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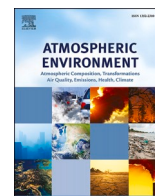
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Source apportionment of indoor PM_{2.5} at a residential urban background site in Malta

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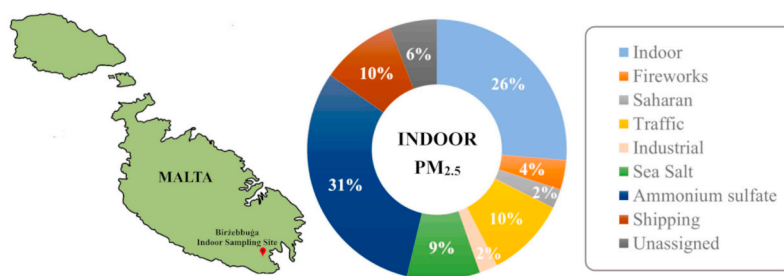
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HIGHLIGHTS

- Eight sources identified for PM_{2.5} at an indoor residential site located Malta.
- (NH₄)₂SO₄ was the highest contributor to indoor PM_{2.5}, followed by indoor sources.
- 6% contribution by fireworks to indoor PM_{2.5} during the summer months.
- Cooking and e-cigarettes were identified as contributors to indoor PM_{2.5}.
- Indoor air quality can be improved by reducing Mediterranean shipping emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study we carry out receptor modelling via Positive Matrix Factorisation (PMF) to identify and quantify the main natural and anthropogenic sources of indoor PM_{2.5} at an urban background site in the island of Malta. Quartz and PTFE filters were collected, analysed gravimetrically and chemically, using ICP-MS, IC and an OC-EC aerosol analyser to determine the concentrations of PM_{2.5}, 18 elements, 5 ions, organic carbon (OC) and elemental carbon (EC). The EPA PMF was used to identify 8 factors that were affecting the receptor site. Seven outdoor sources were identified: ammonium sulfate (31%), traffic (10%), shipping (10%), sea salt (9%), fireworks (4%), Saharan dust (2%) and industrial (2%). An indoor factor was also identified, which contributed 26% to the indoor PM_{2.5}. Cooking and e-cigarette smoking were identified as the main contributors to the indoor factor. The mean indoor PM_{2.5} concentration (5.7 µg m⁻³) at the receptor site was slightly higher than the WHO AQG limit of 5 µg m⁻³. Uniquely for Malta, we have isolated a fireworks factor for indoor PM_{2.5}. Fireworks have been identified as being responsible for most of the Sb and Ba and hence are of great concern due to the health implications of these toxic elements.

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1. Introduction

The Maltese Islands are an archipelago located in the central Mediterranean Sea. The archipelago is geographically small and densely populated (ca. 500 000), with the two largest inhabited islands being Malta (316 km²) and Gozo (67 km²). The daily levels of outdoor particulate matter (PM) measured at the stations representing the most trafficked areas as well urban background areas in Malta exceed the Air Quality Directive limit values of PM_{2.5} and PM₁₀, several instances during the year. This is a recalcitrant problem in Malta (Scerri et al., 2018; Fenech and Aquilina, 2020). Receptor modelling on PM_{2.5} in a coastal town in Malta by Scerri et al. (2018) identified traffic, shipping and fireworks as the main anthropogenic sources contributing over 35% of the PM_{2.5} at that site. Anthropogenic activities were not limited to local emissions, with a significant contribution by ammonium sulfate (23.6%) attributed to regional/long-range transport (Viana et al., 2008). However, no research has been conducted so far on the chemical speciation and source apportionment of airborne indoor PM_{2.5} in Malta.

The correlation of ambient air pollution to health diseases and increased morbidity and mortality is widely established (Brunekreef and Holgate, 2002; IARC, 2015; World Health Organization, 2016) and traditionally studies have been focused on outdoor air quality. Since people spend most of their time indoors (Yao et al., 2015; Bo et al., 2017) indoor air quality is being given significant attention. Many studies have been conducted on indoor air quality, but these studies are generally related to the natural, industrial or urban effects on indoor air quality (Macneill et al., 2014; Krasnov et al., 2015; Almeida-Silva et al., 2016).

Given that people spend most of their times indoors, residential, indoor source apportionment studies are becoming necessary as they provide a better quantification of the exposure to PM_{2.5} than ambient source apportionment studies. Only a limited number of studies carried out source apportionment via receptor models such as Positive Matrix Factorisation (PMF) on indoor residential PM_{2.5} (Larson et al., 2004; Minguillón et al., 2012; Barraza et al., 2014; Molnár et al., 2014; Bari et al., 2015; Suryawanshi et al., 2016) with other PMF studies being carried out in classroom environments (Carrion-Matta et al., 2019). The paucity in indoor PMF studies can be attributed to the extensive chemical speciation required and the logistics required to obtain a large dataset necessary for PMF. Indoor PMF studies can also be challenging as one of the main assumptions of PMF is that source profiles are assumed to be the same across all samples. Several studies have addressed this issue either through factor selection (Molnár et al., 2014) or via expanded receptor models (Hopke et al., 2003; Zhao et al., 2007). Comparing data from different indoor source apportionment studies is not always easy since the sources' absolute and relative contribution may differ as these depend on city size, urban environment, climate, seasonal and cultural activities, building types and ventilation (Molnár et al., 2014). Nonetheless, certain important qualitative comparisons can be made especially on the main sources affecting indoor environments from similar indoor and outdoor environments.

This work aims to use PMF to characterise and quantify the sources affecting indoor PM_{2.5} levels at an urban background site, where the pollution levels are not significantly determined by any single source. Urban background sites represent the integrated contribution from many sources, including all upwind sources. Due to the historic Catholic religious influence in the Maltese Islands, all towns and villages celebrate their local patron saint during a week that is called the *festa* or feast. Several social activities are generally organised during the feast, amongst which a substantial amount of fireworks are let off. Special interest is being given to the effect of seasonal burning of fireworks across the Maltese Islands and whether this has an impact on the indoor air quality of residences that are not located in the vicinity of fireworks displays. Over 30 local pyrotechnic manufacturing sites produce fireworks for the religious feasts, 85 of which are celebrated during the summer months between the end of June and September. In addition, a three-day international fireworks festival is held in April and serves as a

main touristic attraction during a period of relative pyrotechnic inactivity. PM_{2.5} and PM₁₀ originating from fireworks have been recorded in ambient air across the Maltese islands (Camilleri, 2008; Vella et al., 2015; Camilleri and Vella, 2016; Scerri et al., 2018), but there is a dearth of data both locally and abroad on the indoor levels of fine particulate matter originating from fireworks.

2. Materials and methods

2.1. Sampling

The sampling was carried out in a three-storey building occupied by three residents in Birżebbuġa, a village of approximately 10 000 residents, located in the south-eastern part of Malta (Fig. 1) at an urban background site. The building is located on the outskirts of the village, in a residential area comprised of two to three-storey buildings. No retail or industrial activity is carried out in the vicinity. The roads in the area are two-lane residential streets with parking allowed on either side of the street. The area around Birżebbuġa was deemed to be an urban background site since its pollution level is not significantly determined by any single source. Such a description of the built conglomeration was used in an assessment report of air quality in Malta (Stacey and Bush, 2002). The Malta International Airport (at Gudja) lies at approximately 2 km northwest of the site. The liquified natural gas (LNG)-fired power station (at Delimara) and a transshipment hub (at Birżebbuġa port) are in an easterly and south-easterly direction at 1.5 and 2 km, respectively.

Indoor PM_{2.5} was collected using two single filter low volume air samplers (Leckel LVS-3) calibrated with a BGI Tetracal-Ultra and operated at a flowrate of 0.038 m³ min⁻¹. The samplers were placed in the living room of the residence, as shown in Fig. 2. The living room is connected to the kitchen and dining room via an open small window of 0.3 m². One sampler was loaded with PTFE filters and the other with quartz fibre filters (QF).

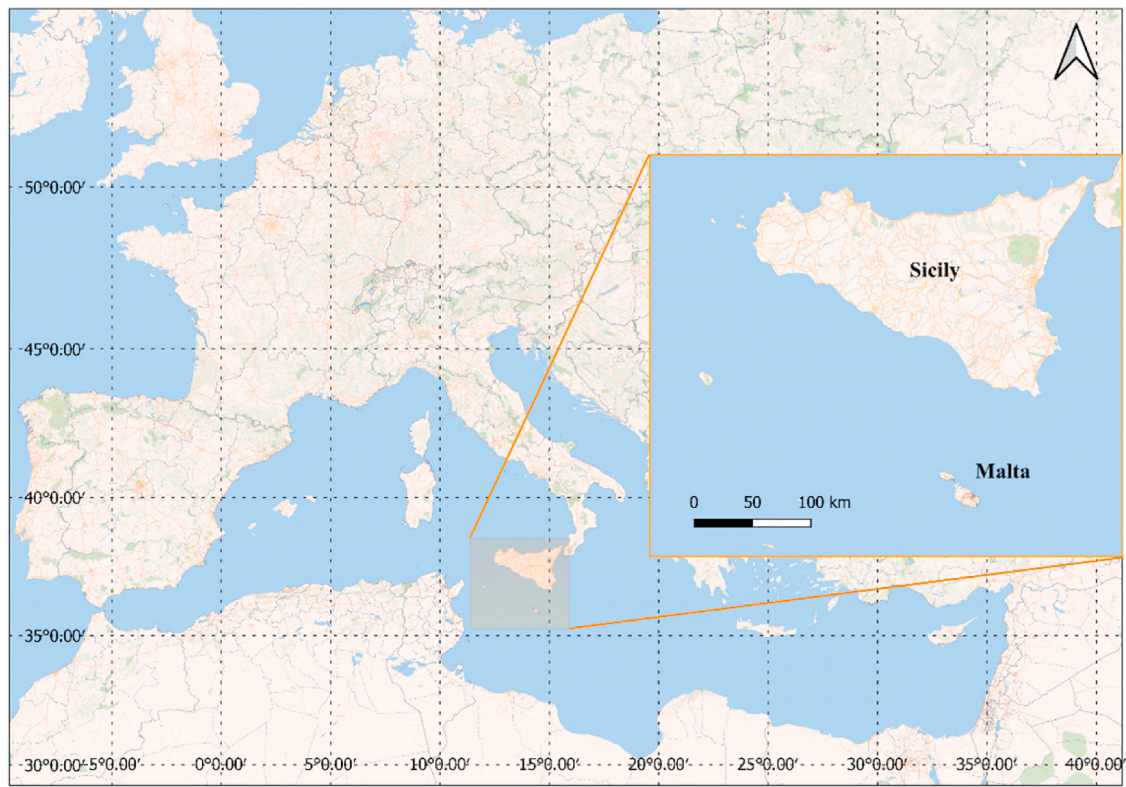
The sampling campaign was carried out between June 2018 and June 2019 and included 159 days of sampling. The 24-h sampling period started at midnight, thrice weekly on Mondays, Thursdays, and Saturdays (except during the feast of the Assumption of Mary in mid-August 2018, where sampling was carried out daily from 13th to 16th August).

2.2. Meteorological data

Indoor and outdoor weather data were collected during the whole period, including non-sampling days. The data included wind speed and direction and rainfall. Less than 10% of the sampling days experienced more than 5 mm of rainfall and hence there weren't enough data points to assess the impact of rainfall on indoor PM_{2.5}. During sampling days, residents kept a daily log of indoor activities such as cooking, heating/cooling, cleaning, smoking, and the opening or closing of outdoor windows. A summary of these activities is given in Table SI.4 in the Supporting Information (SI).

2.3. Analyses

PTFE filters were conditioned and weighed according to EN 12341:2014 (CEN 2014). The weighing room temperature was set at 19 °C–21 °C, and the relative humidity was maintained at 45%–50%. Microwave-assisted acid digestion of the PTFE filters was carried out using a microwave digester (Ethos up with SK-15 rotor). The acid digestion was carried out in a 7 mL PFA microvessel in order to provide a fast, reliable digestion method with minimal losses. Digestion was carried out in 2.5 mL of 69% v/v nitric acid and 30 µL of 50% v/v hydrofluoric acid. The vessels were ramped to 200 °C in 20 min and kept at 200 °C and 16 bar for another 20 min. After cooling, 240 µL of 5% m/v boric acid solution was added to each microvessel using a pipette. These vessels were re-sealed and ramped again to 200 °C in 20 min and kept at 200 °C and 16 bar for another 20 min. The digest was analysed by ICP-



(a)



(b)

Fig. 1. (a) Map indicating the geographic location of Malta and (b) showing the Birżebbuġa sampling site in relation to the Malta International Airport (MIA), the Transhipment hub and the LNG-fired power station.

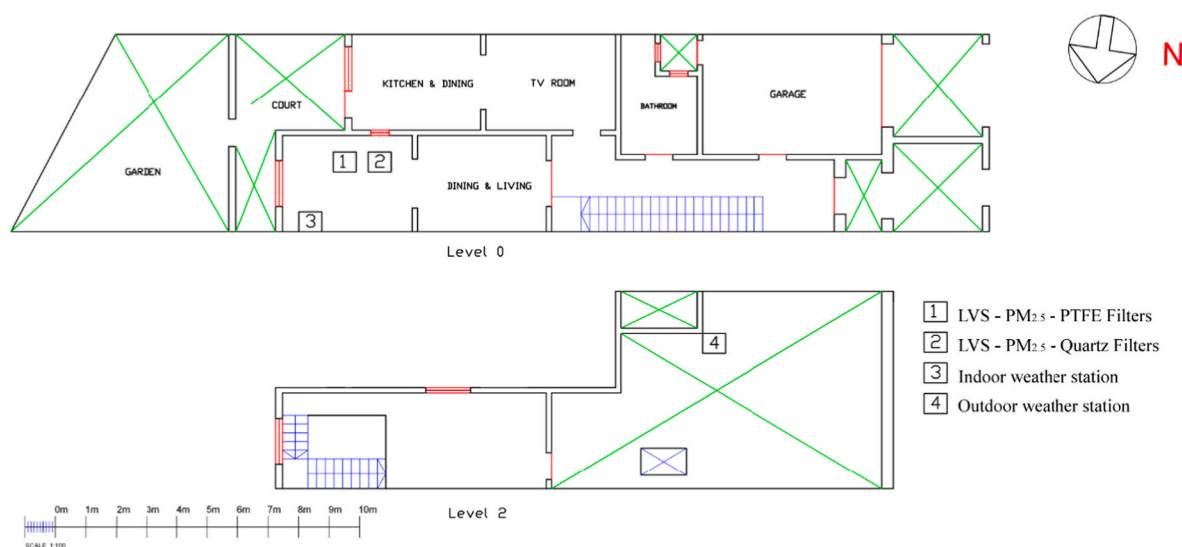


Fig. 2. Schematic diagram of the sampling site detailing the position of the samplers and weather stations.

MS to quantify the concentrations of Al, As, Ba, Ca, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, Ti, V and Zn.

QF filters (Whatman, QM-H, 47 mm) were used for OC-EC analysis of PM_{2.5}. These filters generally have low organic carbon (OC) concentrations ($1.22 \pm 1.11 \mu\text{g cm}^{-2}$) even without pre-firing (Karanasiou et al., 2015), however, in this work the QF filters were pre-fired at 500 °C for 4 h to ensure minimal blank OC concentrations. The QF filters were split into two using an aluminium template and stainless-steel rotary cutter. The stainless-steel cutter was cleaned with a clean filter between individual cuts. The half filters were placed into pre-cooled Petri dishes, sealed inside the polyethylene zip-lock bag and stored in a freezer at -20 °C until analysis.

The details of the method used for the EC-OC analysis are described in the SI. After the QF filters reached room temperature, a 1 cm² punch from all sampled filters and field blanks was taken and analysed using a Sunset Laboratory OC/EC aerosol analyser. With every 10th filter a duplicate punch was analysed for quality control purposes, and the percentage change in total carbon (TC) between the two punches was recorded. The NIOSH 870 OC-EC protocol used was based on a modification of NIOSH 5040, which is detailed in Table SI.2 in the SI.

The remaining half of the sampled QF filters were used for ion chromatography (IC) analysis of PM_{2.5}. The filters were brought to room temperature and transferred to labelled polypropylene centrifuge tubes. Digestion was carried out in 25 mL deionised water with a resistivity of at least 18.2 MΩ cm. The tubes were sonicated for 60 min at a temperature between 20 °C and 25 °C. This was followed by 15 min of shaking and the tubes were then left to rest overnight (12–24 h) at -4 °C. The contents were then filtered through a 0.45 μm PTFE syringe filter. Cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺) were analysed via IC according to EPA 350.1 and anions (Cl⁻, NO₃⁻, SO₄²⁻) were analysed via IC according to ASTM D6919-03. The ammonium ion nitrogen content was determined by colourimetry according to EPA 350.1.

2.4. PMF analysis

Source apportionment using receptor models enables the identification of pollution sources and quantification of the amount that each source contributes at the receptor site. PMF is an advanced factor analysis technique based on the work of Paatero and Hopke (2003). It imposes non-negativity constraints in the factor computational process. This receptor model has been applied for source apportionment of fine PM in ambient air (Kim and Hopke, 2008; Belis et al., 2013; Cesari et al., 2016; Manousakas et al., 2017) and has also been used for indoor source

apportionment (Minguillón et al., 2012; Barraza et al., 2014; Molnár et al., 2014; Suryawanshi et al., 2016).

The model can be written as

$$X = G \cdot F + E \quad (1)$$

where the species concentration matrix X , (that is the known n by m matrix for m number of PM species in n samples) can be factorised into two matrices, G , the factor contribution matrix (given by the $n \times p$) and, F , the factor profile matrix (given by the $p \times m$ matrix of source profiles), where p represents the number of factors extracted. E is the residual matrix, which is the difference between the measured X and the model $G \times F$ and hence is the unapportioned part. More information on the PMF solution is given in the SI.

2.5. Other statistical analysis

The normalised source contributions from the PMF solution were converted into meaningful contributions in ng m⁻³ by multiplying the normalised source contributions against the respective source profiles masses. Albeit non-negativity constraints, PMF 5.0 allows minimal negative source contribution; hence slightly negative source contributions were pulled up to zero before being converted into mass, since negative mass values are meaningless in terms of source contributions. The modelled PMF was compared to the observed gravimetric PM_{2.5} mass, and the un-modelled mass was calculated. The mass source contributions were used to calculate polar plots for each source using OpenAir package in R-studio (Carslaw and Ropkins, 2012). Seasonal contributions were also calculated and seasonal variations were analysed using the Kruskal-Wallis rank-sum test and the Mann Whitney U test in R-Studio.

3. Results and discussion

3.1. The PMF solution

The analytes were screened for their signal-to-noise ratios (S/N) (Paatero and Hopke, 2003; Zhao et al., 2006). In PMF, analytes can be considered as bad, weak, and good. In this solution, no analyte was classified as bad. Analytes with a S/N lower than 4 were down weighted to weak. These include the analytes Na⁺, K, Ca, Cr, Ni, Cu, Zn, As, Sr, Cd, Sb, Cl⁻ and NO₃⁻. EC was also down weighted to weak, even though it had a S/N ratio higher than 4, as a robust solution could not be obtained without down weighting EC.

As PMF is essentially a descriptive model, and the determination of the optimal number of factors that are fitted in the model remains a subjective one (Vecchi et al., 2008), the choice of the number of factors is a compromise. The PMF solution was run for a different number of factors ranging from 5 to 10. All base runs for the different number of factors solutions converged. The final number of factors was chosen depending on the results of the Q(Robust) and Q(True) values for each run, the intra-run residuals, the bootstrap (BS) analysis and the Bootstrap Displacement (BS-DISP) analysis (Norris et al., 2014; Brown et al., 2015). A description of the statistical results for the 5- to 10- factor solutions and the constraints applied to the 8-factor solution are given in the SI.

The BS-DISP analysis showed a more robust 8-factor solution having the lowest rotational ambiguity. This was accepted as the solution that provided the largest number of physically interpretable solutions. The solution achieved a good reconstruction of the PM_{2.5} mass with the modelled mass explaining 93% of the observed mass with a 0.98 coefficient of determination (r^2) for the plot of the observed against the modelled PM_{2.5} (Fig. SI.1).

3.2. PMF results for indoor PM_{2.5}

The profiles for the 8-factor solution are shown in Fig. 3. The uncertainty levels are set to the 5th and 95th percentile of the BS runs for the constrained solution. The yearly and seasonal contributions by each factor to indoor PM_{2.5} are shown in Fig. 4a and b, respectively. The polar plots for the source contributions were plotted using the OpenAir package in R-Studio (Carslaw and Ropkins, 2012) and are shown in Fig. 5.

Factor 1 contributed $1505 \pm 774 \text{ ng m}^{-3}$ of the indoor PM_{2.5} (26%) at the receptor site. The polar plot in Fig. 5 shows that the contributions from this factor are not linked to any particular wind direction factor and the highest concentrations are at the receptor site. This factor was therefore labelled “indoor”. The lowest contribution was registered in summer and the highest during autumn and winter. The seasonal difference in average contributions between summer and the other seasons is statistically significant ($p < 0.01$) but not statistically significant between autumn, winter and spring ($p > 0.01$). This could be possibly explained due to the lower exfiltration from autumn to spring due to lower air exchange rate (AER) at the sampling site, given homes are generally kept more closed during this period. The mean AER measured at the sampling site ranged from 0.195 h^{-1} with closed windows to 1.625 h^{-1} with partially opened windows. The activity summary shown in Table SI.4 shows that 40% of the sampling days were carried out with the residence’s windows either partially or entirely open. Windows were kept closed from mid-October 2018 to mid-May 2019, meaning that windows were only opened during hot summer months. Given the higher AERs during the summer months, outdoor sources are expected to contribute more significantly to indoor PM_{2.5} during this period due to the higher infiltration.

This factor is responsible for half of the OC at the receptor site with an OC/EC ratio of 11.9. The presence of lower amounts of EC in this factor is mainly due to EC being a primary pollutant generated from incomplete combustion, and unlike OC, it is most likely caused by outdoor sources, especially since there was no indoor solid fuel combustion or cigarette smoking. A poor correlation was registered between OC and EC sampled indoors, with the Pearson correlation for log-transformed data at $r = 0.007$. This is also reflected in the PMF results, as indoor EC is mainly obtained from traffic (45.6%) while most of the OC (50.6%) is of indoor origin, which confirms different sources for OC and EC and highlights that most of the EC is of outdoor origin.

OC/EC ratios have been used to characterise emissions of carbonaceous aerosols and the formation of secondary organic carbon (SOC) (Pio et al., 2011). Indoor OC/EC ratios for Chinese cities, ranging from 3.9 to 4.5 (Zhang et al., 2020), which suggested the formation of SOC. This factor’s OC/EC ratios are much higher than that. Pio et al., (2011)

reported an OC/EC minimum ratio of 0.6–0.8 for ambient PM_{2.5} in urban background environments with higher ratios associated with OC of secondary origins. Therefore, this factor’s high OC/EC ratios indicate the presence of SOC resulting probably from gas-to-particle condensation from indoor combustion related to cooking, e-cigarette smoking, and gas heating and also secondary organic aerosols formed from oxidation of cleaning agents. The activity summary in Table SI.4 shows that a flueless butane gas heater was used during 40% of the sampling days. The gas heater was only used during the colder months when outdoor windows were kept closed, resulting in higher indoor OC due to low exfiltration. Cooking using an electric over/toaster was carried out on most sampling days, whilst frying was carried out during 26% of sampling days. Different cooking modes such as frying/grilling/baking/oven or toaster use have different particulate emissions with frying/sauteing producing the highest amount of fine particulate matter (Wallace et al., 2003). E-cigarettes were smoked indoors during 94% of the sampling days. The presence of high levels of Cr and the presence of Ti in this factor indicates the source of these elements could be from heating elements, including those of e-cigarette smoke. Ti and Cr were found to be emitted from e-cigarettes heated filaments, yet conventional cigarettes did not produce these metals (Ruprecht et al., 2017). Given that only e-cigarettes were smoked daily explains the presence of high levels of Cr in this factor. While e-cigarettes also contribute to indoor organic compounds such as ethanal (0.26% that of cigarettes) and methanal (3.4%) albeit significantly lower when compared to conventional cigarettes, they do not contribute any BC emissions (Ruprecht et al., 2017). This is also consonant with the low EC detected in the indoor factor and the high OC/EC ratios.

Factor 1 is also responsible for 26.0% of Na and 26.9% of chloride at the site. These can be attributed to indoor dust resuspension from human activities and cleaning activities such as sweeping and vacuum cleaning, which were carried out during 16% and 8% of the sampling days, respectively. This factor is also the highest contributor for nitrate (31.1%). This may be attributed to the use of an unvented gas heater on 40% of the sampling days. The generation of NO_x from unvented gas combustion is well known (World Health Organization, 2010; Arata et al., 2018). Indoor nitrate production occurs due to lack of NO₂ photolysis. When sufficient O₃ is present from outdoor infiltration, NO_x is oxidised to nitrate. This conversion takes place after combustion stops and ceases to supply NO (Arata et al., 2018).

Factor 2 is the highest source contributor for Sr (60%) and Ba (35%). It is characterised by the elements Cu, Sr, Ba, K, Cl⁻ and NO₃⁻. The contribution from this factor is seasonal and is a source contributor only between June and September which matches the local patron saints’ feast season. Minimal contributions are noticed from October to May. The difference between the average contributions between the periods June to September and October to May is statistically significant ($p < 0.01$). The polar plot shows the highest emissions are mainly from a NW to SW direction as expected due to the receptor site being downwind from fireworks displays in NW to SW winds. This factor is characterised by peak emissions during 14–26 July (feasts in Tarxien, Valletta and Zurriq), the five feasts celebrated in 13–15 August, 01 and 03 September (feasts in Zurriq) and 13 and June 15, 2019 (feasts in Mqabba, Żejtun and Marsa). Reference is made to Fig. SI.4 in the SI for the indication of the areas letting fireworks in the abovementioned time periods with respect to the sampling site. This data is similar to that shown in a study by (Camilleri and Vella, 2010). The increase in metals in PM₁₀ associated with fireworks’ burning was reported to decrease significantly from summer to autumn months in Malta (Camilleri and Vella, 2010). In a similar manner, this study recorded a significant decrease in fireworks related PM_{2.5} at the receptor site from summer to autumn months.

A sudden increase in K concentrations can be used to identify fireworks events (Zhang et al., 2020) due to the prevalence of large amounts of K salts in pyrotechnic compositions. This factor explains 37% of the potassium at the site. During the feast of the 13–15 August, Ba

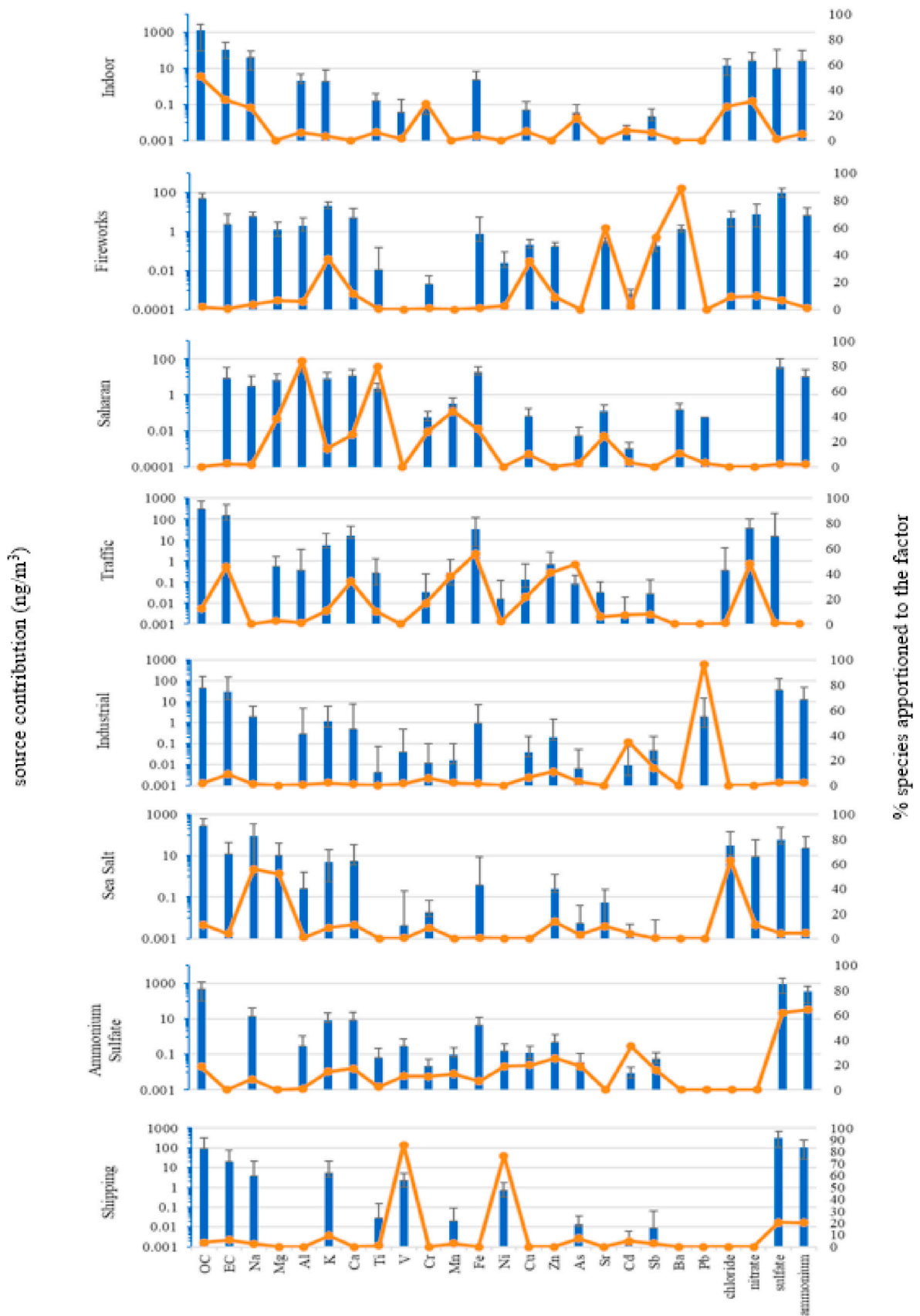


Fig. 3. Factor profiles (bars) and percentage of species apporportioned to each factor (line).

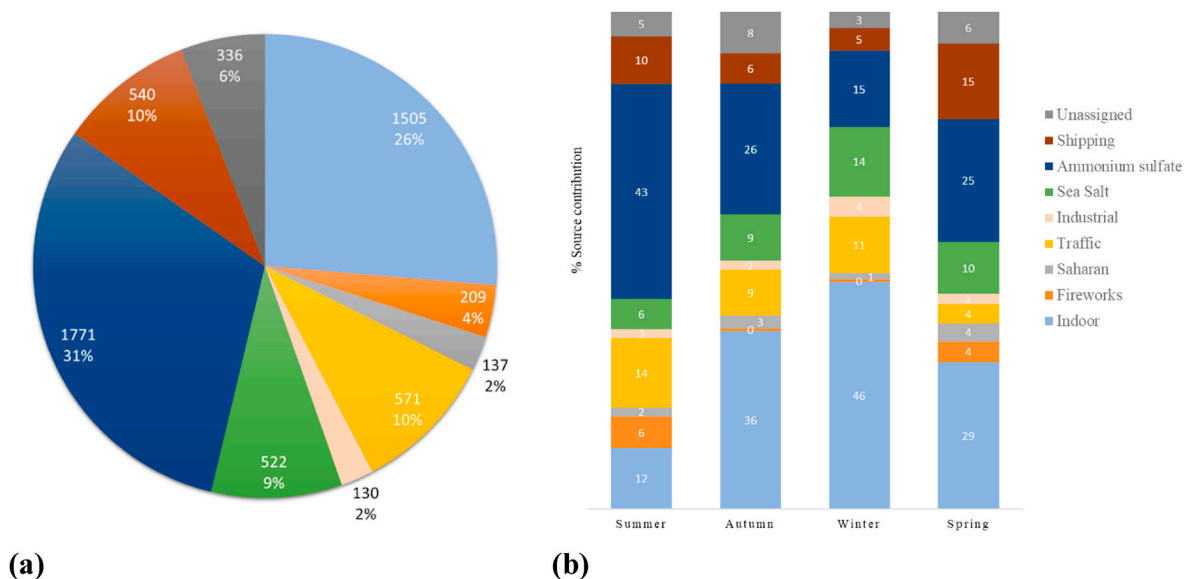


Fig. 4. (a) Annual mean source contributions to indoor PM_{2.5}. The values are given as percentages and in ng m⁻³. (b) Seasonal percentage source contributions to indoor PM_{2.5}.

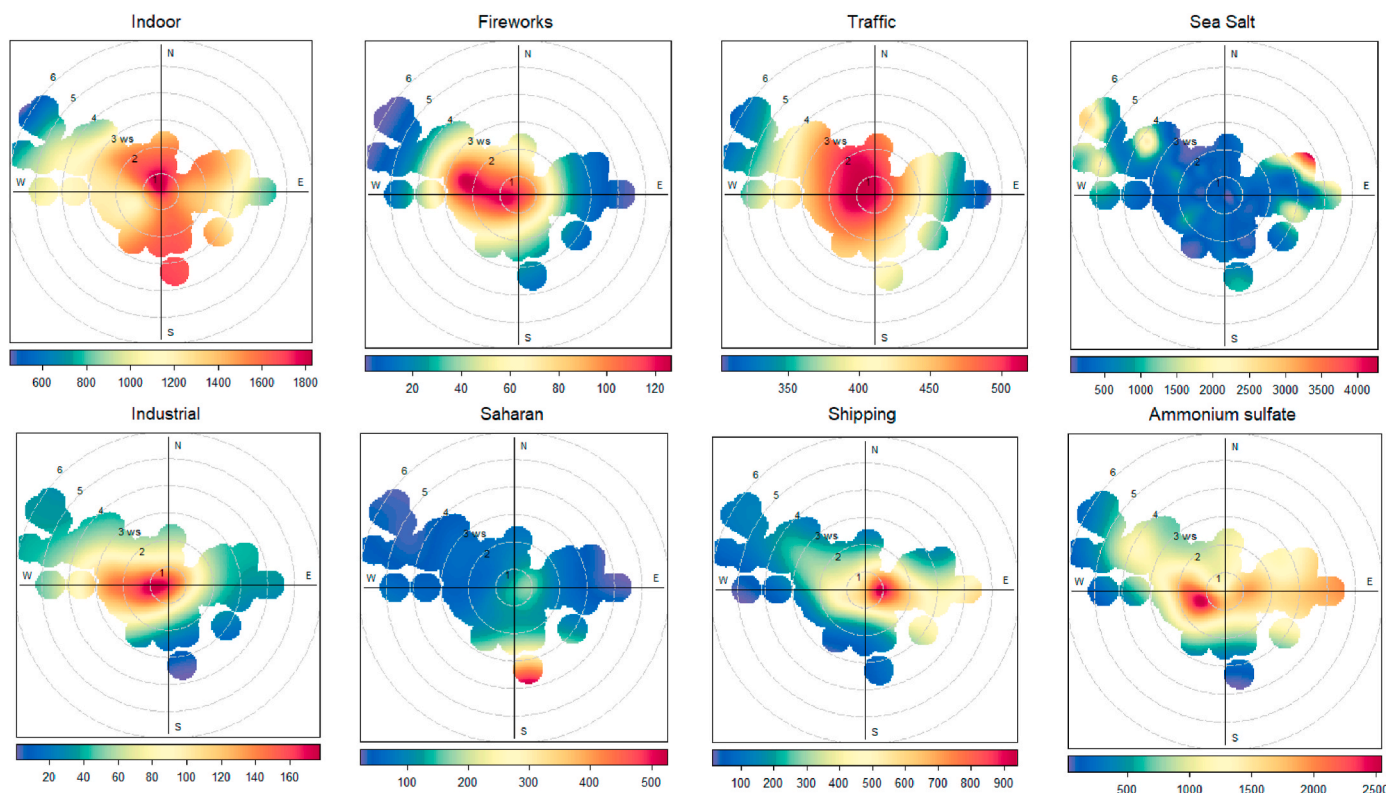


Fig. 5. Polar plot for the source contributions in ng m⁻³.

concentrations exceed 25 ng m⁻³ for several days which represents a 30-fold increase over the annual median concentration for this metal. In contrast, the roadside median concentration of Ba in Marylebone Road in London which is mainly derived from brake wear, was recorded at 15.6 ng m⁻³ (Gietl et al., 2010). This observation is of significance since no feast was celebrated in Birżebbuġa in mid-August and it is a clear indication that the metal-laden PM from nearby villages' fireworks displays disperse substantially to areas close by.

This source contributes 209 ± 769 ng m⁻³ to the indoor PM_{2.5} (4%)

at the site. A 6% contribution is registered for summer. This is a substantial contribution, given that this particulate load is not spread evenly throughout the year but occurs at specific peaks in relation to fireworks activities.

Factor 3 is characterised by the elements Al, Mg, Ca, Ti, Fe, Mn and Sr which are considered markers of Saharan dust (Rodríguez et al., 2002; Viana et al., 2008) and is responsible for 84.5% of the Al, 39.5% of the Mg, 79.5% of the Ti and 44.3% of the Mn at the site. This factor registered peaks that were at least five times the normalised contribution on

06–08 September, 29 October and 13–17 June. HYSPLIT back trajectories were run for all these dates at several heights above ground level (Fig. SI.2). The 1500 m trajectory was considered for the analysis of Saharan dust transport as the air mass at this height is in the upper part of the boundary layer, and surface artefacts are thus avoided. Moreover, this height can be considered as representative of the mean transport wind at a synoptic scale within the upper boundary layer (Salvador et al., 2007). The high factor contributions were all associated with air masses passing over the North African continent before reaching the receptor site. This is also confirmed by the polar plot for this factor which shows the highest contributions associated with S to SE winds.

Except for the September 2018 peaks, the other peaks coincided with Saharan episodes notified by Malta to the European Commission in its report for deduction of the contribution of natural sources from PM₁₀ levels (ERA, 2019; ERA, 2020). Saharan dust episodes only resulted in very high indoor concentration when the windows of the residence were open. Although the contribution of Saharan dust to PM₁₀ was calculated as being in excess of 100 µg m⁻³ on the October 29, 2018 (ERA, 2019) the indoor concentration for PM_{2.5} remained below 10 µg m⁻³. In contrast when the windows were open, a PM₁₀ Saharan dust contribution of 25–31 µg m⁻³ in June 2019 (ERA, 2020) resulted in an indoor PM_{2.5} concentration of 18 µg m⁻³. Given that the windows of the residence were mostly closed throughout the year, this factor only contributes 137 ± 268 ng m⁻³ to the indoor PM_{2.5} (2%). This contrasts with the contributions of Saharan dust to outdoor PM_{2.5} at Msida which were recorded at 15.1% (Scerri et al., 2018).

Factor 4 is the highest source contributor for EC (45.6%), NO₃⁻ (47.9%), Zn (40.9%), Fe (55.9%) and As (47.5%). It is also a main contributor for Ca, Cu and Mn. These elements and compounds are known to be different markers of traffic particulate emissions. Fe, Cu, Zn Cr and Sb are considered tracers for brake-wear (Schauer et al., 2006; Amato et al., 2011), Zn for tyre wear (Amato et al., 2011), OC, EC and NO₃⁻ are considered tailpipe emissions (Schauer et al., 2006) with As being emitted from tailpipe emissions of diesel engines (Talebi and Abedi, 2005). The presence of Ca is indicative of the contribution of re-suspended dust, given that the geology of outcropping rocks in Malta is dominated by limestone (Cassar and Vella, 2003). This factor, therefore, represents both exhaust and non-exhaust vehicular emissions.

OC/EC ratios at urban background sites in Portugal, Spain and the UK were recorded at 2.3–4.0 (Pio et al., 2011) with lower ratios (<2) being registered for urban roadside sites. The traffic factor at the receptor site has an OC/EC ratio of 2.0, which is similar to OC/EC ratios for the urban background sites. The Cu/Sb mass concentration ratio for this factor is 5.2. This ratio indicates that the most likely source is brake-wear particles with this ratio being like that reported for the fine particulate fraction in other studies. Pant and Harrison (2013) found that the Cu/Sb mass ratio in brake-wear particles is dependent on the PM size fraction. Several Cu/Sb mass ratios for PM_{2.5} fractions were reported, including 10 (Barcelona), 2.17 ± 0.83 (Taiwan) and 2.5 (Palermo). This reaffirms that this factor also explains fine PM generated from non-exhaust emissions at this urban background location.

The polar plot in Fig. 5 shows that the highest concentrations from this factor are at the receptor site indicating that this factor represents traffic emissions in the vicinity of the site. This factor contributes 571 ± 600 ng m⁻³ (10%) to the indoor PM_{2.5}. This is substantially lower than that reported by (Scerri et al., 2018) in Msida, where the traffic factor constituted 27.3% of the roadside outdoor PM_{2.5}. This is expected, given that the measurements at Birzebbuga referred to indoor values and also the characteristics of the site are very different. The highest percentage contribution was recorded in summer, with the traffic factor responsible for 14% of the indoor PM_{2.5}. The average contribution by traffic in summer is significantly different (p < 0.01) from that measured in the other seasons. This can be explained due to higher infiltration rates and also higher traffic flows in summer close to the receptor site, given that Birzebbuga is an important seaside holiday destination during the summer months.

Factor 5 is the highest source contributor for Pb (93.9%) and Cd (34.7%) and contributes 9.1% of EC at the site. The presence of high levels of Pb and Cd in this factor indicates industrial emissions. The polar plot shows a single source located in a W-SW direction from the receptor site. The Hal Far industrial zone is located SW of the receptor site at 1.5 km. Steel fabrication, hot dip galvanising and hot asphalt plants located in this area could be the sources of these heavy metals and EC. Hot dip galvanising is known for its emissions of Zn, Pb and Cd (National Pollutant Inventory, 1999).

Factor 5 is the smallest contributor at the site with 130 ± 187 ng/m³ (2%) and shows the highest contributions during winter. Nonetheless, this factor indicates that industrial activity has only a slight impact on the indoor PM_{2.5} levels at the receptor site.

Factor 6 is characterised by high Na, Mg and Cl levels. It is the most important source of Na (55%) and chloride (62%) at the site and contributes 522 (9%) ± 578 ng/m³ of the indoor PM_{2.5} at the receptor site. The Cl/Na ratio of 0.38 is considerably lower than the reported mass ratio for sea spray at 1.8 (Moller, 1990; Seinfeld and Pandis, 2016). Yet the Na/Mg ratio stands at 8.8, which is nearly identical to the ratio of these elements in seawater at 8.36 (Seinfeld and Pandis, 2016). This suggests that these elements are of marine origin and therefore, this factor was labelled as “sea salt”.

The presence of significant nitrate and sulfate in this factor is coupled with low chloride levels. The deficit of chloride ions can be explained by the volatilisation of chloride when NaCl reacts with acidic species such as HNO₃ and H₂SO₄ (Rodríguez et al., 2002; Galindo et al., 2008). In these chemical reactions the chloride ions are replaced by nitrate and sulfate ions forming aged sea salt. Hence this factor is representing aged sea salt. Given that the receptor site is affected by emissions from the nearby harbour and other offshore sources, the fresh sea spray could interact with pollutants such as NO_x and SO₂, producing particles that are enriched in nitrate and sulfate. This factor is in fact, responsible for 11% of the nitrate at the site. The polar plot shows that this factor is not particularly dependent on wind direction. High source contributions are recorded with an increase in wind speed, irrespective of wind direction. This again indicates sea salt as the source, given that sea salt aerosol mass concentration is known to increase with an increase in wind speed (Ovadnevaite et al., 2012). The plots also show that higher source contributions for this factor are associated with NW and E wind directions. Thus, sea salt particles in these air masses react with products of oxidation and hydration of NO_x and SO₂, that are generated both locally from traffic and harbour areas and/or transported, to form aged sea salt.

Factor 7 is the most important factor at the site contributing 1771 ± 1877 ng/m³ (31%) of the PM_{2.5} and is characterised by high amounts of NH₄⁺ and SO₄²⁻ ions. The NH₄⁺/SO₄²⁻ mass ratio for this factor is 0.36, which is nearly identical to the mass ratio of (NH₄)₂SO₄ at 0.376, suggesting that ammonium sulfate is the main component in this source, and hence the factor was labelled “ammonium sulfate”. Given that there are no known major indoor sources of fine SO₄²⁻ (Rivas et al., 2015) this factor can be considered to be of outdoor origin. The mass contribution of 3.79 µg m⁻³ for the ammonium sulfate factor for indoor air during the summer at the receptor site is half that recorded by Scerri et al. for outdoor air in Msida (6.22 µg m⁻³), which confirms the outdoor origins of this factor.

As expected, this factor shows a seasonal variation with the highest contribution registered in summer (43%) and the lowest in winter (15%). The increased photooxidation rates of SO₂ during the summer months explains the increase in particulate sulfate during the summer months (Song et al., 2001; Kim and Hopke, 2008). In a study on aerosol sulfates in the western Mediterranean (Galindo et al., 2008) the correlation coefficients between monthly average concentration and the percentages of secondary sulfates in PM_{2.5} to radiation and temperature were 0.92 and 0.88 respectively, with the highest sulfate concentration recorded in summer months.

The difference between the average percentage contribution during

different seasons was statistically significant ($p < 0.01$) except for autumn and spring. The percentage values are being used, rather than the actual mass contributions, to compensate for any seasonal changes due to changes in infiltration. Given that the oxidation of SO_2 to sulfuric acid is slow (Querol et al., 1998) secondary sulfates are used as indicators of aged air masses (Manousakas et al., 2017; Scerri et al., 2018) and therefore include contributions from long-range transport (Viana et al., 2008). Secondary aerosols originating from local or long-range transport are difficult to separate in factor profiles as they tend to share the same chemical markers (Viana et al., 2008). Fig. 6 shows that air masses associated with the highest contributions for factor 7 pass across Mt. Etna in Sicily, an active volcano with an estimated SO_2 emission of 1.8 kt day^{-1} (Carn et al., 2017). Given that the highest contributions are associated with air masses originating from Italy further corroborates this factor's transboundary nature. This factor is also responsible for 34.7% of the Cd and 19.1% of the As at the site, which suggests a transboundary contribution of these toxic elements.

Factor 8 is the highest source contributor for V (85.8%) and Ni (76.5%) and contributes $540 \pm 767 \text{ ng m}^{-3}$ (10%) of indoor $\text{PM}_{2.5}$. Ni and V are found in higher concentrations in heavy fuel oils that are commonly used by the shipping industry. V/Ni ratios for heavy oil combustion calculated by means of PMF were 3.2 ± 0.8 (Viana et al., 2014) in all PM fractions. For Mediterranean harbours, V/Ni ratios ranging from 2.5 to 5 are markers of shipping emissions (Viana et al., 2009) with non-vessel-derived (land) sources having a V/Ni ratio of 12 (Viana et al., 2014). Given that the V/Ni ratio for this factor is 3.2 it was labelled as "shipping". A similar V/Ni ratio of 2.5 was also recorded for the contribution by shipping at another coastal town in Malta (Scerri et al., 2018).

The polar plot for this factor indicates that the highest source contributions are associated with winds from the easterly direction. This further confirms shipping activities from the Marsaxlokk harbour as the primary source of this factor. The transshipment hub located in this harbour experiences high shipping activity. Given that the power station in Delimara is LNG-powered, shipping can be assumed to be the main source of this factor. Moreover, the bunkering area at Hurd's Bank and the waiting area for Marsaxlokk and Valletta harbours are also located around 15 km offshore in an ENE direction from the sampling site.

The actual and percentage source contributions for this factor are higher in summer and spring. This suggests that the higher contributions are not only due to the increased AERs during the warmer months but

also due to increased emissions arriving at the site. This is similar to that reported by (Manousakas et al., 2017) in Greece and (Scerri et al., 2018) in Malta and is possibly due to increased shipping activity in the warm period.

This factor is responsible for 20.7% of the sulfate at the receptor site. The high levels of sulfate in this factor can be explained by direct emissions of SO_3 by ships, given that ships burn fuel oil with higher sulfur content and oxidation of SO_2 at high flue temperatures is catalysed by V_2O_5 which deposits on the heat exchangers and other stack surfaces. The emitted SO_3 then shows as sulfates at the receptor site following condensation (Kim and Hopke, 2008; Pandolfi et al., 2011).

Many source apportionment studies include an unassigned fraction. In this study, this amounted to $336 \pm 1056 \text{ ng m}^{-3}$ (6%). The seasonal variation in the unassigned mass was not statistically significant ($p > 0.01$). Unassigned mass can be due to structural and absorbed water in the sampled dust remaining during sample conditioning (Yubero et al., 2011) and due to analytical uncertainties.

3.3. Comparison with other studies

A limited number of studies have carried out PMF receptor modelling on residential indoor $\text{PM}_{2.5}$ e.g. (Larson et al., 2004; Minguillón et al., 2012; Barraza et al., 2014; Molnár et al., 2014; Bari et al., 2015; Suryawanshi et al., 2016; Lai et al., 2019). In Table 1 we give a summary of the source apportionment and the percentage contribution in several indoor PMF studies. A PMF study on ambient urban background in another coastal Mediterranean city (Cesari et al., 2016) and the only other $\text{PM}_{2.5}$ PMF source apportionment carried out in Malta (Scerri et al., 2018) are also included. The sources' absolute (and/or relative) contribution may differ between these studies as these depend on the climate classification, meteorology, topography, the urban fabric, building types and ventilation conditions. Although quantitative comparisons can be difficult, certain inferences can be noted.

The residential indoor contribution across these studies ranged from 16.5% to 66.5%, with our study registering the second-lowest indoor contribution at 26%. Studies by Zhao et al., (2006) in the USA and Barraza et al., (2014) in Chile identified cooking as the primary contributor to indoor $\text{PM}_{2.5}$. We, too, conclude that cooking is a major source of the indoor factor and similar to these studies, such profiles included high levels of OC. The other indoor contributions were Secondhand Smoke and cleaning activities characterised by K and Cl

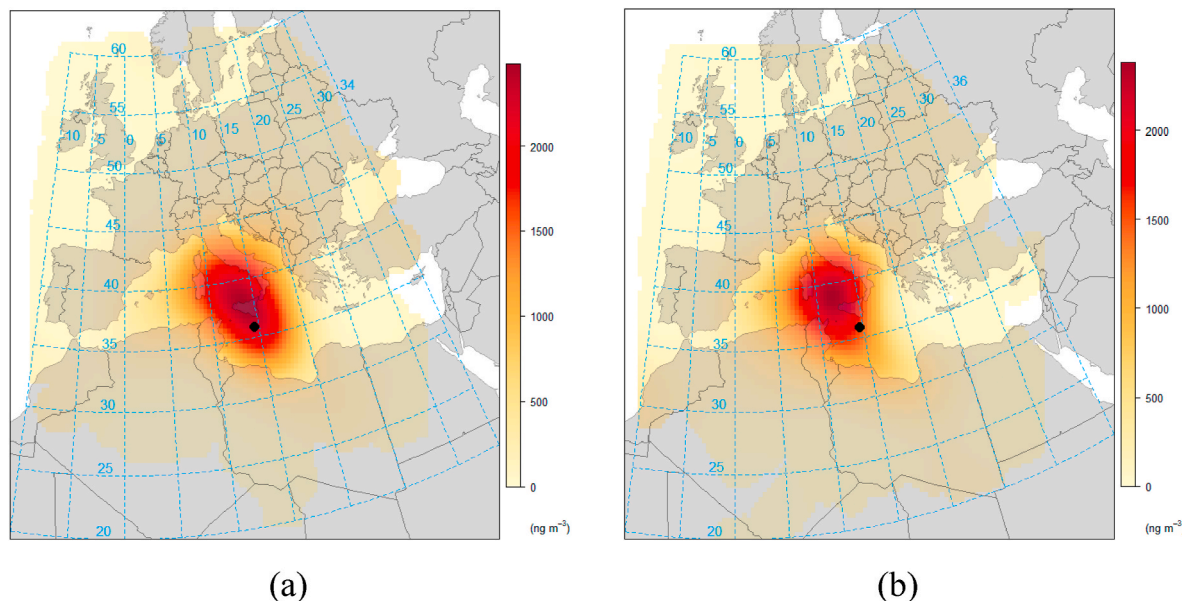


Fig. 6. Concentration field for the ammonium sulfate source contribution (in ng m^{-3}) at an arrival height of (a) 500 m and (b) 1000 m.

Table 1

Factors defined by PMF for indoor residential studies. Urban Background sites are listed as (UB).

Receptor	Type	PM _{2.5} (µg m ⁻³)	Source contribution to PM _{2.5} % (µg m ⁻³)							Article	
			Indoor	Crustal	Traffic	Shipping ^a	SIA	Sea Salt	Industrial		Others
Lecce (Italy)	Ambient (UB)	14.4	–	17.6 (2.5)	16.5 (2.4)	–	29.7 (4.3)	3.6 (0.5)	32.5 (4.7)	Cesari et al. (2016)	
Msida (Malta)	Ambient Traffic	15.1	–	15.1 (2.3)	27.6 (4.1)	5.0 (0.8)	23.6 (3.6)	4.6 (0.7)	24.4 (3.7)	Scerri et al. (2018)	
Birzebbuga (Malta)	Indoor residential	5.7	26 (1.5)	2 (0.1)	10 (0.6)	10 (0.5)	31 (1.8)	9 (0.5)	2 (0.1)	10 (0.5)	This Study
Barcelona (Spain)	Indoor residential			5	4		10	2	1	78	Minguillón et al. (2012)
Gothenburg ^c (Sweden)	Indoor (UB)	8.5	16.5 (1.4)		3.5 (0.3)		54 (4.6)	16.5 (1.4)		9.5 (0.8)	Molnár et al. (2014)
North Carolina (USA)	Indoor residential		66.5 ^b	3.0	7.6		21.9			1.0	Zhao et al. (2006)
Santiago (Chile)	Indoor residential		45.7 (10) ^b		38.8 (8.5)		15.5 (3.4)				Barraza et al. (2014)

Others includes other anthropogenic factors and unassigned fractions. Traffic includes road dust. Crustal includes Saharan.

^a Include Heavy Fuel Oil (HFO) combustion.^b Includes Secondhand Smoke and personal care. Cooking is the major contributor.^c Calculated as not given directly in the study.

ions. Since no smoking occurred at our receptor site, tobacco smoking was not recorded as a contributor, and this could be one of the reasons for the lower indoor contribution when compared to the indoor sites in USA and Chile.

All indoor studies recorded a contribution from traffic, although this varies significantly between studies (3.5%–38.8%). The highest contribution was registered in Santiago (38.8%), given that sampling at this site was carried out in an urban environment. Interestingly the percentage traffic contribution at our receptor site was only slightly lower than that observed in Lecce for an ambient background site (16.5%) but considerably lower than the 27.6% at the ambient traffic site in Msida.

Secondary Inorganic Aerosols (SIAs) are the most important contributor to indoor residential sites (15.5%–54%) with the Birzebbuga site registering one of the highest percentage contributions (31%) for this source. This value was nearly identical to that for ambient PM_{2.5} in Msida (29.7%). This suggests that the air masses in Malta are considerably affected by pollution from long-range/transboundary pollution given the very similar contributions in other coastal Mediterranean cities, with Lecce (UB) 24.3%, Thessaloniki (UB) 33.0% (Cesari et al., 2016; Diapouli et al., 2017).

Although in Europe, SO₂ emissions have decreased during the past 25 years, the relatively lenient limits on the sulfur content of marine fuel in the Mediterranean compared with fuels for land transport means that we now expect that under business-as-usual scenarios, emissions from maritime activities will equal those from land-based sources in the EU (Schembari et al., 2012). SO_x emissions from ships in the Mediterranean account for over 50% of all the European sea regions (Jalkanen et al., 2016). Therefore, with the Malta-Sicily channel being one of the busiest sailing corridors of the Mediterranean, with over 30 000 tankers and large ships sailing through this channel annually (Ellul et al., 2013) maritime emissions constitute a significant contributor both directly, with an estimated 10% contribution at the receptor site, and indirectly via particulate sulfate through secondary formation. Ammonia from land-based emissions in mainland Europe reacts with the products of oxidation and hydration of SO₂ emitted from ships resulting in increased secondary sulfate concentrations along the shipping routes and coastal areas in the central and western Mediterranean (Aksoyoglu et al., 2016).

Uniquely to the local scenario, fireworks are detected as a source in Malta with a 2.9% contribution for ambient air in Msida and 4.0% for indoor air in Birzebbuga. To our knowledge, the only other PMF source apportionment study which calculated the direct and indirect impacts of fireworks was carried out in a megacity in China during the Chinese New

Year (Tian et al., 2014). However, this resulted from a short three-week sampling campaign carried out specifically during the Chinese lantern festival, with fireworks contributing 24.1% of the PM_{2.5} during this period. The identification of fireworks as a source in long sampling campaigns remains purely a Maltese phenomenon.

Approximately 140 tons of fireworks-related material were estimated to have been burnt in the 2012–2014 period in Malta (Camilleri and Vella, 2016). This amount is equivalent to 633 kg per square kilometre per year. In comparison, 93 700 tons of fireworks were burnt in the US (2019) during the same period, which amounts to only 9.9 kg per square kilometre per year. The figure in the US is for the entire firework device (including packaging and inert structural material).

These findings confirm that fireworks are indeed affecting the indoor air quality in Malta, and when the prevalence of pyrotechnic activity is high, the potential for harm to human health cannot be ignored. Even though fireworks contribute 4% of the total PM_{2.5} at the receptor site, they are responsible for most of the Ba (88.9%) and Sb (52.9%). They are also responsible for 35.5% of the Cu measured at the site. Ba causes bronchoconstrictor effects and interferes with the heart and renal functions (Hicks et al., 1986; Kravchenko et al., 2014) and it is suspected to be responsible for the significant increase in asthma during the Diwali festival in India (Murty, 2000). Moreover, Ba derived from fireworks is expected to be more bioavailable since it is present as water-soluble compounds (Steinhauser et al., 2008) in contrast with the less soluble barite from brake pads. The presence of Sb in indoor PM_{2.5} is also problematic given that antimony trioxide is classified as a possible carcinogen to humans (Group 2B) (IARC, 1989; von Uexküll et al., 2005). Pyrotechnic derived PM is also associated with the presence of unreacted perchlorate (Vella et al., 2015), given that potassium perchlorate is the primary oxidiser used in pyrotechnic compositions in Malta (Camilleri and Vella, 2016). Perchlorate is known to interfere with thyroid function as it inhibits the uptake of iodine into the thyroid (Clewett et al., 2004) although the effect of human chronic exposure to low doses of environmental perchlorate is still unclear and subject of study (Gold et al., 2013; Pace and Vella, 2016).

The fact that pyrotechnic metals are present in the indoor environment, is of greater concern as this alone increases the potential for human exposure to these toxic species (Yao et al., 2015; Bo et al., 2017). Moreover, one can expect that the highest episodic indoor concentrations are registered during the night when people are sleeping since most firework displays in Malta take place between 7 p.m.–11 p.m. Fireworks-derived PM could be the easiest controllable source of

particulates on the islands and would be achieved by proper control on the quantity and type of fireworks that are burnt. However, the enthusiasm for fireworks manufacture and display exhibited by the pyrotechnic community and their numerous local supporters is so great that it will be difficult to restrict or regulate the activity. Unfortunately, in recent years, the production of fireworks in Malta is estimated to have actually increased by over 170% (Pace and Vella, 2016).

The WHO annual air quality guideline (AQG) level of $5 \mu\text{g m}^{-3}$ (World Health Organization, 2021) for $\text{PM}_{2.5}$ is applicable to both outdoor and indoor environments. The mean indoor $\text{PM}_{2.5}$ concentrations at the receptor site are slightly higher ($5.7 \mu\text{g m}^{-3}$) than the WHO AQG level while the 24-h limit of $15 \mu\text{g m}^{-3}$ was exceeded twice with shipping and fireworks being responsible for most of the contributions during these two days. Given the high mean indoor concentrations during the summer months ($8.8 \mu\text{g m}^{-3}$), local emissions from fireworks and emissions from shipping in the Mediterranean should be decreased in order to improve indoor air quality in coastal areas in Malta.

4. Conclusion

This study carried out receptor modelling via PMF on indoor $\text{PM}_{2.5}$ at a residential location in an urban background site in Malta. Indoor environments have not been extensively characterised via PMF, and there are very few such studies in the Mediterranean region. This study identified eight factors, including seven outdoor sources namely fireworks (4%), Saharan dust (2%), traffic (10%), industrial (2%), sea salt (9%), ammonium sulfate (31%) and shipping (10%). An indoor factor was also identified, which contributed 26% of indoor $\text{PM}_{2.5}$. Cooking and e-cigarette smoking were identified as the main contributors to the indoor factor.

Indoor $\text{PM}_{2.5}$ at this urban background receptor site is mainly affected by outdoor sources, which generate 68% of indoor $\text{PM}_{2.5}$. The contribution by outdoor sources of $7.3 \mu\text{g m}^{-3}$ (83%) is much higher in summer in both absolute and relative terms. The decrease to $1.8 \mu\text{g m}^{-3}$ (51%) in winter can partially be attributed to lower infiltration as the residence's windows were kept closed during the colder months. The anthropogenic contribution to indoor $\text{PM}_{2.5}$ during the summer months is 75%, with SIAs (mainly as ammonium sulfate), traffic, shipping and fireworks being the most important contributors.

The anthropogenic contribution must be reduced for indoor $\text{PM}_{2.5}$ concentrations to fall below the ambient WHO AQG for annual $\text{PM}_{2.5}$. Pollutant emissions from ships in the Mediterranean region could be reduced through the establishment of an emissions-controlled area. Transboundary ammonia emissions from mainland Europe would also need to decrease in order to reduce the formation of particulate ammonium sulfate in Maltese residences. Locally, the social (non-essential) burning of fireworks could in theory be readily controlled in order to decrease the exposure to toxic elements in the indoor residential environment, but apparently, the opposite trend appears more likely. This work is a first step at untangling and quantifying the principal sources of indoor fine particulate matter as defined by $\text{PM}_{2.5}$ and presents a better picture of the exposure status to $\text{PM}_{2.5}$ of home dwellers in Malta.

CRedit authorship contribution statement

Renato Camilleri: Conceptualization, Methodology, Data curation, Formal analysis, Writing – original draft, Visualization. **Alfred J. Vella:** Conceptualization, Writing – review & editing. **Roy M. Harrison:** Data curation, Writing – review & editing. **Noel J. Aquilina:** Conceptualization, Methodology, Supervision, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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