

The use of positive matrix factorization (PMF) in the source apportionment of ambient aerosol in the Central Mediterranean

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The use of Positive Matrix Factorization (PMF) in source apportionment of ambient aerosol in the Central Mediterranean

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Abstract

Positive Matrix Factorization (PMF) is a widely used receptor modelling technique in order to determine the nature and contribution of the different aerosol sources modulating ambient levels of particulate matter at a receptor. This cumulative thesis together with the papers included within, reports the results of three source apportionment exercises: a) the isolation of the natural contribution to PM₁₀ levels at a rural background site in Malta; b) the estimation of the contributions of the sources driving PM_{2.5} levels at a traffic hotspot in Malta and c) a methodological investigation of how PMF can be used on a smaller dataset using samples taken from an agricultural area in Apulia, South eastern Italy.

The study on the magnitude of the natural contribution to PM₁₀ involved a sampling campaign at a rural background station in Għarb, Gozo (one of the islands in the Maltese archipelago). This sampling campaign resulted in the collection 224 samples, which were subsequently characterised by inductively coupled plasma mass spectrometry (ICP – MS) and ion chromatography (IC) respectively for, their metallic and ionic content. The use of data resulting from this analysis with PMF resulted in the isolation of the two natural sources expected to be of relevance to Malta (marine aerosol and Saharan dust) as well as in the estimation of their apportionment. PMF also resolved three additional sources: a local crustal source, and two secondary inorganic aerosol components (one rich in nitrate and the other rich in sulfate). The natural sources jointly accounted for approximately 39% of the measured PM₁₀, which is at the upper end of the 0.5 – 58% range determined by previous studies for natural contributions in Europe.

A total of 180 membranes sampled throughout 2016 were used in the study on the sources of PM_{2.5} at a traffic site. These membranes were analysed for: elemental concentrations (using X-ray fluorescence spectroscopy, XRF); ionic content (using IC) and for black carbon – BC (using an optical method). The use of this chemical database with PMF resulted in the isolation of 7 aerosol sources, 4 of which were common to the exercise carried out on PM₁₀ at the rural background site (all the sources except for the local crustal source). The additional three sources isolated at this site were traffic, shipping and fireworks. The isolation of the latter component is itself an interesting result, because it shows that a seasonal activity such as the letting of fireworks during the summer village feasts affects the annual levels of PM_{2.5}. Additionally, this component probably has an effect on human health due to its chemical composition. This work will also provide evidence-based information to the policy makers on the emission reductions required in order for the PM_{2.5} levels to be compliant with the annual air quality guideline issued by the World Health Organization.

Finally, a fundamental methodological investigation on how PMF can be used on a small dataset was carried out. This study is based on 29 PM₁₀ and 33 PM_{2.5} samples collected from a rural area in Apulia, Italy. PMF did not work correctly when the datasets for the two different fractions were used

separately. The datasets were therefore aggregated into a single chemical database of 62 samples and this was then used with PMF. A 5-factor model, which exhibited a fairly good rotational stability was the result of this modelling exercise. This was subsequently further improved through the imposition of constraints based on the chemical constitution of the aerosol sources affecting this receptor, which is made possible by the new features included in the United States Environment Protection Agency PMF version 5. Given the size of the dataset the, the uncertainties in the solution returned by PMF were fully characterised using all the error estimation methodologies included in this version of PMF. Additionally, the results of the PMF modelling were validated against those returned by two other models, Constrained Weighted Non-negative Matrix Factorization (CW – NMF) and Chemical Mass Balance (CMB) as well as through the use of other statistical parameters. These results essentially confirm the validity of the model returned by PMF and indicate that the latter model extracted all the information about the aerosol sources affecting the receptor from the speciation data.

Die Verwendung von Positiver Matrix-Faktorisierung (PMF) in der Quellenzuordnung von Außenluft-Aerosolen im zentralen Mittelmeerraum

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Kurzfassung

Die Positive Matrix-Faktorisierung (PMF) ist eine weit verbreitete Rezeptormodellierungstechnik, um den Ursprung und den quantitativen Beitrag von verschiedenen Aerosolquellen zu bestimmen, welche zusammen die Konzentration von Außenluft-Aerosolen an einem Ort bestimmen. Die vorliegende kumulative Doktorarbeit enthält die Ergebnisse von drei Untersuchungen zur Quellenzuordnung: a) die Isolierung des natürlichen Beitrags zu den PM₁₀-Konzentrationen an einem ländlichen Hintergrundsstandort in Malta; b) die Schätzung der Beiträge der Quellen an den PM_{2,5}-Konzentrationen an einem Standort mit starkem Verkehrsaufkommen in Malta, und c) eine methodische Untersuchung zur Verwendung von PMF an einem kleineren Datensatz; letztere wird anhand der Verwendung von Proben aus einem landwirtschaftlichen Gebiet in Apulien, Südostitalien, demonstriert.

Die Studie über das Ausmaß des natürlichen Beitrags zu PM₁₀ umfasste eine Probennahmekampagne an einer ländlichen Hintergrundsstation in Għarb, Gozo (eine der Inseln des maltesischen Archipels). Während dieser Kampagne wurde 224 Proben genommen, die anschließend durch induktiv gekoppelte Plasmamassenspektrometrie (ICP - MS) bzw. Ionenchromatographie (IC) auf ihren metallischen und ionischen Gehalt hin untersucht wurden. Die weitere Untersuchung dieser Analysedaten mittels PMF führte zur Identifizierung und Quantifizierung zweier natürlicher Aerosolquellen (Meeresaerosol und Saharastaub), von denen erwartet wurde, dass sie für Malta relevant sind. PMF löste auch drei weitere Quellen auf: Eine Quelle von lokalen Erdkrustenmaterial und zwei sekundäre anorganische Aerosolkomponenten (die eine reich an Nitrat, die andere reich an Sulfat). Die natürlichen Quellen steuern ungefähr 39% der gemessenen PM₁₀-Konzentrationen bei. Das Ergebnis liegt am oberen Ende des Bereichs von 0.5 bis 58%, den früheren Studien für natürliche Beiträge in Europa gefunden hatten.

Für die Untersuchung der PM_{2,5}-Quellen an einer Verkehrsstation wurden insgesamt 180 täglich beaufschlagten Filter aus dem Jahr 2016 analysiert. Diese Filter wurden wie folgt analysiert: Die Elementkonzentrationen wurden mittels Röntgenfluoreszenzspektroskopie (XRF) bestimmt, der Ionengehalt wurde mit IC gemessen, und Ruß wurde als 'black carbon' unter Verwendung einer optischen Methode analysiert. Die Auswertung dieser Daten mittels PMF führte zur Identifizierung von sieben Aerosolquellen, von denen vier vom Standort im ländlichen Hintergrund bekannt waren, nämlich alle Quellen mit Ausnahme des lokalen Bodenmaterials. Die zusätzlichen drei Quellen an dieser Station waren Verkehr, Schifffahrt und Feuerwerk. Die Identifizierung der letzten Komponente ist für sich selbst genommen schon ein interessantes Ergebnis, da hier gezeigt wird, dass selbst eine saisonale Aktivität wie das Abbrennen von Feuerwerkskörpern während der sommerlichen Dorffeste sich auf die jährlichen PM_{2,5}-Konzentrationen auswirkt. Darüber hinaus wirkt sich diese Komponente aufgrund ihrer chemischen Zusammensetzung wahrscheinlich auf die menschliche

Gesundheit aus. Diese Arbeit liefert den politischen Entscheidungsträgern somit auch grundlegende Informationen, um eine Minderung der PM_{2,5} Emissionen zu erreichen, die für die Einhaltung der Luftqualitätsrichtlinie der Weltgesundheitsorganisation erforderlich sind.

Schließlich wurde eine grundlegende methodologische Untersuchung durchgeführt, nämlich wie PMF an einem kleinen Datensatz verwendet werden kann. Diese Studie basiert auf 29 PM₁₀- und 33 PM_{2,5}-Proben aus einem ländlichen Gebiet in Apulien, Italien. PMF lieferte hier keine interpretierbaren Ergebnisse, wenn die Datensätze für die zwei verschiedenen Größenverteilungen separat verwendet wurden. Die Proben wurden daher in einen einzigen chemischen Datensatz von 62 Proben zusammengefasst, welcher dann mit PMF untersucht wurde. Das Ergebnis dieser Studie war schließlich ein Fünf-Faktor-Modell, welches eine relativ gute Rotationsstabilität aufwies. Dieses Ergebnis wurde anschließend durch a-priori-Vorgaben basierend auf der Kenntnis chemischer Fingerabdrücke von Aerosolquellen weiter verbessert. Letzteres wurde erst durch die neue Funktionalität der PMF-Version 5 der US-amerikanischen Umweltschutzbehörde ermöglicht. Angesichts der Größe des Datensatzes wurden die auf die PMF-Methode zurückgegebenen Unsicherheiten in der Lösung vollständig unter Verwendung aller in dieser Version von PMF enthaltenen Fehlerabschätzmethoden charakterisiert. Darüber hinaus wurden die Ergebnisse der PMF-Modellierung anhand der Ergebnisse von zwei weiteren Modellen validiert: Der Eingeschränkte Gewichtete Nicht-negativ Matrix-Faktorisierung oder ‘Constrained Weighted Non-Negative Matrix Factorization (CW - NMF)’ und der chemischen Massenbilanz oder ‘Chemical Mass Balance (CMB)’, sowie mithilfe weiterer statistischer Parameter. Die Ergebnisse bestätigen im Wesentlichen die Gültigkeit des von PMF ermittelten Ergebnis und zeigen, dass das Modell alle relevanten Informationen zu den Aerosolquellen identifiziert hat, die die chemischen Zusammensetzung an diesem Ort beeinflussen.

L-užu tal-Positive Matrix Factorization (PMF) għas-source apportionment tal-aerosol fir-regjun Ċentrali tal-Mediterran

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Sunt

Il-Positive Matrix Factorization (PMF) hija waħda mill-metodologiji ta' receptor modelling l-iktar użati sabiex jiġu ddeterminati kemm in-natura kif ukoll il-kontribut tas-sorsi kollha ta' aerosol li jafettaw il-livelli ta' partiċelli freċċettur. Din it-teżi kumulattiva kif ukoll l-artikli xjentifici hawn mehmuża, jirappurtaw ir-riżultati ta' tliet eżerċizzji ta' source apportionment: a) l-iżolament tal-kontributi naturali lil-livelli ta' PM₁₀ f'sit fi sfond rurali f'Malta; b) l-istima tal-kontributi tas-sorsi kollha li jikkontribwixxu għal-livelli ta' PM_{2.5} f'sit espost għat-traffiku f'Malta, u c) investigazzjoni metodologika fuq kif il-PMF jista' jintuża fuq dataset iżgħar permezz ta' kampjuni meħuda minn sit agrikolu fil-Pulja, fix-Xlokk tal-Italja.

L-istudju fuq id-daqs tal-kontribut naturali lill-PM₁₀ involva kampanja ta' kampjunament bejn Marzu 2012 u Mejju 2013 f'sit fi-sfond rurali fl-Għarb, Għawdex (waħda mill-gżejjjer fl-arċipelagu Malti). Ir-riżultat ta' din il-kampanja kien il-ġbir ta' 244 il-kampjun li ġew sussegwentement ikaratterizzati permezz tal-inductively coupled plasma mass spectrometry (ICP – MS) u l-ion chromatography. B'hekk ġew mkejjla rispettivament, il-kontenut ta' metalli differenti u ta' ioni fil-PM₁₀. L-užu tad-data li rriżultat minn din l-analiżi bhala wieħed mill-fatturi ta' input għall-mudell PMF, ta lok għall-identifikazzjoni taż-żewġ sorsi naturali li huma mistenija li jkunu ta' rilevanza għal Malta (l-aerosol marin u it-trab tas-Sahara) kif ukoll fl-istima tal-kontribut ta' dawn is-sorsi lill-PM₁₀. Il-PMF identifika ukoll tliet sorsi addizzjonali: crustal material ta' origini lokali u żewġ aerosol sekondarji inorganici (wieħed li fiċċi huwa abbundanti in-nitrat u l-ieħor ikkaraterizzat minn abbundanza ta' sulfat). Is-sorsi naturali flimkien ammontaw għal madwar 39% tal-PM₁₀ imkejjel. Meta mqabbel ma' studji precedenti li saru fl-Ewropa, dan il-valur jitqiegħed fil-parti l-gholja tal-firxa ta' bejn 0.5 – 58%, li ġiet stmata minn għadd ta' studji simili precedenti dwar il-kontribut tas-sorsi naturali fl-Ewropa.

Total ta' 180 membrana li rriżultaw minn kampanjument li sar matul l-2016 intużaw fl-istudju dwar is-sorsi ta' PM_{2.5} fis-sit espost għat-traffiku. Dawn il-membrani ġew analizzati għal livelli elementari (bl-užu X-ray fluorescence spectroscopy, XRF) għall-kontenut ioniku (bl-užu tal-IC) u għall-partiċelli tan-nugrufun/black carbon – BC (permezz ta' metodu ottiku). Il-PMF iżola 7 sorsi ta' aerosol meta ġie mitmugħi id-data tal-karatterizzazzjoni kimika tal-PM_{2.5}. Erbgħa minn dawn is-sorsi kienu inkomuni mas-sorsi li ġew identifikati fl-istudju fuq il-PM₁₀ fis-sit fi-sfond rurali, fl-Għarb (is-sorsi kollha bl-eċċejżi tal-crustal material ta' origini lokali). It-tliet sorsi l-oħra li ġew iżolati għall-dan is-sit huma it-traffiku, it-traffiku marittimu u il-ħruq tal-murtali. L-identifikazzjoni ta' komponent tal-PM_{2.5} li ġej mill-ħruq tal-murtali huwa riżultat interessanti peress li juri li attivitā stagħunali bħall-ħruq ta' murtali waqt il-festi, li jiġi cċelebrati kważi esklussivament fis-sajf, taffettwa l-livelli annwali ta' PM_{2.5}. Għandu jingħad ukoll li dan il-komponent tal-PM_{2.5} għandu probabbilment effett fuq is-saħħa tal-bniedem minħabba l-kompożizzjoni kimika tiegħi. Dan ix-xogħol joffri wkoll informazzjoni bbażata fuq evidenza xjentifika, ta' utilità għat-tfassil ta' politika dwar it-tnaqqis fl-emissjonijiet, li

huwa neċessarju sabiex Malta tilhaq il-linji gwida annwali dwar il-kwalità tal-arja, maħruġa mill-Organizazzjoni Dinjija tas-Saħħa (WHO).

Fl-aħħar, l-istudju metodoloġiku fuq kif il-PMF jista' jintuża fuq dataset żgħir huwa bbażat fuq 29 kampjun tal-PM₁₀ u 33 kampjuni tal-PM_{2.5} li nġabru minn żona rurali fil-Pulja, l-Italja. Meta ntużaw iż-żewġ datasets għaż-żewġ frazzjonijiet tal-aerosol separatament, il-PMF ma' ġadimx sew. Għaldaqstant iż-żewġ datasets ingħabru f'dataset wieħed ta' 62 kampjun u dan id-dataset ġie mitmugħ lill-PMF. Dan l-eżerċizzju rriżulta fmudell ta' 5 fatturi li wera rotational stability pjuttost tajba u li però kellha fejn titranga. Sussegwentement din tranġat permezz tal-impożizzjoni ta' constraints ibbażżetti fuq il-kompożizzjoni kimika tas-sorsi tal-aerosol li għandhom effett fuq is-sit. Dan sar possibbli permezz tal-karatteristiċi l-ġodda inkluži fil-United States Environment Protection Agency (l-Agenzija tal-Harsien tal-Ambjent tal-Istati Uniti) PMF verżjoni 5. Minħabba iċ-ċokon tad-dataset li ntuża mal-PMF, gew stmati l-inċertezzi fis-soluzzjoni li rriżultat mill-PMF billi ntużaw il-metodi kollha għall-istima tal-inċertezzi li hemm inkluži ma' din il-verżjoni tal-PMF. Ir-riżultati tal-PMF ġew ivvalidati permezz ta' paragun mar-riżultati ta' żewġ mudelli oħra, il-Constrained Weighted Non-negative Matrix Factorization (CW – NMF) u l-Chemical Mass Balance (CMB) kif ukoll permezz tal-użu ta' parametri statistici oħra. Dawn ir-riżultati essenzjalment jikkonfermaw li l-mudell li rriżulta mill-PMF huwa validu, kif ukoll li dan il-mudell rnexxielu jislet l-informazzjoni kollha possibbli mill-karaterizzjoni kimika tal-aerosol fir-rigward tas-sorsi ta' aerosol li jaffettwaw is-sit inkwistjoni.

Declaration of Authorship

I, Mark (Mark Mario) SCERRI, hereby declare that I am the sole author of this Dr. rer. nat. thesis and exclusively under the denoted literature. This Dr. rer. nat. thesis has so far not been used in any exam.



Darmstadt

Mark (Mark Mario) SCERRI

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1. About this thesis

This is a cumulative thesis and is based on three publications, in which the author of this thesis is the lead author. These three publications are included with this thesis and are shown below in chronological order:

Paper I:

Scerri, M. M., Kandler, K., & Weinbruch, S. (2016). Disentangling the contribution of Saharan dust and marine aerosol to PM₁₀ levels in the Central Mediterranean. *Atmospheric Environment*, 147, 395-408. doi:10.1016/j.atmosenv.2016.10.028.

Paper II:

Scerri, M. M., Kandler, K., Weinbruch, S., Yubero, E., Galindo, N., Prati, P., Caponi, L., Massabò, D. (2018). Estimation of the contributions of the sources driving PM_{2.5} levels in a Central Mediterranean coastal town. *Chemosphere*, 211, 465-481. doi:10.1016/j.chemosphere.2018.07.104.

Paper III

Scerri, M. M., Genga, A., Iacobellis, S., Delmaire, G., Giove, A., Siciliano, M., Siciliano, T., Weinbruch, S. (2019). Investigating the plausibility of a PMF source apportionment solution derived using a smaller dataset: A case study from a rural receptor in Apulia – South East Italy. *Chemosphere*, 236, 124376. doi://10.1016/j.chemosphere.2019.124376

There are two main aims to this thesis: the characterisation of the Maltese aerosol climate and the investigation of a fundamental methodological issue related to handling smaller datasets with PMF. The characterisation of the Maltese aerosol climate involved studying the contribution of natural sources to PM₁₀ at a rural background site in Malta, and evaluating the importance of the different components of PM_{2.5} aerosol at a station in a traffic hotspot. The methodological issue was addressed through a study carried out at a “simpler” airshed in Apulia, Southeast Italy.

The natural contributions to PM₁₀ were studied in **Paper I**. Directive 2008/50/EC allows Member States the possibility of subtracting exceedances due to natural contributions in order to assess a Member States' compliance with the air quality standards therein. Malta, being a small island in the proximity of the North African coast is affected by two natural sources: sea spray and Saharan dust. The isolation and quantification of these two components was at the basis of this paper. Rural background stations are sited far away from anthropogenic sources and from urban centres and are thus considered ideal for studying the contribution of transboundary sources, therefore explaining the choice of the rural background site. Additionally, the choice of the aerosol fraction to be studied was guided by the considerations that these two sources are considered to have a higher effect on the PM₁₀ fraction, and in fact, so far, the possibility of deducting their contributions can be availed of only for PM₁₀.

Most of the population in Malta inhabits the more urbanised and densely populated part of the island and is therefore exposed to higher ambient aerosol levels than those at the rural background site. This means that a study such as the one in **Paper II**, aimed at assessing the potential for reducing population exposures to PM_{2.5} should have been based at a location, representative of a higher exposure scenario,

explaining the choice of the receptor in this study. **Paper II** and the study on which it is based, should also serve to provide evidence-based guidance to the policy maker on achieving the WHO air quality guidelines for PM_{2.5} by 2020. For this study the PM_{2.5} fraction was chosen, because it is the more relevant fraction, when considering the health implications of chronic exposures to levels of airborne particulate matter in between the WHO guidelines and the EU limit values, which is the case for Malta.

Paper III addresses the methodological issue of running PMF with “smaller” datasets. These “smaller” datasets could result from a number of constraints (such as budgetary, time or accessibility). In this study a dataset made up of 29 PM₁₀ and 33 PM_{2.5} samples and their respective chemical characterizations were used; these two datasets were aggregated into a single chemical database. The aggregated chemical database was used with PMF in order to obtain a well constrained solution (free from rotational ambiguity). Application of aggregated datasets is not new and is based on the assumption of the similarity of source profiles for both aerosol fractions, hence explaining the use of a less complex airshed. The PMF solution was subsequently verified through the use of statistical techniques and through the comparison with the solutions obtained through the use of two other models: Constrained Weighted Non-negative Matrix Factorization (CW – NMF) and Chemical Mass Balance (CMB).

Finally, all the three studies contributed to increasing knowledge about the aerosol sources affecting the Central Mediterranean region, a region, which has not been as extensively studied as the Western or the Eastern Mediterranean.

2. Introduction

2.1 Atmospheric aerosol, PM₁₀ and PM_{2.5}

Aerosols are generally defined as a suspension of particles (solid or liquid) in a carrier gas (Hinds, 1999). In view of the fact, that this thesis deals with atmospheric (tropospheric to be more specific) aerosol, the carrier gas is in this case air. The key parameter when discussing aerosol size distributions is the aerodynamic diameter of the particle, defined as the diameter of a sphere of density 1 g/cm³ and having the same terminal velocity as the particle, when falling freely under the effect of gravity at the prevailing atmospheric conditions. Sizes of atmospheric particulate matter (APM) are considered to range from

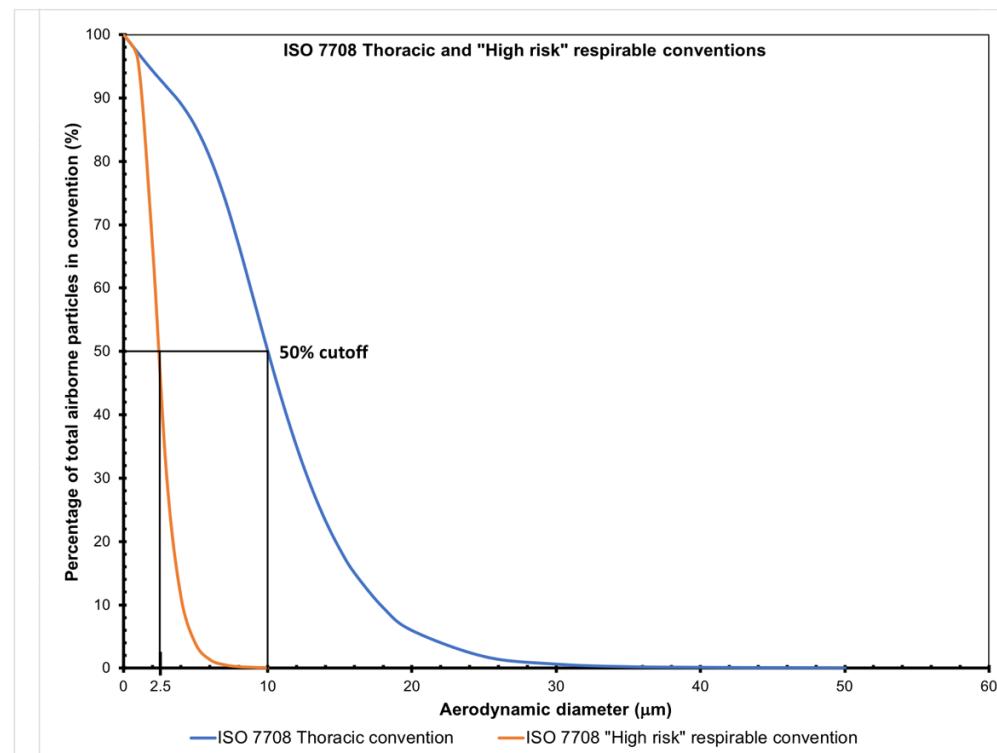


Figure 1: Thoracic and “High risk” respirable conventions according to ISO 7708. Adapted from ISO 7708 (1995).

will deposit in the thorax (Brown et al., 2013), while the smaller particles ($3 - < 1 \mu\text{m}$) will make it all the way up to the alveoli (Thomas, 2013). Two aerosol size distributions are currently defined for the purpose of measuring population exposures to levels of ambient particulate matter. These are the PM₁₀ and the PM_{2.5} fractions (Viegi et al., 2004), respectively the thoracic and the “high risk” respirable conventions in ISO 7708 (1995). PM₁₀ particles penetrate beyond the larynx, while PM_{2.5} particles are capable of deposition within the lower airways up to the alveoli (Samet and Utell, 1991). ISO 7708 (1995) defines PM₁₀ and PM_{2.5} as particles capable of penetrating through a size-selective orifice with an efficiency of 50% at aerodynamic diameter cut-offs of 10 μm for the former and 2.5 μm for the latter, see **Figure 1**

0.001 to 100 μm with the upper limit determined by the maximum size, which would enable the particle to be airborne long enough for it to have an effect on the environment (or human health) and be detected (Kulkarni, Willeke and Baron, 2011). Particles having a relatively large aerodynamic diameter ($\geq 30 \mu\text{m}$) are deposited in the head airways (WHO, 1999), the larger particles ($\leq 5 \mu\text{m}$) not depositing in the head

2.2 Effects of exposure to PM₁₀ and PM_{2.5} on human health

The World Health Organization (WHO) has set the levels of the PM₁₀ and PM_{2.5} aerosol fractions as proxy indicators of air pollution. Epidemiological evidence consistently shows that short term (in the range of hours – days) as well as longer term (in the range of months – years) exposures to both fractions of airborne particulate matter (APM) are conducive to ill-health in humans (WHO, 2000; Pope and Dockery, 2006). Shorter term health endpoints (both for morbidity and for mortality) are mostly affected by PM₁₀ levels while PM_{2.5} is a stronger risk factor with respect to the longer-term ones. The vulnerable fraction of the population such as people with a history of pulmonary or cardiac illness, children, the elderly, etc. is particularly susceptible to pollution by APM. A number of studies based on time series from different cities, have shown the association between diurnal increases in daily mortality and in ambient levels of PM₁₀ and PM_{2.5} to be particularly strong (Levy *et al.*, 2000; Steib *et al.*, 2002; Braga *et al.*, 2001 and Schwartz, 2000; 2003). In this case, mortality is the result of primarily, cardiovascular or respiratory failure (Samet *et al.*, 2000; Analitis *et al.*, 2006). While, a strong association has been determined between cardiopulmonary mortality and long-term exposure to PM_{2.5} (Dockery *et al.*, 1993; Pope *et al.*, 1995; Pope *et al.*, 2004; Jerrett *et al.*, 2005). As far as morbidity is concerned, increases in daily hospital admissions have been linked to short-term increases in the concentrations of both PM₁₀ (Zanobetti *et al.*, 2000; Le Tertre *et al.*, 2002; COMEAP, 2006) and PM_{2.5} levels (Dominici *et al.*, 2006; Stafoggia *et al.*, 2013). On the other hand, Miller *et al.* (2004) found that incidence of non-fatal cardiovascular increases with chronic exposures to PM_{2.5}, while Mc Michael *et al.* (1998) found an analogous exacerbation of chronic disease. Additionally, exposure to particulate matter could also lead to a small increase in the risk of lung cancers incidence (Pope, 1995; Samet and Cohen, 1999).

2.3 European Legislation and the World Health Organization Air Quality Guidelines

The European Union (EU) regulates immission levels of these two aerosol fractions through Directive 2008/50/EC (2008), which sets two air quality standards for the PM₁₀ fraction and one for PM_{2.5}. In fact, PM₁₀ levels are regulated by both a daily limit value (DLV) or shorter-term environmental quality

objective of 50 µg/m³ (and which should be complied with on 90.4% of the days in a calendar year) and by an annual limit value (ALV) or longer-term environmental quality objective of 40 µg/m³. On the other hand, PM_{2.5} is regulated by an ALV of 25 µg/m³. Querol *et al.* (2004), has shown that for Spain complying with the DLV 90.4% of the time is more onerous than complying with the ALV. Figure 2, shows that the annual average concentration would have to be ~31 µg/m³ in order to ensure that the daily concentrations are ≤ 50 µg/m³, 90.4 percent of the times. This is not much different from the situation in Malta where compliance with the DLV requires the ALV to

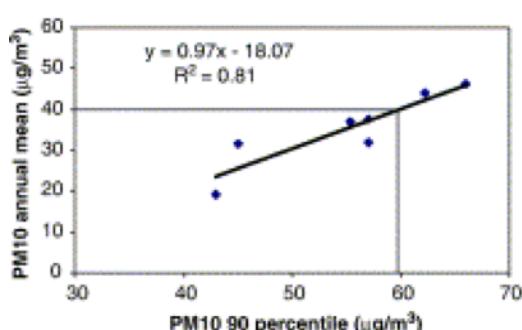


Figure 2: Plot of PM₁₀ annual mean vs. 90.4th percentile of the daily averages for Spain (Querol *et al.* 2004).

be < 34 µg/m³ (ERA, 2019). Furthermore, EEA (2018) shows that generally, the shorter-term environmental quality objective for PM₁₀ is more difficult to comply with across the EU. With only 6 – 8% of the EU population exposed to annual average concentrations of PM_{2.5} > 25 µg/m³ (EEA, 2018), compliance with the ALV for this fraction is generally not considered to be problematic. The EU limit values for PM₁₀ and PM_{2.5} are not considered to be sufficiently protective of human health and in fact the

WHO AQGs are considerably stricter (WHO, 2006), see Table 1, below. It is however worth pointing out that health effects cannot be ruled out even at these levels because no safe threshold has as yet been determined for exposure to PM₁₀ and PM_{2.5} (Pope and Dockery, 2006).

Table 1: The WHO AQGs for PM₁₀ and PM_{2.5}.

Aerosol Fraction	Daily AQG (DAQG)	compliance with DAQG	Annual AQG
PM ₁₀	50 µg/m ³	99% of 365 days	20 µg/m ³
PM _{2.5}	25 µg/m ³	99% of 365 days	10 µg/m ³

The European Environment Agency (EEA) estimated that in 2016, 74 – 85% of the EU population was exposed to PM_{2.5} levels higher than the annual WHO AQG while exposure to PM₁₀ levels higher than the WHO DAQG was in the range of 42 – 52% (EEA, 2018).

2.4 Sources of PM₁₀ and PM_{2.5}

Atmospheric aerosols are complex mixtures of different chemical constituents. They are either emitted directly as primary aerosol or form as a result of chemical reactions between precursors (secondary aerosol). Both primary aerosols and the precursors to secondary aerosol can result from either anthropogenic or natural sources. In Europe, the highest PM levels are measured in the Mediterranean countries (Putaud *et al.*, 2010; Querol *et al.*, 2009). This is attributed to a variety of local/regional factors which primarily affect dust entrainment and secondary aerosol formation, as well as the frequency of African dust events. Dust advected from the Saharan (and sometimes the Sahel) region to Southern Europe is one of the major drivers of both PM₁₀ and PM_{2.5} levels, contributing from 10 – 43% of the PM₁₀ (Pey *et al.*, 2013) and has been shown to affect PM_{2.5} levels too (Viana *et al.*, 2002; Almeida *et al.*, 2005; Nicolás *et al.*, 2011), in fact a contribution of 15% was estimated for Malta (Scerri *et al.*, 2018). The yearly frequency of these events increases along the North – South gradient and this increase is particularly marked for the Central Mediterranean where it reaches a peak of 37% (Pey *et al.*, 2013). In addition, the mineral dust load in the region is incremented by the (natural or anthropogenic) entrainment of local crustal material, which is facilitated by the semi-aridity of the region, while the relatively low precipitation rates make the removal of atmospheric aerosol by wet deposition less effective (Rodríguez *et al.*, 2007). Amato *et al.* (2016a), estimated that in the South of Europe, mineral dust contributes about 10 – 25% of the PM₁₀ and 4 – 10% of the PM_{2.5}.

The occurrence of atmospheric stagnation episodes in the Mediterranean region together with the intensity of solar radiation (particularly during spring – summer) promote the formation of secondary organic and inorganic aerosol (Pey *et al.*, 2013) or SIA and SOA, respectively. SIA is formed from the neutralisation of the photooxidation products of SO₂ and NO₂ by NH₃ (Galindo *et al.*, 2013). The chemical composition of SIA is highly dependent on the ambient temperatures. The thermally stable ammonium sulfate aerosol predominates over ammonium nitrate at the lower latitudes particularly in summer (Tørseth *et al.*, 2012). SIA contributes approximately 15 – 31 % to both PM₁₀ and PM_{2.5}, and is prevalently formed in the fine fraction of atmospheric aerosol (Amato *et al.*, 2016b). SOA is on the other hand formed from the reaction of volatile organic compounds (VOCs) from both natural and anthropogenic sources (Hallquist *et al.*, 2009) with oxidants such as the OH and NO₃ radicals (Warneke *et al.*, 2004). Amato *et al.* (2016a) estimated that in urban background and sub-urban background sites in Southern Europe, SOA dominates the mass of both PM₁₀ (25 – 32%) and PM_{2.5} (32 – 49%) fractions.

Biomass emissions from residential wood burning are expected to have a lower impact on PM levels in Southern Europe, than in Central or Northern Europe, Reche *et al.* (2012). The main sources of aerosol from biomass burning in the region, are summer forest fires and the open field burning of agricultural waste, Puxbaum *et al.*, (2007), particularly olive branches in November – February (Kostenidou *et al.*, 2013). In Greece, contributions of biomass burning of up to 36% and 46%, for PM₁₀ and PM_{2.5} respectively, have been determined by e.g. Diapouli *et al.* (2017).

Other sources of particulate matter pollution which are more affected by local considerations (rather than regional ones) include shipping and traffic. Most of the air pollutants from shipping are emitted at distances of up to 400km away from the coast (Endresen *et al.*, 2003) and affect not only major ports but also medium and small-scale ports, contributing 2 – 10% of the PM₁₀ and 5 – 20% of the PM_{2.5} in coastal areas, Viana *et al.* (2014). Aerosol loads from shipping are due to both primary emissions of e.g. EC, Ni and V (Viana *et al.*, 2008) as well as secondary aerosol (Reche *et al.*, 2011) and occur mostly in the finer fraction. Traffic is one of the major sources of particulate pollution in urban areas, e.g. Viana *et al.* (2008) estimated total traffic contributions in urban and kerbside sites, of 32 – 55% for PM₁₀ and 30 – 49% for PM_{2.5}. Traffic derived APM is divided into an exhaust component and an abrasion and resuspension component. The exhaust component is emitted primarily in the PM_{2.5} fraction (Abu Allaban *et al.*, 2003; Tervahattu *et al.*, 2006; Thorpe *et al.*, 2007; Kam *et al.*, 2012), while the abrasion and resuspension components have a coarser size distribution (Amato *et al.*, 2013).

2.5 Sources of PM₁₀ and PM_{2.5}

Receptor modelling is a tool which is often used in order to determine both the identity of the sources, as well as the contribution of each source to APM levels at a particular receptor (Viana *et al.*, 2008; Belis *et al.*, 2013) or source apportionment. Receptor modelling methodology differs from that for conventional, source based, modelling because it requires speciation data for the aerosol fraction of interest, sampled at the receptor. The underlying assumption in receptor modelling is that the aerosol composition remains invariant from source to receptor, this is not always the case. However, it overcomes the need for full knowledge about the activity of the sources and the dominant meteorological regimes, affecting the receptor, which are the major limiting factors when using source orientated models. Positive Matrix Factorization or PMF (Paatero and Tapper, 1994; Paatero, 1999) is one of the most widely used receptor models (Hopke *et al.*, 2016) for the purpose of solving the source apportionment problem. This model allows the modeller to weight the species to be inputted into the model by the uncertainty in the concentration of the species and can also handle measurements below the limit of detection (BDL), through the setting of the uncertainty of these data points (Manousakas *et al.*, 2017). Additionally, PMF ensures that any outputted factors are more likely to be physically interpretable through the imposition of a constraint on the output of the model which must be ≥ 0 . PMF is essentially a multivariate statistical model and it is therefore data intensive. This means that for the model to function correctly it requires both a relatively large number of (daily) samples as well as the determination of a number of species in the relevant PM Fraction. A number of publications have sought address the issue of defining the minimum acceptable number of species for factor analytic models such as PMF to work correctly. However, there is as yet, no objective criterion, resulting from empirical evidence on this issue. In fact, most of the commonly followed criteria are more “rules of thumb” e.g. Henry *et al.* (1984), suggest using the ratio of the degrees of freedom to the number of determined species, which should be greater than 30; Ito *et al.* (1986), agree with the use of this criterion but suggest taking into account the nature of the airshed under study while other studies have settled for 50

chemically characterised samples (Thurston and Spengler, 1985; Brown and Hafner, 2005 in Belis *et al.*, 2014; Johnson *et al.*, 2011). On the other hand, Norris *et al.* (2014) (the guidebook for the most widely used version of PMF the United States Environment Protection Agency PMF version 5) suggest that for PM_{2.5}, a source apportionment exercise should involve at least 100 samples. In literature, there is even less guidance on the optimal number of chemically determined species for use with models such as PMF. Norris *et al.*, (2014) suggest a range of 10 – 20 species, while the suggestion to rely on the aerosol climate of the site as a guide (Belis *et al.*, 2014; Favez *et al.*, 2019) is even more vague, despite the fact that it is a perfectly sound suggestion. Some studies caution against the inclusion of too many species as this might cause issues with the fitting of the PMF model due to the fact that this adds a source of noise (Reff *et al.*, 2007).

As a receptor model PMF has the advantage that due to its mathematical complexity it can be used in situations in which little to no reliable information about the sources modulating PM levels at a receptor is available, it however requires 10s of chemically characterised samples, which make it relatively expensive. Additionally, one of the main limitations of PMF is, that it is unable to resolve collinear sources, that is, sources having similar chemical profiles (Bove *et al.*, 2018).

3. Materials and methods

This chapter describes the receptor sites and the basics of the receptor modelling technique used to source apportion the different aerosol fractions throughout the work carried out in connection with this thesis: positive matrix factorization (PMF). A detailed description of the analytical procedures and of any additional statistical analysis can be found in the corresponding papers, while descriptions of the two receptor models used to validate the PMF solution in **Paper III** can be found in the latter paper.

3.1. Receptor Characterisation

The rural background station and the traffic station respectively, at basis of the studies in **Papers I** and **II**, form part of the Maltese air quality network operated by the Environmental and Resources Authority and are used by Malta to fulfill its EU reporting obligations under Directive 2008/50/EC (2008).

The rural station is situated in Għarb (36.07°N, 14.20°E and 114 m above mean sea level or AMSL), located in the North western part of Gozo in the Central Mediterranean archipelago of Malta (see Figure 3). The Corine Land Cover (CLC) Database (2012) classifies this as an area “surrounded by agricultural land with significant areas of natural vegetation” or CLC class 2.4.3. The site is relatively remote, with the nearest settlement being a hamlet (within Għarb) at 1 km to the South, having a population of 290, and is accessed only via an un asphalted, dirt track to the East. This means that traffic flows in the area are negligible. Furthermore, the closest “major” road is located at ~5 km to the WNW in the principal Gozitan town of Victoria. The direct contribution of traffic to PM₁₀ levels at the receptor is therefore not expected to be significant. The only major industrial plant in Malta, is a thermal power plant at 30 km to the Southeast and should likewise contribute negligibly (if at all) to the PM₁₀ levels measured in Għarb. On the other hand, some impact on aerosol levels at the receptors is expected from both hardstone and softstone quarries at ~2.5 km to the South.

Msida, a town situated in between Malta’s administrative capital (Valletta) and the town home to the main commercial, tourism and entertainment cluster on the island (Sliema) was chosen to site the traffic station (35.896°N, 14.490°E and 2 m AMSL), see Figure 3. The area around the station is classified by the Corine Land Cover (CLC) Database (2012) as a “port area” or CLC class 123 (due to the presence of a marina at ~70 m to East) and also, as “discontinuous urban fabric” or CLC class 112. Additionally, the area is also in the middle of the densely urbanised part of the island (population density of 5500 /km²), designated by Stacey and Bush (2002) as the agglomeration for the purpose of Directive 2008/50/EC (2008). The station is at ~10 m from a traffic hotspot with yearly traffic flows of ~ 8 million vehicle passages. This receptor is surrounded by busy arterial roads to both the North and the South and is at ~2.5 km to the NNW of Malta’s busiest road with 15 million vehicle passages per year. This means that the PM_{2.5} measured at the station is expected to be significantly affected by traffic derived aerosol. PM_{2.5} levels at this station are also expected to be affected by shipping emissions, due to the fact that the Maltese ports are quite busy, e.g. the total number of port calls in 2016 reached ~26000 (EUROSTAT, 2017) and also, because the receptor is close to the “Grand Harbour Complex (at ~2 km to the South). This complex includes a cruise liner and a catamaran terminal, a shipyard and port reception facilities. In addition, one of the busiest shipping routes in the Mediterranean, the Sicily – Malta canal, lies to the West of the station. The industrial sources shown in Figure 3 are not likely to have a significant effect



Figure 3: The three receptors for Paper I, II and III, respectively Għarb (top), Msida (centre) and Lido Cerano (bottom).

on aerosol levels at the Msida station due to either the scale of the activity or the low operating times (see **Paper II** for more details). The main industrial plant in the island is not visible in the figure and is at over 9 km to the South of the receptor. The use of biomass in spatial heating and to power cooking hobs is uncommon in Malta, making this source not particularly relevant for both PM₁₀ levels at the rural background site and for the PM_{2.5} levels at the traffic site. Both receptors should however be affected by the two natural sources of relevance to Malta: sea salt and Saharan dust due to the closeness to the coast in the case of sea salt (see Figure 3) and due to the fact that Malta is less than 350 km away from Northern Africa in the case of Saharan dust.

The study in **Paper III** is based at a receptor sited beneath the chimney of an industrial site in Lido Cerano, situated at 30 m AMSL along the Brindisi – Casalabate coast (Apulia, Southeastern Italy). The site is considered to be a rural station, because it is surrounded by agricultural land. PM₁₀ and PM_{2.5} levels at the site should not be affected by the chimney emissions. The receptor is however at ~3 km to the East of the “Super Strada Brindisi – Lecce, SS6113” a four – laner and one of the major motorways in the area, therefore traffic emissions are expected to contribute significantly to both fractions. Additionally, the parking area in the facility, in which the samplers are sited is also expected to be a contributor to aerosol levels. Local/regional wind circulation patterns, which characterise the Salento region ensure that the site is often downwind from a number of sources in Brindisi and Taranto (Cesari *et al.*, 2016), respectively at ~7 km to the North west and at ~30 km to the West. These are important when making considerations about secondary inorganic aerosols. Similarly, to the Maltese sites, aerosol levels in Lido Cerano are also expected to be affected by the same natural sources i.e. sea salt (site is at ~0.5 km away from the Adriatic coast) and Saharan dust (the Maghreb is at ~950 km to the South).

3.2. Sampling and analyses

More details on the duration and timing of the sampling campaigns, conditioning of the filter membranes, and on the analytical procedures can be found in Papers I, II and III. However, Table 2 below, shows the species, which were analysed in the three studies together with the respective analytical method.

Table 2: Species determined in each of the three studies and the respective analytical method.

Analyte	Paper I	Paper II	Paper III
Al	ICP – MS	XRF	NA
Si	NA	XRF	XRF
Cl/ Cl^-	IC	XRF	IC
K/ K^+	ICP – MS	XRF	IC
Ca	ICP – MS	XRF	XRF
Ti	NA	XRF	XRF
V	ICP – MS	XRF	XRF
Cr	BDL	XRF	BDL
Mn	NA	XRF	BDL
Fe	ICP – MS	XRF	XRF
Ni	NA	XRF	XRF
Cu	BDL	XRF	XRF
Zn	NA	XRF	XRF
Br	NA	XRF	NA
Sr	NA	XRF	BDL
Ba	NA	XRF	BDL
Pb	BDL	XRF	BDL
NO_3^-	IC	IC	IC
SO_4^{2-}	IC	IC	IC
Na^+/Na	ICP – MS	IC	IC
Mg^{2+}/Mg	ICP – MS	IC	IC
NH_4^+	Deriv + UV Vis	IC	IC
eBC/ EC	NA	MWAA	TOT
OC	NA	NA	TOT

Legend: XRF = X-ray fluorescence spectroscopy, IC = ion chromatography, ICP – MS = inductively couple plasma mass spectrometry, NA = not analysed, BDL = below detection limit, Deriv + UV Vis = derivatisation followed by UV – Visible spectroscopy, MWAA = multiwavelength absorbance analyser, TOT = thermo-optical transmittance. Analytical methods in red indicate that the analysis determined the analyte in red.

3.3. Analysis by PMF

PMF (Paatero and Tapper, 1994; Paatero, 1997) has been used extensively in the three Papers at the basis of this thesis. The algorithm used by PMF in order to carry out this task, is rather complex and is well suited to situations in which very little /no information on both the aerosol sources as well as on their chemical composition is available (Bove *et al.*, 2018), see Figure 4.

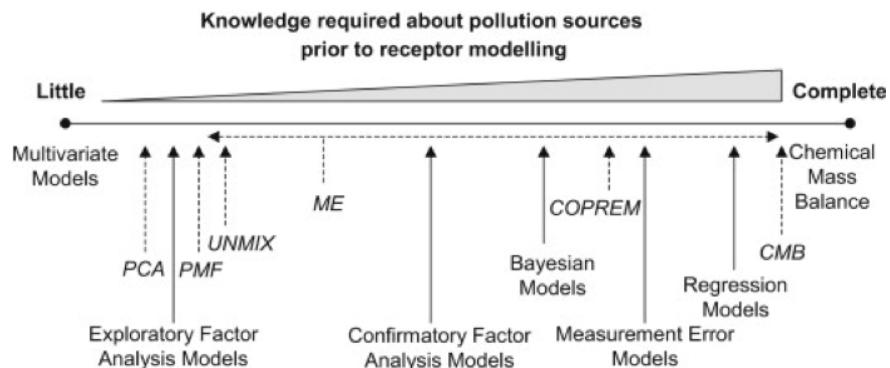


Figure 4: Different source apportionment techniques and the amount of information required about the aerosol sources affecting the receptor. Viana *et al.* (2008).

The source apportionment problem is solved by PMF through the decomposition of x_{ij} , the matrix made up of the j chemical species analysed in the characterisation of the i (daily) samples into the f_{kj} , the matrix representing the chemical composition of each of the p aerosol sources and the g_{ik} , the matrix representing the daily contributions of each source, see equation 1.

$$x_{ij} = \sum_{k=1}^p (g_{ik} \times f_{kj}) + e_{ij} \quad (1)$$

e_{ij} is the matrix of residuals. PMF constrains all the elements in the f_{kj} and g_{ik} matrices such that none of them are significantly negative. In order to weight each of the elements in x_{ij} by its uncertainty, PMF requires the inputting of the uncertainties matrix or u_{ij} . Various methods for the calculation of these uncertainties have been proposed in literature (see Table 1 in Reff *et al.*, 2007). PMF achieves a solution to equation 1 by using the weighted least squares algorithm in order to find the values g_{ik} and f_{kj} which give the minimum value for the quality of fit parameter or Q , see equation 2, below.

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p (g_{ik} \times f_{kj}) + e_{ij}}{u_{ij}} \right]^2 \quad (2)$$

In the studies described in Papers I, III and III, USEPA PMF version 5 was used. USEPA PMF v 5 isolates optimal values of the factor profiles' matrix (f_{kj}) and the factor contributions' matrix (g_{ik}) for the inputted number of factors, through a number of iterations performed by the Multilinear Engine (ME), which underlies the USEPA version(s) of PMF. The algorithm used by ME starts its search for these two matrices with a randomly generated f_{kj} which goes through a succession of modifications using the conjugate

gradient approach until the best fitting solution to equation 1 is identified by the minimum value of Q in equation 2.

Further information on the species inputted in PMF, on how the uncertainties were calculated, and on the number of samples used in each of the studies making up this cumulative thesis, etc. can be found in the Methodology section of **Papers I, II and III**. It is worth pointing out that in **Paper III**, due to the limited number of PM₁₀ and PM_{2.5} samples the chemical speciation data for both aerosol fractions had to be aggregated into a single dataset. Running USEPA PMF v 5 on the sample for each aerosol fraction individually led to the model not functioning correctly. This approach (of aggregating datasets) has been successfully applied (in different circumstances) in numerous other studies (e.g. Amato *et al.*, 2009; Pandolfi *et al.*, 2011; Contini *et al.*, 2014; Tian *et al.*, 2014; Contini *et al.*, 2016; Airuse.eu, 2018). In the three studies the daily source contribution estimates (in mass concentration units) were obtained by multilinear regression analysis (MLRA) using the elements of the source contributions' matrix as the predictor variable and the respective PM fraction as the dependent variable.

3.4. Further tests

Further statistical tests were performed in both **Papers I** and **II** in order to confirm the identity of the factors isolated by PMF. The main aim of **Paper III** was to investigate the suitability of PMF for receptor modelling with smaller datasets and so the results of PMF modelling were compared to those outputted by two other receptor models (CW – NMF and CMB) and statistical tests (including the root mean square error (RMSE) and the absolute fractional bias (AFB), see equations 3 and 4 and the underlying descriptions) were performed in order to compare these results. All these tests are described in more detail in the respective paper.

$$RMSE = \sqrt{\frac{1}{m} \sum_{i=1}^m (M_i - g_i)^2} \quad (3)$$

$$AFB = \frac{2}{m} \times \sum_{i=1}^m \frac{|M_i - g_i|}{(M_i + g_i)} \quad (4)$$

Where m = the number of daily samples, M_i is the measured mass of PM and g_i is the mass of PM reconstructed by the model. The RMSE calculates the spread between M_i and g_i , while the AFB is a measure of the agreement between M_i and g_i with the range of acceptability being 0 – 2 (Cesari *et al.*, 2016).

In **Papers I** and **II** the respective source contribution estimates are disaggregated by season in order to analyse the seasonal behaviour of the isolated sources. Additionally, the concentration weighted trajectories method (Hsu *et al.*, 2003) was used in the three papers, to help with the identification of sources owing their origin to transboundary sources, the method is described thoroughly in **Papers I** and **II** while details about the modelling parameters in each of the three studies can be found in the respective paper, too.

4. Results

This chapter presents a summary of the major results of Papers I, II and III. The first subsection is a generic description of how the optimal PMF solution was achieved in each case, and summarises the characteristics of the solutions retained in the three studies. The source apportionment for these studies as well as the seasonal behaviour of the isolated factors is illustrated in the subsequent sub-chapter. The last subsection, which is the major part of this chapter describes the factors isolated by these studies and describes the reasoning and the evidence backing the attribution to a particular source. Factors common to two or more studies are treated conjointly by the same description, due to the fact that the chemical composition is very similar. Further details can be found in the respective studies.

4.1. PMF Solution

To date there is as yet no “objective” methodology for the determination of the optimal number of factors to be fitted by PMF, in fact this model has been defined as a descriptive one (Vecchi *et al.*, 2008). Throughout the three papers making up the thesis being presented, the following approach was consistently used: the model with the highest number of physically meaningful factors is the one which was retained. This choice is also informed by visually inspecting for any sharp drops in the plots of $Q_{\text{expected}} / Q_{\text{theoretical}}$, IM – the maximum individual column mean and IS – the maximum individual column standard deviation (Lee *et al.* 1999), versus the number of fitted factors. Further details on any refinements which had to be made to the solutions, retained in each of the three studies can be found in the respective sections of Papers I, II and III. Table 3 below provides a brief summary of the characteristics of the model retained in each of the three studies.

Table 3: Summary of the model retained in each of the three studies.

	Paper Number			
	I	II	III	III
PM fraction	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
number of factors explored	3 to 6	4 to 9		4 to 9
factors retained	5	7		5

4.2. Isolated Factors

Table 4 shows the factors isolated by each study as well as the respective source contribution estimate, while **Figures 5a – 5d** show the source apportionment and the seasonal variation in the source contribution estimates for aerosol fractions studied in **Papers I** and **II**, while **Figures 5e and 5f** show the source apportionment for PM₁₀ and PM_{2.5} in **Paper III**. The source profiles describe the chemical composition of the factors isolated by PMF and are therefore used in order to identify the aerosol sources affecting the receptor. **Figure 6** shows only one source profile for every factor in Table 3, because the composition for the common factors is as is expected similar, *mutatis mutandis*, across the three studies. The respective Papers should be consulted for the full set of factor profiles.

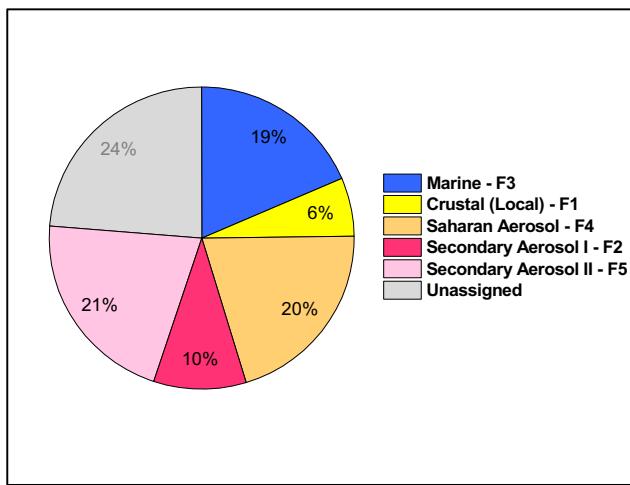


Figure 5a: PM₁₀ source apportionment for Għarb. **Paper I.**

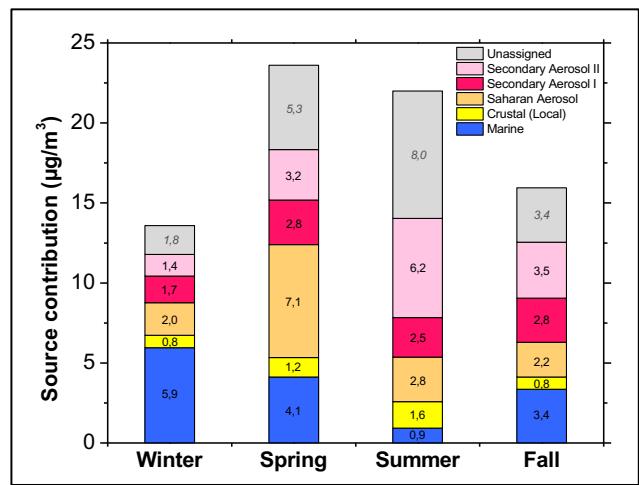


Figure 5b: Seasonal variation in PM₁₀ source contribution. **Paper I.**

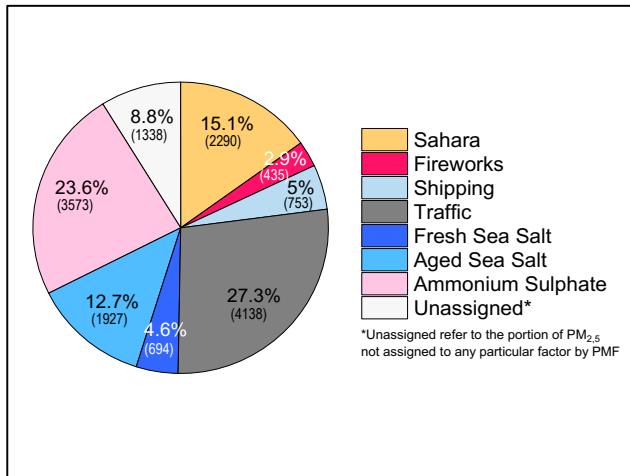


Figure 5c: PM_{2.5} source apportionment for Msida. The numbers in the brackets show the source contribution estimates in ng/m³. **Paper II.**

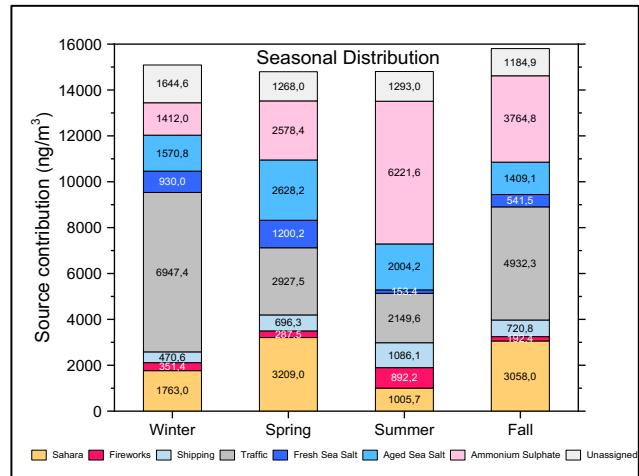


Figure 5d: Seasonal variation in PM_{2.5} source contribution. **Paper II.**

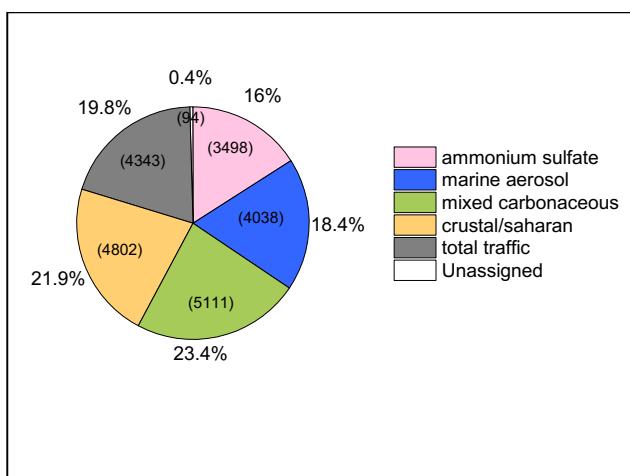


Figure 5e: PM₁₀ source apportionment for Lido Cerano. The numbers in the brackets show the source contribution estimates in ng/m³. **Paper II.**

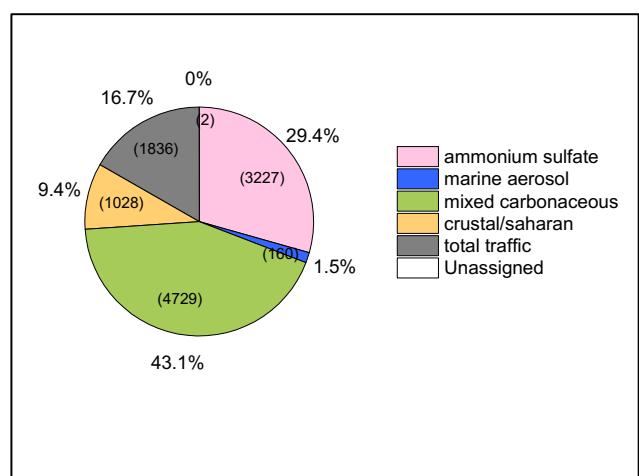


Figure 5f: PM_{2.5} source apportionment for Lido Cerano. The numbers in the brackets show the source contribution estimates in ng/m³. **Paper III.**

There is however a small difference between the source profiles in **Paper I** and those in **Papers II** and **III**. The error bars for the source contribution estimates in **Paper I** were calculated as one half the interquartile range for the bootstrapped runs, while those in **Papers II** and **III** were set at the 5th and 95th percentile of the bootstrapped runs, because according to Paatero (2014) these intervals should not as is customary, be reported as symmetrical ones.

Table 4: Factors isolated in the three studies and relative source contribution estimates.

	Paper I	Paper II	Paper III	Paper III
PM fraction	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Sampling year	2012 - 2013	2016	2015	2015
Crustal/Local	1.14 µg/m ³	NI	NI	NI
Crustal/Saharan	3.73 µg/m ³	2.29 µg/m ³	4.80 µg/m ³	1.03 µg/m ³
Marine (Fresh)	3.37 µg/m ³	0.69 µg/m ³	NI	NI
Marine (Aged)	1.78 µg/m ³	1.92 µg/m ³	4.04 µg/m ³	0.16 µg/m ³
Secondary Sulphate	3.86 µg/m ³	3.57 µg/m ³	3.50 µg/m ³	3.22 µg/m ³
Shipping	NI	0.75 µg/m ³	NI	NI
Total Traffic	NI	4.13 µg/m ³	4.34 µg/m ³	1.84 µg/m ³
Fireworks	NI	0.43 µg/m ³	NI	NI
Mixed Carbonaceous	NI	NI	5.11 µg/m ³	4.73 µg/m ³
PM (modelled)	13.90 µg/m ³	13.78 µg/m ³	21.79 µg/m ³	~10.98 µg/m ³
PM (measured)	18.22 µg/m ³	15.11 µg/m ³	21.89 µg/m ³	10.98 µg/m ³

Legend: NI = not isolated.

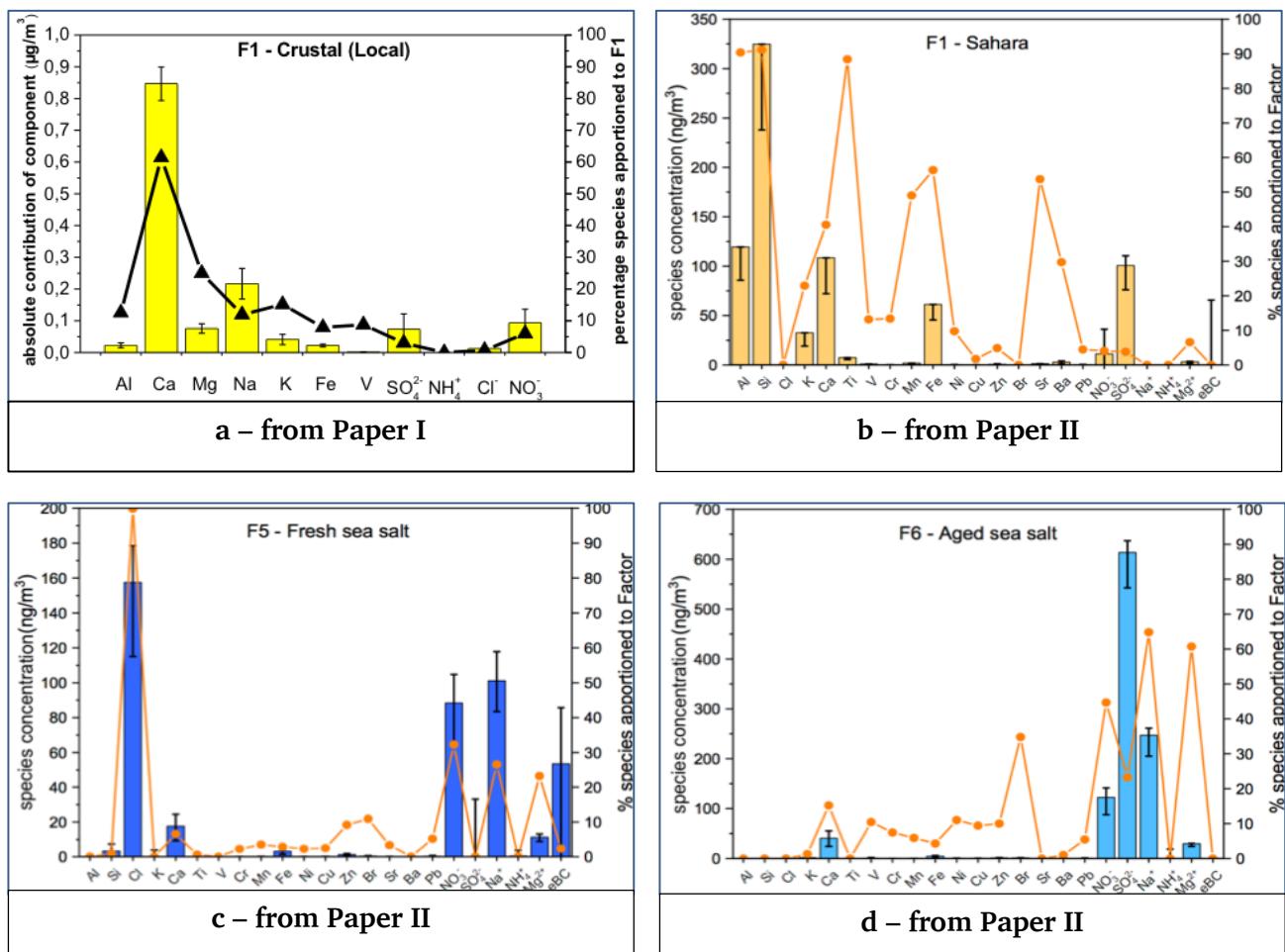


Figure 6: Factor profiles (bars) and percentage of species apportioned to each factor (line).

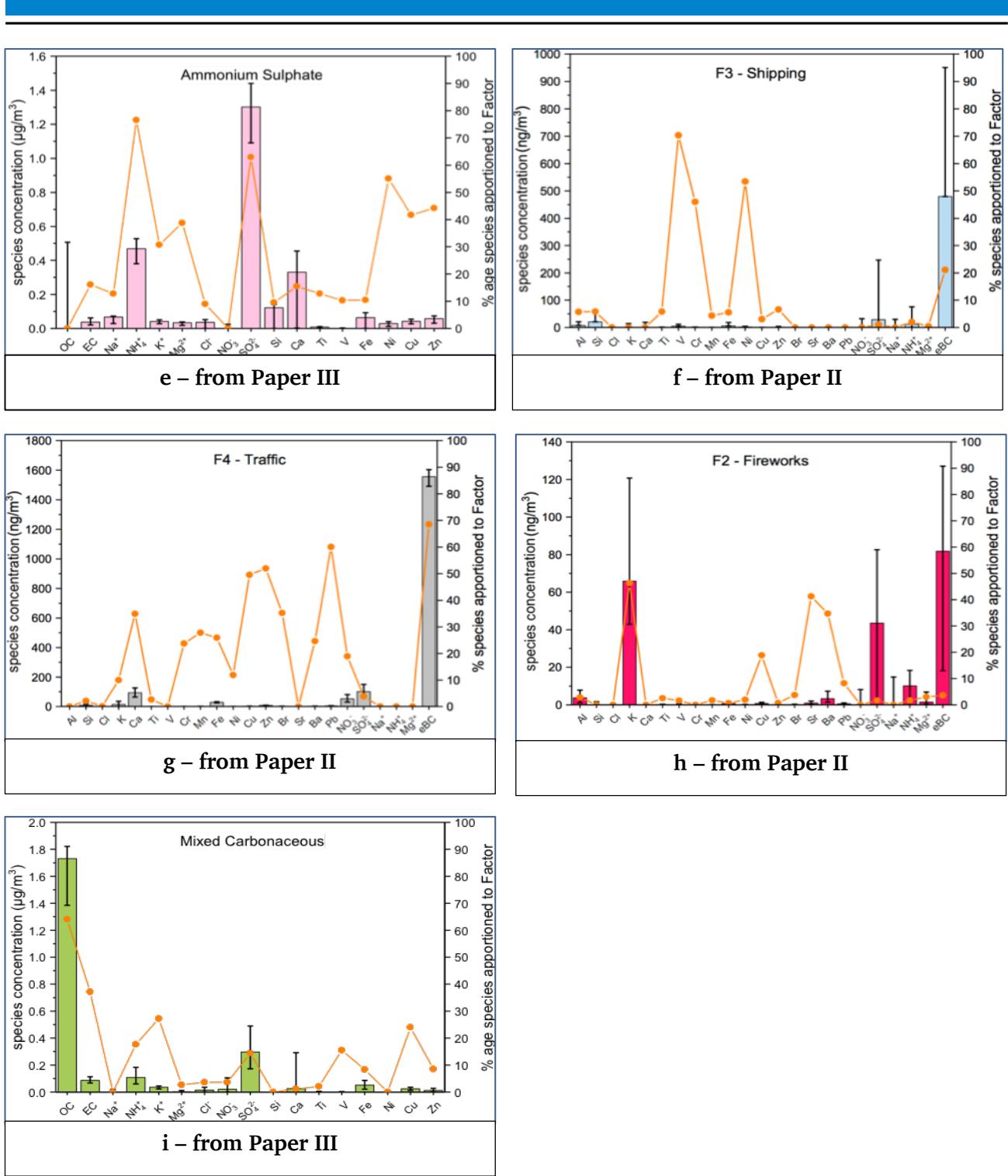


Figure 6 (continued): Factor profiles (bars) and percentage of species apportioned to each factor (line).

4.3. Factor Profiles

The local crustal factor in **Figure 6a** (which was isolated in **Paper I** only) shows high loadings for Ca, mostly. This is interpreted as the contribution from limestone due to the fact that all the surface outcrops in Malta are essentially formations of this rock type and explaining the labelling of this factor as

“Crustal/Local”. This interpretation was aided with a polar plot Figure 7 below, which shows that the highest contribution of this source occurs with wind blowing from the ESE to the SW. This wind segment includes the quarrying activity to the South of the receptor as well the effect of anthropogenic activity from the principal town (at ~5 km to the ESE). Figure 7 also shows that higher contributions from this source are registered at the receptor at wind speeds ≥ 10 m/s, which is not surprising especially in view of the fact that wind is the major agent of dust entrainment. In addition, Figure 5b shows that the contribution of this factor was highest during the driest months Spring and Summer. This was also confirmed statistically, refer to **Paper I** for

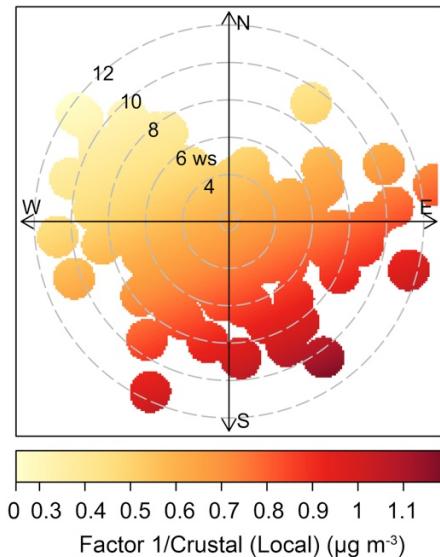


Figure 7: Polar plot for the Crustal/Local Factor in **Paper I**

further details. This is interpreted as a confirmation of the attribution of this factor to local crustal material due to the fact that rain decreases both the resuspension and the emission of dust from quarrying (Amato *et al.*, 2009; Vella and Camilleri, 2005).

The Factor profile in **Figure 6b** was common to the three Papers. This profile shows high loadings for terrigenous species such as Si, Al, Fe and Ca amongst others and normally carries most of the Si and/or Al measured in the samples. These metals are considered as tracer species for African desert dust (Rodríguez *et al.*, 2002; Viana *et al.*, 2008; Scheuvens *et al.*, 2013), explaining the naming of this Factor as “Saharan”. Local origin of a crustal component rich in Si and Al is excluded for Malta on account of the poor Al content in Maltese crustal material (Vella *et al.*, 1997). In the three papers concentration weighted trajectories (see **Figure 8**) were plotted for three arrival heights of relevance to the transportation of Saharan dust (500 m, 1500 m and 3000 m). These plots show that in the three cases high levels of

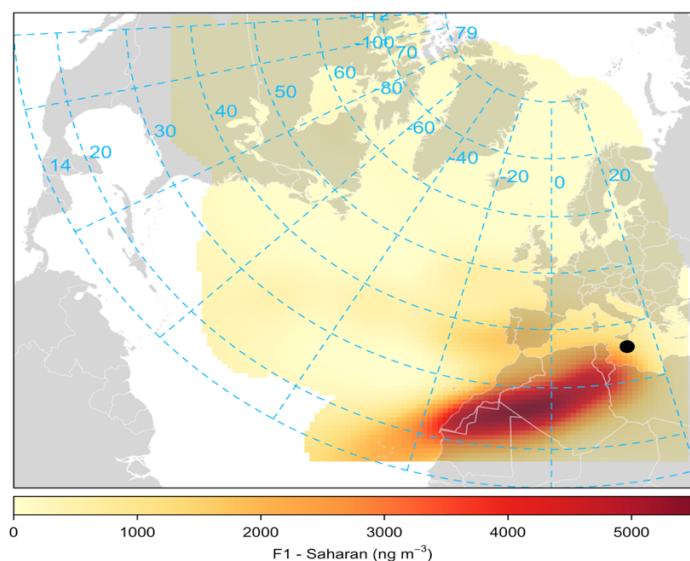


Figure 8: Concentration weighted trajectories for the Saharan Factor for an arrival height of 1500m. **Paper II**.

this source contribution are linked to trajectories spending more time over the Saharan region. Additionally, the Saharan episodes isolated by PMF were checked against national reports on these incidents (**Papers I** and **II**) or against the forecasts of models such as the World Meteorological Organization (WMO) Sand and Dust Storm Warning Advisory System (SDS WAS), see **Paper III**. From Figures 5b and 5d this factor exhibits a marked seasonality, with peaks primarily during Spring, the season mostly associated with these events in the Central Mediterranean. It is worth pointing out that **Papers II** and **III** have shown that Saharan dust is a significant contributor to PM_{2.5} as well in the Central Mediterranean.

The factor labelled as “Fresh marine aerosol” or “Fresh Sea salt” (**Figure 6c**) was isolated in **Papers I** and **II** only. The main tracers of this factor are primarily Na⁺ (Na in **Paper I**) and Cl⁻ (or Cl in **Paper II**) and also Mg²⁺ (or Mg in **Paper I**). Ratios of Cl⁻/Na⁺ and Cl⁻/Mg²⁺ close to reference values of 1.8 and 14.9 respectively (Seinfeld and Pandis, 2016) are considered as indicators of the marine origin of this aerosol component. **Figures 5b** and **5d** show that the strength of the contribution of this factor is also dependent on the season and peaks during the season with the strongest winds, which is, what is expected from its formation mechanism based on bubble bursting due to wind induced shear (Marelli *et al.*, 2007).

The three Papers isolated a factor characterised by the presence of Na⁺ (or Na in **Paper I**), Mg²⁺ (or Mg in **Paper I**) and by the ions NO₃⁻ and SO₄²⁻ (**Figure 6d**). In the three Papers the ratio of Na⁺/Mg²⁺ is close to 8.3, the reference value for sea water (Seinfeld and Pandis, 2016), this possibly indicates that the factor owes its origin to the sea. However, in **Papers I**, **II** and **III** the factor is to varying degrees depleted in Cl. This could be possibly due to the reaction of HNO₃ with NaCl and the loss of Cl through the formation of HCl, hence the descriptor “Aged Marine aerosol”. One feature, which was exclusive to **Paper III** is the fact that at the receptor in Lido Cerano, only an “Aged Marine aerosol” component was isolated, despite the closeness to the coast. This is however not uncommon for both the PM_{2.5} (see e.g. Cesari *et al.*, 2016; Manousakas *et al.*, 2017) and the PM₁₀ (Contini *et al.*, 2010) fractions.

The factor in **Figure 6e**, is characterised by two ionic species NH₄⁺ and SO₄²⁻ and typically carries most of the mass of these two species in the samples analysed. In all the three Papers the ratio of equivalents of SO₄²⁻ / NH₄⁺ is very close to 1, indicating that the factor is due to secondary inorganic sulphate aerosol (SISA), in particular (NH₄)₂SO₄. **Figures 5b** and **5d** show that the levels of this factor are particularly high during summer, in fact it was statistically shown in **Papers I** and **II** that the levels of this factor increase in the months in which the temperatures are higher. This tallies with the fact that the rate of oxidation of the SO₂ precursor is highest in the months with the highest solar intensity (Hidy, 1994; Polissar *et al.*, 2001; Song *et al.*, 2001; Kim *et al.*, 2004), and which are therefore the months with the highest temperatures. The presence of sulphate-containing aerosol is considered an indication of aging of the air masses (Manousakas *et al.*, 2017) due to the slowness in the conversion of SO₂ into H₂SO₄ in the atmosphere, therefore secondary sulphate aerosol is also an indicator of long range/regional transportation, Viana *et al.* (2008). In fact, in **Paper II**, it was shown that high levels of this factor at the receptor are associated with trajectories spending more time over Continental Europe (particularly Italy), see **Figure 9**. From Table 4 one can see that despite the fact that the studies were not carried out during the same year the contribution of this aerosol component to both PM₁₀ (**Paper 1**) and PM_{2.5} (**Paper II**) in Malta is not much different from the contribution of the same component to the respective aerosol fraction in Lido Cerano (**Paper III**), <0.4 µg/m³ for both fractions, which is within the margin of error

reported for this factor in **Paper III**, and highlighting even more the fact that secondary inorganic sulphate aerosol is a regional issue.

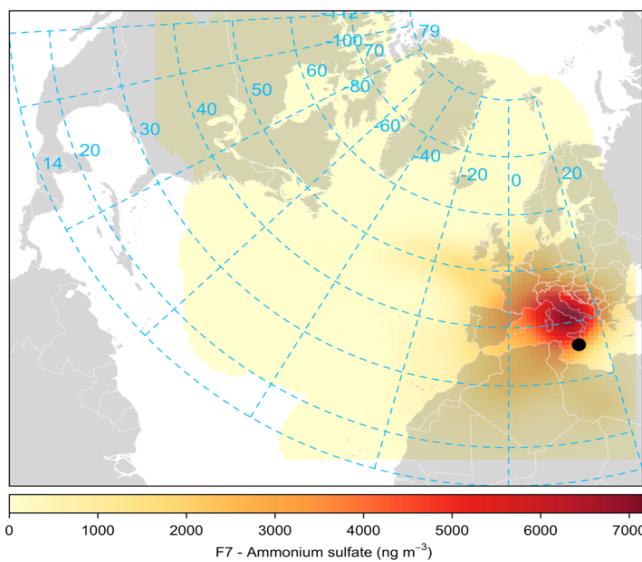


Figure 9: Concentration weighted trajectories for SISA for an arrival height of 1500 m. **Paper II.**

In **Paper II** (only) a factor dominated by the contributions of Ni and V and with an important contribution of equivalent Black Carbon – eBC was isolated (**Figure 6f**). An estimate of the Ni / V ratio yielded a value of 0.4, which is within the range of values considered by Nigam *et al.* (2006) (0.2 – 0.4) and Viana *et al.* (2008) (0.3 – 0.4) as indicators of fuel oil combustion in ships. Hence, this factor was labelled as “Shipping”. The polar plot in Figure 10 supports the assignment of this Factor as it shows that a high influence of this factor is associated with winds from the easterly directions. The harbours in Malta are located on the Eastern side of the island and in addition to that, there is one of the busiest shipping routes in the Mediterranean to the East of Malta. The contribution of the shipping factor peaks during summer and decreases by more than 50% during winter (**Figure 5d**). This is possibly due to the fact that shipping activity increases when the seas are calmer, similar behaviour of this factor was reported by Manousakas *et al.* (2017) for a site in Greece. It is pertinent to point out the relatively high loadings of eBC (**Figure 6f**), this is important especially when discussing the impacts of this activity on human health. The source profile for this factor shows low loadings for both SO_4^{2-} and NO_3^- , this is probably due to the fact that the oxidation of the SO_2 and NO_2 precursor gases to the respective acids is rather slow (particularly for SO_2) and because the emissions occur at a relatively short distance away from the receptor, the secondary component of shipping emissions will in all probability be included

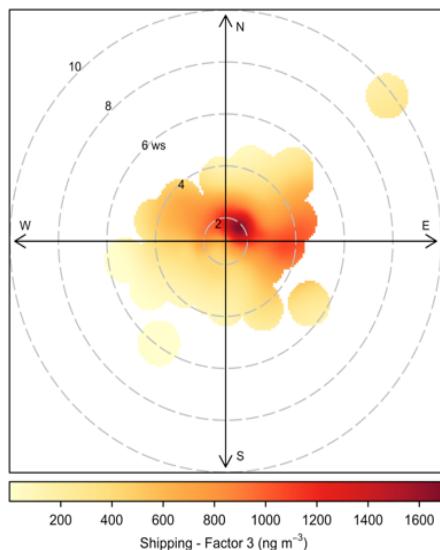


Figure 10: Polar plot for the Shipping Factor. **Paper II**

high loadings of eBC (**Figure 6f**), this is important especially when discussing the impacts of this activity on human health. The source profile for this factor shows low loadings for both SO_4^{2-} and NO_3^- , this is probably due to the fact that the oxidation of the SO_2 and NO_2 precursor gases to the respective acids is rather slow (particularly for SO_2) and because the emissions occur at a relatively short distance away from the receptor, the secondary component of shipping emissions will in all probability be included

with the other secondary inorganic aerosol component, rather than with the component isolated by PMF. It is highly likely that this component represents the primary emissions from shipping.

A Factor which is responsible for most of the eBC (or EC) and for a significant fraction of the NO_3^- together with trace amounts of metals such as (but not limited to) Cu, Zn, Fe, Ni and V was isolated in **Papers II and III** (see **Figure 6g**). All these species are considered as tracers of the various contributors of traffic derived aerosol. Exhaust emissions are normally identified by the presence of both carbonaceous material (EC/eBC and OC) and NO_3^- (Jiang *et al.*, 2005). Zn is used as a tracer of both the combustion of lubricating oil (Viana *et al.*, 2008) and of tyre abrasion (Pakbin *et al.*, 2010; Amato *et al.*, 2011), while Cu, Zn and Fe are associated with the emissions from the abrasion of brakes (Sternbeck *et al.*, 2002; Schauer *et al.*, 2006; Figi *et al.*, 2010; Amato *et al.*, 2011). Ni and V are used as tracers of either fuel oil or gas diesel oil combustion in both land-based and sea-based sources or for the abrasion of the road surface (Lindgren, 1996; Kennedy and Gadd, 2003), due to the presence of bitumen in asphalt. In both **Papers II** and **III** this factor profile shows high loadings for Ca as well; this is considered indicative of a strong contribution from both resuspended road dust as well as from the abrasion of the road surface. The presence of a road surface abrasion contribution was confirmed in **Paper III** by the strong correlation of Ni with V in PM_{10} and the rather poor correlation of these two metals in $\text{PM}_{2.5}$. Aerosol generated from the abrasion of the road surface, due

to its mechanical nature, occurs mostly in the PM_{10} fraction (Ketzel *et al.*, 2007), while emissions from combustion sources should partition heavily in the finer fraction (Amato *et al.*, 2016b). It is highly probable that this Factor is a “Total Traffic fFector” including the exhaust, abraded and resuspended contribution of traffic generated PM. Additionally wind-entrained dust is expected to be chemically similar to the traffic resuspended dust and from the dust abraded from the road surface, meaning that PMF will not be able to distinguish the former component from the rest (Viana *et al.*, 2008). In **Paper II** the “total traffic” source contribution correlated well with the concentration of NO_x in ppb (**Figure 11**), supporting the attribution of this factor to traffic. Moreover, **Figure 5d** shows that the maximum value of this contribution occurs during winter, possibly due to the decrease in the mixing layer height during this season. The polar plot in **Figure 12** shows that the highest concentrations of this contribution occur where the receptor is located (the origin of the plot), which is what one would expect from a site in a traffic hotspot. It was shown in **Paper III** that the contribution of this factor to $\text{PM}_{2.5}$ is 42% of the

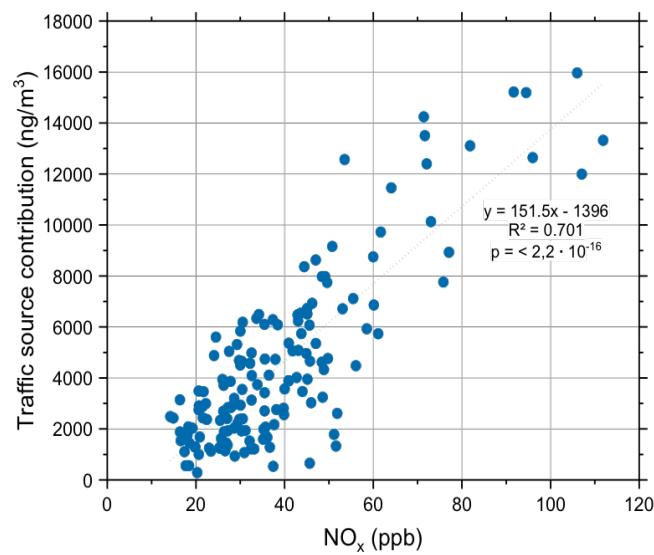


Figure 11: Plot of the traffic source contribution vs. the NO_x concentration. **Paper II**.

contribution of the same factor to PM₁₀. In view of the fact that most of the exhaust fraction is expected to occur in the PM_{2.5} fraction, while the abraded and resuspended contributions should occur in the PM₁₀ fraction, one can conclude that the latter is the major component in traffic derived aerosol. This is similar to the result obtained Weinbruch *et al.* (2014), who have determined a similar split between the exhaust and abraded fractions for a receptor in Germany.

Figure 6h shows a factor which was isolated only in **Paper II**. The source profile of this factor is characterised by K and the presence of the trace metals Ba, Sr and Cu. In **Paper II**, it was shown that this factor is highly seasonal with a peak during a period running from mid-June till the beginning of September coinciding with the Maltese *festa* (a religious feast organised by the various parishes in the Malta, in honour of their patron saint) season. These celebrations include the letting-off of aerial fireworks mainly during the two days preceding the feast, which becomes even more intensive during the day of the feast. The oxidising compounds used in the fireworks explain the presence of K, while the compounds used to give colour to the fireworks explain the presence of Ba, Sr and Cu. Camilleri and Vella (2010) have already shown that this activity affects PM levels during this season. It is worth pointing out that despite the fact that this activity is highly seasonal, its contribution is strong enough for it to have a measurable effect on the annual levels of PM_{2.5}. The presence of K, could have led to the interpretation of this factor as a “biomass combustion factor”, however the marked incidence of this component during the summer months excludes cooking or heating as the source of this factor. The siting of the receptor, in the middle of a densely populated area and (relatively) far away from agricultural activity makes any interference from the burning of agricultural waste a highly remote possibility.

In **Paper III** a factor dominated by OC was isolated (**Figure 6i**). This factor was partly attributed to secondary organic aerosol (SOA), see the paper for further detail. The factor is also characterised by the presence of K⁺ and EC, both considered tracers of biomass combustion. Factor 3 was labelled as “mixed carbonaceous aerosol” factor and is likely to be made up of *inter alia* aged biomass combustion aerosol, which was identified by e.g. Hennigan *et al.* (2010); Hennigan *et al.* (2011) and Cubison *et al.* (2011) as one of the SOA precursors. Siciliano *et al.* (2018) using the same dataset for the carbonaceous species have shown that trajectories reaching the receptor from North-eastern Europe are associated with the peak concentrations of EC, OC and SOA. The North-eastern European air-masses are associated with an increased secondary aerosol loading in Apulia (Di Gilio *et al.*, 2015). This factor was the major contributor to both PM₁₀ and PM_{2.5} at the receptor.

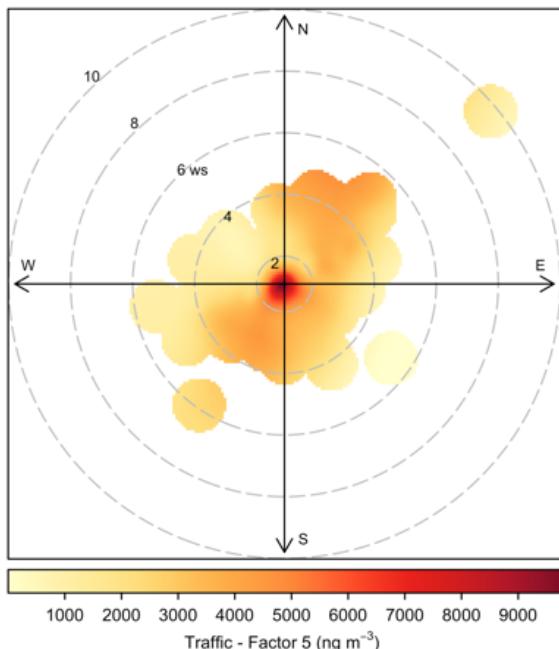


Figure 12: Polar plot for the Total Traffic source contribution. **Paper II**.

The studies in both **Papers II** and **III** included a fraction of the PM mass, which was not assigned to any particular factor (Table 4). This is not uncommon in source apportionment studies and is normally attributed to analytical uncertainties, non-carbonaceous elements in organic matter, which are not determined analytically (Huebert and Charlson, 2000), structural water (Yubero *et al.*, 2011) as well as the hysteresis in the deliquescence – efflorescence cycle of hydrated aerosol particles (EPA, 2004). Despite the unassigned mass the studies in both papers, still reported a high mass closure. On the other hand, the unassigned mass In **Paper III** is insignificant.

5. Discussion

This forthcoming chapter discusses the results obtained by the studies at the basis of **Papers I, II and III**. Section 5.1 treats the issue of the reliability of the solution obtained by Positive Matrix Factorization (PMF) modelling and discusses issues common to the three Papers. The subsequent sections deal with issues specific to each paper: Sections 5.2 and 5.3 address issues related to **Paper I** (reliability issues specific to this Paper and the implications of the results on compliance with Directive 2008/50/EC; Section 5.4 treats the issue of how Malta could achieve compliance with the WHO air quality guidelines (AQGs) in the light of the results of **Paper II**; and Section 5.5 and subsections 5.5.1 and 5.5.2 deal with the validation of the model returned by PMF in **Paper III**.

5.1. Reliability of the PMF solutions

In Europe, the use of receptor modelling techniques in the identification of the major sources of airborne particulate matter (APM) pollution as well as in the quantification of the contribution of each source to ambient levels of the different PM fractions has been harmonised through the protocol compiled by Belis *et al.* (2014) and revised by Favez *et al.* (2019). The use of the recommendations in this protocol together with the guidelines in the USEPA PMF version 5 Guidebook (Norris *et al.*, 2014) as well as the recommendations in Brown *et al.* (2015) for the presentation of the results, in a source apportionment study add reliability to it. The studies at the basis of **Papers I, II and III** were carried out following the above-mentioned guidelines as applicable to each particular situation.

The keystone of any source apportionment exercise by PMF, is the minimisation of the Q fitting parameter. Ensuring that the model achieves a “global” rather than a “localised” minimum has a bearing on the reliability of the model returned by PMF. This was ensured in the three **Papers** by running the model multiple times (10 in **Paper I** and 20 in **Papers II and III**), with each run starting at a different pseudo-random seed and with at least 20 iterations per run (100 in **Paper III**). The procedure adopted in **Paper I** is similar to that in Koçak *et al.* (2011) and Kara *et al.* (2015), while that in the other **Papers** is even more onerous. In the three studies all the multiple PMF runs reached convergence. The minimum Q-values for each of the multiple runs were inspected for any inter-run variations and the insignificant differences between them were interpreted as meaning that a “global” minimum had in fact been achieved. Upon visible inspection, the scaled residuals (d) for all the factors isolated in the respective studies were all within the range $-3 < d < 3$ and were all more or less normally distributed, adding credibility to the solution retained in each of the three studies, Friend *et al.* (2012), Li *et al.* (2013).

The errors in the retained PMF solution can be estimated in USEPA PMF version 5 using three inbuilt error estimation techniques: classical bootstrapping (BS), displacement (DISP) and a combination of these two (BS – DISP). BS and DISP respectively determine the random errors, and the errors due rotational ambiguity, while BS – DISP measures the errors due to both together, Norris *et al.* (2014). In **Papers II and III**, all the three techniques were run on the solutions retained in each of the studies in order to investigate the validity of the respective solution. While in **Paper I** it was possible to run only BS on the final solution, this is a limitation of the particular refinement which had to be applied to the solution (refer to the Results section in the paper), however this should have at least investigated the stability of the chosen solution (Brown *et al.*, 2015). In all three Papers, BS involved 100 runs (the minimum requirement for statistical robustness) with the default minimum R-correlation of 0.6. In the

three cases there was a 100% match between the Base and Bootstrapped factors, meaning that the retained model was well defined. DISP showed no swaps in the factors for both the solutions in **Paper II** and **III**, indicating the respective PMF solutions were rotationally stable for the chosen number of factors. In **Paper II**, BS-DISP accepted 96% of the cases and showed a minimum number of factor swaps (1 – 4), confirming acceptability of the solution (Achilleos *et al.*, 2016) and also that accepted resamples are both robust and reliable (Paatero *et al.*, 2014). However, the BS – DISP carried out on the solution in **Paper III** accepted 88% of the cases but showed numerous identity swaps across most of the factors, meaning that the solution required further refinements. Rotational ambiguity and overall uncertainty increases when running PMF with a smaller dataset (Manousakas *et al.*, 2017) as was the case in **Paper III**. One of the causes of factor swaps (or rotational ambiguity) is the association of species with a particular factor when they are poorly related to it. USEPA version 5 includes rotational tools, such as the possibility of imposing constraints based on external information (such as concentrations of particular species in the F matrix) on the Base solution, which should remove the rotational ambiguity caused by these species. For further detail on the refinement of the Base solution in this study refer to **Paper III**. Once the Base solution was refined, BS-DISP accepted all the cases and showed no factor swaps, indicating that the solution was well constrained. Additionally, when running PMF on a smaller dataset (e.g. in **Paper III**) it is always good practice to include any information available on the error estimates (Manousakas *et al.*, 2017).

Table 5: PMF error estimates for the tracer species of the identified factors. (**Paper III**).

	Factors (Species used as tracers)				
	Secondary Inorganic Sulphate (SO_4^{2-})	Sea Salt (Na^+)	Mixed Carbonaceous (OC)	Saharan (Si)	Total Traffic (Ca)
Constrained Base Value	1.30	0.41	1.73	1.13	1.16
BS 5 th percentile	1.09	0.35	1.39	0.89	1.00
BS Median	1.29	0.42	1.66	1.05	1.14
BS 95 th percentile	1.44	0.48	1.82	1.21	1.63
BS – DISP 5 th percentile	0.81	0.33	1.23	0.89	0.73
BS – DISP Average	1.28	0.43	2.14	1.22	1.27
BS – DISP 95 th percentile	1.76	0.52	3.95	1.55	1.81
DISP Min	1.05	0.37	1.40	0.98	1.02
DISP Average	1.39	0.42	2.07	1.19	1.40
DISP Max	1.73	0.48	2.73	1.39	1.78

Table 5, above shows the error estimates using the three error estimation methodologies in USEPA PMF version 5 for all the species used as tracers of the isolated factors. The errors in this table are not particularly high and this is interpreted as evidence that (despite the smaller dataset) the factors isolated by PMF do in fact correspond to different real, physical sources of aerosol (Manousakas *et al.*, 2017).

Source contribution estimates in Papers I, II and III were calculated using multilinear regression analysis (MLRA). This avoided having to use a total species such as PM₁₀ or PM_{2.5} as a fitting species in PMF, because this could give rise to issues of double counting (Reff *et al.*, 2007) and would have meant artificially constraining the intercept to 0 and overestimating the determined PM mass (Viana *et al.*, 2008). The use of MLRA provides an additional check on the number of factors retained. If all the regression coefficients are >0 , then this is indicative of a non-excessive number of fitted factors, (Buzcu *et al.*, 2003). This was the case in all the three papers. Furthermore, in Papers II and III, all the species making up the different profiles were scaled by respective factor scaling constants (or regression coefficients). The scaled species concentrations were summed across the different profiles and were all < 1 (ng/ng in Paper II and $\mu\text{g}/\mu\text{g}$ in Paper III) for all the profiles in the two Papers, meaning that the fitted number of factors was not too low (Hopke, 2001; Kim *et al.*, 2003). The validity of models determined for the three studies is reinforced by the fact that in the three studies PMF managed to reconstruct most of the PM mass and also because of the high correlation between the measured and the modelled PM mass. This is especially so for Papers II and III. On the other hand, the percentage mass reconstruction and coefficient of determination reported by Paper 1 were $\sim 80\%$ (see the respective papers for more detail). While this shows that the model did not perform as well as it did in the other two papers, this is by no means an isolated incident, in fact there are studies in which mass closure is even less than this e.g. 52% in Yatkin and Bayram (2008), while the coefficient of determination is similar to that reported by e.g. Yubero *et al.* (2011), Vargas *et al.* (2012) and Alam *et al.* (2014). A further test was carried out in Papers II and III in order to measure the ability of PMF to effectively estimate the ambient PM levels. This test, the coefficient of divergence (Buzcu *et al.*, 2003) or CD and it measures the difference between the measured and modelled values. When the CD approaches a value of 1 the measured and the modelled values are significantly different (Wongphatarakul *et al.*, 1998), while lower CD values (such as those reported in Papers II and III) indicate that the sources contributing to the ambient PM levels have been adequately identified (Buzcu *et al.*, 2003).

To sum up all the issues discussed in this section confirm that the solutions reported in the three studies have a high degree of reliability and are therefore credible.

5.2. Reliability issues specific to the study in Paper I

Table 2 shows that As, Cr, Cd and Pb were below the detection limit (BDL) when sampled with a low volume sampler (LVS), this could raise the issue that given that the receptor is located in a less polluted airshed (due to its siting in a rural setup), then perhaps the sampling could have been carried out using a high volume sampler (HVS). While it is true that sampling by HVS could have enabled the measurement of one or a number of the above-mentioned species, the added value of this information is doubtful, at best. This is due the fact that the detection of these species (through HVS sampling) would not have automatically translated into the isolation of more sources by PMF, because if the species are BDL when sampled by an LVS then it means that the effect of the sources emitting them on the receptor is not that marked. PMF (as with receptor models in general) is not normally very good at isolating such minor sources, Jang (2014). It is likely that PMF would have apportioned these metals to one or more of the sources, which have been disentangled for this site, e.g. the resuspended dust component which is likely to include sources such as traffic re-suspension of road dust as well as the abrasion of the road surface, tyres and brake material, leaving the number of isolated factors unchanged. In addition, it is worth pointing out that the aim of this study was to isolate the natural sources in order

to analyse their effects on Malta's compliance with the requirements of Directive 2008/50/EC (2008). It is a well-accepted fact that, compliance with these limits is to be assessed through the use of the reference method as laid down by CEN 12341 (2014), otherwise the equivalence of the measurement method to the reference method would have to be proven. This means that in this case, one would have to carry out the equivalence trial prior to starting the measurement campaign, apart from the fact HVSs would have to be corrected for their uncertainties (CEN 12341, 2014). The carbonaceous fractions EC and OC are normally included in source apportionment studies, so their exclusion, could also raise issues on the effect this could have on the apportionment of the factors which have been isolated. However, one should in this case keep in mind that the natural sources of relevance to Malta, Saharan dust and marine aerosol should not be impacted by the determination or otherwise of EC/OC. In fact, these species are not used as tracers for these two sources. This does not however mean that these species are totally absent from these two factors e.g. it has been shown by Hoffman and Duce (1997), that the finer fraction of marine aerosol component includes a significant contribution from organic material, while Kandler et al., (2007) have shown that Saharan dust includes soot and other carbon containing material.

5.3. Implications of the study in Paper I on compliance with Directive 2008/50/EC

PM₁₀ levels at the receptor in Għarb have been in compliance with both the long-term and the shorter-term standards in Directive 2008/50/EC (2008) since the setting up of the station in 2008. Throughout the period running from 2008 to 2014, the annual averaged PM₁₀ concentrations were within the range 17.9 µg/m³ – 22.3 µg/m³ (18.2 µg/m³ throughout the study period), well below the annual limit value of 40 µg/m³. A comparison to similar stations in the Mediterranean, using the data in (EEA, 2016), shows that range of values measured at the Maltese rural station are indicative of a fairly “clean” Mediterranean rural airshed. In fact, the range of PM₁₀ values for Malta is lower than that measured in Cyprus but higher than that recorded in southern Spain and in Italy, and similar to that measured in Portugal (see Table 6).

Table 6: PM₁₀ concentration ranges in Mediterranean countries measured from 2008 – 2014 (EEA, 2016).

Country	Concentration Range (µg/m ³)		Year		Receptor Location	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cyprus	21.7	36.6	2008	2012	Agia Marina	
Portugal	12.3	23.5	2013	2009	Vaqueiros	Santiago de Cacem
Italy	10.0	23.3	2013	2011	Cetara	Fontechiari
Spain	7.6	20.0	2013	2014	Marita de Maestrazgo	Sa Pobla

Furthermore the number of exceedances of the 50 µg/m³ daily limit value in Malta throughout the same period, varied from 2 to 17, in 2012 and 2010 respectively (ERA, unpublished data) while the maximum number of exceeding days at the Mediterranean stations varied from 11 in Fontechiari (Italy) in 2011 to 13 in Viznar and Calanda (Spain) in 2013 and 39 in Agia Marina (Cyprus) in 2008. Malta Environment and Planning Authority (2012; 2013) attributed these daily exceedances at the receptor in Għarb to Saharan dust episodes.

The receptor in this study is sited at Malta's background site and therefore the Saharan source contribution estimate from this study ($3.7 \mu\text{g}/\text{m}^3$) is applicable throughout the Maltese territory. Directive 2008/50/EC (2008) allows Malta to subtract this contribution together with the marine aerosol contribution from the PM₁₀ levels measured at any site exceeding any one of standards included therein (normally the traffic site). However, the fact that European Union legislation allows Member States to subtract these natural contributions from their exceeding stations should in no way be construed as meaning that these contributions are totally bereft of health effects. This is emphatically stated by the Commission Guidelines on the subtraction of natural sources (European Commission, 2011). Despite the fact that it is not being suggested that the European Union Member States should stop subtracting natural contributions from the PM₁₀ levels at the exceeding stations, chiefly because no regulatory action can be taken in order to control the sources of natural aerosol, however one has to acknowledge that the current approach is inadequate for the protection of human health. It is therefore being strongly suggested that any future revisions of Directive 2008/50/EC (2008) should set obligations on Member States to warn the general public in advance about the occurrence of these events and to ensure that the population is well informed about the human health implications of exposure to elevated PM₁₀ levels during these events.

5.4. Achieving the WHO guidelines by 2020 and the study in Paper II

All the real-time stations in the Maltese Islands have measured PM_{2.5} concentrations below the $25 \mu\text{g}/\text{m}^3$ annual limit value set by Directive 2008/50/EC (2008) from 2008 (the year in which they were set up) onwards and the levels of this aerosol fraction have so far been on the decrease since 2011 (ERA, unpublished data). This is also the case for the traffic station in Msida, the station representative of a high exposure scenario. However, it is a widely accepted fact that compliance with this limit value is not sufficient to protect human health (WHO, 2006). In fact, the air quality guidelines prepared by the WHO set both an annual guideline, which is 2.5 times lower than the EU limit value as well as a daily limit value ($25 \mu\text{g}/\text{m}^3$) to be complied with 99.2% of the time. Additionally, at least two of the EU's major economic competitors (USA and Japan) have limit values for PM_{2.5}, which are closer to the WHO guideline. The "Clean air programme for Europe", issued by the European Commission in 2013, aims to redress this situation through EU-wide emission reductions *inter alia* for PM_{2.5}. These reductions should successively enable the EU to steer the annual limit value towards the WHO guideline by 2020 (European Commission, 2013). In this context the main building block of the EU's emission reduction programme is its emissions reduction commitment for PM_{2.5} to the Gothenburg Protocol of the Convention on Long Range Transboundary Air Pollution (CLRTAP).

The results in **Paper II** have shown that African dust episodes contribute significantly to PM_{2.5} levels as well (15.1% of the total PM_{2.5}), moreover the effect of marine aerosol on this fraction of APM is also measurable. If the WHO guidelines for PM_{2.5} are adopted as EU limit values then the compliance of the Mediterranean countries with these standards (especially the daily limit value) will be heavily impacted by the Saharan dust episodes, while the marine aerosol contribution will have to be given due consideration when considering the compliance of coastal sites with the annual limit value. This should entail a revision of the Commission guidelines on the subtraction of exceedances due to natural sources (currently applicable to PM₁₀ only) in order to cater for the effect of these two sources on PM_{2.5} too.

It has been shown by **Paper II** (and also by **Paper I** and **III**) that secondary inorganic sulphate aerosol (SISA) is one of the chief contributors to ambient PM levels (especially PM_{2.5}) in the Central Mediterranean. According to EEA (2015) atmospheric levels of SISA are driven by the atmospheric concentrations of the NH₃ precursor. This is a consequence of the fact that from 2000 to 2017 atmospheric emissions of SO₂ (the other precursor) have declined by >70%, while those of NH₃ have decreased by <10% (EEA, 2018). In view of the fact that atmospheric concentrations of SISA are more of a regional issue (see results section), the levels of this aerosol component cannot be reduced by countries acting in isolation but through regional or even hemispheric action targeting emissions of NH₃ (of which, industrial farming is a major emitter). The prospects for achieving significant reductions in SISA levels are rather bleak, because the EU Member States have committed themselves to jointly achieve a reduction in NH₃ emissions of only 6% by 2020, over 2005 levels, this will result in a negligible decrease in SISA levels (see **Paper II** for more details).

In coastal areas, particularly in the Mediterranean, shipping is a measurable contributor to aerosol pollution (including PM_{2.5}) see **Figure 13**, below. **Figure 6f** shows that aerosol particles from shipping are laden with BC (or eBC), which has been highlighted by a number of studies as being a serious health

concern (Highwood and Kinnarsely, 2006; Kulkarni *et al.*, 2006; Suglia *et al.*, 2008). This shows that there is even greater scope for stricter emission controls on shipping emissions (current emission regulations are considered lenient when compared to those for land-based sources). In order to remedy this situation, the countries with their coastline along the North Sea have imposed a sulphate and nitrate emission control area (SECA and NECA, respectively) in this sea. The countries along the Mediterranean Sea should do likewise, especially as the report by Cofala *et al.* (2018) has demonstrated the feasibility of this

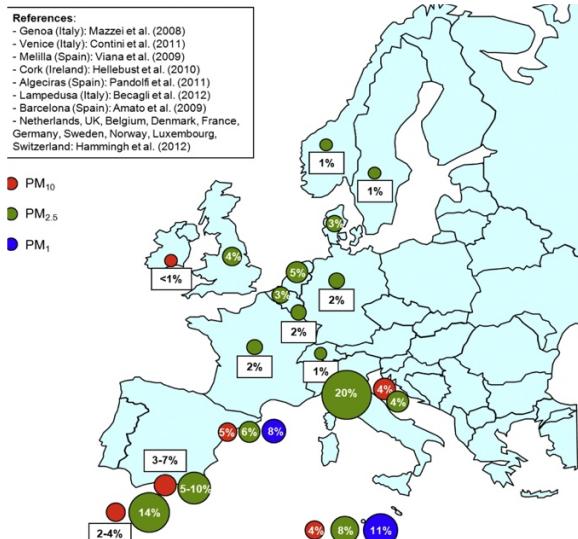


Figure 13: Contribution from shipping emissions to air quality (PM₁₀, PM_{2.5} and PM₁) across Europe. Figure 1 in “Impact of maritime transport emissions on coastal air quality in Europe” by Viana *et al.* (2014).

In practical terms, this means, that the necessary reductions required by Malta in order to achieve the WHO guidelines for PM_{2.5} by 2020 will have to be borne by road traffic, especially in view of the fact that the predicted negligible decrease in ambient levels of SISA throughout the region as well as the reluctance to regulate the shipping sector in the Mediterranean region (see **Figure 14**). Once exceedances due to natural sources are subtracted Malta can achieve the WHO guidelines only after PM_{2.5} immisions due traffic are reduced by at least 2.1 µg/m³ (or a decrease of approximately 51%).

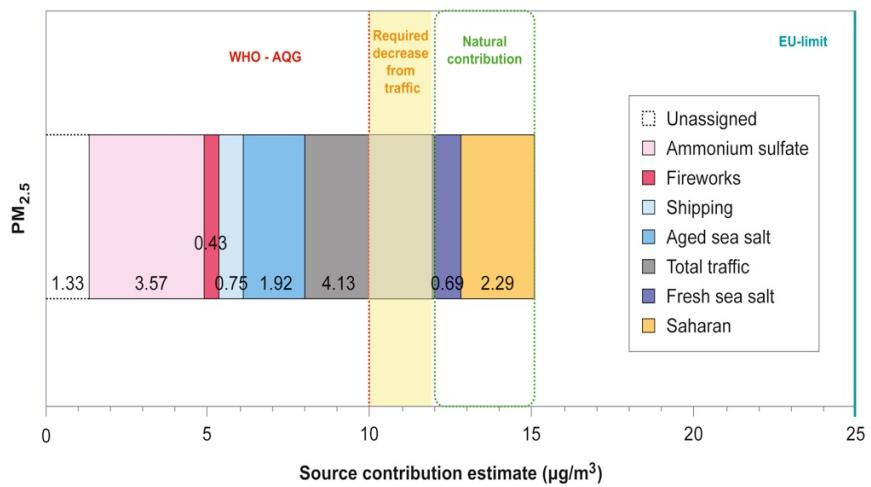


Figure 14: Required emission cuts for Malta to achieve the WHO AQG by 2020.

The letting of fireworks is an activity, which is highly seasonal in nature and yet its contribution is large enough for it to have a significant effect on the annual PM_{2.5} levels. This raises an important concern due to the fact that the fireworks manufactured in Malta use potassium perchlorate as an oxidiser (Vella *et al.*, 2015). This means that PM_{2.5} aerosol from the fireworks is likely to include unreacted perchlorate, which will make it to the bloodstream once it is inhaled. The perchlorate anion reduces thyroxine and triiodothyronine production through the inhibition of iodine uptake in thyroid (Wolff, 1998; Greer *et al.*, 2002). This could, in cases of sustained exposure, amongst other things eventually lead to goiter in subjects with a high iodine deficiency (Greer *et al.*, 2002).

5.5. Validating the model returned by PMF in Paper III

The focus of the study in **Paper III** is the validity of the model returned by PMF rather than the source apportionment *per se*, as was the case in the other two papers. In addition to the tests, which are usually carried out on a PMF solution and discussed in section 5.1, the solution obtained by running PMF was checked against the solutions returned by constrained Weighted Non – negative Matrix Factorization (CW – NMF) and by Chemical Mass Balance (CMB). This was done by comparing the measured mass of PM₁₀ and PM_{2.5} to that reconstructed by the three models as well as through the estimation of the Pearson correlation between the daily source contribution estimates by the three models.

5.5.1. Comparison of the measured and reconstructed mass for PM₁₀ and PM_{2.5}

Table 7a: Model performance for PM₁₀.

Parameter	Models		
	PMF	CW – NMF	CMB
r ² (measured vs. modelled PM ₁₀)	0.97	0.98	0.96
gradient (measured vs. modelled PM ₁₀)	0.99	0.97	1.11
explained PM ₁₀ mass (%)	99.6	99.3	87.2
Root mean square error – RMSE* ($\mu\text{g}/\text{m}^3$)	2.15	2.05	4.68
Absolute fractional bias – AFB*	0.09	0.09	0.20

Table 7b: Model performance for PM_{2.5}.

Parameter	Models		
	PMF	CW – NMF	CMB
r ² (measured vs. modelled PM _{2.5})	0.98	0.97	0.89
gradient (measured vs. modelled PM _{2.5})	~1	1.00	0.97
explained PM _{2.5} mass (%)	~100	99.9	104.1
Root mean square error – RMSE* ($\mu\text{g}/\text{m}^3$)	1.00	1.16	3.76
Absolute fractional bias – AFB*	0.09	0.10	0.17

*See section 3.4 for a description of the test.

Tables 7a and 7b above show that PMF and CW – NMF (the two factor analytic models) reconstruct the mass of both aerosol size fractions well (relatively high r², gradient ~1, explained mass of PM ~ 100%), while CMB underestimates the PM₁₀ mass and overestimated the PM_{2.5} mass, however the percentage of reconstructed mass in both cases is within the acceptable range for CMB of 80% – 120% (Argyropoulos *et al.*, 2017; Shi *et al.*, 2014). Underestimates of the reconstructed mass have been explained as being a consequence of the method used by CMB to calculate the source contribution estimates of the daily samples (Giannini *et al.*, 2013). On the other hand, in situations in which secondary aerosol sources are major contributors to the total PM mass (as is normally the case with PM_{2.5}), CMB can achieve mass closures > 100% (Rizzo and Scheff, 2007). Furthermore, from Tables 7a and 7b one can also conclude that for both aerosol fractions, the spread between the measured and the calculated mass is *quasi* identical and rather low for the two factor analytic models: ~2 $\mu\text{g}/\text{m}^3$ for PM₁₀ and ~1 $\mu\text{g}/\text{m}^3$ for PM_{2.5} (equivalent to ~9% of the average concentration of both fractions throughout the study period), while the low AFB for both models indicates optimal agreement between the measured and reconstructed mass of both PM₁₀ and PM_{2.5}. However, for CMB there is a higher degree of spread between the measured and reconstructed mass for both PM₁₀ and PM_{2.5} respectively 5 $\mu\text{g}/\text{m}^3$ and 4 $\mu\text{g}/\text{m}^3$ (or 21% and 34% of the average concentration of the respective PM fraction during the study period). On the other hand, the low AFB is indicative of an acceptable level of agreement between the measured and modelled mass for both aerosol fractions and is similar to that for PMF and CW – NMF. The results for RMSE show that PMF and CW – NMF manage to model effectively both the PM₁₀ and the PM_{2.5} levels, while CMB models PM₁₀ fairly well, but the higher spread for PM_{2.5} shows that the performance of this model deteriorates for this aerosol fraction. This is probably due the effect of secondary aerosol on mass reconstruction by CMB, which is expected to have a higher effect on PM_{2.5}, due to the higher contribution of secondary aerosol to the PM mass (73% for PM_{2.5} vs. 39% for PM₁₀).

5.5.2. Comparison of the PMF source contribution estimates to those by the other models

The source contribution estimates by PMF were compared to those by CW – NMF and CMB both through the comparison of the average of each source contribution throughout the study period (**Figure 15**) as well as through the calculation of the Pearson correlation coefficient for the daily source contribution estimates by PMF, CW – NMF and CMB (Table 8).

The comparison of the average source contribution in **Figure 15**, shows that most PMF and CW – NMF source contribution estimates are very close to each other and within the respective margin of uncertainty. The mixed carbonaceous aerosol source contribution is the only exception with the CW – NMF estimate higher than the upper uncertainty limit for the PMF estimate. One must be however very careful when interpreting the uncertainties in the source contribution estimates, because as has been argued in **Paper III**, the method used to calculate the error bars does not cover all the errors conducive to uncertainty in the contribution of each factor.

From **Figure 15**, it is also evident that CMB underestimates the contribution for both secondary components in both aerosol fractions. This is not surprising because the difficulties of CMB with the apportionment of secondary aerosol have been highlighted in previous works (e.g. Viana *et al.*, 2008). The source profiles for secondary aerosol components used with CMB are normally assumed to be made up of only one component (e.g. $(\text{NH}_4)_2\text{SO}_4$ only for secondary inorganic sulphate aerosol – SISA), this was the case in this study in **Paper III**, too. The underestimate in the source contribution is probably a consequence of the exclusion of the other species constituting the factor (Cesari *et al.*, 2016). The marine aerosol contribution in PM_{10} is underestimated by CMB by $\sim 1 \mu\text{g}/\text{m}^3$ when compared to PMF and CW – NMF. This is in all probability a result of the exclusion of NO_3^- from the source profile used with CMB. A case similar to this has already been reported in Cesari *et al.* (2016). Furthermore, **Figure 15** also highlights the fact that for PM_{10} , CMB underestimates the total traffic factor by $\sim 3 \mu\text{g}/\text{m}^3$ and over estimates the Saharan contribution by $\sim 5 \mu\text{g}/\text{m}^3$ (and $\sim 4 \mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$). These discrepancies are related to each other (at least for PM_{10}), because while PMF (and CW – NMF) isolated a “pure” Saharan component (see **Paper III**) the profile used with CMB included both local and Saharan crustal material. On the other hand, PMF (and CW – NMF) does not manage to extricate the wind-entrained dust from the traffic resuspended dust and from the road abrasion component on account of their chemical similarity.

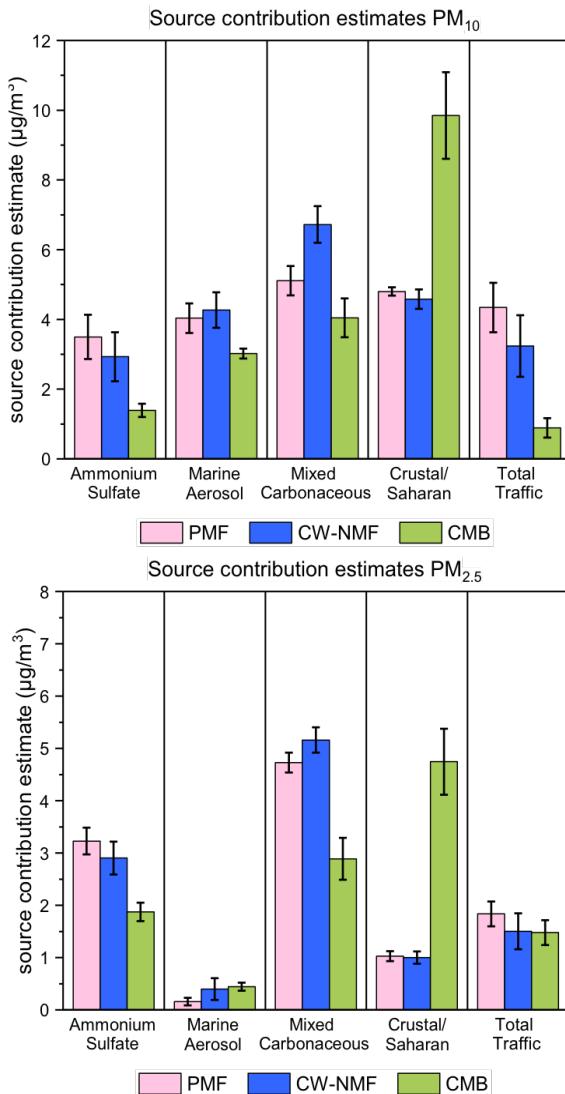


Figure 15: Source contribution estimates by the three models and the respective errors.

probability a result of the exclusion of NO_3^- from the source profile used with CMB. A case similar to this has already been reported in Cesari *et al.* (2016). Furthermore, **Figure 15** also highlights the fact that for PM_{10} , CMB underestimates the total traffic factor by $\sim 3 \mu\text{g}/\text{m}^3$ and over estimates the Saharan contribution by $\sim 5 \mu\text{g}/\text{m}^3$ (and $\sim 4 \mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$). These discrepancies are related to each other (at least for PM_{10}), because while PMF (and CW – NMF) isolated a “pure” Saharan component (see **Paper III**) the profile used with CMB included both local and Saharan crustal material. On the other hand, PMF (and CW – NMF) does not manage to extricate the wind-entrained dust from the traffic resuspended dust and from the road abrasion component on account of their chemical similarity.

Table 8: Pearson correlation coefficients for the daily source contribution estimates by the three models for both fractions. (Paper III).

Fraction	Source contribution	Models being compared		
		PMF vs. CW – NMF	PMF vs. CMB	CW – NMF vs. CMB
PM_{10}	SISA	0.990	0.870	0.901
	marine aerosol	0.999	0.937	0.936
	mixed carbonaceous aerosol	0.975	0.875	0.931
	Saharan	1.000	0.969	0.969
	total traffic	0.984	0.247	0.206
$\text{PM}_{2.5}$	SISA	0.996	0.961	0.982
	marine aerosol	0.878	0.460	0.387
	mixed carbonaceous aerosol	0.994	0.929	0.939
	Saharan	0.999	0.957	0.955
	total traffic	0.937	0.201	0.131

Table 8 above, shows that the daily source contribution estimates for PMF, CW – NMF and CMB correlate well with each other for PM_{10} , with the exception of the total traffic factor for CMB, which correlates poorly with the “same” factor for both factor analytic models. It was shown in Paper III that this situation can be somewhat improved, if using a relatively “crude” method, the wind entrained dust is added to the source contribution estimates determined by CMB for the total traffic factor, supporting the hypothesis that PMF (and CW – NMF) include this component within this factor.

For $\text{PM}_{2.5}$, Table 8 shows a good correlation for the Saharan, mixed carbonaceous aerosol and SISA daily source contribution estimates, a fairly good correlation between the marine aerosol estimates for CMB and those for the other two models, while the correlation between the daily estimates for traffic by CMB and those of the other models is rather poor. In this case the situation did not improve through the application of the same procedure as for PM_{10} , highlighting the difficulties of CMB in the modelling of $\text{PM}_{2.5}$ in this study. It is also worth highlighting that the comparison between the results of CMB and PMF is often a complex task, particularly because the results of the two models frequently differ from each other both in terms of the isolated aerosol sources and of the apportionment of these sources (Giannini *et al.*, 2013). The critical part in the receptor modelling exercise by CMB is the part related to ensuring the accuracy of the inputted source profiles (Lee *et al.*, 2008; Belis *et al.*, 2013), this means that factors such as, the sampling site and its typology and the sampling period considered when the measurement of the profiles was carried out and the aerosol fraction considered, could all potentially influence the output obtained by the model (Yin *et al.*, 2010). In fact, it is normal practice to “calibrate” the profiles inputted in CMB against the profiles outputted by PMF. In this case the results obtained by CMB are similar to those by PMF (see for example, Cesari *et al.*, 2016; Bove *et al.*, 2018). In a context in which CMB (and CW – NMF) is used in order to verify the output of PMF, optimising the profiles to be inputted into CMB as described above, would be tantamount to circular reasoning.

Overall one can conclude that the source contribution estimates for the three models correlate well with each other for PM_{10} , albeit with some “tweaking” of the CMB total traffic factor, indicating that the differences in the absolute values are systematic ones. These discrepancies are probably also due to the fact that CMB achieved a lower mass closure than PMF and CW – NMF ($\sim 87\%$ vs. $\sim 100\%$). Therefore, this comparison has not shown any major faults in the PMF modelling for PM_{10} . The same can be said of three out of the 5 factors isolated by PMF for the $\text{PM}_{2.5}$ fraction (SISA, mixed carbonaceous aerosol

and Saharan aerosol). The lower correlation coefficient obtained for the marine aerosol determined by CMB when compared to both PMF and CW – NMF could be a consequence of the exclusion of NO_3^- from the profile inputted in CMB, and which somehow affected $\text{PM}_{2.5}$ more than it did PM_{10} . The poor correlation between the traffic source contribution estimates by CMB and those by the other two models has no facile explanation. One can only hypothesize that the difference between the source profile used with CMB and that isolated by PMF (and CW – NMF) and which was composed of exhaust, abraded and traffic resuspended components possibly together with the wind resuspended dust, is a likely explanation for this behaviour. Intermixing and source proximity have been highlighted in literature as potentially leading to poor correlation between the PMF and the CMB source contribution estimates (Rizzo & Scheff, 2007).

Notwithstanding the issue of the poor correlation for the traffic factor, the results discussed in this section essentially confer a certain margin of credibility to the model outputted by PMF for $\text{PM}_{2.5}$ as well.

6. Conclusion and Further work

Conclusions and suggestions for further work will be treated separately for the three papers making up this thesis.

The primary aim behind the study in **Paper I** was the extrication and quantification of the two natural contributions (sea spray and Saharan dust) to PM₁₀ in Malta. The study shows that the joint contribution of these two sources amounts to approximately 39% of the PM₁₀ measured at the receptor. In contrast to each other, these two sources show a different seasonal behaviour with the sea spray being more constant throughout the year and the Saharan dust exhibiting a marked seasonality. The marine aerosol contribution depends very much on the wind speed while the Saharan contribution is affected by the development of the right meteorological conditions for its advection and transportation. Furthermore, this study has managed to distinguish between local crustal material and crustal material of Saharan origin, something which is normally not as readily achieved using PMF. The fact that both natural sources can be quantified with a degree of precision provides a sound scientific basis for the deduction of these components. However, the contribution of both is not constant so in order to make the deduction less complex (and expensive), any future work should try to establish ways of relating the contribution of both components to parameters that are more readily measured such as meteorological parameters (for both marine aerosol and Saharan dust) or the short-lived radon progeny (for Saharan dust).

In **Paper II** and the related study seven sources characteristic of a coastal site in the Mediterranean were isolated: traffic (27.3%), secondary inorganic sulphate aerosol (23.6%), Saharan dust (15.1%), aged sea salt (12.7%), shipping (5%), fresh sea salt (4.6%) and fireworks (2.9%). One of the main conclusions of this study is that in order to steer PM_{2.5} levels towards the WHO air quality guidelines, road traffic should be targeted for emission reduction measures. In addition, this study has highlighted the need for stricter controls on ammonia emissions from industrial farms and for the need of regional cooperation (throughout the Mediterranean) on the use of pollution exclusion and control areas in the Mediterranean Sea in order to address the issue of shipping emissions. Despite the fact that the fireworks component is a minor contributor to PM_{2.5}, the fact that this component has an effect on annual levels of this pollutant together with considerations on its chemical composition should serve to kickstart action by the policy makers in order to minimise and eventually eliminate the impact of the letting of fireworks on human health. This study did not however manage to disentangle the various traffic related components from each other. Future work, should try to determine the contribution of tail pipe, abraded and re-suspended components to PM_{2.5} (and ideally PM₁₀ as well). This information would be of help in the designing of policy measures aimed at the replacement of internal combustion engine vehicles with vehicles powered by alternative propulsion systems.

The methodological issue on the use of smaller datasets with PMF is at the basis of **Paper III** and the related study was conducted with a “real world” dataset composed of 29 PM₁₀ and 33 PM_{2.5} samples and their respective chemical characterizations, and which were combined together into a single dataset. The rotational tools included in the USEPA PMF v5 software package were used to better constrain the 5-Factor solution returned by PMF. Due to the small sample size, the uncertainties in the solution were estimated using the three error estimation techniques included in this version of PMF and were found to be reasonable. The comparison with CW – NMF essentially confirms the results obtained by PMF, while some explainable mismatches were evidenced by the comparison with CMB. It is however worth pointing

out that other previous studies reported similar mismatches. The overall conclusion of this methodological study is that PMF can be used with smaller datasets, this is useful in situations in which it is objectively difficult to stick to the currently accepted “rule of thumb” of at least 100 chemically characterised samples. Reporting the uncertainties associated with the solution derived using the smaller dataset is also recommended. Additionally, it cannot be stressed enough, that whenever possible modellers should stick to this rule of thumb. This study too has uncovered areas which warrant further investigation. Any future work should investigate the widely held assumption that the profiles for both PM_{10} and $\text{PM}_{2.5}$ have a similar chemical make-up perhaps through the use of longer time series, which would enable the use of PMF on the datasets for the two aerosol fractions individually. The profiles obtained for both PM_{10} and $\text{PM}_{2.5}$ should then be compared to the profile returned by PMF for an aggregated dataset made up of representative sub-samples from both fractions. This should also help in studying the effect of the size of the sample on the number of factors returned by PMF. Finally, it is being suggested that the assumption of the similarity of profiles for PM_{10} and $\text{PM}_{2.5}$ is in fact affected by the complexity of the airshed for different receptors, should also be investigated.

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Abbreviations

AFB	Absolute fractional bias
ALV	Annual limit value
AMSL	Above mean sea level
APM	Airborne Particulate Matter
AQG	Air quality guideline
BDL	Below detection limit
BS	Bootstrapping
BS - DISP	combination of Bootstrapping and Displacement
CD	Coefficient of divergence
CLRTAP	Convention on long-range transboundary air pollution
CMB	Chemical mass balance
CW - NMF	Constrained weighted non-negative matrix factorization
d	Scaled residuals
DAQG	Daily air quality guideline
DISP	Displacement
DLV	Daily limit value
eBC	equivalent Black Carbon
EC	Elemental carbon
EEA	European Environment Agency
ESE	East south-east
EU	European Union
HVS	High volume sampler
IC	Ion chromatography
ICP - MS	Inductively coupled plasma mass spectrometry
IM	Maximum individual column mean
IS	Maximum individual column standard deviation
LVS	Low volume sampler
ME	Multi-linear engine
MLRA	Multi linear regression analysis
MWAA	Multi-wavelength absorbance analyser
NA	Not analysed
NECA	Nitrate emission control area
NI	Not isolated
NNW	North north-west

OC	Organic Carbon
PM	Particulate Matter
PMF	Positive Matrix Factorization
ppb	Parts per billion
RMSE	Root mean square error
SDS WAS	Sand and Dust Storm Warning Advisory System
SECA	Sulphate emission control area
SIA	Secondary inorganic aerosol
SISA	Secondary inorganic sulphate aerosol
SOA	Secondary organic aerosol
SW	Southwest
TOT	Thermo-optical transmittance
USEPA	United States Environment Protection Agency
UV - VIS	UV - visible spectroscopy
VOC	Volatile organic compounds
WHO	World health organization
WMO	World Meteorological Organization
WNW	West north- west
XRF	X-ray fluorescence spectroscopy

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Paper I

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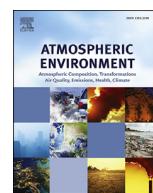
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Disentangling the contribution of Saharan dust and marine aerosol to PM₁₀ levels in the Central Mediterranean



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HIGHLIGHTS

- Two crustal sources (local and Saharan) were isolated at a rural site in Malta.
- Dust of Saharan origin is the second most significant source at the site.
- Marine aerosol is the second most important natural contributor to PM10.
- Natural components (Saharan dust and marine aerosol) contribute 39% to PM10.
- The Natural contribution is within the range reported in previous studies.

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ABSTRACT

The Gharb rural background station located on the northernmost island in the Maltese archipelago has been used to gather PM₁₀ data since 2008. 224 samples from a monitoring campaign carried out from March 2012 to May 2013, were characterized for various metals and ions by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography. This speciation data was used in conjunction with the positive matrix factorization (PMF) model in order to determine the contribution of Saharan dust and marine aerosol to PM₁₀ levels at the receptor. PMF managed to isolate two different crustal source contributions: a local crustal component and a trans-boundary component of North African origin. Marine aerosol, secondary nitrate/aged aerosol, and ammonium sulphate were other source contributions, which were isolated by the model. The trans-boundary crustal component (Saharan aerosol) and the marine aerosol are considered to be of natural origin and their joint contribution to PM₁₀ levels at the site was estimated to be 39%. This value is in the upper part of the range derived from previous studies, for natural contributions to PM₁₀ in Europe (0.5%–58%).

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1. Introduction

According to EEA (2014), mineral dust and marine aerosols are the major contributors to air-borne PM₁₀ in rural background sites.

Two distinct aerosol types characterise marine aerosol, a primary aerosol type, composed mostly of sea salt and formed by the bubble bursting process, due to wind stress at the ocean surface during white-cap formation as well as a secondary aerosol type formed by the gas to particle formation mechanism of organics and

composed of non-sea salt sulphate and biogenic matter, Marelli (2007).

Mineral dust is transported to the Western Mediterranean mainly during the four different meteorological situations described for the Iberian peninsula by Escudero et al. (2005): the surface level North African High (NAH-S), the high altitude North African High (NAH-A), the Atlantic depression (AD) and the North African depression (NAD). The NAD develops when a deep lying low forms over Morocco, Algeria, Tunisia and sometimes the Western Mediterranean. According to Borbély-Kiss et al. (2004), it is responsible for the advection of Saharan dust to Italy and to Central Europe. Consequently it is also expected to be the most relevant for Malta. The NAD scenario is often associated with wet deposition of desert dust (or "red" rain). Each of the four scenarios is associated

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with a different source region. Overall nine different source regions have been identified with the most important regions forming part of the so-called Sahara-Sahel-Chad dust corridor, Prospero et al. (2002). While in principle the geology of the source region determines the chemical characteristics of the parent soil and hence of the dust aerosols, however this has been shown to change during the transportation process, e.g. Scheuvens et al. (2013), particularly in the case of the mixing of airborne dust from different sources regions, Escudero et al. (2011). As a result Saharan mineral dust in Europe does not usually carry a particular source signal.

Airborne particulate matter has been determined to adversely affect human health (e.g., WHO, 2006; Donaldson and Borm, 2006). Saharan dust and marine aerosol are no exception. An increasing body of empirical evidence supports the association between both mortality and morbidity and dust storms, Goudie (2014). Different research groups across the Mediterranean have reported increases in cardiac and respiratory mortality during Saharan episodes, particularly for senior citizens, e.g., Jiménez et al. (2010), Mallone et al. (2011) and Samoli et al. (2011). Research conducted by Pérez et al. (2008) in Barcelona (Spain) has implied that increases in daily mortality during African dust events are related to increases in the coarse fraction ($PM_{10} - PM_{2.5}$) of airborne dust during such episodes. These observations were confirmed by a similar study carried out by Tobías et al. (2011). This increase in mortality has been attributed to the presence of biological material transported with the dust rather than chemical composition, Pérez et al. (2008). Apart from premature death, various human ailments have been attributed to dust storms: respiratory disorders (e.g. Chien et al., 2012; Kanatani et al., 2010; etc.), cardiovascular disorders (e.g. Middleton et al., 2008; Neophytou et al., 2013; etc.), dermatological disorders (Choi et al., 2011), conjunctivitis (Lien et al., 2013) and in regions to exposed heavy dust storms even lung cancer (Giannadaki et al., 2014).

To date there have been no similar reports on the health effects of the marine aerosol component, however Lang-Yona et al. (2014) have argued that it is possible for this component to include a biological fraction, which could have adverse effects on human health.

African dust episodes have also been shown to affect environmental quality. In Southern Spain for example, these episodes are the main drivers behind exceedances of the daily limit value – DLV ($50 \mu\text{g}/\text{m}^3$) for PM_{10} in rural sites during the spring-summer season (Escudero et al., 2007a). This impact, quantified by Escudero et al. (2016) to be in the range of $7\text{--}19 \mu\text{g}/\text{m}^3$, has been attributed to the greater frequency of African dust intrusions and lower levels of precipitation during the warmer seasons. Additionally, Alastuey et al. (2016) have shown that these episodes have a marked effect on PM_{10} levels throughout Southern and Central Europe as well, with the contribution of these episodes to exceedances of the PM_{10} DLV being highly variable and dependent on variations in the meteorology. Through deposition (including wet deposition) the effects of Saharan dust on the environment extend beyond air quality. Saharan dust has been found to increase the pH of rainwater and as a consequence, after deposition, it is possible for this to have negative impacts on soils and the whole ecosystem, Loÿe-Pilot et al. (1986).

Sea salt aerosol (SSA) too, has an impact on air quality. In fact according to Putaud et al. (2004) it can account for up to 80% of the annual airborne particulate concentrations in coastal locations. Manders et al. (2010) have estimated that the aboveground concentration of SSA, across Europe ranges from 0.3 to $13 \mu\text{g}/\text{m}^3$, with the higher concentrations occurring in Ireland. Moreover SSA formed by the bubble bursting mechanism can affect areas distant up to 25 km from the coast, De Leeuw et al. (2000). Once transported inland, SSA can take part in atmospheric chemical reactions

leading to the formation of secondary aerosol, particularly when transported to polluted areas, Athanasopoulou et al. (2008).

In the European Union, ambient levels of PM_{10} are regulated by two limit values, a daily limit value of $50 \mu\text{g}/\text{m}^3$ and an annual limit value of $40 \mu\text{g}/\text{m}^3$. The daily limit value can be exceeded no more than 35 times in one calendar year. Member States are allowed to deduct exceedances attributable to natural sources, (such as marine aerosol and Saharan dust) following the guidelines compiled by the European Commission (European Commission, 2011). The marine aerosol concentration is subtracted from the annual averages of the PM_{10} concentrations, due to the fact that it is present throughout the year. On the other hand episodes of dust advection from Northern Africa occur on an occasional basis and have a short-term duration. Before deducting this contribution, Member States are first required to identify the days on which such episodes occur. The procedure for the deduction of this contribution is a modification of the procedure described by Escudero et al. (2007b).

The different sources contributing to PM_{10} levels at a receptor can be isolated through, amongst other techniques, the use of receptor models such as positive matrix factorization, PMF (Paatero, 1999). Most of the factors isolated by the model are identified by the source profiles and the relative abundance of the constituting species. However the distinction between re-suspended local dust and advected desert dust is not so easily achievable, Viana et al. (2010). This was the case in over 30 studies carried out in Spain, Querol et al. (2008), and in most other studies. In contrast, Nicolás et al. (2008) and Viana et al. (2010), managed to isolate two distinct crustal components (local soil and African dust).

The principle aim of the present investigation is the estimation of the source contributions of Saharan dust and marine aerosol to PM_{10} levels at a rural background location in the Central Mediterranean region. A rural background site was chosen because this type of site is considered ideal for the identification of longer-range trans-boundary sources, due to its distance away from the sources of anthropogenic PM_{10} and from the urban nuclei, Salvador et al. (2008). Thus, the estimated contributions of Saharan dust and marine aerosol to PM_{10} are not significantly influenced by the fact that elemental carbon (EC) and organic carbon (OC) were not measured. Both components are included in the unassigned fraction. Since we do not discuss health effects associated with PM exposure, quantitative knowledge of EC and OC contributions is not necessary. The study has focused on Saharan dust and marine aerosol on account of their being eligible for subtraction as per European Commission (2011) but also due to the paucity of such studies from this region, especially when compared to the western Mediterranean.

2. Experimental

2.1. Sampling

PM_{10} sampling was carried out at a rural background site in Għarb (36.07°N, 14.20°E, 114 m AMSL) located in the Central Mediterranean on the northernmost Island in the Maltese archipelago, Gozo (see Fig. 1). According to the Corine Land Cover (CLC) Database (2012), the area is surrounded by agricultural land with significant areas of natural vegetation (CLC class 2.4.3). This site, forms part of the Maltese air quality network, and is located in the NW of the island of Gozo. The closest inhabited area, a hamlet (within Għarb) with a population of ca. 290 inhabitants (Planning Authority, unpublished data) is at ~1 km to the South. Furthermore this receptor is at ~2.5 km to the North of both hardstone and softstone quarries, and at ~5 km to the WNW from the closest "major" road in the main town, Victoria. The term major should be considered in the context of an island having a surface area of



Fig. 1. Location and characterization of the receptor.

67 km² and a population of 37,000. The station is accessible to motor vehicles only through an un-asphalted track to the east, which means that hardly any cars use the access roads to it. The direct effect of traffic on the receptor is expected to be from minimal to negligible. In addition it has to be pointed out that the site is relatively far away from the two power plants, which were at the time operational in Malta (more than 30 km to the SE, and not visible in Fig. 1). These plants are the only environmentally significant industrial sources in the Maltese Islands. It is also worth mentioning that bio-mass combustion is rarely (if ever) used for spatial heating and never used to power hobs or ovens, unlike Central Europe or the Nordic and Baltic countries, for example. It is expected that due to the closeness of the site to the coast (~0.6 km) and due to the proximity of the archipelago to the Maghreb (~300 km to the east of Tunisia and ~350 km to the north of Libya) aerosol levels at the site will be heavily influenced by both marine aerosol and by air masses originating in North Africa.

Two hundred and twenty four samples were exposed for 24 h each, at a flow rate of 2.3 m³/h, from 01 March 2012 to 09 May 2013 on 46.2 mm PTFE membranes (7592-104) manufactured by Whatman (GE Health Care Life Sciences, Buckinghamshire UK), using a Skypost PM/HV sequential sampler (TCR Tecora S.r.l., Milan Italy). The sampler was leak tested using a TeraCal® Ultra (BGI, Boca Ranton, USA) volumetric flow calibrator. Sampling was carried out as per EN 12341:2014 (Standard gravimetric measurement method for the determination of the PM₁₀ or PM_{2.5} mass concentration of suspended particulate matter). Prior to weighing, the filters were

conditioned for 96 h at a temperature of 20 °C ± 1 °C and at a relative humidity range >45% but ≤50%. The conditioning, handling and weighing of the filters was carried out in a filter weighing system (Mettler – Toledo, Greifensee, Switzerland), which comprises *inter alia*, a robotic auto handler, an environmental monitor and an XP6 microbalance.

2.2. Analytical procedures

Concentrations of Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, and V were determined using the 7500cx ICP-MS (Agilent Technologies Inc., Santa Clara USA), following a microwave assisted high pressure digestion of half a membrane, in an 80% nitric acid (subboiled, 68%) and 20% hydrogen peroxide (suprapure 30%) mixture. Both the digestion and the analysis for metals were carried out following the procedure in UNI EN 14902:2005 (Standard Method for the measurement of Pb, Cd, As and Ni in the PM₁₀ fraction of suspended particulate matter). Anion (Cl⁻, NO₃⁻ and SO₄²⁻) levels were determined using the EPA 300.0 1993 method (Determination of Inorganic Anions by ion chromatography). The sample was mixed for 10 min with 10 ml deionised water (>18 MΩ) and the resulting slurry was filtered through a 0.45 µm membrane. The filtrate was then divided in two portions. 2–3 ml of the first half were analysed by the DIONEX® DX 120 ion chromatograph (Thermo Scientific, Sunnyvale USA). DIONEX® AS-9 HC 2 mm was used as separating column, 9.0 mM Na₂CO₃ at a flow rate of 0.4 ml/min was the eluent and DIONEX® CD 20 was used as the detector. The ammonium ions

(NH₄⁺) in the second portion of the filtrate were converted to indophenol blue through the reaction of the ions with sodium salicylate and sodium isocyanurate in a strongly alkaline solution and catalysed by sodium nitroprusside (method APAT CNR IRSA 4030 A1 Man 29 2003 – Italian Environment Protection Agency and National Research Council Manual for the Analytical Determination of Aqueous Solutions, Volume on non-metallic, inorganic constituents). The amount of indophenol blue and hence the ammonium concentration, was subsequently determined by the 8453 UV-visible spectrometer (Agilent Technologies Inc., Santa Clara USA). The speciation data used throughout this work is the official data used by Malta to comply with its European Union reporting obligations and was obtained directly from the Environment and Resources Authority (ERA), the Maltese Environmental Regulator. All chemical analysis was carried out on behalf of ERA, by Ambiente S.C. in Carrara (Italy), which is accredited for the determination of all the metals and ions included in this work by the respective methods, to UNI CEI EN ISO/IEC 17025:2005 (General requirements for the competence of testing and calibration laboratories). In addition despite the fact that the method used for the digestion and the analysis of metals (EN 14902:2005) mentions only the four metals regulated by EU legislation, it is commonly used by the National Reference Laboratories in the EU Member States for the determination of a wide range metals in PM₁₀, (Gerboles and Buzica, 2008, pp. 15–16), and normally the scope for accreditation is extended to cover this wider range of metals. The procedures described above were also applied to 10 blank filters, which were sent by ERA to the analytical laboratory. The blank filters were used in the determination of the method detection limits (MDL) for all the metals and ions analysed in this work.

2.3. Meteorological parameters

Daily precipitation (mm) as well as daily average temperatures (°C) for the years 2012 and 2013, were obtained from the Meteorological Office at the Malta International Airport situated at ~ 36 km to the south of the monitoring station. 15-minute averages of wind speeds (m/s) and wind direction (degrees) for the same period were measured at the Gharb station using the Wind-Sonic ultrasonic anemometer (Gill Instruments, Hampshire UK). Daily averages for wind speed and wind direction were calculated using the OpenAir package in R-Studio (Carslaw and Ropkins, 2012), and taking into account the circular nature of wind direction. The temperature data was used to apportion the months in three clusters: “warm” (May to October with a daily average temperature of 25.1 °C), “cold” (December, January and February with a daily average temperature of 12.7 °C) and “intermediate” (March, April and November with a daily average temperature of 16.5 °C). The precipitation data was also used to partition months into three clusters: “wet” (September, November, December January and February with a daily precipitation rate of 2.6 mm), “dry” (April to August with a daily precipitation rate of 0.7 mm) and “intermediate” (March and October with a daily precipitation rate of 1.6 mm).

2.4. Statistical analysis

2.4.1. PMF

The Saharan and marine aerosol contributions (together with the other components) affecting PM₁₀ levels in Għarb were determined using positive matrix factorization, (U.S.) EPA PMF version 5.0. PMF is a receptor model developed by Paatero and Tapper (1994) and Paatero (1999). The concentrations of the species analysed in the PM₁₀ sampled throughout the monitoring period (matrix **X**) together with the uncertainty for each measurement (matrix **U**) are used as inputs to the model. **U** allows the analyst to

weight each of the measurements in **X** by the certainty in the measurement. Uncertainties, values below the limit of detection and missing values were handled as per Norris et al. (2014). An additional uncertainty was added to the model to account for measurement errors not included in the uncertainty data (Reff et al., 2007), a conservative value of 15% was chosen, because the uncertainty data was supplied by the laboratory, which analysed the samples and therefore the authors had no control over this data.

PMF resolves **X** into two different matrices the factor contributions matrix, **G** and the factor profiles matrix, **F**:

$$\mathbf{X} = \mathbf{G} \mathbf{F} + \mathbf{E} \quad (1)$$

E is the residuals matrix (the difference between **X** and the product **GF**). All the elements in **G** and **F** are constrained to be ≥ 0 . The PMF algorithm uses a weighted least squares method to minimise parameter Q in equation (2) and estimate both **G** and **F**:

$$Q = \sum_{i=1}^{i=n} \sum_{j=1}^{j=m} \left[\frac{e_{ij}}{u_{ij}} \right]^2 \quad (2)$$

where **e_{ij}** or **E**, is the residuals matrix, **u_{ij}** or **U**, is the uncertainty in the measurement of the parameters in matrix **X**, i represents the number of samples and j represents the different parameters determined by the chemical analysis.

2.4.2. Further statistical tests

Source contributions were determined by multilinear regression analysis (MLRA). According to Reff et al. (2007), the use of PM₁₀ as a fitting species in PMF is considered by some research groups to give rise to issues of double counting. The measured PM₁₀ concentration ($\mu\text{g}/\text{m}^3$) was regressed against the PMF factor scores. MLRA was performed using IBM SPSS (version 23). If all the resolved sources are reasonable all the regression coefficients should have a positive value, Yubero et al. (2011).

Polar plots were plotted using the source contributions obtained by MLRA and the daily averaged wind speed and wind direction data, using the OpenAir package in R-studio, Carslaw and Ropkins (2012). Seasonal variations in each source were investigated by partitioning source contributions by season. Further confirmatory work was carried out on specific factors in order to check for differences between the “warm”, “cold” and “intermediate” seasons as well as for differences between “wet”, “dry” and “intermediate” seasons. In both these cases the seasonal means were calculated and the significance of the inter-seasonal differences were analysed using the non-parametric Dunn test with the p-values corrected by the Bonferroni algorithm (dunn.test package in R-Studio; Dinno, 2015).

2.5. Hybrid receptor modeling

The concentration gradient of the source contributions close to the different source areas was investigated using the concentration weighted trajectories as outlined by Hsu et al. (2003). In this method the average weighted concentration of a grid cell located at *i, j* is modeled by weighting the source contribution *c_l* registered when trajectory *l* reaches the receptor, by the time spent by this trajectory, over this grid cell τ_{ijl} :

$$c_{ijl} = \sum_{l=1}^{l=M} \tau_{ijl}^{-1} \times \sum_{l=1}^{l=M} c_l \times \tau_{ijl} \quad (3)$$

Concentration *c_{ijl}* is calculated for all the grid cells within the modeling domain associated with trajectory *l*. The back trajectories

(trajectory time of 120 h) for the study period were obtained for an arrival height of 1500 m AGL at the receptor, using Hysplit4 (Draxler et al., 2014), and Reanalysis datasets at a resolution of 2.5° on a latitude/longitude grid. The arrival height of 1500 m (corresponding to a geopotential height of 850 hPa) represents the uppermost part of the boundary layer, and was used because it is considered representative of the mean transport winds at the synoptic scale, Stohl (1998) and Salvador et al. (2010). In addition, at this height surface artifacts are filtered out, Salvador et al. (2008). Additional back trajectories were run at arrival heights of 500 and 3000 m AGL (corresponding to geopotential heights of 700 and 950 hPa respectively). The 3000 m arrival height was chosen, because this altitude is considered to be important for African dust transport at the higher altitudes (Escudero et al., 2005), and is representative of the free troposphere, while the 500 m arrival height is considered representative of low altitude transport. Trajectories at heights lower than 500 m are considered to be substantially influenced by the surface (Crosbie et al., 2014) and were therefore excluded. Openair R (Carslaw and Ropkins, 2012) was used in order to plot concentration gradients. As suggested by Carslaw (2015), concentration fields were plotted for contributions with trans-boundary sources only.

3. Results

3.1. PMF solution

A consistency check was carried out by comparing the results of the chemical analysis to the time series for the different species analysed throughout the previous monitoring campaigns. Cu and Ni were excluded from further analysis because their levels showed steep variations, which were unjustified by similar changes in anthropogenic activity in the Maltese Islands. In line with the recommendations of Norris et al. (2014), As, Cd, Cr and Pb were marked as "bad" due to the high percentage of non-detects (>80%), while species, which were not modeled well by PMF, such as Na, V, SO_4^{2-} and Al were down-weighted to "weak". The occurrence of a high percentage of non-detects for As, Cd, Cr and Pb is not surprising given that the ERA has been reporting similar results for these metals since 2008, even when the samples were analysed by a different laboratory, (ERA, unpublished data). In the present work, PMF was run in robust mode and different solutions were explored with the number of factors ranging from 3 to 6. The variations in the $Q_{\text{theoretical}}/Q_{\text{expected}}$ ratio and in the maximum individual column mean (IM), Lee et al. (1999), with the number of factors, as well as the factor profile and factor contribution matrices were investigated. The variation of how well each of the analysed species was predicted (r^2 for modeled vs. measured) with the number of factors was also examined.

The difference in the $Q_{\text{theoretical}}/Q_{\text{expected}}$ ratio and in IM between the 3, 4 and 5-factor solutions was negligible. The differences between these solutions are, that in the 3-factor solution the two secondary aerosol factors are grouped together and the same holds for the two crustal factors, while in the 4-factor solution the two secondary aerosol factors separate. The 5-factor solution was chosen over the others because it predicted species concentrations better. In this context one has to note that ultimately the selection of the number of factors is a subjective one, PMF is a descriptive model with no objective criterion for the determination of the optimal number of factors, Vecchi et al. (2008). Multiple Peak rotations from -0.5 to 0.5 in steps of 0.1 were explored. An Fpeak of -0.3 was enough to solve any issues related to the interpretability of factors and to remove oblique edges in the G-space plots. The 6-factor solution yielded a source, which had no physical interpretability in the context of a background station and was

therefore discarded.

The five-source model explains 76% of the measured PM_{10} concentration in Gharb with a slope of 0.99 and a coefficient of determination (r^2) of 0.8, for the plot of measured vs. modeled concentrations of PM_{10} .

Summary statistics of the contributions of the various factors to PM_{10} are given in Table 1.

3.2. Factor profiles

The factor profiles and the percentage of species apportioned to each factor are shown in Fig. 2, the contribution of the factors to PM_{10} is shown in Fig. 3, while Fig. 4 shows the variation in the different source contributions by season.

Factor 1 is characterized by the predominance of Ca and to a lesser extent by Na. Calcium is a marker for limestone (all the surface outcrops in Malta are constituted of limestone formations). The average contribution of this source to the PM_{10} levels (Fig. 3) was 6% ($1.1 \mu\text{g}/\text{m}^3$). Factor 1 is therefore labeled as "local crustal source". Likely sources for this factor include the re-suspension of street dust and crustal material, fugitive emissions from open pit quarrying, fugitive emissions from construction and demolition works and from other activities related to the use of limestone in the construction industry. The highest absolute contributions of this source occur during spring and summer, the drier months (Fig. 4). In fact a higher contribution for this factor was measured in months classified as "dry" ($1.43 \mu\text{g}/\text{m}^3$) than in those classified as "wet" ($0.69 \mu\text{g}/\text{m}^3$) or "intermediate" ($0.91 \mu\text{g}/\text{m}^3$). The Dunn test showed that the differences between the "wet" and the "dry" months as well as between the "wet" and the "intermediate" months were statistically significant, with the Bonferroni adjusted p-values <0.05 in both cases. This is interpreted as evidence in favour of the attribution of this factor to local crustal sources, since rain is expected to decrease both the re-suspension of dust (Amato et al., 2009) and also fugitive emissions from e.g. quarrying (Vella and Camilleri, 2005). The polar plot for the local crustal source shows that the segment of highest influence from the ESE to the SW (Fig. 5) includes within it, the influence from the quarries to the South of the receptor and the influence from anthropogenic activity in the major town in Gozo (at ~5 km to the ESE). This segment also includes the sector between 120° and 145° , which was defined by Nolle et al. (2002) as the range of wind directions likely to advect to a site close to the receptor, pollutant emissions from the main island (Malta). The occurrence of higher source contributions at the higher wind speeds ($\geq 10 \text{ m/s}$) from the segment of influence is understandable given that wind is one of the major causes of dust entrainment from erodible surfaces.

The main components, which characterise Factor 2 are NO_3^- , SO_4^{2-} and Na (Fig. 2). In addition even though the levels of V are low when compared to the other species, approximately 40% of the V is

Table 1
Summary statistics of the PM_{10} source contributions.

Source Contribution	Minimum $\mu\text{g}/\text{m}^{-3}$	Maximum $\mu\text{g}/\text{m}^{-3}$	Standard Deviation $\mu\text{g}/\text{m}^{-3}$	Mean $\mu\text{g}/\text{m}^{-3}$
Crustal (Local)	0.01	26.16	2.01	1.14
Secondary Aerosol I	0.03	10.15	1.96	1.78
Marine	0.02	25.14	4.06	3.37
Saharan	0.03	151.62	11.14	3.73
Secondary Aerosol II	0.00	18.16	3.72	3.86
Unassigned	0 ^a	28.77	5.93	4.32
PM_{10} (modeled)	3.19	152.17	10.87	13.90
PM_{10} (measured)	1.91	145.79	12.25	18.22

^a 0 means that there are instances in which the concentration of modeled PM_{10} is greater than the concentration of measured PM_{10} .

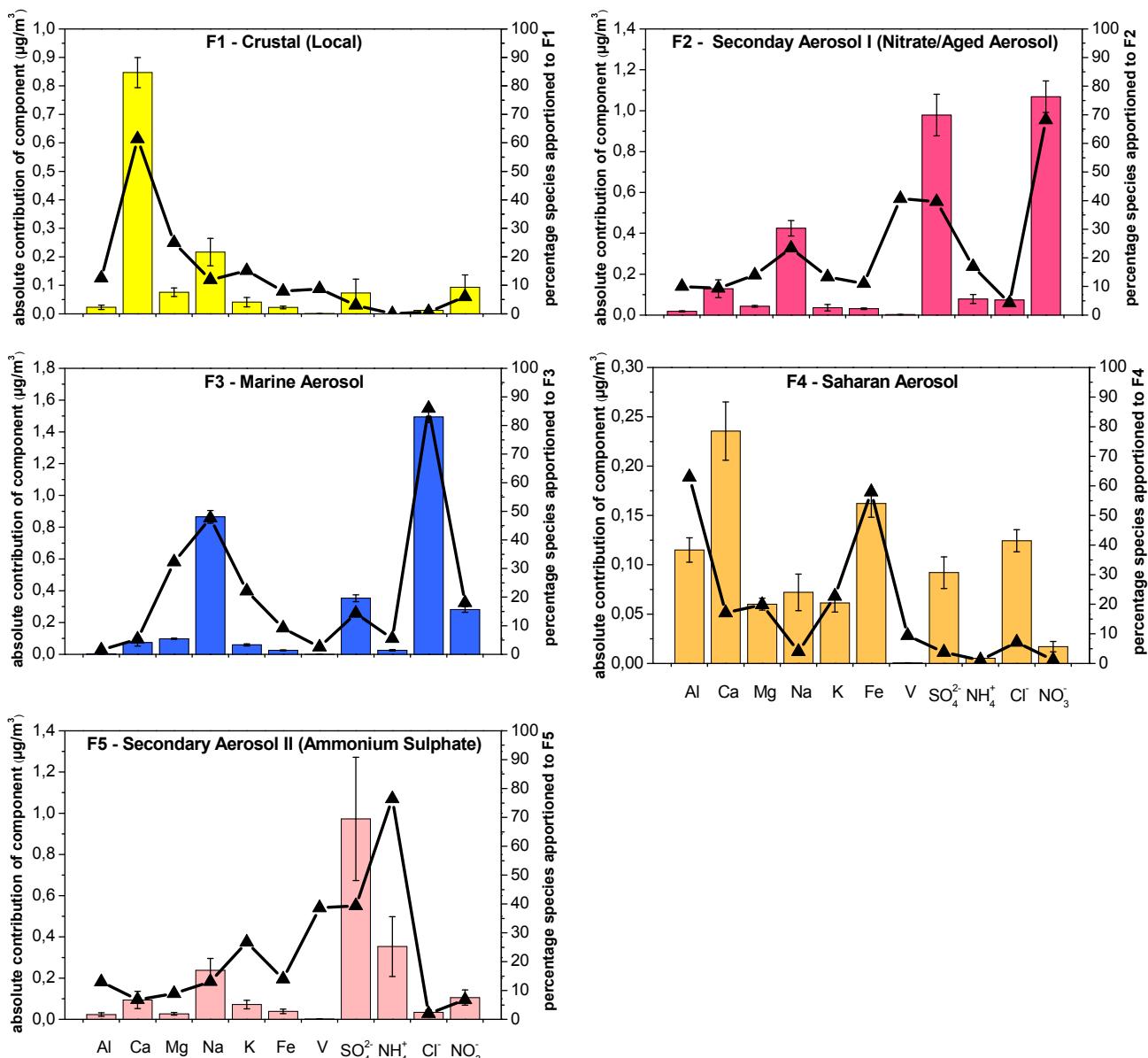


Fig. 2. Factor profiles (bars) and percentage of species apportioned to each factor (black line).

apportioned to this factor (Fig. 2). The high levels of NO₃⁻ (ca. 80% of the measured nitrate is due to this factor), together with the presence of SO₄²⁻, Na (and Ca) indicate that the factor includes a dominant component of aged aerosol (both marine aerosol and mineral dust) hence the labeling as “secondary aerosol – nitrate/aged aerosol”. It is likely that this factor also includes some NH₄NO₃, however the low levels of NH₄⁺ suggest a substantial loss due to the volatilization. The sources of SO₄²⁻ and NO₃⁻ include the conversion of the respective precursor gases (SO₂ and NO₂) into particles. The presence of V might indicate that the precursor gases are emitted by the combustion of fuel oil, moreover it is worth pointing out that there are busy shipping lanes to the east of the Island and the polar plot (Fig. 5) shows a substantial influence from the East even at medium - slow wind speeds (>2 m/s) indicating that the source is probably not a trans-boundary one. Factor 2 contributes 10% (1.8 $\mu\text{g}/\text{m}^3$) to PM₁₀ (Fig. 3). Fig. 4 shows the absence of a seasonal trend for this factor for spring, summer and

fall and drop in the levels of this component during winter. The absence of a seasonal trend for secondary nitrate aerosol has been reported in previous studies across the Mediterranean e.g. in Elche, Spain (Galindo et al., 2008) and particularly in insular sites such as Castillo de Bellver in the Balearics (Pey et al., 2009), The Canary Islands (Querol et al., 2008), and Finokalia in Greece (Bardouki et al., 2003). This lack of seasonal behaviour has been attributed to the fact that the secondary nitrate aerosol in these locations is made up of two components: an aged aerosol component (predominant during the warmer months) and an ammonium nitrate component (which becomes more important during the colder months). It is likely that for Malta the aged aerosol component dominates the behaviour of this aerosol type and that ammonium nitrate plays a minor role. Levels of the aged aerosol component increase during spring and summer due to the increased photo-oxidation of SO₂ (Hidy, 1994) and NO₂ (Matsumoto and Tanaka, 1996) with the latter playing a major role in the reaction with marine aerosol (Zhuang

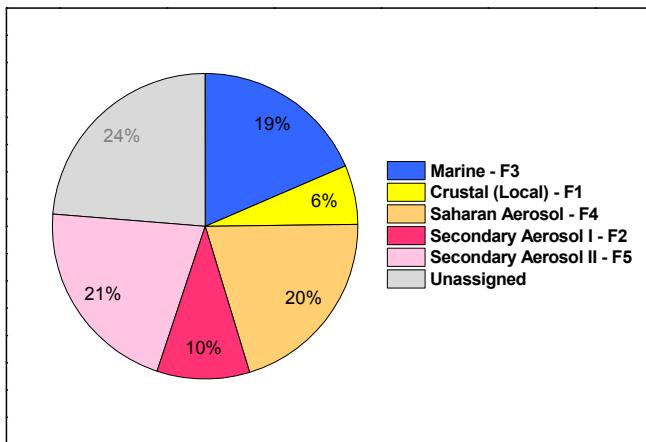


Fig. 3. PM₁₀ source apportionment for Gharb.

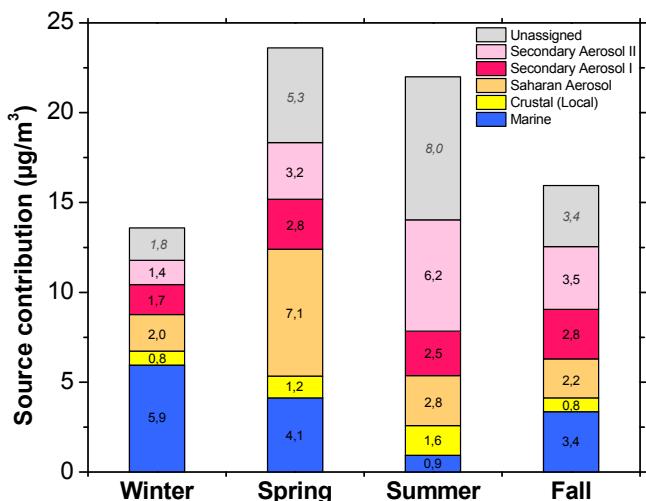


Fig. 4. Variation in source contribution by season.

et al., 1999). The lack of precipitation and the atmospheric stagnation, which characterise the latter part of the Maltese summers favour the accumulation of the aged aerosol component in the atmosphere. This probably leads to sustained levels of this component throughout fall, at least till the atmospheric conditions favour dispersion. Additionally as ambient temperatures start to decrease any losses in the formation of the photochemical component are partially made up for, by ammonium nitrate, whose formation is favoured at the lower temperatures, Matsumoto and Tanaka (1996).

The factor profile for Factor 3 is dominated by Na and Cl⁻ (Fig. 2). Marine aerosol is normally characterized by the presence of Na, Cl and Mg (e.g. Manousakas et al., 2015) and by the abundance of these species relative to each other. Most studies compare the latter to the reference values of the Cl/Na (1.8), Na/Mg (8.3) and Cl/Mg (14.9) ratios from Seinfeld and Pandis (2006). These reference values are very close to those calculated for the marine aerosol in this study (1.7, 8.8 and 15.3 respectively), hence the labeling of this factor as "marine aerosol". The contribution of this factor to PM₁₀ levels is 19% (3.4 µg/m³), Fig. 3. The contribution of this source is higher during winter (Fig. 4), due to the occurrence of stronger winds, which invigorate the formation of marine aerosols through the bubble bursting mechanism, Marelli (2007). The polar plot for the source contribution (Fig. 5), further confirms the dependence of

the marine aerosol contribution on the wind speed (highest source contributions associated with wind speeds >10 m/s) and also shows that since the receptor is located on a small island the contribution is independent of direction.

Factor 4 is the second most important source contributing 20% (3.7 µg/m³) to PM₁₀ (Fig. 3) and is characterized by high contributions of elements typical for crustal material, such as Al, Ca, Mg, K, and Fe, (Fig. 2). It is clear that this factor is a crustal factor of trans-boundary origin due to the abundance of Al (factor contributes ~65% of the total measured Al) and due to the presence of Fe (Fig. 2). Both metals are considered to be good indicators of African dust, Nicolás et al. (2008), Rodríguez et al. (2002), and Scheuvens et al. (2013). In addition concentrations of Al in local crustal material are very low (Vella et al., 1997). The factor was therefore labeled "Crustal Material/Saharan aerosol". The contribution of the factor is felt mostly during spring (Fig. 4) and is highly directional with high contributions being registered at wind directions > 140° but less than 210°, Fig. 5. In Malta winds blowing from the south, particularly in spring, are typically associated with deposition of desert dust. The interpretation of this factor was complemented by a residence time analysis (Fig. 6). For the trajectories arriving at an altitude of 1500 m, high levels of the contribution are strongly associated with air masses passing over the Saharan region (west Algeria, Tunisia and east Libya). This was substantially supported by the back trajectories arriving at 500 and 3000 m, Figure SM1 in the electronic supplement. Additionally all the Saharan events which were notified by Malta to the European Commission throughout the study period, coincided with high contributions from this source, Malta Environment and Planning Authority (2012) and Malta Environment and Planning Authority (2013).

The fifth factor characterized by high contributions of SO₄²⁻ and NH₄⁺ (Fig. 2), is the most important source contributing 21% (3.9 µg/m³) of the PM₁₀ measured in Gharb (Fig. 3). The ratio of equivalents for SO₄²⁻/NH₄⁺ (~1.02) is very similar to 1, the expected value for ammonium sulphate, suggesting that the latter is the dominant component of this factor. In fact the fifth factor was labeled as "secondary aerosol/ammonium sulphate". In addition approximately 40% of the V partitioned onto this factor (Fig. 2). As expected, the contribution of (NH₄)₂SO₄ increases during the summer months (see Fig. 4). In fact the secondary ammonium sulphate source contribution in the "warm" months (5.42 µg/m³) was higher than in the "intermediate" months (2.92 µg/m³) and the lowest contribution was registered during the "cold" months (1.36 µg/m³). The Dunn test showed that the differences between the three clusters were statistically significant with the Bonferroni adjusted p values < 0.05 in all cases. This increase in the "secondary aerosol/ammonium sulphate" source contribution during the warmer months is a result of increased oxidation rate of SO₂ with insolation, Hidy (1994). Ammonium sulphate aerosol results from two precursor gases, NH₃ and SO₂. NH₃ is biogenic (Galindo et al., 2013) while the presence of V is indicative of the fact that SO₂ is anthropogenic, Viana et al. (2008).

Approximately 24% (4.3 µg/m³) of PM₁₀ are not assigned to any one of these 5 factors (Fig. 3). The unassigned portion of PM₁₀ increases considerably throughout summer (Fig. 4), suggesting that secondary organic aerosols (SOAs) play an important role in the unassigned mass, due to the fact that they have been shown to abound during late spring and early summer particularly in rural environments, Rogge et al. (1993). The tracer species for SOAs as well as OC (which would have probably included the cumulative effect of these tracer species) were not determined in this work, and therefore these species are expected to feature in the unassigned fraction. The unassigned fraction is also expected to include a contribution from EC, which should be minor due to the fact that levels of EC in Gharb are expected to be low. In addition non-C

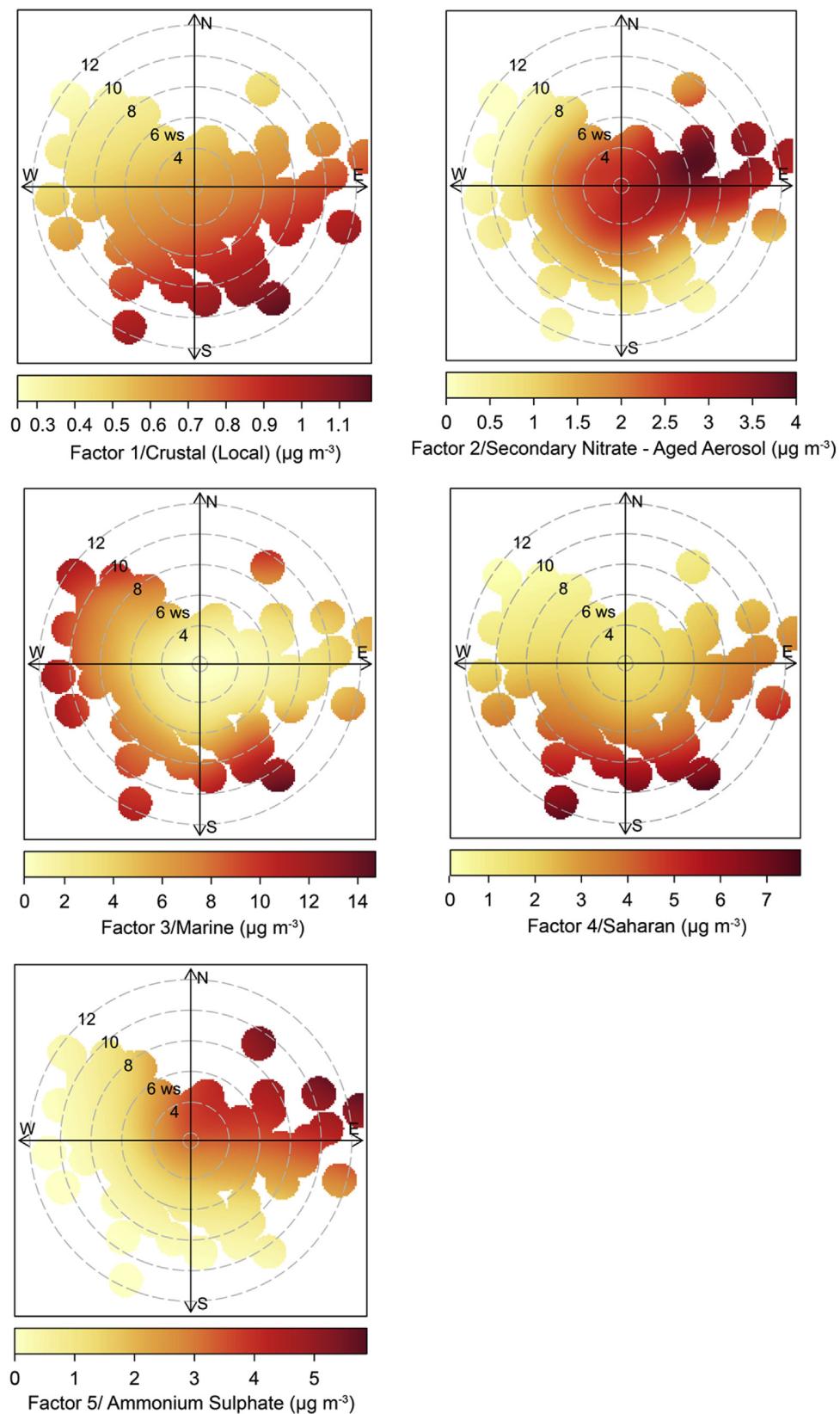


Fig. 5. Polar plots for the 5 source contributions.

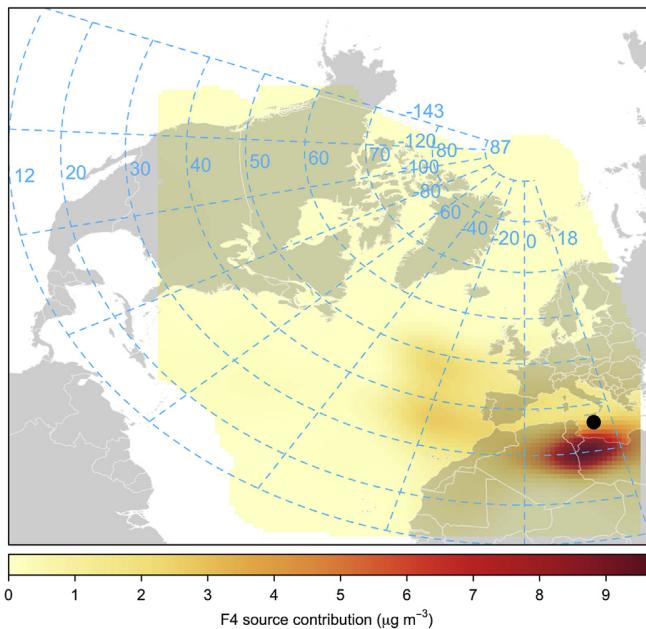


Fig. 6. Concentration field for the Saharan aerosol source contribution (arrival height 1500 m).

atoms of organic matter (Huebert and Charlson, 2000) and water both structural (Yubero et al., 2011) and also due to hysteresis in absorption – desorption cycle (EPA, 2004), are also expected to contribute to the unassigned fraction.

4. Discussion

4.1. Reliability of the PMF solution

The protocol compiled by the JRC (Belis et al., 2014) is intended to harmonize studies based on the use of receptor models such as PMF. Brown et al. (2015) have compiled a set of recommendations for the reporting of PMF results. These guidelines should confer a certain measure of reliability to this type of study. Where applicable these recommendations together with the procedures in the U.S. EPA PMF v5 Guidebook (Norris et al., 2014), were followed throughout this study. It is also worth pointing out that the problems with the analysis of Ni and Cu should not have affected the number of factors isolated. This is due to the fact that levels of Cu at the receptor have included a high percentage of levels below the limit of detection (approximately 80%) at least since 2008. On the other hand V can be used as a tracer species for all the sources impacting the receptor and, which are identified by the presence of Ni.

The use of a high volume sampler (HVS) could have enabled the detection of certain species, which are normally present in trace levels, in background sites. In this study, it could have enabled the determination of the levels of As, Cr, Cd and Pb. It is however doubtful, whether the determination of these metals would have led to the isolation of one or more additional sources. This is because, the fact these metals are present at levels below the detection limit (for the low volume sampler method) is indicative of the fact that their source(s) is/are minor when compared to the other sources, and PMF (as is generally the case with receptor models) is at times incapable of isolating minor sources, Jang (2014). Probably the sources of these metals would have been included with one or more of the five sources determined by this study, particularly the re-suspended local dust factor, which could

include particulate matter from road transport (brake wear, tire wear and road surface abrasion). In addition the use of an HVS would have surely triggered the need for demonstrating equivalence to the method using the low volume sampler (the reference method according to EN 12341:2015). The issue of equivalence was considered critical due to the fact that one of the aims of this work is to determine the effect of natural sources on Malta's compliance with Directive 2008/50/EC. According to this Directive compliance with the limits therein, is to be assessed using the respective reference methods only (unless equivalence is demonstrated for the aerosol climate in Malta). In addition, according to EN 12341:2014, when using HVSs a well-justified allowance would have to be made for their uncertainties.

EC and OC are normally considered as markers for traffic (Viana et al., 2008), and other combustion sources, such as biomass burning, (Andersen et al., 2007). Their exclusion should not have affected the identification of other sources, due to the absence of stationary combustion sources and also because the direct impact of the closest busy road on the site is expected to be small on account of both the traffic volumes involved as well as the distance away from the site (5 km). In addition, EC and OC are included in the unassigned fraction.

A number of publications have attempted to address the issue of sample size and to a lesser extent the minimum number of species to be analysed. According to Johnson et al. (2011) and Brown and Hafner (as cited in Belis et al., 2014), 50 chemically characterized samples are the barest minimum while Henry et al. (1984) and Thurston and Spengler (1985), have proposed equations to determine the optimal number of samples. On the other hand, the issue of the ideal number of species to be analyzed, has received less attention. According to Norris et al. (2014), for PM_{2.5}, 100 samples of 24-h data, for 10 to 20 species are normally sufficient. Other available guidelines include parameters, which are less well defined. According to Belis et al. (2014), for example, the choice of both the number of species and of the species themselves must be guided by knowledge of the aerosol climate of the site. In addition some researchers are of the opinion that the inclusion of too many species introduces a source of noise and interferes with the process of fitting the PMF model, Reff et al. (2007). The present work involving 224, 24-h samples for which 11 different species were used with the PMF model, is in line with the guidelines above. The estimation of the uncertainty matrix is considered critical to PMF; in fact, Polissar et al. (1998), Chow et al. (2007), Norris et al. (2014), amongst others, have all analysed the issue. In Section 2.4.1, it was reported that in this study, uncertainties were estimated according to suggestions in the latter publication.

The PMF algorithm is based on the minimization of the Q parameter, and it is important to ensure that the solution reached, is a global minimum. This was ensured by running PMF 10 times, with 20 iterations per run and with each run starting at a different (pseudo) random seed, similar to Koçak et al. (2011), Kara et al. (2015). The Q values were subsequently inspected for any inter-run differences. All the runs converged and the differences between the Q values were negligible, indicating that the global minimum had been obtained.

The determination of the optimal number of factors in PMF is based *inter alia* on the scaled residuals for the species modeled, Belis et al. (2014). Scaled residuals for all the species included in this study were visually inspected and for the majority of the species they were normally distributed within the range of -3 to +3. This adds confidence in the chosen solution, Friend et al. (2012), Li et al. (2013).

Brown et al. (2015), recommend investigating the stability of the chosen PMF solution by performing a bootstrap on it. One hundred bootstraps (the minimum required for statistical robustness) were

performed; default values for the minimum correlation coefficient and the block size were used (0.6 and 22 respectively). All the base and boot factors were matched, indicating that the solution is stable for the chosen number of factors. The uncertainty ranges in Fig. 2 were set at \pm one half the interquartile range. In addition, all the constants obtained from the MLRA (Section 2.4.2) were positive; this increases the confidence in the selected number of factors, Kim et al. (2003).

The value of the coefficient of determination reported in Section 3.1 shows that 80% of the variability in the measured PM₁₀ values is explained by the linear relationship between measured and modeled values and shows a strong correlation between the two, reinforcing the reliability of the chosen model. Additionally it has to be pointed out that a number of studies estimated an r^2 value which is close to what was being reported by this study, Yubero et al. (2011), Vargas et al. (2012) and Alam et al. (2014) etc., fewer studies reported values of 0.9 or higher e.g. Nicolás et al. (2008) or Farao et al. (2014).

The authors are of the opinion that the five sources identified by PMF include all the sources, which could be reasonably expected to influence PM₁₀ levels at the receptor, given the surroundings of the site, the total absence of significant point sources as well as the distance away from the main town. Secondary organic aerosols are perhaps the only exception. The 24% unassigned mass does not undermine the robustness of the model being presented. It is not uncommon for receptor modeling studies based on factor analysis to have a relatively large percentage of the PM₁₀ not assigned to any particular factor. In literature, unexplained PM₁₀ mass ranged from 48% in Yatkin and Bayram (2008) to 4% in Vargas et al. (2012), and less. However, it is worth mentioning that when performing the MLRA in order to determine the source contributions (see section 2.4.2), the intercept was not constrained to 0, in order not to decrease the unassigned mass artificially. In fact according to Viana et al. (2008), it is possible that studies not reporting an undetermined fraction are over estimating the identified source contributions. A number of factors are considered to contribute to the unassigned mass, such as: undetermined components (including tracers of secondary organic aerosols, EC and OC), artifacts due to hysteresis in the deliquescence – efflorescence cycle, measurement uncertainties in the analysis, etc.

Source profile identification was complemented by additional objective analysis including, species ratios, ionic balance, statistical tests describing the seasonal variations in the estimated source contributions and back-trajectory statistical methods in order to render the identification less subjective.

The exclusion of EC/OC measurements is not expected to have a profound impact on both Saharan and marine aerosol components; in fact these species are never used as tracers for either of these sources. This should not be taken to mean that EC/OC are totally absent from these two contributions e.g. Hoffman and Duce (1977) and others have presented evidence in favour of a non-negligible, measurable content of organic material within the finer fractions of the marine aerosol component, while Kandler et al. (2007) have determined the presence of soot and other carbonaceous material in Saharan aerosol. However the use of MLRA in the determination of the source contributions (see Section 2.4.2) should have minimized any missing mass due to undetermined species such as EC/OC, in both Saharan and marine aerosol components.

In summary the issues discussed above add confidence in the robustness and reliability of the obtained PMF solution.

4.2. Comparison to previous studies

It is not common for studies involving receptor modeling to focus on rural background sites. In fact such studies are mostly

carried out at stations representative of maximum population exposure (urban background sites), or at industrial or traffic sites where exposure to PM₁₀ might constitute a higher health risk, Viana et al. (2008). The use of different samplers and filter types, different analytical methods as well as the use of different receptor models, make the comparison between the source contributions from this study and those in Table 2 rather complex. Different research groups have highlighted the dependence of the chemical composition of PM₁₀ on the geographical location of the receptor. According to Putaud et al. (2010), PM₁₀ is richer in carbonaceous matter in Central Europe, richer in nitrate in Northwestern Europe and richer in mineral dust in Southern Europe. Marine aerosol concentrations vary by distance away from the coast and range from 0.5% of the PM₁₀ mass in inland sites to a maximum of 15% in coastal area, (Tørseth et al., 2012). Pey et al. (2013) estimated that windblown Saharan dust contributes from 10 to 43% of the PM₁₀ measured at rural background or sub-urban sites. Notwithstanding this, it is possible to make a few general comparisons.

The secondary nitrate factor isolated in this study is made up of aged aerosol (both marine and crustal) with some ammonium nitrate and therefore it is difficult to compare it to the results in Table 2. The secondary sulphate contribution in Għarb (21%) is at the higher end of the range in Table 2, which spans from 2% to 24% for Payerne (Minguillón et al., 2012) and Eifel (Beuck et al., 2011), respectively. In the coastal locations, marine aerosol contributed from 8% in Venice (Masoli et al., 2012) to 22% in Galway (Yin et al., 2005). The 19% contribution in Għarb is close to the value for Galway and to the 17% contribution reported for Antalya (Öztürk et al., 2012). All the studies in Table 2 report one crustal component, while the current study has identified two distinct crustal components which together make up 26% of the PM₁₀ mass. This figure is close to the values reported for the Southern European States for example, Querol et al. (2004) and Rodríguez et al. (2004), for Monagrega (26% in both cases), Marenco et al. (2006), for Cimone (27%). The 20% Saharan contribution estimated by this study is also within the range of reported values across the Mediterranean and close to the 24% reported for a site at ~240 km to the North (Bocadifalco, Sicily), Pey et al. (2013).

The Saharan dust contribution (20% or 3.7 µg/m³) and the marine aerosol contribution (19% or 3.4 µg/m³), jointly contribute to 39% (7.1 µg/m³) of the PM₁₀ measured in Għarb, Fig. 3. It is not possible to compare this value to any of the values in Table 2, since most studies identified only a crustal source, which includes both natural and anthropogenic sources.

4.3. Implications for compliance with Directive 2008/50/EC

From 2008 till 2014 the levels of PM₁₀ in Għarb have been compliant with both environmental quality standards set by Directive 2008/50/EC. The range of annual averages registered throughout this 6-year period was always lower than the limit value of 40 µg/m³ (ERA, unpublished data) and varied between 17.9 µg/m³ and 22.3 µg/m³ (18.2 µg/m³ throughout the study period). It is worth pointing out that these annual levels of PM₁₀ are below the limit value, despite the fact that the Saharan contribution has not been subtracted from them. A superficial comparison to the range of PM₁₀ values reported by rural background stations across the Mediterranean throughout the same timeframe, on EEA - Airbase v8, places this range in the same bracket as that for the Portuguese stations (12.3 µg/m³ in Vaqueiros in 2013 to 23.5 µg/m³ in Santiago de Cacém in 2009), on the higher side of the one reported by rural background stations in both Southern Italy (from 10 µg/m³ in Cetara in 2013 to 23.3 µg/m³ in Fontechiari in 2011) and Southern Spain (from 7.6 µg/m³ in Marita del Maestrazgo in 2013 to 20.0 µg/m³ in Sa Pobla in 2014), and on the lower end of the range reported

Table 2
Methodology and location of previous studies (only rural and sub-urban sites). The entry in italics shows the location of the second sampling site included in the study.

Reference	Pio et al. (1996)	Querol et al. (2004)	Rodríguez et al. (2004)	Yin et al. (2005)	Marenco et al. (2006)	Beuck et al. (2011)	Gianini et al. (2012)	Masiol et al. (2012)	Minguillón et al. (2012)	Öztürk et al. (2012)	This Study
Site	Areão	Bemantes	Monagregaa	Galway	Cimone	Eifel	Payerne	Payerne	Antalya	Gharb	
Country	Portugal	Spain	Spain	Ireland	Italy	Germany	Magadino Switzerland	Switzerland	Turkey	Malta	
Sampler (Filter Type)	HVS (QF)	HVS (QF)	Partisol (PTFE)	LVS (PTFE)	HVS (QF)	HVS (QF)	LVS (QF)	HVS (QF)	HVS (cellulose)	LVS (PTFE)	
Receptor Model	APCA/MLRA	PCA/Mass Balance	Mass Closure	APCA/MLRA	PMF	PMF	PMF	PMF	PMF	PMF	MLRA
Identified Factors											
Secondary Nitrate	31% Included as "Secondary Aerosol"	—	—	28% Included as "Secondary aerosol"	—	22%	32%	17%	35%	—	—
Secondary Sulphate	—	—	—	—	—	24%	8%	10%	2%	—	21%
Fossil Fuel Combustion	—	—	—	—	—	17%	21%	—	—	—	—
Aged Aerosol	—	—	—	—	—	23%	—	—	—	32%	—
Industry	—	17%	26%	—	—	20%	—	—	—	—	—
Marine Aerosol	14%	14%	4%	22%	1%	—	—	8%	4%	17%	19%
Resuspended Local dust Resuspended dust - Transboundary Traffic	1% Included as "Soil Contribution"	36% Included as "Crustal"	26% Included as "Crustal"	9% Included as "Resuspended dust"	27% Included as Mineral dust	2%	11% Included as Mineral dust	19% Included as "Mineral dust"	18% Included as Ca dust and Mineral dust	19% Included as "airborne dust"	6%
Other (different sources)	6% Non-ferrous Industry	—	—	—	—	—	17% Factor labeled as "Biomass"	10% Factor labeled as "Mixed Wood Combustion"	31% Factor labeled as "Organic Material".	27% Factor Labeled as "Coal Combustion".	"De-icing salt".

HVS = High Volume Sampler, LVS = Low Volume Sampler, QF = Quartz Fiber Filter, PTFE = Teflon Filter, APC = Absolute principal component analysis, PCA = Principal component analysis, MLRA = Multi linear regression analysis, PMF = Positive Matrix Factorization.

by the Agia Marina station in Cyprus ($21.7 \mu\text{g}/\text{m}^3$ in 2008 to $35.6 \mu\text{g}/\text{m}^3$ in 2012), [EEA \(2016\)](#).

In addition during this 6-year period, the number of exceedances of the daily limit value ($50 \mu\text{g}/\text{m}^3$), ranged from 2 in 2012 to 17 in 2010 (ERA, unpublished data), lower than the maximum allowable value of 35. During the same period the highest number of exceedances of this limit at rural stations across the Mediterranean, ranged from 11 in Fontechiari, Italy (2011) and 13 in Viznar and Calanda in Spain (2008 and 2012 respectively) to 39 in Agia Marina, Cyprus (2008), [EEA \(2016\)](#). Exceedances of the daily limit value in Gharb were attributed to Saharan dust intrusions ([Malta Environment and Planning Authority, 2012](#) and [Malta Environment and Planning Authority, 2013](#)). The Gharb station is the regional background station for all the Maltese territory, therefore the Saharan contribution estimated by this study ($3.7 \mu\text{g}/\text{m}^3$) is applicable to all the stations in the Maltese network, keeping in mind that this value was calculated for a period of 224 days. According to Directive 2008/50/EC, Malta is allowed to subtract this value together with the marine aerosol contribution at the traffic site from the annual levels of PM_{10} at the same site (the traffic site, is normally not in compliance with the 35 exceedances criterion), in order to assess for compliance with its regulatory obligations.

The fact that the European Union Member States are allowed to subtract natural contributions from their regulatory compliance obligations, does not mean that natural contributions to PM_{10} levels are free from adverse health effects. In fact, the Commission Guidelines on Subtraction of Natural Sources, ([European Commission, 2011](#)), emphasizes the fact that aerosols from natural sources are not exempt from human health effects. Whilst acknowledging that the Member States should continue to subtract exceedances due to natural contributions from their compliance obligations, chiefly because these are beyond the Member States' control, we are however of the opinion that this approach alone does not sufficiently safeguard human health. For this reason, we suggest that any future revisions of Directive 2008/50/EC should include a specific obligation on the Member States to issue advance warnings about such occurrences and inform the public on their repercussions on human health.

5. Conclusion.

The principal aim of the current contribution was the isolation and quantification of the two natural PM_{10} source contributions, which are eligible for subtraction according to the Guidelines issued by the European Union and which affect ambient levels of PM_{10} in the Central Mediterranean. It was shown that both contributions are considerable for the Maltese background station. As expected, the marine contribution was found to be more constant and a function of wind speed, whereas the Saharan dust occurred intermittently, when air was advected over the African continent.

One of the major results of this contribution is the isolation of the two crustal components (local re-suspended dust and Saharan aerosol) through the use of the PMF receptor model, a task not often managed before. In this regard, the Saharan aerosol contribution is considerably higher than that of the local re-suspended dust, for this particular receptor.

In addition, the contribution of Saharan aerosol and marine aerosol could be quantified precisely, leading to a rational basis for subtraction of these two natural components from PM_{10} levels. These contributions are not constant, so any future work should investigate the possibility of linking these contributions to a variable, which is easier to determine (e.g. meteorological parameter/s, variations in the levels of the short lived radon progeny, etc.), in order to make the subtraction procedure as precise, and operationally easier.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.10.028>.

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Supplementary Material

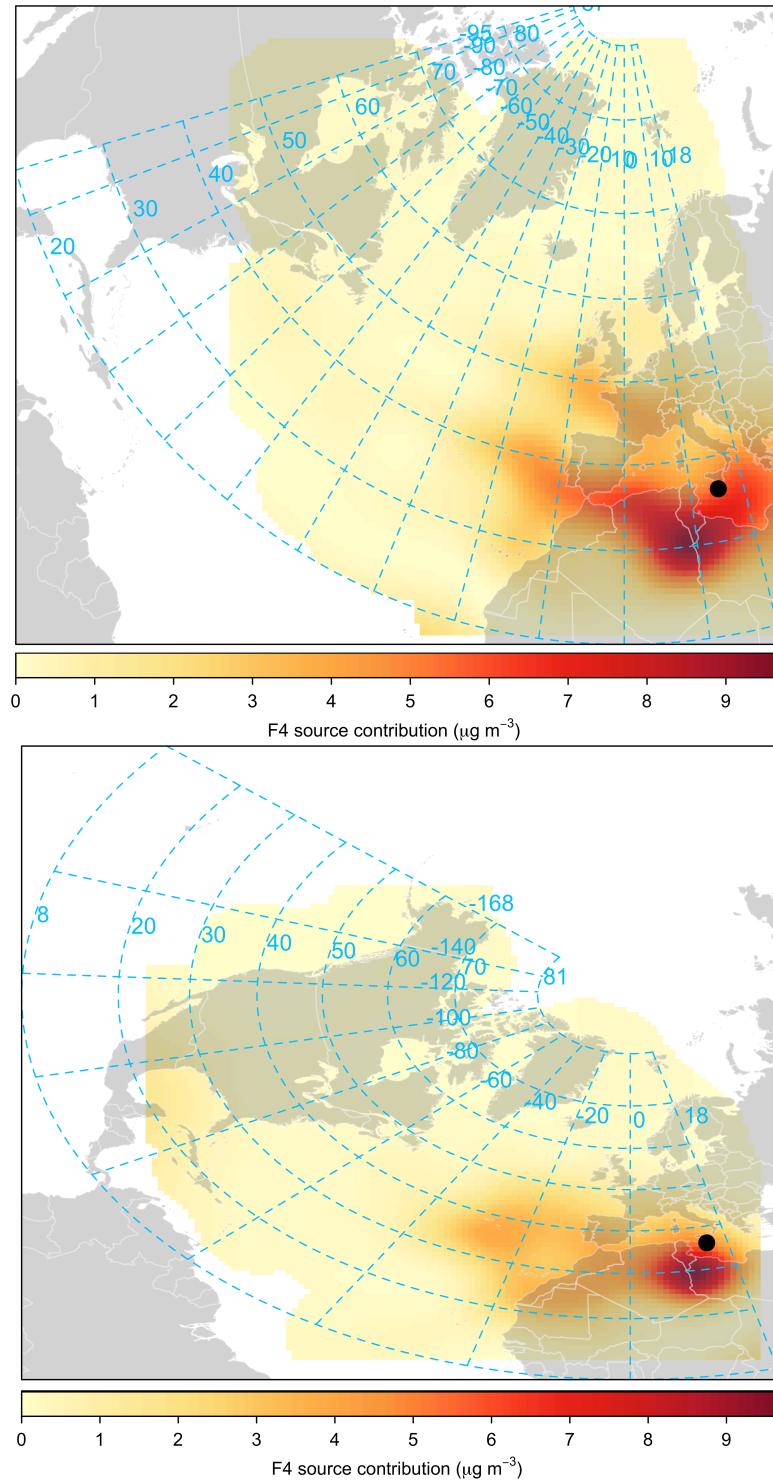


Figure SM1: Concentration field for the Saharan aerosols source contribution at arrival heights of 500m (top) and 3000m (bottom).

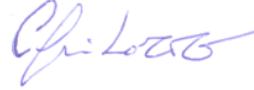
Paper II

Estimation of the contributions of the sources driving PM_{2.5} levels in a Central Mediterranean coastal town. [Chemosphere 211 (2018) 465–481], available from

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The co-authors of the article entitled “Estimation of the contributions of the sources driving PM_{2.5} levels in a Central Mediterranean coastal town” [**Chemosphere 211 (2018) 465–481**] [<https://doi.org/10.1016/j.chemosphere.2018.07.104>.], declare that:

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Estimation of the contributions of the sources driving PM_{2.5} levels in a Central Mediterranean coastal town

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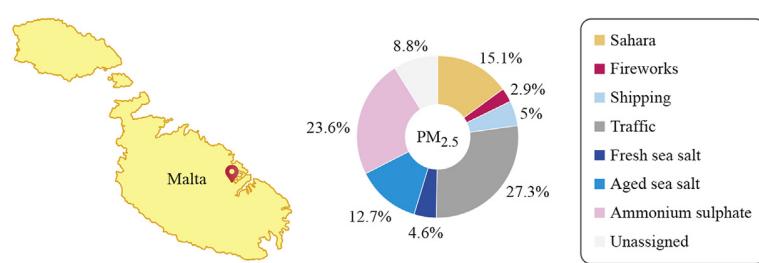
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HIGHLIGHTS

- Seven sources were isolated for a traffic site in a coastal town in Malta.
- Traffic was the most significant contributor to ambient PM_{2.5} levels.
- A component due to letting of fireworks was also identified.
- Traffic should be targeted in order to reduce PM_{2.5} levels and achieve the WHO guidelines by 2020.
- In the long run the countries in the region should also curb emissions from shipping.

GRAPHICAL ABSTRACT



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ABSTRACT

Receptor modelling techniques are widely used in order to identify the main natural and anthropogenic processes driving aerosol levels at a receptor. In this work, Positive Matrix Factorization (PMF) was used to apportion PM_{2.5} levels at a traffic site (Msida) located in a coastal town. 180 filters collected throughout a yearly sampling campaign conducted in 2016, were chemically characterized by light absorbance analysis, x-ray fluorescence and ion chromatography in order to determine the concentrations of black carbon, 17 elements and 5 ions, respectively. The resulting chemical data base was used in conjunction with PMF in order to identify the 7 components affecting the PM_{2.5} levels at the receptor site. Six of these sources are considered to be typical of the atmospheric composition of coastal traffic sites: traffic (27.3%), ammonium sulfate (23.6%), Saharan dust (15%), aged sea salt (12.7%), shipping (5%) and fresh sea salt (4.6%). This is the first time that such a study was carried out in Malta and helps in understanding the aerosol pollution climate of the Central Mediterranean, which is still relatively understudied when compared to the Eastern and Western Mediterranean. Furthermore, we have isolated a factor exclusive to Malta: the fireworks component, which is responsible for 2.9% of the PM_{2.5} and which has health implications due to its chemical composition. The results of this work should also serve to guide the policy

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makers in achieving the necessary emission reductions in order to achieve the WHO guideline for PM_{2.5} by 2020.

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1. Introduction

The fine fraction of airborne Particulate Matter (APM) or PM_{2.5} is defined by ISO 7708 (1995) as particles which pass through a size-selective inlet with a 50% efficiency at the 2.5 μm aerodynamic diameter cut-off and is the metric that is considered to be the high-risk respirable convention. Current epidemiological evidence suggests that PM_{2.5} plays a prominent role in the adverse health effects resulting from exposure to polluting levels of atmospheric PM (Pope and Dockery, 2006). These effects depend on the magnitude of the exposure concentration as well as on the duration of the exposure. Robust associations have been established between PM_{2.5} and both daily mortality (e.g. Schwartz et al., 1996; Burnett et al., 2000; Simpson et al., 2005; Ostro et al., 2006; Perez et al., 2009) as well as long term mortality (e.g. Dockery et al., 1993; Pope et al., 1995; Pope et al., 2002; Pope et al., 2004; Laden et al., 2006). Cardiovascular, cerebrovascular and respiratory illnesses are the main causes of mortality due to acute and chronic exposures to PM_{2.5}. Correlations have also been established between long-term exposures to fine particulate matter and lung cancer e.g. (Dockery et al., 1993; McDonnell et al., 2000). The association between lung cancer and fine particulate matter is particularly significant for diesel exhaust due to the presence of elemental carbon-EC, (Attfield et al., 2012; Silverman et al., 2012), to the extent that IARC (2012) has classified diesel exhaust as a Group 1 carcinogen. Links have also been established between acute exposure to fine particulate matter and cardiovascular (Franchini and Mannucci, 2007; Miller et al., 2007) and respiratory morbidity (Atkinson et al., 2001; Ko et al., 2007). In southern Europe, increases in admissions due to cardiovascular and respiratory causes, with PM_{2.5} levels, have been reported by e.g. Stafoggia et al. (2013). Furthermore, Lanki et al. (2006) and Penttilä et al. (2006) found that PM_{2.5} exacerbated both peak respiratory flow and ischemic heart disease in adults with stable coronary heart disease.

In the European Union (EU-28) ambient levels of PM_{2.5} are regulated by Directive 2008/50/EC, which sets an annual limit value of 25 μg/m³. This limit value is not considered to be sufficiently protective of human health, and in fact the World Health Organization (WHO) recommends an annual air quality guideline (AQG) of 10 μg/m³ and a daily guideline of 25 μg/m³, which can be exceeded 0.5% of the time, WHO (2006). According to the European Environment Agency (EEA, 2016), in the period running from 2012 to 2014, 85–91% of the urban populations in Europe were exposed to PM_{2.5} levels higher than the WHO AQGs. Additionally, according to WHO (2013), the latest available research has highlighted associations between ambient levels of PM_{2.5} and mortality levels at concentrations well below 10 μg/m³ (the current AQG).

PM_{2.5} background levels in the Mediterranean countries tend to be rather high, due to both geographic (closeness to the African continent) as well as meteorological factors such as semi-aridity, modest precipitation rates, weak advection of air masses and the frequency of occurrence of local re-circulation patterns, Rodríguez et al. (2007). The meteorological factors favor higher residence times of particulate matter in the atmosphere, and in fact, the highest concentrations of PM_{2.5} in Europe are measured in near-city, urban background and traffic sites in Southern countries, (Putaud et al., 2010). Closeness to the Saharan region results in a

significant influence of Saharan episodes on the PM immissions in these countries, including on the PM_{2.5} levels (Molinari et al., 1993; Kubilay et al., 2000; Viana et al., 2002; Almeida et al., 2005; Nicolás et al., 2011). In addition, a variety of regional and local sources contribute to the atmospheric levels of PM_{2.5} in the region.

Secondary particulate formation through atmospheric chemical reactions is an important contributor to APM in the region. NO₂ and SO₂ emitted by anthropogenic processes such as fossil fuel combustion (by both land based and maritime sources) are converted by photo-oxidative processes into the respective acids. Particulate matter forms from the reaction of these acids with ammonia, sea salt or mineral dust, Galindo et al. (2013). The prevailing meteorological conditions in the Mediterranean, in particular the insolation rates and higher temperatures, favor the formation of the sulfate (which occurs mostly in the PM_{2.5} fraction) rather than the thermally unstable nitrate.

Sea breezes enhance the troposphere in coastal areas with Na⁺ and Mg²⁺, giving rise to sea salt aerosol which can contribute from 1 to 6% of the PM_{2.5} levels in Southern Europe (Amato et al., 2016a). The metal ions take part in neutralization reactions with nitric and sulfuric acids (particularly during spring and summer) to form nitrate (Nicolás et al., 2009) and sulfate salts of these ions.

Air quality in coastal areas is also adversely affected by maritime transport (Viana et al., 2014), especially due to the fact that 70% of the emissions occur close to the coast (Endresen et al., 2003). Emissions from shipping are still relatively under-regulated when compared to land-based sources (Viana et al., 2009). Particulates emitted by shipping occur mostly in the finer fraction and can be emitted as either primary emissions such as EC, Ni, V, etc. (Viana et al., 2014) or result from gas to particle reactions, (Reche et al., 2011). According to Viana et al. (2014), only 30–40% of the particulates from shipping are emitted as primary particles, while the remaining 60–70% are secondary particles.

Road traffic is widely recognized as one of the major (local) contributors to PM_{2.5} levels in urban areas, (e.g. Viana et al., 2008; Belis et al., 2013), contributing up to a maximum of 49% (Amato et al., 2013) of the fine fraction of APM. Furthermore, in Southern Europe, PM_{2.5} levels increase along the rural background-urban background-kerbside gradient, (Putaud et al. (2010)). Traffic derived atmospheric particulate matter may be divided into exhaust and non-exhaust fractions. Exhaust emissions include both primary and secondary particles. Primary particles are mainly composed of carbonaceous aerosol together with minor amounts of inorganic ions and of metals. Combustion of fuel and lubricant are responsible for the carbonaceous particles (El Haddad et al., 2009), while metal emissions result from engine corrosion (Lough et al., 2005; Sysalová et al., 2012; Varrica et al., 2013) and from the after-treatment systems (Pulles et al., 2012). Secondary particulates, are formed from gas to particle reactions involving the NO_x and VOCs (Amato et al., 2016a) but also SO₂, (Weinbruch et al., 2014). Re-suspended road dust and emissions from abrasion make up the non-exhaust component. The abrasion component results from friction at the brake lining – wheel interface, and at the tyre – road interface. It has been shown that a significant portion of these emissions occurs in the PM_{2.5} fraction both for brake wear (Wählin et al., 2006; Iijima et al., 2007) and tyre wear

(Fauser, 1999; Gustafsson et al., 2008). Road surfaces act as a reservoir for the deposition of fine and coarse particles emitted from any anthropogenic or natural sources (Amato et al., 2009). Air turbulence and tyre shear by the wheels rolling over the road surface cause the re-suspension of these particles.

The aim of this work is to characterize the sources affecting the PM_{2.5} levels in a densely populated, coastal area with an aerosol pollution climate typical of the Central Mediterranean region and representative of a higher exposure situation. It is worth pointing out that the region is relatively understudied in this regard, especially when compared to both the Western and the Eastern Mediterranean. This study should also serve to guide the policy makers in taking the necessary measures in order to achieve the WHO guideline for PM_{2.5}, thereby reducing human health risks.

2. Experimental

2.1. Sampling

PM_{2.5} samples were collected throughout 2016 at the traffic station in Msida (see Fig. 1), forming part of the Maltese air quality network and located at (35.89587°N, 14.48987°E, 2 m AMSL). The Corine Land Cover (CLC) Database (2012) classifies the land coverage in the area around the site as "discontinuous urban fabric" (CLC class 112) and "port area" (CLC class 123) because of the presence of a privately-owned marina at ~70 m east of the station. The station is situated in a traffic hotspot in the central part of the

only agglomeration for the purposes of Directive 2008/50/EC (2008), in the Maltese islands, delineated by Stacey and Bush (2002) and named as the "Valletta – Sliema agglomeration". The agglomeration represents the highly urbanized part of the island with a population density of 5500 inhabitant/km². The Msida station is within 10 m of an important traffic node with traffic flows of ~8.5 million vehicle passages per year and, which links *inter alia* Valletta (Malta's administrative Capital) and Sliema (Malta's tourism, entertainment and commercial hub) and is therefore affected by heavy traffic flows. Additionally, the site is surrounded by heavily trafficked areas to both the north and the south, including Malta's busiest traffic node (approximately 15 million vehicle passages per year) at ~2.5 km to the SSE. PM_{2.5} levels at the sampling site are therefore heavily impacted by road traffic sources. Shipping is also expected to contribute to the fine aerosol levels at the receptor, especially due to the presence of one of most heavily traded routes to the East of the receptor (the Malta – Sicily channel, linking together the West and the East Mediterranean). In addition, the "Grand Harbour complex" is at ~2 km to the SE, from the sampling site. This complex includes a cruise liner terminal, a catamaran terminal, port facilities for mercantile shipping and a private shipyard, and is therefore quite busy, with the total number of ships calling at Maltese ports reaching ~26000 in 2016 (EUROSTAT, 2017). Industrial sources are not likely to have a major effect on PM_{2.5} levels in Msida, due to either the scale (or the yearly operating hours) of the installation or the distance away from the receptor. There are four industrial installations in the area (Fig. 1): a

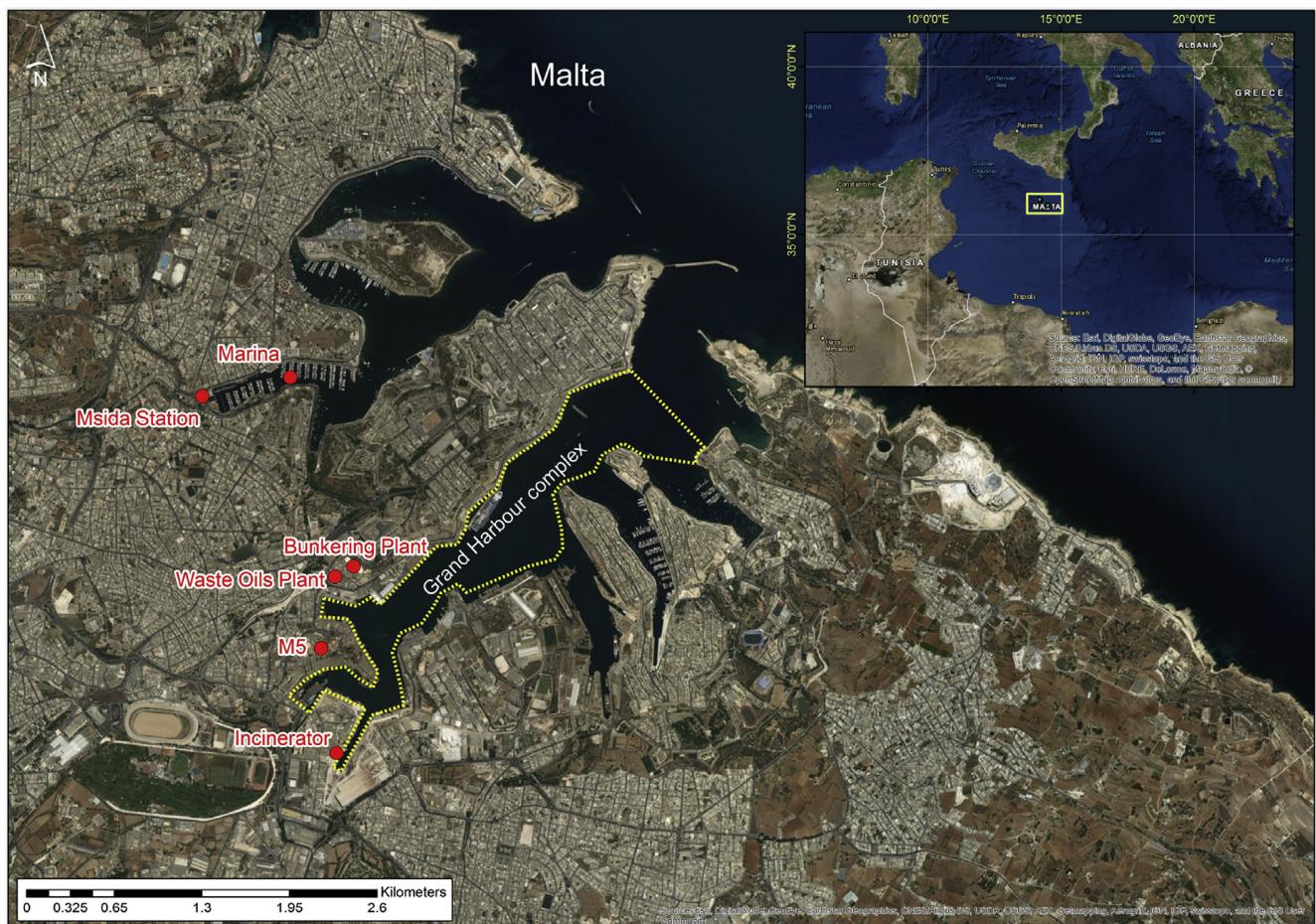


Fig. 1. Location and characterization of the receptor.

waste oil (physical) treatment plant, a bunkering plant, an open cycle gas turbine (M5) and a small incinerator firing mainly abattoir waste. Table SM1 in the electronic supplement, shows that the gas turbine was hardly used in 2016, while the other installations are rather small scale. The only environmentally significant large point source in the island is a thermal power plant located at over 9 km to the SE (not visible in Fig. 1). In Malta, spatial heaters, hobs and ovens rarely if ever fire biomass and therefore the contribution of this source to fine aerosol levels at the receptor should be negligible. However, PM_{2.5} levels at the receptor are expected to be measurably affected by two natural sources in particular, marine aerosol and Saharan dust, respectively due to the small distance away from the coast and the proximity of the archipelago to North Africa (~300 km to the east of Tunisia and ~350 km to the north of Libya).

From a meteorological perspective the sampling year (2016) was characterized by exceptionally low rainfall rates, in fact the Meteorological Office (Malta) reported a total of 325.1 mm of rainfall. This is one of the lowest rainfall rates ever registered in Malta and is outside the 400–800 mm range, which is considered the "normal" rainfall rate for Malta (Galdies, 2011). No other meteorological anomalies were registered throughout this year. In Malta the prevailing wind is the NW (20.7%) followed by WSW, SSW and NNW (cumulatively 24.1%), Galdies (2011). The wind rose for the station (Fig. 2) shows a higher influence from the W to the SW and NNW – N. These anomalous wind patterns probably resulted from a combination of factors, which include topographic and orographic factors as well as the effect of sea breezes from the easterly directions and the bottom of a valley to the W – NW of the station.

The sampling campaign (part of Malta's EU obligations) ran from the 01 January 2016 to the 31 December 2016. 366 samples were collected using an SEQ 47/50 sequential sampler (Sven Leckel GmbH, Berlin, Germany). One quartz fibre (QF) filter, was placed in the sampler cassette for every four Teflon® (PTFE) membranes. The PP47AN, PTFE membranes used, had a diameter of 46.2 mm (pore size 2 µm) and were manufactured by MTL (Measurement Technology Laboratories LLC, Minneapolis, USA), while the MK 360, QF

filters (Munktell – Ahlstrom, Falun, Sweden) used, had a 47 mm diameter. All the filters were exposed for 24 h, at flow rate of 2.3 m³/h, and the sampler was leak tested using a TeraCal® Ultra (BGI, Boca Ranton, USA) volumetric flow calibrator. Sampling was carried out as per CEN 12341 (2014). The filters were conditioned for 96 h at a temperature of 20 °C ± 1 °C and at a relative humidity range >45% but ≤50% in an MTL automated filter weighing system (Measurement Technology Laboratories LLC, Minneapolis, USA), and were subsequently automatically massed using an XP6 microbalance (Mettler – Toledo, Griefensee, Switzerland).

2.2. Analytical procedures

One hundred and eighty filters (approximately one-half of the total number of samples collected) were analyzed in this work. The samples were chosen in such a way that the seasonal weekday and weekend averages of the analyzed filters were as close as possible to those of the full population of filters, and the ratio of weekday/weekend filters was equal to 2.5. BC concentrations were measured optically at a wavelength of 635 nm using the Multi-Wavelength Absorbance Analyzer (MWAA), an optical setup developed at the Physics Department of the University of Genoa, Italy, Cuccia et al. (2010), Massabò et al. (2013) and Massabò et al. (2015). The mass absorption coefficient (MAC) for 7 QF filters was determined by the same institution, from the gradient of a plot of the absorption coefficient of the filters against the EC concentration (gradient = 10.3, r² = 0.99). EC was measured by the Thermal Optical Transmittance Instrument (Sunset Lab Inc., USA; Birch and Cary, 1996), using the NIOSH 5040 protocol. Equivalent BC (eBC) concentrations were obtained by dividing the results of the MWAA by the MAC. Vecchi et al. (2014) and Massabò et al. (2013), report a systematic bias between the absorbance of PTFE and QF filters at 635 nm, due to the absorption of the gaseous phase by the QF filters and not by the PTFE filters. This difference was estimated for Malta by co-locating 2 PM_{2.5} samplers, with the cassette of one sampler loaded with 5 PTFE filters followed by 5 QF filters and vice versa for the cassette of the other sampler. The systematic bias was found to be 41.2%, slightly higher than that reported by Vecchi et al. (2014) and Massabò et al. (2013). The eBC readings were therefore corrected for this difference. The elemental concentrations of (Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba and Pb) were measured with an ARL Quant'x, Energy-Dispersive X-ray Fluorescence Spectrometer (Thermo Fisher Scientific, UK) equipped with an energy-dispersive Si(Li) detector. X-rays were generated with a Rh anode tube (I_{max} and V_{max}, 1.98 Å and 50 kV respectively). The instrument was calibrated using pure thin film standards (Micromatter – XRF Calibration standards, 50 µg/cm², N – Nuclepore® polycarbonate aerosol membranes, USA). A check of the calibration results was periodically performed by comparison against the NIST standard SRM2783 (Air Particulate on Filter Media). The membranes were subsequently analyzed for the concentrations of ions (NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺ and Mg²⁺). The sample was mixed for 30 min with 15 ml deionized water (>18 MΩ) and the resulting slurry was filtered through a 0.45 mm membrane and analyzed by a DIONEX® DX 120 ion chromatograph (Thermo Scientific, Sunnyvale, USA). DIONEX® AS-9 HC, 250 × 4-mm was used as separating column for the anions, with 15.0 mM KOH at a flow rate of 1 ml/min as the eluent. Cations were analyzed using a CS12A (250 × 4-mm) cationic column and 20 mM methanesulfonic acid at a flow rate of 0.8 ml/min, as the eluent. For both anions and cations DIONEX® CD 20 was used as the detector. The lower detection limits for NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺ and Mg²⁺ were respectively 22, 16, 19, 17, 11 and 1 ng/m³. Method detection limits for each of these ions were estimated as three times the standard deviation of the concentrations determined for 10 blank PTFE filters. The percentage of

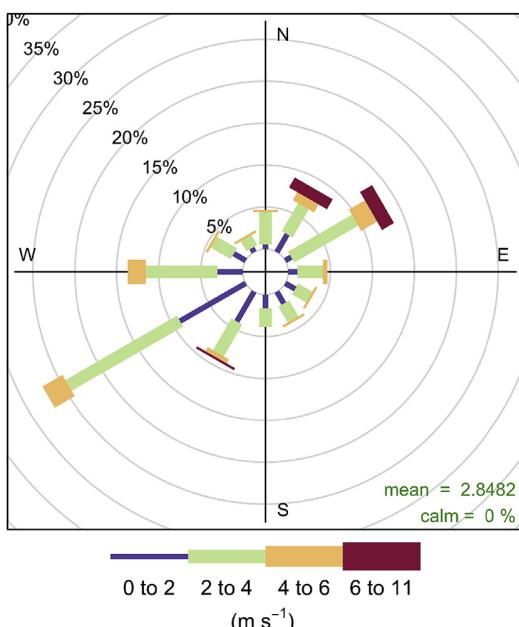


Fig. 2. Windrose for Msida in 2016 showing the frequency of counts (%) by wind direction.

recovery and the analytical precision were assessed by conducting spike-recovery checks. One-half milliliter of a 40 µg/ml standard solution of inorganic ions was added separately to blank samples. Subsequently, a complete extraction procedure was followed and the concentrations of the water-soluble inorganic ions were determined. The recovery rates were found to be within the range of 96%–107%. The precision estimated from the standard deviation of repeated measurements of standards and samples was in the range of 0.8%–9% for all inorganic ions. Both the elemental and the ion concentrations were measured at the Atmospheric Pollution Laboratory of the Miguel Hernández University, Elche (Spain).

2.3. Meteorological parameters

Daily averaged temperatures (°C) were obtained from the Meteorological Office at the Malta International Airport (MIA) at ~6 km to the SW of the Msida station. Wind speed (m/s) and wind direction (degrees) were measured at the receptor as 15-min averages, using a WindSonic ultrasonic anemometer (Gill Instruments, Hampshire, UK). Daily averages were subsequently calculated using the OpenAir package in R-Studio (Carslaw and Ropkins, 2012) using a code which takes into account the circular nature of wind direction.

2.4. Statistical analysis

2.4.1. PMF

Positive matrix factorization PMF, a receptor modelling technique developed by Paatero and Tapper (1994) and Paatero (1999) was used to identify and quantify the sources affecting PM_{2.5} concentrations in Msida. Version 5 of the U.S. EPA PMF was used in this study. Both the species concentrations (matrix **X**) and the uncertainty for each measurement (matrix **U**) are used as inputs to the model. **U** weights each of the measurements in **X** by the uncertainty in the measurement. Uncertainties for both the elements determined using XRF and for eBC measurements were calculated using the method described by Polissar et al. (1998), while the uncertainties of the ions were calculated using the methods described by Zabalza et al. (2006). Analytes below the detection limit (BDL) were treated as suggested by Norris et al. (2014). The uncertainties of eBC were increased by a Factor of 3 during the days affected by Saharan episodes due to the absorption of the Saharan dust at 635 nm. In addition an uncertainty of 10% was added to the model to account for measurement errors not included in the uncertainty data (Reff et al., 2007). PMF decomposes **X** into two matrices **G** and **F** (respectively the factor contributions matrix and the factor profiles matrix), see equation (1):

$$\mathbf{X} = \mathbf{G} \mathbf{F} + \mathbf{E} \quad (1)$$

E is the residuals matrix. The model constrains all the elements in **G** and **F** to be ≥ 0 . A weighted least squares algorithm is used by the model to iteratively minimise parameter Q in equation (2), and estimate both **G** and **F**:

$$Q = \left[\frac{\mathbf{X} - \mathbf{G} \mathbf{F}}{\mathbf{U}} \right]^2 \quad (2)$$

2.4.2. Other statistical tests

The source contributions were converted into physically meaningful units (e.g. ng/m³) by regressing the PM_{2.5} mass concentrations against the factor scores (the elements of the **G** matrix) returned by PMF, (Song et al., 2001). MLRA was performed using

IBM SPSS Statistics, for Macintosh, version 24. Polar plots for the source contributions were plotted using the OpenAir package in R-Studio (Carslaw and Ropkins, 2012). The source contributions were aggregated by season “winter” (December, January, February), “spring” (March, April, May), “summer” (June, July, August) and “autumn” (September, October, November). Average daily temperatures were used to partition months into three groups labelled as “hot” ($\geq 23.7^\circ\text{C}$), “intermediate” ($> 15.4^\circ\text{C}$ but $< 23.7^\circ\text{C}$) and “cold” ($< 15.4^\circ\text{C}$). The seasonal differences, the difference between weekend and weekday averages, differences between “hot”, “intermediate” and “cold” days were all analyzed for specific source contributions using the Mann Whitney *U* test, performed on SPSS (version 24).

2.4.3. Concentration gradients

Concentration weighted trajectories - CWTs (Hsu et al., 2003) were used to investigate the concentration gradient of the source contributions close to the source areas. CWTs weight the source contribution s_l registered when a trajectory l arrives at the receptor by the time spent over a grid cell τ_{ijl} , located at the coordinates i, j , see equation (3).

$$s_{ijl} = \sum_{l=1}^{L=M} \frac{1}{\tau_{ijl}} \times \sum_{l=1}^{L=M} \tau_{ijl} s_l \quad (3)$$

Backtrajectories for 2016 were obtained from HSPLIT (Draxler et al., 2014; Stein et al., 2015) using the Reanalysis dataset (resolution lat/lon of $2.5^\circ/2.5^\circ$). The run time for the trajectories was of 120 h and the arrival height at the receptor was set to 1500 m AGL. The 1500 m arrival height corresponds to a geopotential height of 850 hPa, and was used because it is considered representative of both the mean transport winds at the synoptic scale (Stohl, 1998; Salvador et al., 2010) and the uppermost part of the boundary layer, which is not influenced by surface artefacts (Salvador et al., 2008).

3. Results

3.1. PMF solution

The elements Cr, Sr, Pb, Ba, Zn, Cu, Br, as well as NO₃⁻ were down-weighted in the PMF modelling, to “weak”. In the present study, PMF was run in robust mode. PMF solutions for a different number of factors from 4 to 9 were explored. Plots of $Q_{\text{theoretical}}/Q_{\text{expected}}$, IM – the maximum individual column mean, and IS – the maximum individual column standard deviation (Lee et al., 1999), against the number of fitted factors were investigated for any sharp drops. Furthermore, the different PMF solutions were examined for how well the concentrations of the analyzed species were fitted by the model for the different number of factors considered.

Following this exercise, the solutions with 7–9 fitted factors were retained. The 9-factor solution was discarded because it isolated a factor with no physical interpretability for Malta. The 8-factor solution isolated two-crustal components: one rich in Si and Al and the other rich in Ca, both of which peaked during the days affected by Saharan events. The model isolated these two components even when the number of fitted factors was low (e.g. 5). In an apparently similar case Kim et al. (2005), decreased the weighting of the tracers of the factors showing temporal variability. The model was therefore refined by increasing the uncertainties of tracer species of the Saharan contribution on the Saharan episode days by a factor ranging from 2.5 to 4, relative to the other samples. Following this refinement, PMF returned only one crustal source for 7 fitted factors. This model was retained on grounds that it provided the largest number of physically interpretable solutions. It is

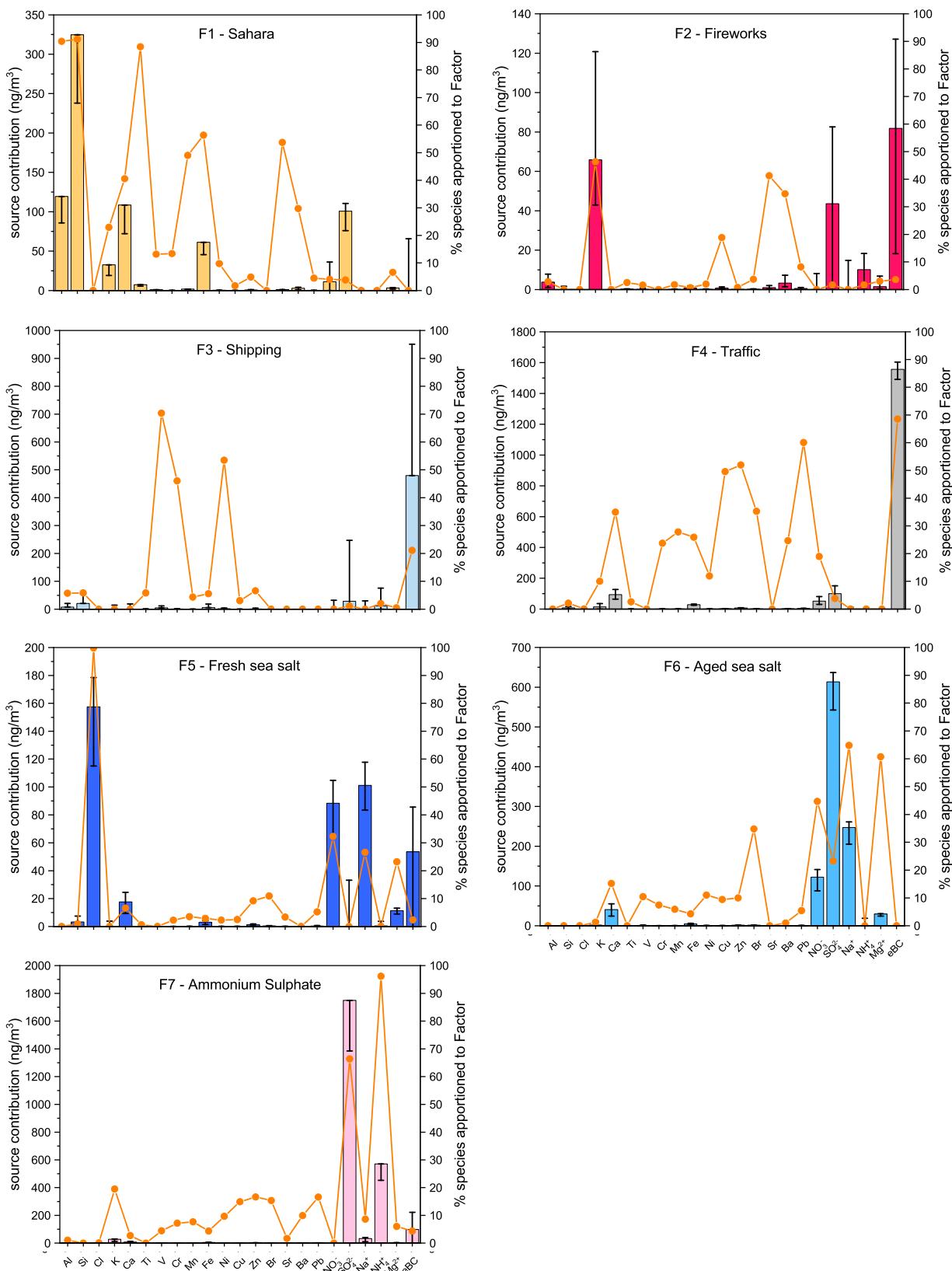


Fig. 3. Factor profiles (bars) and percentage of species apportioned to each factor (orange line).

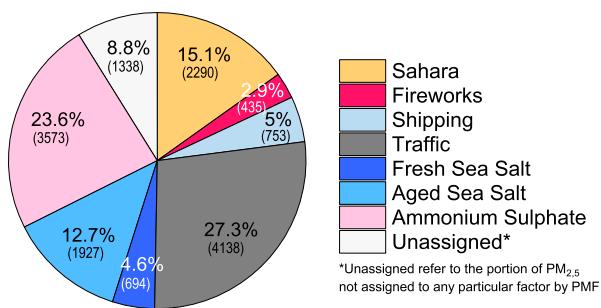


Fig. 4. PM_{2.5} source apportionment for Msida. The numbers in the brackets show the levels of the respective component in ng/m³.

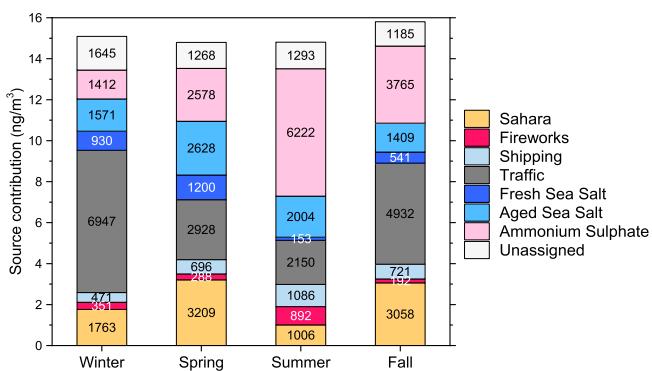


Fig. 5. Variation in source contribution by season.

worth pointing out that PMF is essentially a descriptive model and the determination of the optimal number of factors to be fitted, remains a subjective decision, Vecchi et al. (2008). The chosen solution required the application of some constraints to one of the factors, which was interpreted to be the contribution of fireworks.

Factor contributions, which showed some spikes on 6 days outside the “fireworks season” had to be pulled down, while ensuring that the change in Q was less than 10%. This solution achieved a good PM_{2.5} mass reconstruction explaining over 91% of the PM_{2.5} levels measured at the traffic site with a slope of 1.0 and a coefficient of determination (r^2) for a plot of measured vs modelled PM_{2.5} of 0.95.

3.2. Factor profiles

The factor profiles and the contribution of each factor to the PM_{2.5} levels are shown in Figs. 3 and 4, respectively. The uncertainty ranges in Fig. 3 were set at the 95th and 5th percentile of the bootstrapped runs and were not (as is customary) reported as a symmetric interval, since this is inadequate (Paatero et al., 2014).

Factor 1 is characterized by elements such as Al, Si, Ca, Fe and Sr, which are considered to be markers of African dust (Viana et al., 2008; Scheuvens et al., 2013; Rodríguez et al., 2002) and is responsible for approximately 90% of the total measured Si, and Al. The factor, which is responsible for 15.1% (2290.2 ng/m³) of the annual PM_{2.5} average, shows intense peaks during the days influenced by Saharan episodes and hence the labelling as “Saharan”. The contributions of this factor were highest during spring and autumn (Fig. 5), which is quite common for Malta. The assignment of this factor was further reinforced by a residence time analysis (Fig. 6a), which shows that for trajectories reaching the receptor at 1500 m AGL, high factor contributions are associated with air parcels passing over Morocco, Algeria and Tunisia. The Saharan episodes isolated by this model coincided with the days, notified by Malta to the European Commission in its report on the deduction of the contribution of natural sources from PM₁₀ levels, ERA (2017). It is perhaps worth mentioning, that the two crustal components isolated by the “non-refined” model include a pure Saharan component rich in Si and Al and second crustal factor, rich in Ca. The local origin of the Si (and Al) rich component was excluded because Maltese crustal material is notably, relatively poor in Al (Vella et al., 1997). The Ca-rich source included both a resuspended local component and a Saharan component. This is intuited from a simple comparison between the source apportionments for the

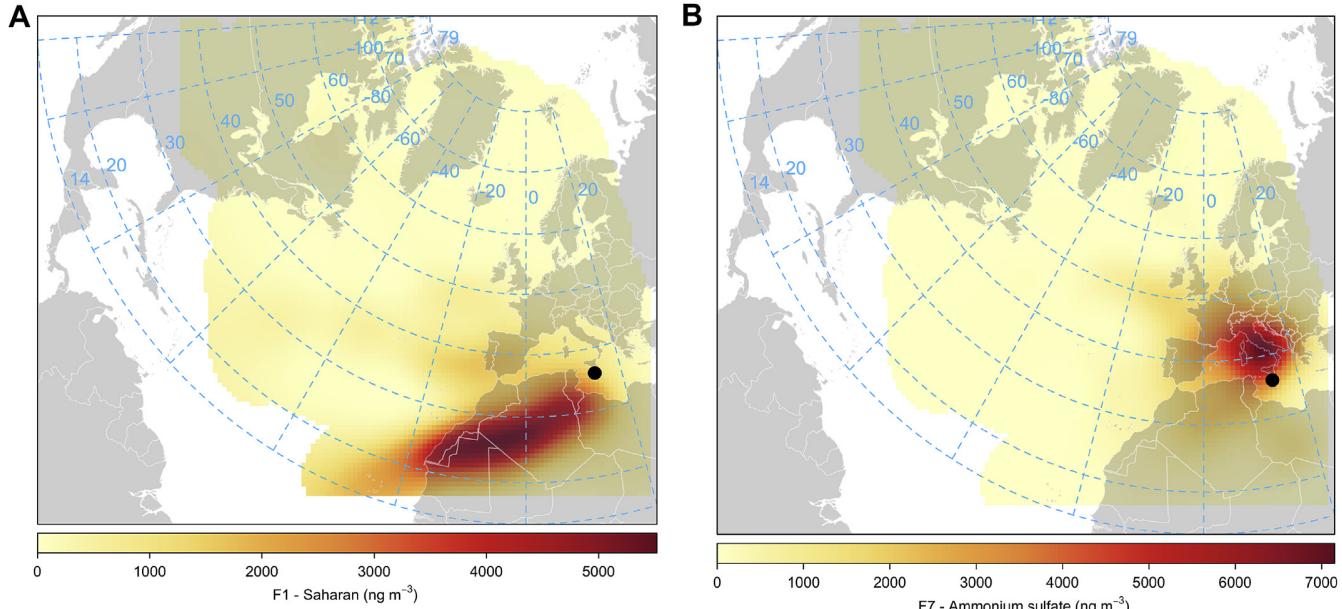


Fig. 6. (a) Concentration field for the Saharan aerosol source contribution (arrival height 1500 m). (b) Concentration field for the ammonium sulfate source contribution (arrival height 1500 m).

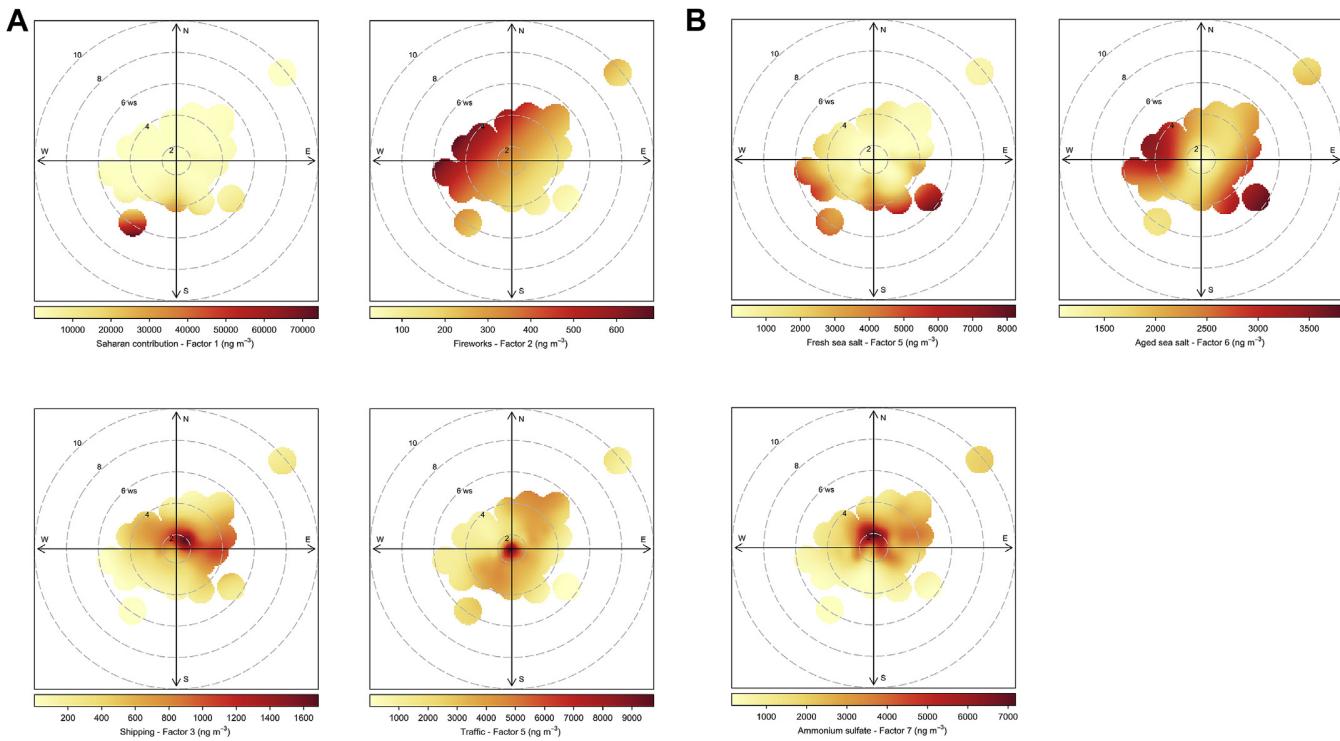


Fig. 7. Polar plots for the source contributions.

"refined" and "non-refined" models, which shows that most of the mass (>85%) of the Ca-rich component is distributed between the Saharan component, the traffic factor and the unassigned PM_{2.5} mass (in decreasing order of magnitude). Additionally, during the Saharan episodes, identified by the higher contributions of the Si-rich component (>3000 ng/m³), a plot of the Ca-rich component shows correlation with the Si-rich component (see Figure SM2 in the electronic supplement), indicating that during the episode days the predominant source of the Ca-rich component and the source of the Si-rich component are the same. On the other hand, the plot for the same components on the "non-episode days" (contributions of the Si-rich component < 3000 ng/m³) shows significant scatter and poor linearity, indicating that the dominant source of the Ca-rich component is different during these other days. The source region in NW Africa is rich in limestone (Scheuvens et al., 2013) and local mineral dust is expected to be rich in the same mineral and without the additional "refinement", PMF was unable to separate the Saharan component from the resuspended component effectively.

Factor 2, contributes 46% of the K in the PM_{2.5}, it is most important source of Ba and the second most important source of Sr, and Cu. The temporal evolution of this factor (Figure SM3 in the electronic supplement) showed a clear seasonal pattern, with intensity peaking from June till September. This period coincides with the season of the *festas* (religious festivals organized in honor of the patron saints of the various parishes). *Festas* are characterized by aerial fireworks displays in the days preceding the feast and climaxing on the day of the feast, and during which petards are let off intermittently. The K in this factor is due to the potassium compounds, which are used as the oxidizing component of fireworks, while Sr, Ba and Cu are used as color generating substances, these substances have been shown to affect PM₁₀ levels during the *festa* season (Camilleri and Vella, 2010). The contribution of this factor amounted to 2.9% (434.5 ng/m³) of the annual PM_{2.5} levels. It is

worth reiterating that in Malta, biomass combustion is seldom used to heat up houses or cook food, and in fact the marked seasonality of this source excludes both spatial heating and cooking as a likely source of this component (neither activity should peak during the summer months). In addition, unlike in Greece (or in other Mediterranean countries), in Malta, there is no burning of olive tree branches from November to February. There is perhaps a remote possibility of some limited interference from the burning of agricultural waste, however one has to keep in mind that the receptor is (relatively) far from the rural areas.

The factor profile for Factor 3 is dominated by the contributions of Ni (~54% due to this factor) and V (70% due to this factor). The Ni/V ratio for this factor is of 0.4. Ratios of 0.2–0.4 (Nigam et al., 2006), or 0.3 to 0.4 (Viana et al., 2009) are generally considered to indicate that fuel oil combustion in shipping is the likeliest source of this contribution. This factor was therefore labelled as "Shipping" and contributes 5% of the PM_{2.5} levels (752.7 ng/m³). High contributions of this factor are associated with winds from the ENE – E, Fig. 7, supporting the assignment of this factor. Shipping source contributions exhibit a maximum in summer and a minimum in winter, with intermediate values during spring and autumn (Fig. 5). This is similar to what Manousakas et al. (2017) describe for a receptor in the Eastern Mediterranean; a maximum in the contribution during the "warm" season, possibly due to increased shipping activity. It should be noted that the factor is responsible for ~20% of the measured eBC, this is important when discussing the health implications of this source. The fact that the source profile for this factor is low in SO₄²⁻ and NO₃⁻ is probably indicative of the fact that this factor is mostly due to primary emissions, this was also the case for e.g. PM_{2.5} levels modelled in the Rotterdam harbour (Hammingh et al., 2012). The emissions occur relatively close to the receptor (Fig. 7) and the oxidation of the precursor gases requires some time (particularly for SO₂). Therefore, most of the secondary particulate from shipping is included in the secondary aerosol

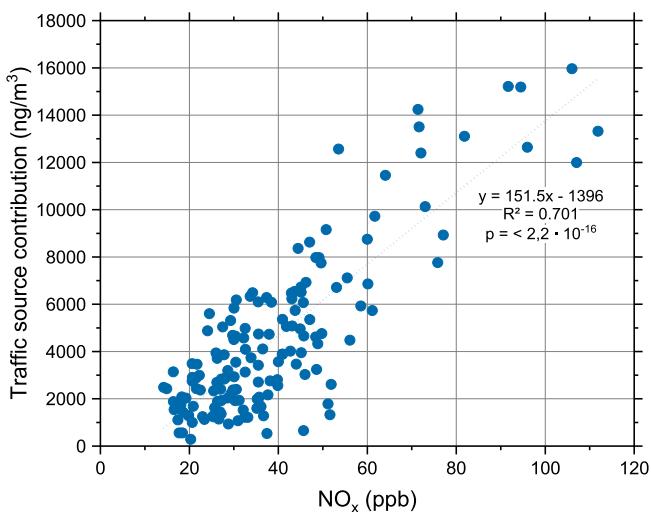


Fig. 8. Plot of the Traffic source contribution (ng/m^3) vs the concentration of NO_x (ppb).

component(s).

Factor 4 is the most important source contribution and is responsible for 27.3% ($4138.0 \text{ ng}/\text{m}^3$) of the $\text{PM}_{2.5}$ concentrations. This factor showed high loadings for eBC (~69%), moderate loadings for NO_3^- (~19%) and the presence of trace amounts of metals such as Pb, Cu, Zn, Mn, Fe, Cr, Ba. These species are known to be markers of the different components of traffic aerosol. Carbon and NO_3^- are considered tracers for tail pipe emissions (Jiang et al., 2005), Zn for the combustion of lubricating oil - (Viana et al., 2008), Ba, Cu, Fe, Mn, Zn, Cr and Pb for brake wear (Sternbeck et al., 2002; Schauer et al., 2006; Amato et al., 2011; Figi et al., 2010), and Pb & Zn for tyre wear (Pakbin et al., 2010; Amato et al., 2011). Ca is indicative of a contribution from re-suspended road dust, due the fact that all the surface outcrops in Malta are constituted of limestone. The tracer species associated with this factor indicate that this most probably is a "total traffic factor" including exhaust and abrasion components. The traffic source contribution showed a good correlation ($r^2 = 0.7$) with the NO_x levels in ppb measured at the site (Fig. 8), similar to e.g. Minguillón et al. (2012). This supports the attribution of this factor to traffic. The traffic source contribution does not show the expected decrease from the weekdays to the weekends as was the case in numerous other studies e.g. Brook et al. (2007), Aldabe et al. (2011), Cusack et al. (2013), etc. Fig. 5, however, shows that the $\text{PM}_{2.5}$ aerosol traffic component has a marked seasonal trend, increasing throughout autumn and winter (4932.3 and $6947.4 \text{ ng}/\text{m}^3$ respectively) and decreasing during spring and summer (2927.5 and $2149.6 \text{ ng}/\text{m}^3$ respectively). The differences between the seasonal averages are statistically significant ($p < 0.05$), with the exception of the difference between spring and summer. NO_x also shows a winter maximum and a summer minimum (average values 50.3 ppb and 29.5 ppb , respectively). The difference between weekday and weekend NO_x levels is also not statistically significant. This is attributed to the fact that there is not much difference between the weekday and weekend traffic flows in this area, while congestion increases greatly after the summer period when the schools start, and peaks during the winter months. In addition, the reduction of the height of the mixing layer in winter could lead to a concentration of air pollutants near the surface. Vanderstraeten et al. (2010) have shown that short term (from one day to the next) decreases in traffic flows are not always accompanied by lower PM levels. The polar plot in Fig. 7, is exactly what one would expect from a traffic derived pollutant measured at a

traffic station i.e. the highest concentrations occurring at the measurement site (the origin).

The factor profile for Factor 5 is characterized by Cl, Na and Mg. These species together with their relative abundance are used to identify the sea salt component of atmospheric particulate matter (APM). The ratios Cl/Na or Cl/Mg in the source profile in Fig. 3 (1.6 and 14.0, respectively) compare well with the reference values for sea water (1.8 for Cl/Na and 14.9 for Cl/Mg) in Seinfeld and Pandis (2016), hence the labelling of this factor as "Fresh sea salt". The average contribution of this factor to $\text{PM}_{2.5}$ levels was of 4.6% ($694.0 \text{ ng}/\text{m}^3$). The contribution of this Factor reaches its maximum during spring and its lowest during summer (Fig. 5), respectively the seasons with the highest (seasonal average 3.4 m/s) and the lowest (seasonal average 2.4 m/s) wind speeds. Stronger winds are associated with the formation of higher amounts of sea salt aerosol through an invigoration of the bubble bursting mechanism, (Marelli, 2007). Additionally, the polar plot in Fig. 7 associates high source contributions for this factor with winds blowing from the sea.

The 6th Factor is responsible for most (~65%) of the Na in the $\text{PM}_{2.5}$ and is the second most important source of SO_4^{2-} and NO_3^- . The ratio of Na/Mg is 8.3 and is the same as the ratio of these two elements in sea water, Seinfeld and Pandis (2016) It is therefore likely that these two elements have a marine origin. Another noteworthy feature of this factor is the almost complete absence of Cl, which indicates that a chemical reaction has used up this element. This factor was therefore labelled "aged sea salt" and its contribution to $\text{PM}_{2.5}$ was 12.7% ($1927.3 \text{ ng}/\text{m}^3$). The contribution of this factor, is highest during spring and summer (Fig. 5), this is due to the increased photo oxidation of SO_2 (Hidy, 1994) and NO_2 (Matsumoto and Tanaka, 1996) during the warmer months. The contribution peaked during spring, probably due to the fact that in 2016, the highest wind speeds in Malta were registered during this season (MIA, unpublished data) and the formation of sea salt is dependent on wind. The polar plot in Fig. 7, shows that the highest concentrations of "aged sea salt" aerosol are associated with winds from the Easterly and Westerly directions. The receptor lies at the bottom of a valley (located to the NW - W) and the development of relatively slow speed re-circulation patterns due to the valley and the sea (all along the Easterly directions) allows time for the SO_2 and NO_2 (both locally emitted and/or transported) to react with the sea salt particles, which are readily available in the Maltese islands.

Factor 7 is the second most important source contributing 23.6% ($3572.7 \text{ ng}/\text{m}^3$) of the $\text{PM}_{2.5}$ and is characterized by high contributions of SO_4^{2-} and NH_4^+ . The sulfate/ammonium equivalents ratio of approximately 1 (1.1) suggests that $(\text{NH}_4)_2\text{SO}_4$ is the dominant component of this aerosol source, and the factor was in fact labelled "ammonium sulfate". As expected, the "Ammonium Sulfate" factor shows a marked seasonal cycle, with the highest average contribution registered during summer (Fig. 5). The difference between the average of the contribution during the "hot", "intermediate" and "cold" months (respectively, $6221.0 \text{ ng}/\text{m}^3$, $2689.5 \text{ ng}/\text{m}^3$ and $1444.0 \text{ ng}/\text{m}^3$) was statistically significant ($p < 0.05$). The increased oxidation rates of the SO_2 precursor during the months with the highest insolation (Hidy, 1994; Polissar et al., 2001; Song et al., 2001; Kim et al., 2004) explains the increase in the source contribution during the hotter months. In view of the fact that the oxidation of SO_2 to H_2SO_4 is rather slow (Querol et al., 1998), sulfates are considered to be indicators of "aged" air masses (Manousakis et al., 2017), and they are often attributed to regional/long range transport, Viana et al. (2008). Fig. 6b, shows that for trajectories reaching Msida at 1500 m AGL, high contributions of ammonium sulfate are associated with air parcels passing over continental Europe, particularly Italy, and further corroborates the attribution of this factor. The mass contribution of the ammonium

sulfate factor ($\sim 3.6 \mu\text{g}/\text{m}^3$) is not much different from that estimated in our previous work (Scerri et al., 2016) for PM_{10} at a rural background site ($\sim 3.9 \mu\text{g}/\text{m}^3$), despite the fact that the sampling campaign for this work was held at least three years after the first one. This shows that as expected the ammonium sulfate component occurs mostly in the finer fraction of PM_{10} .

Source apportionment studies, are likely to include an undetermined fraction and in all probability, studies reporting full apportionment of the PM mass are most probably overestimating the contribution of the identified sources, Viana et al. (2008). In our study the unassigned fraction of 8.8% ($1338.0 \text{ ng}/\text{m}^3$) implies that more than 90% of the particulate mass was apportioned. The unassigned mass can be explained as being due to structural water (Yubero et al., 2011), artefacts caused by hysteresis in the deliquescence/efflorescence cycle (EPA, 2004), and also due to analytical uncertainties. The seasonal differences in the undetermined portion of $\text{PM}_{2.5}$ (Fig. 5), were not statistically significant.

4. Discussion

4.1. Reliability of the 7 factor solution

The reliability of the chosen model depends *inter alia* on ensuring that a global minimum in the Q-parameter has been achieved by PMF. In order to ensure this, PMF was run 20 times, with 20 iterations per run and with each run starting at a different pseudo-random seed, similar to Koçak et al. (2011) or Kara et al. (2015). Scaled residuals for the modelled species were all within the range of -3 to $+3$, with the majority of them normally distributed, therefore adding confidence in the chosen solution (Friend et al., 2012; Li et al., 2013). The coefficients returned by MLRA were all positive, indicating that the number of fitted factors was not excessive, Buzcu et al. (2003). Source profiles (**F** matrix) were scaled by dividing the species in each profile by the respective scaling constants from the MLRA and summed over each source profile. For all 7 scaled source profiles the sums were <1 (ng/ng) and therefore the number of fitted factors was not too low, Hopke (2001). The solution with 7-factors was thus considered to be a physically valid solution, Buzcu et al. (2003). Furthermore, the use of *inter alia*, $\text{PM}_{2.5}$ (or any other total species), and of more than one carbon fraction, as a fitting species in PMF could give rise to issues of double counting, Reffet et al. (2007). In this work, this was avoided by not inputting $\text{PM}_{2.5}$ in PMF and hence determining the source contributions by MLRA, as well as by including only the most relevant carbon fraction (eBC). Additionally, the authors are of the opinion that the inclusion of OC would not have led to the isolation of more sources, because biomass burning is not that important in Malta and all the sources affecting the receptor and for which OC can be used as a tracer species can be identified by the presence of EC (or eBC in our case). The ability of the model to recalculate ambient particle levels was quantified through the coefficient of divergence or CD, calculated according to the equation in Buzcu et al. (2003). A CD ~ 1 is interpreted as meaning that the measured and modelled values are substantially different (Wongphatarakul et al., 1998), while lower values such as the one calculated for this work (CD of 0.28) indicate the identification of all sources contributing to the mass of $\text{PM}_{2.5}$, Buzcu et al. (2003). The stability of the chosen solution was investigated by performing a bootstrap (BS) on it, as recommended by Brown et al. (2015). Overall, 100 BS runs were performed on the 7-Factor solution. The factors were reproduced 100% of the time, implying a well-defined model. In addition, DISP showed no factor swaps, indicating stability for the chosen number of factors. BS-DISP showed a minimal number of factor swaps (1–4) and 96% of the samples were accepted indicating that the error estimates for the accepted

Table 1a
Previous studies in coastal locations in the Western Mediterranean. Pandolfi et al. (2011); Viana et al. (2007); Amato et al. (2009); Amato et al. (2016b); Pérez et al. (2016); Pérez et al. (2016); Viana et al. (2005); Viana et al. (2007); Pandolfi et al. (2011); Amato et al. (2011); Pandolfi et al. (2014); Amato et al. (2014); Amato et al. (2016b).

Receptor	$\text{PM}_{2.5}$ $\mu\text{g}/\text{m}^3$	Traffic	Crustal	Secondary Sulfate	Secondary Nitrate/Aged Sea Salt	Shipping	Fresh Sea Salt	Other	Article
Algeciras (Spain) U	24.2	35.8 (8.7)	8.5 (2.1)*	26.4 (6.4)	8.1 (2.0)	9.5 (2.3) [†]	4.1 (1.0)	7.6 (1.8)	Pandolfi et al., (2011)
Algeciras (Spain) UT	25.0	26.0 (6.5)	4.0 (1.0)*	25.0 (6.3)	12.0 (3.0)	11.0 (2.8) [†]	6.0 (1.5)	16.0 (4.0)	Amato et al., (2014)
Barcelona (Spain) UT	22.5	53.0 (11.9)	20.0 (4.5)*	15.0 (3.4)	—	—	5 (1.1)	7.0 (1.6)	Viana et al., (2007)
Barcelona (Spain) U	27.7	40.0 (11.1)	13.0 (3.6)*	20.0 (5.5)	19.0 (5.3) [†]	6.0 (1.7) [†]	—	2.0 (0.6)	Amato et al., (2009)
Barcelona (Spain) UB	15.0	20.0 (3.0)	7.0 (1.1)	38 (5.7)	16.0 (2.4) [†]	5.0 (0.8) [†]	—	14.0 (2.1.)	Amato et al., (2016b)
Barcelona (Spain) port	17.6	18.8 (3.3)	19.9 (3.7)*	17.6 (3.1)	4.6 (0.8) [†]	13.6 (2.4) [†]	—	25.5 (4.5)	Pérez et al., (2016)
Barcelona (Spain) U	18.1	16.6 (3.0)	2.2 (0.4)*	32.6 (5.9)	5.0 (0.9) [†]	5.5 (1.0) [†]	—	38.1 (6.9)	Pérez et al., (2016)
Bobadela (Portugal) SU	24.0	22.0 (5.3)	16.0 (3.8)*	25 (6.0)	—	8.0 (1.9) [†]	8.0 (1.9)	21.0 (5.0)	Almeida et al., (2005)
Huelva (Spain) UT	18.1	35.0 (6.3)	24.0 (4.3)*	24.0 (4.3)	—	—	7.0 (1.3)	10 (1.8)	Viana et al., (2007)
La Línea (Spain) U	23.4	27.8 (6.5)	8.8 (2.1)*	33.3 (7.8)	8.2 (1.9)	10.3 (2.4) [†]	3.9 (0.9)	5.1 (1.2)	Pandolfi et al., (2011)
La Línea (Spain) UT	20.0	25.0 (5.2)	5.0 (1.1)*	34.0 (6.9)	11.0 (2.3)	13.0 (2.7) [†]	9.0 (1.9)	1.0 (0.1)	Amato et al., (2014)
Los Barrios (Spain) U	31.9	24.5 (7.8)	14.9 (4.8)*	30.5 (9.7)	7.6 (2.4)	8.3 (2.6) [†]	4.6 (1.5)	9.6 (3.1)	Pandolfi et al., (2011)
Los Barrios (Spain) UT	22.0	25.0 (5.0)	5 (1.0)*	34.0 (6.8)	11.0 (2.2)	13.0 (2.6) [†]	3.9 (0.9)	7.8 (1.8)	Amato et al., (2014)
Málaga (Spain) T	23.0	33.0 (7.6)	23.0 (5.3)*	17 (3.9)	—	12.0 (2.8) [†]	10 (2.3)	5.0 (1.2)	Amato et al., (2014)
Porto (Portugal) T	27.0	37.0 (10.0)	15 (4.7)*	13.0 (3.5)	5.0 (1.4)	—	4.0 (1.1)	26.0 (7.0)	Amato et al., (2016b)

UI = urban industrial site, U = urban site, UT = urban traffic site, UB = urban background site, SU = sub urban site and T = traffic site.

*Includes Saharan dust, [†]was included with a fuel oil combustion factor, [‡]isolated both a secondary nitrate factor and an aged sea salt factor.

Other includes other anthropogenic factors as well as unassigned fractions.

Shaded rows indicate studies in which the sampling was carried out less than 5 years or less before this one.

resamples were in all probability both robust and reliable (Paatero et al., 2014) and that the solution is acceptable (Achilleos et al., 2016). The mass of the carbonaceous component of particulate matter was measured using a purely optical method rather than the more widely used thermo-optical methods. Thermo-optical methods require the collection of PM on QF membranes rather than PTFE (or polycarbonate) ones. In order to carry out the source apportionment exercise, a reliable chemical characterization of the PM_{2.5} on the filter is required and QF filters are less well suited for chemical analysis than e.g. PTFE membranes. This is due to their thickness, the presence of contaminants as well as their chemical composition, Massabò et al. (2013). The distribution of particulate matter on the filter is also much less homogenous on QF than on PTFE filters. Vecchi et al. (2009), have also highlighted the fact that the comparison of PM sampled on different media can be problematic due to both positive and negative artefacts. Furthermore, different thermal protocols are currently employed in the thermo-optical analysis (CEN/TR 16243, 2011) and this leads to wide disagreements between results (Subramanian et al., 2006; Piazzalunga et al., 2011).

4.2. Comparative phenomenology of PM_{2.5} in mediterranean coastal urban areas

Tables 1a–c compare the results of 16 different source apportionment studies carried out in 19 different receptors throughout the Mediterranean, from 2001 to date. When comparing these results to those for the current study, one should keep in mind that in this study a sample which is representative of the whole year was analyzed, while some of the studies in Tables 1a–c are based on seasonal samples. This places a limit on the comparability, due to the seasonality of sources such as shipping, traffic, secondary inorganic aerosol, etc. Another factor to keep in mind when comparing source apportionment results across these sites, is the fact that the sites are located in different urban setups, some of them are heavily affected by industrial emissions, while some others by both industrial and traffic emissions, while Msida is affected by traffic emissions, and effects of industrial emissions are not measurable. For the comparative exercise, Msida (Malta) was together with Lecce and Naples (Italy) and Tunis (Tunisia) included in the Central Mediterranean cluster. The PM_{2.5} levels measured in this study (15.1 µg/m³) were not much different from the levels determined in Lecce and Naples (14.4 and 16.0 µg/m³). The levels determined in Tunis were significantly higher (25.0 µg/m³). Similar levels (15.0–18.1 µg/m³) of PM_{2.5} were measured in the Western Mediterranean cluster for studies involving sampling carried out in 2013 and 2014 (with the exception of Porto). The other studies in this cluster reported higher concentrations 20.0–31.9 µg/m³ (with the exception of Huelva). The more recent studies (2012–2014) in the Eastern Mediterranean cluster measured a similar range of PM_{2.5} levels at an urban and suburban site in Cyprus (12.3–14.7 µg/m³) and urban and suburban sites in Athens (11.0–18.0 µg/m³), and higher concentrations in Thessaloniki (25.9–33.3 µg/m³).

The mineral dust fraction in Malta, is due to the advection of crustal material from the Saharan region and contributes 15.1% (2.3 µg/m³) of the PM_{2.5} average concentration. The study in Lecce determined a total crustal fraction which was shown to be significantly influenced by Saharan dust. However, in contrast to Malta, only 2 Saharan events were identified throughout the monitoring period, which might explain why the Saharan contribution was not separated from the other sources of dust. The source apportionment in Tunisia was carried out by chemical mass closure. This approach does not manage to isolate the different crustal components and therefore the 20.0% reported for this site is a total crustal contribution. In spite of this, it is expected that most of the 5 µg/m³

Table 1b
Previous studies in coastal locations in the Central Mediterranean and this study. Cesari et al. (2016); Cesari et al. (2003); D'Alessandro et al. (2003); Kchih et al. (2015).

Receptor	PM _{2.5} µg/m ³	Traffic	Crustal	Secondary Sulfate	Secondary Nitrate/Aged Sea Salt	Apportionment % (µg/m ³)	Shipping	Fresh Sea Salt	Other	Article
Lecce (Italy) U	16.0	37.2 (6.0)	9.7 (1.6)*	24.3 (3.9)	11.1 (1.8)	-	4.2 (0.7)	13.5 (2.2)	Cesari et al. (2016)	
Lecce (Italy) UB	14.4	16.5 (2.4)	17.6 (2.5)*	29.7 (4.3)	11.0 (1.6)	-	3.6 (0.5)	21.5 (3.1)	Cesari et al. (2016)	
Msida (MALTA) T	15.1	27.3 (4.1)	15.1 (2.3)	23.6 (3.6)	12.7 (1.9)	5.0 (0.8)	4.6 (0.7)	11.7 (1.8)	THIS STUDY	
Naples (Italy) U	16.0	39.0 (6.2)	24.0 (3.8)	-	-	6.0 (1.0) [†]	12.0 (1.9)	19.0 (3.0)	D'Alessandro et al. (2003)	
Tunis (Tunisia) U	25.0	24.0 (6.0) ^{††}	20.0 (5.0)*	20.0 (5.0)**	-	-	1.6 (0.4)	34.4 (8.6)	§Kchih et al. (2015)	

U = urban site, UB = urban background site, T = traffic site.

*was included with a fuel oil combustion factor, [†]Study was carried out using chemical mass closure, ^{**}Includes Saharan dust, ^{††}Included in an anthropogenic pollution factor, [§]secondary inorganic aerosol factor, which is mostly secondary sulfate.

Other includes other anthropogenic factors as well as unassigned fractions.

Shaded rows indicate studies in which the sampling was carried out less than 5 years or less before this one.

Table 1 Previous studies in coastal locations in the Eastern Mediterranean. Amato et al. (2016b); Diapouli et al. (2017); Manousakis et al. (2017); Diapouli et al. (2017); Diapouli et al. (2017).

Receptor		Apportionment % ($\mu\text{g}/\text{m}^3$)						Article
Locality (Country)	PM _{2.5} $\mu\text{g}/\text{m}^3$	Traffic	Crustal	Secondary Sulfate	Secondary Nitrate/Aged Sea Salt	Shipping	Fresh Sea Salt	Other
Athens (Greece) SU	11.0	20.0 (2.2)	12.0 (1.3)	33.0 (3.6)	6.0 (3.7)	7.0 (0.8)†	1.0 (0.1)	21.0 (2.3)
Athens (Greece) UB	18.0	20.0 (3.6)	2.0 (0.4)*	25.0 (4.5)	—	6.0 (1.1)†	2.0 (0.4)	45.0 (8.1)
Athens (Greece) SU	12.4	10.0 (1.2)	7.0 (0.9)*	55.0 (6.8)	—	4.0 (0.5)†	1.0 (0.1)	23.0 (2.9)
Larnaca (Cyprus) U	13.2	19.0 (2.5)	13.0 (1.7)*	38.0 (5.0)	—	13.0 (1.7)†	1.0 (0.1)	16.0 (2.1)
Limassol (Cyprus) U	12.7	25.0 (3.2)	17 (2.2)*	32.0 (4.1)	—	10.0 (1.3)†	2.0 (0.3)	14.0 (1.8)
Nicosia (Cyprus) U	14.7	24.0 (3.5)	14.0 (2.1)*	31.0 (4.6)	—	8.0 (1.2)†	2.0 (0.3)	21.0 (3.1)
Paphos (Cyprus) U	12.3	16.0 (2.0)	12.0 (1.5)*	48 (5.9)	—	6.0 (0.7)†	2.0 (0.2)	16.0 (2.0)
Patras (Greece) U	21.8	33.0 (7.2)	2.0 (0.4)	33.0 (7.2)	—	10.0 (2.2)	8.0 (1.7)	14.0 (3.1)
Thessaloniki (Greece) UB	25.9	7.0 (1.8)	2.0 (0.5)*	33.0 (8.5)	20.0 (5.2)	—	2.0 (0.5)	36.0 (9.3)
Thessaloniki (Greece) T	33.3	37.0 (2.3)	2.0 (0.7)*	18.0 (6.0)	—	—	2.0 (0.7)	23.0 (7.7)

Other includes other anthropogenic factors as well as unmentioned fractions

such as massaging the face well as well as

Shaded rows indicate significant differences between Saha and ductile

metres Saharan dust.

reported for this site are due to desert dust. The study in Naples labels the factor as "soil dust" and does not delve into the origin of the dust. Crustal source contributions in the Western Mediterranean cluster ranged from $0.4 \mu\text{g}/\text{m}^3$ in Barcelona to $5.3 \mu\text{g}/\text{m}^3$ in Málaga. In most of the studies this contribution is mainly due to Saharan dust, however the models do not separate the two crustal sources. For the Eastern Mediterranean cluster, the contribution of the crustal source (which also includes Saharan dust) ranged between 0.4 and $2.2 \mu\text{g}/\text{m}^3$ (both measured in Athens).

The traffic contribution in Malta 27.3% ($4.1 \mu\text{g}/\text{m}^3$) is in between the contributions registered by the stations in Lecce 16.5–37.2% ($2.4\text{--}6.0 \mu\text{g}/\text{m}^3$), while that in Naples is somewhat higher 39% ($6.2 \mu\text{g}/\text{m}^3$). For both the Western Mediterranean and the Eastern Mediterranean clusters, the range for the traffic contribution is wider than that for the Central Mediterranean and extends from 16.6 to 53.0% ($3.0\text{--}11.9 \mu\text{g}/\text{m}^3$) for the former and ~7–37% (~ $1\text{--}12.3 \mu\text{g}/\text{m}^3$) for the latter.

In our study, only a secondary sulfate fraction was isolated, contributing 23.6% ($3.6 \mu\text{g}/\text{m}^3$) this is not much different from the contribution in Lecce 24.3–29.7% ($3.9\text{--}4.3 \mu\text{g}/\text{m}^3$). The secondary aerosol fraction for Tunis represents a total secondary inorganic fraction and this was responsible for 20.0% ($5.0 \mu\text{g}/\text{m}^3$) of the total PM_{2.5} concentration. Porto and Málaga (Western Mediterranean cluster) estimated similar source contributions of secondary sulfate aerosol ($\sim 3.7 \mu\text{g}/\text{m}^3$), the apportionment was however different due to differences in composition. In general, however the secondary aerosol source contribution for this cluster was generally higher ($3.5\text{--}9.7 \mu\text{g}/\text{m}^3$). Similarly, the contribution of this source in the Eastern Mediterranean cluster ranged between 3.6 and $8.5 \mu\text{g}/\text{m}^3$.

Two sea salt contributions (fresh and aged) were isolated in both Malta and Lecce, while only a fresh sea salt contribution was isolated in Naples. The contributions of both fractions in Malta are similar to those in Lecce: 4.6% ($0.7 \mu\text{g}/\text{m}^3$) in Malta and 3.6–4.2% ($0.5–0.7 \mu\text{g}/\text{m}^3$) in Lecce, for the fresh fraction and 12.7% ($1.9 \mu\text{g}/\text{m}^3$) for the aged fraction in Malta compared to 11.1% ($\sim 1.8 \mu\text{g}/\text{m}^3$). The contribution of fresh sea salt in Naples is much higher than in Malta, 12.0% ($1.9 \mu\text{g}/\text{m}^3$) while that for Tunis was lower 1.6% ($0.4 \mu\text{g}/\text{m}^3$). Overall fresh sea salt accounts for an approximately a similar fraction in the Eastern cluster 1.0–2.0% ($0.1–0.7 \mu\text{g}/\text{m}^3$), with some exceptions, and a higher fraction in the Western cluster (3.9–10.0% or $0.9–2.3 \mu\text{g}/\text{m}^3$). It is noted that for the latter cluster the contributions are more similar to the one in Naples. Aged sea salt concentrations in the Central Mediterranean were $\sim 2 \mu\text{g}/\text{m}^3$. This is roughly similar to the concentration determined for the Western Mediterranean $\sim 2.4 \mu\text{g}/\text{m}^3$ (with some exceptions), while for the Eastern Mediterranean the concentration of this component was generally higher (3.7–6.0 $\mu\text{g}/\text{m}^3$).

In the Central Mediterranean shipping contributions were isolated in Malta (5%) and Naples (6%) only, with the source contributions $\sim 1 \mu\text{g}/\text{m}^3$. These results compare well with the 8% apportioned by [Becagli et al. \(2012\)](#) for Lampedusa. In most of the studies in the Western Mediterranean shipping was included with a fuel oil combustion factor, while the contribution of shipping in the Algeciras Bay (La Linea, Los Barrios and Algeciras) was slightly higher than for Malta 8.3–13.0% ($\sim 2\text{--}3 \mu\text{g}/\text{m}^3$). In the Eastern Mediterranean cluster, a shipping contribution was isolated in Patras (10.0% or $2.2 \mu\text{g}/\text{m}^3$).

In summary, when comparing the receptor sites across the Mediterranean with PM_{2.5} levels within the 12–18 µg/m³ range, the following conclusions are made: Secondary sulfate contributions in both the Western and the Eastern Mediterranean are higher than in the Central Mediterranean, while traffic tends to contribute more in the Central Mediterranean. Shipping contributes more in the Western than in the Central or Eastern Mediterranean.

4.3. Implications for compliance with the WHO guidelines

The levels of PM_{2.5} registered at the Msida station (the station which registers the highest levels in Malta for all pollutants except ozone), have since the establishment of the monitoring programme always been below the limit value established by Directive 2008/50/EC of 25 µg/m³. This limit value is however not sufficiently protective of human health, and to date no safe threshold for PM_{2.5} has been established (WHO, 2006). In fact, the WHO AQGs for PM_{2.5} are substantially lower. It is at this stage worth mentioning that the US and Japan have already adopted PM_{2.5} limit values, which are closer to the WHO guidelines. In order to close this gap, in 2013 the European Commission issued "The Clean Air Programme for Europe". One of the major aims of this programme was to achieve the necessary emission reductions which would allow the EU to tighten its limit value for PM_{2.5}, towards the WHO air quality guidelines, (European Commission, 2013). The EU plans to achieve these reductions *inter alia* through its 2020 commitments under the Gothenburg Protocol to the Convention on long range trans-boundary air pollution (CLRTAP).

In this context the role of natural contributions to PM_{2.5} levels is important for all the Mediterranean countries. A significant portion of the PM_{2.5} levels in urban areas is due to dust advected from the Northern African desert (15.1% for this study), while the contribution of fresh sea salt to PM_{2.5} levels in coastal areas is non-negligible too. The Saharan contribution will have an impact on the compliance with the (future) daily limit value, while the sea salt contribution will affect the annual limit value of PM_{2.5}. This means that guidelines for the subtraction of exceedances due to both sources should be developed along the lines of the Commission guidelines for the subtraction of natural sources, (European Commission, 2011), which currently apply to PM₁₀ only. The authors would like to stress that exempting natural contributions from regulatory compliance should not be taken to mean that natural sources have no health repercussions, but rather that these sources should be subtracted due to the fact that it is not possible to control them.

Secondary ammonium sulfate aerosol is a major contributor to PM_{2.5} levels in the "Central Mediterranean" (3.6–4.3 µg/m³) as well as in the other regions of the Mediterranean. The formation of secondary aerosols is largely dependent on ammonia levels EEA (2015). This is not surprising given that emissions of SO₂ have decreased by over 70% from 2000 to 2016, while emissions of NH₃ have decreased by <10% over the same period (EEA, 2016). It is evident that a regional (and perhaps a hemispheric) effort, in the form of emission standards for industrial farms, is required in order to reign in the atmospheric levels of NH₃. The EU member states have pledged to cumulatively achieve a 6% reduction in ammonia over 2005, by 2020 (UNECE, 2015). It is not that simple to estimate the resultant decrease in (NH₄)₂SO₄ concentrations, however Backes et al. (2016) estimated that an 11% reduction in NH₃ emissions achieves a 3% reduction in NH₄⁺ levels. Assuming an identical decrease in NH₄⁺ levels for a 6% reduction in NH₃ emissions, will therefore result in a negligible decrease in the secondary sulfate immission levels.

Shipping has been shown to contribute measurably to the PM_{2.5} levels in coastal cities all over the Mediterranean. Additionally, the shipping factor isolated in this study was rich in BC, a component known to have serious implications for human health e.g. Highwood and Kinnersley (2006), Kulkarni et al. (2006), Suglia et al. (2008). Therefore, there is an even greater need to control emissions from shipping, (still relatively under regulated when compared to the land-based sources). The countries along the North Sea have for example managed to plug this regulatory gap with the imposition of a pollutant emission control area (so far only for SO₂ and NO_x) for all the ships sailing within this area.

The negligible decrease expected in the secondary sulfate levels in the Central Mediterranean by 2020 as well as the inertia in regulating shipping emissions, places most of the burden in achieving the WHO guidelines for PM_{2.5} levels by 2020, on reductions from traffic. This is especially true for countries like Malta, where the impact of industrial emissions on PM_{2.5} levels is marginal. If the EU were to deliver on its pledges to the Gothenburg Protocol, it would have to decrease PM_{2.5} emissions from traffic by ~36%, from the current levels to those set by Amann et al. (2012), see Section SM4 in the electronic supplement. Assuming an equivalent decrease in the traffic contribution would cause an overall decrease in PM_{2.5} levels of 6–14% to ~13 µg/m³ (see Section SM5 in the electronic supplement), meaning that compliance with the WHO guidelines would be achieved only after the contributions of natural sources are subtracted.

Fireworks, despite their marked seasonality, have been shown to contribute measurably to the annual levels of ambient PM_{2.5} in Malta. Despite the fact that fireworks displays are not uncommon in Southern Italy and Sicily, the intensive fireworks related activity during the summer is a purely Maltese phenomenon and is considered a "traditional" socio-cultural pastime which is practiced by over 1500 enthusiasts. Fireworks mixtures in Malta include potassium perchlorate as an oxidizer (Vella et al., 2015). Aerosol produced by the blasting of fireworks is therefore likely to contain amongst other components, traces of unreacted perchlorate, which is known to inhibit the uptake of iodine in the thyroid (Wolff, 1998; Greer et al., 2002) therefore reducing thyroxine and triiodothyronine production.

5. Conclusion

This study was conducted in the Central Mediterranean, a region for which the PM_{2.5} levels have not been as extensively characterized as for example the Western or the Eastern Mediterranean. The sources isolated for this receptor are considered to characterize well a coastal site in the region. In all, seven sources were identified: traffic (27.3%), secondary sulfate/ammonium sulfate aerosol (23.6%), Saharan dust (15%), aged sea salt aerosol (12.7%), shipping (5%), fresh sea salt (4.6%) and fireworks (2.9%).

This study has highlighted the following issues: Traffic should be targeted in order to achieve reductions in PM_{2.5} levels in the medium-short term and enable compliance with the WHO air quality guidelines; the countries in the Mediterranean should follow the example of the North sea countries with respect to the imposition of a pollutant emission and control area for ships sailing within the region; and in order to reduce the levels of ammonium sulfate the countries in the region should lobby (with the EU and with other supra-national organisations) for stricter ammonia control measures. Furthermore, this is the first study of its sort to highlight the effect of fireworks on PM_{2.5} levels. We are of the opinion that this should serve to start a discussion on limiting the health effects due to this "pastime".

Future work should try to isolate the different traffic components (tail-pipe, abrasion and resuspension), and this should in turn serve to determine the effect of replacing conventionally powered vehicles with low emission vehicles, on PM_{2.5} levels and guide the policy maker accordingly.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.07.104>.

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Corrigendum

Corrigendum to “Estimation of the contributions of the sources driving PM_{2.5} levels in a Central Mediterranean coastal town” [Chemosphere 211 (2018) 465–481]



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The authors regret that Fig. 3 had the wrong labelling on the primary y-axis, which should have been species concentration (ng/m³) and not source contribution (ng/m³). The figure with the correct labelling is provided here. We apologise for any inconvenience.

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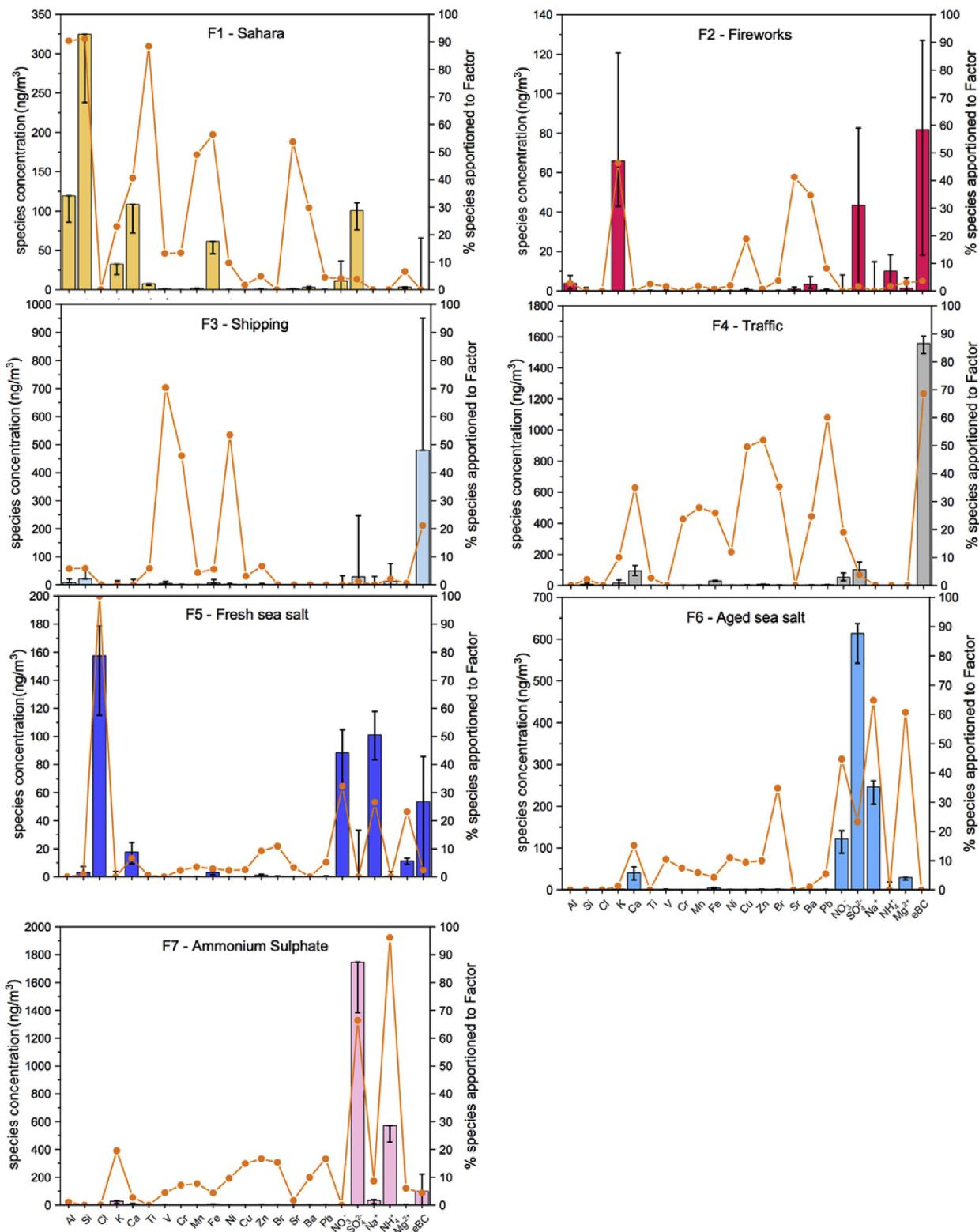


Fig. 3: Factor profiles (bars) and percentage of species apportioned to each factor (orange line).

Supplementary Material

Table SM1: Industrial activity near the receptor

Name	Plant Description	Distance from receptor	Activity Data
Waste Oils Plant	(2×) 3.25 MW _{th} boilers	~ 1.3km to the SSE	300t fuel oil
Bunkering Plant	(3×) 1.25 MW _{th} boilers	~ 1.3km to the SSE	50t light fuel oil & 22t gas diesel oil
M5	(1×) 121 MW _{th} OCGT ^a	~1.7km to the SSE	47t gas diesel oil ^b
Incinerator	rotary kiln incinerator	~2.3km to the SSE	5000 – 7000 t waste/yr

^aOpen cycle gas turbine

^bOperated for only 9.7 hours in 2016

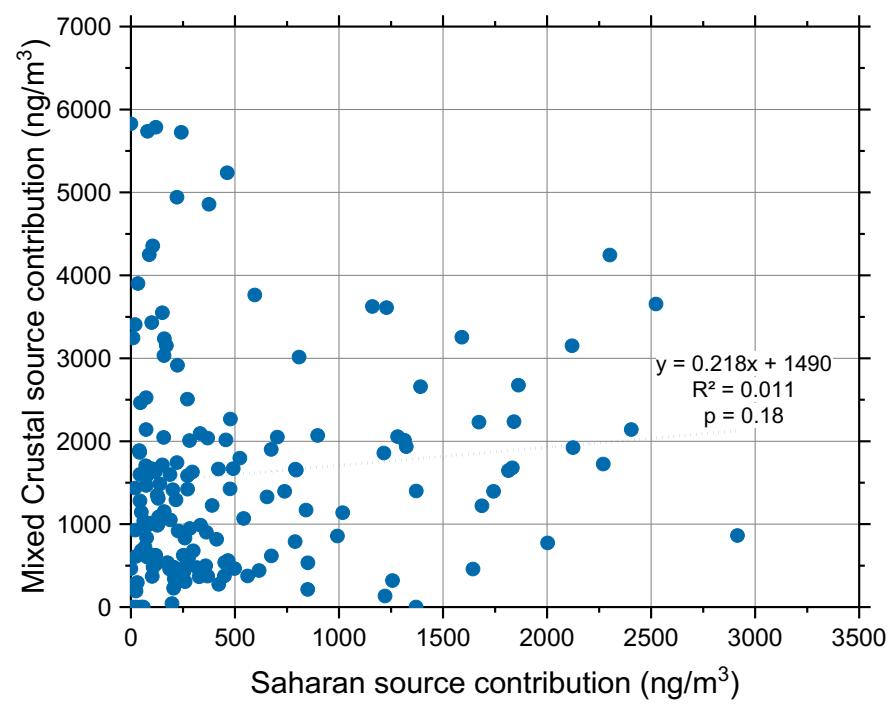
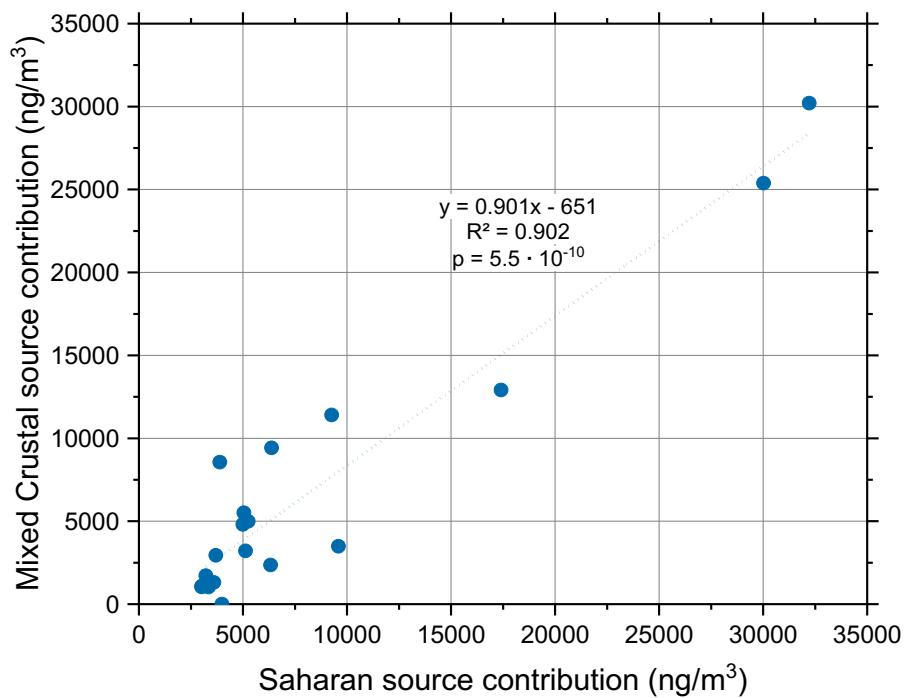


Figure SM2: Plot of the Ca-rich source contribution vs. the Si-rich source contribution Si-rich source contribution $> 3000\text{ng}/\text{m}^3$ (top) and Si-rich source contribution $< 3000\text{ng}/\text{m}^3$ (bottom).

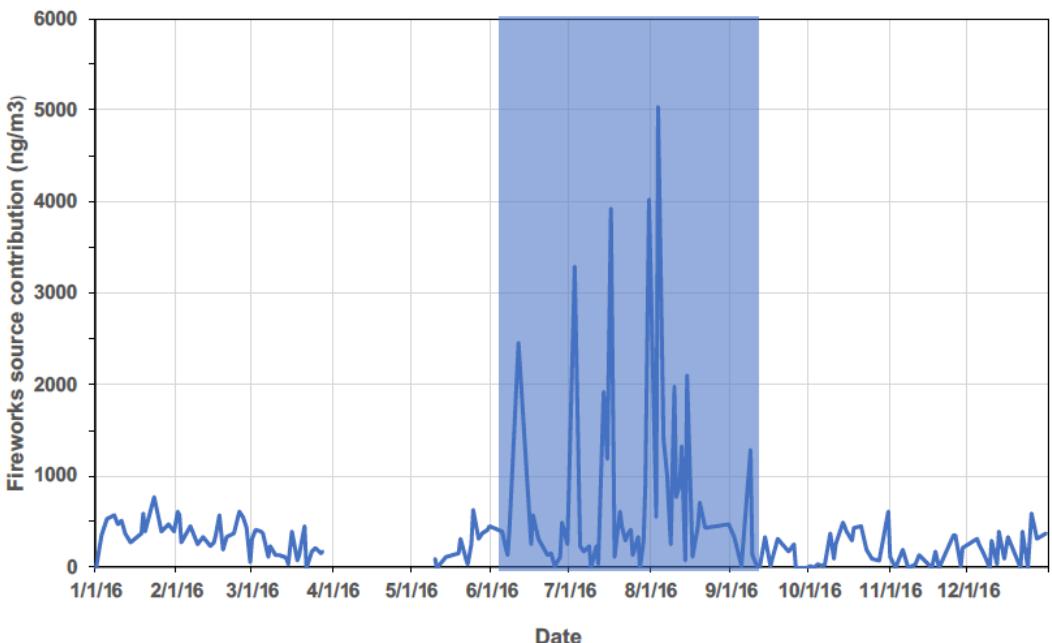


Figure SM3: Temporal variation for the fireworks source contribution. The blue shaded part shows the fireworks season.

Section SM4: Calculation of the required percentage decrease in PM_{2.5} emissions by road traffic

The total PM_{2.5} emissions from road transport by the EU28 in 2015 was 146.7 kt (EEA, 2018).

For the EU to meet its target under the Gothenburg protocol of a 22% reduction in PM_{2.5} emissions relative to 2005 it would have to reduce PM_{2.5} emissions to 94 kt by 2020 (Amann *et al.*, 2012)¹.

Therefore, assuming that the PM_{2.5} emissions from road transport by the EU28 in 2016 are not much different from what they were in 2015, means that ~36% reduction in PM_{2.5} emissions from this sector is required.

Section SM5: Calculation of the percentage reduction in total PM_{2.5} levels resulting from a 36% in the traffic source contribution.

Site	Concentration PM _{2.5} in $\mu\text{g}/\text{m}^3$	Traffic source contribution in $\mu\text{g}/\text{m}^3$	-36% reduction in the Traffic source contribution in $\mu\text{g}/\text{m}^3$	New concentration of PM _{2.5} in $\mu\text{g}/\text{m}^3$	Percentage reduction in the PM _{2.5} concentration
Lecce (urban)	16.0	6.0	3.8	13.8	13.8%
Lecce (urban background)	14.4	2.4	1.5	13.5	6.3%
Naples	16.0	6.2	4.0	13.8	13.8%
Malta	15.1	4.1	2.6	13.6	10%

¹ The report on which the EU based its pledged emission reductions, to the amended Gothenburg Protocol of the 1979 Convention on Long-range Transboundary Air Pollution.

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Paper III

Investigating the plausibility of a PMF source apportionment solution derived using a smaller dataset: A case study from a receptor in a rural receptor in Apulia - South East Italy. [Chemosphere 236 (2019) 124376], available from

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Investigating the plausibility of a PMF source apportionment solution derived using a small dataset: A case study from a receptor in a rural site in Apulia - South East Italy

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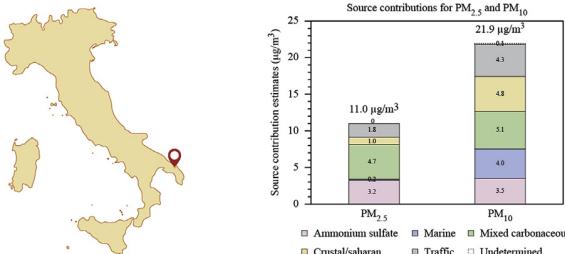
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GRAPHICAL ABSTRACT



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ABSTRACT

Results of a methodological study on the use of Positive Matrix Factorization (PMF) with smaller datasets are being reported in this work. This study is based on 29 PM₁₀ and 33 PM_{2.5} samples from a receptor in a rural setup in Apulia (Southern Italy). Running PMF on the two size fractions separately resulted in the model not functioning correctly. We therefore, augmented the size of the dataset by aggregating the PM₁₀ and PM_{2.5} data. The 5-factor solution obtained for the aggregated data was fairly rotationally stable, and was further refined by the rotational tools included in USEPA PMF version 5. These refinements include the imposition of constraints on the solution, based on our knowledge of the chemical composition of the aerosol sources affecting the receptor. Additionally, the uncertainties associated with this solution were fully characterised using the improved error estimation techniques in this version of PMF. Five factors in all, were isolated by PMF: ammonium sulfate, marine aerosol, mixed carbonaceous aerosol, crustal/Saharan dust and total traffic. The results obtained by PMF were further tested *inter alia*, by comparing them to those obtained by two other receptor modelling techniques: Constrained Weighted Non-negative Matrix Factorization (CW – NMF) and Chemical Mass Balance (CMB). The results of these tests suggest that the solution obtained by PMF, is valid, indicating that for this particular airshed

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1. Introduction

Airborne Particulate Matter (APM) is used by the World Health Organization (WHO) as a proxy indicator for ambient air pollution. PM₁₀ and PM_{2.5} (collectively referred to in this article as PM_x) are currently, the most commonly used metrics for the measurement of ambient levels of particulate air pollution, and hence of population exposures. These fractions of APM are respectively labelled, as the thoracic convention and the "high-risk" respirable convention (ISO 7708, 1995). The definition for both PM₁₀ and PM_{2.5} in ISO 7708 (1995) is based on their ability to penetrate through a size selective orifice at a 50% efficiency for an aerodynamic diameter cut-off at 10 µm for PM₁₀ and at 2.5 µm for PM_{2.5}. The evidence gathered from epidemiological studies shows that both short- and long-term exposures to APM have deleterious effects on human health, (WHO - World Health Organisation, 2000; Pope and Dockery, 2006), with PM₁₀ affecting mostly the former, and PM_{2.5} identified as a stronger risk factor with respect to the latter. Various time series studies, spanning across different cities, have found a statistically robust association between increases in daily mortality and daily increases in both PM₁₀ (Levy et al., 2000; Stieb et al., 2002; Braga et al., 2001) and PM_{2.5} levels (Schwartz, 2000, 2003). For both aerosol fractions mortality results from *inter alia* cardiovascular or respiratory causes (Samet et al., 2000; Analitis et al., 2006). On the other hand, the relationship between chronic exposure to airborne aerosol and cardiopulmonary mortality is particularly strong for the finer fraction or PM_{2.5} (Dockery et al., 1993; Pope et al., 1995, 2004; Jerrett et al., 2005). Additionally, associations between hospital admissions and daily increases in both PM₁₀ (Zanobetti et al., 2000; Le Tertre et al., 2002; COMEAP, 2006) and PM_{2.5} (Dominici et al., 2006; Stafoggia et al., 2013) have been established. Long-term exposures to PM_{2.5} have been reported to accelerate the progress of chronic disease (McMichael et al., 1998) and increase the incidence of non-fatal cardiovascular events (Miller et al., 2004). Vulnerability to particulate air pollution is particularly severe for the elderly and for children as well as for people with pre-existing cardiac or pulmonary disease (WHO - World Health Organisation, 2013). Cohen and Pope (1995) and Samet and Cohen (1999) have also suggested that particulate matter may lead to small increases in the risk of lung cancer incidence.

In the European Union, atmospheric levels of these two aerosol fractions are regulated by Directive, 2008/50/EC (2008), which sets an annual limit value of 25 µg/m³ for PM_{2.5} and two limit values for PM₁₀: an annual limit value (ALV) of 40 µg/m³ and a daily limit value (DLV) of 50 µg/m³ (which should be complied with at least 90.4% of time). The DLV is normally more difficult to comply with than the ALV (EEA - European Environment Agency, 2017), and in fact Querol et al. (2004) have shown (that at least for Spain) complying with the annual limit value is not enough to guarantee compliance with the daily limit value 90.4 percent of the time. The air quality guidelines (AQGs) in WHO - World Health Organisation (2006) are considerably stricter for both PM_{2.5} (ALV of 10 µg/m³ and a DLV of 25 µg/m³) and PM₁₀ (ALV of 20 µg/m³ and a DLV of 50 µg/m³). It is worth pointing out that adverse health effects cannot be excluded even for these levels, as no safe threshold for particulate matter has been determined (Pope and Dockery, 2006). Notwithstanding this, according to EEA - European Environment Agency

(2017), a considerable fraction of the population in the EU continues to be exposed to levels of particulate matter above the WHO's AQGs (82–85% for the PM_{2.5} ALV and 50–62% for the PM₁₀ DLV).

Atmospheric aerosols are complex mixtures of different chemical constituents. They are either emitted directly as primary aerosol or form as a result of chemical reactions between precursors (secondary aerosol). Both primary aerosols and the precursors to secondary aerosols can result from either anthropogenic or natural sources. The identity as well as the contribution of the different sources influencing particulate matter (PM) levels at a receptor are estimated reliably using receptor modelling techniques (Viana et al., 2008; Belis et al., 2013). Receptor models relying on multivariate statistical methods (such as Positive Matrix Factorization – PMF), require the inputting of a matrix composed of a relatively large number of samples to function correctly (Belis et al., 2014). A number of publications have sought to define objective criteria aimed at establishing the minimum number of samples for use with these receptor models. However, the issue is far from settled. Some publications have attempted to derive criteria based on the relationship between the number of samples (m) and the number of chemically characterised species (n) or between the latter and the degrees of freedom or v, (calculated from m and n). Henry et al. (1984), suggest that the ratio of v/n, should not be less than 30 and preferably 50 or even 100. On the other hand, according to Thurston and Spengler (1985) the difference between m and n should be more than 50. Ito et al. (1986), consider the "Henry criterion" to be reasonable however, they conclude that, the complexity of the airshed under study should determine the minimum acceptable number of samples, which for their study (based in New Jersey) was found to be 70. Brown and Hafner (2005) (as cited in Belis et al., 2014) and Johnson et al. (2011) conclude that 50 chemically characterised samples are the absolute minimum. The user guide for the United States Environment Protection Agency – USEPA PMF version 3 (Norris, 2008) simply states that "multiple" samples are required for PMF and that as a "rule of thumb", a concentrations' matrix made up of 100 or more samples is normally used for studies on PM_{2.5}. This "rule of thumb" was carried over to the user guide for USEPA PMF version 5 (Norris et al., 2014), at least as far as the sample size is concerned. This inclusion did not take into consideration the fact that in contrast to PMF version 3, PMF version 5 includes more elaborate methods for the determination of the uncertainties associated with rotational ambiguity (the lack of a physically valid and unique model), which is often an issue with smaller datasets (<100 samples). Manousakas et al. (2017), managed to obtain a well constrained solution for a dataset made up of 50 samples, through the imposition of constraints on the sources' chemical composition and the use of these error estimation methods in USEPA PMF version 5. It has also been shown that the number of samples available for PMF can be increased by grouping together concentrations of the same species measured: at different receptor typologies or for different aerosol size fractions (Belis et al., 2011; Beuck et al., 2011; Mooibroek et al., 2011; Contini et al., 2012; Larsen et al., 2012; Xie et al., 2012; Cesari et al., 2016). In addition Rai et al. (2019) have shown that when sampling time is constrained, PM can be sampled and analysed at hourly intervals (in order to increment the number

of characterised samples). However this could raise issues when dealing with health related studies or with studies related to compliance with air quality standards because both WHO AQGs and limit values are based on either daily or yearly averaged concentrations.

However, there are conceivable situations (due to *inter alia* budgetary, time or receptor accessibility constraints) in which studies involving smaller sample sizes are from a practical perspective unavoidable. This seems to be the case for most health-related studies. In fact, it is not infrequent for PM exposure studies to be based on shorter term measurement campaigns resulting in a low number of samples (<100) (e.g. Csobod et al., 2010; Simoni et al., 2010; Cibella et al., 2014; Balzan et al., 2015; Fsadni, 2015; Sunyer et al., 2015). Additionally, these studies have rarely relied on source apportionment methodologies to identify (and quantify) the sources driving the PM levels, even though a chemical characterization of the PM fraction might have been carried out, (see e.g. Balzan et al., 2015). The fact that source apportionment studies have traditionally required a (relatively) large number of samples is perhaps the major barrier restricting their use in exposure studies, even though they could yield valuable information on the health effects of the different PM components. The principal aim of the current study is a fundamental methodological issue, involving the handling of a relatively small dataset (such as the ones used in many exposure studies) made up of a total of 29 PM₁₀ and 33 PM_{2.5} samples (for a total of 62 samples), such that USEPA PMF version 5, can return a well constrained solution, free from rotational ambiguity. Due to the fact that the assumption behind the technique of aggregating speciation data from both size fractions is that the source profiles for PM₁₀ and PM_{2.5} are similar, we chose to sample PM at a relatively less complex airshed. In addition, the validity of the solutions returned by PMF will be assessed using a number of statistical parameters, as well as through the use of other receptor modelling techniques such as Constrained Weighted Non-negative

Matrix Factorization (CW – NMF) and Chemical Mass Balance (CMB).

2. Experimental

2.1. Sampling

A sampling campaign for both PM₁₀ and PM_{2.5} (PM_x) was carried out between the 17 September and the 16 October 2015 at a rural station along the Brindisi – Casalabate coast in Apulia (South Eastern Italy), see Fig. 1. The receptor which is at an elevation of 30 m above mean sea level (AMSL), is situated in a highly agricultural area, at ~3 km to the East of a four-lane, major, motor way: the "Super Strada Brindisi – Lecce, SS613" and within ~0.5 km of the Adriatic coast. The sampling station is most of the times downwind of a number of sources in Brindisi (~7 km to the North west) and Taranto (~70 km to the West) due to the development of local/regional air re-circulation patterns, which are a characteristic of the Salento (Cesari et al., 2016).

A total of 29 PM₁₀ and 33 PM_{2.5} samples were collected using two Hydra dual channel sequential samplers (FAI Instruments Srl, Rome, Italy) fitted with CEN 12341 (2014) sampling heads for both PM₁₀ and PM_{2.5}. One of the cassettes of both the PM₁₀ and the PM_{2.5} sampler was loaded with 47 mm diameter, pre-heated, quartz fiber (QF) filters (type 1851-047) manufactured by Whatman (GE Health Care Life Sciences, Buckinghamshire, UK). The QF filters were thermally treated at 550 °C for 1 h as per CEN/TR 16243 (2011) and were subsequently used for the determination of organic carbon (OC) and elemental carbon (EC). Teflon® membranes (7952-104) having a diameter of 46.2 mm (and a pore size of 2 µm) manufactured by Whatman (GE Health Care Life Sciences, Buckinghamshire, UK), were loaded in the remaining cassettes of both samplers and used for the analysis of metals and ions. The filters were exposed for 24 h, at a constant flow rate of 2.3 m³/h (with a precision of better

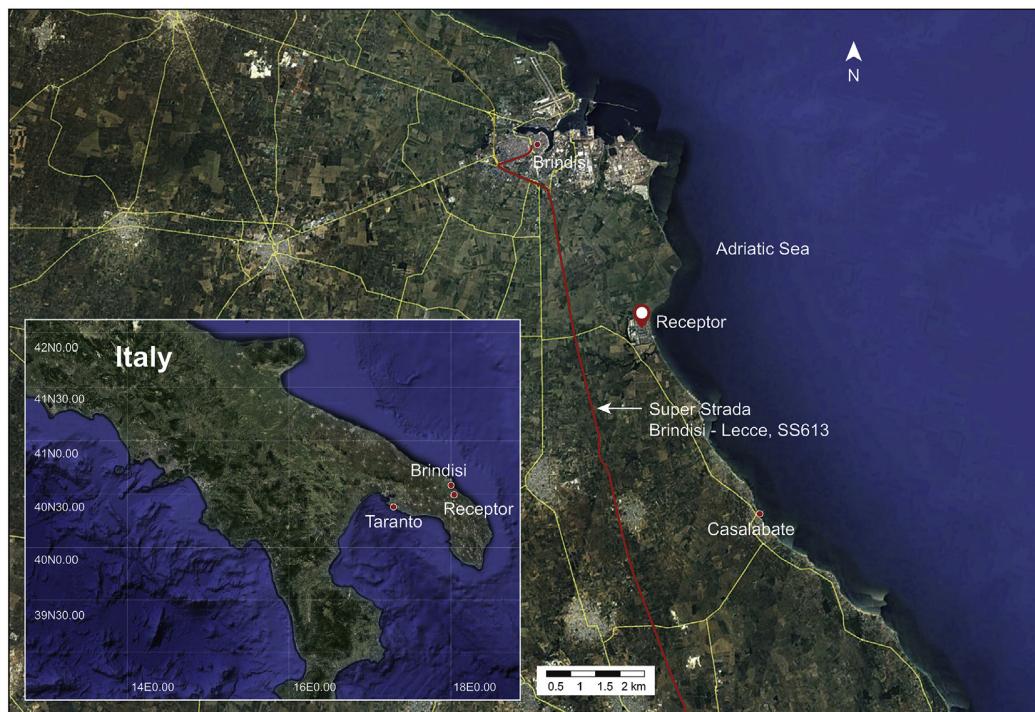


Fig. 1. Location and characterization of the receptor.

than 2%). Before and after the exposure, the filters were conditioned for 48 h at a temperature of $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and at a relative humidity of $50\% \pm 5\%$, in an Activa climatic chamber (Aquaria Srl, Milan, Italy). Subsequently the filters were massed manually on an XS205DU microbalance (Mettler – Toledo, Greifensee, Switzerland). The mass of each filter was measured three consecutive times in order to ensure that the difference between the subsequent measurements was $\leq 20\text{ }\mu\text{g}$. The expanded uncertainties for the mass concentrations of PM_x are less than 5%. The PM_x mass concentrations on the QF and Teflon® membranes were comparable and were on average within $\pm 1\text{ }\mu\text{g/m}^3$ of each other, which is within the experimental uncertainty.

2.2. Analytical procedures

Fig. 2 shows a schematic diagram summarizing the procedures used to characterize both the PM_{10} and the $\text{PM}_{2.5}$ filters by X-ray Fluorescence spectroscopy (XRF), Ion Chromatography (IC) and the thermo-optical transmittance instrument while **Table 1** lists the analytes analyzed by each of these instruments. A more detailed description of the analytical procedures can be found in Section SM2 of the electronic supplement.

2.3. Data analyses

2.3.1. Positive Matrix Factorization, constraint weighted – non-negative Matrix Factorization and chemical mass balance

In this study, Positive Matrix Factorization (PMF) was used in order to apportion the mass of PM_{10} and $\text{PM}_{2.5}$. The results obtained by PMF were subsequently checked against those obtained by Constrained Weighted Non-negative Matrix Factorization (CW – NMF) and Chemical Mass Balance (CMB). Receptor models such as PMF (Paatero and Tapper, 1994; Paatero, 1999), CW – NMF (Delmaire et al., 2010a, 2010b; Hleis, 2010) and CMB (Watson, 1979, 1984) identify and apportion the sources of airborne PM by solving equation (1) (in CMB, the sources profile matrix is inputted by the modeller):

$$\mathbf{X} = \mathbf{G} \times \mathbf{F} + \mathbf{E} \quad (1)$$

PMF and CW – NMF solve equation (1) by decomposing the species concentration matrix \mathbf{X} into the factor contributions matrix \mathbf{G} and the factors profile matrix \mathbf{F} , with the constraint that all the elements in \mathbf{G} (or g_{ik}) and \mathbf{F} (f_{kj}) are positive (or non-negative). \mathbf{E} is the difference between the measured and fitted term. In PMF and CW – NMF, the factor contributions matrix and the factor profiles

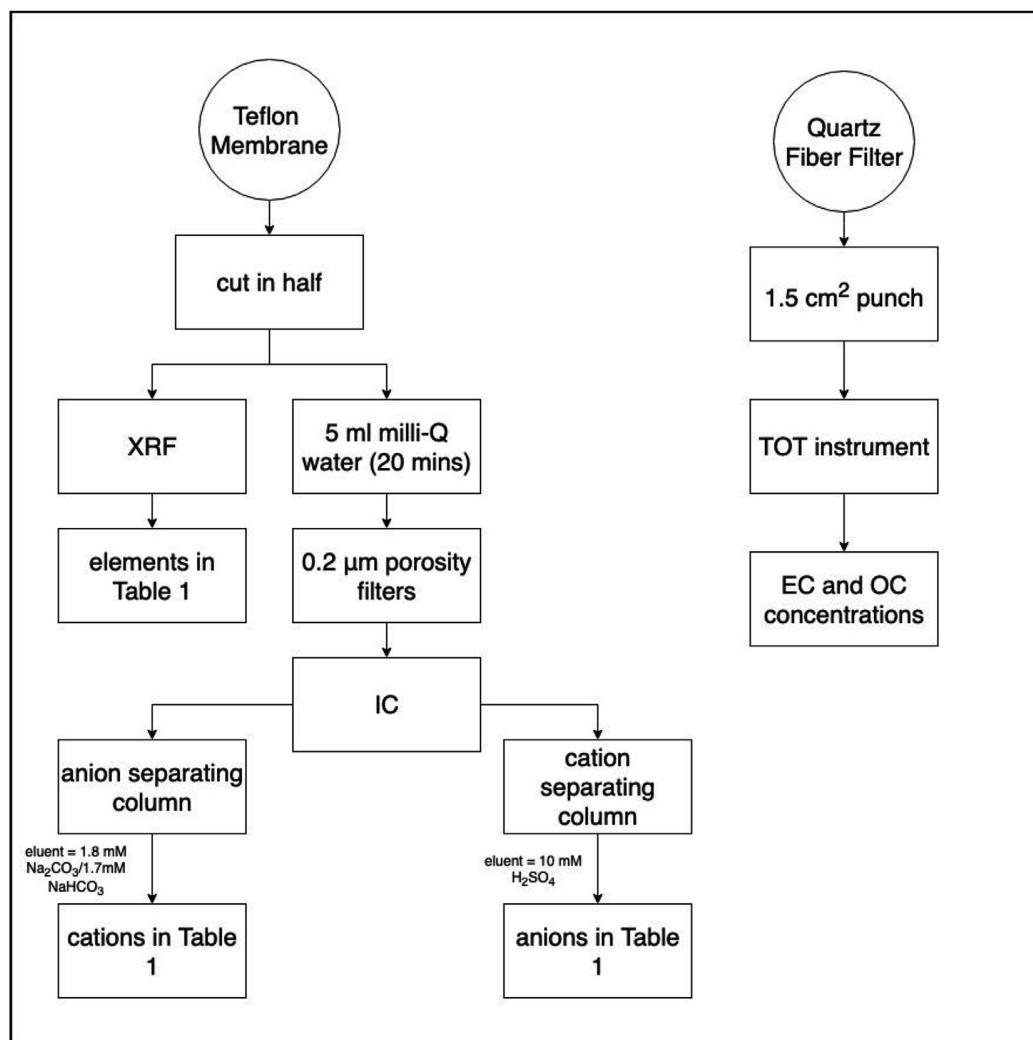


Fig. 2. Schematic diagram for the filter analysis procedure for both PM_{10} and $\text{PM}_{2.5}$.

Table 1

Instrument used for the analysis of each analyte in both the PM10 and the PM2.5 samples.

Analyte	Analyte Type	Instrument
OC EC	Carbonaceous	Thermo-optical transmittance
Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺	Cation	Ion chromatograph
Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻	Anion	
Si Ca Ti V Fe Ni Cu Zn	Element	X-ray Fluorescence Spectroscopy

matrix are estimated using an optimization method, which minimizes the quality of fit parameter (or Q) in equation (2):

$$Q = \sum_{i=1}^m \sum_{j=1}^n \frac{1}{u_{ij}^2} \cdot \mathcal{D}^{(\alpha, \beta)} \left(x_{ij}, \left(\sum_{k=1}^p g_{ik} f_{kj} \right) \right) \quad (2)$$

Where: k is the number of factors, u_{ij} is the uncertainty matrix for \mathbf{X} (x_{ij}) and weights each of the measurements in the species concentration matrix by its uncertainty, and $\mathcal{D}^{(\alpha, \beta)}$ is a function representing the alpha-beta divergence. PMF selects $\alpha = \beta = 1$, reducing equation (2) to its more commonly cited form, see e.g. Norris et al. (2014) and performs its optimization using the weighted least squares method. The CW – NMF optimization algorithm, on the other hand, enables the selection of different values for α and β (Delmaire et al., 2019) in order to find more robust solutions and uses the alternating least squares algorithm to iteratively minimise the term on the right-hand side of equation (2), for fixed \mathbf{F} and respectively \mathbf{G} . CW – NMF enables the modeller to refine the factor profiles matrix \mathbf{F} , by imposing constraints on it using any available knowledge on the chemical composition of the sources contributing to the PM levels. The constraints can take the form of equality relationships (Limem et al., 2014a), which force a determined species in a source profile to a particular value, or else of inequalities (Limem et al., 2014b), which force the value of a species in a specific profile to a preset interval. This makes the profiles less subject to local minima during the calculation process (Kfouri et al., 2016).

USEPA PMF version 5 was used in the current study. Due to the small number of samples for both aerosol size fractions (29 for PM₁₀ and 33 for PM_{2.5}) the two datasets were aggregated into a single dataset. This is possible when the sources affecting both size fractions have similar chemical profiles and temporal variabilities and has the advantage of increasing the number of samples available for PMF. It is worth mentioning that this procedure has already been successfully used in previous source apportionment studies (e.g. Amato et al., 2009; Pandolfi et al., 2011; Contini et al., 2014; Tian et al., 2014; Contini et al., 2016; Airuse. eu, 2018). The size of the aggregated dataset is higher than that of Manousakas et al. (2017) and should enable a good resolution of the factors with PMF. When considering the likely sources of PM_x at the receptor the concentrations of Na⁺, K⁺ and Mg²⁺ rather than the respective elemental concentrations (determined by XRF) were used. Additionally, the elements with a large percentage of samples ($\geq 80\%$) below the detection limit (BDL) were omitted. This effectively

meant that only OC, EC, Si, Ca, Ti, V, Fe, Ni, Cu, Zn, Na⁺, K⁺, Mg²⁺, NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻ were inputted in PMF (EC, Ni, Cu, Zn, Mg²⁺, K⁺ and NO₃⁻ were downweighted to “weak”, further information can be found in Section SM 3 of the electronic supplement). Uncertainties and values BDL were treated as suggested by Norris et al. (2014). PM_x concentrations were not inputted into PMF in order to avoid issues of double counting, Reff et al. (2007). An overall uncertainty of 5% was added to the model in order to account for any possible underestimations in u_{ij} , (Reff et al., 2007).

The CW – NMF model used in this study was developed by the Laboratoire d'Informatique Signal et Image de la Côte d'Opal (LISIC) at the University of Littoral Côte d'Opal (Calais, France) and was run with 100000 iterations. The same concentrations matrix (\mathbf{X}) and uncertainty matrix (\mathbf{U}) as for PMF were used as inputs. The uncertainties inputted into the CW – NMF model took into account the downweighting of the species in PMF as well as any additional user-added, overall uncertainty.

CMB requires full knowledge of the sources affecting the PM levels at the receptor site, because the model requires the inputting of the chemical composition of these sources or source profiles (f_{jk} or the \mathbf{F} matrix) as well as the uncertainty matrix for the source profiles ($u_{f_{jk}}$). In addition, both the species concentrations measured in each sample (x_{ij}) as well as their respective uncertainties ($u_{x_{ij}}$) are also required. The algorithm used by CMB adopts the weighted least squares method in order to minimise the χ^2 parameter in equation (3) and determine the source contributions' matrix (g_k or \mathbf{G}):

$$\chi^2 = \sum_{j=1}^{j=m} \left[\frac{\left(x_{ij} - \sum_{k=1}^p f_{jk} g_k \right)^2}{u_{x_{ij}}^2 + \sum_{k=1}^p u_{f_{jk}}^2 g_k^2} \right] \quad (3)$$

By assuming that $\mathbf{F}(f_{jk})$ is perfectly known, the use of CMB is not limited by the number of samples, to the extent that it can be used on just 1 sample (Belis et al., 2014), this is in contrast to both PMF and CW – NMF, where little prior knowledge is available on \mathbf{F} .

The results reported for CMB in this paper were obtained through the use of USEPA CMB version 8.2. The same species concentrations and measurement uncertainties as for PMF were inputted into the model together with source profiles and source profile uncertainties. Table 2 shows information on the source profiles which were used in the CMB modelling.

Table 2
Profiles used with CMB.

Factor	Type of Profile	Source:
ammonium sulfate	purely stoichiometric	not applicable
marine aerosol	database	SPECIEUROPE 2.0 profile 285
mixed carbonaceous aerosol	chemical mass reconstruction of PM ₁₀ collected in Brindisi/chemical characterization of carbonaceous species in PM ₁₀ and PM _{2.5} from the same area.	Genga et al. (2017) and Siciliano et al. (2018)
crustal/Saharan	chemical analysis of local/Saharan crustal material in PM ₁₀ from the area	Cesari et al. (2016)
total traffic	a combination of components of exhaust and non-exhaust emissions obtained from PM ₁₀ measurements in an underpass within the same area as the receptor	Cesari et al. (2016), SPECIEUROPE 2.0 profile 298

2.3.2. Multilinear regression analysis (MLRA)

The source contributions outputted by PMF and CW – NMF (the 62×5 elements of the \mathbf{G} matrix) were disaggregated into 29×5 factor scores related to the PM₁₀ dataset and the 33×5 factor scores related to the PM_{2.5} dataset. These factor scores were converted into source contribution estimates in $\mu\text{g}/\text{m}^3$ using the method in Song et al. (2001) i.e. by carrying out an MLRA using the PM₁₀ and PM_{2.5} mass concentrations as the dependent variable and the factor scores as the predictor variables. RStudio version 1.1.463 (Rstudio, Inc.) for Macintosh, was used to perform the MLRA. To date USEPA PMF version 5, does not estimate the errors in the source contribution estimates (Paatero et al., 2014). These errors were estimated for both PMF and CW – NMF from the standard errors for the coefficients returned by MLRA, which were converted into concentrations in order to estimate the error margins (Manousakas et al., 2015, 2017; Diapouli et al., 2017). These estimates can be considered to be minimum error estimates because they do not take into account errors due to profile uncertainty and errors due to rotational ambiguity (Manousakas et al., 2017).

2.3.3. Comparison between measured and reconstructed daily PM_x concentrations

The measured daily PM₁₀ and PM_{2.5} concentrations were compared to the concentrations reconstructed by the three models, by calculating the spread and the agreement between the measured and reconstructed mass, respectively the root mean square error (RMSE) defined by equation (4), and the absolute fractional bias (AFB), defined by equation (5).

$$RMSE = \sqrt{\frac{1}{m} \sum_{i=1}^m (M_i - g_i)^2} \quad (4)$$

$$AFB = \frac{2}{m} \times \sum_{i=1}^m \frac{|M_i - g_i|}{(M_i + g_i)} \quad (5)$$

where m is the number of samples, M_i is the measured daily mass concentration of PM_x and g_i is the sum of the 5 source contribution estimates on any day i ($\sum_{k=1}^5 g_{ik}$) during the sampling period or the reconstructed daily PM_x mass. The range of acceptability for the AFB is 0–2 (Cesari et al., 2016).

2.3.4. Concentration gradients

Source contributions for Saharan dust were further investigated using concentration weighted trajectories – CWTs, further details can be found in Hsu et al. (2003). 240 h backtrajectories for 2015, were obtained through HYSPLIT (Draxler et al., 2014; Stein et al., 2015) modelling, using the Reanalysis meteorological dataset, which has a latitude/longitude resolution of $2.5^\circ/2.5^\circ$. The trajectories were modelled for an arrival height of 1500 m above ground level (AGL), which is equivalent to a geopotential height of 850 hPa.

At this height the air parcels are in the upper part of the boundary layer and should not be influenced by surface artefacts, Salvador et al. (2008). Additionally, this height is considered representative of the mean transport winds at the synoptic scale (Stohl, 1998; Salvador et al., 2010). Section SM7, in the electronic supplement includes CWT plots for backtrajectories at arrival heights of 500 and 3000 m.

3. Results

3.1. Descriptive statistics and box and whisker plots

Section SM4 of the electronic supplement includes descriptive statistics for PM₁₀ and PM_{2.5} measurements and their respective chemical characterization as well as box and whisker plots for the PM₁₀ and PM_{2.5} measurements as well as for the 17 different species determined in both fractions.

3.2. PMF solution

Running the model with the datasets for the different PM fractions separately, led to the model not functioning correctly. For the aggregated dataset different PMF solutions were modelled with the number of fitted factors ranging from 4 to 8. The solution with the highest number of physically interpretable sources was the 5-factor solution. Additionally, IS – the maximum individual column standard deviation, IM – the maximum individual column mean and Q_{theoretical}/Q_{expected} were plotted versus the number of factors. These three plots showed sharp drops for 5 factors therefore confirming this solution (Lee et al., 1999). It is pertinent to point out that, the decision on the optimal number of factors to be fitted in PMF is a subjective one, in fact Vecchi et al. (2008) define PMF as a descriptive model.

3.3. Factor profiles

Figs. 3 and 4 respectively show the factor profiles and the source apportionment for PM₁₀ and PM_{2.5}. According to Paatero et al. (2014), uncertainty ranges for the source profile components should not (as is usually done) be reported as symmetric intervals and thus the 95th and 5th percentile of the bootstrapped runs were used to determine uncertainty ranges in Fig. 3.

Factor 1 is the most important source of both NH₄⁺ (>76%) and of SO₄²⁻ (~63%). The ratio of the equivalents of SO₄²⁻/NH₄⁺ is ~1, suggesting that this contribution is primarily (NH₄)₂SO₄ and it was therefore labelled "Ammonium sulfate". Ammonium sulfate contributes 29.4% of the PM_{2.5} ($3.2 \mu\text{g}/\text{m}^3$) and 16.0% of the PM₁₀ ($3.5 \mu\text{g}/\text{m}^3$). This is consistent with the fact that most of the (NH₄)₂SO₄ is expected to occur in the finer fraction due to its formation via a gas to particle conversion. The oxidation of one of the precursors of ammonium sulfate (SO₂) is rather slow (Querol et al., 1998) and therefore the presence of secondary sulfate aerosols is indicative of air mass "ageing" (Manousakas et al., 2017).

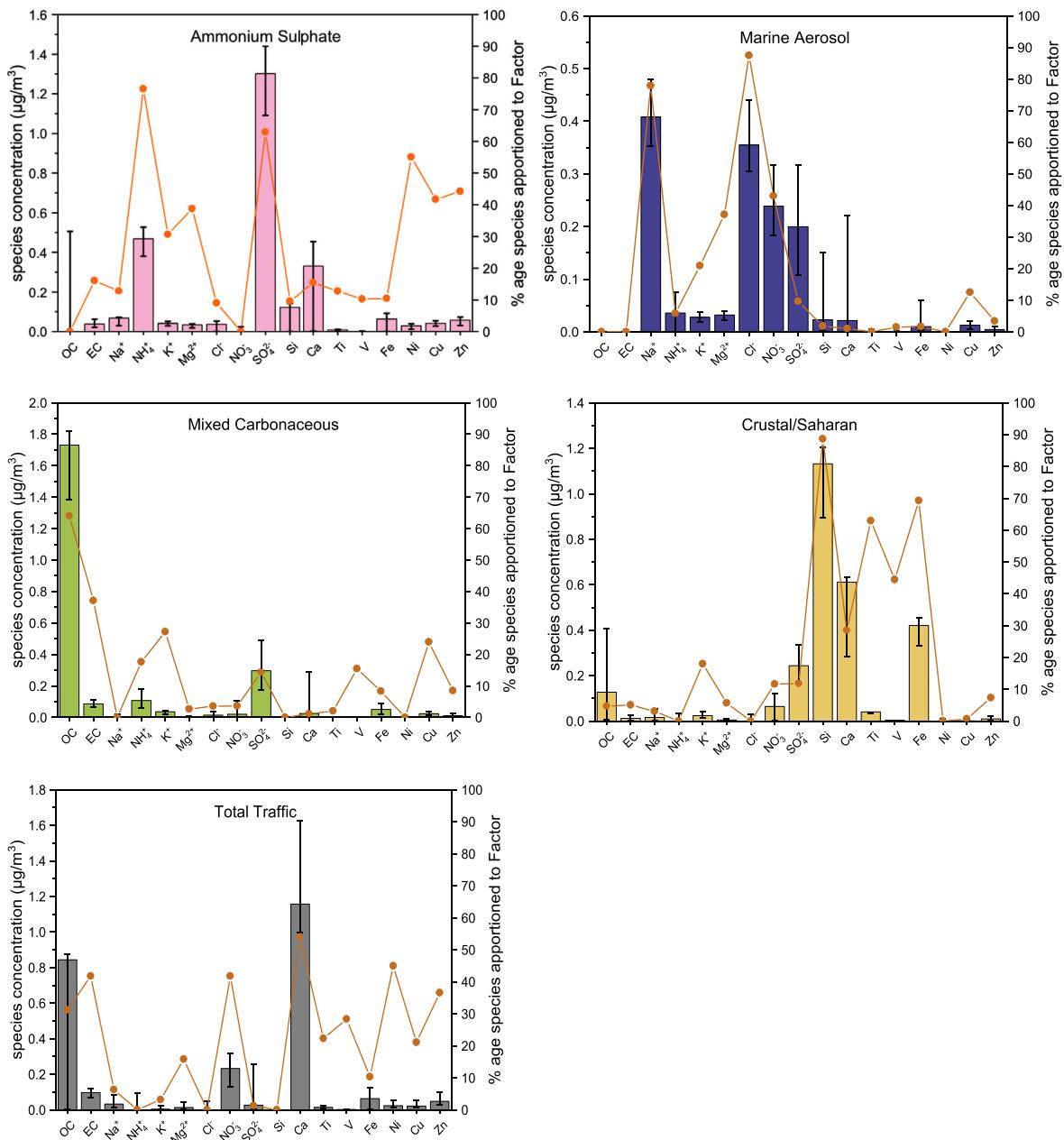


Fig. 3. Factor profiles (bars) and percentage of species apportioned to each factor (orange line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Additionally, secondary sulfate aerosol is more of regional issue due to its association with long range or regional transport (Viana et al., 2008). In fact, the concentrations determined for this site for both fractions are quasi-identical to those determined by Scerri et al. (2018) for $\text{PM}_{2.5}$ and Scerri et al. (2016) for PM_{10} at two different receptors in Malta, (concentrations of this factor in both PM_{10} and in $\text{PM}_{2.5}$ are higher by $0.4 \mu\text{g}/\text{m}^3$ for both studies).

Factor 2, is responsible for most of the mass of Na^+ and Cl^- (~78% and ~88%, respectively). The factor is also responsible for 37% of the Mg^{2+} and 43% of the NO_3^- and was therefore labelled "marine aerosol". The ratios Cl^-/Na^+ (0.88) and $\text{Cl}^-/\text{Mg}^{2+}$ (11.1) are lower than those for sea water (1.8 and 14.9 respectively). Despite the closeness to the coast, the factor is depleted in Cl^- , probably due to the reaction between NaCl and HNO_3 , which converts some of the

fresh sea salt into NaNO_3 and displaces the Cl^- as HCl (Pio and Lopes, 1998), explaining the nitrate content of the factor. Chloride depletion of marine aerosol in coastal sites was also reported by other studies e.g. Cesari et al. (2016) and Manousakas et al. (2017) for $\text{PM}_{2.5}$, Contini et al. (2010) for PM_{10} , etc. "Marine aerosol" is mostly found in the larger fractions of PM (Eleftheriadis et al., 2014) and in fact for this study, marine aerosol contributed 1.5% of the $\text{PM}_{2.5}$ ($0.1 \mu\text{g}/\text{m}^3$) and 18.4% of the PM_{10} ($4.0 \mu\text{g}/\text{m}^3$).

The factor profile for Factor 3 is dominated by the contribution of OC (~64% due to this factor). A comparison of this factor with the secondary organic aerosol (SOA) content, in PM_{10} and $\text{PM}_{2.5}$, which was calculated as per Section SM5 in the Electronic Supplement, shows a good correlation between the two, for both PM fractions, with a correlation coefficient of 0.91 for PM_{10} and 0.95 for $\text{PM}_{2.5}$, see

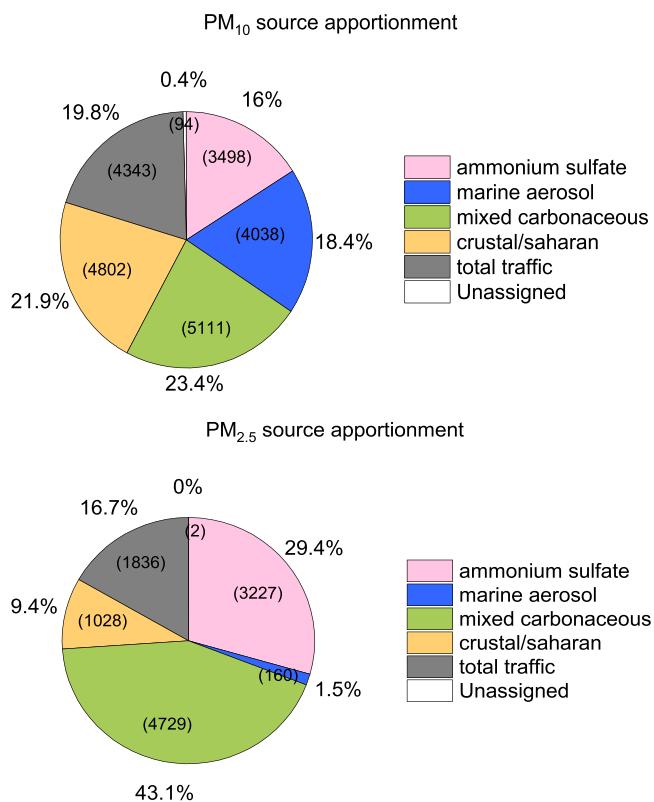


Fig. 4. PM₁₀ and PM_{2.5} source apportionment for Lido Cerano. The numbers in the brackets show the levels of the respective component in ng/m³.

Figure SM5 in the electronic supplement. However, the gradients in the same figure (1.41 for PM₁₀ and 1.91 for PM_{2.5}) show that the SOA calculation method estimates a lower contribution than the factor isolated by PMF. This is due to the fact that, the SOA calculation method estimates a “pure” secondary organic aerosol factor made up of OC only, while Fig. 3 shows that the PMF factor also includes contributions from other species, including tracers of biomass combustion EC (37%) and K⁺ (~27%). Factor 3 is probably a mixed carbonaceous aerosol made up of *inter alia*, aged aerosol from biomass burning, which has been shown to be one of the precursors of SOA (Hennigan et al., 2010, 2011; Cubison et al., 2011). The presence of an aged carbonaceous component is corroborated by the fact that Siciliano et al. (2018), showed that for the same dataset, the maximum concentration of OC, EC and SOA corresponded to airmasses incoming from Northeastern Europe. In Apulia, these air masses are associated with increases in the concentrations of secondary aerosol contributions (Di Gilio et al., 2015). The factor was labelled as “mixed carbonaceous aerosol” and is the most important source of PM_{2.5} (43.1% or 4.7 µg/m³) and of PM₁₀ (23.4% or 5.1 µg/m³), indicating that most of this factor exists in the finer fraction of PM₁₀.

The fourth factor is characterized by high loadings for a combination of metals Si, Ca, Ti and Fe, which is interpreted as a crustal source (Viana et al., 2008; Genga et al., 2012, 2018). The factor is the most important source of Si (>88%), Fe (~69%) and Ti (~63%) and the second most important source of Ca (~29%) and was labelled as “Crustal/Saharan” Factor. Figure SM6 in the electronic supplement shows the time-series for the source contribution for this factor. The days on which the source contributions peaked corresponded to the days in which PM₁₀ concentrations measured by monitoring stations in the region (Brindisi and Lecce) and at the site, peaked

together indicating that a regional phenomenon was responsible for this behavior. 240 hr back trajectories for air parcels reaching Lido Cerano at 500 m, 1500 m and 3000 m were run for these days and the forecasts of the World Meteorological Organization (WMO) Sand and Dust Storm Warning Advisory System (SDS WAS) and of the Monterey Model (U.S. Naval Research Laboratory) were checked for the same days. These checks confirmed that these days were indeed affected by Saharan dust intrusions. Additionally, the CWTs confirmed that for trajectories reaching the receptor at 1500 m, high source contributions are associated with air parcels spending most of the time over Algeria, Fig. 5. Trajectories incoming at the receptor at 500 m and 3000 m (see Figure SM6 in the electronic supplement) also confirm the Northwestern African origin of the air parcels associated with high concentrations of the Saharan source contribution. It can be seen from Figure SM6 in the electronic supplement, that very little would be left if the peaks due to the Saharan events are replaced by the mean of the days not affected by African dust, which is why we are of the opinion that this factor is probably exclusively due to the advection of dust from northern Africa. The presence of Ca is most probably due to the fact that the source region (North west Africa) is rich in limestone, (Scheuvens et al., 2013). The “Crustal/Saharan” factor is the second most important contributor of PM₁₀ and has a higher effect on this fraction than on PM_{2.5}. In fact it contributes only 9.4% of the PM_{2.5} (equivalent to 1.0 µg/m³) compared to 21.9% of the PM₁₀ (equivalent to 4.8 µg/m³). This is expected, since the contribution of mineral dust to PM₁₀ is normally higher than that to PM_{2.5}, Viana et al. (2008).

Factor 5 is responsible for most of the mass of EC (~42%) and of Ca (54%) in PM_x, it also shows strong loadings for OC, NO₃⁻, Ni and Zn and the presence of Cu, Fe, V and Ti, all of which are markers of traffic related aerosol, hence the labelling of this factor as “Total Traffic”. The two carbon fractions and NO₃⁻ (Jiang et al., 2005) and possibly Ni and V (Pant and Harrison, 2013) are considered markers for traffic exhaust emissions, Cu, Fe and Zn for brake wear (Sternbeck et al., 2002; Schauer et al., 2006; Amato et al., 2011; Figi et al., 2010), Zn for the combustion of lubricating oil (Viana et al., 2008) and tyre wear (Pakbin et al., 2010; Amato et al., 2011), Ca, Fe, Ni and V (the latter two species originating from the bitumen in asphalt) for the abrasion of the road surface (Lindgren, 1996; Kennedy and Gadd, 2003).

The metals Ni and V are usually used as tracers of primary aerosol from fuel oil combustion in both land-based and sea-based sources. Particulates from combustion sources are normally emitted in the PM_{2.5} fraction (Amato et al., 2016). However, a good correlation (Pearson correlation coefficient) between the concentration of these two metals was obtained for PM₁₀ only ($r = 0.84$, $p < 0.05$), while the correlation for PM_{2.5} is rather poor ($r = 0.20$, $p < 0.05$). These results may indicate that these two metals owe their origin to the abrasion of the road surface, which occurs mostly in the PM₁₀ fraction (Ketzel et al., 2007), rather than to combustion sources (such as shipping or power generation). Ca and Ti are indicators of resuspended crustal material. In all probability this factor represents the total contribution (exhaust, abraded and resuspended components) of traffic derived aerosol to PM_x. The chemical composition of vehicle resuspended dust and dust from road abrasion is not expected to be different from that of wind entrained dust and therefore the possibility of the latter being included in the factor cannot be excluded because PMF is incapable of isolating factors, when they are very similar chemically (Viana et al., 2008). The “Total Traffic” aerosol contributes 16.7% (1.8 µg/m³) to PM_{2.5} and 19.8% (4.3 µg/m³) to PM₁₀. The exhaust component of traffic aerosol is expected to be predominantly in the finer fractions of APM, while the abrasion component is expected to be in the coarser fraction of APM, due to the mechanical nature of its

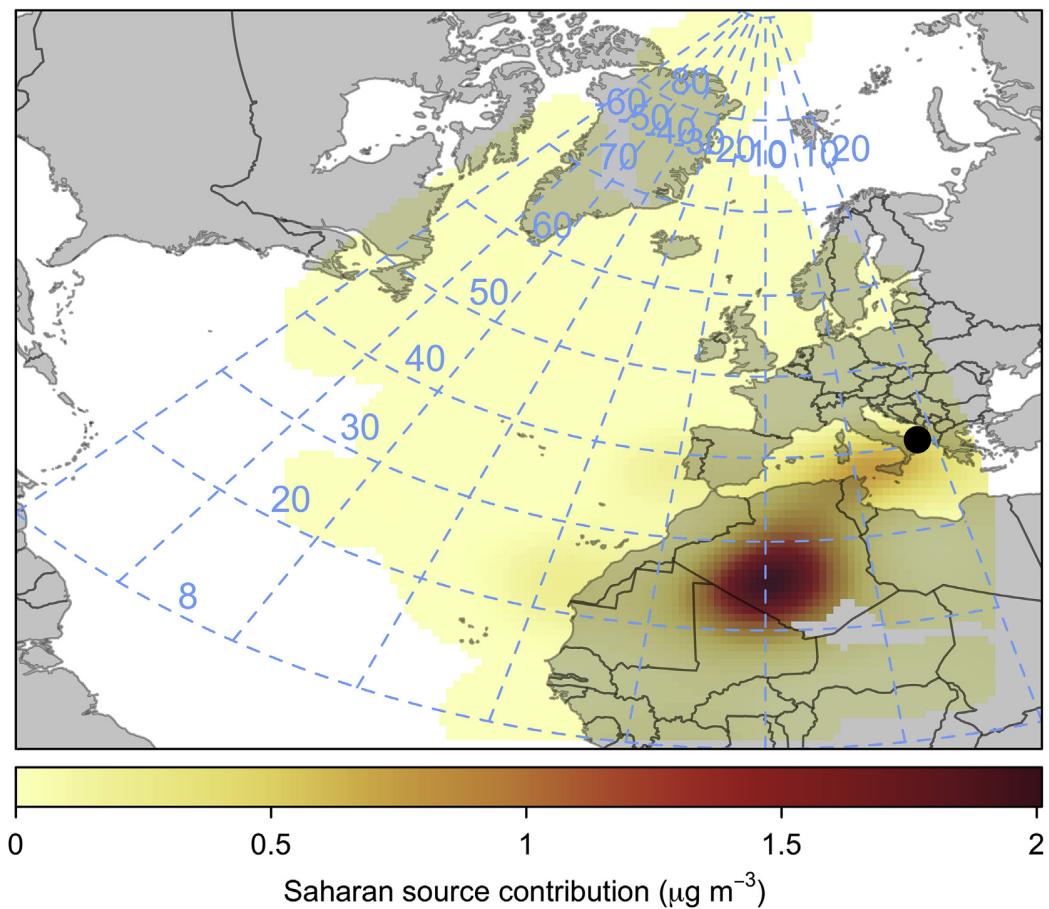


Fig. 5. Concentration field for F4, the Saharan aerosol source contribution (arrival height 1500 m).

formation mechanism. So, the greater mass contribution to PM₁₀ can be explained by the fact that the abraded and resuspended component of the traffic aerosol predominates in this case. This shows that a greater portion of PM emission from road transport is due to the non-exhaust components. In fact, by making a crude assumption that all the exhaust emissions occur in the PM_{2.5} fraction one can derive a percentage contribution of the non-exhaust fraction of ~59%, this is similar to the figure of 58% derived by Weinbruch et al. (2014) for a receptor in Germany.

4. Discussion

4.1. Reliability of the 5 factor PMF solution

The use of datasets with a limited number of samples such as this one, adds some complexity to the PMF modelling due to increases in both rotational ambiguity and overall uncertainty (Manousakas et al., 2017). USEPA PMF version 5, includes three methods for estimating the errors in the solution returned by the model: classical bootstrapping (BS), displacement (DISP) and a combination of both, or BS – DISP. BS captures the random errors, DISP is a measure of the uncertainty due to rotational ambiguity and BS – DISP captures the errors due to both BS and DISP, Norris et al. (2014). These three error estimation techniques were applied to the solution returned by the Base run. BS (with 100 runs and minimum correlation R-value = 0.6) showed that all the factors were reproduced 100% of the time and DISP showed no factor swaps. BS – DISP accepted 88% of the cases and showed that the

solution was however not well constrained due to numerous exchanges of identity (or swaps) across four out of the five factors. These swaps can be caused by the “leakage” of species into factors when they are poorly associated with them, and this is even more probable when running PMF on small datasets. USEPA PMF version 5 includes the possibility of applying constraints on the Base solution in order to clean it from the “interference” due to these species. These constraints include *inter alia* the imposition of external information on the solution through the forcing of species concentrations in the F matrix to a known value, thereby solving rotational ambiguity issues (Paatero et al., 2002; Kim and Hopke, 2004). The marine, mixed carbonaceous, crustal/Saharan and total traffic aerosol factors included one or more species present at very low concentrations (respectively EC & OC, Si, Cu and Si), which were “pulled down maximally” in order to keep the solution rotationally stable rather than to alter it. The ratio of Cl⁻/Na⁺ in the Base solution is < 1 and therefore less than the ratio of these ions in sea water (1.8), this indicates depletion in Cl⁻ content due to aging. The imposition of a constraint adjusting the ratio of these two ions to 1.8 would have substantially altered the source profile for this factor in the Base run and was therefore not included. The final percentage change in the Q robust parameter (%dQ_{robust}) for the constrained run was 0.6%, which is less than the maximum allowable change that is recommended (5%), Norris et al. (2014). The factors did not change significantly when compared to the base run and therefore the factor identity was unaltered. The results for BS and DISP for the constrained solution were identical to those for the Base solution. However, the BS – DISP for the constrained run

Table 3

PMF uncertainty estimates for the tracer species of the identified factors.

	Factors (Species used as tracers)				
	Ammonium Sulfate	Sea Salt	Mixed Carbonaceous	Saharan	Total Traffic
	(SO ₄ ²⁻)	(Na ⁺)	(OC)	(Si)	(Ca)
Constrained Base Value	1.30	0.41	1.73	1.13	1.16
BS 5th	1.09	0.35	1.39	0.89	1.00
BS Median	1.29	0.42	1.66	1.05	1.14
BS 95th	1.44	0.48	1.82	1.21	1.63
BS - DISP	0.81	0.33	1.23	0.89	0.73
BS - DISP Average	1.28	0.43	2.14	1.22	1.27
BS - DISP 95th	1.76	0.52	3.95	1.55	1.81
DISP Min	1.05	0.37	1.40	0.98	1.02
DISP Average	1.39	0.42	2.07	1.19	1.40
DISP Max	1.73	0.48	2.73	1.39	1.78

accepted 100% of the cases with no factor swaps. This confirms the robustness and reliability of the accepted resamples' error estimates (Paatero et al., 2014) and makes the solution acceptable (Achilleos et al., 2016). Table 3, shows the uncertainty estimates for the species used as the tracers for the identified factors and obtained using the error estimation techniques included in USEPA PMF version 5. These uncertainties are all reasonably low meaning that the factors isolated by PMF are really different sources of airborne particulate matter, (Manousakas et al., 2017). In addition, CMB did not converge when more sources were introduced into the model, while CW – NMF gave its best fit for the same number of factors as well. This shows that PMF managed to extract most of the information about the sources from the speciation data.

A critical part of the PMF source apportionment procedure is the achievement of a global minimum in the Q-parameter. In this study, this was achieved by running PMF 20 times (each of the runs initiated at a different pseudo-random seed), with 100 iterations per run. The scaled residuals (d) for the species fitted by PMF were mostly normally distributed and were all within the range $-3 < d < 3$. This adds strength to the identified solution (Friend et al., 2012; Li et al., 2013). The source contributions were determined by regressing PM_{2.5} and PM₁₀ against the respective factor scores, this avoided having to include PM_x in the PMF runs and therefore having to artificially constrain the intercept to 0 and underestimate the undetermined fraction. All the coefficients obtained from the MLRA were non-negative, meaning that the number of fitted sources was not excessive (Buzcu et al., 2003). Scaled source profiles were calculated by dividing the constituent species concentrations by the respective MLRA scaling constant. The sum of each of the scaled source profiles was less than 1. This was interpreted as meaning that the chosen number of factors is not too low (Hopke, 2001; Kim et al., 2003) and confers physical validity to the proposed solution, Buzcu et al. (2003).

The 5-factor solution reconstructed well the mass of both PM₁₀ and PM_{2.5}, explaining respectively 99.5% and ~100% (undetermined fraction was 0.002 µg/m³ out of ~11 µg/m³) of the PM levels

Table 4b
Model performance for PM_{2.5}.

Parameter	Models		
	PMF	CW – NMF	CMB
r ² (measured vs. modelled PM _{2.5})	0.98	0.97	0.89
gradient (measured vs. modelled PM _{2.5})	~1	1.00	0.97
explained PM _{2.5} mass (%)	~100	99.9	104.1
Root mean square error (µg/m ³)	1.00	1.16	3.76
Absolute fractional bias	0.09	0.10	0.17

measured at the receptor with a slope of ~1.00 in both cases and with an r² for a plot of measured vs modelled > 0.97 for both PM₁₀ and PM_{2.5} (see Tables 4a and 4b). Additionally, a coefficient of divergence (CD) was calculated as per Buzcu et al. (2003), in order to estimate the ability of PMF to model ambient particulate levels. When the CD ~1 the measured and modelled values differ significantly (Wongphatarakul et al., 1998). The low values of the CD in our work (0.13 for both PM₁₀ and PM_{2.5}) are indicative of a reliable identification of the sources affecting the levels of particulate matter, Buzcu et al. (2003).

4.2. Comparison between measured and reconstructed mass

The results in Tables 4a and 4b show that the two factor analytic models (PMF and CW – NMF) manage to reconstruct the mass of both PM₁₀ and PM_{2.5} well, while CMB underestimates the PM₁₀ mass and overestimates the mass of PM_{2.5}. Notwithstanding this, the percentage of the mass explained by CMB (87% for PM₁₀ and 104% for PM_{2.5}) is within the 80%–120% range of acceptability for CMB (Argyropoulos et al., 2017; Shi et al., 2014). Gianini et al. (2013) attribute underestimates in the percentage mass closure to the way in which CMB estimates the daily source contributions. However when secondary aerosol sources contribute significantly to the total aerosol mass, the model can sometimes achieve percentages of reconstructed mass >100%, affecting mostly the source apportionment of the finer PM fractions, Rizzo and Scheff (2007).

The RMSE and AFB for PMF and CW – NMF (Tables 4a and 4b) are very similar to each other and indicate that: a) the spread between the measured and reconstructed masses is rather small and equivalent to 9% of the average concentration for both PM₁₀ and PM_{2.5} (RMSE ~2 µg/m³ for PM₁₀ and ~1.0 µg/m³ for PM_{2.5}); and b) that there is agreement between the measured and reconstructed PM_x concentrations, due to the low AFB. For CMB there is however, a higher spread between the measured and reconstructed concentrations of PM_x (RMSE ~5 µg/m³ for PM₁₀ and ~4 µg/m³ for PM_{2.5}, respectively 21% and 34% of the average concentration),

Table 4aModel performance for PM₁₀.

Parameter	Models		
	PMF	CW – NMF	CMB
r ² (measured vs. modelled PM ₁₀)	0.97	0.98	0.96
gradient (measured vs. modelled PM ₁₀)	0.99	0.97	1.11
explained PM ₁₀ mass (%)	99.6	99.3	87.2
Root mean square error (µg/m ³)	2.15	2.05	4.68
Absolute fractional bias	0.09	0.09	0.20

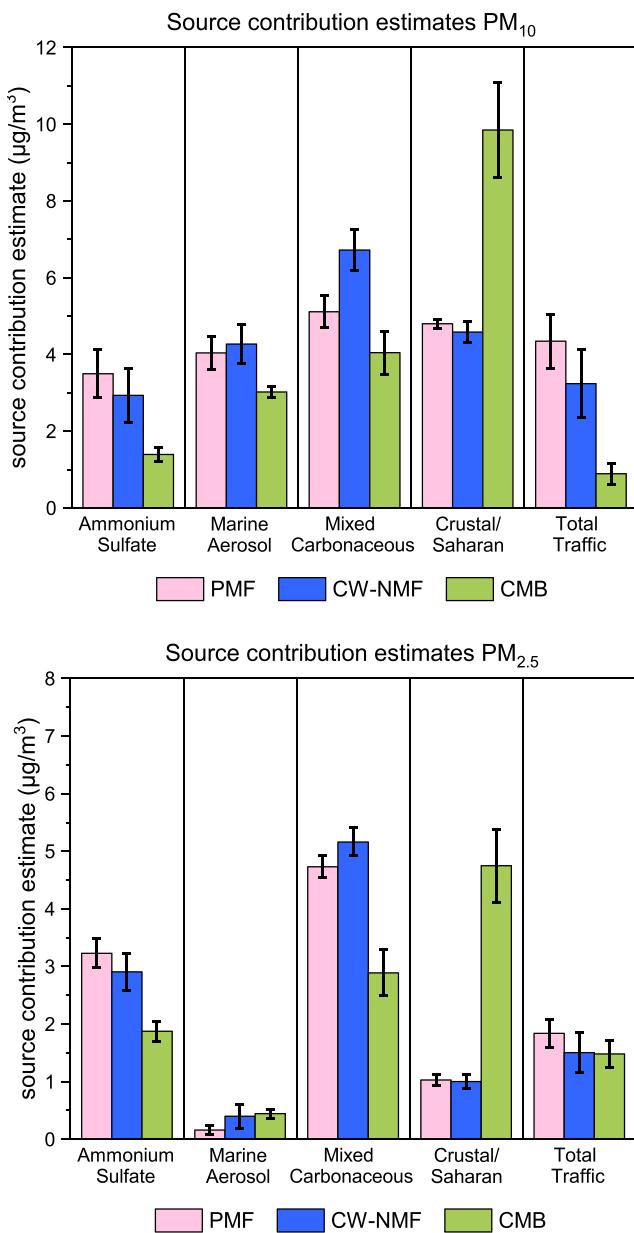


Fig. 6. Source contribution estimates by the 3 models and the respective errors.

while the AFB is within the range of acceptability for both fractions. This indicates that PMF and CW – NMF manage to model well the levels of both PM₁₀ and PM_{2.5}, while the performance of CMB degrades (due to the higher spread) from PM₁₀ to PM_{2.5}. This is probably due to the fact that the effect of secondary aerosols on model performance is expected to be more significant for the finer fraction on account of the higher contribution of these factors to the total particulate mass (73% for PM_{2.5} and 39% for PM₁₀).

4.3. Comparison of the results obtained by PMF with those obtained by the other models

The PMF output was compared to that of the other two models in two ways: a) by comparing the absolute values of the PMF source contribution estimates (together with the respective errors) to

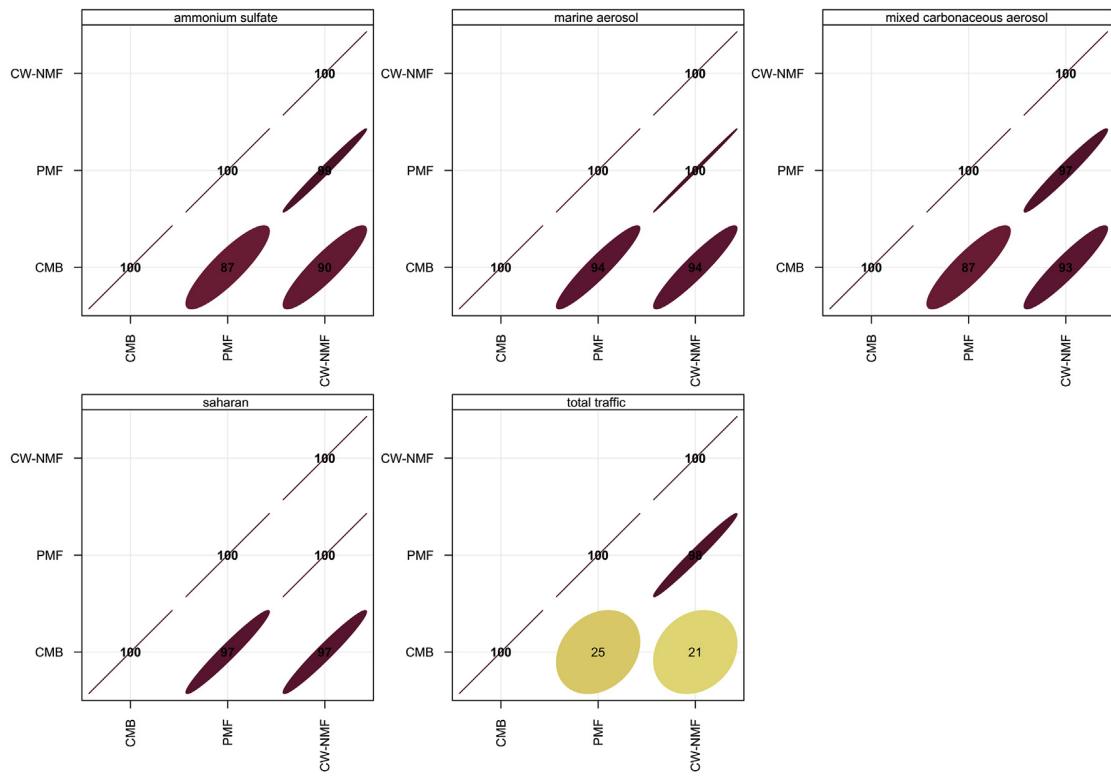
those of the other two models, see Fig. 6, and b) by investigating the Pearson correlation between the source contribution estimates of the three models, see Fig. 7a and Fig. 7b.

Fig. 6 shows that in general the source contributions estimated using PMF and those estimated using CW – NMF are within the respective uncertainties of each other for both fractions. The mixed carbonaceous aerosol in PM₁₀ being an exception due to the slight overestimate by CW – NMF (or underestimate by PMF). This difference is of <1 µg/m³ and one must keep in mind that the errors calculated for both PMF and CW – NMF source contributions are lower-end error estimates. There is a discrepancy between the CMB estimates for the two secondary components (ammonium sulfate and mixed carbonaceous aerosol) and the PMF (and CW – NMF) estimate in both PM₁₀ and PM_{2.5}. This is probably due to the fact that CMB is known, not to apportion secondary aerosols too well (Viana et al., 2008), because the source profiles inputted for these components are often made up of only one compound. This was the case in this study too, and has possibly lead to an underestimation of these factors, due to the fact that the presence of other species associated with them was totally ignored, (Cesari et al., 2016). CMB also underestimates the marine aerosol content in PM₁₀ by ~1 µg/m³ (with respect to PMF and CW – NMF), this is most likely due to the fact that the profile inputted into CMB did not include any NO₃⁻, and is similar to what was reported by e.g. Cesari et al. (2016). The total traffic factor in PM₁₀ estimated by CMB is lower than that estimated by PMF and CW – NMF by ~3 µg/m³, while the Saharan component determined by CMB is higher for both PM₁₀ and PM_{2.5} by respectively ~5 µg/m³ and ~4 µg/m³ when compared to that estimated by the other two models. The discrepancy in the Saharan source contribution estimate is probably caused by the fact that PMF (and similarly CW – NMF) isolates a pure "Saharan" component, while the experimental profile which was inputted in CMB is a mixture of local (wind entrained) and Saharan crustal material. While the fact that, PMF and CW – NMF do not manage to disentangle the wind entrained dust from the resuspended dust and the road abrasion fraction due to their chemical similarity, could explain the discrepancy in the total traffic factor.

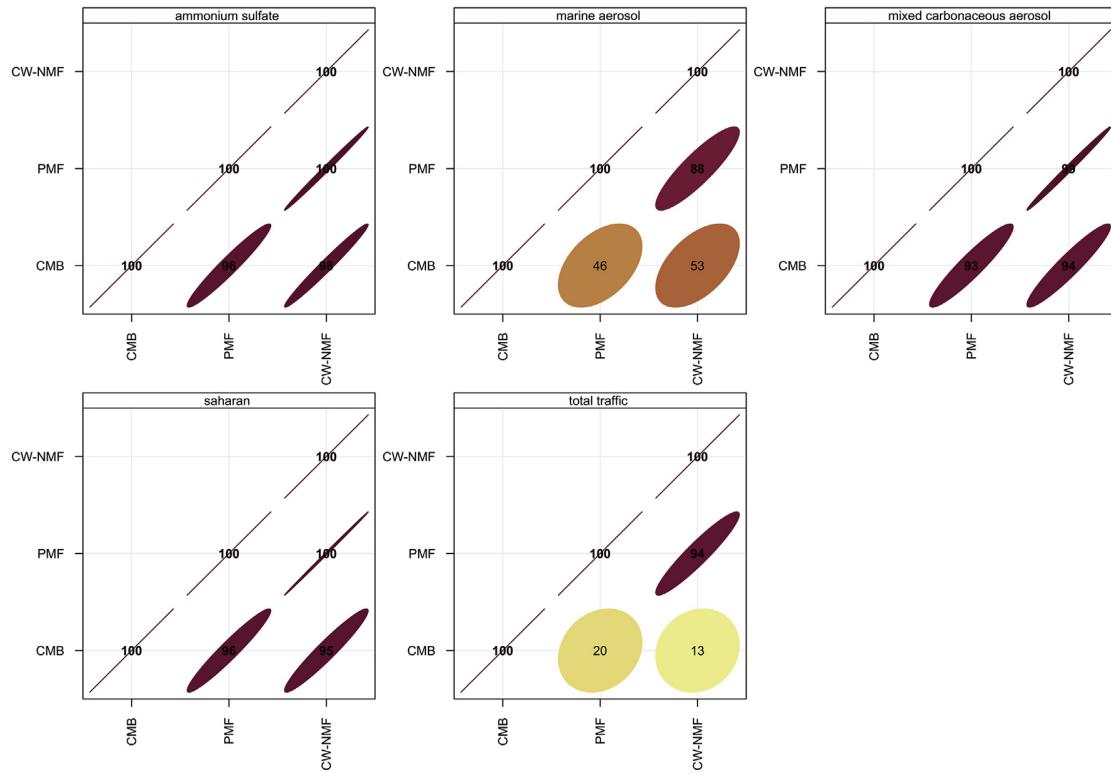
The correlograms in Fig. 7a show, that for PM₁₀ there is good agreement between the daily source contribution estimates of the three models for all factors with the exception of total traffic, where the CMB daily estimates correlate rather poorly with those made by both PMF and CW – NMF. On the other hand a re-constructed CMB traffic source contribution estimate, which includes a crude estimate of the "wind entrained dust" with the traffic components (and calculated as shown in Section SM8 of the electronic supplement), correlates fairly well with the PMF total-traffic source contribution estimate (Figure SM8b in the electronic supplement), indicating that there is a possibility that PMF included the wind entrained dust with the total traffic factor. Discrepancies between PMF and CMB in the apportionment of factors with similar chemical compositions are unavoidable (Begum et al., 2007).

The correlogram for PM_{2.5} (Fig. 7b) shows a good correlation between the source contributions estimated by the 3 models for ammonium sulfate, mixed carbonaceous aerosol and for the crustal/Saharan component, a fair correlation between CMB and the other two models for marine aerosol and a poor correlation between CMB and the other models for total traffic. The procedure adopted for PM₁₀ in Section SM8 of the electronic supplement does not yield a better correlation for PM_{2.5}. This highlights the fact that CMB has some problems with modelling PM_{2.5}.

The intercomparison between PMF and CMB is not always a straightforward exercise and the two models often yield different results in terms of both the sources affecting the receptor as well as the estimates of the contributions of these sources (Gianini et al., 2013). Receptor modelling by CMB is inherently dependent on



a



b

Fig. 7. a: Correlogram for the source contribution estimates by the three models for PM₁₀. The numbers represent the Pearson r coefficient expressed as a percentage, a straight line inclined at 45° represents a correlation of 1, a perfect circle represents a correlation of 0, while the elliptical shape represents the degree of scatter. b: Correlogram for the source contribution estimates by the three models for PM_{2.5}. The numbers represent the Pearson r coefficient expressed as a percentage, a straight line inclined at 45° represents a correlation of 1, a perfect circle represents a correlation of 0, while the elliptical shape represents the degree of scatter.

the accuracy of the inputted source profiles (Lee et al., 2008; Belis et al., 2013), this makes the results obtained by CMB potentially sensitive to the size fraction, sampling site and sampling site typology as well as the sampling period; considered when the source profiles were determined (Yin et al., 2010). The results of CMB are normally aligned to those of PMF after the profiles used as one of the inputs in the CMB model are tweaked using the information obtained from the profiles outputted by PMF (see for example Cesari et al., 2016; Bove et al., 2018). This approach would not have made much sense in the context of a study such as this, where the other models (CW – NMF and CMB) were used in order to check the results obtained by PMF. The correlations between the PM₁₀ source contribution estimates resulting from the three models (including the tweaked CMB traffic factor) show that the same factors are isolated by the models and any discrepancies in the absolute values are due to systematic differences. It is worth mentioning that while the mass reconstructed by the factor analytic models was ~100%, that achieved by CMB was 87.2% and this could have affected these systematic differences. The results for PM₁₀, however show no major flaws in the source apportionment achieved by PMF. The same conclusion can be applied to three of the five factors contributing to the levels of PM_{2.5} (ammonium sulfate, mixed carbonaceous and the crustal/Saharan sources). The fairly good correlation between the marine aerosol source contribution estimated by the factor analytic models and that determined by CMB is probably due to the fact, that the use of the SPECIEUROPE 2.0 profile 285 (Pernigotti et al., 2016), which excluded NO₃, somehow, had a greater effect on PM_{2.5} than on PM₁₀. While the reason for the poor correlation between the CMB traffic source contribution and the PMF and CW – NMF is not readily explainable. We have no doubt that traffic does affect the PM_{2.5} levels at the receptor, the traffic factor isolated by PMF is a composite factor made up of exhaust, abraded and resuspended components and from which PMF does not probably manage to disentangle the wind-entrained dust. Probably the inclusion of all these components in the factor isolated by PMF accentuates the mismatch in PM_{2.5}, such that it cannot be resolved using the same (crude) methodology as for PM₁₀. There are cases in literature in which plots of the daily source contribution estimates by CMB and PMF do not correlate well, due to for example, intermixing or proximity of sources e.g. Rizzo and Scheff (2007). However keeping all the other results in mind, this mismatch should not discredit the results of the apportionment for PM_{2.5}.

5. Conclusion

The main aim of our study was to explore the methodological issue related to PMF receptor modelling with smaller sample sizes (for use in situations in which objective constraints limit the number of samples, which can be availed of). In our case PMF was run on a “smaller”, real world, dataset consisting of 29 PM₁₀ samples and 33 PM_{2.5} samples. The samples for the two fractions were aggregated and the in-built rotational tools in the USEPA PMF version 5 package were used to refine the PMF solution. We have shown that the solution is made more stable through the application of constraints based on external information about the site. The results of the error estimation techniques in PMF (BS, DISP and BS – DISP) show reasonable uncertainties in the tracer species, indicating strongly that the identified factors are physical sources. PMF returned a 5-factor solution, which is plausible on the basis of what is known about the airshed at the receptor and the prevailing air mass transportation patterns. The comparison between the source contribution estimates for PM₁₀ and PM_{2.5} and the source apportionment for the two fractions is also consonant with what is currently known about the chemical composition of these two

fractions, chiefly that secondary aerosols are found predominantly in the finer fractions, while the marine aerosol and the abraded and re-suspended factors are almost exclusively found in the PM₁₀ fraction. In addition the model outputted by PMF was compared to those returned by CW – NMF and CMB. The PMF results were confirmed by CW – NMF, while the CMB estimates show some explainable deviations in PM₁₀ and in PM_{2.5}. However, these deviations are not exclusive to this study and the comparison with the other models reinforces our confidence in the PMF results.

Overall we can conclude that scientifically meaningful source apportionments can be obtained by running PMF on datasets consisting of a small number of samples (less than the currently accepted rule of thumb) and through the judicious imposition of constraints on the solution. The key result of the methodological question we sought to answer through this work, is that when there are constraints on the number of samples that can be taken/analyzed, one can still extract useful information by PMF. Notwithstanding our conclusion we still believe that whenever possible one should stick to the currently accepted practice of at least 100 samples. Finally, we believe that our work has highlighted the potential for future investigations on this subject. In our view any future work should investigate the effect of sample size on the number of factors isolated by PMF. Additionally it would also be interesting to check whether the assumption of the similarity of profiles for both PM₁₀ and PM_{2.5} holds for different receptor typologies (such as urban background, industrial and traffic to name a few).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124376>.

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Supplementary Material

Section SM1: Abbreviations

AFB	Absolute Fractional Bias
AGL	Above Ground Level
ALV	Annual Limit Value
AMSL	Above Mean Sea Level
APM	Airborne Particulate Matter
AQGs	Air Quality Guidelines
BDL	Below Detection Limit
BS – DISP	combination of bootstrapping and displacement (error estimation method on PMF)
BS	Bootstrapping (error estimation method in PMF)
CD	coefficient of divergence
CMB	Chemical Mass Balance
CW – NMF	Constrained Weighted Non-negative Matrix Factorization
CWT	Concentration Weighted Trajectory
d	scaled residual
DISP	Displacement (error estimation method in PMF)
DLV	Daily Limit Value
EC	Elemental Carbon
EEA	European Environment Agency
IM	the maximum Individual column Mean
IS	the maximum Individual column Standard deviation
MLRA	Multilinear Regression Analysis
OC	Organic Carbon
PM	Particulate Matter
PMF	Positive Matrix Factorization
QF	Quartz Fiber
RMSE	Root Mean Square Error
SDS WAS	Sand and Dust Storm Warning Advisory System
SOA	Secondary Organic Aerosol
USEPA	United States Environment Protection Agency
WHO	World Health Organization
WMO	World Meteorological Organization
XRF	X – ray Fluorescence Spectrometer

Section SM2: Analytical procedures.

The OC and EC concentrations were measured using the Thermal Optical Transmittance Instrument (Sunset Lab Inc., USA; Birch and Cary, 1996), applying the NIOSH 5040 protocol. A 1.5 cm² hole was punched through the QF filters and the punch was used for the analysis of OC/EC. The concentrations of the major and minor elements Si, Ti, Fe, Mg, Ca, Na, K, P as well as of the trace elements Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Y, Zr, Nb, La, Cd, Nd, and Pb on one half of the PTFE filter, were measured using a Spectro X-Lab 2000, Energy-Dispersive X-ray Fluorescence Spectrometer – XRF (Spectro Analytical Instruments GmbH, Kleve, Germany) fitted with a Si(Li) detector. A Rh anode tube was used to generate X-rays (I_{max} and V_{max} , 1.98A and 50kV respectively). The instrument was calibrated against pure, thin film standards (Micromatter – XRF Calibration standards, 50 µg/cm², N – Nucleopore® polycarbonate aerosol membranes, USA). The NIST standard SRM2783 (Air Particulate on Filter Media) was used for periodic calibration checks. The other membrane halves were analyzed for the concentrations of ions (NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, K⁺, NH₄⁺, and Mg²⁺) according to CEN/TR 16269 (2011). The sample was extracted by leaching in 5 ml of Milli-Q water for 20 minutes in an ultrasonic bath. The resulting slurry was filtered through 0.2 µm porosity filters, and ion concentrations were determined by ion chromatography using the DIONEX® 600 IC (Thermo Scientific, Sunnyvale, USA) fitted with a CD 25 conductivity detector. DIONEX® AS – 4A SC, 250 × 4-mm was used as separating column for the anions, with 1.8 mM Na₂CO₃/1.7 mM NaHCO₃ at a flow rate of 2.0 ml/min as the eluent and using a CSRS – Ultra 4mm Cation Self-Regenerating Suppressor. Cations were analyzed using a DIONEX® CS12 – SC (250 × 4-mm) column together with an ASRS – Ultra 4mm Anion Self-Regenerating suppressor. In this case the eluent was 10 mM H₂SO₄ at a flow rate of 1.0 ml/min (Perrone *et al.*, 2016; Perrone *et al.*, 2018). The method detection limits were estimated as three times the standard deviation of the concentration for 10 blank membranes and were found to be 0.3, 6.2, 0.6, 0.1, 0.7, 0.3, and 0.2 ng/m³ respectively for Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, and Mg²⁺. Analytical precision and percentage recovery were determined through spiked sample recovery check. The blank samples were spiked with 0.5 ml of a 40 µg/ml inorganic ions' standard solution followed by the full extraction procedure and by the determination of the concentrations of the aqueous ions. The rates of

recovery were within the range of 97 – 104 %. The standard deviation of 10 repeated measurements was used to calculate precision, which was determined to be in the range of 3.1 to 5.8%.

Section SM3: Further details on the species downweighted for the PMF modelling:

Table SM3:
Downweighted species

Species	Reason
EC	Q / Q _{exp} ratio > 2 for some factors
Ni	Relatively low S/N ratio
Cu	Relatively low S/N ratio
Zn	Relatively low S/N ratio
K ⁺	Less optimal fit by the model
NO ₃ ⁻	Less optimal fit by the model

Section SM4: Descriptive statistics for PM10 and PM2.5 measurements and their respective speciation.

Table SM4a:

Basic statistics for PM₁₀ and PM₁₀ speciation

Analyte	Geometric mean ($\mu\text{g}/\text{m}^3$)	Geometric standard deviation ($\mu\text{g}/\text{m}^3$)	95 th percentile ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	5 th percentile ($\mu\text{g}/\text{m}^3$)	Interquartile range ($\mu\text{g}/\text{m}^3$)
OC	2.376	2.188	7.552	2.230	3.194	0.738	1.513
EC	0.242	1.668	0.501	0.259	0.272	0.111	0.091
Na ⁺	0.861	1.695	1.874	0.833	0.992	0.445	0.312
NH ₄ ⁺	0.513	1.749	0.926	0.593	0.578	0.164	0.138
K ⁺	0.138	1.890	0.411	0.134	0.169	0.052	0.056
Mg ²⁺	0.106	1.669	0.248	0.092	0.122	0.063	0.037
Cl ⁻	0.637	2.294	1.835	0.622	0.886	0.160	0.373
NO ₃ ⁻	1.008	1.542	2.114	0.914	1.116	0.568	0.277
SO ₄ ²⁻	2.060	1.639	4.480	2.112	2.300	0.875	0.474
Si	0.741	3.510	10.693	0.489	1.976	0.172	0.293
Ca	2.271	2.128	8.392	2.167	2.931	0.837	0.740
Ti	0.057	2.271	0.381	0.045	0.091	0.028	0.018
V	0.008	1.781	0.031	0.007	0.010	0.005	0.002
Fe	0.521	2.779	4.455	0.405	0.973	0.161	0.228
Ni	0.056	1.087	0.064	0.056	0.056	0.050	0.003
Cu	0.122	1.333	0.150	0.123	0.123	0.099	0.010
Zn	0.144	1.228	0.197	0.147	0.147	0.096	0.013
PM ₁₀	19.198	1.657	46.748	17.974	21.886	9.856	4.475

Table SM4b:

Basic statistics for PM_{2.5} and PM_{2.5} speciation

Analyte	Geometric mean $\mu\text{g}/\text{m}^3$	Geometric standard deviation $\mu\text{g}/\text{m}^3$	95 th percentile $\mu\text{g}/\text{m}^3$	Median $\mu\text{g}/\text{m}^3$	Mean $\mu\text{g}/\text{m}^3$	5 th percentile $\mu\text{g}/\text{m}^3$	Interquartile range $\mu\text{g}/\text{m}^3$
OC	1.499	2.200	4.721	1.241	2.278	0.508	0.926
EC	0.193	1.652	0.361	0.186	0.231	0.096	0.069
Na ⁺	0.077	1.732	0.181	0.079	0.097	0.034	0.015
NH ₄ ⁺	0.527	1.773	1.093	0.606	0.642	0.151	0.191
K ⁺	0.075	1.835	0.165	0.068	0.106	0.041	0.021
Mg ²⁺	0.066	1.342	0.081	0.077	0.069	0.039	0.001
Cl ⁻	0.056	2.143	0.178	0.032	0.078	0.029	0.038
NO ₃ ⁻	0.125	1.336	0.190	0.121	0.136	0.090	0.024
SO ₄ ²⁻	1.520	1.754	3.166	1.674	1.920	0.586	0.468
Si	0.201	3.293	0.914	0.190	0.679	0.074	0.060
Ca	1.132	1.839	1.675	1.233	1.471	0.307	0.204
Ti	0.030	1.818	0.061	0.030	0.045	0.020	0.004
V	0.006	1.606	0.009	0.006	0.008	0.004	0.001
Fe	0.166	2.480	0.491	0.163	0.357	0.072	0.046
Ni	0.057	1.096	0.065	0.056	0.058	0.050	0.005
Cu	0.115	1.111	0.134	0.112	0.116	0.100	0.012
Zn	0.140	1.150	0.167	0.140	0.145	0.122	0.008
PM _{2.5}	8.519	1.701	17.157	8.497	10.980	4.496	2.785

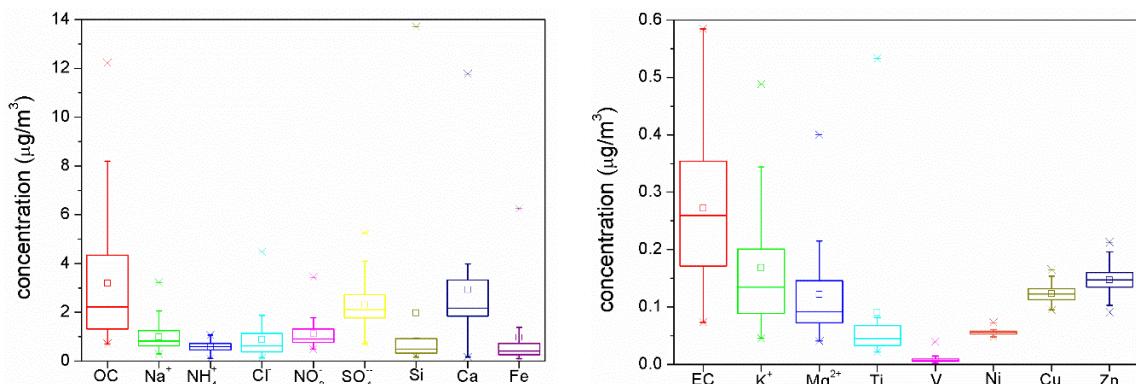


Figure SM4a: Box plot for the species determined in PM₁₀. The plot on the right shows the species present at higher concentrations, while the plot on the left shows the species present at lower concentrations.

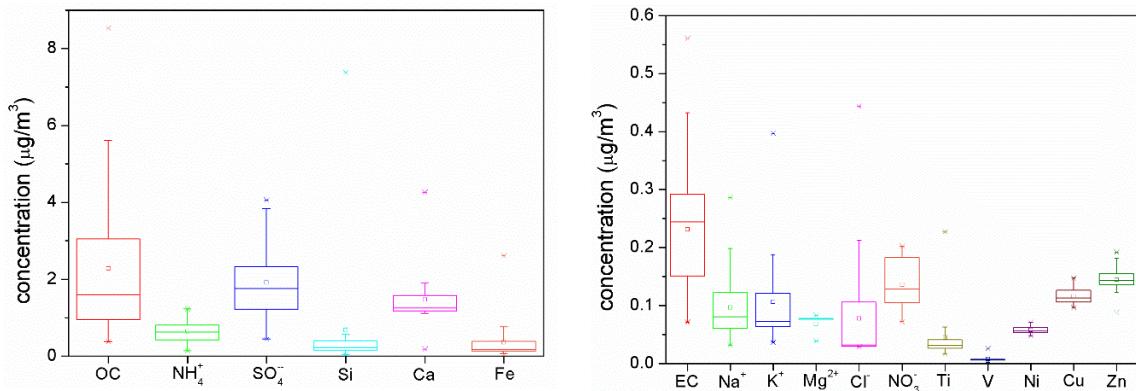


Figure SM4b: Box plot for the species determined in PM_{2.5}. The plot on the right shows the species present at higher concentrations, while the plot on the left shows the species present at lower concentrations.

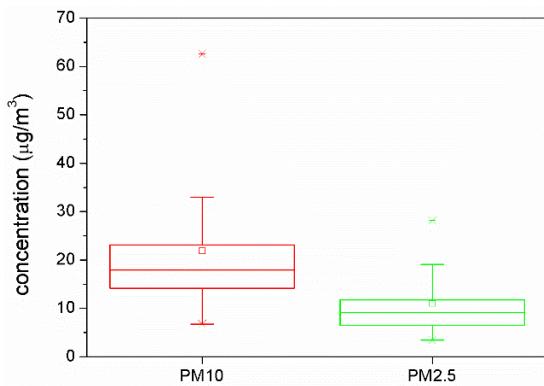


Figure SM4c: Box plot for the PM₁₀ and the PM_{2.5} concentrations.

Section SM5: Determination of the concentration of SOA in PM_x.

The calculation of the concentration of secondary organic aerosol SOA in both PM₁₀ and PM_{2.5} required the calculation of the parameter OC_{sec}, (see equation SM5, below) using the OC/EC minimum ratio method (Turpin and Huntzicker, 1995; Pio *et al.*, 2011; Genga *et al.*, 2017). A detailed description of this calculation is reported in Siciliano *et al.* (2018).

$$[\text{SOA}] = \frac{f_{\text{OM}}}{\text{OC}} \times [\text{OC}_{\text{sec}}] \quad (\text{SM5})$$

Where f_{OM/OC} was set at 1.8 in between the values in Turpin and Lim (2001) for urban (1.6 ± 0.2) and aged aerosols (2.1 ± 0.2).

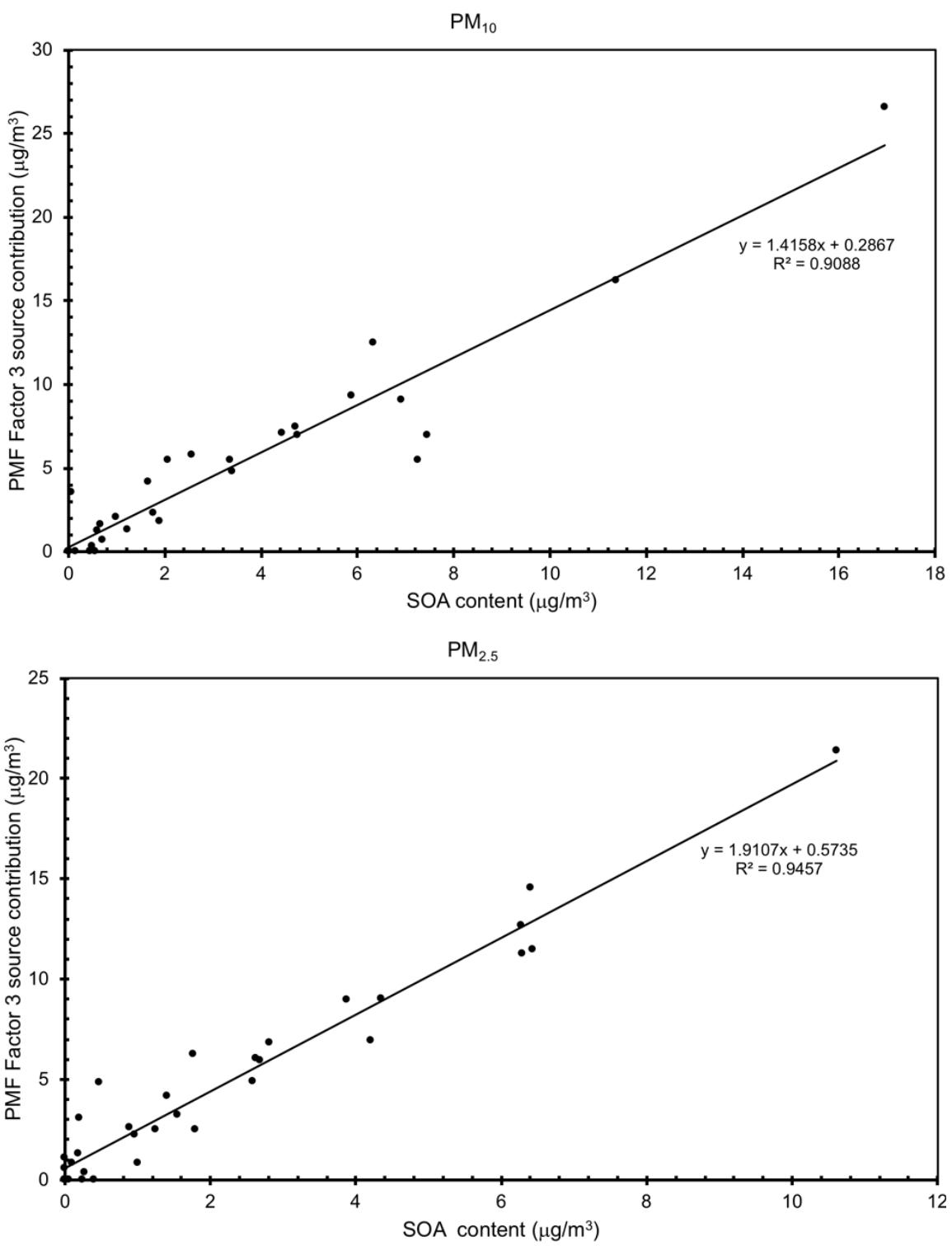


Figure SM5: Plot of concentration of PMF Factor 3 source contribution vs SOA content of for PM₁₀ (top) and PM_{2.5} (bottom).

Section SM6: Saharan episodes.

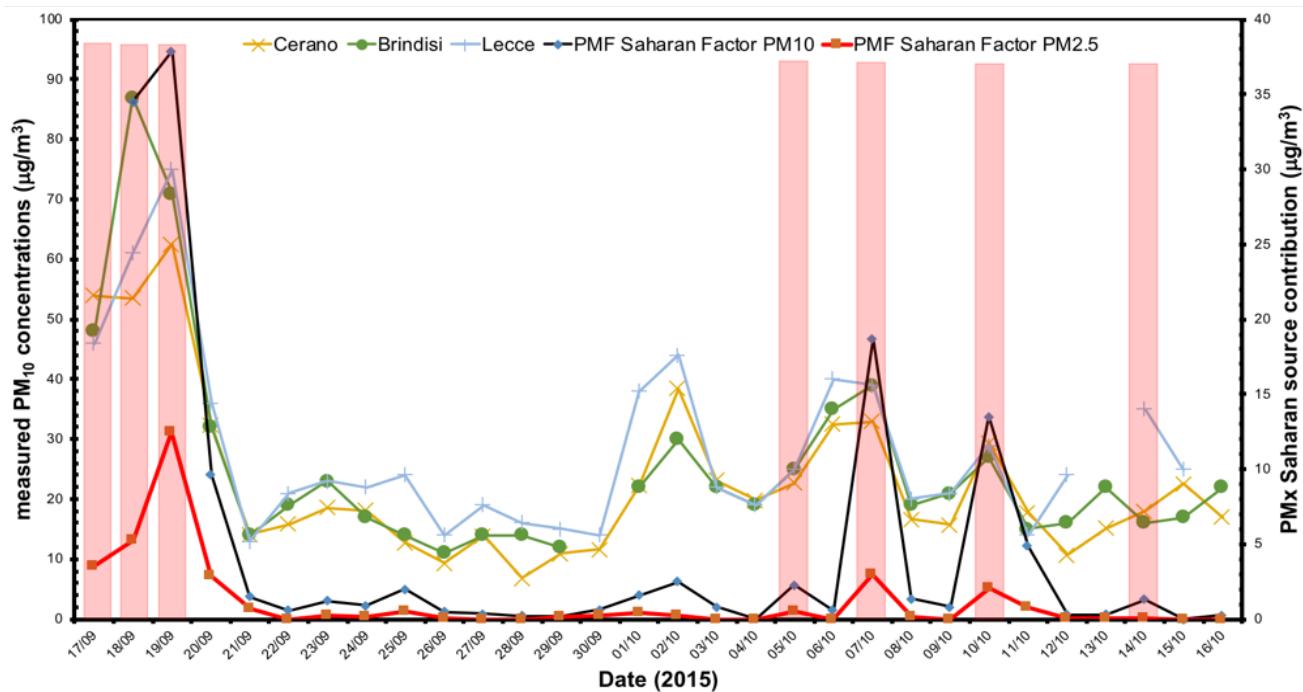


Figure SM6: Time series for the PM₁₀ (black) and PM_{2.5} (red) Saharan source contribution and for the PM₁₀ concentrations in the region. (Both stations in Lecce and Brindisi are in urban background sites).

The pink bars show the identified Saharan intrusion days.

Section SM7: Additional CWT plots.

Two additional CWT plots (Figure SM7) with the backtrajectory arrival heights set at 500 and 3000 m were plotted for the Saharan Factor. The 500 m arrival height (geopotential height of 750 hPa) is considered to be representative of transport below the boundary layer (Dvorská *et al.*, 2009), while 3000 m arrival height (geopotential height of 950 hPa) is considered to be important for the high altitude transportation of desert dust (Escudero *et al.*, 2005).

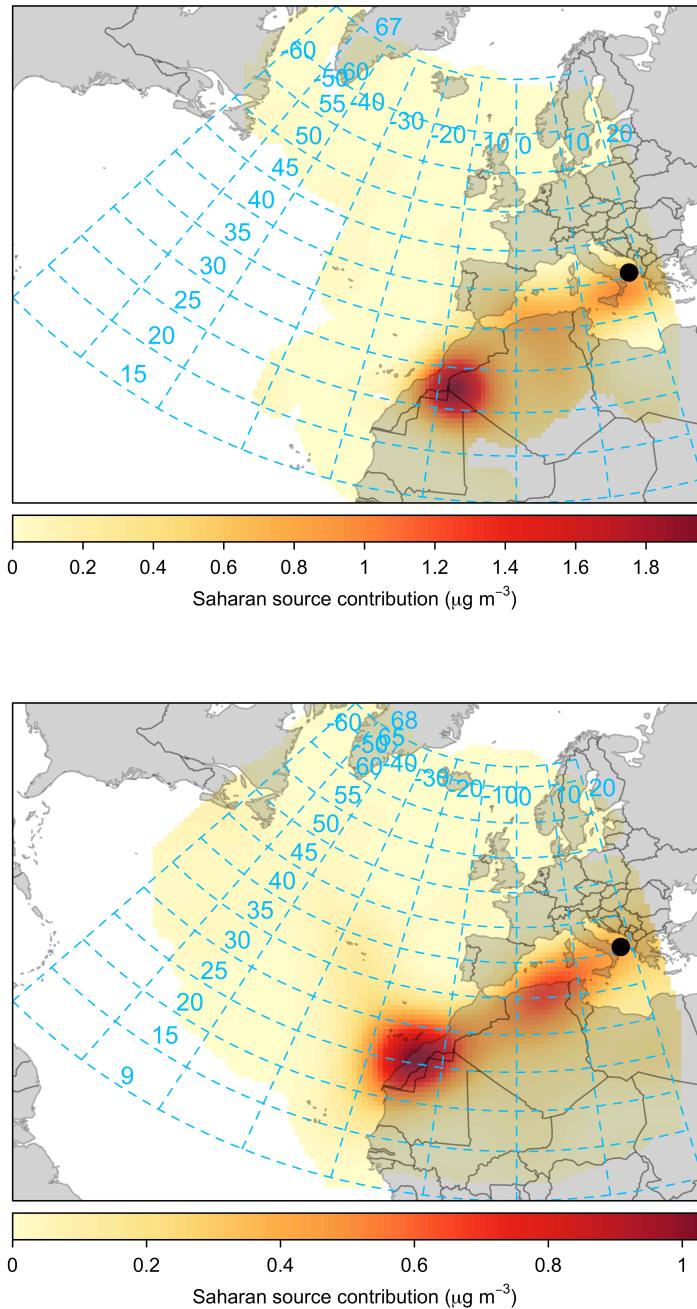


Figure SM7: CWT plots with backtrajectory arrival heights at 500 m (top) and 3000 m (bottom)

Section SM8: Time-series for the source contribution estimates by the three models

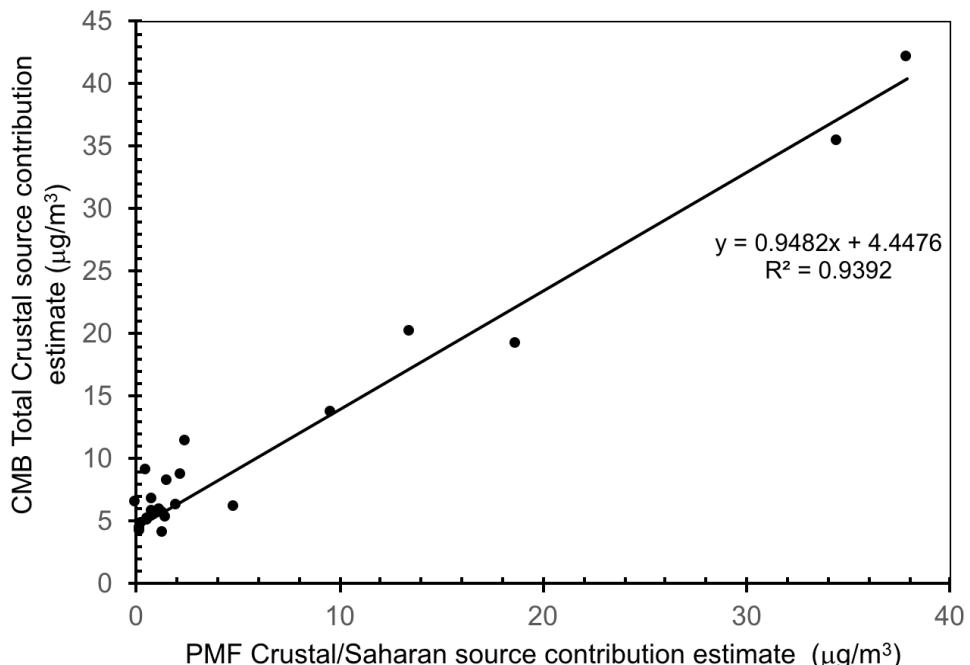


Figure SM8a: Plot of the CMB Total Crustal Factor vs, the PMF Crustal/Saharan source contribution estimate.

The total crustal factor isolated by CMB (TCF) was plotted against the Saharan factor isolated by PMF (SAH) obtaining the graph in figure SM5a and having the equation $TCF = 4.45 + 0.95 \times SAH$. Assuming that the difference between TCF and SAH is entirely due to the “wind-entrained” local dust, one can calculate the minimum value of this wind entrained component from the intercept in Figure SM8a. The days affected by this wind-entrained component are therefore those in which $TCF - SAH \geq 4.45 \mu\text{g}/\text{m}^3$. On these days the traffic factor isolated by CMB is incremented by the value of TCF - SAH to calculate a reconstructed CMB source contribution estimate. This is plotted against the PMF traffic source contribution estimate (see Figure SM8b).

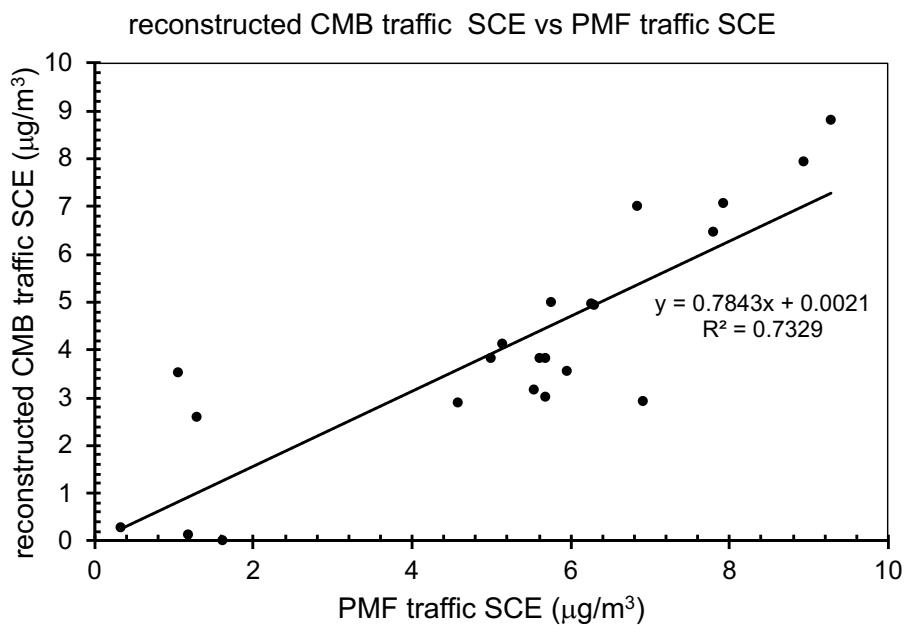


Figure SM8b: Plot of the reconstructed CMB source contribution estimate versus the PMF source contribution estimate.

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