen from higher altitudes. The SeaWifs image, corresponding to 3 June, shows low stratocumulus in the northern part of the

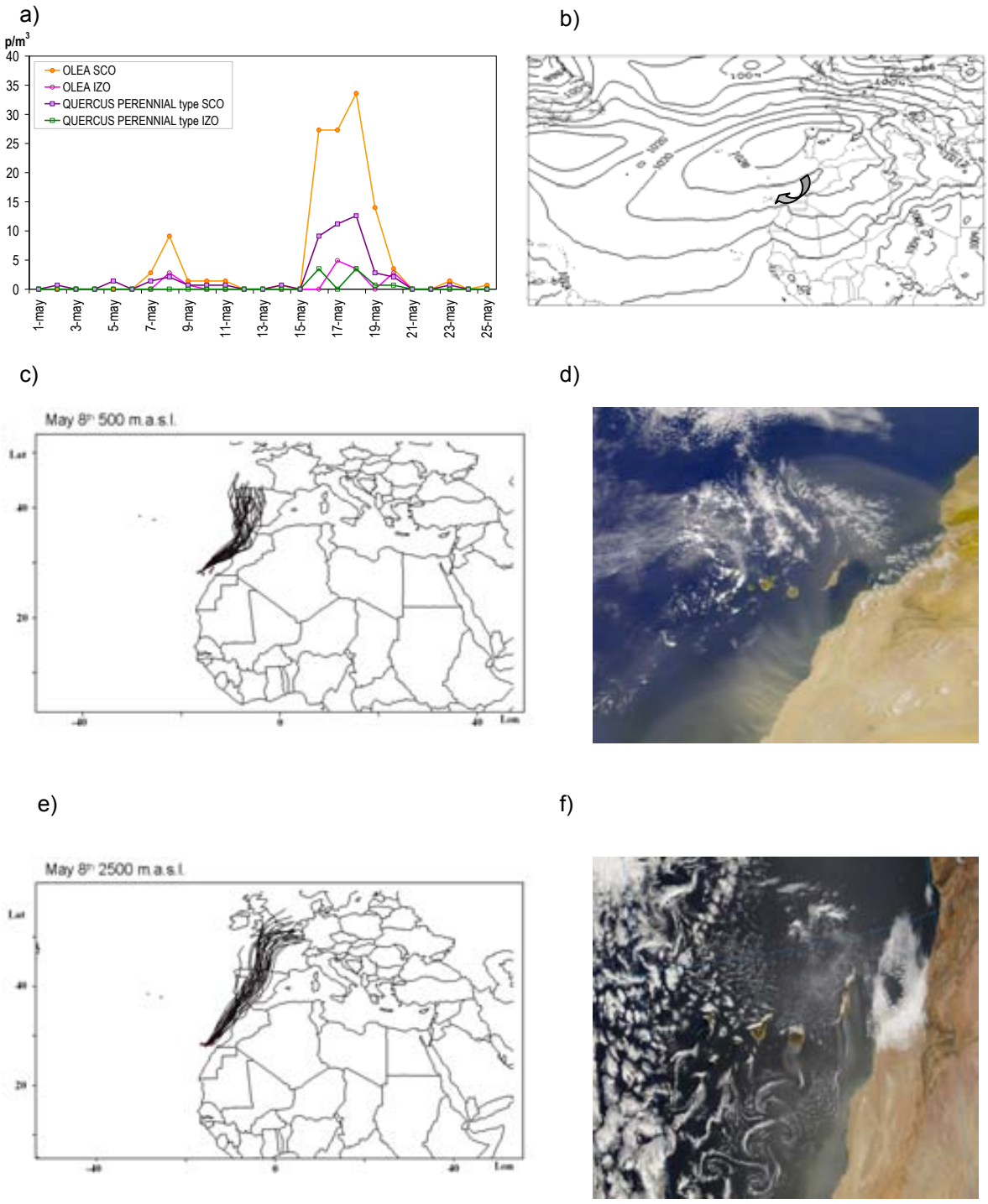


Figure 6 Episodes from 7 to 21 May 2007 at SCO and IZO: a) mean daily pollen concentration; b) synoptic weather map showing sea level pressure (hPa) from ECMWF on 8 May 2007. *Arrow* Movement of the air mass; c) Four-day ensemble back trajectories calculated at 500 m asl altitude at 00:00 UTC on 8 May 2007; d) SeaWifs image on 8 May 2007; e) Four-day ensemble back trajectories calculated at 2500 m asl altitude at 00:00 UTC on 8 May 2007; f) MODIS image on 16 May 2007.

islands and a “dust-shadow” in the south part of them (Fig. 7d). These two facts indicate that the dust cloud moving southwards only affected to the high lands of Tenerife (IZO).

The synoptic meteorological situation was characterized by a high-pressure system over the north Atlantic in front of the Iberian Peninsula, and a low-pressure system situated over Sardinia and Corsica (Fig. 7b). In the previous days, i.e., 1-2 June, several nuclei of low pressure formed also in North Africa. Under this atmospheric situation, ensemble back trajectories (Fig. 7c,e) and the forecast of the DREAM dust model indicated that air masses moved to the Canary Islands from the south of the Iberian Peninsula. A combined transport was also observed in this case, stemming from a similar pattern from the previously described: first, the air mass was moved from Morocco and Western Sahara to the Atlantic under the action of the North African low, and then this was mixed with the air mass coming from Iberian Peninsula to Tenerife. The identified pollen types during this episode are characteristic of Mediterranean vegetation assemblages (Belmonte and Roure, 1991), except for *Casuarina.* Hence the MBL pollen transport was from Iberian Peninsula air masses (Fig. 7c), whereas the FT pollen dynamic was characterized by the combined transport (Fig. 7e) confirmed by the important arrival of *Casuarina* from Western Saharan and southern Morocco mixed with Mediterranean pollen types at IZO.

Year 2006	**SCO**	**IZO**
	%	
Olea	89	
Vitis	88	
Quercus deciduous type	86	
Cyperaceae	57	
Poaceae	29	
Chenopodiaceae-Amaranthaceae	27	
Year 2007		
	%	*%*
Olea	94	97
Quercus perennial type	44	62
Poaceae	--	33

Table 2. Percent contribution of long-range transported pollen to total annual counts, calculated from the sum of peak events in each year.

As seen by these meteorological transport pathways and the nature of the pollen types, the Mediterranean region (broadly comprising southern Iberian Peninsula and African Mediterranean region) or the Sahara-Sahel are probable source areas for many of these pollens. Therefore, the meteorological information indicates that transport during these pollen peak days was from long-range transport. Based on this premise, we have evaluated the pollen contribution of peak days (extra-regional transport) and related it to the total counts. In Table 2 the percent contribution of the extra-regional sources is shown for the two sites. It can be seen that *Olea*, *Vitis* and *Quercus* deciduous type were mostly of extra-regional origin (percentages between 86-97%). In other taxa (Cyperaceae and *Quercus* perennifolia), outside sources predominated though with less importance (percentages of long-range transport 57-62%). On

the other hand, for very common and ubiquitous plants as the Poaceae and Chenopodiaceae/Amaranthaceae, only one third of the annual counts was from extra-regional sources.

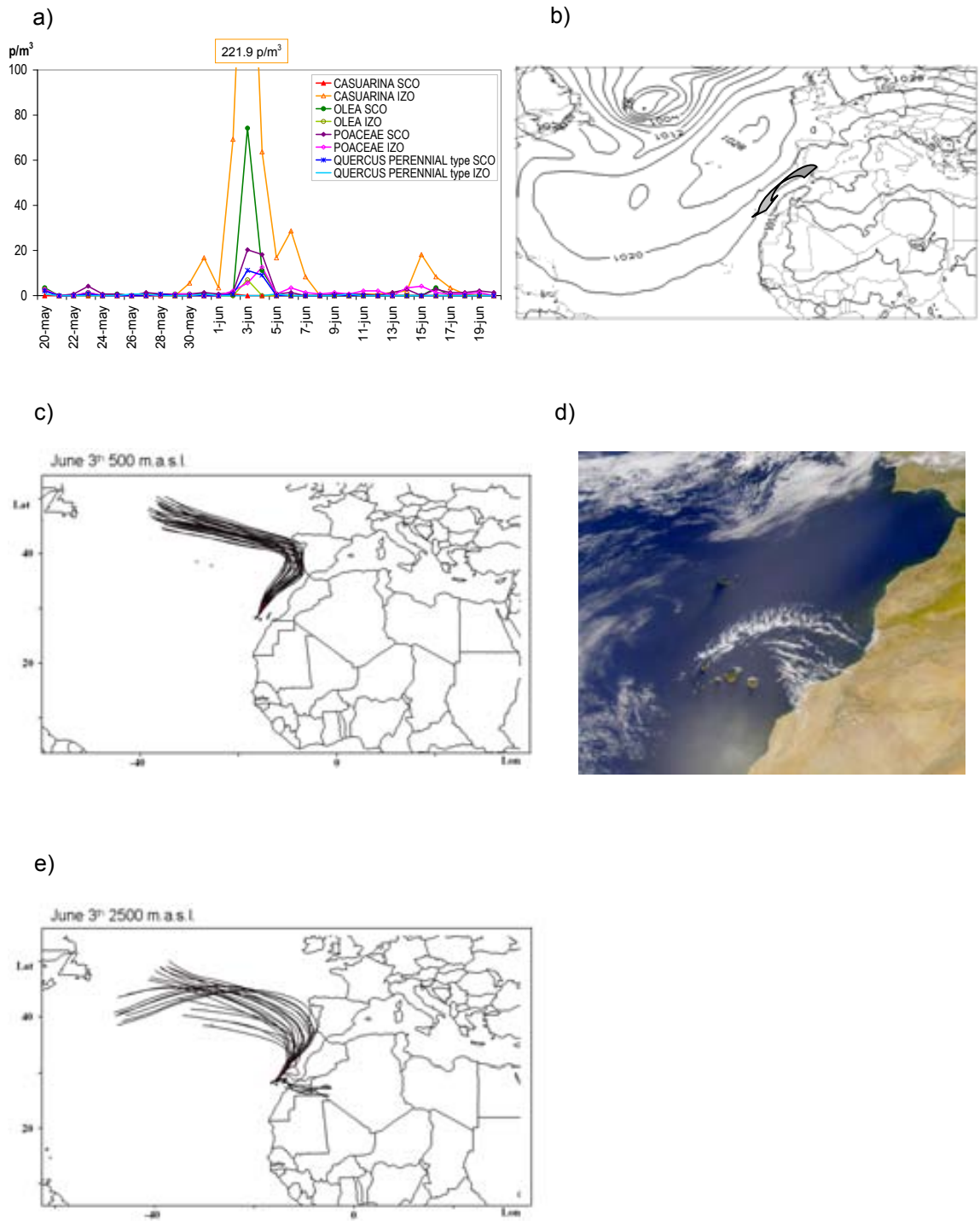
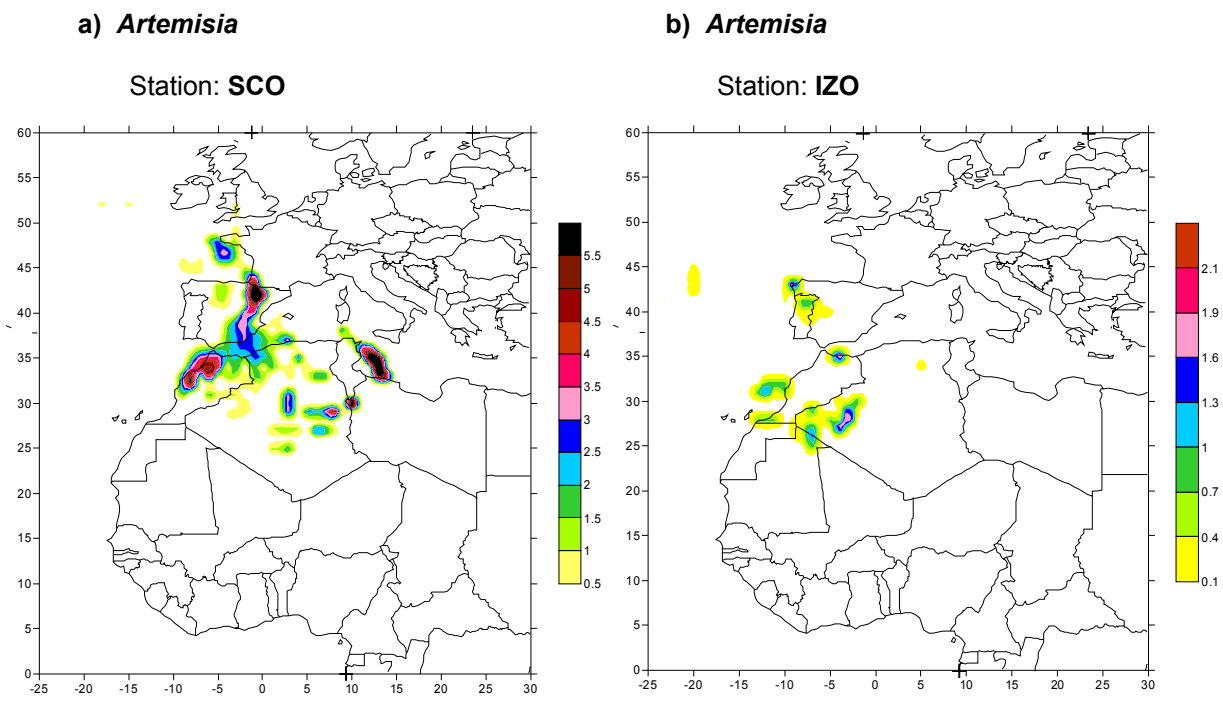


Figure 7. Episodes on 2-5 June 2007 at SCO and IZO: a) mean daily pollen concentration; b) synoptic weather map showing sea level pressure (hPa) from ECMWF on 3 June 2007. *Arrow* Movement of the air mass; c) Four-day ensemble back trajectories calculated at 500 m asl altitude at 00:00 UTC on 3 June 2007; d) SeaWifs image on 3 June 2007; and e) Four-day ensemble back trajectories calculated at 2500 m asl altitude at 00:00 UTC on 3 June 2007.

Source-receptor model

To further investigate the origins of the extra-regional pollen, a source-receptor model was applied to the taxa that indicated provenances from North Africa, Europe and Sahara-Sahel in the ANOVA analysis and the taxa that showed outstanding peaks (see above). Source-receptor models were applied to *Artemisia*, Chenopodiaceae/Amaranthaceae and Poaceae wild type at SCO and IZO, and to Arecaceae, Cyperaceae and *Olea* only at SCO (Fig. 8).

According to the maps of pollen concentration obtained with the source-receptor model (Fig. 8), the probable source areas were: North Africa and the Mediterranean region for Poaceae wild type; the Mediterranean region for *Artemisia* and *Olea*; Sahara and Sahel for Chenopodiaceae/Amaranthaceae and Arecaceae; and the Sahel for Cyperaceae.



Figre 8. Pollen concentration maps (p/m^3) derived from the application of Seibert et al. (1994) source-receptor model: a) *Artemisia* at SCO; b) *Artemisia* at IZO.

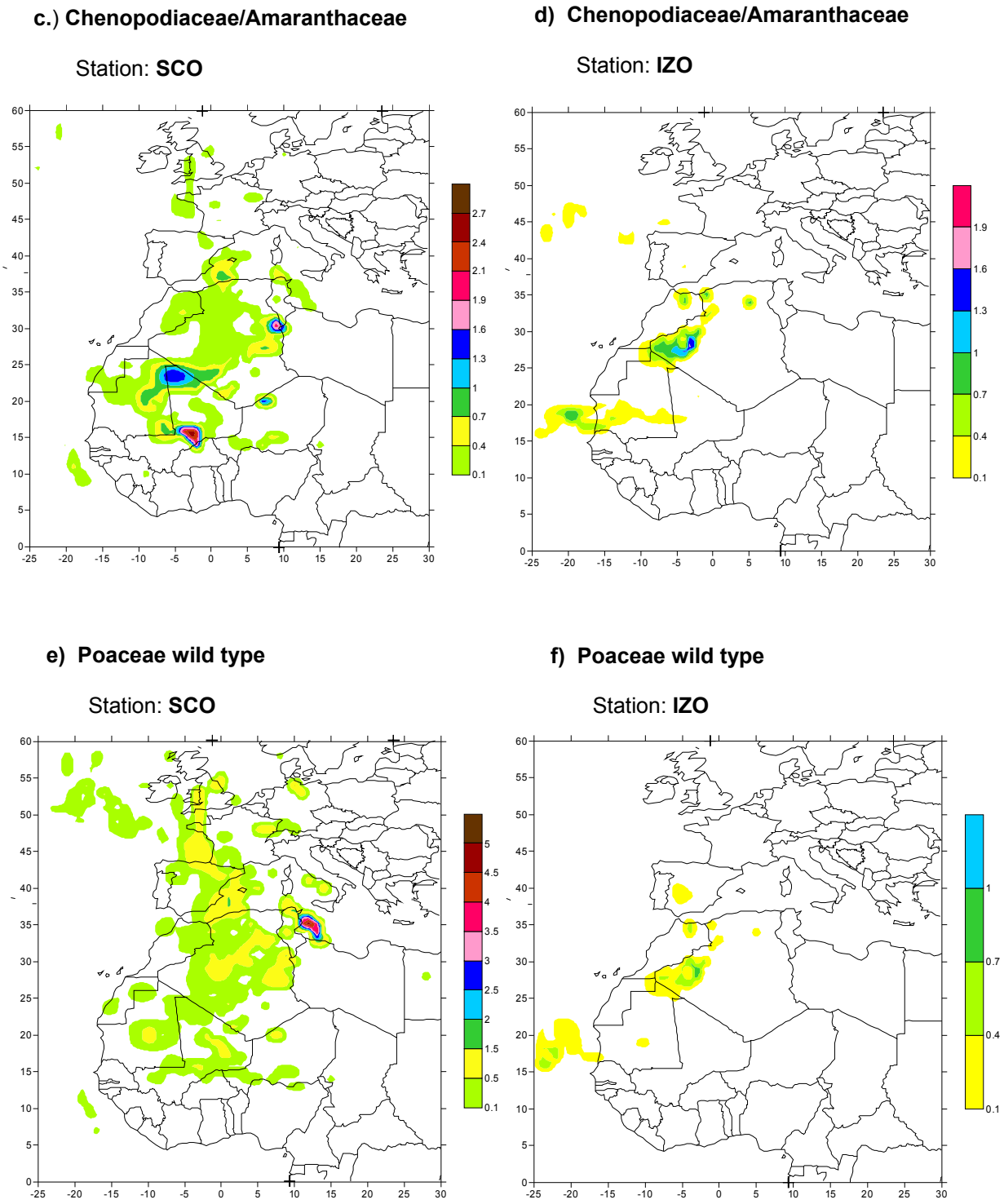


Figure 8. Pollen concentration maps (p/m^3) derived from the application of Seibert et al. (1994) source-receptor model: c) Chenopodiaceae/Amaranthaceae at SCO; d) Chenopodiaceae/Amaranthaceae at IZO.

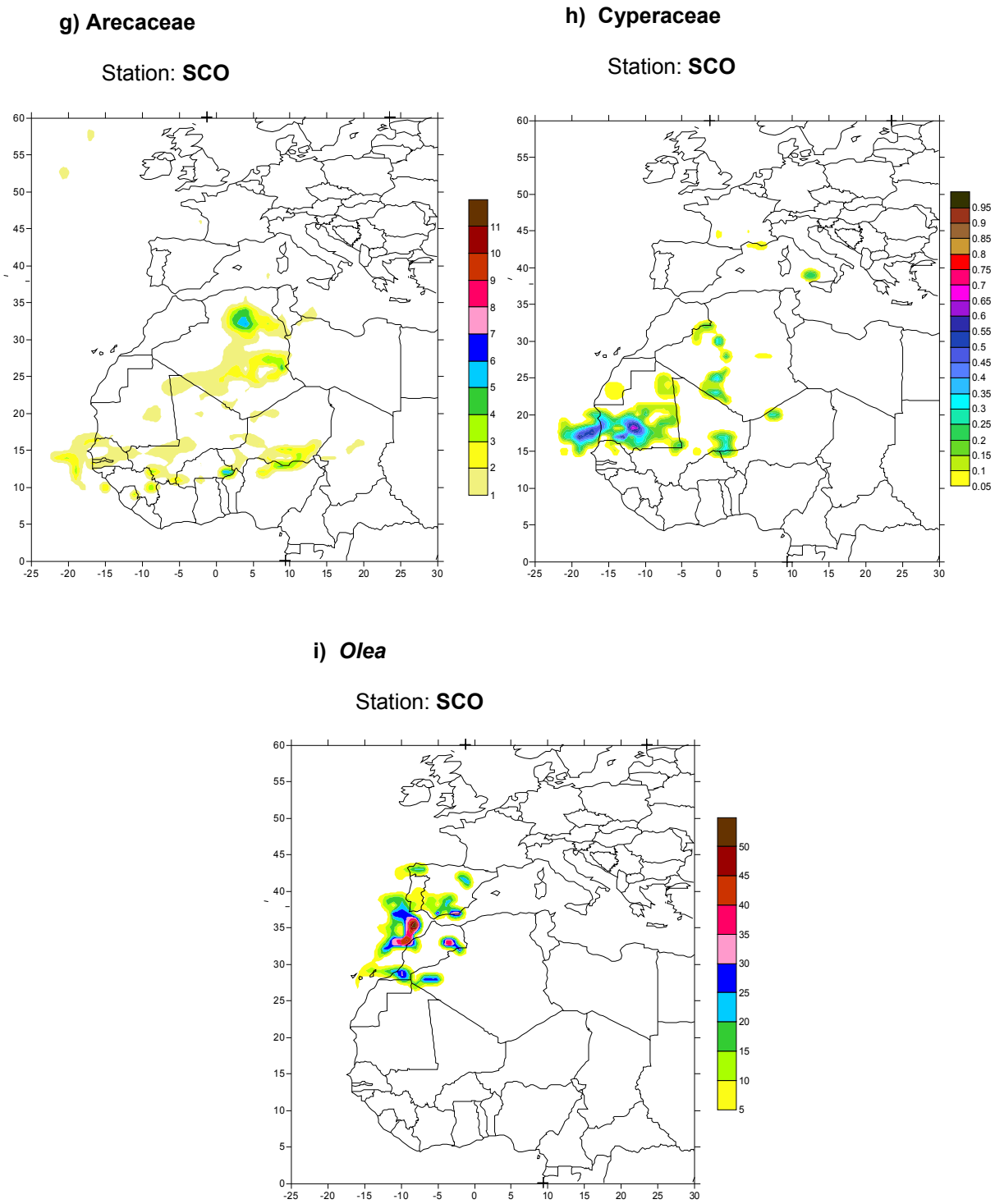


Figure 8. Pollen concentration maps (p/m^3) derived from the application of Seibert et al. (1994) source-receptor model: g) Arecaceae at SCO; h) Cyperaceae at SCO; and i) *Olea* at SCO.

Table 3. Summary of the evidence supporting an extra-regional pollen transport to Tenerife. Probable source areas are proposed and references supporting this hypothesis are included. Period Index is the sum of the mean daily pollen concentrations during the study period (01/01/2006-31/12/2007 at SCO and 11/06/2006-11/11/2006 and 23/04/2007-04/11/2007 at IZO). References: [1]Van Campo and Quet 1982; [2]Calleja et al. 1993; [3]Franzen et al. 1994; [4]Romero et al. 2003; [5]Cariñanos et al. 2004; [6]Hooghiemstra et al. 2006; [7]Waisel et al. 2008.

		Period Index (pollen)	Provenance by sectors from ANOVA	Date	Area of provenance for Specific case studies	Source area from source-receptor models	Probable extra-regional origin and Supporting references
Olea	SCO	295	-	May 06 May 07 June 07	Mediterranean	Mediterranean (Iberian Peninsula and Morocco)	Mediterranean [2,3,6] (SCO)
	IZO	23	-	May 07 June 07	Mediterranean	-	
***Quercus* deciduous type**	SCO	14	-	May 06 June 07	Mediterranean	-	Mediterranean
	IZO	8	EU+MED-NAF	-	-	-	
***Quercus* perennial type**	SCO	102	-	May 07 June 07	Mediterranean	-	Mediterranean [2,6]
	IZO	13	-	May 07 June 07	Mediterranean	-	
Vitis	SCO	4	-	May 06 June 07	Mediterranean	-	Mediterranean (SCO)
Artemisia	SCO	985	-	-	-	Mediterranean-Saharan Transitional Steppes	African Mediterranean Region [2,3,4,6]
	IZO	68	MED-NAF	-	-	Mediterranean	
Casuarina	SCO	26	MED-NAF	-	-	-	African Mediterranean Region [1,2,5]
	IZO	704	-	June 07	African Mediterranean region	-	
Poaceae wild type	SCO	449	-	May 06 Nov. 06 June 07	Mediterranean Sahara-Sahel	Sahel, Sahara desert and Mediterranean	Mediterranean and North Africa [2,4,6]
	IZO	97	-	June 07	Mediterranean	Sahara desert	
Chenopodiaceae / Amaranthaceae	SCO	269	North Africa	Nov. 06 June 07	Mediterranean Sahara	Sahara desert and Sahel (Mauritania, Mali, Algeria)	North Africa [2,3,4,6,7]
	IZO	0			-		
Arecaceae	SCO	720	SAHEL-SGR	-	-	Sahel and Sahara desert (Algeria)	Sahel and Sahara desert (Algeria)[7] (SCO)
	IZO	6	-	-	-	-	
Cyperaceae	SCO	15	SAHEL-SGR	Nov. 06	Sahara	Sahel and Sahara desert	Sahel and Sahara desert [3,4]
	IZO	15	-	-	-	-	

Discussion

All pollen types identified as having a possible extra-regional origin in the island of Tenerife correspond to vegetation also present in the island, which shows the complexity of the subject studied. Most pollen transport occurs within the island, but local pollen concentrations are usually low and they show a narrow range of variation (Fig. 3). In the study cases presented here, pollen peaks increased drastically from background concentrations (Figs. 4 to 7). Furthermore, in all the presented cases, the pollen increase coincided with specific meteorological situations driving air masses from regions in which the plants providing the observed pollen are present. A synthesis of the evidence supporting long-range transport for pollen is summarized in Table 3. Considering the three approaches used to determine the transport (provenance analysis, specific case studies and source receptor modelling), four of the ten studied pollen types were associated with a possible Mediterranean origin: *Olea, Quercus* both deciduous and perennial types and *Vitis*. It was estimated that 86-97% of these taxa pollen count were from extra-regional sources. *Artemisia* and *Casuarina* were specifically related with the African Mediterranean Region. Arecaceae and Cyperaceae were probably transported from regions in the Sahel and the Sahara desert. Probable provenances for Chenopodiaceae/Amaranthaceae were North Africa, and for Poaceae wild type was North Africa together with the Mediterranean region. Other authors (see citations in Table 3) have also reported pollen transport from the proposed areas. The aerobiological study of Calleja et al. (1993) and the paleopalynological studies of Romero et al. (2003) and Hooghiemstra et al. (2006) reinforce the assumption of pollen transport from North Africa and from the southern Mediterranean to Tenerife for *Artemisia, Casuarina,* Chenopodiaceae/Amaranthaceae, Cyperaceae*, Olea, Quercus* perennial type and Poaceae wild type. Others studies carried out in Europe (Van Campo and Quet, 1982; Franzen et al. 1994; Cariñanos et al. 2004) and at the Mediterranean Sea (Waisel et al. 2008) have also reported long-range transport of Arecaceae*, Artemisia,* Cyperaceae*, Casuarina,* Chenopodiaceae/Amaranthaceae and *Olea* originating in the Mediterranean area. The presence of these plants in the proposed source areas (African Flowering Plants Database, version 3.1, http://www.ville-ge.ch/musinfo/bd/cjb/) supports the assumption exposed in this paper.

The strong influence of the trade winds from the northeast over Tenerife (Rodríguez, 1999) together with the high plant diversity of the vegetation in the Mediterranean region can explain the high number of pollen types related with a Mediterranean provenance. In contrast, pollen types originated in the Sahel and the Sahara desert would correspond to vegetation in extreme environmental conditions that only occasionally finds adequate climatic conditions to pollinate. Except for the palm trees (Arecaceae), taxa from the African provenance were clearly characterized by the predominance of herbaceous taxa, similarly to the findings of Hooghiemstra et al. (2006). Finally, the wide provenance area found for Chenopodiaceae/ Amaranthaceae and Poaceae wild type pollen is explained for these families being cosmopolitan (Mabberley, 1987)

The period index (Table 3) is the sum of the mean daily pollen concentrations during the study period. This value was larger at SCO than at IZO, except for *Casuarina.* Higher values at SCO come from: (1) the study period being for a longer period at this site, and (2) the local vegetation at SCO producing higher numbers of pollen (for example, of Arecaceae and *Artemisia*). However, the observed higher period index for *Casuarina* at IZO was due to a combined mechanism in which the air mass containing this pollen was uplifted and moved to the west in a cyclonic motion by the action of the north African low already described above. Then this pollen crossed the top of the MBL and entered the FT, where it could be transported by the eastern branch of the north Atlantic anticyclone (Fig. 7).

Concerning to long range transport, the values observed in the period index along with evidence from the case studies indicate that most of the transport would occur through the trade winds. In some cases (such as Chenopodiaceae-Amaranthaceae at SCO and IZO, Cyperaceae at SCO and Poaceae wild type at IZO) the three approaches we have used indicate the same provenance, and other work supports this result (see references in Table 3). Although these taxa could also have a regional origin due to its cosmopolitism (Mabberley, 1987), the exposed evidences reinforce the hypothesis of a long range transport.

For other taxa (such as Arecaceae at SCO, *Artemisia* at IZO and *Olea* at both sites) two of our approaches support the designation of a provenance which is also supported by the bibliography. Again, although these taxa can have a regional origin, evidence for provenance from far away regions is found.

For other taxa or for a given station, only one analysis suggested an extra-regional provenance and for some of these taxa (*Quercus* deciduous type and *Vitis*) no bibliographical reference has been found. Finally, we have found no evidence of transport from foreign areas for Arecaceae, Cyperaceae, and *Vitis* at IZO.

Conclusions

In conclusion, our results indicate several extra-regional pollen transport episodes to Tenerife. Main provenances were: First, from the Mediterranean region, especially from the southern Iberian Peninsula and Morocco through the trade winds in the MBL. These episodes were characterized by the presence of tree pollen (*Casuarina, Olea, Quercus* perennial and deciduous types) and mixed with herbaceous pollen *(Artemisia,* Chenopodiaceae-Amaranthaceae and Poaceae wild type*)*. Second, transport from the Saharan sector at the MBL level, carrying principally herbaceous pollen (Chenopodiaceae-Amaranthaceae*,* Cyperaceae and Poaceae wild type) and in one case *Casuarina* pollen, uplifted to the free troposphere. And third, from the Sahel, which appears as episodes of low frequency associated to high pressure systems over north Africa and characterised by low concentrations of the transported pollen taxa (Arecaceae, Chenopodiaceae-Amaranthaceae, Cyperaceae and Poaceae wild type*)*.

The capacity for sensitization to pollen is theoretically universal. Several of the studied taxa with an extra-regional origin (such as *Artemisia,* Chenopodiaceae/Amaranthanceae*, Olea*, Poaceae wild type and *Quercus* perennial type) are among the ones causing most common allergies (Bousquet et al. 2008). Other studied taxa (Arecaceae, *Casuarina* and Cyperaceae) have also been recognised as allergenic (Lewis et al. 1983). The prevalence (percentage of the pollen causing the allergy) observed in Tenerife in patients with confirmed pollinosis has been: *Artemisia* 64.5%, Gramineae or Poaceae 45.2%, Urticaceae 24.5%, *Chenopodium* 9.4% and *Salsola* 6.2% (Belmonte et al. 2008b). This research shows that sporadic events of long-range pollen transport need to be taken into consideration as responsible for respiratory allergy episodes, as has been also found in other studies (Estrella et al. 2006; Skjøth et al. 2007; Siljamo et al. 2007, 2008).

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Chapter 6

Conclusions

The main outcomes of this thesis are summarised as follows:

Chapter 2

The comparison of collection methods to determine atmospheric deposition in Montseny (NE Spain) showed that:

I. The removal of atmospheric compounds occurred mainly by wet deposition, which contributed 74% of total deposition (wet+dry).

II. Dry deposition was characterized by the predominance of crustal ions such as Ca^{2+} and Mg^{2+} or crustal-biological such as K^{+}.

III. Although the recovery of deposited particles after the last rain (DSP) only contributed 8% to total deposition (wet+dry), this is an important measurement to include, since bulk deposition plus DSP accounted for 97% of total deposition (wet+dry).

IV. Total deposition estimated by wet plus dry and bulk plus deposited particles after the last rain (DSP) was generally equivalent, with the exception of K^{+} and NH_4^{+}.

Thus, in Mediterranean rural environments, when field conditions do not favor the set up of wet-only/dry-only devices, bulk plus DSP measurements can be implemented because, as shown in this work, they accounted for most of the sum of wet and dry deposition. However, it should be kept in mind that these measurements are an approximation to the real deposition to the landscape, since direct dry deposition sampling methods underestimate deposition of gases and fine particles. Therefore this method for collecting dry deposition mostly applies for elements deposited as coarse aerosols.

Chapter 3

Some ions in the precipitation in the Montseny Mountains (NE Spain) showed significant changes over time during the last 25 years (1984-2009). For these elements, source receptor models have been applied to interpret the changes, and indicated that:

V. The general atmospheric circulation over the NE Iberian Peninsula has changed and shown a 10% decrease of Atlantic advections (from 39% in 1984-1993 to 31% in 1998-2005) and a 5% increase of African (from 9% to 13%) and European (from 13% to 18%) air flows.

VI. The seasonal pattern for rainy days indicated that precipitation in winter and spring was originated mostly from the Atlantic, in autumn from North Africa and in summer, from Europe and the regional recirculation.

VII. Precipitation collected in Montseny from 1983 to 2009 showed a significant decrease of SO_4^{2-} and H^+ and an increase of NO_3^-. In the initial period (1984-1993) these anthropogenic pollutants (SO_4^{2-}, H^+ and NO_3^-) were mostly originated in central and Eastern Europe. The implementation of stricter environmental policies for the abatement of sulphur emissions over central Europe resulted in a significant temporal decrease of SO_4^{2-} and H^+ in precipitation collected in Montseny. The increase of emissions from traffic ships and the industrialisation of developing countries in Eastern Europe and North Africa may account for the location of the main source areas of SO_4^{2-}, H^+ and NO_3^- over North Sea, Eastern Europe and North Africa region in the more recent period (1998-2009).

This knowledge must be taken into account for designing effective abatement strategies to reduce air pollution and its effects on ecosystems and human health. Particularly, further emission controls are needed to reduce SO_2 and NO_x emissions from ships, which have an increasing role in particle formation and transport that can affect sites far away from maritime routes.

Chapter 4

The estimation of atmospheric phosphorous (P) deposition to the western Mediterranean Sea showed that:

VIII. Dry deposition accounted for ~50% of total annual particulate phosphorus deposition which amounts to 576 μmols P m^{-2} y^{-1}. This indicates that the dry deposition pathway needs to be considered when nutrient budgets for the Mediterranean are calculated.

IX. African events were very relevant in the annual budget accounting for 2/3 of total annual particulate phosphorus deposition. In these African events, wet deposition dominated over dry deposition.

X. Total annual particulate phosphorus deposition in north-eastern Spain lies toward the lower range of reported values for Corsica and the eastern Mediterranean, in agreement with an increasing impact of African dust from west to east in the Mediterranean.

XI. On an annual basis, atmospheric-derived soluble P contributed < 1% of annual new primary production in the western Mediterranean. However, one strong African dust event (22-27 May, 2008) accounted for 24-33 % of the atmospheric P-induced annual new production, thus suggesting the important role of sporadic high dust-loaded events in the Mediterranean productivity.

This study corroborates the findings of other research in the Western Mediterranean indicating that P deposition from African dust events, despite its low P dissolution rate (8-15%), may

represent an important source of nutrients to surface waters, especially when they occur during the stratification period when nutrients are depleted at the surface.

Chapter 5

The study of source areas and long-range transport of pollen from continental land to Tenerife (Canary Islands) indicated that:

XII. The main provenances of long-range pollen transport episodes detected in Tenerife were: (1) The Mediterranean region, especially from the South of the Iberian Peninsula and Morocco, through the trade winds in the marine boundary layer (MBL). These episodes were characterized by the presence of pollen from trees (*Casuarina, Olea, Quercus* perennial and deciduous types) mixed with pollen from herbs (*Artemisia,* Chenopodiaceae-Amaranthacea and Poaceae wild type). (2) The Saharan sector, through transport at the MBL level carrying mainly pollen from herbs (Chenopodiaceae-Amaranthaceae*,* Cyperaceae and Poaceae wild type) and, in one case, *Casuarina* pollen uplifted to the free troposphere. And (3) the Sahel, which appears as episodes of low frequency associated to high pressure systems over north Africa and characterised by transport of pollen from palm trees (Arecaceae) and herbs (Chenopodiaceae-Amaranthaceae, Cyperaceae and Poaceae wild type).

XIII. Several of the studied taxa from an extra-regional origin (such as *Artemisia,* Chenopodiaceae/Amaranthanceae*, Olea*, Poaceae wild type and *Quercus* perennial type) are among the ones causing most common allergies. Other studied taxa (Arecaceae, *Casuarina* and Cyperaceae) have also been recognised as allergenic.

Thus, this research shows that sporadic events of long-range pollen transport need to be taken into consideration as possible cause of respiratory allergy episodes, which up to now have been mostly attributed to dispersion of local pollen.

Further research

Several points that are raised in this thesis require further research, as discussed below.

The study of the transport and deposition of atmospheric compounds is essential for the understanding of spatial variations, temporal trends and the possible effects of pollutant deposition on ecosystems and human health. Several aspects of concern warrant further long-term atmospheric monitoring. In particular more research is needed about: temporal trends of nitrogen deposition, impacts and control of new source areas attributed to ship emissions, and newly industrialisation of areas in North Africa, the effect of phosphorus atmospheric deposition in nutrient budgets of terrestrial and marine ecosystems and ecosystem productivity, and the

long range transport and viability of bioaerosols (pollen, bacteria and fungi) after dispersion. The interactions in the atmosphere between anthropogenic pollutants, mineral dust and biological organisms constitute an important field of research that is revealing unexpected implications on the functioning of the environment.