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AIR POLLUTION ACROSS THE MEDITERRANEAN BASIN: MODELLING, MEASUREMENTS AND POLICY IMPLICATIONS

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CHAPTER 1

Introduction

The Mediterranean Basin still does suffer from the impact of anthropogenic pressures which lead to environmental degradation. Chemical pollution, maritime transport and climate change are key factors causing air quality degradation at both regional and local scales. On the other hand, air pollutant dynamics and distribution in the Mediterranean region are closely related to its unique geographical characteristics and specific weather conditions that favour the enhancement of air pollutant photochemical production and accumulation. Poor air quality within the Mediterranean Basin has effects on human health, ecosystem conditions and economic resources. Already existing measures to manage pressures have been proven inadequate and the EC proposed new policies and environmental legislation, both currently close to adoption. Owing to this context, the work developed during this PhD focuses over the Mediterranean region in order to investigate key pressure affecting Mediterranean regional air quality, to gain further insight into the atmospheric mechanisms leading to high air pollutant levels across the Mediterranean Basin and to describe the resulting trade-offs that will have to be dealt by management and policy. These overall goals have been achieved through the application of innovative modelling techniques as well as the assimilation and integration of monitoring-based data, with the supporting facilities of both ENEA (National Agency for New Technologies, Energy and Environment) – Casaccia Research Centre and CNR-IIA (Institute of Atmospheric Pollution Research of the Italian National Research Council) - Division of Rende (CS). The DPSIR (*Driver-Pressure-State-Impacts-Response*) conceptual framework has been followed in the PhD dissertation to highlight the several factors influencing this complex study. The DPSIR model, adopted by the European Environmental Agency, is in fact useful in describing the relationships between the origins and consequences of environmental problems; furthermore, in order to understand their dynamics, it is also useful to focus on the links between DPSIR elements. In this way, the relationship between the *Driving forces* and the *Pressure* from the Italian economic activities as well as the effectiveness of some *Responses*, like the measures taken into account in the Italian Regional Air Quality Management Plans (AQMPs), were investigated through the RAINS-Italy model and within the convention between the Ministry of the Environment, Land and Sea (MATTM) and ENEA. As reported in ***Chapter 2***, the application of the RAINS-Italy model, starting from the Italian official energy and production activities scenario and transmitted to the EU Commission for the Emission Trading National Allocation Plans, provided the related Current Legislation (CLE) emission scenarios of SO_2, NO_x, PM_{10}, $PM_{2.5}$, VOC and NH_3. The effectiveness in air pollution emission reduction at the target year, 2010, of the Italian Regional AQMPs was then assessed comparing the Current Legislation (CLE) and an alternative scenario, which contains all the measures that the Regional administrations intend to adopt to preserve air quality within their territory. The efficacy of all AQMPs measures at 2010 was shown in terms of SO_2, NO_x and PM_{10} emissions avoided and PM_{10} concentration reductions together with the improvements of the health impact indicator, the Life Expectancy Reduction (LER), defined as months lost attributable to $PM_{2.5}$ concentrations. The carried out analyses show that the Italian Regional AQMPs contain Technical and Non-Technical Measures especially in the energy, domestic and transport sectors both having a crucial role, although the normative compliance is not assured everywhere. The identification and quantification of the main natural and anthropogenic sources (*Drivers*) affecting air pollutant levels in the Southern Italy were, otherwise, carried out by refining a range of multivariate and linear modelling techniques for covariance and time series analysis (***Chapter 3***). Principal Component Analysis (PCA) statistical method was also applied to the available air pollutant levels in order to decouple the sample amounts into estimated source profiles and source contributions to each sample. The air quality assessment, representing the *State* of the air matrix within the DPSIR framework, was then carried out through observational measurements obtained from both land-based and over-water monitoring campaigns (***Chapters 4, 5*** and ***6***). The PhD dissertation specifically focuses on three priority pollutants: Particulate Matter (PM), Ozone (O_3) photo-chemically produced and Mercury (Hg) that is long-lived in the atmosphere (from 6 months to 1 year on average) and thus representative of hemispheric/global pollutants which are subject to long-range transport. The air quality, in term of variations of the above mentioned air pollutant levels was furthermore evaluated in relation to both natural and anthropogenic sources. Central-Southern Mediterranean Basin, especially in summertime, is heavily affected by natural sources, like Saharan dust outbreaks and wildfire events, therefore a focus on their influence on both oxidizing capacity of the atmosphere and air quality over Calabria region, southern Italy was addressed and presented in ***Chapter 4***. During summer 2007 an intensive sampling campaigns on PM_{10} and O_3 concentrations have been simultaneously performed at three monitoring stations of the CNR-IIA - Division of Rende, the Marine, Urban and High Altitude monitoring sites. The results obtained were then coupled with both backward trajectories analysis and satellite derived products which were useful to understand the aerosol sources and transport pathways. These crossed analysis permitted to register some Saharan dust intrusion, highlighting that a huge rise in PM_{10} levels with a concurrent decrease in O_3 values usually characterized these transport events. According to the Air Quality Directive 2008/50/EC and skipping the obtained net dust load from the measured PM_{10} levels, a notably reduction in the number of daily excedancees was observed highlighting the large influence of this natural source over the air quality in the southern Mediterranean regions. Moreover, even if further analysis should be conducted to better evaluate the specific amount of O_3 and PM_{10} concentrations directly due to wildfire emissions, the observations carried out suggest that during favourable weather conditions, the contribution of biomass fires on both tropospheric O_3 and aerosol concentrations cannot be neglected during specific periods of summertime. The influence of anthropogenic sources was otherwise assessed in ***Chapter 5*** focusing on the " Large Industrial Point Sources" (regulated by the IPPC Directive 2008/1/EC) that refer to the major combustion plants, including chemicals production and steel plants, refineries and incinerators. Atmospheric mercury emissions from all IPPC activities located in Italy were checked on the INES (Inventario Nazionale delle Emissioni e delle loro Sorgenti) register. The results showed that the highest value of mercury emissions in air, ranging from 1062 to 1385 Kg yr^{-1}, refers to the largest pig iron and steel facility in Europe (ILVA S.p.a) located in the city of Taranto, whereas the second contribution, in terms of absolute mercury emission values, comes from the refinery (SYNDIAL S.p.A. - ex EniChem S.p.A.) located at Augusta-Priolo city in Sicily. Moreover, it could be observed that within the mercury emissions related to all IPPC activity, the largest part (about 74%), come from those IPPC facilities whose involved area has been defined as a National Interest Rehabilitation Site (Law n. 426/1998 and Ministerial Decree 468/2001). Measurements of atmospheric mercury species were also performed across both the Tyrrhenian and the Adriatic sea aboard the Research Vessel (*RV*) Urania of the Italian CNR during three oceanographic campaigns within MEDOCEANOR project, in order to assess the spatial distribution and temporal variation of mercury species concentrations in Marine Boundary Layer close to industrial contaminated sites. Two of these three cruise campaigns were performed across the Adriatic sea following the same route in different meteorological conditions during two seasons, autumn 2004 (27th of October to 12nd of November) and summer 2005 (17th to 29th of June) whereas the third one took place across the Tyrrhenian sea during 2007 (12nd of September to 1st of October). Furthermore, to gain more insight into the atmospheric mechanisms leading to high air pollutant levels across the Mediterranean Basin, the measurements performed during six cruise campaigns on board the CNR *RV* URANIA, from 2003 to 2009 and within the CNR MED-OCEANOR programme, were synthesized, integrated and then analysed in a coherent way (***Chapter 6***). Sampling periods of each of this six cruise campaigns refer to: summer 2003 (6 to 27 August); autumn 2004 (27 October to 12 November); summer 2005 (17 to 29 June); summer 2006 (5 to 20 July); autumn 2007 (12 September to 1 October) and summer 2009 (5 to 30 June). In the Mediterranean marine environment the maritime transport became a “hot” issue in the past decade for atmospheric research and air pollution and climate policy. Despite implications on both human health and radiative budget involve an increasing interest, data referring to air pollutants directly measured on the sea are yet relatively scarce. Owing to this context, the overview reported in ***Chapter 6*** holds a relevant interest in that it fills in part the observation gaps over the Mediterranean basin. Specifically, for each oceanographic cruise campaigns performed on board the CNR *RV* URANIA, temporal and spatial variations of both fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particles concentrations along with ozone and meteorological parameters were examined. Elemental composition of both $PM_{2.5}$ and $PM_{2.5-10}$ were furthermore determined in order to identify specific tracers for different classes of particles that can be found in the Mediterranean atmosphere. Shipping emissions, representing both local harbours and maritime traffic across the basin, were also tested using the marker ratio of V and Ni, showing a quite large contribution to the total aerosol load. Variations of the two size range of inhalable particulate matter ($PM_{2.5-10}$, $PM_{2.5}$) over the eastern and western sector of the Mediterranean basin were also investigated in respect to source-receptor relationships. Finally, in ***Chapter 7***, the role of atmospheric pollution on harmful health effects (*Impacts*) are investigated. Within the CNR Environment and Health Inter-departmental (PIAS) Project, recent findings on toxicity routes attributable to particulate and gaseous pollutants are reviewed. Toxicity routes are discussed as evidence or hypothetical relationships between sources, diffusion paths, receptor sites and susceptible populations. The body of knowledge which has received during the whole PhD activity was thus necessary and essential for the acquisition of a methodology which proved to be really suitable for the evaluation of complex problems relating to air pollution in the Mediterranean Basin. The results obtained during this study give a valuable contribution to our current understanding of how and why regional air quality may change in the Mediterranean region and could provide important information for scientists and policy implications.

CHAPTER 2

The integrated assessment of the regional Air Quality Management Plans through the Italian national model

The Italian Air Quality legislation underwent sweeping changes with the implementation of the 1996 European Air Quality Framework Directive when the Italian administrative Regions were entrusted with air quality management tasks. The most recent Regional Air Quality Management Plans (AQMPs) highlighted the importance of Non-Technical Measures (NTMs), in addition to Technical Measures (TMs), in meeting environmental targets. The aim of the present work is to compile a list of all the TMs and NTMs taken into account in the Italian Regional AQMPs and give in the target year, 2010, an estimation of SO_2, NO_x and PM_{10} emission reductions, of PM_{10} concentration and of the health impact of $PM_{2.5}$ concentrations in terms of Life Expectancy Reduction. In order to achieve this objective the RAINS-Italy, as part of the National Integrated Modeling system for International Negotiation on atmospheric pollution (MINNI), has been applied. The management of TMs and NTMs inside RAINS have often obliged both the introduction of exogenous driving force scenarios and the control strategy modification. This condition has inspired a revision of the many NTM definitions and a clear choice of the definition adopted. It was finally highlighted that only few TMs and NTMs implemented in the AQMPs represent effective measures in reaching the environmental targets.

2.1 Introduction

A new approach to air quality assessment was introduced in 1996 with the publication of the European Air Quality Framework Directive (EC,1996), which defined for the first time howair quality should be assessed and managed in the Member States. Together with the subsequently issued four daughter directives (EC, 1999, 2000, 2002, 2004), a common framework for the assessment and reporting of air quality was set, the pollutants for which air quality standards and objectives were to be considered in the legislation were specified. The new Directive 2008/50/EC on ambient air quality and cleaner air for Europe (EC, 2008) confirms substantially the planning and management approach to air quality, even introducing new limit values for $PM_{2.5}$, the assessment of the contribution of natural sources and other new features. The Italian Air Quality legislation underwent sweeping changes through the Italian Government Decree no. 351 issued under Parliamentary Delegation on 1999 (Italian Government, 1999) to implement the European Directive 96/62/EC. The air pollution prevention, improvement and preservation have been assigned to the 20 Italian administrative Regions while the European Directive implementation remains at a national level. This institutional division implies the elaboration of different Regional Air Quality Management Plans (AQMPs), a fundamental phase of the entire assessment process, planning and management where air quality measures should be defined and adopted in order to meet established air quality targets. The most powerful tool to verify the compliance with those targets seems to be the integrated assessment models, and among them the RAINS model, already applied in many negotiation processes (RAINS, 2007). Many options are available to reduce emissions from the different sources and they can be generally divided into technical (e.g. end-of-pipe measures), structural (e.g. fuel switch) and behavioural measures. The RAINS-Italy model in its current version is restricted to the analysis of end-of-pipe measures, while behavioural measure evaluation is reflected through alternative exogenous scenarios of the driving forces (Amann et al., 2004). The Italian Regional AQMPs include both Technical and Non- Technical Measures and in this work their assessment have been carried out with the RAINS-Italy model comparing the Current LEgislation (CLE) and an alternative scenario, which contains all the measures the Regional administrations intend to adopt to preserve air quality in their territory. The CLE scenario is based on the assumptions that at the target year the air pollution laws and directives at European, national and local level have been applied. Translated into the RAINS model language, this assumption means that the CLE trends reflect an energy and non-energy activity level scenario and a control strategy which takes into account the technological abatement evolution expressed for each fuel/sector/technology as implementation rate of the abatement technologies. The alternative scenario (AQP scenario) considers in addition the TMs and NTMs adopted by the Regions in the Air Quality Management Plan. To take into account the single measure, both TM and NTM, modification of energy/activity levels and control strategy was often made at the same time, not representing these two clusters of RAINS model input data a clear boundary line between TMs and NTMs. The cost analysis is thus not feasible in a direct way at this stage and it has been put off to future works. The aim of this work is to draw up a reasoned list about all the Technical and Non-Technical Measures assessed into the Italian Regional AQMPs revising critically the more spread classification systems and to give an estimation of the emissions saved at the target year, 2010, using RAINS-Italy as a part of the National Integrated Modeling system for International Negotiation on atmospheric pollution (MINNI). The efficacy of all AQMPs measures at 2010 is shown in terms of SO_2, NO_x and PM_{10} emissions avoided and PM_{10} concentration reductions together with the improvements of the health impact indicator, the Life Expectancy Reduction (LER), defined as months lost attributable to $PM_{2.5}$ concentrations.

2.1 National modeling system: the MINNI project

Integrated Assessment Models (IAMs) have been widely applied since the first Regional Air Pollution Information and Simulation (RAINS) model version (Alcamo et al., 1990) has been used as reference tool for policy makers in developing cost-effective solution to complex problems (Warren and ApSimon, 1999). IAMs are transdisciplinary tools in combining the scientific research results in different field like atmospheric chemistry, meteorology, economy, abatement technologies, policies and influences on human health. The most used IAM tool in Europe is the RAINS model (Amann et al., 1999), developed at the International Institute for Applied Systems Analysis (IIASA),which provides a framework for the analysis of emission reduction strategies, focusing on acidification, eutrophication and tropospheric ozone. The RAINSmodel considers emissions of SO_2, NO_x, PM_{10}, $PM_{2.5}$, VOC and NH_3 (Amann et al., 2001), provides deposition and concentration maps and addresses threats to human health posed by fine particulates and ground-level ozone (Amann et al., 2004). It has now been extended to greenhouse gases (Klaasen et al., 2005; Ho¨glund-Isaksson and Mechler, 2005; Winiwarter, 2005) evolving to the GAINS model (GAINS, 2009). The same approach has been adopted in Italy where ENEA, since 2002 and on behalf of the Italian Ministry of the Environment, the Land and the Sea, has been leading the National Integrated Modeling system for International Negotiation on atmospheric pollution (MINNI) project.

The MINNI project consists of two different but connected models (Fig. 2.1):

- the Atmospheric Modeling System (AMS-Italy), simulating air pollution dynamics and multiphase chemical transformations;
- the RAINS-Italy model, calculating emission scenarios, cost curves, impact analysis on environment and health.

The AMS-Italy (Zanini et al., 2005) consists of three main components:

- RAMS (Regional Atmospheric Modeling System), a non-hydrostatic meteorological model (Pielke et al., 1992; Cotton et al., 2003), provides the hourly 3D meteorological fields using a 2- way nested grid system, the outer one covering large part of central Europe and the Mediterranean Sea with a 60 km resolution and the inner one being the target area. Input data come from the ECMWF (European Centre forMedium rangeWeather Forecast) analyses and surface synoptic observations, assimilated during the whole model simulation using nudging technique. Planetary boundary layer scaling parameters, diffusivities and deposition velocities of the chemical species of interest have been then computed with a diagnostic post-processing module;
- an emissions processing system prepares hourly gridded emissions for air quality simulations starting from yearly inventory data, using sets of activity-specific thematic layers, time modulation and speciation profiles. Reference data employed are the province-based Italian inventory and the EMEP (Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) inventory for surrounding European countries (EMEP, 2003). Emissions from maritime activities included are also considered, as well as volcanoes, whereas some almost 300 large point sources are treated explicitly, taking directly into account plume rise effect;
- the Flexible Air quality Regional Model (FARM) (ARIANET, 2004), derived from STEM (Carmichael et al., 1998), a threedimensional Eulerian chemical-transport model modelling advection–diffusion and multiphase chemistry of atmospheric pollutants, and including different chemical schemes and aerosol modules. Time-varying chemical boundary conditions have been assigned from the three-dimensional fields produced by the EMEP Eulerian model for the same period.

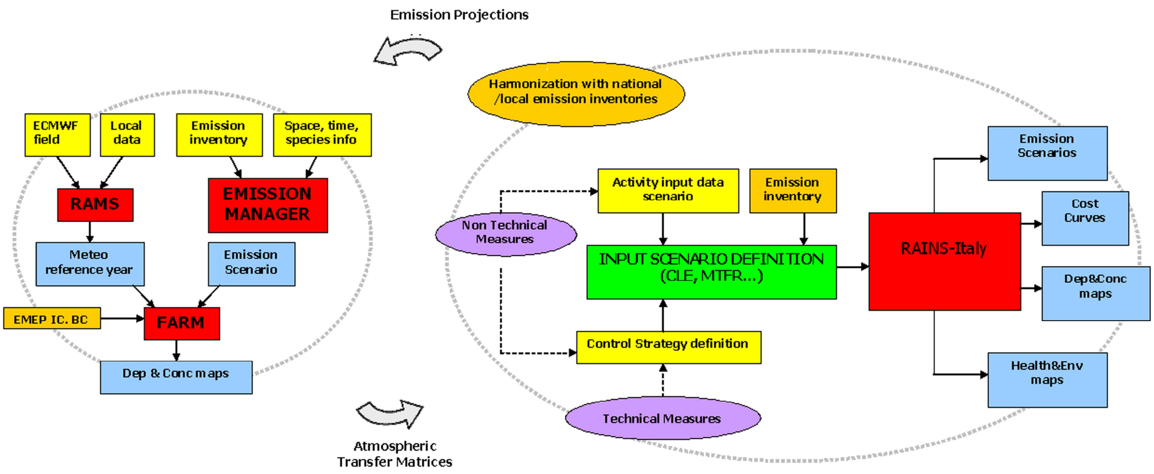


Figure 2.1: *The simplified flow-chart of the MINNI national modelling system.*

In order to better capture sub-national characteristics, e.g. stagnation inside the Po Valley, a large plane downwind the Alps, the local circulation induced by the complex coastal peculiarities of the Italian Peninsula, both affecting pollutant dispersion and transformation, and to consider a higher resolution land-use definition and consequently a more precise reconstruction of deposition processes, the spatial resolution ranges between 20 km _ 20 km for preparing the Atmospheric Transfer Matrices (ATMs) to 4 km_ 4 km for more detailed calculation. The ATMs provide the link between the AMS and RAINS-Italy. RAINS-Italy (Vialetto et al., 2005) is the national version of the RAINS-Europe model, and considers as emission source areas either the nation as a whole or the 20 administrative Regions; moreover, it considers the national sea traffic. The autonomy of the Regions in defining air quality reduction measures, together with the high orographic and meteorological regional variability requires an administrative regional approach. So 20 km _ 20 km ATMs have been calculated by AMS-Italy (compared to GAINS-Europe 50 km _ 50 km ATMs calculated by EMEP). By means of these transfer matrices, for any of the calculated emission projection, RAINS-Italy quickly generates ambient concentration, deposition and impact maps, allowing the assessment of fine particle health impacts through the Life Expectancy Reduction indicator. These evaluations are obviously affected by simplified assumptions about emission–concentration relations. In RAINS-Italy, the Energy and Production Activities Scenarios, which drive the emission projections in the target years (every 5 years up to 2030) starting from the base year (2000), are developed by ISPRA and ENEA with the optimization model MARKAL (MARKet ALlocation) (Gracceva and Contaldi, 2005). The energy scenario

(Contaldi, 2005) represents the Italian official energy scenario transmitted to the EU Commission for the Emission Trading National Allocation Plans (2005), with updated assumptions on the development of natural gas consumption. Both scenarios were downscaled to a regional level and then compared with the scenarios developed by Regional Administrations themselves. In this way, the RAINS model attempts to develop a holistic understanding of a complex reality through a variety of reductionistic steps.

2.3 Definition of Technical and Non-Technical Measures

An emerging issue in meeting policy targets for air pollution is the need to consider Non-Technical Measures (NTMs) for pollution abatement in addition to Technical Measures (TMs) (Oxley and ApSimon, 2007). In spite of their increasing importance, no comprehensive and often contrasting definitions are given in literature as underlined by the UNECE workshop (ASTA, 2005; UNECE, 2006). In the MERLIN Project TM and NTM definition is based respectively on emission factor and activity data changes (Reis, 2005),while in the RAINS perspective, Technical Measures are seen mainly as end of- pipe while Non-Technical Measures as structural and behavioural changes (Schucht, 2005). It is, however, more complicated than this. The NTMs, often supported by fiscal/economic incentives, are actually not completely independent from technology changes even if they are rather geared towards changing the behaviour of technology users (Sternhufvud et al., 2006). Therefore, the definition itself and the assumptions used for NTMs assessment could result in an evaluation process lacking in transparency. An initial attempt to ‘‘translate’’ NTMs both for transport and energy sectors has been implemented in the RAINS-Italy model. In order to do this, the classification followed in the present study derives from Barrett who defines NTMs as measures where the behaviour of people changes such as to reduce a given environmental impact (Barrett, 2005). This means that consumption reduction, substitution, but also technology choice and technology use could be classified as NTMs, while in RAINS view these measures are strictly treated as TMs. In this perspective, although technology changes occurred and, in RAINS language, a control strategy modification was introduced (see Fig. 2.1), measures like the purchase of photovoltaic solar panel to produce electricity instead of fossil fuels or the purchase of high efficiency domestic boilers have been classified as NTMs. The assessment of some NTMs in RAINS-Italy requires consequently modifications of both control strategy and energy consumption, the last ones to take into account different people behaviours towards technology uptake rates with or without regional incentives, so implying a different emission reduction for the same measure. The methodology followed to translate these measures in RAINS-Italy is further explained and the results of the classification adopted in the present work are reported in Table 2.1.

SECTOR	TYPE of MEASURES	
ENERGY	Photovoltaic	NTM
	Wind	TM
	Hydroelectric	TM
	Geothermic Well	TM
	Urban Waste incineration with heat recovery	TM
	District heating Plant	TM
	Biogas recovery in agricultural and in farming sectors	TM
DOMESTIC	High efficiency domestic boilers	NTM
	Energy efficiency in building	NTM
	Residential heating accountability	NTM
	Heat pumps	NTM
	Regulation of some fuel use	NTM
	Efficiency improvements in fireplaces and stoves	TM
	Solar heating systems	NTM
	Incentives for shift to natural gas in domestic boilers	NTM
ROAD TRANSPORT	Low emission zones	NTM
	Road traffic restriction	NTM
	Pollution charge	NTM
	Car sharing	NTM
	Motorway speed limits	NTM
	Bike sharing	NTM
	Incentives for new cars	TM
	Incentives for new diesel heavy duty	TM
	Antiparticulate filter	TM
	Incentive for hydrogen cars	TM
	New methane service stations	TM
	Incentives for biofuel public transport	TM
	Opening new rail lines	NTM
	Opening new underground lines	NTM
	Cycle paths	NTM
	Sea motorway	NTM
	Bus investment (new buses, service extension, frequency increase)	NTM
	Rationalising load transport in urban area	NTM

Table 2.1: *Technical and Non-Technical Measures adopted in the Italian Regional AQMPs.*

2.4 RAINS and NTMs in the Italian experience with Regional Air Quality Plans

The aim of the activities undertaken in 2008 in close cooperation with all the Italian Regions was to support their institutional functions in air pollution assessment and management by means of a model able to create multiple emission scenarios starting from a coherent and shared input data assessment. The central task was the analysis of emission reduction strategies followed in the Regional Air Quality Plans to meet environmental quality targets by means of Technical and Non-Technical Measures. In particular, the PM_{10} emission reductions achieved at 2010 will be hereby the focus of the analysis being this pollutant still a challenge for air quality policies; furthermore results for SO_2 and NO_x will be shown. The TM and NTM effect on air quality will be shown as PM_{10} concentrations and losses in Life Expectancy attributable to exposure to fine particulate matter, the health impact indicator in RAINS for anthropogenic $PM_{2.5}$ (Mechler et al., 2002).

2.4.1 Scenario analysis

The activity premise was an acceptable harmonization, at a given base year, between regional emission inventories, set up with a bottom–up approach, and RAINS-Italy emissions, estimated with a top–down approach. When the total emission difference between the two estimations was around 5%, the harmonization process (Pignatelli et al., 2007) stopped. The RAINS-Italy regional emission reference scenarios were so developed for the future years downscaling on Regions the baseline national energy and non-energy activity level scenarios with proxy variables and the CLE control strategy. Once defined the regional baseline scenarios, the regional air quality scenarios result from the assessment of the additional measures both technical and non-technical implemented in the Regional AQMPs. At national level, the 2010 CLE total emission scenario shows 213 kt of PM_{10}, 376 kt of SO_2 and 1057 kt of NO_x with reductions, respect to 2000, the reference year, respectively of 7.9%, 50.1% and 24.0% (D'Elia et al., 2007). The resulting PM_{10} yearly average concentrations (Fig. 2.2a) show exceedances of 40 ($\mu g\ m^{-3}$), the standard value, at the most important Italian metropolitan areas. Furthermore, the whole Po Valley shows critical conditions considering that in the first runs of AMS model, from which atmospheric transfer matrices were calculated (see Paragraph 2.2), the organic component of primary PM was not considered. Regarding health impacts (Fig. 2.3a), the most important Italian metropolitan and industrial areas have a loss of average Life Expectancy in a range of 12–23 months in 2010. These first evidences highlight the need to implement air quality plans to reduce the PM_{10} and $PM_{2.5}$ concentrations in urban agglomerations where the greatest part of population lives and to preliminarily assess the efficacies of the reduction measures. The AQMPs adopted by 15 of the 20 Italian Regions were so analysed and assessed (see Paragraph 2.4.2). If compared to the 2010 CLE scenario, the 2010 AQMP scenario reduces PM_{10}, NO_x and SO_2 emission of respectively 2.8%, 2.4% and 0.5% and both the variables mapped in Figs. 2.2 and 2.3 do not show significant improvements. Regions with a more effective AQMP reach higher PM_{10} yearly average concentrations reductions, with peaks of 7.5% in northern and central Italy, even if not sufficient to assure the compliance at 2010 with air quality standard (Fig. 2.2b). Similarly the improvement in losses of average Life Expectancy indicator achieves 1 month only in Lombardy Region (Fig. 2.3b).

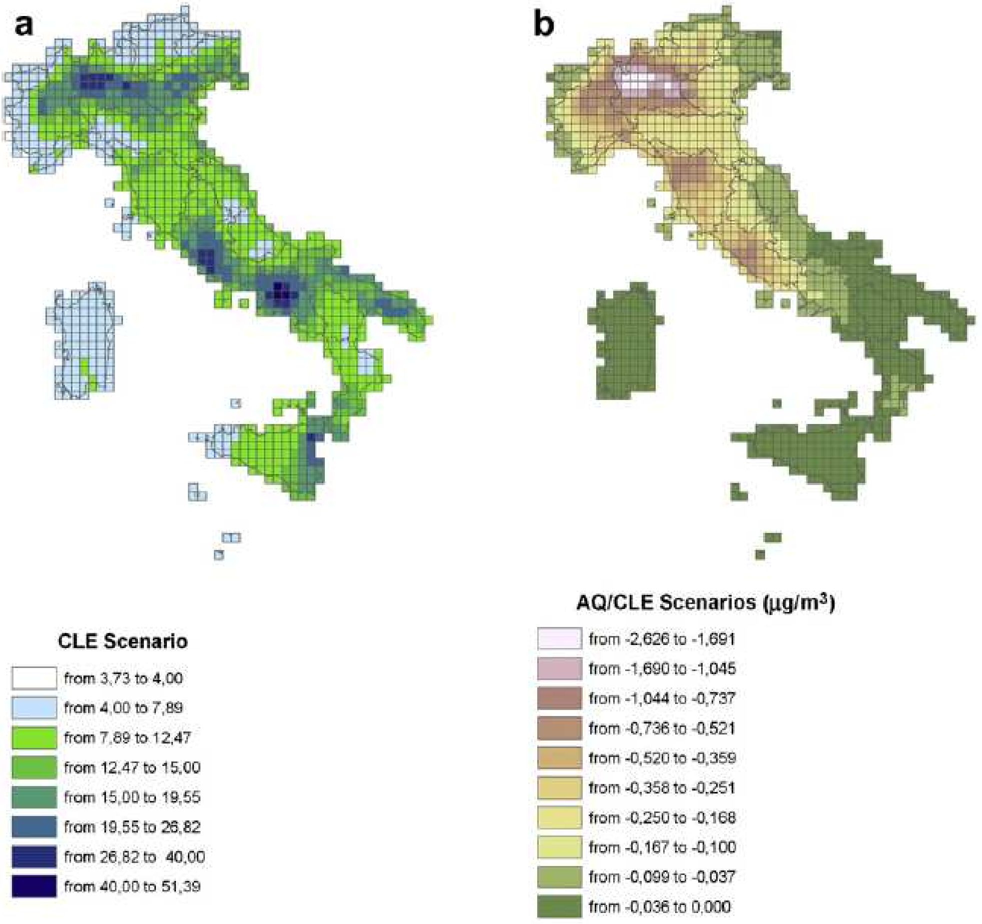


Figure 2.2: *PM_{10} mass concentration ($\mu g\ m^{-3}$) at target year 2010: a) CLE scenario; b) difference ($\mu g\ m^{-3}$) between Air Quality Management Plan scenario and CLE scenario.*

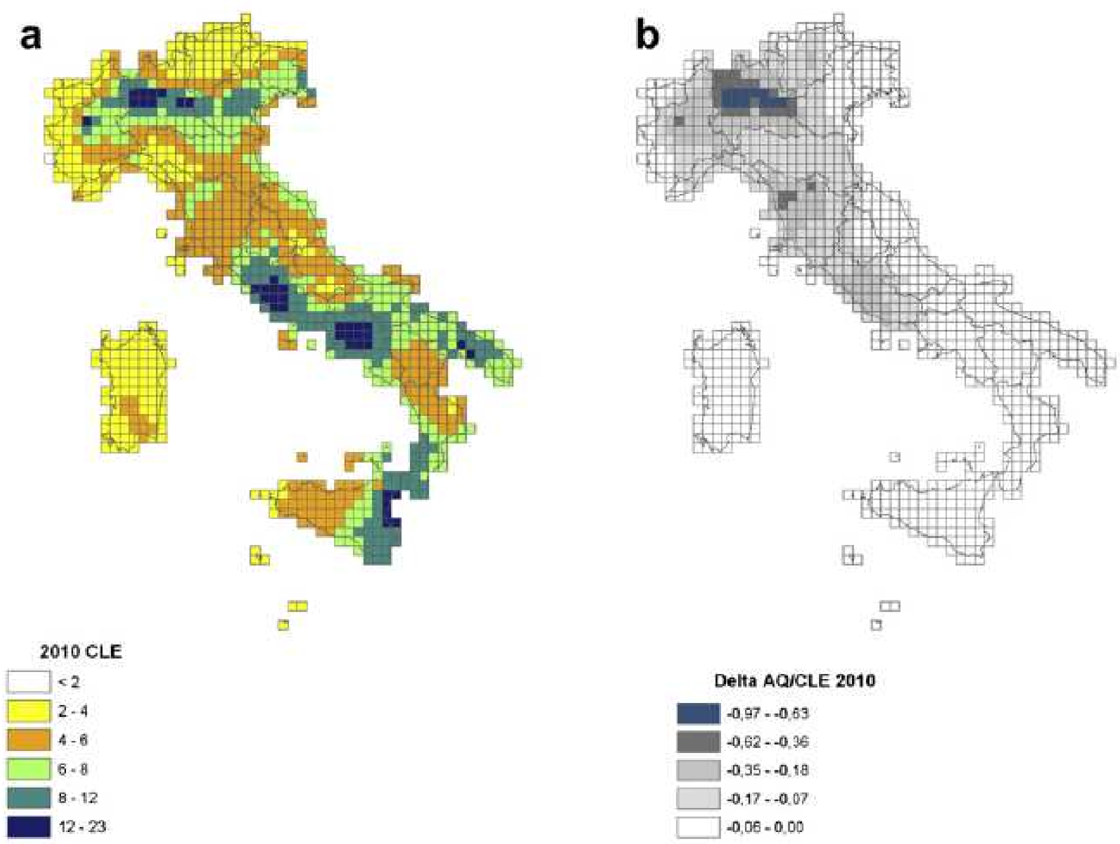
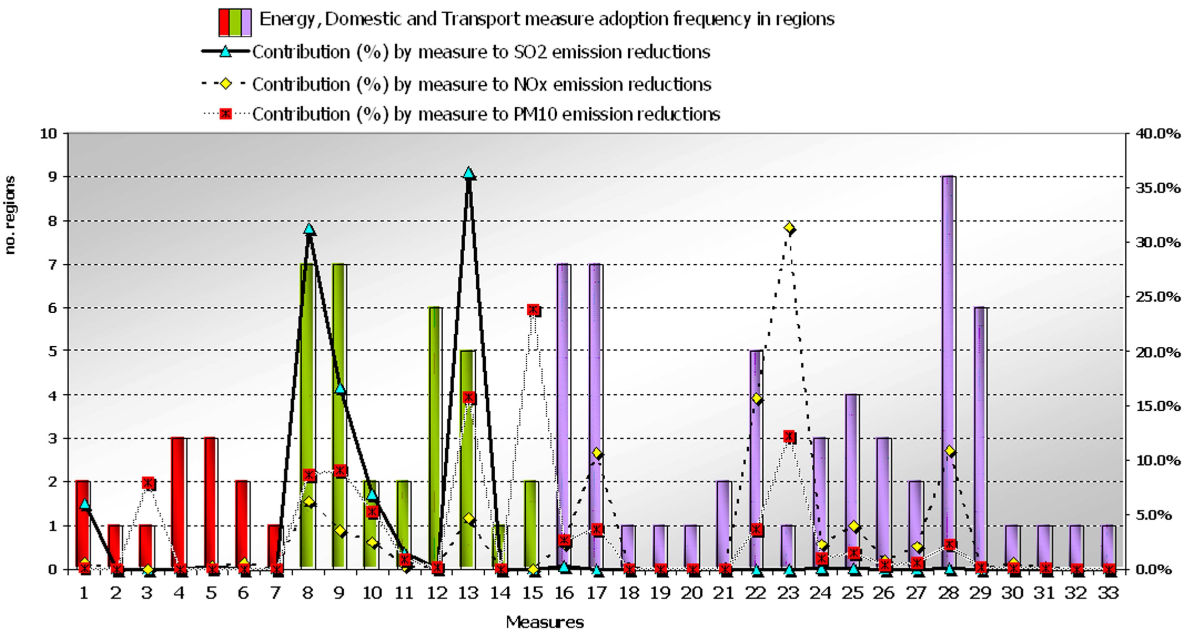


Figure 2.3: *Losses in average Life Expectancy (months) attributable to* $PM_{2.5}$ *concentrations at 2010: a) CLE scenario; b) difference (months) between Air Quality Management Plan scenario and CLE scenario.*

2.4.2 Measures analysis

The complete list of the measures adopted in the AQMPs is presented in Table 2.1. A first level of classification is used to refer to the macro-sectors of the activities involved in the adopted measures: Energy, Domestic and Transport. For these macro-sectors, according to the definition used in this work (see Paragraph 2.3), each measure is firstly defined as TM or NTM (see Table 2.1) and then analysed in terms of SO_2, NO_x and PM_{10} emission reductions (Fig. 2.4). In Fig. 2.4, the adoption frequency in Regions, shown by the bars, is overlaid with three plot lines, which report the percentage contribution by measure to SO_2, NO_x and PM_{10} emission reductions. The figure highlights how the most common measures not always allow the higher emission reductions. In the energy sector, most of the regional AQMPs measures consist of the promotion of renewable energy sources, including electricity and heat generated from solar, wind, hydropower, geothermal resources, biomass and biofuels. These measures do not alter the energy services for consumers in terms of a ‘‘technical’’ change in energy supply structures. The energy policy assumptions in the AQMPs support power and/or heat regional-based Plant installation. Therefore, the related incentives have not a consequence on consumer behaviour. The ‘‘Photovoltaic’’ measure provides instead domestic building-integrated photovoltaic systems whose installation depends directly on people’s agreement with the measure and, as already said in Paragraph 2.3, the behaviour could be affected by regional incentives. For this reason, according to the definition adopted in this study, the ‘‘Photovoltaic’’ measure is NTM whereas the other energy measures are TMs. In comparison to the other sectors, the energy measures have a low adoption frequency, varying from 1 to 3 times and their total contribution to SO_2, NO_x and PM_{10} emission reductions is respectively 6.3%, 1.5% and 8.0%. In the domestic sector almost allmeasures have been classified as NTMs, concerning prevalently energy conservation/efficiency strategies with or without the support of command and control policies or economic incentives. The total domestic measure contribution to emission reductions is 17.4% for NO_x, 93.0% for SO_2 and 63.6% for PM_{10}. Among all these measures, the ‘‘Regulation of residential biomass, oil and coal use’’ reaches the highest contribution to the reduction of SO_2 emissions (36.4%) and contributes to the 15.8% of PM_{10} emission reduction. This measure, together with the most effective measure in reducing PM_{10} emissions (23.8%), the ‘‘Efficiency improvements in fireplaces and stoves’’, highlight another important problem concerning PM_{10} emissions: the biomass burning for heating, a measure sustained by greenhouse gas reduction policies that originates trade-off with air quality policies. Regarding the road transport sector, the predominant measures are NTMs, whose contribution is strongly needed to achieve a notable NO_x emission reduction. All transport measures achieve a total contribution to emission reductions of 0.7% for SO_2, 28.3% for PM_{10} and 81.1% for NO_x; of this last reduction, 31.4% was reached through the implementation of ‘‘Incentives for new diesel heavy duty’’. Although its high efficacy, only one Italian Region adopted it, while the contribution of the ‘‘Low emission zones’’, one of the most common measures adopted by 7 regions, is 2.3%. Therefore, modeling NTMs, but also TMs, with RAINS-Italy has not always been a simple task because some measures act in different ways for different pollutants (e.g. motorway speed limits) and others require quantitative assumptions to translate the given input data (e.g. km of new cycle paths) in a suitable RAINS-Italy input data (e.g. energy consumption of cars). These quantitative assumptions often deal with a behavioural component measure and their local applicability; transparency is then required when related impact is shown.



1 = Urban Waste incineration with heat recovery;
2 = Biogas recovery in agricultural and in farming sectors;
3 = District heating Plant ;
4 = Photovoltaic;
5 = Wind;
6 = Hydroelectric;
7 = Geothermic Well;
8 = High efficiency domestic boilers;
9 = Energy efficiency in building;
10 = Residential heat meter;
11 = Heat pumps;
12 = Solar heating systems;
13 = Regulation of residential biomass, oil and coal use;
14 = Incentives for shift to natural gas in domestic boilers;
15 = Efficiency improvements in fireplaces and stoves;
16 = Low emission zones;
17 = Road traffic restriction;
18 = Pollution charge;
19 = Car sharing;
20 = Motorway speed limits;
21 = Bike sharing;
23 = Incentives for new diesel heavy duty;
24 = Opening new rail lines;
25 = Opening new underground lines;
26 = Cycle paths;
27 = Modal shifts from cars/lorries to ships;
28 = Bus investment (new buses, service extension, frequency increase);
29 = Particulate filter;
30 = Incentives for biofuel public transport;
31 = New methane service stations;
32 = Incentive for hydrogen cars;
33 = Rationalising load transport in urban area.

Figure 2.4: *AQMP measure adoption frequency in regions, shown by the bars, and percentage contribution by measure to SO_2, NO_x and PM_{10} emission reductions, reported by the three plot lines.*

To cope with the complexity of the subject and to better point out the methodological approach, a focus on only 6 of all the AQMP measures is reported. The choice arises from the remarkable relevance of these 6 measures in terms of both their results and their modeling through RAINS-Italy. Two measures have been chosen for each macro-sector and reported (Fig. 2.5) in terms of SO_2, NO_x and PM_{10} sectorial emission reductions respect to the 2010 regional CLE scenario. In this graph (Fig. 2.5) the stacked bars, whose patterns represent a different administrative region, showthe different sectorial emission reduction for each Region where the AQ measures were applied. Being NTMs dependent on people’s behaviour and varying the hypotheses about measure implementation among Regions, different responses to the same measures have been observed throughout the country with a broad variation of each single measure effect on SO_2, NO_x and PM_{10} sectorial emissions, as shown in Fig. 2.5. In the energy sector, the 2 selected measures are ‘‘Urban Waste incineration with heat recovery’’ and ‘‘District heating Plant’’ which, involving a district heating distribution network, are both combined heat and power generation measures. Their modeling through RAINS-Italy produces an increase in renewable energy consumptions (waste and biomass) in the Power Plant sector with an equivalent reduction of fossil fuel consumptions both in the Power Plant and the Domestic sector. The translation of these measures in a suitable RAINS-Italy input has required the definition and quantification of some parameters, as for example, the estimation of biomass increase and fossil fuel decrease, type of new waste incineration plant (in terms of emission factors and efficiency), fossil fuel power plant and domestic boiler efficiency, and spatial application of the measures. For the ‘‘Urban Waste incineration with heat recovery’’, adopted by two Italian Regions, the relative bars reported in the graph show only one contribution since the regional CLE scenarios often contain preliminary hypotheses about some of the AQMP measures therefore influencing their assessment. However, this measure shows a nearly null SO_2 emission reduction and a slight decrease, 2.9% and 1.9% respectively, for NO_x and PM_{10} emissions in the two involved sectors. For the ‘‘District heating Plant’’, a remarkable sectorial emission increase for SO_2 (13.7%) and NO_x (6.5%) has been highlighted. This occurred because the policy assumptions for ‘‘District heating Plant’’ capacity are very powerful and the involved existing district heating plant technologies do not ensure an efficient SO_2 and NO_x emission abatements. Contrarily, the PM_{10} abatement technologies and the related emission factor are such to make an effective PM_{10} emission reduction (6.6%). It could be expected that the new district heating plant generation will improve its technological structure allowing to overcome the trade-off above described. For the domestic sector, ‘‘High efficiency domestic boilers’’ and ‘‘Energy efficiency in building’’ are selected. The first measure is reported in RAINS-Italy variables as decrease of fossil fuel consumptions and an increase of technology diffusion in Domestic sector. Moreover, the following parameters have to be quantify: the substitution rate and the efficiency of domestic boiler, the new domestic boiler emission factor, the allocation of domestic fuel reduction through the different fuels and the spatial application of the measure. This measures show a wide range of domestic emission reduction, from 0.0% to 11.9% for SO_2, from 0.0% to 10.0% for NO_x and from0.0% to 10.0% for PM_{10}. The other measure required the quantification of the fossil fuel consumption decrease and its allocation through the different fuels, an accurate evaluation of the buildings involved in the measure divided in old and new and the spatial application of the measure. In this case, it has been also verified the energy requirement to reach in new and old buildings in comparison with those assumed in the CLE scenario. Also in this case a wide emission reduction range has been noticed: from 0.0% to 11.4% for SO_2, from0.0% to 5.4% for NO_x and from 0.0% to 9.9% for PM_{10}.

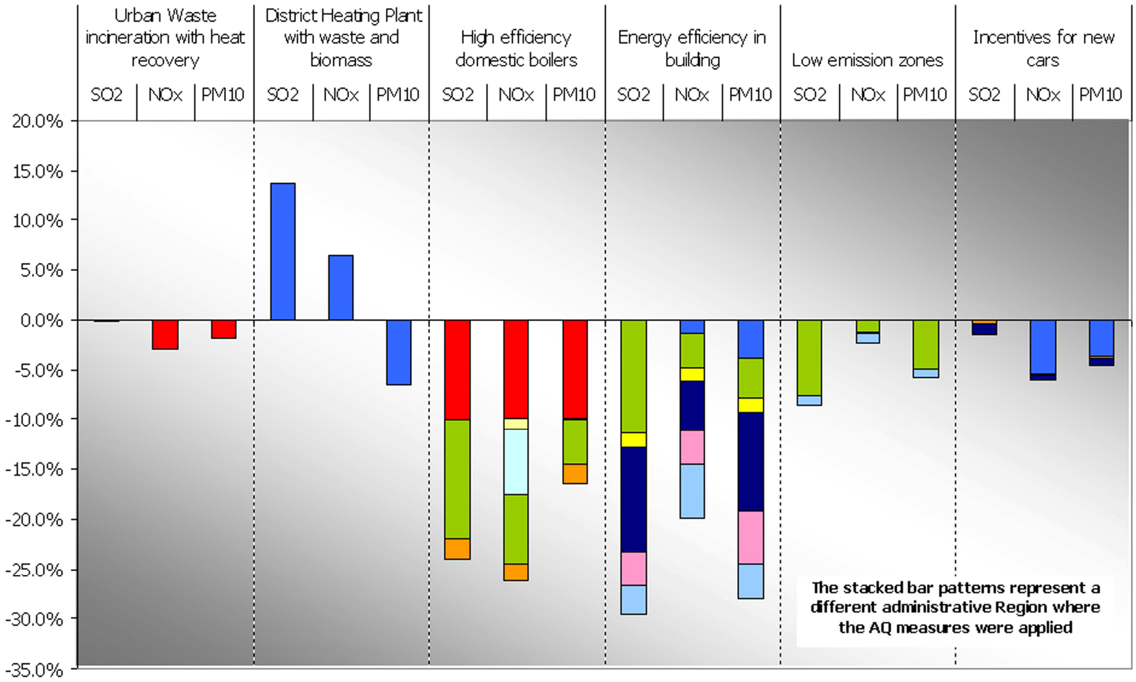


Figure 2.5: *SO_2, NO_x and PM_{10} emission reductions (in %) on regional sector emissions calculated respect to the 2010 CLE scenario for the 6 selected measures. The stacked bars, whose patterns represent a different administrative Region, show the sector emission reductions for each Region where the AQ measures were applied.*

Referring to the transport sector, the 2 chosen measures are the ‘‘Low emission zones’’ and the ‘‘Incentives for new cars’’. A wide range of SO_2, NO_x and PM_{10} transport emission variation resulted for these measures due to different evidences: first of all the mandatory level in applying the same measure among the Regions and then the different regional car fleet involved. Where a higher reduction has been estimated an older car fleet was involved. The aim of these types of measures was sometimes to make easier the car substitution and it has so been detected by people. The translation of the first transport measure through RAINS-Italy model consists in a modification of either control strategy and energy scenario, involving the quantification of a large numbers of parameters such as: the low emission zone extension, the fleet involved by the measure, the urban speed, the measure spatial application, the car substitution and/or a modal shift. Being the ‘‘Incentives for new cars’’ measure modelled as anticipation of future European car standard Directives, hypotheses only on control strategy have been formulated, taking into account the fleet involved, the spatial application of the measure and the car replaced by the incentives. Although being two of the most adopted AQ measures, the results achieved are not much effective since the higher transport emission reductions for SO_2, NO_x and PM_{10} are respectively 0.1%, 0.5% and 0.9% for the former one and 0.0%, 2.3% and 0.7% for the latter one. Similar analysis have been carried out in terms of SO_2, NO_x and PM_{10} total regional emission whose results globally show lower values in comparison to those reported above which are instead referred to the sector.

2.5 Conclusions and future directions

In implementing the European Air Quality Directive 96/62/EC, the Italian Regions have been entrusted with air pollution prevention, improvement and preservation tasks. The Regional Air Quality Management Plans formally adopt air quality measures to meet environmental targets. The adoptable measures can be either technical and non-technical, but no more Technical Measures alone are enough to meet targets, changes are also required in our behaviours both as individuals and societies (Oxley and ApSimon, 2007). All the uncertainties in the NTMs definition, as seen in Section 3, may influence the results of inter-comparison studies and introduce a lack of transparency in their efficacy assessment making complex the desirable realization of a unique guideline where it is possible to find their air pollution impact, their market and non-market costs, the possible implementation instruments, their social effects and so on. In this sense, the integrated assessment models represent a powerful tool but it is necessary to pay attention to Non-Technical Measures approach, in particular when treating cost analysis (UNECE, 2006). Many efforts are already going in that direction (UCL, 2009) and the scientist debate is still open. The Italian Regional AQMPs contain Technical and Non-Technical Measures especially in the energy, domestic and transport sector and the analyses carried out show the crucial role of both, although the normative compliance is not assured everywhere. It has to be noticed that the measures mostly adopted in the AQMPs do not always represent the most effective measures in reducing PM_{10} concentrations and improving the loss in average Life Expectancy at 2010. Furthermore, some climate change policies (like the use of biomass as fuel) are likely to produce trade-offs on air quality and vice versa (AQEG, 2007) and the next challenge is to use integrated assessment modeling to explore the synergies and trade-offs among different groupings of pollutants. A step ahead will be possible with the Italian version of the GAINS (Greenhouse gas Air pollution INteractions and Synergies) model, but further analysis still need to be carried out especially about costs.

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CHAPTER 3

Source Identification through Multivariate Receptor Modeling

Integrated analytical approaches have been carried out in order to assess the Saharan dust contributions to PM_{10} levels in southern Italy. Aerosol mass concentrations and aerosol chemical composition determinations have been performed at an urban, suburban and rural background monitoring sites between July and August 2007. PM_{10} samples were collected using a dual channel particulate matter sampler and analysed using ICP-MS to determine trace elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sb, V and Na) concentrations. In order to identify the source-receptor relationships, a multivariate statistical technique, Principal Component Analysis (PCA), was used. Four PM_{10} source categories for the urban site [crustal particles, traffic-related particles, agricultural practices and glassware production]; five main sources at the suburban site [crustal particles, traffic-related particles, agricultural practice, boat oil burning and sea salt] and, four source categories at the rural site [crustal particles, rust proofing, textile manufacturing and farming] were identified. The analysis, coupled with computation of back trajectories, complemented with satellite images, showed that 23% of the PM_{10} data collected at the urban, 16% at the suburban and 5% at the rural site exceeded the EU daily limit value in conjunction with Saharan dust outbreaks. The relevance of this source category, impacting at all sampling sites, highlighted the need of more detailed measurements than just PM_{10} mass concentration to implement an appropriate air quality control strategy in this area, and also to prevent apparent air quality parameter exceedances resulting from high levels of crustal material in routine sampling.

3.1 Introduction

The European Commission covered PM management and assessment in the Air Quality Framework Directive (EC, 1996) and in the first Daughter Directive (EC, 1999) establishing for PM_{10} an annual limit value of 40 $\mu g\ m^{-3}$ and a daily limit value of 50 $\mu g\ m^{-3}$ with a maximum allowed number of exceedances of 35 times per year. This directive included the possibility to skip exceedances due to natural events which result in concentrations significantly in excess of normal background levels from natural sources. In the new Directive 2008/50/EC, that substantially confirms the planning and management approach to air quality, PM_{10} limit values have been retained, however, few things have changed which relate to their application (Brunekreef and Maynard, 2008). The update gives indeed the possibility of skipping exceedances due to natural sources regardless of the amount of their contribution; therefore assessment of natural contributions to the PM_{10} concentration, even for small additions causing the daily limit value exceedance, has become a primary task for both scientists and policy makers. Multivariate receptor models have been developed and improved in order to identify and quantify the contribution of both natural and anthropogenic PM sources (Marcazzan et al., 2003). These methods have, in fact, the great advantage that there is no need for a priori knowledge of emission inventories and are based on the measured ambient concentrations of different PM fractions and components (Chio et al., 2004). Among natural sources, the sporadic but intense outbreaks from Saharan dry regions have a strong impact on the Mediterranean region (Sprovieri and Pirrone, 2008). Many authors studied the influence of Saharan dust in different part of Italy (Rogora et al., 2004) and in cities such as Rome (Gobbi et al., 2007) and Naples (Pisani et al., 2005). Their analysis pointed out, besides, that the Saharan dust intrusions into the Mediterranean area occurs more often in summer and with an increasing influence as the latitude decreases (Meloni et al., 2007; Matassoni et al., 2009). As reported in the Italian Government Decree no. 351 (Italian Government, 1999), the air pollution prevention, improvement and preservation have been assigned to the 20 Italian administrative regions implying the elaboration of different Regional Air Quality Management Plans (D’Elia et al., 2009). Therefore, to efficiently implement the entire process of regional air quality planning and management, an appropriate emission sources assessment that fill the gap on the natural sources burden at regional and local scale is needed as well. Pertaining to this context, our work have been carried out during summer 2007 to assess the Saharan dust burden affecting PM_{10} levels in Calabria region, Southern Italy. Three sampling campaigns have been performed simultaneously at an urban, suburban and rural background monitoring sites between July and August 2007. PM_{10} mass concentrations and elemental chemical composition were analysed. In order to identify the potential natural and anthropogenic sources impacting each monitoring site, a multivariate statistical technique such as PCA was applied. PCA has been also coupled with Multi-Linear Regression Analysis (MLRA) for the quantification of source contributions at each monitoring site. These statistical analysis were complemented with satellite derived products of global dust distributions that were useful to understand the dust source regions and transport pathways.

3.2 Methodology

3.2.1 Sampling and Analytical Methods

PM_{10} sampling was performed simultaneously at three monitoring sites located in selected areas of Calabria region characterized by different prevailing meteorological conditions. According to Decision 2001/752/EC and the “Criteria for EUROAIRNET” document, the air quality monitoring stations involved in this work were classified as Urban, Suburban and Rural Background Stations with regard to the site of Rende (N39°20'0" E16°11'0"), San Lucido (N39°19'22" E16°02'44") and Longobucco (N39°23'39" E16°36'49"), respectively. PM_{10} samples were collected on pre-weighed and preconditioned 47-mm Teflon filters, over a 24h sampling period from 18th of July to 30th of August 2007 using an EN 12341 reference high volume sampler with a flow rate of 38 L min^{-1}.

During the sampling, conventional meteorological parameters were routinely recorded. After the sampling, PM_{10} filters were hot digested with 5 mL of a 10% HNO_3 solution and analyzed for their elemental content using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent Technologies, model 7500 CE). Concentrations of Al, As, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Pb, Sb, Ni, V were determined in all samples. Since the Suburban Background station, due to its coastal location, is very likely influenced by natural marine aerosols, the Na concentrations were also determined in the samples collected at this site. A parallel analysis of blanks was carried out to quantify possible contamination. As a first indication of the relative contribution of crustal and non-crustal sources, the enrichment factor method was applied. The Enrichment Factors (EFs) have been calculated for each detected element, considering Al as the reference element and using the crustal composition given by Greenwood and Earnshaw. In order to investigate the relationships among heavy metals in both fine and coarse fractions, the Principal Component Analysis (PCA) was then performed utilizing the orthogonal transformation method with Varimax rotation and retention of principal components. This technique is used to explain the statistical variance of a given data set in terms of a minimum number of significant components. Factor loadings indicate the correlation of each pollutant species with each component and are related to the source emission composition. PCA was applied to each dataset obtained from the three monitoring sites to identify and estimate the strength of possible PM_{10} sources. The accuracy of the PCA technique was tested plotting the model-predicted daily PM_{10} concentrations with the experimental values.

3.2.2 Multivariate Receptor Modeling

3.2.2.1 Principal Component Analysis (PCA)

Source categories for PM_{10} were identified by Principal Component Analysis (PCA) using SYSTAT$^{®}$ version 10. PCA is a statistical technique which can be applied to a set of variables in order to reduce their dimensionality (Hopke, 2003b). The orthogonal transformation method with Varimax rotation and retention of principal components whose eigenvalues were greater than unity (Kaiser criterion) was used. Careful selection of modelling parameters and the number of factors is essential in obtaining sensible results from PCA (Liu et al., 2003b; Huang et al., 2005). In this analysis, appropriate sets of selected elements were included in all source apportionment models. It should be pointed out that Henry (2003) suggested that the minimum number of samples (n) to obtain appreciable results by PCA should be:

$$\underline{n} > 30 + (m + 3) / 2 \qquad (1)$$

where *m* is the number of chemical species analysed.

The matrix principal component model is represented by the following equation:

$$X = GF^{T} + E \qquad (2)$$

where **X** (n × m) is the measured composition matrix and n and m are the number of samples and species, respectively. **G** (n × p) is the source contribution matrix where p is the number of source factors extracted, and **F** (m × p) is the source profile matrix which is transposed in this analysis. **E** (n × m) is the unexplained part of **X**. The objective of PCA analysis is to minimize the value of $\boldsymbol{x_{ij}}$ which is defined as:

$$x_{ij} = \sum_{K=1}^{p} g_{ik} f_{jk} + e_{ij} \qquad (3)$$

where x_{ij} is the j^{th} species concentration measured in the i^{th} sample, g^{th} is the particulate mass concentration from the k^{th} source contributing to the i^{th} sample, f_{kj} is the j^{th} species mass fraction from the k^{th} source, e_{ij} is residual associated with the j^{th} species concentration measured in the i^{th} sample, and p is the total number of independent sources (Hopke, 2003b).

3.3 Results and discussion

3.3.1 Chemical composition

Time series of the recorded PM_{10} levels are shown Figure 3.1 whereas in Table 3.1 a statistical analysis of the detected element concentrations in PM_{10} are reported for the urban, suburban and rural sites, respectively. The daily mean PM_{10} levels were 35.4 μg m^{-3}, 38.4 μg m^{-3} and 24.6 μg m^{-3} at the urban, suburban and rural sites, respectively. The average PM_{10} concentration at the suburban site was 1.1 and 1.6 times higher than those observed at the urban and rural site respectively. Pertaining the elemental composition, the Al mean concentration was highest at urban and rural sites while at the suburban the Na contribute was considerable. The Al percentage contribution to total elemental mass concentration, as sum of only elements detected in this study, was 86% and 84% at urban and rural site, respectively. At suburban site, where Na contribution was 69%, the Al content accounted for 28% of the total. All other metals showed a trace content. Particularly the As, Cd and Ni concentrations were lower than the target values reported in the European Directive 2004/107/EC (EC, 2004) and the Pb levels lesser than the relative limit value established in the European directive 1999/30/EC (EC,1999). The concentration range of each element was very wide resulting in high standard deviations from the mean concentration. Such high standard deviations are not unusual for the data obtained in the Mediterranean atmosphere (Rodríguez et al., 2002; Rodríguez et al., 2004; Querol et al., 2004a). The high variability of each element and the large standard deviation observed at each monitoring site, suggests that the ambient air concentrations varied depending on non-local sources such as for instance Saharian dust, whose sporadic but intense occurrences have a strong impact on the Mediterranean aerosol (Sprovieri and Pirrone, 2008). The African dust occurrences was firstly evaluated by comparing crustal derived metals such as Al, Ca, Fe, K, Mg and Mn time series with PM_{10} levels. During these events the concentrations of the crustal elements, as it can see in Figure 4.1, reached levels in excess respect to the background concentrations by up to one or two orders of magnitude (Kubilay and Saydam, 1995; Güllü et al., 1998; Kubilay et al., 2000; Herut et al., 2001; Herut, 2001). Back trajectories-based analysis complemented with the NAAPs based dust concentration maps (see Figure 4.2) suggested that the observed high mineral dust concentrations were reached at each our site during African dust outbreaks with a concurrent raising in PM_{10} levels.

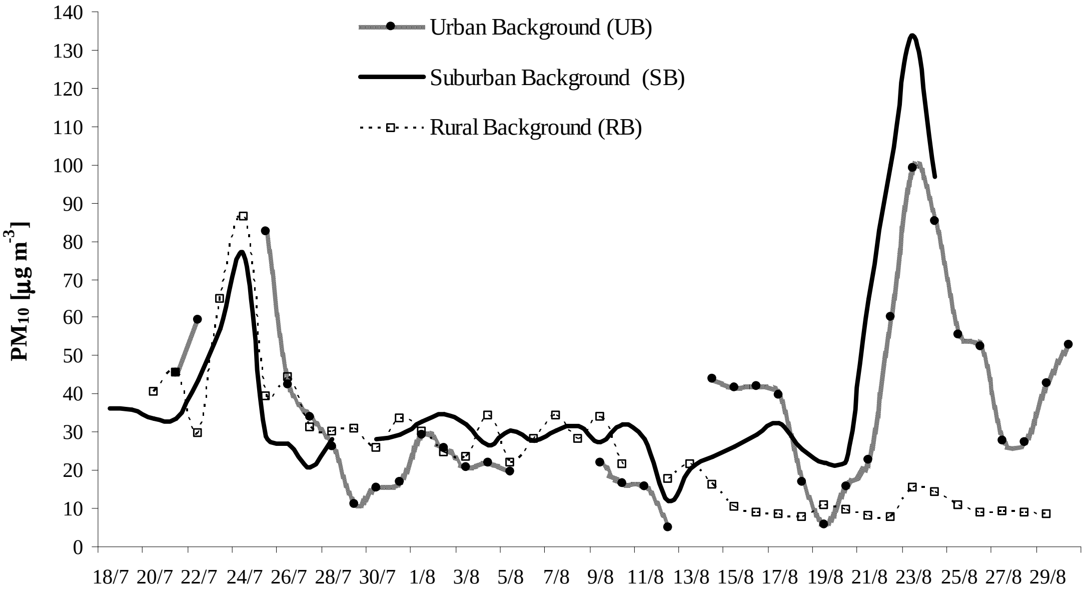

Figure 3.1 *Time series of PM_{10} levels recorded at a Suburban, Urban and Rural Background sites*

Parameter	*Unit*	*Urban Background*				*Suburban Background*				*Rural Background*			
		n=37				n=38				n=40			
		Mean	Max	min	SD	Mean	Max	min	SD	Mean	Max	min	SD
PM_{10}	$\mu g\ m^{-3}$	35.38	99.30	1.10	22.73	38.43	134.00	11.80	25.10	24.64	86.36	7.70	16.61
Al	$ng\ m^{-3}$	347.92	1451.46	8.87	391.80	586.53	2439.14	102.86	566.80	336.17	2102.01	18.38	452.46
As	$ng\ m^{-3}$	0.20	0.94	0.00	0.21	0.14	1.18	0.00	0.29	0.00	0.00	0.00	0.00
Cd	$ng\ m^{-3}$	0.20	7.60	0.00	1.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	$ng\ m^{-3}$	0.10	0.90	0.00	0.20	0.02	0.80	0.00	0.13	0.00	0.00	0.00	0.00
Cr	$ng\ m^{-3}$	8.83	12.22	2.65	2.06	5.56	13.63	2.18	2.18	3.12	7.31	1.49	1.46
Cu	$ng\ m^{-3}$	14.02	41.71	2.13	7.28	19.99	158.76	6.86	27.15	37.13	400.19	1.88	87.17
Mn	$ng\ m^{-3}$	12.08	41.77	0.00	10.67	15.75	52.74	2.35	11.89	8.53	41.39	0.00	9.02
Ni	$ng\ m^{-3}$	4.75	17.70	0.69	10.92	6.66	17.49	1.64	3.77	1.16	3.50	0.00	0.87
Pb	$ng\ m^{-3}$	12.99	46.05	1.62	11.06	15.40	207.36	4.76	32.17	17.56	61.78	3.90	15.50
Sb	$ng\ m^{-3}$	1.67	3.70	0.16	0.75	1.34	4.21	0.26	0.65	0.94	1.64	0.54	0.26
V	$ng\ m^{-3}$	2.97	6.45	0.00	1.88	5.73	21.18	1.57	3.58	1.22	3.66	0.10	1.06
Na	$ng\ m^{-3}$	-	-	-	-	1450.71	4367.13	383.22	947.48	-	-	-	-

Table 3.1 *Statistical summary of PM_{10} and trace element mass concentrations at the three sampling sites*

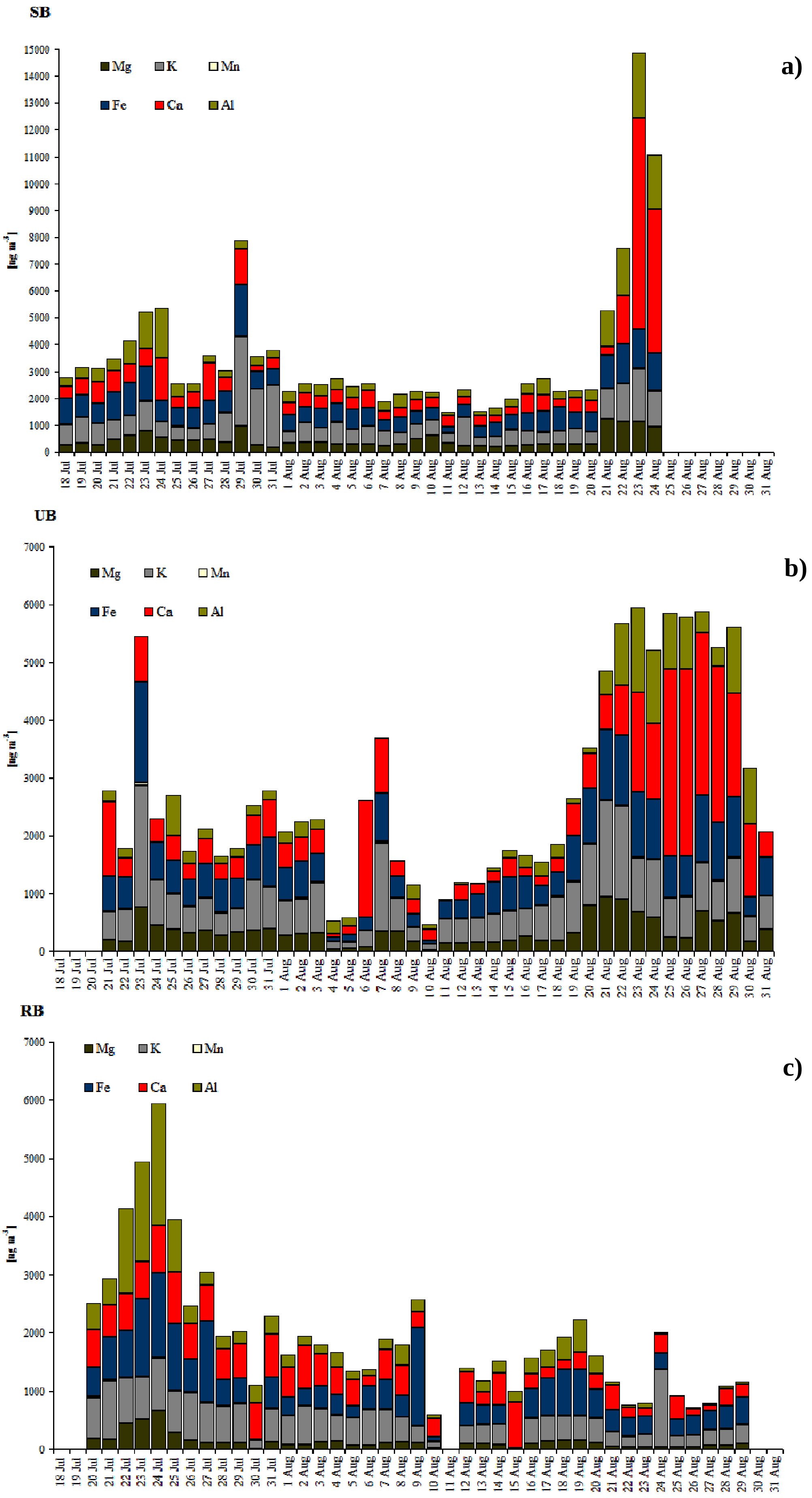

***Figure 3.2** Time series of crustal element levels recorded at: a) SB; b) UB and c) RB sites*

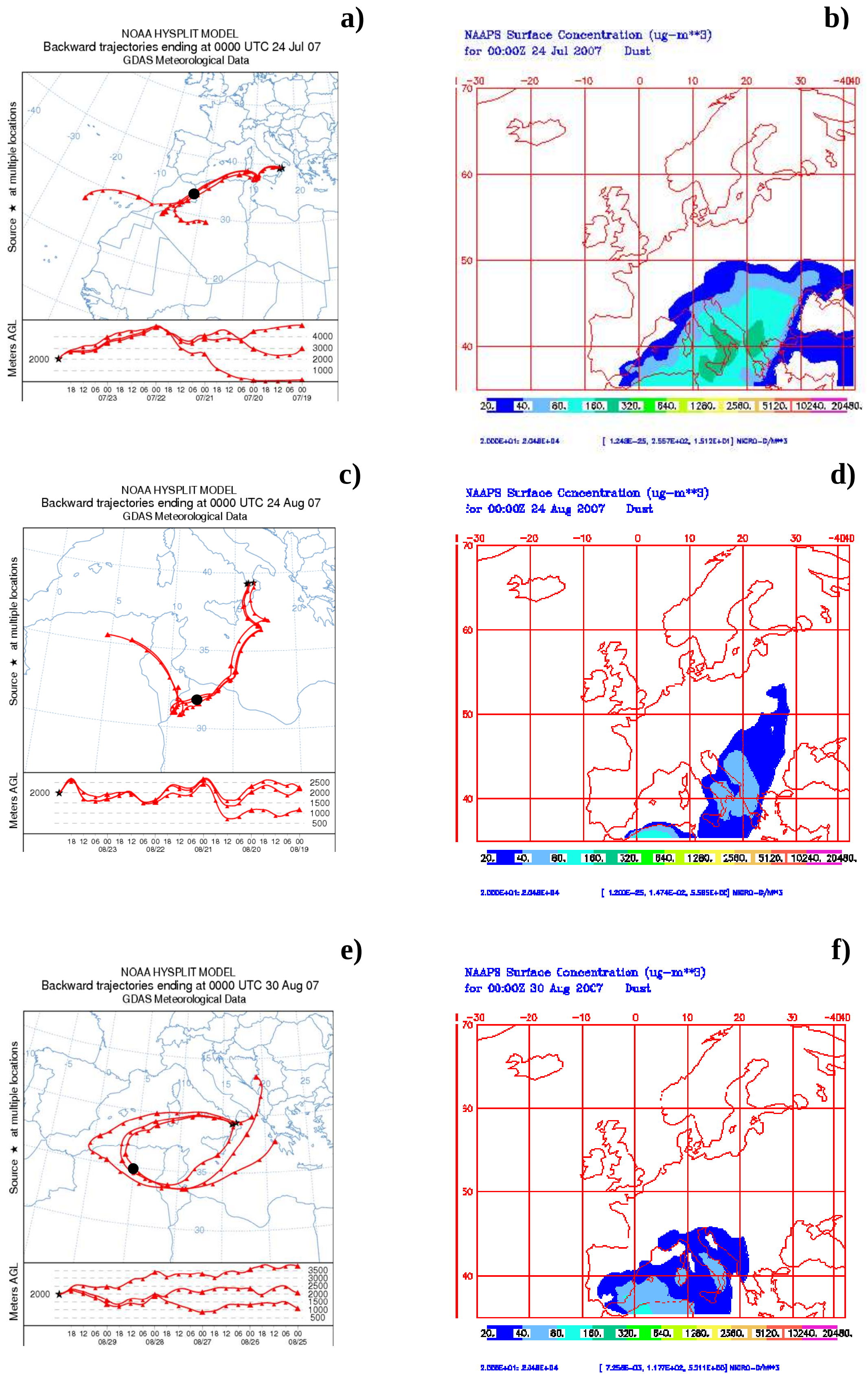

Figure 3.3 *Saharan dust outbreaks occurred over the southern Italy. On the left panels shows 5-days HYSPLIT backward trajectories are reported for the: a) 24th of July; c) 24th of August and e) 30th of August. On the right panels NAAPs based dust concentration maps for the: b) 24th of July; d) 24th of August and f) 30th of August are reported*

3.3.2 Meteorological influence

Average PM_{10} concentrations as function of wind direction are shown in Figure 4.3. The PM_{10} concentrations were observed to be high when the wind was blowing from the southeast over the urban site, from the Northeast at suburban and Northwest at the rural site. Because of the predominant wind direction the contribution of all pollutants from this specific direction at each measuring site is significant compared to other directions. Statistical analysis of daily mass concentration and relevant meteorological parameters such as daily mean values of temperature, relative humidity, precipitation, atmospheric pressure, wind speed and direction, were performed (Figure 4.4). Negative correlation with wind speed was observed giving the prominence to the efficiency of the atmospheric horizontal mixing as a dilution mechanism. This was most evident at the suburban site where the wind speed values were highest compared to those recorded at the urban and rural sites. A positive correlation was, indeed, found for the temperature parameter. The PM_{10} peak concentrations occurred correspondingly with high temperature values. No significant correlation was found between PM_{10} and relative humidity and between PM_{10} and pressure.

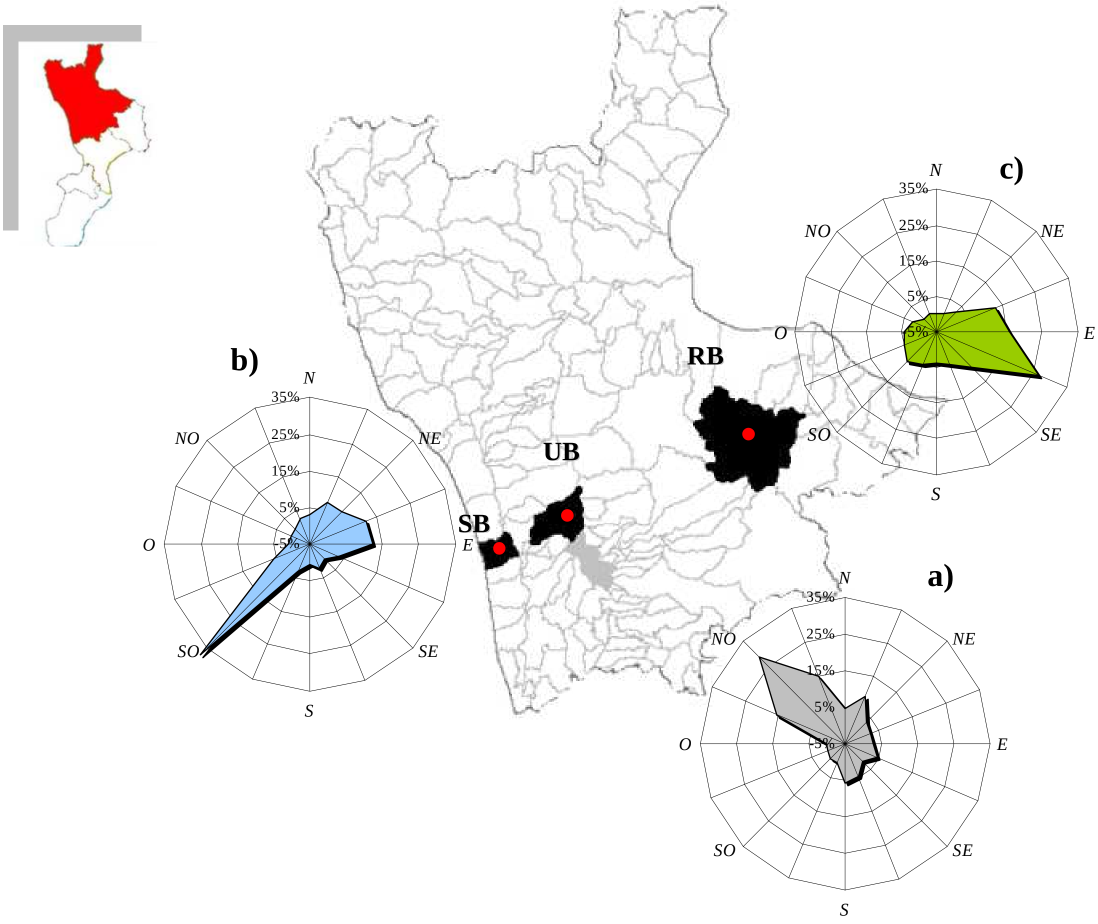

Figure 3.4 *Sampling sites in Calabria region; inset wind direction distribution of* PM_{10} *average concentration at: a) Urban, b) Suburban and c) Rural Background sites*

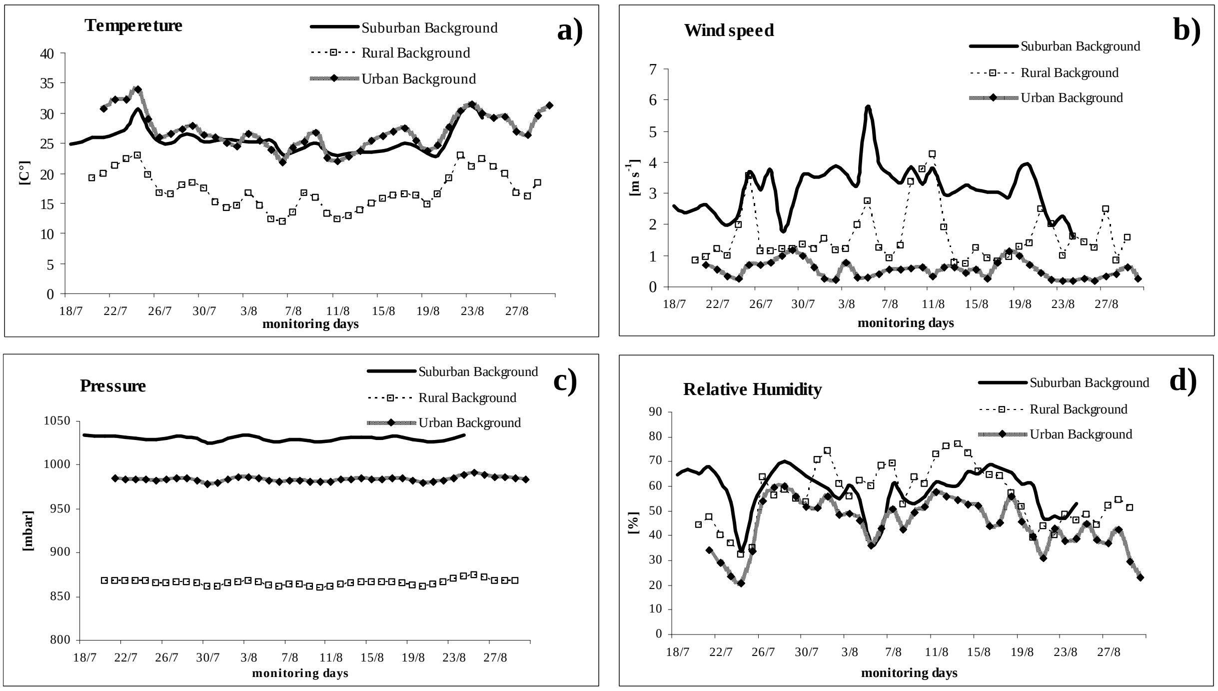

Figure 3.5 *a)Temperature, b) Wind Speed, c) Pressure and d) Relative Humidity behaviour observed at the Urban, Suburban and Rural Background monitoring stations*

3.3.3 Enrichment Factor analysis

The degree to which trace elements in the aerosols are enriched or depleted relatively to specific sources can be assessed using the Enrichment Factor (EF) analysis (Chester et al., 1999).The content of trace elements in crude soil could arise from the geochemical background of the soil or from anthropogenic contributions. According to crude soil values of EF<10 indicate that local resuspension of crude soils is the origin of elements. Values of EF in the range of 10-5000 indicate that the elements are mostly emitted from anthropogenic emission sources (Hlavay et al., 1996). The EF of trace elements was calculated according to the formula:

$$\mathrm{EF} = \frac{\mathrm{C}_{X\,\mathrm{a}} / \mathrm{C}_{R\,\mathrm{a}}}{\mathrm{C}_{X\,\mathrm{c}} / \mathrm{C}_{R\,\mathrm{c}}} \qquad (3)$$

where,

$\mathrm{C}_{X\,\mathrm{a}}$ = trace metal *X* concentration in the aerosol;
$\mathrm{C}_{R\,\mathrm{a}}$ = reference element *R* concentration in the aerosol;
$\mathrm{C}_{X\,\mathrm{c}}$ = trace metal *X* concentration in average crustal material;
$\mathrm{C}_{R\,\mathrm{c}}$ = reference element *R* concentration in average crustal material.

As the reference element must be abundant in the crude soil, the choice of the reference element R is limited (Si, Al or Fe). To have a first indication on the extent of the contribution of anthropogenic emissions to atmospheric elemental levels, the enrichment factor (EF) in this study has been calculated for each detected element, using Al as reference element and the crustal composition given by Mason (1966). In general, an internationally accepted average crustal composition is used to calculate trace element EFs for ambient aerosols (Odabasi et al., 2002). By convention, the average elemental concentration of the natural crust is used instead of the continental crust composition of the specific area, as detailed data for different areas are not easily available. Moreover, particles are subject to transport phenomena and the definition of a specific area is quite difficult.

In Figure 4.5 mean enrichment factors are represented. Elements with EF next to unity have a strong natural component while elements with high enrichment factors have mainly an anthropogenic origin. In PM_{10} fraction Mn has EF next to 1 whereas Pb, Cd and Sb show elevated values of enrichment; As, Cr, Ni and V otherwise appear to be enriched even if to a lesser extent. The resuspension of previously settled particles of anthropogenic origin can increase the EF values. In this study, the EF values up to 10 and below 100 were considered as contributors to resuspention. In this way, it was ascertained that local resuspension had no influence on the content of Pb and Sb in the atmospheric aerosol, whereas dust originating through long-range transport and through resuspension of settled dust particles, significantly contributes to the content of As, Cr, Ni and V in the atmospheric aerosol. The other investigated elements originated partly from crude soil but also from some other emission sources in the region.

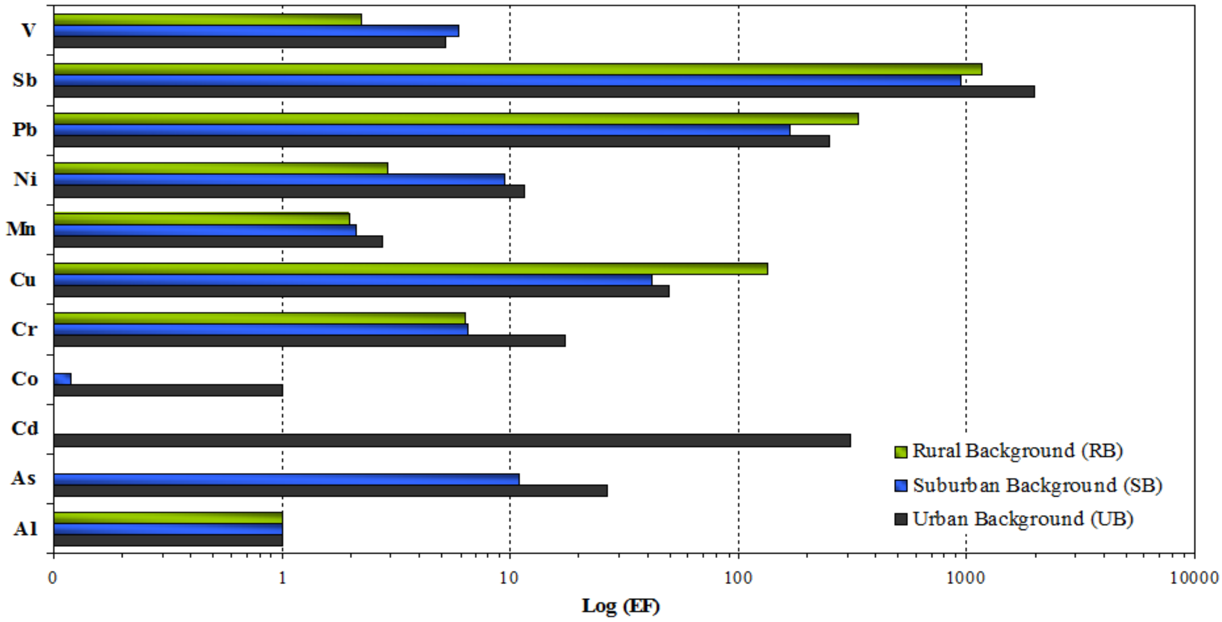

Figure 3.6 *Enrichment factors (EF) of trace elements detected at SB, UB and RB site locations*

3.3.4 Source identification and apportionment

Principal component analysis was performed on *Urban*, *Suburban* and *Rural* data sets. The results, in term of loadings, as well as the percent of the explained variance are presented in Tables 4.2, 4.3 and 4.4, respectively. To determine the number of sources, it was reasonable to test different numbers of sources and use the one that both adequately fits the data and provides the most physically meaningful results. To test the accuracy of the applied PCA technique, the model-predicted daily PM_{10} concentrations were correlated with the experimental values. The R^2 quite high values for urban, suburban and rural site (0.72, 0.81 and 0.87 respectively) show a good agreement between monitored and modelled data.

Trough the PCA five independent factors for the *Suburban* site and four independent factor for the *Urban* and *Rural* site were extracted. The crustal factor was common to any of the three monitoring locations. Other two sources like traffic and agricultural practice, were common to both *Urban* and *Suburban* sites. The sources labelled as oil burning and marine were only found in the San Lucido site. Glassware production were only found to contribute to the Rende PM_{10} levels, whereas rustproofing, textile manufacturing and farming were indentified to be the fingerprint sources in the Longobucco site. The source profiles of the PM_{10} sources are shown in Figures. 3.7 (*Urban site*) 3.9 (*Suburban site*) and 3.11 (*Rural site*). Estimated mass contributions from each identified source category obtained by Multiple Regression Linear Analysis are moreover shown in Figures 3.8, 3.10 and 3.12. Due to the limitation in analysed sources species, 22.8 % at the urban site, 18.6% at the suburban and 17.8% at the rural site, respectively, could not be apportioned to any possible sources by this technique.

The crustal source with Al and Mn as main tracers was common to either of the three monitoring site involved in this work. This source represents inputs of mineral particulate matter of local origin (local/regional dust resuspension) but also of African origin resulting from the incidence of African dust outbreaks in the study area. The other sources are detailed, for each monitoring site, in the further paragraphs.

3.3.4.1 Case Study #1: Rende (Urban site)

Four factors were determined in PM_{10}, which explained 75.3% of the variance (see Table 3.2). The first component (PCU1) extracted for the Urban site data set is represented by the crustal source which accounted for 28.9% of the total variance , consisted of Al and Mn with high loading levels. The second component (PCU2) explained 23.1% of the variance with major contributions from Pb, Cu, Ni, Cr and V in descending order of their loading levels. This factor was selected as a traffic-related source corresponding to the re-suspension of road dust generated by abrasion of vehicle-parts and road surfaces as tyre and brake wear (Kummer et al., 2009; Sternbeck et al., 2002; Adachi and Tainosho, 2004). The source identified as agricultural practice represents the third factor (PCU3) which explained 14.6% of the variance. It was associated with As whose loading is the only one with a high value in this principal component. The As was assumed to be a tracer of various insecticides used for agricultural practices (Peryea, 1998; Zang and Shan, 2001; Otero et al., 2005). Although this inorganic arsenic compound is nowadays banned for human health damage caused by its toxicity, in the last half century, Mono Sodium Methyl Arsenate (MSMA) and Di-Sodium Methyl Arsenate (DSMA), a less toxic organic form of arsenic, has replaced lead arsenate's role in agriculture. The fourth and last component (PCU4) extracted for the Urban site data set explained 8.8% of the variance. It was primarily associated with Sb that in mixtures of its sulphide and oxide, is used as pigment in glass processing. Since many factories involved in the glass manufacturing are located near the Urban monitoring site, this component was confidently identified as related to glassware production.

3.3.4.2 Case Study #2: San Lucido (Suburban site)

Five principal components were extracted accounting for 82.3% of the cumulative variance (Table 3.3). The first three components PCS1 (Traffic), PCS2 (Crustal) and PCS3 (Agricultural Practice), with 26.0%, 23.8% and 13.3% of the explained variance, are common to those identified in the Urban site with similar tracers. In the Traffic component, the loading values are high for the tracers (Pb, Cu, Sb and Cr) which are related to the abrasion of vehicle parts. Several studies have shown that Pb, Cu, Sb and Cr are indicator elements for traffic emissions (Querol et al., 2001; Manoli et al., 2002). The fourth component (PCS4) was associated with V and Ni tracers and represents emission from oil combustion since nearby there is a small harbour and motor-boat traffic constitutes a constant source of oil combustion emissions. The fifth component (PCS5) was associated with the marine salt element, Na with a high loading (0.95) that can be considered as tracer of marine aerosol, transported from the coast towards the study area.

3.3.4.3 Case Study #3: Longobucco (Rural site)

Four factors were determined in PM_{10} at the rural site (Table 3.4). Besides the first component identified as crustal source (PCR1) with 24.6% of explained variance, three others components were extracted for the Longobucco data set, whose interpretation was not straightforward. The second principal component (PCR2), shows high loading only for Pb and probably identifies the red lead (Pb3O4) that is a red crystalline dust used as pigment in the rustproofing paint for iron and steel. The third principal component (PCR3) was associated with Sb, Ni and Cr, whose inorganic salts are used as mordants in the textile industry to fix dyes. Since the traditional textile manufacturing is still an important part of the Longobucco economy, this component could be solely interpreted as textile manufacturing. Finally, the major contributor to the fourth principal component (PCR4) was Cu. Copper sulphate is used as a fungicide and bactericide on plants, famously grapes in “Bordeaux mixture”, (artisanal wine making is still common in the area), and it is also used as disinfectant for livestock. Therefore, since the Longobucco economy is also based on cattle-farming with a small scale agricultural component, Cu was identified as manuring and farming source. For V any relevant correlations, with the identified sources, were founded.

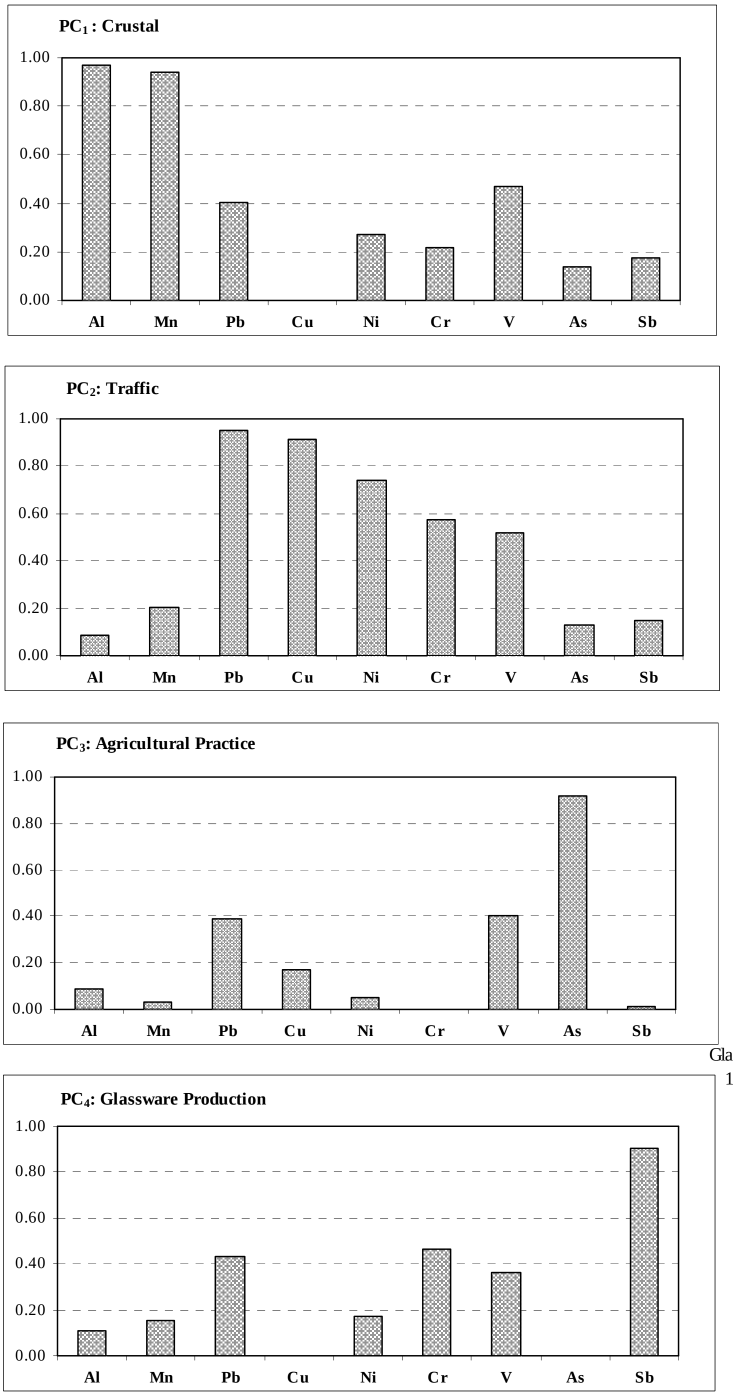

Figure 3.7 *Source profile for PM$_{10}$ collected at the Urban site*

	PC$_1$	PC$_2$	PC$_3$	PC$_4$
Al	0.97	0.08	0.09	0.11
Mn	0.94	0.20	0.03	0.16
Pb	0.41	0.95	0.39	0.44
Cu	-0.10	0.91	0.17	-0.03
Ni	0.27	0.74	0.05	0.17
Cr	0.21	0.58	-0.34	0.46
V	0.47	0.52	0.40	0.36
As	0.14	0.13	0.92	-0.02
Sb	0.18	0.15	0.01	0.90
Eigenvalues	3.94	1.55	1.18	0.73
Variance (%)	28.89	23.06	14.57	8.75
Cumulative (%)	28.89	51.95	66.52	75.27

Table 3.2 *Varimax rotated factor matrix for Urban site*

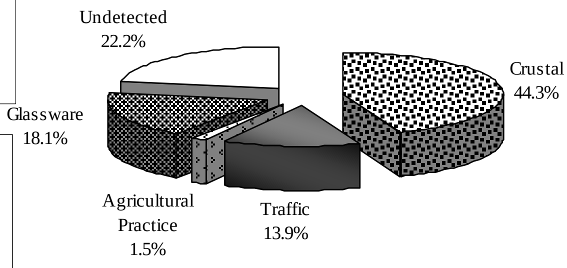

Figure 3.8 *Source apportionment of PM$_{10}$ at the Urban site*

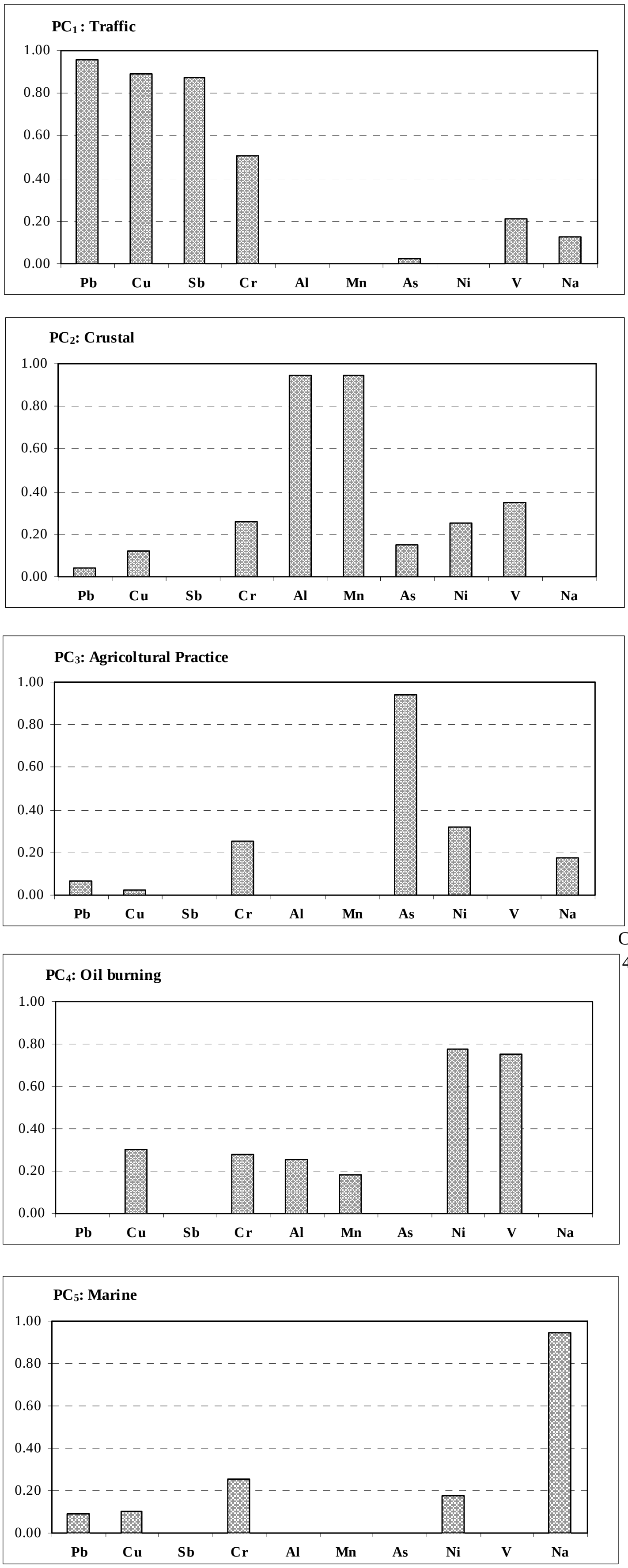

Figure 3.9 *Source profile for PM_{10} collected at the Suburban site*

	PC_1	PC_2	PC_3	PC_4	PC_5
Pb	0.96	0.04	0.07	-0.01	0.09
Cu	0.89	0.12	0.02	0.30	0.10
Sb	0.87	-0.06	-0.28	-0.08	-0.06
Cr	0.50	0.26	0.25	0.28	0.26
Al	-0.03	0.94	-0.03	0.26	-0.02
Mn	-0.03	0.94	-0.13	0.18	-0.09
As	0.02	0.15	0.94	-0.07	-0.18
Ni	-0.02	0.25	0.32	0.78	0.18
V	0.21	0.35	-0.21	0.75	-0.23
Na	0.12	-0.04	0.18	0.00	0.95
Eigenvalues	4.57	3.00	2.10	1.70	1.14
Variance (%)	26.00	23.80	13.30	10.50	8.70
Cumulative (%)	26.00	49.80	63.10	73.60	82.30

Table 3.3 *Varimax rotated factor matrix for Suburban site*

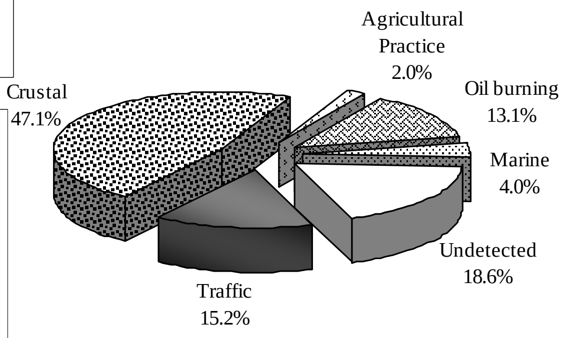

Figure 3.10 *Source apportionment of PM_{10} at the Suburban site*

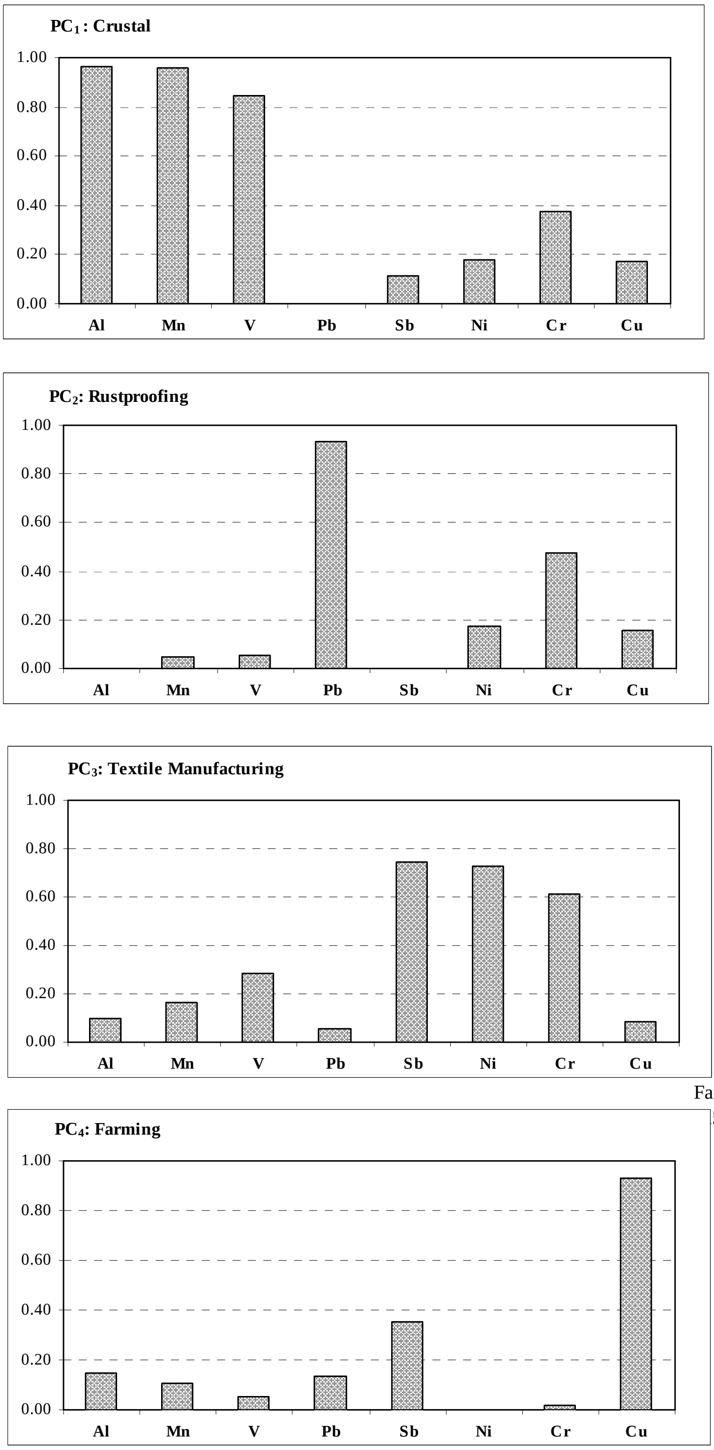

Figure 3.11 *Source profile for PM_{10} collected at the Rural site*

	PC$_1$	PC$_2$	PC$_3$	PC$_4$
Al	0.96	-0.01	0.10	0.15
Mn	0.96	0.05	0.16	0.11
V	0.84	0.05	0.28	0.05
Pb	-0.02	0.93	0.05	0.14
Sb	0.11	-0.23	0.75	0.35
Ni	0.18	0.18	0.73	-0.07
Cr	0.38	0.47	0.61	0.02
Cu	0.17	0.16	0.09	0.93
Eigenvalues	3.53	1.28	0.94	0.86
Variance (%)	34.64	15.76	19.88	13.06
Cumulative (%)	34.64	50.40	70.28	83.34

Table 3.4 *Varimax rotated factor matrix for Rural site*

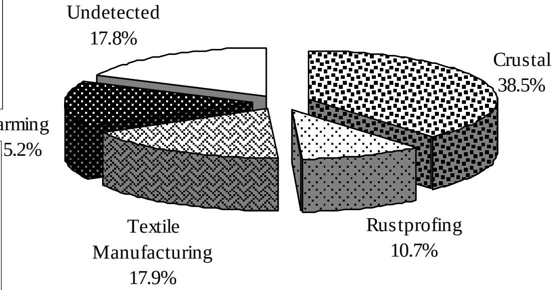

Figure 3.12 *Source apportionment of PM_{10} at the Rural site*

3.4 Conclusions

This study provided a detailed analysis of the PM_{10} elemental composition affecting an urban, suburban, and rural area in Calabria and evaluated the atmospheric transport patterns as well as the potential source regions affecting PM_{10} levels. The PCA application showed that few number of principal components is enough to explain over than 75% of the total variance for each dataset. The analysis indicated the existence of complex processes of emission and transport of trace elements from local, natural and anthropogenic sources, but also from remote sources. The PM_{10} levels at the three monitoring sites were affected, in different ways, by transport, agricultural, marine and manufacturing activities source emissions, but the common source impacting largely at each site, was the Saharan dust. The PM_{10} concentrations in each monitoring site were not very high, though, some exceedances, related just to Saharan dust outbreaks have been detected. These events were identified combining the information from the PCA procedure with that from other independent tools. Satellite data and results of HYSPLIT Model, specifically developed to simulate dust mobilization and transport, were used. The identified Saharan dust outbreaks showed in each sites a relevant contribution with a sharp raising in PM_{10}, Al, Mg, K, Ca, Fe and Mn levels. This consideration highlighted the importance of the PM_{10} source apportionment jointly with others integrated analytical approaches that can be used in long-term health-impact based studies and can support policy making in order to achieve an effective air quality management. The extent to which exposure to ‘natural’ PM itself is harmful to health is, in fact, still a matter of debate (Brunekreef and Maynard, 2005). In the absence of a single, recognised standard procedure, more studies will have be conducted to assess the correct Saharan dust impact on PM_{10} concentrations in the Mediterranean area with a special regard to the southern regions.

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CHAPTER 4

Natural Sources: Aerosol-Ozone variability at a Marine, Urban and High Altitude monitoring stations in Southern Italy during summer 2007

Central-Southern Mediterranean basin, especially in summertime, is heavily affected by Saharan dust outbreaks and wildfire events. A focus on their significant influence on either oxidizing capacity of the atmosphere and air quality over Calabria region, southern Italy, was here presented. Since the frequency of these events is expected to increase due to climate change, similar studies could even be a valid effort to better understand and characterise such atmospheric variations. In particular, during summer 2007, the south of Italy and largely the Calabria region was affected by a quite severe fire season with the highest total area burned (estimated for Calabria at 9 608 ha) occurred in Italy. In order to evaluate the spatial variation of aerosol (PM_{10}) and ozone (O_3) concentrations under the influence of both anthropogenic and natural sources and characterize the atmospheric conditions that lead both O_3 and PM_{10}-rich episodes in southern Italy, an intensive sampling campaign was simultaneously performed from the middle of July to the end of August 2007 at a Marine, Urban and High Altitude monitoring stations in Calabria region. Among natural sources, Saharan dust intrusion and Biomass Burning, have shown to involve a marked impact on the data recorded. Typical fair weather of Mediterranean summer and persisting anticyclone system at synoptic scale, were indeed favourable conditions to the arrival of heavily dust loaded air masses over three period of consecutive days. A cluster analysis, based on the prevailing air mass backward trajectories was performed allowing to discriminate the contribution of different air masses origin and paths. Results have shown that both PM_{10} and O_3 levels reached similar high values when air masses coming from the industrialized and densely populated continental Europe as well as under the influence of wildfire emissions. During the indentified dust outbreaks a huge rise in PM_{10} levels with a concurrent decrease in O_3 values was otherwise observed. Spatial and meteorological variability between observations performed at the three sampling locations were furthermore presented highlighting the coherence with measurements previously recorded around the Mediterranean Basin.

4.1 Introduction

During the last decade, the long-range transport of pollutants across the Mediterranean sea has received considerable attention due to the high level of industrialization and dense population around the basin which provide a significant effects on pollution of this area (Lelieveld et al., 2002; Millàn et al., 2006). Research studies carried out in the Mediterranean region have shown that the Mediterranean atmosphere consists of a mixture of anthropogenic and natural contributions thus confirming this region to be a major crossroad of different air mass transport processes (Duncan et al., 2008). The contributions of these two components within the region depend on different factors such as the relative distance between sources and receptor sites and the meteorological conditions.

Different classes of particles can be found in the Mediterranean atmosphere due to the variety of the regions around the basin: desert dust, originated from North Africa (Saharan dust) and from the arid regions of the Iberian Peninsula; polluted particles, produced mainly in urban and industrial areas of Continental and Eastern Europe; marine aerosol, continuously originated over the Mediterranean itself or transported from the North Atlantic; and biomass burning particles, often produced from forest fires (Pace et al., 2006) Moreover, the Mediterranean basin is a unique area with the highest aerosol optical depths in the world (Ichoku et al., 2002; Husar et al., 1997) and maximum direct radiative forcing values due to the accumulation of aerosols favoured by meteorological conditions, small cloudiness and prolonged exposure to solar radiations (Hatzianastassiou et al., 2004) Similarly, ozone (O_3) is of particular interest in the Mediterranean region. In fact, compared to Central Europe, O_3 concentrations over the Mediterranean are up to 20–40% (10–12 ppb) higher (Kalabokas et al., 2007) Increasing ozone concentrations have further been observed from North to Central-South Europe (Lelieveld et al., 2002)

The high levels of solar radiation observed in the Mediterranean in combination with several factors such as, anthropogenic and biogenic O_3 precursor emissions, trans-frontier transport of pollutants, frequent biomass fires and thermally induced recirculation near the densely populated coast, favor intense photochemical O_3 production (Millàn et al., 2006; Pace et al., 2006; Rodriguez et al., 2001; Auvray et al., 2005; Vautard et al., 2003; Gerasopoulos et al., 2005; EEA, 2005-2007). Results observed in previous studies highlighted the importance in the Southern Mediterranean Basin of PM_{10} and O_3 pollution events occurring in summertime (April-October).[2,12,15] These episodes, related with meteorological conditions that favour enhanced photochemical O_3 production and aerosol accumulation, have shown to cause an additional violations per year of both the European health standard for O_3 (8-h average < 60 ppbv)[3,16] and the European daily PM_{10} target value ($< 50\ \mu g\ m^{-3}$).[15] Moreover, an increase in mortality, often registered during summertime, seem also to be related to these worse air quality conditions other than to the highest temperature of the typical Mediterranean summer season. Particularly, during the three heat wave episodes occurred in summer 2007, significant excess in mortality was observed mainly in the south of Italy with a percent increase between 11-56%.[17] Owing to this context, during summer 2007 in Calabria region, Southern Italy, properly sampling campaigns concerning PM_{10}, tropospheric O_3 along with selected parameters were simultaneously performed at a Marine, Urban and High Altitude monitoring stations. The results obtained were then coupled with both backward trajectories analysis and satellite derived products which were useful to understand the aerosol sources and transport pathways. These crossed analysis permitted to assess some Saharan dust intrusion, highlighting that low O_3 concentrations usually accompany these transport events. These findings were confirmed by soundings of O_3, humidity and temperature recorded at other existing monitoring stations over Calabria area, besides ours. Fire hot-spots were identified by the MODIS Rapid Response System (http://rapidfire.sci.gsfc.nasa.gov/) which provides for specific locations and daily frequency of biomass burning. Finally, a cluster analysis based on the prevailing air mass influence, was performed allowing to discriminate the contribution of different air mass origin and paths and to better characterize the correlation between O_3 and PM_{10} concentrations. In order to assess the Saharan dust contribution in exceeding PM_{10} target values a statistical based methodology was applied to the three PM_{10} data set obtained. Spatial and meteorological variability between observations performed at our three sampling locations and their comparison with previously measurements performed across the Mediterranean Basin were furthermore presented.

4.2 Materials and Methodologies

4.2.1 Monitoring Sites

From 18th of July to 30th of August 2007, ground-based air measurements were simultaneously performed at three sampling stations located in Calabria region, Southern Italy

(Figure 4.1). Main characteristics of each sampling site are summarized in Table 4.1. According to (18) the air quality monitoring stations involved in this work were classified as Urban (UB), Suburban (SB) and Rural Background (RB) Stations with regard to Rende (N39°20'0" E16°11'0"), San Lucido (N39°19'22" E16°02'44") and Longobucco (N39°23'39" E16°36'49") sites, respectively.

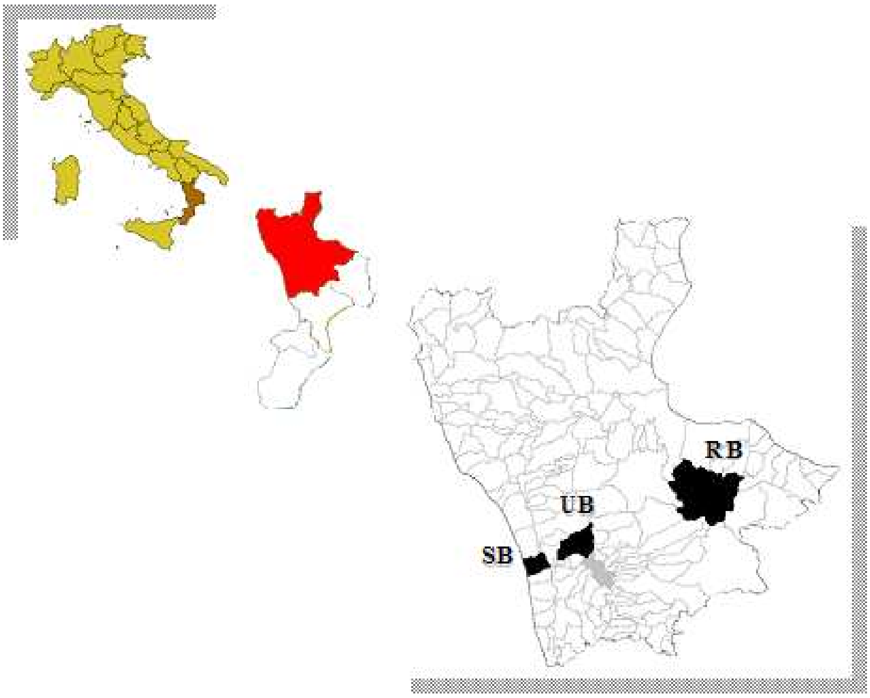


Figure 4.1: *Monitoring site locations: Suburban Background (SB), Urban Background (UB) and Rural Background (RB) sites.*

Site	***Town***	***Altitude* [m a.s.l]**	***Latitude***	***Longitude***	***Monitoring Station Classification*** *
SB	San Lucido	49	39° 19' 22"	16° 02' 44"	Suburban Background
UB	Rende	250	39° 20′ 0″	16° 11′ 0″	Urban Background
RB	Longobucco	1379	39° 23' 39"	16° 36' 49"	Rural Background

** according to Decision 2001/752/CE*

Table 4.1: *Coordinates and monitoring station classification for each sampling site*

Urban Background (UB) station is located inside the campus of the University of Calabria in Rende. This town is about 4 kilometres far from the major urban area of Cosenza even if the two conurbations now effectively run into each other constituting one continuous urbanised area of roughly 100 000 inhabitants. The increasing urbanisation of the area led to a 4% increase in fuel consumption between 2002 and 2006 and the traffic flow is the major local source of air pollution.[19] The A3 motorway crosses the area at about 1km east of the measurement site with a considerable traffic flow, including heavy-duty vehicles.

Suburban Background (SB) station is located on the Thyrrenian coast of Calabria on a small headland 49 m asl, near San Lucido, a village with a population of 5 906 inhabitants. During the summer season, particularly in July and August, this seaside area attracts a large number of tourists with a resulting rapid increase in population and traffic flow. The nearest major road, the SS 18, located at about 600 m east the sampling site, follows the coast line and has a traffic count in the summer season of approximately 3 000 cars per day.[20]

Rural Background (RB) site is at a relatively high altitude (1379 m asl), situated near the village of Longobucco in the Sila Massif, between the Tyrrhenian and Ionian seas. The area surrounding the sampling station is a mixture of seasonal pasture and woodland. Longobucco has a population of about 4 000 inhabitants, but is situated in a valley some km away. The local economy is based particularly on cattle-farming and on textile manufacturing.

4.2.2 Sampling and Analysis Procedures

PM_{10} samples were collected on pre-weighed and preconditioned 47-mm Teflon filters, over a 24h sampling period from 18th of July to 30th of August 2007 using a dual channel high volume particulate matter sampler with a flow rate of 38 L min^{-1}. A total of 44 samples were obtained at each monitoring site. O_3 measurements, available for UB and RB sites, were performed by an automatic Teledyne UV absorption ozone analyser (Model 400E). The ozone analysers were calibrated every 24 h by routine automated additions of known concentrations of gaseous ozone supplied by an internal permeation source. A sampling flow rate of 0.8 L min^{-1} was used to measure the ozone concentration every 5 min. At only SB site CO measurements were carried out by an automatic CO analyser Teledyne (Model 300E). Meteorological parameters were continuously measured at all three monitoring stations.

4.2.3 Data Analysis Treatment

For each monitoring sites the data set consists of PM_{10} daily mass concentrations (µg m^{-3}) and daily meteorological parameters average values [(temperature T (°C); relative humidity RH (%); precipitation (mm); daily mean wind vector along with component wind speeds WS (m s^{-1}) and wind direction □ (deg)]. In addition, 5-minute O_3 average values were available for UB and RB stations whereas 5-minute carbon monoxide (CO) levels were recorded only at the SB site. For each measured variable, the explorative statistical parameters of data distribution have been performed. To investigate the different source regions of air masses reaching the study area and to better understand the occurrence of specific events affecting PM_{10} and O_3 levels at each monitoring site, 5-days backward trajectories at different altitudes (500, 1 000 and 1 500 m a.g.l.) for each sampling day were calculated using the HYSPLIT4 model.[21] Several tools, such meteorological maps, numerical models and satellite images, were also analyzed as useful sources of information. In particular, the influence of African dust transport was investigated following the methodology described in the next section. The sulphate concentration maps provided by NAAPs model (http://www.nrlmry.navy.mil/aerosol/) were instead used to identify events of transboundary transport of pollutants from the European continent. Otherwise, for fire events identification the MODIS true-colour images (http://rapidfire.sci.gsfc.nasa.gov/) and the NAAPs based smoke concentration maps were in addition used to identify the origins and the extension of fire plumes. Specific locations and daily total fire hot-spots over the Cosenza province were then obtained from the Fire Information for Resource Management System (FIRMS) (http://maps.geog.umd.edu/firms) which integrates remote sensing and GIS technologies to deliver global MODIS hotspot/fire locations to natural resource managers and other stakeholders around the world.

4.2.4 Methods applied for the identification of Saharan dust outbreaks in Calabria Region

The identification of Saharan Dust Outbreaks (SDO) was performed applying the methodology well described in (22). Five-day back-trajectories ending at each of our sampling location at 2000 and 4000 m a.g.l. altitude were thus calculated by HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model,[21] including the vertical wind. As stated by the used methodology, the air masses are loaded with Saharan dust through entrainment in the mixed layer or through permanence over the Sahara for a long fraction of time. The entrainment condition requires that the trajectory approaches the mixed layer within 500 m of the layer top or enters the mixed layer; in this case the most probable loading area is located where the distance between the trajectory and the mixed layer is the lowest, or where the intrusion into the mixed layer is the deepest. Thereby, the entrainment condition was checked for the trajectory ending at 4000 m first and then for that ending at 2000 m. If the entrainment condition was never met along both trajectories, the permanence condition was checked for the trajectory at 2000 m. In order to account wet deposition events, the entrainment and the permanence conditions were accepted only if it did not rain after the dust loading; this condition should be eliminate as stated by the followed methodology. Otherwise, in order to corroborate the identified dust events, additional information was obtained from satellite observations reporting Aerosol Index, performed by Earth Probe/Total Ozone Mapping Spectrometer (EP/TOMS),[23] and from model results of dust optical depth from NAAPS – Navy Aerosol Analysis and Prediction System[24,25] (http://www.nrlmry.navy.mil/aerosol/). Furthermore, specific SDO events were analyzed in relation to the NCEP based 700 mbar level geopotential height and temperature (http://www.cdc.noaa.gov/) in order to assess their seasonal differences and the main circulation patterns driving these events through the Central Mediterranean basin to our three sites. All the NCEP maps have been taken considering an area of 10°–60° N and 30° W–40° E. Finally, for the quantification of the daily African PM_{10} load during dust outbreaks, the method based on the statistical data treatment of PM_{10} levels time series[26] was used. The daily dust load was obtained by applying a monthly moving 30th percentile to the PM_{10} time series at a reference rural station, located at Firmo (N39°43’22’’ E16°10’15’’, 370 m a.s.l.), in Cosenza province, after a prior extraction of the days with Saharan dust influence. The recorded PM_{10} time series at the rural station considered in this study, are indeed available since 2004 and can be easily downloaded by the BRACE dataset (http://www.brace.sinanet.apat.it/web/struttura.html). Then, for a given day under Sahara influence, the net dust was obtained by subtracting the calculated value from 30th percentile to the measured PM_{10} concentration. The thus calculated net African dust load, valid for the whole region, as stated by the used methodology, was thereby subtracted from the daily PM_{10} levels recorded at each of our sampling stations only on days when the occurrence of African dust outbreaks was observed.

4.3 Results and Discussion

4.3.1 Overview on PM_{10} and O_3 levels recorded during summer 2007

Sampling campaigns were performed from 18th of July to 30th of August, when typical fair weather conditions of the Mediterranean summer prevailed. No precipitations were generally recorded (only an exception occurred at RB, during the 23rd of August) and the hourly maximum of air temperature reached values of 37.0, 42.4 and 31.7 °C at SB, UB and RB sites, respectively. Local winds were quite weak while a persisting anticyclone system often occurred at synoptic scale. Temporal series of PM_{10} concentrations recorded at the three sites are reported in Figure 4.2. A common pattern can be observed with particular evidence in the raising values, even though the second and third peak values, reached at both SB and UB sites, did not appeared at RB. At each sampling site, a total of 44 values of PM_{10} daily concentrations were determined, ranging from 11.8 to 134.0 μg m^{-3}, from 1.1 to 99.3 μg m^{-3} and from 7.7 to 86.4 μg m^{-3} at SB, UB and RB site, respectively. PM_{10} concentrations ranged very wide resulting also in high standard deviations (23.8 μg m^{-3} at SB, 22.7 μg m^{-3} at UB and 16.0 μg m^{-3} at RB) from the mean concentrations that were 39.7 μg m^{-3}, 35.5 μg m^{-3} and 24.7 μg m^{-3} at the SB, UB and RB site. Such high standard deviations are not unusual for data obtained in the Mediterranean atmosphere[27,28] suggesting that ambient air concentrations varied depending on non-local sources.[29] Measured PM_{10} mean values were both lower than the yearly limit value of 40 μg m^{-3} while a number of 9, 10 and 2 days exceeding the daily PM_{10} limit value[30] were recorded at SB, UB and RB sites, respectively. In order to discuss these observations, the PM_{10} data presented in this study were compared with PM_{10} mass-levels previously recorded across the Mediterranean Basin (MB). In this area, as reported in (15), PM_{10} concentrations reach the maximum values during summertime as result of the higher frequency of African dust outbreaks, lower precipitation, higher (local/regional) resuspention owing to the dryness of soils, increased formation of secondary aerosols caused by the maximum solar radiation and recirculation of air masses that prevent air renovation. In (15) summer mean PM_{10} mass-levels across the MB are reported. These values revealed clear W-E and N-S increasing trends ranging from 12.7 μg m^{-3} in the Northern to 28.8 μg m^{-3} in the Southern Italy and from about 15.0 μg m^{-3} in the Western to 34.1 μg m^{-3} in the Eastern Basin. A larger summer period (from April to September) to which the above reported PM_{10} values are referred in respect to our summer reference period (from 18th of July to 30th of August) could explain the slightly lower values of literature. Otherwise, the above reported PM_{10} mean values agree rather well with our results moreover with regard to the site location. In fact, in terms of mean concentration, PM_{10} trend observed at our sampling stations (SB > UB > RB) was in line with PM_{10} values measured across the MB that are usually lower at the high mountain areas and higher at island and coastal sites (due to the sea spray contribution).[15] Pertaining O_3 levels the results obtained during the sampling campaigns are summarized in Table 4.2 which reports daily O_3 maximum, mean and standard deviation values besides maximum 1 h mean and maximum daily 8-hour mean. This latter parameter, over 15 days at UB and 31 days at RB site, exceeded the ozone long-term objective for the protection of human health (i.e., a daily maximum 8-hour average concentrations higher than 120 μg m^{-3}) whereas hourly mean values were at both stations ever less than the information threshold.[31] These O_3 concentrations during summer, were quite higher than those recorded, at the same site locations during wintertime,[19] thus corroborating the tropospheric seasonal cycle of background O_3. In fact, over the Mediterranean region and in southern Europe, O_3 levels are usually dominated by the presence of a broad spring–summer peak,[32,33,34,35,36] due to the superposition of the hemispheric-scale spring maximum (April–May) and the increased photochemical production of O_3 that characterises the lower troposphere during summer.[1,37] Similar O_3 behaviours were pointed out by (38) for two measurement sites located in the southern Italian Alps and Pre-Alps (Alpe Motta, 1800 m and Passo S. Marco, 1900 m), where a winter minimum (from 26 to 32 ppbv) was followed by a spring peak (46–49 ppbv) and subsequent summer peak (47–55 ppbv). Measurements performed at Mt. Cimone (northern Italian Apennines; 2165 m), during the period 1996–2004,[39] have also revealed the presence of a seasonal O_3 cycle (yearly mean value: 54 ppbv) with two peaks in spring (average 59 ppbv) and in summer (average 63 ppbv). These O_3 values agree notably with those observed at our sampling stations considering that tropospheric O_3 concentrations increase with altitude.[40] This phenomenon, owing to the influence on O_3 concentrations of air mass transport from the stratosphere and to the high efficiency of O_3 dry deposition and removal at the surface,[41] could also partially explain the difference in ozone levels observed at our sampling stations (RB > UB). The relative vicinity of the UB to the motorway leads otherwise to lower measured ozone concentrations, most likely explained due to titration by NO,[19] in respect to those observed at the RB site. The results obtained during our sampling measurements, whose an overview has been above presented, were further investigated and discussed in the following sections, in respect to specific events that produced a noticeable influence on PM_{10} and O_3 levels.

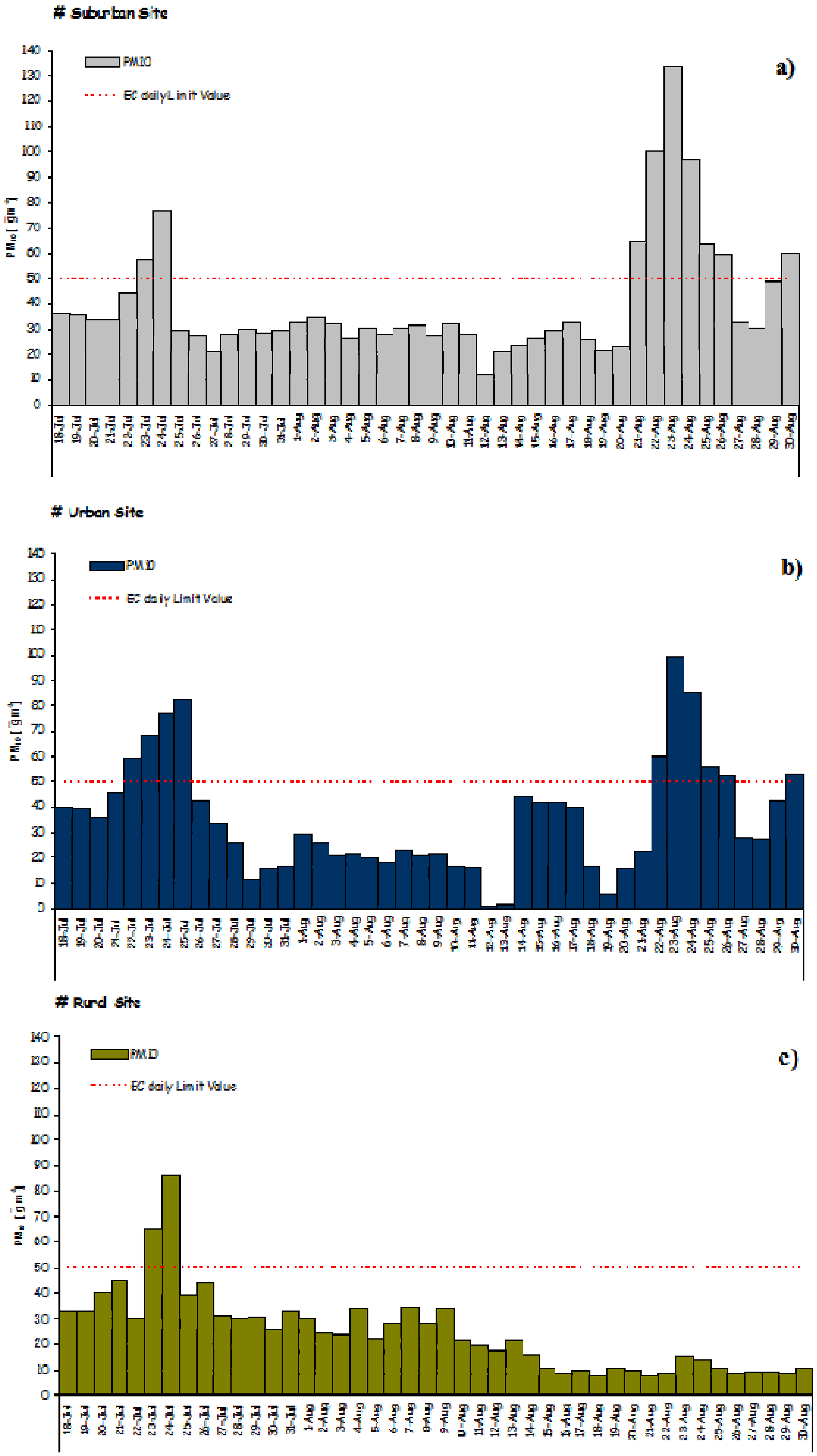


Figure 4.2: *Time series of PM_{10} levels recorded at: a) SB; b) UB and c) RB sites.*

	O_3 [ppb]				
	Max 24 h	Mean 24 h	S.D. 24h	Max 1h	Max 8h
SB	-	-	-	-	-
UB	57.5	43.8	6.8	82.3	71.2
RB	63.6	50.9	6.2	82.9	80.4

Table 4.2: *Descriptive statistics for ozone levels.*

4.3.2 Saharan Dust Outbreak influence on PM_{10} and O_3 levels

Saharan storms export more mineral dust than any other area of the world, injecting into the atmosphere amount of desert particles as 130-760 Tg yr^{-1} to about 1 600 Tg yr^{-1} [42] whose a non negligible part is transported by synoptic circulation across the Mediterranean Basin. At ground level, dust outbreaks are well known for the dust load magnitude they generate and their implication to current and future European Union directives on air quality.[43] The presence of mineral dust in the atmosphere may contribute to climatic variations and influence the behaviour of some tropospheric trace gases, changing the oxidizing capacity of the atmosphere.[44] In particular, those mineral aerosol particles, which are characterised by very large surface area, can strongly absorb the shortwave solar radiation, influencing the radiative forcing of climate,[45] or causing a photolysis rate reduction, thus inhibiting ozone production. Mineral dust injected in the troposphere can also indirectly influence the tropospheric O_3 concentrations. In fact, aerosols can either increase or decrease the actinic flux (depending on scattering and absorption properties at UV wavelengths) affecting the photochemical ozone changes.[46] In addition, through surface processes, mineral aerosol may influence tropospheric O_3 formation by affecting O_3-precursors and the tropospheric oxidation capacity.[47] In particular, HNO_3 and NO_3 depletion on dust particulate can remove a fraction of O_3 precursors (i.e., NOx) favouring a reduction of photochemical O_3 production efficiency.[48] Owing to these meaningful implications and in order to assess the impact strength of Saharan Dust Outbreaks on our ground-based air sampling measurements a thorough investigation on their dynamic evolution has been carried out.

The intrusion of SDO during the sampling campaigns at our monitoring stations occurred for a period of three consecutive days. Periods of 4 days (from 22nd to 25th of July), 5 (from 22nd to 26th of August) and 2 days (from 29th to 30th of August) have been recorded. For each of these SDO event (which will be referred to as 1st, 2nd and 3rd event) the back-trajectory analysis allowed to locate over the Saharan desert the most probable loading regions which are highlighted as black circles in the Hysplit-based maps (Figure 4.3, left panels). These maps show the loading areas for both three SDO events located above 30° N and specifically at the border line between Marocco and Northern Algeria, in North-Western of Lybia and in Northern Algeria in respect to the 1st, 2nd and 3rd period of the identified SDOs. These specific cases were analysed in relation to the NCEP based 700 mbar level geopotential height and temperature (this latter not presented), in order to identify the main circulation patterns driving SDOs through the Mediterranean until the Calabria region. The 1st episode, was particularly governed by a trough extending over the Great Britain and a high pressure system present in North Africa above 35 °N (Figure 4.3a). This configuration, characterized by a warm kernel in North-Western Sahara with a tongue extending north-eastward towards Sicily, caused strong south-westerly flows from the Sahara towards Sourthern Italy (Figure 4.3b). The synoptic situation characterizing instead the 2nd SDO event was a well defined low over the Iberian peninsula descending through the Western Africa, and a high pressure that moved from the Northern Lybia with a ridge extending from Southern Italy to South-Eastern Europe (Figure 4c). The air masses resulting from these two pressure systems (Figure 4.3d), travelled along S - N stream flows. During the 3rd SDO event, indentified at the end of August 2007, dust transport was driven otherwise by a persisting anti-cyclonic circulation over the Mediterranean Basin (Figure 4.3e). This synoptic condition was favourable for the clockwise motion of the air masses that moved through Tunisia and Algeria prior to ending at our sampling stations in Calabria region (Figure 4.3f). Concerning PM_{10} concentrations, the strength impact of these characterised SDO events, showed some differences between the ground-based air measurements performed at the three sampling sites. The 1st SDO episode was the single one that caused at each of the sites a similar raising in PM_{10} levels reaching peak values between the 24th and 25th of July. A common pattern in PM_{10} levels can be observed also during the 2nd and 3rd SDO episodes even though the following PM_{10} peak values, reached at both SB and UB site, did not appeared at RB (see Figure 4.2). Regarding the 2nd SDO, a rainfall checked along the trajectory followed by the air masses prior to ending at RB (at 00:00 of the 23rd of August) was the most likely reason causing the difference between PM_{10} levels at SB and UB and those measured at the RB. The related outcome was just a slight increase in PM_{10} mass-levels (15.6 $\mu g\ m^{-3}$) at RB station in contrast to the huge raises that reached peak values of 134.0 and 99.3 $\mu g\ m^{-3}$ at SB and UB site, respectively. During 3rd SDO episode some differences occurred in the air-mass loading with Saharan dust.

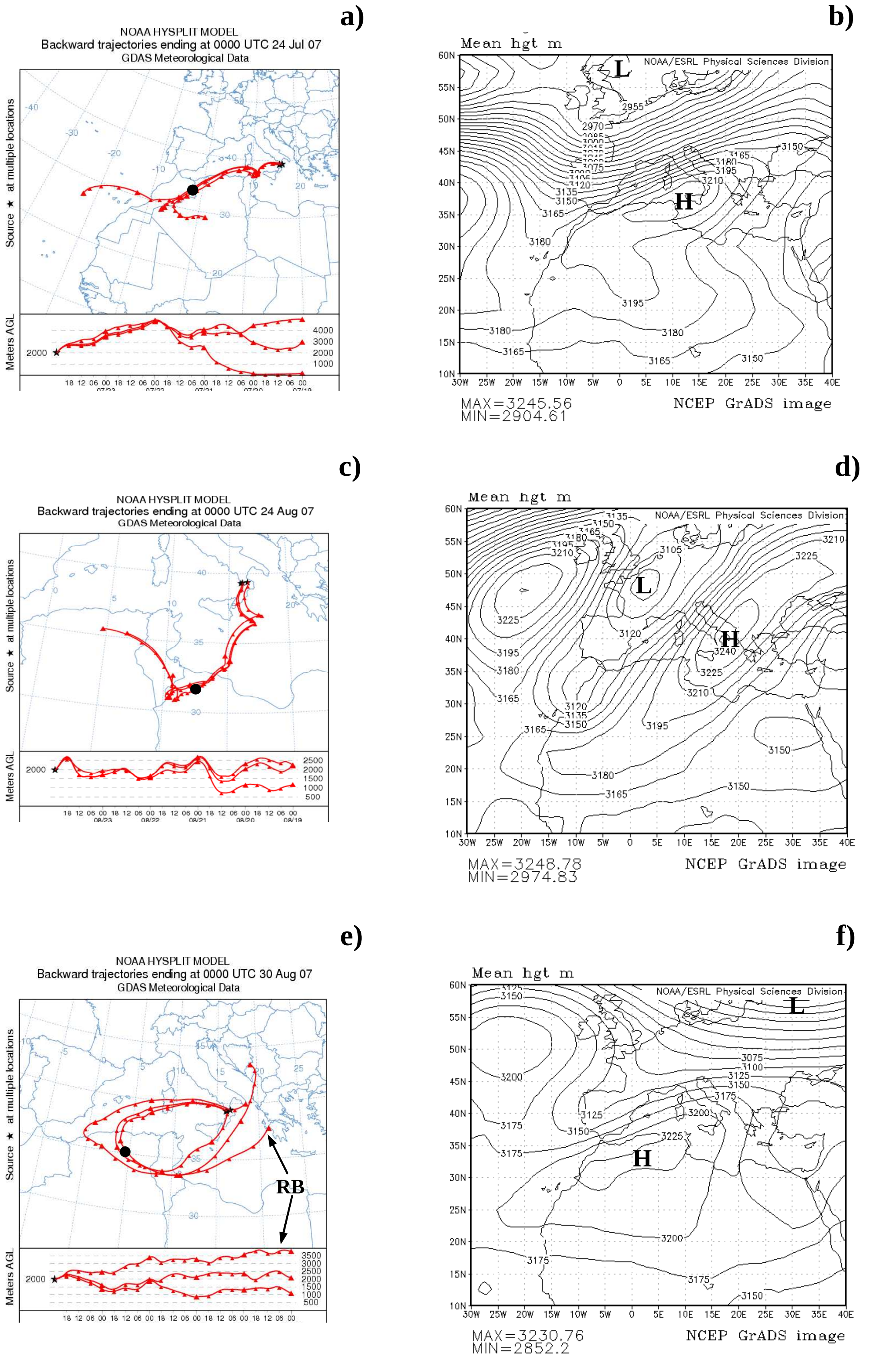


Figure 4.3: Saharan dust outbreaks occurred over the southern Italy. On the left panels 5-days HYSPLIT backward trajectories are reported for the: a) 24th of July; c) 24th of August and e) 30th of August. On the right panels NCEP-based 700 mbar geopotential height (m) for the: b) 24th of July; d) 24th of August and f) 30th of August are reported.

As assumed in (22), air masses are loaded with Saharan dust through entrainment in the mixed layer, requiring that the trajectory approaches the mixed layer within 500 m of the layer top or enters the mixed layer. Regarding our sampling stations, during the 3rd SDO period the entrainment condition, with trajectory entering the mixing layer, was met along both trajectories ending at SB and UB sites (see Figure 4.4a-b). Conversely, according to Figure 4.4c, the entrainment of the trajectory ending at RB, that followed a slightly different pathway (see Figure 4.3c), did not occur and the loading with Saharan dust did not take place. Thereby, it could be confidently held that 2nd and 3rd SDO did not affect RB measurements. In order to assess the influence of the above described SOD episodes over both PM_{10} and O_3 levels a graph reporting both their time series was made. Figure 4.5 (left panels) shows at both the sampling stations a decrease in O_3 levels in conjunction with a huge increase in PM_{10} values for each identified SDO event (highlighted with gray bars). Similar trends were also detected in RH [%] and T [°C] values, whose time series are even reported in Figure 4.5 (right panels). A selection of the days with and without SDO influence has been then performed obtaining an explorative statistical analysis summarised in Table 4.3. The identified SDO days, in terms of percentage variation (Δ%) over days without SDO influence, showed an average increase in PM_{10} concentrations of 135.5% at the SB, 167.4% at the UB, 103.6% at the RB site and an opposite trend in O_3 levels with an average decrease of 17.7% and 13.9% at the UB and the RB site, respectively. These outcomes agree quite well with previously both laboratory and modelling studies[49,50,51] as well as observations focused directly on this issue.[52,53,54,55] PM_{10} and O_3 levels recorded in others existing monitoring stations over Calabria area, besides ours, were furthermore checked. During the same sampling period, two stations, both defined as rural, one located at Saracena (N39°46’44’’ E16°09’28’’, 606 m asl) and the other one at Firmo (N39°43’22’’ E16°10’15’’, 370 m asl), 68 km and 61 km NNE respectively far from our site in Rende (UB), performed ground-based air measurements available at the BRACE database (http://www.brace.sinanet.apat.it/web/struttura.html). The reported values in Figure 4.6 show a clear increases in PM_{10} in conjunction with O_3 levels decreasing during the same SDO events detected for our sampling stations. These occurrence corroborate that Saharan dust transport is a large scale phenomena that could modify significantly both PM_{10} and O_3 concentrations.

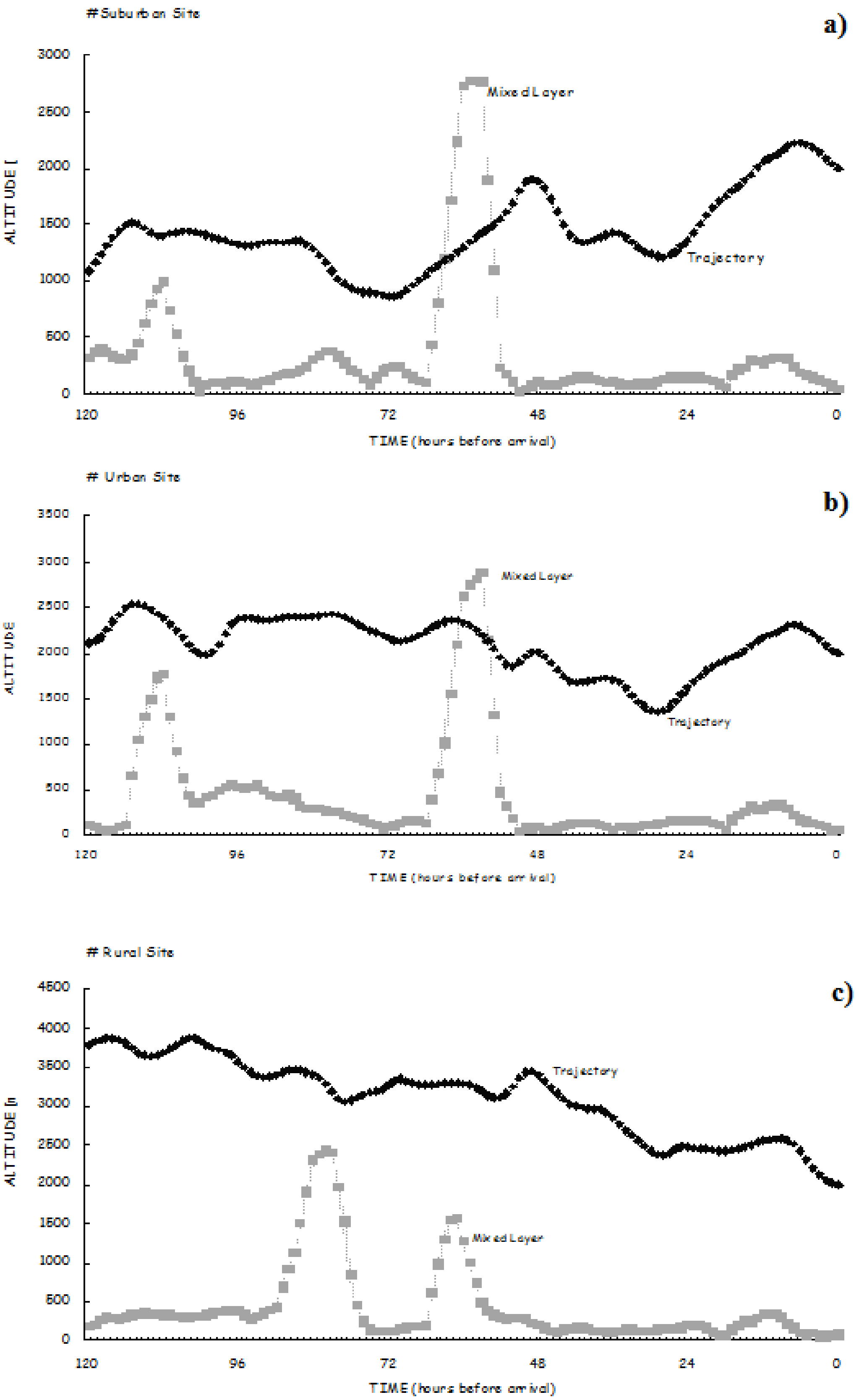


Figure 4.4: *Trajectory and Mixed Layer altitudes along the path followed by backward trajectory before their arrival at: a) SB; b) UB and c) RB sites, respectively on 30th of August.*

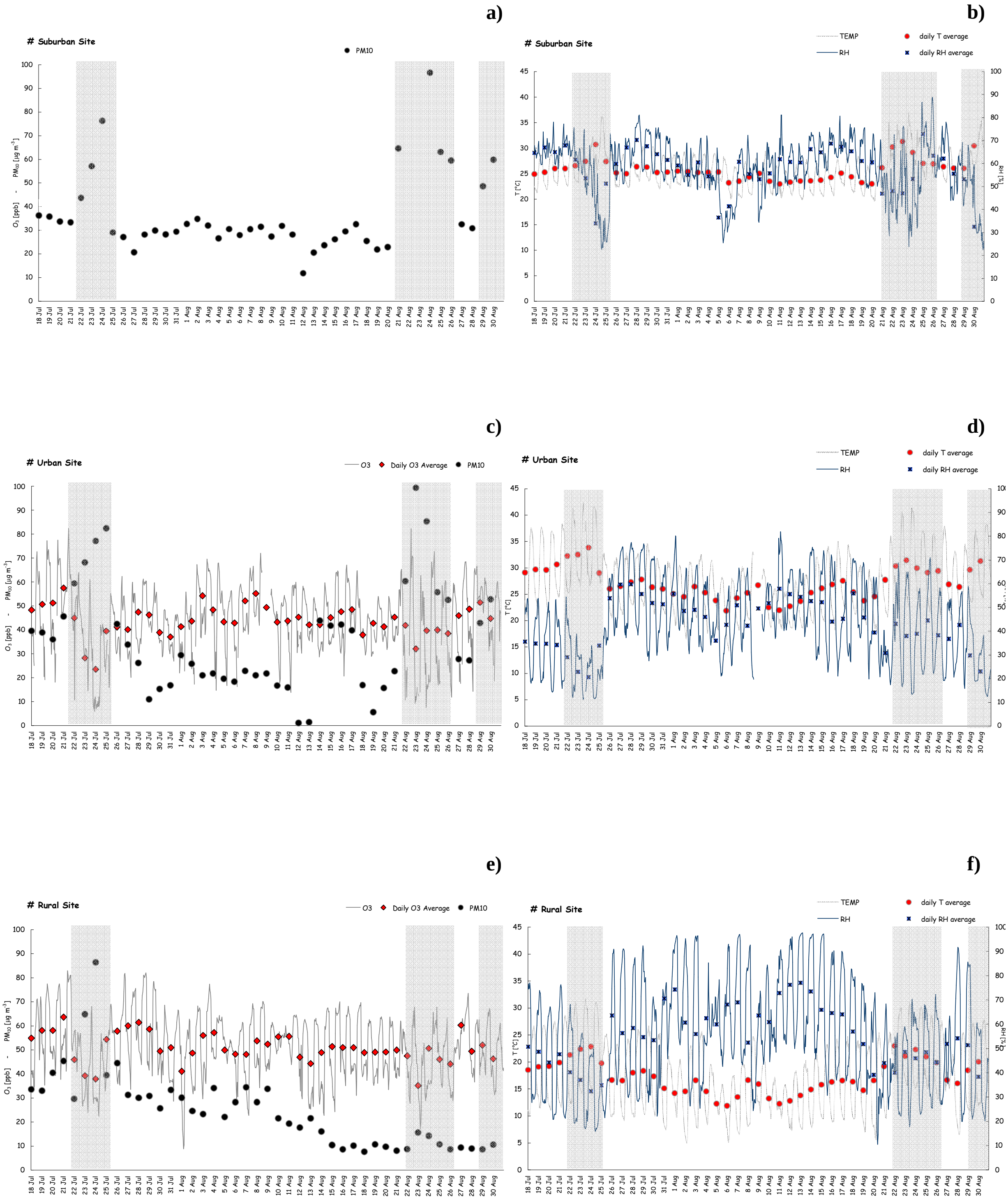
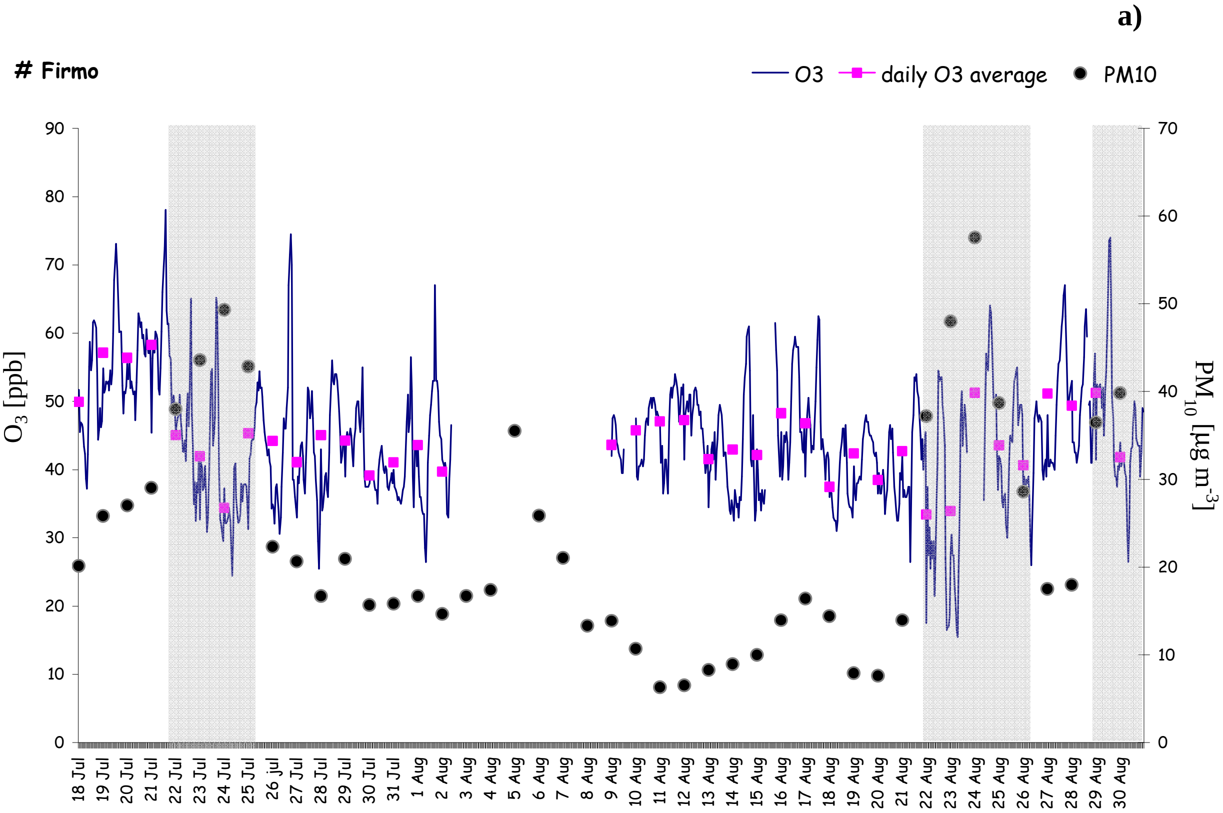


Figure 4.5: *Time series of PM$_{10}$-O$_3$ levels (left panels) and of T-RH values (right panels) for: a)-b) SB; c)-d) UB and e)-f) RB sites, respectively. Grey bars highlight the periods in which the identified SDO occurred.*



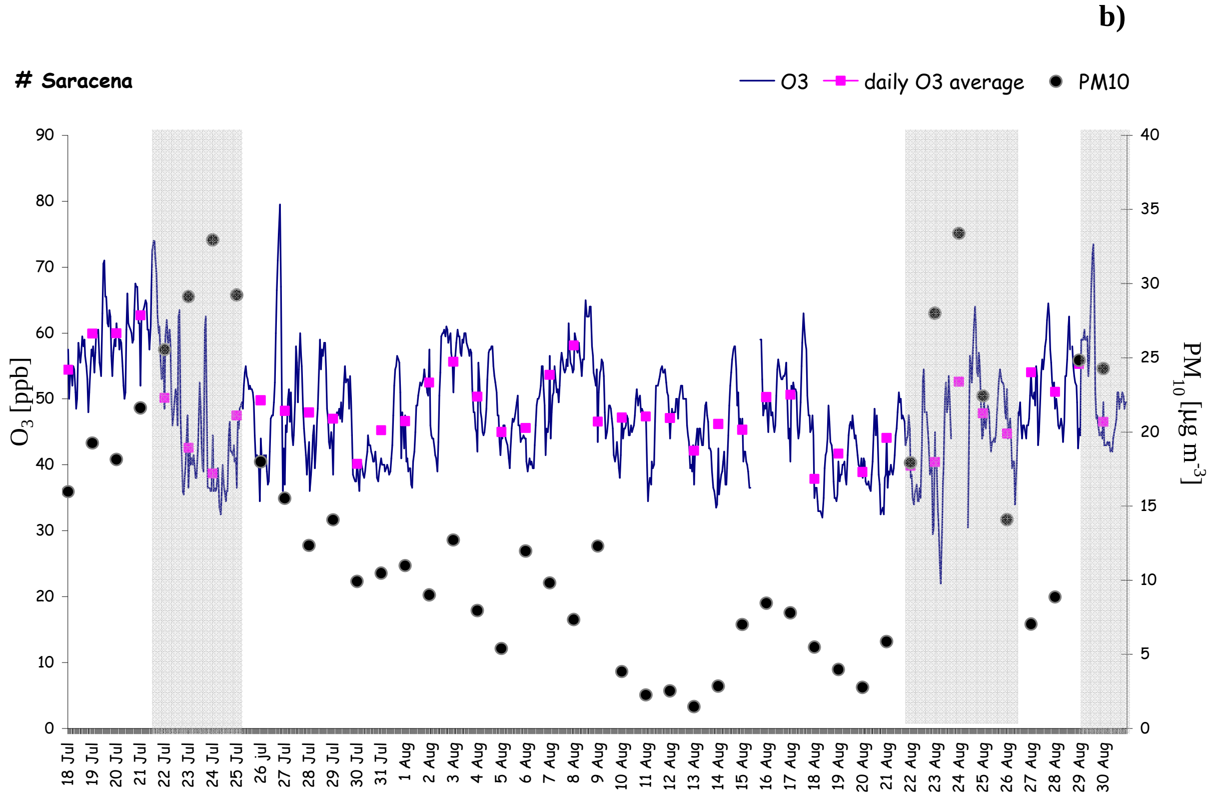


Figure 4.6: *Time series of PM_{10} and O_3 levels recorded at: a) Firmo and b) Saracena rural sites.*

	PM_{10} [µg m^{-3}]						
	During SDO			Without SDO			Δ%
	min	Max	mean	min	Max	mean	
SB	29.0	134.0	69.8	11.8	64.6	29.6	135.5%
UB	42.9	99.3	66.9	1.1	45.6	25.0	167.4%
RB	29.6	86.4	55.1	8.6	86.4	27.0	103.6%
Firmo	28.6	57.6	41.8	6.3	35.5	16.7	151.1%
Saracena	14.1	33.4	25.6	1.5	21.6	9.5	170.1%

	O_3 [ppb]						
	During SDO			Without SDO			Δ%
	min	Max	mean	min	Max	mean	
SB	-	-	-	-	-	-	-
UB	23.0	51.5	36.9	37.0	57.5	44.8	-17.7%
RB	37.9	54.4	44.4	35.1	63.6	51.5	-13.9%
Firmo	33.4	51.3	42.0	37.5	58.3	45.4	-7.5%
Saracena	38.7	55.2	46.0	37.9	62.7	97.8	-5.9%

	T [°C]						
	During SDO			Without SDO			Δ%
	min	Max	mean	min	Max	mean	
SB	26.0	31.3	28.5	23.0	26.4	24.8	14.9%
UB	29.0	33.8	30.8	21.9	30.7	25.9	19.0%
RB	19.8	22.9	21.6	11.9	23.0	16.7	28.9%

	RH [%]						
	During SDO			Without SDO			Δ%
	min	Max	mean	min	Max	mean	
SB	32.5	72.9	51.9	36.5	70.2	60.3	-13.9%
UB	20.7	44.6	32.9	30.9	59.8	47.2	-30.3%
RB	32.4	40.2	36.1	38.4	77.1	57.1	-36.8%

Table 4.3: *Comparison of* PM_{10}, O_3, *T and RH explorative statistic values recorded during days with and without SDO. Percent variation (Δ%) between mean values calculated over days with and without SDO is also reported.*

4.3.3 Biomass Burning events

In the troposphere, among the major sources of atmospheric pollutants and climate altering species, an important role is played by Biomass Burning (BB) events.[56,57] Elevated concentrations of trace gases (i.e., O_3, CO) and aerosol particles have been observed in connection with BB events in various regions of the world.[56,58,59,60,61,62,63,64] The dominant fraction of BB emissions is released as carbon with CO_2 and CO being responsible for about 90–95% of the total carbon emitted.[59] Most of the remaining carbon is composed of CH_4 and other volatile organic carbon compounds while less than 5% of the carbon is emitted as particulate matter.[65] Previous studies have shown that the atmospheric compounds directly emitted by BB or produced by photochemical processes within BB plumes can be transported over long distances, thus affecting both air quality and climate on the regional and global scales.[66] In Europe, the Mediterranean Basin is affected by large wildfire events, especially during summer. As an example, during the extreme dry and hot summer of 2003, the large forest fires in Spain, Portugal, Greece and Italy, significantly influenced trace gas composition and aerosol properties both in the boundary layer and the free troposphere.[67,68] In Italy, from the 1st of January to 2nd of September 2007, as presented in the annual accounts of the State Forestal Body, Calabria region reported the largest wooded area (as well as 9 608 ha) affected by BB with a total number of 1 614 fires. During our sampling period and specifically for Cosenza province a high number of fires was recorded by the MODIS Rapid Response System (http://rapidfire.sci.gsfc.nasa.gov/) which provides for specific locations the daily frequency of biomass burning (see Figure 4.7). The graph reported in Figure 4.7 highlights that the frequency of the daily total fire hot-spots over Cosenza province shows a striking similarity with PM_{10} time series observed at our sampling sites. A roughly apportionment of the number of fire hot-spots affecting singularly each of our station has been further performed taking into account only those falling in an area extending less than 5 km from each sampling location. The outcomes, reported as dots in Figure 4.7, showed that the highest frequency of the daily fire hot-spots occurred in conjunction with PM_{10} peak values recorded at each sampling site. Thus it was likely to suppose that a fraction of the high PM_{10} values showed in this study could originate also from aerosols production related to biomass burning effluents emitted by the identified fires in Cosenza province. Biomass Burning occurrence in Calabria region was furthermore confirmed by the Naval Research Laboratory Aerosol Analysis and Prediction System-NAAPS (http://www.nrlnmry.navy.-mil/aerosol/)[69] which provides for simulations of emission and transport of smoke plumes in the atmosphere. The NAAPS-based maps (not shown) referring to the study period showed a plume characterized by an aerosol optical depth of 0.1–0.2 suggesting large smoke emissions from Calabria region during 23rd – 25th July and 23rd – 30th August. The effective influence of Biomass Burning over measurements performed at SB site was corroborated by CO levels that reached two peak values, both of about 180 ppb, on the 24th of July and 23rd of August. Values of 45 ppb in CO concentrations were instead recorded during days with a lower frequency in fire hot-spots. At UB and RB sites, for which CO measurements, unfortunately, were not available, a throughout investigation in the daily prevalence of local winds was carried out. In this way it was possible to check if the local circulation favoured air masses, prior to ending at UB and SB site, to pass over the identified fire hot-spots with a likely entrainment of Biomass Burning products.

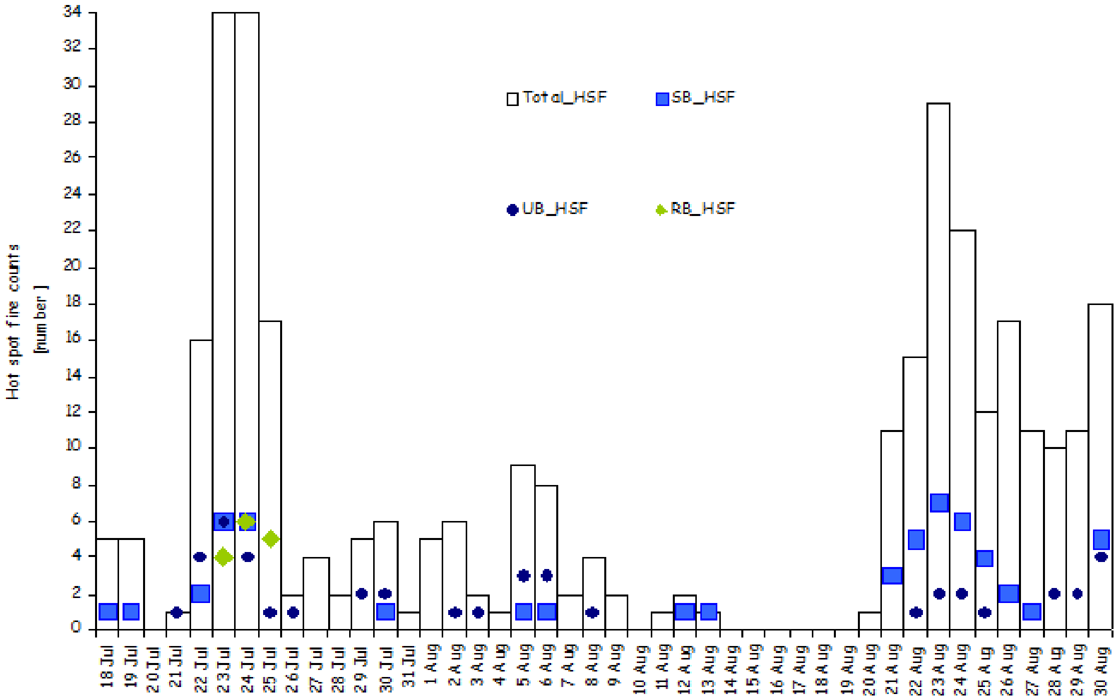


Figure 4.7: *Daily total hot-spots fire (HSF) over Cosenza Province (Calabria Region), from the MODIS Rapid Response System-Web Fire Mapper (http://maps.geog.umd.edu). Dots represent the number of hot-spots fire singularly affecting each sampling site.*

4.3.4 Air mass back-trajectory analysis

In order to evaluate the contribution of different air mass origins and paths on PM_{10} and O_3 levels recorded at the three sampling stations during the study period, back-trajectory analysis was carried out. Sampling days were classified in six different clusters:

1. WMED - Western MEDiterranean basin: air masses originating and/or passing over West Mediterranean;
2. NATL - Nord ATLantic: air masses having 5-day origin over the Nord Altantic at altitudes above 3 000 m a.s.l. and descending lower before reaching the measurement sites;
3. CEU - Continental EUrope: air masses passing over this highly industrialized and densely populated area (Central - Eastern Europe);
4. SDO - Saharan Dust Outbreak: air masses showing to be loaded with Saharan dust over Nord Africa prior to arriving at the sampling sites;
5. BB - Biomass Burning: air masses travelling in the lower troposphere over the areas where, as observed by MODIS, widespread forest and brush fires occurred;
6. SDO&BB - Saharan Dust Outbreaks and Biomass Burning: air masses being affected by both this events.

The occurrence frequencies of the above described air mass classes at our sampling sites were reported in Figure 4.8 (right panels). The weight of air mass influences was quite similar at SB and UB sites with 45% and 48% of each sampling campaign that was respectively affected by natural events. In particular, BB and SDO&BB clusters prevailed over the influence of SDO that accounted only for 5% and 2%. Overall, the NATL class showed the largest weight whereas the CEU the lowest one. Influence of natural events, at RB site, have shown to account poorly with a total occurrence frequency of 9% (2% for SDO and 7% for SDO&BB). The NATL cluster prevailed also at this sampling location, followed by WMED and CEU. Within the obtained clusters, for each sampling station, basic statistics for PM_{10} and O_3 levels as well as for T [°C] and RH [%] values were further calculated. The respective average values were thus reported in Figure 4.8 (left panels) in order to better evaluate for which air mass circulation PM_{10} and O_3 were more enhanced during the sampling period. In general, significant differences were observed for the different air mass classes. Particularly, it can be noted that the polluted industrial and densely populated continental Europe (CEU) represented the major sources of O_3 concentrations during the study period. When air masses arrived from these regions, the mean O_3 level was the highest at both UB and RB sites with mean value of 47.9 and 54.3 ppb, respectively. As reported by EEA,[70] during summer 2007, O_3 target value for human health protection was exceeded in a significant part of Europe with the most significant ozone episode occurring from the 14th to 21st of July. During this period, in EU area, 45% of the total number of exceedances of the information threshold, 39% of exceedances of the alert threshold and 12% of long-term objective exceedances were observed. [70] Thus, the continental Europe can be considered as an important source for tropospheric O_3 during fair weather, when meteorological conditions are favourable for photochemical production and build-up of O_3. From the 18th to 21st of July, a CEU influence was properly detected at our sampling stations. Over the whole sampling campaign, the hourly maximum values of 82.2 ppb at UB and 82.8 ppb at RB were just recorded on 21st of July. Conversely, O_3 concentrations of 43.7 ppb for UB and 46.3 ppb for RB were recorded when air masses arrived from Western Mediterranean basin (WMED), an area characterized by lower anthropogenic contributions. Lower values than those recorded within CEU occurrence, were also recorded over the NATL influence with values of 43.0 ppb at UB and 52.9 ppb at RB site. The higher values recorded at RB site over NATL influence was most likely explained by the air mass pathway. In fact, even though both trajectories had origin over Nord Atlantic, those arriving at RB often crossed through Italian peninsula and Po valley whereas the other one followed a pathway over the Mediterranean sea prior to arrive at SB. As expected, lowest O_3 concentrations were recorded in conjunction with SDO events when the air masses come from North Africa. Due to the relative lack of pollution sources and to the action of mineral dust on tropospheric O_3,[54] North Africa is in fact not considered a source of tropospheric O_3 for Europe.[71,72] It is relevant to note that during the alone BB influence (occurred only at UB), O_3 levels reached an average value (46.4 ppb) quite close to those measured over CEU circulation class. Therefore, as observed at SB site, even if the highest O_3 concentrations were related with polluted air masses travelling over continental Europe, the contribution of biomass fires on tropospheric O_3 concentrations was not negligible. Otherwise, in concurrence of BB with SDO, the role played by BB events on the enhancement of O_3 levels was not evident at both SB and RB sites. This could be most likely explained by the huge presence of mineral dust that could have partially hindered O_3 production. In fact, the average PM_{10} concentrations over SDO&BB influence at UB was about three times higher than that calculated during BB occurrence and 1.3 - 2.1 times higher than those obtained under the alone SDO influence at UB and RB site, respectively. Overall, at each sampling stations, even at SB site, SDO&BB contribution to PM_{10} concentrations broadly prevailed. Analogously to O_3 levels, the lowest PM_{10} values at SB and UB sites were observed when air masses coming from Nord Atlantic (NTAL) and at RB under the WMED influence.

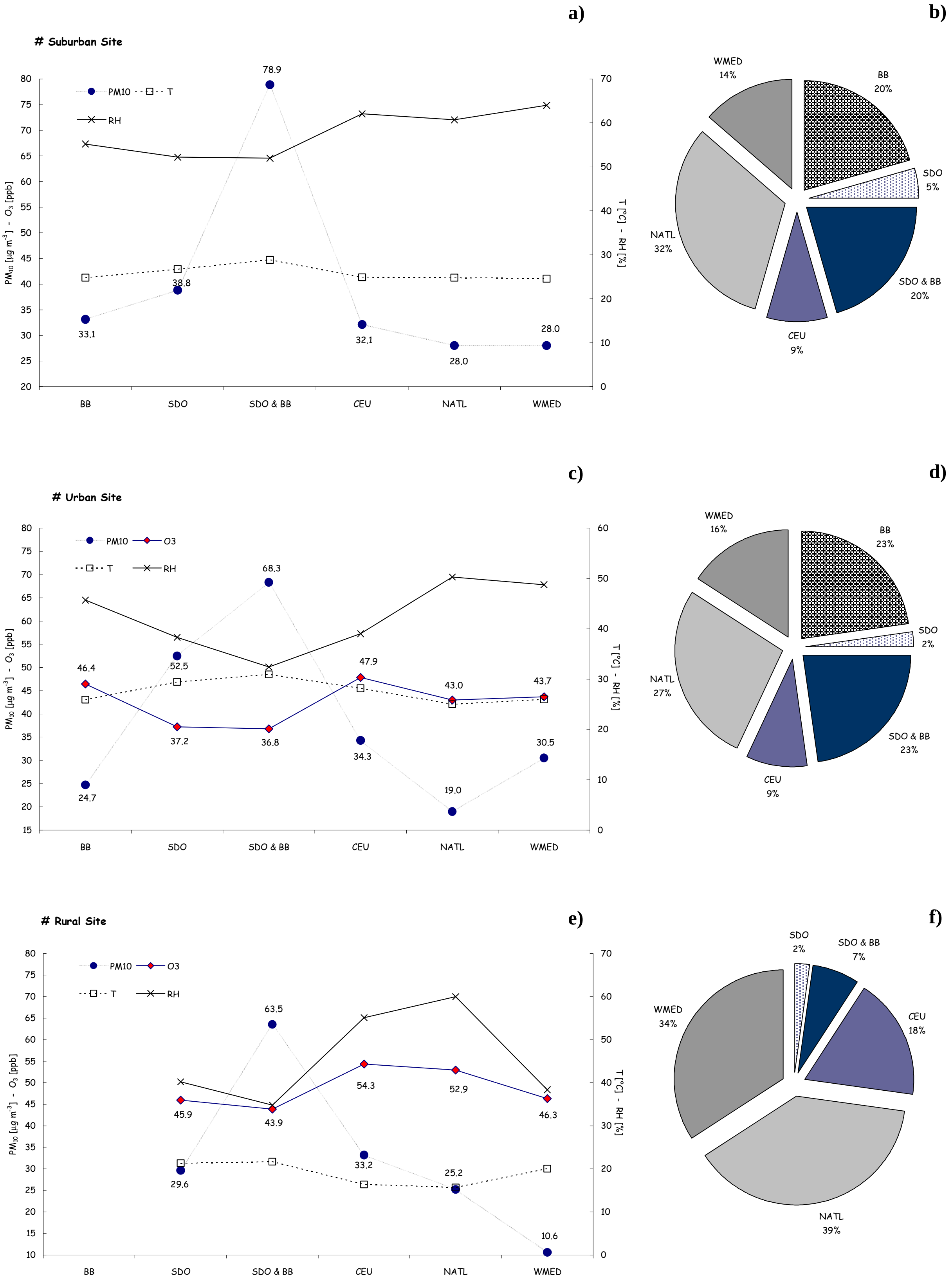


Figure 4.8: *Cluster analysis based on the prevailing air mass trajectories and paths. Average values for PM_{10}, O_3, T and RH over each kind of influence (left panels) and occurrence frequencies of the identified air mass classes (right panels) are reported for: a)-b) SB; c)-d) UB and e)-f) RB sites, respectively.*

4.3.5 PM_{10} Exceedences evaluation

Since contributions from natural sources can be assessed but can not be controlled, the new Directive 2008/50/EC[30] gives the possibility of skipping exceedances due to natural sources with regard to the amount of their contribution. Therefore, where natural contributions to pollutants in ambient air can be determined with sufficient certainty and the exceedances are due prevalently to these natural contributions, these may be subtracted when assessing compliance with air quality limit values. In southern Europe, natural episodes with the greatest impact on the PM_{10} levels are represented by the intrusions of African air masses frequently with high dust loads.[73,74,75,76] In order to determine quantitatively the daily African dust contribution to PM_{10} mass-levels during Saharan Dust Outbreaks at our sampling sites, the methodology presented by (26), based on statistical data treatment of time series of PM_{10} levels, was used. It was thus possible to quantify the African dust contribution without the need for PM speciation. The results are presented in Figure 4.9 (left panels) in which the absolute values of dust contribution were reported as black bars. The net dust contribution was quite large with a weight that accounted for 29.3 - 93.3% at SB, 32.9 - 72.1% at UB and 38.9 - 77.0% at RB within the days affected by Saharan transport. Skipping the obtained net dust load from the measured PM_{10} levels, a notably reduction in the number of daily excedanceees can be observed, getting down from 9 to 3 at SB, from 10 to 2 at UB and from 2 to 1 at RB site. In Figure 4.9 (right panels), for each monitoring site, numbers of exceedances, as absolute and percentage values, were reported with and without Saharan Dust contribution. Since days with exceedance were all classified as SDO and SDO&BB, those remaining without Saharan contribution could be attributed most likely to BB influence, whose contribution to PM_{10} daily limit exceedances seems not to be negligible.

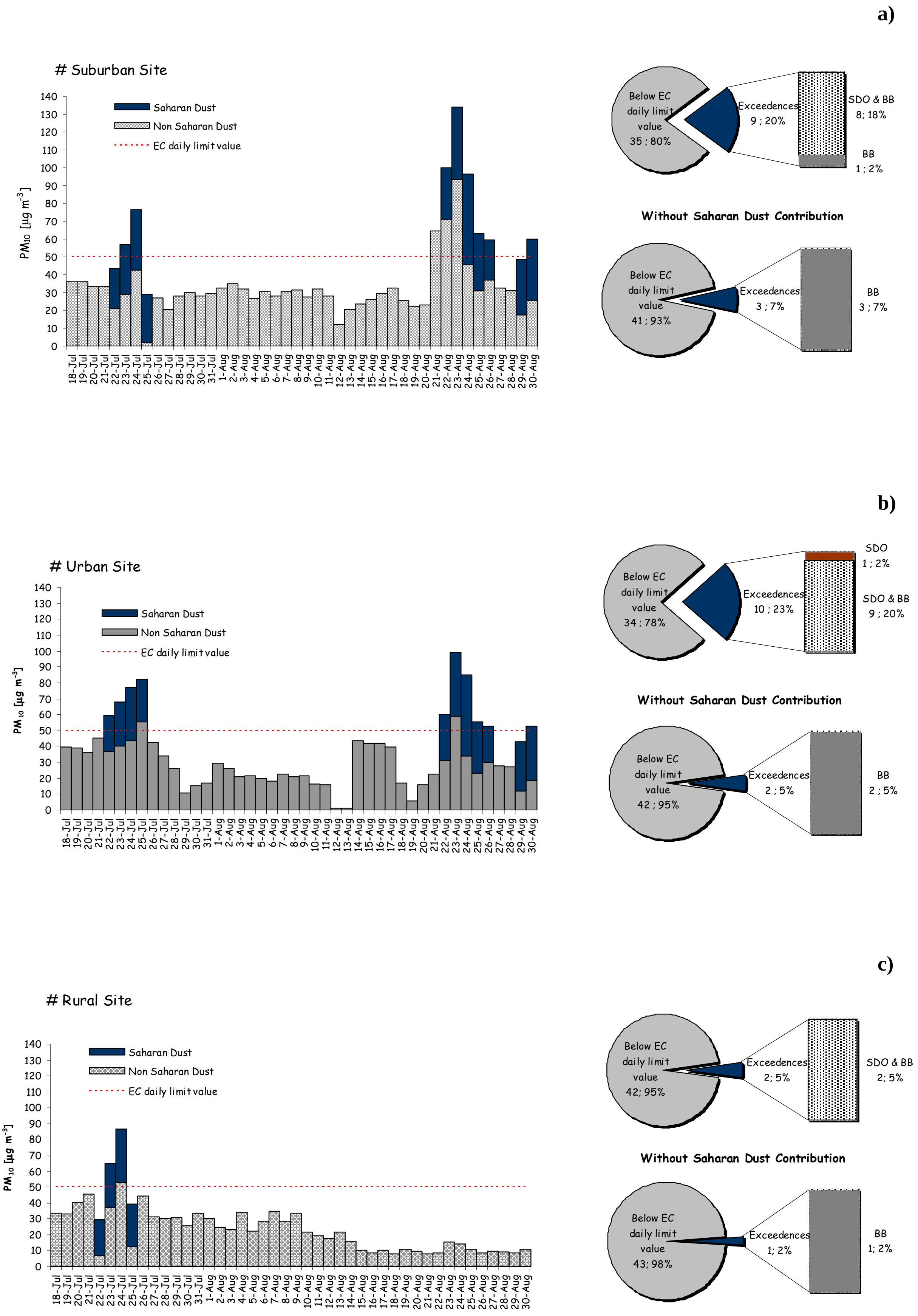


Figure 4.9: *Assessment of the net African dust load. Left panels report time series of PM*$_{10}$ *concentrations along with the the absolute dust load (black bars) calculated for days with SDO influence. Absolute and percent values of number of exceedances are showed on the right panels with and without Saharan dust contribution. Either graphs refer to: a) SB; b) UB and c) RB sites, respectively.*

4.4 Conclusions

During summer 2007, at three background monitoring station located in Calabria region, high levels of trace gases (O_3 and CO) were recorded, as well as significant variations in the aerosol concentrations (PM_{10}). The observations presented in this study showed that such variations were probably related to air masses coming from continental Europe connected with event of mineral dust transport from North Africa and Biomass Burning products. Since Calabria region is located in the southern Mediterranean basin, the observations carried out here can provide useful information for better understand the role played by different transport processes in modifying the tropospheric background conditions. Five-days backward trajectories were useful to determine air mass origin, showing that continental Europe was the major pollution source areas for O_3, whereas the north African desert regions were the most important source areas for PM_{10} and low O_3 concentrations. During dust events, in fact, at SB, UB and RB sites the mean concentration levels for PM_{10} were respectively 69.8, 66.9 and 55.1 $\mu g\ m^{-3}$ with respect to 29.6, 25.0 and 27.0 $\mu g\ m^{-3}$ PM_{10} values averaged over days without Saharan dust intrusions. Preliminary results on the possible impact of dust transport over O_3 values observed in Southern Italian at an urban and rural areas showed that during the greater number of the dust events, significant O_3 decreasing have occurred in Calabria region with a percent values of 18% and 14% at UB and RB sites, respectively. Moreover, even if further analysis will be carried out to better evaluate the specific amount of O_3 concentrations directly due to wildfire emissions, our observations suggested that in presence of favourable weather conditions, the contribution of biomass fires on tropospheric O_3 concentrations cannot be neglected during specific periods of summertime. Since in the future, the strength and frequency of such phenomena as well as Saharan dust and wildfire emissions could be affected by climate change,[77] the investigation of their impact on background O_3 in the southern Europe and Mediterranean area still appears necessary. Recently there is considerable interest in quantifying the background PM_{10} and O_3 concentrations, their variability and trends, also with the purpose of evaluating the effectiveness of measures adopted to reduce anthropogenic photochemical O_3 production and PM_{10} emissions to support policy makers in defining an effective air quality management. Otherwise, when assessing compliance with EU legislation, a statistical based methodology, as that adopted for our PM_{10} data sets, is useful to assess the amount of Saharan dust contribution. In our case study this application showed that more than half of PM_{10} daily exceedances could be confidently attributed to Saharan dust. Since contributions from natural sources can be thus assessed but not be controlled, dealing with air quality management scope, their contribution can be removed. Anyway, their impact as reported in several epidemiological studies, raise concerns about adverse health effects and appropriate interventions by health authorities. Therefore, a thorough knowledge of such events, such as Saharan dust and wildfire emissions, over the southern Mediterranean basin, could be of interest even to their correct parameterization into air quality models that could thus support an adequate health alert system. Results presented in this work could be considered as an exploratory study that needs further improvements. In particular, chemical analysis of aerosol appears as a necessary step to identify unambiguously the presence of mineral dust and biomass burning products at the measurements sites. Overall, in the absence of a single, recognised standard procedure, more studies will be conducted to assess the correct impact of these two natural sources on PM_{10} concentrations and their influence over O_3 levels in the Mediterranean area with a special regard to the southern regions.

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CHAPTER 5

Large Industrial Point Sources: a focus on mercury emissions and concentrations

Human health is intimately connected to the surrounding environment but it is usually very difficult to identify cause-and-effect relationships, however linking environmental pollution to human health helps to redefine priorities. Soil contamination requiring clean up is present in approximately 250,000 sites in the European Environment Agency-EEA member countries, the number is estimated to grow by 50% by 2025. Several thousands of these sites are located in Italy where 54 qualify for national remediation intervention (Ministerial Decrees n. 486, 2001 and n. 308, 2006) because of contamination documented in qualitative and/or quantitative terms and of potential health impact. This section attempts to summarise most recent estimates of mercury emissions and concentrations from contaminated sites to which industrial sites and manufacturing processes can be ascribed.

5.1 Contaminated Sites of National Interest (SIN) in Italy

The remediation of contaminated sites has become in last years one of the most important environmental emergencies in Italy as well as in Europe. In Italty there are currently about 50 sites (over an area of about 100.000 hectares, i.e. 0.3% of the overall surface of the national country) whose remediation is considered to be of national interest based on their environmental relevance. These sites are directly ruled by the Ministry of the Environment under the National Programme for Site Remediation, Law n. 426/1998 and Ministerial Decree 468/2001. A public financial support of about 750 millions of Euro is already available, mainly for preliminary actions such as site characterisation and emergency containment of contamination at these sites. Figure 5.1 shows the location of the 54 contaminated Sites of National Interest (SINs). Among the SINs, the major anthropogenic pressure derives from industrial plants, including chemicals production and steel plants, refineries, landfills and incinerators; other pressure derives from asbestos-related risk plants and mines.

Figure 5.1 Location of the National Interest Rehabilitation Sites in Italy.

Valle D'Aosta
1. Emarese

Piemonte
2. Pieve Vergonte
3. Balangero
4. Basse di Stura
5. Casale Monferrato
6. Serravalle Scrivia

Liguria-Piemonte
7. Cengio e Saliceto

Liguria
8. Cogoleto - Stoppani
9. Pitelli (La Spezia, Lerici, Arcola)

Lombardia
10. Sesto San Giovanni
11. Pioltello - Rodano
12. Milano - Bovisa
13. Cerro al Lambro
14. Broni
15. Brescia Caffaro
16. Mantova- Laghi e Polo Chimico

Trentino-Alto Adige
17. Bolzano
18. Trento nord

Friuli Venezia-Giulia
19. Trieste
20. Laguna di Grado e Marano

Veneto
21. Porto Marghera
22. Mardimago - Ceregnano (Rovigo)

Emilia-Romagna
23. Fidenza
24. Sassuolo - Scandiano

Marche
25. Falconara Marittima
26. Basso bacino del fiume Chienti

Toscana
27. Massa e Carrara
28. Livorno
29. Piombino
30. Grosseto
31. Orbetello - Area Ex Sitoco

Umbria
32. Terni - Papigno

Lazio
33. Fiume Sacco (Prov. di Roma e Frosinone)
34. Frosinone

Abruzzo
35. Fiumi Saline e Alento

Molise
36. Campobasso - Guglionesi II

Campania
37. Litorale Domizio Flegreo ed Agro Aversano
38. Napoli Bagnoli - Coroglio
39. Napoli Orientale
40. Area litorale vesuviano
41. Sarno

Puglia
42. Manfredonia
43. Bari - Fibronit
44. Brindisi
45. Taranto

Basilicata
46. Tito
47. Val Basento

Calabria
48. Cassano - Crotone

Sicilia
49. Milazzo
50. Biancavilla
51. Augusta-Priolo Gargallo
52. Gela

Sardegna
53. Sulcis-Iglesiente-Guspinese
54. Porto Torres

Table 5.1 *List of the National Interest Rehabilitation Sites in Italy.*

Additionally to the 54 contaminated sites of national interest, it has been estimated that there are about 15.000 contaminated sites of regional or local relevance to be remediated or at least monitored, with an estimated cost of about 25-30 billions € in the next 15 years. The state of the art of the national sites in Italy is that a strong diffuse contamination occurs in the homogeneous (from the hydrogeological point of view) Pianura Padana (Padana Plain) in the North of Italy. In this large area are concentrated several national and local sites mainly contaminated by chlorinated solvents and heavy metals. In particular, most of the sites are located in the Lombardia Region and especially in the Province of Milano and Brescia. A special consideration should be made about the largest National contaminated site, Porto Marghera, Venice (which is indicated as number 21 in Figure 5.1), that is strongly contaminated by a large spectrum of chemicals with a prevalence of chlorinated solvents and heavy metals. At the national level it should also be considered a number of coastal sites, mainly in the south of the country, deriving from the presence of refineries and induced petrochemical industries. By this regard, the national sites of Manfrendonia, Brindisi and Taranto in Puglia Region, and Gela and Priolo-Agusta in Sicily have to be considered. All these sites are strongly contaminated by hydrocarbons with a frequent occurrence of separated phases, often combined with chlorinated solvents. The area surrounding Taranto, in particular, is affected by a large industrial facility including one of the largest European steel factories. A particular relevance holds the impact on the environment of large mining activities mainly located in large areas in Sardinia and some spot in Tuscany and Calabria Regions, with a strong contamination of soils and aquifers by heavy metals. Regarding each SIN, available data on pollutants in different environmental matrices were collected: the most investigated components were soil, groundwater and sediments. The first receptor of site contamination in Italy is considered the groundwater beneath the site itself because the contaminants usually migrate downward to the groundwater. The particular Italian geographical situation (dense areas, direct uses of groundwater, connection with deep groundwater and/or surface resources) implies a large use of emergency containment actions. Data on surface water, biota and air were also collected but they are scanty. It is important to highlight the lack of data on foods, especially animal products, fish and vegetables, which are a key element in assessing the potential population exposure through diet. It is also relevant to point out that the environmental characterization of contaminated sites may represent an important tool to understand the health impact of environmental pollution on populations residing in the investigated areas.

5.2 Mercury as a Hazardous Air Pollutant

Mercury (Hg) is a hazardous air pollutant and bioaccumulative neurotoxin. It is a naturally occurring element in the earth’s crust released to the atmosphere through natural and anthropogenic activities. The form of Hg in the atmosphere is predominantly inorganic and non-bioaccumulative (Schroeder and Munthe, 1998); however, once Hg is deposited in the terrestrial or aquatic ecosystem it can be converted to the more toxic organic form, methylmercury, which bioaccumulates in marine and freshwater environments and can ultimately threaten human and environmental health (Schroeder and Munthe, 1998). Elevated levels of Hg have been observed in several wildlife species, including the common loon (Evers et al., 2007) whose exposure to Hg has resulted in reduced reproductive success (Burgess, 2005). A primary concern for humans is the ability for Hg to bioaccumulate within the aquatic food chain, as ingestion of contaminated fish can lead to neurological damage including impaired cognitive thinking, memory loss, and reduced fine motor skills. Those at greatest risk for these effects are the developing fetus, infants, young children, women of childbearing age, and anyone who consumes large amounts of commercial seafood or relies on self-caught fish as a major source of sustenance. All forms of mercury are more or less toxic to humans, because it is widely distributed in the body and many systems are affected. The toxic effects of mercury, reported in Table 5.2, vary according to form: elemental, inorganic or organic; dose: high dose acute poisonings versus low dose chronic effects; timing: prenatal, infancy, childhood or adult. In children, the central nervous system is the most vulnerable. The International Agency for Research on Cancer (IARC) has classified methyl-mercury as being group 2B: the agent (mixture) is possibly carcinogenic to humans. Quantification of atmospheric Hg emission, transport, chemistry, and deposition is therefore vital to understanding the impact of mercury pollution on the society and the environment.

Toxic Effects of Mercury

- Neurotoxicity;
- Nephrotoxicity;
- Teratogenicity: MeHg is a teratogen (Minamata disease);
- CVS: elevated risk of heart attack, hypertension;
- Carcinogenicity: MeHg is a possible human carcinogen;
- Mutagenesis: Hg seems not to be mutagen;
- Reprodution: no clear evidence of effect;
- Immunotoxicity: under scientific discussion.

WHO, 2008

Table 5.2 *Toxic effects of Mercury as reported by the World Health Organisation (WHO, 2008).*

5.3 Mercury in the Atmosphere

5.3.1 Speciation and Chemistry

Mercury exists in three main forms in the atmosphere: gaseous elemental Hg (Hg^0), fine particle bound Hg (Hg^P), and divalent reactive gaseous Hg (RGM). Hg^P and RGM are commonly referred to collectively as $Hg^{(II)}$ or Hg^{2+}. Hg^0 comprises more than 90% of Hg in ambient air (Slemret al., 1985, Lin and Pehkonen, 1999). It has low solubility in water and is relatively stable in the environment, allowing it to be transported long distances in the atmosphere (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999). Deposited Hg can also be re-emitted to the atmosphere as Hg^0 due to its high volatility, further contributing to the global atmospheric Hg pool (Schroeder and Munthe, 1998). RGM, on the other hand, is much more reactive than Hg^0 (Lin and Pehkonen, 1999). Consequently RGM has a much shorter atmospheric lifetime than Hg^0 and deposits readily through wet and dry deposition, not only close to emission sources but also following Hg^0 oxidation in the atmosphere (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999). Hg^p is released directly from emission sources (Keeler et al., 1995) but may also form when gas-phase Hg binds to particles (Pirrone et al., 2000; Forlano et al., 2000). Similar to RGM, Hg^p is also readily removed through wet and dry deposition (Lin and Pehkonen, 1999). As a result of the varying behaviour of these species, Hg can be considered a local, regional, and global pollutant. Distinguishing the relative contributions from of local, regional, and global sources on Hg deposition in a given region is critical to effectively regulating mercury emissions to the atmosphere. Additionally, there are a range of gas phase, aqueous phase, and heterogeneous reactions that Hg can undergo in the atmosphere following emission. Hg^0 can be oxidized to $Hg^{(II)}$ in the gas and aqueous phases by hydroxyl radicals, ozone, and reactive halogen compounds (Munthe, 1992; Lin and Pehkonen, 1997; Hynes et al., 2009). The oxidized $Hg^{(II)}$ can subsequently be removed from the atmosphere through wet and dry deposition (Lin et al., 2006). Hg^0 may also be removed through dry deposition (Schroeder and Munthe, 1998; Lin et al., 2006). Reduction of Hg^{2+} can also occur in the aqueous phase by sulfite, halogen species, and hydroperoxyl radicals (Lin and Pehkonen, 1999; Hynes et al., 2009; Munthe et al., 1991), as well as through photochemical reactions and heterogeneous reactions in cloud droplets (Lin and Pehkonen, 1997; Seigneur et al., 1994). The relative importance of these reactions will vary seasonally and geographically based on the availability of oxidizing and reducing species. Halogen reactions, on the other hand, are typically important in Arctic environments (Lindberg et al., 2002) and the marine boundary layer (Hedgecock and Pirrone, 2001; Lin et al., 2006); however, industrial halogen sources (Carpi, 1997) could also contribute to Hg^0 oxidation. The variable behaviour of emitted Hg species and the inter-conversions that Hg undergoes in the atmosphere following emission add great complexity to understanding the spatial scale of source impacts and makes regulating Hg emissions particularly challenging.

5.3.2 Global Emissions Sources

Mercury is released to the atmosphere from a variety of natural and anthropogenic sources (Pirrone et al., 1996; Pacyna et al., 2001; Pirrone et al., 2003).. Their estimates are highly uncertain, and the relative contribution from natural and anthropogenic sources will vary geographically and temporally. Natural emissions occur through geologic processes, including volcanoes and geothermal activity, as well as through biomass burning, marine emissions, and evasion from terrestrial and aquatic surfaces (Nriagu, 1989; Gustin et al., 2008). Given that Hg can be rapidly recycled back to the atmosphere following deposition (Lindberg et al., 2007), it is estimated that a substantial portion of the emissions from terrestrial or aquatic surfaces represent the re-emission of previously deposited natural or anthropogenic Hg (Schroeder and Munthe, 1998; Gustin et al., 2008; Lindberg et al., 2007). Anthropogenic emissions include point sources such as combustion (utility and industrial boilers, hazardous waste combustors, and crematories) and manufacturing (chlor-alkali, cement, batteries, byproduct coke, and refineries), and area sources such as agricultural burning, landfills, and mobile sources (Pirrone et al., 2010). While emissions from natural sources are predominantly Hg^0, anthropogenic emissions contain varying amounts of Hg^0, RGM, and Hg^p (Carpi, 1997; Landis et al., 2004; Seigneur et al., 2006; Cohen et al., 2007). Variability in the speciation of emissions by source type consequently influences the relative amounts of emitted Hg that can be rapidly removed following emission or instead be transported downwind.

On global scale natural sources, which include the contribution from oceans and other surface waters, rocks, top soils and vegetation, volcanoes and other geothermal activities and biomass burning are estimated to release annually about 5207 Mg of mercury, part of which represent previously deposited anthropogenic and natural mercury from the atmosphere to ecosystem-receptors due to historic releases and part is a new contribution from natural reservoirs. Natural sources contribute to the global budget by 66% with oceans releasing most of the mercury (35%) followed by biomass burning (forest 9% and agriculture 2%), deserts and metalliferous zones (7%), tundra and grassland (6%), forest (4%), evasion after mercury depletion events (3%) and volcanoes (1%) (Pirrone et al., 1996; Pirrone et al., 2001, Pirrone et al., 2008). Current anthropogenic sources, which include a large number of industrial point sources are estimated to release about 2905 Mg of mercury on annual basis (updated from Pirrone et al., 2008). The major contribution is from fossil fuels fired power plants (1443 Mg y^{-1}, 18%), artisanal small scale gold mining (400 Mg y^{-1}, 5%), non-ferrous metals manufacturing (310 Mg y^{-1}, 2%), cement production (226 Mg y^{-1}, 2%) waste disposal (166 Mg y^{-1}, 2%) and caustic soda and chlorine production (163 Mg y^{-1}, 2%). Summing up the contribution from natural and anthropogenic sources nearly 8112 Mg of mercury is released annually to the global atmosphere. Despite important gaps have been filled in the recent assessment (Pirrone et al., 2008) (i.e. mercury emission from coal bed fires and from biomass burning) some concern exists when considering assessment of mercury release from contaminated sites like abandoned mines or heavy polluted industrial sites.

5.4 Mercury Emissions from Large Industrial Point Sources in Italy

Emissions from large industrial point sources are currently regulated by the Directive 2008/1/EC of the European Parliament and of the Council concerning Integrated Pollution Prevention and Control (IPPC). It replaces the Council Directive 96/61/EC on the same subject matter. The European register EPER (European Pollutant Emission Register), established within the Directive 96/61/EC and implemented by the Decision 2000/479/EC, represents the first step at a European level towards a truly integrated pollutant emissions register, an experience which is going to improve further with the forthcoming introduction of the E-PRTR (European Pollutant Release and Transfer Register). Operating since 2003, EPER collects the information provided by 9377 facilities spread over EU15 countries plus Norway and Hungary. Concerning Italy, in accordance with European EPER, a national pollutant emission register has been established, called INES (Inventario Nazionale delle Emissioni e delle loro Sorgenti). INES has been operating since 2003 (first reporting year, 2002) and the last available updating refers to 2006. Mercury and its compounds is included in the Annex III of The Directive 2008/1/EC within the list of the main polluting substances to be taken into account if they are relevant for fixing emission limit values. In air, the emission threshold value for mercury has been fixed by the European Decision 479/2000 to 10 kg yr^{-1}. The INES register has then been browsed and queried on the following web-page: http://www.eper.sinanet.apat.it in order to check the atmospheric mercury emissions from all IPPC activities located in Italy. Results are shown in Figure 5.3 in which atmospheric emissions of mercury are classified according to IPPC code activity (see Table 5.2 for an explanation). In order to accounting for the emissions coming from contaminated sites (as defined by the Law n. 426/1998) the IPPC activities identified to be located over SIN areas have been referred as the code numbering reported in Figure 5.1. Comparing the absolute contribution from each single facilities, it is evident that the highest value of mercury emissions in air, ranging from 1062 to 1385 Kg yr^{-1}, refers to the facility number 45 (ILVA S.p.a). This is one of the largest pig iron and steel facility in Europe that is located in the city of Taranto and whose involved area has been defined as a National Interest Rehabilitation Site. The second one contribution, in terms of absolute mercury emission values, comes from the facility with SIN code equal to 51 (SYNDIAL S.p.A. - ex EniChem S.p.A.). located at Augusta-Priolo city, Sicily.

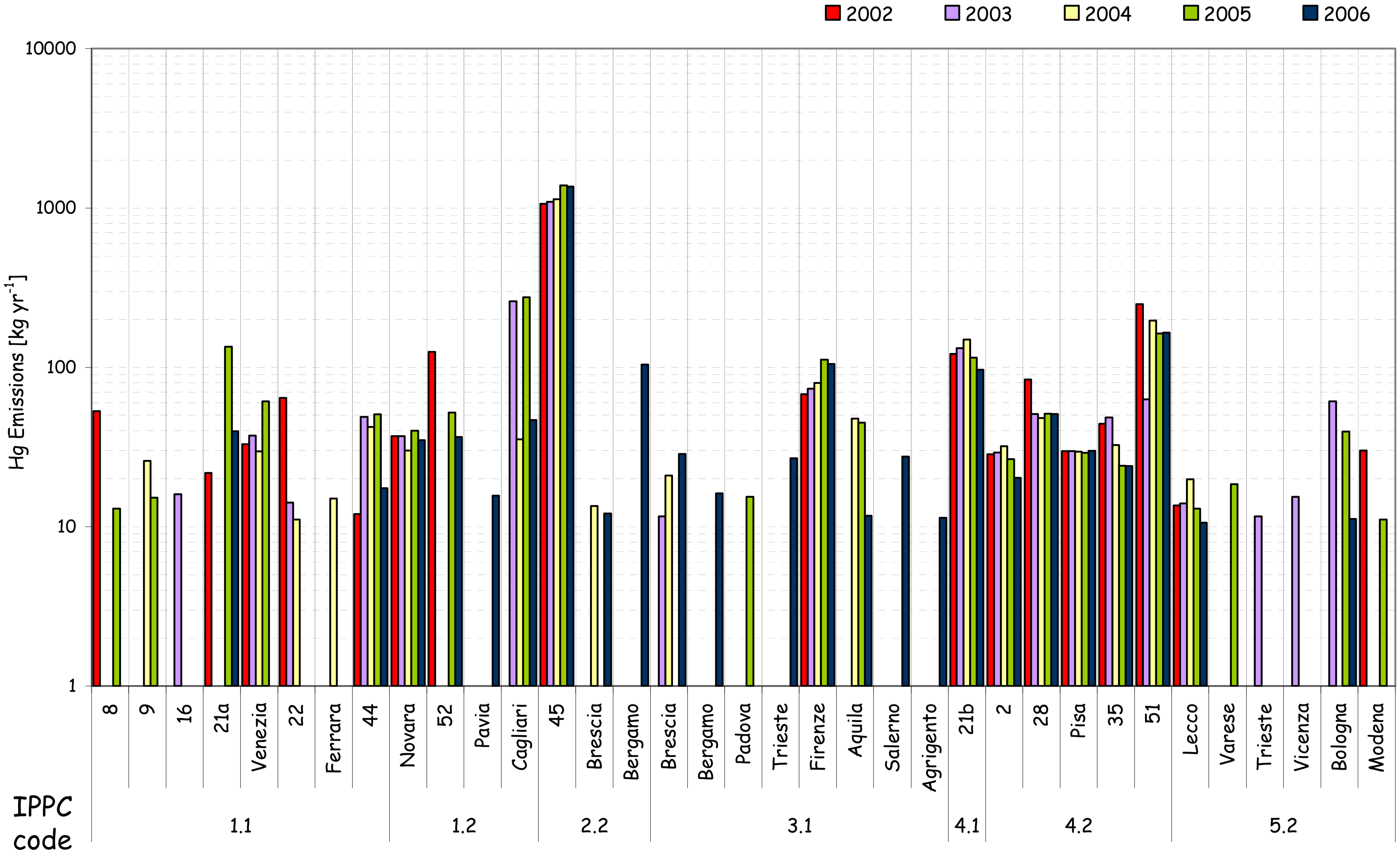


Figure 6.3 *Mercury emissions referring to each single IPPC facilities in Italy, 2002-2006*

1	Energy Industry	1.1	Combustion installations with a rated thermal input exceeding 50 MW
		1.2	Mineral oil and gas refineries
2	Production and processing of metals	2.1	Metal ore (including sulphide ore) roasting or sintering installations
		2.2	Installations for the production of pig iron or steel (primary or secondary fusion) including continuous casting, with a capacity exceeding 2,5 tonnes per hour.
3	Mineral industry	3.1	Installations for the production of cement clinker in rotary kilns with a production capacity exceeding 500 tonnes per day or lime in rotary kilns with a production capacity exceeding 50 tonnes per day or in other furnaces with a production capacity exceeding 50 tonnes per day.
4	Chemical industry	4.1	Chemical installations for the production of basic organic chemicals
		4.2	Chemical installations for the production of basic inorganic chemicals
5	Waste management	5.2	Installations for the incineration of municipal waste (household waste and similar commercial, industrial and institutional wastes) with a capacity exceeding 3 tonnes per hour.

Table 5.3 *IPPC activity definition.*

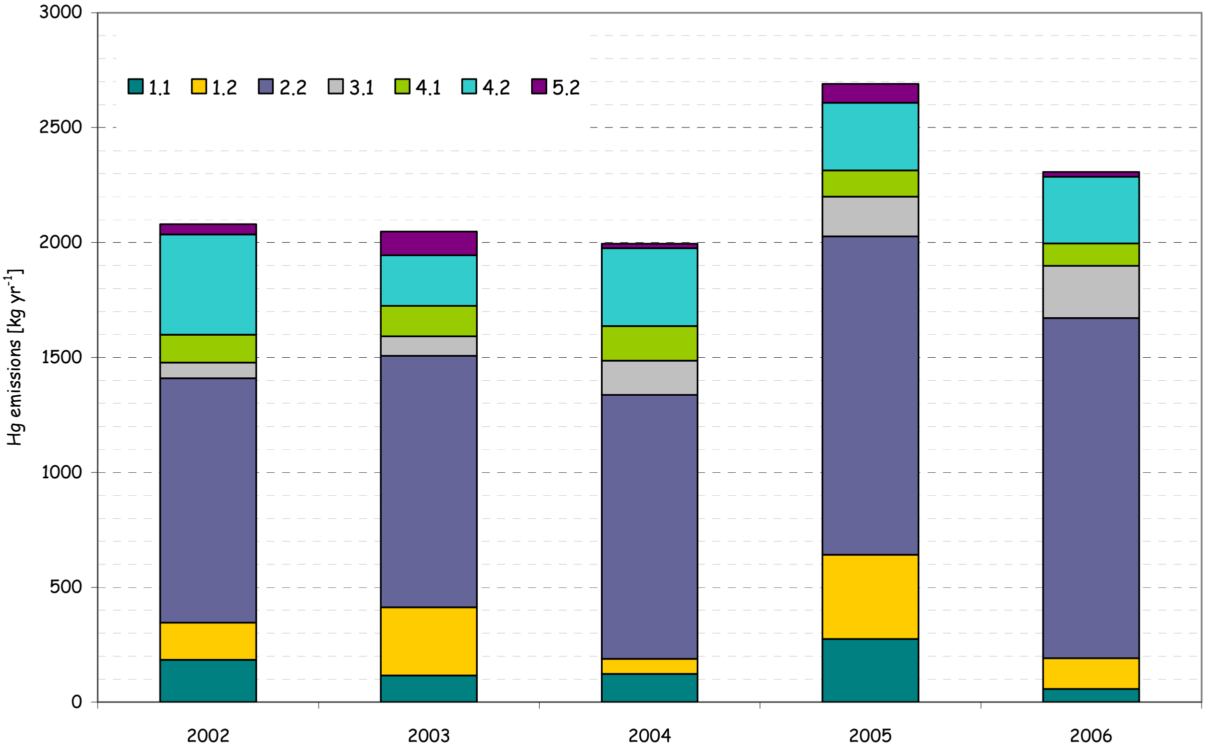


Figure 5.3 *Mercury emissions referring to IPPC activities as a whole, 2002-2006.*

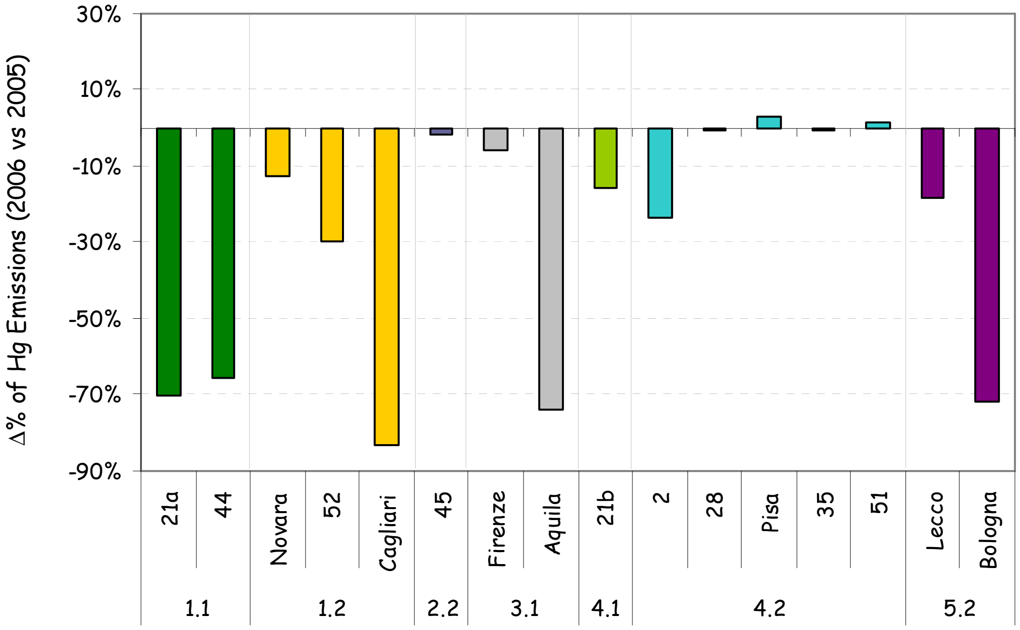


Figure 5.4 *Percentage variation (Δ%) between 2006 and 2005 mercury emissions referring to each single IPPC facilities.*

5.5 Mercury Emission Control: Current Policies and Effect of Existing Technologies

Under section 129 of the Clean Air Act Amendments, the U.S. EPA specifically targeted emission reduction from solid waste combustors, previously one of the largest anthropogenic sources of atmospheric Hg (U.S. EPA, 1997). Restrictions placed on stack emissions from municipal and medical waste incinerators lead to ~95% reductions in total Hg emissions from these sources (Cohen et al., 2007). Declines in emissions occurred due to controls placed on stacks as well as bans on the use of Hg in manufactured products, such as batteries and paint, which reduced the amount of Hg in waste (U.S. EPA). These reductions occurred across the U.S., with some of the largest declines observed in the Northeast States where Hg emissions declined from 15.9 tpy to 4.7 tpy between 1998 and 2002 (Butler et al., 2008). However, emissions from coal-fired utility boilers and other major anthropogenic sources in the United States have remained fairly constant (Cohen et al., 2007; Butler et al., 2008). In 2005 the Clean Air Mercury Rule (CAMR) was proposed, suggesting a cap-and-trade approach to regulating Hg emissions from coal-fired power plants. CAMR was developed based on the framework of the Clean Air Interstate Rule (CAIR), which was also issued in 2005 to regulate emissions of SO_2 and NO_x under similar regulatory techniques. The intention of CAMR was to ultimately reduce Hg emissions by 70%. The rule was overturned in 2008 in favor of using maximum available control technologies (MACT) to reduce Hg emissions, as proposed in the 1990 Clean Air Act Amendments (U.S. EPA). To date EPA has yet to promulgate its final ruling as to how MACT will be implemented.

The installation of the Best Available Technologies (BATs) in industrial plants plays a fundamental role in the emission control as most technologies can reduce mercury emissions up to 95% (USEPA, 1997, 2002a,b; Wang et al., 2010). Removal efficiency depends from adopted technology and production process (Table 5.4). Fossil fuels-fired power plants are the largest point sources of mercury released to the atmosphere, though other emission sources (e.g. artisanal gold mining) provide an important contribution to the global atmospheric budget (Pirrone et al., 2009). World coal consumption in 2006 was 6118 Tg, representing the primary fuel used in electrical power generation facilities (42%) and accounts for about the 27% of world’s energy consumption (EIA, 2009). Although it is very difficult to generalize the mercury concentration in coal, the literature indicates that the mercury content in coal varies between 0.01 and 1.5 g per Mg (Toole-O’Neil et al., 1999; Mukherjee et al., 2008; Pirrone et al., 2009) (Table 5.5). The concentration of mercury is somewhat lower in lignite coals than in bituminous and sub-bituminous coals. However, the lower heating values of lignite coals relative to bituminous and subbituminous coals suggest that the amount of lignite burned perMWof energy produced is higher compared to other coal types (Tewalt and Finkelman, 2001).

Technology	**Coal**	**Cement**	**Waste**	**Soda**	**Battery**
ESP	32	25			
FF	42	50			75
FGD	34 (18-97)	-			
SDA + ESP	67 (23-83)	-			
SDA + FF	30 (6-97)	-			
AC			50-95		
GSC				90	
ME				90	
AAC				90	

ESP=Electrostatic precipitators; FF=Fabric Filter; FGD=Flue Gas Desulfurization; SDA=Spry Drier Absorber; AC=Activated Carbon; GSC=Gas Stream Cooling; ME=Mist Eliminators; AAC=Adsorption on Activated Carbon

Table 5.4 *Median mercury removal efficiency (%) for some technologies and different categories (from (USEPA, 1997, 2002a,b; Wang et al., 2010)).*

Control Technology	Effect on Oxidized Hg	Effect on Elemental Hg	Effect on Particulate Hg
ESP	Little if any	Little if any	Efficient removal
Fabric Filter	Adsorption on fly ash Decrease due to oxidation in some cases	Adsorption on fly ash Decrease due to oxidation in some cases	Efficient removal
Flue Gas Desulfurization	Efficient removal	Little if any removal Increase due to reduction of adsorbed oxidized mercury in some cases	No effect
SCR	Increase due to oxidation	Decrease due to oxidation	Increase in some cases
SNCR	No effect	No effect	No effect

Table 5.5 *Effect of existing control technologies on atmospheric Hg species.*

5.6 Mercury Measurements

5.6.1 Experimental

Measurements of atmospheric mercury species were conducted across both the Tyrrhenian and the Adriatic sea aboard the R. V. Urania of the Italian CNR, during three oceanographic campaigns of which two were performed along the same route during two seasons, autumn (26 October to 15 November) 2004 and summer (15 June to 5 July) 2005 whereas the third one took place during autumn (12 September to 1 October) 2007. The campaigns aimed to assess how mercury species concentrations and distribution in MBL change with vicinity to industrial contaminated sites. The cruise paths of the Med-Oceanor campaigns to date are shown in Figure 5.5. The 2004 and 2005 cruise paths (solid and dotted white lines) were identical in the Adriatic, but the 2005 cruise started from Napoli and finished at Messina. Collection and analysis of Hg^0, $Hg^{II}_{(g)}$ and Hg^P was performed using an automated Tekran (Toronto, Canada) Model 2537A CVAFS, Tekran Model 1130 speciation unit, and Tekran Model 1135 Hg^P system (Landis et al., 2002). The integrated mercury system was mounted on the top deck of the R. V. Urania with the inlet at about 10m above the sea surface. Hg^0 samples (5 min) were continuously quantified by the 2537A analyser. The technique is based on amalgamation on two Au traps within the analyser working alternately, and mercury detection by CVAFS. The integrated Tekran speciation system was configured to collect 2 h $Hg^{II}_{(g)}$ and Hg^P samples on a quartz KCl-coated annular denuder and quartz filter assembly, respectively. Particles larger than 2.5 μm are removed from the air stream by a cyclone before entering the denuder, and smaller particles pass through without deposition on the reactive inner surface under the proper flow rate conditions (10 l min^{-1}). After the 2 h sampling period, a one hour analysis procedure begins by flushing the 1130 and 1135 systems with mercury free air. The Hg^P and $Hg^{II}_{(g)}$ collected on the quartz filter and annular denuder, respectively, were thermally decomposed (at 800 and 500 °C respectively) into the mercury free air stream and detected as Hg^0. During the campaign denuders were re-coated and replaced weekly. The Tekran 2537A analysers were calibrated on a daily basis using the internal permeation tubes. The permeation tube in each of the Tekran 2537A instruments was calibrated just prior to the study as described in Landis et al. (2002) using a Tekran model 2505 primary calibration unit. The detection limit for $Hg^{II}_{(g)}$ and Hg^P under the operating conditions used was less than 2 pgm^{-3}.

5.6.2 Mercury concentrations near contaminated sites

Figure 5.5 *The R. V. Urania cruise paths during the 2004, 2005 and 2007 Mediterranean oceanographic campaigns.*

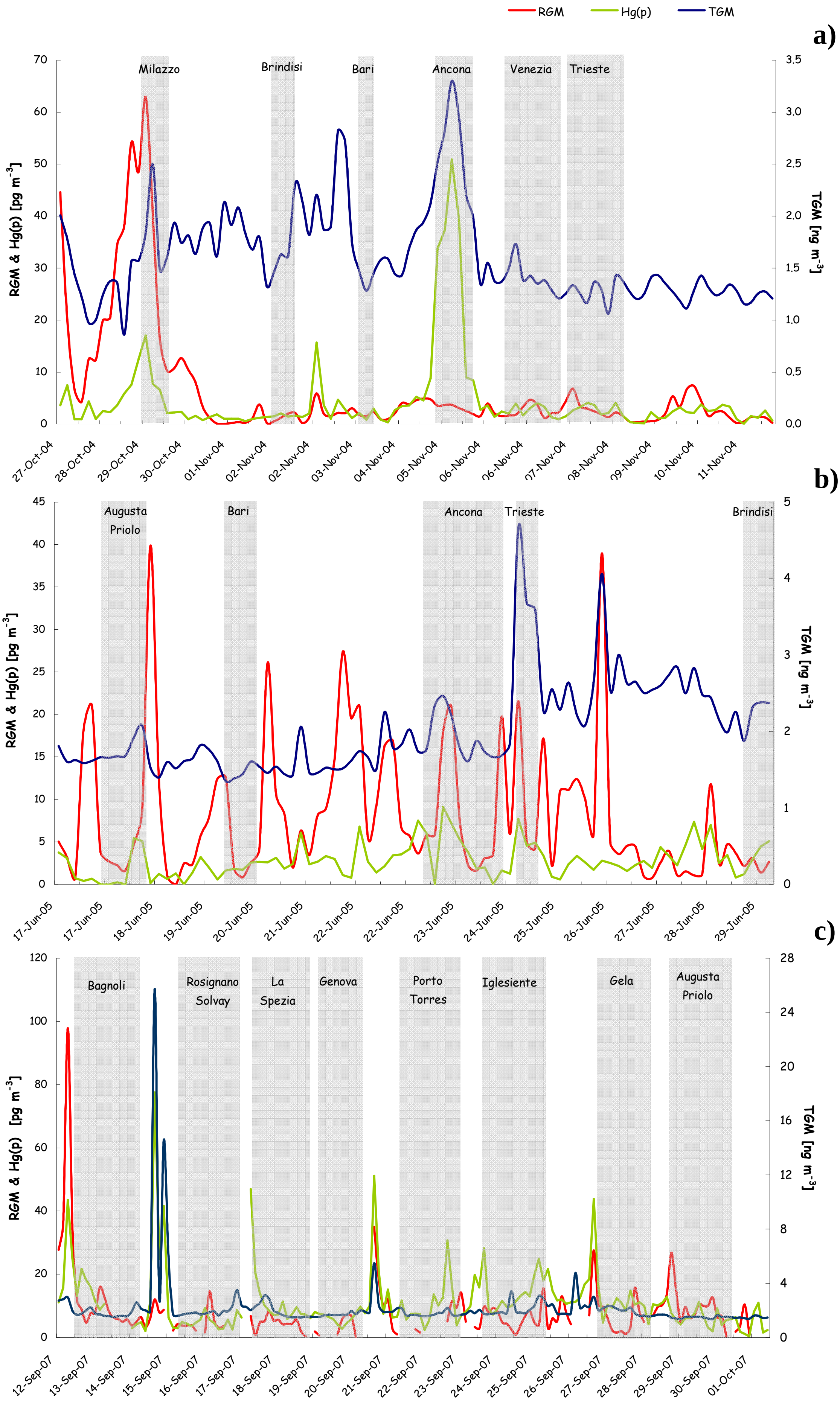
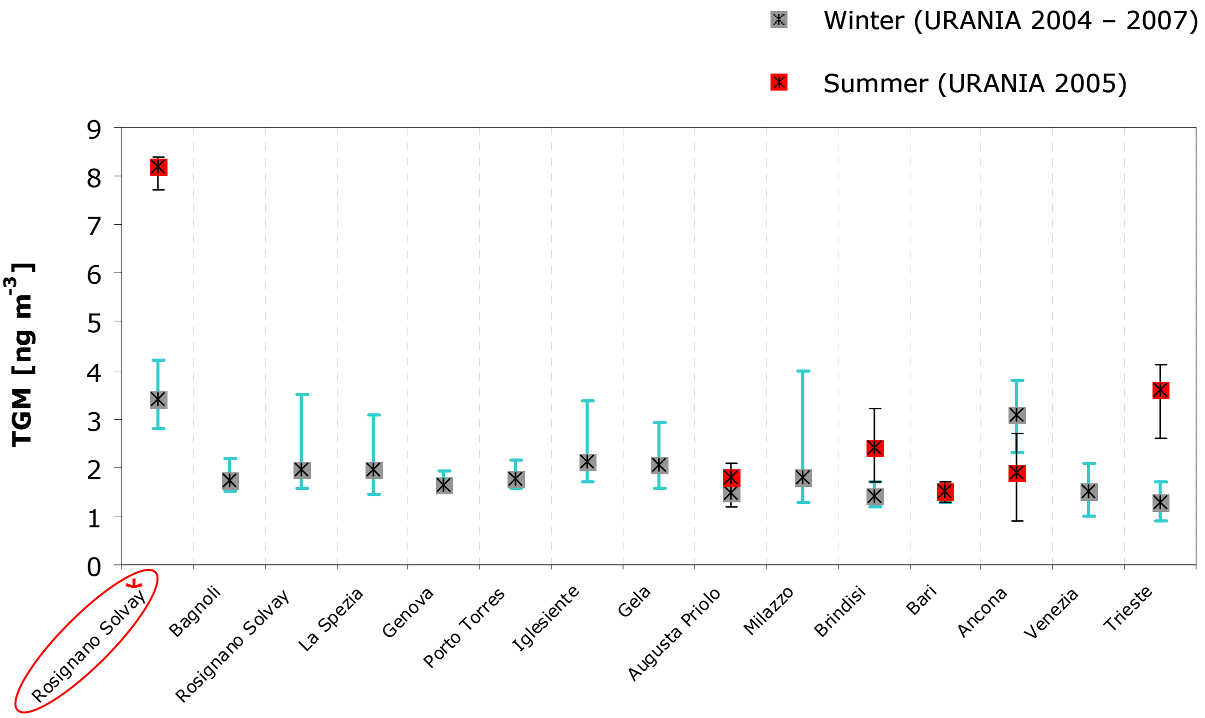


***Figure 5.6** TGM, RGM and Hg(p) measurements recorded during: a) 2004; b) 2005 and c) 2007 URANIA Cruise Campaign.*

5.6.3 Comparison of Results to Previous Studies



** D. Gibičar et al., 2009*

Figure 5.7 *TGM comparison between values published in D. Gibičar et al., 2009 and those presented in this work. Data refer to winter and summer sampling periods.*

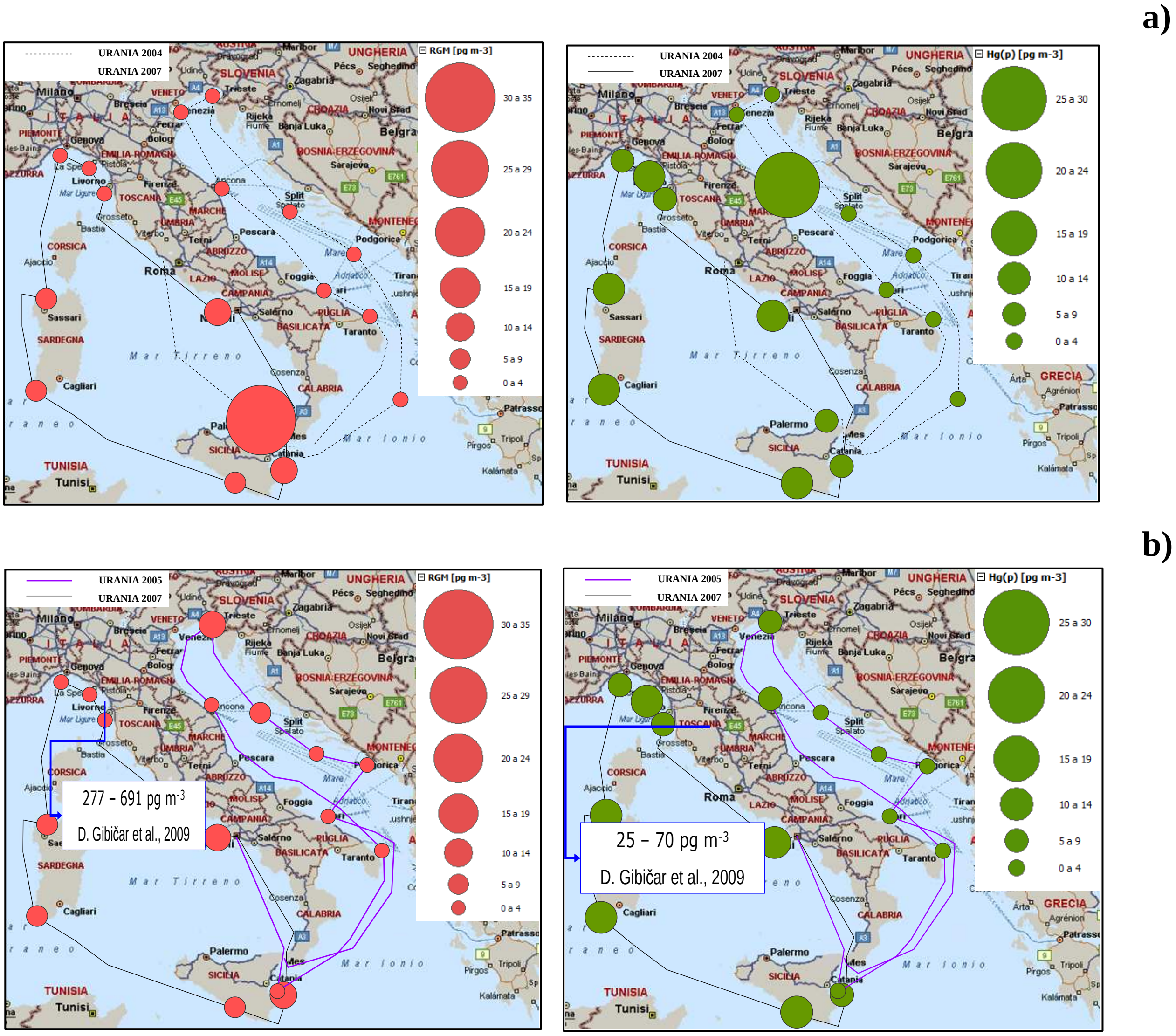


Figure 5.8 Spatial distribution of RGM (left panels) and Hg(p) (right panels) concentrations observed during: a) 2004-2007 and b)2005-2007 cruise campaigns performed onboard the CNR Research Vessel URANIA along the reported tracks.

5.7 Conclusions

Additional research is required to reduce uncertainty in emissions estimates from contaminated sites. The uncertainty is mostly related to the limited measurement of fluxes from ancient mercury mines (e.g. only in Italy there are more than 15 ancient mines), from heavy polluted industrial sites (e.g. chlor-alkali and cement plants) and from coal-bed fires. A coordinated geo-referenced database will certainly improve the estimates. These uncertainties affect emission estimates, model and policy development, and human welfare. Atmospheric mercury models developed in recent years for assessing the relationship between emission source regions and receptor regions show a limited accuracy. The ability to determine the accuracy of current models is severely limited by the lack of a unified global emission inventory that accounts for a better emission source characterisation. Delineation of mercury "hot spots" and knowledge of ecological processes that lead to their formation can reduce uncertainty and can help mitigation and outreach efforts of reducing health costs. This improved knowledge of the sources, transport and fate of environmental mercury would lead to realistic risk assessments, efficient mitigation efforts, and effective outreach to minimize adverse impacts on coastal ecosystems and human populations.

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CHAPTER 6

Air pollution over the Mediterranean Basin: observations through six cruise campaigns on board the CNR Research Vessel URANIA

The Mediterranean basin, due to its semi-enclosed configuration, is one of the areas heavily affected by air pollutants. Despite implications on both human health and radiative budget involve an increasing interest, monitoring database measuring air pollution over these area are yet relatively scarce. Owing to this context, concentrations of fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particles along with ozone and meteorological parameters were measured during six oceanographic cruise campaigns covering the whole Mediterranean Basin. Elemental composition of both $PM_{2.5}$ and $PM_{2.5\text{-}10}$ were also determined in order to identify specific tracers for different classes of particles that can be found in the Mediterranean atmosphere. A comparison analysis between the data sets recorded during either cruise campaigns was further performed in order to point out the correlation structure among the pollutants and their relationship with meteorological parameters. According to aerosol optical properties and chemical composition, European continental influence, Saharan dust storms, wildfire events and Maritime transport have been identified during either cruise campaigns as the leading cause of the aerosol-ozone variation. Shipping emissions, representing both local harbours and maritime traffic across the basin, were also tested using the marker ratio of V/Ni, showing a quite large contribution to the total aerosol load. Peak values observed for coarse fraction have shown to be driven by the occurrence of African dust events. Conditions favouring high ozone levels have been also highlighted by analysis of weather maps and back trajectories. Spatial variability resulted in larger fine particle concentrations and higher ozone levels over the eastern Mediterranean compared respect to the western sector, mainly due to the background contribution of anthropogenic compounds.

6.1 Introduction

Air pollutants in the marine environment comprise a complex and variable mixture of natural and anthropogenic sources. In addition, data from monitoring stations as well as results of measurement campaigns show that aerosol and ozone concentrations in the Mediterranean Basin appear to be relatively high (Querol, et al.; Lelieveld et al., (2002)). Available nowadays PM and O_3 measurements suggest that the whole Mediterranean region is characterised not only by “hot-spot” episodes in urban areas, but also by high background concentrations. Results from a 3-D chemistry transport model also suggest that ozone concentrations over the Mediterranean Sea are higher than those observed for the rest of Europe (e.g. Johnson et al., 2001). One of major questions in the scientific community is to what extend the background PM and O_3 concentrations are related to sources within the Mediterranean basin and how much it results from long range transport emitted outside the basin. The ozone behaviour and distribution in the Mediterranean region is closely related to the unique geographical characteristics and specific weather conditions. During the summer period, the Mediterranean area is directly under the descending branch of the Hadley circulation, caused by deep convection in the tropics (Lelieveld, 2009). The region incorporates the world’s largest inland sea, which is surrounded by relatively high mountain ridges on almost every side; its climate is in general warm and dry (Bolle, 2003). The Mediterranean summers, connected with high pressure situations leading to subsidence, stability, clear sky and high solar radiation intensity enhance photochemical processes and emissions of biogenic volatile organic compounds to the atmosphere (Millan et al., 2002). However, based on observational and modelling data, also long range transport of European air toward the Mediterranean Basin has been claimed to be a main cause of elevated aerosol and ozone concentrations in the Mediterranean area (Lelieveld et al., 2002). Otherwise the atmosphere in the Mediterranean Marine Boundary Layer (MBL) appears to be one of the most polluted in the world (Kouvarakis et al., 2000) with a significant contribution of dense ship traffic and highly industrialized population centres surrounding the basin itself (Marmer and Lang-mann, 2005). A large influence is also due to natural sources like Saharan dust and biomass burning (Pace et al., 2005; Sprovieri and Pirrone, 2008; Pirrone et al., 2010). The transport of mineral dust and anthropogenic aerosols from land into the marine environment is of considerable interest, not at least for its potential impact on ocean ecosystems, world climate and air quality. Fertilisation of ocean waters by dust increasing Fe/N and P/N ratios, for example, is known to favour phytoplankton growth and thus influence marine cycles. Furthermore, physical effects of major outbreaks of desert aerosols into the oceanic environment include changes to outgoing long-wave radiation and visibility reduction in many low latitude regions of the world (Haywood et al., 2005). In addition to these different impacts, anthropogenic emission in busy shipping lanes and large port cities are important sources of pollution plumes containing a wide range of particulate and gaseous pollutants (Healy et al., 2009). Ship emissions and their impacts on environment became a “hot” issue in the past decade for atmospheric research and air pollution and climate policy. In 2008, the International Maritime Organization (IMO) unanimously adopted amendments to the MARPOL Annex VI regulations to reduce SO_x, NO_x and particulate emissions from ships (IMO, 2008). The revised Annex VI entered into force in July 2010 and the emission reduction measures will be phased in over the following decade. In support of the policy, research studies are required to investigate how the implementation of these regulation, combined with the predicted future growth of ship traffic and geographical expansion of waterways and ports are going to affect the atmospheric composition. However, whereas there is already a large monitoring database measuring air pollution at surface land-based sites and in ports, there is a relatively little information on atmospheric aerosol directly measured on the sea. PM_{10} mass concentrations have been monitored by national and international air pollution monitoring networks for two decades (see e.g. EMEP and AirBase data bancks), whereas $PM_{2.5}$ measurements are still being started up at many sites, because the new European Directive 2008/50/EC establishes target values for $PM_{2.5}$ concentration and exposure to be met by 2010. In a recent work physical and chemical aerosol characteristics observed over a network of more than 60 sites across Europe were presented and discussed (Putaud et al., 2010). However, only a few of these stations are located close to the sea and they do not cover the whole area. To fill the observation gaps in the Mediterranean basin and to gain more insight into the atmospheric mechanisms leading to high surface aerosols levels, the Institute of Atmospheric Pollution Research of the National Research Council (CNR-IIA) has started regular cruise measurement campaigns in the Mediterranean Sea since 2000 (Sprovieri et al. 2003; Hedgecock et al., 2003; Sprovieri et al., 2008; 2010). In this work a focus on the aerosols and ozone observations in both Western and Eastern Mediterranean basin has been performed. The main purpose of this work, in particular, is to present the datasets collected during six cruise campaigns from 2003 to 2009 on board the CNR Research Vessel URANIA and to characterize the specific sources and conditions leading to high aerosols and ozone levels. Variation in two size range of inhalable particulate matter

($PM_{2.5-10}$, $PM_{2.5}$) over the eastern and western sector of the Mediterranean basin has also been investigated linking their spatial variability to source-receptor relationship.

6.2 Experimental Section

Ozone and aerosol levels measurements were performed during six cruise campaigns onboard the Research Vessel (*RV*) URANIA of the CNR from 6th to 27th August 2003, from 27th October to 12th November 2004, from 17th to 29 June 2005, from 5th to 20 July 2006, from 13th September to 2nd October 2007 and from 4th to 30th June 2009. Specific tracks are reported in Figure 5.1. Measurement equipments were fixed on front of the ship to avoid contamination from the ship exhaust itself. O_3 measurements were performed by an automatic Teledyne UV absorption ozone analyser (Model 400E). The ozone analysers were calibrated every 24 h by routine automated additions of known concentrations of gaseous ozone supplied by an internal permeation source. A sampling flow rate of 0.8 L min^{-1} was used to measure the ozone concentration every 5 min. Daily 24-h ambient $PM_{2.5-10}$ and $PM_{2.5}$ samples were otherwise collected using a Manual Andersen Dichotomous Sampler (Model 241) on 37ømm Teflon filters, over a 24-hour sampling period at a flow rate of 1.67 L min^{-1} and about 15 L min^{-1} respectively, for a total operational flow rate of 16.7 L min^{-1}. The filters were conditioned and pre-weighed using a 1µg sensitivity microbalance (Gibertini Microcristal Model) in the laboratories of the CNR Institute of Atmospheric Pollution Research before and after the sampling period to assess $PM_{2.5-10}$ and $PM_{2.5}$ concentrations by standard gravimetric procedures. A total of 110 fine and coarse particulate samples were then collected across the Mediterranean basin the performed tracks. Once the gravimetric determination was completed the filters were digested with 5 mL of a 10% HNO_3 solution and subsequently analyzed for their elemental composition using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent Technologies, model 7500 CE). Concentrations of Al, As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl, V were determined in all samples. Meteorological data were also provided from an automatic meteorological station on the *RV*, therefore, among others, information concerning the position, speed and direction of the *RV* were available also for identifying situations of contamination due to the emissions from the ship itself. In order to characterize the daily atmospheric scenarios influencing the particulate and ozone levels, a number of complementary tools were used to investigate different source regions of air masses reaching the study area. These included NCEP meteorological maps (Kalnay et al., 1996) and daily back-trajectories calculated by HYSPLIT4 model (Draxler and Rolph, 2003; see detailed methodology in Escudero et al., 2005). The occurrence of African dust outbreaks was also detected using the same tools coupled to information obtained from the NAAPS aerosol maps from the Marine Meteorology Division of the Naval research Laboratory, USA (NRL) (http://www.nrlmry.navy.mil/aerosol). The sulphate concentration maps provided by NAAPs model (http://www.nrlmry.navy.mil/aerosol/) were instead used to identify events of transboundary transport of pollutants from the European continent. Otherwise, for fire events identification the MODIS true-colour images (http://rapidfire.sci.gsfc.nasa.gov/) and the NAAPs based smoke concentration maps were in addition used to identify the origins and the extension of fire plumes.

6.3 Results and discussions

6.3.1 Overview of the data recorded

The variation of PM_{10} concentrations as sum of fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particle concentrations recorded during the six cruise campaigns at both off-shore and coastal sites are displayed in Figure 5.1. PM_{10} concentrations ranged very wide from 8.7 to 56.6 µg m^{-3} with a mean value of 27.8 µg m^{-3} across the whole Mediterranean basin. Away from major port cities, as the Figure 5.1 shows, the higher PM_{10} mass levels were recorded at the extremity of the basin where dust intrusions from Nord Africa (NAF) and smoke plumes from biomass burning in sub-Saharan Africa and Greek have been identified as the main sources of contribution. $PM_{2.5}/PM_{10}$ ratio and daily O_3 mean referring to each cruise campaigns have been overlaid to the time series of fine and coarse particle levels and reported in Figure 5.2 a) and b), respectively. As this graph shows, ratio between $PM_{2.5}$ and PM_{10} mass concentrations ranged between 0.2 and 0.9 and daily O_3 levels from 21 to 74 ppm. A closer examination reveals that during the 2004 cruise campaign, $PM_{2.5}/PM_{10}$ ratios raise the peak values and slightly increase with PM_{10} levels at many sites indicating that pollution periods are predominantly due to increase in $PM_{2.5}$ mass concentration at these locations. The highest fine concentrations was observed along this same 2004 track and particularly during the passage through the Messina Straits. A strong anti-correlation, during this time period, between fine particles and ozone levels was found, as expected, because the high fine levels in this area are likely caused by maritime transport source that also emit NO that destroy ozone by a fast “titration” reaction (Velchev et al., 2010). Overall, $PM_{2.5}/PM_{10}$ ratios slightly to sharply decrease with increasing PM_{10} levels. Significant contributions to higher PM_{10} concentrations of coarse mineral dust suspended from the ground or transported from African deserts could explain this observation. The highest coarse concentrations have been observed when the “regional anticyclone” is embedded in a synoptic scale high pressure system extending south-northward towards the Mediterranean thus favouring Saharan dust intrusion.

Significant correlation for $PM_{2.5}$ and PM_{10} mass concentrations was otherwise observed (R^2= 0.8, n=105) indicating that $PM_{2.5}$ and PM_{10} main source strengths co-vary and/or that both concentrations are driven by a common phenomenon: pollution dispersion due to meteorological condition. Descriptive statistics (mean, Maximum and minimum) for meteorological parameters referring to each cruise campaigns are summarized and compared in Figure 5.3. As it can see, wind speed, relative humidity and air pressure showed a large range of values within each single cruise campaign but the relative mean values were substantially comparable each others. Wind speed mean values ranged from 6 ms^{-1} (referring to 2003 cruise campaign) to about 8 ms^{-1} (2006 cruise campaign). Both air pressure and relative humidity mean value changed poorly varying from 1009 to 1013 hPa and from 75 to 78%, respectively. Only in comparing temperature and atmospheric radiation (not shown) mean values significant differences were observed The lowest temperature mean value (~18°C) was recorded during the 2004 track since this cruise campaign was performed during autumn (27th October - 12th November). The highest temperature mean value (~30°C) was otherwise observed along the 2005 track performed in summer period (17th – 29 June) followed by those recorded during 2003 (6th – 27th August), 2006 (5th – 20th July) and 2009 (4th – 30th June) cruise campaigns. As expected and as evident in comparing Figure 5.3a) and b) a strong correlation was found between ozone mean levels and both temperature and atmospheric radiation mean values. Any relevant influences of local meteorological parameters over fine and coarse particle levels were observed. As it will described in the next section, sources strength and synoptic atmospheric conditions were the main drivers of fine and coarse variation across the Mediterranean basin rather than local whether.

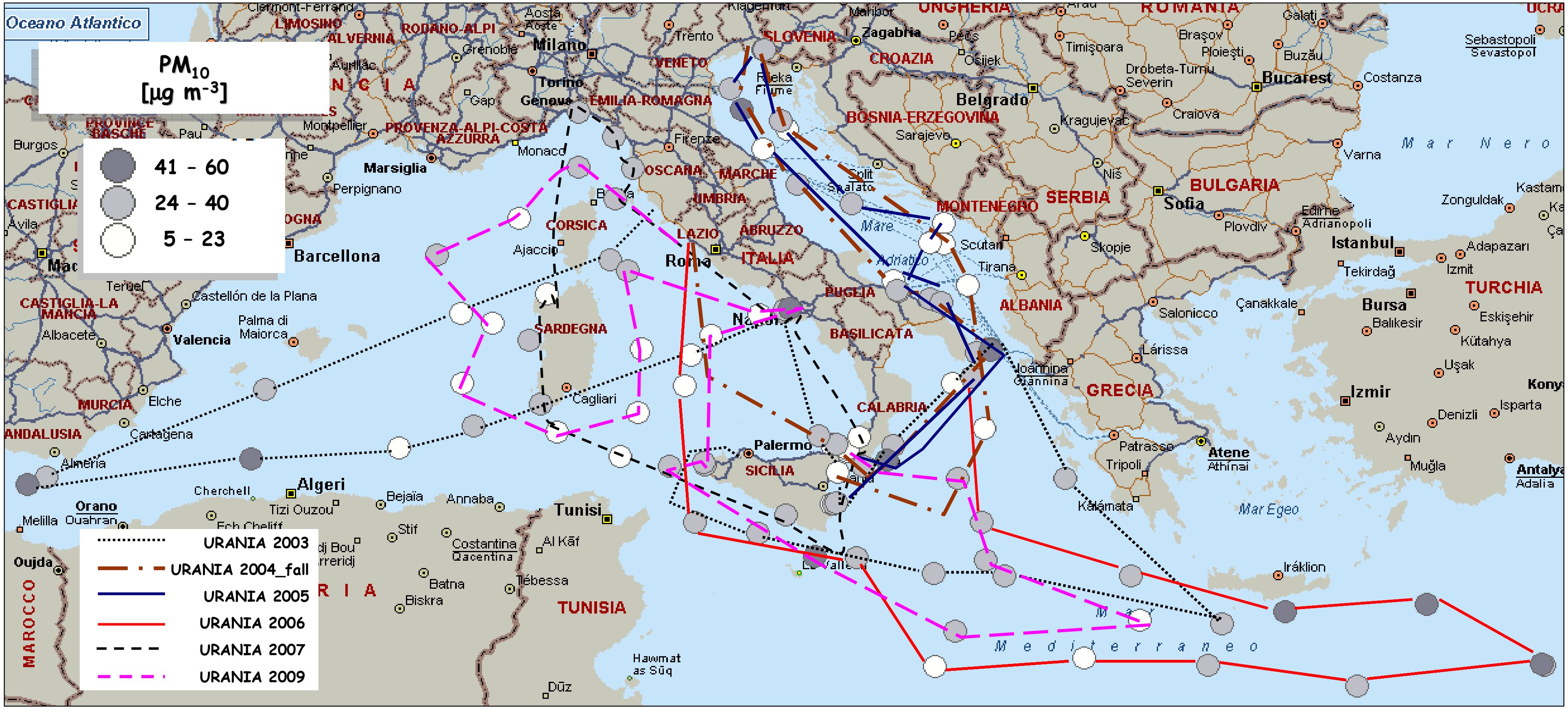

Figure 5.1 Spatial distribution of PM_{10} concentrations observed during six cruise campaigns performed onboard the CNR Research Vessel URANIA along the reported tracks.

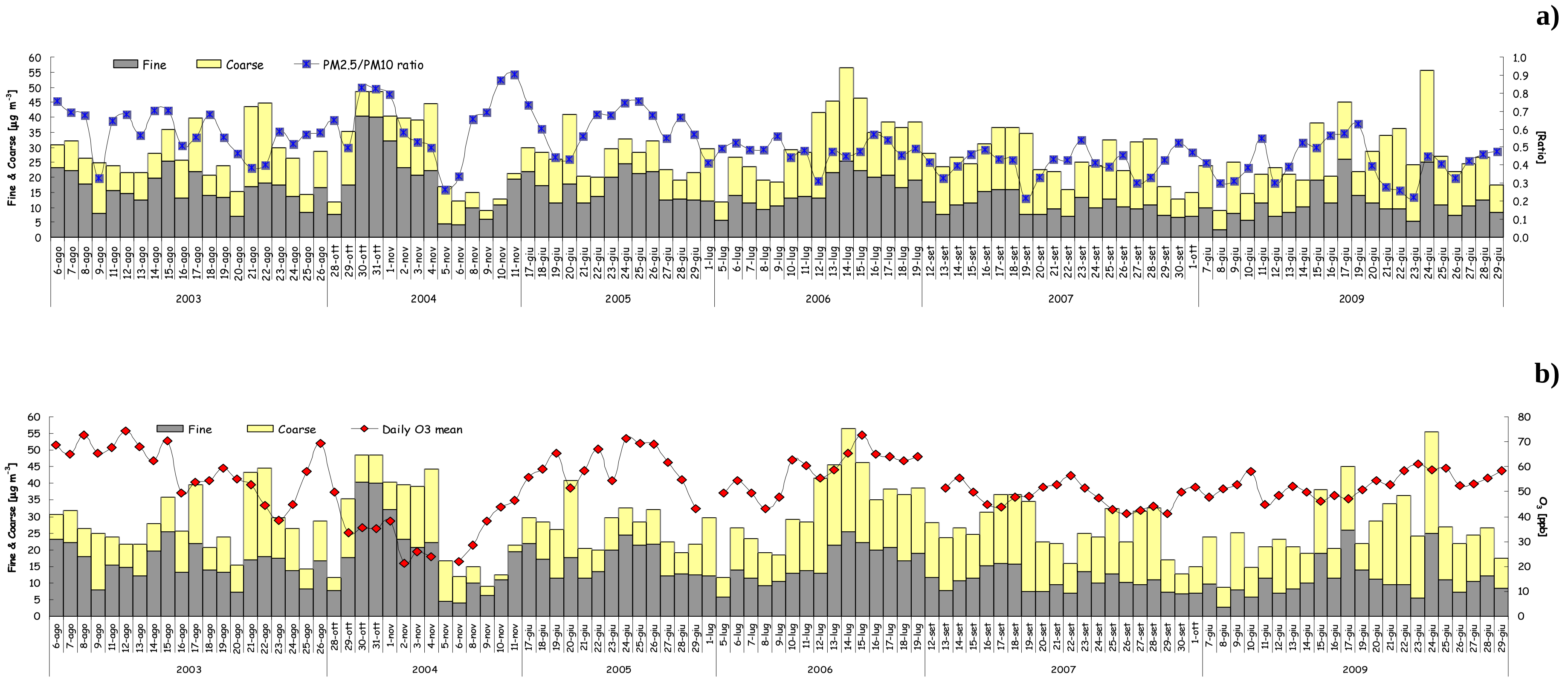

Figure 5.2 Time series of fine and coarse particle levels overlaid to a) $PM_{2.5}/PM_{10}$ ratio and b) daily O_3 mean values referring to each cruise campaigns.

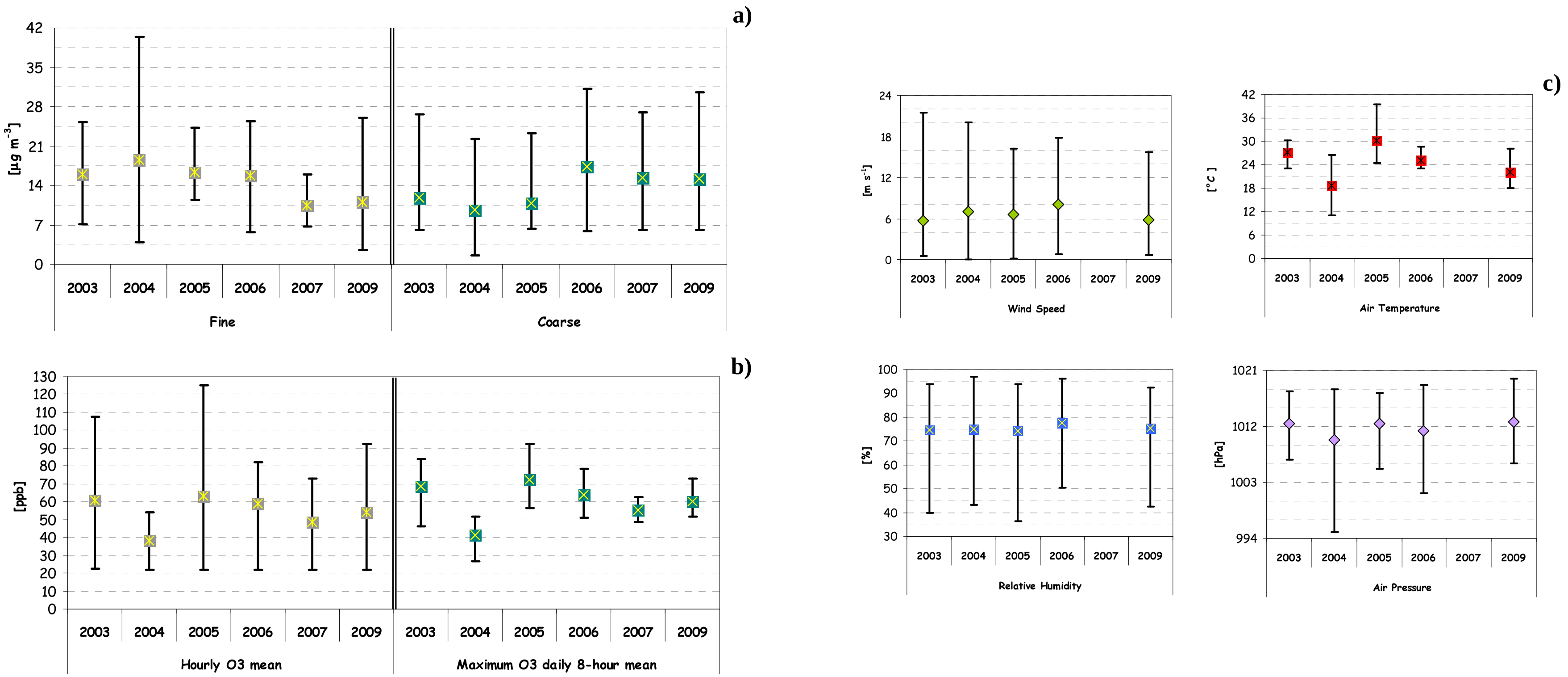

Figure 5.3 *Descriptive statistics: mean (as a dots), Maximum and minimum (as the highest and lowest shaft) for a) fine and coarse particle; b) hourly* O_3 *mean and Maximum* O_3 *daily 8-hour mean and c) meteorological parameter values referring to each cruise campaign.*

6.3.2 Aerosol-Ozone variation within Western and Eastern Mediterranean sectors

For a more detailed evaluation of the data set recorded the investigated Mediterranean area was separated in two regions, the Western Mediterranean (WM), (6W to 15E) and the Eastern Mediterranean (EM) (16E to 36E). Data of fine and coarse particle concentrations and the computed Maximum O_3 daily 8-hour mean were then separated as they refer to the Western or Eastern Mediterranean sector and thus reported in Figure 5.4 a) and b). As it can see the 2010EU target value for annual $PM_{2.5}$ mean concentration (25 $\mu g\ m^{-3}$) was exceeded four time (8.3%) in the Eastern sector and two time (3.5%) in the Western one. Considering the two sectors of the Mediterranean Sea region (WM and EM) and as reported in Figure 5.5a) a fine mean value was found to be significantly larger in EM side (16.4 $\mu g\ m^{-3}$) compared to that observed in the WM (12.4 $\mu g\ m^{-3}$). In contrast, higher coarse average value was observed in the Western (14.3 $\mu g\ m^{-3}$) and lower in the Eastern sector (12.8 $\mu g\ m^{-3}$). In terms of mean percentage contribution of fine concentrations to the total particle levels the values of 56% and 47% in EM and WM sectors, was found respectively (see Figure 5.5a) and b)). Otherwise, considering the whole Mediterranean region, fine and coarse concentrations showed comparable values with an average value of 14.2 $\mu g\ m^{-3}$ and 13.6 $\mu g\ m^{-3}$, respectively and with a slightly higher percentage contribution of 51% of fine fraction over the coarse one (see Figure 5.5c), bottom panel). The resulting average PM_{10} concentrations (as sum of fine and coarse fractions) showed therefore comparable values along the whole Mediterranean basin with a larger contribution of fine fraction in the Western sector compared to the Eastern side where the background contribution of anthropogenic compounds prevails. Pertaining O_3 values (see Figure 5.4b)), the relative Health Threshold value, established by the new Directive 2008/50/EC as the Maximum O_3 daily 8-hour mean: 120 $\mu g\ m^{-3}$ (~60 ppb), was exceeded 20 days (35%) in the Eastern Mediterranean sector reporting a mean value of 51.3 ppb. In the Western side the number of days with exceedences of the ozone long-term objective for the protection of human health were found to be 29, equal to the 60% over the total observations done over this sector.

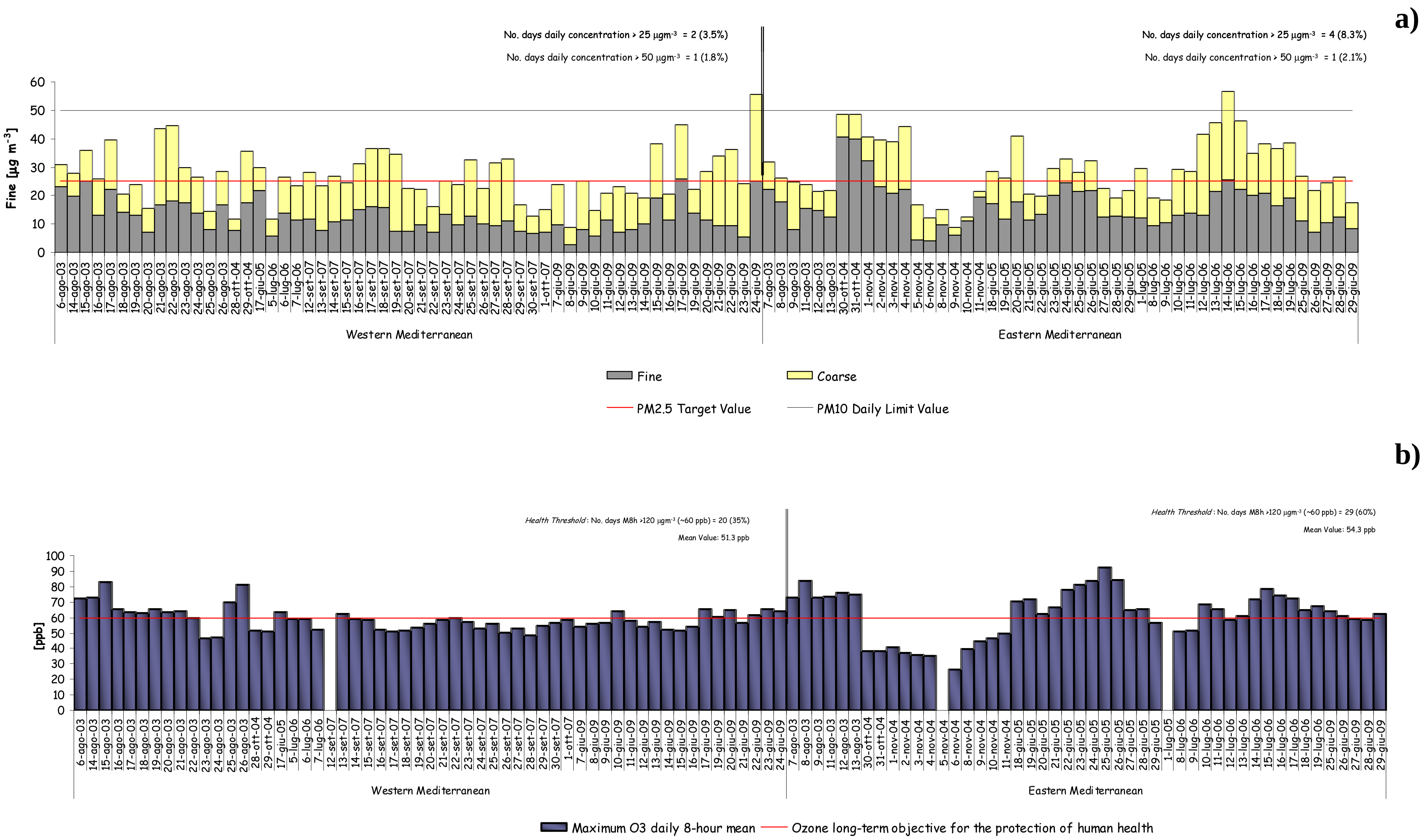

Figure 5.2 *Time series of a) fine and coarse particle levels and b) Maximum O_3 daily 8-hour mean values referring to Western and Eastern Mediterranean sectors.*

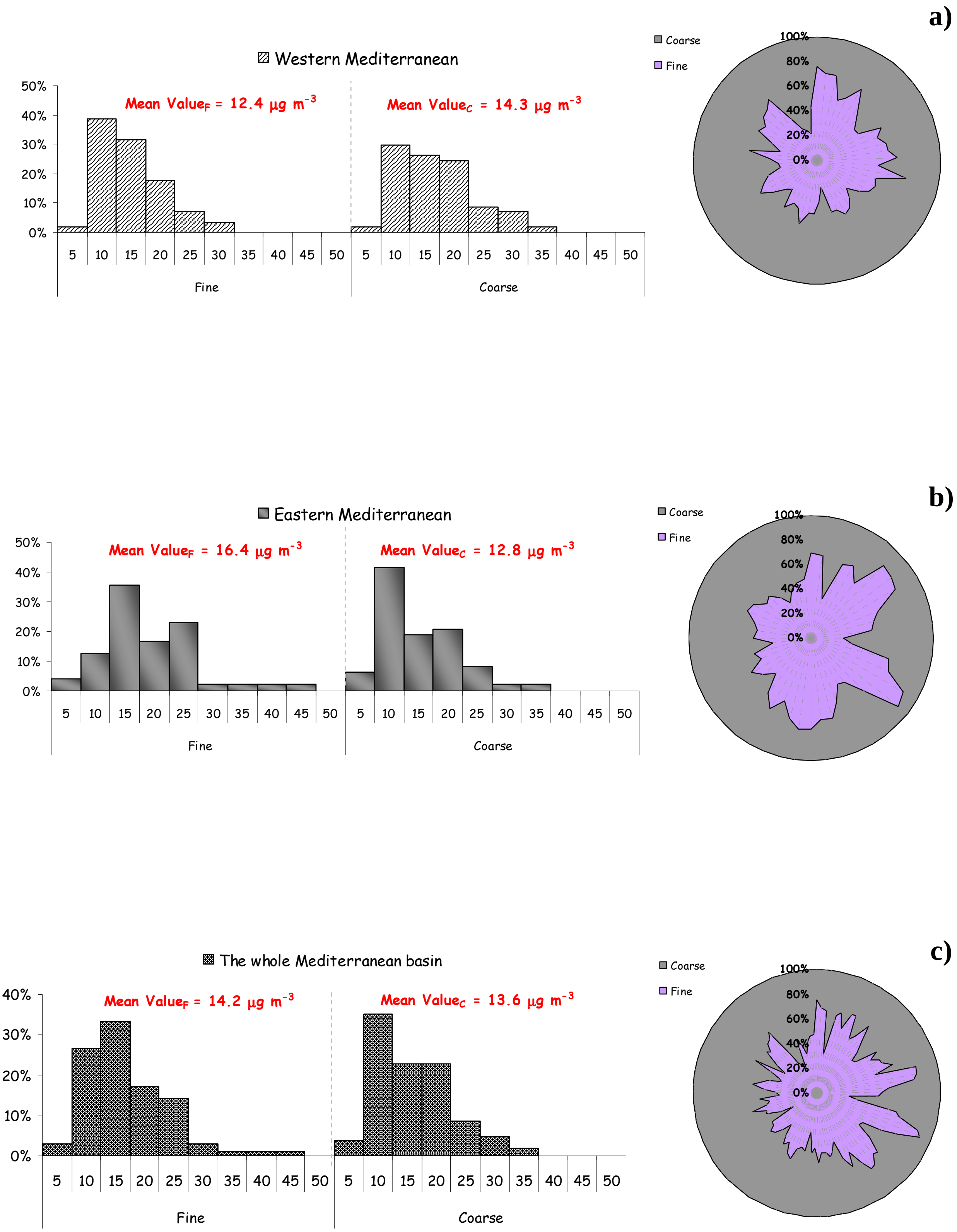

Figure 5.5 *For a)Western; b) Eastern and c) the whole Mediterranean area, fine and coarse frequency distribution and relative contribution are reported in the left and right panels, respectively.*

6.3.3 Observations along each single cruise campaign

In order to examine the data recorded at sea in more detail, each single cruise campaign will be considered in the next sections focussing on concentrations of different aerosol size fractions (fine and coarse) and on ozone levels. These data were integrated with variations in the major PM transition (heavy) metals along with their distribution within finer and coarser aerosols during the journey. Spatial and temporal variations of the recorded data will be furthermore reported highlighting the events that were identified as the main influencing factors.

6.3.3.1 Urania Cruise Campaign 2003

During the 2003 cruise campaign the URANIA Research Vessel followed firstly a track along south-eastern Mediterranean sea from Sicily to Creta island, passed through the Strait of Messina and then, after a brief stop at Napoli harbour, continued in the Western Mediterranean sector until the Strait of Gibraltar and returned back ending the journey at the Livorno harbour (Figure 5.6). The whole cruise involved 20 days at sea from 6th to 27th August during which the temperature was quite high (23-30 °C) and the high-pressure system (anti-cyclone) prevailed. These hot and dry persistent weather conditions, well-known as the 2003 “heat-wave”, have trigged numerous wildfires, enhanced the pollution accumulation in the boundary layer and caused a lot of premature deaths. Wildfire emissions particularly, as confirmed by the NAAPs-based smoke maps (showed as an example in Figure 5.8, upper panel) , have had a large impact over the whole Mediterranean area favouring enhanced photochemical O_3 production and aerosol accumulation. As it was expected, O_3 levels were therefore very huge reaching peak values equal to 140 ppb and exceeding the European health standard for O_3 (8-h average < 60 ppbv) almost in all sampling days (see Figure 5.7). Stagnant meteorological condition along with wildfire plumes influenced aerosol concentrations in the way that the finer fraction levels prevailed, with an average value equal to 57%, over the coarser one almost always. It is interesting to point out, as it can see in Figure 5.7 , that in the period from 21st to 24th August after the increasing of the coarse concentrations beyond the fine ones the corresponding ozone levels consistently decreased and, as exception over the entire cruise, the O_3 health standard was respected. This occurrence has been identified to be influenced by a Saharan dust storm whose outbreak has been confirmed by HYSPLIT-based backward trajectories (coming from Nord-Africa) and by TOMS-based Aerosol Index maps (with AI>1.5) (see Figure 5.8 bottom panel).

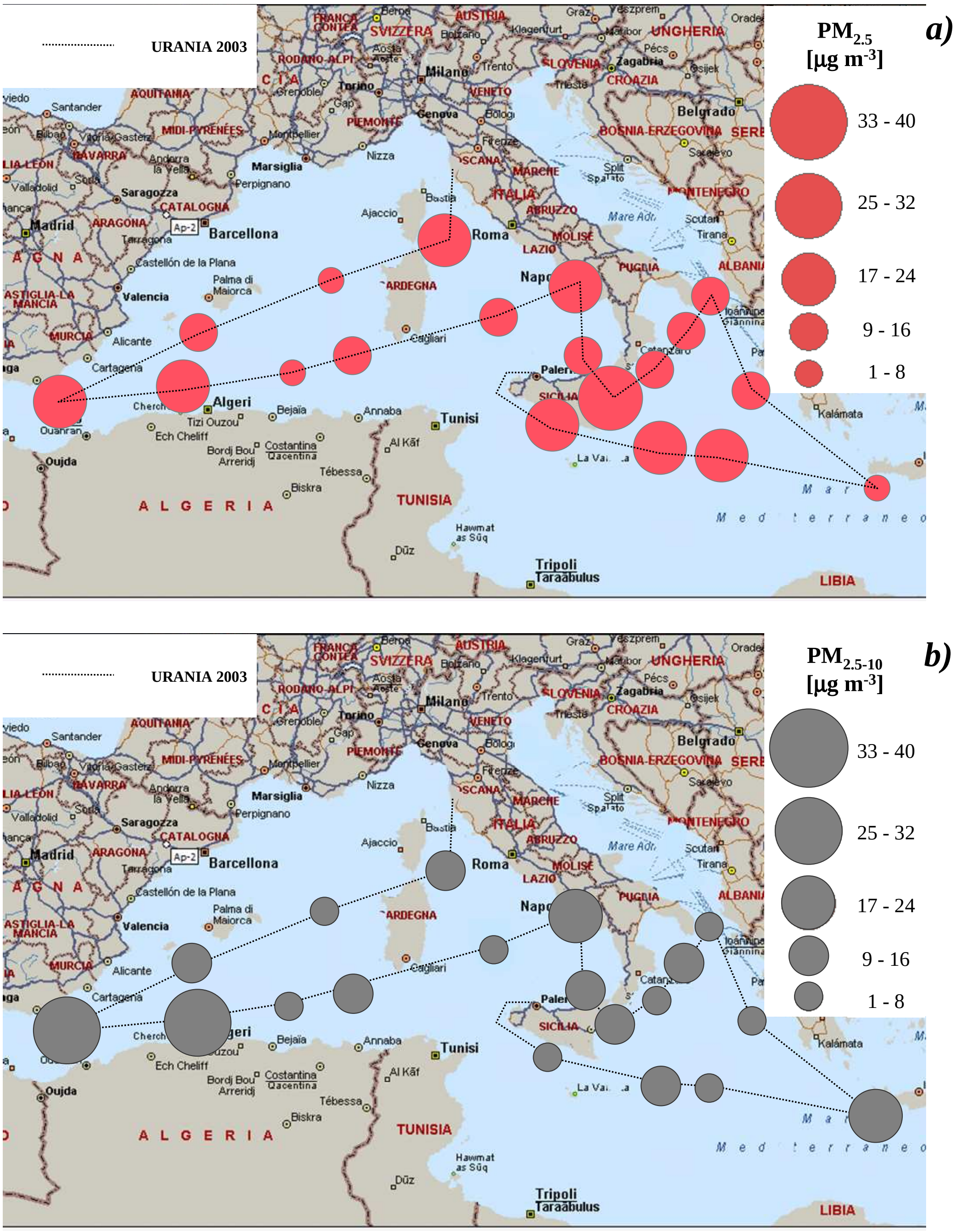

***Figure 6.6** Spatial distribution of a) fine and b) coarse particle concentrations observed during the 2003 cruise campaign performed onboard the CNR Research Vessel URANIA along the reported track.*

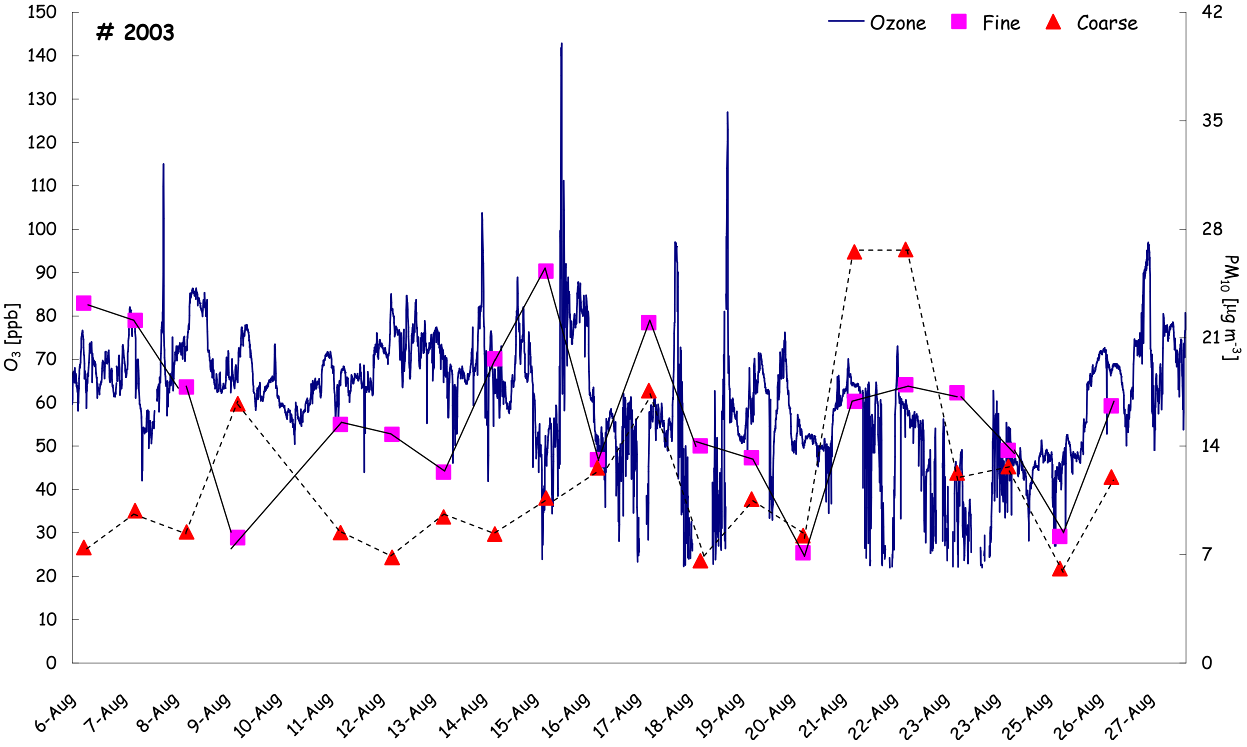

Figure 6.7 *Time series of fine and coarse particle concentrations and ozone levels recorded during the 2003 cruise campaign.*

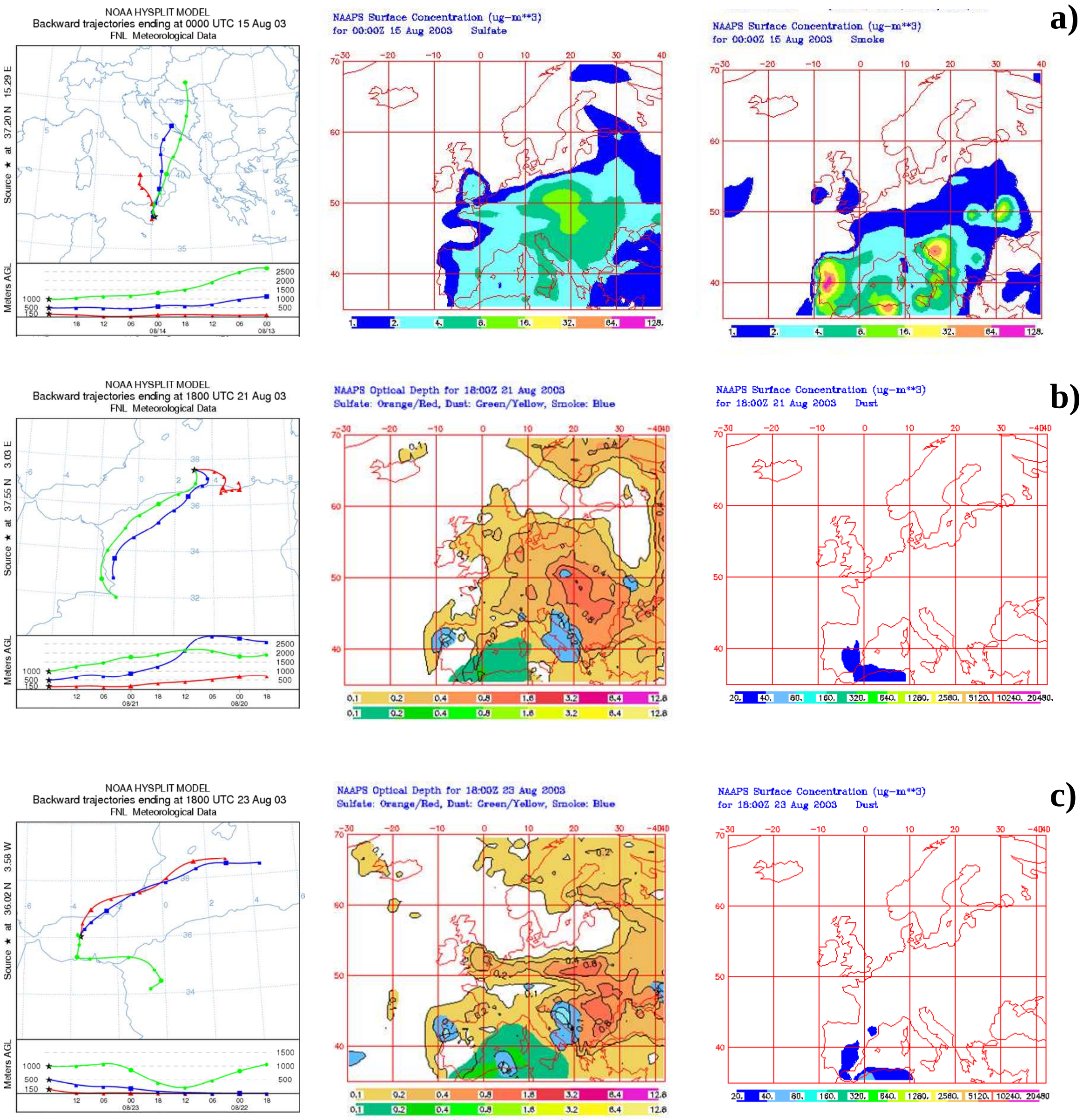

Figure 5.8 *Hysplit and NAAPS-based maps showing: back-trajectories and ship position in the left panels, sulphate concentrations or optical depth in central panels and smoke or dust concentrations for a) 15*th*; b) 21*st *and c) 23*rd *August 2003, respectively.*

6.3.3.2 Urania Cruise Campaign 2004

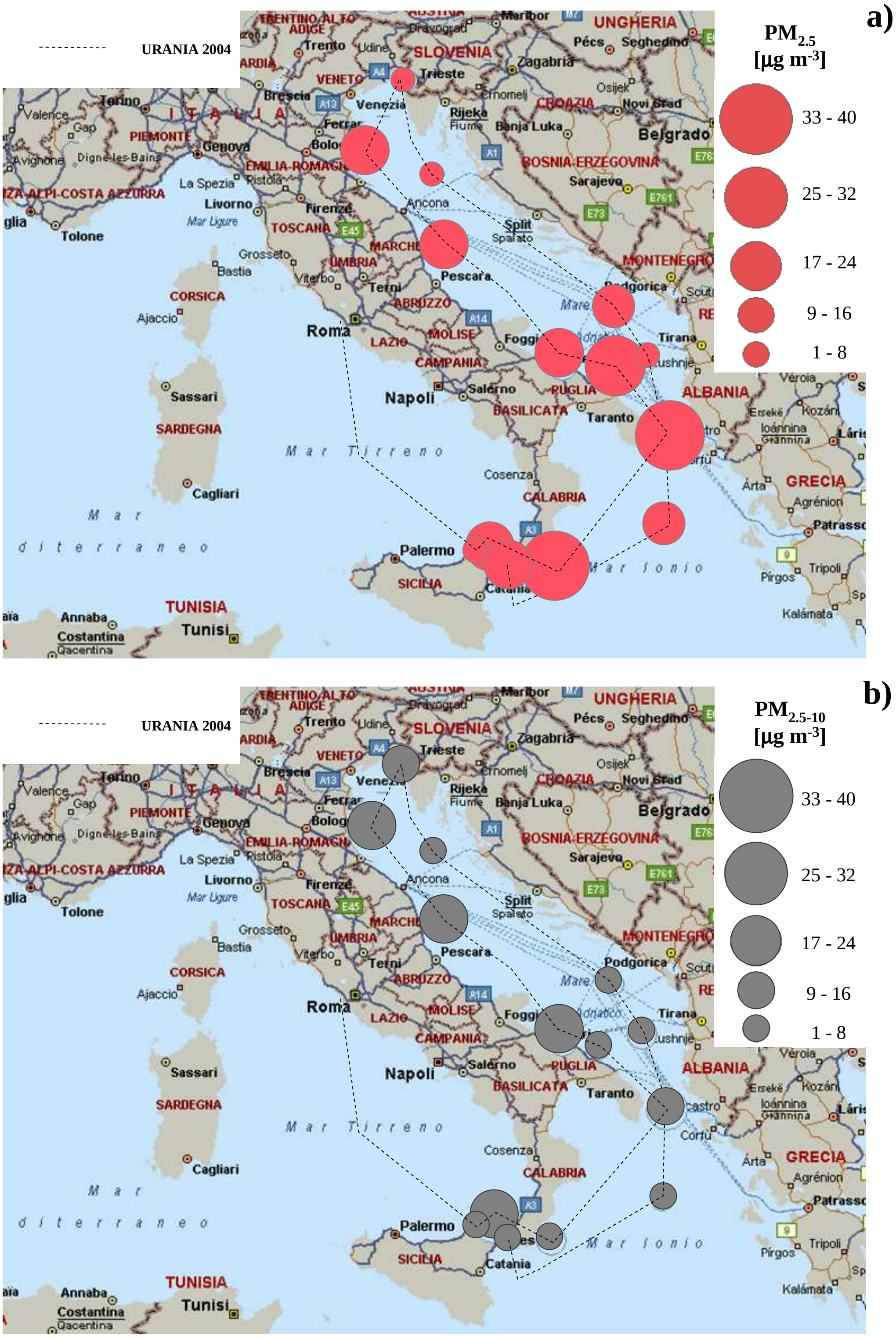

Figure 6.9 *Spatial distribution of a) fine and b) coarse particle concentrations observed during the 2004 cruise campaign performed onboard the CNR Research Vessel URANIA along the reported track.*

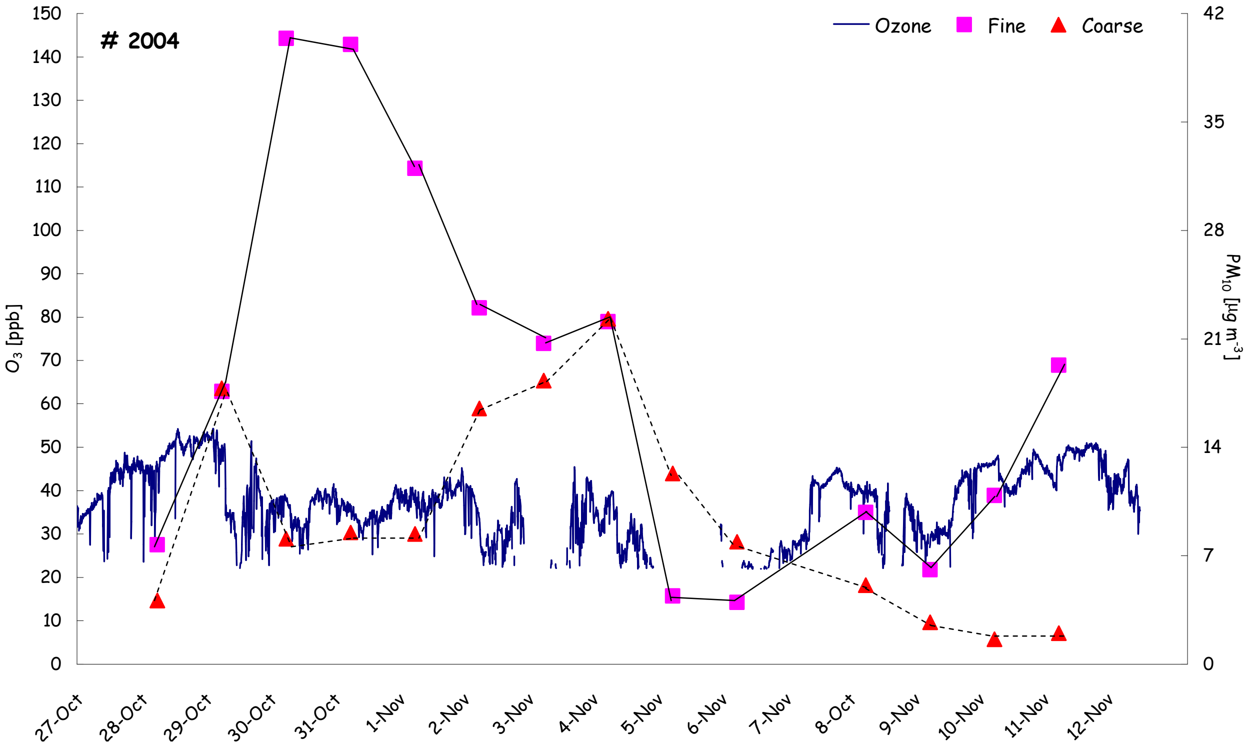

Figure 6.10 *Time series of fine and coarse particle concentrations and ozone levels recorded during the 2004 cruise campaign.*

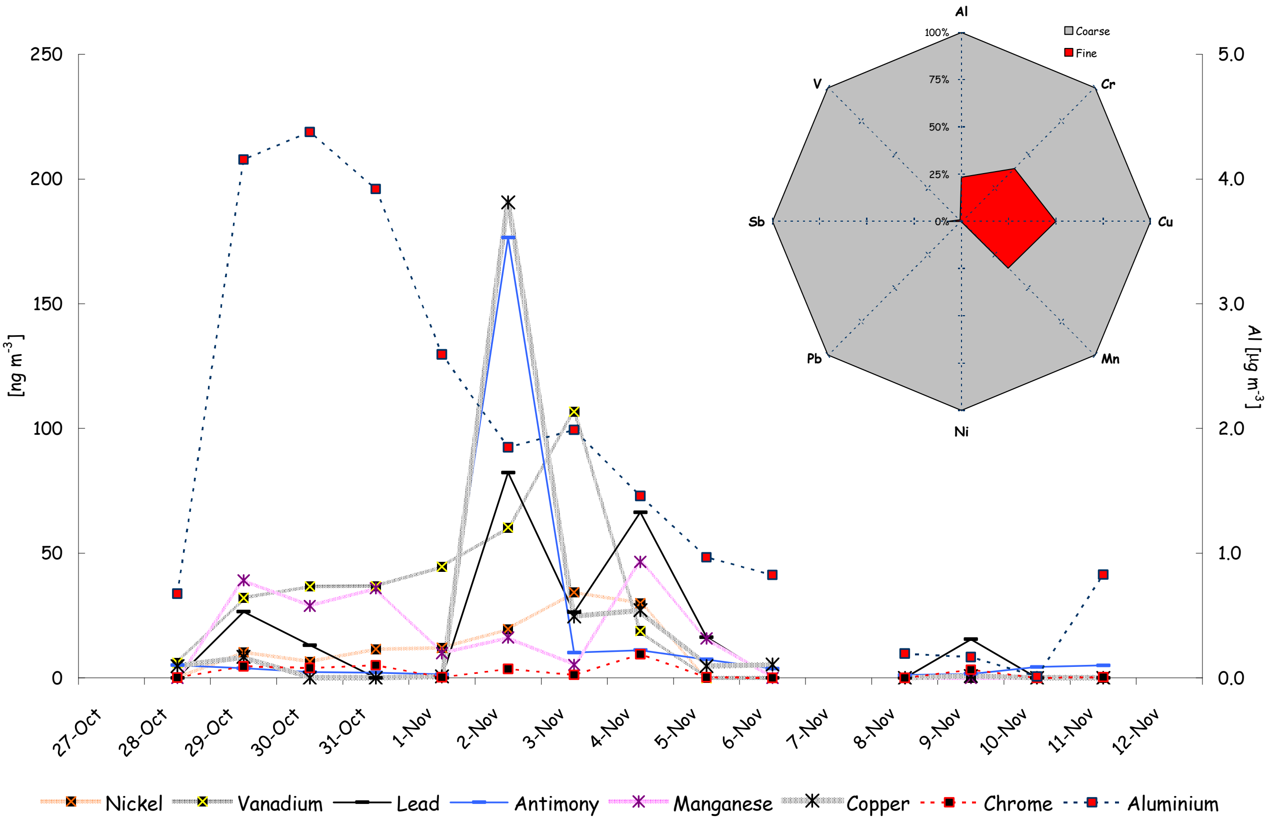

Figure 6.11 *Time series of Al, Cr, Cu, Mn, Ni, Pb, Sb and V concentrations associated to the aerosol particles during the 2004 cruise campaign. Distribution between fine and coarse size fraction is also reported.*

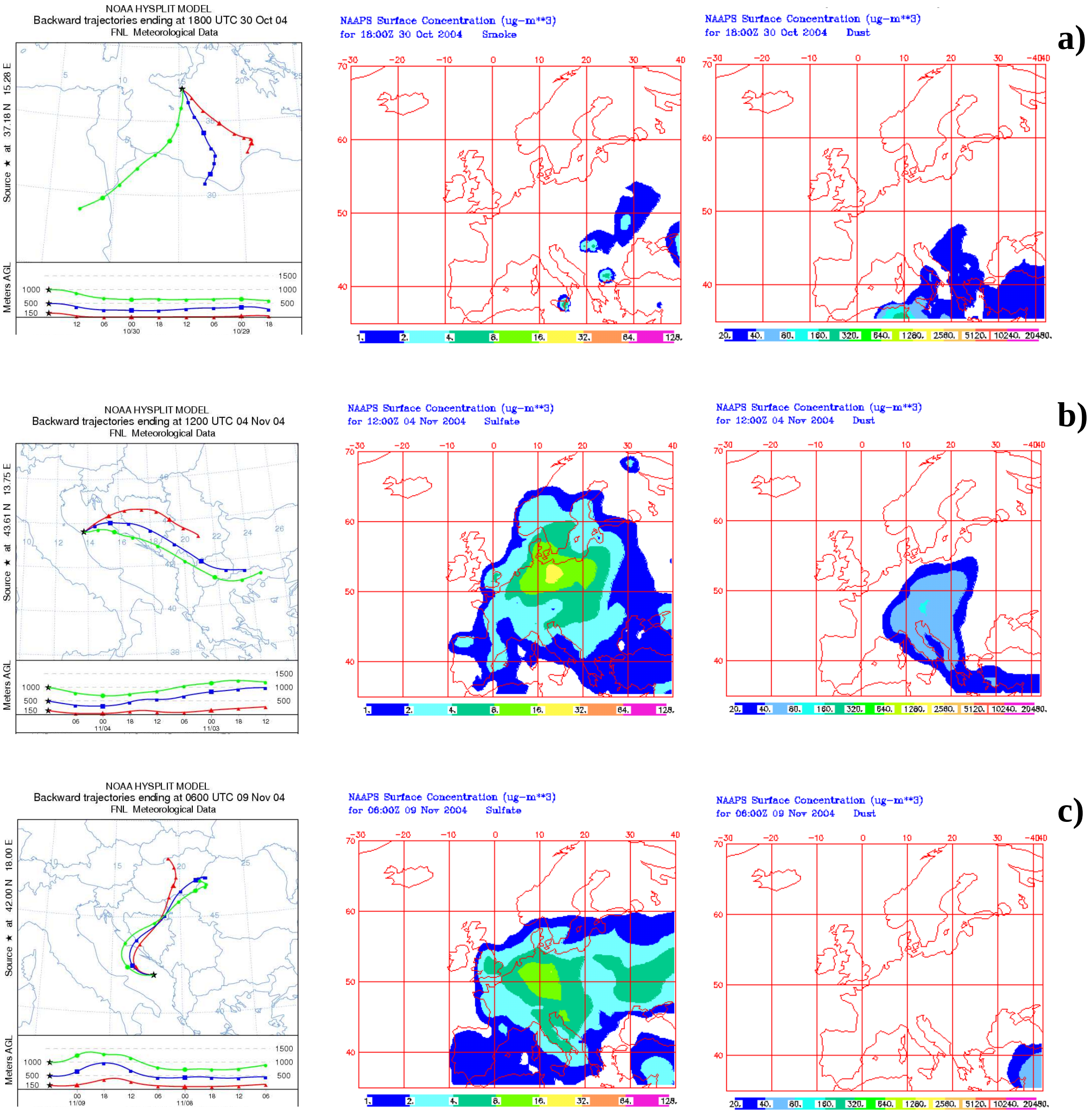

Figure 6.12 *Hysplit and NAAPS-based maps showing: back-trajectories and ship position in the left panels, smoke or sulphate concentrations in central panels and dust concentrations for a) 30*th *October; b) 4*th *and c) 9*th *November 2004, respectively.*

6.3.3.3 Urania Cruise Campaign 2005

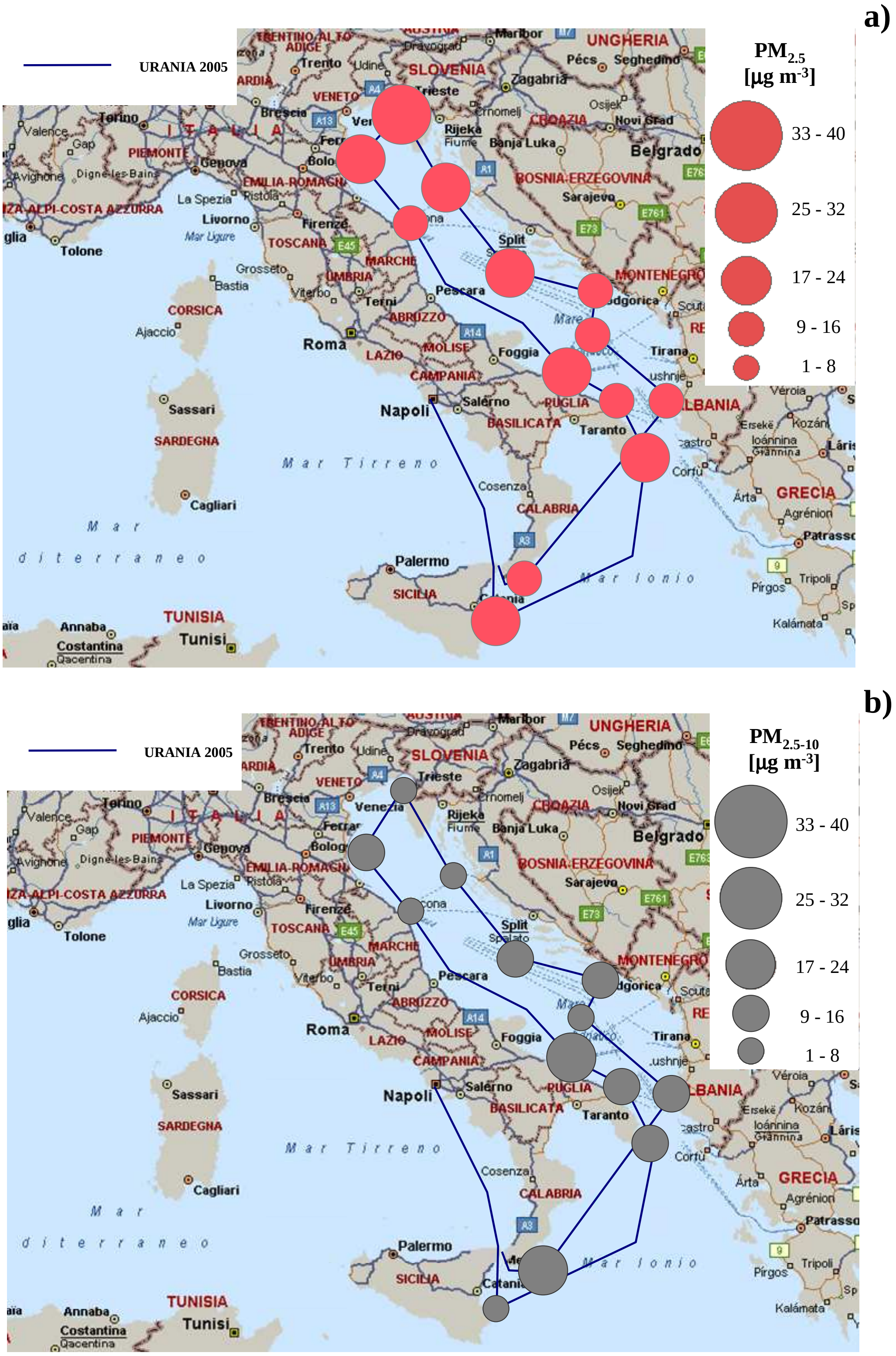

***Figure 6.13** Spatial distribution of a) fine and b) coarse particle concentrations observed during the 2005 cruise campaign performed onboard the CNR Research Vessel URANIA along the reported track.*

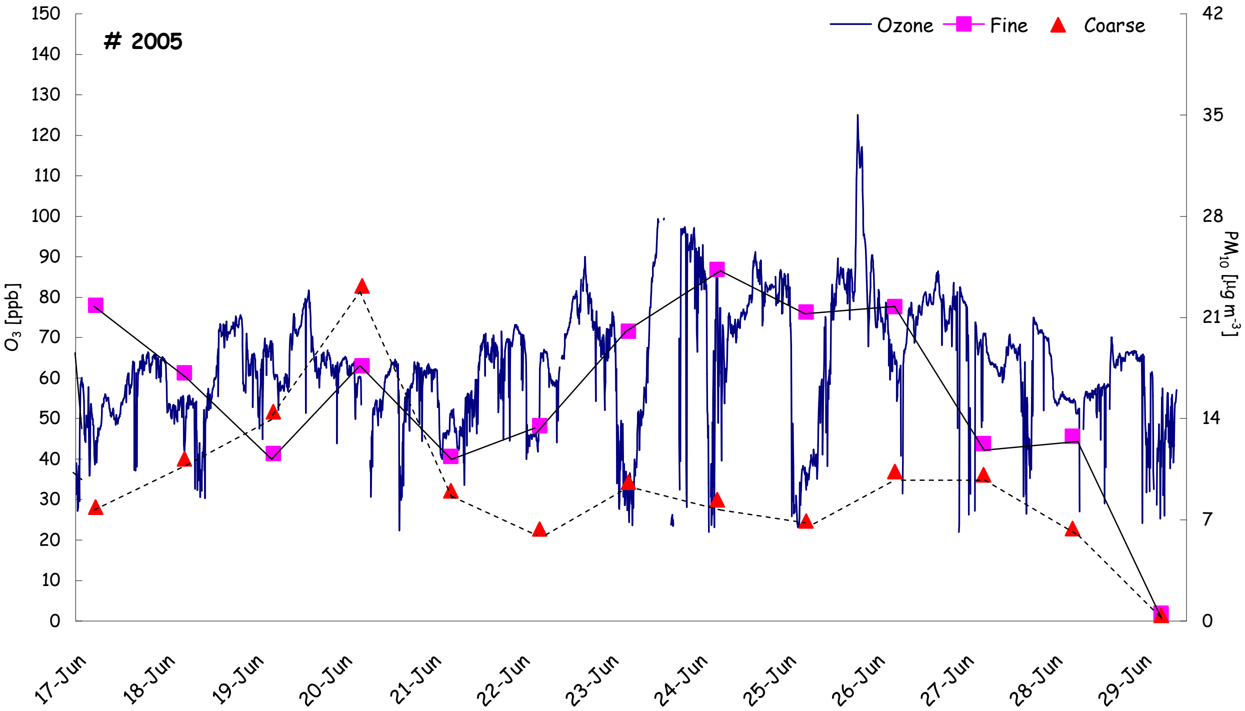

Figure 6.14 *Time series of fine and coarse particle concentrations and ozone levels recorded during the 2005 cruise campaign.*

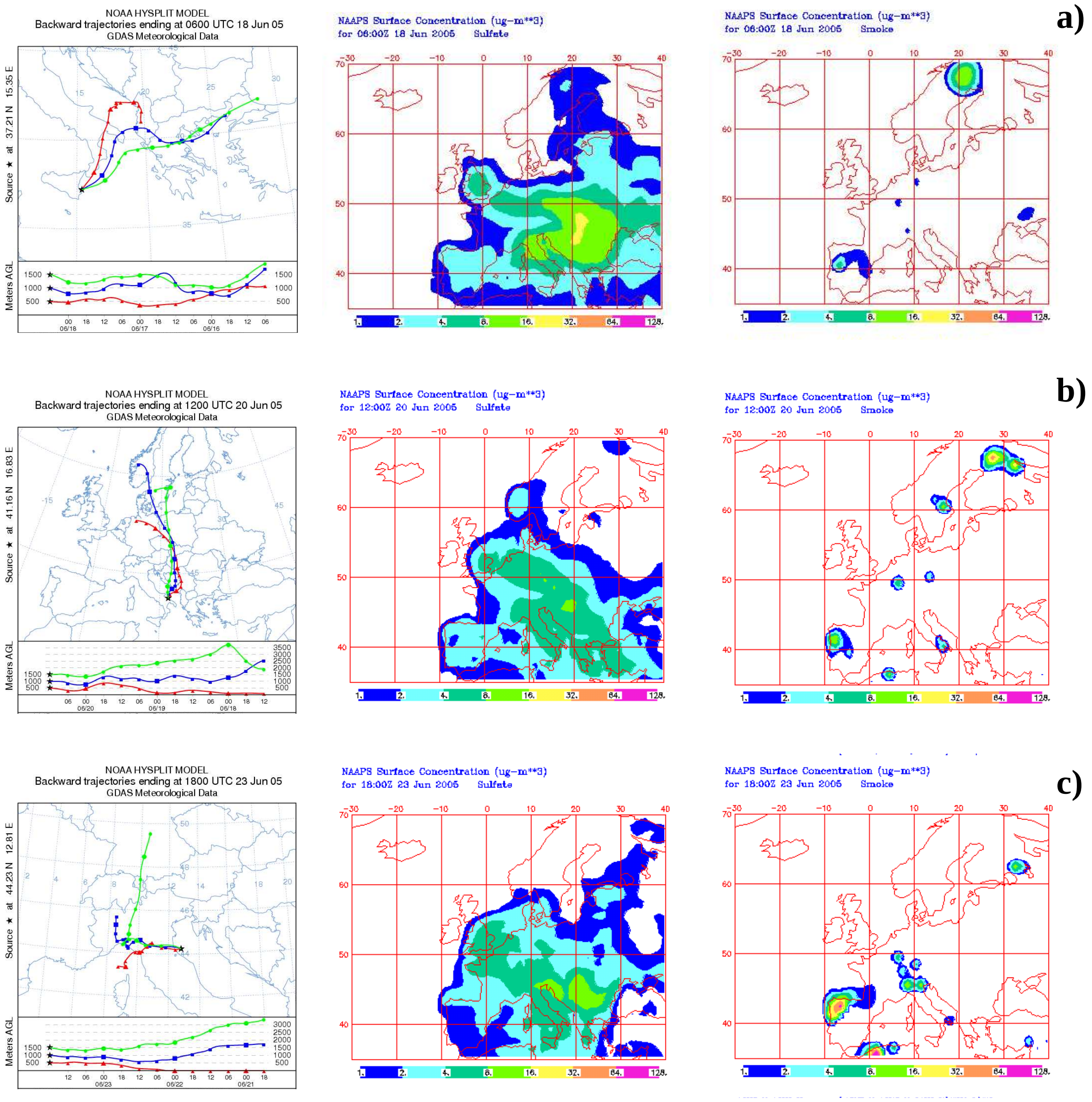

Figure 6.15 *Hysplit and NAAPS-based maps showing: back-trajectories and ship position in the left panels, sulphate concentrations in central panels and smoke concentrations for a) 18th; b) 20th and c) 23rd June 2005, respectively.*

6.3.3.4 Urania Cruise Campaign 2006

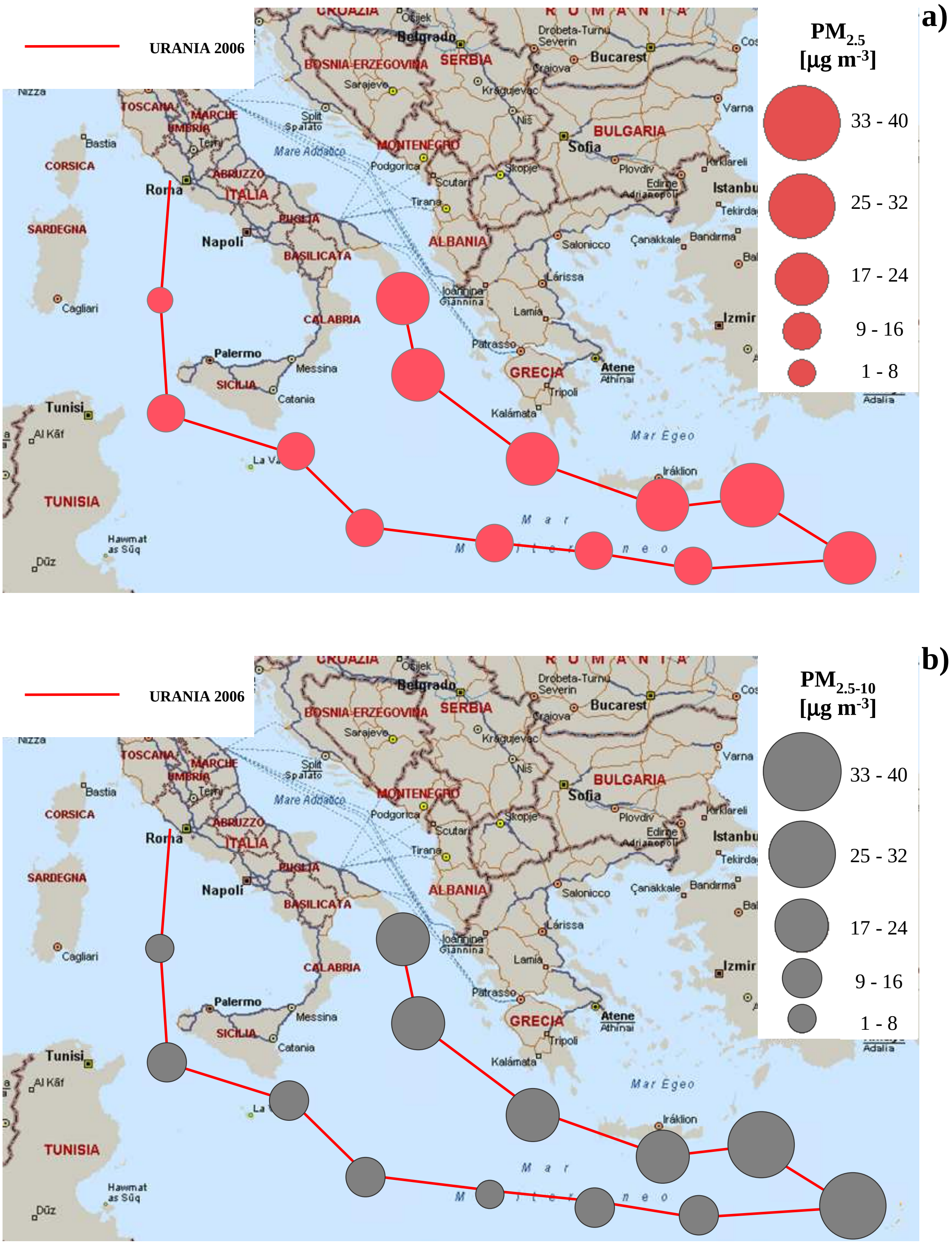

Figure 6.16 *Spatial distribution of a) fine and b) coarse particle concentrations observed during the 2006 cruise campaign performed onboard the CNR Research Vessel URANIA along the reported track.*

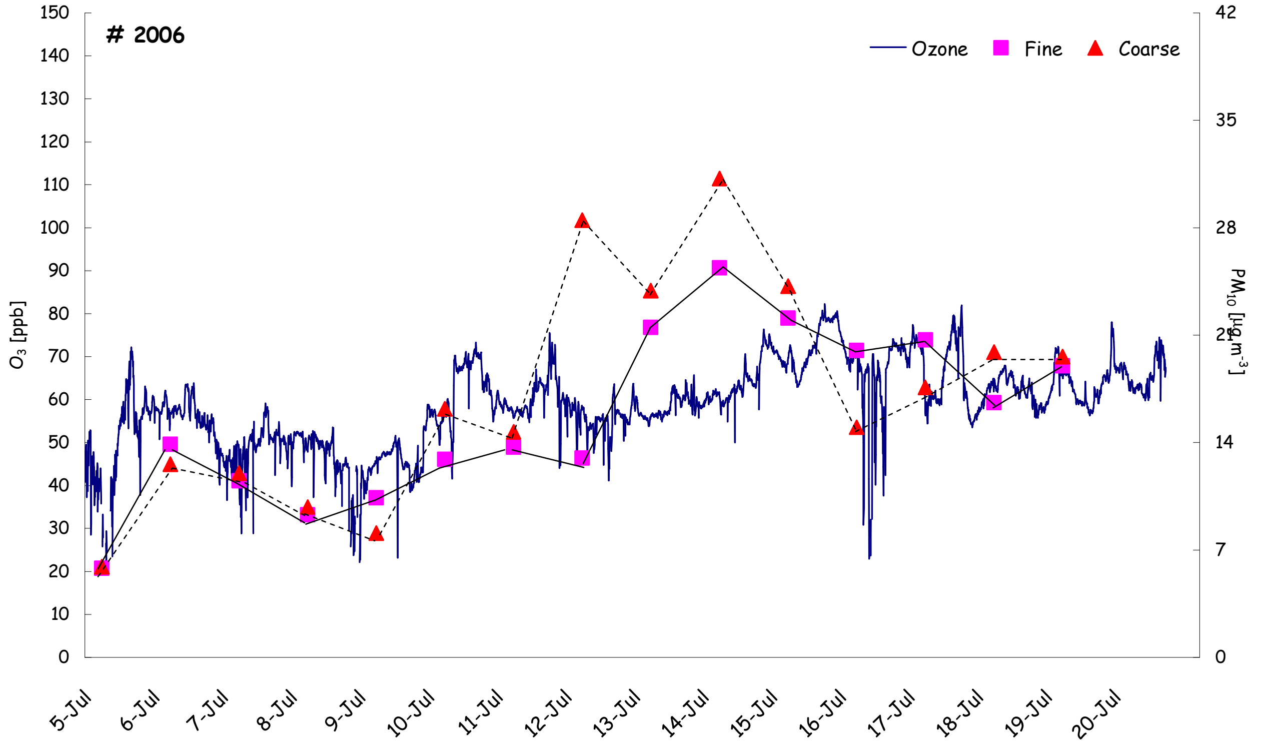

Figure 6.17 *Time series of fine and coarse particle concentrations and ozone levels recorded during the 2006 cruise campaign.*

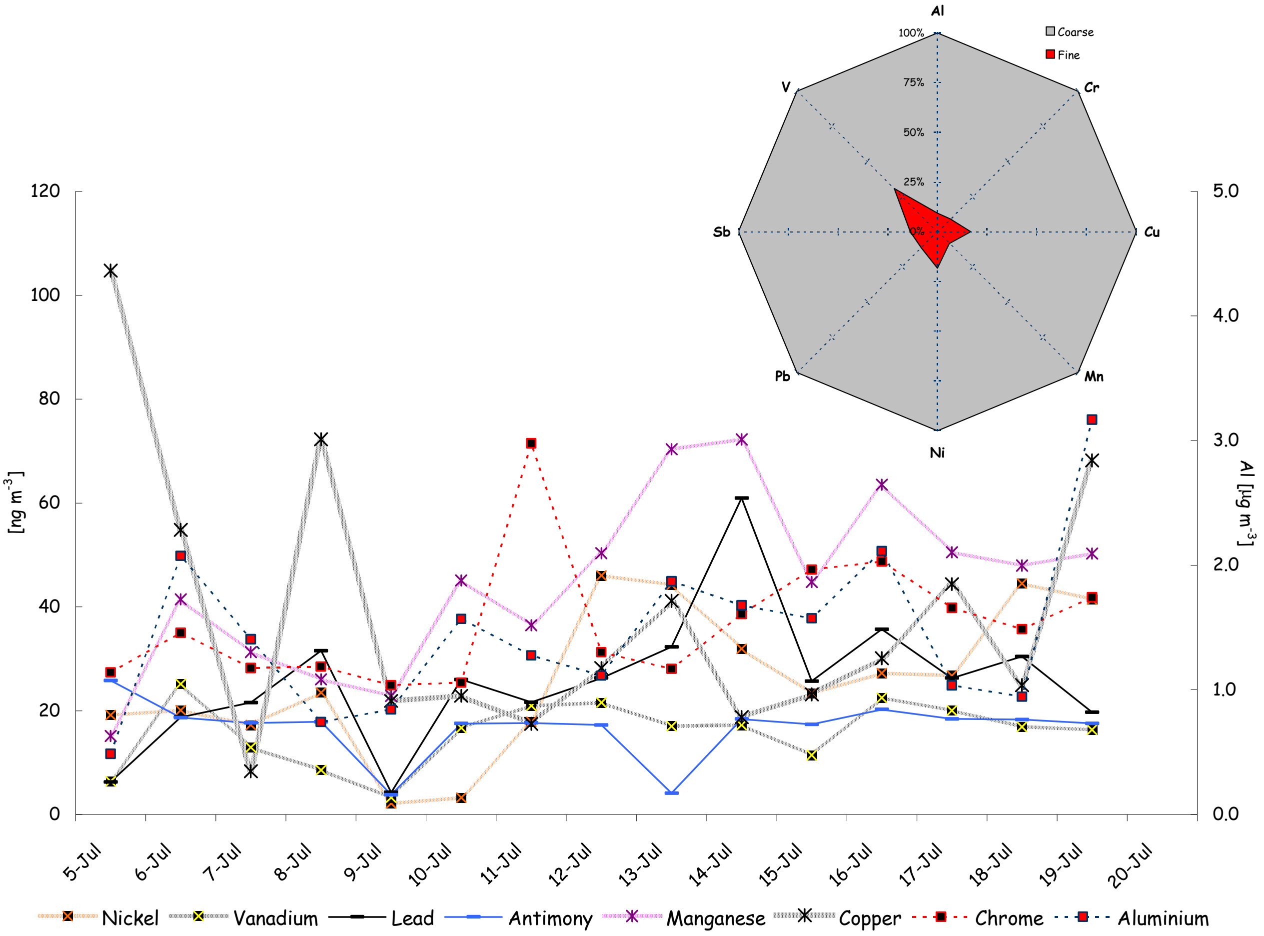

Figure 6.18 *Time series of Al, Cr, Cu, Mn, Ni, Pb, Sb and V concentrations associated to the aerosol particles during the 2005 cruise campaign. Distribution between fine and coarse size fraction is also reported..*

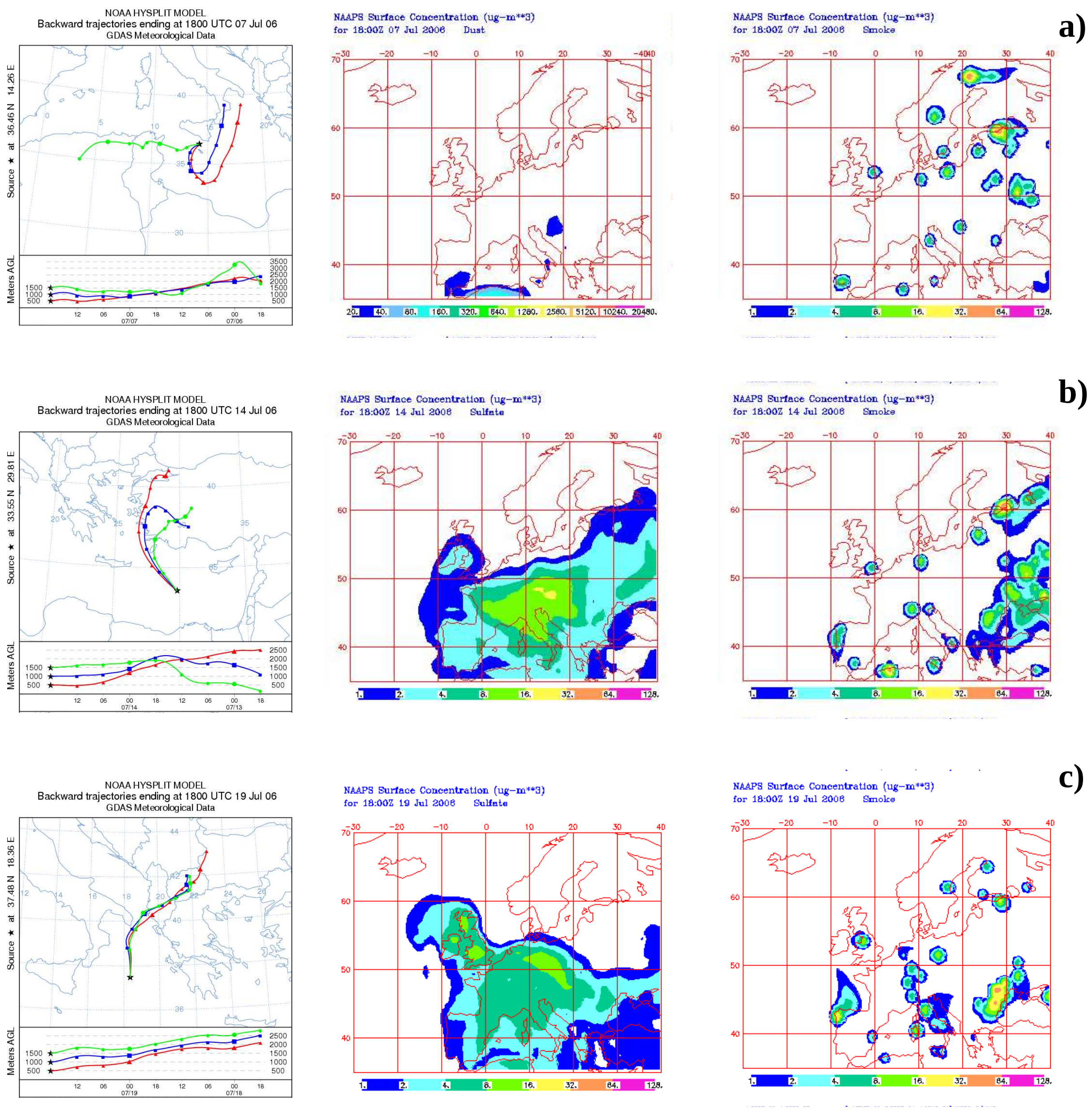

***Figure 6.19** Hysplit and NAAPS-based maps showing: back-trajectories and ship position in the left panels, sulphate concentrations in central panels and smoke concentrations for a) 7th; b) 14th and c) 19th July 2006, respectively.*

6.3.3.5 Urania Cruise Campaign 2007

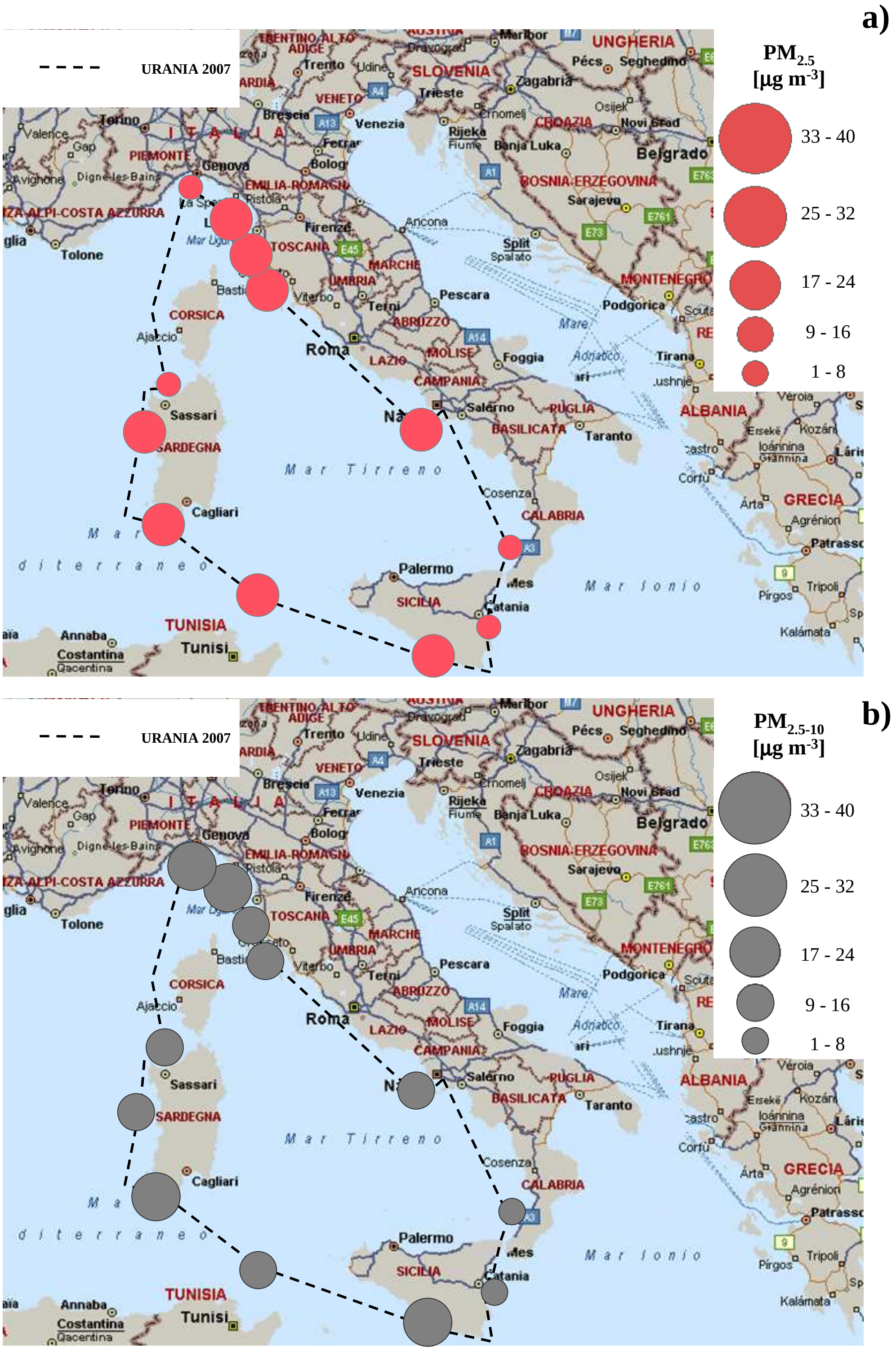

***Figure 6.20** Spatial distribution of a) fine and b) coarse particle concentrations observed during the 2007 cruise campaign performed onboard the CNR Research Vessel URANIA along the reported track.*

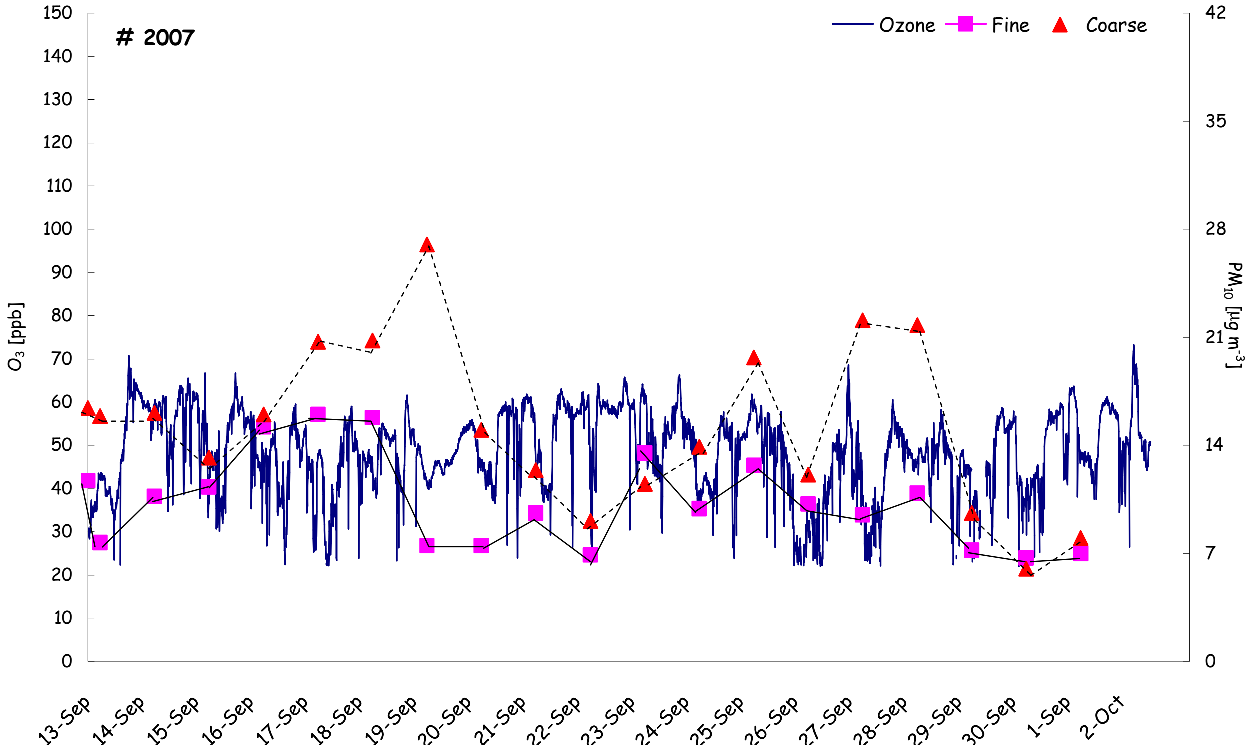

Figure 6.21 *Time series of fine and coarse particle concentrations and ozone levels recorded during the 2007 cruise campaign.*

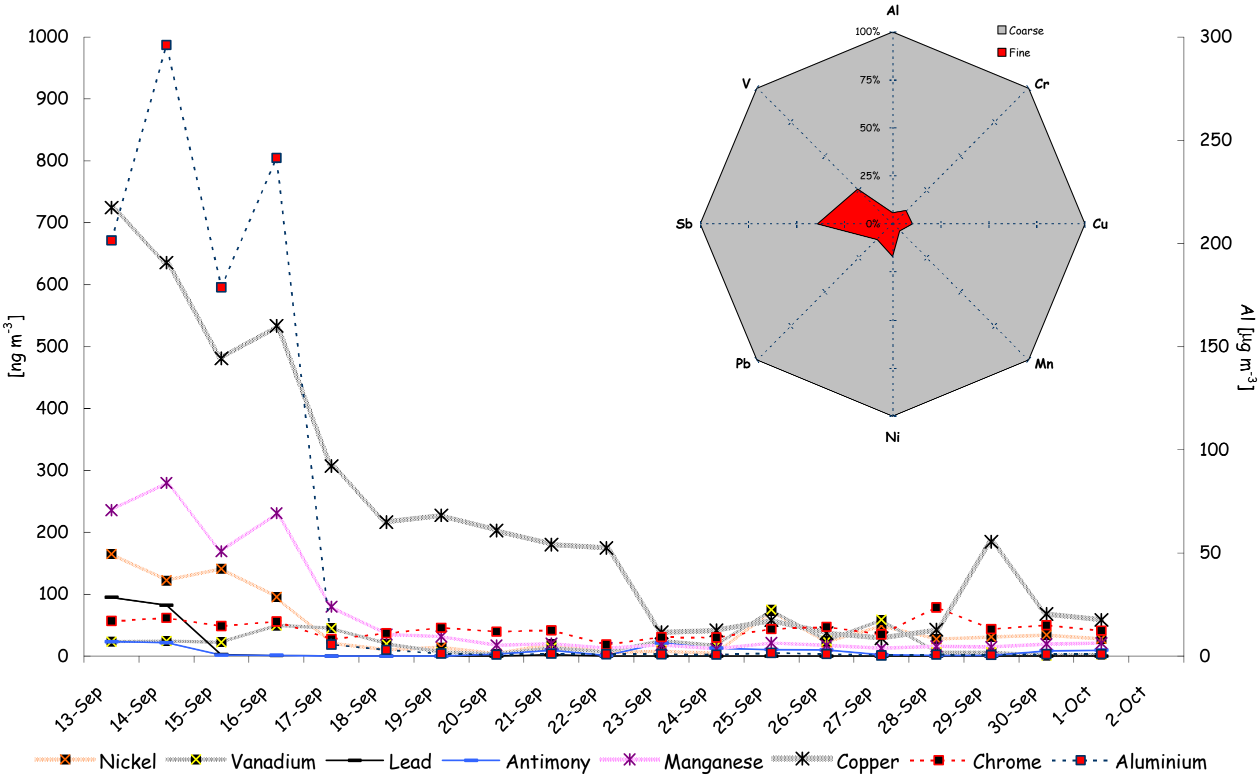

Figure 6.22 *Time series of Al, Cr, Cu, Mn, Ni, Pb, Sb and V concentrations associated to the aerosol particles during the 2007 cruise campaign. Distribution between fine and coarse size fraction is also reported..*

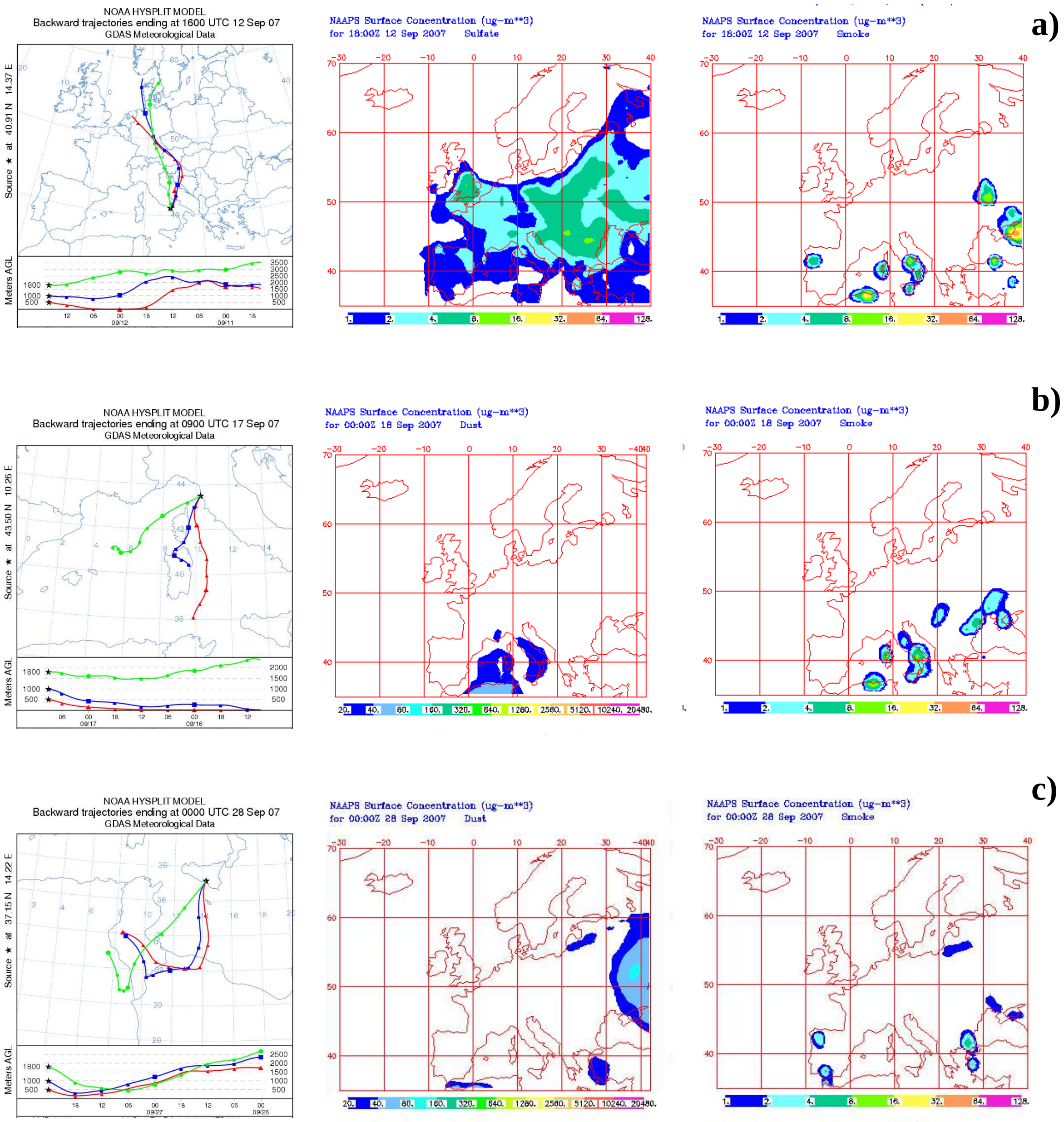

Figure 6.23 *Hysplit and NAAPS-based maps showing: back-trajectories and ship position in the left panels, sulphate or dust concentrations in central panels and smoke concentrations for a) 12th; b) 17th and c) 28th September 2007, respectively.*

6.3.3.6 Urania Cruise Campaign 2009

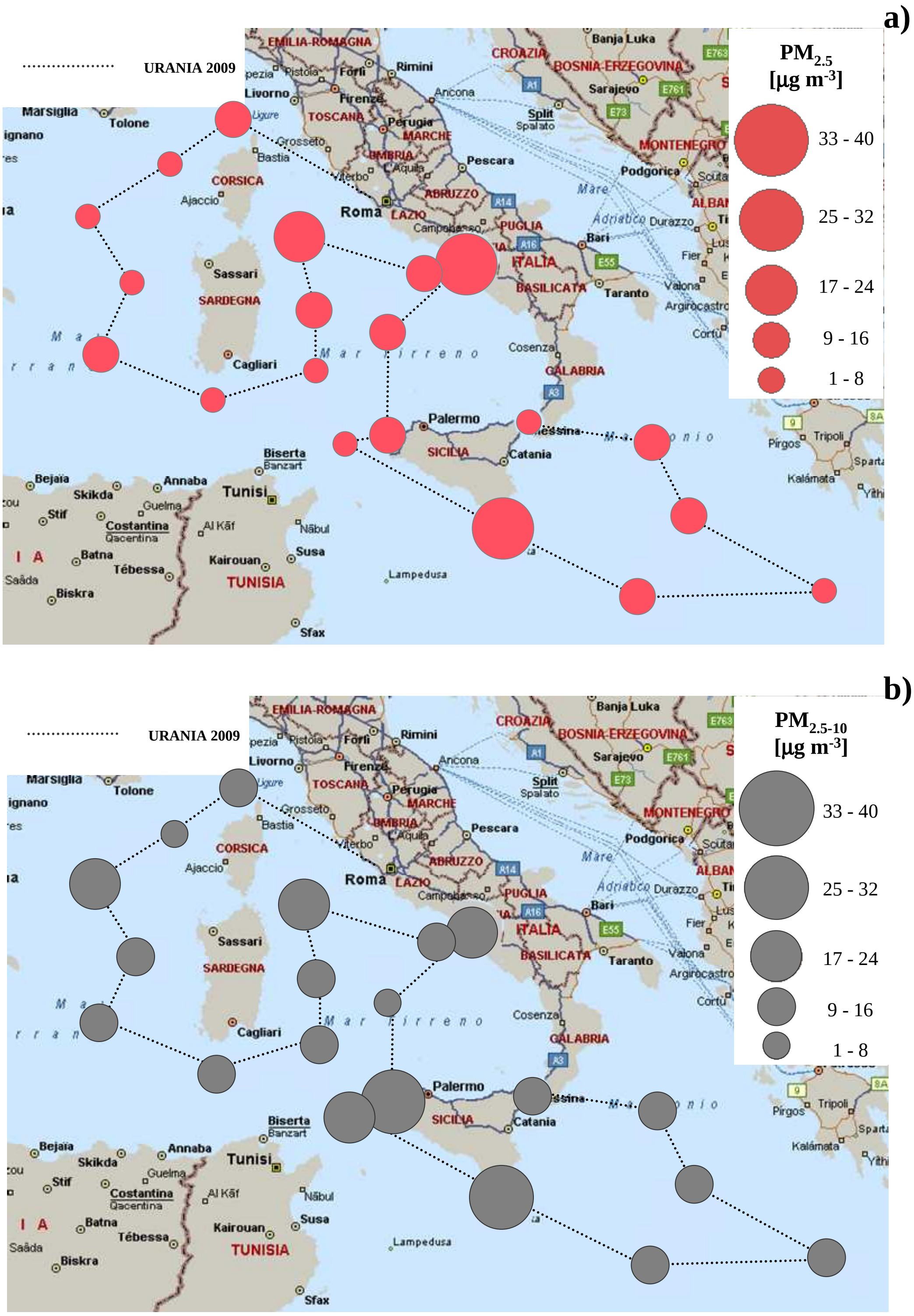

***Figure 6.24** Spatial distribution of a) fine and b) coarse particle concentrations observed during the 2009 cruise campaign performed onboard the CNR Research Vessel URANIA along the reported track.*

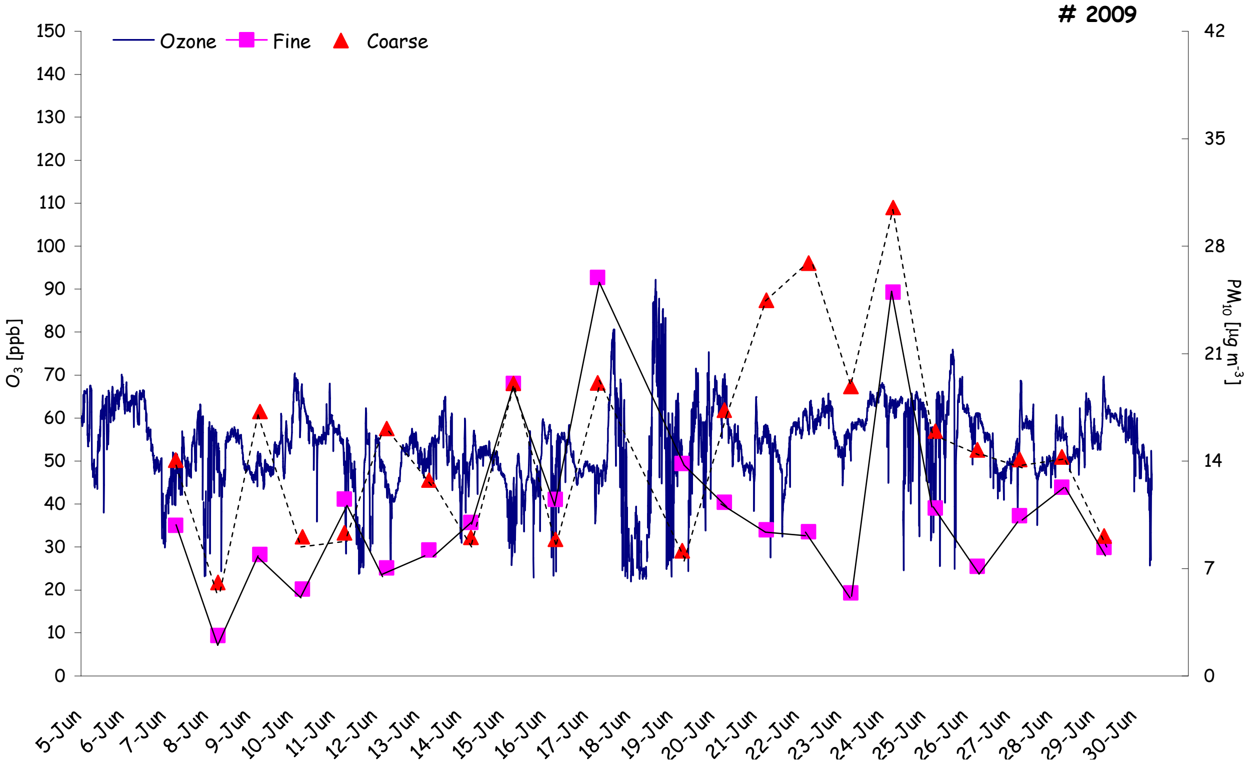

Figure 6.25 *Time series of fine and coarse particle concentrations and ozone levels recorded during the 2009 cruise campaign.*

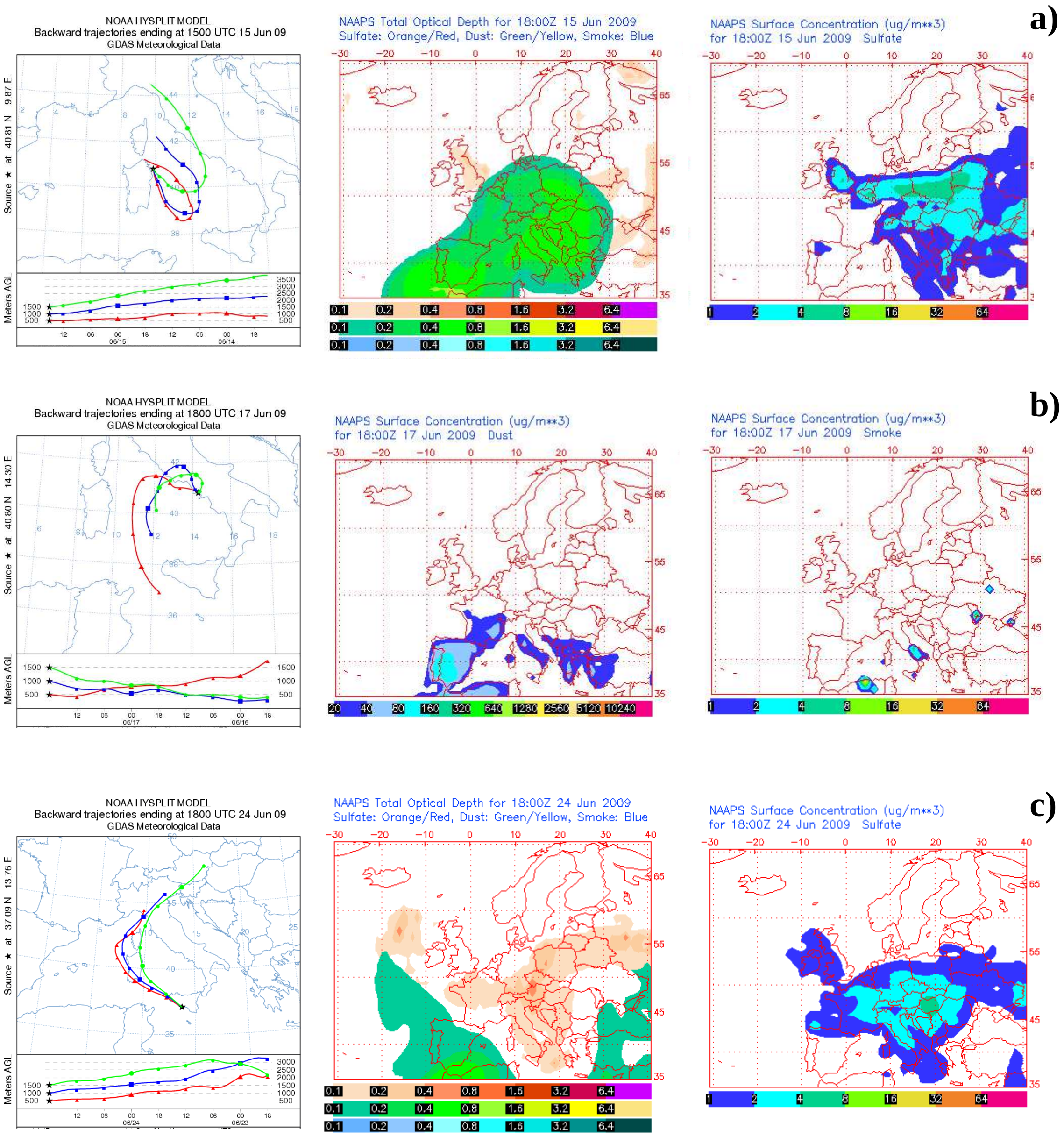

Figure 6.26 *Hysplit and NAAPS-based maps showing: back-trajectories and ship position in the left panels, optical depth or dust concentrations in central panels and sulphate or smoke concentrations for a) 15th; b) 17th and c) 24th June 2009, respectively.*

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CHAPTER 7

Role of Atmospheric Pollution on Harmful Health Effects

Gaseous and particulate matter in ambient and indoor air has a key role on the increased morbidity or mortality observed in many clinical studies. Knowledge of the main toxicity patterns of atmospheric pollutants is still at an initial stage, especially as concerns particulate matter. This is mainly due to the varying size distributions and chemical composition of PM_{10} and $PM_{2.5}$ and to the many-sided toxicity mechanisms of ultrafine particles (UFPs). In this chapter, recent findings on toxicity routes attributable to PM matter to UFPs and to gases, are reviewed. Toxicity routes are discussed as evidence or hypothetical relationships between sources, diffusion paths, receptor sites and susceptible populations.

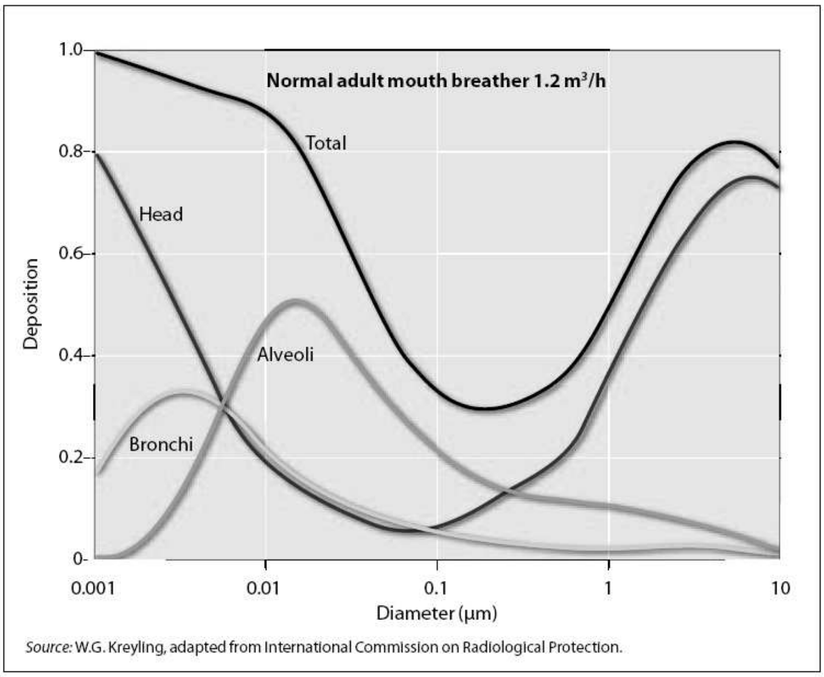
7.1 Introduction

Adverse health effects of atmospheric pollutants have been well documented in Europe and in other parts of the world. These include many diseases and an estimated reduction of a year or more in life expectancy for people living in European cities. There is also evidence of increased infant mortality in highly polluted areas. Concerns about these health effects have led to the implementation of regulations to reduce harmful air pollutants emissions and their precursors at international, national, regional and local levels. Further measures – while necessary to reduce the health effects of air pollution – are becoming increasingly expensive. There is thus a growing need for accurate information on the health effect of air pollution to plan scientific, effective and well targeted strategies to reduce these effects. In July 2002 the European Parliament and the Council adopted the Decision 1600/2002/EC on the Sixth

Community Environment Action Programme (Sixth EAP). This Programme sets out the key environmental objectives to be attained in the European Community, one of which (Article 2) is to establish "….a high level of quality of life and social well being for citizens by providing an environment where the level of pollution does not give rise to harmful effects on human health …"(1). The activities of the European Commission to implement the Sixth EAP currently take place within the Clean Air for Europe (CAFE) programme (2). This programme, launched in early 2001, aims at developing long-term, strategic and integrated policy advice to protect against significant negative effects of air pollution on human health and the environment. The World Health Organization (WHO) in support to the CAFE process, provided updated information on health effects of air pollutants establishing the project "Systematic Review of Health Aspects of Air Quality in Europe" (3) in the course of which the current state of knowledge concerning health impacts of air pollution has been reviewed. The body of evidence of air pollution effects on health at the pollution levels currently common in Europe has been considerably strengthened by the contribution of both epidemiological and toxicological studies. The latter provide new insights into possible mechanisms to analyse the hazardous effects of air pollutants on human health and complement the large body of epidemiological evidence, showing, for example, consistent associations between daily variations in air pollution and some health outcomes. Exposure to ambient air pollution has been linked to a number of different health outcomes, starting from modest transient changes in the respiratory tract and impaired pulmonary function, to restricted activity/reduced performance, emergency room visits and hospital admissions and mortality. There is also increasing evidence of air pollution adverse effects not only on the respiratory system, but also on the cardiovascular system. This evidence stems from studies on both acute and chronic exposure. Short-term epidemiological studies suggested that a number of sources are associated with health effects, especially motor vehicle emissions, and also coal combustion. These sources produce primary as well as secondary particles, both of which have been associated with adverse health effects. If long-term exposure to a specific pollutant is linked to some health effects, cohort studies provide a basis to estimate chronic diseases and lifespan reduction in a given population. This is the case for mortality linked to PM long-term exposure. An expert group led by WHO – the Joint UNECE/WHO-ECEH Task Force on Health Aspects of Long Range Trans-boundary Air Pollution – recommended the use of risk coefficients from the American Cancer Society (ACS) study (4) to estimate the effects of chronic exposure to particulate matter (PM) on life expectancy in Europe. This study is the largest cohort study published in the scientific literature on the association between mortality and exposure to PM in air, and has involved 550,000 persons between 1982 and 1998. The risk estimated from this study were also used in the WHO Global Burden of Disease project (5). This project estimated that exposure to fine PM in outdoor air leads to about 100,000 deaths and 725,000 years of life lost each year in Europe. It is clear that there is a significant health risk associated with PM. It is also evident that there is a yet not known safe threshold for exposure but that there appears to be a linear relationship between exposure and risk. In addition, it has not yet been possible to identify with confidence which PM chemical constituents are primarily responsible for the different health effects. Therefore, even though the evidence on the relationship between exposure to different air pollutants and health effects has increased considerably over the past few years, there are still large uncertainties and important gaps in knowledge. These gaps can be reduced only by targeted scientific research. Areas in which such research is urgently needed include exposure assessment, dosimetry, toxicity of different components, biological mechanisms of effects, susceptible groups and individual susceptibility (taking into account gene–environment interactions), effects of mixtures versus single substances, and effects of long-term exposure to air pollution. The “Systematic Review” clearly demonstrated the need to set up a more comprehensive air pollution and health monitoring and surveillance programme in different European cities. Air pollutants to be monitored include coarse PM, $PM_{2.5}$,PM_1, ultrafine particles, PM chemical composition, including elemental and organic carbon, and gases such as ozone, nitrogen dioxide and sulphur dioxide. The value of black smoke and ultrafine particles as indicators of traffic-related air pollution should also be evaluated. Furthermore, periodic surveillance of health effects requires better standardization of routinely collected health outcome data. The “Systematic Review” also showed the need of a system to maintain a literature database and develop meta-analysis in order to monitor research findings, summarize the literature on health effects and health impact assessment.

7.2. Air Pollution and Health

Ambient air pollution consists of a highly variable, complex mixture of different substances, which may occur in the gas, liquid or solid phase. Several hundred different components have been found in the troposphere, many of them potentially harmful to human health and the environment. The main sources of air pollution are transport, power generation, industry, agriculture, and heating. All these sectors release a variety of air pollutants – sulphur dioxide, nitrogen oxides, ammonia, volatile organic substances, and particulate matter – many of which interact with others to form new pollutants. These are eventually deposited and have a whole range of effects on human health, biodiversity, buildings, crops and forests. Air pollution results in several hundreds of thousands of premature deaths in Europe each year, increased hospital admissions, extra medication, and the loss of millions of working days. The health costs for the European Union are huge. The pollutants of highest concern for human health are airborne particulates and ozone – indeed no safe levels have yet been identified for either of them. Nevertheless, the "Systematic Review" focused on three pollutants: particulate matter (PM), ozone and nitrogen dioxide, as requested by the CAFE Steering Group. This is not to imply that other substances do not pose a considerable threat to human health and the environment at the current levels present in Europe. It should also be mentioned that PM itself is a complex mixture of solid and liquid constituents, including inorganic salts such as nitrates, sulphates and ammonium and a large number of carbonaceous species (elemental carbon and organic carbon). Thus PM implicitly covers a number of different chemical pollutants emitted by various sources. The term 'particulate matter' (PM) is used to describe airborne solid particles and/or droplets. These particles may vary in size, composition and origin. Several different indicators have been used to characterize ambient PM. Classification by size is quite common because size governs the transport and removal of particles from the air and their deposition within the respiratory system, and is at least partly associated with the chemical composition and sources of particles. Based on size, urban PM tends to be divided into three main groups: coarse, fine and ultrafine particles. The border between the coarse and fine particles usually lies between 1 μm and 2.5 μm, but is usually fixed by convention at 2.5 μm in aerodynamic diameter ($PM_{2.5}$) for measurement purposes. The border between fine and ultrafine particles lies at about 0.1 μm. PM_{10} is used to describe particles with an aerodynamic diameter smaller than 10 μm. The particles contained in the PM_{10} size fraction may reach the upper part of the airways and lung. Figure 7.1 shows schematically where particles are deposited in the respiratory tract, depending on their size. Smaller particles (in particular $PM_{2.5}$) penetrate more deeply into the lung and may reach the alveolar region. Ultrafine particles contribute only slightly to PM_{10} mass but may be important from a health point of view because of their large numbers and high surface area. They are produced in large numbers by combustion (especially internal combustion) engines. As reported in (3) the most severe effects in terms of the overall health burden include a significant reduction, by a year or more, in average life expectancy linked to the long-term exposure to high levels of air pollution due to fine PM. Many studies have found that fine particles (usually measured as $PM_{2.5}$) have serious effects on health, such as increased mortality rates and emergency hospital admissions for cardiovascular and respiratory reasons. Thus there is good reason to reduce exposure to such particles. Coarse particles (usually defined as the difference between PM_{10} and $PM_{2.5}$) seem to have effects on, for example, hospital admissions for respiratory illnesses, but their effect on mortality is less clear.



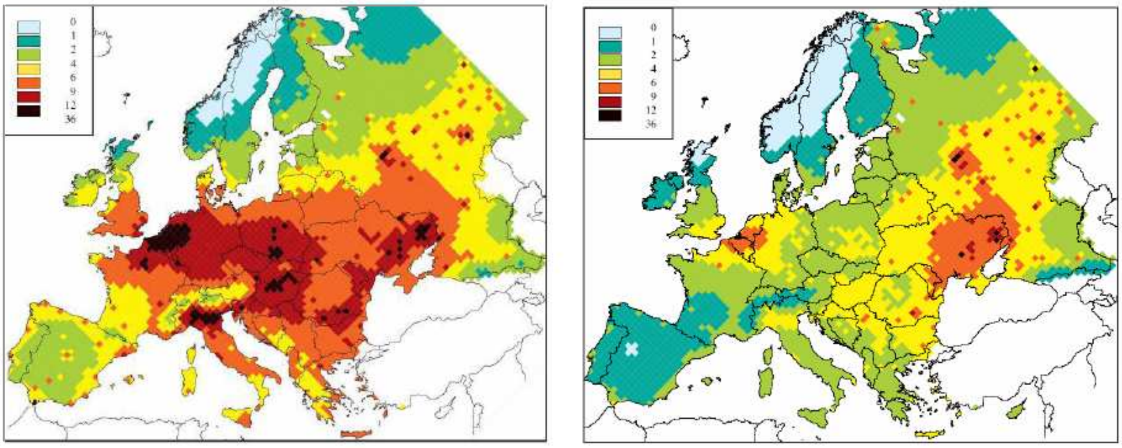
Source: W.G. Kreyling, adapted from International Commission on Radiological Protection.

Figure 7.1 *Deposition probability of inhaled particles in the respiratory tract according to particle size.*

Similarly, ultrafine particles are different in composition, and probably to some extent in effect, from fine and coarse particles. Nevertheless, their effect on human health have been insufficiently studied to permit a quantitative evaluation of health risks due to exposure to such particles. As stated above, PM in ambient air has various sources. In targeting control measures, it would be important to know if PM from some sources or of a specific composition gave rise to special health concern due to their high toxicity. The few epidemiological studies that have addressed this important issue specifically suggest that combustion sources are particularly important for health. Toxicological studies have also pointed to primary combustion derived particles as having an higher toxic potential. These particles are often rich in transition metals and organic compounds, and also have a relatively high surface area. By contrast, several other single components of the PM mixture (e.g. ammonium salts, chlorides, sulphates, nitrates and wind-blown dust such as silicate clays) have been shown to have a lower toxicity in laboratory studies. Despite these differences found among the constituents studied in laboratory, it is currently not possible to quantify the contributions of the different sources and different PM components on the health effects caused by exposure to ambient PM.

7.2.1 Modelling approach on health impact

Health impact assessment allows to quantify the effects of exposure to an environmental hazard. It plays a central role in assessing the potential health effects of different policies and measures, thereby providing a basis for decision-making. A detailed knowledge of several factors is required for any such assessment. Crucial information on exposure to air pollutants is provided by an integrated approach on ambient air quality monitoring and modelling study. Air quality modelling, particularly the Integrated Assessment Modelling (IAM), is important in linking pollution levels to emission sources and integrating population data, findings from epidemiological studies, information about the formation and dispersion of fine particles in the atmosphere, assessment of current and future levels of emissions of fine particles and their precursors. In the frame of the UN-ECE Convention on Long-Range Trans-boundary Air Pollution (CLRTAP), and in the context of the Community Environmental policies of the EU Commission, the RAINS-Europe model provides one of the most relevant examples of successful application of Integrated Assessment Modelling (IAM). The RAINS model (6), developed at the International Institute for Applied Systems Analysis (IIASA), considers emissions of SO_2, NO_x, PM_{10}, $PM_{2.5}$, VOC and NH_3, provides deposition and concentration maps and addresses threats to human health posed by fine particulates (7). The assessment of fine particle health impacts is implemented through the Life Expectancy Reduction indicator (LER), defined as months lost attributable to $PM_{2.5}$ concentrations. Awaiting further refinements in the scientific disciplines, the quantitative implementation should be considered as preliminary and needs to be revised as soon as more substantiated scientific information becomes available. The Task Force on Health of the United Nations Economic Commission, when conducting the in-depth review of the RAINS approach for modelling health impacts of fine particles (TFH, 2003), noted: “some data suggested that different components contributing to $PM_{2.5}$ mass might not be equally hazardous”. In particular, the discussion focused on the role of the secondary inorganic aerosols (including nitrates and sulphates). It concluded that, due to the absence of compelling toxicological data about the active different PM components of a complex mixture, it was not possible to quantify the relative health impact importance of the main PM components at this stage. Therefore, it was recommended to relate health impacts to total mass of $PM_{2.5}$ until more specific evidence becomes available (8). The methodology used in the RAINS model, at European and national scale, to estimate losses in life expectancy due to air pollution represents an initial implementation assessing the implications of present and future European policies to control exposure to particulate matter. In Figure 7.2, an example of the changes in life expectancy loss in EU in 2000 and in the interim objective in 2020 (9) is reported.



2000

Strategy in 2020

Figure 7.2 *Changes in EU life expectancy loss in 2000 and in the interim objective in 2020 (Strategy).*

The impact assessment of different policies is based on the analysis of a set of technological measurements, within the RAINS model, relating to various emission reduction scenarios. The ambition level of the Strategy is based on a set of specific measurements which would need to be undertaken at Community and Member State level. In recent years, some European countries such as, among others, Italy, have tackled the issue of implementing the RAINS model at national level, introducing higher spatial resolution in similar models, pursuing the ultimate objective of a more adequate response to the need of evaluating, at national level, cost-effective policy measures to reduce air pollutant emissions, and consequently, the pressure on environment and human health. As a result, the RAINS-Italy model (10) as the national version of the RAINS-Europe model was defined considering as emission source areas either the nation as a whole or the 20 administrative Regions. In a recent work (11), the RAINS-Italy model was used to assess the emission reduction strategies followed in the Regional Air Quality Management Plans (AQMPs) to meet environmental quality targets by means of Technical and Non-Technical Measures. Regarding health impacts, the most important Italian metropolitan and industrial areas show an average Life Expectancy loss ranging between 12 to 23 months in the 2010-CLE scenario. This higher resolution map, yet reported in Chapter 2 as Figure 2.3a), shows a better definition of the hot spots present in the urban areas of Turin, Milan, Rome and Naples, as well as in the industrial sites of eastern Sicily and Taranto, in the Apulia region (12). The above mentioned study showed that if compared to the 2010 CLE scenario, in the 2010 AQMP scenario the improvement in the average Life Expectancy loss indicator (Figure 2.3b)) is of 1 month only in Lombardy (11).

7.2.2 Indoor vs outdoor air pollution

As it is the case for other air pollutants, the total exposure of an individual to suspended particulate matter (of whatever size) is the result of contributions from the two microenvironments, outdoor air and indoor air. The indoor air compartment can be further subdivided into homes, restaurants, car, buses and aircraft, workplaces etc. Consequently, in studies to detect and quantify the health effects of particles, attention must be paid that exposure is characterised adequately. Generally there are two different ways to obtain such characterization. One is by *measuring* total air exposure using personal sampling: the persons under study are provided each with a personal sampler that they have to carry on them or position as close to them as possible for 24 hours consecutively. Since this is cumbersome for a study participant, the following alternative can be used: total exposure is *modelled* taking into account the time spent in the various microenvironments (indoors and outdoors) and the concentrations observed in these microenvironments. Personal sampling provides a concentration level that represents the integration of all the concentration levels in all compartments visited by the studied person during the 24-h (or longer) measurement period and, thus, it cannot detect the individual contribution of any compartment. In contrast, the modelling process using the combination of the pollutant concentrations in the different microenvironments and the time spent therein permits to assess the contribution of total exposure to each of these microenvironments. This kind of source apportionment can be of great help to decide what measurements should receive priority in controlling pollutant concentrations. A recent publication on exposure to $PM_{2.5}$ describing the results of a model approach (13) stated that the “indoor-residential” microenvironment had the greatest influence on total exposure to $PM_{2.5}$, compared to the other microenvironments considered, namely outdoor and non-residential indoor (office, school, store, restaurant, bar, in-vehicle). It turned out that the outdoor compartment was responsible for a *direct* contribution of about 5% on average. Another 35% was due to an *indirect* contribution via infiltration of outdoor air into indoor spaces. Thus, about 60% of the total exposure to $PM_{2.5}$ could not be influenced by control measurements taken to reduce outdoor air $PM_{2.5}$ levels.

7.3 Inorganic Air Pollutants

7.3.1 Gaseous matter

Air pollution by inorganic gaseous matter was dealt with since the first major pollution events (i.e. the Great Smog of London, 1952; etc.) put on evidence the strict relationship between levels of chemical species in the ambient (and indoor) air their harmful effects on health and ecosystems. Among inorganic gases, carbon monoxide (CO) is one of the most common air pollutants. It has a low reactivity and a low water solubility and it is mainly released into the atmosphere as a product of incomplete combustion. CO is not only directly released in the air, but can also originate from the chemical reactions of organic air pollutants, such as methane. Its latency in the atmosphere is about three months. Since at moderate latitudes air masses travel for months and since the CO formation from organic air pollutants takes place everywhere in the atmosphere, a global background level of CO exists, ranging between 0.05 and 0.15 ppmv (0.06 and 0.17 mg m^{-3}) (14). It is estimated that about one-third of CO, including that derived from hydrocarbon oxidation, originates from natural sources. CO levels in busy city streets are higher than those present near highways, since the amount of CO emissions per kilometre strongly decreases with vehicle speed and also because ventilation in city streets is less. Ambient CO levels are usually highest in winter, because cold engines release much more CO than hot engines and also because the atmosphere tends to be more stable than in summer. It has to be reminded, however, that usually CO ambient levels do not exceed neither WHO guidelines for health protection nor the limits of the EU directives on air quality. Although CO is hardly removed from the air in atmospheric transport at continental level, long range transport does not lead to concentrations of concern at both rural and urban background level. Also at points of high traffic in large cities, levels exceeding legislation are only occasionally observed. Industrial areas may be affected by large CO emissions; however, when these emissions are released through high chimneys, local ambient concentrations show poor increases and do not pose risks for human health. CO toxicity patterns are linked to its reaction with haemoglobin in the human blood to form carboxy-haemoglobin (COHb). The affinity of haemoglobin for CO is 200- 250 times higher than for oxygen, and as a result this binding reduces the oxygen carrying capacity of the blood and impairs the release of oxygen to extra vascular tissues. The most important variables determining the COHb level are CO in inhaled air, duration of exposure and lung ventilation. Physical exercise accelerates the CO uptake process. The formation of COHb is a reversible process; however, the half-life elimination of COHb is much longer in the foetus than in the pregnant mother. The effects of CO exposure on cardiovascular disease have been studied for a long time (15). However, only limited information is available about the possible cardiac effects of gaseous pollutants at concentrations close to those present in ambient air. Apart from hazards due to high CO concentrations, other health effects seem to originate from the association between CO and other gaseous and particulate matter, especially exposure to exhausts from motor engines. Although attention has recently been focused on the cardiovascular effects of PM, few studies show evidence of the relationship between some cardiovascular diseases and the exposure of different populations to road traffic exhausts. For example, experimental studies have demonstrated mild cardiac effects from both sulphur dioxide (SO_2) and ozone (O_3)(16). Other studies, where personal exposure to different pollutants has been investigated, have suggested that the estimated cardiac effects attributed to gases, including SO_2, are actually effects of other pollutants, specifically PM (17). At this stage of knowledge, however, it is difficult to differentiate between the effects of PM and those of gases because people are normally exposed to both types of pollutants at the same time. Because of these uncertainties, it seems prudent to further investigate both the effects that low concentrations of gaseous pollutants, alone or in combination with PM, might have on cardiovascular diseases, and the possibility that the associations with gaseous pollutants may actually reflect the effects of PM or some component that is not currently being studied for its health effects (16). Anthropogenic sulphur dioxide (SO_2) results from the combustion of sulphur containing fossil fuels (mainly coal and heavy oils) and the smelting of sulphur containing ores. Over the past years, however, there has been a net tendency towards emission reduction in Countries where low-sulphur fuels and emission control measures have been adopted. In addition, the source pattern has changed and moved from small multiple sources (domestic, commercial, industrial) to large single sources releasing SO_2 from tall stacks. Volcanoes and oceans are the major natural sources of SO_2. After being released in the atmosphere, sulphur dioxide is further oxidized to sulphate ($SO_4^{=}$) and sulphuric acid forming an aerosol often associated with other pollutants in droplets or solid particles having a wide range of sizes. SO_2 and its oxidation products are removed from the atmosphere by wet and dry deposition. Nowadays, it is also recognized that sulphate aerosols play an important cooling role in the radiative climate of the Earth through the phenomena of sunlight scattering in cloud free air and as cloud condensation nuclei. Sulphur dioxide is an irritant and when inhaled at high concentrations may cause breathing difficulties in people exposed to it. People suffering from asthma and chronic lung disease may be especially susceptible to the adverse effects of sulphur dioxide. Nevertheless adverse effects from high concentrations of SO_2 have been observed both on healthy people and asthma patients (18). Oxidized nitrogen compounds (NO_2, NO_x, NO_y) and ozone (O_3) join common patterns in atmospheric formation chemistry, environmental fate and adverse effects on health and the ecosystem. NO is directly released by all combustion processes; once in the atmosphere, it reacts with oxygen and a number of other inorganic (e.g. O_3, OH radical, halogens) and organic (VOCs) gases to form NO_2, NO_3, HONO, HNO_3, PAN, nitro – PAH and other organic and halogen nitrates, in the gaseous or particulate phase. Ozone and oxidized nitrogen compounds are strongly oxidant and this aspect mainly characterizes their harmful health action. In particular, the oxidizing potential of these compounds is commonly referred to as “odd oxygen” (Ox) or “odd nitrogen” (NO_x), i.e families of chemical compounds that interconvert rapidly among themselves on time scales that are shorter than those necessary to form or destroy the family . Another family is that defined as “NO_z”, which refers to the sum of NO_x oxidation products (19).

$$NO_x = NO + NO_2 \qquad [1]$$

$$O_x = \Sigma\ (O(^3P) + O(^1D) + O_3 + NO_2) \qquad [2]$$

$$NO_z = \Sigma\ (HNO_3 + HNO_4 + NO_3 + 2NO_2O_5 + PAN + \text{other organic nitrate} + \text{halogen nitrate} + \text{particulate nitrate}) \qquad [3]$$

Unlike some other compounds whose formation rates vary directly with the emissions of their precursors, O_3 differs in that its production changes nonlinearly with the concentrations of precursors. At the low NO_x concentrations found in most environments ranging from remote continental areas to rural and suburban areas, the O_3 net production increases with the increasing of NO_x. At the high NO_x concentrations found in downtown metropolitan areas especially near busy streets and roadways and in power plants, there is a net destruction of O_3 by titration reaction with NO. Between these two regimes is a transition stage in which O_3 shows only a weak dependence on NO_x concentrations. In the high NO_x regime, NO_2 scavenges OH radicals which would otherwise oxidize VOCs to produce peroxy radicals, which in turn would oxidize NO into NO_2. In the low NO_x regime, VOC oxidation generates, or at least does not consume, free radicals, and O_3 production varies accordingly. Sometimes the terms ‘VOC-limited’ and ‘NO_x-limited’ are used to describe these two regimes; also, the terms NO_x-limited and NO_x-saturated are used. The chemistry of OH radicals, that are responsible of the initiation of hydrocarbons oxidation, shows a behaviour similar to that of O_3 with respect to NO_x concentrations (19). These considerations introduce a high degree of uncertainty into attempts to relate changes in O_3 concentrations to precursors emissions. It should also be noted at the outset that in a NO_x-limited (or NO_x-sensitive) regime, O_3 formation is not insensitive to radical production or the flux of solar UV photons, but O_3 formation is more sensitive to NO_x. For example, global tropospheric O_3 is sensitive to CH_4 concentrations even if the troposphere is predominantly NO_x-limited. To get information about the O_3-NO_x-VOCs relationships and sensitivity, the ratio of summed VOC to NO_x concentrations determining whether conditions are NO_x-sensitive or VOC sensitive is not sufficient to describe O_3 formation, since other factors - i.e. the effect of biogenic VOCs (which are not present in urban centres in early morning) - and some important individual differences in VOCs ability to generate free radicals, have to be considered. The difference between NO_x-limited and NO_x-saturated regimes is also reflected in measurements of hydrogen peroxide (H_2O_2), another strong oxidant of ambient air. H_2O_2 formation takes place by self-reaction of photo chemically generated HO_2 radicals, so that there is large seasonal variation in H_2O_2 concentrations, and values in excess of 1 ppb are mainly limited to summer months, when photochemistry is more active (20). Hydrogen peroxide is produced in abundance only when O_3 is produced under NO_x-limited conditions. The transition from NO_x-limited to NOx-saturated conditions is highly space and time dependent. In the upper troposphere, responses to NO_x additions from commercial aircraft have been found that are very similar to those in the lower troposphere. Moreover, the complex interplay between chemical and meteorological processes gives rise to uncertainties in understanding ozone formation. This is especially true for regions of complex topography. In coastal regions around the Mediterranean Basin, for instance, the combination of mountain and sea breeze re-circulations significantly affects ozone phenomenology. Ozone can also have very specific distributions in mountain areas, and observed concentrations differ significantly between mountain peaks and valleys (20). Nitro-polycyclic aromatic hydrocarbons (nitro- PAHs) are generated from incomplete combustion processes through PAHs electrophilic reactions in the presence of NO_2 (21). Among combustion sources, diesel emissions have been identified as the major source of nitro-PAHs in ambient air. Direct emissions of nitro-PAHs in PM vary with the type of fuel, vehicle maintenance, and ambient conditions (22). In addition to being directly released, nitro-PAHs can also be formed from both PAHs gaseous and heterogeneous reactions with gaseous nitrogenous pollutants in the atmosphere. After formation, nitro-PAHs with low vapour pressures (such as 2NF and 2NP) immediately migrate to particles under ambient conditions; therefore harmful effects related to nitro – PAHs are better investigated in the organic fraction of particulate matter. Also in indoor environments NO_2 plays a key role in adverse health effects. It is indeed produced by NO reactions with ozone or peroxy radicals generated by indoor air chemistry involving O_3 and unsaturated hydrocarbons such as terpenes found in air fresheners and other household products (23). Nevertheless indoor NO_2 is also contributed by indoor – outdoor air exchange. The relationship between personal NO_2 exposure and ambient NO_2 can be modified by the indoor environment. For example, during the infiltration processes, ambient NO_2 can be lost through penetration and decay (chemical and physical processes) in the indoor environment, and the concentration of indoor ambient NO_2 is not just the ambient NO_2 concentration but the product of the ambient NO_2 concentration and the infiltration factor (Finf, or α if people spend 100% of their time indoor). Indoor NO_2 is removed by gas phase reactions with ozone and assorted free radicals and by surface promoted hydrolysis and reduction reactions. The concentration of indoor NO_2 also affects PAN decomposition. These processes are important not only because they influence the indoor NO_2 concentrations to which humans are exposed, but also because some products of indoor chemistry may confound attempts to examine associations between NO_2 and health. As a matter of fact, NO_2 is an oxidant and lipid per-oxidation is believed to be a major molecular event responsible for its toxicity. As a result, there has been considerable attention paid to NO_2 effect on the antioxidant defence system in the epithelial lining fluid and in pulmonary cells. Repeated exposure to indoor NO^2 at concentrations ranging from 0.04 to 33 ppm has been shown to alter low molecular weight antioxidants such as glutathione, vitamin E, and vitamin C, as well as some enzymes involved in cell oxidant homeostasis. NO_2 effects on structural proteins of the lungs have raised concern because elastic recoil is lost after exposure. It has been observed that the latter increases collagen synthesis. This, in turn, shows increases in total lung collagen which, if sufficient, could result in pulmonary fibrosis after longer periods of exposure. Such correlation has yet to be confirmed by in vivo studies involving NO_2 exposure; nevertheless some evidence shown in animal studies about asthma, emphysema and other lung diseases. Similarly to O_3, NO_2 is absorbed throughout the lower respiratory tract, but the major delivery site is the centriacinar region, i.e, the junction between the conducting and respiratory airways in humans and animals (21). Ozone is a strong oxidant, and as such can react with a wide range of cellular components and biological materials: damage can occur to all parts of the respiratory tract. The time pattern of these changes in the respiratory system, as determined in laboratory animals as well as in epidemiological investigations, is complex. During the first few days of exposure, inflammation occurs and then persists at an attenuated level. At the same time, epithelial hyperplasia progresses, and reaches a plateau after about one week of exposure. When the exposure ceases, these effects slowly disappear. In contrast to this, interstitial fibrosis increases slowly and can persist even when exposure ceases. In a large number of controlled human studies, significant impairment of pulmonary function has been reported. Field studies in children, adolescents, and young adults have indicated that pulmonary function decrements, similarly to those observed in controlled studies, can occur as a result of short term exposure to ozone concentrations in the range of 120-240 $\mu g\ m^{-3}$ and higher. In comparison with adults, children have a higher intake of ozone and other air pollutants. This is due to a higher basal metabolic rate, resulting in a higher breathing volume per minute and a higher breathing frequency. Furthermore, their respiratory tract is still under development until the age of six and a half, and it is therefore more susceptible to the inflammatory effects of ozone. Children's immune systems are not yet fully developed and are generally under bigger stress. For these and other reasons, children are at higher risk when exposed to ambient ozone concentrations. Hospital admissions for respiratory causes and exacerbation of asthma are observed both in exposures to ambient ozone (and co-pollutants) and in controlled exposures to O_3 alone. Other groups at risk are those people exercising outdoors during evening hours or whenever ozone concentrations tend to be highest (e.g. in photochemical smog events). Due to the irritant nature of ozone, capable of inducing airway inflammation and broncho-constriction, asthma patients are deemed to be at enhanced risk from exposure to ozone and photochemical smog, because inflamed airways contribute to the pathogenesis and exacerbation of the disease and to morbidity and mortality for asthma. Results from recent epidemiologic studies have suggested that ozone might have serious cardiovascular effect (24 and references therein). Although a large number of toxicity animal studies have been performed on respiratory and other effects of NO_2, O_3 and other gaseous pollutants on metabolic and physiological functions (body weight, hepatic, renal, brain, etc.), results are often affected by serious limitations, due to both the necessary animal-to-human extrapolation of concentration-response data and the fact that controlled exposures to a single pollutant alone provide incomplete information. Human clinical studies attempt to recreate in laboratory the atmospheric conditions of ambient pollutant atmospheres, paying great attention to concentrations, duration, timing, and other conditions which may impact responses. These studies allow the measurement of health symptoms and physiological markers resulting from air breathing. This carefully controlled environment allows researchers to identify responses to individual pollutants, to characterize exposure-response relationships, to examine interactions among pollutants, and to study the effects of other variables such as exercise, humidity, or temperature. Susceptible populations, including individuals with acute and chronic respiratory and cardiovascular diseases, can participate with appropriate limitations based on subject comfort and protection from risk. Endpoint assessment has traditionally included symptoms and pulmonary function, but more recently a variety of markers of pulmonary, systemic, and cardiovascular function have been used to assess pollutant effects. It is reasonable to consider, however, that human clinical studies have limitations. For practical and ethical reasons, studies must be limited to relatively small groups, to short durations of exposure, and to pollutant concentrations that are expected to produce only mild and transient responses. Findings from the short-term exposures in clinical studies may provide limited insight about the health effects of chronic or repeated exposures. Moreover, the choice of previous- and after-exposure time lags for the observation of health effects is critical in assessing the role of a pollutant in toxicity events. Many studies have shown that NO_2 has a fairly consistent, immediate effect on health outcomes, including respiratory hospitalizations and mortality. Several studies also observed significant NO_2

effects over longer cumulative lag periods, suggesting that in addition to single-day lags, multiday lags should be investigated to fully capture a delayed NO_2 effect on health outcomes. Finally it should be kept in mind that, although many biochemical changes are not necessarily toxic manifestations of the pollutant per se, such changes may anyway impact the metabolism and toxicity of other chemicals in humans and animal species (21). The EU regulates the main harmful inorganic gaseous pollutants by the EC legislation of the Air Quality Framework (25). Other legally binding Protocols have been established since the 1979 Geneva Convention on Long Range Transboundary Air Pollution (LRTAP) (26). Guideline levels aimed at health and environment protection have been set by WHO and other institutions, too, to be used for impact assessment. The first edition of the WHO "Air quality guidelines for Europe (AQG)" was published in 1987 (27). To determine critical or guideline levels, quantitative relationships between the pollutant exposure and its studied effect are needed. However, any such relationships have a certain degree of uncertainty, and the data necessary to produce them are often scarce. Therefore, the establishment of guideline values, such as levels at which acute (or chronic) effects on public health or ecosystems are likely to be not relevantly harmful, impose the support of biological, clinical and epidemiological evidence, often not available or inadequate. Different legal tools aimed at protecting and improving the health and quality of ecosystems from air pollution have been used in recent years. The 1992 fifth action programme of the European Commission (EAP) on the environment recommended "the establishment of long-term air quality objectives" for many inorganic gaseous pollutants (CO, NO_2 and NO_x, SO_2, O_3). The list of key requirements, also includes the need for "studies to analyze the effects [on health ant ecosystems] of the combined action of various pollutants or sources of pollution and the effect of climate on the activity of the various pollutants examined". Under the 5th EAP the Air Quality Framework was established, within which the 96/62/EC Directive and the following four Daughter Directives have been adopted. This law establishes limits and threshold values for SO_2, NO_2 and NO_x under the 99/30/EC, CO under the 2000/69/EC and O_3 under the 2002/03/ EC for EU Member States. In the 6th EAP, further steps have been taken toward health / environment protection by the Clean Air for Europe (CAFE) programme. The CAFÉ is conceived as a process based on technical analysis and policy development to achieve the adoption of a Thematic Strategy on Air Pollution. The major elements of the CAFE programme are outlined in Communication COM(2001)245 (2). The programme, launched in early 2001, aims at the development of a long-term, strategic and integrated policy advice to protect against the significant negative effects of air pollution on human health and the ecosystem. Within this process, the 2008/50/EC Directive on ambient air quality and cleaner air for Europe has been adopted and will enter into force as from 11 June 2010, when the Directives 96/62/EC, 1999/30/EC, 2000/69/EC and 2002/3/ EC shall be repealed.

7.3.2 Particulate Matter

The history of air pollution is very long, and since its very first occurrence – smoke from heating and cooking activities in prehistoric dwellings - particles have been addressed as one of the most important issues. Pollution from combustion sources and specifically suspended particles have been responsible for the most relevant pollution disasters (e.g. Mause Valley, Belgium, 1930, the Big Smoke, London, 1952), which led to increasing efforts towards pollution monitoring, the understanding of main pollution processes, political awareness and, finally, regulations. At European level, pollution from particulate matter (PM) has been first addressed by the First Daughter Directive (1999/30/EC) to the Air Quality Framework Directive (1996/62/EC); recently, a new Directive (2008/50/EC, published in June 2008) summarised most of the existing legislation on ambient air and introduced some new requirements. As far as PM is concerned, the First Daughter Directive addressed only PM_{10}, setting limits for its annual average concentration (40 $\mu g\ m^{-3}$) and the number of exceedances (35 per year) of the 50 $\mu g\ m^{-3}$ daily concentration limit. Air quality limits also for $PM_{2.5}$ were introduced only by the recent Directive 2008/50/EC (25 $\mu g\ m^{-3}$, with a 20% margin of tolerance that will be reduced to zero on 1st January 2015). In addition to the measurement of PM mass concentration, Directive 2008/50/EC also includes the measurement of $PM_{2.5}$ chemical composition in background sites, listing a number of components that must necessarily be determined in each $PM_{2.5}$ sample (sulphate, nitrate, chloride, sodium, ammonium, potassium, calcium, magnesium). This new issue is related to the increasing awareness of the complexity of this “pollutant”, which is a mixture of thousands of different chemical species, each one with its own properties and possibly its own environmental and health effects. Unlike gaseous pollutants, where the concentration is generally sufficient to define the system, for the atmospheric aerosol many parameters have to be defined. Physical parameters include the geometric and aerodynamic diameter, shape (spheres, fibres, etc.), phase (solid, liquid, mixture of both), density, electrical charge, hygroscopicity etc. and are necessary to understand particles behaviour in the atmosphere as well as inside the respiratory system. The most complex issue in aerosol characterisation, however, is its chemical composition, which includes a variety of components, whose determination requires a variety of analytical techniques. The knowledge of health effects caused by inhalation of atmospheric particles has been improved a lot during the last decade and there is no doubt that particles can be harmful to human health. PM is associated with a wide variety of both acute and chronic cardiovascular and respiratory effects. Acute effects include increased hospital admittance for respiratory disease or premature mortality for cardiovascular disease, while chronic effects include a number of diseases leading to longevity reduction. The increase in respiratory and cardiovascular morbidity and mortality is in the order of a few percent for a PM increase of 10 $\mu g\ m^{-3}$ (28-34). The study of the link between particulate matter and health is extremely complex and poses many problems, including the difficulties in assessing the role of particle size and particle composition, in quantifying the real exposure and understanding the biological mechanisms that are responsible for the effects, in evaluating the impact of the different sources and, last but not least, in detecting the real concentration and composition of the atmospheric aerosol. The size of atmospheric particles varies among five orders of magnitude, from a few nanometres to hundreds of micrometers. The size of the aerosol influences its lifetime in the atmosphere (and thus the spatial range of influence of any single source) as well as its pathway inside the human body. Basically, the atmospheric aerosol consists of three modes, which are closely linked to their formation mechanism: the coarse mode, predominantly mechanically generated (e.g. by erosion and by resuspension), the accumulation mode, produced by condensation from vapours and coagulation from smaller particles, and the nucleation mode, which includes particles smaller than 0.1 μm originating from combustion processes (e.g. vehicle exhausts, biomass burning). Natural aerosol, originating from the sea and the soil, is mostly in the coarse mode and is generally considered as less harmful than anthropogenic aerosol, generated by combustion sources, found mainly in the fine mode and able to penetrate deeply in the respiratory tree. The harmful role of nanoparticles, able to reach the alveoli and to be directly transported inside the body cells, is still a matter of debate. The chemical composition of an atmospheric particle depends on its source as well as on its "story" from the time of its emission or formation to the time when it reaches the receptor (e.g. the human body). Some particles are directly released from their source into the atmosphere (primary PM), but the characterisation of any emission source is quite complex, as it generally changes with time and operative conditions. In addition, once formed, particles often undergo chemical and physical transformations and for this reason what is measured at the receptor may be also very different from what is released at the source. Even more difficult to trace are the other particles formed in the atmosphere as a result of chemical reactions between gaseous compounds or gas-to-particle conversion; of particular relevance, in this framework, is the oxidation of biogenically released VOCs. Information about PM sources can be obtained by analysing their chemical composition. Only a limited number of compounds constitute more than 1% of the overall PM mass: a few metals (Al, Si, Fe), the main anions and cations (chloride, nitrate, sulphate, carbonate, sodium, ammonium, potassium, magnesium and calcium), elemental carbon and organic material. This last category is the most important, as it generally represents 20 – 60% of PM, but, unlike the other main components, it is not a single chemical compound but it is constituted by many hundreds of compounds, none of which constitute more than 1% of the total PM mass. Although the determination of the listed compounds is in most cases sufficient to obtain the mass closure (i.e the sum of the single components equals the gravimetric mass), the determination of micro-components is generally necessary to obtain a picture of PM sources and effects (35-45). Although quite complex, the determination of most inorganic PM components has been one of the targets of field research during the last 10-20 years. By determining inorganic PM macro-components it is possible to trace natural sources (sea-spray, desert dust, local crustal components) and to measure the contribution of secondary compounds (ammonium sulphate and ammonium nitrate); inorganic micro-components, on the contrary, may be of help in determining the contribution of anthropogenic sources, e.g. dust re-suspension and industrial sources (46-48). Much less understood and quantified is the organic fraction, as the chemical analysis is generally able to identify no more than 15-20% of total organic mass. Once we are able to measure PM concentration and to determine its chemical composition, we need to clarify the link between concentration and exposure. This is a critical point in the scientific studies about health effects, as the reference PM values are generally those measured by local Protection Agencies, i.e. outdoor values sometimes taken at traffic hotspots, while people generally spend most of their time in indoor environments, including homes, working places and vehicles, and only a small part of their time outdoors. Considerable work is still needed to develop models able to simulate the behaviour of individuals in indoor microenvironments. Also, we need information about the composition of indoor PM, that may greatly differ from the composition of outdoor particles (49-56). For example, in indoor environments we may be exposed to much more particles produced by peculiar sources such as domestic wood burning or cooking than to particles emitted by traffic sources. As a consequence of the many difficulties arising when relating PM concentration to the results of epidemiological studies, the scientific community is now trying to find a relationship between health effects and individual chemical components. This attempt requires the availability of long time series of PM composition study and is still in its infancy.

The other pathway to elucidate the link between PM and health effects is the study of the PM toxicological effects, that is the specific mechanisms that lead PM to cause the observed health impacts. These studies include animal models, human exposure during occupational activities and experimental exposures. The mechanisms of PM effects on human health are still quite uncertain, but given the variety and degree of observed health associations, it is likely that more than one of them are involved. Basically, particles entering the tissue cells may cause inflammation; researchers increasingly find that reactive oxygen compounds (in the PM or produced by stimulated cells) play a role. Because of the presence of particles in the respiratory tract, changes in the respiratory function may occur. Particles in the blood may increase viscosity, causing thrombosis or myocardial infarct. Of course, individuals with pre-existing deficiencies of the cardiovascular or respiratory system may suffer more severe effects (56-61). It is clear that a more integrated approach is needed to get insights into PM health effects. In particular, the link between health effect and PM component and size and the biological specific mechanism of its action requires further combined interdisciplinary studies.

7.4 Future Perspectives and Developments

Despite the increasing amount of data provided by both laboratory and field studies, the nature and role of aerosol particles responsible for health effects, as well as of gaseous mixtures especially in urban areas, is still a matter of debate. In the former case the issue is of importance also because the different constituents of the aerosol exhibit distinct sources and emission/formation processes. Therefore, linking toxicological and epidemiological impacts of atmospheric particulate matter to chemical composition is a key for the evaluation of effective pollution abatement strategies. Results of size-segregated aerosol chemical analyses for Italian stations have already been published during the last ten years and are available in the peer reviewed literature and in project reports (40). These data generally refer to sparse measurements employing multi-stage impactors in both urban (e.g, Bologna, Catania, Rome) and rural/background sites (e.g, Monte Cimone); information on the inorganic and organic composition of ultrafine to coarse particles have been retrieved by chemical determinations of size-segregated fractions. Nevertheless, an increasing series of data on the aerosol chemical composition and size-distribution has been provided by short-term intensive field studies performed in the frame of national and European research projects (46). During these experiments, state-of-the-art instrumentation has been deployed for aerosol characterization. In this view, a further step forward will be to identify systematic behaviours in the contributions of inorganic and organic chemical constituents as a function of particles size, and depending on site classification (urban, sub-urban, rural, marine, high-altitude, etc.), as well as to provide a summary of the constituents of ultrafine particles. This will help interpreting clinical and epidemiological observations under an enhanced awareness of the behaviour of particulate pollutants in different environments. Finally, a comparison with published results of analogous measurements performed in other European countries will be carried out, to identify singularities to be further investigated in the future. New directions of research in the field of understanding impact routes of ambient and indoor air on health relate to selected species showing a precise toxicant action and to their size-segregated behaviour in aerosols. In this view, research activities will be run concerning either the characterization or the toxicant and reactive behaviour of the water-soluble organic fraction of PM. Besides transition metals and PAHs, on which some peer-reviewed literature already exist, the chemical analysis of fine particulate samples has shown that even in urban areas the water-soluble fraction of the aerosol contains large amounts of poorly-characterized organic compounds (WSOC, “water-soluble organic carbon”), in contrast to the paradigm of many toxicological studies which attributes the organic-soluble and water-soluble fractions of the aerosol to organic and inorganic compounds, respectively. On the contrary, recent findings point to WSOC as a major agent for aerosol toxicity and oxidizing properties (56,116). Although a number of bioassays have been adopted in previous studies to provide fast and sensitive measurement of the aerosol chemical reactivity, mechanistic pathways for toxicity were not established. Relevant bioassays will be thus tested, for the scopes of evaluating the oxidative potential of airborne aerosol in humans and animals. Among possible bioassays, those will be selected which are sensitive to reactive oxygen species, like superoxide and hydrogen peroxide. The latter species, indeed, can be produced in biological liquids and tissues by organic compounds via redox reactions. Such tests include for instance those based on dithiothreitol (DTT) consumption rate, or employing dichlorofluorescin (DCFH) (56,156). The key importance of testing these methods to provide, i.e, an optimal application to the analysis of the water-soluble organic extracts of ambient aerosol samples is a matter of evidence. Finally, a state of- the-art analytical technique like the Aerosol Mass Spectrometry (AMS) will be employed for the quantitative mass determination of Ultra Fine Particles. This is at date an obligate step towards enhancing the knowledge about responsibilities of the atmospheric pollution on health impacts. Indeed, the AMS is currently the only technique providing unique information on the short-term processes controlling the concentration and composition of ultrafine particles and their interaction with larger particles. Moreover, the data analysis of the emerging results from AMS will allow comparison with the more consolidated outcomes from available measurements by multi-stage impaction methods.

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