Universitat
de les Illes Balears

DOCTORAL THESIS

2020

STUDY AND CHARACTERIZATION OF REGIONAL BACKGROUND ATMOSPHERIC AEROSOL IN THE BALEARIC ISLANDS, WESTERN MEDITERRANEAN

José Carlos Cerro Garrido

Universitat
de les Illes Balears

DOCTORAL THESIS

2020

Doctoral Programme of Chemical Science and Technology

STUDY AND CHARACTERIZATION OF REGIONAL BACKGROUND ATMOSPHERIC AEROSOL IN THE BALEARIC ISLANDS, WESTERN MEDITERRANEAN

José Carlos Cerro Garrido

Director: Jorge Pey Betrán

Director: Víctor Cerdà Martín

Tutor: José Manuel Estela Ripoll

Doctor by the Universitat de les Illes Balears

Universitat
de les Illes Balears

Dr Víctor Cerdà Martín, of the Universitat de les Illes Balears, and Jorge Pey Betrán, of the Instituto Pirenaico de Ecología

WE DECLARE:

That the thesis titles *Study and Characterization of regional background atmospheric aerosol in the Balearic Islands, Western Mediterranean,* presented by José Carlos Cerro Garrido to obtain a doctoral degree, has been completed under our supervision and meets the requirements to opt for an International Doctorate.

For all intents and purposes, we hereby sign this document.

Signature

Víctor Cerdà Martín

Jorge Pey Betrán

Palma, 2nd December 2020

This PhD thesis is composed by a compendium of scientific articles derived from the investigation carried out.

The complete list of references as well as the Impact Factor of the journals are shown below:

1. Cerro J.C., Cerda V., Pey J.: Trends of air pollution in the Western Mediterranean Basin from a 13-year database: A research considering regional, suburban and urban environments in Mallorca (Balearic Islands), Atmos. Environ., 103, 138-146, 2015. [Impact Factor: 4.012]

2. Cerro J.C., Cerdà V., Querol X., Alastuey A., Bujosa C., Pey J. Variability of air pollutants, and PM composition and sources at a regional background site in the Balearic Islands: Review of western Mediterranean phenomenology from a 3-year study. Science of the Total Environment 717 (2020) 137-177. [Impact Factor: 6.551]

3. Cerro J.C., Cerdà V., Caballero S., Bujosa C., Alastuey A., Querol X., and Pey J. Chemistry of dry and wet atmospheric deposition over the Balearic Islands, NW Mediterranean: source apportionment and African dust areas. Science of the Total Environment 747 (2020) 141187. [Impact Factor: 6.551]

Journals focused in aerosol science, or air quality, usually range Impact Factor from 0.5 to near 6, being the most prestigious journals Atmospheric Chemistry and Physics [Impact Factor: 5.414] and Science of the Total Environment [Impact Factor: 6.551].

Other publications related to this thesis:

Conference Papers:

1. José C. Cerro, Jorge Pey, Carles Bujosa, Sandra Caballero, Andrés Alastuey, Michael Sicard, Begoña Artiñano, Xavier Querol, *Regional background aerosols over the Balearic Islands over the last 3 years: ground-based concentrations, atmospheric deposition and sources*, Geopysical Research Abstracts, Vol. 15, EGU2013-14226, EGU General Assembly, Viena, Austria, 2013.

2. Michaël Sicard, Jorge Pey, Jose Carlos Cerro, Diego Lange, Sandra Caballero, Antonio Tovar-Sanchez, Rafael Morales-Baquero, Adolfo Comerón, Carles Bujosa, Xavier Querol, Begoña artiñano, Lucas Alados-Arboledas, Andres Alastuey, Francesc Rocadenbosch, Alvaro Muñoz, Constantino Muñoz, David García-Vízcaino, Jordi Bach, Xavier Bush, *Spanish activities in the framework of the ChArMEx project since 2009: a summary*, 1st Iberian Meeting on Aerosol Science and Technology , RICTA 2013, Évora, Portugal , 2013 (ISBN:978-989-20-3962-6)

3. J.C. Cerro, S. Caballero, C. Bujosa, A. Alastuey, X. Querol, J. Pey, *Aerosol deposition in Balearic Islands as overlook of the deposition in the western Mediterranean*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014. (ISBN: 978-84-695-9978-5)

4. J.C. Cerro, V. Cerdà, J. Pey, *Trends in air pollution between 2000 and 2012 in the Western Mediterranean: A zoom over regional, suburban an urban environments in Mallorca (Balearic Islands)*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014. (ISBN: 978-84-695-9978-5)

5. J. Pey, J.C. Cerro, S. Hellebust, H.L. Dewitt, B. Temime-Roussel, M. Elser, N. Pérez, A. Sylvestre, D. Salameh, G. Mocnik, A.S.H. Prévôt, Y. L. Zhang, S. Szidat, N. Marchand, *Ground based atmospheric monitoring in Mallorca and Corsica in summer 2013 in the context of ChArMEx: Results on number-size distributions, on-line and off-line aerosol chemistry, and volatile organic compounds*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014. (ISBN: 978-84-695-9978-5)

6. Jorge Pey, José Carlos Cerro, Stig Hellebust, H. Langley DeWitt, Brice Temime-Roussel, Miriam Elser, N. Pérez, Alexandre Sylvestre, Dalia Salameh, Grisa Mocnik, Andre Prévôt, Yanlin Zhang, Soenke Szidat, Nicolas Marchand, Atmospheric Monitoring in the Western

Mediterranean in Summer 2013: Overview of Physic-chemical Properties and Variability, AAAR 2014 Conference, Proceedings book.

7. H. Langley Dewitt, Jorge Pey, Stig Hellebust, Brice Temime-Roussel, Aurelie Mizzi, Dalia Salameh, Alexandre Sylvestre, Miriam Elser, N. Pérez, José Carlos Cerro, Jean-Luc Jaffrezo, Grisa Mocnik, Andre Prévôt, Nicolas Marchand, Comparison of the Sources of Organic Aerosol (OA) Using Aerosol Mass Spectrometry at Two Mediterranean Islands: Corsica and Mallorca, AAAR 2014 Conference, Proceedings book.

8. J.C. Cerro, J. Pey, N. Pérez, V. Cerdà, H.L. DeWitt , S. Hellebust, M. Elser, A.S.H. Prévôt, B. Temime-Roussel and N. Marchand, *Source apportionment of Organic Aerosol in a remote Mediterranean using a combination of offline and online approaches*. European Aerosol Conference 2016, Tours, France

9. J.C. Cerro, V. Cerdà and J.Pey, *Semi-quantitative methodology to assess efficiency of local air pollution abatement policies in contrast to national or continental ones*. European Aerosol Conference 2016, Tours, France

10. Cerro J. C., Cerda V., Querol X., Alastuey A., Pey J., *3-years background gas and aerosol measurements in Mallorca Island, in WMB: preliminary source apportionment outputs* 5th Iberian Meeting on Aerosol Science and Technology, IDAEA-CSIC, Barcelona, 2017.

Other publications not derived from this thesis: during this period José Carlos Cerro Garrido has collaborated with other works not corresponding to this Thesis:

Books:

José Carlos Cerro Garrido, Josep Ferran Bádenas Jovani, Francisco Javier Lladó Arrieta, Maria Luisa Tobar Santamaría, Carme Pons Bonafé, Paula Maria Elias Mir, *Qualitat de l'Aire a les Illes Balears 2010/2015*, Govern de les Illes Balears (ISBN: 978-84-697-5493-1) (517 pp).

Research papers:

1. Genestar C., Pons C., Cerro J. C., Cerdà V.: *Different decay patterns observed in a nineteenth-century building (Palma, Spain)*, Environ. Sci. Pollut. Res. 21(14): 8663-8672, 2014.

2. Alastuey A., Querol X, Aas W, Lucarelli F, Pérez N, Moreno T., Cavalli F., Areskoug H, Balan V, Catrambone M, Ceburnis D., Cerro J.C., Conil S., Gevorgyan L., Hueglin C., ImreK., Jaffrezo J.L., Leeson S.R., Mihalopoulos N., Mitosinkova M., O'Dowd C.D., Pey J., Putaud J.P., Riffault V., Ripoll A., Sciare J., Sellegri K., Spindler G., and Yttri K.E.: *Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013*, Atmos. Chem. Phys., 16, 6107–6129, 2016.

3. Kevin Berland, Clémence Rose, Jorge Pey, Anais Culot, Evelyn Freney, Nikolaos Kalivitis, Giorgios Kouvarakis, José Carlos Cerro, Marc Mallet, Karine Sartelet, Matthias Beckmann, Thierry Bourriane, Greg Roberts, Nicolas Marchand, Nikolaos Mihalopoulos, and Karine Sellegri, *Spatial extent of new particle formation events over the Mediterranean Basin from multiple ground-based and airborne measurements*, Atmos. Chem. Phys., 17, 9567–9583, 2017 (doi.org/10.5194/acp-17-9567-2017).

4. Pey J., Larrasoaña J.C., Pérez N., Cerro J.C., Castillo S., Tobar M.L., de Vergara A., Vázquez I., Reyes J., Mata M.P., Mochales T., Orellana J.M., Causapé J., 2020. *Phenomenology and geographical gradients of atmospheric deposition in southwestern Europe: results from a multi-site monitoring network*, Sci. Total Environ. 140745, https://doi.org/10.1016/j.scitotenv.2020.140745.

Conference Papers:

1. Mochales, T; Larrasoaña, JC; Pey, J; Pérez, N; Cerro, JC; Tobar, M; de la Parra, I; Castillo, S., Reyes, J; Mata, P. (2017) *Evaluación magnética de partículas atmosféricas (Proyecto Donaire)*. MAGIBER X (Magnetismo de Iberia). Valle del Grío (España. Septiembre 2017

2. Mochales, T; Larrasoaña, JC; Pey, J ;Pérez, N; Cerro, JC; Tobar, M; de la Parra, I; Reyes, J; Mata, P. (2017) *Preliminary magnetic evaluation of air quality monitoring in north-east Spain (DONAIRE Project)*. PAGES OMG 2017, Zaragoza, Mayo 2017.

3. Pey, J; JC, Larrasoaña ; Pérez, N; Cerro, JC ; Tobar, M; Mochales, T; de la Parra, I; de Vergara, A; Váquez, I; Reyes, J; Navarro, E; Sancho, MC (2017). *The DONAIRE project "Atmospheric deposition in natural and anthropized environments over northeastern Spain; integrated geochemical and magnetic characterization": first results*. conference: PAGES OMG 2017, Zaragoza, Mayo 2017

4. Larrasoaña J.C., Mochales T., Pey J., Pérez N., Cerro J.C., Tobar M.L., de la Parra I., Reyes J., Mata M.P. (2017). *Rock magnetic characterization of atmospheric deposition in northeastern Spain: Preliminary results from the DONAIRE Project*. IAPSO-IAMAS-IAGA Joint Assembly 2017. Cape Town, South Africa, 27 August-1 September 2017.

Acknowledgements

First of all I would like to thank the PhD directorVíctor Cerdà to let me join the research group, the Laboratory of Environmental Analytical Chemistry.

I gratefully acknowledge the regional government, through its Atmosphere department, my work, because it has given to me the passion for air pollution.

I would like to thank the IDAEA-CSIC team (Xavi, Andrés, Noemí, Teresa, Marco, Angeliki and all the rest) for giving me the opportunity to join them and spend so many pleasure stages in Barcelona.

I am grateful for the Aix-Marseille University people (Brice, Adrien, Dafne, Sylvan, Elodie, Daliah, Alex, Amelie…) for hosting me in Marseille and treat me so well. Special mention to Nicolas Marchand, who trained me as I would have been his little grasshopper.

Finally I would like to thank my PhD director Jorge Pey, who has worked with me, side by side, day by day, since the beginning of this thesis. This work could not have been possible without his persistence.

At last, I would like to thank my family and friends, especially to my parents, to Macià for giving to me the strength, and to Roberto for being always there.

This thesis has been funded with the following grants:

- Spanish Ministry of Science and Innovation (Spain) through the project and the European Funds for Regional Development (European Union) CGL2011-13580-E/CLI (IDAEA-CSIC)
- Spanish Ministry of Science and Innovation (Spain) through the project CTQ2013-47461-R (Universitat de les Illes Balears)

- Spanish Research Agency (AEI – Spain) through the grant RYC 2013-14159 (Jorge Pey).
- French Research Agency (France) through the project ANR-Blanc SAF-MED, grant n° SIMI6 ANR-12-BS06-0013 (Aix Marseille Université)
- Spanish Research Agency (AEI – Spain) and the European Funds for Regional Development (FEDER - European Union) through the project CTQ2016-77155-R (Universitat de les Illes Balears)
- Spanish Research Agency (AEI – Spain) and the European Funds for Regional Development (FEDER - European Union) through the project CGL2015-68993-R (Instituto Pirenaico de Ecología-CSIC)
- La Caixa mobility grants

List of abbreviations

ACSM	Aerosol Chemical Speciation Monitor
AF	African
AMS	Aerosol Mass Spectrometer
ANT	Anthropogenic
ARAID	Fundación Aragonesa para la Investigación y el Desarrollo
ASOA	Ammonium Sulphate Associated Organic Aerosol
AT	Atlantic
BB	Biomass Burning
BC	Black Carbon
BSC	Barcelona Supercomputing Center
ChArMEx	Chemistry-Aerosol Mediterranean Experiment
CLL	Can Llompart
CMB	Chemical Mass Balance
CP	Cap Pinar
CPC	Condensation Particle Counter
CSIC	Consejo Superior de Investigaciones Científicas
DD	Dry Deposition
DL	Detection Limit
DMA	Differential Mobility Analyser
DMS	Dimethyl Sulphide
DREAM	Dust Regional Atmospheric Model
EB	Earthbound
EC	Elemental Carbon
EMEP	European programme for monitoring and evaluation Pollutants
ENDESA	Environment department-ENDESA
EU	European
FAIRMODE	Forum for Air Quality Modelling in Europe
GDAS	Global Data Assimilation System
GMT	Greenwich Mean Time
GOIB	Laboratory of the atmosphere-Govern de les Illes Balears
HM	Algerian-Hoggar Massif’s
HR-ToF-AMS	High Resolution-Time of Flight-Aerosol Mass Spectrometer
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectories
IDAEA-CSIC	Institute of Environment Assessment and Water Research
IGME	Geological Survey of Spain

INFN	Univ. di Firenze and Instituto Nazionale di Fisica Nucleare
INS	Insoluble
IPE	Instituto Pirenaico de Ecología
LCE	Lab. of Environmental Chemistry – Univ. Aix-Marseille
LI	Tunisian-Libyan
LOOA	Low-volatile Oxygenated Organic Aerosol
MED	Mediterranean
MERIS	Medium Resolution Imaging Spectrometer Instrument
MODIS	Moderate Resolution Imagin Spectroraidometer
MRA	Multiple Regression Analysis
N	Particle Number
NAAPS	Navy Aerosol Analysis and Prediction System
NAF	North-African
NAOi	North Atlantich Oscillantion index
NRL	Naval Research Laboratory
OA	Organic Aerosol
OC	Organic Carbon
OM	Organic Matter
OMI	Ozone Measurment Instrumentation
OOA	Oxygenated Organic Aerosol
PBL	Planetary Boundary Layer
PCA	Principal Component Analysis
PM	Particulate Matter
PM10	Particulate Matter with aerodynamic diameter below 10 µm
PM2.5	Particulate Matter with aerodynamic diameter below 2.5 µm
PM1	Particulate Matter with aerodynamic diameter below 1 µm
PMF	Positive Matrix Factorization
PNC	Particle Number Concentration
PSA	Particle Source Area
PSI	Paul Schrerrer Institute
PTR-MS	Proton-transfer-reaction mass spectrometry
RB	Rural/remote Background
REG	Regional
SB	Sub-urban Background
SeaWIFS	Sea-viewing Wide Field of view Sensor
SMPS	Scanning Mobility Particle Sizer Spectrometer

SN(R)	Signal to noise (ratio)
SOA	Secondary Organic Aerosol
SOL	Soluble
SR	Summer Regional
SVOOA	Semi-volatile Oxygenated Organic Aerosol
TD	Total Deposition
TOC	Total Organic Carbon
UB	Urban background
UMH	Miguel Hernández University
VOC	Volatile Organic Compounds
WD	Wet Deposition
WM	Western Mediterranean
WMB	Western Mediterranean Basin
WMED	Western Mediterranean
WR	Winter Regional
WS	Western Saharan
WSOC	Water Soluble Organic Carbon

List of contents

Abstract

This thesis sets out to present a number of outcomes regarding air pollution in the Western Mediterranean. In this work there is an analysis of the current status of atmospheric pollutants over the Balearic Islands and their recent trends (2000-2012). Furthermore, there is a detailed study of the chemical characterization of atmospheric aerosols and their sources (2010-2012). In addition, a parallel study of aerosol deposition to obtain atmospheric fluxes, including some pollutants and nutrients (2010-2012). Finally, there is an investigation about organic aerosol sources taking the opportunity to apply an innovative method developed in the framework of this PhD and applied to an internation field campaing developed in summer 2013.

Chapter 1 collects a global introduction to focalize the main subject of this research.

Chapters 2 to 5 correspond to several publications derived from this research. These chapters are divided into a number of sections homogeneously structured in order to favour better reading and understanding: first, an abstract of the chapter; second an introduction about the global interest of the topic, context, previous research and main objectives; third, methodology; fourth, highlighted results that have been worthy and innovative enough to be published; fifth, discussion about the outcomes and the opportunities; sixth, the main conclusions derived from our investigation. At the end, each chapter has its own bibliography, on the purpose of better findings.

Chapter 2 discusses about trends 2000-2012 of air pollution considering regional, suburban and urban environments in Mallorca. This chapter is focused on the evolution of NO, NO_2, SO_2, O_3 and PM_{10} concentrations. In addition, this work interprets daily, weekly, seasonal and inter-annual patterns of diverse pollutants in different environments. The combined assessment at different environments allows us to discern changes induced by the implementation of regional policies from those caused by the enactment of continental strategies. Moreover, the effect of North Atlantic Oscillation index (NAOi) on different metrics, environments and seasons is assessed.

Chapter 3 deals with a 3-years study (2010-2012) of variability of air pollutants, PM composition and sources at a regional background site in the Balearic Islands.Furthermore, during three intensive observation periods real-time concentrations of particle number, black carbon and ammonia were measured.In addition, our study intends to evaluate the impact of increasing tourism (2010-2018) in this region as a regional source of pollution. Such a scenario is typically provoking during the warm season: 1) a much higher power supply demand; 2) a significant increment of vehicles all over the Island; 3) the increase in the amount of cruises, yachts and merchant ships; 4) a sharp increase in air traffic.

Source apportionment studies have been conducted in order to elucidate the importance of anthropogenic and natural sources or the co-variance of certain sources or the relevance of specific sources during some meteorological scenarios or seasons.

Chapter 4 discloses a 2 years campaign (Sept. 2010-Aug. 2012) studying fluxes and chemical composition of atmospheric deposition.Wet and dry deposition samples were collected separately. Time series and long-range-transport scenarios were studied. A Positive Matrix Factorization study has been carried out integrating both dry and wet deposition. Element ratios were investigated to discern differences among the origins of the mineral component. Patterns of clay and carbonate deposition have been also taken into account. And finally correlation of dry and wet deposition chemistry with PM10 chemical composition were investigated, in function of the meteorological scenario, in order to assess when and which components could present better linear regression.

Chapter 5 aims to integrate real-time HR-ToF-AMS data with off-line filter analysis, and to detect their synergies and challenges when evaluating organic sources. An extensive campaign was conducted in summer 2013. Thus including multiple devices based on off-line and real time techniques.

Chapter 6 reflects on the outcomes obtained, assesses the current situation of the western Mediterranean air basin, and discusses opportunities for the future.

Finally, Chapter 7 assembles the main conclusions derived from this thesis.

Besides, annexes contain:

- Scientific articles derived from this thesis
- List of communications, conference attendances or workshops where results have been presented
- International work involved during this thesis

Resum

Aquesta tesi està orientada a millorar el coneixement sobre la contaminació atmosfèrica en la Mediterrània occidental. Aquest treball conté una anàlisi de l'estat dels contaminants atmosfèrics, el seu comportament i l'estat evolutiu (2000-2012-2018). A més, es realitza un estudi de la caracterització química de l'aerosol atmosfèric i es determina la contribució de les fonts de fons existents (2010-2012). Adicionalment, es fa un estudi paral·lel per tal de conèixer els fluxos atmosfèrics de deposició d'alguns contaminants i nutrients (Setembre 2010-Agost 2012). Finalment, s'investiguen les fonts d'aerosols orgànics secundaris aprofitant una innovadora meteodologia desenvolupada durant aquesta tesis i aplicada a una campanya de mesura duta a terme durant l'estiu de 2013.

El capítol 1 recull una introducció global per focalitzar el tema principal d'aquesta investigació.

Els capítols 2 a 5 corresponen a diverses publicacions derivades d'aquesta investigació. Aquests capítols es divideixen en diverses seccions estructurades de manera homogènia per tal de tenir una millor comprensió i lectura: primer, un resum del capítol; en segon lloc, es descriu l'interès global de la qüestió, el context, la investigació prèvia i els objectius principals; tercer, la metodologia; quart, destaca resultats que són prou rellevants i innovadors per ser publicats; cinquè, discussió sobre els resultats i les oportunitats; sisè, les principals conclusions derivades de la nostra investigació. Al final, cada capítol té la seva pròpia bibliografia amb l'objectiu de que sigui més fàcil de trobar.

El capítol 2 tracta sobre les tendències de la contaminació atmosfèrica 2000-2012 tenint en compte entorns regionals, suburbans i urbans a Mallorca. Aquest capítol està centrat en l'evolució de les concentracions de NO, NO_2, SO_2, O_3 i PM_{10}. A més, aquest treball interpreta patrons diaris, setmanals, estacionals i interanuals de diversos contaminants en diferents entorns. L'avaluació combinada en diferents entorns ens permet distingir els canvis induïts per l'aplicació de polítiques regionals de les provocades per la promulgació d'estratègies continentals. A més, s'avalua l'efecte de l'índex d'oscil·lació de l'Atlàntic Nord (NAOi) sobre diferents mètriques, ambients i temporades.

Capítol 3 versa sobre un estudi de tres anys (2010-2012) sobre la variabilitat dels contaminants atmosfèrics, la composició del PM i les fonts d'un lloc regional de les Illes Balears. A més, durant tres períodes d'observació intensius es van mesurar concentracions en temps real de nombre de partícules, carboni elemental i amoníac. A més, el nostre estudi pretén avaluar l'impacte del creixent turisme (2010-2018) a aquesta regió com a font regional de contaminació. Aquest escenari provoca típicament en la temporada càlida: 1) una demanda de subministrament d'energia molt més elevada; 2) un increment significatiu de vehicles a tota l'illa; 3) l'augment de la quantitat de creuers, iots de creuers i vaixells mercants; 4) Un fort augment del transport aeri.

S'han realitzat estudis de contribució de fonts per dilucidar la importància de fonts naturals, antropogèniques o la convergència de fonts o la rellevància de fonts específiques durant alguns escenaris meteorològics o estacions.

El capítol 4 mostra una campanya de dos anys (setembre de 2010 a agost de 2012) que estudia els fluxos i la composició química de la deposició atmosfèrica. Les mostres de deposició humida i en seca es van recollir per separat. Es van estudiar sèries temporals i escenaris de transport de llarga distància. S'ha realitzat un estudi de Positive Matrix Factorization integrant la deposició en sec i humida. S'han investigat els ratios entre elements per detectar diferències entre els orígens de la component mineral. També s'han tingut en compte els patrons de deposició d'aluminosilicats i carbonats. I finalment es va investigar la correlació de la química de deposició seca i humida amb la composició química PM_{10} en funció de l'escenari

meteorològic, per tal de valorar quan i quins components podrien presentar una millor regressió lineal.

El capítol 5 té com a objectiu integrar dades de HR-ToF-AMS en temps real amb anàlisis de mostres de filtres i detectar les seves sinergies i reptes a l’hora d’avaluar fonts orgàniques. L'estiu de 2013 es va dur a terme una extensa campanya, incloent-hi diversos dispositius basats en tècniques manuals i en temps real.

El capítol 6 fa una reflexió sobre els resultats obtinguts, avalua la situació actual de la conca aèria a la Mediterrània occidental i fa un extracte sobre les oportunitats al futur.

Finalment, el capítol 7 recull les principals conclusions derivades d’aquesta tesi.

A més, els annexes contenen:

- Articles científics derivats d'aquesta tesi

- Llistat de comunicacions, asistència a conferències o grups de treball on s’han presentat els resultats

- Treball internacional corresponent a aquesta tesis

Resumen

Esta tesis está orientada a mejorar el conocimiento sobre la contaminación atmosférica en el Mediterráneo occidental. Este trabajo contiene un análisis del estado de los contaminantes atmosféricos, su comportamiento y el estado evolutivo (2000-2012-2018). Además, se realiza un estudio de la caracterización química del aerosol atmosférico y se determina la contribución de las fuentes de fondo existentes (2010-2012). Adicionalmente, se hace un estudio paralelo para conocer los flujos atmosféricos de deposición de algunos contaminantes y nutrientes (Septiembre 2010-Agosto2012). Finalmente, se investigan las fuentes de aerosoles orgánicos secundarios aprovechando una innovadora meteodologia desarrollada durante esta tesis y aplicada a una campaña de medida llevada a cabo durante el verano de 2013.

El capítulo 1 recoge una introducción global para focalizar el tema principal de esta investigación.

Los capítulos 2 a 5 corresponden a varias publicaciones derivadas de esta investigación. Estos capítulos se dividen en varias secciones estructuradas de manera homogénea para tener una mejor comprensión y lectura: primero, un resumen del capítulo; en segundo lugar, se describe el interés global de la cuestión, el contexto, la investigación previa y los objetivos principales; tercero, la metodología; cuarto, destaca resultados que son suficientemente relevantes e innovadores para ser publicados; quinto, discusión sobre los resultados y las oportunidades; sexto, las principales conclusiones derivadas de nuestra investigación. Al final, cada capítulo tiene su propia bibliografía con el objeto de que sea más fácil de encontrar.

El capítulo 2 trata sobre las tendencias de la contaminación atmosférica 2000-2012 teniendo en cuenta entornos regionales, suburbanos y urbanos en Mallorca. Este capítulo está centrado en la evolución de las concentraciones de NO, NO_2, SO_2, O_3 y PM_{10}. Además, este trabajo interpreta patrones diarios, semanales, estacionales e interanuales de varios contaminantes en diferentes entornos. La evaluación combinada en diferentes entornos nos permite distinguir los cambios inducidos por la aplicación de políticas regionales de las provocadas por la promulgación de estrategias continentales. Además, se evalúa el efecto del índice de oscilación del Atlántico Norte (NAOi) sobre diferentes métricas, ambientes y temporadas.

Capítulo 3 versa sobre un estudio de tres años (2010-2012) sobre la variabilidad de los contaminantes atmosféricos, la composición del PM y las fuentes de un sitio regional de las Islas Baleares. Además, durante tres períodos de observación intensivos se midieron concentraciones en tiempo real del número de partículas, carbono elemental y amoníaco. Además, nuestro estudio pretende evaluar el impacto del creciente turismo (2010-2018) en esta región como fuente regional de contaminación. Este escenario provoca típicamente en la temporada cálida: 1) una demanda de suministro de energía mucho más elevada; 2) un incremento significativo de vehículos en toda la isla; 3) el aumento de la cantidad de cruceros, yates de cruceros y barcos mercantes; 4) Un fuerte aumento del transporte aéreo.

Se han realizado estudios de contribución de fuentes para dilucidar la importancia de fuentes naturales, antropogénicas o la convergencia de fuentes o la relevancia de fuentes específicas durante algunos escenarios meteorológicos o estaciones.

El capítulo 4 muestra una campaña de dos años (septiembre de 2010 a agosto de 2012) que estudia los flujos y la composición química de la deposición atmosférica. Las muestras de deposición húmeda y seca se recogieron por separado. Se estudiaron series temporales y escenarios de transporte de larga distancia. Se ha realizado un estudio de Factorización Matricial Positiva integrando la deposición seca y húmeda. Se han investigado los ratios entre elementos para detectar diferencias entre los orígenes de la componente mineral. También se han tenido en cuenta los patrones de deposición de aluminosilicatos y carbonatos. Y

finalmente se investigó la correlación de la química de deposición seca y húmeda con la composición química PM10 en función del escenario meteorológico, para valorar cuándo y qué componentes podrían presentar una mejor regresión lineal.

El capítulo 5 tiene como objetivo integrar datos de HR-ToF-AMS en tiempo real con análisis de muestras de filtros y detectar sus sinergias y retos a la hora de evaluar fuentes orgánicas. El verano de 2013 se llevó a cabo una extensa campaña, incluyendo varios dispositivos basados en técnicas manuales y en tiempo real.

El capítulo 6 hace una reflexión sobre los resultados obtenidos, evalúa la situación actual de la cuenca aérea en el Mediterráneo occidental y hace un extracto sobre las oportunidades en el futuro.

Finalmente, el capítulo 7 recoge las principales conclusiones derivadas de esta tesis.

Además, los anexos contienen:

- Artículos científicos derivados de esta tesis

- Listado de comunicaciones, asistencia a conferencias o grupos de trabajo donde se han presentado los resultados

- Trabajo internacional correspondiente a esta tesis

Chapter 1: Introduction

1.1. State of the art

Atmospheric pollution is one of the most challenging environmental problems with which contemporary societies are faced. Most serious pollutants, in terms of harm to human health, are particulate matter (PM), nitrogen dioxide (NO_2) and tropospheric ozone (O_3) (WHO, 2005). Some population groups are more affected by air pollution than others, because they are more exposed or vulnerable to environmental hazards (WHO, 2013). Lower social-economic groups tend to be more exposed to air pollution, while older people, children and those with pre-existing health conditions are more vulnerable (EEA, 2019). Air pollution also has considerable economic impacts, cutting lives short, increasing medical costs and reducing productivity through working days missed across the economy (EEA, 2019).

1.1.1. Pollutants

Air emissions have natural or anthropogenic origins, which include industrial activities, power plants, waste incineration plants, traffic (road, shipping or air), or residential heating. Air pollutants comprise primary and secondary air pollutants. Primary air those which are emitted directly from sources. They include, but are not limited to, particulate matter (PM), sulphur dioxide (SO_2), nitric oxides (NO_x), hydrocarbon (HC), volatile organic compounds (VOCs), carbon monoxide (CO), and ammonia (NH_3). Secondary air pollutants are those formed through complex physical and/or chemical reactions, e.g., coagulation and condensation or photochemical reactions, chemical reactions of primary pollutants, among them or by reactions with normal atmospheric constituents.

Examples of secondary air pollutants are ground level ozone, formaldehyde, smog, and acid mist.

Particulate matter is a mixture of solid particles and liquid droplets suspended in the air. It is a two-phase system consisting of particles and the gas in which they are suspended. Particulate matter can be both primary pollutants and secondary pollutants that are sent directly into the atmosphere in the form of windblown dust and soil, sea salt spray, pollen, and spores, or smoke, fumes, and haze with a natural or anthropogenic origin.

Air pollutants, Volatile organic compounds (VOCs) are chemicals that contain carbon and/or hydrogen and evaporate easily. VOCs are the main air emissions from the oil and gas industry, as well as indoor consumer products and construction materials, such as new fabrics, wood, and paints. VOCs have been found to be a major contributing factor to ground-level ozone, a common air pollutant, and a proven public health hazard. Sulphur dioxide (SO_2) and nitric oxides (NO_x) are two major gaseous air pollutants generated through combustion processes. Carbon monoxide (CO) and hydrocarbon (HC) are generated from incomplete combustion and are converted into CO_2 through a complete combustion process.

Atmospheric physics and knowledge of chemistry are disciplines with a long road of research ahead.

Most gaseous air emissions such as NO_x, SO_2, HC, VOCs, and ammonia (NH_3) are converted into PM.

1.1.1.1. Particulate Matter

Atmospheric particulate matter (PM) is defined as all those solid and/or liquid particles (with the exception of pure water) that enter the atmosphere due to natural or anthropogenic causes (Mészáros, 1999). Another term used is that of atmospheric aerosol, or airborne. In the environmental field, the concentration of PM per unit volume of air can be expressed as mass concentration or number per unit volume of air (µg or ng/m^3, n/cm^3).

PM is characterized by its great variability in terms of its physical and chemical characteristics, and its complexity. There are a large number of sources of both natural and anthropogenic. Depending on these sources, their physical properties (size, mass, specific surface, density, morphology) and their chemical and mineralogical composition will vary. The residence time of the particles in the atmosphere and their transported distance will also depend on all these properties.

PM can be removed from the atmosphere through the deposition process, which is defined as the continuous flow of matter from the atmosphere to the Earth's surface per unit area and time (mg-µg/m^{2}day, or g-mg/m^{2}year).

Classification and distribution

There are several types of PM classifications, mainly according to their generation process, or according to their origin. Neither of these classifications excludes the other, but they are complementary.

Depending on its formation mechanism, the PM can be of primary or secondary origin. Particles of primary origin are those emitted directly into the atmosphere as solids or aerosols from their emitting source. Those of secondary origin are formed in the atmosphere, by chemical reactions from precursor gases, or by the interaction between gas and liquid or between gas and particle (Warneck P., 1988).

Depending on its origin, PM can be classified into natural particles and anthropogenic particles. Natural particles are those that are suspended in the atmosphere from natural emission sources. A large fraction of this type of particle that is emitted into the atmosphere on a global scale is of mineral origin from the resuspension of desert or semi-desert soils.

Another fraction comes from volcanic emissions, which although more occasional, its effects become significant since they can produce a negative radiative balance that can last for some years (IPCC, 2001). These emissions are made up of both mineral matter (ash) and secondary components from the oxidation of volcanic SO_2 emissions. Another important component in the natural fraction of the PM on a global scale is the marine aerosol since the oceans emit a large volume of particles into the atmosphere, which depend on the force and speed of the wind (O'Dowd et al., 1993).

There are also natural sources of a biogenic type. They are known as bioaerosols. Mainly, they are made up of plant remains, pollen, spores, and small micro-organisms such as viruses, bacteria, fungi, protozoa or algae. Typically they are coarser fraction particles, except viruses and bacteria that are <2 µm in diameter. In addition to these biogenic particles, mainly of primary origin, we must highlight the emissions of secondary particles originated from biogenic emissions of organic gaseous precursors (SOA), such as forest emissions of compounds such as terpenes and isoprenes.

It can be concluded that although most of the particles of natural origin tend to be of the primary type, secondary particles of natural origin are also produced, such as sulphates, nitrates and secondary organic compounds (SOA), which come from precursors such as emitted gases by volcanic eruptions, by forest, soil, marine emissions, or atmospheric processes such as lightning.

Anthropogenic particles make up a significant proportion of PM. They are emitted into the atmosphere by anthropogenic action (e.g., industrial, urban, agricultural, mining emissions or by air, sea or land transport). Its main sources are therefore located in urban and industrial areas. Within anthropogenic particles, we can also distinguish between primary and secondary particles. According to numerous studies, in urban areas anthropogenic particles of primary origin are normally associated with traffic, such as direct emissions from vehicle engines (black carbon and gaseous precursors of secondary particles: SO_2, NO, NH_3 and volatile organic compound components), or wear of the road surface, tires and brakes, and resuspension of material deposited on the road. Other urban emissions such as those produced in construction, demolition and heating can also be important. In industrial areas the primary particulate matter of anthropogenic origin comes from the emissions from chimneys of certain industrial processes such as the combustion of coal, the smelting of metals (Zn, Cu), or the production of cements, bricks or ceramics.

Another type of primary anthropogenic emissions is the so-called fugitive emissions, which are those produced due to the handling and resuspension of powdery materials. They also occur due to agricultural activities such as tillage, emissions of waste or burning of biomass.

Among the anthropogenic particles of secondary origin, the sulphates generated by oxidation of SO_2 dominate, emitted for example by thermal power plants and industrial plants, or nitrates that come from the oxidation of nitrogen oxides (NO_x) emitted by automobiles, certain generation processes electrical and industrial or by intensive livestock activities (NH_3 emission) and/or slurry application in agriculture. The hydrocarbons emitted by the burning of biomass or fossil fuels emitted by traffic and by a great variety of industrial processes also give rise to organic compounds of secondary origin.

As previously mentioned, both the particle size distribution and the chemical composition of PM depend, among other factors, on the nature of its emitting focus. Focusing on the particle size distribution of PM, it can vary from nanometers, to tens of microns. There is a classification of PM collected by Warneck (1988) and modified by the EPA (1996) and by Seinfeld and Pandis (2016), in which several grain size distributions are differentiated, which are called “modes”, based on their formation mechanism.

A) Nucleation mode

Includes particles with a diameter <0.02 μm. This mode has a maximum between the 5-15 nm diameter range. These types of particles have an average lifespan in the atmosphere of hours, since they quickly become coarser by coagulation with other particles, or by reaction with other components (gaseous or liquid), whether organic or inorganic.

The formation of these particles depends on the precursor gas, on temperature and on humidity, their formation is favoured by a decrease in temperature or by an increase in relative humidity (Eastern and Peter, 1994). Currently, the only known precursor gases to form particles by homogeneous nucleation in the atmosphere are H_2SO_4, NH_3, and H_2O (EC, 2003). Another type of situation that may favour the increase of particles in this particle size range is the photochemical conversion of gas to particle due to the increase in solar radiation, which mainly affects the formation of particles between 3 and 7 nm. An increase in particles in this range can be seen when the radiation is higher (noon) (McGovern et al., 1996; Harrison, 1997, 1999).

B) Aitken mode

It includes particles with a size range between 0.02 and 0.1 μm. They have a natural and anthropogenic origin both primary and secondary and can be formed by coagulation of the nucleation mode particles, by condensation, or by liquid phase reactions. One type of particle within this range is carbonaceous particles, mostly of primary origin (soot) which is originated in fossil fuel combustion processes. They usually have diameters of 100 nm (generally> 30 nm), and can reach diameters of up to 150-200 nm (Matter et al., 1999). In urban areas the main source of soot is diesel engines (EC, 2003).

Ultrafine particles are defined as particles less than 0.1 μm in diameter and encompass both nucleation mode particles and part of the Aitken. Sometimes this term is used exclusively for nucleation fashion particles. These are the particles that dominate in terms of number in PM in general and especially in urban environments (Harrison et al., 1999), but contribute in a very low proportion to the total mass of PM (Jaenicke, 1993). According to WHO (2013) this range of particles (<0.1 μm), is the one that has the most negative effects on health.

C) Accumulation mode

It is the one that includes the particles with a range between 0.1-1 μm. The particles included in this mode are mainly formed by liquid phase reactions (such as those that may occur in water droplets from clouds) of particles from the Aitken mode. The high concentration of water and the high speed of reaction within the clouds favour these reactions. The transfer of mass that occurs in these reactions may occur by gas condensation and/or by coagulation of the nucleation mode particles. The particles of this mode have a long residence time in the atmosphere, unlike those of the nucleation mode (which agglomerate rapidly among them to give rise to coarser particles).

There are environments in which the conversion of particles from nucleation and Aitken fads to the accumulation mode, by coagulation or condensation, is most encouraged, such as in highly polluted atmospheres (Seinfeld. J and Pandis S., 2016). In contrast, in oceanic air masses, these two modes appear well differentiated.

D) Coarse mode

It is made up of particles with a diameter> 1 μm. They are mainly primary particles that enter the atmosphere through mechanical processes, such as erosion of the Earth's surface (mineral matter) or other processes such as the bursting of bubbles on the surface of seas and oceans (marine aerosol). PM of secondary origin also plays an important role within this fraction. The reaction of gases with particles of mineral or marine origin gives rise to new coarse particulate material. This mode of particles is the one that contains most of the mass of PM but the least number of particles.

Generally, fine particles are those that are below 1 µm, and coarse particles are those that are above 1 μm. This 1 μm limit is not accidental. The growth of fine fraction particles by different processes (nucleation, coagulation or condensation) has been found to be limited to diameters <1 µm approximately. On the other hand, the mechanical processes that generate the primary particles are not effective to generate particles with diameters <1 μm due to energy limitations.

In terms of air quality and epidemiology, this limit between fine and coarse particles is 2.5 μm, which is primarily due to epidemiological and equipment design criteria, rather than the presence of two groups of particles in the fractions> 2.5 μm and <2.5 μm.

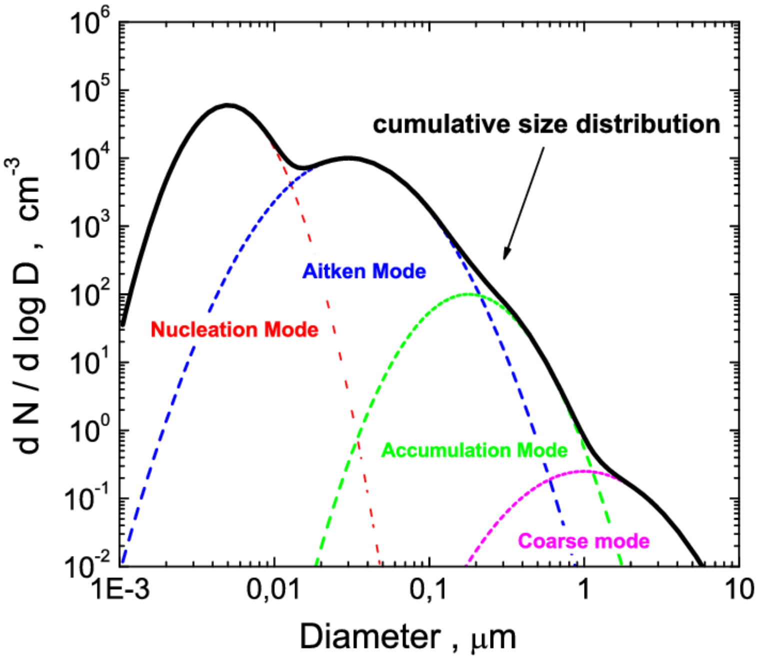


Figure 1.2. Idealised evolution of tropospheric aerosol size distribution with four modes (Lambert et al., 2011)

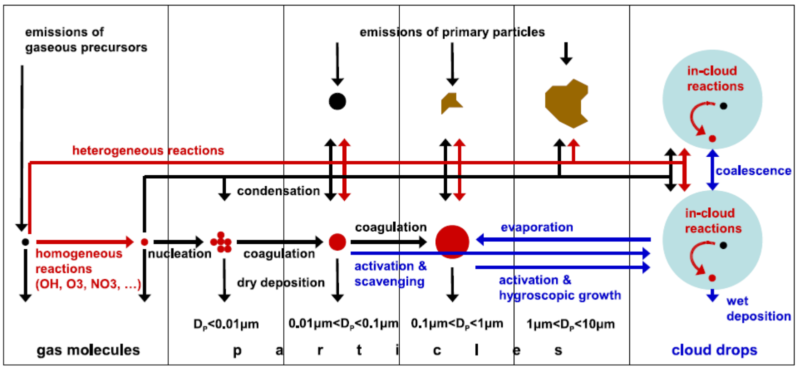


Figure 1.3. Evolution of tropospheric Aerosol (Lambert et al., 2011)

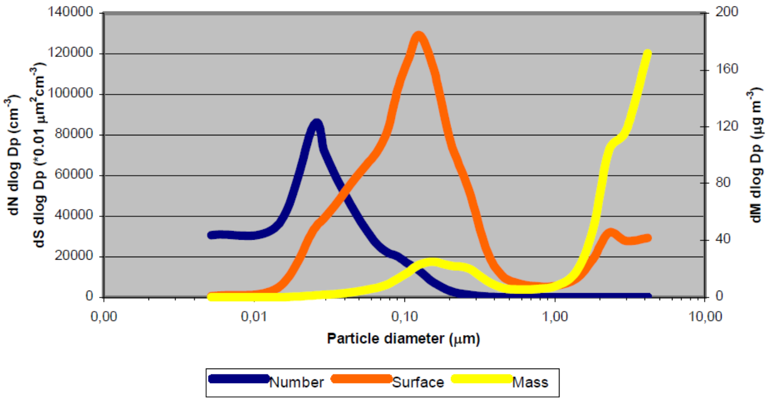


Figure 1.4. Size distribution of airborne particulate matter in function of their number, surface and mass (EC, 2003).

Deposition

The atmospheric dynamics provides the main route for dispersion and transport of pollutants in gaseous and aerosol forms among different environmental systems. The trajectories followed by the pollutants in the atmosphere and the distance they travel depend on different factors, such as meteorological conditions. Finally, most of the pollutants return to the surface of the earth trough wet or dry deposition, or through direct absorption of gaseous compounds by surface waters, plants or soil. In Europe, most of the atmospheric deposition occurs in the form of wet deposition, but in southern European regions the role of dry deposition is equally important or even dominant when compared to wet deposition (López et al., 2013).

Dry deposition is defined, usually and in our case, as the fraction of particulate matter and gases per unit area that returns to the surface in the absence of precipitation. Therefore, wet deposition is defined as the flux of a chemical compound (in gas or particle phase) to the earth's surface by precipitation (in whatever form falls into the collector), and total deposition as the sum of both (Mészáros et al., 1999).

The level of turbulence in the atmosphere, especially at the levels closest to the surface, will govern the amount of particulate material that is deposited on the surface. The size, density and shape of the particles can determine whether or not capture of particulate material occurs from the surface. Finally, the nature of the surface is important in allowing the capture of different species.

The general dry deposition estimation assumes that the dry deposition flux is directly proportional to the concentration of the species being deposited by taking a height above the surface of less than 10 m (Herut et al., 1999 and 2002):

$F = -v_d C$

where F represents the vertical flux of dry deposition (amount of material deposited per unit area per unit of time), v_d represents the proportional constant between the flux and the concentration known as deposition rate (measured in units of length per unit of time), and C the concentration of the species per unit volume of air. By convention the vertical deposition flow is negative, so the deposition rate is always positive. The dry deposition process is summarized in three steps (Mészáros et al., 1999):

1) vertical aerodynamic transport from the atmosphere,

2) transport through a sublayer of stagnant air above the earth's surface called the quasi-laminar sublayer, and

3) interaction with the surface.

The particle transport processes in the metres closest to the surface are by turbulence, aided in the case of the coarser particles by the action of gravity. Transport processes in the quasi-laminar sublayer occur by diffusion, where fine particles are transported by Brownian movements and coarse particles by intersection, inertial forces, and sedimentation. Settling particles (> 30 μm) are deposited directly by gravity, while coarse (1-10 μm) and fine (<1 μm) are deposited by diffusion processes. There is a range of particles between 0.1-1 μm in which the above processes are generally not very effective. Each of the previous steps contributes to the value of the deposition rate constant v_d. Once the particles fall to the surface they are adhered while the gases are absorbed by the surface. It may happen that if the force that supports the particle on the surface is less than the lifting force of the surface, the particle rises again to the atmosphere, which is known as resuspension. This resuspension accounts in our case as positive dry deposition, since it rises from the soil surface and makes its way into our dry collector.

Wet deposition might occur through several different routes. Various forms of precipitation, including liquid or solid play an important role in this process.

Other processes of deposition could be attributed to the wet fraction, but due to our collector system, they will be sampled in the dry fraction, e.g., dew, or atmospheric pollutants might also be transferred to the ground from fog or cloud droplets through direct fog water deposition, or direct surface condensation and (or) deposition and dragging of waters particles raised from the Sea surface by wind.

The composition of wet deposition might be significantly altered on contact with surfaces, both natural and artificial.

In our latitudes, of all the previous processes, the one that has the most relevance is rain. Inside the precipitation the deposition of particulate matter can be carried out by two mechanisms: the in-cloud scavenging or rainout, and the below-cloud scavenging or washout.

In-cloud scavenging is the flushing mechanism that takes place within the cloud. Atmospheric compounds and raindrops are united by nucleation or collision in the case of particles, or by dissolution in the case of gases. Raindrop growth occurs, allowing more particles to be captured by coalescence. Sulphates and nitrates are two examples of condensation nuclei for their hygroscopic characteristics. The below-cloud scavenging is the flushing mechanism that takes place under the cloud. In the path that the drops fall freely, they will collide and drag a part of the particulate material (particles with a diameter> 1 μm) present in the lower layers. Coarser particles are more easily deposited by wet deposition than fine particles.

1.1.1.2. Gaseous Pollutants

The most commonly monitored gaseous pollutants (SO_2, NO, NO_2, O_3, CO) are featured because of their health or ecosystem effects, or the environmental effect known as acid rain (also known as acid deposition), or others such as eutrophication.

Gaseous pollutants (SO_2, NO, NO_2 and NH_3)

A variety of processes can result in the transfer of acidifying pollutants from the emissions to the final turn to the surface. The major pollutants of interest are compounds of sulphur (particularly sulphuric acid (H_2SO_4)) and oxidized and reduced nitrogen (particularly nitric acid (HNO_3), nitrate (NO_3) and ammonia (NH_3)).

These pollutants can be present as gas or in liquid/particle phase. What will influence in their dynamics, reactivity, lifetime…

Across Europe and North America, signatories to the 1979 UNECE Convention on Long Range Transboundary Air Pollution (LRTAP) oblige countries to reduce the annual total emissions, the national ceiling emissions.

Primary pollutants, such as SO_2, NO, NO_2 and ammonia (NH_3), undergo chemical transformation as they are dispersed in the atmosphere and produce secondary pollutants (sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+)). These secondary pollutants are usually in aerosol form and display different properties. The understanding of atmospheric chemistry is still being developed.

The most important transformations are brought about by oxidation. There are different types of oxidants in the atmosphere. Oxidation may take place in gas or aqueous phase. The main oxidant in the troposphere is OH· (the hydroxyl radical) which results in photochemical conversion. Ozone (O_3) and hydrogen peroxide (H_2O_2) can also be important.

Sulphur oxide oxidation

Photochemical oxidation of SO_2 gas to soluble sulphate aerosol:

$$SO_2 + OH\cdot\ (+O_2 + H_2O) \leftrightarrow H_2SO_4 + HO_2\cdot$$

If the SO_2 dissolves in water droplets in cloud, bisulphite (HSO_3^-) or sulphite (SO_3^{2-}) ions are formed, depending upon the pH. These may then be oxidized by either O_3 or H_2O_2 to yield sulphate in solution:

$$(HSO_3^- + O_3 \text{ or } H_2O_2 \leftrightarrow SO_4^{2-} + H^+ + SO_3^{2-}) + O_3 \text{ or } H_2O_2 \leftrightarrow SO_4^{2-}$$

H_2O_2 is rapidly consumed by this reaction so the importance of this reaction is limited by the availability of H_2O_2 in the atmosphere.

Oxidation by O_3, however, is really limited only by pH, becoming very slow when pH drops below 4.5. Because of this pH dependence, the importance of O_3 oxidation of sulphur is dependent on the presence in the atmosphere of neutralizing species such as ammonia.

Oxidized nitrogen reactivity

Gaseous nitrogen oxides play a role in acidification, eutrophication and ozone production. Many of the reactions are reversible. Oxidation of NO by O_3 to yield nitrogen dioxide:

$$NO + O_3 \leftrightarrow NO_2 + O_2$$

In daylight, however, NO_2 is rapidly converted back into NO as a result of photolysis (sunlight). This rapid interconversion (over time periods of minutes) is described as a photo stationary state. The mechanism also produces O_3. NO can also be converted to NO_2 by reactions with free radicals; the photolysis of the resulting NO_2 is a net source of O_3.

NO_2 is also oxidized by O_3 to form the nitrate radical, but in daylight the NO_3 is rapidly photolysed.

At night, the NO_3 persists and reacts further with NO_2 to give dinitrogen pentoxide (N_2O_5). This then reacts with water vapour to form nitric acid.

The key reaction for removing NO_x from the atmosphere during daylight is the oxidation of NO_2 by the hydroxyl radical to produce gaseous nitric acid (HNO_3). Nitric acid is readily deposited, dissolved in water droplets or reacts with ammonia to form particles:

$$NO_2 + OH \rightarrow HNO_3$$

OH can also oxidize NO to yield nitrous acid (HONO). HONO is rapidly broken down by sunlight (back into OH and NO), but can be dissolved into water vapour producing nitrite ions. In this aqueous phase, HONO (or NO_2) can be oxidized by H_2O_2 to produce nitrate.

Ammonia reactivity

Ammonia gas is highly reactive and can be readily deposited back to the surface close to its place of origin. Ammonia also reacts with acidic compounds H_2SO_4, HNO_3 or HCl to yield particulate ammonium which can then be removed from the atmosphere in rain.

Ozone

Ozone (O_3) is a secondary pollutant product of photolytic and photochemical reactions.

The vast majority of ozone occurs in the stratosphere where it is produced as a result of photolysis of molecular oxygen by UV radiation. We focus on tropospheric, and more especially, surface ozone.

Tropospheric ozone is largely produced by photochemical reactions involving oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Carbon monoxide (CO) and methane (CH_4) also play an important role. Fumigation from the stratosphere is also an important source of tropospheric concentrations. Ozone is an important oxidant, but in an unpolluted atmosphere does not accumulate. In areas downwind of high concentrations of its major precursor pollutants, NO_x and VOCs, and in the presence of sunlight, high concentrations of O_3 can be generated. NO_x anthropogenic emissions come mainly from transport, power plants and industrial sources. The largest sources of NM-VOCs are road transport and solvents. Most affected areas are usually outskirts of urban areas or downwind from industries where ozone forms an important element of photochemical smog. Plumes of high concentration can travel thousands of km from the source region, which convert ozone into a global problem in the northern hemisphere. Biogenic emissions of VOCs (isoprene, monoterpenes…) can be significant and exceeds anthropogenic emissions.

Ozone reactivity

Net photochemical production of O_3 occurs when peroxy radicals (HO_2 and RO_2) are generated, which can then react with NO to NO_2 without the consumption of O_3 effectively disturbing the photo stationary state:

$$NO + HO_2 \rightarrow NO_2 + OH$$

These peroxy radicals can be produced by the oxidation of CO, CH_4 or non-methane VOCs (NM-VOCs) by OH. In these reactions, OH is regenerated. Although globally the majority of OH reacts with CO and CH_4, at the regional/local scale reactions with NM-VOCs from anthropogenic sources (such as solvent use and road transport) become dominant. The peroxy (free) radicals produced by the oxidation of these hydrocarbons enable O_3 concentrations to build up in urban areas where they would otherwise be low. The number of oxidation cycles the OH/peroxy radicals can go through before reaching terminating reactions (i.e. final sinks for the radicals) dictates how much excess O_3 can be produced. The number of cycles is described as the ‘chain length’ for ozone formation (Porg et al., 1997), and efforts to reduce ozone concentrations should shorten these ‘chain lengths’.

It is possible to predict O_3 concentrations for different initial concentrations of NO_x and VOCs (and sunlight). Where the ratio of NO_x to VOC is high, the system is said to be VOC-limited, while for low NO_x to VOC ratios, the system is NOx-limited. In a VOC-limited system ‘chain length’ is shortened by reducing VOC emissions. However, if policy brought about a reduction in NOx, but not VOCs, in a VOC-limited area, then O_3 concentrations would increase (longer ‘chain length’). The implementation of policies for ozone reduction is, therefore, a complex process, especially as the definition of a region as VOC- or NO_x-limited may vary depending on wind direction in relation to pollution sources. The implications of demands to reduce NO_x emissions in order to address problems associated with acid deposition should also be considered.

Deposition of gaseous pollutants

The direct deposition of gases and particles onto a surface is known as dry deposition. For acidification, the gases of interest are SO_2, NO_2, HNO_3 and HCl, and NH_3 by its alkaline properties. The largest sink for tropospheric ozone is dry deposition to terrestrial surfaces. A small proportion will be lost through uptake into cloud water droplets.

Dry deposition will depend on several factors, such as vegetation height, the affinity of a particular pollutant for an individual type of surface or wind speed. In general terms, dry deposition is important when it is close to sources of pollutants, while wet deposition is more important when it is remote from sources.

The direct deposition of water droplets from clouds is called cloud water interception or occult deposition. This process becomes important in areas where cloud cover regularly blankets the surface (usually on hill tops) or fog at valleys. The deposition of cloud droplets will be enhanced in forested upland areas because of their surface roughness, so inputs of acidity in forested areas regularly under cloud may be particularly important.

Wet deposition occurs due to the removal of pollutants from within clouds or beneath clouds as precipitation falls. It is dominated by the removal of acidic aerosol species and so occurs largely remote from sources, once the chemistry of the air has had time to evolve. Wet deposition, therefore, usually predominates in rural and upland areas.

1.1.2. Dynamics

The residence times of pollutants in the atmosphere and the distances over which they can travel after being emitted are determined primarily by the altitude of the emissions and meteorological conditions (type of atmospheric circulation, air temperature, wind direction and speed, etc.). Once in the atmosphere, the pollutants undergo dispersion and (or) transformation(s), depending on their properties and meteorological conditions. Ultimately, most of the pollutants return to the surface of the earth (sometimes very far from the emission source) through wet or dry deposition, or through direct sorption of gaseous compounds by surface waters, plants, or soil.

The Western Mediterranean Basin (WMED) is a crossroad region in between South-Western Europe, Northern Africa and the Atlantic Ocean, characterized by particular atmospheric dynamics. Actually, although the WMB is located in mid-latitudes and therefore should be strongly impacted by the movements of westerly air masses, the quasi-permanent influence of the Azores high and the mountainous coastline all around the Basin favour and reinforces meso-scalar atmospheric circulations (Millán et al., 2002). In this atmospheric context, a number of intrinsic factors such as the increasing level of human pressure; the strong influence of Northern African dust (Querol et al., 2001, Rodríguez et al., 2003, Escudero et al., 2006, Pérez et al., 2008, Querol et al., 2009a, Pey et al., 2009a, 2013b); the occurrence and recurrence of forest fires all around the Basin, especially in summer; and the intensity of photochemical processes in the Mediterranean atmosphere make aerosol phenomenology especially complex. Furthermore, climate change scenarios reflect the vulnerability of this particular region. All these characteristics compel us to investigate current aerosol and gaseous pollutant dynamics in a representative regional background location in the WMB.

Air mass origins

The long-range transport of air masses was classified in 5 types: transport from northern Africa (AF); from the Mediterranean (MED); from Europe (EU); from Atlantics (AT); and lack of advection (REG). The effect in air pollution generated by these phenomena is extensively explained in Pey et al. (2013) and Cerro et al. (2017).

Regional episodes

It is a stagnation period dominated by high barometric pressures. We find it predominantly in summer and winter. Usually this phenomenon takes place because the Azores high pressure system is located in high latitude. It reaches much of Western Europe, the Iberian mainland and the Mediterranean basin.

During these episodes, the renewal of the air masses is poor, leading to an increase in the concentration of pollutants in the atmosphere and facilitating the formation of secondary pollutants. In summer periods the sun warms the surface considerably and in the daytime can generate a very high mixing layer. The emitted pollutants react among them and some as nitrogen oxides and sulphur oxides give rise to nitrates and sulphates to form secondary particles. This favours a decrease in the concentration of these gases, but transforms them into other pollutants that also affect public health. In winter, however, the cold makes the mixing layer thinner, reducing the possibility of dispersal of pollutants. In fact, concentration of primary pollutants during these situations is the higher.

Europe

These situations usually occur during the end of autumn and beginning of winter or in early spring. Anthropogenic pollutants emitted in Central Europe can reach the Balearic Islands. The main sources of emission would be in this case the heavy industry and large thermal power plants existing in Central Europe, with high emission of nitrogen oxides and sulphur dioxide. This results in secondary particles formed by nitrates and sulphates that reach our location.

Mediterranean episodes

This situation occurs when winds come from the Mediterranean Sea. Usually, Libyan desert outflows reach our location through this trajectory, and accompanied by rainfall. Then these episodes can be loaded with particles. On the other hand, some oil refineries and emissions from Stromboli or Etna volcanoes characterize the Italian coast.

Atlantic

The arrival of winds from the Atlantic causes a renewal of the air masses, leading to a significant decrease in the concentration of pollutants. In addition, they often come with wind and rainfall, due to the passage of a front from the north, thus causing an important cleansing of the local atmosphere.

African episodes

Outbreaks of desert dust from northern Africa are the situations when maximum concentrations of PM are recorded.

Dust can travel in the atmosphere at different altitudes from the troposphere reaching the Balearic Islands, whether at high altitudes or even on the surface. There is a significant increase in particles smaller than 10 microns, but the increase in particles smaller than 1 micron is not so noticeable. The intensity of the phenomenon will depend on different factors: whether it reaches the surface or the particles stay high; if there is wet deposition due to precipitation; if the air masses have travelled much since their resuspension and have diluted.

This phenomenon is commonly encountered in the summer because the latitude of the Azores anticyclone favours the resuspension in the Sahara and the arrival in the South of the Peninsula and the Balearic Islands. But we also find it in February and March when a low pressure system is generated over north-western Africa.

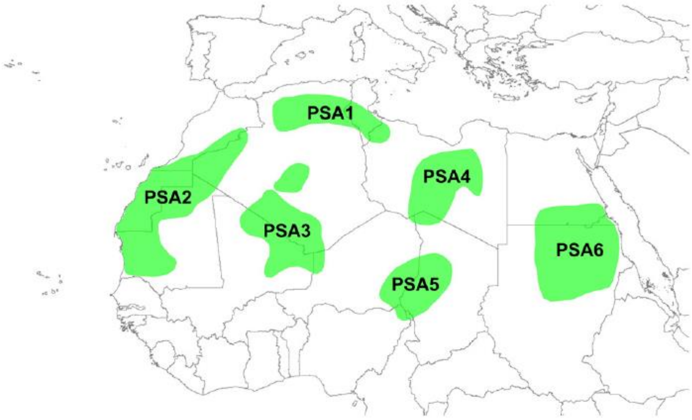


Figure 1.4. Maps of Northern Africa with major dust production areas based on TOMS aerosol index (Scheuvens et al., 2013 and references therein).

1.1.3. Effects

1.1.3.1. Human health effects

Airborne particles, in terms of mass and number concentrations, are associated with different adverse impacts on human health (WHO, 2005, 2013; Samoli et al 2013; Stafoggia et al 2013). Similarly, exposure to nitrogen oxides (NO_x), ozone (O_3), sulphur dioxide (SO_2) ammonia (NH_3) can induce some cardiovascular and lung diseases, premature deaths and carcinogenic effects (WHO, 2005; 2013).

Some international organizations try to sum up all the effects that air pollution causes on human health. The World Health Organization is the organism in charge of elaborating and updating recommendations to protect the population from this issue. On the other hand, the Environmental European Agency elaborates a report every year which summarizes the main findings regarding the effects of air pollution on health (EEA, 2019 and references therein).

Air pollution is a major cause of premature death and disease and is the single largest environmental health risk in Europe, causing around 400 000 premature deaths per year in the EEA-39 (excluding Turkey), mainly related to heart disease and stroke, lung diseases and lung cancer. Air pollution, and specifically PM, has been officially classified as carcinogenic.

Elderly people and children are the most sensitive, since both short and long-term exposure can hamper lung function, provoke respiratory infections and asthma. Other consequences have been studied in recent years: fertility, pregnancy, newborns, cognitive development, diabetes, obesity, systematic inflammation, Alzheimer's disease or dementia.

1.1.3.2. Ecosystems and agriculture

In addition, these atmospheric pollutants may also affect ecosystems (Bytnerowicz et al., 2007), agriculture (Gonzalez-Fernandez et al., 2014). For example, nitrogen oxides and ammonia (NH_3) emissions imply an excess of nutrients to terrestrial and aquatic ecosystems and lead to eutrophication. NO_X, together with SO_2, also contribute to the acidification of soil, lakes and rivers, causing loss of biodiversity. Finally, ground level O3 damages agricultural crops, forests, and plants by reducing their growth rates, and has negative impacts on biodiversity and ecosystem services (EEA, 2019).

1.1.3.3. Climate Change

In addition, atmospheric aerosols are key drivers in certain atmospheric and climate processes and they are influencing the Earth's radiative balance (IPCC, 2007).

Amongst different aerosol types, black carbon (BC) is the one drawing more attention because of its well-known potential for warmth (IPCC, 2013). Other kinds of particles can contribute also to the global dimming (IPCC, 2007). Tropospheric O_3 also is a short-lived climate forcer and contributes directly to global warming. Other PM components, such as organic carbon, ammonium (NH_4^+), sulphate (SO_4^{2-}) and nitrate (NO_3^-), have a cooling effect (IPCC, 2013).

1.1.3.4. Other effects

Air pollution can damage materials, properties, buildings and artworks, including historical heritage (Genestar et al., 2014). Damage includes corrosion (caused by acidifying compounds), biodegradation and soiling (caused by particles), and weathering and fading of colours (caused by O3) (EEA, 2019).

The economic implications of air pollution include reduced productivity of workers, additional health expenditure, and crop and forest yield losses. The Organisation for Economic Co-operation and Development (OECD, 2016) estimated that the total costs of ambient air pollution for the OECD region amounted around EUR 1.100 per capita for 2015, corresponding to about 5 % of income in 2015.

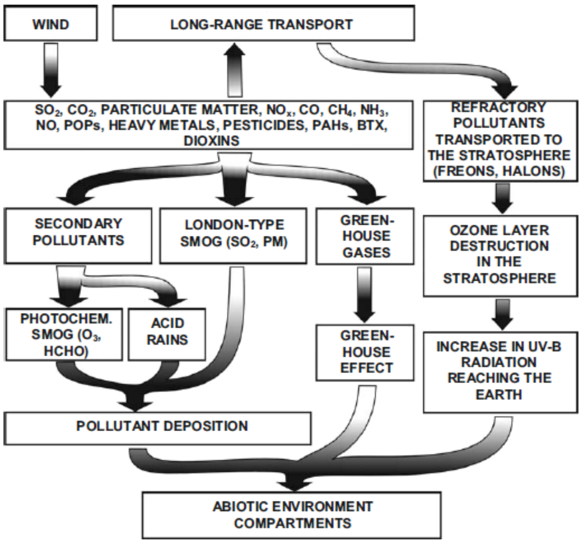


Figure 1.5. Effect of pollutants emitted to the atmosphere on other environmental compartments (Polkowska et al., 2011).

1.1.4. Legislation

Several strategies have been displayed throughout the continent to improve air quality during the period in study (2000-2018): All the directives about air quality surveillance (96/62/CE, 1999/30/CE, 2000/69/CE, 2002/3/CE, 2004/107/CE, 2008/50/CE); the Clean Air For Europe Programme (CAFE, 2005); several laws focused on industries, such as the limitation of emissions of Volatile Organic Compounds (1999/13/EC); Waste Incineration Plant Emissions (2000/76/EC); National Emission Ceiling Directive (2001/81/EC, 2016/2284/EU); Large Combustion Plant Emissions (2001/80/EC); Integrated Pollution Prevention and Control Directives (1996/61/EC, 2008/1/EC); Industrial Emission Directive (2010/75/EU); Medium Combustion Plant Directive (2015/2193/EU); measures focused on transport, such as EURO3 to EURO6 European emission standards; Shipping Emission Directives (1999/32/EC, 2012/33/EU) were also applied.

At a local scale, a number of abatement strategies have been implemented since 2000, mainly in Palma de Mallorca. Specifically, a considerable promotion of public transport was launched in 2000; bus-taxi lanes were delimited in 2002; several underground car parks were built in 2003; park-pay neighborhood restricted and pedestrian areas have been implemented since 2004; improvements in the ring road have been introduced since 2005; the use of low consumption vehicles have been encouraged since 2006; investments in public transport were made in 2007; and a wide range of measures, included in the Palma Air Quality Improvement Plan 2008 (Balearic Government, 2008) were adopted in the period 2008-2011. As a consequence of the economic crisis, a less ambitious plan (Palma Air Quality Improvement Plan 2011-2015) was finally approved (Balearic Government, 2013). Definitely, the financial crisis was one of the most effective abatement measures: a 4% yearly reduction in vehicular traffic was estimated from 2009 to 2012, reversing the evolution from 2000 to 2008.

Although air quality in Mallorca can be currently considered of good quality from a legislative point of view, particulate matter concentrations and specific gaseous pollutants exceed the European Directives targets in different areas, like the limit value for human health protection for NO_2 at urban areas, or the target value for human health protection for O_3 at regional environments.

1.1.5. Air quality monitoring network in the Balearic Islands

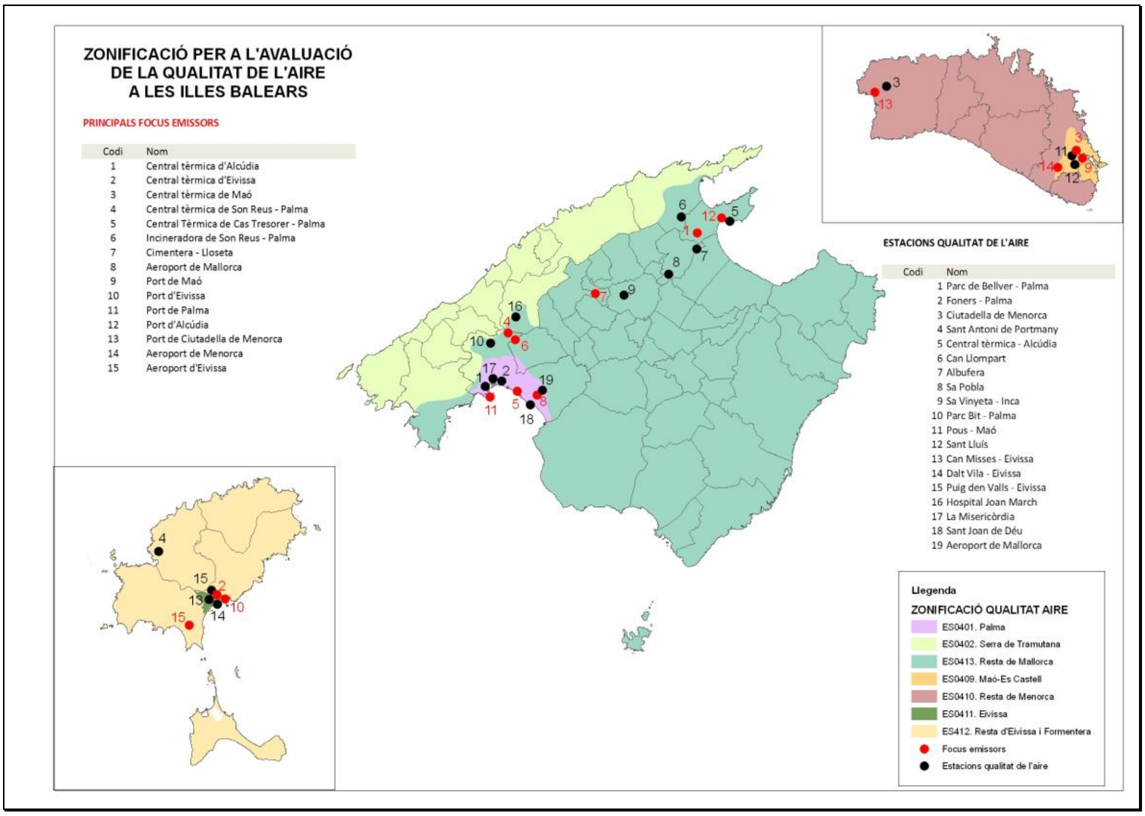
CLL, the main location in our study, is part of the regional air quality monitoring network.

The Balearic network is managed by the Balearic Government and consists of several fix and mobile stations monitoring pollutants and meteorological parameters in real time or off line.

The framework of this network is dynamic and began to be developed essentially in 1996, although previous studies were carried out during early 1990's.

The stations are distributed throughout the islands with the intention of controlling the influence of local sources. CLL is part of the coal fired power plant control subnetwork. A previous study of historic temporal series of the whole network reflected that this site was the one least affected by local sources, consequently, the most suitable to investigate the remote background environment.

The air quality network configuration and the main local sources can be appreciated in figure 1.6.



PRINCIPALS FOCUS EMISSORS

Codi	Nom
1	Central tèrmica d'Alcúdia
2	Central tèrmica d'Eivissa
3	Central tèrmica de Maó
4	Central tèrmica de Son Reus - Palma
5	Central Tèrmica de Cas Tresorer - Palma
6	Incineradora de Son Reus - Palma
7	Cimentera - Lloseta
8	Aeroport de Mallorca
9	Port de Maó
10	Port d'Eivissa
11	Port de Palma
12	Port d'Alcúdia
13	Port de Ciutadella de Menorca
14	Aeroport de Menorca
15	Aeroport d'Eivissa

ESTACIONS QUALITAT DE L'AIRE

Codi	Nom
1	Parc de Bellver - Palma
2	Foners - Palma
3	Ciutadella de Menorca
4	Sant Antoni de Portmany
5	Central tèrmica - Alcúdia
6	Can Llompart
7	Albufera
8	Sa Pobla
9	Sa Vinyeta - Inca
10	Parc Bit - Palma
11	Pous - Maó
12	Sant Lluís
13	Can Misses - Eivissa
14	Dalt Vila - Eivissa
15	Puig den Valls - Eivissa
16	Hospital Joan March
17	La Misericòrdia
18	Sant Joan de Déu
19	Aeroport de Mallorca

Figure 1.6. Air quality monitoring network in the Balearic Islands. Coloured areas indicate local air basins. Red dots correspond to main emission focus. Black dots correspond to air quality stations.

1.1.6. Previous studies

Particulate matter concentrations and gaseous pollutants (NO_x, SO_2, CO and O_3) have been measured on a regular basis in several European regions since the beginning of the 90's. This has allowed the investigation of trends at certain European regions (Colette et al., 2011; Barmpadimos et al., 2012; Cusack et al., 2012; Cerro, 2013; Querol et al., 2014). However, it is not always straightforward to discriminate the origin of the observed trends. Part of the observed PM_{10} changes in the NW Mediterranean can be explained by a decrease in African dust contributions (Pey et al., 2013b). Similarly, a partial decrease has been attributed to the occurrence of favourable meteorological situations connected with the atmospheric circulation over the northern Atlantic (Jerez et al. 2013). In addition, the vast implementation of abatement strategies over specific areas and/or the impact of the economic crisis can be the main reasons to explain such a decrease (Cusack et al., 2012).

To this date, the University of the Balearic Islands have led a number of studies on air pollution in the Balearic Islands (Mateu et al., 1998 and references therein). Additionally, a campaign performed in the suburbs of Palma de Mallorca in 2004-2005 was devoted to studying PM_{10} and $PM_{2.5}$ concentrations, composition and sources (Pey et al., 2009a, 2013a).

Concerning the profound study of chemical composition and dynamics of aerosols, contemporary similar studies have been carried out in recent years, some from the continent (e.g. Minguillón et al., 2015; Ripoll et al., 2015), and some from islands (Chrit et al., 2018; Fu et al., 2017), some of them even connecting results all around (Alastuey et al., 2016; Berland et al., 2017). All together constitute a Task Force that aims to obtain better knowledge of air pollution and the potential effects of climate change in the Mediterranean.

This Thesis reviews all data available from other studies at remote environments all around the Western Mediterranean, representing a Metaanalysis research of the existing knowledge for the same period as ours. Previous Metaanalysis have been conducted focus on this region (Querol et al., 2009) for the beginning of the millennium or for deposition results (Guieu et al., 2010; Fu et al., 2017).

These findings claim for an extra effort to understand the phenomenology and the sources of PM in regional background sites. For these purposes, Can Llompart (CLL) and Cap Pinar (CP) represent properly the WMB aerosol phenomenology over regional background environments.

1.1.8. State of the art of air quality research

This section has been focused on the current research in air pollution. This scientific field is multidisciplinary. An overview of the main magnitudes and matrix is presented. Furthermore, tools or devices that are commonly used are here listed. Main networks around the globe created around these magnitudes, matrix and/or tools are also presented. And finally, a list of the main type of research studies in this field is displayed. Figure 1.7 reflects the interactions among the subsections.

It all constitutes an updated global picture of the atmospheric environmental research.

Biological pollutants (Pollen-aerobiology, bacteria, virus, entomology…), electromagnetic levels or radioactivity, constitute other global research fields, separated from air quality management or air pollution.

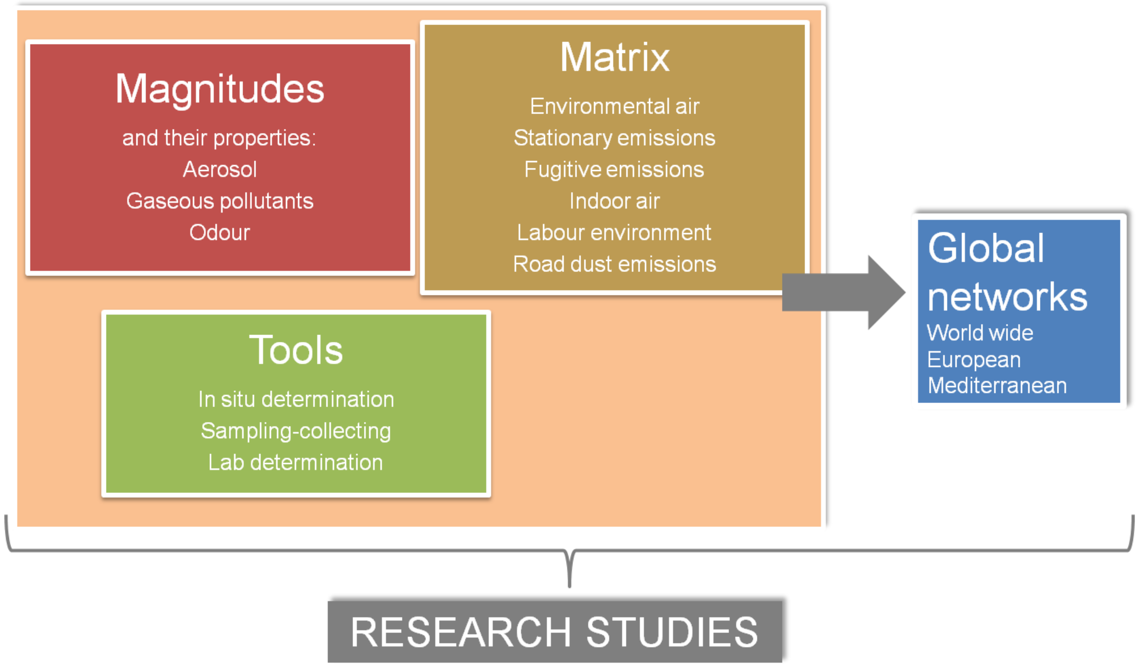


Figure 1.7. Infographic about the relationship among main inputs that the research studies based on atmosphere have.

In the following sections a classification has been elaborated in function of magnitude, matrix, tools and the subsequent type of research. The aspects in which this Thesis has been developed are highlighted in blue.

1.1.8.1. Magnitudes

Aerosol

Aerosol formation and aging: molecular clustering, nucleation processes, new formation particles, coalescence, coagulation, reactions (thermodynamics, kinetics, catalysis, higroscopy, photochemistry…).

> Tools: In lab experiments: reaction chambers, smog chambers; in situ determinations: chromatography (U-HPLC or GC-MS) and spectrophotometries.

Meteorological and climate properties: Cloud Condensation Nuclei, radiative absorption-reflection, ice melting.

> Tools: spectroscopy; Multi-Angle Absorption Photometer (MAAPS); Aethalometer.

Concentration and Size distribution: particles with aerodynamic diameter under 1, 2.5 or 10 µm (PM_1, $PM_{2.5}$, PM_{10}), total suspended particles (PST), ultrafine particles (0.1-1 µm), nanoparticles (<0.1 µm), settling particles (>30 µm), asbestos. In terms of mass and/or number.

> Tools: Collection and gravimetry, microbalance, beta-absorption, laser interferetion, Condensation Particle Counter (CPC), Scanning Mobility Particle Sizer Spectrometer (SMPS).

Chemical composition: inorganic compounds (major, minor and traces), OC/EC, organic compounds.

> Tools: major ions: Ionic Chromatography (anions and cations), SIA (NH_3, NO_3^-), selective ion electrode (NH_3), potenciometry (Cl^-), major elements (ICP-AES, AA-GF), traces elements (ICP-MS, AA-GF), Thermal Optical Transmittance Analyzer-Sunset (OC/EC), Total Organic Carbon Analyzer (WSOC), GC-MS (apolar organic compounds) and HPLC-MS (polar organic compounds), Scan Electron Microscopy (SEM), X-ray Fluorescence (XRF), PIXE analysis (all elements), Aerosol Chemical Speciation monitor (ACSM) and Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (not refractory inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-…) and VOCs), Multi-Angle Absorption Photometer (MAAPS), Aethalometer (PM-BC).

Mineralogy: mineralogy and crystallography.

> Tools: Scan Electron Microscopy (SEM), X-ray Fluorescence (XRF), X-ray Diffraction (XRD).

Physical properties: Aerosol Optical Depth (AOD), vertical profile of the atmosphere, magnetism…

> Tools: in situ: aethalometer, MAAPs, remote sensing ground level: Electronique multiband sun photometer (CIMEL), Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR); satellites: MODIS (NASA) and Copernicus (ESA).

Gaseous pollutants:

Inorganic: NO, NO_2, O_3, CO_2, NH_3, SH_2, heavy metals (Hg, Pb). Patterns, Trends, Dynamics, reactions (molecular clustering thermodynamics, kinetics, catalysis, photochemistry…).

> Tools: spectroscopic sensors, chemiluminiscence sensors, Differential Optical Absorption Spectroscopy (DOAS), retroreflectors, AA-GF (Pb), ICP-MS (Pb), Cold Vapour Atomic Fluorescence Spectroscopy (Hg).

Organic: PAHs, Dioxines and Furanes, BTX, COVs-O3 precursors, biogenic (isoprenes and aged isoprenes), Levoglucosan (biomass burning indicators). Patterns, Trends, Dynamics, reactions (aging, thermodynamics, kinetics, catalysis, photochemistry…).

Tools: FID/PID; in situ chromatography-FID/PID…; resin or filter collecting, thermal desorption or extraction, HPLC or GC-MS; PTR-ToF-MS.

Odour

Odour.

Tools: Lindvall box, diluents devices, panel teams.

Odour compounds: NH_3, SH_2, VOCs: Alcohols, Aldehydes, Aliphatic Hydrocarbons, Amines, Aromatic Alcohol, Aromatic compounds, Cyclic Hydrocarbons, Esters, Ethers, Furans, Halogen-containing comp., Ketones, Lactones, Mercaptanes, Nitrogen-containing comp., Organic Acids, Oxygen-containing comp., Sulphur-containing comp., Terpenes, Heterogroups. Odour factor determination, intensity, synergistic and antagonistic effects.

Tools: electrochemical sensors (NH_3, SH_2), converter-chemiluminiscence (NH_3), converter-spectroscopy SH_2), FID (TOCs), PID (TOCs), GC-MS, HPLC-MS.

1.1.8.2. Matrix

Environmental air: intense traffic environments, urban, suburban, rural, remote, industrial or artificial (reaction chambers, smog chambers) sites.

Tools: air quality stations, mobile/portative stations, PM collectors, settling particles collectors, passive and semi-passive samplers, personal collectors-dosimeters, low cost sensors (nanosensors), ships sites, aircraft sites, balloons, drones; remote sensing devices at ground level: Differential Optical Absorption Spectroscopy (DOAS), retroreflectors, Electronique multiband sun photometer (CIMEL), Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR); satellites: MODIS (NASA) and Copernicus (ESA); dispersion models.

Stationary emissions: waste incineration plants, power plants, ceramic plants, refinery plants, siderurgy plants, chemical plants, other industrial plants, boilers, fireplaces, impregnation industries, transport combustion engines. Emission characterization, abatement systems optimization and factor emission calculations.

Tools: isokinetic determinations (PST, SO_2, SH_2, HF, HCl, PAH, Metals, PCDDFs), electrochemical determination (CO, CO_2, O_2, NO_x, SO_2, NH_3, SH_2), spectroscopy (SO_x, SH_2, CO), chemiluminiscence (NO_x, NH_3), paramagnetism (O_2), FID/PID (CH_4, TOC, VOCs), Fourier-transform infrared spectroscopy (FTIR), Opacimeters (PST, BC).

Fugitive emissions: construction, quarries, concrete factories, asphalt plants, other industries.

Tools: similar as environmental air (different sensitive range) and Differential Optical Absorption Spectroscopy (DOAS), retroreflectors.

Indoor air: schools, underground, hospitals, house, halls, airports, gym…

Tools: Similar to environmental air's.

Labour environment: quarries, confined environments, ATX environments, impregnation emissions, asbestos…

Tools: Personal collectors, dosimeters, handled analyzer (CH_4, VOCs), PM collectors.

Road dust emissions: breaks, tyres, resuspension, engine friction.

Tools: road dust samplers and lab determination.

1.1.8.3. Tools

In situ determination:

Air quality stations: spectroscopy sensors (SO_2, SH_2, CO, O_3), chemiluminiscence sensors (NO_x, NH_3), beta absorption (PM), microbalance (PM), nephelometry-scattering (PM), laser (PM); FID/PID (CH_4, TOC), chromatography (BTX, derivates and O_3 precursors).

Air quality supersites: Condensation Particle Counter (CPC), Scanning Mobility Particle Sizer Spectrometer (SMPS), Aerosol Chemical Speciation monitor (ACSM) (not refractory inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-…) and VOCs), Multi-Angle Absorption Photometer (MAAPS) (BC), Aethalometer (PM-BC).

Emerging techniques in campaigns or supersites: X-ray Fluorescence (XRF) (Metals and other elements), Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (not refractory inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl_-….) and VOCs), PTR-ToF-MS (VOCs).

Remote sensing ground level: Differential Optical Absorption Spectroscopy (DOAS), retroreflectors, Electronique multiband sun photometer (CIMEL) (AOD and PM in vertical column), Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR) (AOD and PM depending on height).

Satellites: MODIS (NASA) (PM, NO_x, SO_2, O_3) and Copernicus (ESA) (PM, NO_x, SO_2, O_3).

Stack emissions: spectroscopy sensors (SO_2, SH_2, CO, O_3), chemiluminiscence sensors (NO_x, NH_3), paramagnetism (O_2), opacimeters, electrochemical sensors (SO_2, SH_2, CO, CO_2, O_3, NO_x, NH_3, O_2), Fourier-transform infrared spectroscopy (FTIR) (SO_2, SH_2, CO, CO_2, O_3, NO_x, NH_3, O_2), FID (TOC), PID (TOC).

Sampling-collecting

PM collectors (PST, PM_{10}, $PM_{2.5}$, PM_1, waterfall impactors), settling particles collectors (Bulk, Precipitation, WD-DD), semi-passive and passive collectors-dosimeters, resin or filter collecting followed by thermal desorption or extraction, Lindvall box, isokinetic samplers (Stack emissions), road dust samplers.

Lab determination

Artificial environments: reaction chambers, smog chambers

Lab techniques: gravimetry, spectrophotometry, Ionic Chromatography (anions and cations), Flow injection analysis (FIA) and Sequential injection analysis (SIA)-spectroscopy (NH_3, NO_3^-), selective ion electrode (NH_3, F^-), potenciometry (Cl^-), ICP-AES, AA-GF/Flame (major elements), ICP-MS (traces elements), AA-GF (traces elements), Thermal Optical Transmittance Analyzer-Sunset (OC/EC), Total Organic Carbon Analyzer (WSOC), GC-MS (apolar organic compounds) and HPLC-MS (polar organic compounds), Scan Electron Microscopy (SEM), X-ray Fluorescence (XRF), PIXE analysis (all elements), X-ray Fluorescence (XRF), X-ray Diffraction (XRD), AA-GF (Pb), ICP-MS (Pb), Cold Vapour Atomic Fluorescence Spectroscopy (Hg), diluents devices (Odour).

1.1.8.4. Type of research studies

Levels, dynamics and/or patterns of pollutants (daily, weekly, seasonal…).

Magnitudes: aerosol, gaseous pollutants, odour.

Matrix: Environmental air in all environments (traffic, urban, suburban, rural, remote)

Tools: air quality stations, mobile/portative stations, PM collectors, settling particles collectors, passive and semi-passive samplers, personal collectors-dosimeters, low cost sensors (nanosensors), ships sites, aircraft sites, balloons, drones; remote sensing devices at ground level: Differential Optical Absorption Spectroscopy (DOAS), retroreflectors, Electronique multiband sun photometer (CIMEL), Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR); satellites: MODIS (NASA) and Copernicus (ESA); dispersion models.

Trends calculations.

Magnitudes: aerosol, gaseous pollutants, aerosol chemical composition.

Matrix: Environmental air in all environments (traffic, urban, suburban, rural, remote)

Tools: air quality stations, mobile/portative stations, PM collectors, settling particles collectors, passive and semi-passive samplers; remote sensing devices at ground level: Differential Optical Absorption Spectroscopy (DOAS), Electronique multiband sun photometer (CIMEL), Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR); satellites: MODIS (NASA) and Copernicus (ESA); dispersion models.

Chemical reactions, reaction mechanism, catalyst and physical processes (molecular clustering, coagulation, settling).

Magnitudes: aerosol, gaseous pollutants.

Matrix: Environmental air, indoor air.

Tools: Artificial environments: reaction chambers, smog chambers, spectroscopy, GC-MS, Fourier-transform infrared spectroscopy (FTIR), Differential Optical Absorption Spectroscopy (DOAS).

New particle formation.

Magnitudes: aerosol.

Matrix: Environmental air.

Tools: Artificial environments: reaction chambers, smog chambers; beta absorption (PM), microbalance (PM), nephelometry-scattering (PM); Condensation Particle Counter (CPC), Scanning Mobility Particle Sizer Spectrometer (SMPS), Aerosol Chemical Speciation monitor (ACSM) (not refractory inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-…) and VOCs).

Source apportionment.

Magnitudes: Aerosol, gaseous pollutants, odour.

Matrix: Environmental air, fugitive emissions, indoor air, labour environments, stationary emissions.

Tools: air quality stations, mobile/portative stations, PM collectors, settling particles collectors, Lindvall box, diluents devices, panel teams, electrochemical sensors (NH_3, SH_2), converter-chemiluminiscence (NH_3), converter-spectroscopy SH_2), FID (TOCs), PID (TOCs), GC-MS, HPLC-MS.

Health affection: toxicological and epidemiological studies.

Magnitudes: Aerosol, gaseous pollutants, and within components.

Matrix: Environmental air, indoor air, labour environment.

Tools: lab toxicological tools (tissue degradations…) and epidemiological statistics associated to air quality data.

Ecosystem affection

Magnitudes: Aerosol, gaseous pollutants, and within components.

Matrix: environmental air, fugitive emissions.

Tools: ecological tools (demography, patterns, seasonality…) associated with air quality data and deposition.

Elements and compounds, geological cycles

Magnitudes: Periodic table elements, aerosol, gaseous pollutants, and within components.

Matrix: Environmental air as part of the global cycle and fluxes from and to other matrix (soil, water…).

Tools: settling particles and gas deposition collectors, interphase chambers (sea surface, soil surface), environmental air tools and in lab determination.

Investigation of emission factors.

Magnitudes: Aerosol, gaseous pollutants, and within components.

Matrix: Stationary emissions, Fugitive emissions.

Tools: isokinetic determinations (PST, SO_2, SH_2, HF, HCl, PAH, Metals, PCDDFs), electrochemical determination (CO, CO_2, O_2, NO_x, SO_2, NH_3, SH_2), spectroscopy (SO_x, SH_2, CO), chemiluminiscence (NO_x, NH_3), paramagnetism (O_2), FID/PID (CH_4, TOC, VOCs), Fourier-transform infrared spectroscopy (FTIR), Opacimeters (PST, BC), Differential Optical Absorption Spectroscopy (DOAS), retroreflectors, road dust samplers, and environmental air tools.

Dispersion Model Developments:

Focus on air quality: models for evaluating levels of pollutants (globals, regionals, street canyon…); forecasting pollutant levels; assessing what specific policy decisions could suppose; source contributions.

Focus on emission sources: model dispersion of specific emissions sources, peaks and estimating risks (forward trajectories); detecting sources of specific episodes (backtrajectories); inventories elaboration.

Optical properties (AOD, PM, BC).

Magnitudes: Aerosols.

Matrix: environmental air (surface and vertical column).

Tools: Multi-Angle Absorption Photometer (MAAPS) (BC), Aethalometer (PM-BC), Electronique multiband sun photometer (CIMEL) (AOD and PM in vertical column), Light Detection and Ranging o Laser Imaging Detection and Ranging (LIDAR) (AOD and PM depending on height), Satellites.

Climate change: radiative properties-warm potential factor determination.

Magnitudes: Aerosols, gaseous pollutants.

Matrix: environmental air.

Tools: Multi-Angle Absorption Photometer (MAAPS) (BC), Aethalometer (PM-BC), satellites.

Cloud Condensation Nuclei.

Magnitudes: Aerosols and within components.

Matrix: Environmental air.

Tools: environmental air tools.

Quality control and quality assurance.

Magnitudes: all

Matrix: all

Tools: all

Analytical Chemistry development.

Magnitudes: all

Matrix: all

Tools: all

Nanoparticles generation-control of processing systems.

Magnitudes: aerosol

Matrix: artificial chambers.

Tools: Condensation Particle Counter (CPC), Scanning Mobility Particle Sizer Spectrometer (SMPS).

1.1.8.5. Current global networks related to this field

WORLD WIDE NETWORKS:

Global Atmosphere Watch (GAW) Programme

Within the United Nations, it is the responsibility of WMO to provide the authoritative voice on the state and behaviour of the atmosphere and climate of the Earth. To this end, the Atmospheric Research and Environment Branch (ARE) of the Research Department co-ordinates and stimulates research on the composition of the atmosphere and weather forecasting, focusing on extreme weather events and socio-economic impacts. ARE supports global research initiatives under programmatic guidance from the Commission for Atmospheric Science (CAS). It does this through two programmes: the Global Atmosphere Watch (GAW) Programme and the World Weather Research Programme (WWRP). WWRP supports research to develop improved and cost-effective forecasting techniques and their application for socio-economic benefit and in decision-making. Activities are conducted related to synoptic forecast verification and linking forecast products to societal benefit areas. ARE leads the WMO Sand and Dust Storm Warning System. It also supports sound science practices in weather modification research. CAS is closely linked to the World Climate Research Programme with which it shares support of the Working Group on Numerical Experimentation (WGNE) and through the WWRP, a growing number of joint research initiatives. GAW focuses on the coordination and application of global observations of atmospheric greenhouse gases, ozone, ultraviolet radiation, aerosols, selected reactive gases, precipitation chemistry and the GAW urban meteorology and environment project (GURME). It supports international conventions on ozone depletion, climate and long-range transport of air pollution. With community support it issues WMO Ozone Bulletins and Greenhouse Gas Bulletins.

Aerosol Robotic Network (AERONET)

The AERONET (AErosol RObotic NETwork) project is a federation of ground-based remote sensing aerosol networks established by NASA and PHOTONS (PHOtométrie pour le Traitement Opérationnel de Normalisation Satellitaire; Univ. of Lille, CNES, and CNRS-INSU) and is greatly expanded by networks (e.g., RIMA, AeroSpan, AEROCAN, and CARSNET) and collaborators from national agencies, institutes, universities, individual scientists, and partners. For more than 25 years, the project has provided long-term, continuous and readily accessible public domain database of aerosol optical, microphysical and radiative properties for aerosol research and characterization, validation of satellite retrievals, and synergism with other databases. The network imposes standardization of instruments, calibration, processing and distribution.

EUROPEAN NETWORKS:

Aerosols Clouds and Trace gases Research Infraestructure Network (ACTRIS)

ACTRIS (Aerosol, Clouds and Trace Gases Research Infrastructure) is a pan-European initiative consolidating actions amongst European partners producing high-quality observations of aerosols, clouds and trace gases. Different atmospheric processes are increasingly in the focus of many societal and environmental challenges, such as air quality, health, sustainability and climate change. ACTRIS aims to contribute in the resolving of such challenges by providing a platform for researchers to combine their efforts more effectively, and by providing observational data of aerosols, clouds and trace gases openly to anyone who might want to use them.

EUROCHAMP-2020 is a separately run project coordinating the activities of atmospheric measurement chambers in Europe, but aims to merge in ACTRIS at the end of the project.

EIONET: European Topic Centre on Air Pollution and Climate Change Mitigation

The ETC on Air Pollution, Transport, Noise and Industrial Pollution (ETC/ATNI) is an international consortium working with the European Environment Agency under a framework partnership agreement for the period 2019-2021. The lead institution for ETC/ATNI is Stiftelsen Norsk Institutt for luftforskning (NILU), Norway.

The main tasks of the ETC are:

Integrated activities in the areas of air pollution, noise, industry, energy and transport;

Air pollutant emissions monitoring, reporting and verification;

Air pollutant mitigation assessments and indicators;

Air quality and noise data;

Air quality and noise assessments and indicators;

ETC management and capacity building in EEA member and cooperating countries.

Copernicus Atmosphere Monitoring Service

The Copernicus Atmosphere Monitoring Service aims to provide continuous data and information on atmospheric composition. The service describes the current state of the atmosphere, forecasts for several days ahead, and consistently analyses data records for past periods. It supports many applications in a variety of domains including health, environmental monitoring, renewable energies, meteorology, and climatology.

The service builds on a series of projects developed within the Framework Programmes 6 and 7 (FP6/FP7), funded by the EC, and on ESA's GMES Service Element project PROMOTE.

The Copernicus Atmosphere Monitoring Service is also supported by the Sentinel satellites.

EMEP (European Monitoring and Evaluation Programme)

EMEP is the co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe. It is a scientifically based and policy driven programme under the UNECE Convention on Long-range Transboundary Air Pollution. EMEP's activities are supported through the work of a number of EMEP centres and task forces.

MEDITERRANEAN NETWORKS:

Chemistry-Aerosol Mediterranean Experiment (ChArMEx)

As part of the international multidisciplinary program MISTRALS (Mediterranean Integrated Studies At Local And Regional Scales) (http://www.mistrals-home.org/), ChArMEx (the Chemistry-Aerosol Mediterranean Experiment) (http://charmex.lsce.ipsl.fr/) is an international cooperative research program that aims at a better understanding and quantification of tropospheric chemistry and its impacts in the Mediterranean with a focus on air quality, regional climate, and biogeochemistry, and of their future evolution. ChArMEx is composed of many scientific projects and involves a large research community from various disciplines and methodological backgrounds.

MISTRALS is finally part of the Plan Bleu task force, which was created from the Barcelona convention (COP21). Plan Bleu framework serves as a diagnosis and generation of knowledge to understand the human impact on the Mediterranean and to obtain knowledge in order to improve its resilience to face the impacts of climate change.

This Thesis project has been founded with the aim of being a project with international involvement and international projection. It appeared as a complement of the international multi-team programme ChArMEx.

Other projects around the Mediterranean Sea were also carried out in this context, like ADRIMED (Aerosol Direct Radiative Impact on the regional climate in the MEDiterranean region) or SAF-MED (Mediterranean Experiment SOP summer 2013). This PhD Thesis collaborated with those projects in its second phase.

1.2. Objectives

The global aim of this project consists in estimating the footprint of anthropogenic activity in the Mediterranean air background environment. Thus, in a context of a non-stop increasing human pressure and the challenge that climate change reflects.

1.2.1. General Objectives

The overall objective of this study is to obtain the current diagnosis of air pollution in the Western Mediterranean, with attention to the atmospheric impact of recent socio-economic changes and to the implementation of mitigation policies. This PhD aims at supporting future efficient strategies to counteract air pollution in the Western Mediterranean, as well as to support health and ecosystems impact studies.

The general objectives of this thesis are:

1. To determine the current state and recent trends of atmospheric pollutants in the Western Mediterranean observed at three environments: urban, suburban and rural/remote, and their relation with atmospheric dynamics, mitigation policies and socio-economic changes.

2. To investigate fine and coarse aerosol composition and sources at the regional background of the Balearic Islands from a long-term monitoring campaign, with a focus on tourism as a potential socio-economic activity having an impact on air quality at the regional scale.

3. To study wet and dry aerosol deposition in terms of chemical fluxes and sources, with special attention to the contribution of anthropogenic sources and African dust origin.

4. To advance in source apportionment of organic aerosols by developing a methodology based on the combination of conventional and state of the aerosol composition data.

1.2.2. Specific objectives

The specific objectives were:

1. To determine the state of atmospheric pollutants in the western Mediterranean, their patterns and their relation with atmospheric dynamics.

2. To calculate trends of these pollutants from 2000 to the present, differentiating for urban, suburban and rural-regional-remote environments.

3. To evaluate the effect of the policies implemented to reduce air pollution, trying to discern the effect of local from those of continental level.

4. To carry out a long-term measurement and sampling campaign (two and a half years) in a remote location in the Balearic Islands, in order to deliver representative results of the background environment of the centre of the western Mediterranean, with special attention to spring and summer seasons, when the most intense particulate matter contamination phenomena occur.

5. To study the pattern of gases (SO_2, NO_2, O_3, NH_3), particles (in terms of fractions mass and number) and black carbon, and influence of the meteorological situations. Additionally, to compare gases and particulate matter concentrations from remote sites around the Western Mediterranean.

6. To perform a chemical characterization study of atmospheric aerosol for fractions PM_{10} and PM_1. Elaborate a comparison of chemical components for the Western Mediterranean collecting existing studies between the mid 2000's and 2013.

7. To conduct a source apportionment study for PM_{10} and PM_1 in order to separate and quantify the main sources, natural or anthropogenic.

8. To evaluate whether increasing human activity, and in particular tourism and related activities, such as power plants, cruises or air traffic, can affect air pollution, and the counteracted effect of the European upcoming restrictions on emissions.

9. To study separately the wet and the dry deposition of gases and particles with a long-term sampling campaign (1 and a half years).

10. To chemically characterise settling fluxes for a wide range of parameters. In addition, to cluster components in different groups, including mineral and marine fractions, nutrients and trace elements of human origin to analyse deposition fluxes in function of air mass origin.

11. To identify main sources contributing to deposition, separating their influence on the wet and dry components.

12. To study the main case studies of intense deposition for both, wet and dry, with special treatment for African episodes, in which a separate analysis has been conducted for the main mineral dust source areas in order to investigate their chemical footprint. Furthermore to compile and compare this type of studies.

13. To compare and to study how off-line particle studies, with 24-hour sampling on the filter, can connect with avant-garde devices that release real-time data on the non-refractory fractions of the particles.

1.2.3. PhD performance, collaborations and chronology.

The main monitoring campaign of this PhD Thesis was developed at Can Llompart. It was initially headed by the IDAEA-CSIC team (leaded by Jorge Pey, Xavier Querol and Andres Alastuey) in coordination with UIB (José C. Cerro and Victor Cerdà), and in collaboration with the Laboratory of the Atmosphere from de Balearic Islands Government (José C. Cerro, Maria Luis Tobar), and the environment department of ENDESA-ENEL power supply company (Carles Bujosa).

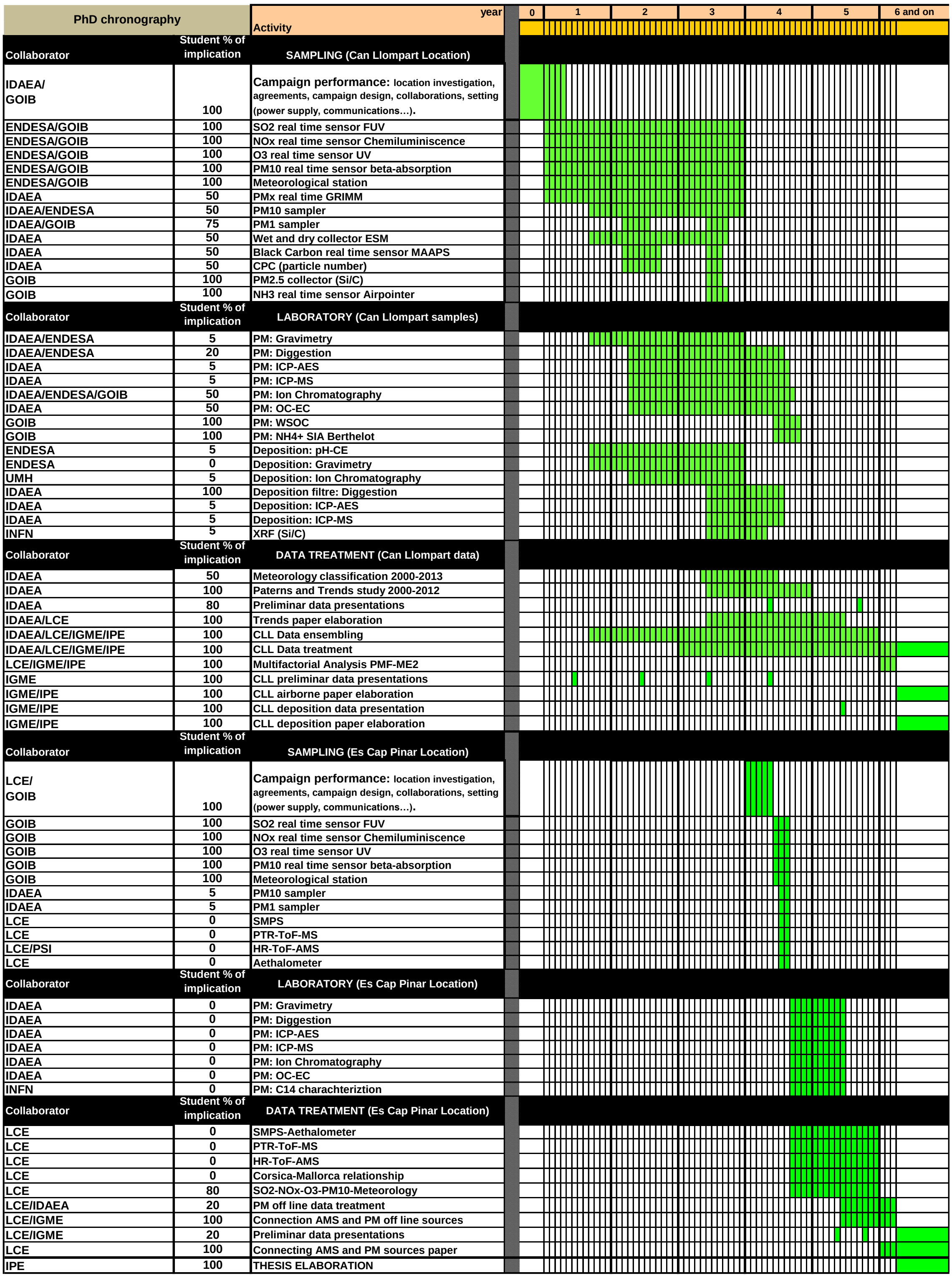
Most of sample treatments and determinations were done at the IDAEA-CSIC facilities. Few determinations took place at others laboratories: ENDESA's; Laboratory of the Atmosphere; Miguel Hernández University; and Nuclear Physics National Institute of Italy.

Activities, institutions involved, and the implication of the student are shown in Figure 1.8.

Complementary to the main campaign, an additional study was performed 6 months after the closure of the Can Llompart monitoring. That campaign was directed by the Laboratory of Environmental Chemistry - Université d'Aix-Marseille and located at Cap EsPinar, which is located only 6 km northwards of Can Llompart. The objective of that campaign was to advance in the knowledge of secondary organic aerosol formation in this region, with special attention to the role of marine emissions in this process. To this end, a number of state-of-the-art instruments together with different conventional monitors were deployed. This campaign offered me an excellent opportunity to connect the outputs retrieved from the long-term campaign and to go beyond in some of the aspects, such as the origin of the organic aerosol.

Institution	Abbreviation	Main collaborators
Environment department-ENDESA	ENDESA	Carles Bujosa
Laboratory of the atmosphere-Govern de les Illes Balears	GOIB	José C. Cerro
Institute of Environment Assessment and Water Research – CSIC	IDAEA	Jorge Pey, Xavier Querol, Andrés Alastuey and Noemí Pérez.
Geological Survey of Spain	IGME	Jorge Pey
Università di Firenze and Instituto Nazionale di Fisica Nucleare	INFN	Franco Lucarelli
ARAID Foundation -Instituto Pirenaico de Ecología – CSIC	IPE	Jorge Pey
Laboratory of Environmental Chemistry - Université d'Aix-Marseille	LCE	Nicolas Marchand, Jorge Pey, Brice Temime-Roussel, Stig Hellebust and H. Langley DeWitt.

Paul Schrerrer Institute	PSI	Miriam Elser, Andre Prévôt
Miguel Hernández University	UMH	Sandra Caballero



Collaborator	Student % of implication	Activity
Collaborator	**Student % of implication**	**SAMPLING (Can Llompart Location)**
IDAEA/ GOIB	100	Campaign performance: location investigation, agreements, campaign design, collaborations, setting (power supply, communications…).
ENDESA/GOIB	100	SO2 real time sensor FUV
ENDESA/GOIB	100	NOx real time sensor Chemiluminiscence
ENDESA/GOIB	100	O3 real time sensor UV
ENDESA/GOIB	100	PM10 real time sensor beta-absorption
ENDESA/GOIB	100	Meteorological station
IDAEA	50	PMx real time GRIMM
IDAEA/ENDESA	50	PM10 sampler
IDAEA/GOIB	75	PM1 sampler
IDAEA	50	Wet and dry collector ESM
IDAEA	50	Black Carbon real time sensor MAAPS
IDAEA	50	CPC (particle number)
GOIB	100	PM2.5 collector (Si/C)
GOIB	100	NH3 real time sensor Airpointer
Collaborator	**Student % of implication**	**LABORATORY (Can Llompart samples)**
IDAEA/ENDESA	5	PM: Gravimetry
IDAEA/ENDESA	20	PM: Diggestion
IDAEA	5	PM: ICP-AES
IDAEA	5	PM: ICP-MS
IDAEA/ENDESA/GOIB	50	PM: Ion Chromatography
IDAEA	50	PM: OC-EC
GOIB	100	PM: WSOC
GOIB	100	PM: NH4+ SIA Berthelot
ENDESA	5	Deposition: pH-CE
ENDESA	0	Deposition: Gravimetry
UMH	5	Deposition: Ion Chromatography
IDAEA	100	Deposition filtre: Diggestion
IDAEA	5	Deposition: ICP-AES
IDAEA	5	Deposition: ICP-MS
INFN	5	XRF (Si/C)
Collaborator	**Student % of implication**	**DATA TREATMENT (Can Llompart data)**
IDAEA	50	Meteorology classification 2000-2013
IDAEA	100	Paterns and Trends study 2000-2012
IDAEA	80	Preliminar data presentations
IDAEA/LCE	100	Trends paper elaboration
IDAEA/LCE/IGME/IPE	100	CLL Data ensembling
IDAEA/LCE/IGME/IPE	100	CLL Data treatment
LCE/IGME/IPE	100	Multifactorial Analysis PMF-ME2
IGME	100	CLL preliminar data presentations
IGME/IPE	100	CLL airborne paper elaboration
IGME/IPE	100	CLL deposition data presentation
IGME/IPE	100	CLL deposition paper elaboration
Collaborator	**Student % of implication**	**SAMPLING (Es Cap Pinar Location)**
LCE/ GOIB	100	Campaign performance: location investigation, agreements, campaign design, collaborations, setting (power supply, communications…).
GOIB	100	SO2 real time sensor FUV
GOIB	100	NOx real time sensor Chemiluminiscence
GOIB	100	O3 real time sensor UV
GOIB	100	PM10 real time sensor beta-absorption
GOIB	100	Meteorological station
IDAEA	5	PM10 sampler
IDAEA	5	PM1 sampler
LCE	0	SMPS
LCE	0	PTR-ToF-MS
LCE/PSI	0	HR-ToF-AMS
LCE	0	Aethalometer
Collaborator	**Student % of implication**	**LABORATORY (Es Cap Pinar Location)**
IDAEA	0	PM: Gravimetry
IDAEA	0	PM: Diggestion
IDAEA	0	PM: ICP-AES
IDAEA	0	PM: ICP-MS
IDAEA	0	PM: Ion Chromatography
IDAEA	0	PM: OC-EC
INFN	0	PM: C14 charachteriztion
Collaborator	**Student % of implication**	**DATA TREATMENT (Es Cap Pinar Location)**
LCE	0	SMPS-Aethalometer
LCE	0	PTR-ToF-MS
LCE	0	HR-ToF-AMS
LCE	0	Corsica-Mallorca relationship
LCE	80	SO2-NOx-O3-PM10-Meteorology
LCE/IDAEA	20	PM off line data treatment
LCE/IGME	100	Connection AMS and PM off line sources
LCE/IGME	20	Preliminar data presentations
LCE	100	Connecting AMS and PM sources paper
IPE	100	THESIS ELABORATION

Figure 1.8. Chronography performance of the activities related to the studies carried out at Can Llompart and Cap Es Pinar, indication of the collaborator institution and the implication of the student that defences this Thesis.

1.3. Introduction to methodological aspects

This section aims to elaborate the methodological aspects developed during this Thesis, which are specifically described in the corresponding chapters.

In order to reach the general objective 1 (see Section 1.2.1.), historic available air quality data (2002-2012 and 2013-2018) was integrated and a database was built. Different Openair (r-project) tools were used to determine patterns and trends: timeVariation, pollutionRoses, Theil-Sen…

Furthermore, for the period 2002-2012, Hysplit backward trajectories were calculated and satellite observations and modelizations were consulted with the aim of determining daily air mass advections. Thus, it allows us to study separate patterns and trends, and to discern the effect of the air pollution mitigation policies.

The general objective 2 (see Section 1.2.1.) implied a 3-years sampling campaign (2010-2012) with a number of sensors and collectors at Can Llompart site: gaseous pollutant analysers, meteorological sensors, real time particulate matter sensors based in beta absorption and laser, and a PM_{10} collector. Occasional sensors and collectors were additionally displayed during intensive campaigns: PM_1 collector, particle counter CPC, Black Carbon sensor and a NH_3 sensor. PM_{10} and PM_1 samples were treated and analysed with the purpose of determining the chemical composition. A Positive Matrix Factorization calculation was conducted with the intention of identifying and quantifying the different aerosol sources that contribute to the Western Mediterranean background.

A parallel 2-years campaign of atmospheric deposition sampling was carried out in order to achieve the objective 3 (see Section 1.2.1.). A separate collection of wet and dry deposition and a further chemical composition laboratory analysis were made in order to study specific patterns and sources.

The influence of atmospheric dynamics was investigated for the previous objectives.

Finally, for objective 4 (see Section 1.2.1.), an extra campaign was conducted during summer 2013 in which different avant-garde devices were deployed at Cap Pinar site (a PTF-ToF-MS, an aethalometer, a SMPS and a HR-ToF-AMS), all of them in combination with conventional sensors for gaseous pollutants, meteorology and particulate matter. Additionally two PM collectors were displayed, one with a PM_{10} inlet and another with PM_1. Chemical composition was determined likewise at Can Llompart campaigns. A methodology was developed to combine the organic compounds source contribution outputs of the HR-ToF-AMS with the chemical composition of the PM_1 filters.

1.3.1. Sampling sites and monitoring strategy

The selected monitoring site is located on the Island of Mallorca (Balearic Islands, Spain) (39.838”N, 03.024”E, 45 m a.s.l.), in the core of the WMED (Figure 1.9). The Can Llompart observatory (CLL) is placed in the north of the island, with the Tramuntana mountain range in its north-western side. This mountain range, emerging from the western coastline of the island, conforms a chain of mid-altitude peaks (up to 1445 m a.s.l) with south-west to north-east direction which, in addition to sea breezes, drives most of wind regimes (Pey et al., 2009a). Thus, sea to land breezes from the east blows during the day, while vespertine land-to-sea breezes occur from the south. Two key sources of emission are located nearby CLL (Figure 1.9.c): 1) a 540 MW coal-fired power plant (Es Murterar-Alcudia, 6,5 Km distant in SE direction); 2) a commercial harbour (Alcudia Port, 9,1 Km distant in E direction). Micro-implantation characteristics can be appreciated in Figure 1.9.d.1, showing the site in the middle of crop lands and forest, at 70 m of a moderately-transited road (around 1000 vehicles per day) on the eastern side.

An additional campaign was conducted during summer 2013 at Cap Pinar (CP) (Figure 1.9), few kilometres away from CLL. CP site was set-up exclusively for the summer 2013 campaign at the end of June, being fully operative from July 3rd to August 13th. CP was built in the "Es Cap Pinar" military facilities belonging to the Spanish Ministry of Defence. The environment is a non-urbanized area surrounded by pine forested slopes, being one of the most insulated zones in the Mallorca Isle, in between the Alcudia and Pollença bays. The exact location of the site is 39.885°N, 3.195°E, at around 20 m a.s.l., at a distance of about 0.08 Km to the eastwards coastline, 0.55 Km to the westwards one and 0.90 Km to the northwards one (Figure 1.9.d.2).

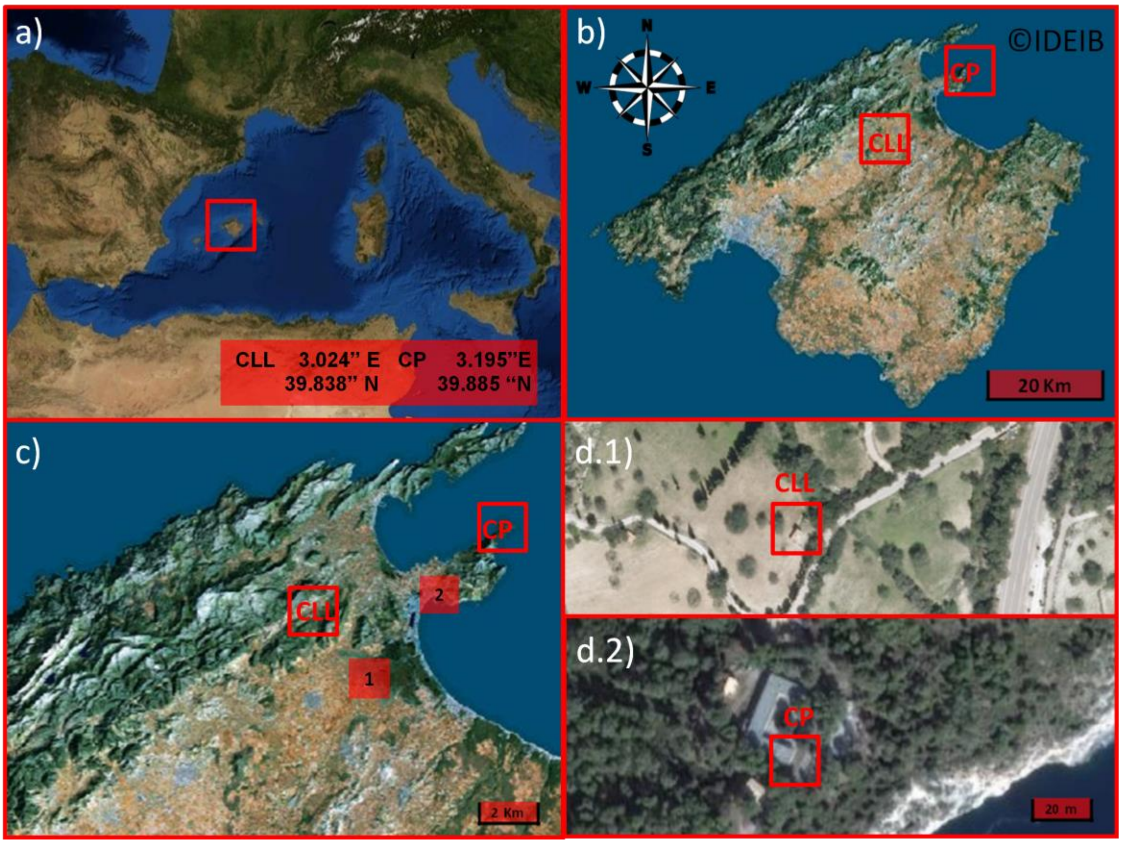


Figure 1.9. Sites, Can Llompart (CLL) and Cap Pinar (CP), location are displayed in decreasing scale from left to right and up to down, from the situation in the core of the Western Mediterranean Basin (a) to microimplantation (d). c) reflects main emission focus: 1. The "Es Murterar-Alcudia" coal-fired power plant; 2. The Alcudia harbour. d) shows the microimplantation of both sites.

Pictures of sites can be seen in figures 1.10 to 1.13. Figure 1.10 shows the regular sampling at Can Llompart; Figure 1.11 reflects the views all around the Can Llompart sampling point; Figure 1.12 shows the additional deployment of instruments at Can Llompart during intensive observation periods; Figure 1.13 shows the deployment of sampling inlets at Cap Pinar site.

Figure 1.10. 1) Inlet for gaseous sampling (SO_2, NO, NO_2, O_3) with conventional instrumentation; 2) Grimm optical particle counter (PM_{10}, $PM_{2.5}$, PM_1); 3) Inlet for the beta absorption monitor; 4) Sequential high-volume PM_{10} sampler; 5) Automatic collector of dry and wet deposition; 6) meteorological tower (temperature, relative humidity, pressure, wind direction and velocity); 7) rainfall collector.

Figure 1.11. Three 120º angle views at CLL site

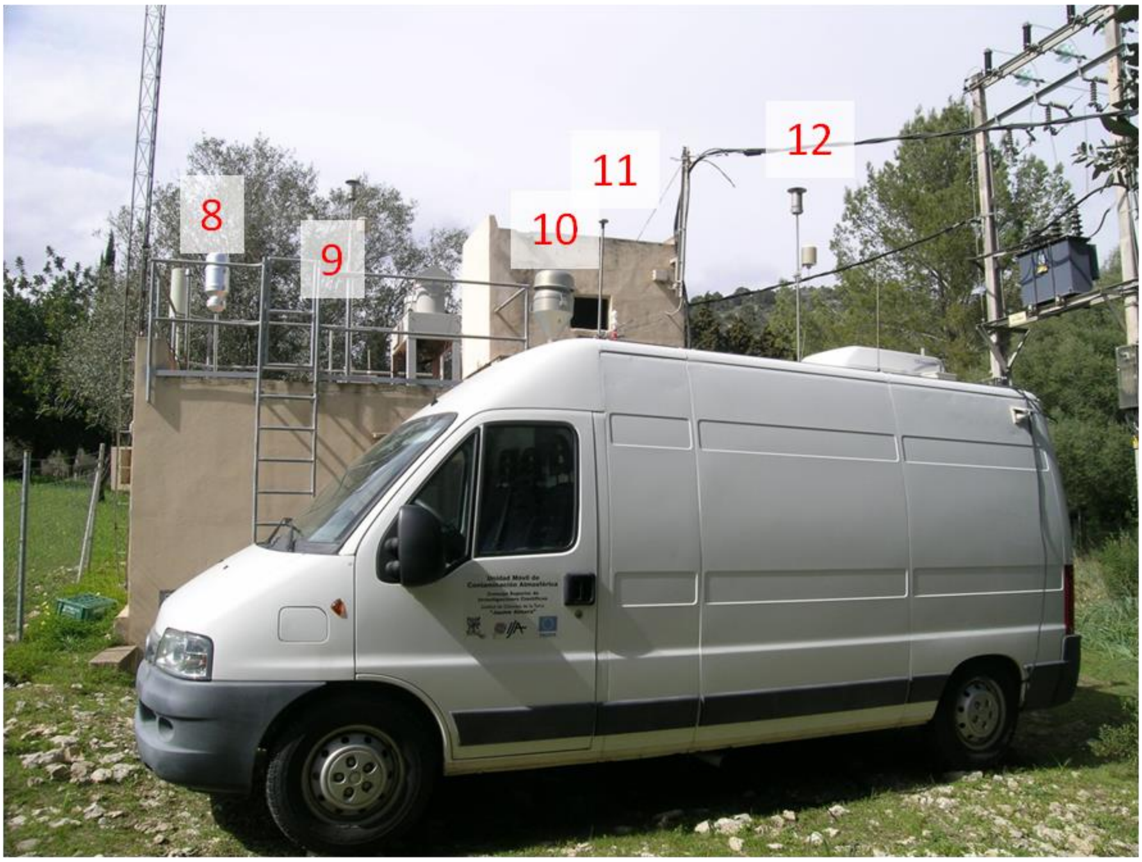


Figure 1.12. Additional equipment displaying during intensive campaigns: 8) New inlet for Sequential high-volume PM_{10} sampler; 9) Inlet for Condensation Particle Counter (Number of particles); 10) Inlet for Sequential high-volume PM_1 sampler; 11) Inlet for MAAPS sensor (Black Carbon); 12) Inlet for an additional beta absorption monitor.

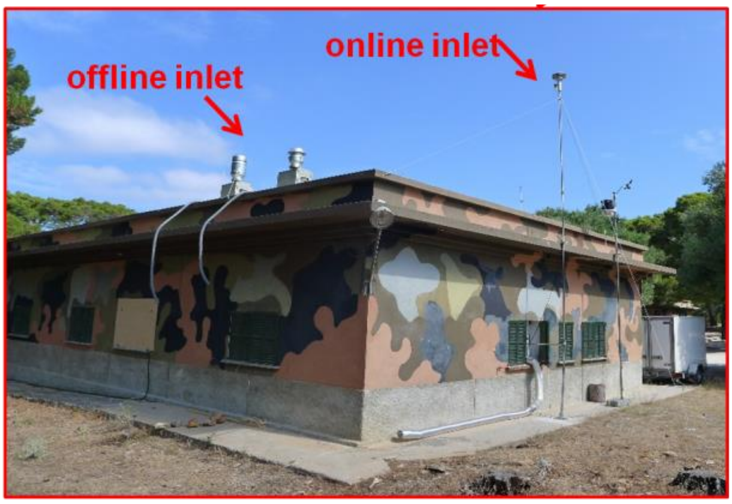


Figure 1.13. Es Pinar Cape off line inlets indicated on the left site and on line measurements inlet on the right side.

1.3.2. Field and laboratory methodologies

Specific methodology is explained in each chapter. Here we introduce the general vision of the common methodology used in these kinds of studies.

Gaseous Pollutants

The EN method for determination of SO_2, NO_2 and O_3 describe the operating characteristics, and establish criteria for the influence of losses on pollutant concentrations; air conditioning and residence time of the sample from the entrance to the analyzer: Calibrations should be performed at least once every 3 months and after repair; Verification of zero and span should be at least once every two weeks, with acceptance criteria of zero (≤ 5 nmol / mol_{air}) and span (≤ 5.0% of initial span gas value).

Regarding maintenance, the EN standards indicate change of particulate filter at least once every 3 months and change of the sampling lines at least once every 6 months.

SO_2 EN 14212 standard defines characteristics and requirements for real time sulphur dioxide measurement sensors by ultraviolet fluorescence method. UV fluorescence is based on the emission of SO_2 excited molecules by previous excitation with UV rays.

NO_2 and NO EN 14211 standard defines characteristics and requirements for real time nitrogen dioxide and nitrogen monoxide measurement sensors by chemiluminescence method. The converter efficiency should be ≥ 95%.

O_3 EN 14625 standard defines characteristics and requirements for real time ozone measurement sensors by UV photometry.

Calibration must be done by in situ ozone generation with a UV lamp.

Aerosols

Airborne particles and components within, PM EN-ISO 12341 standard defines collectors performance, sampling and gravimetric determination of PM fractions (10 and 2.5).

A collector consists of a sampling head inlet, which separates particles greater than 10, 2.5 or 1 micron. The head makes the air enter through nozzles and is forced to hit a surface. This surface must be impregnated with petroleum jelly. Larger particles will collide on this surface by centripetal acceleration and remain trapped there. The air is then passed through a filter with a particle retention efficiency of more than 99.5 %. The standard establishes two types of heads, one with a low flow rate and another with a high flow rate.

In this work, a MCV-CAV-A/MSb sequential high-volume sampler was used for PM_{10} collection and a DIGITEL high-volume sampler for PM_1, both on 150 mm quartz micro-fibre filters.

Then the PM mass captured in the filter must be determined gravimetrically. The sampling time should be 24 h. Filters must be driven to a established contain of humidity.

Despite the reference standard is the previously mentioned (EN 12341), there are several alternative technologies with the capacity to deliver real time PM concentrations.

Two of them have been used in this Thesis: the beta attenuation and laser light scattering.

Beta attenuation consists in filtering air through a filter tape generating a spot. The attenuation of beta radiation through the spot is measured with a determined time interval. Every hour the tape turns and the filtering starts again in a new spot. Absorption of beta rays would depend on the type of particle. Therefore it is necessary to correlate this method with the reference one periodically. Different beta sources can be used.

Light scattering measurements is the most widespread optical method, especially laser scattering. These systems separate PM in different aerodynamic size fractions, entering the detector through different particle size channels. Numbers of particles depending on their size can be integrated in mass concentration. Again this will depend on the type of particle, therefore it is necessary also to correlate with the reference method.

Metals EN 14902 standard establishes the method for determining the air quality concentration of Pb, Cd, As and Ni in the PM filter fraction. Most common heavy metals circulate in the atmosphere adhering to the particles.

Deposition and its components

Bibliography presents a wide range of methodologies to sample deposition. It depends mostly on the type of samples that we aim to obtain: soluble, non-soluble; bulk, wet and/or dry. The ESM Andersen sampler used consists of two polypropylene containers, 40 cm height and 29.14 cm diameter, placed in a robust device fitted with a rain sensor, which activates a mechanism when it begins to rain. In normal conditions, the DD container is open to receive atmospheric transfers, and the wet-deposition one is covered. The rain sensor activates the automatic mechanism, provoking the overturn of atmospheric deposition capture. At CLL, the instrument was located on the roof of the air quality monitoring site, at around 4 m above ground level.

The main standards taken into account were the EN 15841 to determine metals, and EN 16913 to determine soluble ions. But in all cases the type of sampler reported is only indicative.

Laboratory analysis

PM_{10} and PM_1 24h quartz fibre filters were analysed to determine the ambient concentration of major and trace elements, soluble ions, and organic and elemental carbon. To this end, a fraction of the filter was digested using a mixture of inorganic acids (HNO_3–HF–$HClO_4$) (Querol et al., 2001, Pey et al., 2009b) and the quantitative analysis of metals and trace elements was performed using ICP–AES for major elements (Al, Ca, Na, Mg, K, Fe, P) and ICP–MS for trace elements (Li, P, Ti, V, Cr, Mn, Co, Ni, , Zn, Ga, Ge, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, La, Ce, Pb, among others). Major ions (SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) were analysed by ionic chromatography. OC and EC fractions were quantified using the thermal optical transmittance (TOT) method, with a Sunset Lab analyser, using EUSAAR 2 protocol (Cavalli et al., 2010). Water Soluble Organic Carbon (WSOC) was determined by combustion catalytic oxidation method. Colorimetric method for NH_4^+ was applied using a segmented flow analysis device.

The experimental SiO_2/Al_2O_3 ratio obtained during a specific monitoring campaign was 2.54, according to results published by Alastuey et al. (2016). CO_3^{2-} content was estimated from Ca values considering that all Ca is in the form of calcite, thus according to their stechiometric relation.

Likewise, the OM/OC ratio used in this work (1.97) corresponds to the experimental values obtained during a specific campaign conducted in 2013 in which the Aiken et al. (2008) methodology was used. The results of that were already presented by DeWitt et al. (2014).

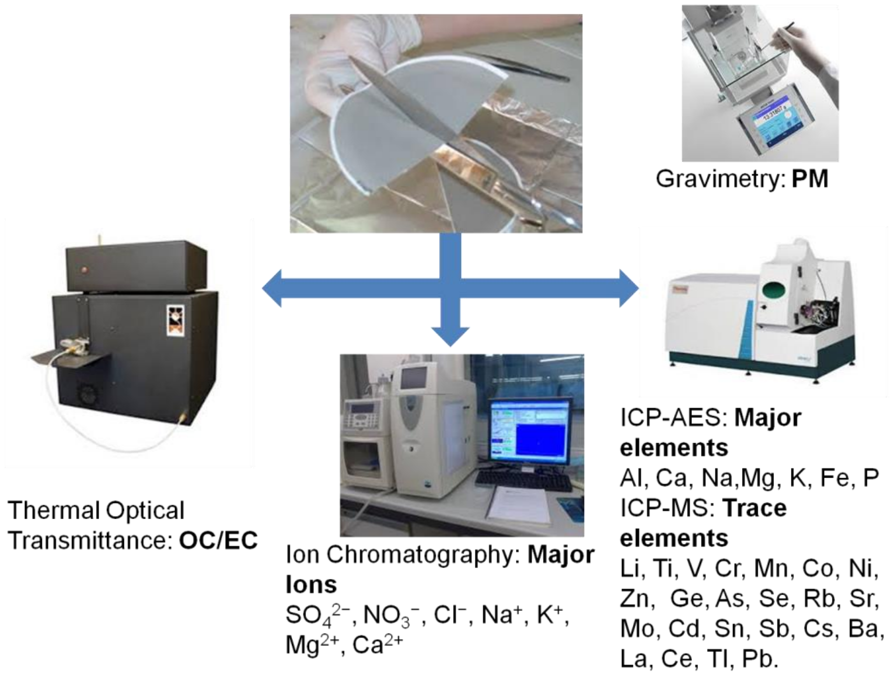


Figure 1.14. Schematic representation of the PM 24 h-filters and insoluble deposition samples analysis methodology.

Avant-garde techniques for aerosol monitoring

Traditionally, PM composition has been investigated by offline studies that comprise 24h sampling and subsequent laboratory treatment and analysis, a laborious and time consuming methodology. Time resolution does not allow us to appreciate daytime variability. Conversely, filters allow for a wide range of investigations that cannot be carried out, for the moment, by on-line systems.

In recent years, different types of mass spectrometers have been developed to analyse real time submicron aerosol or volatile organic compounds.

CPC

Condensation particle counters (CPC) detect and count aerosol particles by first enlarging them by using the particles as nucleation centres to create droplets in a supersaturated gas, and then particles can be detected by usual techniques, such as laser nephelometry (measurement of light pulses scattered by the grown-up particles) or a DMA (Differential Mobility Analyser).

An extensive description can be consulted at Hermann et al. (2007) and Petäjä et al. (2006).

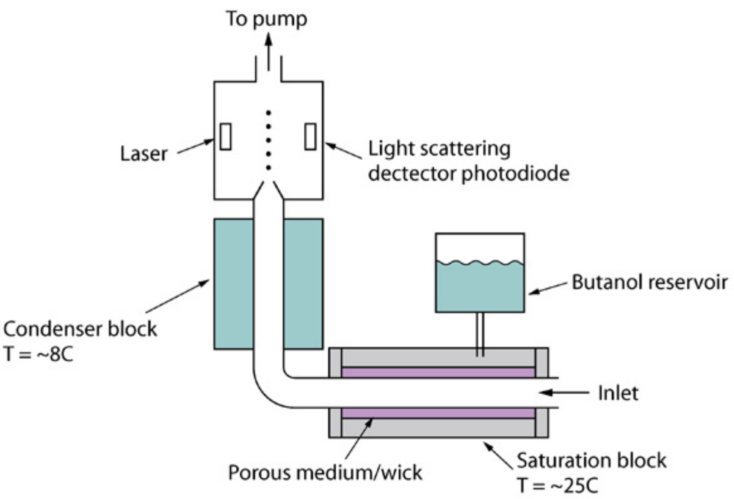


Figure 1.15. Schematic performance representation of the Condensation Particle Counter (CPC).

HR-ToF-AMS

The Aerodyne Aerosol Mass Spectrometer (AMS) provides quantitative size and chemical mass loading information in real-time for non-refractory sub-micron aerosol particles. The AMS couples size-resolved particle sampling and mass spectrometric techniques into a single real-time measurement system.

A wide performance description is written at Aiken et al. (2008) and Allan et al. (2003) and (2004).

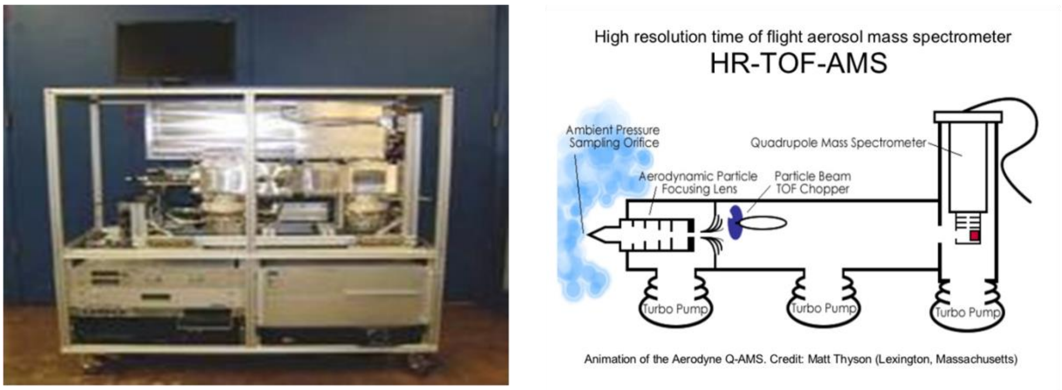


Figure 1.16. The HR-ToF-MS system. Left: external view. Right: schematic performance representation from the Aerodyne Q-AMS animation (credit: Matt Thyson from Lexington, Massachusetts).

Satellite observations, and models consultation

The interpretation of the origin of air masses is of enormous relevance in multiple atmospheric studies. In the case of insular locations such as Mallorca, a 3600 Km^2 island, this characterization is even more relevant since the arrival of particular air masses can provoke drastic variations on certain metrics. For example, air masses transported from North Africa are frequently enriched in particulate matter (Pey et al. 2013b), airflows from continental areas may induce PM and O_3 increments, or advections from marine sectors are generally linked to low atmospheric pollutant loads. Thus, a study to evaluate the origin of the air masses reaching and/or residing over the Balearic Islands has been carried out following the methodology used in Pey et al., 2009a.

The identification of the daily origin of air masses that influence the study area (2000-2013) on different days was based on the calculation of back-trajectories and the observation of aerosol maps and satellite images aided with geopotential pressure maps.

Overall, 6 meteorological scenarios were accounted (Figure 1.17): Atlantic (AT), Mediterranean (MD), European (EU), North African (AF), and two situations representing a lack of advection, differentiated according to the season in which they occur, summer regional (SR, from May to October) and winter regional (WR, from November to April).

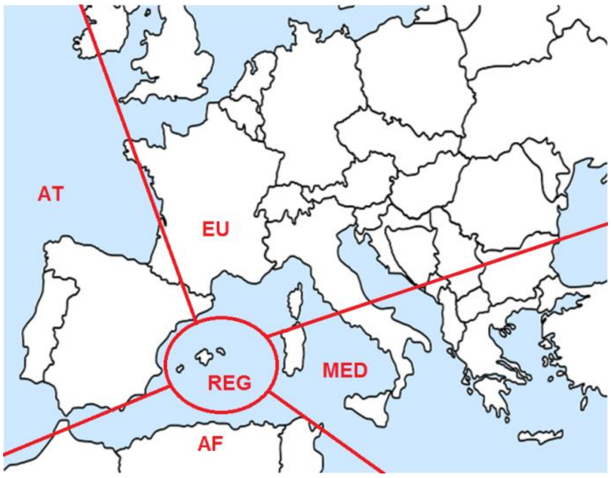


Figure 1.17. Origins of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional and Winter Regional (REG).

HYSPLIT

For the calculation of air mass back-trajectories the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectories) (Stein et al., 2015) calculation model was used. The calculation of long-range transport is based on the calculation of the vertical speeds of the air masses. The back-trajectories were calculated daily for 12h GMT taking the transport from 5 days ago for the period 2000-2013. They were calculated for three heights of starting points for the calculation of back-trajectories over Mallorca airport, 750, 1500 and 2500, and taking into account GDAS 1º data.

This tool has low spatial resolution (90 km), so it is suitable for detecting episodes of long-distance transport. An output example is shown in figure 1.18.

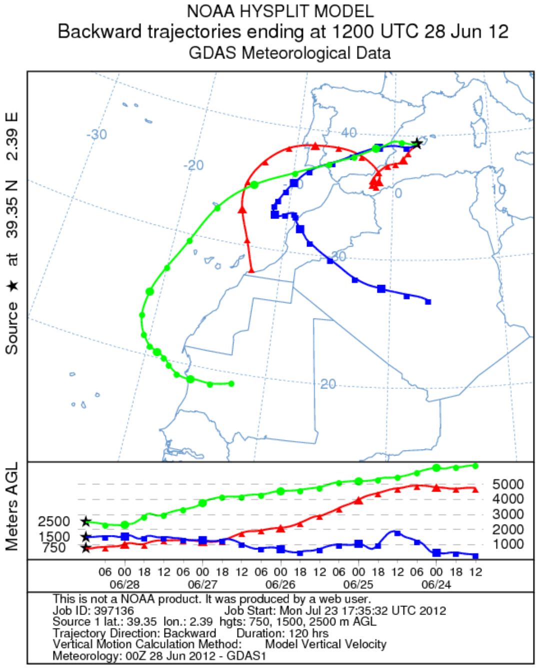


Figure 1.18. Example of Hysplit output calculation of backward trajectories. The example reflects one long-range transport of air masses getting to the site from AF origin: 28th June 2012.

Pressure Maps

Maps of geopotential pressure at sea level and at 850 mb provided by the Physical Sciences Laboratory from NOAA (https://psl.noaa.gov/data/composites/hour/) provide pressure maps every 6h that can be integrated. An example is shown in figure 1.19.

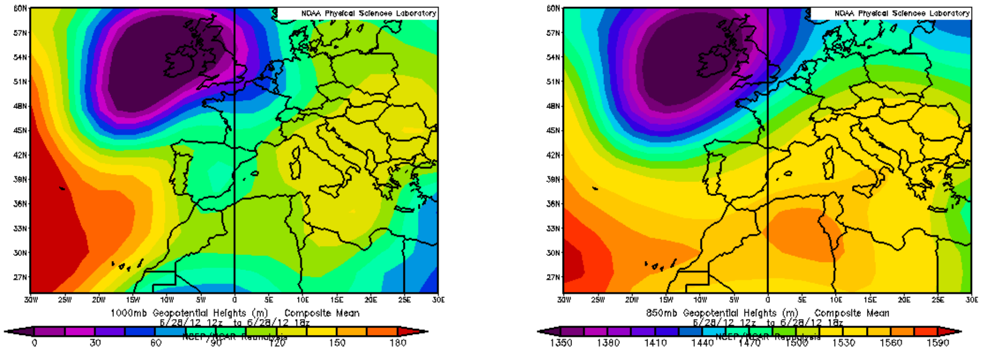


Figure 1.19. NOAA pressure map example: a) Sea Level; b) 850 mb. The example reflects one long-range transport of air masses getting to the site from AF origin: 28th June 2012.

Mineral dust

In order to detect African outbreaks influencing our location different dispersion models and satellite images were consulted.

- Aerosol maps of the Marine Meteorology Division del Naval Research Laboratory, USA (NRL) (http://www.nrlmry.navy.mil/aerosol) including sulphate, mineral dust and smoke concentrations, as well as total column aerosol optical depth. Thus maps correspond to the NAAPS model (Navy Aerosol Analysis and Prediction System) elaborated from MODIS (moderate resolution image spectroraidometer) (https://modis.gsfc.nasa.gov/tools/) observations. Additionally MODIS observations were also consulted. Examples are shown in figure 1.20 and 1.21.

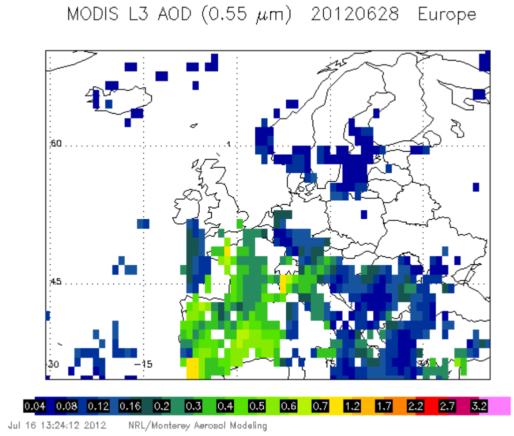


Figure 1.20. MODIS observation from Terra satellite. The example reflects one long-range transport of air masses getting to the site from AF origin: 28th June 2012.

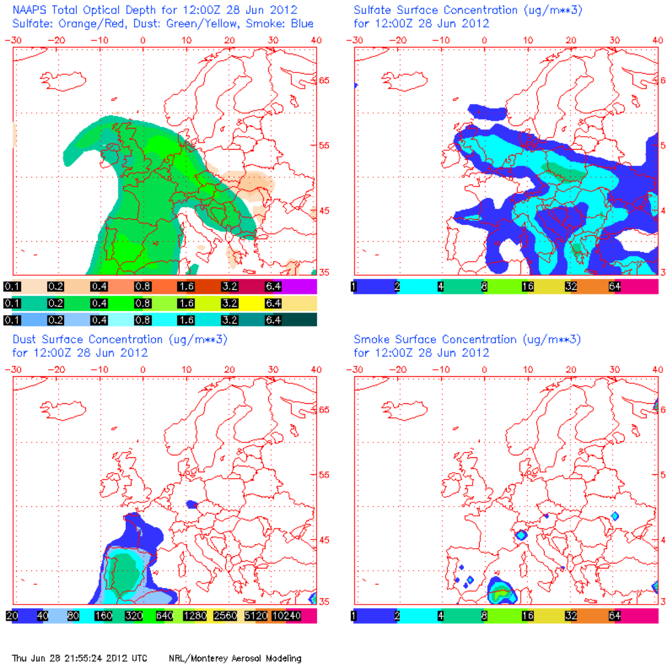


Figure 1.21. NAAPS modelization. The example reflects one long-range transport of air masses getting to the site from AF origin: 28th June 2012.

- DREAM model (Dust Regional Atmospheric Model) of the Euro-Mediterranean Centre on Insular Coastal Dynamics installed in the Barcelona Supercomputing Centre (BSC) (https://ess.bsc.es/bsc-dust-daily-forecast) produce mineral dust concentration maps every 12 hours for Europe and Northern Africa. Additionally wet and dry deposition of mineral dust is also available. An example is shown in figure 1.22.

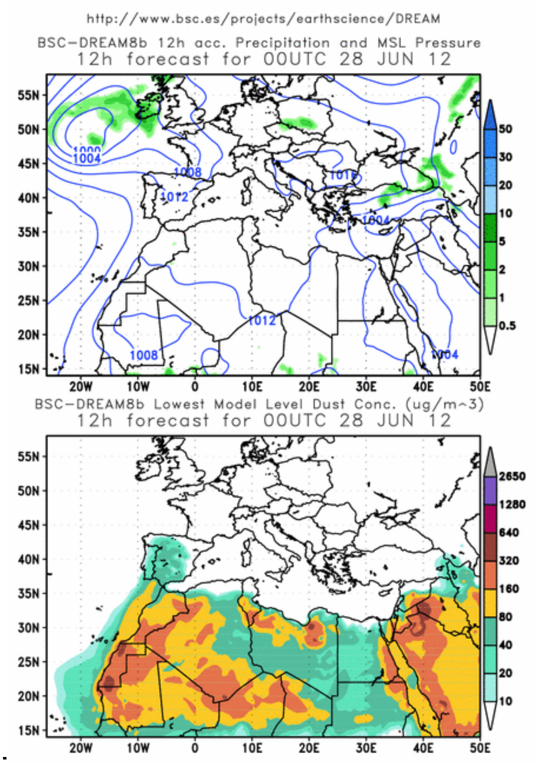


Figure 1.22. BSC-DREAM8b modelization. The example reflects one long-range transport of air masses getting to the site from AF origin: 28th June 2012.

True colour images

Occasionally, NASA NEO project (https://neo.sci.gsfc.nasa.gov) can provide true colour Earth surface images from Terra and Aqua satellites, as well as Sea-viewing Wide Field of view Sensor (SeaWIFS) Project Image Archive (https://seawifs.gsfc.nasa.gov/). These kind of images allow us visualise outbreaks from Northern Africa and its influence over the Mediterranean. An example is shown in figure 1.23.

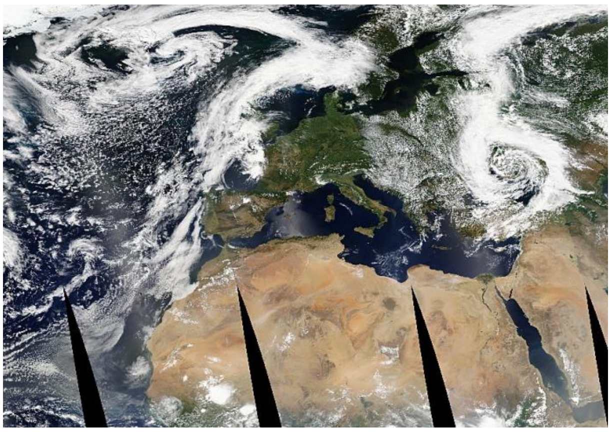


Figure 1.23. SeaWIFS true colour example. The example reflects one long-range transport of air masses getting to the site from AF origin: 28th June 2012.

Globcolour

Globcolour (globcolour.info) from ESA contributes additionally with several tools, among them, Medium Resolution Imaging Spectrometer Instrument (MERIS) display chlorophyll activity over the sea surface, and enable to estimate sea blooms generated by a wide contribution of nutrients. An example is shown in figure 1.24.

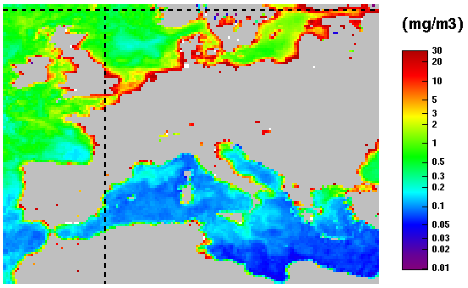


Figure 1.24. GlobColour monthly MERIS product Chlorophyll-a concentration example of May 2011.

BSC-Caliope

The system operationally provides air quality forecast at 24h and 48h for Europe (12x12 km), the Iberian Peninsula and Balearic Islands (4x4 km), and it possibilities to consult historical archive. BSC Caliope consists of three main parts: meteorological forecast (WRF-ARW model); emission forecast (HERMES model) (nitrogen oxides (NO and NO_2), volatile organic compounds (VOCs), carbon monoxide (CO), sulphur dioxide (SO_2) and particulate matter (PM)); and finally it delivers air quality forecast (Chemical transport CMAQ model and the already mentioned DREAM for mineral dust) (O_3, NO_2, CO, SO_2, PM_{10}, $PM_{2.5}$ and benzene).

Giovanni

NASA Giovanni project (https://giovanni.gsfc.nasa.gov/giovanni/) based on models applied to the MODIS satellite observations, provide a number of air quality tools, among others, sulphur dioxide surface concentrations, tropospheric nitrogen dioxide concentrations, tropospheric ozone.

Copernicus

Copernicus is the European Union's Earth Observation Programme. It offers information services based on satellite Earth Observation and in situ (non-space) data.

Copernicus products have been designed during the period of this Thesis, in fact, validation concerning air quality data is still ongoing. In consequence, the tools that this programme offers have not been taken into account, but the possibilities that it gives to the future are quite relevant.

NAO index

Additionally, North Atlantic Oscillation Index (NAOi) values were used in order to take into consideration the potential effect of meteorology in the observed trends. Thus, monthly NAOi values were downloaded from http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/nao.shtml. Then, they were merged into seasonal averages and discussed together with seasonal means calculated for each pollutant at each type of environment.

Positive Matrix Factorization

The source apportionment to the particulate matter was investigated by applying Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) using the Multilinear Engine (ME-2) (Paatero, 1999). The method describes the measurements with a bilinear factor model:

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + \theta_{ij}$$

being X_{ij} is the j_{th} species concentration measured in the i_{th} sample, p is the number of sources, g_{ik} is the contribution of the k_{th} source to the i_{th} sample, f_{kj} is the concentration of the j_{th} species in the k_{th} source and θ_{ij} is the residual associated with the j_{th} species concentration measured in the i_{th} sample. The values g_{ik} and f_{kj} are adjusted until a minimum for the objective function Q for a given number of factors p is found:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{\theta_{ij}}{\sigma_{ij}} \right)^2$$

being σ_{ij} is the user defined uncertainty for the j_{th} species in the i_{th} sample.

In the present study the source apportionment to OA was performed applying ME-2 using the toolkit SoFi (Source Finder) version 4.7 described in Canonaco et al. (2013).

ME-2 was used in order to run the same calculations than those carried out for the organic aerosol investigation (HR-ToF-AMS).

1.4. References

Aiken A.C., Decarlo P.F., Kroll J.H., Worsnop D.R., Huffman J.A., Docherty K.S., Ulbrich I.M., Mohr C., Kimmel J.R., Sueper D., Sun Y., Zhang G., Trimborn A., Northway M., Ziemann P.J., Canagaratna M.R., Onasch T.B. Alfarra M.R., Prevot A.S.H., Dommen J., Duplissy J., Metzger A., Baltensperger U., and Jimenez J.L.: *O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry*, Environ. Sci. Technol., 42, 4478–4485, 2008.

Alastuey A., Querol X, Aas W, Lucarelli F, Pérez N, Moreno T., Cavalli F., Areskoug H, Balan V, Catrambone M, Ceburnis D., Cerro J.C., Conil S., Gevorgyan L., Hueglin C., ImreK., Jaffrezo J.L., Leeson S.R., Mihalopoulos N., Mitosinkova M., O'Dowd C.D., Pey J., Putaud J.P., Riffault V., Ripoll A., Sciare J., Sellegri K., Spindler G., and Yttri K.E.: *Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013*, Atmos. Chem. Phys., 16, 6107–6129, 2016.

Allan J. D., Jimenez J. L., Williams P. I., Alfarra M. R., Bower K. N., Jayne J. T., Coe H., and Worsnop D. R. 2003. *Quantitativesampling using an Aerodyne aerosol mass spectrometer: 1. Tech-niques of data interpretation and error analysis*, J. Geophys. Res.-Atmos., 108, 4090,doi:10.1029/2002JD002359.

Allan J. D., Delia A. E., Coe H., Bower K. N., Alfarra M. R., Jimenez J. L., Middlebrook A. M., Drewnick F., Onasch T.B., Canagaratna M. R., Jayne J. T., and Worsnop D. R. 2004. *A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data*, J.Aerosol Sci., 35, 909–922.

Barmpadimos I., J. Keller, D. Oderbolz, C. Hueglin, and A. S. H. Prévôt, 2012. *One decade of parallel fine (PM2.5) and coarse (PM10–PM2.5) particulate matter measurements in Europe: trends and variability*. Atmospheric Chemistry and Physics, 12, 3189–3203.

Berland K., Rose C., Pey J., Culot A., Freney E., Kalivitis N., Kouvarakis G., Cerro J.C., Mallet M., Sartelet K., Beckmann M., Bourriane T., Roberts G., Marchand N., Mihalopoulos N., and Sellegri K., 2017. *Spatial extent of new particle formation events over the Mediterranean Basin from multiple ground-based and airborne measurements*, Atmos. Chem. Phys., 17, 9567–9583, 2017 (doi.org/10.5194/acp-17-9567-2017).

Bytnerowicz A., Omasa K. and Paoletti E., 2007. *Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective*. Environmental Pollution 147: 438-445.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.. *SoFi, an IGOR based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data,* Atmos. Meas. Tech., 6, 3649–3661, doi:10.5194/amt-6-3649-2013, 2013.

Cavalli F., Viana M., Yttri K.E., Genberg J., and Putaud, J.P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79–89, 2010.

Cerro J.C., 2013. Comportament i tendències de la contaminació atmosfèrica a Mallorca, com a referent del Mediterrani Occidental. Master Thesis. Universitat de les Illes Balears.

Cerro J.C., Bádenas J.F., Lladó F.J., Tobar M.L., Pons C., Elias P.M., *Qualitat de l'Aire a les Illes Balears 2010/2015*, Govern de les Illes Balears (ISBN: 978-84-697-5493-1) (517 pp).

Chrit M., Sartelet K., Sciare J., Pey J., Nicolas J.B., Marchand N., Freney E., Sellegri K., Beekmann M., and Dulac F.: *Aerosol sources in the western Mediterranean during summertime: a model-based approach*, Atmos. Chem. Phys., 18, 9631–9659, 2018.

Colette, Granier C., Hodnebrog, Jakobs H., Maurizi A., Nyiri A., Bessagnet B., D'Angiola A., D'Isidoro M., Gauss M., Meleux F., Memmesheimer M., Mieville A., Rouïl L., Russo F., Solberg S., Stordal F., and Tampieri F., 2011. *Air quality trends in Europe over the past decade: a first multi-model assessment*. Atmospheric Chemistry and Physics, 11, 11657–11678.

Cusack M., Alastuey A., Pérez N., Pey J., Querol X., 2012. *Trends of particulate matter (PM2.5) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010)*. Atmospheric Chemistry and Physics 12, 8341-8357.

DeWitt H.L., Pey J., Hellebust S., Temime-Roussel B., Mizzi A., Salameh D., Sylvestre A., Elser M., Pérez N., Cerro J.C., Jaffrezo J.L., Mocnik G, Prévôt A., Marchand N., *Comparison of the Sources of Organic Aerosol (OA) Using Aerosol Mass Spectrometry at Two Mediterranean Islands: Corsica and Mallorca*. AAAR Conference 2014.

Eastern R.C. and Peter L.K., 1994. *Binary homogeneous nucleation: temperature and relative humidity fluctuations, nonlinearity, and aspects of new particles production in the atmosphere*. Journal of Applied Meteorology, 33, 775-784.

EC-European Comission, 2003. *Second Position Paper on Particulate Matter*. European Comission.

EEA-European Environmental Agency, 2020. *Air Quality Report 2019*. EEA.

EPA-Environmental Pollution Agency (USA), 1996. *Air Quality Criteria for Particulate Matter*. EPA. Vol. 1.

Escudero M., Stein A., Draxler R.R., Querol X., Alastuey A., Castillo S. and Ávila A.: *Determination of the contribution of Northern Africa dust source areas to PM10 concentrations over Central Iberan Peninsula using the HYSPLIT model*, J. Geophys. Res. Atmos., 111, D06210, 2006.

Fu Y., Desboeufs K., Vincent J., Bon Nguyen E., Laurent B., Losno R., and Dulac F. *Estimating chemical composition of atmospheric deposition fluxes from mineral insoluble particles deposition collected in the western Mediterranean region*. Atmos. Meas. Tech., 10, 4389–4401, 2017

Genestar C., Pons C., Cerro J. C., Cerdà V., 2014. *Different decay patterns observed in a nineteenth-century building (Palma, Spain)*. Environmental Science and Pollution Research, Apr.

González-Fernández I., Calvo E., Gerosa G., Bermejo V., Marzuoli R., Calatayud V., and Alonso R., 2014. *Setting ozone critical levels for protecting horticultural Mediterranean crops: Case study of tomato*. Environmental Pollution, 185: 178-187.

Guieu C., Loÿe-Pilot M. D., Benyahya L., Dufour A., 2010. *Spatial variability of atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole Mediterranean from a* *one-year monitoring experiment: Biogeochemical implications*. Marine Chemistry 120 (2010) 164–178. doi:10.1016/j.marchem.2009.02.004

Harrison R.M. y Kito A.M.N., 1990. *Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants. Atmospheric Environment24, 2633-2640*.

Harrison R.M. y Jones M., 1995. *The chemical composition of airborne particles in the UK atmosphere*. The Science of the Total Environment168, 195-214.

Harrison R.M. y Grieken R.E.v., 1998. *Atmospheric Particles. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems*. J Buffle and H P van Leeuwen. John Wiley & Sons, pp 610.

Hermann M., Wehner B., Bischof O., Han H.S., Krinke T., Liu W., Zerrath A., Wiedensohler A. 2007. *Particle counting efficiencies of new TSI condensation particle counters*. Journal of Aerosol Science, 38(6), 674-682, https://doi.org/10.1016/j.jaerosci.2007.05.001.

Herut B., Krom M.D., Pan G., Mortimer R., 1999. *Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact*. Limnology and Oceanography 44, 1683-1692.

Herut B., Collier R. and Krom M.D., 2002. *The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean*. Limnology and Oceanography 47, 870-878.

IPCC-Intergovernmental Panel on Climate Change, 2001. *Climate Change 2001: The Scientific Basis*. IPCC. Cambridge University Press.

IPCC-Intergovernmental Panel on Climate Change, Core Writing Team, Pachauri, R.K. and Reisinger, A. (Eds.), 2007. *Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Geneva, Switzerland. pp 104

IPCC- Intergovernmental Panel on Climate Change, Core Writing Team, Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp., 2013.

Jaenicke R., *Chapter 1 Tropospheric Aerosols*, International Geophysics, Academic Press, Volume 54, 1993, Pages 1-31, https://doi.org/10.1016/S0074-6142(08)60210-7.

Jerez S., Jimenez-Guerrero P., Montávez J.P., Trigo R.M., 2013. *Impact of the North Atlantic Oscillation on European aerosol ground levels through local processes: a seasonal model-based assessment using fixed anthropogenic emissions*. Atmospheric Chemistry and Physics, 13, 11195-11207.

Lambert A., *Dakar's urban pollution plume: A SAMUM-II case study on the plume structure and the influence of urban emissions on dust physico-chemical and radiative properties*, PhD Thesis, 2011.

López P., Gelado-Caballero M.D., Santana-Castellano D., Suárez de Tangil M., Collado-Sánchez C., Hernández-BritoJ.J., 2013, A three-year time-series of dust deposition flux measurements in

Gran Canaria, Spain: A comparison of wet and dry surface deposition samplers, Atmospheric Environment 79 (2013) 689e694. https://doi.org/10.1016/j.atmosenv.2013.07.044.

Mateu J., Bauzá de Mirabó F., Forteza R. and Cerdà V., 1998. *Heavy metals in the aerosols collected at two stations in Majorca (Spain)*. Water, Air and Soil Pollution, 112, 1-15

Matter U., Siegmann H.C. and Burtcher H., 1999. *Dynamic field measurements of submicron particles from diesel engines*. Environmental Science and Technology33, 1946-1952.

McGovern F.M., Nunes M.J., Raes F. and Gonzales-Jorge H., 2002. *Marine and anthropogenic aerosols at Punta Del Hidalgo, Tenerife, and the aerosol nitrate number paradox*. Journal of Geophysical Research107 (D24), 4766, 1-10.

Mészáros E., 1999. *Fundamentals of Atmospheric Aerosol Chemistry*, Akadémiai Kiado Mészáros.

Millán M. M., Sanz M. J., Salvador R., and Mantilla E.: *Atmospheric dynamics and ozone cycles related to nitrogen deposition in the western Mediterranean*, Environ. Pollut., 118: 167-186, 2002.

Minguillón M.C., Ripoll A., Pérez N., Prévôt A. S. H., Canonaco F., Querol X., and Alastuey A.: *Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor,* Atmos. Chem. Phys., 15, 6379–6391, 2015.

OECD, 2016. *The economic consequences of outdoor air pollution, Organisation or Economic Co-operation and Development*, Paris (https://doi. org/10.1787/9789264257474-en)

O'Dowd C. D. and Smith M. H., 1993. *Physicochemical properties of aerosols over the northeast Atlantic: Evidence for wind-speed related submicron sea-salt aerosol production*, J. Geophys. Res., 98, 1137–1149, https://doi.org/10.1029/92JD02302.

Paatero, P. and Tapper, U. 1994. *Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values*, Environmetrics, 5, 111–126.

Paatero, P. 1999. *The multilinear engine – a table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model*, J. Comput. Graph. Stat., 8, 854–10 888.

Pérez, N., Pey, J., Castillo, S., Viana, M., Alastuey, A., Querol, X.: *Interpretation of the variability of regional background aerosols in the Western Mediterranean*, Sci. Total Environ., 407, 527–540, 2008.

Petäjä T., Mordas G., Manninen H., Aalto P.P., Hämeri K. & Kulmala M. 2006. *Detection Efficiency of a Water-Based TSI Condensation Particle Counter 3785*, Aerosol Science and Technology, 40:12, 1090-1097, DOI: 10.1080/02786820600979139.

Pey J., Querol X., Alastuey A., 2009a. *Variations of levels and composition of PM10 and PM2.5 at an insular site in the Western Mediterranean*. Atmospheric Research, 94, 285-299.

Pey J., Pérez N., Castillo S., Viana M., Moreno T., Pandolfi M., López-Sebastián J.M., Alastuey A., Querol X., 2009b. *Geochemistry of regional background aerosols in the Western Mediterranean*. Atmospheric Research, 94, 422-435.

Pey J., Alastuey A., Querol X., 2013. *PM10 and PM2.5 sources at an insular location in the western Mediterranean by using source apportionment techniques*. Science of the Total Environment, 456-457, 267-277.

Polkowska Z., Górecki T., and Namieśnik J., *Determination of atmospheric pollutants in wet deposition*, Environ. Rev. 19: 185–213 (2011) doi:10.1139/A11-006.

Porg, 1997. *Ozone in the United Kingdom*. 4th Report of the Photochemical Oxidants Review Group.

Querol X., Alastuey A., Rodríguez S., Plana F., Ruiz C.R., Cots N., Massagué G., and Puig O.: *PM_{10} and $PM_{2.5}$ source apportionment in the Barcelona Metropolitan area, Catalonia, Spain*, Atmos. Environ., 35, 6407-6419, 2001.

Querol X., Pey J., Pandolfi M., Alastuey A., Cusack M., Perez N., Moreno T., Viana M., Mihalopoulos N., Kallos G., Kleanthous S.: *African dust contributions to mean ambient PM10 mass-levels across the Mediterranean Basin*, Atmos. Environ., 43(28), 4266-4277, 2009a.

Querol X., Alastuey A., Pey J., Cusack M., Perez N., Mihalopoulos N., Theodosi C., Gerasopoulos E., Kubilay N., and Kocak M.: *Variability in regional background aerosols within the Mediterranean*, Atmos. Chem. Phys., 9, 4575–4591, 2009b.

Querol X., Alastuey A., Pandolfi M., Reche C., Pérez N., Minguillón M. C., Moreno T., Viana M., Escudero M., Orio A., Pallarés M., Reina F., 2014. *2001-2012 trends on air quality in Spain*. Science of The Total Environment, 06, 490C:957-969.

Ripoll A., Minguillón M.C., Pey J., Pérez N., Querol X., and A. Alastuey A.: *Joint analysis of continental and regional background environments in the Western Mediterranean: PM1 and PM10 concentrations and composition, Atmos.* Chem. Phys., 15, 1129-1145, 2015.

Rodríguez S., Querol X., Alastuey A., Viana M., Mantilla E.: *Events Affecting Levels and Seasonal Evolution of Airborne Particulate Matter Concentrations in the Western Mediterranean*, Environ. Science Tech., 37(2), 216-22, 2003.

Samoli E., Stafoggia M., Rodopoulou S., Ostro B, Declercq C., Alessandrini E., Díaz J., Karanasiou A., Kelessis A., Le Tertre A., Pandolfi P., Randi G, Scarinzi C., Zauli-Sajani S., KatsouyanniK., Forastiere F., 2013. *Associations between Fine and Coarse Particles and Mortality in Mediterranean Cities: Results from the MED-PARTICLES Project*. Environmental Health Perspectives 121, 8.

Scheuvens D., Schütz L., Kandler K., Ebert M., Weinbruch S., 2013. *Bulk composition of northern African dust and its source sediments — A compilation*. Earth-Science Reviews 116 (2013) 170–194. http://dx.doi.org/10.1016/j.earscirev.2012.08.005

Seinfeld. J and Pandis S., 2016. *Atmospheric chemistry and physics 3rd edn*, chapter 8 properties of the atmospheric aerosol.

Stafoggia M., Samoli E., Alessandrini E., Cadum E., Ostro B., Berti G., Faustini A., Jacquemin ., Linares C., Pascal M., Randi G., Ranzi A., Stivanello E., Forastiere F., 2013. *Short-term Associations between Fine and Coarse Particulate Matter and Hospitalizations in Southern Europe: Results from the MED-PARTICLES Project*. Environmental Health Perspectives 121, 9.

Warneck P., *Chemistry of the Natural Atmosphere*, Science 07 Oct 1988:Vol. 242, Issue 4875, pp. 121-122,DOI: 10.1126/science.242.4875.121-a

World Health Organization, 2005. *Air quality guidelines global update 2005*. *Report on a Working Group meeting*, Bonn, Germany, 18-20 October.

World Health Organization, 2013. *Review of evidence on health aspects of air pollution-REVIHAAP Project. Technical Report.* Bonn, Germany.

Chapter 2. Trends of air pollution in the Western Mediterranean Basin from a 13-year database: a research considering regional, suburban and urban environments in Mallorca (Balearic Islands)

Trends of air pollution in the Western Mediterranean Basin from a 13-year database: a research considering regional, suburban and urban environments in Mallorca (Balearic Islands)

This chapter corresponds to the Research Paper: *Trends of air pollution in the Western Mediterranean Basin from a 13-year database: a research considering regional, suburban and urban environments in Mallorca (Balearic Islands)*

Authors: Jose Carlos Cerro[1,2], Victor Cerdà[1] and Jorge Pey[3]

[1] Laboratory of Environmental Analytical Chemistry, Illes Balears University, Ctra. Palma-Valldemossa, Km 7.2, 07122, Palma de Mallorca, Spain.

[2] Laboratory of the Atmosphere, Balearic Islands Government, C/Corredors, 10, 07009, Palma de Mallorca, Spain.

[3]Aix Marseille Université, CNRS, LCE FRE 3416, 13331 Marseille, France.

Published in Atmospheric Environment journal, 103, 138-146, 2015.

http://dx.doi.org/10.1016/j.atmosenv.2014.12.014

Abstract

This study is focused in the evolution of NO, NO_2, SO_2, O_3 and PM_{10} concentrations, from 2000 to 2012, at urban, suburban and regional observatories in the Balearic Islands (Spain), an insular region in the Western Mediterranean.

At urban and suburban areas, daily patterns of most pollutants are strongly linked to land-traffic emissions, being the regional background less influenced. SO_2 variations, however, are mostly driven by the impact of other sources different from road traffic, including shipping emissions and power generation. Urban NO_x, SO_2 and PM_{10} concentrations exhibit a common weekly pattern, with a very slight accumulation during the weekdays and sharp decreases (15-39%) on weekends.

Our long-term database displays clear decreasing NO and NO_2 concentrations from 2000 onwards, prominent in the urban environment (-1.1 $\mu g/m^3$year), and moderate in suburban and regional areas (up to -0.3 $\mu g/m^3$year). At urban sites, O_3 behaviour (+1.0 $\mu g/m^3$year) is opposite to that of NO, one of its main depletion agents. A moderate O_3 increasing trend (+0.5 $\mu g/m^3$year) is detected at regional background areas, whereas a modest decreasing trend occurred at the suburban background (-0.4 $\mu g/m^3$year), probably caused by enhanced vehicular emissions over these areas induced by urban planning and mobility policies. Finally, substantial PM_{10} drops are obvious, -0.7 $\mu g/m^3$year at urban and suburban areas, and -0.5 $\mu g/m^3$year in the regional background. Our results link the sharpest declines to air masses from western to northern sectors, pointing to effective pollution abatement strategies at a European scale. Some additional benefits are connected to the implementation of diverse local policies.

The effect of the North Atlantic Oscillation (NAO) was investigated. Negative NAO phases were related to additional air quality benefits, while positive phases mostly contributed to air degradation.

Keywords: air quality, PM_{10}, NOx, SO_2, O_3, abatement strategies, air mass origin, NAO index.

2.1. Introduction

Atmospheric pollution is one of the most challenging environmental problems to which contemporary societies are faced. Airborne particles are associated with different adverse impacts on human health (WHO, 2005, 2013; Samoli et al 2013; Stafoggia et al 2013). Similarly, exposure to nitrogen oxides (NO_x), ozone (O_3) or sulphur dioxide (SO_2) can induce some cardiovascular and lung diseases, premature deaths and carcinogenic effects (WHO, 2005; 2013). In addition, these atmospheric pollutants may also affect ecosystems (Bytnerowicz et al., 2007), agriculture (Gonzalez-Fernandez et al., 2014) and historical heritage (Genestar et al., 2014). Furthermore, one of the most relevant effects of atmospheric pollutants is on climate (IPCC, 2007).

Several strategies have been displayed throughout the continent to improve air quality during the period in study. Several laws focused on industries, such as the following directives: limitation of emissions of Volatile Organic Compounds (1999/13/EC); Waste Incineration Plant Emissions (2000/76/EC); National Emission Ceiling Directive (2001/81/EC); Large Combustion Plant Emissions (2001/80/EC); Integrated Pollution Prevention and Control Directives (1996/61/EC, 2008/1/EC); Industrial Emission Directive (2010/75/EU). In addition, measures focused on transport, such as EURO3, EURO4 and EURO5 European emission standards entered into force in January 2000, January 2005 and September 2009, respectively; and Shipping Emission Directives (1999/32/EC, 2012/33/EU) were also applied.

Particulate matter concentrations and gaseous pollutants (NO_x, SO_2, CO and O_3) have been measured on a regular basis in several European regions since the beginning of the 90's. This has allowed the investigation of trends at certain European regions (Colette et al., 2011; Barmpadimos et al., 2012; Cusack et al., 2012; Cerro, 2013; Querol et al., 2014). However, it is not always straightforward to discriminate the origin of the observed trends. Part of the observed PM_{10} changes in the NW Mediterranean can be explained by a decrease in African dust contributions (Pey et al., 2013b). Similarly, a partial decrease has been attributed to the occurrence of favourable meteorological situations connected with the atmospheric circulation over the northern Atlantic (Jerez et al. 2013). In addition, the vast implementation of abatement strategies over specific areas and/or the impact of the economic crisis can be the main reasons to explain such decrease (Cusack et al., 2012).

Since the 60's tourism is the most relevant economic sector in Mallorca. Besides of vehicular traffic, which is a major atmospheric pollution source in Mallorca, important emissions to the atmosphere are released from the energy sector, from a large waste incineration plant and from a cement factory. Furthermore, harbour and airport emissions may be significant at specific areas and/or for certain pollutants, especially during the warm season. Although air quality in Mallorca can be currently considered as good from a legislative point of view, particulate matter concentrations and specific gaseous pollutants exceed in different areas the European Directives targets, like the limit value for human health protection for NO_2 at urban areas, or the target value for human health protection for O_3 at regional environments. Up to date, the University of the Balearic Islands have led a number of studies on air pollution in the Balearic Islands (Mateu et al. 1998 and references therein). Additionally, a campaign performed in the suburbs of Palma de Mallorca in 2004-2005 was devoted to study PM_{10} and $PM_{2.5}$ concentrations, composition and sources (Pey et al., 2009a, 2013a).

At a local scale, a number of abatement strategies have been implemented since 2000, mainly in Palma de Mallorca. Specifically, a considerable promotion of public transport was launched in 2000; bus-taxi lanes were delimited in 2002; several underground car parks were built in 2003; park-pay neighborhood restricted and pedestrian areas have been implemented since 2004; improvements in the ring road have been introduced since 2005; the use of low consumption vehicles have been promoted since 2006; investments in public transport were done in 2007; and a wide range of measures, included in the Palma Air Quality Improvement Plan 2008 (Balearic Government, 2008) were adopted in the period 2008-2011.As a consequence ofthe economic crisis,a less ambitious plan (Palma Air QualityImprovement Plan 2011-2015) was finally approved(Balearic Government, 2013). Definitely, the financial crisis has been one of the most effective abatement measures. A 4% yearly reduction in vehicular traffic has been estimated since 2009, reversing the evolution from 2000 to 2008.

In this work we present a synopsis of recent trends (2000-2012) observed in the Mallorca Isle on various air quality metrics. This work interprets daily, weekly, seasonal and inter-annual patterns of diverse pollutants at different environments. The combined assessment at different environments allows to discern changes induced by the implementation of regional policies from those caused by the enactment of continental strategies. Moreover, the effect of North Atlantic Oscillation index (NAOi) on different metrics, environments and seasons is evaluated.

2.2. Methodology

2.2.1. Monitoring network and data availability

More than a decade of uninterrupted measurements by the air quality monitoring network of the Balearic Islands Government provide, for the first time at an insular location in the Western Mediterranean Basin, the opportunity to study the trends and the variability of different air quality metrics. Hourly data of NO, NO_2, SO_2, O_3 and PM_{10} from 2000 to 2012 were compiled, being thereafter revalidated and used in this study.

According to the criteria included in the European Directive 2008/50/EC, the monitoring sites used in this work are classified in urban, suburban, and regional background. The location of the different monitoring sites is presented in Figure 2.1.

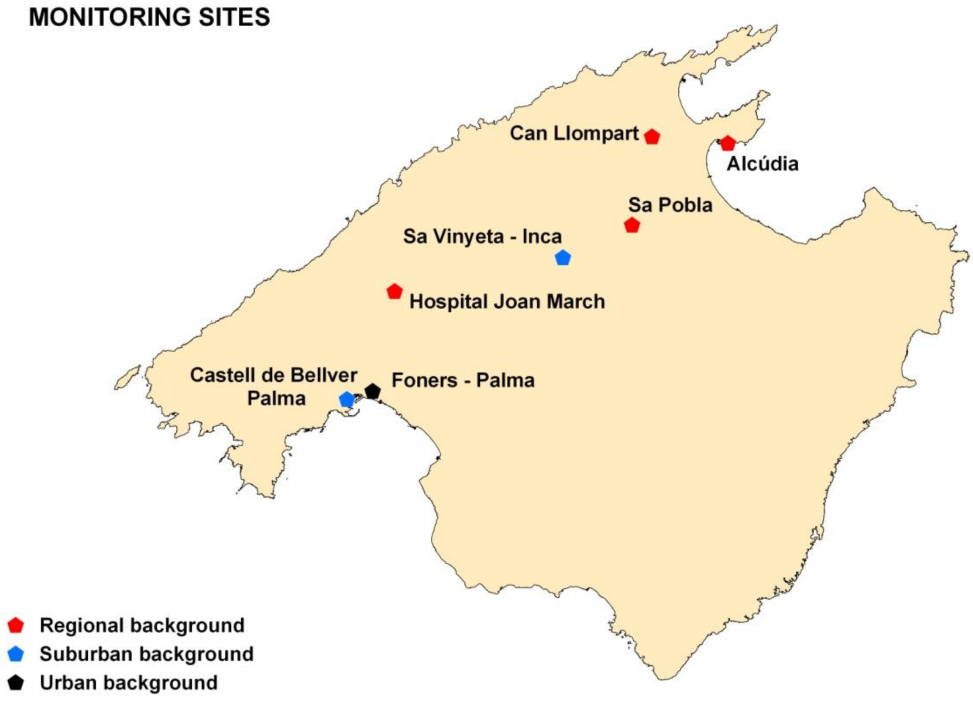


Figure 2.1. Location of the monitoring sites considered in the study.

In order to simplify the analysis, a merged database for each pollutant (O_3, NO, NO_2, SO_2 and PM_{10}) was built-up for each type of environment, as in Cerro (2013). This decision smoothens sporadic local influences in the case of the regional background conditions (4 sites), and converges into a better representation of suburban background conditions in Mallorca (2 sites). In the following sections urban, suburban and regional background environments will be referred to as a UB, SB and RB respectively.

For this study, only those pollutants measured uninterruptedly since 2000 were considered: ozone (O_3), nitrogen monoxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), and particulate matter PM_{10}. In addition, two essential criteria included in the guidelines of the European Environmental Agency (EEA, 2009) have been followed to decide which monitoring sites were selected for the analysis of trends: 1) the annual data coverage should be over 75%; 2) at least 8 of the last 10 years of data exist.

2.2.2. Monitoring techniques and data quality

All the measurements performed in the air quality network of the Balearic Islands comply with the European directives in terms of reference methods (as EN standards), or equivalent ones after the demonstration of their equivalence with respect to those. Specifically, EN 14212 for SO_2, based on ultraviolet fluorescence spectrophotometer; EN 14211 for NO_2, based on chemi-luminescence detection; and EN 14625 for O_3, based on ultraviolet spectrophotometry, were used. These methods describe the measurement principle and operating characteristics of the equipment, but also specify the minimum criteria for quality assurance in a week maintenance, two-week verification and quarter calibration. These criteria have been strictly followed in the monitoring network under study.

The methods used for PM_{10} monitoring comprised real-time absorption of beta radiation and tapered oscillating microbalance. In both cases, routinely intercomparisons against the gravimetric reference method were performed to retrieve the correction factors.

2.2.3. Air mass origins

The interpretation of the origin of air masses is of enormous relevance in multiple atmospheric studies. In the case of insular locations such as Mallorca, a 3600 Km^2 island, this characterization is even more relevant since the arrival of particular air masses can provoke drastic variations on certain metrics. For example, air masses transported from North Africa are frequently enriched in particulate matter (Pey et al. 2013b), airflows from continental areas may induce PM and O_3 increments, or advections from marine sectors are generally linked to low atmospheric pollutant loadings. Thus, a study to evaluate the origin of the air masses reaching and/or residing over the Balearic Islands has been carried out following the methodology used in Pey et al., 2009a. Overall, 6 meteorological scenarios were accounted (Figure 2.2.): Atlantic (AT), Mediterranean (MD), European (EU), North African (AF), and two situations representing a lack of advection, differentiated according to the season in which they occur, summer regional (SR, from May to October) and winter regional (WR, from November to April).

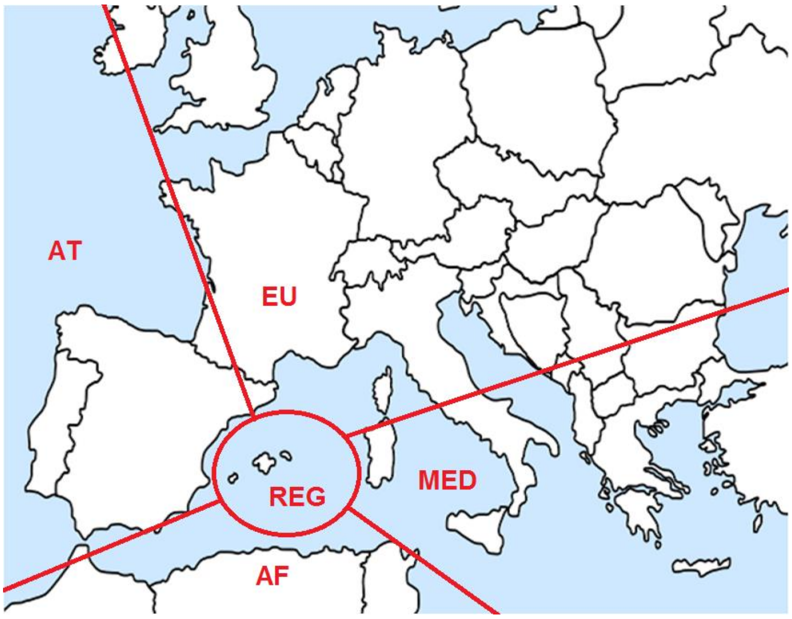


Figure 2.2. Origins of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional and Winter Regional (REG).

Additionally, NAOi values were used in order to take into consideration the potential effect of meteorology in the observed trends. Thus, monthly NAOi values were downloaded from http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/nao.shtml. Then, they were merged into seasonal averages and discussed together with seasonal means calculated for each pollutant at each type of environment.

2.2.4. Statistical treatment

All the statistical calculations have been performed by using the software developed by the R project (http://www.R-project.org/). Particularly, we used the Openair package (Carslaw and Ropkins, 2012; Carslaw, 2014), which was specifically designed for air pollution data treatment.

One of the most used tools in the present study concerns the calculation of trends in various atmospheric pollutants. Theil-Sen methodology of Openair package derives from the non-parametric Mann-Kendall test (Kendall, 1976; Hipel and McLeod, 2005), and is more robust and provides more accurate confidence intervals when punctual variations and absurd values occur.

2.3. Results

2.3.1. Quantification of urban, suburban and regional concentrations

The simultaneous monitoring at UB, SB and RB environments located in the same region allows the application of the Lenschow et al. (2001) methodology, successfully applied previously by Pey et al. (2010) in the Barcelona region. Basically, for a given pollutant, the subtraction of RB concentrations to the SB will provide the estimation of the suburban input. Similarly, the discount of RB concentrations to the UB will result in the urban contribution. The results of these calculations are presented in Table 2.1.

Table 2.1. Average concentrations (2000-2012) of NO, NO_2, SO_2, O_3 and PM_{10} (µg/m^3) at UB (urban background), SB (suburban background) and RB (regional background) environments. Subtraction of RB concentrations to UB and SB, in µg/m^3 and in %.

Averages (µg/m^3)	NO	NO_2	SO_2	O_3	PM_{10}

UB	26.2	47.9	2.8	38.3	30.0
SB	2.4	11.4	3.2	66.8	21.0
RB	1.6	6.3	2.3	66.1	19.5
Partitioning (µg/m^3)	NO	NO_2	SO_2	O_3	PM_{10}
UB minus RB	24.6	41.6	0.5	-27.8	10.5
SB minus RB	0.8	5.0	1.0	0.7	1.5
Partitioning (%)	NO	NO_2	SO_2	O_3	PM_{10}
UB minus RB	94	87	18	-58	35
SB minus RB	33	45	28	1	7

The UB is the dominant source of NO and NO_2, mostly due to vehicular emissions. On average, 94 and 87% of the urban concentrations of NO and NO_2 are due to city emissions. Likewise, the UB is an active source of PM_{10}, as 35% of the PM_{10} concentrations measured in the city are produced within the urban area. Less marked is the urban increase of SO_2, only 18% higher than in the RB. By contrast, O_3 concentrations are effectively depleted in the city, being 58% of those measured in the RB. In general, SB experiences an enrichment of NO_x and SO_2 with respect to the RB, with concentrations enhanced between 28 and 45%. On the contrary, O_3 and PM_{10} concentrations are rather similar at SB and RB environments.

Overall, most NO_x are urban in origin; the regional SO_2 component is very relevant as the largest SO_2 sources are located out of the city (namely the Alcudia coal-fired power plant and the ship traffic), causing a diffuse SO_2 contamination all over the island; urban O_3 concentrations are half than those measured at SB and RB areas, which is directly related to the urban consumption of O_3 in oxidation processes; and PM_{10} is mostly related to regional and long-range transport, although a non-negligible urban contribution occurs.

2.3.2. Daily and weekly patterns

NO, NO_2 and PM_{10} concentrations display two daily peaks at all backgrounds, early in the morning and in the afternoon, coincident with land-traffic rush hours (Figure 2.3). The dislike behaviour of SO_2 from the previous reinforces its dependence on other sources including power generation and shipping emissions, the latter affecting mostly suburban and urban sites (Figure 2.7). Ozone displays a clear diurnal trend with maximal concentrations after midday and minimal early in the morning coinciding with the traffic rush hours (at SB and RB environments) and absent photochemical activity (at all environments).

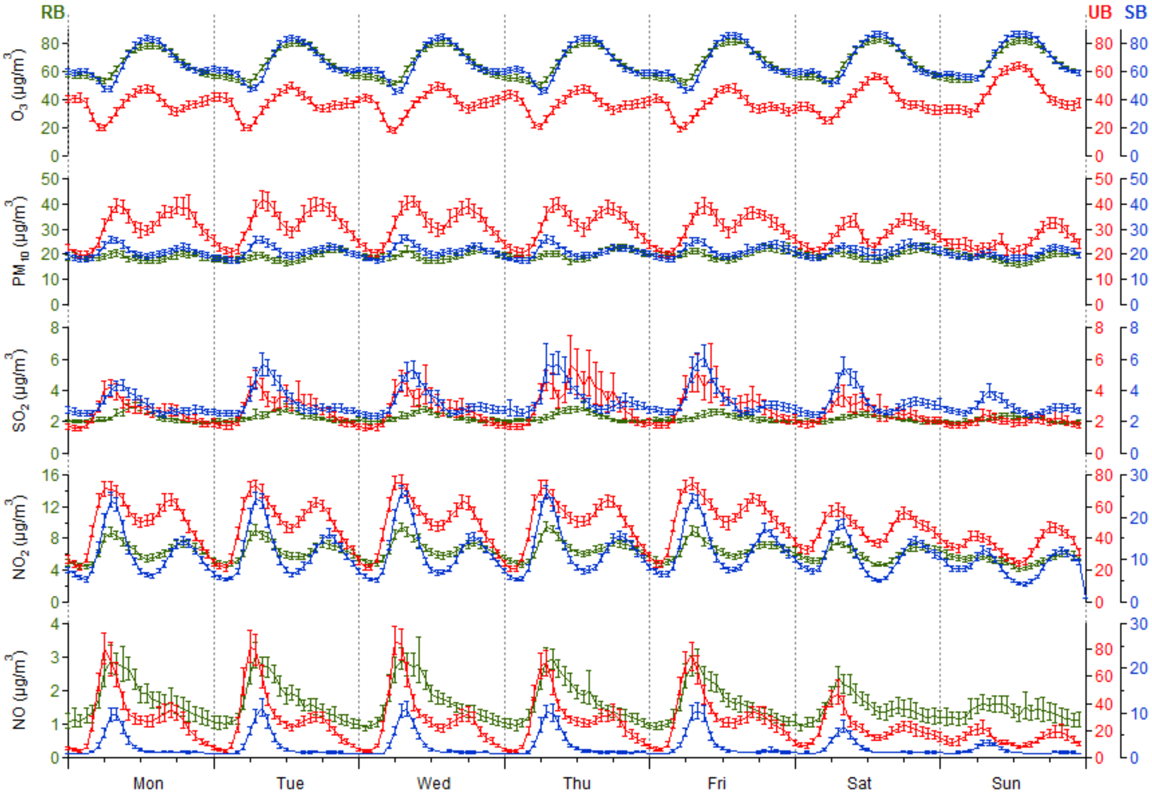


Figure 2.3. Weekly variation (hourly averages 2000-2012) of NO, NO_2, SO_2, PM_{10} and O_3 (in µg/m³) at UB (urban background), SB (suburban background) and RB (regional background) environments. Note different concentration scales for specific pollutants.

NO, NO_2, SO_2 and PM_{10} exhibit a similar weekly pattern, with higher concentrations during the weekdays and much reduced during weekends, especially on Sundays (Figure 2.3). As seen in Table 2.2, the reduction in these atmospheric pollutants is significant at the urban area, with a decrease up to 39% in the case of NO, and between 15 and 21% for the other three pollutants. The changes observed in the SB are akin to those in the UB only for NO and NO_2, smaller for SO_2 (only 6% less) and insignificant for PM_{10}. Similarly, RB NO and NO_2 experience a significant decrease (up to 15%) during weekends, but tiny variations in SO_2 and PM_{10}. On the other hand, ozone concentrations increase during weekends in all types of environment, from an anecdotic increment in the RB and SB (2-3%) to a moderate augment in the UB (14%). No significant variations in the concentrations of the different atmospheric pollutants occur during weekdays, thus indicating a lack of accumulation of locally-derived pollutants over the region. This is not the case of continental Mediterranean regions, where this phenomenon occurs at urban and regional scales (Pey et al., 2008; Ripoll et al., 2014). Thus, the insularity of our region avoids the accumulation of local pollutants over extended time periods and consequently this location may be regarded as an excellent observatory of the western Mediterranean atmosphere, ideal to study long-scale variations in atmospheric pollutants.

Table 2.2. Average concentrations (2000-2012) of NO, NO_2, SO_2, O_3 and PM_{10} (µg/m³) from Monday to Sunday at urban, suburban and regional background environments. Week-end benefit (in %).

µg/m³	Urban					Suburban					Regional				
	NO	NO_2	SO_2	O_3	PM_{10}	NO	NO_2	SO_2	O_3	PM_{10}	NO	NO_2	SO_2	O_3	PM_{10}
Monday	30.1	50.1	2.6	36.6	31.0	2.5	11.3	3.0	65.9	21.0	1.7	6.4	2.3	65.6	18.9
Tuesday	29.0	49.3	2.8	37.0	32.1	2.7	11.9	3.3	66.2	21.0	1.7	6.5	2.3	65.8	19.0

Wednesday	29.3	49.5	2.8	37.2	31.7	2.7	12.0	3.2	66.0	21.3	1.7	6.7	2.3	65.4	19.6
Thursday	28.2	50.2	3.3	37.4	31.3	2.8	12.2	3.5	66.2	20.9	1.7	6.7	2.3	65.2	19.9
Friday	30.9	53.4	3.1	36.1	30.8	2.8	12.7	3.4	66.3	21.4	1.6	6.6	2.3	66.4	20.2
Saturday	21.7	46.2	2.6	39.5	27.9	2.0	10.7	3.3	67.7	21.3	1.5	6.1	2.2	67.2	20.0
Sunday	14.3	36.6	2.0	44.6	25.3	1.5	8.7	2.9	69.0	20.1	1.4	5.4	2.1	67.0	18.9
Week-days	29.5	50.5	2.9	36.8	31.4	2.7	12.0	3.3	66.1	21.1	1.7	6.6	2.3	65.7	19.5
Week-end	18.0	41.4	2.3	42.1	26.6	1.8	9.7	3.1	68.3	20.7	1.4	5.7	2.2	67.1	19.4
Week-end benefit (%)	**-39**	**-18**	**-22**	**14**	**-15**	**-35**	**-19**	**-6**	**3**	**-2**	**-15**	**-13**	**-5**	**2**	**0**

2.3.3. Inter-annual variations

In order to analyse possible trends for air pollutants at the UB, SB and RB, Theil-Sen trends were calculated for NO, NO_2, SO_2, O_3 and PM_{10} concentrations for the period 2000-2012 (Table 2.3).

Table 2.3. Theil-Sen concentration trends (2000-2012) for NO, NO_2, SO_2, O_3 and PM_{10} (in µg/m³ year) and their 95% confident intervals (in brackets), at urban, suburban and regional background environments.

µg/m³year (p>0.95)	NO	NO_2	SO_2	O_3	PM_{10}
Urban	-1.11 (-1.59, -0.64)	-1.02 (-1.56, -0.47)	0.01 (-0.06, 0.08)	1.04 (0.32, 1.83)	-0.73 (-0.95, -0.52)
Suburban	-0.01 (-0.05, 0.04)	-0.28 (-0.39, -0.16)	0.09 (0.02, 0.16)	0.48 (-0.05, 0.96)	-0.75 (-1.01, -0.51)
Regional	-0.24 (-0.29, -0.20)	-0.18 (-0.28, -0.07)	-0.07 (-0.13, -0.03)	0.48 (-0.05, 0.96)	-0.55 (-0.72, -0.41)

-Nitrogen Oxides (NO and NO_2)

A clear reduction of NO has been detected at UB and RB locations (Figure 2.4 A). Such reduction has been remarkable at the UB (-1.11 µg/m³ per year) and moderate at the RB (-0.24 µg/m³ per year). Conversely, no change has been observed at the SB (-0.01 µg/m³ per year). Likewise, NO_2 concentrations have been reduced (Figure 2.4 B) at all types of environments (-1.02, -0.28 and -0.18 µg/m³ per year at UB, SB and RB respectively). It is important to mention that diesel vehicles have been nationally promoted in recent years due to its low consumption, so the growth of the vehicle fleet has been followed by its progressive dieselization (Figure 2.5). It is well known that diesel vehicles emit a substantial proportion of primary NO_2 with respect to gasoline vehicles (Grice et al., 2009; Anttila et al., 2011). Actually, the UB NO drop has been much more pronounced than that of NO_2 (Figure 2.6).

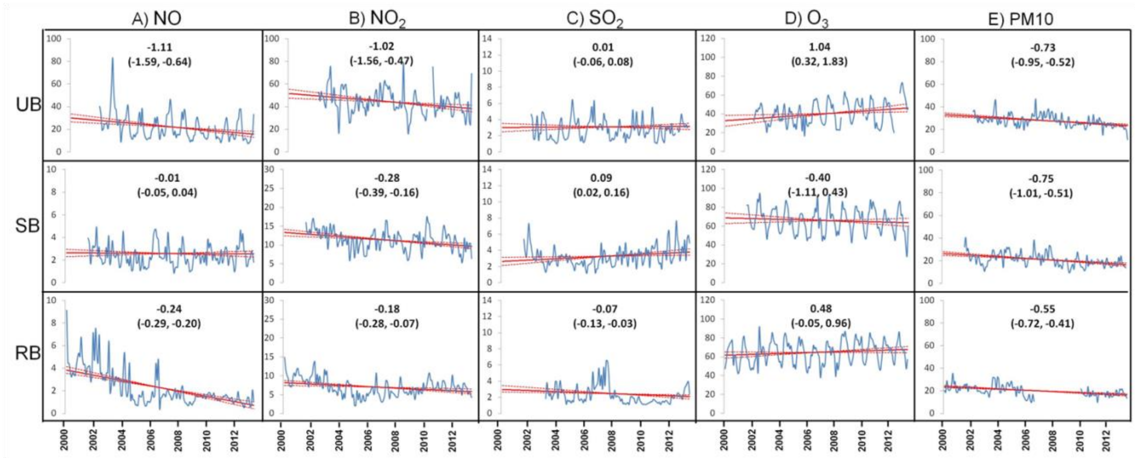


Figure 2.4. Monthly averages and Theil-Sen trends (2000-2012) for NO, NO_2, SO_2, PM_{10} and O_3 (in µg/m^3) at at UB (urban background), SB (suburban background) and RB (regional background) environments. Different concentration scales for specific pollutants.

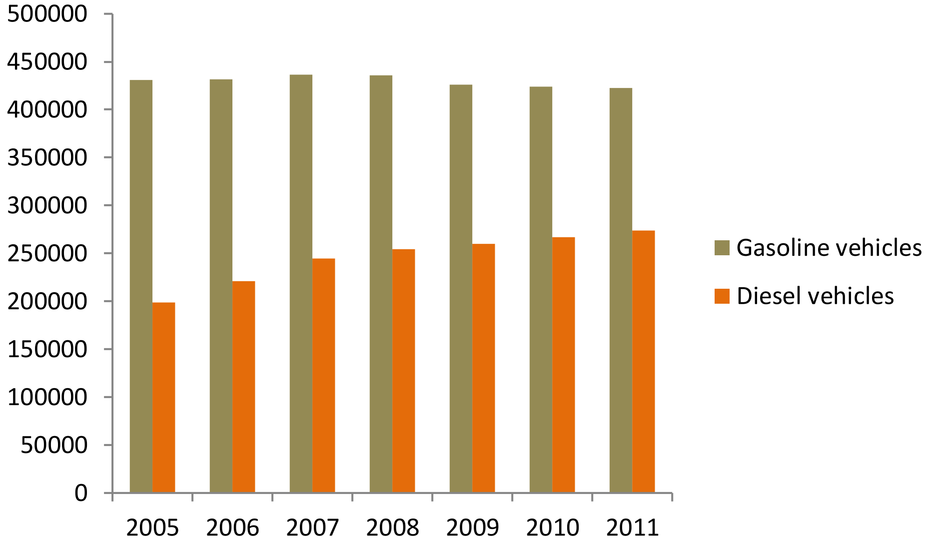


Figure 2.5. Evolution of the car gasoline/diesel fleet in Mallorca

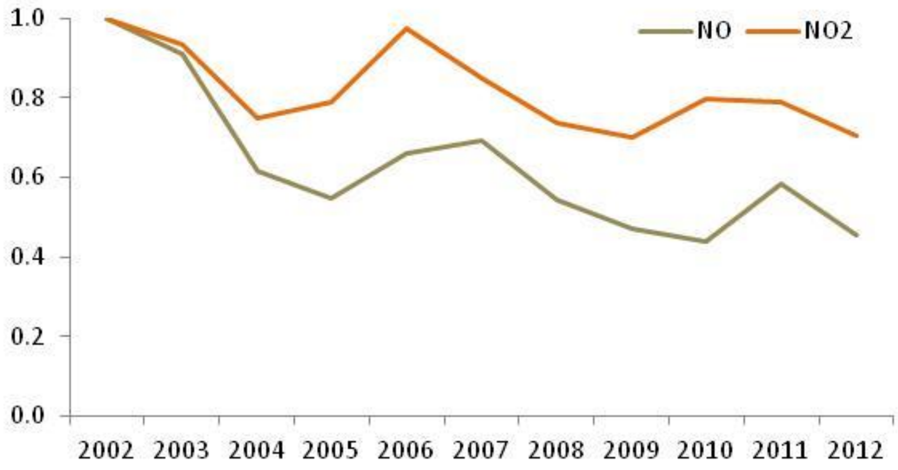


Figure 2.6. Normalised urban NO and NO_2 concentrations since 2002 at urban environment.

-Sulphur Dioxide (SO2)

Insignificant changes have been observed for SO_2 (Figure 2.4 C). A slightly reduction of SO_2 has been detected in the RB (-0.07 µg/m^3 year). Such reduction may be the result of the desulphurisation system installed in the Alcudia power plant.

A little rise of SB SO_2 has been noticed (0.09 µg/m^3 year), which may be caused by increased maritime traffic, despite the entering into force of the Directive 2005/33/EC in 2010, limiting considerably the sulphur content in ship fuels (Schembari et al., 2012).

In contrast, urban SO_2 concentration does not show any variation (0.01 µg/m^3 year). Whereas maritime traffic rose, the harbour activity was progressively shifted from the old dock (in front of the city centre) to the western dock (closer to one of the suburban sites) (Figure 2.7).

Figure 2.7. Locations of the Old and the Western docks in respect to the city, and location of an UB site (Foners) and a SB site (Bellver).

-Ozone (O_3)

The concentrations of ozone have experienced opposite trends with respect to NO (Figure 2.4 D). In particular, O_3 has significantly increased in the UB (+1.04 µg/m^3 per year), moderately in the RB (0.48 µg/m^3 per year), but showing a decreasing trend in the SB (-0.4 µg/m^3 per year).

On one hand, the NO reduction observed in the UB explains the dissimilar trend in O_3. Likewise, the unaltered NO concentrations in the SB may be an indicator of increasing traffic over these environments, which could explain the moderate reduction of ozone. Finally, the RB O_3 augment is consistent with observations at other European background areas (Ordonez et al., 2005; EEA, 2012).

-Particulate Matter (PM10)

The evolution of PM_{10} concentrations shows a clear diminution over all types of areas (Figure 2.4 E). The decrease is more important in UB and SB areas (-0.73 and -0.75 µg/m^3 per year respectively), but also significant over the RB (-0.54 µg/m^3 per year). These results are in agreement with other studies carried out across Europe (Cusack et al., 2012; Barmpadimos et al., 2012). Whilst a 0.54 µg/m^3 per year decrease has been recorded over the RB, an additional 0.20 µg/m^3 diminution per year is patent at UB and SB sites, probably connected to the combination of improved vehicle technologies and to the application of abatement plans (Balearic Government, 2008, 2013). The RB decrease is attributed to the implementation of mitigation strategies across the continent (Cusack et al., 2012; Schembari et al., 2012), to the impact of the financial crisis over southern Europe (Cusack et al., 2012), and to the lower contribution of Saharan dust since 2006-2007 (Pey et al., 2013b).

2.3.4. 2000-2012 trends and its relation with the origin of air masses

Theil-Sen inter annual trends for the period 2000-2012 were also assessed for air mass origins (Table 2.4, Figures 2.8 a-e). The most frequent situations were AT (44%) and AF (22%), followed by SR (15%), WR (9%) and EU (8%). Mediterranean advection occurred only 4% of the time, and consequently this scenario was not considered representative enough to deal with. From this analysis it will be possible to make a distinction between changes affecting local to continental scales, such as those concerning PM_{10} or O_3 (whose concentrations may be substantially driven by external origins), and those changes at a local to regional scale, such as those affecting NO_x and SO_2.

Table 2.4. Theil-Sen concentration trends (2000-2012) for NO, NO_2, SO_2, O_3 and PM_{10} (in µg/m^3 year) and their 95% confident intervals, according to the origin of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional (SR) and Winter Regional (WR).

µg/m³year (p>0.95)		AT	EU	AF	SR	WR
NO	Urban	-1.33 (-1.92, -0.83)	-1.64 (-2.55, -0.89)	-0.83 (-1.31, -0.37)	-0.72 (-1.17, -0.25)	-1.20 (-2.27, -0.02)
	Suburban	-0.02 (-0.07, 0.04)	-0.02 (-0.11, 0.05)	0.02 (-0.04, 0.08)	-0.01 (-0.08, 0.06)	0.11 (-0.03, 0.22)
	Regional	-0.25 (-0.30, -0.20)	-0.22 (-0.33, -0.17)	-0.22 (-0.28, -0.17)	-0.22 (-0.29, -0.16)	-0.17 (-0.31, -0.06)
NO_2	Urban	-1.46 (-2.14, -0.89)	-1.28 (-2.57, -0.30)	-1.09 (-1.92, -0.26)	0.11 (-0.84, 1.09)	-0.84 (-1.81, 0.10)
	Suburban	-0.30 (-0.43, -0.16)	-0.48 (-0.66, -0.27)	-0.27 (-0.47, -0.05)	-0.21 (-0.47, 0.06)	-0.18 (-0.55, 0.17)
	Regional	-0.22 (-0.35, -0.10)	-0.24 (-0.44, -0.07)	-0.11 (-0.24, 0.02)	-0.06 (-0.20, 0.08)	-0.14 (-0.42, 0.10)
	Urban	0.00 (-0.08, 0.07)	0.03 (-0.14, 0.18)	0.05 (-0.03, 0.13)	0.14 (0.03, 0.23)	-0.07 (-0.22, 0.06)

SO_2	Suburban	0.04 (-0.04, 0.12)	0.01 (-0.11, 0.11)	0.16 (0.08, 0.24)	0.10 (-0.02, 0.24)	0.16 (0.00, 0.30)
	Regional	-0.07 (-0.12, -0.02)	-0.04 (-0.14, 0.07)	-0.09 (-0.14, -0.04)	0.00 (-0.07, 0.06)	-0.12 (-0.22, -0.03)
O_3	Urban	0.94 (0.14, 1.79)	1.65 (0.70, 2.68)	1.65 (0.23, 2.80)	1.26 (0.30, 2.42)	0.13 (-1.25, 1.34)
	Suburban	-0.40 (-1.10, 0.33)	-1.75 (-3.38, -0.31)	-0.29 (-1.30, 0.57)	-0.78 (-1.63, -0.21)	-0.14 (-1.08, 0.88)
	Regional	0.43 (-0.09, 0.97)	0.01 (-1.01, 1.07)	-0.01 (-0.66, 0.65)	0.43 (-0.19, 1.04)	0.20 (-0.86, 1.09)
PM_{10}	Urban	-1.00 (-1.34, -0.72)	-0.57 (-1.13, 0.01)	-0.41 (-1.23, 0.40)	-0.87 (-1.46, -0.38)	-0.52 (-1.33, 0.31)
	Suburban	-0.74 (-1.00, -0.50)	-0.48 (-0.87, -0.13)	-0.44 (-0.85, 0.06)	-1.23 (-1.62, -0.78)	-0.27 (-0.67, 0.14)
	Regional	-0.62 (-0.77, -0.45)	-0.62 (-0.85, -0.33)	-0.77 (-1.16, -0.39)	-0.73 (-1.09, -0.48)	-0.35 (-0.75, -0.08)

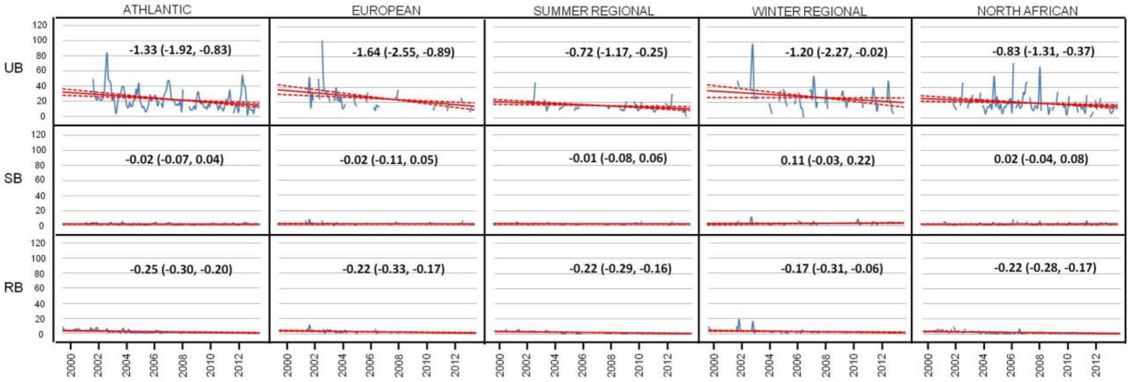


Figure 2.8.a. Monthly averages and Theil-Sen trends (2000-2012) for NO (in µg/m^3) at UB (urban background), SB (suburban background) and RB (regional background) environments, according to the origin of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional (SR) and Winter Regional (WR).

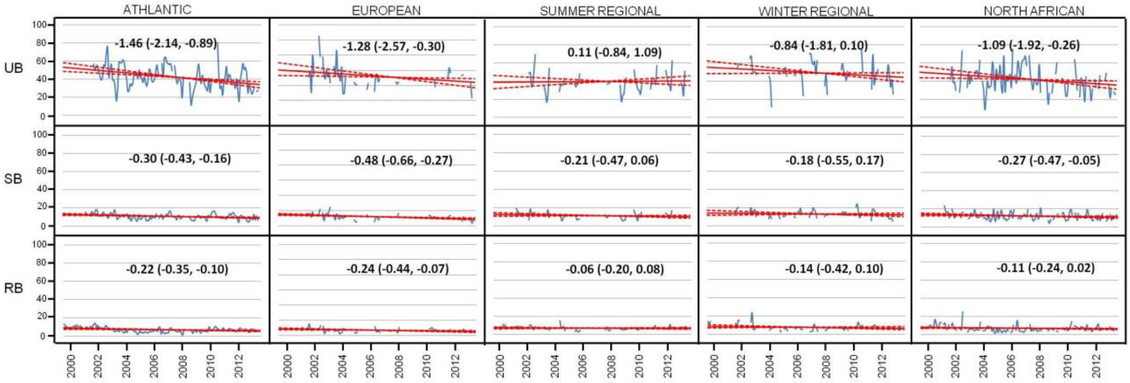


Figure 2.8.b. Monthly averages and Theil-Sen trends (2000-2012) for NO_2 (in µg/m^3) at UB (urban background), SB (suburban background) and RB (regional background) environments, according to the origin of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional (SR) and Winter Regional (WR).

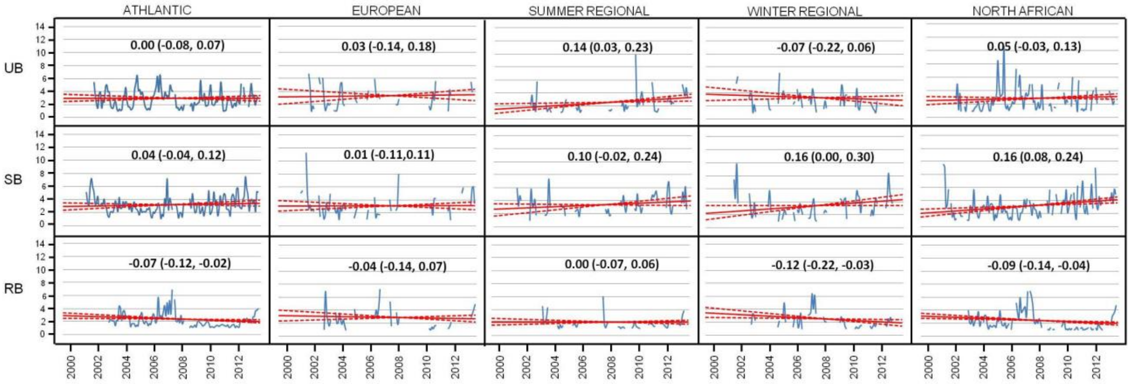


Figure 2.8.c. Monthly averages and Theil-Sen trends (2000-2012) for SO_2 (in µg/m^3) at UB (urban background), SB (suburban background) and RB (regional background) environments, according to the origin of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional (SR) and Winter Regional (WR).

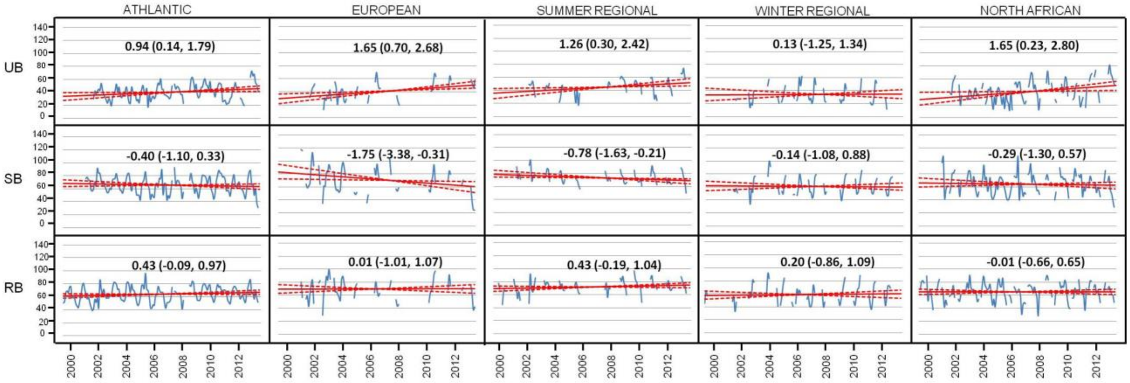


Figure 2.8.d. Monthly averages and Theil-Sen trends (2000-2012) for O_3 (in µg/m^3) at UB (urban background), SB (suburban background) and RB (regional background) environments, according to the origin of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional (SR) and Winter Regional (WR).

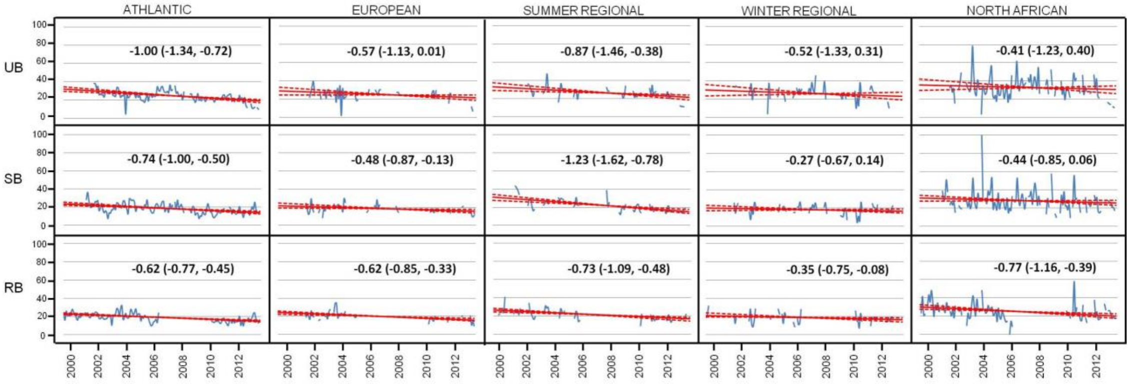


Figure 2.8.e. Monthly averages and Theil-Sen trends (2000-2012) for PM_{10} (in µg/m^3) at UB (urban background), SB (suburban background) and RB (regional background) environments, according to the origin of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional (SR) and Winter Regional (WR).

A significant decrease of NO and NO_2 concentration occurred in the UB for most types of episode. However, NO was less markedly reduced during SR situations at the same time that NO_2 slightly rose. A possible explanation could be the uninterrupted increment of tourists in summer, when SR events occur. This is again connected to a prominent increase in SO_2 during these situations.

The drop (in µg/m^3 year) of NO during WR situations (-1.20) was comparable to that during AT and EU scenarios (-1.33 and -1.64). The situation for NO_2 is moderately different. Whereas the decline during AT and EU was very similar as for NO (-1.28 and -1.46), it was much lower during WR (-0.84). This could be connected with the progressive dieselization of the vehicular fleet (Figure 2.5), associated with higher primary NO_2 emissions (Grice et al., 2009; Anttila et al., 2011).

Whereas SO_2 has slightly fallen down at RB areas (already commented), steady or slight increments occurred at UB and SB environments, in parallel with the augment of maritime traffic. This is not observed during WR situations at the UB area (-0.07). As discussed in previous sections this could be explained by the progressive reallocation of the harbour activity from the old to the western dock (Figure 2.7). It has to be noted that atmospheric emissions remain in the vicinity of the source during WR episodes.

UB O_3 concentrations rose in parallel to the decline of NO. O_3 concentrations at SB felt down according to the augment of the progressive increase of vehicular traffic. Noticeably, one of the most interesting observations at RB areas concerns the dissimilar O_3 trends in function to air mass origins. When comparing AT, EU and AF scenarios, it is evident that O_3 increment is only linked to AT events. Therefore, our observations suggest that the O_3 augment in the northern hemisphere (EEA, 2012) observed in the last years is not directly related to European or North African sources since no O_3 trends from these sectors are visible. Thus, this could indicate a partial success of European policies to abate ozone precursors, and no major changes in North Africa in the last decade.

The drop of PM_{10} is generally higher in the UB than the RB, except for the AF episodes. This fact can be related to the double effect of continental measures: the implementation of different EURO standards has reduced European atmospheric emissions, with a clear effect over the continental background but also at a local scale (with less primary emissions and secondary precursors in our cities). During AF scenarios, the PM_{10} drop is more pronounced at the RB than at the UB (and SB). It is well known that a mix of SO_2 and African dust tend to generate calcium sulphate particles (Alastuey et al., 2005). In our particular context, with moderate positive SO_2 trends in the UB and SB areas during SR and AF scenarios, the enhancement of this phenomenon is likely. This is reinforced with the fact that most African dust incursions occur in summer, the busiest maritime traffic interval. Thus, the formation of calcium sulphate particles around SO_2 emission sources may partially compensate its natural decline.

PM_{10} trends at RB and SB areas under WR events (when the influence of local and regional sources is dominant) are less pronounced when compared to other scenarios. Specifically, a decline of 0.35 µg/m^3 year is detected at the RB and 0.27 µg/m^3 year at the SB. These values contrast with those for other meteorological scenarios, usually in the range 0.44 to 1.23 µg/m^3 year. The lower PM_{10} decline during WR events could reflect less success of abatement measures adopted at regional scale with respect to those at continental level. It should be taken into account that measures throughout the continent have been adopted in different emission sectors (traffic, energy, industry, among others). In Mallorca, the lack of large industrial installations implies that the local benefit will arise mostly from land transport. Having in mind that vehicular traffic has grown during the studied period, the reduction in PM_{10} can be explained by the introduction of successive EURO standards. When focusing in urban PM_{10} trend, a higher decrease is apparent (-0.52), probably because of the aforementioned EURO standards, but also due to local measures applied locally. In contrast, a lower decrease in SB area has been observed (-0.27) with respect to the RB decrease. This may be explained by the fact that part of the vehicular traffic has been moved from the city centre to the periphery as a result of different mitigation strategies and urban planning policies.

2.3.5. Air pollution and hemispheric atmospheric circulation: a comparison with NAO index

NAO conditions varied markedly in the period 2000-2012, from a more positive phase during the first interval towards prevailing negative conditions during the second one (Figure 2.9).

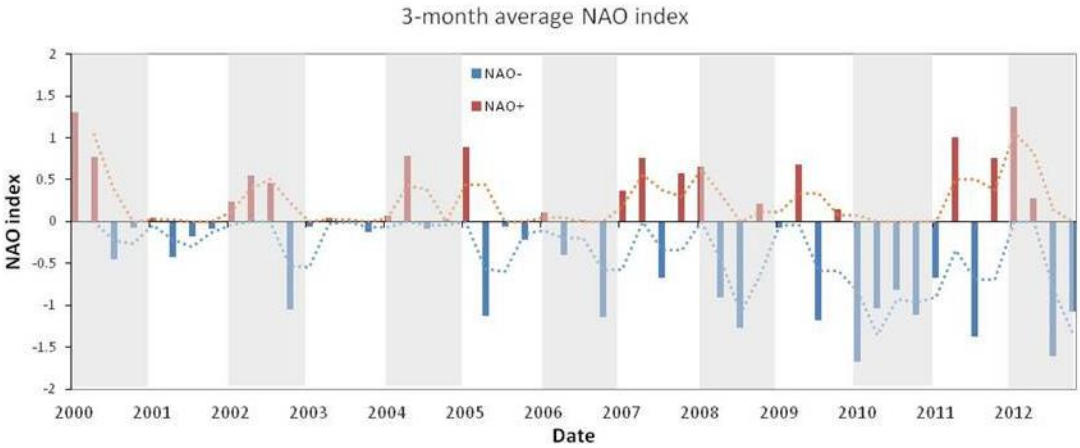


Figure 2.9. Seasonal NAO index for the period 2000-2012. Negative NAO phases (blue) and positive NAO phases (red). Dashed lines reproduce the moving average.

Seasonal mean concentrations for each pollutant were plotted against their corresponding NAOi values. Figure 2.10 depicts a selection of the main correlations obtained for the different seasons:

Spring (March-May)

In spring, NAOi exerted an influence on certain pollutants such as O_3, NO and NO_2. The correlation is more evident for NO and NO_2 at SB and UB areas, in which negative NAO phases were linked to lower NO_x concentrations. O_3 tended to be higher during negative NAO periods, especially at the RB.

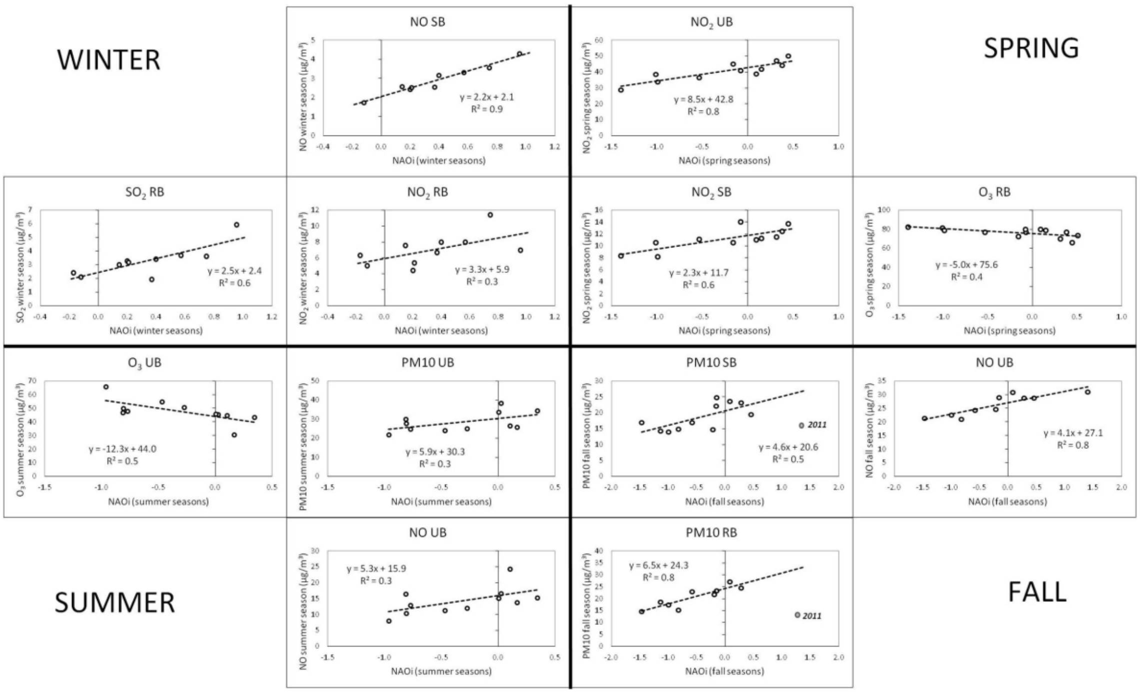


Figure 2.10. Selected scatter-plots between NO, NO_2, SO_2, PM_{10} and O_3 (in µg/m³) and NAOi at UB (urban background), SB (suburban background) and RB (regional background) environments for winter, spring, summer and fall seasons.

Summer (June-August)

In summer, partial correlations are observed at certain environments and for specific pollutants. Indeed, negative NAO periods were related to lower PM_{10} concentrations, which may be linked to less frequent Saharan dust episodes (Pey et al., 2013b). O_3 and NO concentrations at the UB vary inversely in function of NAO conditions. Thus, negative NAO periods were associated to lower NO, but higher O_3 concentrations. Conversely, a slight decrease of SO_2 concentrations over all types of environments is detected as NAOi is progressively more positive.

Fall (September-November)

During fall, there is a clear NAOi effect on PM_{10}, especially at SB and RB environments, with much lower PM_{10} concentrations as NAOi became more negative. The behaviour of NO at the UB was exactly the same as PM_{10} in RB and SB. Such NAOi effect is partially seen on NO_2.

Winter (December-February)

During winter, clear effects on NO and SO_2 at the SB can be seen, with NAOi negative phases favouring the occurrence of lower concentrations of both pollutants. A similar pattern for NO_2 at RB areas can be drawn.

Overall, NAOi emerges as a partial indicator to predict and explain certain behaviours in air pollutant concentrations in our region. More precisely, negative NAO periods seem to favour atmospheric dispersion as NO_x concentrations are generally lower when comparing with more positive NAO phases. Moreover, such negative NAO periods, when observed during the typical Saharan dust season (summer-fall), diminish the transport of dust towards the NW Mediterranean, resulting in additional air quality benefits. Conversely, O_3 concentrations display inverse patterns, both in UB (less O_3 consumption by NO_x oxidation) and RB environments.

2.4. Conclusions

A 13-year database of different air quality parameters has been investigated in this work. The analysis of weekly patters reveals a limited degree of accumulation of locally emitted pollutants over Mallorca, thus highlighting the adequateness of Mallorca as an observatory of the Western Mediterranean atmosphere.

The design of our study has allowed the discrimination of UB and SB contributions. Most of NO and NO_2 are urban, whereas PM_{10} and O_3 are clearly connected to regional sources and long-range transport processes despite a moderate UB contributions. SO_2 arise from regional sources, especially from power generation and shipping emissions.

Trend calculations reflect a clear improvement of the air quality in all environments, with a considerably drop of NO_x and PM_{10} concentrations at UB and RB areas. Such downward trend is less evident at SB areas as they have been increasingly exposed to road-traffic emissions as a result of urban planning policies and mitigation strategies. Slight SO_2 inter-annual variations have been observed despite the new regulations in sulphur content in shipping fuel (in force since 2010) and the desulfurization system installed in the main coal power plant. The increased maritime traffic may have counteracted all these abatement measures.

Our results show that the most significant decreasing trends occurred when air masses came from western to northern sectors, suggesting the effectiveness of certain European strategies to tackle air pollution. Some additional benefits are connected to the implementation of diverse local policies.

We have investigated also the role of the North Atlantic Oscillation. Our region has been benefited of favorable atmospheric conditions since 2006-2007 (a negative NAO period) which, together with the implementation of continental and regional/local policies and the impact of the financial crisis, has resulted in a prominent decrease of atmospheric pollutants. Our findings suggest that the atmospheric dispersion effect linked to the NAO sign is not negligible. Indeed, most of the higher NOx and PM_{10} concentrations recorded during the 13-year study were observed during positive NAO phases. Therefore, it would be highly recommendable to anticipate further local measures for the moment when atmospheric conditions will be adverse and the economic crisis overcome.

2.5. Acknowledgements

The authors acknowledge the financial support from the Spanish Ministry of Science and Innovation through the project CTQ2013-47461-R and the French Research Agency through the project ANR-Blanc SAF-MED, grant n° SIMI6 ANR-12-BS06-0013.

2.6. References

Alastuey A., Querol X., Castillo S., Escudero M., Avila A., Cuevas E., Torres C., Romero P.M., Exposito F., Garcia O., Diaz J.P., Dingenen R.V., Putaud J.P., 2005. *Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan dust episode (July 2002)*. Atmospheric Environment, 39, 4715–4728.

Anttila P., Tuovinen J.P., Niemi J.V., 2011. *Primary NO_2 emissions and their role in the development of NO2 concentrations in a traffic environment*. Atmospheric Environment, 45, 986-999.

Balearic Government, 2008. *Pla de Millora de la Qualitat de l'Aire de Palma 2008*. Palma, Spain.

Balearic Government, 2013. *Pla de Millora de la Qualitat de l'Aire de Palma 2011-2015*. Palma, Spain.

Barmpadimos I., J. Keller, D. Oderbolz, C. Hueglin, and A. S. H. Prévôt, 2012. *One decade of parallel fine (PM2.5) and coarse (PM10–PM2.5) particulate matter measurements in Europe: trends and variability*. Atmospheric Chemistry and Physics, 12, 3189–3203.

Bytnerowicz A., Omasa K. and Paoletti E., 2007. *Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective*. Environmental Pollution 147: 438-445.

Carslaw, D.C. and K. Ropkins, 2012. *Openair — an R package for air quality data analysis*. Environmental Modelling & Software. Volume 27-28, 52-61.

Carslaw, D.C., 2014. *The openair manual — open-source tools for analysing air pollution data. Manual for version 1.0*, King's College London.

Cerro J.C., 2013. Comportament i tendències de la contaminació atmosfèrica a Mallorca, com a referent del Mediterrani Occidental. Master Thesis. Universitat de les Illes Balears (in Catalan).

Colette, Granier C., Hodnebrog, Jakobs H., Maurizi A., Nyiri A., Bessagnet B., D'Angiola A., D'Isidoro M., Gauss M., Meleux F., Memmesheimer M., Mieville A., Rouïl L., Russo F., Solberg S., Stordal F., and Tampieri F., 2011. *Air quality trends in Europe over the past decade: a first multi-model assessment*. Atmospheric Chemistry and Physics, 11, 11657–11678.

Cusack M., Alastuey A., Pérez N., Pey J., Querol X., 2012. *Trends of particulate matter (PM2.5) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010)*. Atmospheric Chemistry and Physics 12, 8341-8357.

Environmental European Agency, 2009. *Assessment of ground-level ozone in EEA member countries, with a focus on long-term trends*. Copenhagen, Denmark.

Environmental European Agency, 2012. *The contribution of transport to air quality. TERM 2012: transport indicators tracking progress towards environmental targets in Europe*. EEA Report No 10/2012. ISSN 1725-9177. Copenhagen, Denmark.

Genestar C., Pons C., Cerro J. C., Cerdà V., 2014. *Different decay patterns observed in a nineteenth-century building (Palma, Spain)*. Environmental Science and Pollution Research, Apr.

González-Fernández I., Calvo E., Gerosa G., Bermejo V., Marzuoli R., Calatayud V., and Alonso R., 2014. *Setting ozone critical levels for protecting horticultural Mediterranean crops: Case study of tomato*. Environmental Pollution, 185: 178-187.

Grice S., Stedman J., Kent A., Hobson M., Norris J., Abbott J., Cooke S., 2009. *Recent trends and projections of primary NO_2 emissions in Europe*. Atmospheric Environment, 43, 2154–2167.

Hipel K. W. and McLeod A. I., 2005. *Time Series Modelling of Water Resources and Environmental Systems*. Elsevier, Amsterdam.

Intergovernmental Panel on Climate Change, Core Writing Team, Pachauri, R.K. and Reisinger, A. (Eds.), 2007. *Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Geneva, Switzerland. pp 104

Jerez S., Jimenez-Guerrero P., Montávez J.P., Trigo R.M., 2013. *Impact of the North Atlantic Oscillation on European aerosol ground levels through local processes: a seasonal model-based assessment using fixed anthropogenic emissions*. Atmospheric Chemistry and Physics, 13, 11195-11207.

Kendall M. G., 1976, *Rank Auto Correlation Methods*, 4 ed., Griffin, Oxford.

Lenschow P, Abraham H.J., Kutzner K., Lutz M., Preuß J.D.and Reichenbächer W., 2001. *Some Ideas about the Sources of PM10*. Atmospheric Environment, 35, Supplement No. 1, S23 – S33

Mateu J., Bauzá de Mirabó F., Forteza R. and Cerdà V., 1998. *Heavy metals in the aerosols collected at two stations in Majorca (Spain)*. Water, Air and Soil Pollution, 112, 1-15

Ordóñez C., Mathis H., Furger M., Henne S., Hüglin C., Staehelin J., and Prévôt A. S. H., 2005. *Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003*. Atmospheric Chemistry and Physics, 5, 1187–1203.

Pandolfi M., Gonzalez-Castanedo Y., Alastuey A., de la Rosa J.D., Mantilla E., Sánchez de la Campa A., Querol X., Pey J., Amato F., Moreno T., 2011. *Source Apportionment of PM10 and PM2.5 at Multiple*

Sites in the Strait of Gibraltar by PMF: Impact of Shipping Emissions. Environmental Science and Pollution Research 18, 260-269.

Pey J., Querol X., Alastuey A., 2009a. *Variations of levels and composition of PM10 and PM2.5 at an insular site in the Western Mediterranean*. Atmospheric Research, 94, 285-299.

Pey J., Pérez N., Castillo S., Viana M., Moreno T., Pandolfi M., López-Sebastián J.M., Alastuey A., Querol X., 2009b. *Geochemistry of regional background aerosols in the Western Mediterranean*. Atmospheric Research, 94, 422-435.

Pey J., Querol X., Alastuey A., 2010. *Discriminating the regional and urban contributions in the North-Western Mediterranean: PM levels and composition*. Atmospheric Environment, 44, 1587-1596.

Pey J., Alastuey A., Querol X., 2013a. *PM10 and PM2.5 sources at an insular location in the western Mediterranean by using source apportionment techniques*. Science of the Total Environment, 456-457, 267-277.

Pey J., Querol X., Alastuey A., Forastiere F., Stafoggia M., 2013b. *African dust outbreaks over the Mediterranean Basin during 2001–2011: PM10 concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology*. Atmospheric Chemistry and Physics, 13, 1395-1410.

Querol X., Alastuey A., Pandolfi M., Reche C., Pérez N., Minguillón M. C., Moreno T., Viana M., Escudero M., Orio A., Pallarés M., Reina F., 2014. *2001-2012 trends on air quality in Spain*. Science of The Total Environment, 06, 490C:957-969.

Ripoll A., Pey J., Minguillón M. C., Pérez N., Pandolfi M., Querol X., Alastuey A., 2014. *Three years of aerosol mass, black carbon and particle number concentrations at Montsec (southern~Pyrenees, 1570 m a.s.l.)*. Atmospheric Chemistry and Physics,14, 4279-4295.

Samoli E., Stafoggia M., Rodopoulou S., Ostro B, Declercq C., Alessandrini E., Díaz J., Karanasiou A., Kelessis A., Le Tertre A., Pandolfi P., Randi G, Scarinzi C., Zauli-Sajani S., KatsouyanniK., Forastiere F., 2013. *Associations between Fine and Coarse Particles and Mortality in Mediterranean Cities: Results from the MED-PARTICLES Project*. Environmental Health Perspectives 121, 8.

Schembari C., Cavalli F., Cuccia E., Hjorth J., Calzolai G., Pérez N., Pey J., Prati P., Raes F., 2012. *Impact of a European directive on ship emissions on air quality in Mediterranean harbours*. Atmospheric Environment 61, 661-669.

Stafoggia M., Samoli E., Alessandrini E., Cadum E., Ostro B., Berti G., Faustini A., Jacquemin ., Linares C., Pascal M., Randi G., Ranzi A., Stivanello E., Forastiere F., 2013. *Short-term Associations between Fine and Coarse Particulate Matter and Hospitalizations in Southern Europe: Results from the MED-PARTICLES Project*. Environmental Health Perspectives 121, 9.

Stein A.F., Draxler R.R., Rolph G.D., Stunder B.J.B., Cohen M.D., Ngan F., 2015. *NOAA's HYSPLIT atmospheric transport and dispersion modeling system*. Bull. Amer. Meteor. Soc. 96, 2059–2077

World Health Organization, 2005. Air quality guidelines global update 2005. *Report on a Working Group meeting*, Bonn, Germany, 18-20 October.

World Health Organization, 2013. *Review of evidence on health aspects of air pollution-REVIHAAP Project. Technical Report.* Bonn, Germany.

Chapter 3: Variability of air pollutants, and PM composition and sources at a regional background site in the Balearic Islands: review of western Mediterranean phenomenology from a 3-year study

This chapter corresponds to the Research Paper: *Variability of air pollutants, and PM composition and sources at a regional background site in the Balearic Islands: review of western Mediterranean phenomenology from a 3-year study*

Authors: José C. Cerro[1,2], Víctor Cerdà[1], Xavier Querol[3], Andrés Alastuey[3], Carles Bujosa[4†] and Jorge Pey[5]

[1]Laboratory of Environmental Analytical Chemistry, Illes Balears University, Palma de Mallorca, 07122, Spain

[2]Laboratory of the Atmosphere, Govern Illes Balears, Palma de Mallorca, 07009, Spain

[3]Institute of Environmental Assessment and Water Research, IDÆA-CSIC, Barcelona, 08028, Spain

[4]ENDESA, Palma de Mallorca, 07007, Spain

[5]ARAID-Instituto Pirenaico de Ecología - CSIC, Zaragoza, 50059, Spain

Published in Science of the Total Environment 717 (2020) 137-177

DOI: https://doi.org/10.1016/j.scitotenv.2020.137177

Abstract

The present study discloses the results of a comprehensive 3-years campaign (2010-2012) of air pollution measurements over a regional island background area (Can Llompart-Balearic Islands, Spain), contextualized with other measurements in the western Mediterranean region.

Gaseous pollutants and particulate matter fractions were measured in real time; and PM_{10} and PM_1 daily samples were obtained regularly from which chemical analyses were performed. Furthermore, during three intensive observation periods, real-time concentrations of particle number, black carbon and ammonia were additionally measured.

Our results display particular diurnal and seasonal patterns for certain pollutants such as O_3 and particle number concentration.

Our study reveals that concentrations of air pollutants and aerosol chemical composition are rather similar all over the central and western Mediterranean basin. The most abundant chemical components in PM_{10} were mineral dust, followed by organic matter, sea spray and SO_4^{2-}; in PM_1 organic matter and SO_4^{2-} dominated, with significant contribution of mineral dust.

Furthermore, a source apportionment Positive Matrix Factorization analysis was conducted. Natural sources exert most of the impact on the coarse-mode fraction, while most of fine-mode aerosols are linked to anthropogenic sources coming from local, regional or long range transport emissions.

Prevalence of Atlantic air masses in 2010 had a positive effect in air quality, lowering mineral dust, SO_4^{2-} and EC concentrations. On the contrary, the high incidence of African dust and regional recirculation situations during the 2012 warm season favoured an overall PM load increase governed by mineral dust, SO_4^{2-} and trace elements associated to dust aerosols.

The continuous increase in tourists in the Balearic Islands, and in general all around the Mediterranean, is clearly changing air quality patterns: while urban air pollution has strongly decreased since 2010, such downward trend is less pronounced at the regional scale, thus related to crescent sources such as maritime and air transport.

3.1. Introduction

Atmospheric pollution is one of the most important environmental challenges to which contemporary societies are faced with. Among the hundreds of substances that compose air pollution, gaseous compounds such as nitrogen dioxide (NO_2), ozone (O_3), sulphur dioxide (SO_2), ammonia (NH_3) and atmospheric particulate (in terms of mass and number concentrations) and their chemical components attract most of the attention. While health effects derived from NO_2, SO_2 and O_3 pollution points to cardiovascular and lung diseases, or even premature deaths (WHO, 2005; 2013), the effects caused by aerosol pollution are more severe. Actually, atmospheric particulate matter (PM) is associated with increasing mortality and morbidity (Pope III and Dockery, 2006; Samoli et al., 2013; Stafoggia et al. 2013; WHO, 2013). In addition, atmospheric aerosols are key drivers in certain atmospheric and climate processes and they are influencing the Earth's radiative balance (IPCC, 2007). Amongst different aerosol types, black carbon (BC) is the one drawing more attention because of its well-known potential for warmth (IPCC, 2013) and its classification as carcinogenic (WHO, 2013). Air components may also affect the ecosystems, as they can be either pollutants (heavy metals), either fertilizers (Bytnerowicz et al., 2007); the agriculture, with special concern to tropospheric O_3 (Eugster et al., 2010; Gonzalez-Fernandez et al., 2014); and the historical heritage (Genestar et al., 2014).

The Western Mediterranean Basin (WMED) is a crossroad region in between South-Western Europe, Northern Africa and the Atlantic Ocean, characterized by particular atmospheric dynamics. Actually, although the WMB is located in mid-latitudes and therefore should be strongly impacted by westerly air masses movements, the quasi-permanent influence of the Azores high and the mountainous coastline all around the Basin favour and reinforces meso-scalar atmospheric circulations (Millán et al. 2002). In this atmospheric context, a number of intrinsic factors such as the increasing level of human pressure; the strong influence of Northern African dust (Querol et al., 2001, Rodríguez et al., 2003, Escudero et al., 2006, Pérez et al., 2008, Querol et al., 2009a, Pey et al., 2009a, 2013b); the occurrence and recurrence of forest fires all around the Basin, especially in summer; and the intensity of photochemical processes in the Mediterranean atmosphere make aerosol phenomenology especially complex. Furthermore, climate change scenarios reflect the vulnerability of this particular region. All these characteristics compel us to investigate current aerosol and gaseous pollutants dynamics in a representative regional background location in the WMB.

Cerro et al. (2015) demonstrated that regional background sites in the Balearic Islands in the period 2002-2012 represent properly the WMB aerosol phenomenology. Formerly, Pey et al. (2009a and 2009b) investigated aerosol concentrations and sources in a suburban site in the Majorca Isle, near the capital city. In those studies they corroborated the influence of urban sources (vehicular emissions and harbour dusts) and the highlighted importance of regional background aerosols. The study by Cerro et al. (2015) gave evidence of a very prominent decrease in PM concentrations in Majorca Island in the recent years, more pronounced in urban sites than in regional background environments. These results are in line with those shown by Querol et al. (2014) for continental Spain and match the observations from other areas in Northern and Western Europe (Barmpadimos et al., 2012; Cusack et al., 2012). Thus, regional PM is decreasing slowly than urban PM. These findings claim for an extra effort to understand the phenomenology and the sources of PM in regional background sites. For these purposes, Can Llompart (CLL) represents properly the WMB aerosol phenomenology over regional background environments. In addition, our study intends to evaluate the impact of the increasing tourism in this region as a regional source of pollution. Such a scenario is typical provoking during the warm season: 1) a much higher power supply demand; 2) a significant increment of vehicles all over the Island; 3) the increase in the amount of cruisers, cruiser yachts and merchant ships; 4) a sharp increase in air transport

With this in mind, the present study seeks to evaluate in detail the concentrations and time variation of different fractions of PM, SO_2, NO_2 and O_3. Chemical composition of both PM_{10} and PM_1 fractions are analyzed and source apportionment analysis has been carried out. Other parameters such as BC, NH_3 and particle number concentration (PNC), recorded during intensive observation periods, are also investigated. All the interpretations presented in the manuscript take into account meteorological influences, both at micro and meso scales, and of course accounting for long-range transport influences. Overall, a representative diagnosis of the WMED atmospheric environment is intended. The current assessment will let to evaluate in the future trends in the regional background ambient and to investigate the causes.

Source apportionment studies at regional and remote environments usually extract mixed sources and/or atmospheric processes (Pey et al., 2013a; Minguillón et al., 2015) owing to the intrinsic nature and phenomenology of aerosols at these areas: they come from a number of widespread sources, subjected to the variations of atmospheric dynamics. Despite such limitations, source apportionment studies are useful to elucidate the importance of anthropogenic and natural sources or the co-variance of certain sources or the relevance of specific sources during some meteorological scenarios or seasons.

3.2. Methodology

3.2.1. Sampling and measurements

The selected monitoring site is located in the Island of Mallorca (Balearic Islands, Spain) (39°50’16”N, 03°01’25”E, 45 m a.s.l.), in the core of the WMED (Figure 3.1.A). The Can Llompart observatory (CLL) is placed in the north of the island, with the Tramuntana mountain range in its north-western side. This mountain range, emerging from the western coastline of the island, conforms a chain of mid-altitude peaks (up to 1445 m a.s.l) with south-west to north-east direction which, in addition to sea breezes, drives most of wind regimes (Pey et al., 2009a). Thus, sea to land breezes from the east blows during the day, while vespertine land to sea breezes occur from the south (Figure 3.1.B). Two key sources of emission are located nearby CLL: 1) a 540 MW coal-fired power plant (Es Murterar-Alcudia, 6,5 Km distant in SE direction); 2) a commercial harbour (Alcudia Port, 9,1 Km distant in E direction) (Figure 3.1.C.). Micro-implantation characteristics can be appreciated in Figure 3.1.D, showing the site in the middle of crop lands and forest, at 70 m of a moderately-transited road (around 1000 vehicles per day) on the eastern side.

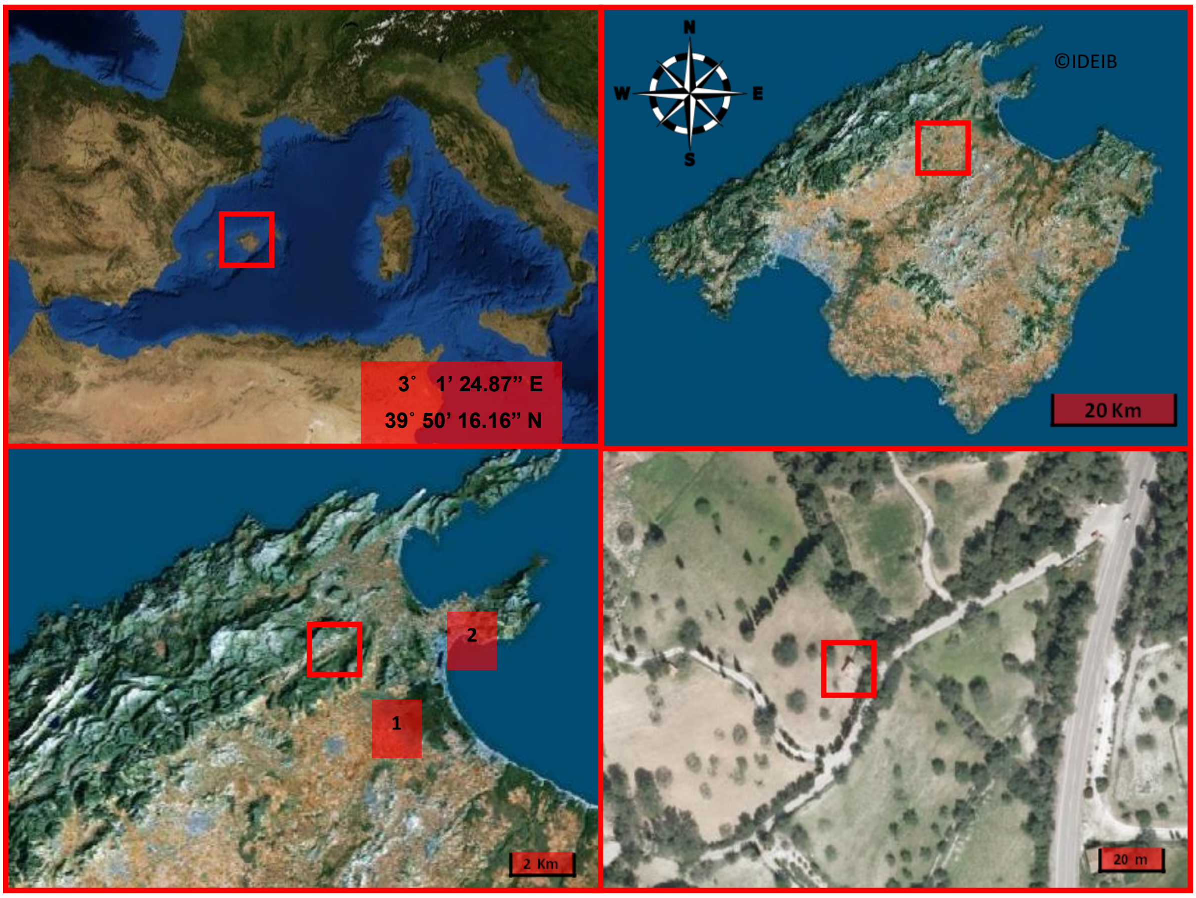
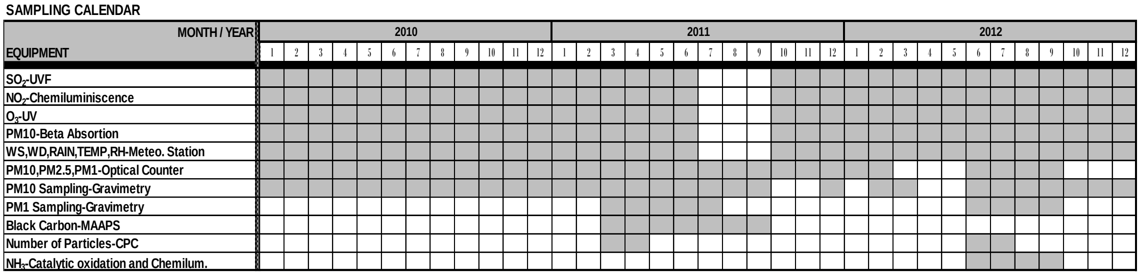


Figure 3.1. Site location is displayed in decreasing scale from up to down and left to right, from the situation in the core of the Western Mediterranean Basin to microimplantation. 1. The "Es Murterar-Alcudia" coal-fired power plant; 2. The Alcudia harbour.

The measurements at CLL comprised three consecutive years, starting in January 2010 and ending in December 2012. Data availability for each type of measurement is shown in Figure 3.2 of the supplementary document. PM_{10} was measured by using a beta absorption monitor. Gaseous pollutants were measured with reference methods according to EN standards. Specifically, EN 14212 for SO_2, based on ultraviolet fluorescence spectrophotometer; EN 14211 for NO_2, based on chemiluminescence detection; EN 14626 for CO, based on near infrared spectrophotometers; and EN 14625 for O_3, based on ultraviolet spectrophotometry, were used. Fortnightly verifications and quartely calibrations were carried out.



SAMPLING CALENDAR

MONTH / YEAR	2010												2011												2012											
EQUIPMENT	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
SO_2-UVF	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
NO_2-Chemiluminiscence	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
O_3-UV	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
PM10-Beta Absortion	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
WS,WD,RAIN,TEMP,RH-Meteo. Station	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
PM10,PM2.5,PM1-Optical Counter	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨			
PM10 Sampling-Gravimetry	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			▨		▨	▨			▨	▨	▨	▨	▨	▨	▨
PM1 Sampling-Gravimetry															▨	▨	▨	▨	▨											▨	▨	▨	▨			
Black Carbon-MAAPS															▨	▨	▨	▨	▨	▨	▨															
Number of Particles-CPC															▨	▨														▨	▨					
NH_3-Catalytic oxidation and Chemilum.																														▨	▨	▨	▨			

Figure 3.2. Data availability for gaseous pollutants, meteorological parameters and PM sampling during the campaign in CLL.

For the 3-year monitoring period, other instruments were installed, including: 1) a MCV-CAV-A/MSb sequential high-volume sampler for PM_{10} collection on 150 mm quartz micro-fibre filters; 2) an optical particle counter GRIMM 1107, which converts number concentrations into mass concentrations by applying intrinsic algorithms, to determine real time concentrations of

PM_{10}, $PM_{2.5}$ and PM_1. PM_x hourly data were day-averaged and adjusted by comparison with 24-h gravimetry measurements of PM_{10} (recorded during the three years) and PM_1 (measured during intensive campaigns). The PM_{10} factor was used to correct $PM_{2.5}$ concentrations.

Overall, hourly concentrations of NO_2, SO_2, O_3, PM_{10}, $PM_{2.5}$, PM_1, air temperature, wind direction and wind speed, atmospheric pressure and precipitation were measured during the period 2010-2012.

The summer season, with higher PM concentrations and presumably very often impacted by African dust, enhanced tourism and cruise activities, was thought as the most suitable time for intensive campaigns in order to address the impacts as well as possible. Moreover, spring, when the highest biogenic emissions occur, was selected as another period of interest to develop intensive and more detailed observations. Therefore, in addition to the continuous measurements, three intensive campaigns were performed: the first in March–April 2011; the second in July–August 2011; and the third in June–August 2012. During intensive observation periods, PM_{10} and PM_1 samples were collected daily and additional instruments were deployed. Detailed information on monitoring intervals can be found in Figure 3.2.

During March-September 2011 BC concentrations were determined by using a Multi Angle Absorption Photometer (MAAP, model 5012, Thermo, Petzold et al., 2004). The MAAP instrument measure absorption coefficient at 636 nm (Müller et al., 2011) and converts these values to BC. Equivalent BC concentrations were calculated by comparing BC with elemental carbon as Pérez et al. (2010).

Measurements of particle number concentrations (PNC) were carried out using a low-size detection (detects particles down to 5 nm) water-based condensation particle counter (TSI, WCPC 3785) during spring intensive campaign in 2011 and summer intensive campaign in 2012.

An NH_3 monitor was deployed during the 2012 summer campaign. This sensor is based on chemiluminiscence detection after the catalytic conversion of ammonia into NO_2, and subsequently to NO. This monitor was implemented in a commercial portable device called Airpointer (www.airpointer.com). Hourly concentration values were obtained and weekly average results were compared with NH_3 passive samples.

3.2.2. Offline PM analysis

PM_{10} and PM_1 24h quartz fibre filters were analysed to determine the ambient concentration of major and trace elements, soluble ions, and organic and elemental carbon. To this end, a fraction of the filter was digested using a mixture of inorganic acids (HNO_3–HF–$HClO_4$) (Querol et al., 2001, Pey et al., 2009b) and the quantitative analysis of metals and trace elements was performed using ICP–AES for major elements (Al, Ca, Na, Mg, K, Fe, P) and ICP–MS for trace elements (Li, P, Ti, V, Cr, Mn, Co, Ni, , Zn, Ga, Ge, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, La, Ce, Pb, among others). Major ions (SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) were analysed by ionic chromatography. OC and EC fractions were quantified using the thermal optical transmittance (TOT) method, with a Sunset Lab analyser, using EUSAAR 2 protocol (Cavalli et al., 2010). Water Soluble Organic Carbon (WSOC) was determined by combustion catalytic oxidation method. Colorimetric method for NH_4^+ was applied using a segmented flow analysis device.

The experimental SiO_2/Al_2O_3 ratio obtained during a specific monitoring campaign was 2.54, according to results published by Alastuey et al. (2016). CO_3^{2-} content was estimated from Ca values considering that all Ca is in the form of calcite, thus according to their stoichiometric relation.

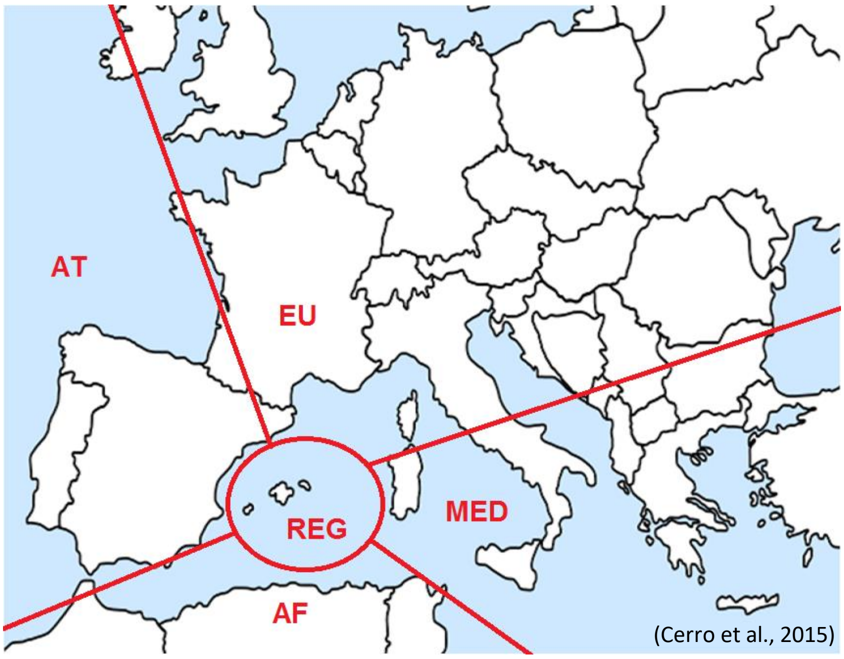
Likewise, the organic matter/organic carbon (OM/OC) ratio used in this work (1.97) corresponds to the experimental values obtained during a specific campaign conducted in

2013 in which the Aiken et al. (2008) methodology was used. The results of that were already presented by DeWitt et al. (2014).

The chemical components of the PM were grouped as crustal or mineral (sum of Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P); sea spray (sum of Cl^- and Na^+); organic matter and elemental carbon (OM+EC); sulphate (SO_4^{2-}); nitrate (NO_3^-); ammonium (NH_4^+); and trace elements (Mn, Li, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, La, Ce, and Pb).

3.2.3. Origin of air masses

A meteorological study based on the interpretation of HYSPLIT (https://www.arl.noaa.gov/hysplit/) (Stein et al., 2015; Rolph et al., 2017) 120-hours back-trajectories to evaluate the origin of the air masses reaching and/or residing over the Balearic Islands was conducted, as in Pey et al. (2009a) and Cerro et al. (2015) distinguishing five advection scenarios (Figure 3.3): Atlantic (AT), Mediterranean (MD) and European (EU) air mass origins, African dust outbreaks (AF), and a lack of advection scenario, named Regional (REG).



(Cerro et al., 2015)

Figure 3.3. Origins of air masses: Atlantic (AT), European (EU), North African (AF), Summer Regional and Winter Regional (REG).

3.2.4. Air quality trends

Trends in air pollutant concentrations have been studied as in Cerro et al. (2015). The period 2010-2018 has been considered here. Three sites representing different environments have been investigated: Foners-urban site; Bellver-suburban site; Can Llompart-regional site.

3.2.5 Regional air quality compilation

Data from regional background sites all around WMED Basin were investigated in order to compare with CLL results. EMEP, VAG and European network (Airbase) were considered to obtain pollutant levels of the study period, from January 2010 to December 2012. Specifically, 10 French, 6 Italian and 14 Spanish stations were considered (Figure 3.4). Morocco, Algeria (SAMASAFIA network) and Tunisia had no rural background sites near Mediterranean Sea for that time. SO_2, NO_2 and O_3 were considered in addition to PM_{10} and $PM_{2.5}$ aerosol fractions.

Sites have been grouped on in regions as is shown in Figure 3.4.

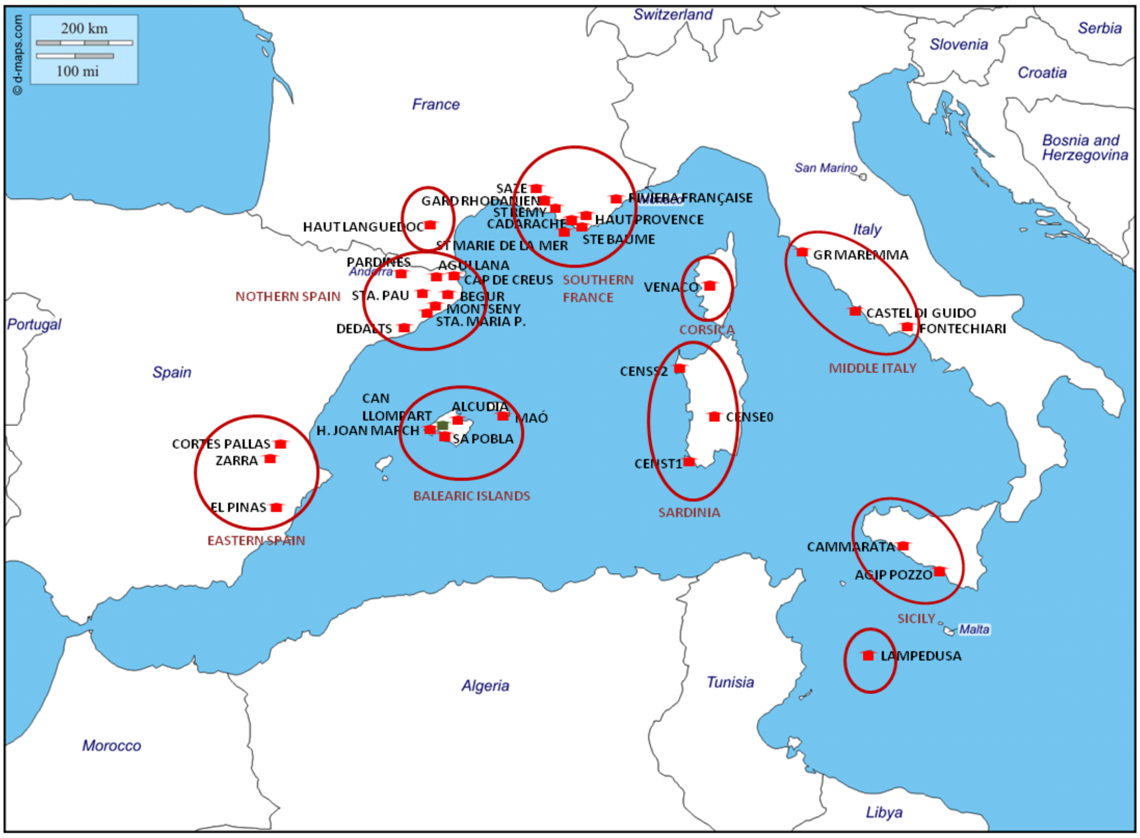


Figure 3.4. Regional background sites considered to compare the results of this study with other sub-regions in the Western Mediterranean.

3.2.6. Source Apportionment to PM_{10} and PM_1

A receptor model has been conducted to discern source apportionments for the PM_{10} and PM_1 24h filters. Specifically, Positive Matrix Factorization (PMF) statistics (Paatero and Tapper, 1994; Lanz et al., 2007; Ulbrich et al., 2009) have been applied by using the SoFi tool interface (Canonaco et al., 2013) which includes the Multilinear Engine ME-2 program (Paatero, 1999). This tool was designed to easily process Aerosol Mass Spectrometer data, although off-line data can be also managed. In this work, only 24h-offline data are shown (those corresponding to the 3-year study), but other real-time data from a complementary campaign were processed almost in parallel (Cerro et al., 2016), and therefore, the use of a single tool was chosen. Detection limits (DL) and uncertainties were jointly established for PM_1 and PM_{10}. Briefly, values under the DL have been replaced for half of DL value (Polissar et al., 1998). Species having more than 50% of data under the DL and with low signal-to-noise were not included in the analysis (Brown & Hafner, 2005): Li, Be, B, P, Sc, Cr, Ge, Y, Zr, Nb, Mo, Cs, Ba, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Bi, Th, U. After this procedure 36 species were used.

Initial uncertainties were considered depending on the analysis methodology, DL and coefficients of variation. A factor of 4 was multiplied to all uncertainty values corresponding to those species estimated from others, such as SiO_2 (from Al) and CO_3^{2-} (from Ca) in order to underrrate them. Afterwards, a gradual uncertainty was calculated as function of the concentration obtained, with linear increase for most of the species and stepwise increment for mineral species (Reff et al., 2007, Karagulian et al., 2012). Subsequently, a trial-and-error process was carried out to obtain the best model performance by evaluating the results according to Q values (Figures 3.25 and 3.30), the distribution of the residuals and the results from multiple regressions (Polissar et al., 2001).

3.3. Results

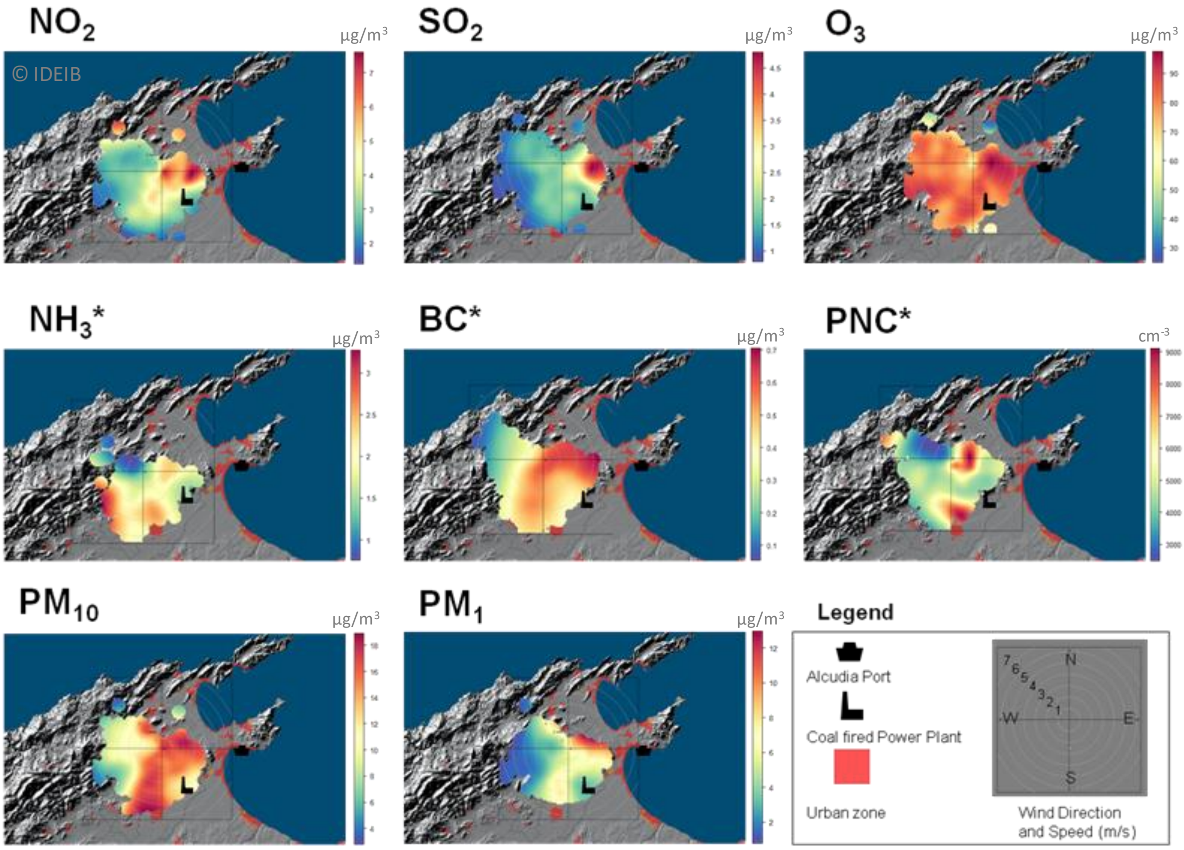
3.3.1. Micro and Mesoscale influence

Wind roses for the concentration of gaseous and PM_x are shown in Figure 3.5. Wind roses elucidate major affection from eastern direction, probably due to the road and the harbour activities, mixed with the power plant emissions.

Particle number concentration reflects two main spots, one coinciding with lack of wind, that would be related to local particle emission/formation, and another from south-eastern direction probably caused by inland pollution from mixed sources.

NH_3 higher concentrations are detected when southern and western wind directions occur. This pattern is dissimilar to the rest of pollutants. Definitively, besides the influence of power plant emissions, ammonia arises from other sources, especially agricultural and farming activities, and wastewater treatment plants.

PM_{10} increases mostly under southern and north-eastern winds, in the first case, partly accompanied with BC and NO_2, owing to the combined influence of episodic AF contributions and regular inland pollutants, and in the second case because of different sources, including harbour emissions and marine aerosols.



*Only intensive observations periods for NH_3, BC and PNC concentrations and consequently not strictly comparable with the other metrics measured during the 3-year campaign (Figure 3.2).

Figure 3.5.Pollutant roses of gases and PM fractions over a region around CLL (40 km of longitude and 25 km of latitude), and its main anthropogenic focus: urban areas, the Alcudia port and the coal-fired power plant.

Overall, a nearby influence is detected due to road traffic, shipping and power plant emissions accomplished by other regional sources, altogether impacting on NO_2, SO_2, BC, PM_{10} and PM_1 concentrations episodically.

3.3.2. Variability of air quality metrics from 2010 to 2012

Mean NO_2 concentration is 5.0 µg/m^3. Maximum of hourly NO_2 values reached 68.6 µg/m^3 (27/06/2010 10 GMT), and 13.6 µg/m^3 for daily means (15/02/2011).

SO_2 presents an average concentration of 2.0 µg/m^3, and hourly maximum of 105.3µg/m^3 (27/06/2010 10h GMT), causing the highest daily average, 11.1 µg/m^3.

All previous pollutants display concentrations much lower than thresholds, targets or limit values established in air quality regulations.

O_3 mean concentration was 67.6 µg/m^3. Its maximum is reached during spring time (145 µg/m^3 26/05/2011 13h GMT), as already observed by Pey et al. (2009). This value was far from the limit value considered to report to the general public (180 µg/m^3). The limit value to protect human health (120 µg/m^3 as maximum daily-8-hour mean) was exceeded 30 times, an average of 10 times per year, lower than the 25 exceedances allowed by the European regulations, but exceed World Health Organization guidelines (WHO 2005) recommendations, set at 100 µg/m^3 for daily maximum 8-hour mean. This threshold would have been exceeded 185 days, 17% of the total period.

PM_{10} presents an average concentration of 16.0 µg/m^3, far from the human health annual target for European Commission, 40 µg/m^3. However not far from the WHO (WHO 2005) guidelines for annual average, 20 µg/m^3.

An hourly maximum of 125 µg/m^3 (02/11/2011 8h GMT).

The daily limit value to protect human health, 50µg/m^3, was exceeded 16 times, an average lower than 6 times per year, much lower than the 35 exceedances allowed by the European regulations.

$PM_{2.5}$ and PM_1 values were not available during the whole campaign (Figure 3.2), but a suitable coverage was attained. $PM_{2.5}$ presents an average concentration of 10.7µg/m^3, far from the human health annual target for European Commission, 25µg/m^3, and for the long term target 20 µg/m^3. In contraposition, it oversteps the annual guideline for WHO, 10 µg/m^3.

An hourly maximum of 65µg/m^3 (21/03/2010 15h GMT) was measured, coincident with an intensive dust outbreak from northern Africa. Hence attributed to the crustal component existing in $PM_{2.5}$ fraction. The guideline value indicated for daily means by the WHO is 25µg/m^3. 16 WHO-daily exceedances were measured during the campaign, 3% of the entire period of the $PM_{2.5}$ measurement.

PM_1mean is 7.1 µg/m^3. No target is defined from European Commission or WHO for this fraction. An hourly maximum of 54 µg/m^{3}was reached (12/02/2010 11h GMT), coincident also with an intensive African dust outcome. A 40 µg/m^3 daily maximum was recorded (02/03/2010).

Daily, weekly and seasonal patterns

-Daily variations

A clear daily cycle is appreciated for NO_2, with two peaks, early in the morning and in the afternoon, related to land-traffic rush hours (Figure 3.6). These two peaks are not well defined, mixing them up during spring time.

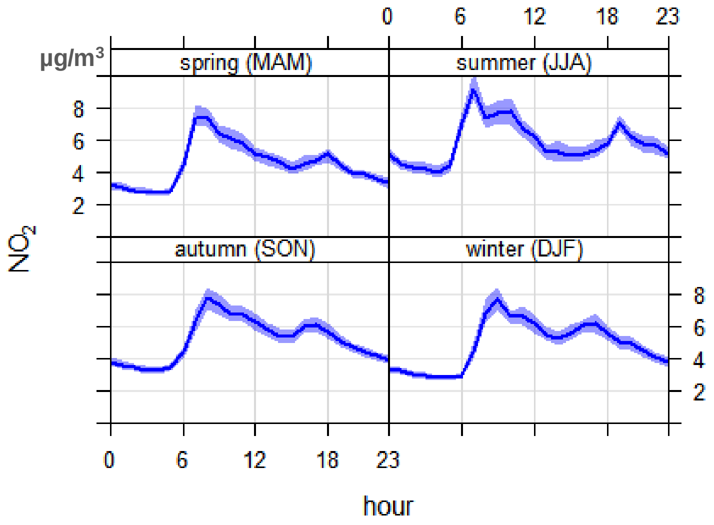


Figure 3.6. NO_2 daily pattern in function of the meteorological season, concentrations in µg/m³.

Similar to NO_2, SO_2 displays no clear daily peaks, except for summer period, although midday peak can be appreciated throughout the year (Figure 3.7). These midday impacts are meteorologically induced: inversion of the breeze regime (sea-land breezes carry shipping emissions to the continent during the day), and variations of the boundary layer depth, which favours the mixing of the pollution at a wider scale.

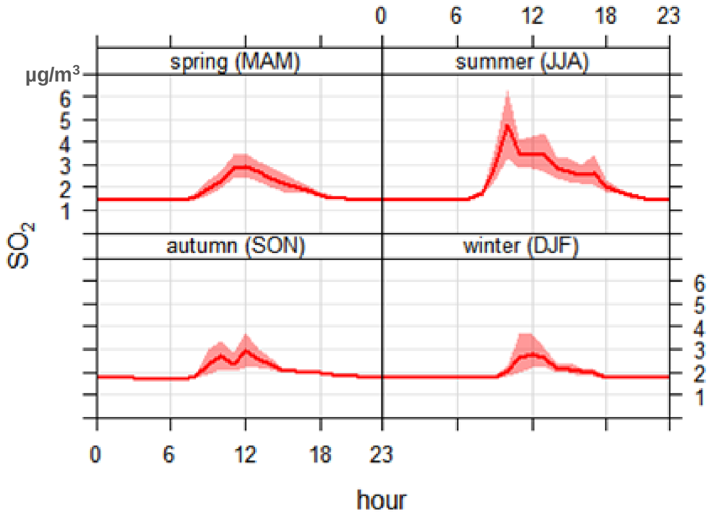


Figure 3.7. SO_2 daily pattern in function of the meteorological season, concentrations in µg/m³.

Ozone displays a clear diurnal trend with maximal concentrations after midday related to photochemical activity, and minimal early in the morning (Figure 3.8). This minimal is much marked during weekdays due to the reaction with nitrogen oxides.

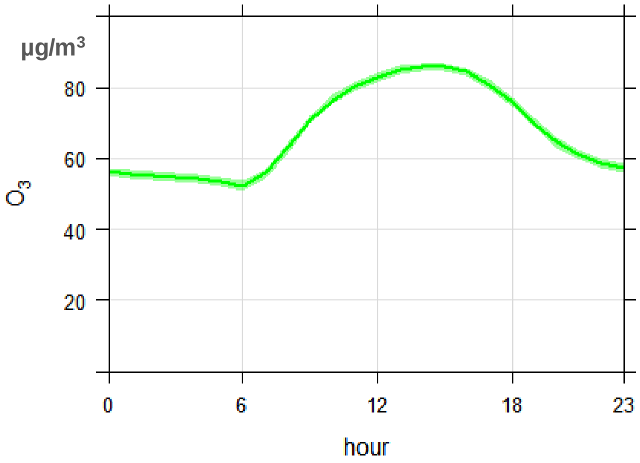


Figure 3.8. O_3 daily pattern, concentrations in µg/m³.

The diurnal cycle for particulate matter concentrations was less marked than that for ozone. Daily variability of particulate matter concentrations is driven by nucleation and coagulation processes. Fine particle concentrations increase midday on related with the photochemical activity and particle formation from conversion of gases in less volatile compounds. PM_{10} increase beyond due to accumulation processes during vespertine hours, whilst fine particle start to decrease (Figure 3.9).

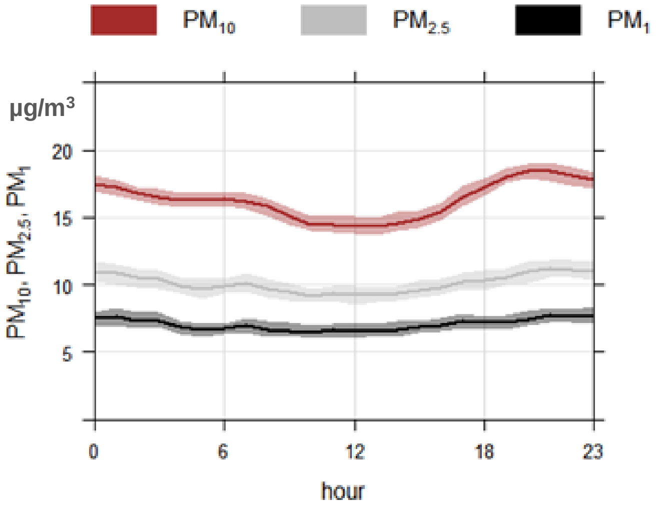


Figure 3.9. PM daily patterns, concentrations in µg/m³.

Ammonia and SO_2 increase during the day to reach its maximum around midday, aligned with PNC concentrations pattern (Figure 3.10), probably suggesting the presence of non-negligible nearby sources, like power plant and shipping activity.Under clear sky conditions, which are prevalent in the region, and in presence of gas precursors, a number of intense new-particle formation bursts took place during which no or slight PM mass increments were followed. Most of these events were registered in spring; being the most noticeable the one occurred on 19th March 2011 at 11h (GMT), with 120.000 particles cm^{-3} and a concentration of 3 µg/m³ for PM_1. After midday a decrease in PNC is observed, which could be related to subsequent particle processes such as coagulation between particles (thus decreasing PNC) and condensation of semi-volatile species onto them (keeping PNC stable but increasing PM mass).

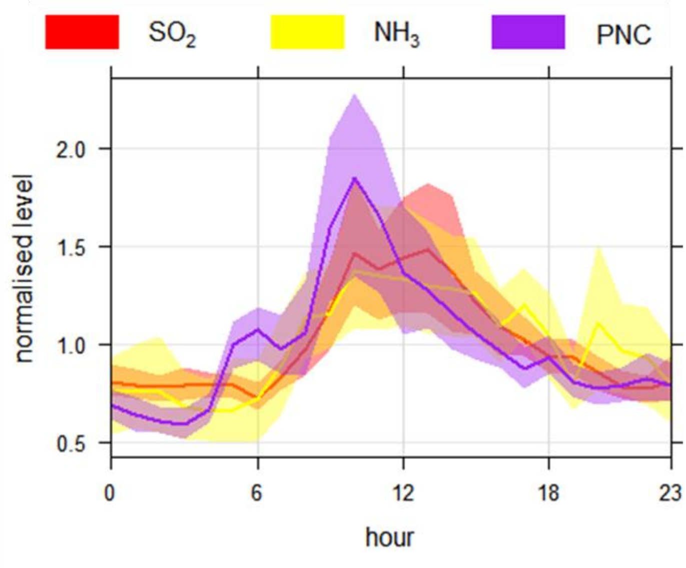


Figure 3.10. Daily variation (hourly normalized concentrations) of SO_2, NH_3 and PNC corresponding to the period in which NH_3 measurements were available.

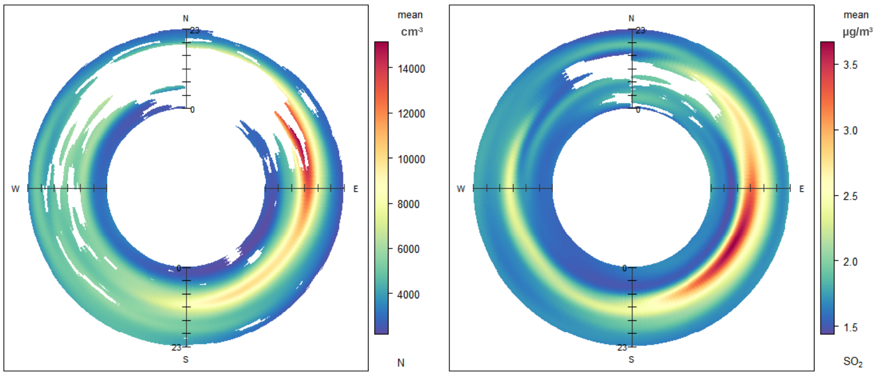


Figure 3.11. PNC (left) and SO_2 (right) hourly concentrations, in colour shown, depending on the wind direction.

Taking into account the regional pollutant inventory for 2011, around 9 ktSO_x where emitted by the power plant located nearby, and around 6 ktSO_x where emitted by shipping and aircraft emissions mainly occurring in the southern harbour and airport.

Figure 3.11 reflects how SO_2 and PNC share the same wind direction prevalence and daily pattern, which lead to think that main nucleation source is coincident with SO_2 emission focus.

-Weekly variations

In order to assess significant differences between weekdays and weekends (Figure 3.12) Mann Whitney U test was applied, in which only two non-parametric data groups are considered, Monday-Friday and Saturday-Sunday. A significant drop was obtained for NO_2 and BC, with near 100% of probability, reflecting a strong weekly pattern probably driven by traffic emissions. SO_2reflects a less marked weekly pattern, with a probability of 89% of significant differences. In the case of PM fractions, the highest difference between weekdays and weekends corresponds to PM_{10}, with a 78%, followed by $PM_{2.5}$, with a 71% and PM_1, with only 59%. These results suggest that the temporal variability of fine particles is less driven by the impact of nearby sources. On the other hand, as it was expected, O_3 does not reveal a weekly pattern, with significance below 20%. PNC and NH_3 do not reflect major differences.

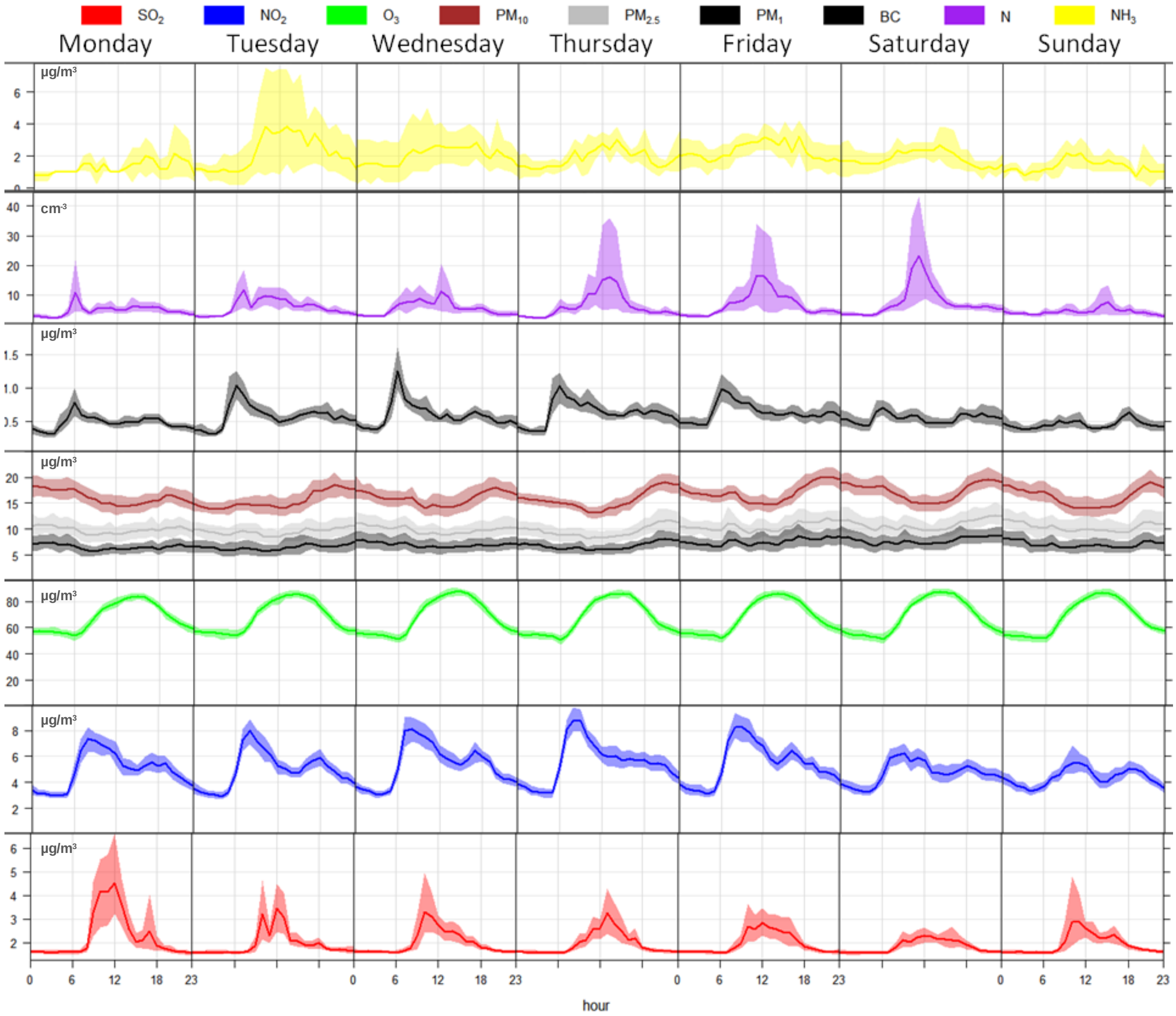


Figure 3.12. Weekly variation (hourly averages in µg/m³ and cm-3) of SO_2, NO_2, O_3, PM_{10}, $PM_{2.5}$, PM_1, BC, N (PNC), and NH_3.Only intensive observations periods for BC, N (PNC) and NH3 (Figure 3.2) and consequently not strictly comparable with the other metrics measured during the 3-year campaign.

In a day by day basis it can be observed that NO_2 maximum is displayed on Thursdays, while SO_2 is greater on Mondays. Related to NO_2 maximum O_3 minimum occurs on Thursdays also. PM fractions reflect a slight accumulation during week, with a maximum on Saturdays and drops on Sundays.

A clear daily cycle is appreciated for BC, with two peaks, higher early in the morning and lower in the afternoon, related to land-traffic rush hours. Average concentration for BC is 0.55 µg/m³. Minimum hourly averaged concentrations measured for BC are around 0.3 µg/m³, and maximum concentrations reach 1.5 µg/m³ (Figure 3.12).

Particle number concentration shows different patterns between the two studied periods, spring and summer season. In both periods, daily pattern of PNC concentrations displays two peaks: an early one at rush hours, concurrent with BC (Figure 3.12), NO_2 (Figures 3.6 and 3.12), PM_{10} (Figures 3.9 and 3.12) concentrations, and mostly related to primary emissions occurring nearby; and a second and much higher peak appearing at midday, probably due to photochemical nucleation. This peak is accentuated when high concentrations of SO_2 and NH_3 are measured (Figure 3.10). Moreover, this process is emphasized during spring time (Figure 3.13) when the bloom of volatile organic emissions from biogenic sources occurs, which is added to anthropogenic gases (Minguillon et al., 2015a), enough solar radiation and not very high PM_1 concentrations (Rodriguez et al., 2015), showing the highest peak on 19th March 2011 at 11h (GMT), with 120.000 particles cm^{-3} and a concentration of 3 µg/m^3 for PM_1.

In summer this midday peak is also detected, but it is not as intense as the spring one (Figure 3.13). This fact could be due to the presence of higher PM_1 concentrations that favour the coagulation and condensation processes rather than new particle formation.

It is interesting to highlight the delay between PNC and PM_1 concentrations peak in summer (Figure 3.13): while PNC maximizes at 10h GMT, PM_1 reach its maximum at 16-17h GMT, probably reflecting the concatenation of the atmospheric processes during the day (from the nucleation mode to the accumulation mode).

Concerning to the weekly pattern, in spring a clear increase of PNC during weekdays is observed, while this accumulation is not well defined in the warm season (Figure 3.13), probably due to tourism activity, as one of the most relevant contributions, is hold throughout the week.

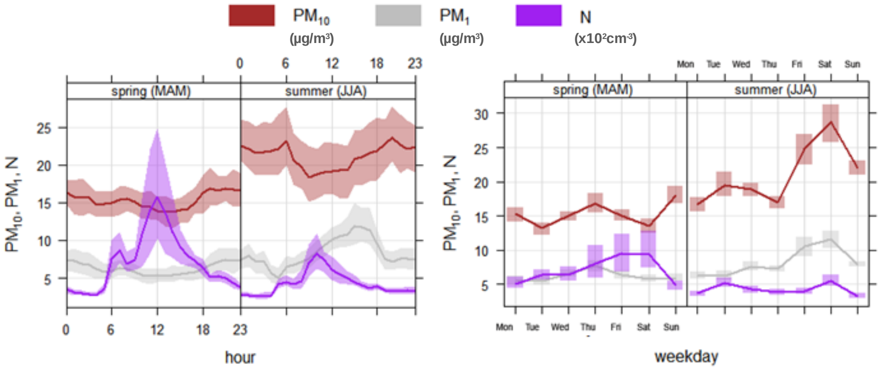


Figure 3.13. Concentrations in µg/m^3 for PM and x10^2cm^{-3} for N (corresponding to the period of PNC measurements) of PM_{10}, $PM_1$and N. Left graph: daily variation (hourly concentrations) in spring and summer seasons; right graph: weekly variation (daily concentrations) in spring and summer seasons.

BC concentrations do not decrease below 0.3 µg/m^3 even during weekends (Figure 3.12). Therefore, this value (0.3) could be considered as the WMB background contribution, being the difference (0.25 µg/m^3, 45% of the average concentration) the contribution from nearby sources and regional emissions.

-Seasonal variations

Relevant seasonal variation were displayed in all parameters as it can be observed in Figures 3.14 and 3.15, with maximum concentrations in summer and minimum in winter, which is typical of regional background environments in the WMB (Rodríguez et al., 2003).

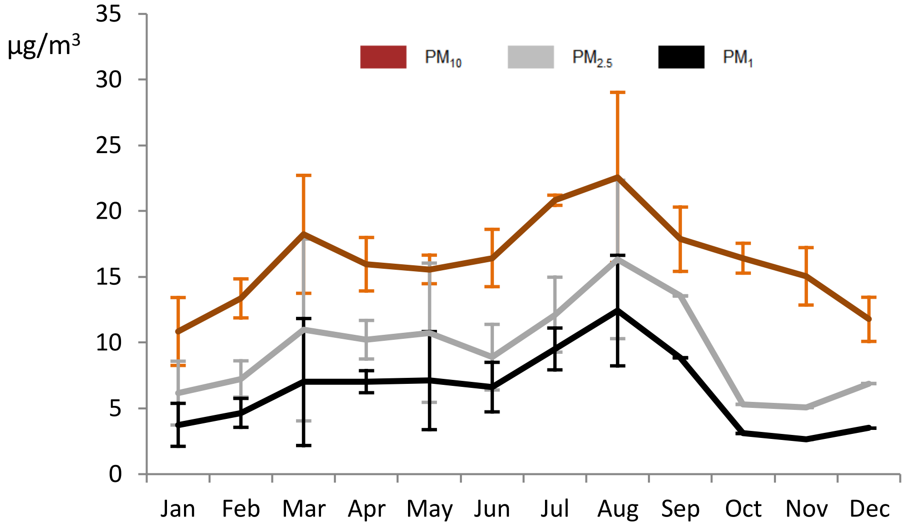


Figure 3.14. Seasonal variation (monthly averages and standard deviations in µg/m3) of PM_{10} (in brown), $PM_{2.5}$ (in grey) and PM_1 (in black).

Nitrogen dioxide reaches its maximum in summer (Figure 3.15), which is an opposite trend with respect to urban sites, clearly related to the seasonal population increase all over the island. Likewise, SO_2 is higher in summer (Figure 3.15), probably caused by the increment of shipping emissions liked to the vacation season. NO_2 and SO_2 time series measured by Nasa OMI (Ozone Monitoring Instrument: https://aura.gsfc.nasa.gov/omi.html) consulted by the Giovanni data system (https://giovanni.gsfc.nasa.gov/giovanni/) plotted in figures 3.16 to 3.18 confirm these patterns.

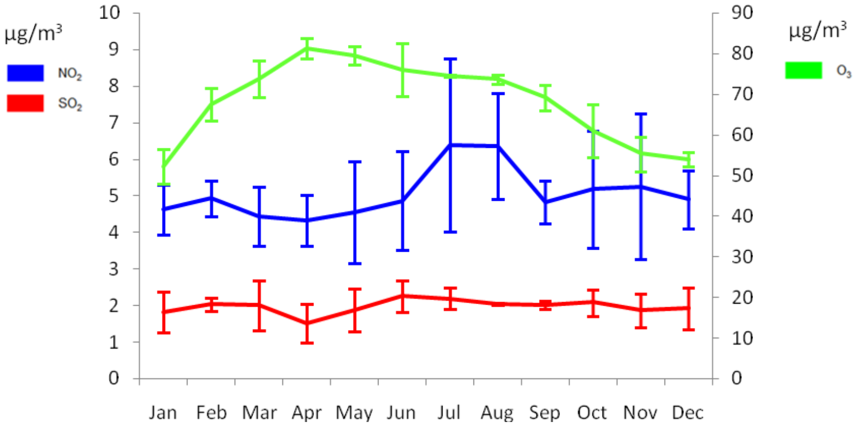


Figure 3.15. Seasonal variation (monthly averages and standard deviations in µg/m3) of SO_2 and NO_2 (left axis), and O_3 (right axis).

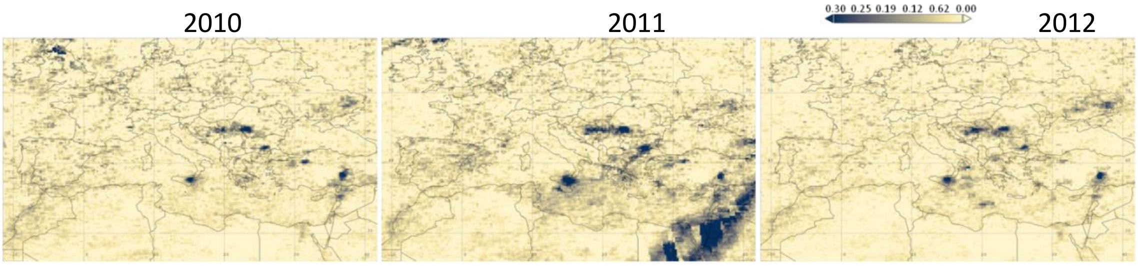


Figure 3.16.Time average map of SO_2 Column amount (PBL) (Dobson Units).Years 2010-2011-2012. NASA SO_2 OMI level 3. Plotted using the Giovanni online data system, developed and maintained by the NASA GES DISC.

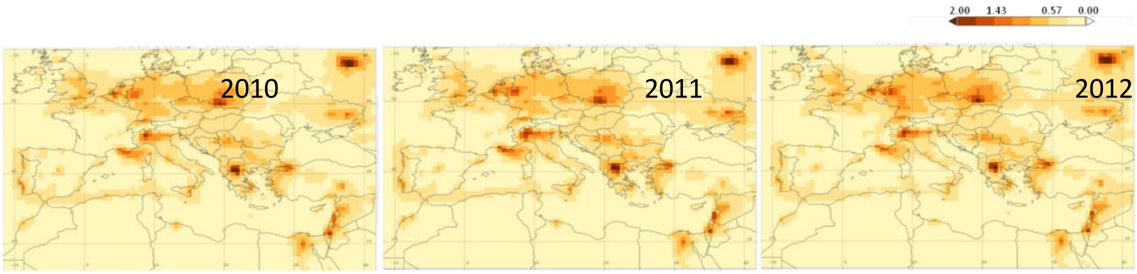


Figure 3.17. Time average map of SO_2 surface concentrations kgx $10^{-8}/m^3$ from mean monthly values. NASA SO_2 OMI level 3. Years 2010-2011-2012. Plotted using the Giovanni online data system, developed and maintained by the NASA GES DISC.

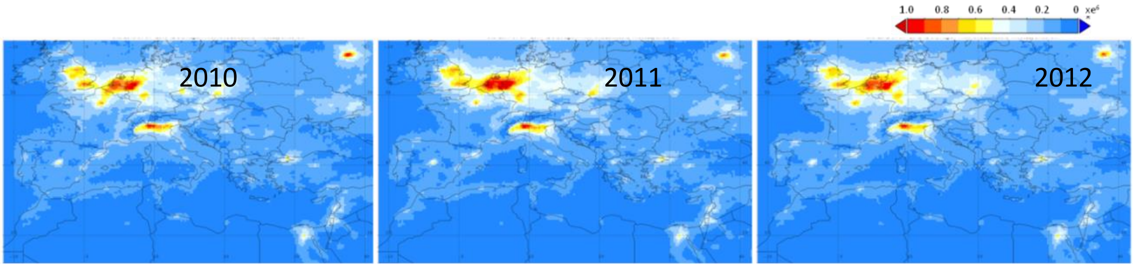


Figure 3.18. Mean annual tropospheric NO_2 column (clear, 0-30% cloud) (10^{14}molec/cm^2). NASA NO_2 OMI level 3. Years 2010-2011-2012.Plotted using the Giovanni online data system, developed and maintained by the NASA GES DISC.

A prominent O_3 maximum is recorded in spring over the Balearic Islands (although data from CLL are only shown here) (Figure 3.15), instead of a summer maximum as usually observed at continental sites in the WMED (Castell-Balaguer et al., 2012; Millán et al., 1997).

PM_{10} and PM_1 are usually aligned all year long (Figure 3.14), except in March (sometimes this is observed in February, e. g., 2004, 2017), when short but severe Saharan dust episodes are registered (Pey et al., 2013b) causing sharp peaks in PM_{10} not measured in PM_1.

A previous study in Mallorca background environments (Pey et al., 2013a, Cerro et al., 2015) has demonstrated that PM_{10} concentrations showed a strong seasonal pattern driven by the transport of African dust and by the contribution of regional dust resuspension, both enhanced in summer. Similar seasonal variations for PM finer fractions were observed. This has been concluded for different regional and continental background sites (e.g. Querol et al., 1998; Cozic et al., 2008; Rodríguez et al., 2003; Ripoll et al., 2014).

Finer PM fractions summer maximum can be linked with the enhanced accumulation of pollutants over the WMB as a result of stagnant conditions (Millan et al., 1997), in a context of higher emissions over the whole region. Additionally, PM fine fraction peaks can be also related to AF episodes, not due to as a direct source, but as an adjuvant of condensation and accumulation processes and a compression of the PBL (Pandolfi et al., 2014). Moreover, during NAF episodes south origin advections predominate over sea breezes with a PM apportionment throughout the day (Jorba et al., 2013). Furthermore, higher temperature and photochemistry enhances the formation of SOA. Spring and summer seasons are related to greater biogenic emissions (Seco et al., 2011). Finally the prevalence of wildfires and DMS concentrations can be taken into account.

Daily PM variations have been studied for each season in order to detect differences or similarities. Sea breeze blow strongly in warmer time and drive air convections more clearly than for colder periods for the islands. This behavior contrasts with those for continental areas.

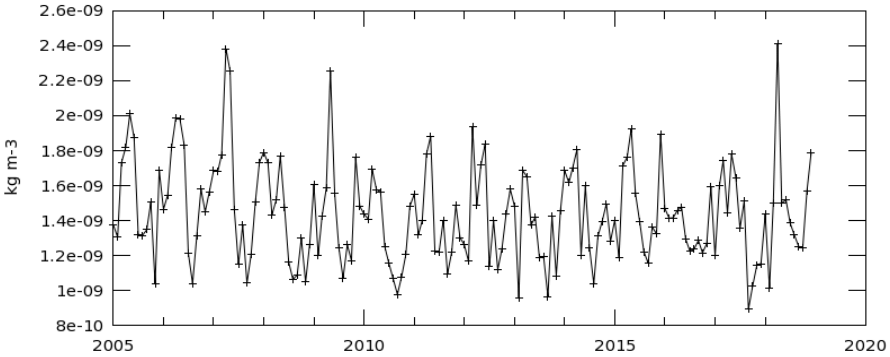


Figure 3.19. OMI NASA Satellite Measurements. Time Series, Area-Averaged of SO_2 Surface Mass Concentration (ENSEMBLE) monthly 0.5 x 0.625 deg. [MERRA-2 Model M2TMNXAER v5.12.4] kg m-3 over 2005-Jan-2018-Dec, Region 1.25E, 38N, 4.375E, 40.5N.

3.3.3. Long range transport scenarios and contribution

Concentrations were studied according to the origin of air masses (Table 3.1). The most frequent situations were AT (36%) and REG (34%), followed by AF (20%), EU (8%) and finally MED (2%). Particle number concentration, NH_3 and BC concentrations where only measured during intensive campaigns and specific discussion is given in this section.

Table 3.1. Mean values (standard deviation) of each pollutant (all in μg/m^3 except PNC, in cm^{-3}) depending on the air mass origin.

μg/m^3	SO_2	NO_2	O_3	PM_{1-10}	PM_1	NH_3*	BC*	PNC(cm^{-3})*
AT (36%)	1.80 (0.69)	4.64 (2.12)	65.4 (13.2)	9.7 (3.7)	5.0 (4.7)	2.00 (1.82)	0.47 (0.21)	6299 (5420)
EU (8%)	1.91 (0.52)	4.95 (1.67)	76.7 (14.4)	7.7 (2.2)	7.2 (4.1)		0.73 (0.23)	4769 (2224)
MED (2%)	2.23 (0.75)	4.85 (2.12)	69.5 (14.6)	16.9 (1.0)	3.9 (0.3)		0.47 (0.19)	
AF (20%)	1.87 (0.82)	5.82 (2.23)	65.5 (15.6)	12.0 (6.2)	9.2 (5.8)	2.40 (1.87)	0.63 (0.28)	4853 (1498)
REG (34%)	2.20 (1.30)	4.98 (2.02)	70.4 (16.2)	8.8 (2.6)	8.0 (4.6)	1.63 (1.12)	0.56 (0.17)	6305 (4055)

* Only intensive observations periods for these metrics and consequently not strictly comparable with the other metrics measured during the 3-year campaign.

Meteorologically, 2010 was characterized by a higher frequency of AT, reduced impact of AF (Table 3.2), and rainfall above normal values. On the other hand, 2012, under the most negative NAO Index, was characterized by a rainy spring season, followed by a warm season in which AF and REG dominated, and relatively low frequency of AT took place. In conclusion, the 3-years campaign has covered the whole variation range of Mediterranean climate conditions which is, in several cases, behind of the observed aerosol phenomenology.

Table 3.2. Sampled filters, season (cold season is assigned to the period November to April, and warm season to the period May to October), raining days coinciding with sampling and advection scenarios.

year	season	fraction	nº filters	rainy days	Episode				
					A	EU	MED	AF	REG
2010	cold	PM_{10}	25	8	12	5	0	1	7
		PM_1	0	0	0	0	0	0	0
	warm	PM_{10}	32	2	10	1	0	6	15
		PM_1	0	0	0	0	0	0	0
2011	cold	PM_{10}	56	6	15	10	1	9	21
		PM_1	32	2	9	6	0	5	17
	warm	PM_{10}	95	5	31	1	1	12	50
		PM_1	48	5	12	3	2	3	28
2012	cold	PM_{10}	26	4	12	4	0	1	9
		PM_1	0	0	0	0	0	0	0
	warm	PM_{10}	59	2	17	1	1	26	14
		PM_1	59	0	13	1	1	31	13

PM_{10}, as expected, is greater during AF. NO_2, BC and PM_1 maximize during AF, surely due to two synergistic reasons: AF occur more usually in summer, when anthropogenic emissions are at their highest all around the archipelago; the higher concentration provoked by the compression of the boundary layer during those situations (Pandolfi et al., 2014). In addition to the unfavourable dispersive conditions, the transport of pollutants from populated areas located southwards, and reaching CLL simultaneously, should not be neglected. SO_2 concentrations rose during REG and MED, surely due to prevalence of sea to land winds carrying maritime transport emissions to CLL. Notice that O_3 concentrations decrease during AF, probably due to a combination of factors, such us boundary layer compression, which provokes enhancement of O_3 depleting compounds, the consumption of O_3 by mineral dust particles (Soler et al., 2016), and the presumably lower O_3 concentrations intrinsically associated to air masses from AF (Han et al., 2018). Regional scenarios, encompassing accumulation processes, present also high values. In addition to the aforementioned high concentrations of PM_1 during AF, the few MED advections observed displayed PM_1 and SO_2 high concentrations, suggesting the influence of shipping emissions.

If prevalence of each air mass origin is combined with the associated concentration of every individual pollutant (Table 3.1), relative loads for each pollutant and each episode can be obtained (Table 3.3). Afterwards, contributions can be weighted by average concentrations to obtain influence in percentage terms (Table 3.3).

Table 3.3. Contribution (in µg/m³ or cm⁻³, and in %) of each scenario to the mean pollutant value.

	SO_2		NO_2		O_3		PM_{1-10}		PM_1		NH_3*		BC*		PNC*	
	µg/m³	%	µg/m³	%	µg/m³	%	µg/m³	%	µg/m³	%	µg/m³	%	µg/m³	%	cm^{-3}	%
AT	0.64	33	1.66	33	23.4	34	3.4	34	1.8	26	0.72	41	0.17	30	2258	39
EU	0.16	8	0.41	8	6.4	9	0.6	7	0.6	9		0	0.06	11	396	7
MED	0.06	3	0.12	2	1.7	3	0.4	4	0.1	1		0	0.01	2		0
AF	0.37	19	1.14	23	12.9	19	2.4	24	1.8	26	0.47	27	0.12	22	953	17
REG	0.74	38	1.68	33	23.8	35	3.0	30	2.7	39	0.55	32	0.19	34	2128	37

* Only intensive observations periods for these metrics and consequently not applicable for the 3-years campaign.

Table 3.3 shows that REG and AT are the most relevant loaders for all pollutants since they are the most frequent. Although SO_2 is highest under MED advections, its contribution is neglected compared with REG or AT. The same occurs for O_3, whose concentration maximizes under EU, but the main contributors are REG and AT. AF raise PM_{1-10} level significantly, but they add less to the PM_{1-10} budget when compared with the dominant input associated to AT, followed closely by REG. Conversely, the contribution linked to REG dominates PM_1 closure, followed by AT and AF.

Note that similar results for PM_{1-10} contribution from AF (2.4 µg/m³) were extracted using the official European calculation (2.1 µg/m³ in Table 3.4 and Figure 3.21), which reinforces the strength of this complementary method to assess AF loads.

Table 3.4. SO_2, NO_2, O_3, PM_{10} and $PM_{2.5}$ (in µg/m³) annual averages at regional background sites in different regions across the WMED during the period under study (2010-2012). Max:...; Min:...; Mean:... , with indication of the number of sites considered.

		SO_2			NO_2			O_3			PM_{10}				$PM_{2.5}$		
	number of sites	max	min	Mean	max	min	mean	max	min	mean	max	min	mean	Af. Dust	Max	min	Mean
E-SPAIN	3	3.4	0.3	1.4	5.1	2.4	3.4	85	65	77	17	10	12	2.2**	5.6	5.5	5.6
N-SPAIN	8	1.5	0.3	0.8	3.9	1.7	3.0	80	48	69	19	16	17	1.3**	13.0	7.9	10.8
BALEARIC ISL.	4	3.7	1.4	1.8	10.6	3.9	6.7	86	59	71	19	13	17	1.1**	9.1	6.3	7.6
HAUT-LANGU.	1							92	82	88							
S- FRANCE	8	2.1	1.8	2.0	2.4	2.4	2.4	84	52	66				1.6***			
C-ITALY	3	1.0	1.0	1.0*	19.1	3.4	9.4	83	46	65	19	19	19*	1.2 (2010)			
CORSICA	1				1.0	1.0	1.0				18	18	18*		9.0	9.0	9.0*
SARDINIA	3	0.8	0.3	0.6	5.0	1.3	3.2	72	72	72*	18	18	18*	1.1 (2010)			
SICILY	2	3.0	2.9	3.0				88	88	88*				4.8***			
LAMPEDUSA	1							78	78	78*				5.4****			
CAN LLOMPART	1	2.3	1.6	2.0	6.2	4.1	5.0	69	66	68	17	15	16	**2.1**	12.1	8.6	10.3

* Only one-year data is available

** Annual contribution declared by the Spanish government.

*** Pey et al. (2013b)

**** Marconi et al. (2014)

NH_3 concentrations are rather similar (1.6-2.4 µg/m^3) for the episodes registered and episode apportionments were also comparable (27-41%). BC concentrations vary in a very narrow range, from 0.47 µg/m^3 (AT, MED) to 0.73 µg/m^3 (EU). REG and AT, are the main contributors (34 and 30%, respectively), followed by AF (22%), EU (11%) and only 2% ascribed to MED. It is interesting to note that BC concentrations during AT and MED are very similar to the background level estimated in section 3.2. PNC presents very similar concentrations during AT and REG (6299 and 6305 cm^{-3}) and very similar contributions to the global budget (39 and 37%). Lower but similar concentrations are measured for EU and AF (4769 and 4853cm^{-3}); however different contributions were obtained (7 and 17%).

3.3.4. Regional air quality over western Mediterranean

3.3.4.1. Gaseous pollutants and PM_x patterns

Regional background sites have been joined in different sub-regions as is described in section 2.5. Average 2010-2012 concentrations of each sub-region are shown in Figure 3.20. Other relevant information (mean values, maximum and minimum annual concentrations) are indicated in Table 3.4.

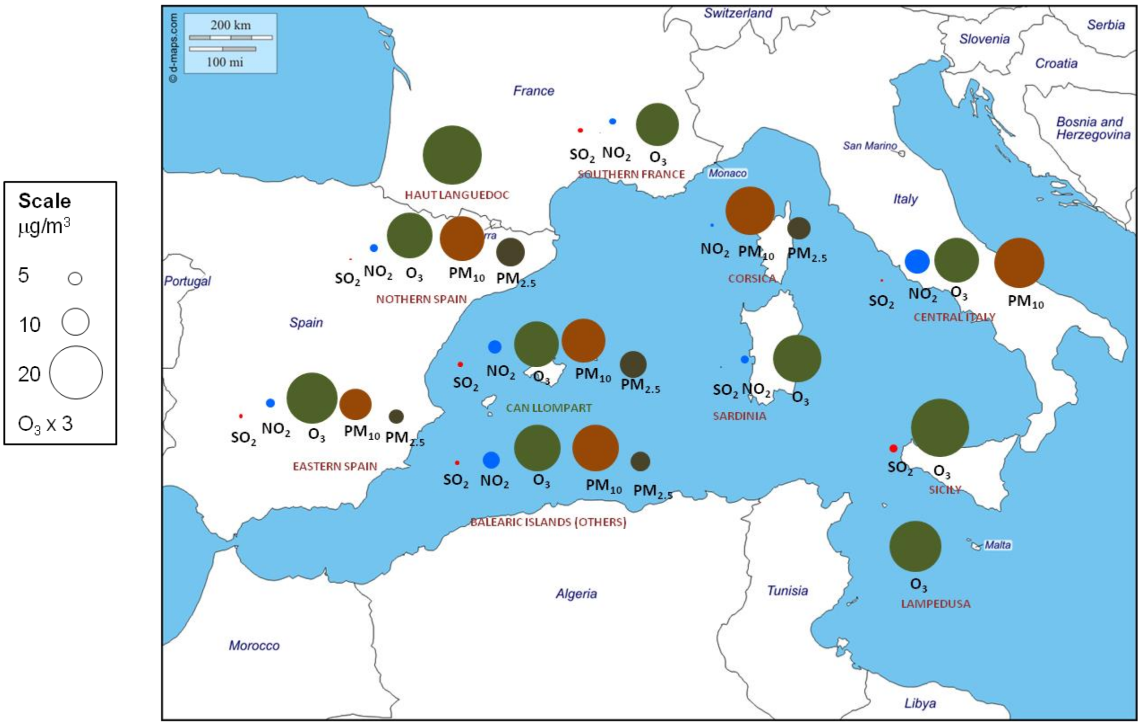


Figure 3.20. Average 2010-2012 concentrations (in µg/m^3) of SO_2, NO_2, O_3, PM_{10}, and $PM_{2.5}$ over regional background regions in the WMED. Note the different scale for O_3 (it should be multiplied by 3).

On average WMED sites display similar levels of air pollutants, with some particularities. In spite of the very low concentrations of SO_2 and the low concentrations of NO_2, the highest SO_2 (3.0 µg/m^3 annual mean) concentrations are observed in Sicily, probably due to the impact of shipping emissions (Becagli et al, 2017), the petrochemical activity in the area, and the emission of the Etna volcano. Nasa SO_2 OMI (https://giovanni.gsfc.nasa.gov/giovanni/) plotted in figures 3.16 and 3.17 illustrate this situation. The highest of NO_2 concentrations (9.4 µg/m^3 annual mean) are recorded in Central Italy, probably caused by the influence of the Roma's plume, followed by the Balearic Islands (6.7 µg/m^3) due to the high density of anthropogenic sources all over the island.

Ozone is registered in slightly higher concentrations at continental (65-88 µg/m^3) than at island sites (68-78 µg/m^3). This could be due to the combined effect of recirculation of air masses affecting continental regions from NO_x coastal cities plume (Millán et al., 2002) and the enhanced generation of ozone from biogenic VOCs.

Annual averages of PM_{10} vary between 16 and 19 µg/m^3 except for eastern Spain, where these concentrations are slightly lower probably due to the relatively high altitude of the monitoring sites (between 642 to 1150 m a.s.l.), which prevent the arrival of coastal PM (mostly sea spray and anthropogenic emissions) under specific meteorological circumstances (Ripoll et al., 2014). African dust contributes between 6 to 18% to the total PM_{10} mass, reflecting a dependency on the latitude as is described in Querol et al. (2009a) and Pey et al. (2013b). Among the scarcity of $PM_{2.5}$ data, CLL and the North-Eastern region share the highest concentrations, and Eastern Spanish sites the lowest.

Overall, concentrations of air pollutants are rather similar all over the WMB. This region may be understood as a unique atmospheric basin in which topography and emission sources confer a number of particularities at the different receptor points. CLL is a suitable location, subjected to moderate anthropogenic influence, to investigate gaseous and aerosol phenomenology in this region.

3.3.4.2. PM_x chemical characterization

Figure 3.21 depicts the average chemical composition of PM_1 (2010-2011), PM_{10} (2010-2012), and PM_{1-10} (2011-2012) fractions in CLL. The most abundant components in PM_{10} were mineral dust (21 %), followed by sea spray (19 %), OM (18 %) and SO_4^{2-} (15%), all adding up to for 73% of the total mass. The amount of NO_3^- (6 %), NH_4^+ (3 %), EC (2 %) and traces (0.4 %) constitute only a fraction of 12%, being the rest undetermined PM_{10} mass. The most relevant components in PM_1 were OM (38 %), followed by SO_4^{2-} (27 %), together accounting for 61% of the mass. Mineral dust is also a relatively abundant PM_1 component (9%), similar to NH_4^+ (8%), and higher than NO_3^- (6%), EC (4%) and sea spray (2%). Mineral dust in PM_1 is relatively more abundant than at other WMED regional and remote background sites (Ripoll et al. 2015), in which the abundance is around 5%. PM_{1-10} composition is estimated subtracting PM_1 to PM_{10} concentrations, only considering simultaneous periods. Coarse PM massis essentially driven by sea spray and mineral components, which conforms 64% of the total coarse mass. The AF contribution to PM_{10} is calculated by using the methodology proposed by Escudero et al. (2010), which was thereafter adopted as the European reference method for the estimation of Saharan dust contributions (EC 2011 and Pey et al., 2013b). Natural AF dust contribution entails 2.1 µg/m^3 in PM_{10}. Taking into account that the mineral component during AF in PM_1 accounts for 0.9 µg/m^3, and the average contribution of mineral dust in PM_1 during non-AF is 0.8 µg/m^3, only 0.1 µg/m^3 of the PM_1 mineral component could be attributed to the AF. Consequently, it can be considered that regional sources contribute 1.3 µg/m^3 to the PM_{1-10} fraction. Furthermore, certain chemical components usually found in the accumulation mode, such as NO_3^- (10 %), SO_4^{2-} (7 %) and OM (4 %), are relatively significant. It is well known that aerosol processing in Mediterranean atmospheres leads to the formation of secondary components especially during warm season, such as $NaNO_3$, $Ca(NO_3)_2$, Ca-$MgSO_4$ (Pey et al., 2009b, and references therein).

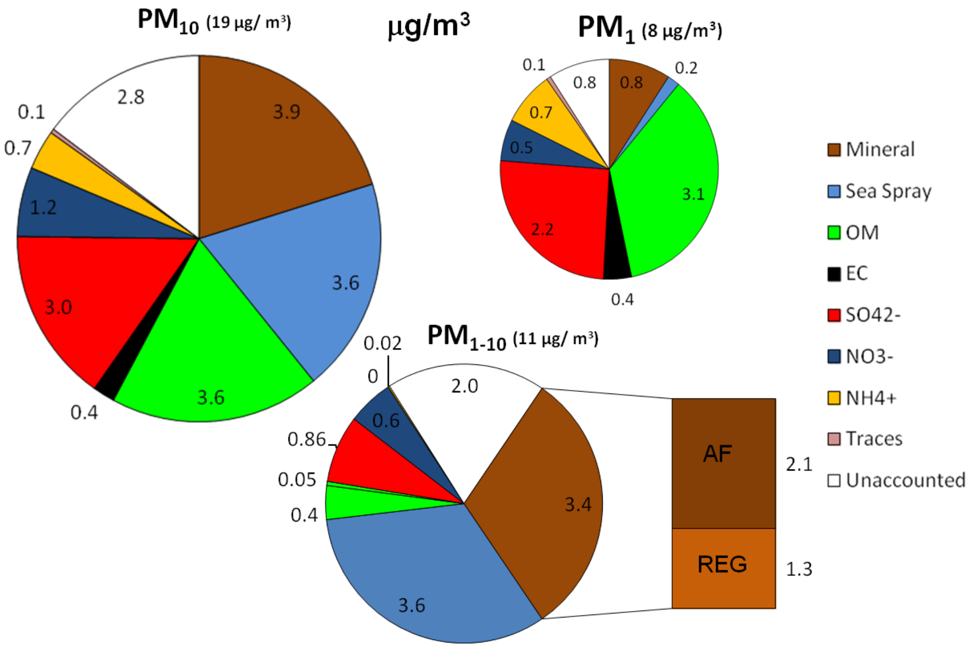


Figure 3.21. Average chemical composition (in µg/m³) at Can Llompart: PM_{10} (2010-2012), PM_1 (2011-2012) and PM_{1-10} (2011-2012).

Monthly averages of the main chemical component groups (EC, OM, NO_3^-, NH_4^+, SO_4^{2-}, mineral dust, sea spray, and traces) in PM_{10} and PM_1 are presented in Figure 3.22. This figure evidences that the beginning of the study was characterized by lower concentrations of most of the chemical component groups, whereas the converse pattern is found at the end.

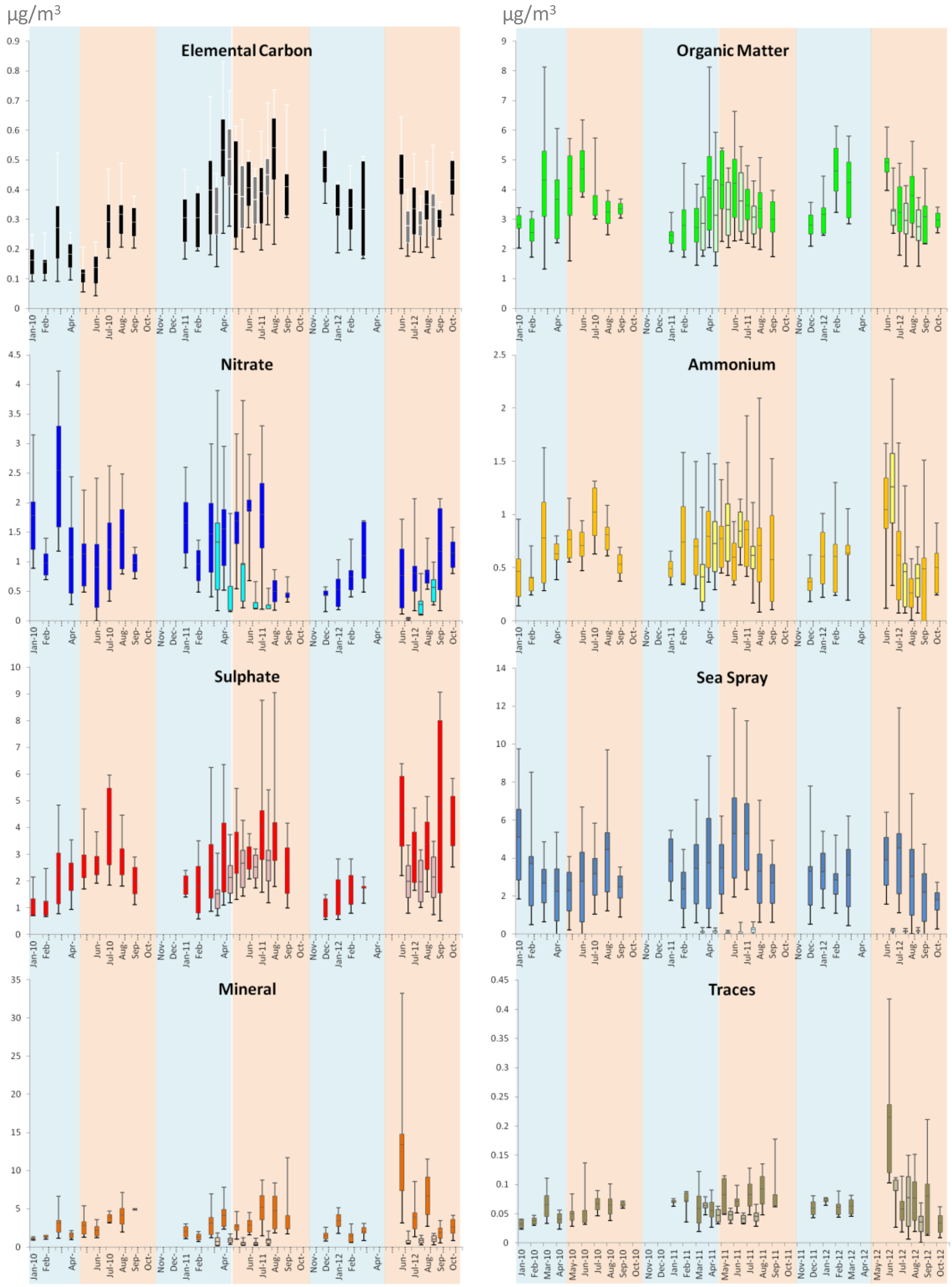


Figure 3.22. Monthly averages of main chemical component groups in PM$_{10}$ (intense colour) and PM$_1$ (light colour). Median (black line within the boxes) and percentiles (5-25-75-95, boxes and whiskers) of monthly concentrations in µg/m^3. Monthly data with less than four samples have been not taken into account.

Figure 3.22 reflects that EC and OM are always shifted to the fine fraction. In the case of NH$_4^+$, higher concentrations have even been measured in PM$_1$ than in PM$_{10}$, which is only possible if we assume that certain sampling artifacts have occurred, such as the volatilization of NH$_4$Cl owing to the reaction between NaCl and NH$_4$NO$_3$ particles in PM$_{10}$ filters (Cheng et al., 2012). The rest of components are partially or mainly found in the crustal PM$_{1-10}$ fraction. The best example of a coarse component is mineral dust. Nitrate and SO_4^{2-}, being mostly secondary in origin, typically linked to NH_4^+ (accumulation-mode aerosols), are found in the case of CLL in significant amounts in the coarse fraction, presumably forming $NaNO_3$, $Ca(NO_3)_2$ and Mg-$CaSO_4$. Actually, PM_1/PM_{10} ratios for NO_3^- and SO_4^{2-} calculated for the intensive campaigns are 0.41 and 0.70 respectively.

Meteorology determined the inter-annual variation as is explained in section 3.3. EC, mineral dust, SO_4^{2-} and trace elements were clearly lower in 2010. OM, NH_4^+ and sea spray do not show any significant inter-annual variability. Nitrate is the only component found in higher concentrations in 2010. Therefore, the higher frequency of AT and rainy conditions had a positive effect in the global aerosol cocktail, which is explained by the lowering of mineral dust, SO_4^{2-}, trace elements and EC. Warm periods, which are mostly driven by the concatenation of REG and AF, are related to an overall PM load increase. Mineral, SO_4^{2-} and traces are the most enhanced components during warm season. Actually, the 2012 summer season was characterized by very intense AF.

To date, chemical characterization of atmospheric aerosols at regional background environments in the WMED is scarce, and only few comprehensive studies have been performed. Besides of certain specific studies to investigate aerosol composition and sources at individual sites (Pey et al. 2009; Cusack et al., 2012) or particular regions (Ripoll et al.; 2015), the most complete is the one by Querol et al. (2009b), in which they compared the PM composition at several sites in the Mediterranean Basin, from the westernmost site (Montseny, Spain) to the easternmost side (Erdemli, Cyprus), passing through Finokalia (Greece). In that study they highlighted the increasing PM towards eastern sites, explained by the enrichment in anthropogenic sulphate and North African mineral dust.

Our integrated PM composition database contains average concentrations and chemical composition at different locations in the WMED (Table 3.5). Few long-term studies on PM chemical characterization at regional background sites around WMED have been conducted, especially in PM_1 fraction. In addition, those studies cover different time periods. Therefore, no global conclusion on chemical composition should be extracted. Nevertheless, primary observations arose from this comparison. Figure 3.23 summarizes the most significant features from Table 3.6. Beyond the differences in PM_{10} mass (PM_{10} increases from the West to the East), most of the chemical components display a strong variability among the different sites. Thus, sea salt decreases significantly in function of the distance to the coastline; organic components (OC and EC) and NO_3^- are clearly enhanced in South-Alpine sites, probably because of biomass-burning (see also the higher K concentrations in Table 3.6) and traffic emissions (some typical traffic tracers are also enhanced, mainly Cu, Sb or Zn); mineral dust displays a south to north decreasing gradient, mostly coincident with the impact of AF (Querol et al., 2009a and Pey et al. 2013b) with the exception of Montelibretti that could be affected by the Rome plume (Alastuey et al., 2016). In this comparative analysis, CLL stands out because of the evident impact of sea salt particles, and a moderate to high mineral dust and sulphate loads.

Table 3.5. Regional background sites with PM chemical composition available in the Western Mediterranean.

Site	Country	Altitude m a.s.l	Distance km from sea	Coordinates	Period	PM10	References	PM1	References
Can Llompart	*Spain*	*45*	*7*	*39°50’16”N-03°01’25”E*	*2010-2012*	*X*	This study	*X*	This study
Montsec	*Spain*	*1590*	*114*	*42°03'05"N-0°43'46"E*	*2010-2013*	*X*	Ripoll et al. (2014)	*X*	Ripoll et al. (2014)
Montseny	*Spain*	*740*	*26*	*41°46'00"N-02°21'00"E*	*2010-2013*	*X*	Ripoll et al. (2014)	*X*	Ripoll et al. (2014)
Aitana	*Spain*	*1558*	*18*	*38°39'05"N 0°17'54"O*	*2010-2012*	*X*	Galindo et al. (2016)	*X*	Galindo et al. (2016)
Montelibretti	*Italy*	*48*	*45*	*42°06'00"N-12°38'00"E*	*2012-2013*	*X*	Alastuey et al. (2016)		
Lampedusa	*Italy*	*48*	*20*	*35°31'01"N 12°37'48"E*	*2007-2008*	*X*	Calzolai et al. (2015)		
Payerne	*Switzerland*	*489*	*350*	*46°48'47"N - 06°56'41"E*	*2008-2009*	*X*	Minguillón et al. (2012)	*X*	Minguillón et al. (2012)
Magadino	*Switzerland*	*200*	*177*	*46°09'36”N-08°55'48”E*	*2008-2009*	*X*	Gianini et al. (2012)		

Table 3.6. PM_{10} chemical composition in different Western Mediterranean sites, grouped in zones.

	BALEARIC ISLANDS	EASTERN SPAIN	NORTHERN SPAIN		SOUTHERN ALPS		CENTRAL ITALY	LAMPEDUSA
	This Study CLL	**Aitana (high altitude)**	**Montsec (high altitude)**	**Montseny**	**Payerne**	**Magadino**	**Montelibretti**	**Lampedusa**
PM	19	13	12	16	19	21	28	32
Undet	3.6	2.9	2.3	4.3	3.0	2.6	8.0	11.4
EC	0.37	0.07	0.12	0.23	0.70	1.50	1.21	
OM	3.7	3.7	3.2	4.0	5.6	8.8	7.44	
NO_3^-	1.2	0.8	0.8	1.2	3.8	2.1	1.74	2.1
NH_4^+	0.7	0.4	0.5	0.5	1.6	1.2		0.7
SO_4^{2-}	3.0	1.5	1.3	1.9	1.9	1.9	2.3	3.7
Sea salt	3.6	0.4	0.3	0.5	0.1	0.2	1.2	8.3
Cl^-	2.4	0.1	0.1	0.3	0.0	0.1	0.5	4.3
Na	1.2	0.3	0.1	0.3	0.1	0.1	0.7	3.2
Mineral	3.9	3.3	3.0	2.8	1.8	1.9	5.5	5.8
CO_3^{2-}	0.8	0.6	0.5	0.4			1.3	1.3
SiO_2	1.3	1.4	1.1	1.1			1.6	1.7
Al_2O_3	0.5	0.6	0.5	0.4			0.7	0.7
Ca	0.5	0.4	0.3	0.3	0.2	0.1	0.8	0.9
K	0.1	0.1	0.1	0.1	0.2	0.3	0.4	0.3
Mg	0.2		0.1	0.1	0.0	0.0	0.2	0.4
Fe	0.2	0.2	0.1	0.2	0.1	0.3	0.3	0.3
P	15.0		9.0	11.0			6.5	
Ti	19.2	20.0	14.0	12.4	2.2	4.9	21.0	30.0
Mn	4.2	6.1	4.0	3.8	2.9	5.1	6.6	5.3
Traces	0.03	0.03	0.02	0.03	0.60	0.80	0.06	0.02
Li	0.3		0.2	0.2				
V	3.6	4.0	1.1	2.0	0.5	0.6	2.9	5.2
Cr	2.0	1.3	0.8	0.9	0.7	1.4	3.2	
Co	0.1		0.1	0.1				
Ni	2.5	2.7	0.5	1.1	0.7	0.9	2.2	2.0
Cu	3.2	1.0	1.1	3.0	4.0	9.0	8.4	1.8
Zn	10.8	7.1	7.0	10.0	19.0	21.0	18.7	
As	0.2		0.1	0.2	0.5	0.7	0.2	
Se	0.2		0.1	0.2	0.4	0.4	0.4	
Rb	0.4		0.3	0.3	0.5	0.6	3.5	
Sr	2.2	2.6	1.5	1.1	0.6	0.6	3.8	7.0
Cd	0.05		0.03	0.06	0.09	0.10		
Sn	0.4		0.4	0.7				
Sb	0.5		0.1	0.3	0.6	1.0		
Ba	3.6	8.2	2.0	3.0	1.7	3.0	7.4	
La	0.2		0.2	0.1	0.1	0.1		
Pb	2.0	1.4	1.1	2.0	4.0	4.0	4.1	2.9
Ga	0.1							

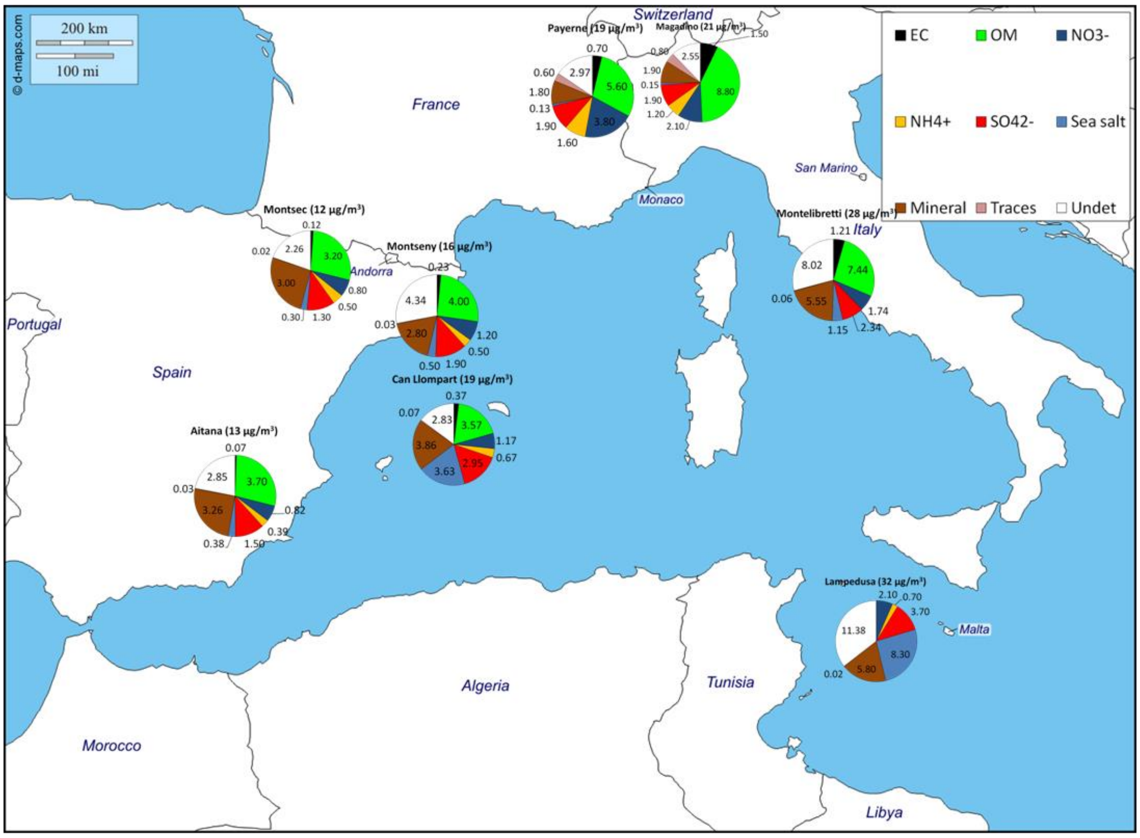


Figure 3.23. PM_{10} chemical composition in regional background sites of the WMED, integrated in 9 components: Elemental Carbon EC, Organic Matter OM, Nitrate NO_3^-, Ammonium NH_4^+, Sulphate SO_4^{2-}, Sea Salt, Mineral, Traces, Undetermined. See references in Table 3.5.

PM_1 mean loads are summarized in Table 3.7 and the chemical composition is displayed in Figure 3.24. PM_1 mass concentrations among the different sites vary in a quite narrow interval, from 5 µg/m³ at Aitana (SE of Spain) to 9 µg/m³ at Payerne (Switzerland), being the NE of Spain and the Balearic Islands in an intermediate situation (from 7 to 8 µg/m³). At CLL, PM_1 contains the highest amount of mineral dust. When compared with Aitana, which is the second site in mineral dust contribution in PM_1, lower amount of $AlSiO_4^-$ are detected but enhanced CO_3^{2-} components are measured in CLL, probably of local to regional origin. Similarly, SO_4^{2-} at CLL is much higher than at the other sites, probably reflecting the higher impact of shipping and power plant emissions, which are accomplished with well-known tracers including V, Ni, Cr and Co. Finally, OM, EC, NO_3^-, Sb and Zn, considered as tracers from vehicle exhaust and non-exhausts emissions, are enhanced in CLL and some of them in Payerne.

Overall, CLL displays rather similar PM_1 concentrations than other sites in the NE Mediterranean and only slightly lower than those at Payerne, but the anthropogenic impact at CLL is, in general, more evident and this is probably due to the closer proximity of the emission sources at this site.

Table 3.7. PM_1 chemical composition in different Western Mediterranean sites, grouped in zones.

	BALEARIC ISLANDS	NORTHERN SPAIN		EASTERN SPAIN	SOUTHERN ALPS
	This Study CLL	**Montsec**	**Montseny**	**Aitana**	**Payerne**
PM	8	7	8	5	9
Undet	0.1	2.0	2.4	0.7	1.8
EC	0.36	0.09	0.17	0.07	0.45
OM	3.1	2.8	2.9	2.1	2.9
NO_3^-	0.5	0.2	0.3	0.1	1.1
NH_4^+	0.7	0.5	0.5	0.4	0.9
SO_4^{2-}	2.2	1.2	1.5	1.0	1.3
Sea salt	0.2	0.1	0.1	0.1	0.1
Cl^-	0.1	0.1	0.1	0.1	
Na	0.06	0.02	0.03	0.06	
Mineral	0.8	0.3	0.3	0.5	0.5
CO_3^{2-}	0.16	0.05	0.01	0.09	
SiO_2	0.19	0.10	0.10	0.26	
Al_2O_3	0.07	0.03	0.04	0.09	
Ca	0.11	0.03	0.01	0.06	
K	0.08	0.02	0.05	0.07	
Mg	0.06	0.01	0.01	0.01	
Fe	0.04	0.01	0.01	0.02	
P	6.61	3.00	3.20		
Ti	2.4	1.1	0.8	4.0	
Mn	1.2	0.9	0.7	1.0	
Traces	0.06	0.02	0.02	0.01	0.06
Li	0.07	0.01	0.01		
V	3.22	0.70	1.20	2.00	
Cr	2.71	0.70	0.50		
Co	0.14	0.05	0.03		
Ni	2.70	0.40	0.80	1.00	
Cu	1.53	0.40	1.50		
Zn	8.55	5.00	6.00	2.00	
As	0.13	0.06	0.10		
Se	0.13	0.06	0.09		
Rb	0.11	0.05	0.07		
Sr	0.44	0.10	0.10	1.00	
Cd	0.04	0.02	0.05		
Sn	0.25	0.20	0.40		
Sb	0.34	0.01	0.10		
Ba	1.05	1.30	0.60	1.00	
La	0.09	0.06	0.03		
Pb	1.36	0.80	1.60	1.00	
Ga	0.04				

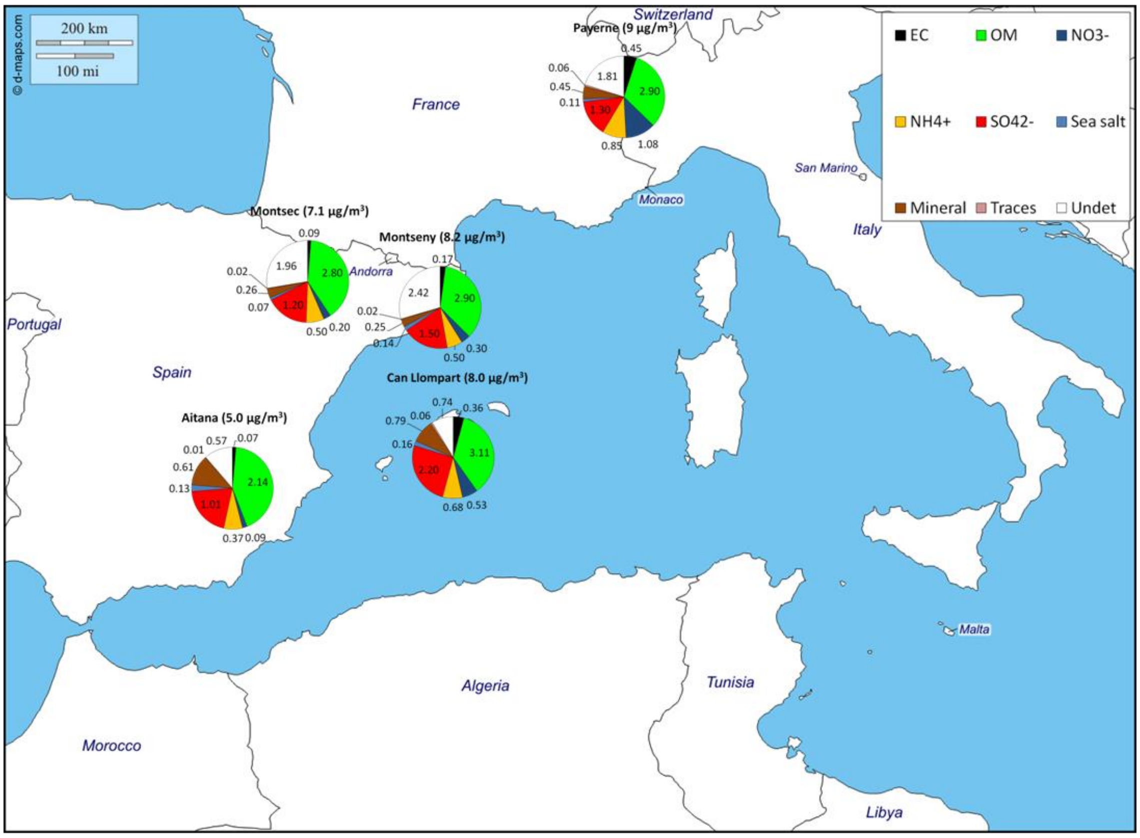


Figure 3.24. PM_1 chemical composition in regional background sites of the WMED, integrated in 9 components: Elemental Carbon EC, Organic Matter OM, Nitrate NO_3^-, Ammonium NH_4^+, Sulphate SO_4^{2-} , Sea Salt, Mineral, Traces, Undetermined. See references in Table 3.5.

3.3.5. PM_x Source Apportionment

3.3.5.1. PM_{10} Solution

PMF exploration was run under seed mode from 1 to 10 factors, with 10 iterations for each factor. A parabolic vertex Q/Qexp value was detected at 4 factors (Figure 3.25. Right). All iterations displayed similar Q/Qexp ratios for 4 factors (Figure 3.25. Left).

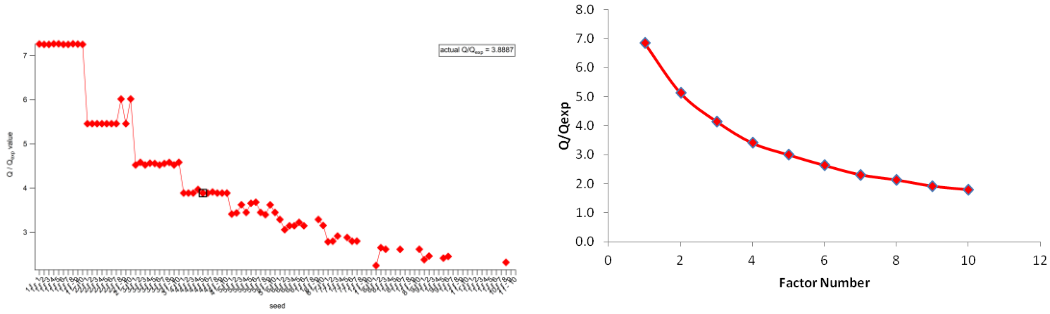


Figure 3.25. Q/Qexp ratios obtained considering different number of factors solution. Left: all iteration Q/Qexp results; Right: number of factors Q/Qexp averaged results.

4 factors displayed high concordance (Figure 3.26), including two characterized mostly by anthropogenic species, and one characterized by mineral and marine species.

3 and 5 factors were also investigated: Considering 3 factors, anthropogenic and natural species were mixed all over the three factors. 5 factors were investigated, but iterations were not stable.

Before considering 4 factors the most suitable solution, time-series were studied and compared with meteorological episodes and external tracers as conventional pollutant gases.

Rotational ambiguity was studied by varying Fpeak from -2 to 2 with steps of 0.2 (Figure 3.27). Regularly results approaches to one were obtained from -1.4 to 0.2, and no stable results over 0.0 Fpeak were achieved.

50 pseudorandom starting-points (seeds) were verified to study the influence of initial conditions and none was dissimilar.

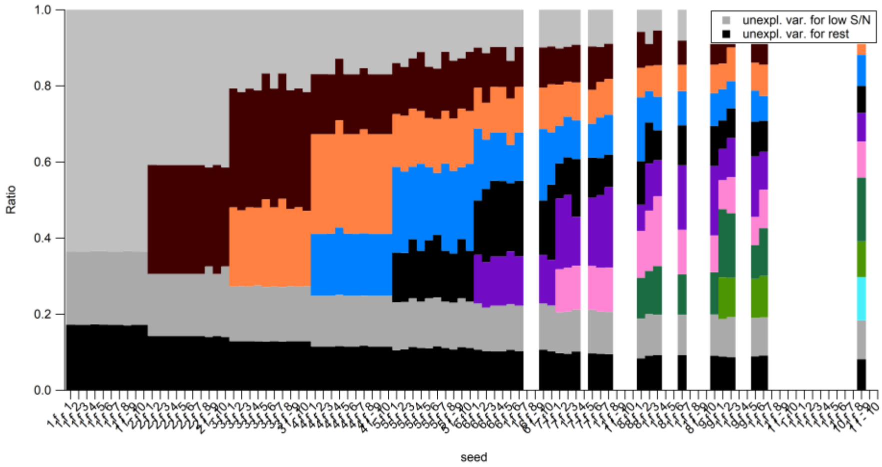


Figure 3.26. Mass fraction of each factor for all iterations.

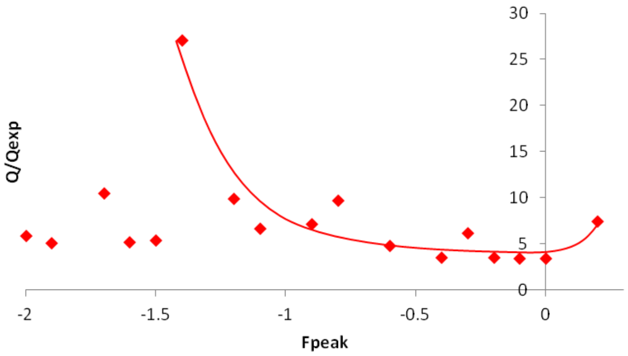


Figure 3.27. Fpeak from -2 to 2 with steps of 0.2.

The most suitable solution for the PMF source apportionment analysis yields 4 factors, which include two characterised mostly by anthropogenic species, one characterised by mineral species, and another based in marine species (Figure 3.28).

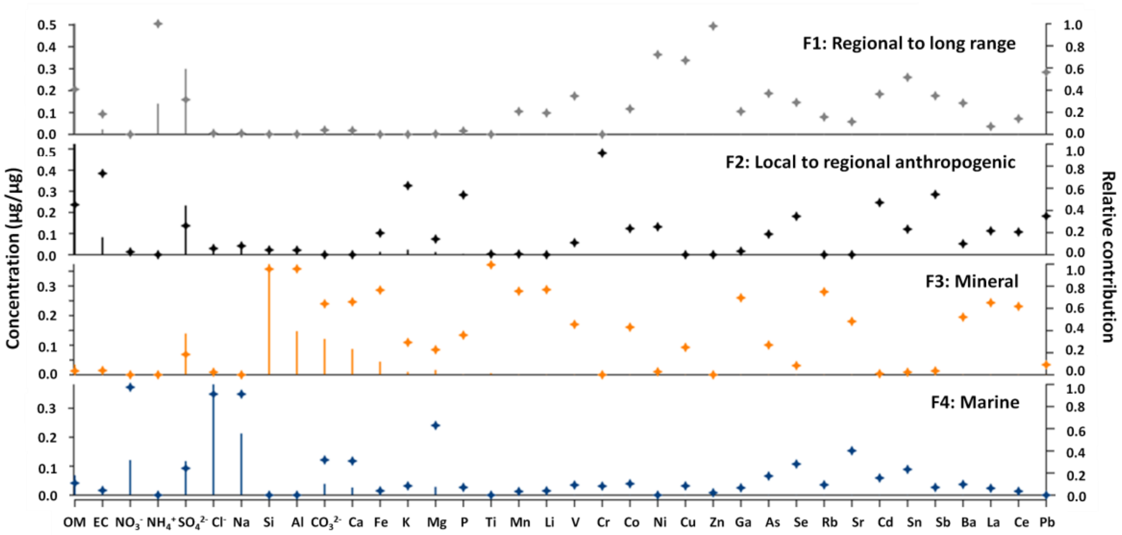


Figure 3.28. Concentration in µg/µg (with bars) and relative contribution (with dots) of chemical components for the 4-factor solution in PM_{10}.

The four sources were labelled according to their characteristic tracers.

Factor 1 is characterized by Zn, NH_4^+, Cu, Ni, Pb and Sn, and to a lesser extent by OM, SO_4^{2-}, V, As, Cd and Sb. This fingerprint does not correspond to a single pollution source but it could be a mixture of various anthropogenic sources, including coal-fired power plant emissions (Querol et al., 1998; Cesari et al., 2016) and heavy oil combustion probably related to shipping (Pandolfi et al., 2011, Pey et al., 2013c), but also mixed with road traffic emissions (Amato et al., 2012). This factor could be partially related to nearby shipping and power plant emissions given the proximity of these sources to CLL but it is also related to regional and long-range transported aerosols. Taking into account the temporal variability of Factor 1 contributions (Figure 3.29) and the preferential association with certain meteorological conditions (Table 3.8), we have interpreted it as ***regional-to-long range*** influence. Overall, it accounts for 2.4 µg/m^3 of the total PM_{10} mass. In order to weight the influence of the different sources a number of ratios have been evaluated (Table 3.9).

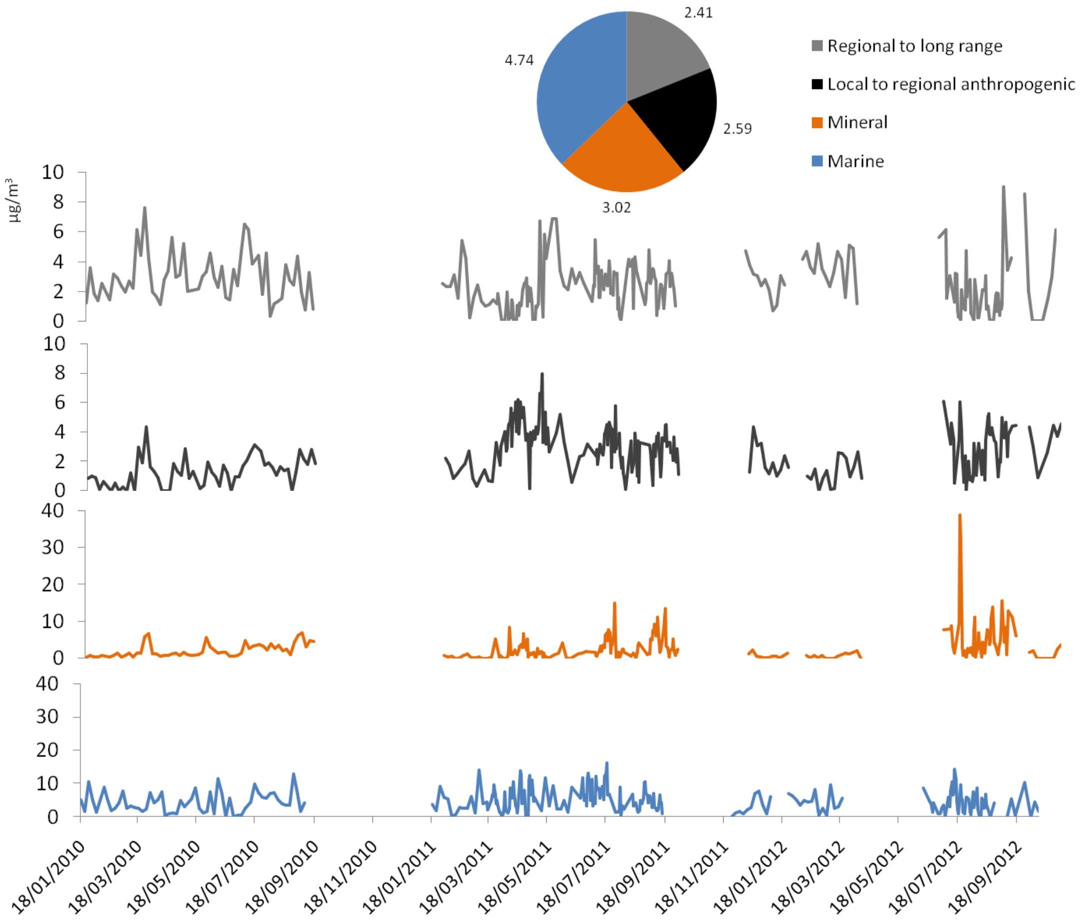


Figure 3.29. Time series concentration of the PM$_{10}$ factors, in µg/m3. Notice different scale for anthropogenic and natural factors.

Table 3.8. PM_{10} factors' mean contribution (in µg/m³) according to: year; warm/cold (warm period: April-October; cold period: November-March); season; and air mass origin.

µg/m³	Num. samples	regional-to-long range	local-to-regional	Mineral	Marine
2010	57	3.0	1.3	2.2	4.4
2011	149	2.3	3.1	2.5	5.2
2012	76	2.3	2.6	4.7	4.2
Warm	210	2.2	2.9	3.6	4.9
Cold	72	2.8	1.7	0.9	4.1
Spring	77	2.1	3.2	1.8	4.7
Summer	143	2.3	2.7	4.5	5.0
Autumn	11	3.0	2.9	1.1	2.9
Winter	51	2.8	1.4	0.8	4.4
AT	86	2.0	2.1	2.0	5.0
EU	22	3.3	2.5	1.1	4.9
MED*	3	3.3	3.0	5.1	3.0
AF	63	1.9	3.2	5.8	4.9
REG	108	2.8	2.6	2.6	4.5

* only three samples, then not statistically significant

Table 3.9. Mass ratio between different tracers of shipping and/or coal-fired power plant emissions.

	This study CLL	**Primary shipping emissions¹**	**Coal-fired power plant emissions²**
V/Ni	0.69	0.27	0.66
Zn/V	8.36	1.0	4.5
SO_4^{2-}/V	733	21	393
NH_4^+/V	532	5.6	19
SO_4^{2-}/NH_4^+	1.4	3.7	21
Mn/V	0.69	0.05	3.0

1 Pey et al. 2013c

2 Cesari et al. 2016

Factor 2 is defined by OM, EC, SO_4^{2-}, K, P, Cr, Se, Cd, Sb, and it is related again to road traffic (OM, EC, Sb) and coal combustion (SO_4^{2-}, Cr, Cd, Se) (Pey et al. 2013a; Amato et al. 2016). In this case these contributions are mixed with tracers from other sources such as agricultural emissions (K, P), occurring nearby but sporadically. This factor is thought as more local in origin than the previous one and finally it is labelled as ***local-to-regional anthropogenic*** emissions**.** The contribution of Factor 2 comprises 2.5 µg/m³ of PM_{10} on average.

Factor 3 includes typical soil related elements such as Si, Al, CO_3^{2-}, Ca, Fe, Ti, Mn, Li, V, Co, Ga, Rb, Sr, Ba, La, Ce, and consequently was labelled as ***mineral*** (Pey et al. 2013a). Mineral dust accounts for 3.0 µg/m^3 and it comes, either from local soil resuspension (enriched in calcium), either from long-range transport of dust aerosols from North Africa, in this case shifted to a more aluminosilicate composition. The bias between the PMF estimation and the experimental determination of mineral dust (3.9 µg/m^3, see Figure 3.21 and Table 3.8) is explained because part of the mineral components (Ca, CO_3^{2-}) have been incorporated in the next factor.

Factor 4 is mainly composed by Na, Cl, NO_3^-, and to a less extent by Mg, SO_4^{2-} and Ca, species typically related to fresh and aged ***marine*** emissions (Pey et al. 2013a; Amato et al. 2016). At CLL, the marine source is the most weighted factor (4.7 µg/m^3), partially due to natural sea-salt particles, partially because it contains other non-natural salts such as sulphates and nitrates. The recurrent atmospheric processing affecting sea spray aerosol is well known, leading to the formation of Na_2SO_4 and $NaNO_3$ (Harrison & Pio, 1983; Pey et al., 2009b). Actually, experimental sea salt concentration is 3.6 µg/m^3, being the extra 1.1 µg/m^3 linked to the aforementioned reactions and to the incorporation of some mineral dust in this factor. This processes explained the coarse size distribution of NO_3^- in summer.

Overall, these factors explain 76% of the variability, with 16%, 17%, 27% and 16% respectively. 13% of the variability is involved in the signal to noise background, and only 10% is unexplained.

Factor time series are shown in Figure 3.29. The contribution of the regional-to-long range transport factor (factor 1) slightly decreases along the campaign, which is comparable with gradual descend of the emissions from these sources according to the regional inventories (16% of SO_2 reduction from 2010 to 2012 (http://atmosfera.caib.es) and the SO_2NASA OMI observations (Figure 3.17). Meteorological conditions in 2010, with a much higher prevalence of AT, favoured atmospheric dispersion, which is clearly observed in the local-to-regional contribution (factor 2) and for mineral loads (factor 3). Daily contributions of the marine factor varied from very low values to significant amounts (around 10-15 µg/m^3).

Seasonal average factor contribution is shown in Table 3.8. The contribution of local-to-regional sources is reduced during the cold period, in line with NO_2 patterns. Despite the prevalence of low-dispersive atmospheric conditions in the cold season, local activity is strongly reduced with respect to that occurring in the warm season owing to the massive arrival of tourists in summer. Regional-to-long range transport factor is slightly higher during the cold season, probably due to the impact of the coal-fired power plant emissions taking place nearby the site in a less-dispersive atmosphere. Mineral dust is clearly enhanced in the warm season, as AF and REG become more frequent. Finally, the marine influence is only slightly higher in summer, probably due to the increase in the sea-to-land breezes carrying fresh and aged marine particles inland. Only eleven 24-hour samples were collected during fall season, consequently results obtained should not be considered representative enough.

By combining the daily variation of factors' contributions together with the classification of these contributions according to air mass origins (Table 3.8), the following conclusions can be identified:

-The regional-to-long range transport factor is enhanced under EU and REG, thus supporting the double contribution to this factor: medium and long range transport of PM and local sources.

-The local-to-regional influence is greater when AF occur, which is aligned with NO_2 results. This issue could be related with the compression of the boundary layer associated to most of these situations described by Pandolfi et al. (2014), and discussed formerly in section 3.3., and the fact that AF episodes and tourist season are concomitant during the warm season.

-The highest frequency of AF in summer 2012 is perfectly reflected in the mineral factor, with the highest peak up to 39µg/m³ on a daily basis (Figure 3.29) and a clear enhancement during that episodes (Table 3.8).

3.3.5.2. PM$_1$ solution

PMF exploration was run under seed mode from 1 to 10 factors, with 10 iterations for each factor. A parabolic vertex Q/Qexp value was detected at 3 factors (Figure 3.30. Right). All iterations displayed similar Q/Qexp ratios for 3 factors (Figures 3.30. Left).

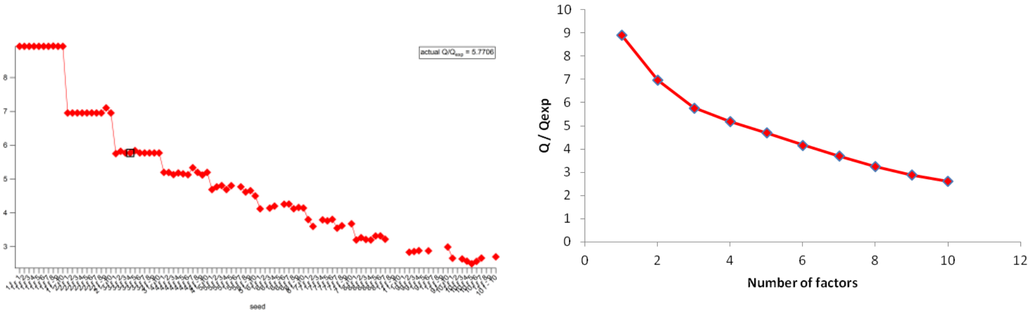


Figure 3.30. Q/Qexp ratios obtained considering different number of factors solution. Left: all iteration Q/Qexp results; Right: number of factors Q/Qexp averaged results.

3 factors displayed high concordance (Figure 3.31), including two characterized mostly by anthropogenic species, and one characterized by mineral and marine species.

2 and 4 factors were also investigated: Considering 2 factors, anthropogenic and natural species were mixed all over the two factors. 4 factors were investigated, but iterations were not stable.

Before considering 3 factors the most suitable solution, time-series were studied and compared with meteorological episodes and external tracers as conventional pollutant gases.

Rotational ambiguity was studied by varying Fpeak from -2 to 2 with steps of 0.2 (Figure 3.32). Regularly results approaches to one were obtained from -1.4 to 0.0, and no stable results over 0.0 Fpeak were achieved.

50 pseudorandom starting-points (seeds) were verified to study the influence of initial conditions and none was dissimilar.

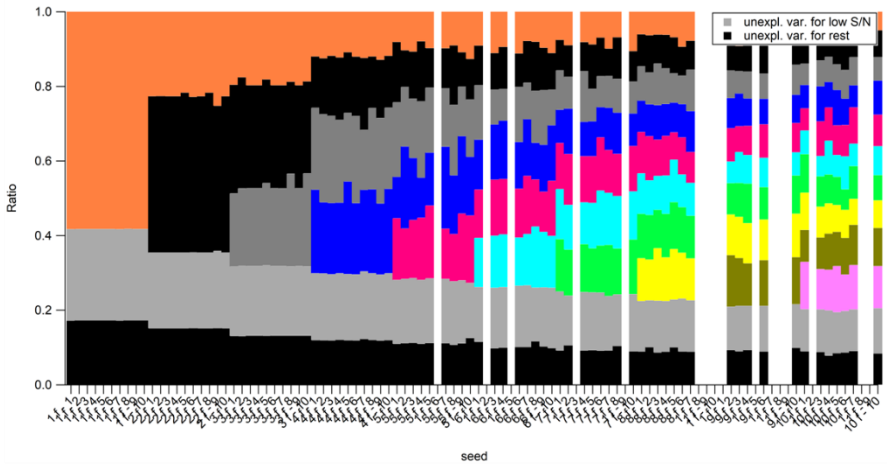


Figure 3.31. Mass fraction of each factor for all iterations.

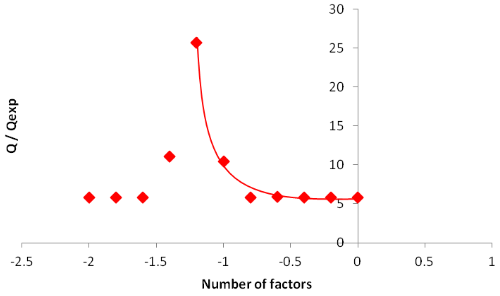


Figure 3.32. Fpeak from -2 to 2 with steps of 0.2.

3-factors solution for PM_1 was identified as the most suitable, including two factors characterized mostly by anthropogenic species, and one characterized by mineral and marine species.

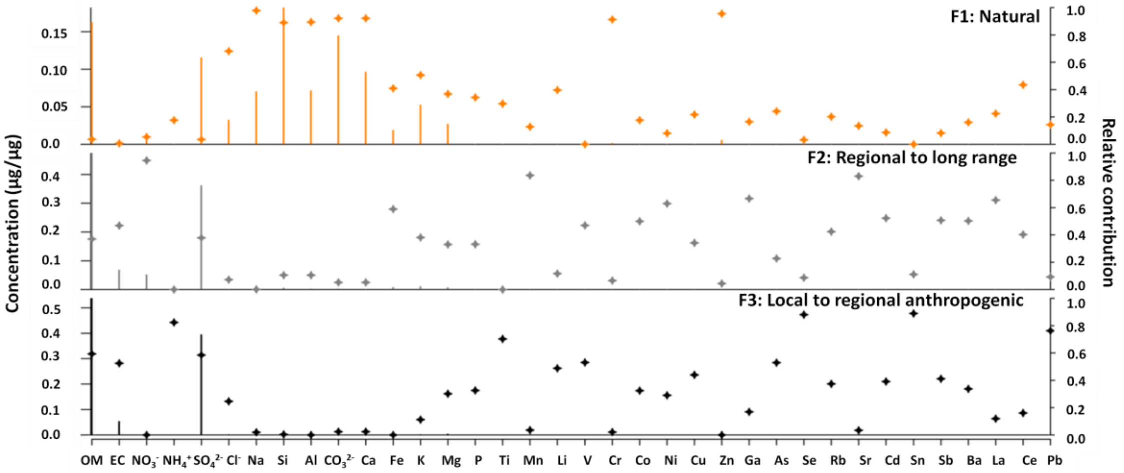


Figure 3.33. Concentration in µg/µg (with bars) and relative contribution (with dots) of chemical components for the 3-factor solution in PM_1.

The three sources were labelled according to their characteristic tracers as: a mix of crustal and marine species ***Natural*** (Cl, Na, Si, Al, CO_3^{2-}, Ca, Fe, K, Mg, Li, Cr, Zn, Ce), a ***regional-to-long range*** anthropogenic influence (OM, EC, NO_3^-, SO_4^{2-}, Fe, Mn, V, Co, Ni, Ga, Sr, Cd, Sb, Ba, La, Ce) and a ***local-to-regional*** source (OM, EC, NH_4^+, SO_4^{2-}, Ti, Li, V, As, Se, Cd, Sn, Pb). Again, the interpretation of these factors is not straightforward and the prevalence during specific meteorological conditions of some of them has been considered. Thus, the enrichment of Factor 2 during EU and REG situations (Table 3.10) led us to interpret that factor as more related to regional and long range transport emissions than Factor 3, which is clearly enhanced under AF episodes, as occurred in PM_{10}.

OM, EC, V, Cu, Cd, Sb and Ba are distributed rather equally among the two anthropogenic factors, while Fe, Mn, Ni, Ga, Sr and La are rather tracing the first one; and Ti, Li, As, Se, Sn and Pb the second one. Nitrate is aligned with an anthropogenic source (regional-to-long range) in PM_1, contrasting with what happen in PM_{10}, in which NO_3^- is mostly in marine factor. While in PM_1 NO_3^- particles are mainly forming NH_4NO_3, in PM_{1-10} are confirming the prevalence of aged marine aerosols.

The natural factor accounts for 0.6 µg/m^3 of PM$_1$. The two anthropogenic factors are not well separated and they are both mixed with some mineral species. The first one, could be more local in origin since it contains tracers from vehicular exhaust and non-exhaust emissions, and accounts for 2.2 µg/m^3; while the second one could be attributed to the impact of regional and long-range transport of aerosols owing to the presence of SO_4^{2-} and NH_4^+, although influenced by nearby sources as reflected in certain trace elements, and constitutes 2.7 µg/m^3 of PM$_1$. 1.9 µg/m^3 of the total determined mass rest unexplained.

The 3-factor solution for PM$_1$ explains 68% of the variability, 20% by the natural factor, 21% by local-to-regional, and 28% by regional-to-long range factor, and 19% explained by signal to noise.

Figure 3.34 shows PM$_1$ factors´ concentration time series. Natural factor expresses more variability during 2012 than 2011, surely related to the high frequency of AF occurred in 2012.

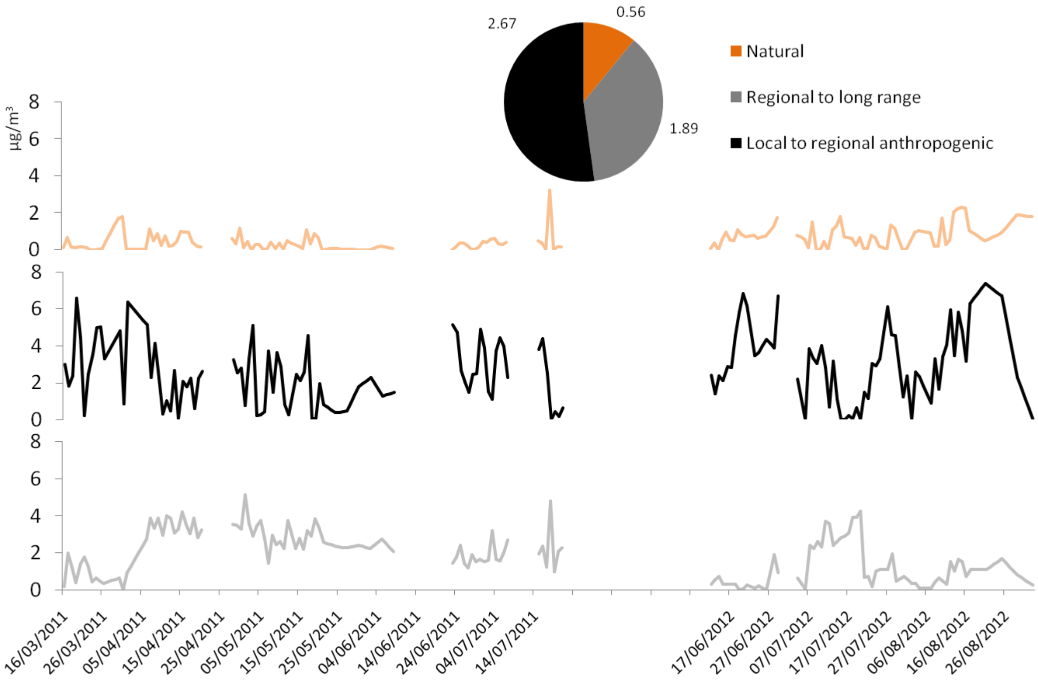


Figure 3.34. Time series concentration of the PM1 factors, in µg/m3.

Table 3.10 shows PM$_1$ factors' load average depending on the air mass origin. The natural factor shows its highest concentrations during AF (long range transport of dust), followed by AT (local dust resuspension). In all cases, its variability is mostly driven by mineral dust since average values of this component are 4 times higher than those of marine aerosols in PM$_1$ (Figure 3.34). The first anthropogenic factor, which is the one more linked to regional and long-range transport is enhanced during EU (average values from a low number of samples from early spring 2011), followed by REG and AT, and much lower concentrations under AF. Conversely, the second anthropogenic factor, which is more associated to local sources including coal and heavy oil combustion, increased clearly under AF, followed by REG scenarios.

Table 3.10. PM_1 factors' mean contribution (in µg/m^3) according to: year; season; and air mass origin.

µg/m^3	Num. samples	Natural	Regional-to-long range	Local-to-regional
2011	80	0.3	2.3	2.4
2012	59	0.8	1.1	3.3
Spring	68	0.4	2.4	2.4
Summer	71	0.7	1.6	2.8
AT	30	0.7	2.2	2.1
EU	10	0.5	2.9	1.7
MED*	3	0.4	2.3	3.4
AF	37	0.9	0.9	3.8
REG	59	0.3	2.2	2.4

* only three samples, then not statistically significant

The natural factor is clearly enhanced in summer as higher frequency of AF is registered; the impact of local-to-regional was more important during the spring campaign in 2011; and the regional-to-long range factor was only slightly higher in summer.

It is important to remark that the PMF results from the PM_1 solution are not directly comparable to those of PM_{10} for two main reasons: 1) factors in PM_{10} are in some cases a mixture of sources but are better separated than those in PM_1; 2) PM_{10} data included in the model cover all seasons (276 PM_{10} filters) while PM_1 sampling period only covers spring and summer campaigns in 2011 and 2012 (138 PM_1 filters).

3.3.6. Gaseous pollutants and PM10 trends in the period 2010-2018

From 2010 to 2018, a sharp increase in the number of tourists in the Balearic Islands has occurred (Table 3.13 and Figure 3.35). According to the statistics, around 11.5 million of tourists visited the Balearic Islands in 2010, from which 11% (1.2 million) arrived by maritime transport and the remaining 89% by air. The situation in 2018 was significantly different. The number of tourists rose to 16.5 million, and those arriving by maritime transport have doubled those in 2010 (2.4 million), overall representing 15% of the arrivals. Regional emissions remain at similar levels in 2017 when compared with those in 2010 (Table 3.11). The increasing trend in the arrival of tourists is decoupled with the global emission of pollutants: while global emissions remain at similar levels since 2010 (only with some variability related to the financial crisis and the recovery of the economy), certain sources such as power plant and road traffic have reduced their emissions but other sources including maritime and air transport display an overall increase, enough to compensate the implementation of specific mitigation plans (Cerro et al., 2015). Specifically, maritime SO_2 and NO_x emissions increased from 49.7 and 51.7 % of the total in 2010 to 67.6 and 64.6% in 2017, respectively (Table 3.12). Likewise, total suspended particle emissions augmented in the same way, from 42.3 to 54.9 % of the total between 2010 to 2017 (Table 3.12). A comparable increasing trend in the case of NO_x owing to air transport emissions is detected, shifting from 7.5 to 10% of the total emissions.

Table 3.11. SO_2, NO_x and PST (total suspended particles) emission tones by sector published by Balearic Islands Government (atmosfera.caib.es) in the period 2010-2017.

Sector		Power Plant Emissions	Small and Medium emission plants	Combustion Industrial Emissions	Non combustion Industrial Emissions	Fossil fuel extraction and distribution	Solvents and other related products	Road Transport	Other transports (including maritime and air transport)	Waste manag.	Agriculture	Other sources	**Total**
2010	**SOx (t)**	11.234	246	239			0	12	12.613	26	0	8	**24.377**
		46.1%	1.0%	1.0%			0.0%	0.0%	51.7%	0.1%	0.0%	0.0%	
	NOx (t)	23.556	851	613			3	9.220	55.194	207	275	39	**89.958**
		26.2%	0.9%	0.7%			0.0%	10.2%	61.4%	0.2%	0.3%	0.0%	
	PST (t)	545	969	87	493		63	784	2.867	146	476		**6.430**
		8.5%	15.1%	1.4%	7.7%		1.0%	12.2%	44.6%	2.3%	7.4%		
2011	**SOx (t)**	9.357	230	147			0	11	16.137	65	0	31	**25.977**
		36.0%	0.9%	0.6%			0.0%	0.0%	62.1%	0.2%	0.0%	0.1%	
	NOx (t)	20.990	833	610			6	8.764	64.825	314	261	154	**96.756**
		21.7%	0.9%	0.6%			0.0%	9.1%	67.0%	0.3%	0.3%	0.2%	
	PST (t)	538	972	91	447		98	733	3.593	154	460		**7.085**
		7.6%	13.7%	1.3%	6.3%		1.4%	10.4%	50.7%	2.2%	6.5%		
2012	**SOx (t)**	8.538	217	173			0	11	13.312	48	0	5	**22.303**
		38.3%	1.0%	0.8%			0.0%	0.0%	59.7%	0.2%	0.0%	0.0%	
	NOx (t)	19.026	842	864			2	8.145	55.090	284	256	24	**84.534**
		22.5%	1.0%	1.0%			0.0%	9.6%	65.2%	0.3%	0.3%	0.0%	
	PST (t)	433	984	97	341		43	686	2.981	152	466		**6.182**
		7.0%	15.9%	1.6%	5.5%		0.7%	11.1%	48.2%	2.5%	7.5%		
2013	**SOx (t)**	7.092	241	130			0	11	13.276	35	0	38	**20.822**
		34.1%	1.2%	0.6%			0.0%	0.1%	63.8%	0.2%	0.0%	0.2%	
	NOx (t)	13.404	707	714			4	8.021	51.103	272	285	189	**74.700**
		17.9%	0.9%	1.0%			0.0%	10.7%	68.4%	0.4%	0.4%	0.3%	
	PST (t)	339	996	70	283		65	669	2.906	151	442		**5.920**
		5.7%	16.8%	1.2%	4.8%		1.1%	11.3%	49.1%	2.6%	7.5%		
2014	**SOx (t)**	7.351	201	121			0	12	15.988	33	0	2	**23.708**
		31.0%	0.8%	0.5%			0.0%	0.0%	67.4%	0.1%	0.0%	0.0%	
	NOx (t)	11.521	649	626			4	8.138	58.596	328	361	8	**80.229**
		14.4%	0.8%	0.8%			0.0%	10.1%	73.0%	0.4%	0.4%	0.0%	
	PST (t)	292	993	47	312		65	672	3.466	151	497		**6.496**
		4.5%	15.3%	0.7%	4.8%		1.0%	10.3%	53.4%	2.3%	7.6%		
2015	**SOx (t)**	5.598	177	189			0	12	15.636	39	0	2	**21.655**
		25.8%	0.8%	0.9%			0.0%	0.1%	72.2%	0.2%	0.0%	0.0%	
	NOx (t)	9.306	644	683			3	8.042	62.363	384	290	11	**81.727**
		11.4%	0.8%	0.8%			0.0%	9.8%	76.3%	0.5%	0.4%	0.0%	
	PST (t)	218	979	88	350		59	671	3.464	153	425		**6.407**
		3.4%	15.3%	1.4%	5.5%		0.9%	10.5%	54.1%	2.4%	6.6%		
2016	**SOx (t)**	7.586	192	220			0	13	17.157	38	0	14	**25.221**
		30.1%	0.8%	0.9%			0.0%	0.1%	68.0%	0.2%	0.0%	0.1%	
	NOx (t)	12.909	678	693			3	8.098	67.828	364	272	70	**90.915**
		14.2%	0.7%	0.8%			0.0%	8.9%	74.6%	0.4%	0.3%	0.1%	
	PST (t)	224	999	87	282		54	688	3.783	155	377		**6.648**
		3.4%	15.0%	1.3%	4.2%		0.8%	10.4%	56.9%	2.3%	5.7%		
2017	**SOx (t)**	6.908	199	218			0	13	17.106	43	0	14	**24.501**
		28.2%	0.8%	0.9%			0.0%	0.1%	69.8%	0.2%	0.0%	0.1%	
	NOx (t)	11.265	682	640			3	7.795	67.178	371	280	70	**88.285**
		12.8%	0.8%	0.7%			0.0%	8.8%	76.1%	0.4%	0.3%	0.1%	
	PST (t)	193	1.004	87	301		56	686	3.751	153	365		**6.596**
		2.9%	15.2%	1.3%	4.6%		0.9%	10.4%	56.9%	2.3%	5.5%		

Table 3.12. SO_2, NO_x and PST (total suspended particles) emission tones by transport mode published by Balearic Islands Government (atmosfera.caib.es) in the period 2010-2017.

	2010						2017					
Sector	SOx (t)		NOx (t)		PST (t)		SOx (t)		NOx (t)		PST (t)	
Road Traffic	12	0.0%	9.220	10.2%	784	12.2%	13	0.1%	7.795	8.8%	686	10.4%
Maritime transport	12.118	49.7%	46.529	51.7%	2.720	42.3%	16.566	67.6%	57.007	64.6%	3.620	54.9%
Air Transport	395	1.6%	6.704	7.5%	67	1.0%	513	2.1%	8.838	10.0%	88	1.3%

Table 3.13. Number of flight passengers, ship passengers and tourists in the Balearic Islands in the period 2010-2018.

year	Flight passengers	Ship passengers	Tourists
2010	14.283.000	1.260.000	11.477.000
2011	15.414.000	1.618.000	12.436.000
2012	15.345.000	1.304.000	12.626.000
2013	15.484.000	1.538.000	13.050.000
2014	15.917.000	1.590.000	13.579.000
2015	16.477.000	1.963.000	14.011.000
2016	18.364.000	1.958.000	15.372.000
2017	19.592.000	2.115.000	16.340.000
2018	20.252.000	2.446.000	16.596.000

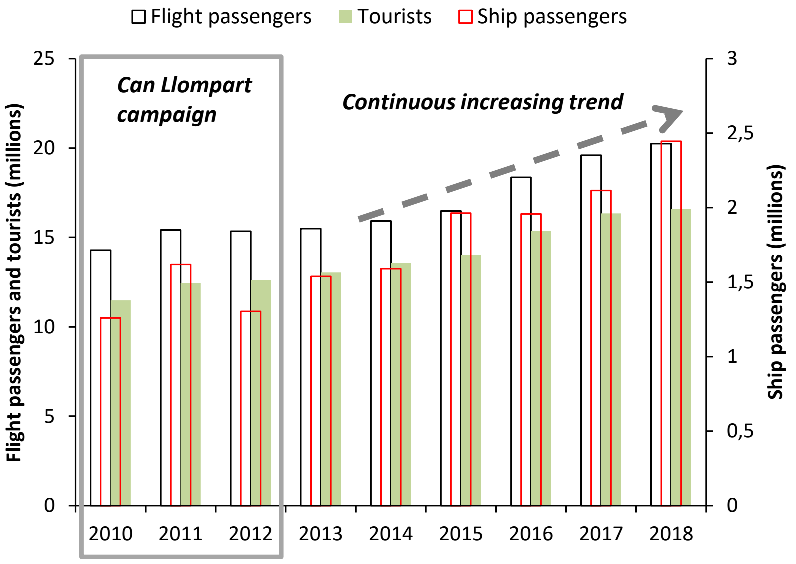


Figure 3.35. Number of flight passengers, ship passengers and tourists (in millions) in the Balearic Islands from 2010 to 2018.

Results of air quality trends over an urban, a suburban and a regional site in Mallorca are shown in Figure 3.36 and summarized in Table 5. A strong decrease of NO_2 and PM_{10} is observed in the urban area, which is not observed in the suburban site (Bellver) and is very slight over the regional background. Our hypothesis, already discussed in Cerro et al. (2015), suggests that a significant part of the decrease registered in Palma is associated to the combination of the improvement in vehicle's technology and the implementation of certain urban policies to improve air quality. However, the increasing arrival of tourists during this period has provoked the rise of emissions from various sources at the regional scale, including maritime, air and land transport. As a result, the concentrations of air pollutants all over the Islands are being homogenized progressively.

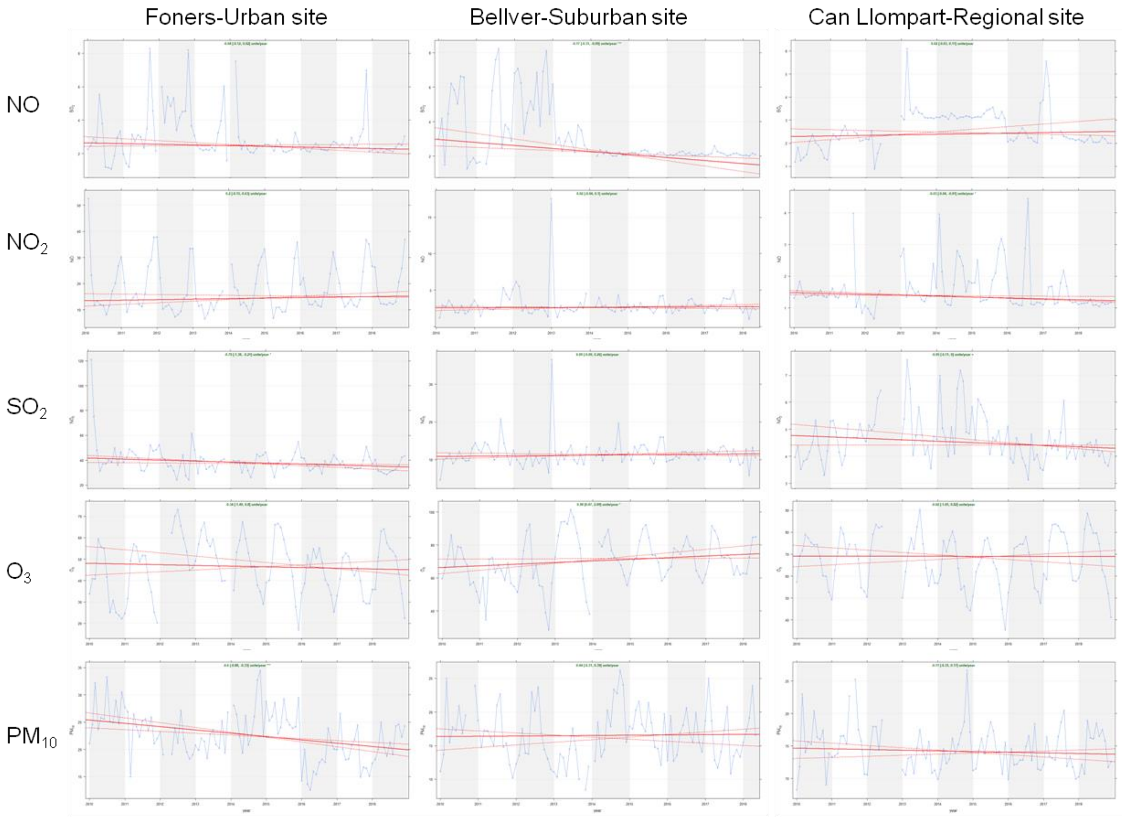


Figure 3.36. Monthly averages and Theil-Sen trend (2010-2018) for NO, NO_2, SO_2, O_3 and PM_{10} in (µg/m^3) at Foners (urban background), Bellver (suburban background) and Can Llompart (regional background) sites. Different concentration scales for specific pollutants.

Table 3.14. Theil-Sen trends (2010-2018) for NO, NO_2, SO_2, O_3 and PM_{10} in (µg/m^3 per year) at Foners (urban background), Bellver (suburban background) and Can Llompart (regional background) sites, and their 95% confident intervals (in brackets).

Trends 2010-2018 Δµg/m^3 year	NO	NO_2	SO_2	O_3	PM_{10}
Foners-Urban	0.20 (-0.15, 0.63)	-0.79 (-1.38, -0.21)	-0.04 (-0.12, 0.02)	-0.34 (-1.49, 0.80)	-0.60 (-0.88, -0.33)
Bellver-Suburban	0.02 (-0.04, 0.10)	0.09 (-0.09, 0.26)	-0.17 (-0.31, -0.09)	0.98 (0.07, 2.09)	0.04 (-0.31, 0.39)
Can Llompart-Regional	-0.03 (-0.04, -0.01)	-0.05 (-0.11, 0.00)	0.02 (-0.03, 0.11)	-0.02 (-1.05, 0.82)	-0.11 (-0.35, 0.17)

3.4. Discussion

Our study fulfils a deep knowledge gap concerning regional background aerosol composition and sources in the WMED. Cerro et al. (2015) evidenced and interpreted interesting downward trends for ambient concentrations for most of atmospheric pollutants (with the exception of O_3) over the Balearic Islands in the period 2000-2013, more pronounced at urban sites (1.0 µg/m^3 annual PM_{10} decrease) than at the regional background (0.6 µg/m^3 annual PM_{10} decrease), thus reflecting the efficiency of abatement measures adopted at the urban scale, but not as clear as the regional background decline. Future air quality regulations will need a complete study of the air pollution in general and the aerosol composition specifically in the isolated regional background of the WMED in order to propose realistic abatement strategies.

This is the first published work reporting long-term monitoring campaign on gases (SO_2, NO_2, O_3, NH_3), aerosol composition (PM_1 and PM_{10}), other pollutants (BC, PNC) and sources carried out over an insular site (the Balearic Islands) in the WMED. Comparable long term observations are available in the North-Eastern of Iberia Spain (Minguillón et al., 2015; Ripoll et al., 2014 and 2015) and rather similar can be found in the Lampedusa Island (Calzolai et al., 2015). Several extensive and short-term measurements are available in Corsica (Chrit et al., 2018; Michoud et al., 2017).

During the course of this 3-year study we had the opportunity to verify the strong variability of aerosol phenomenology in our region. On one hand, the Mediterranean climate is very irregular from one year to another. In our region, the effect of the North Atlantic Oscillation (NAO) is patent (Pey et al., 2013b) and it controls, for example, the arrival of air masses from North Africa or the Atlantic. The monitoring campaign of this work started under a very negative phase of the NAO in 2010 and finished under a moderate positive phase in 2012. On the other hand, anthropogenic emissions taking place in the Balearic Islands decreased from 2010 to 2012 at the local-to-regional scale. However, a progressive increase of PM, mineral dust and SO_4^{2-} was registered from 2010 to 2012, thus reflecting the strong effect of large-scale atmospheric circulation patterns. As a result, this 3-year study represents much better the so-called “annual average” than any single annual average in the period 2010-2012.

It is well known that the separation of individual emission sources of PM using receptor models such as PMF is not straightforward. It is also clear that source-splitting is trickier from a regional background database, where atmospheric particles from different sources are frequently mixed and ageing processes have affected, than from an urban background database, where the emissions from nearby sources are occurring and the effect of atmospheric ageing is less remarkable. The results obtained here reflect the impact of anthropogenic sources on PM_1 to explain almost 80% of the mass, while natural sources register the impact on the coarse fraction to represent around 50% of PM_{10}. While marine and mineral dust sources have been well separated (probably because the episodic nature of them), the anthropogenic ones are not. Tracers suggest two different factors both in PM_1 and PM_{10}: a mix of local-to-regional sources corresponding to emissions taking place in the Island (road traffic, shipping and power plant emissions), and a mix of regional-to-long range sources corresponding to aged aerosols from various sources transported to the Island (potentially mixed with regional emissions). The weight of both factors is very similar and they are preferentially encountered in the fine aerosol mode.Nevertheless, in order to retrieve more information about the impact of individual sources at regional background sites, the complementation with other measurements would be desirable. To give an example, in summer 2013, an enormous scientific effort was conducted in the WMED in the framework of several research projects, many of them aligned with ChArMEx (p.e. Ancellet et al., 2016; Schepanski et al., 2016 ; Michoud et al., 2017; Chrit et al., 2018 ; Guth et al., 2018 ; Cholakian et al., 2018). In the case of the Balearic Islands, a regional background site in the northernmost edge of the island was selected (at few kilometers from the CLL). Cerro et al., (2016) presented the results of a novel source apportionment approach combining the results retrieved from a classic PMF analysis on off-line samples, as in this study, together with the source apportionment outputs from AMS data. The results of that exercise revealed that oxygenated organic aerosols were associated with anthropogenic emissions of local (without SO_4^{2-}) and regional (enriched in SO_4^{2-}) origins.

To contextualize our campaign (2010-2012) in the current context we have analysed the overall trend of air quality parameters in the period 2010-2018. The main city in Mallorca, Palma, has experienced a significant air quality improvement. However, such improvement is not extensive to suburban areas or to the regional background. Probably, the considerable increase of the touristic sector, with enhanced emissions from air and maritime transport, has masked the progressive reduction from other sources. In light of this new reality, the forthcoming air quality plans should be based on a more integrated strategy rather than focalised on urban emissions or specific hotspots.

3.5. Conclusions

The present paper contributes to a better knowledge of air pollution dynamics in the WMED. Can Llompart, a regional background air monitoring site in the Balearic Islands, was selected for a detailed study on gaseous pollutants phenomenology, and aerosol composition and their sources.

Diurnal and seasonal variations of SO_2, NO_2, O_3, PM_{10}, $PM_{2.5}$ and PM_1 concentrations were studied. Typical patterns were found for most of these pollutants. However, some particularities were encountered:

- O_3 maximizes in late spring probably due to the combined effect of the elevated biogenic VOC emissions as precursors of O_3 together with the relatively low amount of O_3 suppressors (e.g. NO_x), which are clearly enhanced in summer due to tourist season;

- PM_{10} and PM_1 concentrations are usually aligned throughout the year. February and March are frequently affected by short and intense Saharan dust episodes. As a result of that, differences between the fine and coarse-mode concentrations are accentuated.

Gaseous pollutants and PM concentrations in Western and Central Mediterranean behave is a similar way all over this region. However, O_3 concentrations are slightly higher at continental sites (65-88 µg/m^3) than at insular locations (68-78 µg/m^3), which is probably due to the combined effect of recirculation of air masses across the continental coastline and the enhanced generation of biogenic VOCs from vegetation.

Intensive observation periods allowed us to:

- estimate the WMED background for black carbon (0.30 µg/m^3) and decoupling it from the contribution of nearby sources (0.25 µg/m^3);

- detect the occurrence of extreme photochemical nucleation bursts in spring at noon (up to 120.000 particles cm^{-3}), under clear-sky conditions and coinciding with the bloom of VOC emissions from biogenic sources.

A detailed PM_{10} and PM_1 chemical characterization has been done. Mineral dust, mostly supplied by Saharan dust outbreaks, followed by OM, sea spray and SO_4^{2-} prevail in PM_{10}, whereas OM, SO_4^{2-}, mineral dust and NH_4^+ control PM_1 composition.

The scarcity of long-term aerosol chemistry data across regional background areas in the Western and Central Mediterranean restricts some conclusions regarding an overall comparison. Nevertheless, a number of features can be highlighted: a) the two insular regions, Lampedusa and Mallorca, register the highest influence of sea salt and SO_4^{2-}, reflecting the impact of natural and anthropogenic emissions occurring in the Mediterranean Sea; b) OM and NO_3^- are clearly enhanced in the South-Alpine region and in Central Italy, indicating the strong influence of biomass burning in the first case, and urban emissions in the second case; c) mineral dust decrease northwards which is mostly connected to the African dust distribution in the region.

4 factors were extracted in PM_{10} and 3 factors in PM_1. In $PM_{10,}$ two of these factors are clearly anthropogenic: one attributed to regional-to-long range transport sources characterized by

secondary SO_4^{2-} influenced by coal-fired emissions (Power plant) and heavy oil (Shipping) combustion, mixed with road traffic emissions, and another attributed to local-to-regional sources more directly related to road traffic tracers. The other two factors in PM_{10} differentiate mineral sources and sea spray emissions. In PM_1, the same two anthropogenic factors as in PM_{10} were found, and a third natural mixed factor was obtained. Overall, natural sources exert most of the impact on the coarse-mode fraction, while most of fine-mode aerosols are linked to anthropogenic sources. Such anthropogenic influence is clearly enhanced in summer as a result of the combined effect of atmospheric stagnant conditions and the increased anthropogenic pressure in this region and all around the Mediterranean. Taking into account the atmospheric dynamics in this region of the globe, it is rather difficult to separate local-insular from pan-regional influences.

Our results indicate that the year-to-year increase in the number of tourists in Balearic Islands has a clear impact in air quality at the regional scale. Air pollution has diminished substantially in the main city, Palma, since 2010 but this has not occurred in the regional background, where the impact of regional-to-long range transport sources augmented enough as the local-to-regional sources decreased. Therefore, air pollution exposure between urban and rural inhabitants is getting comparable. Upcoming air quality mitigation actions should be built-up on a more integrated strategy, in which the Balearic Islands region as a whole needs to be consider.

3.6. Acknowledgements

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication. The authors also wish to thank D. C. Carslaw and K. Ropkins for providing the Openair software used in this paper (Carslaw, 2012; Carslaw and Ropkins, 2012), and the Paul Scherrer Institut for providing the SoFi (Source Finder) program based on PMF/ME-2, especially F. Canonaco and H. Prévôt.

The Spanish Agencia Estatal de Investigación (AEI – Spain) and the European Funds for Regional Development (FEDER – European Union) are gratefully acknowledged for financial support through CTQ2016-77155-R and CGL2015-68993-R projects (AEI/FEDER, UE). The RYC 2013-14159 grant is also acknowledged.

3.7. References

Aiken A.C., Decarlo P.F., Kroll J.H., Worsnop D.R., Huffman J.A., Docherty K.S., Ulbrich I.M., Mohr C., Kimmel J.R., Sueper D., Sun Y., Zhang G., Trimborn A., Northway M., Ziemann P.J., Canagaratna M.R., Onasch T.B. Alfarra M.R., Prevot A.S.H., Dommen J., Duplissy J., Metzger A., Baltensperger U., and Jimenez J.L.: *O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry*, Environ. Sci. Technol., 42, 4478–4485, 2008.

Alastuey A., Querol X, Aas W, Lucarelli F, Pérez N, Moreno T., Cavalli F., Areskoug H, Balan V, Catrambone M, Ceburnis D., Cerro J.C., Conil S., Gevorgyan L., Hueglin C., ImreK., Jaffrezo J.L., Leeson S.R., Mihalopoulos N., Mitosinkova M., O'Dowd C.D., Pey J., Putaud J.P., Riffault V., Ripoll A., Sciare J., Sellegri K., Spindler G., and Yttri K.E.: *Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013*, Atmos. Chem. Phys., 16, 6107–6129, 2016.

Amato F., Karanasiou A., Moreno T., Alastuey A., Orza J.A.G., Lumbreras J., Borge R., Boldo E., Linares C. and Querol X.: *Emission factors from road dust resuspension in a Mediterranean freeway,* Atmos. Environ. 61: 580–587, 2012.

Amato F., Alastuey A., Karanasiou A., Lucarelli F., Nava S., Calzolai G., Severi M., Becagli S., Gianelle V.L., Colombi C., Alves C., Custódio D., Nunes T., Cerqueira M., Pio C., Eleftheriadis K., Diapouli E., Reche C., Minguillón M.C., Manousakas M.I., Maggos Th., Vratolis S., Harrison R.M., and Querol X.: *AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five Southern European cities*, Atmos. Chem. Phys., 16, 3289–3309, 2016.

Ancellet G., Pelon J., Totems J., Chazette P., Bazureau A., Sicard M., Di Iorio T., Dulac F., and Mallet M.: *Long-range transport and mixing of aerosol sources during the 2013 North American biomass burning episode: analysis of multiple lidar observations in the western Mediterranean basin,* Atmos. Chem. Phys., 16, 4725-4742, 2016.

Barmpadimos I., Keller J., Oderbolz D., Hueglin C., and Prévôt A. S. H.: *One decade of parallel fine (PM2.5) and coarse (PM10–PM2.5) particulate matter measurements in Europe: trends and variability*, Atmos. Chem. Phys., 12, 3189–3203, 2012.

Becagli S., Anello F., Bommarito C., Cassola F., Calzolai G., Di Iorio T., di Sarra A., Gómez-Amo J.L., Lucarelli F., Marconi M., Meloni D., Monteleone F., Nava S., Pace G., Severi M., Sferlazzo D.M., Traversi R., and Udisti R.: *Constraining the ship contribution to the aerosol of the central Mediterranean*, Atmos. Chem. Phys., 17, 2067–2084, 2017.

Brown S.G., Hafner H.: *Multivariate Receptor Modeling Workbook.*Sonoma Technology Inc. Petaluma, CA. U.S.A. 236 pp, 2005. http://www.sonomatechdata.com/sti_workbooks/

Bytnerowicz A., Omasa K. and Paoletti E.: *Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective*, Environ. Pollut., 147, 438-445, 2007.

Calzolai G., Nava S., Lucarelli F., Chiari M., Giannoni M., Becagli S., Traversi R., Marconi M., Frosini D., Severi M., Udisti R., di Sarra A.,. Pace G., Meloni D., Bommarito C., Monteleone F., AnelloF., and Sferlazzo D.M.: *Characterization of PM10 sources in the central Mediterranean*, Atmos. Chem. Phys., 15, 13939–13955, 2015.

Canonaco F., Crippa M., Slowik J.G., Baltensperger U., and Prévôt A.S.H.: *SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data*, Atmos. Meas. Tech., 6, 3649–3661, 2013.

Castell-Balaguer N., Tellez L., Mantilla E.: *Daily, seasonal and monthly variations in ozone levels recorded at the Turia river basin in Valencia (Eastern Spain)*, Env. Sci. Pollut. R., 19(8), 3461–3480, 2012.

Cavalli F., Viana M., Yttri K.E., Genberg J., and Putaud, J.P.: *Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol*, Atmos. Meas. Tech., 3, 79–89, 2010.

Cerro J.C., Cerda V., Pey J.: *Trends of air pollution in the Western Mediterranean Basin from a 13-year database: A research considering regional, suburban and urban environments in Mallorca (Balearic Islands),* Atmos. Environ., 103, 138-146, 2015.

Cerro J.C., Pey J., Pérez N., Cerdà V., DeWitt H.L., Hellebust S., Elser M., Prévôt A.S.H., Temime-Roussel B. and Marchand N.: *Source apportionment of Organic Aerosol in a remote Mediterranean using a combination of offline and online approaches*. European Aerosol Conference 2016.

Cesari D., Donateo A., Conte M., Contini D.: *Inter-comparison of source apportionment of PM10 using PMF and CMB in three sites nearby an industrial area in central Italy,* Atmos. Res., 182, 282–293, 2016.

Cheng Y., Duan F-k., He K-b., Du Z-y., Zheng M., Ma Y-l.: *Sampling artifacts of organic and inorganic aerosol: Implications for the speciation measurement of particulate matter,* Atmos. Environ., 55, 229-233, 2012.

Cholakian A., Beekmann M., Colette A., Coll I., Siour G., Sciare J., Marchand N., Couvidat F., Pey J., Gros V., Sauvage S., Michoud V., Sellegri K., Colomb A., Sartelet K., Langley-DeWitt H., Elser M., Prévot A.S.H., Szidat S., and Dulac F.: *Simulation of fine organic aerosols in the western Mediterranean area during the ChArMEx 2013 summer campaign,* Atmos. Chem. Phys., 18, 7287-7312, 2018.

Chrit M., Sartelet K., Sciare J., Pey J., Nicolas J.B., Marchand N., Freney E., Sellegri K., Beekmann M., and Dulac F.: *Aerosol sources in the western Mediterranean during summertime: a model-based approach*, Atmos. Chem. Phys., 18, 9631–9659, 2018.

Colette A., Granier C., Hodnebrog O., Jakobs H., Maurizi A., Nyiri A., Bessagnet B., D'Angiola A., D'Isidoro M., Gauss M.,Meleux F., Memmesheimer M., Mieville A., Rouïl L., Russo F., Solberg S., Stordal F., and Tampieri F.: *Air quality trends in Europe over the past decade: a first multi-model assessment*, Atmos. Chem. Phys., 11, 11657–11678, 2011.

Cozic J., Verheggen B., Weingartner E., Crosier J., Bower K. N., Flynn M., Coe H., Henning S., Steinbacher M., Henne S., CollaudCoen M., Petzold A., and Baltensperger U.: *Chemical composition of free tropospheric aerosol for PM1 and coarse mode at the high alpine site Jungfraujoch*, Atmos. Chem. Phys., 8, 407–423, 2008.

Cusack M., Alastuey A., Pérez N., Pey J., Querol X.: *Trends of particulate matter (PM2.5) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010)*, Atmos. Chem. Phys., 12, 8341-8357, 2012.

DeWitt H.L., Pey J., Hellebust S., Temime-Roussel B., Mizzi A., Salameh D., Sylvestre A., Elser M., Pérez N., Cerro J.C., Jaffrezo J.L., Mocnik G, Prévôt A., Marchand N., *Comparison of the Sources of Organic Aerosol (OA) Using Aerosol Mass Spectrometry at Two Mediterranean Islands: Corsica and Mallorca*. AAAR Conference 2014.

EC (2011). *Commission Staff Working Paper 6771/11 establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources under the Directive 2008/50/EC on ambient air quality and cleaner air for Europe*, European Commission, Brussels, Belgium (accessed online on 12th November 2019 at: http://register.consilium.europa.eu/pdf/en/11/st06/st06771.en11.pdf).

Escudero M., Stein A., Draxler R.R., Querol X., Alastuey A., Castillo S. and Ávila A.: *Determination of the contribution of Northern Africa dust source areas to PM10 concentrations over Central Iberan Peninsula using the HYSPLIT model*, J. Geophys. Res. Atmos., 111, D06210, 2006.

Escudero M., Querol X., Pey J., Alastuey A., Pérez N., Ferreira F., Alonso S., Rodríguez S., Cuevas E.: *A methodology for the quantification of the net African dust load in air quality monitoring networks,* Atmos. Environ., 41, 5516–5524, 2007.

Eugster W., Moffat A. M., Ceschia E., Aubinet M., Ammann C., Osborne B., Davis P. A., Smith P., Jacobs C., Moors E., Le Dantec V., Béziat P., Saunders M., Jans W., Grünwald T., Rebmann C., Kutsch W., Czerný R., Moureaux C., Dufranne D., Carrara A., Magliulo V., Di Tommasi P., Olesen J. E., Schelde K., Olioso A., Bernhofer C., Cellier P., Larmanou E., Loubet B., Wattenbach M., Marloie O., Sanz M. J., Sogaard H., and Buchmann N.: *Management effects on European cropland respiration,* Agr. Ecosyst. Environ., 139, 346-362, 2010.

Galindo N., Yubero E., Nicolás J.F., Crespo J., Varea M., Gil-Moltó J.: *Regional and long-range transport of aerosols at Mt. Aitana, Southeastern Spain*, Sci. Total Environ., 584–585, 723–730, 2017.

Genestar C., Pons C., Cerro J. C., Cerdà V.: *Different decay patterns observed in a nineteenth-century building (Palma, Spain)*, Environ. Sci. Pollut. Res. 21(14): 8663-8672, 2014.

Gianini M.F.D., Gehrig R., Fischer A., Ulrich A., Wichser A., Hueglin C.: *Chemical composition of PM10 in Switzerland: an analysis for 2008/2009 and changes since 1998/1999*, Atmos. Environ., 54, 97–106, 2012.

Guth J., Marécal V, Josse B., Arteta J., and Hamer P.: *Primary aerosol and secondary inorganic aerosol budget over the Mediterranean Basin during 2012 and 2013,* Atmos. Chem. Phys., 18, 4911-4934, 2018.

Han H., Liu J., Yuan H., Zhuang B., Zhu Y., Wu Y., Yan Y., and Ding A.: *Characteristics of intercontinental transport of tropospheric ozone from Africa to Asia*, Atmos. Chem. Phys., 18, 4251–4276, 2018.

Harrison R.M., Pio C.: *Size differentiated composition of inorganic aerosol of both marine and continental polluted origin*. Atmos. Environ., 17, 1733–1738, 1983.

IPCC, Core Writing Team, Pachauri, R.K. and Reisinger, A. (Eds.). *Contribution of Working Group I to the Fith Assessment Report of the Intergovernmental Panel on Climate Change. Climate Change, the physical science basis (point 8.5)*. Geneva, Switzerland. pp 104, 2007.

IPCC, Core Writing Team, Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp., 2013.

Jorba O., Perez Garcia-Pando C., Spada M., Baldasano J. M., and Janjic Z.: *Modeling and evaluation of the global sea-salt aerosol distribution: sensitivity to emission schemes and resolution effects at coastal/orographic sites*, Atmos. Chem. Phys., 13, 11735-11755, 2013.

Karagulian F., Belis C. A., Borowiak A.: *Results of the European Intercomparison exercise for receptor models 2011-2012*. Part I. JRC Report EUR 25727 EN, 2012.

Lanz V.A., Alfarra M.R., Baltensperger U., Buchmann B., Hueglin C., and H. Prévôt A.S.: *Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra*, Atmos. Chem. Phys., 7, 1503-1522, 2007.

Michoud V., Sciare J., Sauvage S., Dusanter S., Léonardis T., Gros V., Kalogridis C., Zannoni N., Féron A., Petit J.E., Crenn V., Baisnée D., Sarda-Estève R., Bonnaire N., Marchand N., DeWitt H.L., Pey J., Colomb A., Gheusi F., Szidat S., Stavroulas I., Borbon A., and Locoge N.: *Organic carbon at a remote site of the western Mediterranean Basin: Sources and chemistry during the ChArMEx SOP2 field experiment*, Atmos. Chem. Phys., 17, 8837–8865, 2017.

Millán M.M., Salvador R. Mantilla E., Kallos G.: *Photo-oxidant Dynamics in the Mediterranean Basin in summer: Results from European Research Projects*, J. Geophys. Res. Atmos., 102, D7, 8811-8823, 1997.

Millán M. M., Sanz M. J., Salvador R., and Mantilla E.: *Atmospheric dynamics and ozone cycles related to nitrogen deposition in the western Mediterranean*, Environ. Pollut., 118: 167-186, 2002.

Minguillón M.C., Querol X., Baltensperger U., Prévôt A.S.H.: *Fine and coarse PM composition and sources in rural and urban sites in Switzerland: Local or regional pollution?,* Sci. Total Environ., 427–428, 191-202, 2012.

Minguillón M.C., Ripoll A., Pérez N., Prévôt A. S. H., Canonaco F., Querol X., and Alastuey A.: *Chemical characterization of submicron regional background aerosols in the western*

Mediterranean using an Aerosol Chemical Speciation Monitor, Atmos. Chem. Phys., 15, 6379–6391, 2015.

Müller, T., Henzing, J. S., de Leeuw, G., Wiedensohler, A., Alastuey, A., Angelov, H., Bizjak, M., CollaudCoen, M., Engström, J. E., Gruening, C., Hillamo, R., Hoffer, A., Imre, K., Ivanow, P., Jennings, G., Sun, J. Y., Kalivitis, N., Karlsson, H., Komppula, M., Laj, P., Li, S.-M., Lunder, C., Marinoni, A., Martins dos Santos, S., Moerman, M., Nowak, A., Ogren, J. A., Petzold, A., Pichon, J. M., Rodriquez, S., Sharma, S., Sheridan, P. J., Teinilä, K., Tuch, T., Viana, M., Virkkula, A., Weingartner, E., Wilhelm, R. and Wang, Y. Q.: *Characterization and intercomparison of aerosol absorption photometers: result of two intercomparison workshops*, Atmos. Meas. Tech., 4(2), 245–268, 2011.

Paatero, P. and Tapper, U.: Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, 1994.

Paatero, P.: *The multilinear engine – A table-driven, least squares program for solving multilinear problems, including the n-wayparallel factor analysis model*. J. Comput. Graph. Stat., 8, 854–888, 1999.

Pandolfi M, Gonzalez-Castanedo Y, Alastuey A, de la Rosa JD, Mantilla E, Sánchez de la Campa A, Querol X., Pey J., Amato F. and Moreno T., 2011. *Source apportionment of PM10 and PM2.5 at multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions*. Environmental Science and Pollution Research; 18:260–9.

Pandolfi M., Tobias A., Alastuey A., Sunyer J., Schwartz J., Lorente J. and Querol X.: *Effect of atmospheric mixing layer depth variations on urban air quality and daily mortality during Saharan dust outbreaks*. Sci. Total Environ., 494–495:283–289, 2014.

Pérez, N., Pey, J., Castillo, S., Viana, M., Alastuey, A., Querol, X.: *Interpretation of the variability of regional background aerosols in the Western Mediterranean*, Sci. Total Environ., 407, 527–540, 2008.

Pérez N., Pey J., Cusack M., Reche C., Querol X., Alastuey A. and Viana M., 2010. *Variability of Particle Number, Black Carbon, and PM10, PM2.5, and PM1 Levels and Speciation: Influence of Road Traffic Emissions on Urban Air Quality,* Aerosol.Sci. Tech., 44(7), 487-499, 2010.

Petzold A. and Schönlinner, M.: *Multi-angle absorption photometry – a new method for the measurement of aerosol light absorption and atmospheric black carbon*, J. Aerosol Sci., 35, 421–441, 2004.

Pey J., Querol X., Alastuey A.: *Variations of levels and composition of PM_{10} and $PM_{2.5}$ at an insular site in the Western Mediterranean,* Atmos. Res., 94, 285-299, 2009a.

Pey J., Pérez N., Castillo S., Viana M., Moreno T., Pandolfi M., López-Sebastián J.M., Alastuey A., Querol X.: *Geochemistry of regional background aerosols in the Western Mediterranean*, Atmos. Res., 94, 422-435, 2009b.

Pey J., Alastuey A., Querol X.: *PM_{10} and $PM_{2.5}$ sources at an insular location in the western Mediterranean by using source apportionment techniques,* Sci. Total Environ., 456-457, 267-277, 2013a.

Pey J., Querol X., Alastuey A., Forastiere F., Stafoggia M.: *African dust outbreaks over the Mediterranean Basin during 2001–2011: PM10 concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology*, Atmos. Chem. Phys., 13, 1395-1410, 2013b.

Pey J., Perez N., Cortes J., Alastuey A. and Querol X.: *Chemical fingerprint and impact of shipping emissions over a western Mediterranean metropolis: Primary and aged contributions*, Sci. Total Environ., 463-464, 497-507, 2013c.

Polissar, A.V., Hopke P.K., Paatero P., Malm W.C., and Sisler J.F.: *Atmospheric aerosol over Alaska 2. Elemental composition and sources*, J. Geophys.Res. Atmos., 103(D15), 19045-19057, 1998.

Polissar A.V., Hopke P.K. Poirot R.L.: *Atmospheric aerosol over Vermont: chemical composition and sources*. Environ. Science Tech., 35, 4604-4621, 2001.

Pope III C.A. and Dockery D.W.*: Health Effects of Fine Particulate Air Pollution: Lines that Connect,* J. Air & Waste Manage. Assoc., 56(6), 709–742, 2006.

Querol X., Alastuey A., Puicercus J.A., Mantilla E., Ruiz C.R., Lopez-Soler A., Plana F. & Juan R.: *Seasonal evolution of suspended particles around a large coal-fired power station: chemical characterisation,* Atmos. Environ., 32, 719–731, 1998.

Querol X., Alastuey A., Rodríguez S., Plana F., Ruiz C.R., Cots N., Massagué G., and Puig O.: *PM_{10} and $PM_{2.5}$ source apportionment in the Barcelona Metropolitan area, Catalonia, Spain*, Atmos. Environ., 35, 6407-6419, 2001.

Querol X., Pey J., Pandolfi M., Alastuey A., Cusack M., Perez N., Moreno T., Viana M., Mihalopoulos N., Kallos G., Kleanthous S.: *African dust contributions to mean ambient PM10 mass-levels across the Mediterranean Basin*, Atmos. Environ., 43(28), 4266-4277, 2009a.

Querol X., Alastuey A., Pey J., Cusack M., Perez N., Mihalopoulos N., Theodosi C., Gerasopoulos E., Kubilay N., and Kocak M.: *Variability in regional background aerosols within the Mediterranean*, Atmos. Chem. Phys., 9, 4575–4591, 2009b.

Querol X., Alastuey A., Pandolfi M., Reche C., Pérez N., Minguillón M. C., Moreno T., Viana M., Escudero M., Orio A., Pallarés M., Reina F.: *2001-2012 trends on air quality in Spain*, Sci. Total Environ., 490, 957-969, 2014.

Reff, A., Eberly, S.I., Bhave, P.V.: *Receptor modelling of ambient particulate matter data using Positive Matrix Factorization: review of existing methods,* J. Air & Waste Manage. Assoc., 57, 146-154, 2007.

Ripoll A., Pey J., Minguillón M. C., Pérez N., Pandolfi M., Querol X., Alastuey A.: *Three years of aerosol mass, black carbon and particle number concentrations at Montsec (southern~Pyrenees, 1570 m a.s.l.)*, Atmos. Chem. Phys., 14, 4279-4295, 2014.

Ripoll A., Minguillón M.C., Pey J., Pérez N., Querol X., and A. Alastuey A.: *Joint analysis of continental and regional background environments in the Western Mediterranean: PM1 and PM10 concentrations and composition, Atmos.* Chem. Phys., 15, 1129-1145, 2015.

Rodríguez S., Querol X., Alastuey A., Viana M., Mantilla E.: *Events Affecting Levels and Seasonal Evolution of Airborne Particulate Matter Concentrations in the Western Mediterranean*, Environ. Science Tech., 37(2), 216-22, 2003.

Rolph, G., Stein, A., and Stunder, B.: *Real-time Environmental Applications and Display sYstem: READY,* Environ. Modell.Softw., 95, 210-228, 2017.

Samoli E., Stafoggia M., Rodopoulou S., Ostro B, Declercq C., Alessandrini E., Díaz J., Karanasiou A., Kelessis A., Le Tertre A., Pandolfi P., Randi G, Scarinzi C., Zauli-Sajani S., KatsouyanniK., Forastiere F.: *Associations between Fine and Coarse Particles and Mortality in Mediterranean Cities: Results from the MED-PARTICLES Project*, Environ. Health Persp., 121(8), 932-938, 2013.

Schembari C., Cavalli F., Cuccia E., Hjorth J., Calzolai G., Pérez N., Pey J., Prati P., Raes F.: *Impact of a European directive on ship emissions on air quality in Mediterranean harbours,* Atmos. Environ., 61, 661-669, 2012.

Schepanski K., Mallet M., Heinold B., and Ulrich M.: *North African dust transport toward the western Mediterranean basin: atmospheric controls on dust source activation and transport pathways during June–July 2013,* Atmos. Chem. Phys., 16, 14147-14168, 2016.

Seco R., Peñuelas J., Filella I., Llusià J., Molowny-Horas R., Schallhart S., Metzger A., Müller M., and Hansel A.: Contrasting *winter and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: the effect of local biogenic emissions*, Atmos. Chem. Phys., 11, 13161-13179, 2011.

Soler R., Nicolas J. F., Caballero S., Yubero E., Crespo J.: *Depletion of tropospheric ozone associated with mineral dust outbreaks*, Environ. Sci. Pollut. Res., 23(19):19376-19386, 2016.

Stafoggia M., Samoli E., Alessandrini E., Cadum E., Ostro B., Berti G., Faustini A., Jacquemin ., Linares C., Pascal M., Randi G., Ranzi A., Stivanello E., Forastiere F.: *Short-term Associations between Fine and Coarse Particulate Matter and Hospitalizations in Southern Europe: Results from the MED-PARTICLES Project*, Environ. Health Persp., 121(9), 1026-1033, 2013.

Stein A.F., Draxler R.R, Rolph G.D., Stunder B.J.B., Cohen M.D., and Ngan F.: *NOAA's HYSPLIT atmospheric transport and dispersion modeling system*, Bull. Amer. Meteor. Soc., 96, 2059-2077, 2015.

Ulbrich I.M., Canagaratna M.R., Zhang Q., Worsnop D.R., and Jimenez J.L.: *Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data,* Atmos. Chem. Phys., 9, 2891–2918, 2009.

WHO, 2005. Air quality guidelines global update 2005. *Report on a Working Group meeting*, Bonn, Germany.

WHO, 2013.*Review of evidence on health aspects of air pollution-REVIHAAP Project. Technical Report.* Bonn, Germany.

Chapter 4: Chemistry of dry and wet atmospheric deposition over the Balearic Islands, NW Mediterranean: source apportionment and African dust areas

This chapter corresponds to the Research Paper: *Chemistry of dry and wet atmospheric deposition over the Balearic Islands, NW Mediterranean: source apportionment and African dust areas*

José C. Cerro[1,2], Víctor Cerdà[1], Sandra Caballero[3], Carles Bujosa[4†], Andrés Alastuey[5], Xavier Querol[5], and Jorge Pey[6]

[1]Laboratory of Environmental Analytical Chemistry, Illes Balears University, Palma de Mallorca, 07122, Spain

[2]Laboratory of the Atmosphere, Govern Illes Balears, Palma de Mallorca, 07009, Spain

[3]Atmospheric Pollution Laboratory (LCA), Miguel Hernández University, Elche, 03202, Spain

[4]ENDESA, Palma de Mallorca, 07007, Spain

[5]Institute of Environmental Assessment and Water Research, IDÆA-CSIC, Barcelona, 08028, Spain

[6]ARAID-Instituto Pirenaico de Ecología - CSIC, Zaragoza, 50059, Spain

Published 24th July 2020 in Science of the Total Environment 747 (2020) 141187

Abstract

Wet and dry aerosol deposition samples were collected from September 2010 to August 2012 at a remote background site in the Mallorca Isle (Western Mediterranean). Ions and major and trace elements were determined in soluble and insoluble fractions. Temporal variations of chemical components are discussed and interpreted. The overall pattern associated to long-range-transport air masses is studied: Dry/Wet deposition ratios, charges and composition depend clearly on the meteorological scenario. E.g. Dry/Wet ratio is 1:1 when air comes from North Africa, in contrast to a 1:9 ratio under the mainland Europe influence.

Moreover, an innovating source apportionment study was conducted integrating both dry and wet deposition samples. Six sources were revealed, including marine aerosols (32%); two different mineral factors, African dust (15%) and regional dust (12%); two anthropogenic factors, one related to road traffic (8%) and another to regional sources (17%); and a mixed factor having biomass burning emissions and others sources (17%). Temporal variations and influence from long-range-transport air masses are also investigated.

Fertilization deposition trends have also been explored, observing nutrients settling, as well as nitrate and sulphate, due to their agricultural interest. An important peak during January-February 2012 is studied in depth.

Having in mind the strong impact of African dust on the global deposition budget, the analysis of elemental ratios between key dust components was investigated in order to identify major source areas affecting Western Mediterranean: Western Sahara, Algeria-Hoggar Massif and Tunisia-Libya. Differences among these regions are evident. E.g. the impact of industrial emissions is well-detected under outbreaks from Tunisia-Libya, with relatively high content of Ni and Pb.

4.1. Introduction

Most of the emitted elements to the atmosphere return to the surface through wet or dry deposition (WD or DD). In Europe, most of the atmospheric deposition occurs in the form of WD, but in southern European regions the role of DD can be even equally to WD (Castillo et al., 2017).

Dynamics controlling WD and DD fluxes are clearly different (Mészáros, 1999). The individual investigation of the wet and dry fractions contributes to a better understanding of the whole Earth cycles and the derivate effects.

The deposition of particulate matter might have a direct effect on the ecosystems by harming (pollutant deposition) or benefiting (nutrients deposition). The scavenging of atmospheric particles is the main process of the dissolved/particulate exchange in the surface waters of the Mediterranean Sea (Sarthou and Jeandel, 2001). Acidification is a major soil-forming process (Muhs et al., 2010; Stuut et al., 2009), thus, added to the acidifying deposition, makes it a significant environmental issue (Cecchini et al., 2019; Genestar et al., 2014). Furthermore, sediment cores from the deep Balearic Basin Sea provide evidence for the accumulation of Cd, Pd and Zn in the top few centimetres of the abyssal Mediterranean sea-bed (Angelidis et al., 2011).

Moreover, Southern Europe has been identified as a major Saharan dust receptor area (Rogora et al., 2004 and references therein). Dust areas affecting Western and Eastern sides of the Mediterranean are different (Guerzoni et al., 1999; Molinareli et al., 1995, 1996 and 1999), displaying a slightly different mineralogical composition. Some ratios have emerged as good indicators to discern the potential source area (Gelado-Caballero et al., 2012; Moreno et al., 2006; Scheuvens et al., 2013 and references therein), and the most common have been used in this study. Also Guieu et al. (2010) used typical Al ratios with respect to different anthropogenic tracers, such as Cd, Pb and Zn, to elucidate the contamination of mineral dust by Northern African emissions.

Atmospheric phenomenology over Islands is comparable to that occurring over sea and, therefore, the observed patterns can be better extrapolated than when monitoring over coastal areas in the continent. In this case, our observations from the Balearic Islands could be regarded as representative of the Western Mediterranean region.

From a 2-year monitoring campaign of wet and dry deposition, the goal of this research is to characterise atmospheric particulate matter deposition in the regional background site of Can Llompart (Cerro et al., 2020) in terms of aerosol fluxes and their chemical composition.

Generally, most of the available research focuses on a limited number of species: macronutrients such as P, N and S (Avila et al., 2012 and 2020; Izquierdo et al., 2012; Longo et al., 2014; Marty et al., 2012; Moon et al., 2014; Sanz et al., 2002); Guieu et al. (2010), focused on Al, Fe, Cd, Zn, Pb and P across the Mediterranean; Alastuey et al. (1999) and Calvo et al. (2010) studied SO_4^{2-}, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, K^+, Na^+ and NH_4^+; Jordi et al. (2012) studied Cu ecosystem inhibition effect; Castillo et al. (2017) investigated soluble species of dry and wet deposition discerning African dust events from others; and Desboeufs et al. (2018) and Bergametti et al. (1989) expanded their studies to mineral dust elements, anthropogenic tracers and nitrogen species at a remote coastal site on the west coast of Corsica; Vincent et al. (2016) and Fu et al. (2017) evaluated bulk deposition in several areas of the Mediterranean. Furthermore, the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) aims, among other objectives, deepening the knowledge of elementary cycles of gases and aerosols, with atmospheric deposition being one of the main axes of this network. In the Balearic Islands there is an EMEP station in the Menorca Isle, but it lacks of a regular monitoring program and with a limited number of chemical species.

This study expands to wet and dry deposition fluxes, chemical composition and sources, with a special focus on origin of the air mass. The impact of the long range transport and the influence of local-to-regional sources were assessed by a receptor modelling source apportionment analysis.

4.2. Methods

4.2.1. Monitoring site and sample collection

The monitoring station for atmospheric deposition sampling is the regional background site of Can Llompart (CLL) (39°50′16″N, 03°01′25″E, 45 m a.s.l.), located in the Isle of Mallorca (Balearic Islands, Spain). Details about the monitoring site are given in Cerro et al. (2020).

DD and WD samples were recorded separately by means of an ESM Andersen sampler. EN 15841 (Cd, Pb, As, Ni) standard was considered both for collection and determination.

Sampling mechanism

The ESM Andersen sampler consists of two polypropylene containers, 40 cm height and 29.14 cm diameter, placed in a robust device fitted with a rain sensor, which activates a mechanism when a rain event starts. In normal conditions, the DD container is open to receive atmospheric transfers, and the wet-deposition one is covered. The rain sensor activates the automatic mechanism, provoking the overturn of atmospheric deposition capture. At CLL, the instrument was located on the roof of the air quality monitoring site, at around 4 m above ground level.

Sampling, transport and preservation of the sample

In each field visit two clean containers were carried out to the site in order to replace the ones exposed. Those containing atmospheric deposition were covered with plastic film and carried to the laboratory to extract atmospheric deposition samples. The one corresponding to the dry deposition inputs was washed out with 250 ml of bi-distilled water and subsequently filtered onto a quartz fiber filter. The WD sample was also filtered following the same procedure, but in this case liquid volume was quantified and pH was measured. Containers were always changed at around midday local time.

Accordingly, up to four sub-samples were obtained for each sampling: 1) a DD filter (insoluble DD); 2) a DD aliquot (soluble DD); 3) only during precipitation periods, a WD filter (insoluble WD); 4) only during precipitation periods, a WD aliquot (soluble WD).

Insects or vegetative detritus were removed from the sample manually by using plastic tweezers. Once collected, samples were preserved in dark conditions in the fridge at 4ºC. Filtration took place in the following three days, and the soluble sub-sample was analysed in most cases in less than a week.

Filters were previously dried at 45ºC for 72h. Then they were allowed to temperate and stabilize in a desiccator during 24h, being thereafter weighed twice with a difference of 24h. After filtration the same procedure was applied. Filters were then preserved in cold, awaiting treatment for further analysis. Acceptance criterion of weighing was 0.1 mg.

Dry and wet deposition was sampled from 6th June 2010 to 22nd August 2012, delivering 58 dry and 40 wet deposition samples. Sampling frequency during the first 1.5 year varied between 7-15 days (in general, a weekly sampling interval was followed). Owing to human resources limitations, the last quarter of the campaign followed a 6-week sampling interval.

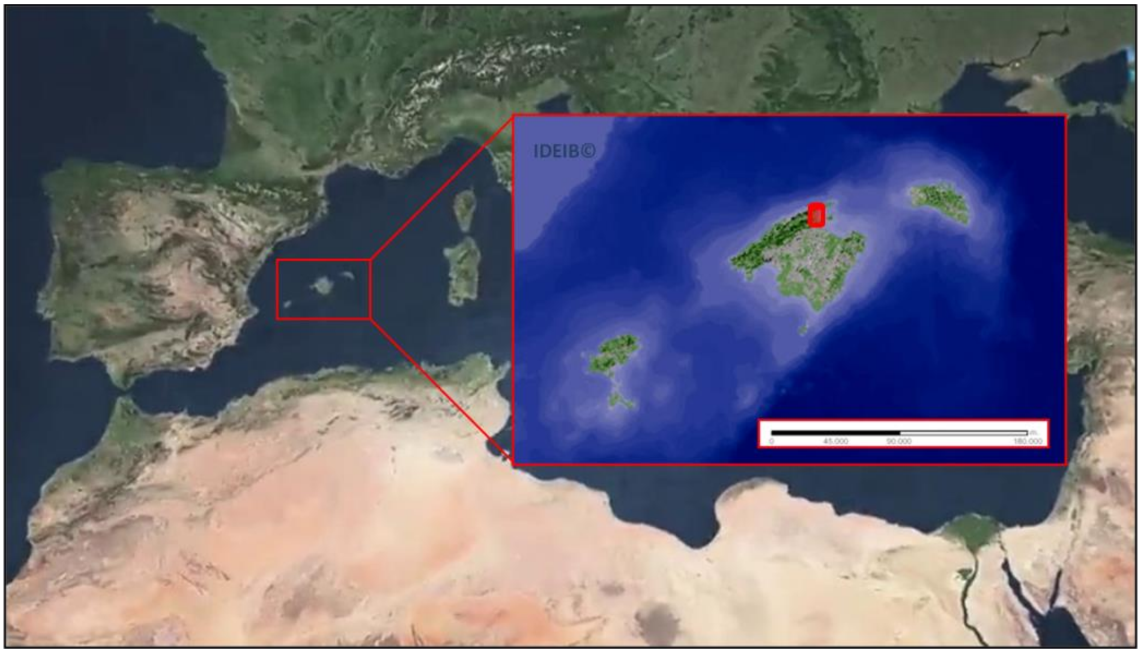


Figure 4.1. Satellite view of site location in the Balearic Islands, Western Mediterranean.

4.2.2. Analytical procedures

Aliquots were analysed by Ionic Chromatography (Dionex, DX-120) to determine water soluble ions SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+. CO_3^{2-} content was estimated from Ca^{2+} values considering that all Ca^{2+} is in the form of calcite, thus according to their stoichiometric relation. The sum of all these components recovers the amount of soluble atmospheric deposition. The quality of analytical data was checked by cation-anion balance.

Insoluble total deposition was obtained by gravimetric determination in both cases, WD and DD by weighing filters before and after sampling. Filters were analysed for major and certain trace elements following the procedures described in Querol et al. (2001). Briefly, each filter was completely digested in PTFA containers in a mixture of $HF:HNO_3:HClO_4$ acids, driven to complete dryness, re-dissolved in HNO_3 (5% concentration) and finally derived to an Inductively Coupled Plasma Atomic Emission Spectroscopy instrument (IRIS Advantage TJA solutions, THERMO). Concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, V and Zn were obtained. For each set of samples analysed, a number of blank filters (to remove the filter contribution) and an amount of the NIST 1633b coal fly ash (to assure the quality of the analytical determinations) were also analysed.

Data Quality Assurance

Quality assurance is based on the EN 15841 standard.

Reactive, laboratory and field blanks have been used. Reactive and field blank were used to calculate the detection limit (DL) as standard deviation of 10 reactive-field blanks multiplied by a factor of 2 (rounded t student for 95% of confidence). Laboratory blank were only used to prevent contamination of samples.

Finally DLs were rounded and jointly established for soluble and insoluble species in order to conduct the source apportionment (Table 4.1)(see section 4.2.5).

Main contributions to uncertainty, according to EN 15841 standard, are: field sampling; analysis; and handling (washing of containers…).

The major contribution should come from field sampling. To evaluate this uncertainty inter-laboratory participation and/or different collectors are required. It was not possible in our case.

Analysis uncertainties were previously calculated from standard deviation of sub-samples. Different environments were considered in order to have different levels of concentrations. Reproducibility conditions were taken into account.

EN 15841 standard recommends a fixed bias for the sampling uncertainty contribution (including handling), which could reach 20% in the case of some traces. In our case this uncertainty has been estimated in function of the quantities to recover. The less quantity the higher uncertainty, from 5% for the soluble species to the 12% for minor traces (Table 4.1).

Then, sampling uncertainty was quadratically combined with analysis uncertainty to obtain the combined typical uncertainty. Finally, a factor of 2 (t student) was considered to approach the expanded uncertainty for a level of confidence of 95% (Table 4.1).

		DL µgm^{-2}d^{-1}	Sampling Uncertainty %	Analysis Uncertainty %	Combined typical Uncertainty %	Expanded Uncertainty %
sol	Cl$^-$	20	5	3.3	6	**12**
	NO$_3^-$	20	5	3.3	6	**12**
	SO$_4^{2-}$	20	5	3.3	6	**12**
	CO$_3^{2-}$	20	5	3.3	6	**12**
	Na$^+$	20	5	3.3	6	**12**
	NH$_4^+$	20	5	3.3	6	**12**
	K$^+$	20	5	3.3	6	**12**
	Mg^{2+}	20	5	3.3	6	**12**
	Ca^{2+}	20	5	3.3	6	**12**
ins	Al	0.3	8	6.0	10	**20**
	Ba	0.3	12	9.0	15	**30**
	Ca	0.3	8	6.0	10	**20**
	Cu	0.3	12	9.0	15	**30**
	Fe	0.3	8	6.0	10	**20**
	K	0.3	8	6.0	10	**20**
	Mg	0.3	8	6.0	10	**20**
	Mn	0.3	12	9.0	15	**30**
	Na	0.3	12	9.0	15	**30**
	Ni	0.3	12	9.0	15	**30**
	P	0.3	12	9.0	15	**30**
	Pb	0.3	12	9.0	15	**30**
	S	0.3	12	9.0	15	**30**
	Sr	0.3	12	9.0	15	**30**
	Ti	0.3	8	6.0	10	**20**
	V	0.3	12	9.0	15	**30**
	Zn	0.3	12	9.0	15	**30**

Table 4.1. Detection Limits (DL) of total (TD), dry (DD) and wet (WD) deposition of soluble (sol) and insoluble (ins) species in mgm^{-2}yr^{-1}. Detection Limit (DL) are calculated for a week sampling period, considering 250 ml of washing volume. Table-right shows sampling and analysis uncertainties, combination of both, and expanded uncertainty considering a t student factor of 2 (95% of confident) in %.

CLL site was also equipped with online air quality monitors for the measurement of the levels of gaseous pollutants and size-resolved aerosol fractions (PM$_{10}$, PM$_{2.5}$ and PM$_1$) on hourly basis. Details on field monitoring and analytical procedures are given in Cerro et al. (2020).

4.2.3. Meteorological interpretations/Clustering

A combination of meteorological tools was used to identify the most relevant atmospheric conditions for each sampling interval along the campaign. These include the outputs of the NAAPs modeling for smoke, sulphate and desert dust surface concentrations from the NRL Monterey Aerosols Laboratory (https://nrlmry.navy.mil/aerosol/), the NASA-MODIS-satellite imagery (https://modis.gsfc.nasa.gov), and the HYSPLIT analysis (https://www.arl.noaa.gov/hysplit/m, NOAA, Stein et al., 2015) of integrated air mass back-trajectories. Back-trajectories were computed in the vertical velocity model (starting point at 12 UTC from LEPA coordinates (Lat.: 39.55; Long.: 2.73) run frequency-backwards for the whole sampled period plus 96 hours) at 500 m.a.s.l. Five clusters of air mass origins were considered for back trajectories as in Cerro et al. (2015 and 2020): Atlantic (AT), Mediterranean (MD) and European (EU) air mass origins, African dust outbreaks (AF), and a lack of advection scenario named Regional (REG). Taking into account the significance of African dust deposition in our region, together with their particular chemical fingerprints (Avila et al., 2003; Roda et al., 2002) special attention was paid to the incidence of these scenarios.

4.2.4. Data treatment

Real time precipitation was monitored, and accumulation compared with the WD volume collected. The precipitation sampled was in agreement with the recovered rainfall records.

Insoluble total deposition (TD) was obtained by gravimetric determination of the insoluble WD+DD, whereas soluble TD was assessed considering the amount of inorganic soluble species analysed and adding up an indirectly-estimated amount of water soluble organic carbon (WSOC) in PM_{10} for the same sampling site according to Cerro et al. (2020).

In order to estimate the insoluble fraction analysed, concerning the total mass, oxide weights were considered. The experimental SiO_2/Al_2O_3 ratio obtained during a specific monitoring campaign was 2.54, according to results published by Alastuey et al. (2016).

There are a variety of units to express deposition fluxes, with references to periods of days, weeks or years; masses of µg, mg, g, kg or even tonnes; and surfaces of m^2, ha or km^2. Here the yearly basis has been used for global results, referred to deposition per m^2, while the daily basis has been used for specific periods of the study.

4.2.5. Source apportionment

Positive Matrix Factorization, PMF (Paatero and Tapper, 1994), was used to identify and quantify the source contributions to atmospheric deposition samples, following the same data preparation as in Cerro et al., (2020). Detection limits (DL) and uncertainties were jointly established for soluble and insoluble species. Briefly, values under the DL have been replaced for half of DL value (Polissar et al., 1998). Species having more than 50% of data under the DL and with low signal-to-noise were not included in the analysis (Brown & Hafner, 2005). Initial uncertainties were considered depending on the analysis methodology, DL and coefficients of variation. A factor of 4 was multiplied to all uncertainty values corresponding to those species estimated from others, such as SiO_2 (from Al) and CO_3^{2-} (from soluble Ca^{2+}) in order to underrate them. Subsequently, a trial-and-error process was carried out to obtain the best model performance by evaluating the results according to Q values, the distribution of the residuals and the results from multiple regressions (Polissar et al., 2001). Finally, 9 soluble species (Cl^-, NO_3^-, SO_4^{2-}, $CO_3^{2-}{}_{estimated}$, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), and 17 insoluble species (Al, $SiO_{2\text{-}estimated}$, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, V, Zn) were included in the PMF analysis. To run the PMF software, each sampled included the soluble and insoluble fraction for WD and DD. A matrix having 26 elements or compounds and 98 samples (58DD+40WD) was used.

PMF solutions considering from two to seven factors were evaluated. Finally, the six-factor result was selected as the best meaningful solution, coupling a good agreement with our understanding of source identification and the indicator of PMF optimization.

4.2.6. Case studies

High deposition episodes of specific interest were selected for a more detailed interpretation. The first case study focuses on the extremely high dust deposition event occurring during the main African dust outbreak (AF) in March 2011. The second case study verses on the deposition of nutrients (N-$NH_4^+{}_{sol}$, P_{ins}, $K^+{}_{sol}$, Fe_{ins}) (Claustre et al., 2002; Desboeufs et al., 2018; Guerzoni et al., 1999; Guieu et al., 2010), and secondary aerosol components with agricultural interest (N-$NO_3^-{}_{sol}$, S-$SO_4^{2-}{}_{sol}$) (Pieri et al., 2010), throughout the campaign, with especial attention to the main peak occurred in January-February 2012.

4.2.7. African dust source regions

Prior studies have investigated the mineralogy and the elemental ratios of atmospheric dust to trace African dust source regions (Desboeufs et al., 2018; Gelado-Caballero et al., 2012; Marconi et al., 2014; Meskhidze et al., 2005; Morales-Baquero et al., 2013; Moreno et al., 2006; Scheuvens et al., 2013; Stuut et al., 2009; Marconi et al., 2014; Molinaroli et al., 1999; Moreno et al., 2006). The following ratios are very useful to split those contributions from other crustal sources: Ca_{total}/Al, K/Al, Mg/Al, Fe/Al, Na/Al, P/Al, (Ca_{total}+Mg)/Fe.

4.3. Results

4.3.1. Deposition Fluxes

Annual TD flux obtained from 6th June 2010 to 22nd August 2012, with the 58 sample pairs reached 22.8 $gm^{-2}yr^{-1}$, and it is mainly driven by WD (13.7 $gm^{-2}yr^{-1}$), with lower proportion of DD (9.1 $gm^{-2}yr^{-1}$) (Table 4.2). These results, however, highlight the relevance of DD in this region, much higher than in NE Iberia (Castillo et al., 2017). The atmospheric deposition collector used in this study lasts about a minute in changing from the DD-mode to the WD one and, consequently, part of the bellow-cloud scavenging occurred at the beginning of WD events is partially assimilated into the DD. This was not a critical point in most cases, but it became during an intense Saharan dust event. Accordingly, light rain, not significant enough to activate the rain sensor, left a large amount of dried rain droplet patches of mineral dust at the bottom DD collector.

Averaged and median daily fluxes reached 62 and 31 $mgm^{-2}d^{-1}$, respectively. The large difference is caused by the occurrence of very intense TD episodes, which enhance significantly the average over the median.

Total deposition was enhanced during the cold seasons, coinciding with precipitation periods and greater WD contributions (Table 4.2). Conversely, DD/WD was markedly higher in summer, influenced by the increase frequency of African dust and the magnification of regional dust emissions owing to the scarcity of precipitations (Pey et al., 2009), but also accounting for the increasing load of atmospheric pollution derived, among other causes, from the tourist season (Cerro et al., 2020). Actually, DD drives the global deposition recorded in summer, trebling the contribution from WD events. Around 80% of the

WD occurred in the cold seasons (autumn and winter), whereas DD was more evenly distributed over the year.

Table 4.2.A. Average of Total Deposition (TD), Dry Deposition (DD) and Wet Deposition (WD) annual fluxes in gm^{-2}yr^{-1}, and their soluble (sol) and insoluble (ins) fractions. The upper table shows seasonal values and the bottom table reflects values depending on the origin of air mass in mgm^{-2}d^{-1}: Atlantic (AT), Mediterranean (MD), European (EU), African (AF), and Regional (REG). Accumulated precipitation (Ac. Prec.) is reported in ml.

	TD	DD	sol_DD	ins_DD	WD	sol_WD	ins_WD	Ac. Prec.
(gm^{-2}yr^{-1})								(mm)
Total	22.8	9.1	5.0	4.1	13.7	12.6	1.1	984
(mgm^{-2}d^{-1})								(mm)
Spring	30.2	13.6	6.0	7.6	16.6	11.8	4.8	201
Summer	40.5	29.2	12.5	16.7	11.3	9.3	2.0	80
Autumn	93.1	30.5	24.2	6.3	62.6	60.2	2.3	374
Winter	88.6	25.8	12.2	13.6	62.8	59.3	3.5	329
(mgm^{-2}d^{-1})								(mm)
AT	32.4	8.6	5.9	2.7	23.7	22.9	0.8	82
AF	74.7	37.5	18.1	19.4	37.2	32.1	5.0	344
REG	33.7	18.3	11.0	7.4	15.4	13.6	1.8	185
MED	88.9	25.0	21.2	3.8	63.9	59.2	4.7	120
EU	101.4	11.9	9.3	2.7	89.5	88.0	1.5	253

$mgm^{-2}d^{-1}$		Total	spring	summer	autum	winter	AT	AF	REG	MED	EU
TD	AVERAGE	62.3	30.2	40.5	93.1	88.6	32.4	74.7	33.7	88.9	101.4
	DESVEST		20.6	36.1	111.9	117.7	28.7	106.9	39.7	109.9	92.5
	MIN	4.9	5.5	10.1	10.0	4.9	4.9	8.3	5.5	14.2	10.0
	MAX	501.1	85.5	164.8	501.1	436.5	110.8	501.1	188.9	303.2	332.4
DD	AVERAGE	24.7	13.6	29.2	30.5	25.8	8.6	37.5	18.3	25.0	11.9
	DESVEST		10.1	33.4	47.1	60.8	5.9	61.7	7.0	22.2	9.6
	MIN	0.0	4.3	0.0	6.0	2.7	0.0	3.8	5.5	7.9	2.7
	MAX	302.3	34.6	164.8	227.4	302.3	24.5	302.3	34.6	62.0	34.1
DD_sol	AVERAGE	13.6	6.0	12.5	24.2	12.2	5.9	18.1	11.0	21.2	9.3
	DESVEST		4.7	12.1	44.9	14.5	4.2	36.4	6.3	20.8	8.9
	MIN	0.0	1.7	0.0	2.9	2.1	0.0	1.7	2.6	3.9	2.1
	MAX	216.7	17.5	64.7	216.7	56.5	17.0	216.7	27.6	56.5	32.2
DD_ins	AVERAGE	11.1	7.6	16.7	6.3	13.6	2.7	19.4	7.4	3.8	2.7
	DESVEST		6.2	22.4	7.6	54.6	1.9	44.5	3.8	2.5	2.1
	MIN	0.0	2.5	0.0	0.9	0.5	0.0	0.6	0.9	0.9	0.5
	MAX	269.8	21.9	100.1	29.6	269.8	7.5	269.8	17.1	7.3	6.9
WD	AVERAGE	37.5	16.6	11.3	62.6	62.8	23.7	37.2	15.4	63.9	89.5
	DESVEST		16.0	21.7	84.4	88.0	30.0	68.1	34.9	89.2	96.0
	MIN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.2	0.0
	MAX	400.5	52.5	110.8	400.5	329.7	110.8	400.5	160.4	241.2	329.7
WD_sol	AVERAGE	34.4	11.8	9.3	60.2	59.3	22.9	32.1	13.6	59.2	88.0
	DESVEST		10.1	20.7	83.8	86.4	28.7	66.1	34.0	88.2	96.9
	MIN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.2	0.0
	MAX	400.1	27.5	105.5	400.1	329.6	105.5	400.1	160.2	235.9	329.6
WD_ins	AVERAGE	3.1	4.8	2.0	2.3	3.5	0.8	5.0	1.8	4.7	1.5
	DESVEST		8.2	2.7	3.4	13.0	1.4	11.2	4.6	3.7	3.7
	MIN	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0
	MAX	64.3	28.7	13.0	11.0	64.3	5.3	64.3	22.1	11.0	13.0

Table 4.2.B. Statistics for Total Deposition (TD), Dry Deposition (DD) and Wet Deposition (WD) fluxes in $mgm^{-2}d^{-1}$, and their soluble (sol) and insoluble (ins) fractions. Table shows statistics for recordings within the corresponding season (left) or air mass origin (right). Air mass origins are Atlantic (AT), Mediterranean (MD), European (EU), African (AF), and Regional (REG).

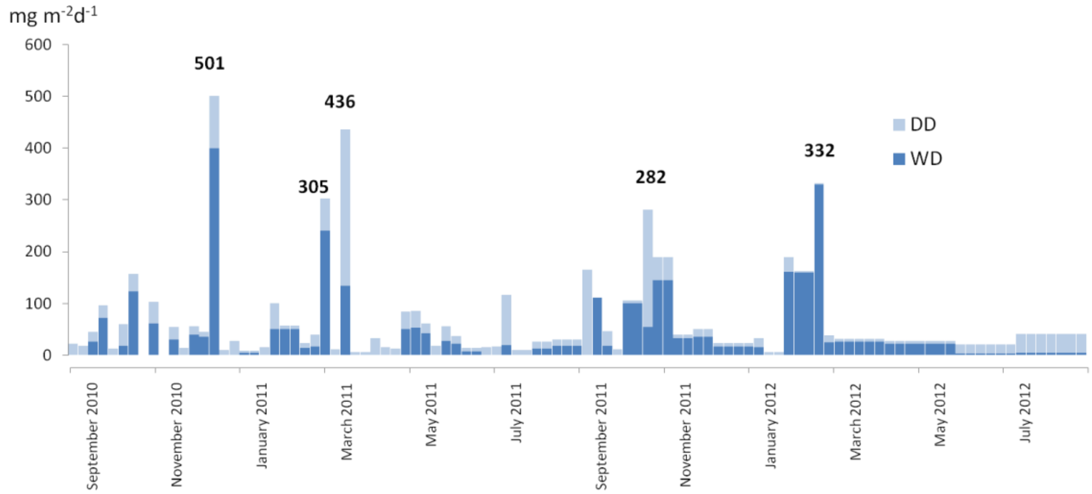


Figure 4.2. Temporal series of Dry Deposition (DD, light blue) and Wet Deposition (WD, intense blue) fluxes, accumulative values in mgm^{-2}d^{-1}.

Figure 4.2 shows that time trends are highly affected by the occurrence of specific peak events rather than by seasonal patterns, but the occurrence of these intense events yield the seasonal differences reported in Table 4.2. The episodic nature of these contributions have been already discussed by several authors (Avila et al., 2003; Castillo et al., 2017; Guieu et al. 2010; Loÿe-Pilot and Martin et al., 1996; Roda et al., 2002), which highlighted not only the control exerted by such short but intense events in the overall seasonality, but also in the inter-annual variations.

The origin of the air masses over CLL during each sampling period was investigated by calculating the HYSPLIT air back-trajectories and aerosols modelling maps reported in the methodology section. According to this evaluation, the influence of African air masses (AF) was the most frequent (42% of the total), followed by stagnant periods (25%), AT (15%), EU (12%) and Mediterranean (7%).

The most intense TD peak shown in Figure 4.2 was recorded during the sampling period 17th to 20th December 2010, reaching 501 mgm^{-2}d^{-1} (total amount of 1.50 gm^{-2}, 6.6% of the annual TD flux), coincident with an intense Saharan dust outflow. The second highest peak, but the most intense episode, as it corresponds to a longest sampling period (13th to 19th March 2011), again caused by an African dust outbreak, reaching 436 mgm^{-2}d^{-1}, and contributing 2.62 gm^{-2}, which constitutes 11% of the annual TD flux. The third peak episode was a Mediterranean cyclonic situation on 14th-21st February 2012. The average contribution was 332 mgm^{-2}d^{-1} (contributing with 2.32 gm^{-2}, 10% of the annual TD) and it was mainly driven by WD.

The lowest TD fluxes occurred under AT advections (Table 4.2), and during stagnation situations, typically reaching 32 to 35 mgm^{-2}d^{-1}.

Wet deposition pH ranged from neutral (6.8) to alkaline (8.9), probably due to the contribution of regional and long-range transport of neutralised ammonium sulphate and nitrate, and in a minor proportion to the neutralization of locally emitted acid by local and exogenous mineral dust (Levin et al.,1996).

4.3.2. Chemical composition: soluble and insoluble components

As shown in Table 4.2, WD is mainly water soluble. However, during DD contribution of the insoluble fraction may dominate. This is more obvious in summer and winter due to the higher impact of African dust outbreaks and lower rainfall. Table 4.3 summarizes mean, median and maximum values of the analysed species in WD and DD samples during the 2-years campaign.

Soluble components

Soluble components display the highest deposition rates for WD, with sea salt (SS) elements rising over the rest. Cl^- and Na^+ are the main components in WD, with 5.62 and 2.83 $gm^{-2}yr^{-1}$ mean fluxes, and peaks up to 207 and 120 $mgm^{-2}d^{-1}$, respectively. Mean and peak fluxes of SS in DD reached 2.02 and 0.98 $gm^{-2}yr^{-1}$, and 118 and 52 $mgm^{-2}d^{-1}$, respectively. After SS, NO_3^-, SO_4^{2-} and Ca^{2+} are also relevant. Thus, WD mean fluxes were 1.14, 2.25 and 0.61$gm^{-2}yr^{-1}$, with peaks up to 35, 100 and 21 $mgm^{-2}d^{-1}$, respectively. Mean and peak fluxes of these elements in DD reached 0.33, 0.47 and 0.45 $gm^{-2}yr^{-1}$, increasing up to 9.9, 18.8 and 16.8$mgm^{-2}d^{-1}$, respectively.

Insoluble components

Insoluble TD at CLL is clearly dominated by DD, and this, among the analysed species, by deposition of Ca (mean of 659 $mgm^{-2}yr^{-1}$), Al (345), Fe (203), Mg (155) and K(103). In insoluble WD, the same analysed elements but in a different order control the overall flux: Al (average of 127 $mgm^{-2}yr^{-1}$), Fe (77), K (39), Mg (31), and finally Ca (30). Interestingly, Ca and Mg are very relevant in DD samples (pointing to local-to-regional soil contributions), and much reduced in WD.

Regarding trace elements, those linked to mineral dust (Mn, Ti, P, Ba, and Na) display a very similar partitioning as Al and Fe, with WD/DD reaching 0.3-0.4. However, anthropogenic tracers such as V, Ni, Pb, Cu or Zn are shifted towards the WD (DW/DD=0.5-0.9).

Table 4.3. Total deposition (TD), dry deposition (DD) and wet deposition (WD), average (av), median (med) and maximum (max) fluxesof determined soluble (sol) and insoluble (ins) species in mgm^{-2}yr^{-1}(except for maximum values, which are expressed in µgm^{-2}d^{-1}). Ratios between WD and DD are also reflected. Values from this work and other indicated references.

		Our work: Can Llompart (N Mallorca Island)								Montseny (Barcelona)[1]		Le Casset (Southern French Alps)[2]		Corsica[2]		Ses Salines (Southern Mallorca Island)[2]		Lampedusa[2]		Frioul (Marseille)[2]	
		TD	DD			WD			ratio	TD	Ratio	TD	Ratio	TD	ratio	TD	Ratio	TD	ratio	TD	ratio
		Av	Av	med	Max	av	Med	Max	WD/DD	av	WD/DD	Av	WD/DD	av	WD/DD	Av	WD/DD	Av	WD/DD	av	WD/DD
sol	Cl^-	7640	2020	833	118257	5620	1393	206614	2.8	1030	4.6										
	NO_3^-	1470	326	218	9938	1143	558	35046	3.5	1621	3.3										
	SO_4^{2-}	2726	474	252	18799	2251	634	100492	4.7	1686	4.8										
	CO_3^{2-}	854	402	221	11116	451	83	28513	1.1												
	Na^+	3804	976	463	52277	2829	680	119755	2.9	543	5.5										
	NH_4^+	208	19	11	1097	189	108	6907	9.7	575	5.1										
	K^+	618	244	117	6468	375	101	13064	1.5	233	1.1										
	Mg^{2+}	489	127	57	6674	363	127	12966	2.9	145	2.1										
	Ca^{2+}	1063	450	294	16812	613	355	20999	1.4	2620	2.7										
ins	Al	472	345	110	26346	127	35	7448	0.4			405	2.4	778	7.3	1950	6.1	1304	1.2	377	2.4
	Ba	3.2	2.5	1.2	164	0.8	0.3	45	0.3												
	Ca	689	659	352	32510	30	11	660	<0.1												
	Cu	1.0	0.7	0.5	12.0	0.3	0.1	8.7	0.5			0.4	1.9	0.5	5.3	0.9	3.2	0.9	1.8	2.1	4.6
	Fe	280	203	89	14438	77	29	4358	0.4			217	2.6	494	8.1	1119	4.0	935	1.5	160	2.1
	K	142	103	37	8237	39	14	2419	0.4												
	Mg	186	155	75	7528	31	9	1710	0.2												
	Mn	4.2	3.1	1.2	242	1.1	0.3	74	0.4			2.6	2.2	4.8	10.1	10.7	4.3	10.2	1.9	2.3	2.0
	Na	32	23	13	1036	9	4	307	0.4												
	Ni	0.5	0.3	0.1	11.2	0.2	0.1	10.9	0.8			0.2	2.1	0.6	5.3	1.2	4.9	1.0	1.9	0.3	2.7
	P	19	13.9	7.7	457	4.7	2.3	143	0.3			12.5	3.8	9.9	10.1	19.3	4.0	51.6	2.0	51.6	1.5
	Pb	0.4	0.2	0.1	3.0	0.2	0.0	6.4	0.9												
	S	10	7.6	5.5	73	2.4	2.7	27	0.3												
	Sr	1.6	1.4	0.6	76	0.2	0.1	10	0.2												
	Ti	40	29	11	1650	11	4	502	0.4												
	V	0.7	0.4	0.1	16.9	0.3	0.1	9.3	0.7			0.6	2.3	1.3	7.3	2.4	4.3	2.1	1.4	0.5	2.3
	Zn	5.4	3.5	2.4	60	1.9	0.9	68	0.5			1.1	2.3	1.7	5.7	3.0	3.2	18.0	1.6	6.0	2.6

*Total N (sum of NO_3^-, NO_2^-, and NH_4^+)

[1] Castillo et al., 2017. From August 2002 to July 2003

[2] Fu et al., 2017.From 2011 to 2013.Only Saharan dust deposition episodes.

When comparing our data to other studies in nearby regions (Table 4.3), CLL displays higher TD fluxes for SS than those at Monstseny (40 km inland Barcelona), as marine influence decreases with altitude and distance to the sea (Castillo et al., 2017). On the other hand, deposition measurements during African dust outbreaks in the Western Mediterranean (Fue et al., 2017) recorded a high variability that can be appreciated in the Al, Fe or Mn average fluxes and in the WD/DD partitioning (Table 4.3). As an example, S Mallorca recorded the greatest Al average for AF scenarios, 1.95 $gm^{-2}yr^{-1}$, much higher than Al total deposition at CLL (northern Mallorca), 0.47 $gm^{-2}yr^{-1}$, which could be also connected to the large inter-annual variability of this source (Avila et al., 2003; Castillo et al., 2017; Guieu et al. 2010).

Regarding deposition of some anthropogenic traces (Pb, Ni, V, Zn), CLL reached TD values in a similar range of the observed in the Western Mediterranean (Table 4.3) and lower to the Eastern Mediterranean (Guieu et al., 2010). CLL, unlike the rest of the locations, presents higher affinity of insoluble fraction for DD. First of all, it could be related to the bias that our sampler system offers (see section 2.1.), but also to the relevance of local resuspension phenomena at CLL and the influence of regional and local sources, including a coal fired power plant, road traffic and a harbour (Cerro et al., 2020).

4.3.3. Source apportionment

4.3.3.1. PMF solutions

To our knowledge, this is the first source apportionment study integrating WD and DD components.

We evaluated different PMF solutions from two to seven factors, similarly to Cerro et al. (2020). A 6-factor solution was finally selected (Figure 4.3), coupling a good agreement with our understanding of source identification and the indicator of PMF optimization (Figures 4.4 and 4.5). The scaled residuals presented in Figure 4.4 display a Gaussian distribution around the 0 value, in general lower than 2, what reflects the consistence of the solution.

The six-factor solution was the most stable, with a sharper decrease in the $Q=Q_{exp}$ trend and a constant global minimum Q value among 100 random runs. In terms of the stability of the PMF analysis, all factors of the six-factor solution were reproduced in 100% of bootstrap runs, demonstrating that this solution was stable.

In general, low correlation among the six factors has been observed, indicating that they are sufficiently representative of different sources. However, the two mineral factors obtained in this study shared a number of similarities and, on certain occasions, varied in parallel.

The six-factor solution enables us to apportion the results among the six sources: 1) Marine or SS, characterised by Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, and partially by NO_3^- or Ca^{2+}; 2) Anthropogenic, including a number of road traffic tracers such as Cu and Zn (Amato et al., 2016), but also from other anthropogenic sources, such as Ni and Pb (Querol et al., 1998; Cesari et al., 2016); 3) African dust, related to Al, Ba, Fe, K, Mn, Na, Ti, V, and to a lesser extent by Ca^{2+}, Mg, or P, already identified by Pey et al. (2013) in a source apportionment study at Mallorca; 4) Biomass burning, associated to K^+ (Amato et al., 2016) and a smaller amount of NO_3^- and Zn; 5) Regional dust, characterised by Ca, Mg, P, Sr, and less by Ca^{2+}, Al, Ba, Ti (Pey et al., 2013; Querol et al., 2001); and 6) Regional pollution, correlated with NO_3^-, NH_4^+, Ca^{2+}, and SO_4^{2-}. Factor contributions are given in Table 4.4 and their temporal variability is depicted in Figure 4.6.

This source identification is based on the presence of tracer elements as well as on the ratio of the elements in the source profile. The source identification was also supported by the seasonal contributions of each source to the atmospheric fluxes shown in Table 4.4. The identification of factors was supported by previous works on source apportionment of aerosol particles in the western Mediterranean (Cerro et al., 2020; Pey et al., 2013).

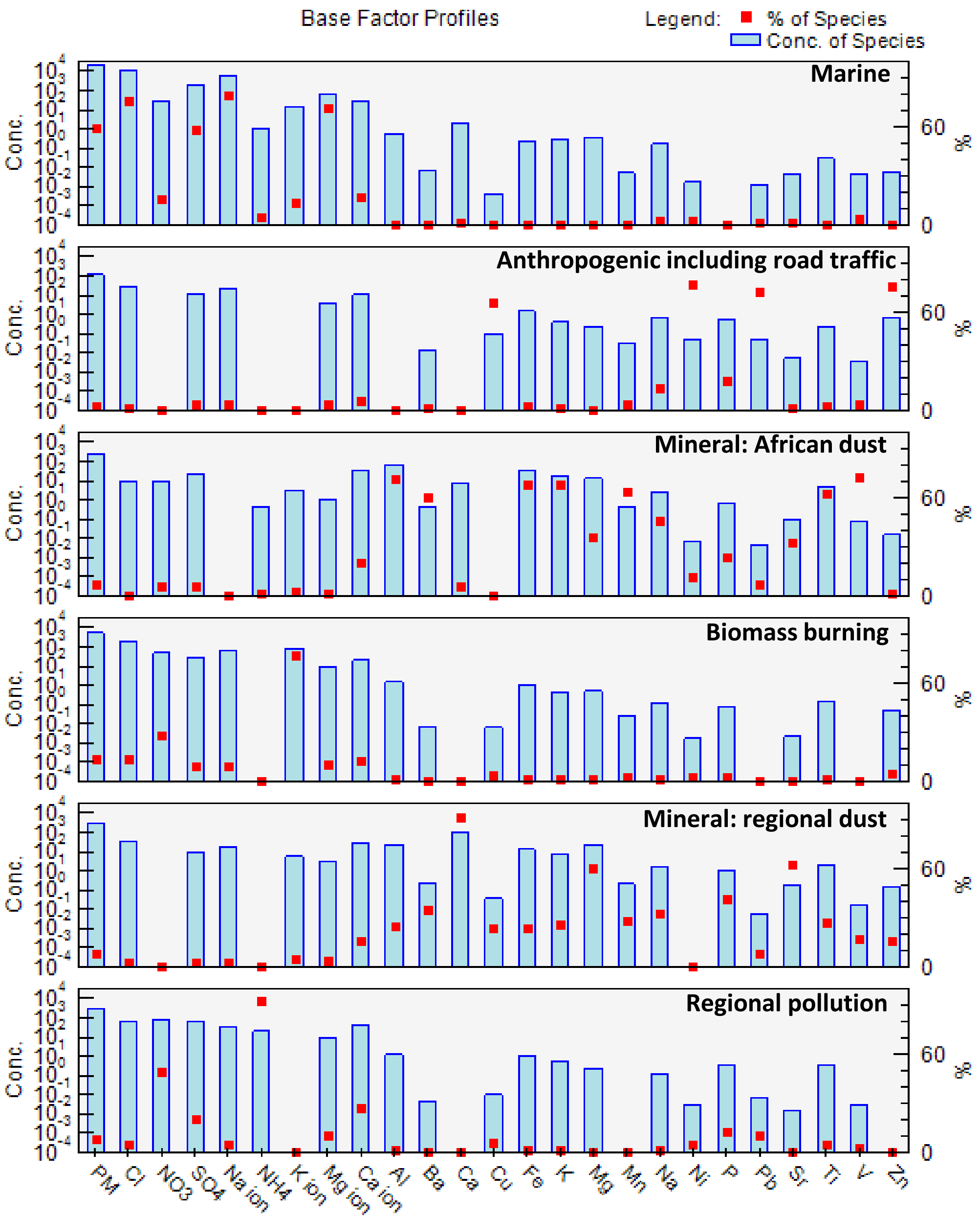


Figure 4.3. Deposition fluxes (DD and WD integrated) in $mgm^{-2}d^{-1}$ (with bars) and relative contribution (with dots) of chemical components for the 6-factor solution.

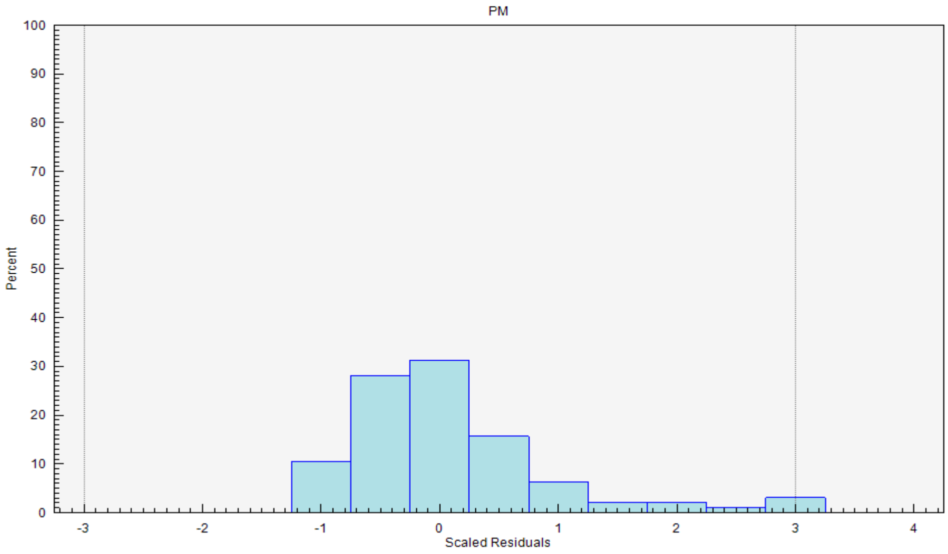


Figure 4.4. Distribution of scaled residuals

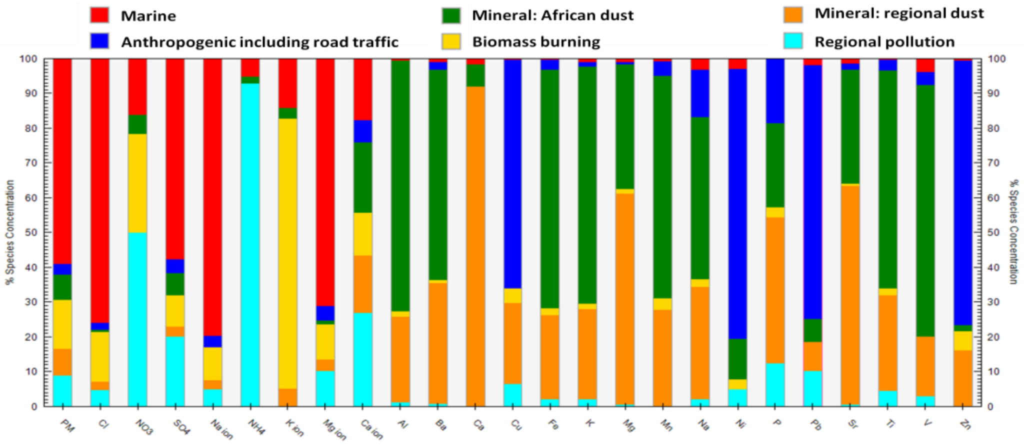


Figure 4.5. Mass distribution of each specie among the 6-factors solutions of the Positive Matrix Factorization.

4.3.3.2. Sources patterns

Table 4.4 shows average contribution of each source to DD and WD. Table 4.4 also reflects seasonality and results in function of the meteorological scenarios. It is well-known that the origin of air masses control geochemical variations in airborne PM in this region (Pey et al., 2009; Cerro et al., 2020). This analysis provides information regarding whether or not certain types of aerosols are preferentially deposited under prevailing meteorological conditions.

The marine component is a mass-relevant factor at CLL due to the proximity of the monitoring site to the coastline. The PMF solution splits the contribution of this factor as follows: 0.95 $gm^{-2}yr^{-1}$ for DD and 4.69 $gm^{-2}yr^{-1}$ for WD. In general, higher amounts of this source occurred in autumn-winter seasons, and much reduced in spring-summer (Table 4.4). Severe marine fluxes are registered (Figure 4.6). This was the case of the period 17th to 20th December 2010, when the deposition of marine aerosols reached 30 and 256 $mgm^{-2}d^{-1}$ in DD and WD, respectively. This episode was recorded under intense north-eastern winds and precipitations. Thus, the huge amount of marine aerosols could be derived from in-cloud (acting as CCN) and below-cloud scavenging processes of sea salt particles. It was already known that the emission of sea salt particles varies in parallel to the intensity of surface wind speed (O'Dowd et al., 1993). Overall, AT scenarios, associated with intense winds and important precipitation, are the main contributors to this source.

The mineral dust influence from Saharan dust is (Figure 4.6) is likewise important in DD (1.45 $gm^{-2}yr^{-1}$) and WD (1.17$gm^{-2}yr^{-1}$) (Table 4.4). Short but intense peaks stand out from the rest, especially in late winter and summer under the influence of Saharan dust outbreaks. The most significant event occurred from 13th to 19th March 2011, reaching daily fluxes up to 84 $mgm^{-2}d^{-1}$ for DD and 48 $mgm^{-2}d^{-1}$ for WD, but the most significant period in which African dust episodes were registered was spring-summer 2012. A specific treatment of March 2011 episode is displayed in section 3.4.1. Other summer-fall episodes, mainly recorded in 2011, registered concentrations significantly above average.

The local mineral contribution is directly related to the soil resuspension induced by natural and non-natural processes. The chemical composition of this mineral source clearly contrasts with the AF signature. In Mallorca, surface soils and geological terrains are strongly enriched in carbonates, which could explain the chemical nature of this factor, dominated by Ca, Mg, Sr and Ba. Nevertheless, its fingerprint also incorporates other mineral elements, probably indicating a mixture of mineral sources encountered at the regional scale. The contribution of this factor is strongly shifted to DD (1.98 $gm^{-2}yr^{-1}$), being almost negligible in WD (0.05 $gm^{-2}yr^{-1}$). The local mineral influence is recorded independently of the origin of the air mass, but main peaks are coincident with MED and REG scenarios.

Soluble K^+ is commonly associated with waste/biomass burning or wood combustion (Nava et al., 2015; Alastuey et al., 2016). Then this factor has been labeled as biomass burning, but other sources could be implicit. It accounts for 0.76 $gm^{-2}yr^{-1}$ to the DD and 2.24 $gm^{-2}yr^{-1}$ to the WD. The peak of this source deposition takes place during fall and winter seasons. This is aligned with the time in which agricultural burning is permitted, and contrast with other studies in the Mediterranean in which the peak of biomass is reached in summer due to intense forest fires (Bossioli et al., 2016). This factor is related to REG events, but also to AT that are normally related to precipitation, cold and windy events, again coincident with the available days for agricultural fires. Furthermore, it is partially related to EU events, suggesting that European PM pollution is enriched in biomass burning emissions.

The anthropogenic factor contributes in the same magnitude to DD and WD, being 0.84 $gm^{-2}yr^{-1}$ to the DD and 0.58 $gm^{-2}yr^{-1}$ to the WD. The homogeneous contribution of this factor claims for a permanent pollution background in this Mediterranean region (Guieu et al., 2010). A number of peaks were detected for this component (Figure 4.6), the most significant in spring 2011. The highest contribution of source coincided with the most intense AF event. According to the observations made by other authors (Gelado-Caballero et al., 2012; Guieu et al., 2002), part of this anthropogenic pollution could be transported from North Africa. However, before African dust particles reached CLL they were mixed with the anthropogenic inputs from Mallorca sources.

Regional pollution factor is the second major contribution of nitrogen and sulphur and it appears mixed with Ca^{2+} and slightly with P, and it indicates a clear combustion signature behind this source. The strong prevalence of this source under AT, REG and EU situations, and the chemical signature, suggest that coal-burning emissions from the nearby power plant, shipping emissions and those taking place in central and Eastern Europe may mix to explain this factor. It contributes 0.31 $gm^{-2}yr^{-1}$ to the DD and 2.63 $gm^{-2}d^{-1}$ to the WD, thus suggesting the role of these hygroscopic aerosols in forming Cloud Condensation Nuclei.

Table 4.4. Average contribution (Total) of each PMF factor to total (TD), dry (DD) and wet (WD) deposition in mgm^{-2}yr^{-1} and %, and values in function of the season and in function of air mass origin in µgm^{-2}d^{-1}: Atlantic (AT), Mediterranean (MD), European (EU), African (AF), and Regional (REG).

	Marine			Mineral: African dust			Mineral: regional dust			Biomass burning			Regional pollution			Anthropogenic including road traffic		
	TD	DD	WD	TD	DD	WD	TD	DD	WD	TD	DD	WD	TD	DD	WD	TD	DD	WD
Total mgm^{-2}yr^{-1}	5640	954	4686	2619	1453	1166	2030	1983	47	2992	756	2236	2931	305	2626	1414	837	577
%	32	15	41	15	23	10	12	32	0	17	12	20	17	5	23	8	13	5
µgm^{-2}d^{-1}																		
Spring	981	75	906	6005	1430	4575	3729	3659	70	1894	780	1114	6064	352	5713	2427	889	1538
Summer	2707	1727	980	8921	7589	1332	6700	6474	225	1788	1233	555	2088	798	1290	2075	1590	486
Autumn	24265	7103	17162	5845	1936	3909	6965	6850	115	13417	3541	9875	13890	1277	12613	6456	3780	2675
Winter	33535	1239	32295	6617	3341	3276	3876	3821	55	15837	2666	13171	11269	745	10524	4243	2387	1856
µgm^{-2}d^{-1}																		
AT	54764	1525	53239	2666	1336	1330	3155	3100	54	21524	2896	18628	13370	942	12428	4449	3386	1063
AF	5798	2036	3762	10334	6567	3767	6047	5857	190	2696	1317	1378	4921	1053	3868	3537	2248	1289
REG	15949	7221	8728	4702	3989	713	7266	7178	88	8585	4562	4023	5871	495	5376	4237	3085	1152
MED	6946	1982	4964	9008	8213	795	12178	11872	306	3950	956	2993	8191	99	8092	6375	2320	4055
EU	7375	450	6925	6348	484	5864	3958	3881	77	9519	868	8650	12000	762	11238	3475	951	2524

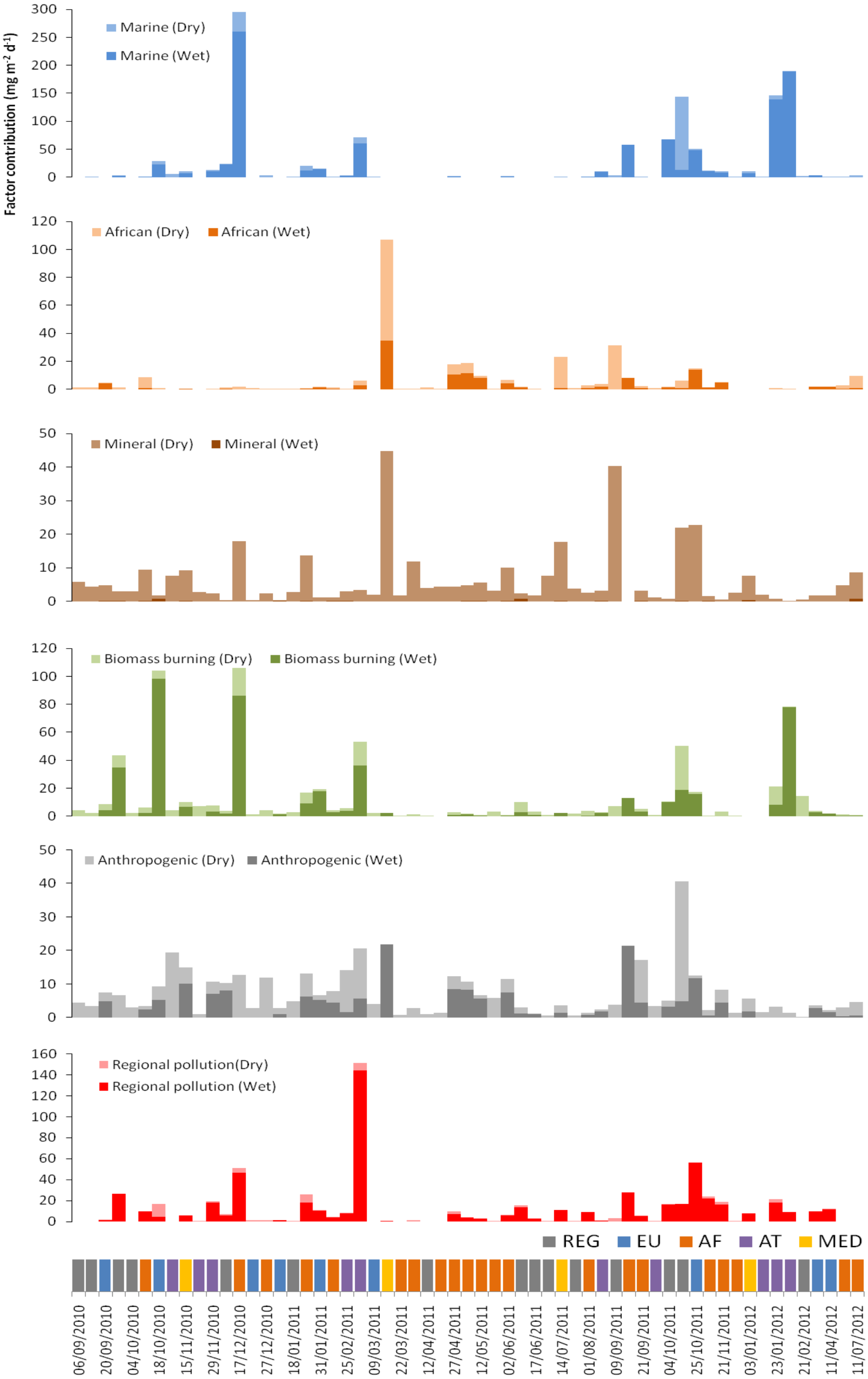


Figure 4.6. Time series of fluxes of the deposition factors (accumulative values, light colour for DD and intense colour for WD) in mgm^{-2}d^{-1}. Notice that X axis represents sample sequence instead of chronology.

These clear PMF outputs contrast with those obtained for PM_{10} and PM_1 at the same site for similar periods (Cerro et al., 2020), where anthropogenic sources became a mixture not easy to separate. Probably, the integration of DD and WD in the same calculation adds some extra variance to PMF runs which helps to separate sources.

4.3.4. Case studies

3.4.1. High impact African dust deposition events

Few but intense episodes contribute largely to annual TD (Loÿe-Pilot and Martin, 1996; Guieu et al., 2010). The most significant of these extreme events corresponded to a dust outbreak from Northern Africa sampled on 13th to 19th March 2011 (Figure 4.7). The outbreak started on 13th and finished on 16th March, with only few hours of slight rain. Therefore it can be said that real time peak of DD flux reached greater values than those of the composed sample for the whole period. But WD rate major peak surely multiply the average measured for this period. Mean fluxes of mineral dust during the episode reached 84 $mgm^{-2}d^{-1}$ for DD and 48 $mgm^{-2}d^{-1}$ for WD, corresponding to 20 % and 22% of the total mineral matter recorded during the 2-year campaign in WD and DD, respectively. This episode is also characterised by relevant deposition of anthropogenic traces. This is in agreement with other observations that previously indicated that AF dust episodes are accompanied by several transition and heavy metals (Scheuvens et al., 2013; Gelado-Caballero et al., 2012; Guieu et al., 2002).

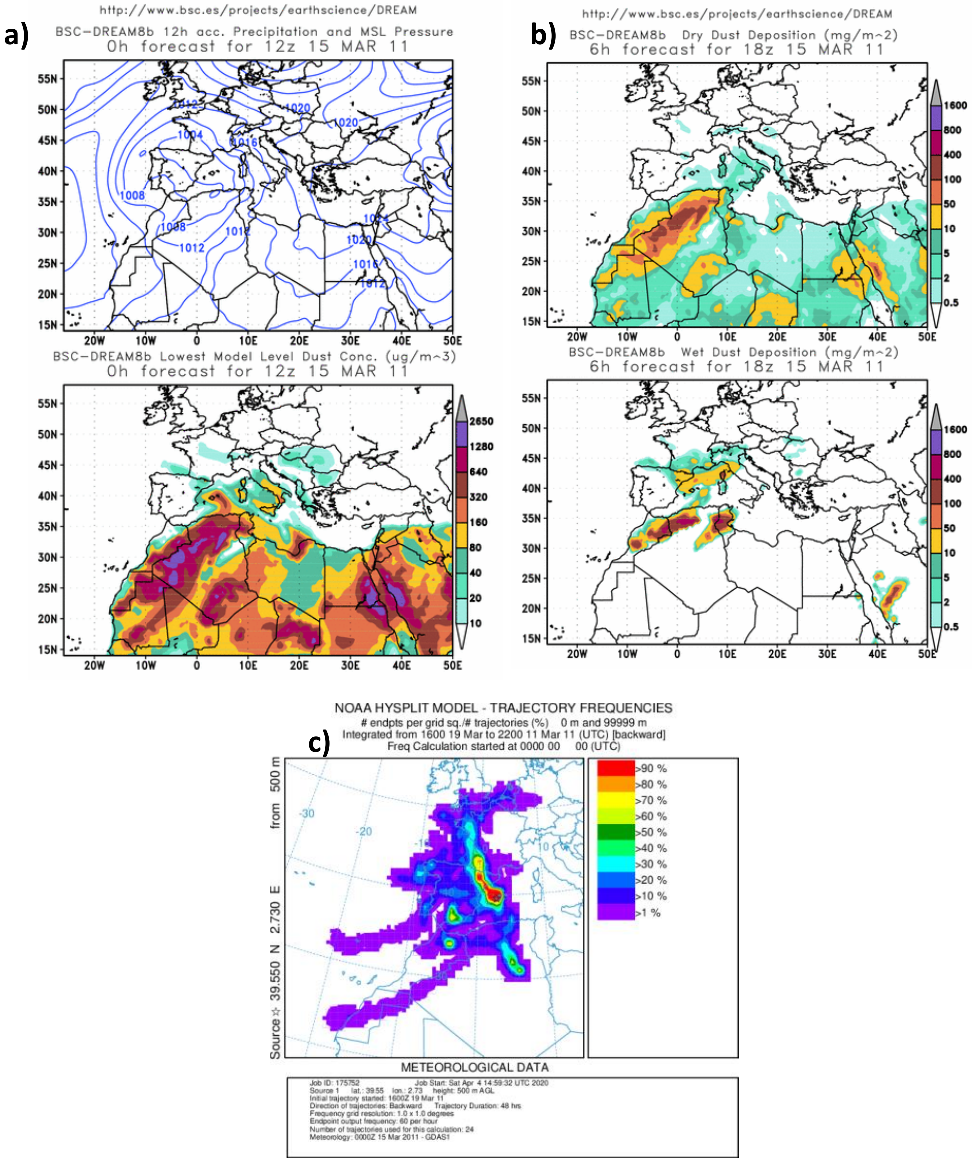


Figure 4.7. a) BSC-DREAM8b dust concentration map for 15th March 2011, reflecting also the meteorological situation; b) BSC-DREAM8b dust deposition maps for dry and wet deposition on 15th March 2011; c) HYSPLIT calculation of 48h backtrajectory frequencies for the period 11th-19th March 2011.

The analysis of dust concentration maps reveals a short but intense event affecting the Balearic Islands. Air mass back-trajectories and satellite images corroborate the influence of African air masses and the presence of dust aerosols over the Balearic Islands. However, the calculation of mineral dust in PM_{10} reached only 28 μgm^{-3} on 15th March (following the Escudero et al., 2007 procedure). The meteorological scenario, characterised by a deep low pressure system moving fast from the Atlantic towards the Mediterranean throughout the Iberian Peninsula, clearly favoured dust transport from Western Sahara and Mauritania (Hoggar Massif). This was the most intense event in 2 years of observations, but we recorded most of the DD. As stated above, the light rain observed during most of the event and the time lapse in changing from dry to wet mode could be the causes of disturbance in this case. Consequently, most of the referred dry-sample was actually related to wet-scavenging processes insufficiently intense to activate the collector sensor.

4.3.4.2. Nutrients, including secondary inorganic aerosols

The study of deposition of some species is relevant because they constitute a limiting nutrient for oceans and seas ($N\text{-}NH_4^+{}_{sol}$, P_{ins}, $K^+{}_{sol}$, Fe_{ins}) (Claustre et al., 2002; Desboeufs et al., 2018; Guerzoni et al., 1999; Guieu et al., 2010), or because they have agricultural interest for land crops ($N\text{-}NO_3^-{}_{sol}$, $S\text{-}SO_4^{2-}{}_{sol}$) (Moon et al., 2016; Pieri et al., 2010).

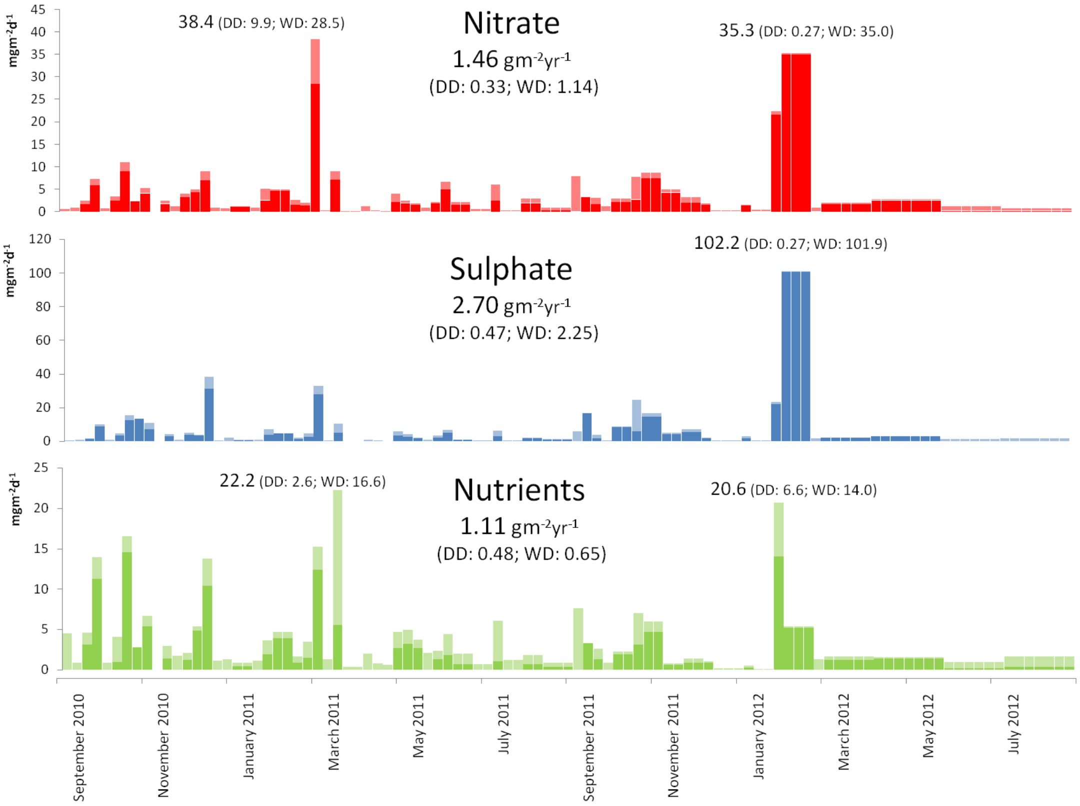


Figure 4.8. Nitrate, sulphate and nutrients ($N\text{-}NH_4^+{}_{sol}$, P_{ins}, $K^+{}_{sol}$, Fe_{ins}) time series, accumulative values in $mgm^{-2}d^{-1}$. Dry deposition (DD, light colour) and wet deposition (WD, intense colour).

Nitrate and sulphate deposition rates display rather similar patterns among them and akin to those of the marine factor (see section 3.3.2). These preferentially occur as WD, and in fall and winter (Table 4.5). Nitrate DD fluxes reached 0.33 $gm^{-2}yr^{-1}$ while 1.14 $gm^{-2}yr^{-1}$ in WD. Sulphate, DD and WD reached 0.47 and 2.21 $gm^{-2}yr^{-1}$ respectively. High TD peaks of these pollutants occurred in January-February 2012 (35.3 $mgm^{-2}d^{-1}$ for nitrate and 102.2 $mgm^{-2}d^{-1}$ for sulphate), with a dominant EU air mass transport (see below), and in February 2011 (38.4 $mgm^{-2}d^{-1}$ for nitrate, and sulphate fluxes).

Table 4.5. Nitrate, sulphate and nutrients (N-$NH_4^+{}_{sol}$, P_{ins}, $K^+{}_{sol}$, Fe_{ins}) average contribution (Total) of total (TD), dry (DD) and wet (WD) deposition fluxes in mgm^{-2}yr^{-1}, and values in function of air mass origin in µgm^{-2}d^{-1}: Atlantic (AT), Mediterranean (MD), European (EU), African (AF), and Regional (REG).

	TD			DD			WD		
	Nitrate	Sulphate	Nutrients	Nitrate	Sulphate	Nutrients	Nitrate	Sulphate	Nutrients
(mgm^{-2}yr^{-1})									
Total	1455	2699	1114	326	474	480	1143	2251	645
(µgm^{-2}d^{-1})									
AT	1723	3654	1648	338	511	503	1385	3144	1145
AF	2928	4962	3052	919	1746	1616	2009	3217	1435
REG	2607	2967	2893	896	1032	1498	1711	1934	1396
MED	9004	9960	4783	2399	2008	1298	6606	7952	3485
EU	11224	29138	4518	748	930	903	10476	28208	3615

Maximum TD fluxes of nitrate and sulphate arose under EU influence (11.2 and 29.1 mgm^{-2}d^{-1}, respectively, Table 4.5), with 93% and 97% as WD.

The deposition of nutrient species was rather regular throughout the study, displaying a number of events with fluxes highly exceeding average values (Figure 4.8). Most of the observed peaks matched those of nitrate and sulphate, and they are clearly controlled by the NH_4^+ concentration. The partitioning between DD and WD was similar (0.48 and 0.65 gm^{-2}yr^{-1}, respectively). These reached major records under EU and MED air mass transport, with TD ranging from 4.5 to 4.8 mgm^{-2}d^{-1}. As for most components, the lowest fluxes were obtained for AT air masses.

January-February 2012 nitrate and sulphate TD peak

High contributions of nitrate (35.3 mgm^{-2}d^{-1}) and sulphate (102.2 mgm^{-2}d^{-1}) to TD were measured from 31st January 2012 to 21st February 2012 (Figure 4.8), with these high fluxes being shifted toward WD (99% for both pollutants). This period is characterised by a mostly EU air mass transport alternating with short stagnation intervals (Figure 4.9).

During this period, a relatively high (79 mm) and alkaline (7.9 pH) rainfall (79 mm) was recorded. Nutrients reached high WD fluxes: 1.75 mgm^{-2}d^{-1} NH_4^+ and 3.45 mgm^{-2}d^{-1} K^+; whereas those of Fe and P were negligible in WD but high for DD (25.4 and 5.5 µgm^{-2}yr^{-1}, respectively). This period accumulated 40 % of the overall sulphate, 26 % of the total nitrate and 27 % of the recorded K^+. Definitively, secondary particles from long-range transport sources located in mainland EU contributed significantly to the observed deposition of nutrients, especially those of secondary origin although not discarded the contribution to Fe and P.

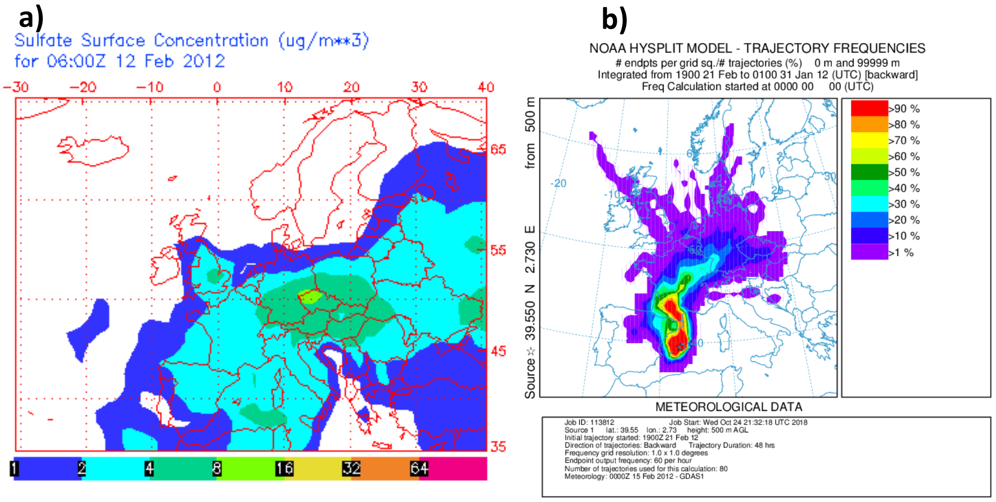


Figure 4.9. a) Map of modelled surface sulphate by NRL Monterey Aerosol in the day 12th February. b) HYSPLIT trajectory frequencies calculated for the period 31st January to 21st February 2012.

4.3.5. Sources of African dust

More than one third of the collected samples (23 out of 59) were taken under the influence of African dust outbreaks. To evaluate to what extent the different source regions of dust alter the chemical composition of the samples, a number of elemental ratios have been calculated and discussed (see section 2.6). Source areas of African dust were inferred from the interpretation of integrated back-trajectories for each monitoring period. Three main source areas affected the Balearic Islands during the monitoring campaign: the Western Saharan (WS), recorded 54 % of the AF events, the Algeria-Hoggar Massif (HM), observed 34 % of the AF episodes, and the Tunisia-Libya (LI), registered 12 % of the AF dust outbreaks. WS and HM sources got to Mediterranean mixed for 3 sample periods. WS corresponds to the Principal Source Area (PSA) 2 indicated by Scheuvens et al. (2013), HM to PSA1 and 3, and LI to PSA4 and partly PSA1. Figure 4.10 depicts three examples of integrated back-trajectories for each type of source-region.

Dust outbreaks from WS are frequently observed in autumn and winter, when low-pressure systems travel from the Atlantic towards the western coast of Iberia or the north-western African coast, causing the rapid transport of dust particles to the western Mediterranean. Wet deposition is common under this type of scenario. Mineral dust from Algeria-HM occurs preferentially in summer, in combination with stagnant atmospheric conditions at surface levels. Mineral dust is transported progressively, not in very high concentrations, and its fall-out occurs preferentially as dry-deposition. In some cases, extreme events of dust deposition integrate dust from different source areas, especially WS and HM. Actually, the most intense event registered during the campaign, from 13th to 19th March 2011, is a good example of this phenomenon. Finally, outflows from Tunisia-Libya reach the Balearic Archipelago after longer distance over the Mediterranean Sea, accumulating other sources of pollution such as shipping or petrochemical exhaust emissions. These scenarios are normally characterised by high humidity and frequently they cause intense rainfalls over the region under study.

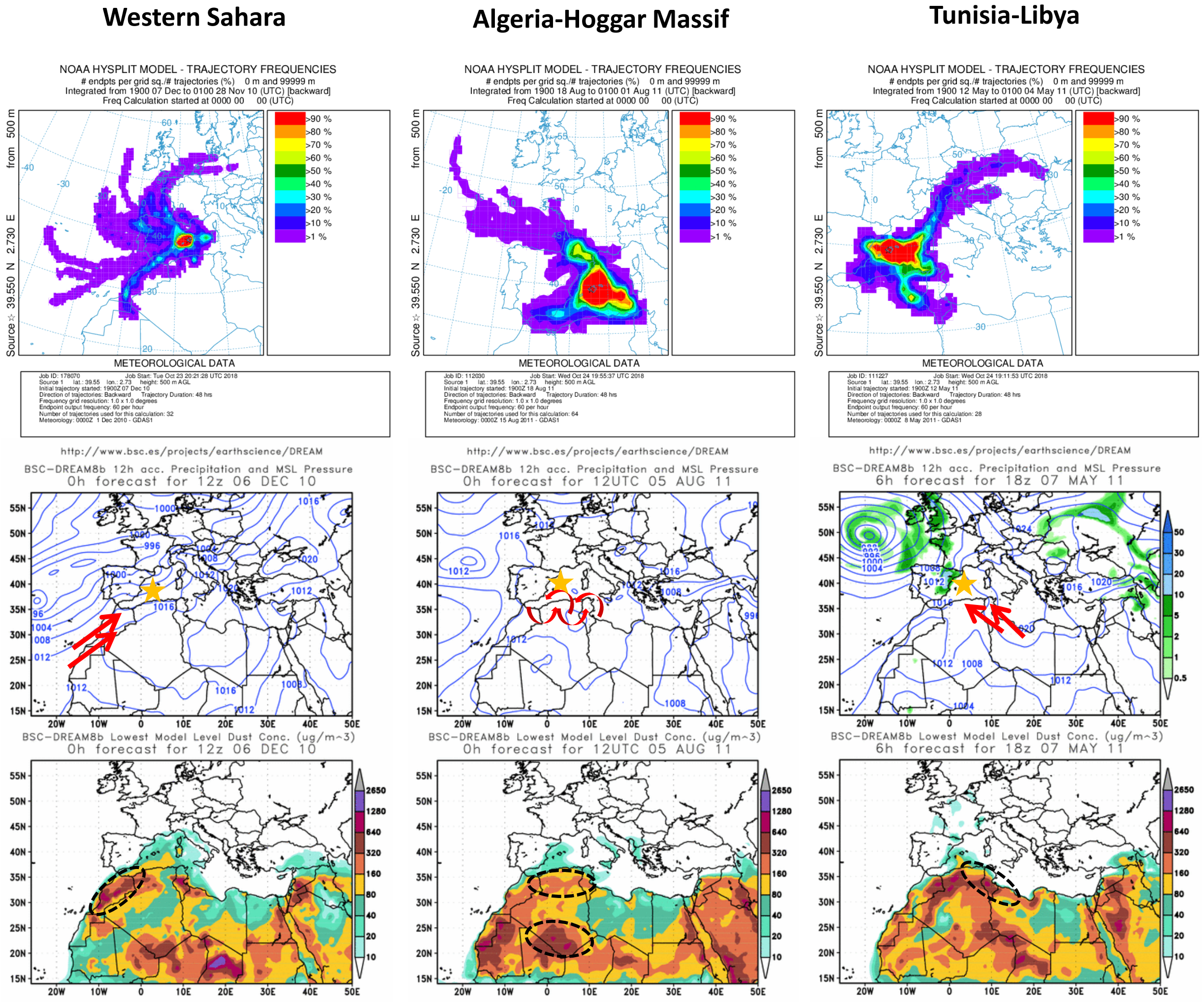


Figure 4.10. Top: integrated back-trajectories for a Western-Sahara, a Algeria-Hoggar Massif and Tunisia-Libya dust outbreak; bottom: BSC-DREAM8b dust concentration maps for specific days of each type of episode, with indication of main air-transport direction (red arrows) and the most active dust sources affecting the Balearic islands (dashed ellipses).

In order to investigate whether or not the arrival of dust particles from different regions alter the chemical composition of the mineral dust, Ca_{total}/Al, Mg/Al, Fe/Al, K/Al, Na/Al, P/Al and (Ca_{total}+Mg)/Fe ratios were calculated for each AF sampling period (Table 4.6). V/Ni and V/Pb ratios have been calculated in order to infer the contamination of the mineral dust in origin or during transport towards the Balearic Islands.

Table 4.6. Mean ratios obtained in this work according to source regions of dust in North Africa. Comparison with ratios reported in other studies. Deposition: Total Deposition (TD), Dry (DD), Wet (WD); Soil (S). Note that Ca includes the soluble and insoluble fraction.

Ratios	Ca/Al	Mg/Al	Fe/Al	(Ca+Mg)/Fe	K/Al	Na/Al	P/Al	V/Ni	V/Pb
This work (DD)									
W. Sahara	8,1	0,90	0,76	12,6	0,66	0,17	0,23	3,5	2,8
H. Massif	3,3	0,53	0,63	5,9	0,29	0,06	0,05	2,3	3,0
Libya	7,0	0,60	0,56	12,9	0,35	0,12	0,13	1,8	2,0
This work (WD)									
W. Sahara	9,6	0,41	0,78	8,1	0,49	0,20	0,07	2,6	2,9
H. Massif	1,8	0,26	0,60	0,8	0,30	0,04	0,01	1,3	3,1
Libya	4,7	0,22	0,60	3,2	0,31	0,06	0,04	0,9	1,3
Marconi et al (2014) (TD)									
Algeria-Tunisia	2,3-4,8	0,9-2,5	0,4-0,8	2,5-8,0					
Lybia	1,0-3,0	0,1-0,7	0,5-0,7	2,0-6,0					
S. Algeria				0,6-1,2					
S. Algeria-Sahel	<0,5								
Sub-sahara				<0.85					
Scheuvens et al (2013) (TD)									
PSA2: W. Sahara	4,0-6,8	0,8-0,9	0,6-0,7	7,3-12,6	0,36-0,41		0,02-0,03		
PSA3: H. Massif									
Scheuvens et al. 2013 (S)									
PSA2: W. Sahara	1,9-6,5	0,3-1,0	0,5-3,7	3,4-11,5	0,34-0,42	0,14-0,48	0,01-0,02		
PSA3: H. Massif	0,20-0,36	0,1-0,3	0,3-0,8	0,6-1,2	0,23-0,37	0,12-0,33	0,04-0,14		
Moreno et al. 2006 (S)									
W. Sahara	2.0-3,4	0,37-0,43	0,26-0,55	6,7-14,4	0,17-0,21	0,07-0,11		4,5-8,4	2,3-4,9
H. Massif	0,20-0,22	0,13-0,14	0,25-0,27	1,3	0,13-0,14	0,08-0,10		2,8-3,6	1,4-2,9
Chad	0,13-0,16	0,07-0,10	0,27-0,32	0,73-0,90	0,08-0,10	0,03-0,05		3,2-5,3	1,8-4,5

When regarding Ca_{total}/Al, Mg/Al and (Ca_{total}+Mg)/Fe ratios (Table 4.6) some differences can be appreciated for this study, both for DD and WD samples, and among samples from different origins. Dry deposition samples, mostly registered in summer, are enriched in Ca with respect to WD ones (higher Ca_{total}/Al and (Ca_{total}+Mg)/Fe occur), probably indicating a contribution of local soil resuspension. Western Sahara and LI samples display a more carbonate composition than HM as higher ratios are observed (Table 4.6). These patterns coincide with those reported by Moreno et al. (2006), Marconi et al. (2014) or Scheuvens et al. (2013). The ratios obtained in this study are highly comparable to those reported from these source regions. Likewise, K/Al, Na/Aland P/Al are higher for WS and LI air masses in comparison with HM (Table 4.6). These results are comparable to those reported in Scheuvens et al. (2013).

In order to detect the possible contamination of dust with anthropogenic pollutants in North Africa, the variations of V/Ni and V/Pb ratios have been studied. According to the results presented by Rodriguez et al. (2011), Pb, As, Ni and V may trace North African anthropogenic emissions, including those from petrochemical states. From the results by Moreno et al. (2006), higher V/Ni and V/Pb ratios occur in WS samples related to the enrichment of V by clay content, and slightly lower in HM soils. Influence from shipping emissions in the Mediterranean is expected to lead V/Ni ratio to 2.5 to 3.0 values (Alastuey et al., 2016). Our results follow these trends in the case of V/Ni (Table 4.6), although lower ratios in our case, indicating depletion in V and/or enrichment in Ni. These patterns are accentuated for LI air masses, for which V/Ni ratios from 0.9 to 1.8 were measured for DD and WD samples, what could be related to metallurgical activities or oil refining with a different V/Ni ratio. Likewise, V/Pb ratio decreases considerably from WS (2.8-2.9) towards LI samples (1.3-2.0), probably indicating a relative enrichment in Pb in air masses coming from this source region. These findings are akin to those reported by Rodriguez et al. (2011) (see Figure 15 from that work), who found a significant impact of industrial emissions in dusty air masses reaching the Izaña observatory. From that study, the calculated V/Ni and V/Pb ratios from “source 2” (anthropogenic emissions) are very similar to the obtained ratios from LI air masses in our study. This fact could demonstrate the relatively high contamination of such mineral dust by anthropogenic emissions released in that region.

4.4. Discussion

The atmospheric circulation is an efficient conveyor belt distributing pollutants and nutrients around the Globe. Relevance of atmospheric deposition in the global budget of nutrients and pollutants has been assessed in several studies. As an example, it is well known that Fe is the limiting element in the oceans when generating biomass. Atmospheric iron fertilization of sea will feed phytoplankton (trapping atmospheric CO_2) to finally be stored in marine sediments, becoming an important sink for greenhouse gases. According to our results, atmospheric deposition spreads out in the Western Mediterranean every year more than 200.000 Tn of Fe, contrasting with human macro-experiments, like the LOHAFEX project, that supposed a total artificial supply of 7.6 Tn.

Our work provides new information to the existing knowledge in this Southern European region. In the Balearic Islands, and in general over the Mediterranean Sea, dust DD is frequent during the warm season and it is equally relevant in terms of dust fluxes than red-rains. However, it is equally true that a single WD event may transfer the same amount of dust as the sum of all the warm-season DD events. In this line, we have observed that DD of Saharan dust carries, apart from mineral particles, a substantial amount of anthropogenic trace metals. Thus, the nutrient contribution is not constrained to Fe deposition but also other anthropogenic species. It has been described in a previous work (Cerro et al., 2020) that seasonal tourism in the Balearic Islands (which coincides with the African dust season) has a significant impact in terms of air quality impairment at the regional scale. Such a scenario is certainly increasing the amount of atmospheric nutrients in the atmosphere, but also the concentration of potentially toxic trace metals. It could happen that the extra contribution of anthropogenic nutrients is counteracted by the presence of enhanced trace metals such as Cu, Pb or Zn.

When regarding the origin of African dust travelling towards the Balearic Islands, three main source regions were found: the Western Sahara, the Algeria-Hoggar Massif and Tunisia-Libya. Our results have revealed significant chemical differences of dust arising from these regions, which are related to geological differences of source lands. Thus, Western sources are characterized by the abundance of Ca-minerals (especially calcite and dolomite) associated to widespread Cenozoic and Mesozoic calcareous deposits, while Eastern sources are fed by the weathering of the Paleozoic Craton, rich in igneous and metamorphic minerals (such as Na-Ca-K feldspars ormica-group silicates). Saharan dust might be evidently enriched in anthropogenic pollutants, especially that from Libya, as this study and those by Guieu et al. (2002) and Gelado-Caballero et al. (2012) demonstrated.

Our study lacks dedicated characterization of mineralogical abundances and is not dealing with the organic aerosol fraction. To go further in these subjects, the DONAIRE network (Pey et al., 2020), in which two sites in the Mallorca Isle take part, is regarding the inorganic and organic fraction, mineralogy, magnetic properties and bioavailability of the elements, overall to infer the impact on the ecosystem.

Positive Matrix Factorization calculations are traditionally used for airborne aerosol source identification. This study has revealed that the model was appropriate to separate sources from these low time-solved samples, even for TD. In our case the application of PMF has elucidated the weight of soil emissions at local and regional level, which is comparable to the input from Northern African dust. Likewise, although biomass burning emissions at the regional scale are scarce and mainly concentrated in certain periods of the year, this source is the third one in importance, and it is mostly the result of long-range transport processes from mainland Europe. Similarly, a significant amount of the regional pollution factor (the second one in importance) can be attributed to long-distance sources. Policies related to the Convention on Long-Range Trans-boundary Air Pollution would suppose reduction of acidification and pollutant traces and, at the same time, less deposition of certain secondary substances with fertilizing properties. On the other hand, the industrialization of Northern Africa and the sustained increase in construction and tourism will cause an increase in atmospheric pollution in that region. In insular areas such as the Balearic archipelago, the incidence of air masses from different origins must be considered since the amount of imported pollution is much higher than what is emitted locally, and their chemical nature varies significantly according to the region.

4.5. Conclusions

A comprehensive geochemical study of dry and wet atmospheric deposition at an insular regional background site in the Western Mediterranean is presented, where a number of soluble and insoluble species were analysed, among mineral, marine, nutrient or anthropogenic tracers. The total deposition flux for the sampling period (September 2011-August 2012) was 22.8 $gm^{-2}yr^{-1}$ (wet deposition: 13.7 $gm^{-2}yr^{-1}$; dry deposition: 9.1 $gm^{-2}yr^{-1}$). The most intense event was in spring 2011, with an average flux of 436 $mgm^{-2}d^{-1}$ during six days, amounting 2.62 gm^{-2}, and contributing 11% of the annual contribution.

The application of Positive Matrix Factorization to the integrated database including dry and wet deposition species has resolved six factors: marine, anthropogenic including road traffic, African dust, biomass burning, regional dust, and regional pollution. The overall anthropogenic contribution reached 42%: biomass burning (17%), regional pollution (17%) and the anthropogenic that includes road traffic (8%). Thereafter, among the natural sources, the marine factor was the main contributor (32%), followed by African dust (15%) and regional dust (12%), which is regularly observed, also when African dust occurs.

Marine aerosols and African dust variability is marked by several intense peaks normally accompanied by precipitation. While regional dust is omnipresent and is equally related to dry and wet deposition. Fluxes of anthropogenic sources are continuously observed, which urges us to consider the presence of a background baseline in the Mediterranean Sea. In general anthropogenic sources are related to Regional, Mediterranean and mainland Europe air mass transport, but also to the African ones, which suggest a clear affection by long-range transport sources from Eastern Mediterranean and continental Europe.

A specific investigation has been conducted to study trends on nutrients ($N\text{-}NH_4^+{}_{sol}$, P_{ins}, $K^+{}_{sol}$, Fe_{ins}) and components of agricultural interest ($N\text{-}NO_3^-{}_{sol}$, $S\text{-}SO_4^{2-}{}_{sol}$) deposition. Nitrate and sulphate depend on specific episodes near 100% driven by wet deposition that usually occur during fall or winter seasons, while the settling of nutrients is more constant throughout the year and more balanced between dry and wet deposition.

African dust origin has been studied coupling the interpretation of integrated back-trajectories and the variations of elemental ratios. Western Sahara, Algeria-Hoggar Massif, and Tunisia-Libya dust sources were recognized. Significant differences in elemental ratios were recognized, especially relevant for Ca_{total}/Al, K/Al, Mg/Al and $(Ca_{total}+Mg)/Fe$, in most cases related to the carbonate content in dust samples. Western Sahara and Tunisia-Libya are enriched in carbonates with respect to Algeria-Hoggar Massif. Furthermore, the evaluation of V/Ni and V/Pb ratios has revealed the enhanced contamination of mineral dust from Tunisia-Libya source with anthropogenic pollutants.

To conclude, our work displays separate results of soluble and insoluble species, for dry and wet deposition, while most of the investigations are focused on one of these fractions and/or consider solely bulk or wet deposition. In consequence, this study leads to a better understanding of Western Mediterranean deposition fluxes of mineral, marine, or anthropogenic sources, as well as nutrients and species of agricultural interest.

4.6. Acknowledgements

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication; the Barcelona Supercomputing Center for providing the images from NMMB/BSC-Dust or BSC-DREAM8b model (http://www.bsc.es/ess/bsc-dust-daily-forecast/); the Naval Research Laboratory for providing images from their aerosol observations and modelling; the NASA for their MODIS satellite imagery; and EPA PMF developers for providing an engine to calculate source apportionments.

The Spanish Agencia Estatal de Investigación (AEI – Spain) and the European Funds for Regional Development (FEDER – European Union) are gratefully acknowledged for financial support through CTQ2016-77155-R and CGL2015-68993-R projects (AEI/FEDER, UE). The RYC 2013-14159 grant is also acknowledged.

4.7. References

Alastuey A., Querol X., Chaves A., Ruiz C. R., Carratala A., Lopez-Soler A., 1999. *Bulk deposition in a rural area located around a large coal fired power station, northeast Spain*. Environmental Pollution, 106, 359–367.

Alastuey A., Querol X., Aas W., Lucarelli F., Pérez N, Moreno T., Cavalli F., Areskoug H., Balan V., Catrambone M., Ceburnis D., Cerro J.C., Conil S., Gevorgyan L., Hueglin C., ImreK., Jaffrezo J.L., LeesonS.R., Mihalopoulos N., Mitosinkova M., O'Dowd C.D., Pey J., Putaud J.P., Riffault V., Ripoll A., Sciare J., Sellegri K., Spindler G., and Yttri K.E., 2016. *Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013*, Atmos. Chem. Phys., 16, 6107–6129, 2016.

Amato F., Alastuey A., Karanasiou A., Lucarelli F., Nava S., Calzolai G., Severi M., Becagli S., Gianelle V. L., Colombi C., Alves C., Custódio D., Nunes T., Cerqueira M., Pio C., Eleftheriadis K., Diapouli, E., Reche C., Minguillón M. C., Manousakas M.-I., Maggos T., Vratolis S., Harrison R. M., and Querol X., 2016. *AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five southern European cities*. Atmos. Chem. Phys., 16, 3289–3309, https://doi.org/10.5194/acp-16-3289-2016, 2016.

Angelidis M.O., Radakovitch O., Veron A., Aloupi M., Heussner S., Priced B, 2011. *Anthropogenic metal contamination and sapropel imprints in deep Mediterranean sediments.* Marine Pollution Bulletin, 62(5), 1041-1052, May 2011, https://doi.org/10.1016/j.marpolbul.2011.02.030

Avila A. and Alarcón, 2003. *Precipitation chemistry at a rural Mediterranean site: Between anthropogenic pollution and natural emissions*. Journal of Geophysical Research Atmospheres, Volume 108, Issue D9. https://doi.org/10.1029/2002JD002565

Avila A., and Roda F., 2012. *Changes in atmospheric deposition and stream water chemistry over 25 years in undisturbed catchments in a Mediterranean mountain environment*, Sci. Total. Environ., 434, 18-27, doi: 10.1016/j.scitotenv.2011.11.062.

Avila A., Molowny-Horas R., Camarero L., 2020. *Stream chemistry response to changing nitrogen and sulfur deposition in two mountain areas in the Iberian Peninsula*. Sci. Total. Environ., 711, 134697.

Bossioli E., Tombrou M., Kalogiros J., Allan J., Bacak A.,Bezantakos S., Biskos G., Coe H., Jones B. T., Kouvarakis G.,Mihalopoulos N., and Percival C. J., 2016. *Atmospheric compositionin the Eastern Mediterranean: Influence of biomass burning during summer time using the WRF-Chem model*. Atmos. Environ., 132, 317–331, https://doi.org/10.1016/j.atmosenv.2016.03.011.

Brown S.G., Hafner H., 2005. *Multivariate Receptor Modeling Workbook*. Sonoma Technology Inc. Petaluma, CA. U.S.A. 236 pp. http://www.sonomatechdata.com/sti_workbooks/

Calvo A.I., Olmo F.J., Lyamani H., Alados-Arboledas L., Castro A., Fernández-Raga M., Fraile R., 2010. *Chemical composition of wet precipitation at the background EMEP station in Víznar (Granada, Spain) (2002–2006)*. Atmospheric Research 96 (2010) 408–420. doi:10.1016/j.atmosres.2010.01.013

Castillo S., Alastuey A., Cuevas E., Querol X. and Avila A, 2017. *Quantifying Dry and Wet Deposition Fluxes in Two Regions of Contrasting African Influence: The NE Iberian Peninsula and the Canary Islands.* Atmosphere 2017, 8, 86.

Cecchini G., Andreetta A., Marchetto A., Carnicelli S., 2019. *Atmospheric deposition control of soil acidification in central Italy.* Catena, Volume 182, November 2019, 104102, https://doi.org/10.1016/j.catena.2019.104102.

Cerro J.C., Cerda V., Pey J., 2015. *Trends of air pollution in the Western Mediterranean Basin from a 13-year database: A research considering regional, suburban and urban environments in Mallorca (Balearic Islands)*, Atmos. Environ., 103, 138-146, 2015.

Cerro J.C., Cerdà V., Querol X., Alastuey A., Bujosa C., Pey J., 2020. *Variability of air pollutants, and PM composition and sources at a regional background site in the Balearic Islands: Review of western Mediterranean phenomenology from a 3-year study.* Science of the Total Environment 717 (2020) 137-177.

Cesari D., Donateo A., Conte M., Contini D., 2016. *Inter-comparison of source apportionment of PM10 using PMF and CMB in three sites nearby an industrial area in central Italy*, Atmos. Res., 182, 282–293.

Claustre H., Morel A., Hooker S.B., Babin M., Antoine D., Oubelkheir K., Bricaud A., Léblanc K., Quéguiner B., and Maritorena S., 2002. *Is desert dust making oligotrophic waters greener?* Geophys.Res. Lett., 29, 10.1029/2001GL014056.

Desboeufs K., Leblond N., Wagener T., Bon Nguyen E., and Guieu C., 2014. *Chemical fate and settling of mineral dust in surface seawater after atmospheric deposition observed from dust seeding experiments in large mesocosms*. Biogeosciences, 11, 5581–5594, https://doi.org/10.5194/bg-11-5581-2014.

Desboeufs K., Bon Nguyen E., Chevaillier S., Triquet S., and Dulac F., 2018. *Fluxes and sources of nutrient and trace metal atmospheric deposition in the northwestern Mediterranean*. Atmos. Chem. Phys., 18, 14477–14492, 2018. https://doi.org/10.5194/acp-18-14477-2018.

Fu Y., Desboeufs K., Vincent J., Bon Nguyen E., Laurent B., Losno R., and Dulac F. *Estimating chemical composition of atmospheric deposition fluxes from mineral insoluble particles deposition collected in the western Mediterranean region*. Atmos. Meas. Tech., 10, 4389–4401, 2017

Gelado-Caballero M.D., López-García P., Prieto S., Patey M.D., Collado C., Hérnández-Brito J.J., 2012. *Long-term aerosol measurements in Gran Canaria, Canary Islands: particle concentration, sources and elemental composition*. Journal of Geophysical Research 117 (D3), D03304.

Genestar C., Pons C., Cerro J. C., Cerdà V., 2014. *Different decay patterns observed in a nineteenth-century building (Palma, Spain)*, Environ. Sci. Pollut. Res. 21(14): 8663-8672.

Guerzoni S., Chester R., Dulac F., Herut B., Loÿe-Pilot M.D., Measures C., Migon C., Molinaroli E., Moulinc C., Rossinia P., Saydami C., Soudinej A. and Ziverik Guerzoni P., 1999. *The role of atmospheric deposition in the biogeochemistry in the Mediterranean Sea*. Progress in Oceanography Volume 44, Issues 1–3, Pages 147–190, August 1999.

Guieu C., Loye-pilot M.-D., Ridame C., and Thomas C., 2002. *Chemical characterization of the Saharan dust end-member; some biological implications for the western Mediterranean*. Journal of Geophysical Research, 10.1029/2001JD000582.

Guieu C., Loÿe-Pilot M. D., Benyahya L., Dufour A., 2010. *Spatial variability of atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole Mediterranean from a one-year monitoring experiment: Biogeochemical implications*. Marine Chemistry 120 (2010) 164–178. doi:10.1016/j.marchem.2009.02.004

Jordi A., Basterretxea G., Tovar-Sánchez A., Alastuey A., Querol X., 2012. *Copper aerosols inhibit phytoplankton growth in the Mediterranean Sea*. Proceedings of the National Academy of Sciences 109, 21246–21249. https://doi.org/10.1073/pnas.1207567110.

Levin Z., Ganor E. and Gladstein V., 1996. *The effects of desert particles coated with sulfate on rain*

formation in the Eastern Mediterranean. Journal of Applied Meteorology 35, 1511–1523.

Longo A.F., Ingall E.D., Diaz J.M., Oakes M., King L.E., Nenes A., Mihalopoulos N., Violaki K., Avila A., Benitez-Nelson C.R, Brandes J., McNulty I., and Vine D.J., 2014.*P-NEXFS analysis of aerosol phosphorus delivered to the Mediterranean Sea*.Geophys. Res. Lett., 41, 4043–4049, doi:10.1002/2014GL060555.

Loÿe-Pilot M. D., and Martin J. M., 1996.*Saharan dust input to the Western Mediterranean: an eleven years record in Corsica, in the impact of desert dust across the Mediterranean*, edited by Guerzoni S. and Chester R., Kluwer Acad. Publ., 191 – 199.

Marconi M., Sferlazzo D. M., Becagli S., Bommarito C., Calzolai G., Chiari M., di Sarra A., Ghedini C., Gómez-Amo J.L., Lucarelli F., Meloni D., Monteleone F., Nava S., Pace G., Piacentino S., Rugi F., Severi M., Traversi R., and Udisti R., 2014. *Saharan dust aerosol over the central Mediterranean Sea:* PM_{10} *chemical composition and concentration versus optical columnar measurements*. Atmos. Chem. Phys., 14, 2039–2054, 2014, https://doi.org/10.5194/acp-14-2039-2014

Marty J.C., Chiav!erini J., Pizay M.D., Avril B., 2002. *Seasonal and interannual dynamics of nutrients and*

phytoplankton pigments in the western Mediterranean Sea at the DYFAMED time-series station (1991–1999). Deep-Sea Research II 49 (2002) 1965–1985.

Meskhidze N., Chameides W. L., and Nenes A., 2005. *Dust and pollution: A recipe for enhanced ocean fertilization?* Journal of Geophysical Research, Vol. 110, D03301, doi:10.1029/2004JD005082, 2005.

Mészáros E., 1999. *Fundamentals of Atmospheric Aerosol Chemistry*, Akadémiai Kiado Mészáros.

Molinaroli E., Ibba G., 1995. *Characterisation of palygorskite in dust of desertic provenance in aerosols and rains, Sardinia, western Mediterranean*. Giornale di Geologia e Geologia Marina 51, 67–76.

Molinaroli E., 1996. *Mineralogical characterisation of Saharan dust with a view to its final destination in Mediterranean sediments*.Environmental Science and Technology Library book series (ENST, volume 11)

Molinaroli, E., Pistolato, M., Rampazzo, G., Guerzoni, S., 1999. *Geochemistry of natural and anthropogenic fallout (aerosol and precipitation) collected from the NW Mediterranean: two different multivariate statistical approaches*. Applied Geochemistry 14, 423–432.

Moon J.-Y., Lee K., Tanhua T., Kress N., and Kim I.-N., 2016. *Temporal nutrient dynamics in the Mediterranean Sea in response to anthropogenic inputs.* Geophys.Res. Lett., 43, 5243–5251, doi:10.1002/2016GL068788.

Morales-Baquero R., Pulido-Villena E. and Reche I., 2013. *Chemical signature of Saharan dust on dry and wet atmospheric deposition in the south-western Mediterranean region.* Tellus B, 65, 18720, 2013

Moreno T., Querol X., Castillo S., Alastuey A., Cuevas E., Herrmann L., Mounkaila M., Elvira J., Gibbons W., 2006. *Geochemical variations in aeolian mineral particles from the Sahara–Sahel Dust Corridor*. Chemosphere 65 (2006) 261–270. doi:10.1016/j.chemosphere.2006.02.052

Muhs D.R., Budahn J., Avila A., Skipp G., Freeman J., Patterson D., 2010. *The role of African dust in the formation of Quaternary soils on Mallorca, Spain and implications for the genesis of Red Mediterranean soils*. Quaternary Science Reviews 29 (2010) 2518 e 2543.

Nava S., Lucarelli F., Amato F., Becagli S., Calzolai G., Chiari M., Giannoni M., Traversi R., and Udisti R., 2015. *Biomass burningcontributions estimated by synergistic coupling of daily andhourly aerosol composition records.* Sci. Total Environ., 511, 11–20, https://doi.org/10.1016/j.scitotenv.2014.11.034.

O'Dowd C. D. and Smith M. H., 1993. *Physicochemical properties of aerosols over the northeast Atlantic: Evidence for wind-speed related submicron sea-salt aerosol production.* J. Geophys. Res., 98, 1137–1149, https://doi.org/10.1029/92JD02302.

Paatero P. and Tapper U., 1994. *Positive matrix factorization: a nonnegative factor model with optimal utilization of error estimates of data values*. Environmetrics, 5, 111–126.

Pey J., Querol X., Alastuey A., 2009. *Variations of levels and composition of PM10 and PM2.5 at an insular site in the Western Mediterranean*. Atmos. Res., 94, 285-299.

Pey J., Larrasoaña J.C., Pérez N., Cerro J.C., Castillo S., Tobar M.L., de Vergara A., Vázquez I., Reyes J., Mata M.P., Mochales T., Orellana J.M., Causapé J., 2020. *Phenomenology and geographical gradients of atmospheric deposition in southwestern Europe: resultsfrom a multi-site monitoring network*, Sci. Total Environ. (underreview).

Pieri L., Matzneller P., Gaspari N., Marotti I., Dinelli G., Rossi P., 2010. *Bulk Atmospheric Deposition in the Southern Po Valley (Northern Italy)*. Water Air Soil Pollut (2010) 210:155–169, DOI 10.1007/s11270-009-0238-y

Polissar A.V., Hopke P.K., Paatero P., Malm W.C., and Sisler J.F., 1998. *Atmospheric aerosol over Alaska 2. Elemental composition and sources*. J. Geophys.Res. Atmos., 103(D15), 19045-19057.

Polissar A.V., Hopke P.K. Poirot R.L., 2001. *Atmospheric aerosol over Vermont: chemical composition and sources*. Environ. Science Tech., 35, 4604-4621, 2001.

Querol X., Alastuey A., Puicercus J.A., Mantilla E., Ruiz C.R., Lopez-Soler A., Plana F. & Juan R., 1998. *Seasonal evolution of suspended particles around a large coal-fired power station: chemical characterisation*, Atmos. Environ., 32, 719–731, 1998.

Querol X., Alastuey A., Rodríguez S., Plana F., Ruiz C.R., Cots N., Massagué G., and Puig O., 2001. *PM10 and PM2.5 source apportionment in the Barcelona Metropolitan area, Catalonia, Spain*. Atmos. Environ., 35, 6407-6419.

Roda F., Avila A., Rodrigo R, 2002. *Nitrogen deposition in Mediterranean forests*. Environmental Pollution Volume 118, Issue 2, July 2002, Pages 205-213. https://doi.org/10.1016/S0269-7491(01)00313-X

Rodríguez S., Alastuey A., Alonso-Pérez S., Querol X., Cuevas E., Abreu-Alfonso J., Viana M., Pérez N., Pandolfi M., and de la Rosa J., 2011. *Transport of desert dust mixed with North African industrial pollutants in the subtropical Saharan Air Layer.* Atmos. Chem. Phys., 11, 6663-6685.

Rogora M., Mosello R., Marchetto A., 2004. *Long-term trends in the chemistry of atmospheric deposition in Northwestern Italy: the role of increasing Saharan dust deposition*. Tellus B, Vol 56, DOI: 10.3402/tellusb.v56i5.16456

Sanz M.J., Carratala A., Gimeno C., Millán M.M., 2002. *Atmospheric nitrogen deposition on the east coast of Spain: relevance of dry deposition in semi-arid Mediterranean regions*. Environmental Pollution 118 (2002) 259–272.

Sarthou G. and Jeandel C., 2001. *Seasonal variations of iron concentrations in the Ligurian Sea and iron budget in the western Mediterranean*. Marine Chemistry, 74, 115 – 129

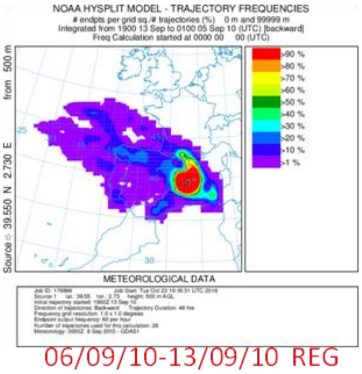
Scheuvens D., Schütz L., Kandler K., Ebert M., Weinbruch S., 2013. *Bulk composition of northern African dust and its source sediments — A compilation*. Earth-Science Reviews 116 (2013) 170–194. http://dx.doi.org/10.1016/j.earscirev.2012.08.005

Stein A.F., Draxler R.R., Rolph G.D., Stunder B.J.B., Cohen M.D., Ngan F., 2015. *NOAA's HYSPLIT atmospheric transport and dispersion modeling system*. Bull. Amer. Meteor. Soc. 96, 2059–2077

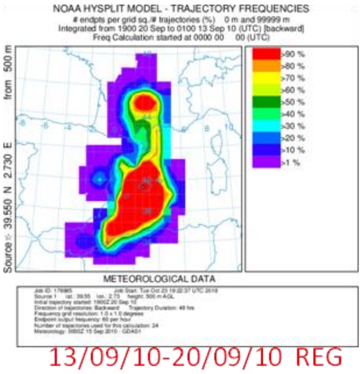
Stuut J.-B., Smalley I., O'Hara-Dhand K., 2009. *Aeolian dust in Europe: African sources and European deposits*. Quat. Int. 198, 234–245.

Vincent J., Laurent B., Losno R., Bon Nguyen E., Roullet P., Sauvage S., Chevaillier S., Coddeville P., Ouboulmane N., di Sarra A. G., Tovar-Sánchez A., Sferlazzo D., Massanet A., Triquet S., Morales Baquero R., Fornier M., Coursier C., Desboeufs K., Dulac F., and Bergametti G., 2016. *Variability of mineral dust deposition in the western Mediterranean basin and south-east of France*. Atmos. Chem. Phys., 16, 8749–8766, https://doi.org/10.5194/acp-16-8749-2016.

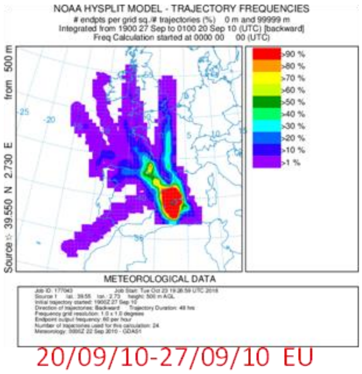
Appendix: Integrated back-trajectories



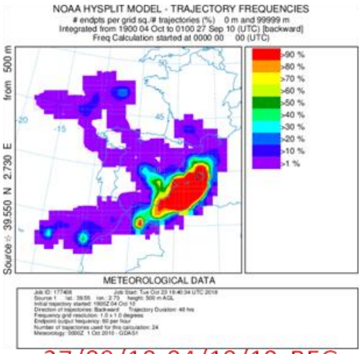
06/09/10-13/09/10 REG



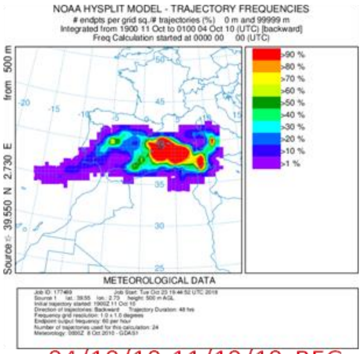
13/09/10-20/09/10 REG



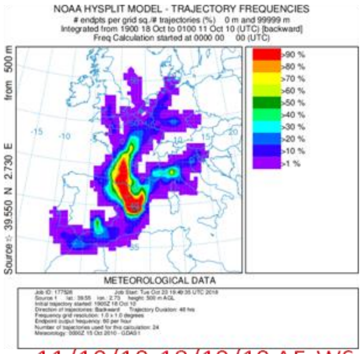
20/09/10-27/09/10 EU



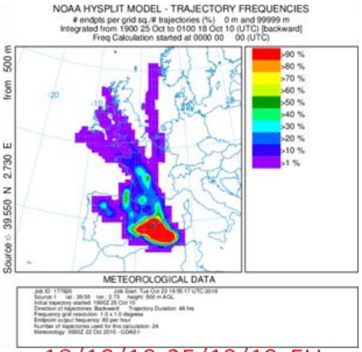
27/09/10-04/10/10 REG



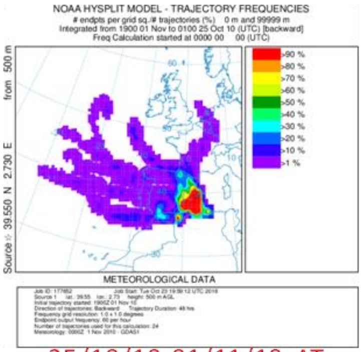
04/10/10-11/10/10 REG



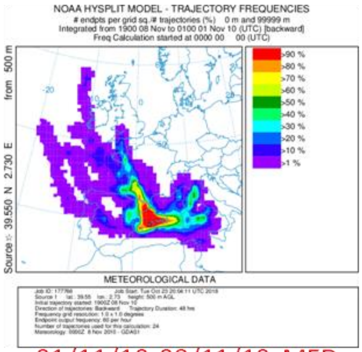
11/10/10-18/10/10 AF-WS



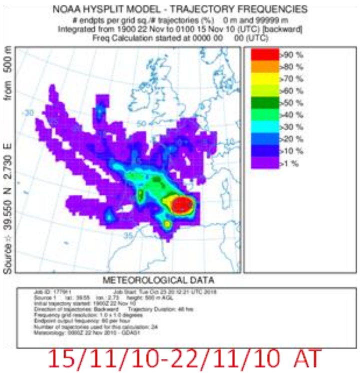
18/10/10-25/10/10 EU



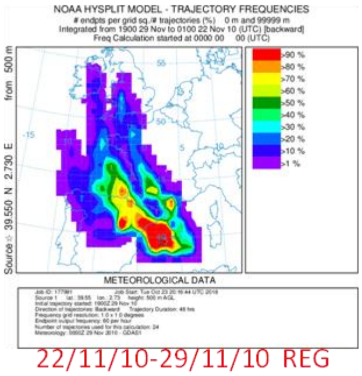
25/10/10-01/11/10 AT



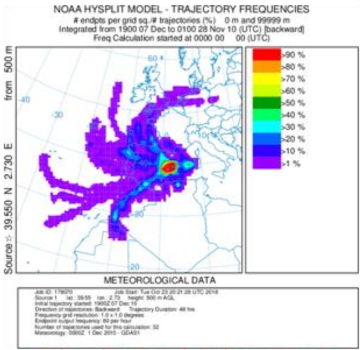
01/11/10-08/11/10 MED



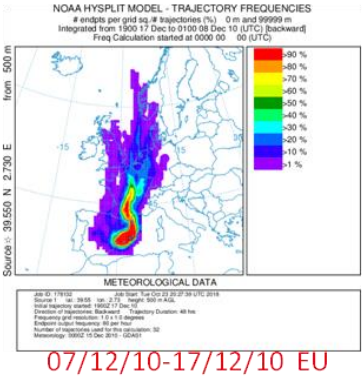
15/11/10-22/11/10 AT



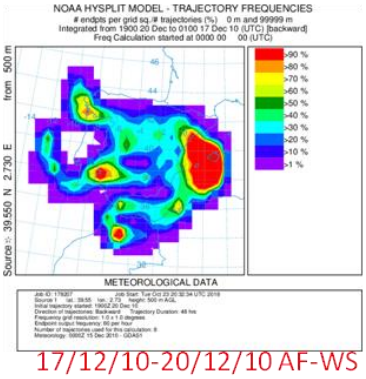
22/11/10-29/11/10 REG



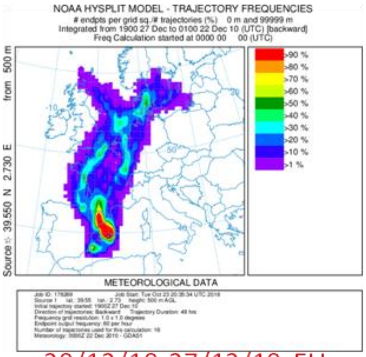
29/11/10-07/12/10 AF-WS



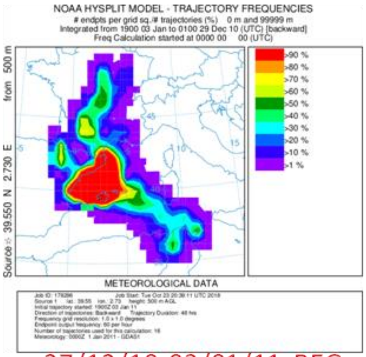
07/12/10-17/12/10 EU



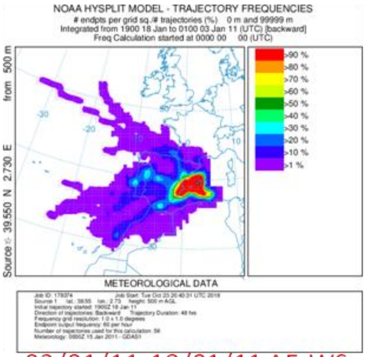
17/12/10-20/12/10 AF-WS



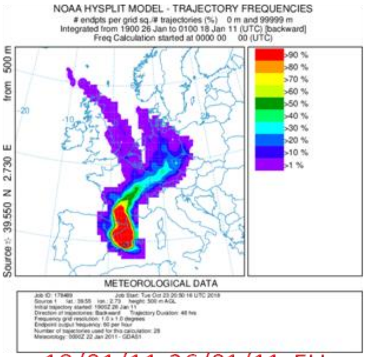
20/12/10-27/12/10 EU



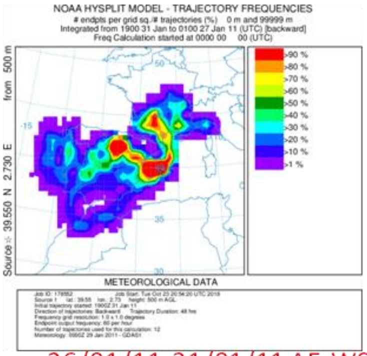
27/12/10-03/01/11 REG



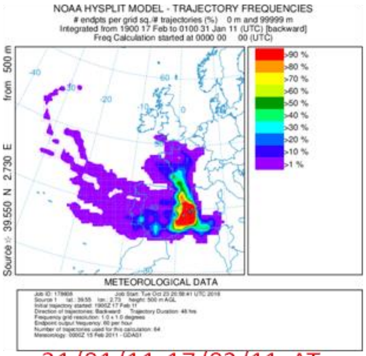
03/01/11-18/01/11 AF-WS



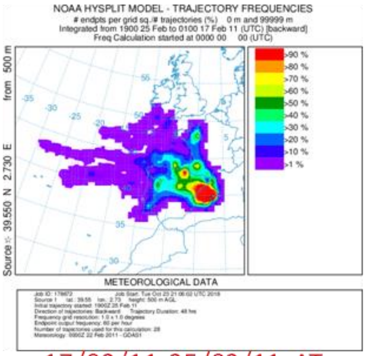
18/01/11-26/01/11 EU



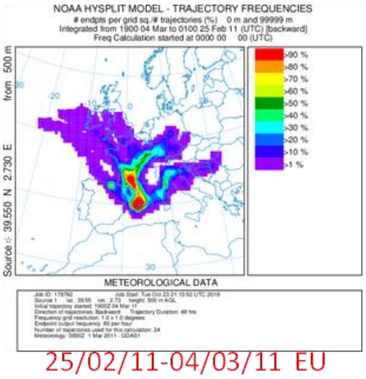
26/01/11-31/01/11 AF-WS



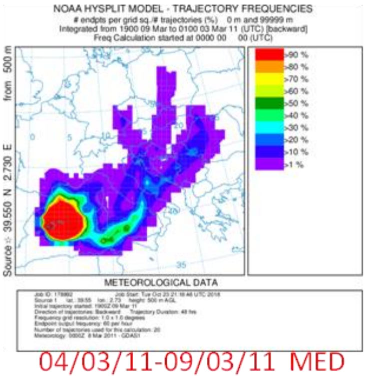
31/01/11-17/02/11 AT



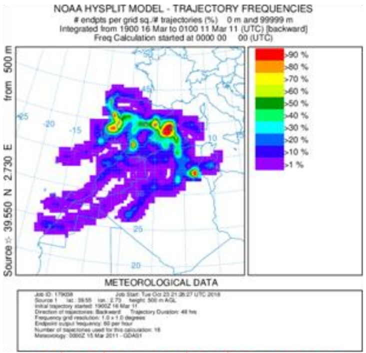
17/02/11-25/02/11 AT



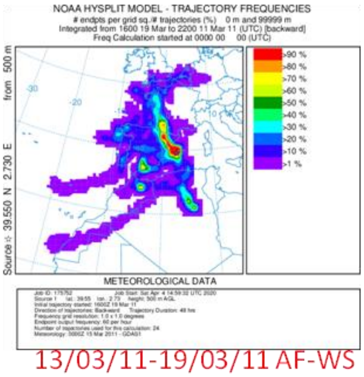
25/02/11-04/03/11 EU



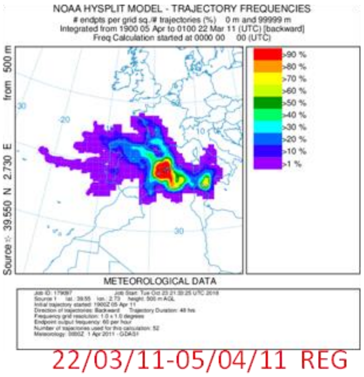
04/03/11-09/03/11 MED



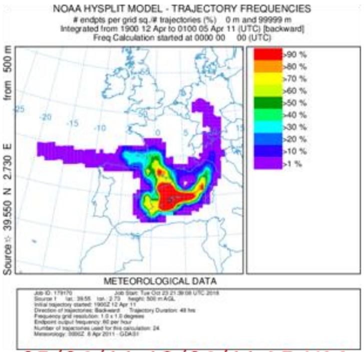
09/03/11-16/03/11 AF-WS



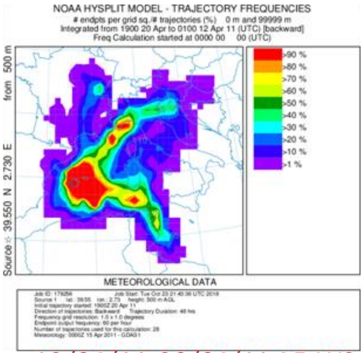
13/03/11-19/03/11 AF-WS



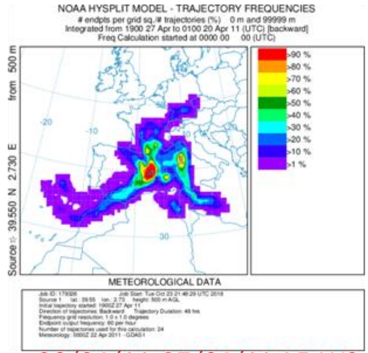
22/03/11-05/04/11 REG



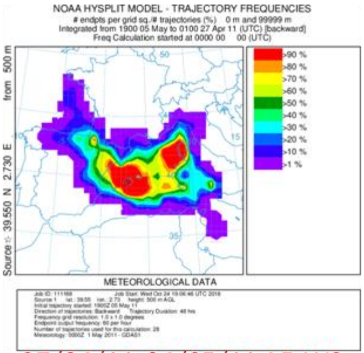
05/04/11-12/04/11 AF-HM



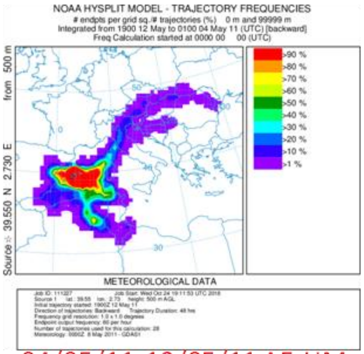
12/04/11-20/04/11 AF-WS



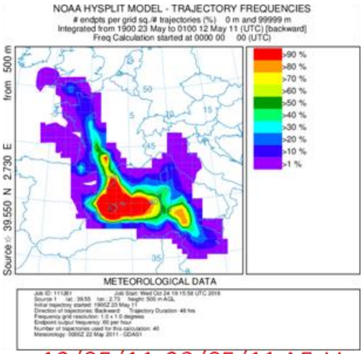
20/04/11-27/04/11 AF-WS



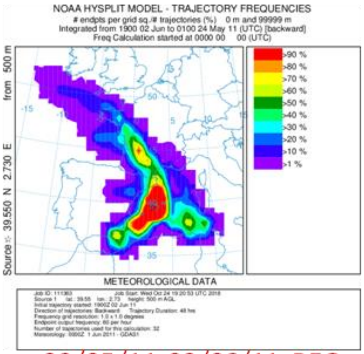
27/04/11-04/05/11 AF-WS



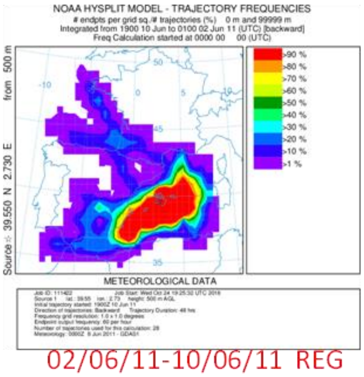
04/05/11-12/05/11 AF-HM



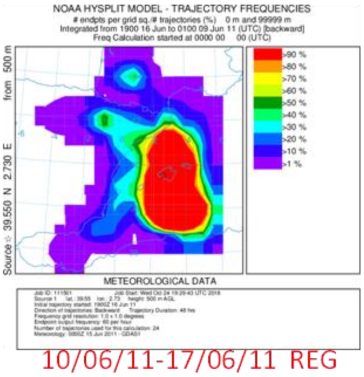
12/05/11-23/05/11 AF-LI



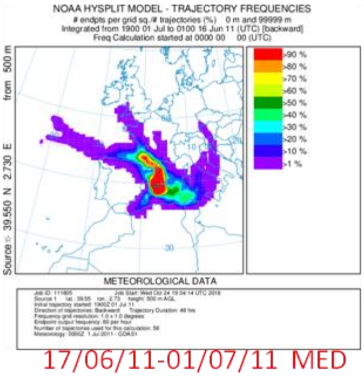
23/05/11-02/06/11 REG



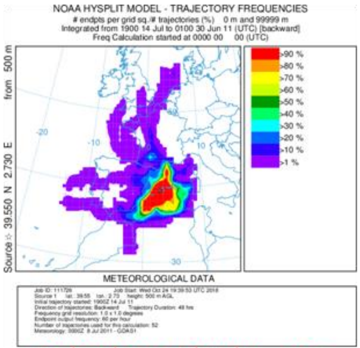
02/06/11-10/06/11 REG



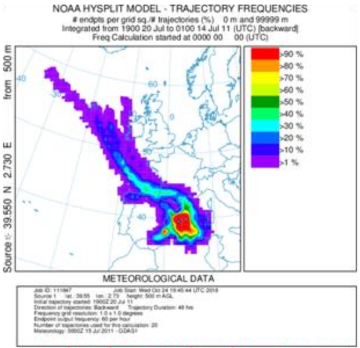
10/06/11-17/06/11 REG



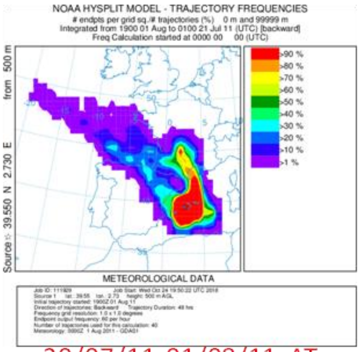
17/06/11-01/07/11 MED



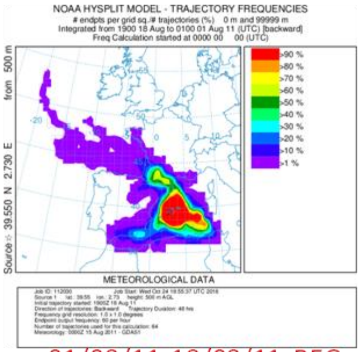
01/07/11-14/07/11 REG



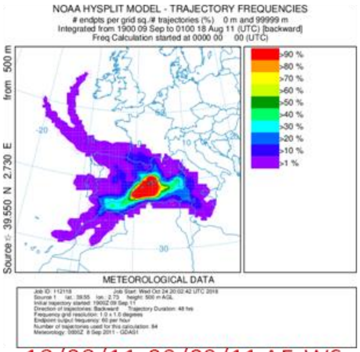
14/07/11-20/07/11 AF-HM



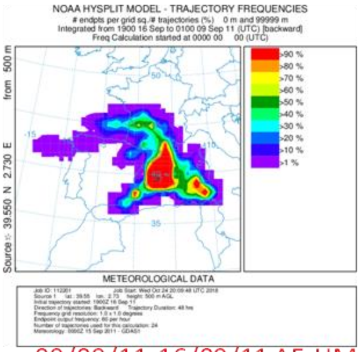
20/07/11-01/08/11 AT



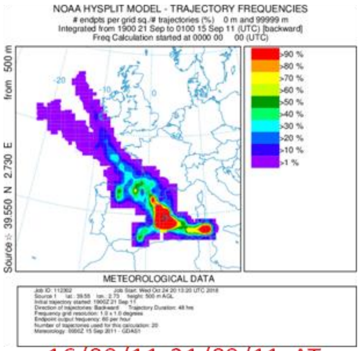
01/08/11-18/08/11 REG



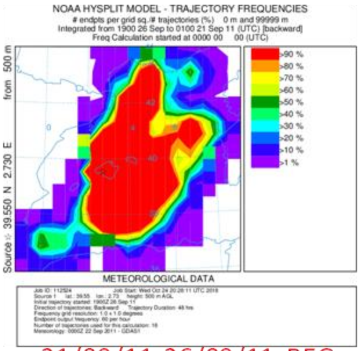
18/08/11-09/09/11 AF-WS



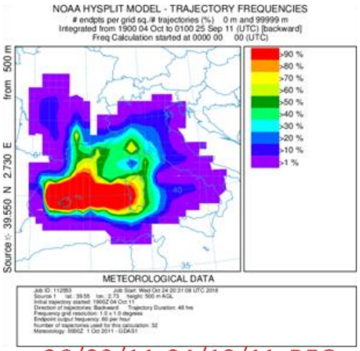
09/09/11-16/09/11 AF-HM



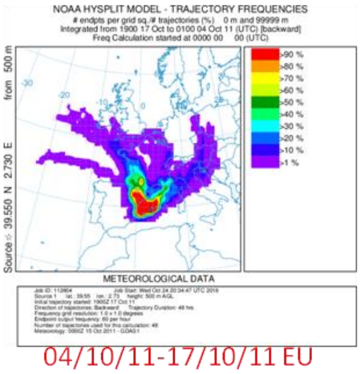
16/09/11-21/09/11 AT



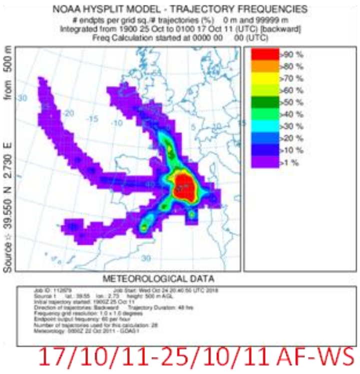
21/09/11-26/09/11 REG



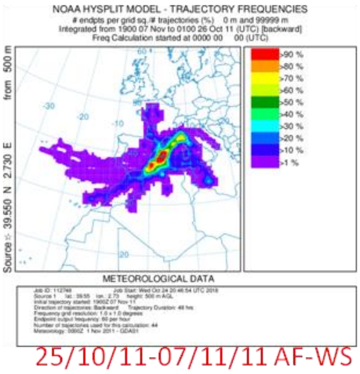
26/09/11-04/10/11 REG



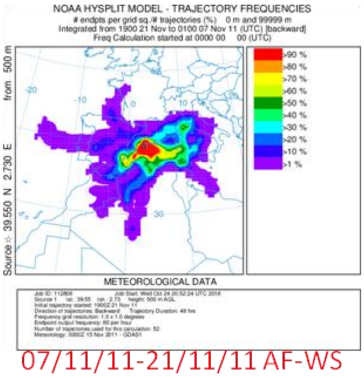
04/10/11-17/10/11 EU



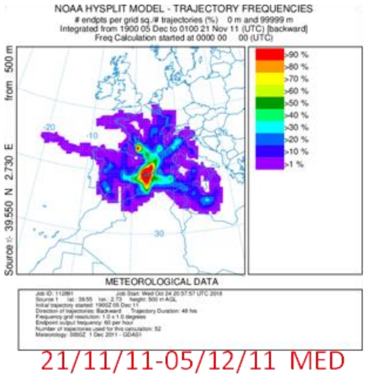
17/10/11-25/10/11 AF-WS



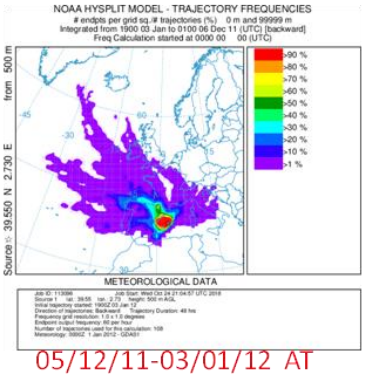
25/10/11-07/11/11 AF-WS



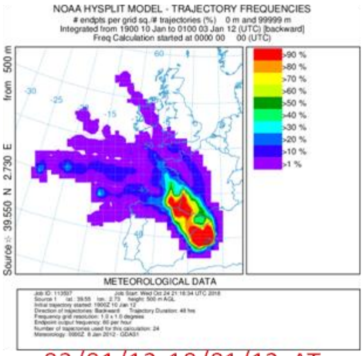
07/11/11-21/11/11 AF-WS



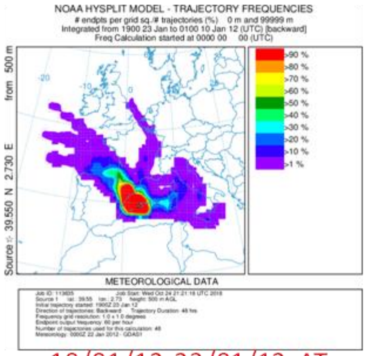
21/11/11-05/12/11 MED



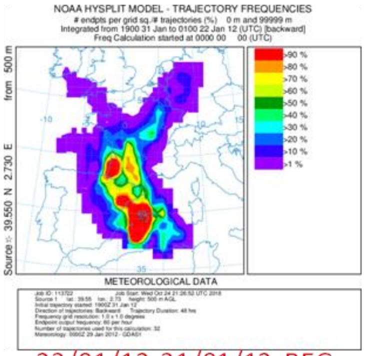
05/12/11-03/01/12 AT



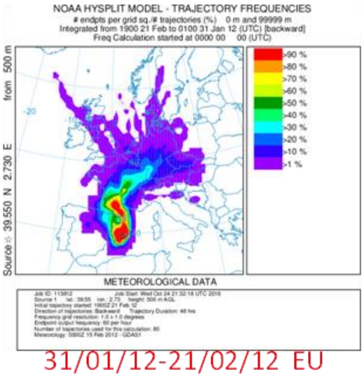
03/01/12-10/01/12 AT



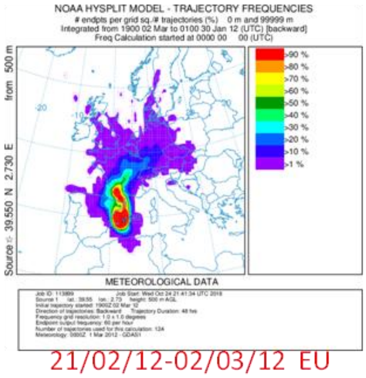
10/01/12-23/01/12 AT



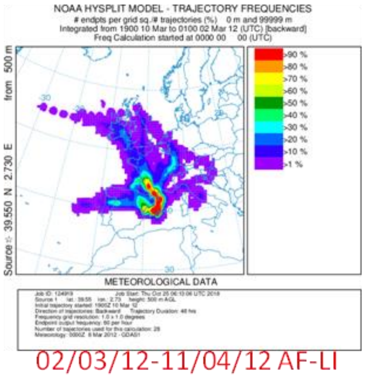
23/01/12-31/01/12 REG



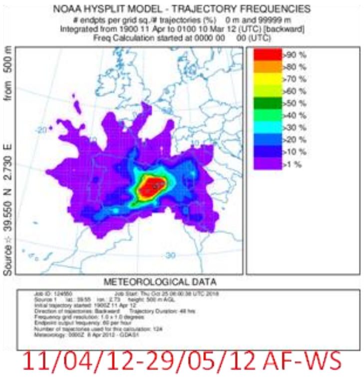
31/01/12-21/02/12 EU



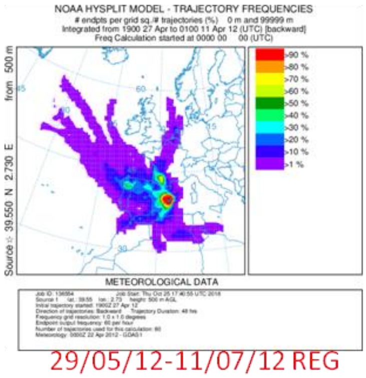
21/02/12-02/03/12 EU



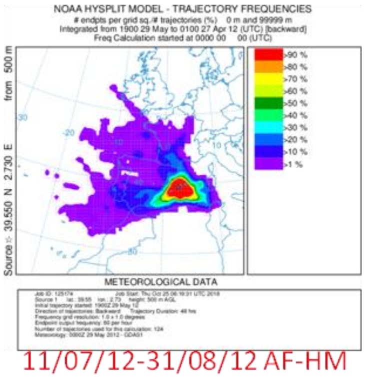
02/03/12-11/04/12 AF-LI



11/04/12-29/05/12 AF-WS



29/05/12-11/07/12 REG



11/07/12-31/08/12 AF-HM

Chapter 5: Source apportionment of Organic Aerosol in a remote Mediterranean site using a combination of offline and online approaches

This chapter is unedited, but based on conference paper: *Source apportionment of Organic Aerosol in a remote Mediterranean site using a combination of offline and online approaches*

Authors: J.C. Cerro[1,2], J. Pey[3,4], N. Pérez[5], V. Cerdà[1], H.L. DeWitt[3] , S. Hellebust[3,6], M. Elser[7], A.S.H. Prévôt[7], B. Temime-Roussel[3] and N. Marchand[3]

[1] Laboratory of Environmental Analytical Chemistry, Illes Balears University, Palma, 07122, Spain

[2] Laboratory of the Atmosphere, Balearic Islands Government, Palma, 07009, Spain

[3] Aix Marseille Université, CNRS, LCE UMR 7376, 13331 Marseille, France

[4] Spanish Geological Survey, Zaragoza IGME Unit, Zaragoza, 50006, Spain

[5] Institute of Environmental Assessment and Water Research CSIC, Barcelona, 08034, Spain

[6]Centre for Research into Atmospheric Chemistry, University College, Cork, Ireland

[7] Gasphase and Aerosol Chemistry Group, Paul Scherrer Institute, 5232, Villigen, Switzerland

Keywords: Source Apportionment, Organic Aerosol, AMS.

Presenting author email: jose.carlos.cerro.garrido@gmail.com

Abstract

Southern Europe displays elevated concentrations of aerosols, mostly secondary in origin and strongly enhanced during the warm season. The high state of oxidation of organic aerosols (OA) in this region, as a result of recirculation of air masses and intensive aerosol ageing, sources are largely unknown. With the aim of advancing in the knowledge of OA sources in the Mediterranean region, an intensive field campaign was carried out in summer 2013 in the regional background site of “Cap Pinar” (Mallorca, Spain) within the framework of SAF-MED (Secondary Aerosol Formation in Mediterranean) and ChArMEx (Chemistry Aerosol Mediterranean Experiment) actions. Real time measurements of particle composition were performed by using an Aerosol Mass Spectrometer (HR-ToF-AMS) combined with daily collection of PM_1 samples for further analysis (OC/EC, major ions, major and trace elements), from the 3rd July to the 12th August.

A source apportionment study was carried out with a ME-2 approach finder (SoFi toolkit, Canonaco et al. 2013) on both off-line and on-line measurements. In addition, to integrate online and offline source apportionment solutions a methodology based on Multiple Regression Analysis was applied. From the application of this novelty approach, it could be possible to integrate PM_1-24h-OA factors and AMS-OA sources.

Our findings revealed that an earthbound (EB) factor (a mix of marine and mineral aerosols) was related to the sulphate oxygenated organic aerosol (SO4_OOA) factor (mainly marine sulphate) (50.6 %); a regional earthbound (REG EB) source (mix of nearby mineral and marine) was clearly influenced again by SO4_OOA (64.3 %); an anthropogenic (ANT) source was constituted mainly by oxygenated organic aerosol (OOA), probably related to a mix of combustion processes, (55.7 %); and a regional anthropogenic (REG ANT) factor (more local) was constituted mainly by ammonium sulphate associated organic aerosol (ASOA) (usually related to road traffic) (44.5 %) and OOA (43.8 %) sources.

1. Introduction

Traditionally, PM composition has been investigated by offline studies that comprise 24h sampling and subsequent laboratory treatment and analysis, a laborious and time consuming methodology. Time resolution does not allow us to appreciate daytime variability. Conversely, filters allow a wide range of investigations that cannot be carried out, for the moment, by on-line systems. In recent years, different types of mass spectrometers have been developed to analyse real time submicron aerosol. Aerodyne Research aerosol mass spectrometers (AMS) are the most widely used. Otherwise, refractory fractions cannot be determined, including a vast range of inorganic species, such as metals, salts or minerals.

The submicron Organic Aerosol (OA) formation comprises multiple processes of further studies, from the primary emissions to removal, going through reversible phase partitioning, chemical and photochemical transformations (Canagaratna et al., 2010; Hallquist et al., 2009; Jimenez et al., 2009; Kroll et al., 2008). OA comprises 20-90% of the total mass for PM_1 (Jimenez et al., 2009) and a quantitative understanding is necessary to reduce some of the largest uncertainties that currently exist. Southern Europe displays elevated concentrations of aerosols, mostly secondary in origin and strongly enhanced during the warm season. Due to the high oxidation state of OA in such environment sources are still largely unknown.

Furthermore, Organic Aerosol mass and chemical analysis becomes a challenge since it comprises a wide range of compounds with diverse oxidation state and physical properties (Goldstein et al., 2007; Kanakidou et al., 2005; Seinfeld et al., 2003).

Source apportionment research is important to know which are the contributions for Airborne Particulate Matter and, consequently, to settle better knowledge of the causes of air pollution. This leads to more efficient abatement policies. The number of source apportionment studies published has increased considerably during last 15 years. The Forum for Air Quality Modelling in Europe (FAIRMODE), in its sub-group 2, has developed a guide for considering how Source Apportionment studies have to be performed. Fragkou et al. (2012) report that, in the case of Europe, countries opt for Principal Component Analysis (PCA) modelling as the mainly tool used to investigate contributions for PM, followed by back-trajectories analysis, receptor models such as Positive Matrix Factorization (PMF), Chemical Mass Balance (CMB)... Additionally a great part of the countries have used dispersion models, mainly Eulerian chemical transport models, followed by Lagrangian and Gaussian. Ultimately a combination of tools is usually implemented by the countries.

Despite the current decay in PM concentrations in background ambient all around Europe (Cusack et al., 2012; Barmpadimos et al., 2012) and particularly, in western Mediterranean (Cerro et al., 2015 and 2020; Pey et al., 2013b), summer season is still critical from the point of view of air quality regulations. Target values for PM are still exceeded and a more extensive knowledge about its formation processes should be achieved in order to prevent, or to predict, high concentration episodes. A wide range of primary sources contribute to western Mediterranean PM, such as shipping and traffic emissions, industrial emissions, biogenic emissions, marine aerosol, biomass burning, Saharan dust and other long transport influences (Querol et al., 2009; Cerro et al., 2020; Pey et al., 2013b). All these contributions are displayed in summer during the maximum photochemical activity and secondary aerosol formation. Therefore, background ambient air is affected by a mixture of aerosols, and trying to measure contributions becomes challenging.

An extensive campaign was conducted in summer 2013 in Es Pinar Cape in Mallorca (Figure 5.1.) as part of SAF-MED project and more globally in the framework of ChArMEx (https://charmex.lsce.ipsl.fr/), including multiple devices based in off line and real time techniques (Pey et al., 2014). Time-resolved online measurements of particle composition were performed using a HR-ToF-AMS combined with daily collection of PM_{10} and PM_1 for further analysis, since 3rd July to 12th August. Other metrics were determined in parallel as indicated in Pey et al., 2014.

A receptor model has been conducted to discern source apportionments for PM_1 and AMS results. Specifically, Positive Matrix Factorization (PMF) statistics (Paatero and Tapper, 1994;

Lanz et al., 2007; Ulbrich et al., 2009) have been applied using the Multilinear Engine ME-2 program (Paatero et al., 1999) and its interface SoFi (Canonaco et al., 2013).

On board we aim to integrate the AMS source apportionment result obtained by H. Langley DeWitt, with the 24 hours PM_1 filter analysis source apportionment solution, in favour of discerning the origin of the Organic Matter contained in this fraction. Also, we are in process of bounding PM_1.

5.2. Methodology

5.2.1. Location

The campaign was conducted during summer 2013 at es Cap Pinar (CP)(Figure 5.1). CP site was set-up exclusively for the summer 2013 campaign at the end of June, being fully operative from July 3rd to August 13th. CP was built in the “Es Pinar” military facilities belonging to the Spanish Ministry of Defence. The environment is a non-urbanized area surrounded by pine forested slopes, being one of the most insulated zones in the Mallorca Isle, in between the Alcudia and Pollença bays. The exact location of the site is 39.885°N, 3.195°E, at around 20 m a.s.l., at a distance of about 0.08 Km to the eastwards coastline, 0.55 Km to the westwards one and 0.90 Km to the northwards one.

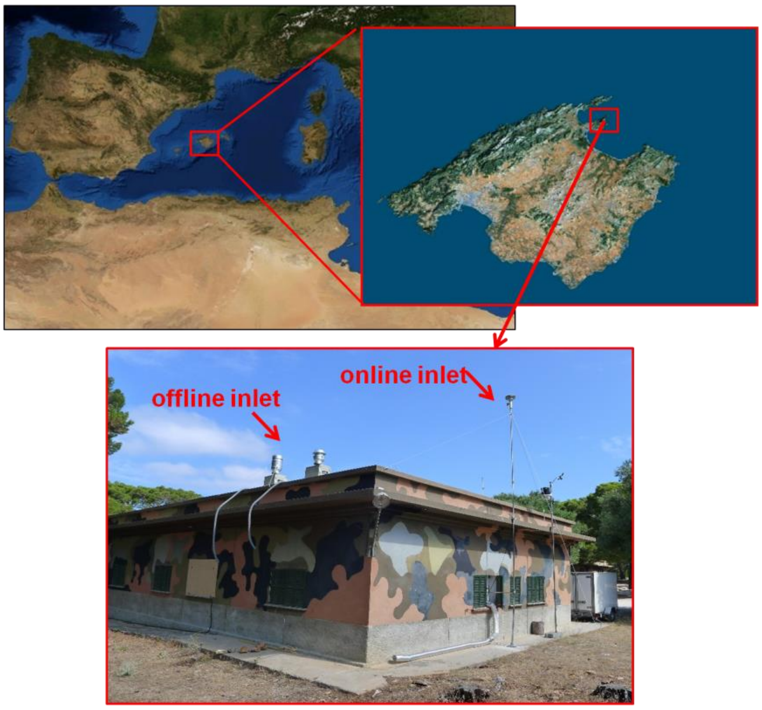


Figure 5.1. Es Pinar Cape (Cap Pinar) location and off line inlets indicated on the left site and on line measurements inlet on the right side.

5.2.2. 24 h filter collection and analysis

PM_1 24h quartz fibre filters collection was carried out according to the EN 12341 standard. Filters were further analysed. For the determination of the elemental compositions, a fraction of the filter was digested using a mixture of inorganic acids (HNO3:HF:HClO4) (Querol et al., 2001; Pey et al., 2013a; Cerro et al., 2020). The quantitative analysis of metals and trace elements was performed using ICP–AES (inductively coupled plasma– atomic emission spectrometry) for major elements (Al, Ca, Na,Mg, K, Fe, P) and an ICP–MS (inductively coupled plasma– mass spectrometry) for trace elements (Li, Be, B, P, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th, U). OC and EC fractions were quantified using the thermal optical transmittance (TOT) method, with a Sunset Lab analyzer. Major ions (SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) were analyzed by ionic chromatography. Quantification of NH_4^+ was achieved by a selective electrode. ^{14}C content of total carbonaceous aerosol (TC=OC+EC) was measured in a selection of filters representing all meteorological situations using ARTEMIS accelerator mass spectrometry (El Haddad et al., 2013).

More extensive description of methodology and quality assurance is pending to be published by Jorge Pey.

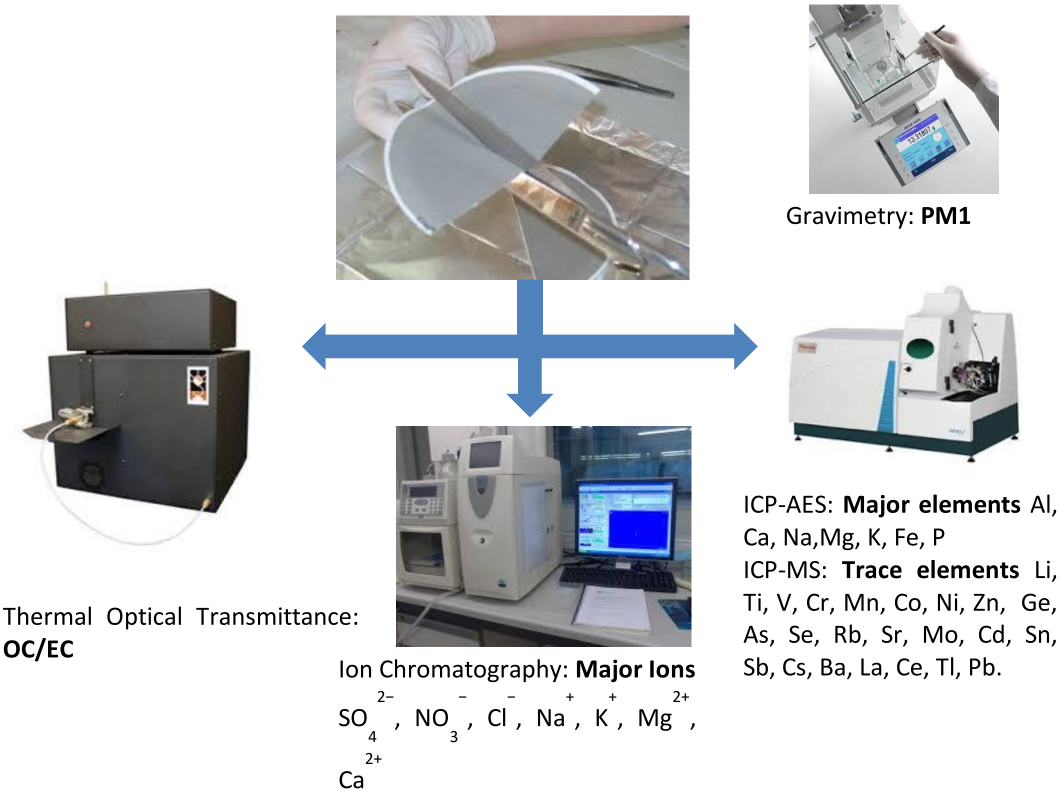


Figure 5.2. Off-line aerosol analysis methodology: daily collection of PM_1 samples for further analysis (OC/EC, major ions, major and trace elements).

5.2.3. AMS measurement

AMS provides online quantitative mass spectra of the non refractory components of the submicron aerosol fraction with high time resolution, via thermal vaporization (typically at 600 °C) and 70 eV electron impact ionization (IE) (Canagaratna et al., 2007).

HR-ToF-AMS principle has been detailed by DeCarlo et al. (2006). The AMS calibration procedure and analysis protocol are described in detail elsewhere (e.g., Canagaratna et al., 2007).

Mass concentrations were corrected using a Collection Efficiency (CE) to account for the particle bounce of aerosols on the vaporizer. The composition-dependent CE was calculated as described in Middlebrook et al. (2012).

IE for each of specie is expressed relatively to the IE of the nitrate moiety (calibrated with pure ammonium nitrate particles) by the Relative Ionization Efficiency (RIE) (Jimenez et al., 2003). The ammonium nitrate calibration described by Ng et al. (2011) was performed using an atomizer (TSI, Constant Output Atomizer Model 3076) for primary aerosol generation, followed by a silica-gel diffusion dryer.

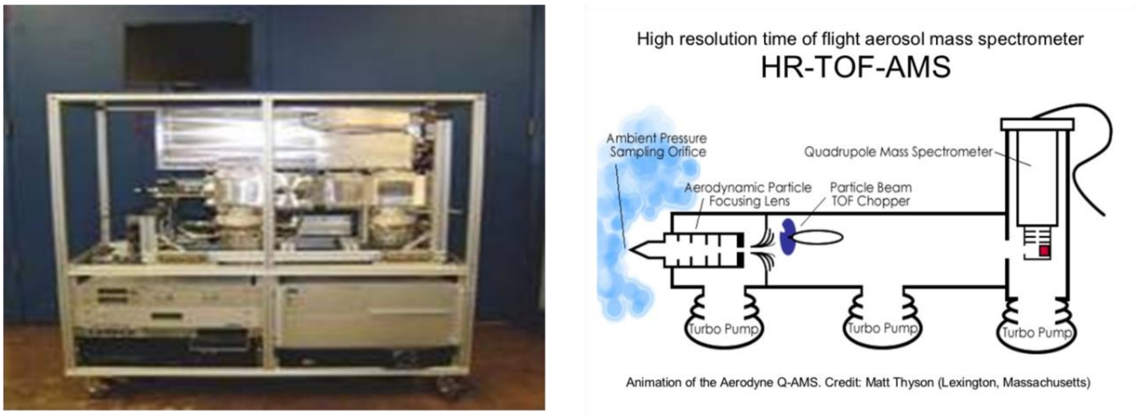


Figure 5.3. On-line aerosol analysis methodology: Highly time-resolved on-line measurements of particle composition were performed using an Aerosol Mass Spectrometer (HR-ToF-AMS).

5.2.4. Data treatment

The AMS data processing procedure has been carried out (DeWitt et al., 2014).

The AMS Unit-Mass-Resolution (UMR) data and the AMS High-Resolution (HR) data were applied using the data analysis toolkits Squirrel (Allan et al., 2003; Aiken et al., 2007, 2008) and Pika (Sueper et al., 2013) subsequently, in order to convert m/z signals in Organic and Inorganic species.

Posterior treatment requires as inputs the data matrix and the associated uncertainty matrix, both obtained here with the Squirrel tool. Uncertainties were modified following the recommendations of Ulbrich et al. (2009).

Time series obtained for inorganic compounds (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+) and Organic Matter were compared with PM_1 offline results, in the same average periods, to study their correlations.

Elemental analysis (Aiken et al., 2007, 2008) was performed for organics with HR data to obtain the oxygen-to-carbon atomic ratio (O:C), the hydrogen-to-carbon atomic ratio (H:C), the nitrogen-to-carbon atomic ratio (N:C) and the ratio of organic matter to organic carbon (OM=OC). It allows us to reflect the degree of oxygenation of organics in two ways. The first is the O:C directly from elemental analysis (Aiken et al., 2007, 2008; El Haddad et al., 2013) and the second is the average carbon oxidation state (OSC), which can be approximated by 2xO:C–H:C (Kroll et al., 2011).

Afterwards Positive Matrix Factorization (PMF) was performed to obtain source contributions for PM_1 filters and AMS results. PMF is a statistical source apportionment tool that uses constrained, weighted least squares estimation to determine source profiles and strengths. Specifically, PMF is a variant of a factor analysis method with non-negative factor elements and it takes into account error estimations of observed data values (Paatero and Tapper, 1994; Lanz et al., 2007; Ulbrich et al., 2009). The Multilinear Engine ME-2 was used to solve these multilinear and quasi-multilinear problems (Paatero, 1999). Particularly, it solves models where the data values are fitted by sums of products of unknown factor elements.

In favour of facilitating the choice of the initial conditions for the ME-2 engine and the analysis of the results, SoFi (Source Finder) interface was used (Canonaco et al., 2013).

In order to have better understanding same initial tools were used to carry out the PM_1 24h filters source apportionment: ME-2 and SoFi.

Values under detection limit have been replaced for half of detection limit concentration (Polissar et al., 1998). Species including more than 50% of data under detection limit and with low signal-to-noise have been removed (Brown and Hafner, 2005): Li, Be, B, P, Sc, Cr, Ge, Y, Zr, Nb, Mo, Cs, Ba, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Bi, Th, U.

Initial uncertainties were considered depending on the analysis methodology, limit detection and coefficients of variation. Afterwards gradual uncertainty was calculated as function of the concentration analyzed, with linear increase for most of the species and stepwise increment for mineral species (Reff et al., 2007, Karagulian & Belis, 2012). Next step a trial-and-error process was carried out to obtain the best model, evaluating results using Q values, distribution of residuals and results from multiple regressions (Polissar et al., 2001).

Thereupon Organic Matter concentration time series were extracted for PM_1 and for AMS factors (by H. L. DeWitt), both corresponding to the same fraction of Particulate Matter.

To go in depth of Organic Aerosol origins, the AMS factor time series were combined with PM_1 factor time series. Multiple Regression Analysis (MRA) was carried out considering the four AMS factors as independent variables for each corresponding Organic Matter offline factor as dependent variable, assuming intercept=0 in order to achieve major explanation.

These combinations are based on mass balance equations, in with each of the AMS factors is considered to comprise the four OM fractions obtained in the PM_1 offline factors. The technique is essentially based on the co-variability between the AMS factor time series and the time series of the Organic Matter obtained in each offline factor. Conceptually, it assumes constant contribution of each Organic portion AMS factor to each OM offline factor fraction. Negative loadings were considered to be 0.

5.3. Results

5.3.1. Results for PM_1 24h filters and Source Apportionment Solution

The two species more abundant analyzed for PM_1 are OM (3.02 μgm^{-3}) and sulphate (2.74 μgm^{-3}), followed by ammonium (1.09 μgm^{-3}). Below them mineral (0.26 μgm^{-3}), EC (0.21 μgm^{-3}) and sea spray (0.18 μgm^{-3}) are presented. Finally traces represent the lower contributor (0.02 μgm^{-3}). These results are consistent with the previous obtained at Can Llompart site (Cerro et al., 2020).

The OA contribution varied throughout the campaign, reaching 4.81 μgm^{-3} the 15/07/2013 during a Regional S meteorological episode, with a bottom of 1.60 μgm^{-3} the 30/07/2013 during Atlantic advection.

PMF exploration was run under seed mode from 1 to 10 factors, with 10 iterations for each factor. A parabolic vertex Q/Qexp value was detected at 4 factors for PM_1. All iterations displayed similar Q/Qexp ratios for 4 factors.

Therefore, 4 factors were investigated for PM_1, followed by 3 and 5 factors.

4 factors displayed high concordance, including two characterized mostly by anthropogenic species and two mostly characterized by mineral or marine species. Time series were studied and compared with the meteorological episodes (Pey et al., 2014) and external tracers as conventional pollutant gases. Finally, one non anthropogenic factor was title as “earthbound” (EB), as it is characterized by Al_2O_3, Fe, Ti and other mineral species, but also with Na, Mg, NO_3^- and others that could have its origin in sea aerosol. Another non anthropogenic factor was titled “regional earthbound” (REG EB), as it relates mainly to Ca and other mineral species, except for Al_2O_3 and Fe, what fits with the island soil composition. Also it is constituted by other species that could be related to sea aerosol.

One Anthropogenic factor named “Anthropogenic” (ANT). And another anthropogenic factor was titled as “Regional Anthropogenic” (REG ANT), as it contains part of Ca or other species that could be mostly regional.

3 factors were investigated too, but no coherence was obtained, since all kind of species, anthropogenic and non anthropogenic, were mix in the three.

Rotational ambiguity was investigated by varying Fpeak from -2 to 2 with steps of 0.1. Regularly results close to 1.3 Q/Qexp were obtained from -2 to 0, and no stable results over 0.

60 pseudorandom starting-points (seeds) were verified to study the influence of initial conditions and only 3 of them were slightly dissimilar.

Organic Matter is distributed in different manners among all the factors, with highest abundance in ANT factor (1.26 µgm^{-3}), closely followed by REG ANT (1.16 µgm^{-3}) and with less abundance in EB factor (0.20 µgm^{-3}) and much less in REG EB (0.07 µgm^{-3}). In terms of relative weight of the measured species in each factor different sorted is achieved, with the highest weight of Organic Carbon in EB (90%), followed by ANT (79%), REG ANT (45%) and REG EB (12%).

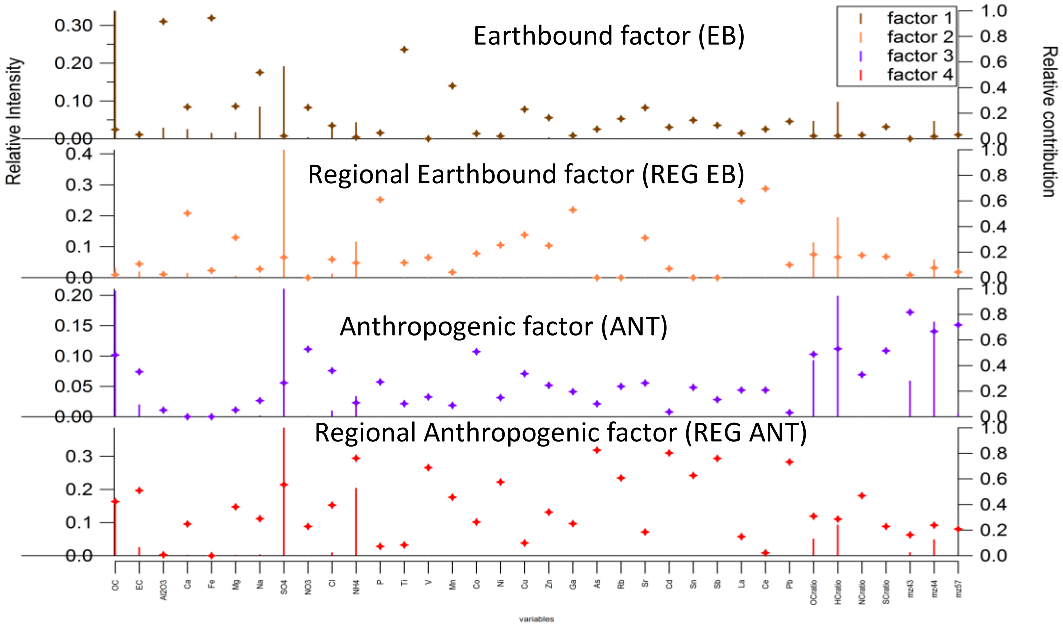


Figure 5.4. Concentration (Relative Intensity) in µg/µg (with bars) and relative contribution (with dots) of chemical components for the 4-factor solution in PM$_1$.

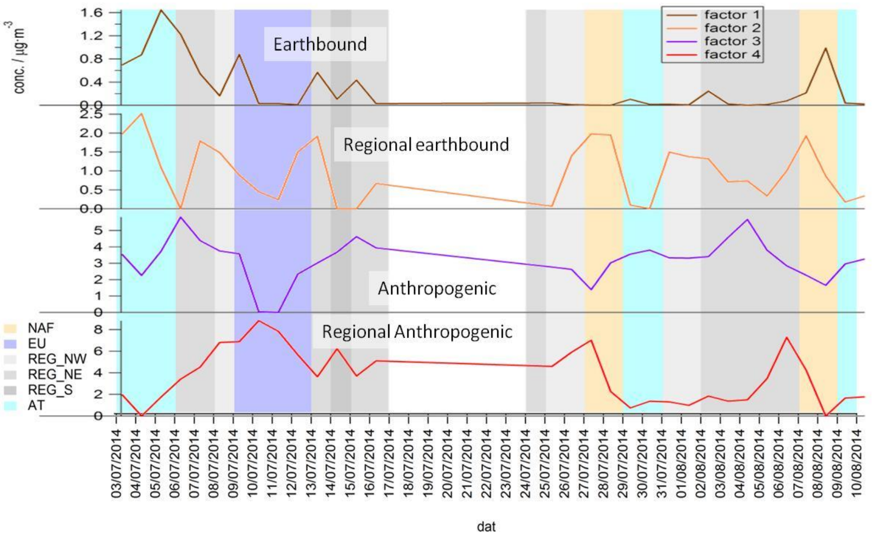


Figure 5.5. Time series concentration of the PM_1 factors, in µgm^{-3}. Colours on the background represent the meteorological scenario: NAF-North African; EU-European; REG-NW-Regional from North West; REG-NE Regional from North East; REG-S-Regional from South; AT-Atlantic.

5.3.1. Results for AMS measures and Source Apportionment Solution

An important consideration in the quantitative analysis of AMS data is the collection efficiency (CE) related to particle bounce. CE was estimated through comparison of the aggregate mass of OA, NH_4^+, NO_3^- and SO_4^{2-} from AMS and EC from Sunset with volume distributions from a collocated SMPS (TSI: DMA 3081, classifier 3080, and CPC 3775). We assessed the CE for the campaign as 0.55±0.14 (22% uncertainty), comparable to values typically found for ambient aerosol (0.5, Middlebrook et al., 2012). Data presented below are all corrected for CE.

Since calibration of IE for all species is not feasible, IE for each of the specie is expressed relative to the IE of the nitrate moiety (calibrated with pure ammonium nitrate particles) by the Relative Ionization Efficiency (RIE) (Jimenez et al., 2003). The ammonium nitrate calibration described by Ng et al. (2011) was performed using SMPS (Scanning Mobility Particle Sizer) composed by a differential mobility analyzer (DMA) model TSI 3936, and a condensation particle counter (CPC, TSI 3772). Monodisperse 300 nm ammonium nitrate aerosol particles were used, covering a range of nitrate concentrations from 2 to 15 µgm^{-3}. An IE of $2.2 \cdot 10^{-11}$ was obtained. The RIE for ammonium was measured as part of the ammonium nitrate calibration, and found to be 5.4. The RIE values used in this study for the rest of the species were those usually applied in AMS ambient concentrations: 1.4 for OA and 1.1, 1.2, and 1.3 for nitrate, sulphate, and chloride, respectively (Canagaratna et al., 2007). RIE for sulphate was experimentally determined before/after the campaign and was found to be very close to 1.2 and hence the default value was used for the current dataset.

The comparison between ion concentrations measured by HR-ToF-AMS against PM_1 concentrations determined by offline techniques displayed strong correlation for sulphate, OM and ammonium (with squared Pearson correlation coefficient of R^2 = 0.78, 0.75, 0.76 and slopes of 1.26, 1.17, 0.91, respectively) (Figure 5.6.). EC was also compared with black carbon concentrations retrieved from the aethalometer, displaying again a very good correspondence (R^2=0.87 and slope=1.29). Other ions, such as chloride and nitrate displayed poor correlations, probably due to sampling artifacts in filters (Cheng et al., 2012).

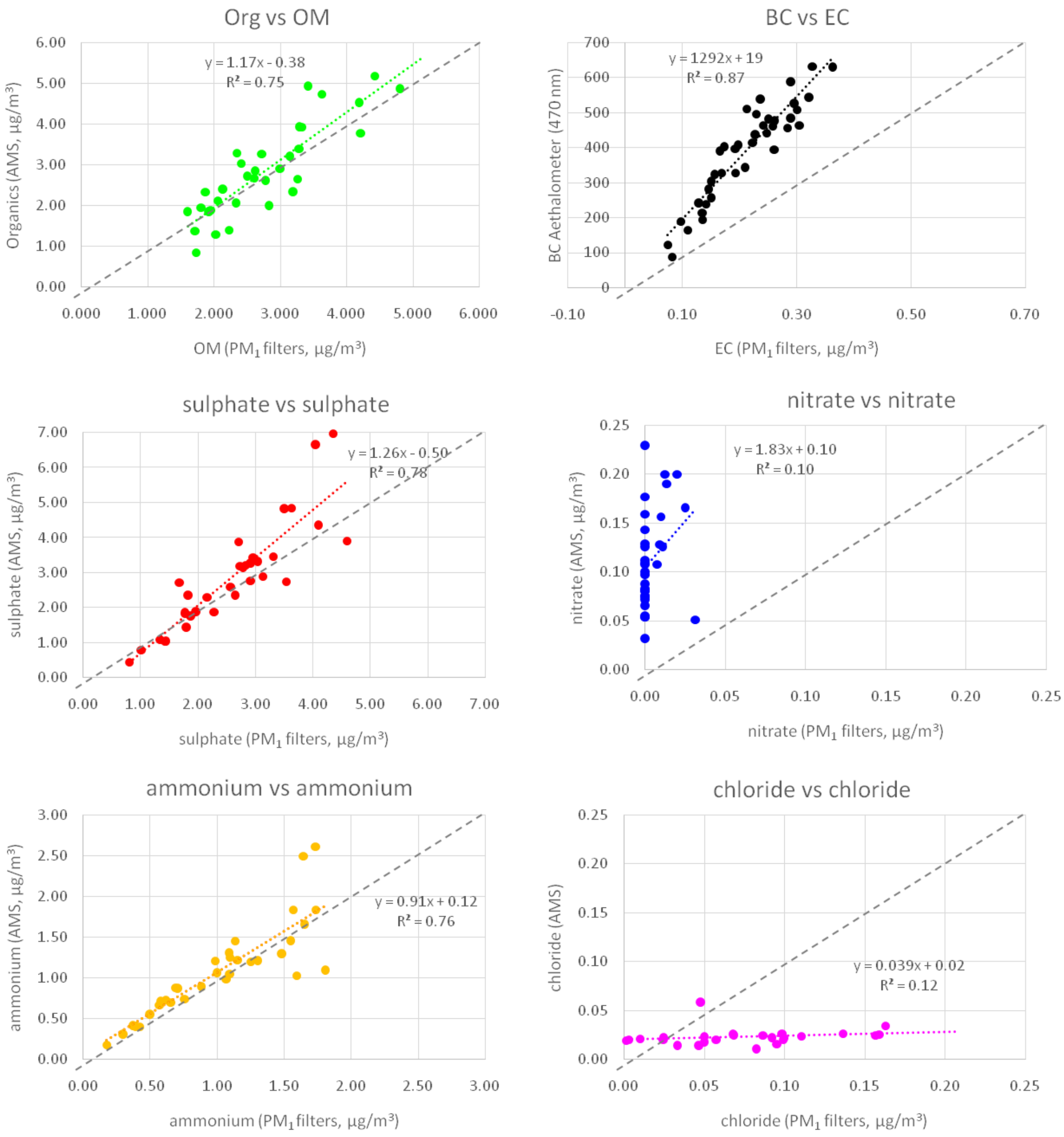


Figure 5.6. AMS daily averages in front of 24h-filters composition values, indicating R^2 regression index and equation obtained, for OM, Sulphate, Nitrate, Ammonium, and Chloride. In the case of EC the AMS value has been represented in front of daily Black Carbon Aethalometer result.

PMF studies were conducted apportioning the measured organic mass spectra. Only signals between 12-115 m/z ratio were used, considering that it explains most of the mass and avoiding naphthalene signals at m/z 127, 128, and 129 (Miguillón et al. 2015).

HR-ToF-AMS displayed performance problems since July 17th to 24th, and this period was not taken into account.

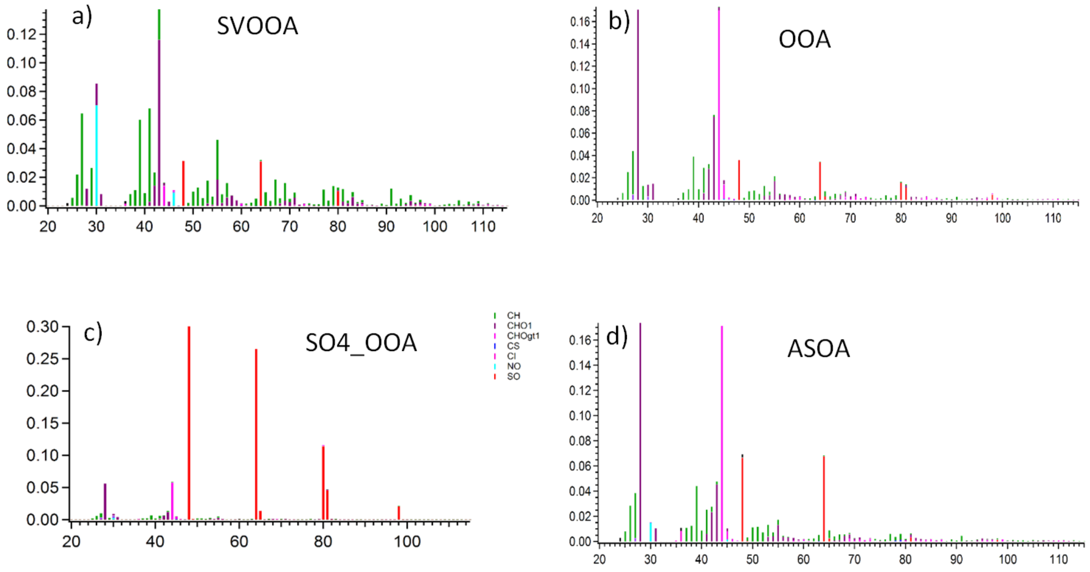


Figure 5.7. Organic species profiles extracted (Relative Intensity) from the PMF analysis done by H.L. Dewit: a) Semivolatile Oxygenated Organic Aerosol (SVOOA); b) Oxygenated Organic Aerosol (OOA); c) Sulphate Oxygenated Organic Aerosol (SO4_OOA); d) Ammonium Sulphate (AS).

Concentration (Relative Intensity) in µg/µg (with bars) and relative contribution (with dots) of chemical components for the 4-factor solution in PM_1 are shown.

Ions with a signal-to-noise ratio (SNR) < 0.2 were removed, while ions with a 0.2 < SNR < 2 were down-weighted by a factor of 2. Ions with duplicated information were further underrated (Li et al., 2013).

PMF exploration was run under seed mode from 2 to 7 factors, with 10 iterations for each factor. A parabolic vertex Q/Qexp value was detected at 4 factors. And all iterations displayed similar Q/Qexp ratios for these 4 factors.

After fixing the number of sources in 4, the PMF solutions were analysed for rotational ambiguity by varying the Fpeak parameter (Paatero et al., 2002). PMF was run with fPeak varying from -1 to 1 in steps of 0.1 for p (number of factors) from 2 to 7. Solutions with four factors were chosen to minimize residuals approach Q/Qexp ratio to 1. These factors were compared investigated with Polar Rose and compared with external tracers such as Black Carbon, DMS or Toluene. Finally, a four-factor solution was obtained: first characterised by Semivolatile Oxygenated Organic Aerosol (SVOOA), one by Low Volatile Oxygenated Organic Aerosol (OOA), one by Oxygenated Organic Aerosol accompanied by sulphate and related to DMS-marine (SO4_OOA), and one led by Ammonium Sulphate (AS).

O:C (0,64), H:C (1.25) and N:C (0.01) ratios obtained demonstrate that the impact of primary sources was very reduced during the campaign (El Haddad et al., 2013) and therefore, aged OA was predominant.

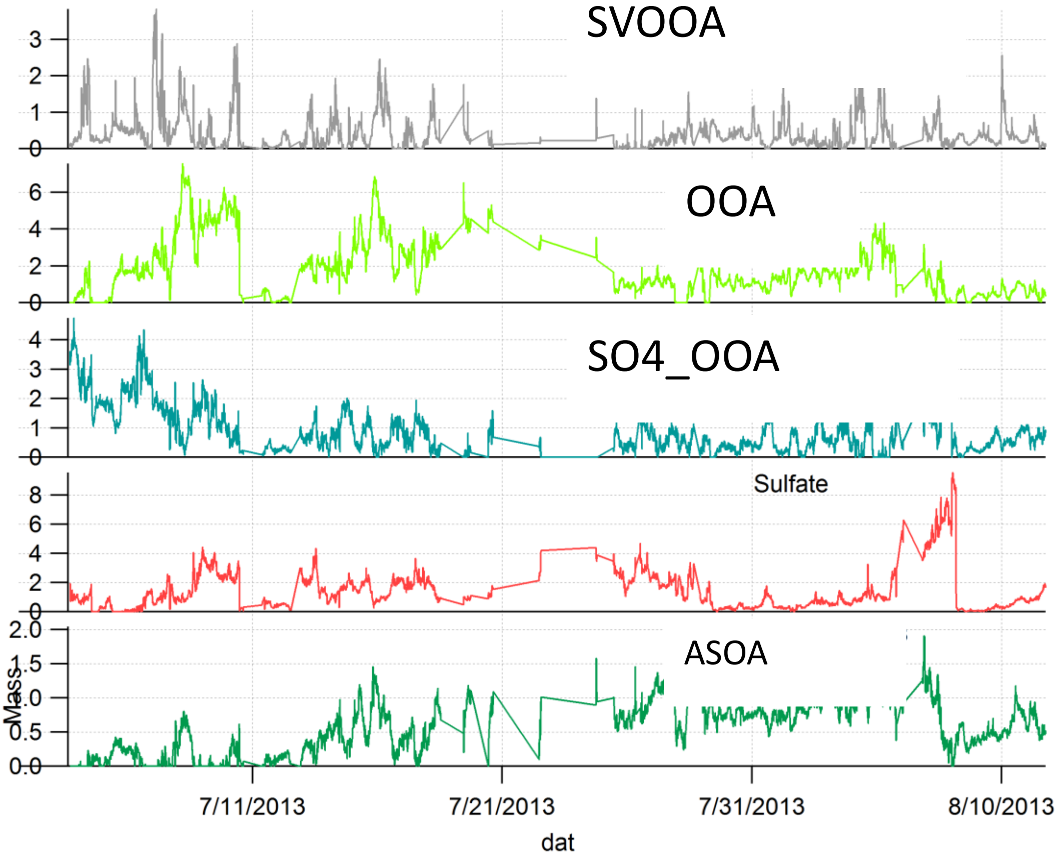


Figure 5.8. Time series concentration of the AMS-OA factors, in µgm^{-3}. Semivolatile Oxygenated Organic Aerosol (SVOOA); Oxygenated Organic Aerosol (OOA); Sulphate Oxygenated Organic Aerosol (SO4_OOA); Sulphate; Ammonium Sulphate (ASOA).

Considering these results obtained for AMS PM$_1$ OA is split into 4 fractions. Extraction of the organic mass within the time series of the factors was done removing inorganic species (Figure 5.8.). The most abundant fraction of Organic Matter corresponds to the named factor Oxygenated Organic Aerosol (OOA) (1.46 µgm^{-3}), followed by sulphate-marine Oxygenated Organic Aerosol (SO4_OOA) (0.62 µgm^{-3}), Semivolatile Organic Aerosol (SVOOA) (0.54 µgm^{-3}), and Ammonium Sulphate related Organic Aerosol (ASOA) (0.47 µgm^{-3}).

Results are consistent with the radiocarbon analysis, which reveals that 34,5 % of the Total Carbon corresponds to fossil carbon, with dissimilar results for OC (27,5% is fossil) and EC (69,4% is fossil).

86% of the EC is included in the anthropogenic factors for PM$_1$.

5.3.1. Connecting Offline PM$_1$24h filters with real time HR-ToF-AMS measurements-Synergies

AMS investigation delivers main organic elements (C, O, H, N) concentrations, which allows calculating the ratio between Organic Carbon to Organic Matter for each day. The OM/OC average obtained was 1.97.

OA from AMS factor time series were compared with PM$_1$ factor time series after extracting inorganic components, and both were compared with OM analysed time series (Figure 5.9.).

As it can be observed in Figure 5.9, a clear correlation was obtained for the three time series, being the AMS-OA the one that presents on or two clear outliers.

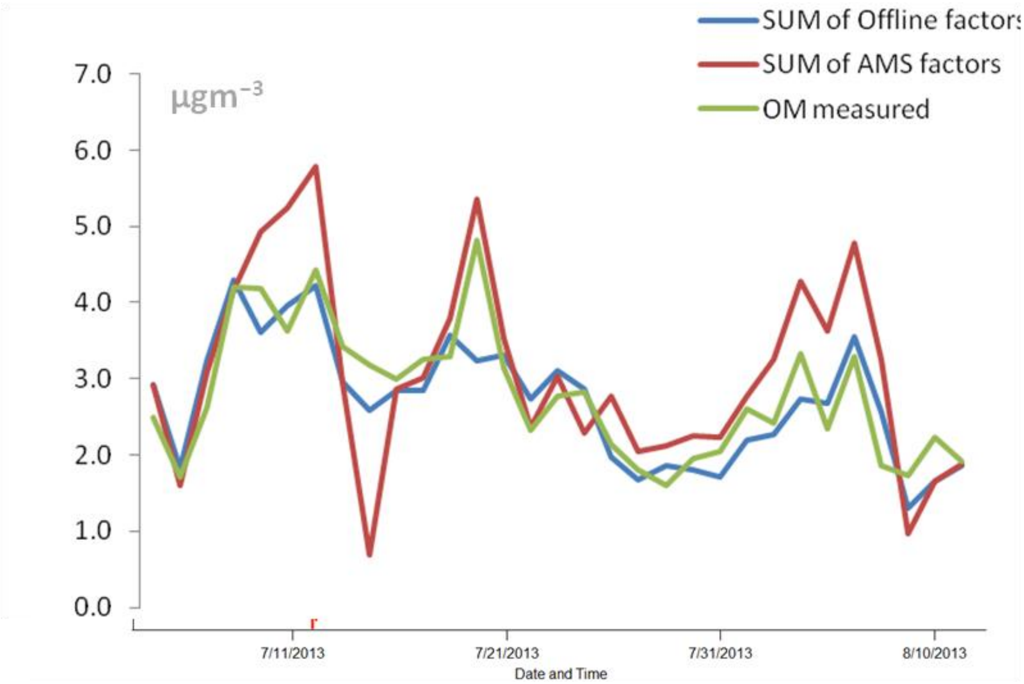


Figure 5.9. Time Series of on-line and off-line source apportionment solutions for OA are displayed respect to measured OA.

Table 5.1 reflects time series values of the organic component of the PM1-24h sources in green, and the organic component of the AMS-OA factors in orange. Results have been coloured in order to establish a visual reference that some relationship can be extracted.

Table 5.1. Time series, µgm^{-3}, of PM1-24h sources in green (ED, REG EB, ANT, REG ANT OA), and the organic component of the AMS-OA factors in orange (SVOOA, OOA, SO4_OOA, ASOA).

Date	OA EB	OA REG EB	OA ANT	OA REG ANT	SVOOA	OOA	SO4_OOA	ASOA
03/07/2013	0.51	0.14	1.59	0.68	0.68	0.41	1.40	0.43
04/07/2013	0.64	0.18	1.01	0.00	0.38	0.10	0.95	0.17
05/07/2013	1.10	0.07	1.53	0.55	0.68	1.29	1.02	0.10
06/07/2013	0.82	0.00	2.40	1.07	1.12	1.55	1.11	0.39
07/07/2013	0.36	0.11	1.76	1.38	0.92	3.07	0.44	0.49
08/07/2013	0.11	0.10	1.57	2.18	0.31	3.15	0.84	0.95
09/07/2013	0.58	0.06	1.45	2.13	0.68	3.77	0.39	0.95
10/07/2013	0.02	0.03	0.02	2.89	0.55	1.61	0.23	0.55
11/07/2013	0.02	0.02	0.00	2.55	0.23	0.15	0.17	0.15
12/07/2013	0.01	0.10	0.96	1.77	0.48	1.39	0.34	0.65
13/07/2013	0.38	0.12	1.23	1.12	0.50	1.55	0.43	0.52
14/07/2013	0.07	0.00	1.53	1.98	0.37	2.13	0.72	0.57
15/07/2013	0.28	0.00	1.84	1.12	1.04	3.42	0.41	0.48
16/07/2013	0.02	0.04	1.64	1.62	0.34	2.02	0.54	0.63
25/07/2013	0.03	0.00	1.20	1.51	0.10	0.97	0.65	0.64
26/07/2013	0.01	0.09	1.11	1.90	0.23	1.22	0.85	0.74
27/07/2013	0.00	0.12	0.56	2.17	0.48	0.64	0.70	0.47
28/07/2013	0.00	0.12	1.18	0.67	0.77	1.00	0.64	0.37
29/07/2013	0.06	0.01	1.38	0.22	0.55	1.09	0.36	0.04
30/07/2013	0.01	0.00	1.46	0.40	0.62	1.01	0.38	0.10
31/07/2013	0.01	0.09	1.31	0.39	0.53	1.07	0.46	0.19
01/08/2013	0.00	0.09	1.32	0.30	0.40	1.30	0.44	0.09
02/08/2013	0.16	0.08	1.39	0.57	0.34	1.55	0.68	0.19
03/08/2013	0.01	0.04	1.80	0.41	0.75	1.70	0.56	0.24
04/08/2013	0.00	0.05	2.23	0.45	0.81	2.61	0.48	0.36
05/08/2013	0.01	0.02	1.56	1.09	0.25	1.87	0.78	0.74
06/08/2013	0.05	0.06	1.17	2.28	0.71	1.46	1.16	1.47
07/08/2013	0.14	0.12	0.94	1.34	0.33	0.51	0.92	1.49
08/08/2013	0.62	0.05	0.63	0.00	0.39	0.31	0.26	0.01
09/08/2013	0.02	0.01	1.13	0.49	0.63	0.55	0.36	0.13
10/08/2013	0.01	0.02	1.29	0.54	0.50	0.83	0.56	0.27

Multiple Regression Analysis (MRA):

The aim in this case is to know how each AMS-OA factor is contained inside the 24h-filter-OA source. Therefore OA concentration for every 24h-PM$_1$ factor was taken as the dependent variable, and AMS-OA results were considered as independent variables. MRA was applied to each individual OA factor time series.

If the aim would have been the opposite, i.e., to know how each 24h-filter-OA source is contained inside the AMS-OA factor, then AMS-OA values would have been considered as the dependent variable, and 24h-PM$_1$ factor would have been taken as the independent variable.

Table 5.2. Multiple Regression Analysis outputs considering each 24h-filter-OA source the dependent variable and AMS-OA daily values as the independent variables.

OA_EB	*Coefficients*	*St. Error*	*t Statist*	*Probability*	*Lower 95%*	*Over 95%*	*Lower 95.0%*	*Over 95.0%*
SVOOA	0.1463	0.2029	0.7211	0.4770	-0.2699	0.5625	-0.2699	0.5625
OOA	0.0237	0.0609	0.3892	0.7002	-0.1013	0.1487	-0.1013	0.1487
SO4_OOA	0.3890	0.1618	2.4036	0.0234	0.0569	0.7211	0.0569	0.7211
ASOA	-0.3018	0.1584	-1.9057	0.0674	-0.6268	0.0231	-0.6268	0.0231

OA_REG EB	*Coefficients*	*St. Error*	*t Statist*	*Probability*	*Lower 95%*	*Over 95%*	*Lower 95.0%*	*Over 95.0%*
SVOOA	0.0170	0.0392	0.4327	0.6687	-0.0635	0.0975	-0.0635	0.0975
OOA	-0.0043	0.0118	-0.3618	0.7203	-0.0284	0.0199	-0.0284	0.0199
SO4_OOA	0.0754	0.0313	2.4086	0.0231	0.0112	0.1397	0.0112	0.1397
ASOA	0.0196	0.0306	0.6394	0.5279	-0.0433	0.0825	-0.0433	0.0825

OA_ANT	*Coefficients*	*St. Error*	*t Statist*	*Probability*	*Lower 95%*	*Over 95%*	*Lower 95.0%*	*Over 95.0%*
SVOOA	0.5100	0.2589	1.9697	0.0592	-0.0213	1.0413	-0.0213	1.0413
OOA	0.3908	0.0778	5.0259	0.0000	0.2313	0.5503	0.2313	0.5503
SO4_OOA	1.1275	0.2066	5.4574	0.0000	0.7036	1.5514	0.7036	1.5514
ASOA	-0.5615	0.2022	-2.7772	0.0098	-0.9763	-0.1467	-0.9763	-0.1467

OA_REG ANT	*Coefficients*	*St. Error*	*t Statist*	*Probability*	*Lower 95%*	*Over 95%*	*Lower 95.0%*	*Over 95.0%*
SVOOA	0.1992	0.5533	0.3601	0.7216	-0.9360	1.3345	-0.9360	1.3345
OOA	0.1890	0.1661	1.1376	0.2653	-0.1519	0.5299	-0.1519	0.5299
SO4_OOA	-0.0843	0.4414	-0.1910	0.8500	-0.9900	0.8214	-0.9900	0.8214
ASOA	1.5572	0.4320	3.6046	0.0012	0.6708	2.4436	0.6708	2.4436

Coefficients were considered (Table 5.3. A). Negative coefficients were considered to have zero contribution (Table 5.3. B). Therefore, the obtained sum of coefficients for each factor was normalized to 1 (Table 5.3. C). Then coefficients were rebuilt in mass apportionment considering total mass (Table 5.3. D). Finally, AMS-OA factors mass percentage in PM$_1$ factor solutions can be calculated (Table 5.3. E).

Table 5.3. A: Multiple Regression Analysis output coefficients (PM$_1$-24h-filters OA Vs. AMS-OA factors); B: Only positive values for coefficients; C: Normalized to 1 coefficients; D: AMS-OA rebuilt apportions to PM$_1$-24h-filters OA in μgm^{-3}; E: AMS-OA apportions to PM$_1$-24h-filters OA in %.

A. Coeffic.	OA EB	OA REG EB	OA ANT	OA REG ANT	Total mass μgm^{-3}
SVOOA	0.15	0.02	0.51	0.20	0.54
OOA	0.02	0.00	0.39	0.19	1.46
SO4_OOA	0.39	0.08	1.13	-0.08	0.62
ASOA	-0.30	0.02	-0.56	1.56	0.47
B. Coeffic.(+)	OA EB	OA REG EB	OA ANT	OA REG ANT	
SVOOA	0.15	0.02	0.51	0.20	
OOA	0.02	0.00	0.39	0.19	
SO4_OOA	0.39	0.08	1.13	0.00	
ASOA	0.00	0.02	0.00	1.56	
C. Norm.Coeffic.	OA EB	OA REG EB	OA ANT	OA REG ANT	
SVOOA	0.17	0.02	0.58	0.23	
OOA	0.04	0.00	0.65	0.31	
SO4_OOA	0.24	0.05	0.71	0.00	
ASOA	0.00	0.01	0.00	0.99	
D. μgm^{-3}	OA EB	OA REG EB	OA ANT	OA REG ANT	Total Mass
SVOOA	0.09	0.01	0.31	0.12	0.54
OOA	0.06	0.00	0.95	0.46	1.46
SO4_OOA	0.15	0.03	0.44	0.00	0.62
ASOA	0.00	0.01	0.00	0.46	0.47
E. %	OA EB	OA REG EB	OA ANT	OA REG ANT	
SVOOA	30.2	22.9	18.5	11.8	
OOA	19.2	0.0	55.7	43.8	
SO4_OOA	50.6	64.3	25.8	0.0	
ASOA	0.0	12.8	0.0	44.5	

Table 5.3.D and E let us to know how PM_1-24h-factors are related to the AMS-OA:

EB factor is composed mainly by SO4_OOA (50.6 %) and SVOOA (30.2 %), what could be related to marine influence and isoprene derivatives (Seinfeld et al., 2003) respectively.

REG EB source is clearly influenced again by SO4_OOA (64.3 %) and SVOOA (22.9 %).

In both cases, EB and REG EB, a partly of AMS-OA anthropogenic influenced factors are displayed, OOA (19.2 %) in the first case and ASOA (12.8 %) in the second.

ANT is related to aged secondary organic aerosol-OOA (55.7 %), but also to SO4_OOA (25.8 %), the marine one that could be related to shipping emission too.

REG ANT is constituted mainly by ASOA (44.5 %), normally associated to road traffic emissions, and OOA (43.8 %).

5.4. Discussion and conclusions

The study of aerosol phenomenology is a complex matter everywhere, but it becomes complicated when intense ageing processes occur. This is the case of the Mediterranean region in summer, especially in its western part (Pey et al., 2009; Cerro et al., 2015 and 2020). The co-emission of natural and anthropogenic sources together with recirculation of air masses at the regional scale results in intensive aerosol processing and ageing. The intensive campaign conducted in summer 2013 combined online and offline techniques to advance in the knowledge of secondary aerosols in this region. This campaign took place after the 3-year campaign on which this PhD is based. Therefore, a profound knowledge about aerosol patterns and components was obtained from that extensive study.

The state-of-the-art techniques used during the summer 2013 campaign allowed us to obtain new knowledge about dynamics and patterns of pollutants or sources contribution. As a result of that observation period, a number of patterns and characteristics were revealed:

-OA was the most abundant component of the PM_1 fraction (3.0 μgm^{-3}) representing 40% of the PM mass.

-The PM_1 24h filter source apportionment exhorted a 4-factor solution as the most appropriate. Among these 4 factors, one is clearly from natural origin, here named “earthbound” (EB). It is characterized by Al_2O_3, Fe, Ti and other mineral species, but also marine species Na, Mg. Another one, probably natural in origin but with a more regional nature, has been called “regional earthbound” (REG EB), as it relates mainly to Ca, consistent with the island’s soil composition, and also to sea salt aerosol. Two anthropogenic factors were obtained; “Anthropogenic” (ANT), characterized by EC, SO_4^{2-}, and “Regional Anthropogenic” (REG ANT), as it contains part of Ca.

-OA is distributed among all the factors, with the highest abundance in the ANT factor (1.26 μgm^{-3}), closely followed by REG ANT (1.16 μgm^{-3}) and with less abundance in the EB factor (0.20 μgm^{-3}). It is negligible in REG EB (0.07 μgm^{-3}).

-Regarding AMS, ME-2 was applied to the entire mass spectra (organic and inorganic ions). Again a 4 factors solution was obtained (DeWitt ongoing publication): a Semi volatile Oxygenated Organic Aerosol fraction (SVOOA) (0.54 μgm^{-3}), a Semi Volatile Oxygenated Organic Aerosol (SVOOA) (1.46 μgm^{-3}) fraction, another Oxygenated Organic Aerosol fraction that was strongly associated with sulphate and DMS characteristic ion (SO4_OOA) (0.62 μgm^{-3}), and an Ammonium Sulphate fraction (AS) (0.47 μgm^{-3}).

-In order to combine online and offline source apportionment solutions for OA, different statistical approaches were applied. Multiple Regression Analysis was considered to provide the best solution in terms of how AMS-OA factors were distributed among PM_1-OA’s. OA concentration for every PM_1 factor was taken as the dependent variable, and AMS-OA results were considered as independent variables. MRA was applied to each individual OA factor time series. Negative factors were considered to have zero contribution. Finally, the extracted coefficients were normalized to sum 1.

-Results exhort that an EB 24h-filter factor is composed mainly by SO4_OOA AMS factor (50.6 %) and SVOOA AMS (30.2 %); a 24h-filter REG EB factor is clearly influenced again by SO4_OOA AMS (64.3 %) and SVOOA AMS (22.9 %) factors; a 24h-filter ANT source is constituted mainly by OOA (55.7 %) and also by SO4_OOA (25.8 %); a REG ANT factor is constituted mainly by ASOA source (44.5 %) and OOA (43.8 %). Overall, SVOOA is an important fraction in all PM_1-offline solutions, OOA is the major Anthropogenic OA factor, SO4_OOA is mostly associated with natural factors and ASOA with REG ANT.

-To date, OA species have been important but poorly known fraction of airborne particulate matter in this region. The AMS has emerged as a powerful toolkit for identification of OA sources and quantitative source apportionment of atmospheric aerosols. Low-volatile and semi-volatile aerosols are associated with anthropogenic and long-range-transported secondary OA and, conversely, more volatile aerosols are related to recently-produced biogenic OA. The combination of offline and online source apportionment results has permitted a better knowledge regarding OA origins.

5.6. Acknowledgments

This work was supported by the ANR-12-BS060013-02 French project; CTQ2013-47461-R Spanish project; RYC-2013-14159 Spanish project; La Caixa mobility grants.

5.7. References

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L. *Elemental analysis of organic species with electron ionization high-resolution mass spectrometry*, Anal. Chem., 79, 8350–8358, 2007.

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L. *O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry*, Environ. Sci. Technol., 42, 4478–4485, 2008.

Allan J.D., Jimenez J.L., Williams P.I., Alfarra M.R., Bower K.N., Jayne J.T., Coe H., and Worsnop D.R. 2003. *Quantitative sampling using an Aerodyne aerosol mass spectrometer. Part 1: techniques of data interpretation and error analysis*. J Geophys Res-Atmos 108(D3):4090. doi:10.1029/2002JD002358

Barmpadimos I., J. Keller, D. Oderbolz, C. Hueglin, and A. S. H. Prévôt, 2012. *One decade of parallel fine (PM2.5) and coarse (PM10–PM2.5) particulate matter measurements in Europe: trends and variability*. Atmospheric Chemistry and Physics, 12, 3189–3203.

Brown S.G., Hafner H., 2005. Multivariate Receptor Modeling Workbook. Sonoma Technology Inc. Petaluma, CA. U.S.A. 236 pp. http://www.sonomatechdata.com/sti_workbooks/

Canagaratna M.R., Jayne J.T., Jimenez J.L., Allan J.D., Alfarra M.R., Zhang Q., Onasch T.B., Drewnick F., Coe H., Middlebrook A., Delia A., Williams L.R., Trimborn A.M., Northway M.J. 2007. *Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer*. Mass Spectrom Rev 26:185–222. doi:10.1002/mas.20115

Canagaratna M.R., Onasch T.B., Wood E.C., Herndon S.C., Jayne J.T., Cross E.S., Miake-Lye R.C., Kolb C.E., and Worsnop D.R. 2010. *Evolution of vehicle exhaust particles in the atmosphere*. J Air Waste Manag Assoc 60 (10):1192–1203. doi:10.3155/1047-3289.60.10.1192

Canonaco F., Crippa M., Slowik J.G., Baltensperger U., and Prévôt A.S.H. (2013). *SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data*, Atmos. Meas. Tech., 6, 3649–3661.

Cerro J.C., Cerda V., Pey J.: *Trends of air pollution in the Western Mediterranean Basin from a 13-year database: A research considering regional, suburban and urban environments in Mallorca (Balearic Islands),* Atmos. Environ., 103, 138-146, 2015.

Cerro J.C., Cerda V, Querol X., Alastuey A., Bujosa C. and Pey J., 2020. *Variability of air pollutants, andPMcomposition and sources at a regional background site in the Balearic Islands: Review of western Mediterranean phenomenology from a 3-year study*. Science of the Total Environment 717 (2020) 137177

Cheng Y., Duan F-k., He K-b., Du Z-y., Zheng M., Ma Y-l.: *Sampling artifacts of organic and inorganic aerosol: Implications for the speciation measurement of particulate matter,* Atmos. Environ., 55, 229-233, 2012.

Cusack M., Alastuey A., Pérez N., Pey J., Querol X.: *Trends of particulate matter (PM2.5) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010)*, Atmos. Chem. Phys., 12, 8341-8357, 2012.

DeCarlo P.F., Kimmel J.R., Trimborn A., Northway M.J., Jayne J.T., Aiken A.C., Gonin M., Fuhrer K., Horvath T., Docherty K.S., Worsnop D.R., Jimenez J.L. 2006. *A field-deployable high-resolution time-of-flight aerosol mass spectrometer*. Anal Chem 78(24):8281–8289. doi:10.1021/ac061249n

El Haddad I, D'Anna B., Temime-Roussel B., Nicolas M., Boreave A., Favez O., Voisin D., Sciare J., George C., Jaffrezo J.L., Wortham H., and Marchand M. *Towards a better understanding of the origins, chemical composition and aging of oxygenated organic aerosols: case study of a Mediterranean industrialized environment, Marseille*. Atmos. Chem. Phys., 13, 7875–7894, 2013

DeWitt H.L., Pey J., Hellebust S., Temime-Roussel B., Mizzi A., Salameh D, Sylvestre A., Elser M., Pérez N., Cerro J.C., Jaffrezo J.L., Mocnik G., Prévôt A. and Marchand N. (2014). *Comparison of the Sources of Organic Aerosol (OA) Using Aerosol Mass Spectrometry at Two Mediterranean Islands: Corsica and Mallorca,* Proc. Book 3rnd AAAR Annual Conference.

Fragkou E., Douros I., Moussiopoulos N., Belis C.A., 2012. *Current trends in the use of models for source apportionment of air pollutants in Europe*. Int. J. Environment and Pollution, Vol. 50, Nos. 1/2/3/4, 2012

Goldstein A, Galbally I. 2007. *Known and unexplored organic constituents in the earth's atmosphere*. Environ Sci Technol 41 (5):1514–1521. doi:10.1021/es072476p

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J. *The formation, properties and impact of secondary organic aerosol: current and emerging issues*, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X. F., Smith, K. A., Morris, J. W., and Davidovits, P. *Ambient aerosol* *sampling using the aerodyne aerosol mass spectrometer*, Geophys. Res. Atmos., 108, 8425, doi:10.1029/2001JD001213s, 2003.

Jimenez J. L., Canagaratna M. R., Donahue N. M., Prevot A. S. H., Zhang Q., Kroll J. H., DeCarlo P. F., Allan J. D., Coe H., Ng N. L., Aiken A. C., Docherty K. S., Ulbrich I. M., Grieshop A. P., Robinson A. L., Duplissy J., Smith J. D., Wilson K. R., Lanz V. A., Hueglin C., Sun Y. L., Tian J., Laaksonen A., Raatikainen T., Rautiainen J., Vaattovaara P., Ehn M., Kulmala M., Tomlinson J. M., Collins D. R., Cubison M. J., Dunlea J., Huffman J. A., Onasch T. B., Alfarra M. R., Williams P. I., Bower K., Kondo Y., Schneider J., Drewnick F., Borrmann S., Weimer S., Demerjian K., Salcedo D., Cottrell L., Griffin R., Takami A., Miyoshi T., Hatakeyama S., Shimono A., Sun J. Y, Zhang Y. M., Dzepina K., Kimmel J. R., Sueper D., Jayne J. T., Herndon S. C., Trimborn A. M., Williams L. R., Wood E. C., Middlebrook A. M., Kolb C. E., Baltensperger U., Worsnop D. R.. 2009. *Evolution of organic aerosols in the atmosphere*. Science 326:1525–1529. doi:10.1126/science.1180353

Kanakidou M., Seinfeld J.H., Pandis S.N., Barnes I., Dentener F.J., Facchini M.C., Van Dingenen R., Ervens B., Nenes A., Nielsen C.J., Swietlicki E., Putaud J.P., Balkanski Y., Fuzzi S., Horth J., Moortgat G.K., Winterhalter R., Myhre C. E. L., Tsigaridis K., Vignati E., Stephanou E. G., and Wilson J. 2005. *Organic aerosol and global climate modelling: a review*. Atmos Chem Phys 5:1053–1123. doi:10.5194/acp-5-1053-2005

Karagulian F., Belis C.A, 2012. *Enhancing Source Apportionment with receptor models to Foster the Air Quality Directive Implementation,* International Journal of Environmental Pollution. 50: 190-199.

Kroll J.H, Seinfeld J.H. 2008. *Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere*, Atmos Environ 42:3593–3624. doi:10.1016/j.atmosenv.2008.01.003

Kroll J.H., Donahue N.M., Jimenez J.L., Kessler S.H., Canagaratna M.R., Wilson K.R., Altieri K.E., Mazzoleni L.R., Wozniak A.S., Bluhm H., Mysak E.R., Smith J.D., Kolb C.E., Worsnop D.R. 2011. *Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol*. Nat Chem 3:133–139. doi:10.1038/NCHEM.94

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Pr´evˆot, A. S. H.. *Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra*, Atmos. Chem. Phys., 7, 1503–1522, doi:10.5194/acp-7-1503-2007, 2007.

Li, Y. J., Lee, B. Y. L., Yu, J. Z., Ng, N. L., and Chan, C. K.. *Evaluating the degree of oxygenation of organic aerosol during foggy and hazy days in Hong Kong using high-resolution time-offlight aerosol mass spectrometry (HR-ToF-AMS)*, Atmos. Chem. Phys., 13, 8739–8753, doi:10.5194/acp-13-8739-2013, 2013.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.. *Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data*, Aerosol Sci. Technol., 46, 258–271, doi:10.1080/02786826.2011.620041, 2012.

Minguillón M.C., Ripoll A., Pérez N., Prévôt A. S. H., Canonaco F., Querol X., and Alastuey A.: *Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor,* Atmos. Chem. Phys., 15, 6379–6391, 2015

Ng NL et al (2011) An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol. Aerosol Sci Technol 45(7):770–784. doi:10.1080/02786826.2011.560211 Paatero, P. and Tapper, U. *Positive matrix* *factorization: a non-negative factor model with optimal utilization of error estimates of data values*, Environmetrics, 5, 111–126, 1994.

Paatero, P. *The multilinear engine – A table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model*, J. Comput. Graph. Stat., 8, 854–888, 1999.

Pey J., Querol X., Alastuey A.: *Variations of levels and composition of PM10 and PM2.5 at an insular site in the Western Mediterranean,* Atmos. Res., 94, 285-299, 2009.

Pey J., Alastuey A., Querol X.: *PM10 and PM2.5 sources at an insular location in the western Mediterranean by using source apportionment techniques,* Sci. Total Environ., 456-457, 267-277, 2013a.

Pey J., Querol X., Alastuey A., Forastiere F., Stafoggia M.: *African dust outbreaks over the Mediterranean Basin during 2001–2011: PM10 concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology*, Atmos. Chem. Phys., 13, 1395-1410, 2013b.

Pey J., Cerro J.C., Hellebust S., DeWitt H.L., Temime-Roussel B., Elser M., Pérez N., Sylvestre A., Salameh D., Mocnik G., Prévôt A., Zhang Y., Szidat S., Marchand N. (2014). *Atmospheric Monitoring in the Western Mediterranean in Summer 2013: Overview of Physic-chemical Properties and Variability,* Proc. Book 3rnd AAAR Annual Conference.

Polissar, A. V., Hopke P. K., Paatero P., Malm W. C., and Sisler J. F., 1998. *Atmospheric aerosol over Alaska 2. Elemental composition and sources,*Journal of Geophysical Research D: Atmospheres, 103(D15), 19045-19057.

Polissar A.V., Hopke P.K. Poirot R.L., 2001. *Atmospheric aerosol over Vermont: chemical composition and sources*, Environmental Science and Technology. 35, 4604-4621.

Querol X., Alastuey A., Rodríguez S., Plana F., Ruiz C.R., Cots N., Massagué G., and Puig O.: *PM10 and PM2.5 source apportionment in the Barcelona Metropolitan area, Catalonia, Spain*, Atmos. Environ., 35, 6407-6419, 2001.

Querol X., Pey J., Pandolfi M., Alastuey A., Cusack M., Perez N., Moreno T., Viana M., Mihalopoulos N., Kallos G., Kleanthous S.: *African dust contributions to mean ambient PM10 mass-levels across the Mediterranean Basin*, Atmos. Environ., 43(28), 4266-4277, 2009.

Reff, A., Eberly, S.I., Bhave, P.V., 2007. *Receptor modelling of ambient particulate matter data using Positive Matrix Factorization: review of existing methods*. Journal of Air & Waste Management Association 57, 146-154.

Seinfeld JH, Pankow JF (2003) Organic atmospheric particulate material. Annu Rev Phys Chem 54:121–140. doi:10.1146/annurev.physchem.54.011002.103756

Sueper, D. *ToF-AMS data analysis software*, available at: http://cires.colorado.edu/jimenez-group/ToFAMSResources/ ToFSoftware/index.html, last access: 1 December 2013.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L., 2009.*Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data*. Atmos. Chem. Phys., 9, 2891–2918, doi:10.5194/acp-9-2891-2009.

Chapter 6. Discussion

Atmospheric pollution and climate change are among the most relevant environmental challenges at present. The Mediterranean Basin is subjected to an extreme anthropogenic pressure and will be one of the regions most affected by global change (IPCC, 2019). Atmospheric dynamics in the WMED is strongly dependent on the general atmospheric circulation in middle latitudes in the Northern Hemisphere, which is modulated in our case by the seasonal displacement of the quasi-permanent high pressure system located around the Azores archipelago (Millan et al., 2002). The combination of atmospheric dynamics, including the recirculation of air masses at the regional scale (Jorba et al., 2013a), together with the impact of long range transport of atmospheric pollutants and the emissions from local and regional sources, make the Mediterranean region an intricate area, but at the same time, a permanent laboratory (Querol et al., 2009; Pey et al., 2013; Karanasiou et al., 2014; Ancellet et al., 2016; Schepanski et al., 2016; Michoud et al., 2017; Chrit et al., 2018; Guth et al., 2018; Cholakian et al., 2018). The WMED is surrounded by continental areas in which thermal lows are developed in the warm season, whereas the subsidence of air masses occurs typically over the Balearic Sea. In this particular context, the above mentioned factors behave in a different way as they do it over continental areas. As a result, the accumulation and ageing of pollutants over this WMED maritime region could be enhanced.

Atmospheric pollution in the Western Mediterranean Basin has been assessed in several studies, most of them performed over continental areas facing the Mediterranean coast (Chazette et al., 2019; Chrit et al., 2018a and 2018b; Cozic et al., 2008; Cusack et al., 2012; Escudero et al., 2005; Galindo et al., 2017; Guth et al., 2018; Jorba et al., 2013b; Minguillón et al., 2015; Pandolfi et al., 2014; Pey et al., 2009a; Reche et al., 2011; Ripoll et al., 2014 and 2015; Rodríguez et al., 2002; Sorribas et al, 2015). As mentioned formerly, studies performed in insular locations are crucial to better understand the atmospheric processes and their related aerosol phenomenology in these environments. Since air renovation over islands is permanent, the variations of their composition and degree of pollution are more sensitive to pan-regional variations than to local inputs. Therefore, atmospheric dynamics, aerosol loadings and their removal processes at these environments can be regarded as comparable to those occurring in their vicinity regions over the sea. To date, a number of studies have been performed over islands. This is the case of those by Calzolai et al. (2015), Becagli et al. (2017), Liuzzi et al. (2017), Mailler et al. (2016) and Mallet et al. (2019) in the Lampedusa Island, in which they have revealed PM summer chemical composition and its sources, aerosol optical properties, and the specific influence of ship emissions. Likewise, those by Arndt et al. (2017), Chrit et al. (2018a), Claeys et al. (2017), Debevec et al. (2020), Desboeufs et al. (2018) and Michoud et al. (2017 and 2018) have been conducted in Corsica, bringing new knowledge regarding organic aerosol sources in this region, sometimes impacted by outflows from polluted regions nearby such as the Po and Rhone Valleys, or the Marseille area (Berland et al., 2017). Eastwards in the Mediterranean, most of the available studies have been developed in the Finokalia Island (Crete) and Cyprus. In the first case a supersite experiment has been implemented (Pikridas et al., 2019) and nucleation processes has investigated (Kalivitis et al., 2019). In the second case, volatile organic compounds have been studied (Debevec et al, 2017 and 2018). Other occasional studies have been carried out from other islands, like the Aegean

Archipelago (Athnasopoulou et al., 2015) or Minorca Island (Chazette et al., 2016). Several studies have been focused on comparison of different islands or in their relationship (Alastuey et al., 2016; Ancellet et al., 2016; Berland et al., 2016; Fu et al., 2017 and Mallet et al., 2016).

Several strategies have been displayed throughout the continent to improve air quality since the beginning of the 21stcentury, in the Framework of the "Clean Air For Europe" (CAFE) Programme. Several laws focused on industries, such as the following directives: limitation of emissions of Volatile Organic Compounds (1999/13/EC); Waste Incineration Plant Emissions (2000/76/EC); National Emission Ceiling Directive (2001/81/EC, 2016/2284/EU); Large Combustion Plant Emissions (2001/80/EC); Integrated Pollution Prevention and Control Directives (1996/61/EC, 2008/1/EC); Industrial Emission Directive (2010/75/EU). In addition, measures focused on transport, such as EURO3 to EURO6 European emission standards; and different Shipping Emission Directives (1999/32/EC, 2012/33/EU) have been also applied. Added to continental efforts countries, regions, and municipalities, have been tackling with air pollution, and its improvement. In general, citizens, companies and civil society have been involved sensitive to this problem. The result is that some of the common problems of air pollution, in regional terms, have been reduced: photochemical smog, acid rain, eutrophization caused by air pollution, and, in consequence, healthy problems have decreased, and better maintain of our ecosystems and historical heritage has been evidenced when compared with 80s and 90s.

Despite these efforts, there are some problems that still persist (e.g. airborne aerosol, polycyclic aromatic hydrocarbon or nitrogen oxides concentrations), or that have increased during recent years (e.g. tropospheric ozone or benzene concentrations), or that have not even been localized in the legislation (e.g. Chemical composition, ultrafine particles, most of heavy metals, most of the organics, road dust or indoor pollutants). The scientist knowledge is relevant to put the eye on these issues, even more in this context of global change. Future air quality regulations will need a complete study of the air pollution in general, and the aerosol composition specifically.

This has been the scientific and social-economic context in which this PhD thesis has been built. In this sense, the initial conception of the ChArMEx international action was devoted to fulfil the scientific gaps regarding atmospheric and aerosol phenomenology over the Mediterranean Sea. The experimental part of this PhD emerged in response to this international action, although the final experimental set-up was covered by different projects at national level. For different reasons, the regional background site of Can Llompart, in the Mallorca Isle (Balearic Islands), was selected. This PhD has evaluated the air quality impacts derived from the implementation of continental and local abatement strategies; it has investigated the current situation regarding atmospheric aerosol composition and their sources at the regional scale; and it has quantified the fluxes and sources of atmospheric aerosols transferred back from the atmosphere to the surface.

6.1. References

Alastuey A., Querol X, Aas W, Lucarelli F, Pérez N, Moreno T., Cavalli F., Areskoug H, Balan V, Catrambone M, Ceburnis D., Cerro J.C., Conil S., Gevorgyan L., Hueglin C., ImreK., Jaffrezo J.L., Leeson S.R., Mihalopoulos N., Mitosinkova M., O'Dowd C.D., Pey J., Putaud J.P., Riffault V., Ripoll A., Sciare J., Sellegri K., Spindler G., and Yttri K.E. 2016. *Geochemistry of PM10 over*

Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013, Atmos. Chem. Phys., 16, 6107–6129.

Ancellet G., Pelon J., Totems J., Chazette P., Bazureau A., Sicard M., Di Iorio T., Dulac F., and Mallet M., 2016. *Long-range transport and mixing of aerosol sources during the 2013 North American biomass burning episode: analysis of multiple lidar observations in the western Mediterranean basin.* Atmos. Chem. Phys., 16, 4725–4742, https://doi.org/10.5194/acp-16-4725-2016, 2016

Arndt J., Sciare J., Mallet M., Roberts G.C., Marchand N., Sartelet K., Sellegri K., Dulac F., Healy R.M., and Wenger J.C. 2017. *Sources and mixing state of summertime background aerosol in the north-western Mediterranean basin*. Atmos. Chem. Phys., 17, 6975–7001, https://doi.org/10.5194/acp-17-6975-2017

Becagli S., Anello F., Bommarito C., Cassola F., Calzolai G., Di Iorio T., di Sarra A., Gómez-Amo J.L., Lucarelli F., Marconi M., Meloni D., Monteleone F., Nava S., Pace G., Severi M., Sferlazzo D.M., Traversi R., and Udisti R. 2017. *Constraining the ship contribution to the aerosol of the central Mediterranean*, Atmos. Chem. Phys., 17, 2067–2084.

Berland K., Rose C., Pey J., Culot A., Freney E., Kalivitis N., Kouvarakis G., Cerro J.C., Mallet M., Sartelet K., Beckmann M., Bourriane T., Roberts G., Marchand N., Mihalopoulos N., and Sellegri K., 2017. *Spatial extent of new particle formation events over the Mediterranean Basin from multiple ground-based and airborne measurements*, Atmos. Chem. Phys., 17, 9567–9583, 2017 (doi.org/10.5194/acp-17-9567-2017).

Calzolai G., Nava S., Lucarelli F., Chiari M., Giannoni M., Becagli S., Traversi R., Marconi M., Frosini D., Severi M., Udisti R., di Sarra A., Pace G., Meloni D., Bommarito C., Monteleone F., Anello F., and Sferlazzo D.M., 2015. *Characterization of PM10 sources in the central Mediterranean*. Atmos. Chem. Phys., 15, 13939–13955, https://doi.org/10.5194/acp-15-13939-2015, 2015

Chazette P., Totems J., and Shang X., 2019. *Transport of aerosols over the French Riviera – link between ground-based lidar and spaceborne observations*. Atmos. Chem. Phys., 19, 3885–3904, https://doi.org/10.5194/acp-19-3885-2019

Cholakian A., Beekmann M., Coll I., Ciarelli G., and Colette A., 2018. *Biogenic secondary organic aerosol sensitivity to organic aerosol simulation schemes in climate projections.* Atmos. Chem. Phys., 19, 13209–13226, https://doi.org/10.5194/acp-19-13209-2019, 2019

Chrit M., Sartelet K., Sciare J., Pey J., Nicolas J.B., Marchand N., Freney E., Sellegri K., Beekmann M., and Dulac F., 2018a. *Aerosol sources in the western Mediterranean during summertime: a model-based approach.* Atmos. Chem. Phys., 18, 9631–9659, https://doi.org/10.5194/acp-18-9631-2018

Chrit M., Sartelet K., Sciare J., Majdi M., Nicolas J., Petit J.E., and Dulac F., 2018b. *Modeling organic aerosol concentrations and properties during winter 2014 in the northwestern Mediterranean region*. Atmos. Chem. Phys., 18, 18079–18100, https://doi.org/10.5194/acp-18-18079-2018

Claeys M., Roberts G., Mallet M., Arndt J., Sellegri K., Sciare J., Wenger J., and Sauvage B. 2017. *Optical, physical and chemical properties of aerosols transported to a coastal site in the western Mediterranean: a focus on primary marine aerosols*. Atmos. Chem. Phys., 17, 7891–7915, https://doi.org/10.5194/acp-17-7891-2017

Cozic J., Verheggen B., Weingartner E., Crosier J., Bower K. N., Flynn M., Coe H., Henning S., Steinbacher M., Henne S., CollaudCoen M., Petzold A., and Baltensperger U.: *Chemical composition of free tropospheric aerosol for PM1 and coarse mode at the high alpine site Jungfraujoch*, Atmos. Chem. Phys., 8, 407–423, 2008.

Cusack M., Alastuey A., Pérez N., Pey J., Querol X.: *Trends of particulate matter (PM2.5) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002–2010)*, Atmos. Chem. Phys., 12, 8341-8357, 2012.

Debevec C., Sauvage S., Gros V., Sciare J., Pikridas M, Stavroulas I., Salameh T., Leonardis T., Gaudion V., Depelchin L., Fronval I., Sarda-Esteve R., Baisnée D., Bonsang B., Savvides C., Vrekoussis M., and Locoge N. 2017. *Origin and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus)*. Atmos. Chem. Phys., 17, 11355–11388, https://doi.org/10.5194/acp-17-11355-2017

Debevec C., Sauvage S., Gros V., Sellegri K., Sciare J., Pikridas M., Stavroulas I., Leonardis T., Gaudion V., Depelchin L., Fronval I., Sarda-Esteve R., Baisnée D., Bonsang B., Savvides C., Vrekoussis M., and Locoge N. 2018. *Driving parameters of biogenic volatile organic compounds and consequences on new particle formation observed at an eastern Mediterranean background site*. Atmos. Chem. Phys., 18, 14297–14325, https://doi.org/10.5194/acp-18-14297-2018

Debevec C., Sauvage S., Gros V., Salameh T., Sciare J., Dulac F., and Locoge N. 2020. *Seasonal variation and origins of volatile organic compounds observed during two years at a western Mediterranean remote background site (Ersa, Cape Corsica)*. Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-607

Desboeufs K., Bon Nguyen E., Chevaillier S., Triquet S., and Dulac F., 2018. *Fluxes and sources of nutrient and trace metal atmospheric deposition in the northwestern Mediterranean*. Atmos. Chem. Phys., 18, 14477–14492, 2018. https://doi.org/10.5194/acp-18-14477-2018.

Escudero M., Castillo S., Querol X., Avila A., Alarcón M., Viana M.M., Alastuey A., Cuevas E., Rodríguez S., 2005. *Wet and dry African dust episodes over eastern Spain*. J. Geophys. Res. Atmos., 110, D18.

Fu Y., Desboeufs K., Vincent J., Bon Nguyen E., Laurent B., Losno R., and Dulac F. *Estimating chemical composition of atmospheric deposition fluxes from mineral insoluble particles deposition collected in the western Mediterranean region*. Atmos. Meas. Tech., 10, 4389–4401, 2017

Galindo N., Yubero E., Nicolás J.F., Crespo J., Varea M., Gil-Moltó J.: *Regional and long-range transport of aerosols at Mt. Aitana, Southeastern Spain*, Sci. Total Environ., 584–585, 723–730, 2017.

Guth J., Marécal V., Josse B., Arteta J., and Hamer P., 2018. *Primary aerosol and secondary inorganic aerosol budget over the Mediterranean Basin during 2012 and 2013.* Atmos. Chem. Phys., 18, 4911–4934, https://doi.org/10.5194/acp-18-4911-2018

IPCC, 2019. *IPCC Special Report on the Ocean and Cryosphere in a Changing Climate* [H.-O. Pörtner, D.C. Roberts, V. Masson-Delmotte, P. Zhai, M. Tignor, E. Poloczanska, K. Mintenbeck, A. Alegría, M. Nicolai, A. Okem, J. Petzold, B. Rama, N.M. Weyer (eds.)]. In press

Jorba O., Pandolfi M., Spada M., Baldasano J.M., Pey J., Alastuey A., Arnold D., Sicard M., Artiñano B., Revuelta M.A., Querol X., 2013a. *Overview of the meteorology and transport patterns during the DAURE field campaign and their impact to PM observations*. Atmos.Environ., 77, 607-620. http://dx.doi.org/10.1016/j.atmosenv.2013.05.040

Jorba O., Perez Garcia-Pando C., Spada M., Baldasano J. M., and Janjic Z., 2013b. *Modeling and evaluation of the global sea-salt aerosol distribution: sensitivity to emission schemes and resolution effects at coastal/orographic sites*, Atmos. Chem. Phys., 13, 11735-11755.

Kalivitis N., Kerminen V.M., Kouvarakis G., Stavroulas I., Tzitzikalaki E., Kalkavouras P., Daskalakis N., Myriokefalitakis S., Bougiatioti A., Manninen H.E., Roldin P., Petäjä T., Boy M., Kulmala M., Kanakidou M., and Mihalopoulos N.. 2019. *Formation and growth of atmospheric nanoparticles in the eastern Mediterranean: results from long-term measurements and process simulations*. Atmos. Chem. Phys., 19, 2671–2686, https://doi.org/10.5194/acp-19-2671-2019

Karanasiou A., Querol X., Alastuey A., Perez N., Pey J., Perrino C., Berti C., Gandini M., Poluzzi V., Ferrari S., de la Rosa J., Pascal M., Samoli E., Kelesis A., Sunyer J., Alessandrini E., Stafoggia M., 2014. *Particulatematter and gaseouspollutants in theMediterranean Basin: Results from the Med-Particles project*. Sci. Tot. Environ., 488-489, 297-315, http://dx.doi.org/10.1016/j.scitotenv.2014.04.096

Liuzzi G., Masiello G., Serio C., Meloni D., Di Biagio C., and Formenti P. 2017. *Consistency of dimensional distributions and refractive indices of desert dust measured over Lampedusa with IASI radiances*. Atmos. Meas. Tech., 10, 599–615, https://doi.org/10.5194/amt-10-599-2017

Mailler S., Menut L., di Sarra A.G., Becagli S., Di Iorio T., Bessagnet B., Briant R., Formenti P., Doussin J.F., Gómez-Amo J.L., Mallet M., Rea G., Siour G., Sferlazzo D.M., Traversi R., Udisti R., and Turquety S. 2016. *On the radiative impact of aerosols on photolysis rates: comparison of simulations and observations in the Lampedusa island during the ChArMEx/ADRIMED campaign*. Atmos. Chem. Phys., 16, 1219–1244, https://doi.org/10.5194/acp-16-1219-2016

Mallet M., Dulac F., Formenti P., Nabat P., Sciare J., Roberts G., Pelon J., Ancellet G., Tanré D., Parol F., Denjean C., Brogniez G., di Sarra A., Alados-Arboledas L., Arndt J., Auriol F., Blarel L., Bourrianne T., Chazette P., Chevaillier S., Claeys M., D'Anna B., Derimian Y., Desboeufs K., Di Iorio T., Doussin J.-F., Durand P., Féron A., Freney E., Gaimoz C., Goloub P., Gómez-Amo J. L., Granados-Muñoz M. J., Grand N., Hamonou E., Jankowiak I., Jeannot M., Léon J.-F., Maillé M., Mailler S., Meloni D., Menut L., Momboisse G., Nicolas J., Podvin T., Pont V., Rea G., Renard J.-B., Roblou L., Schepanski K., Schwarzenboeck A., Sellegri K., Sicard M., Solmon F., Somot S., Torres B, Totems J., Triquet S., Verdier N., Verwaerde C., Waquet F., Wenger J., and Zapf P. 2016. *Overview of the Chemistry-Aerosol Mediterranean Experiment/Aerosol Direct Radiative Forcing on the Mediterranean Climate (ChArMEx/ADRIMED) summer 2013 campaign*. Atmos. Chem. Phys., 16, 455–504, https://doi.org/10.5194/acp-16-455-2016

Mallet M.D., D'Anna B., Même A., Bove M.C., Cassola F., Pace G., Desboeufs K., Di Biagio C., Doussin J.F., Maille M., Massabò D., Sciare J., Zapf P., Giorgio di Sarra A., and Formenti P. 2019. *Summertime surface PM_1 aerosol composition and size by source region at the Lampedusa island in the central Mediterranean Sea*. Atmos. Chem. Phys., 19, 11123–11142, https://doi.org/10.5194/acp-19-11123-2019.

Michoud V., Sciare J., Sauvage S., Dusanter S., Léonardis T., Gros V., Kalogridis C., Zannoni N., Féron A., Petit J.E., Crenn V., Baisnée D., Sarda-Estève R., Bonnaire N., Marchand N., DeWitt H.L., Pey J., Colomb A., Gheusi F., Szidat S., Stavroulas I., Borbon A., and Locoge N., 2017. *Organic carbon at a remote site of the western Mediterranean Basin: Sources and chemistry during the ChArMEx SOP2 field experiment*. Atmos. Chem. Phys., 17, 8837–8865.

Michoud V., Sauvage S., Léonardis T., Fronval I., Kukui A., Locoge N., and Dusanter S., 2018. *Field measurements of methylglyoxal using proton transfer reaction time-of-flight mass spectrometry and comparison to the DNPH–HPLC–UV method.* Atmos. Meas. Tech., 11, 5729–5740, https://doi.org/10.5194/amt-11-5729-2018, 2018

Millán M. M., Sanz M. J., Salvador R., and Mantilla E., 2002. *Atmospheric dynamics and ozone cycles related to nitrogen deposition in the western Mediterranean*, Environ. Pollut., 118: 167-186.

Minguillón M.C., Ripoll A., Pérez N., Prévôt A. S. H., Canonaco F., Querol X., and Alastuey A., 2015. *Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor,* Atmos. Chem. Phys., 15, 6379–6391.

Pandolfi M., Querol X., Alastuey A., Jimenez J.L., Jorba O., Day D.A., Ortega A., Cubison M., Comerón A., Sicard M., Mohr C., Prévôt A., Minguillón M.C., Pey J., Baldasano J., Burkhart J.F., Seco R., Peñuelas J., van Drooge B.L., Artiñano B., Di Marco C., Nemitz E., Schallhart S., Metzger A., Hansel A., Lorente J., Ng N.L., Jayne J., Szidat S., 2014. *Effects of Sources and Meteorology on Particulate Matter in the Western Mediterranean Basin: An overview of the DAURE campaign*. Journal of Geophysical Research-Atmospheres 119, 4978–5010, doi:10.1002/2013JD021079.

Pey J., Pérez N., Castillo S., Viana M., Moreno T., Pandolfi M., López-Sebastián J.M., Alastuey A., Querol X., 2009a. *Geochemistry of regional background aerosols in the Western Mediterranean*. Atmospheric Research, 94, 422-435.

Pey J., Querol X., Alastuey A., Forastiere F., Stafoggia M., 2013. *African dust outbreaks over the Mediterranean Basin during 2001–2011: PM10 concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology*. Atmospheric Chemistry and Physics, 13, 1395-1410.

Pikridas M., Bougiatioti A., Hildebrandt L., Engelhart G. J., Kostenidou E., Mohr C., Prévôt A. S. H., Kouvarakis G., Zarmpas P., Burkhart J. F., Lee B.-H., Psichoudaki M., Mihalopoulos N., Pilinis C., Stohl A., Baltensperger U., Kulmala M., and Pandis S. N. 2010. *The Finokalia Aerosol Measurement Experiment –2008 (FAME-08): an overview*. Atmos. Chem. Phys., 10, 6793–6806, 2010 www.atmos-chem-phys.net/10/6793/2010/doi:10.5194/acp-10-6793-2010

Querol X., Alastuey A., Pey J., Cusack M., Pérez N., Mihalopoulos N., Theodosi C., Gerasopoulos E., Kubilay N., Koçak M., 2009. *Variability in regional background aerosols within the Mediterranean*. Atmospheric Chemistry and Physics, 9, 4575-4591.

Reche C., Viana, M. Moreno T., Querol X., Alastuey A., Pey J., Pandolfi M., Prévôt A., Mohr C., Richard A., Artiñano B., Gomez-Moreno F.J., Cots N., 2011. *Peculiarities in atmospheric particle number and size-resolved speciation in an urban area in the western Mediterranean: Results from the DAURE campaign*. Atmospheric Environment, 5282-5293.

Ripoll A., Pey J., Minguillón M. C., Pérez N., Pandolfi M., Querol X., Alastuey A., 2014. *Three years of aerosol mass, black carbon and particle number concentrations at Montsec (southern~Pyrenees, 1570 m a.s.l.)*. Atmos. Chem. Phys., 14, 4279-4295, doi:10.5194/acp-14-4279-2014.

Ripoll A., Minguillón M.C., Pey J., Pérez N., Querol X., and A. Alastuey A., 2015. *Joint analysis of continental and regional background environments in the Western Mediterranean: PM1 and PM10 concentrations and composition, Atmos.* Chem. Phys., 15, 1129-1145.

Rodríguez S., Querol X., Alastuey A., Mantilla E., 2002. *Origin of high summer PM10 and TSP concentrations at rural sites in Eastern Spain*. Atmos. Environ., 36, 3101-3112.

Schepanski K., Mallet M., Heinold B., and Ulrich M., 2016. *North African dust transport toward the western Mediterranean basin: atmospheric controls on dust source activation and transport pathways during June–July 2013.*Atmos. Chem. Phys., 16, 14147–14168, https://doi.org/10.5194/acp-16-14147-2016

Sorribas M., Ogren J.A., Olmo F.J., Quirantes A., Fraile R., Gil-Ojeda M., Alados-Arboledas L., 2015. *Assessment of African desert dust episodes over the southwest Spain at sea level using in situ aerosol optical and microphysical properties*. Tellus B 2015, 67, 27482, doi:10.3402/tellusb.v67.27842

Chapter 7. Conclusions and future research

This thesis provides new understanding about the quality of air and aerosol phenomelogy in the Western Mediterranean. This work has been based on the extensive existing knowledge, going beyond in different matters:

1. The current state and recent trends of atmospheric pollutants in the western Mediterranean has been assessed. The analysis reveals that air masses over Mallorca area good approximation to Western Mediterranean atmospheric phenomenology. Air pollutants at urban and regional background areas behave as expected, with higher pollution in winter over the cities and more homogeneous pollution over the region in summer. Contrary to remote continental sites, ozone reaches its higher concentrations in spring or at the end of the summer period, probably due to the combined effect of enhanced biogenic VOC emissions and lower NO_x concentrations, the latest clearly enhanced in summer as a result of tourism. Regarding the origin of air pollutants, NO and NO_2 are clearly urban, while PM_{10} and O_3 are mostly due to regional and long-range transport, in spite of non-negligible urban contributions. SO_2 originates from regional sources, especially from power generation and shipping emissions.

Trends of air pollutants displayed a clear improvement of the air quality in all environments for the period 2000-2012, but less pronounced thereafter (2010-2018). Such downward trends are explained thanks to the implementation of certain European strategies to tackle air pollution, combined with some actions at local and regional level, without forgetting the dramatic impact of the financial crisis. The initial drop of NO_x and PM_{10} concentrations at urban areas evolved into a slight decrease during the second period, with even an upturn for NO_2 coincident with the economy recovery and absence of new abatement policies at regional level. Local strategies were expected to shift to alternative mobility, but they promote the spreading of vehicular emissions rather than a change towards a greener mobility. As a result, pollution levels at suburban areas decreased less than in the main city, except for SO_2, which was substantially reduced as a result of the entering in force of the new regulations limiting sulphur content in fuels, and the de-sulphuring system implemented in early 2000's in the coal power plant. Regarding O_3, the slight increase detected at the regional background environment was attributed to the overall increase on the continental scale, as suggested by their high load under Atlantic air-mass origin.

The role of the North Atlantic Oscillation (NAO) was also assessed, and this region was benefited several times by negative NAO phases, in which atmospheric dispersion is enhanced: 2002, 2005-2007, 2008, 2010-2011, or the second semester of 2012-2013. Globally, meteorology during the interval 2000-2012 favored the reduction of air pollution, while this benefit was not encountered afterwards. Therefore, the meteorological conditions could influence the steepness of the downward trend during the period 2000-2012 but not in the downward trend itself. The persistence of opposite meteorological conditions during the second period was not enough to counteract the achieved air quality benefits.

2. We conducted a long-term measurement and sampling campaign (2010-2012), with intensification of the observations in spring and summer seasons in which other metrics such as NH_3, particle number concentrations or black carbon were also measured. During the course of the 3-year campaign we had the opportunity to verify the strong variability of aerosol phenomenology in this region. Thus, the effect of the NAO index together with the intrinsic

variability of the Mediterranean climate led us to conclude that a 3-year average represents much better the so-called “annual average” than any single annual average, smoothing meteorological impacts or short-term socioeconomic phases. The 3-year campaign started under a very negative NAO phase and finished under positive phase. Likewise, anthropogenic emissions over the Balearic Islands decreased from 2010 to 2012 as a consequence of the financial crisis and the implementation of different abatement strategies. Such a scenario, however, led to a progressive increase of PM, mineral dust and SO_4^{2-} from 2010 to 2012, thus reflecting the relevance of large-scale atmospheric circulation.

The chemical characterisation of PM_{10} reflects that this fraction is mostly composed of mineral dust, followed by organic matter, sea spray and sulphate. PM_1 is mainly formed by organic matter, sulphate, but also mineral dust and ammonium. The comparative study with other parts of the Western Mediterranean reveals that insular regions register higher values of SO_4^{2-}, as a result of summing up natural and anthropogenic emissions, but organic matter and NO_3^- are clearly enhanced in the South-Alpine region and in Central Italy, indicating the strong influence of biomass burning and urban emissions, respectively. Mineral dust decreases northwards as a reduction in African dust is occurring.

Source apportionment results show that anthropogenic sources on PM_1 explain almost 80% of the mass, while natural sources register the impact on the coarse fraction to represent around 50% of PM_{10}. Marine and mineral dust sources have been well separated (probably because the episodic nature of them), while the anthropogenic ones are not, since they get to our site all mixed in an aged aerosol, as expected for a remote environment. Finally PMF solution split anthropogenic influence in two different factors both in PM_1 and PM_{10}: a mix of local-to-regional sources corresponding to emissions taking place in the Island (road traffic, shipping and power plant emissions), and a mix of regional-to-long range sources corresponding to aged aerosols from various sources transported to the Island (potentially mixed with regional emissions). Such anthropogenic influence is clearly enhanced in summer as a result of the combined effect of atmospheric stagnant conditions and the increased anthropogenic pressure in this region and all around the Mediterranean.

Intensive campaigns were important to estimate the background concentration of black carbon in the Western Mediterranean (0.30 $\mu g/m^3$) and to document the occurrence of extreme new-particle formation events in spring, coinciding with the bloom of biogenic VOCs and O_3 peaks.

3. The separate study of wet and dry deposition (September 2010-August 2012) and its chemical characterisation of soluble and insoluble species showed some new findings. Average deposition flux for the sampling period was 32 $gm^{-2}yr^{-1}$. Total deposition flux is mainly driven by wet deposition and by the impact of Saharan dust. From time to time, intense peaks of nitrate and sulphate occur, especially under north-eastern flows, giving evidence of the transport of pollutants from mainland Europe. A specific investigation was conducted to study trends on nutrients ($N\text{-}NH_4^+{}_{ss}$, P_{nss}, K^+_{ss}, Fe_{nss}) and components of agricultural interest ($N\text{-}NO_3^-{}_{ss}$, $S\text{-}SO_4^{2-}{}_{ss}$) deposition. Nitrate and sulphate depend on specific episodes almost 100% driven by WD that usually occur during autumn or winter seasons, while with nutrients settling is more constant throughout the year and more balanced between dry and wet deposition. The contribution of the different sources was distinguished: marine, anthropogenic including road

traffic, African dust, biomass burning, regional dust, and regional pollution. When regarding the origin of African dust travelling towards the Balearic Islands, three main source regions were found: the Western Sahara, the Algeria-Hoggar Massif and Tunisia-Libya. Our results have revealed significant chemical differences among dust-particles from these regions which are related to intense geological variations. Saharan dust is, sometimes, evidently enriched in anthropogenic pollutants. This is especially true for the few Libyan samples.

4. Additionally, in 2013, another summer intensive campaign allowed as to establish new combined knowledge between the avant-garde AMS-OA outputs and the conventional PM_1-24h-filter organic fractions. Results obtained show that Semivolatile organic aerosol an important fraction in all PM_1-offline solutions, Oxygenated Organic Aerosol (not related to sulphate) is the major anthropogenic factor, while Oxygenated Organic Aerosol associated with high sulphate concentrations is mostly associated with marine factors. Finally, the clear sulphate factor was more associated with regional anthropogenic factors, surely affected by shipping emissions or the coal fired power plant.

Definitively this thesis constitutes a wide diagnosis of the current air pollution dynamics and trends in the Western Mediterranean, concentrations, sources and fluxes; and composes a “fitness-check” of the mitigation strategies, from local to continental level, in contrast to the human activity trends.

7.1. Highlights

First part (Chapter 2 and Chapter 3):

- Patterns and trends of air pollutant concentrations in the Western Mediterranean (2002-2012-2018): urban, suburban and remote environments
- Specific NAO conditions contributed positively to air quality improvement
- Abatement policies and economic crisis explain most of the observed trends
- The impact of local and continental abatement measures was differentiated when patterns and trends where calculated in function of air mass dynamics

Second part (Chapter 3):

- Insular and pan-regional aerosol phenomenology of air pollutants and aerosol chemistry composition is discussed and revised
- Aerosol sources in the insular regional background of the Western Mediterranean
- Local to regional sources are increasing, while long-range transport is decreasing
- Level of background air pollution remain due to boosted maritime and air transport

Third part (Chapter 4):

- Dry Vs Wet, Soluble Vs Insoluble, Deposition fluxes in the Western Mediterranean, comparison with other studies.
- Source apportionment study integrating Dry and Wet Deposition results
- African (differentiating dust source areas) dust and nutrients deposition in the Western Mediterranean, case studies

Fourth part (Chapter 5):

- Combination of conventional aerosol studies with the avant-garde Aerosol Mass Spectrometer outputs led to obtain better understanding of Organic Aerosol sources.

7.2. Future research

Thanks to this Thesis we have a better knowledge about gaseous pollutants and aerosol patterns and dynamics in the Western Mediterranean, and how global and local policies have contributed to their trends. On the opposite side, we have assessed the counteracting effect of the constant growth of tourism activity. We have compared results about the chemical composition of coarse and fine particles and we have found out which are the main sources. Furthermore we have determined the main fluxes of aerosol deposition in the middle of the Western Mediterranean, its sources and compared with other sites around this Basin. We have studies how contemporary in situ analysers and conventional techniques can be integrated in order to establish a better understanding of organic aerosol sources.

However, as a result of this research, we have figured out that some studies should be conducted in deep, e.g.:

- Ozone dynamics and specially its reactivity

- The specific effect of some mitigation policies

-The importance of nanoparticles in our region has been evidenced, but the lack of instrumental facilities has permitted only an initial assessment. The investigation of long—term data on nanoparticles and their origin would be desirable and would help in understanding better a number of aerosol processes described in this PhD.

- Contemporary sensors enable to real-time measurements of volatile organic compounds (PTR-ToF-MS) and organic aerosol (ACSM and HR-ToF-AMS).

-A multidisciplinary action integrating ecosystem responses to aerosol fluxes.

- The new tools that telemetric sensors offer, from land surface and from satellites, should allow us to establish real-time concentration cartographies of some pollutants.

- Nanosensors and Big data should be properly integrated with the “citizen science”.

-Other field of research may put the eye on emerging pollutants and biological indicators.

- Indoor pollutants and their patterns are still starting to be studied.

ANNEX I: Publications

I.I. Thesis Publications

1. Cerro J.C., Cerda V., Pey J.: Trends of air pollution in the Western Mediterranean Basin from a 13-year database: A research considering regional, suburban and urban environments in Mallorca (Balearic Islands), Atmos. Environ., 103, 138-146, 2015.

http://dx.doi.org/10.1016/j.atmosenv.2014.12.014

Atmospheric Environment 103 (2015) 138–146

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Trends of air pollution in the Western Mediterranean Basin from a 13-year database: A research considering regional, suburban and urban environments in Mallorca (Balearic Islands)

J.C. Cerro [a, b, *], V. Cerdà [a], J. Pey [c, d]

[a] *Laboratory of Environmental Analytical Chemistry, Illes Balears University, Ctra. Palma-Valldemossa, Km 7.2, 07122, Palma de Mallorca, Spain*
[b] *Laboratory of the Atmosphere, Balearic Islands Government, C/Corredors, 10, 07009, Palma de Mallorca, Spain*
[c] *Aix Marseille Université, CNRS, LCE FRE 3416, 13331, Marseille, France*
[d] *Instituto Geológico y Minero de España, Unidad de Zaragoza, C/Manuel Lasala 44, 9B, 50006 Zaragoza, Spain*

HIGHLIGHTS

- 13-years data of regulated air pollutants have been studied in Mallorca Island.
- Mallorca represents Western Mediterranean atmospheric phenomenology.
- Abatement policies and economic crisis explain most of the observed trends.
- Specific NAO conditions contributed positively to air quality improvement.
- The impact of local and continental abatement measures was differentiated.

ARTICLE INFO

Article history:
Received 6 October 2014
Received in revised form
5 December 2014
Accepted 6 December 2014
Available online 11 December 2014

Keywords:
Air quality
PM_{10}
NO_x
SO_2
O_3
Abatement strategies
Air mass origin
NAO index

ABSTRACT

This study is focused in the evolution of NO, NO_2, SO_2, O_3 and PM_{10} concentrations, from 2000 to 2012, at urban, suburban and regional observatories in the Balearic Islands (Spain), an insular region in the Western Mediterranean.

At urban and suburban areas, daily patterns of most pollutants are strongly linked to land-traffic emissions, being the regional background less influenced. SO_2 variations, however, are mostly driven by the impact of other sources different from road traffic, including shipping emissions and power generation. Urban NO_x, SO_2 and PM_{10} concentrations exhibit a common weekly pattern, with a very slight accumulation during the weekdays and sharp decreases (15–39%) on weekends.

Our long-term database displays clear decreasing NO and NO_2 concentrations from 2000 onwards, prominent in the urban environment (-1.1 μg/m^3 year), and moderate in suburban and regional areas (up to -0.3 μg/m^3 year). At urban sites, O_3 behaviour ($+1.0$ μg/m^3 year) is opposite to that of NO, one of its main depletion agents. A moderate O_3 increasing trend ($+0.5$ μg/m^3 year) is detected at regional background areas, whereas a modest decreasing trend occurred at the suburban background (-0.4 μg/m^3 year), probably caused by enhanced vehicular emissions over these areas induced by urban planning and mobility policies. Finally, substantial PM_{10} drops are obvious, -0.7 μg/m^3 year at urban and suburban areas, and -0.5 μg/m^3 year in the regional background. Our results link the sharpest declines to air masses from western to northern sectors, pointing to effective pollution abatement strategies at a European scale. Some additional benefits are connected to the implementation of diverse local policies.

The effect of the North Atlantic Oscillation (NAO) was investigated. Negative NAO phases were related to additional air quality benefits, while positive phases mostly contributed to air degradation.

1. Introduction

Atmospheric pollution is one of the most challenging environmental problems to which contemporary societies are faced. Airborne particles are associated with different adverse impacts on

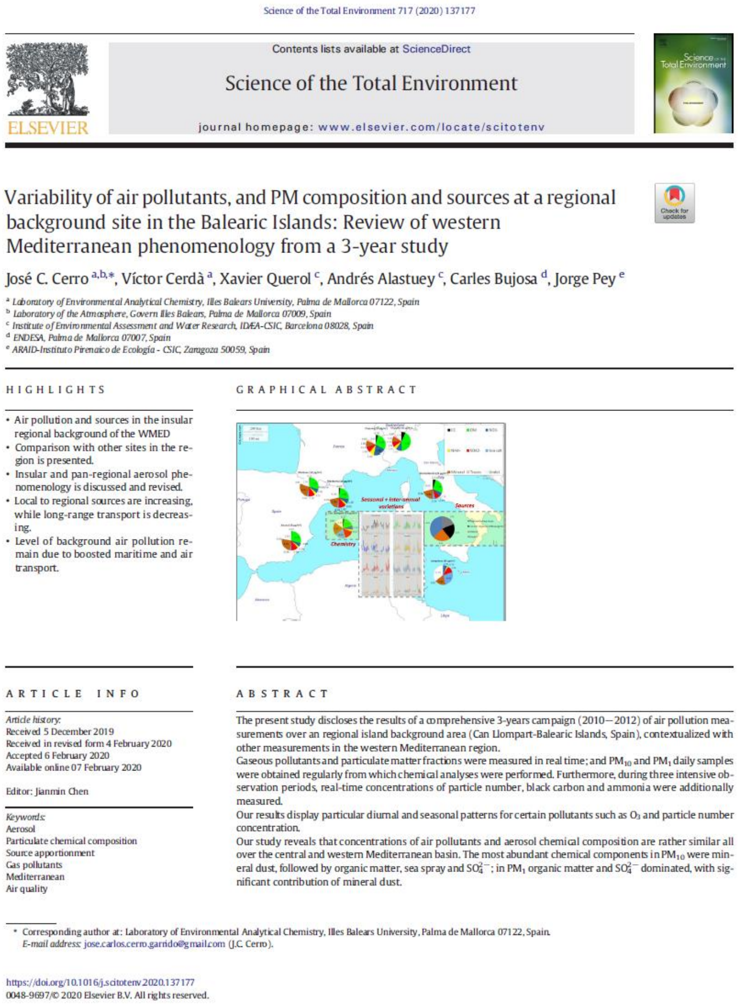
---

[*] Corresponding author. Laboratory of the Atmosphere, Balearic Islands Government, C/Corredors, 10, 07009, Palma de Mallorca, Spain.
E-mail address: aristotilxxi@gmail.com (J.C. Cerro).

http://dx.doi.org/10.1016/j.atmosenv.2014.12.014
1352-2310/© 2014 Elsevier Ltd. All rights reserved.

2. Cerro J.C., Cerdà V., Querol X., Alastuey A., Bujosa C., Pey J. Variability of air pollutants, and PM composition and sources at a regional background site in the Balearic Islands: Review of western Mediterranean phenomenology from a 3-year study. Science of the Total Environment 717 (2020) 137-177.

https://doi.org/10.1016/j.scitotenv.2020.137177



Science of the Total Environment 717 (2020) 137177

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Variability of air pollutants, and PM composition and sources at a regional background site in the Balearic Islands: Review of western Mediterranean phenomenology from a 3-year study

José C. Cerro [a,b,*], Víctor Cerdà [a], Xavier Querol [c], Andrés Alastuey [c], Carles Bujosa [d], Jorge Pey [e]

[a] *Laboratory of Environmental Analytical Chemistry, Illes Balears University, Palma de Mallorca 07122, Spain*
[b] *Laboratory of the Atmosphere, Govern Illes Balears, Palma de Mallorca 07009, Spain*
[c] *Institute of Environmental Assessment and Water Research, IDÆA-CSIC, Barcelona 08028, Spain*
[d] *ENDESA, Palma de Mallorca 07007, Spain*
[e] *ARAID-Instituto Pirenaico de Ecología - CSIC, Zaragoza 50059, Spain*

HIGHLIGHTS

- Air pollution and sources in the insular regional background of the WMED
- Comparison with other sites in the region is presented.
- Insular and pan-regional aerosol phenomenology is discussed and revised.
- Local to regional sources are increasing, while long-range transport is decreasing.
- Level of background air pollution remain due to boosted maritime and air transport.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 5 December 2019
Received in revised form 4 February 2020
Accepted 6 February 2020
Available online 07 February 2020

Editor: Jianmin Chen

Keywords:
Aerosol
Particulate chemical composition
Source apportionment
Gas pollutants
Mediterranean
Air quality

ABSTRACT

The present study discloses the results of a comprehensive 3-years campaign (2010−2012) of air pollution measurements over an regional island background area (Can Llompart-Balearic Islands, Spain), contextualized with other measurements in the western Mediterranean region.
Gaseous pollutants and particulate matter fractions were measured in real time; and PM_{10} and PM_1 daily samples were obtained regularly from which chemical analyses were performed. Furthermore, during three intensive observation periods, real-time concentrations of particle number, black carbon and ammonia were additionally measured.
Our results display particular diurnal and seasonal patterns for certain pollutants such as O_3 and particle number concentration.
Our study reveals that concentrations of air pollutants and aerosol chemical composition are rather similar all over the central and western Mediterranean basin. The most abundant chemical components in PM_{10} were mineral dust, followed by organic matter, sea spray and SO_4^{2-}; in PM_1 organic matter and SO_4^{2-} dominated, with significant contribution of mineral dust.

---

[*] Corresponding author at: Laboratory of Environmental Analytical Chemistry, Illes Balears University, Palma de Mallorca 07122, Spain.
E-mail address: jose.carlos.cerro.garrido@gmail.com (J.C. Cerro).

https://doi.org/10.1016/j.scitotenv.2020.137177

3. Cerro J.C., Cerdà V., Caballero S., Bujosa C., Alastuey A., Querol X., and Pey J. Chemistry of dry and wet atmospheric deposition over the Balearic Islands, NW Mediterranean: source apportionment and African dust areas. Science of the Total Environment 747 (2020) 141187.

https://doi.org/10.1016/j.scitotenv.2020.141187

Science of the Total Environment 747 (2020) 141187

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Chemistry of dry and wet atmospheric deposition over the Balearic Islands, NW Mediterranean: Source apportionment and African dust areas

José C. Cerro [a,b,*], Víctor Cerdà [a], Sandra Caballero [c], Carles Bujosa [d,†], Andrés Alastuey [e], Xavier Querol [e], Jorge Pey [f]

[a] *Laboratory of Environmental Analytical Chemistry, Illes Balears University, Palma de Mallorca 07122, Spain*
[b] *Laboratory of the Atmosphere, Govern Illes Balears, Palma de Mallorca 07009, Spain*
[c] *Atmospheric Pollution Laboratory (LCA), Miguel Hernández University, Elche 03202, Spain*
[d] *ENDESA, Palma de Mallorca 07007, Spain*
[e] *Institute of Environmental Assessment and Water Research, IDÆA-CSIC, Barcelona 08028, Spain*
[f] *ARAID-Instituto Pirenaico de Ecología - CSIC, Zaragoza 50059, Spain*

HIGHLIGHTS

- Dry Vs Wet, Soluble Vs Insoluble, Deposition fluxes in the Western Mediterranean
- Source apportionment study integrating Dry and Wet Deposition results
- Comparative of Western Mediterranean Depositions
- African dust and nutrients deposition in the Western Mediterranean, case studies
- Dry and Wet chemical composition from Northern African Dust Source Areas

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 6 May 2020
Received in revised form 20 July 2020
Accepted 21 July 2020
Available online 24 July 2020

Editor: Pavlos Kassomenos

Keywords:
Air pollution
Aerosol
Airborne aerosol
Deposition

ABSTRACT

Wet and dry aerosol deposition samples were collected from September 2010 to August 2012 at a remote background site in the Mallorca Isle (Western Mediterranean). Ions and major and trace elements were determined in soluble and insoluble fractions. Temporal variations of chemical components are discussed and interpreted. The overall pattern associated to long-range-transport air masses is studied: Dry/Wet deposition ratios, charges and composition depend clearly on the meteorological scenario. E.g. Dry/Wet ratio is 1:1 when air comes from North Africa, in contrast to a 1:9 ratio under the mainland Europe influence.
Moreover, an innovating source apportionment study was conducted integrating both dry and wet deposition samples. Six sources were revealed, including marine aerosols (32%); two different mineral factors, African dust (15%) and regional dust (12%); two anthropogenic factors, one related to road traffic (8%) and another to regional sources (17%); and a mixed factor having biomass burning emissions and others sources (17%). Temporal variations and influence from long-range-transport air masses are also investigated.

---

[*] Corresponding author at: Laboratory of the Atmosphere, Govern Illes Balears, Palma de Mallorca 07009, Spain.
E-mail address: jose.carlos.cerro.garrido@gmail.com (J.C. Cerro).
[†] Deceased.

https://doi.org/10.1016/j.scitotenv.2020.141187

I.II. Other Publications

Other publications related to this thesis:

Conference Papers:

1. José C. Cerro, Jorge Pey, Carles Bujosa, Sandra Caballero, Andrés Alastuey, Michael Sicard, Begoña Artiñano, Xavier Querol, *Regional background aerosols over the Balearic Islands over the last 3 years: ground-based concentrations, atmospheric deposition and sources*, Geopysical Research Abstracts, Vol. 15, EGU2013-14226, EGU General Assembly, Viena, Austria, 2013.

2. Michaël Sicard, Jorge Pey, Jose Carlos Cerro, Diego Lange, Sandra Caballero, Antonio Tovar-Sanchez, Rafael Morales-Baquero, Adolfo Comerón, Carles Bujosa, Xavier Querol, Begoña artiñano, Lucas Alados-Arboledas, Andres Alastuey, Francesc Rocadenbosch, Alvaro Muñoz, Constantino Muñoz, David García-Vízcaino, Jordi Bach, Xavier Bush, *Spanish activities in the framework of the ChArMEx project since 2009: a summary*, 1st Iberian Meeting on Aerosol Science and Technology , RICTA 2013, Évora, Portugal , 2013 (ISBN:978-989-20-3962-6)

3. J.C. Cerro, S. Caballero, C. Bujosa, A. Alastuey, X. Querol, J. Pey, *Aerosol deposition in Balearic Islands as overlook of the deposition in the western Mediterranean*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014. (ISBN: 978-84-695-9978-5)

4. J.C. Cerro, V. Cerdà, J. Pey, *Trends in air pollution between 2000 and 2012 in the Western Mediterranean: A zoom over regional, suburban an urban environments in Mallorca (Balearic Islands)*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014. (ISBN: 978-84-695-9978-5)

5. J. Pey, J.C. Cerro, S. Hellebust, H.L. Dewitt, B. Temime-Roussel, M. Elser, N. Pérez, A. Sylvestre, D. Salameh, G. Mocnik, A.S.H. Prévôt, Y. L. Zhang, S. Szidat, N. Marchand, *Ground based atmospheric monitoring in Mallorca and Corsica in summer 2013 in the context of ChArMEx: Results on number-size distributions, on-line and off-line aerosol chemistry, and volatile organic compounds*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014. (ISBN: 978-84-695-9978-5)

6. Jorge Pey, José Carlos Cerro, Stig Hellebust, H. Langley DeWitt, Brice Temime-Roussel, Miriam Elser, N. Pérez, Alexandre Sylvestre, Dalia Salameh, Grisa Mocnik, Andre Prévôt, Yanlin Zhang, Soenke Szidat, Nicolas Marchand, Atmospheric Monitoring in the Western Mediterranean in Summer 2013: Overview of Physic-chemical Properties and Variability, AAAR 2014 Conference, Proceedings book.

7. H. Langley Dewitt, Jorge Pey, Stig Hellebust, Brice Temime-Roussel, Aurelie Mizzi, Dalia Salameh, Alexandre Sylvestre, Miriam Elser, N. Pérez, José Carlos Cerro, Jean-Luc Jaffrezo, Grisa Mocnik, Andre Prévôt, Nicolas Marchand, Comparison of the Sources of Organic Aerosol (OA) Using Aerosol Mass Spectrometry at Two Mediterranean Islands: Corsica and Mallorca, AAAR 2014 Conference, Proceedings book.

8. J.C. Cerro, J. Pey, N. Pérez, V. Cerdà, H.L. DeWitt , S. Hellebust, M. Elser, A.S.H. Prévôt, B. Temime-Roussel and N. Marchand, *Source apportionment of Organic Aerosol in a remote Mediterranean using a combination of offline and online approaches*. European Aerosol Conference 2016, Tours, France

9. J.C. Cerro, V. Cerdà and J.Pey, *Semi-quantitative methodology to assess efficiency of local air pollution abatement policies in contrast to national or continental ones*. European Aerosol Conference 2016, Tours, France

10. Cerro J. C., Cerda V., Querol X., Alastuey A., Pey J., *3-years background gas and aerosol measurements in Mallorca Island, in WMB: preliminary source apportionment outputs* 5th Iberian Meeting on Aerosol Science and Technology, IDAEA-CSIC, Barcelona, 2017.

Other publications not derived from this thesis: during this period José Carlos Cerro Garrido has collaborated with other works not corresponding to this Thesis:

Books:

José Carlos Cerro Garrido, Josep Ferran Bádenas Jovani, Francisco Javier Lladó Arrieta, Maria Luisa Tobar Santamaría, Carme Pons Bonafé, Paula Maria Elias Mir, *Qualitat de l'Aire a les Illes Balears 2010/2015*, Govern de les Illes Balears (ISBN: 978-84-697-5493-1) (517 pp).

Research papers:

1. Genestar C., Pons C., Cerro J. C., Cerdà V.: *Different decay patterns observed in a nineteenth-century building (Palma, Spain)*, Environ. Sci. Pollut. Res. 21(14): 8663-8672, 2014.

2. Alastuey A., Querol X, Aas W, Lucarelli F, Pérez N, Moreno T., Cavalli F., Areskoug H, Balan V, Catrambone M, Ceburnis D., Cerro J.C., Conil S., Gevorgyan L., Hueglin C., ImreK., Jaffrezo J.L., Leeson S.R., Mihalopoulos N., Mitosinkova M., O'Dowd C.D., Pey J., Putaud J.P., Riffault V., Ripoll A., Sciare J., Sellegri K., Spindler G., and Yttri K.E.: *Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013*, Atmos. Chem. Phys., 16, 6107–6129, 2016.

3. Kevin Berland, Clémence Rose, Jorge Pey, Anais Culot, Evelyn Freney, Nikolaos Kalivitis, Giorgios Kouvarakis, José Carlos Cerro, Marc Mallet, Karine Sartelet, Matthias Beckmann, Thierry Bourriane, Greg Roberts, Nicolas Marchand, Nikolaos Mihalopoulos, and Karine Sellegri, *Spatial extent of new particle formation events over the Mediterranean Basin from multiple ground-based and airborne measurements*, Atmos. Chem. Phys., 17, 9567–9583, 2017 (doi.org/10.5194/acp-17-9567-2017).

4. Pey J., Larrasoaña J.C., Pérez N., Cerro J.C., Castillo S., Tobar M.L., de Vergara A., Vázquez I., Reyes J., Mata M.P., Mochales T., Orellana J.M., Causapé J., 2020. *Phenomenology and geographical gradients of atmospheric deposition in southwestern Europe: results from a multi-site monitoring network*, Sci. Total Environ. 140745, https://doi.org/10.1016/j.scitotenv.2020.140745.

ANNEX II: Additional training and knowledge spreading

Related official courses with the PhD

Riesgo en Instalaciones Radioactivas, 5h, UIB, Palma, 2016

PMF Training Course, AIRUSE LIFE11 project, 19h, Barcelona, 2016

Treball en Altura, Escola Balear de l'Administració Pública, 10h, Palma, 2017

Norma UNE-EN ISO/IEC 17025, Escola Balear de l'Administració Pública, 10h, Palma, 2017

Taller de Imágenes Satélite, Colegio Oficial de Ingenieros de Caminos y Puertos, 2,5h, 2019.

Advanced Openair and R-data analysis and Hysplit joint training seminar, hold by Universidad de Huelva, 22 h, 2019.

Conferences, Seminars, Congress and Workshop attendances

Jornada sobre Gestión de Ozono Troposférico en España, Madrid, 6h, desember 2013

Resonancia Magnética Nuclear y Reconocimiento Molecular, Universitat Illes Balears, 2h, Palma, 2014

***Workshop Aerosol: Mediterranean Experiment SOP summer 2013*, Marseille, 4-10th May 2014**

Saharan dust in southern Europe in the period 2001-2011: estimation and geographical distribution, Universitat de les Illes Balears, Palma, 2014

***2nd Iberian Meeting on Aerosol Science and Technology-RICTA 2014*, Tarragona, 7-9th July 2014.**

Seminario Transporte marítimo, energía y medio ambiente, hold by Gas Natural Fenosa, 6h, Palma, 2014

Influence of industrial activities on concentration and chemical composition of ambient aerosol particles,1h, hold by Laboratorie de Chimie de l'Environnement of the University Aix-Marseille, Marseille, 2015.

Applying new techniques of Chromatography to Environmental Analysis, 1h, hold by Laboratorie de Chimie de l'Environnement of the University Aix-Marseille, Marseille, 2015

Etude de la réactivité hétérogène de NO_2 avec des surfaces internes propres à l'habitat, 1h, hold by Laboratorie de Chimie de l'Environnement of the University Aix-Marseille, Marseille, 2015

Chimie de l'atmosphère et glaciologie, 1h, hold by Laboratorie de Chimie de l'Environnement of the University Aix-Marseille, Marseille, 2015

Heterogeneous reactions of ozone with commonly used pesticides adsorbed on silica particles, 1h, hold by Laboratorie de Chimie de l'Environnement of the University Aix-Marseille, Marseille, 2015

Métodos cuantitativos de la evaluación diaria de la contribución de polvo africano en el ambiente en niveles de Materia particulada en Europa Workshop, organized by AIRUSE LIFE project and DIAPASON project, hold by Institut de Diagnosi Ambiental i de l'Aigua-CSIC, Barcelona, 2015

Climate Change- An introduction for staff and volunteers (French), International Federation of Red Cross, 2015.

Calidad del Aire en el Metro Workshop, organized by IMPROVE Life project, hold by Institut de Diagnosi Ambiental i de l'Aigua-CSIC, Barcelona, 2015

Calidad del Aire: problemas y soluciones, hold by Generalitat Valenciana, Valencia, 2016

Cambio Climático y Medio Marino, hold by Ministerio de Agricultura y Medio Ambiente, Madrid, 2016

Cambio Climático y Medio Marino, hold by Ministerio de Agricultura y Medio Ambiente, Madrid, 2016

***European Aerosol Conference 2016*, Tours, France, 4-9 septiembre.**

RICTA17, 5th Iberian Meeting on Aerosol Science and Technology, IDAEA-CSIC, Barcelona, 2017.

***Climate Change Conference of the parties COP22*, organised by UN, Marrakech, 2016.**

***International Blue Carbon Scientific Group Workshop*, organised by Blue Carbon Initiative, Eivissa, 9 to 12th October 2017.**

International Smart Islands Congress, hold by Feria de Barcelona, Calvia, 2018.

DONAIRE project Workshop, hold by Instituto Geológico y Minero de España, 6h, Zaragoza, 2018.

Jornada de Canvi Climàtic i Resiliència: Reptes Territorials, hold by Govern de les Illes Balears and Consell de Mallorca, 6h, Porreres-Mallorca, 2018.

Estudi territorialitzat de la vulnerabilitat davant del canvi climàtic, hold by Conselleria de Territori, Energia i Mobilitat, Palma, 2018.

Primeres Jornades sobre Canvi Climàtic a les Illes Balears, hold by Universitat de les Illes Balears-Laboratori Interdisciplinar sobre el Canvi Climàtic, Palma, 25 to 26th October 2018.

Agendes Urbanes seminar, hold by Conselleria de Territori, Energia i Mobilitat and Ministerio de Fomento, 4,5h, Palma, 2019.

***Climate Change Conference of the parties COP25*, organised by UN, Madrid, hold by Chile Government, 2019.**

Talks and defences

Talk: *Balearic Islands monitoring network: situation during summer 2013*, Mediterranean Experiment SOP summer 2013 workshop, hold by Laboratory of Environmental Chemistry (LCE) from the Université d'Aix-Marseille, 4th to the 10th May 2014.

Talk: *Trends in air pollution between 2000 and 2012 in the Western Mediterranean: A zoom over regional, suburban an urban environments in Mallorca (Balearic Islands)*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014.

Poster defence: 3. J.C. Cerro, S. Caballero, C. Bujosa, A. Alastuey, X. Querol, J. Pey, *Aerosol deposition in Balearic Islands as overlook of the deposition in the western Mediterranean*. 2n Iberian Meeting on Aerosol Science and Technology, RICTA 2014, Tarragona, Spain, 2014.

Poster defence: J.C. Cerro, J. Pey, N. Pérez, V. Cerdà, H.L. DeWitt , S. Hellebust, M. Elser, A.S.H. Prévôt, B. Temime-Roussel and N. Marchand, *Source apportionment of Organic Aerosol in a remote Mediterranean using a combination of offline and online approaches*. European Aerosol Conference 2016, Tours, France

Poster defence: J.C. Cerro, V. Cerdà and J.Pey, *Semi-quantitative methodology to assess efficiency of local air pollution abatement policies in contrast to national or continental ones*. European Aerosol Conference 2016, Tours, France

Talk: *Contaminació atmosfèrica i qualitat de l'aire*, organised by the Col·legi Oficial de Químics de les Illes Balears, Palma, 2017.

Talk: *Desafiaments climàtic i oportunitats de negoci verd*, organised by Logicament-*ECO4CLIM17*-Universitat de les Illes Balears, Palma, 2017.

Talk: *Canvi Climàtic: propostes de canvi per no canviar el clima*, organised by Fons Pitiús de Cooperació, Eivissa, 2017.

Defence: *Balearic Islands Climate Change policies*, *In-country review of the 7th National Communication and 3rd Biennal Report of Spain*, hold by Ministerio de Agricultura y Pesca, Alimentación y Medio Ambiente for UN, Madrid, 2018.

Talk: *Encuentro sobre cambio climático*, organised by Observatorio de Medioambiente Urbano del Ayuntamiento de Málaga, Málaga, 2018.

Talk: *Colaboración en el proyecto DONAIRE en les Illes Balears, DONAIRE workshop*, organised by Instituto Geológico y Minero de España, Zaragoza, 2018.

Talk: *Vulnerabilitat davant del canvi climàtic a les Illes Balears, Estudi territorialitzat de la vulnerabilitat davant del canvi climàtic seminar*, organised by Govern Illes Balears, Palma, 2018.

Talk: *Jornadas sobre la prevención de olores provenientes de las plantas de tratamiento de residuos urbanos*, organised by Consell de Mallorca, Palma, 2019.

Conferences, Seminars, and Workshop organizations

Jornada Kick off procès participació de la llei de canvi climàtic de les Illes Balears, Palma, 2016, and repliques at Menorca, Ibiza and Formentera.

Jornada de actualización de organismos de control autorizados en materia de atmósfera de las Illes Balears, organised by Govern Illes Balears, Palma, 2016.

Jornada d'Ecomunicipalisme, organised by Govern Illes Balears in collaboration with Consell de Mallorca, Palma, 2017

Jornada de Canvi Climàtic i Resiliència: Reptes Territorials, organised by Govern Illes Balears, Mallorca, 2018.

Estudi territorialitzat de la vulnerabilitat davant del canvi climàtic, organised by Govern Illes Balears, Palma, 2018.

1ª reunió del grup de treball d'experts de canvi climàtic de l'Euroregió Pirineus Mediterrània, Palma, 2019.

Cicle Taules redones focalitzades en canvi climàtic, organised by Govern Illes Balears, Mallorca, 2019.

ANNEX III: International mention meritation

This thesis was born with the aim of being a project with international involvement and international projection. It appeared in the context of, but not belonging to, the Chemistry Aerosol Mediterranean project (ChArMEx). At the same time, ChArMEx project belongs to the Mistral project, which extends to all environmental vectors. Mistral is finally part of the Plan Bleu task force, which was created from the Barcelona convention (COP21). Plan Bleu framework serves as a diagnosis and generation of knowledge to understand the human impact on the Mediterranean and to obtain knowledge in order to improve its resilience to face climate change impacts.

In its final part (campaign in Cap Es Pinar) an international collaboration was also established within the SAFMED project "Mediterranean Experiment SOP summer 2013". That collaboration has led the student to do a stage in the Laboratory of Environmental Chemistry - Université d'Aix-Marseille.

Furthermore the student has attended several curses, congresses, conferences, seminars and workshops of international sphere. Most of them are indicated in the *Additional training and knowledge spreading* annex.

Additionally, he has attended other curses with the only aim of improving his skills in international dealing, and also he has obtained some recognition in foreign languages:

Trainings

Workshop on financing Creation and Development of Enterprises, 16h, Palma, 2013

Communication skills in English: written and oral expression (1st module), 30h, Universitat de les Illes Balears, Palma, 2014

Communication skills in English: written and oral expression (2nd module), 30h, Universitat de les Illes Balears, Palma, 2014

H2020-SME Instrument Grants, organised by Centre Balears Europa, 2h, Palma, 2014.

Introduction to Monitoring and Evaluation (in French), International Federation of the Red Cross, 2h, 2015.

Program/Project Planification (in French), International Federation of the Red Cross, 2h, 2015.

Sessió informativa sobre el programa LIFE+ de la Unió Europea, Centre Balears Europa, Palma, 5h, 2016

Redacció i Gestió de projectes Europeus, organised by Centre Balears Europa, Alda and Fundació Universitat i Empresa, 24h, Palma, 2017.

Selecció d'empleats públics a les institucions europees, Escola Balear de l'Administració Pública, 1,5h, Palma, 2017.

Prioritats de despesa del futur pressupost de la Unió Europea: marc financer plurianual 2021-2027, hold by Centre Balears Europa de la Conselleria de Vicepresidència i la Conselleria d'Innovació, Recerca i Turisme, 4 h, Palma, 4 de febrero de 2019.

Languages learning recognitions

Obtained the European B2 English Level by the Cambridge University and by the Language Official School, and C by the British Council.

Obtained the European A2 French Level by the Alliance Française.

International projects proposals

The student has participated as the technical contact of the regional Belaric Islands Government in several European programme calls. Bellow the line only those where the student has developed a more active role are highlighted:

- *Joint Actions for the development of Sustainable Mediterranean Islands Network in Europe* (JASMINE), INTERREG MED-PROGRAMME 2015, with the aim of constitute a Mediterranean islands network of energy agencies in order to develop Sustainable Energy Plans for islands, directed by the Cyprus Energy Agency, and involving twenty partners from 7 countries.
- *Renewable energy from WAVES in low energY coasts In the balEaric isLanDs* (WAVES YIELD), LIFE+ 2016, with the aim of tasting a a undimetric system to take advantatge of the energy contained in low energy seas, like the Mediterranean. The proposal was directed by the student, and it involved 9 partners from Italy and Spain, and a budget of 2.5 M€.
- *Islands DecarbonisatiOn* (IDO), Horitzon 2020-Building a low-carbon, climate resilient future: secure, clean and efficient energy- 2018, topic LC-SC3-ES-4-2018-2019-2020, with the aim of implementing Energy smart management and renewable energy penetration in islands throughout Europe. The proposal was directed by the student, and it involved 20 partners from 5 countries, and a budget of 11.2 M€.

All previous proposals were submitted, but none was selected, despite very high score was obtained in all cases.

Some international projects developed where the student has participated only as a supporter and in interest of knowing and spreading the knowlodge exhorted are:

- *Testing and development of air quality mitigation measures in southern Europe* (AIRUSE), LIFE.
- *Implementing Methodologies and Practices to reduce air pollution of the subway environment* (IMPROVE), LIFE.

Others

Additionaly the student was awarded as the *Best Reviewer Award in the year 2017* of the Air&Waste Management Association Journal.