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$PM_{2.5}$ elemental composition in indoor residential environments and co-exposure effects on respiratory health in an industrial area

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ABSTRACT

This study aimed to identify and characterise indoor sources of particulate matter (PM) in domestic environments. 74 inhabited apartments located in the urban area of Gela (Sicily, Italy), close to a refinery, and in three villages of the hinterland were evaluated, in real-world conditions, for the elemental composition of $PM_{2.5}$. The samples were collected simultaneously inside and outside each apartment for 48 h. In addition, two of the apartments were simultaneously studied for four weeks.

The elemental composition of $PM_{2.5}$ was determined by applying a chemical fractionation procedure followed by inductively-coupled plasma spectrometry analysis, with both optical emission and mass detection. The extractable, more bio-accessible fraction ($_{ext}$), and the mineralised residual fraction ($_{res}$) of each element were determined, thus increasing the selectivity of elements as source tracers.

Indoor air in the considered apartments was affected by both outdoor pollution and specific indoor emission sources. The behaviour of each source was studied in detail, identifying a reliable tracer: Ti_{res} for soil, As_{ext} for industrial sources, V_{ext} for heavy oil combustion, Ce for cigarette smoking and Mo for the use of vacuum dust cleaners. As_{ext} and V_{ext} showed an excellent infiltration capacity, while the concentration of Ti_{res} was affected by a low infiltration capacity and by the contribution of particles re-suspension caused by the residents' movements. In the case of Ce and Mo, indoor concentrations were much higher than outdoor with a high variability among the apartments, due to the inhabitants' habits concerning cigarette smoke and use of electric appliances. To test the overall effect of the concomitant exposure to the identified sources on Wh12 M and on DDA, a WQS analysis was conducted. Cigarette smoking and heavily oil combustion driven the Wh12 M odds increase, while the DDA odds increase was mainly driven by heavily oil combustion and the use of vacuum dust cleaners.

1. Introduction

It is well known that the quality of air in indoor environments plays a key role in determining people exposure to atmospheric pollutants, as the amount of time that we all spend in homes, workplaces, schools, transport media and other closed environments dramatically exceeds the time we spend outdoors (Schweizer et al., 2007, Mannan and Al-Ghamdi, 2021). Air quality studies aimed to evaluate the exposure to indoor pollutants are of fundamental importance for sensitive populations such as children, elderly, and sick persons, who typically spend an even higher fraction of their time indoors. Moreover, getting information about indoor air quality is essential in polluted industrial areas, as the chemical species emitted by the industrial plants also affect indoor non-working environments, with substantial consequences on occupants' health (Zammit et al., 2020).

It is also known that indoor air quality depends on both the infiltration of pollutants from outdoors and the strength of indoor sources related to occupants' activities. These include cooking, smoking, using electronic machines, household appliances and personal hygiene products, wood heating, candle burning, re-suspension of deposited dust due to people's movements, temporary activities such as renovations, among others (Ferro et al., 2004; Qian et al., 2014; Yu et al., 2015; Chithra and Shiva Nagendra, 2018; Drago et al., 2018; Tran et al., 2020).

The case of atmospheric particulate matter (PM), characterised by a

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wide chemical, physical, dimensional, and morphological variety, is much more complex than that of individual gaseous pollutants, and the determination of its chemical composition is essential to identify its sources and strength and to evaluate its health effects. Moreover, indoor PM has been demonstrated to be toxicologically more active than outdoor air (Oeder et al., 2012; Tran et al., 2020; Zammit et al., 2020), making the study of the chemistry of the indoor atmospheric aerosol a complex but crucial scientific target.

From a practical perspective, the study of PM chemical composition in indoor sites requires collecting samples in inhabited environments that often have small dimensions. This means that the sampling devices must be small and quiet enough to avoid annoyance to the inhabitants and that their flow rate must be low enough not to modify the ambient concentration. Because of these difficulties, many literature studies about indoor PM in small, inhabited environments have been limited to mass or number concentration or some chemical components only (Fuoco et al., 2015; Isaxon et al., 2015; Mazaheri et al., 2016; Liu and Zhang, 2019). However, some detailed studies reporting a complete chemical characterization were carried out both in schools (Amato et al., 2014; Rivas et al., 2015; Tofful and Perrino, 2015) and homes, undoubtedly the most sensitive environment to the presence of bulky and noisy equipment, especially during the night (Perrino et al., 2016). Concerning the elemental composition, which is a valuable tool to identify PM sources, some indoor studies report data collected in schools (Molnár et al., 2007; Viana et al., 2015; Ruggieri et al., 2019; Martins et al., 2020), while only a few studies were carried out in populated domestic environments (Molnár et al., 2006; Anand et al., 2022; Camilleri et al., 2022).

Numerous epidemiological studies have demonstrated that short and long-term exposure to particulate matter with an aerodynamic diameter <2.5 μm ($PM_{2.5}$) can cause adverse respiratory outcomes (Drago et al., 2018; Schraufnagel et al., 2019; Xu et al., 2020, among others). To a large extent, the chemical components and emission sources determine the particulate matter detrimental health effects. Indeed, $PM_{2.5}$ is a complex mixture of chemical and biological species and the potential interaction between its different constituents can lead to different magnitude of health effects. Evaluating the joint effects of indoor $PM_{2.5}$ constituents remains a major challenge in the elucidation of health risks of fine particulate exposure.

This work aimed to study the in-out variations in the elemental composition of $PM_{2.5}$ in 74 inhabited apartments located in the industrial area of Gela (Sicily, Italy) and the background area behind the city. The secondary, first degree schools located in the same geographical area had been already evaluated for PM composition in previous work (Ruggieri et al., 2019). The study of Ruggieri et al. showed that the composition of the atmospheric aerosol collected indoors reflected the outdoor composition and that the air quality in the industrial area was worse than in the background sites, not only outdoors but also indoors.

In this paper, the elemental composition was studied with the purpose to trace the main PM sources. To this aim, the extractable and residual fraction of each element was determined, according to a chemical fractionation procedure previously validated and reported in the literature (Canepari et al., 2006, 2009). Chemical fractionation assures an improvement of the selectivity of elements as source tracers, as different PM sources release the elements in various chemical forms that may have different solubility (Ren et al., 2021; Massimi et al., 2022). Furthermore, the soluble fraction gives indications about the bio-accessibility of toxic elements, a characteristic that is rarely addressed in literature studies about indoor exposure and may be crucial for a correct evaluation of the health risks associated to PM (Anand et al., 2022). In each apartment, indoor and outdoor samplings were always simultaneous, allowing a reliable evaluation of the infiltration of PM and its components. In two of the apartments, PM was collected for four weeks, during summer and winter, to study the seasonal differences in the traced sources and extensively examine the covariance of groups of elements tracing the same sources. Moreover, we used WQS regression analysis to examinate the overall effect of the identified sources on the exposure of children living in the evaluated apartments as concerns respiratory symptoms.

2. Materials and methods

2.1. Study design

Between March and December 2012, in the context of the "RESPIRA" Cross-Border Program Italy-Malta 2007–2013, an epidemiological survey was performed in Sicily, in the southern Mediterranean area. Within the RESPIRA project, 1325 schoolchildren were randomly selected from all the secondary schools, first degree, of the Gela Health District. The local Ethical Committee approved the study, and all parents of the investigated children signed an informed consent. Moreover, parents were asked to complete a modified version of the ISAAC questionnaire (Asher et al., 1995) regarding respiratory symptoms and personal information: 1190 parents' questionnaires were obtained (Drago et al., 2018). Episode of wheezing in the last twelve months (Wh12 M) was defined as a positive answer to the question: "In the past 12 months, has your child had wheezing or whistling in the chest?". A child having "doctor-diagnosed asthma" (DDA) was defined as a positive answer to the question "Has your child ever had asthma diagnosed by a doctor? ". Information on the possible confounders or effect modifiers was also collected. Skin prick test panel, including Dermatophagoides, Alternaria, Parietaria, Graminacee, Dog, Olea, *Blattella germanica*, Cat extracts plus positive and negative controls, was performed for each subject according to EAACI recommendations (Dreborg and Frew, 1993). Allergic sensitization was defined as at least one skin reaction to allergens with a mean wheal diameter of 3 mm or larger.

$PM_{2.5}$ was collected for 48 h in 72 apartments located in the urban area of Gela (77,000 inhabitants, 35 apartments), located on the south coast of the Sicily island (southern Italy) close to one of the largest oil refineries in Europe, and in the villages of Niscemi, Mazzarino, and Butera (26,400, 11,800 and 4900 inhabitants, respectively, 37 apartments), located at 15 km, 25 km, and 14 km, respectively, from Gela. A map of the sampling area is shown in Fig. 1.

All the samplings were carried out between June 2012 and February 2013, when the Gela refinery was fully operating. At the end of 2014, the petrochemical refinery closed down to be subsequently converted into a biorefinery, in operation since 2019.

In each apartment, $PM_{2.5}$ was simultaneously collected indoors and outdoors using very quiet devices (<35 dB) operating at the flow rate of 10 l min^{-1} (SILENT Sequential Air Sampler, FAI Instruments, Fonte Nuova, Rome, Italy) and equipped with 47 mm Teflon filters (TEFLO, 47 mm, 2.0 μm pore size, PALL Life Sciences).

Two other apartments located in the centre of Gela were simultaneously monitored for two weeks in summer (July 4–17, 2013) and two weeks in winter (February 13–26, 2014), using the same procedure and instrumentation.

2.2. Analytical procedure

To calculate $PM_{2.5}$ mass concentration, the filters were weighted before and after sampling using an automated microbalance mod. ME5, 1 μg sensitivity (Sartorius AG, Goettingen, Germany) after conditioning at 50% R.H. and 20 °C for 48 h.

Elemental analysis was performed according to a method optimised and validated in its development stage on both standard certified material and pairs of environmental samples (Canepari et al., 2006). The filters were extracted for 20 min under ultrasounds in acetate buffer (CH_3COOH/CH_3COOK 0.01 M; pH 4.3) and filtered on cellulose nitrate membranes (0.45 μm pore size; Millipore, MA-USA). This extracting solution was chosen to increase the selectivity of elements as PM source tracers, but also to estimate their environmental mobility and bio-accessibility (Canepari et al., 2010). The extracts ($_{ext}$) were analysed

Fig. 1. Map of the study area (upper panels) and of the apartments in Gela (35 apartments monitored for 48 h, plus 2 apartments, H1 and H2, monitored for 4 weeks) (lower panel).

by inductively coupled plasma with both optical emission (ICP-OES; Vista MPX CCD Simultaneous, Varian, Mulgrave, Australia) and mass detection (ICP-MS; 820 MS, Bruker). Cu, Fe, Mg, Mn, Na, S were quantified by ICP-OES and As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, La, Li, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V by ICP-MS. The residual fraction ($_{res}$) was then subjected to microwave-assisted acid digestion, using HNO_3:H_2O_2 (2:1) (Ethos Touch Control with HPR 1000/6 S rotor, Milestone); it was then filtered again at 0.45 μm and analysed by ICP-OES and ICP-MS (same elements as for the extracted fraction, with the exception of Cr, which is inefficiently mineralised in the digestion mixture, and Na and S which are contained only in the extractable fraction). Matrix-matched standard solutions were used for calibration; Y and Sc were used as internal standard; the collision reaction interface (CRI) was activated for As determination.

2.3. Statistical analysis

Elemental concentration was expressed as mean, median, standard deviation, and 10th–90th percentiles. Differences between indoor and outdoor concentration was evaluated by means of the Wilcoxon signed-rank test for paired data. The limits of detections (LODs) were calculated as the mean value plus three times the standard deviation of the blanks. In the calculations, concentrations below the limit of detection were replaced with LOD/2, as recommended for small datasets (Hornung and Reed, 1990; Clarke, 1998; Hewett and Ganser, 2007; Helsel, 2010).

Principal Component Analysis (PCA) was carried out using the statistical software CAT (Chemometric Agile Tool) based on the R-project for statistical computing, Ver. 3.0, 32-bit. The data matrix was transformed by performing row and column autoscaling to correct variations in the different scaling of the examined variables.

The weighted quantile sum (WQS) regression model was used to assess the relationship between indoor air pollutants and respiratory symptoms. This model produces a weighted linear index and an associated weight for each pollutant, ranging from 0 to 1, which reflects how much the exposure to each identified PM component or source contributes to the overall association with the outcome. The bootstrap was set to 100 times, and it was assumed that the direction of association was positive for all the exposures tested. All regression models were adjusted for gender and atopic state. The analyses were performed using R package gWQS within R software version 3.6.1.

We categorized indoor air pollutants levels into tertiles, with the 1st tertile representing the lowest level of exposure. For the indoor sources – cigarette smoking and vacuum dust cleaner – we created tertiles using total Ce and Cu concentration, respectively. As regards the sources with high seasonality (i.e., industrial emission – As_{ext}, and heavy oil combustion – V_{ext}), the tertiles were created taking separately into account the season in which the measurements were performed.

The association between each exposure tertile, and both Wh12 M and DDA was also assessed using logistic regression models adjusted for age and allergic sensitization of subjects.

3. Results and discussion

The mean and median values, standard deviation, 10th and 90th percentiles of the indoor and outdoor concentrations of the two elemental solubility fractions in the 72 apartments are reported in Tables 1 and 2. The LODs and the number of determinations > LOD, expressed as a percentage of the total number of determinations, are also reported. An asterisk indicates the elements showing indoor values significantly different from outdoor values (Wilcoxon signed-rank test; $p < 0.002$).

It is worth noting that the LODs of the extracted fraction are much lower than those of the residual fraction. Therefore, the chemical fractionation method allows evaluating elements that would have been below the detection limit if detected using the usual total digestion procedure. This is the case of Cadmium and other potentially toxic elements.

The results in Tables 1 and 2 show that some elements were contained mainly in the extractable and more bio-accessible fraction (e.g., Cd, Rb), while other elements were almost totally in the mineralised residual fraction (e.g., Ba, Ce, Fe, La, Sn, Ti). This indicates that most of the detected elements were scarcely bio-accessible and potentially less dangerous for the human health.

Following the typical abundance in the atmospheric aerosol, the concentrations of the detected elements were very variable: from some fractions of pg/m^3 (Be, Ce, Cs, La, U) to tens or hundreds of ng/m^3 (Fe, Mg, Na, S).

Among the extractable/residual fractions of all the detected elements, we identified some robust tracers of indoor PM sources, following the procedure reported below. First, we removed the elements/solubility fractions having more than 30% of the concentration values below the LOD (indoors or outdoors). This was done as a precautionary measure to make the data processing more robust (Kang et al., 2014). Then, we run an explorative PCA to highlight the cases when the extractable and residual fractions were covariant. For these elements, we replaced the two solubility fractions with the total element concentration. The final dataset included As_{ext}, Cd_{ext}, Ce, Cu, Fe, La, Mg_{ext}, Mg_{res}, Mn, Mo, Na_{ext}, Ni_{ext}, Pb, Rb_{res}, S_{ext}, Sb, Sn_{res}, Ti_{res}, Tl_{ext}, and V_{ext}.

A new run of the PCA, including the indoor and outdoor concentrations of the selected elements/fractions in the 72 apartments, yielded the results shown in Fig. 2. Five components were extracted, explaining 72.9% of the total variance. The loadings of the five components are reported in Supplementary Material, Table S1.

These results show that the elemental composition was able to differentiate between the industrial/urban area of Gela and the hinterland. Samples collected in Gela, both indoor and outdoor, show higher values on the x-axis (component 1, explaining 29.6% of the total variance) with respect to the other sites. This component is related to the

Table 1
Descriptive statistics of the elemental concentration (extractable fraction) inside and outside the 72 apartments. Concentrations are expressed as ng/m^3.

	LOD	OUT						IN					
		% < LOD	Mean	Median	SD	10%	90%	% < LOD	Mean	Median	SD	10%	90%
As[a]	0.05	7	0.18	0.17	0.07	0.09	0.27	7	0.24	0.20	0.14	0.12	0.41
Ba[a]	0.1	39	0.21	0.14	0.22	<LOD	0.45	28	0.31	0.23	0.34	<LOD	0.62
Be[a]	0.0002	46	0.0005	0.0004	0.0004	<LOD	0.0009	32	0.0006	0.0006	0.0004	<LOD	0.0011
Bi	0.001	51	0.002	<LOD	0.003	<LOD	0.006	51	0.002	<LOD	0.003	<LOD	0.004
Cd[a]	0.02	3	0.06	0.03	0.06	0.03	0.12	4	0.19	0.07	0.37	0.03	0.42
Ce[a]	0.0001	3	0.0070	0.0038	0.0091	0.0004	0.015	1	0.031	0.0069	0.066	0.0012	0.099
Co	0.004	71	0.003	<LOD	0.003	<LOD	0.007	72	0.003	<LOD	0.004	<LOD	0.007
Cr	0.03	65	0.07	<LOD	0.09	<LOD	0.23	64	0.10	<LOD	0.13	<LOD	0.33
Cs	0.002	37	0.004	0.003	0.003	<LOD	0.010	26	0.005	0.004	0.004	<LOD	0.011
Cu[a]	0.2	17	0.8	0.7	0.8	<LOD	1.5	4	3.9	2.3	5.8	0.7	8.7
Fe	0.3	26	2.4	1.8	2.2	0.2	5.9	24	2.5	1.6	2.5	<LOD	5.9
La[a]	0.0005	13	0.0066	0.0036	0.010	0.0050	0.017	6	0.031	0.005	0.067	0.001	0.090
Li[a]	0.006	25	0.014	0.007	0.018	<LOD	0.028	32	0.020	0.015	0.022	<LOD	0.043
Mg	4	1	32	29	22	14	49	6	31	29	15	15	50
Mn	0.2	18	0.9	0.5	0.9	<LOD	2.1	11	1.1	0.8	1.4	0.2	2.1
Mo	0.001	25	0.18	0.030	0.72	<LOD	0.10	17	0.17	0.04	0.56	<LOD	0.14
Na	50	1	344	308	218	122	595	4	370	348	220	143	707
Ni	0.2	25	0.6	0.4	0.6	<LOD	1.4	18	0.6	0.3	0.6	<LOD	1.4
Pb	0.06	3	0.59	0.45	0.46	0.21	1.1	3	0.64	0.53	0.48	0.21	1.1
Rb	0.1	31	0.5	0.5	0.4	<LOD	1.0	26	0.5	0.4	0.4	0.1	1.0
S	100	7	549	356	453	135	1279	4	582	366	513	161	1447
Sb	0.05	6	0.39	0.20	0.61	0.07	0.90	3	0.36	0.17	0.57	0.07	0.73
Se	0.2	39	0.2	0.2	0.2	<LOD	0.5	39	0.2	0.2	0.2	<LOD	0.5
Sn[a]	0.008	49	0.025	0.009	0.037	<LOD	0.06	15	0.070	0.043	0.085	<LOD	0.17
Sr[a]	0.1	43	0.3	0.2	0.3	<LOD	0.7	15	0.4	0.3	0.3	<LOD	0.9
Ti	0.004	56	0.014	<LOD	0.019	<LOD	0.043	50	0.011	0.005	0.013	<LOD	0.030
Tl	0.01	18	0.043	0.020	0.064	<LOD	0.12	17	0.06	0.03	0.09	<LOD	0.15
U	0.0006	72	0.0006	>LOD	0.0006	<LOD	0.0014	71	0.0006	<LOD	0.0004	<LOD	0.0012
V	0.01	8	1.2	0.5	1.6	0.1	3.4	6	1.1	0.5	1.6	0.1	3.3

[a] Indoor values significantly different from outdoor values (p-value<0.002).

Table 2
Descriptive statistics of the elemental concentration (mineralised residual fraction) inside and outside the 72 apartments. Concentrations are expressed as ng/m^3.

	LOD	OUT						IN					
		% < LOD	Mean	Median	SD	10%	90%	% < LOD	Mean	Median	SD	10%	90%
As	0.4	31	0.5	0.5	0.2	<LOD	0.7	32	0.48	0.51	0.23	>LOD	0.74
Ba	1.0	38	1.6	1.2	1.5	<LOD	3.1	28	1.9	1.5	1.8	<LOD	3.2
Be	0.001	57	0.001	<LOD	0.002	<LOD	0.003	54	0.002	<LOD	0.002	<LOD	0.004
Bi	0.01	46	0.04	0.03	0.03	<LOD	0.06	56	0.05	0.03	0.05	<LOD	0.08
Cd	0.06	83	0.08	<LOD	0.15	<LOD	0.18	74	0.11	<LOD	0.19	<LOD	0.37
Ce[a]	0.001	1.4	0.15	0.13	0.14	0.020	0.31	0	1.0	0.26	1.6	0.03	3.1
Co	0.009	71	0.012	<LOD	0.005	<LOD	0.019	76	0.012	0.011	0.005	<LOD	0.017
Cs	0.005	43	0.008	0.006	0.007	<LOD	0.017	36	0.009	0.007	0.008	>LOD	0.016
Cu[a]	1	17	3.2	2.7	2.3	<LOD	5.7	1.4	13	9.8	12	3.2	27
Fe	10	15	80	61	63	20	173	2.8	91	73	75	21	152
La[a]	0.001	1.4	0.13	0.100	0.153	0.013	0.28	0	0.60	0.18	0.88	0.02	1.8
Li	0.02	42	0.05	0.04	0.05	<LOD	0.12	26	0.11	0.06	0.18	<LOD	0.20
Mg	10	1.4	36	30	15	19	59	0.0	38	35	19	22	58
Mn	0.5	29	1.4	1.1	1.3	<LOD	3.1	19	2.0	1.1	5.3	<LOD	2.7
Mo[a]	0.02	29	0.36	0.09	1.24	<LOD	0.28	5.6	0.68	0.38	1.29	0.08	0.98
Ni	0.7	58	1.3	<LOD	1.0	<LOD	2.7	60	1.2	0.7	0.9	<LOD	2.4
Pb	0.2	6.9	2.9	2.1	2.6	0.6	6.6	1.4	3.1	2.1	3.6	0.7	6.7
Rb	0.1	18	0.2	0.2	0.1	<LOD	0.3	18	0.2	0.2	0.1	<LOD	0.3
Sb	0.05	1.4	0.63	0.26	1.11	0.10	1.5	0	0.67	0.33	0.97	0.12	1.8
Se	0.5	36	0.6	0.7	0.3	<LOD	1.0	32	0.6	0.6	0.3	<LOD	1.0
Sn[a]	0.1	4.2	0.3	0.2	0.2	0.1	0.6	1.4	0.6	0.5	0.5	0.2	1.0
Sr	0.3	51	0.3	<LOD	0.4	<LOD	0.9	51	0.3	<LOD	0.4	<LOD	0.6
Ti[a]	0.3	1.4	1.5	0.7	1.5	0.5	3.4	0	2.4	2.1	2.4	0.5	3.6
Tl	0.05	61	0.08	<LOD	0.15	<LOD	0.14	50	0.08	<LOD	0.11	<LOD	0.19
U	0.001	36	0.003	0.003	0.003	<LOD	0.008	32	0.004	0.004	0.005	<LOD	0.008
V	0.10	43	1.7	1.2	1.6	0.6	3.7	43	1.6	1.1	1.5	<LOD	3.9

[a] Indoor values significantly different from outdoor values (p-value<0.002).

concentration of most elements and indicates condition of high pollution. Moreover, some indoor samples show higher values for component 2, which explains 16% of the total variance (upper left area of the score plot). The same area of the loading plot indicates that in these apartments there were much higher concentrations of La, Ce, Cd_{ext}, Tl_{ext}, Mo and Cu.

The PCA results indicate that, in most cases, the quality of the outdoor atmosphere had a strong influence on indoor air, as, for each site, indoor and outdoor data are found in the same area of the score plot. In some apartments, independently of their geographical location, there were, instead, additional indoor sources.

In the loading plot, there are groups of elements that are very well correlated and share the same emission sources. These sources can be identified as cigarette smoking (La, Ce, Cd_{ext}, Tl_{ext}) (Drago et al., 2018), use of vacuum dust cleaners and other brush motor electric appliances (Mo and Cu) (Manigrasso et al., 2019; Ruggieri et al., 2019, Viana et al., 2015), heavy oil combustion (Ni_{ext}, $S_{ext,}$ V_{ext}) (Perrino et al., 2020), and natural sources (Mg_{ext} and Na_{ext} for sea-spray; Fe, Mg_{res}, Mn, Rb_{res}, Ti_{res} for soil; Canepari et al., 2014). As_{ext} and Sn_{res}, which are mostly of industrial origin, as well as Sb and Pb, which are generally considered tracers of traffic emission (Canepari et al., 2014), are also located in the right sector of the loading plot, indicating higher concentration in the urban-industrial area of Gela.

To briefly describe the infiltration behaviour of the particles released by the above sources, we chose one of the elements belonging to each group: Ce for cigarette smoking, Mo for vacuum dust cleaners, V_{ext} for heavy oil combustion, Ti_{res} for soil, As_{ext} for industrial sources. The Exploratory Data Analysis (EDA) plots for these five source tracers are shown in Fig. 3.

The data show that for the tracers of heavy oil combustion (V_{ext}) and industrial emission (As_{ext}), the distributions of the indoor and outdoor data populations were similar, as well as the median values. This behaviour is due to the excellent infiltration capacity of these particles, which are of small dimensions, and to the negligible contribution of internal sources for the chemical species containing these elements.

For the tracer of the elements contained in particles produced and re-suspended from soil (Ti_{res}), indoor and outdoor median values were comparable, although with slightly higher values indoors, but the distributions of indoor and outdoor data were quite different, with a higher proportion of medium and high values recorded indoors. These results may be due to particles re-suspension caused by the residents' movements, which compensates for and exceeds the low infiltration capacity of these particles, typically of large dimensions (Wu and Takaro, 2007).

Concerning the tracers of cigarette smoke (Ce) and of the use of electrical appliances equipped with brush motors, such as vacuum cleaners, (Mo), the indoor values were much higher than those recorded outdoors. In the case of Ce, the distribution of the indoor values was very different from those from outdoors, and there were some cases of values much higher than the average concentration recorded in the other apartments. These values can be ascribed to the presence of heavy smokers.

In the case of Mo, instead, the lower concentration variability is justified by the fact that the same vacuum cleaner was used in all the apartments to collect samples of deposited dust (results not discussed in this paper). For this reason, the data were more homogeneous than in the case of Ce, and the distribution of indoor values was similar to the distribution recorded outdoors, although shifted towards higher concentrations. It is worth noting that the use of electric appliances equipped with brush motors is responsible for the increase in the indoor concentration of elements that are potentially harmful to human health (Canepari et al., 2010). Among these elements, Cu has been identified as a possible trigger of oxidative stress processes inside cells (Tabner et al., 2011), and for this element the increase in the indoor concentration was even higher (about 20 times) than in the case of Mo. It is also worth underlining that the vacuum cleaner was used in each apartment for some minutes only, and that this very short emission was so strong that it conditioned the 48-h average concentration.

Many literature studies carried out around the world report elemental concentration in PM, but the direct comparison of concentration levels among areas where the PM source strength may vary of order of magnitudes is of little value. Instead, the studies reporting I/O ratios (Xu et al., 2020; among others) allow a more effective comparison. However, it is worth noting that the main studies addressing the indoor/outdoor elemental concentration in PM generally compare total

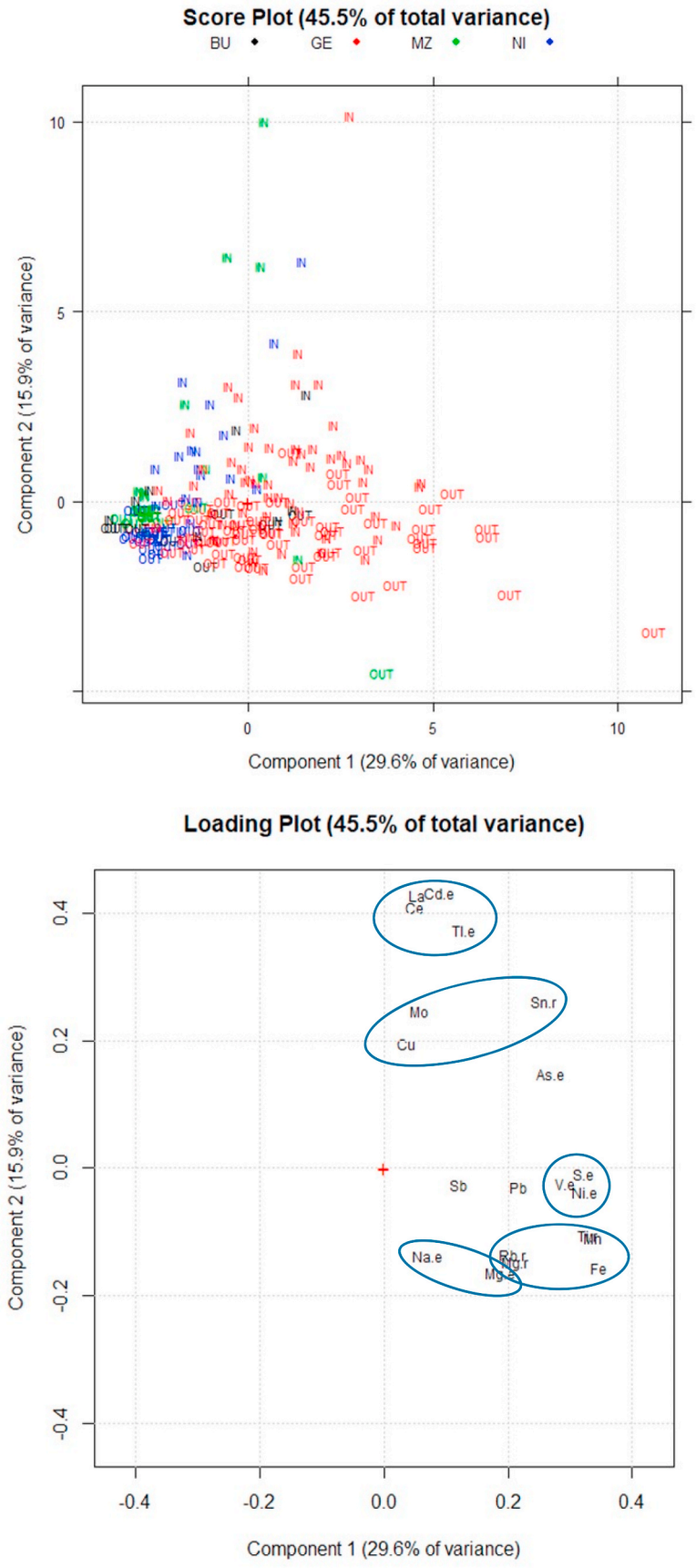

Fig. 2. PCA of indoor and outdoor elemental concentrations. Score plot (upper panel) and loading plot (lower panel) of components 1 and 2. The colour codes differentiate among the four sampling sites. The extractable and residual fractions are indicated as "e" and "r" after the element symbol. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

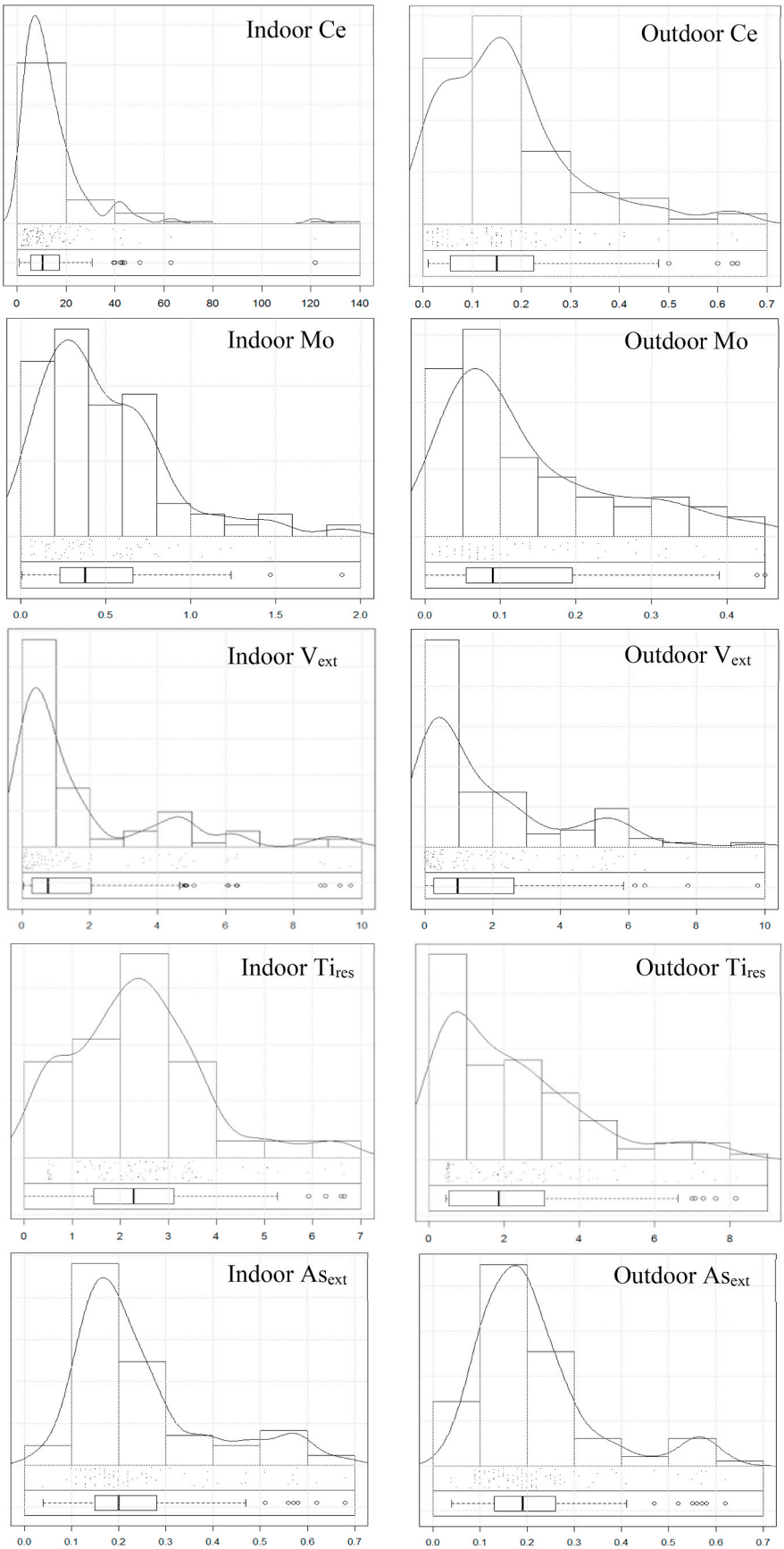

Fig. 3. EDA plots of indoor and outdoor concentrations of a tracer for each considered source.

concentration levels (Zammit et al., 2020; among others); instead, we chose to determine the extractable and residual fraction of each element to make the identification and tracing of PM sources more reliable. Considering this methodological difference, our I/O values for V and As are very close to the results of Liu and Zhang, 2019); regarding Ce, however, in this work the I/O value of this element is slightly higher than 1 (it is 4.4 in our study), probably because there were no smokers in the considered environment (a commercial building). Despite the higher concentration levels of all elements, Ji et al. (2018) report I/O values for As and V close to one, as in our study, but a very low ratio (0.33) for Ti (0.78 in our study). Low I/O value for Ti (0.39) are also reported by Adgate et al. (2007). These differences are not surprising, as I/O ratios are generally very site-specific, especially for elements that are contained in coarse particles. The infiltration of atmospheric particles, in fact, depends on the characteristics of the buildings (materials used, type and tightness of window frames, presence of air conditioners) and the habits of inhabitants (frequency of window opening), which can be highly variable. These parameters have a more pronounced effects on coarse particles, which infiltrate less and are more efficiently removed by air conditioners than fine particles.

To give a comprehensive picture of the different behaviour of the considered PM sources in indoor and outdoor environments, Fig. 4 compares the concentration of the five tracers in the 72 apartments during the three considered seasons. It is worth noting that seasonal variability is one of the issues generally taken into account in environmental studies since, in most geographical areas, the time of year

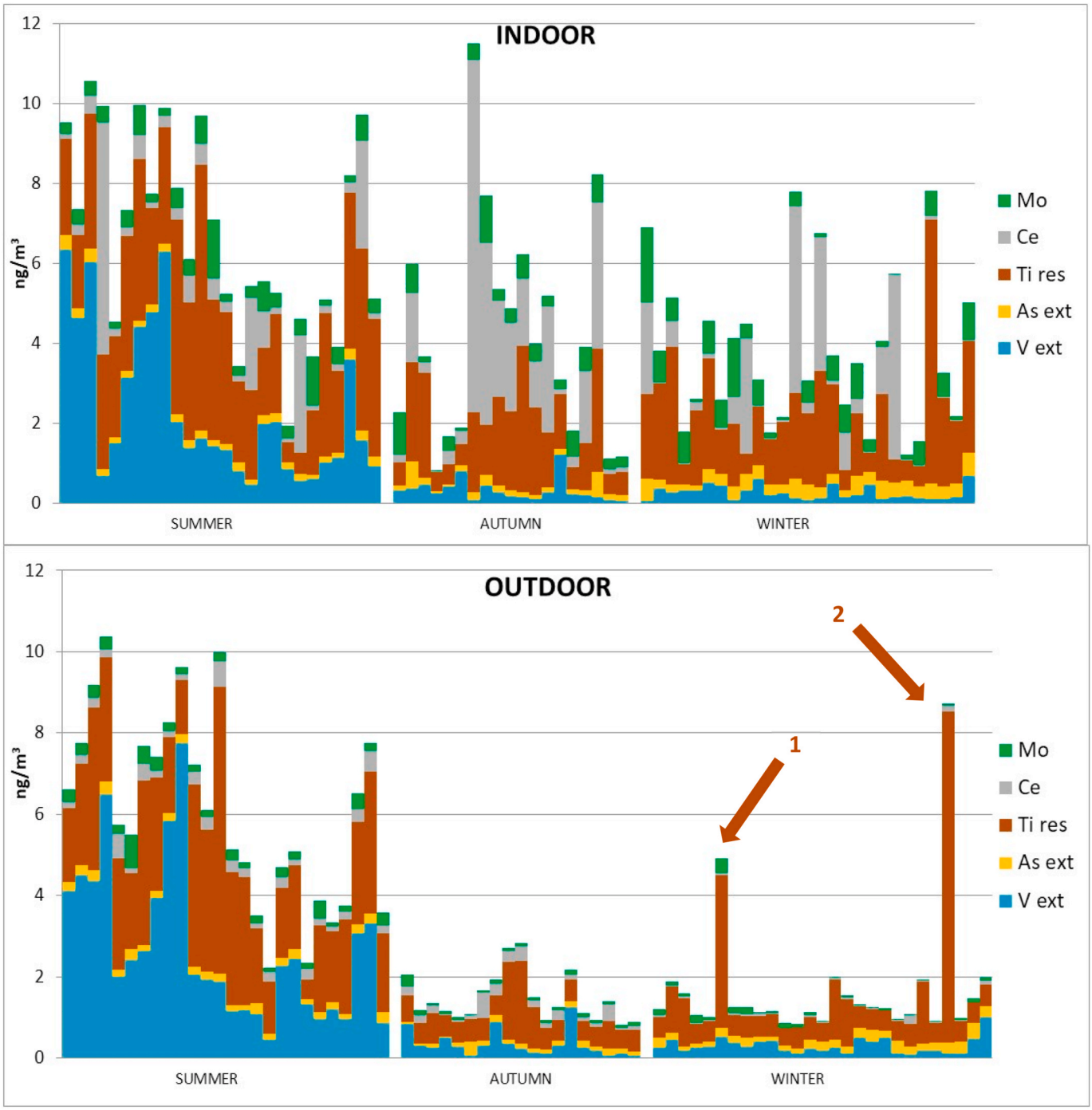

Fig. 4. Time pattern of the five source tracers inside and outside the 72 considered apartments.

influences both the meteorological conditions and the intensity of emission sources (Canepari et al., 2019; Javin et al., 2020; Kong et al., 2020; Tofful et al., 2021). In addition, climatic conditions affect the amount and frequency of natural ventilation, which can affect PM infiltration.

The indoor and outdoor patterns were very alike for the elements that easily infiltrate from outdoors towards the indoor environments (V_{ext} and As_{ext}). Instead, a very variable, often much higher, indoor concentration was recorded for Ce and, to a lesser extent, Mo, which both have an indoor source of strong intensity.

Ti_{res} also showed higher indoor values, particularly during the autumn and winter. A build-up during the cold season is visible for all the indoor sources and is probably due to a weaker natural ventilation in the apartments. This is consistent with the results of Sánchez-Soberón et al. (2019), who studied the seasonal variations of PM infiltration in Spain, Abdel-Salam (2021) in Egypt, Zhao et al. (2020) in Berlin, and many others. An exception is constituted by the two winter events of high Ti_{res} concentration (brown arrows in Fig. 4). The two events were due to a local re-suspension of dust, probably caused by construction works (1), and to the long-range transport of desert dust (2). Only in these two cases, due to the very high concentration recorded outdoors, the contribution of PM infiltration greatly exceeded that of the internal sources, and the ratio of the indoor to outdoor concentration (I/O) was lower than 1.

A visible seasonal pattern is also shown by the concentration of V_{ext}, which may be ascribed to a more frequent transit of ships occurring along the coast during the summer period. Summer increase of vanadium concentration in the Mediterranean basin is consistent with the finding of Cusack et al. (2012), Salameh et al. (2018) and Galindo et al. (2018), who attributed the increase to intense cruise ship traffic during the warm season.

Table 3 reports the I/O ratio calculated for the tracers of the five considered sources and referred to the three seasonal periods. These results are a further confirm of the above findings: the values recorded for V and Asext, which have negligible internal sources, were close to one, and showed small seasonal variations; - the I/O values of the other three elements, which trace relevant indoor sources, were lower during the warmer period (winter > autumn > summer), due to increased natural ventilation in the apartments, and show greater variability (Zhao et al., 2020; Tofful et al., 2021); very high I/O values were obtained for Ce, which is a particularly sensitive tracer of cigarette smoking.

In addition to the 72 apartments that were monitored during different periods, we also carried out simultaneous measurements in two additional apartments (H1 and H2) during two 2-weeks periods (summer 2013 and winter 2014). Fig. 5 reports the concentration pattern of the five tracers. In the case of brush motors, we selected Cu as the best tracer. Mo, in fact, is a very specific tracer but it is released only by some, older, models of vacuum cleaners (and by the one used in the considered 72 apartments). Cu, instead, is contained in the emission of all brush motors (Manigrasso et al., 2019).

The data in Fig. 5 confirm the robustness of the above discussion, which was made on the basis of non-simultaneous observations. The outdoor patterns of the five tracers at H1 and H2, located about 1.5 km apart, were in good agreement, indicating that the air quality in the considered area was quite homogeneous.

Table 3
Seasonal IN/OUT concentration ratios of the five source tracers.

		As_{ext}	Ce	Mo	Ti_{res}	V_{ext}
Winter	Mean	1.2	17	9.5	2.4	0.9
	St. dev.	0.5	24	7.7	1.3	0.5
Autumn	Mean	1.1	7.0	5.5	2.3	1.0
	St. dev.	0.5	5.5	3.0	1.4	0.8
Summer	Mean	1.0	3.5	1.8	1.2	0.9
	St. dev.	0.3	6.6	1.5	0.7	0.4

A different behaviour was shown by Ti_{res} at H2 during the winter period, due to construction works carried out in the street facing the house. The concentration of the two elements that have negligible internal sources (V and As_{ext}) showed very similar indoor and outdoor time patterns. This indicates a fast exchange between the external and internal air masses. Moreover, the concentration values of V and As_{ext} during the summer were much higher than during the winter, indicating a higher intensity of the emission sources during the warm season.

Differently, Ce and Cu showed much higher concentrations indoors, and the time patterns were asynchronous, with relevant differences between H1 and H2 and between indoor and outdoor concentration in the same apartment. This is due to the prevalence of the internal sources: smoking (Ce) was more frequent at H1, while the use of a vacuum cleaner (Cu) was more frequent at H2.

The characteristics of the 72 children residing in the evaluated dwellings are reported in Table 4. WQS technique has been widely utilized as a multiple-pollutant model to derive the overall health effect of simultaneous environmental exposures (Butler et al., 2019, Yitshak-Sade et al., 2020)

In our WQS analysis, the overall effect of the considered pollution sources produced a 9.3-fold increase in the adjusted odds of DDA status (OR = 9.34, 95% CI [1.79–48.7]). Heavy oil combustion (52.2%) and vacuum dust cleaners (27.8%) showed a predominant role in driving the observed association. As concerns Wh12 M, the WQS adjusted model produced a 14.2-fold odds increase (14.15 [1.77–113.16]). Only cigarette smoking and heavy oil combustion contributed meaningfully to the overall effect with a weight of 39.8% and 40.2% respectively (Fig. 6 panels A and B).

As showed in our results, the WQS analysis allowed us to consider both indoor and outdoor $PM_{2.5}$ source contributions in evaluating children respiratory symptoms. The DDA-associated positive WQS index was driven by both an outdoor source (heavy oil combustion) and an indoor source (vacuum dust cleaner). In agreement with our results, Patel and Miller found a significant association between concentrations of ambient Ni and V and wheeze symptoms in children up to 2 years old (Patel and Miller, 2009). It is worth noting that the contribution of heavy oil combustion, traced by Vanadium and Nickel concentration, contains also many other organic and inorganic pollutants that may be co-responsible for significant health effects (Chianese et al., 2021) Moreover, heavy oil combustion represents a health threat due to its high infiltration rate from outdoor emission sources into indoor environments. The vacuum dust cleaner contribution might depend on the chemical characteristics of its tracers, Cu and Mo, previously associated with respiratory symptoms (Strak et al., 2012) and to the very small dimensions of the particles emitted by this source, in the nano range (Manigrasso et al., 2019). However, it should be considered that in homes of subjects with DDA the very frequent use of vacuum dust cleaner, which is recommended to reduce asthma triggers (Wu and Takaro, 2007), may be responsible for an increase in the concentration of these source tracers.

Despite the relationship existing between DDA and Wh12 M, our WQS results show that the Wh12 M -positive WQS index was driven by heavy oil combustion and cigarette smoking, with a similar weight. Among all the tested emission sources, the ability of cigarette smoking in triggering and exacerbating respiratory symptoms is in accordance with our previously studies, in which smoke tracers (Cd, Tl, Ce, La) were associated with the occurrence of respiratory health effects on children (Drago et al., 2018).

4. Conclusions

Measurement of the elemental composition of $PM_{2.5}$ inside and outside 72 apartments located in an industrial and background area of Siciliy (Italy) has allowed us to explore the variations in the strength of some relevant indoor sources of PM. Our results suggest that the study of indoor PM sources may benefit from the separate analysis of the

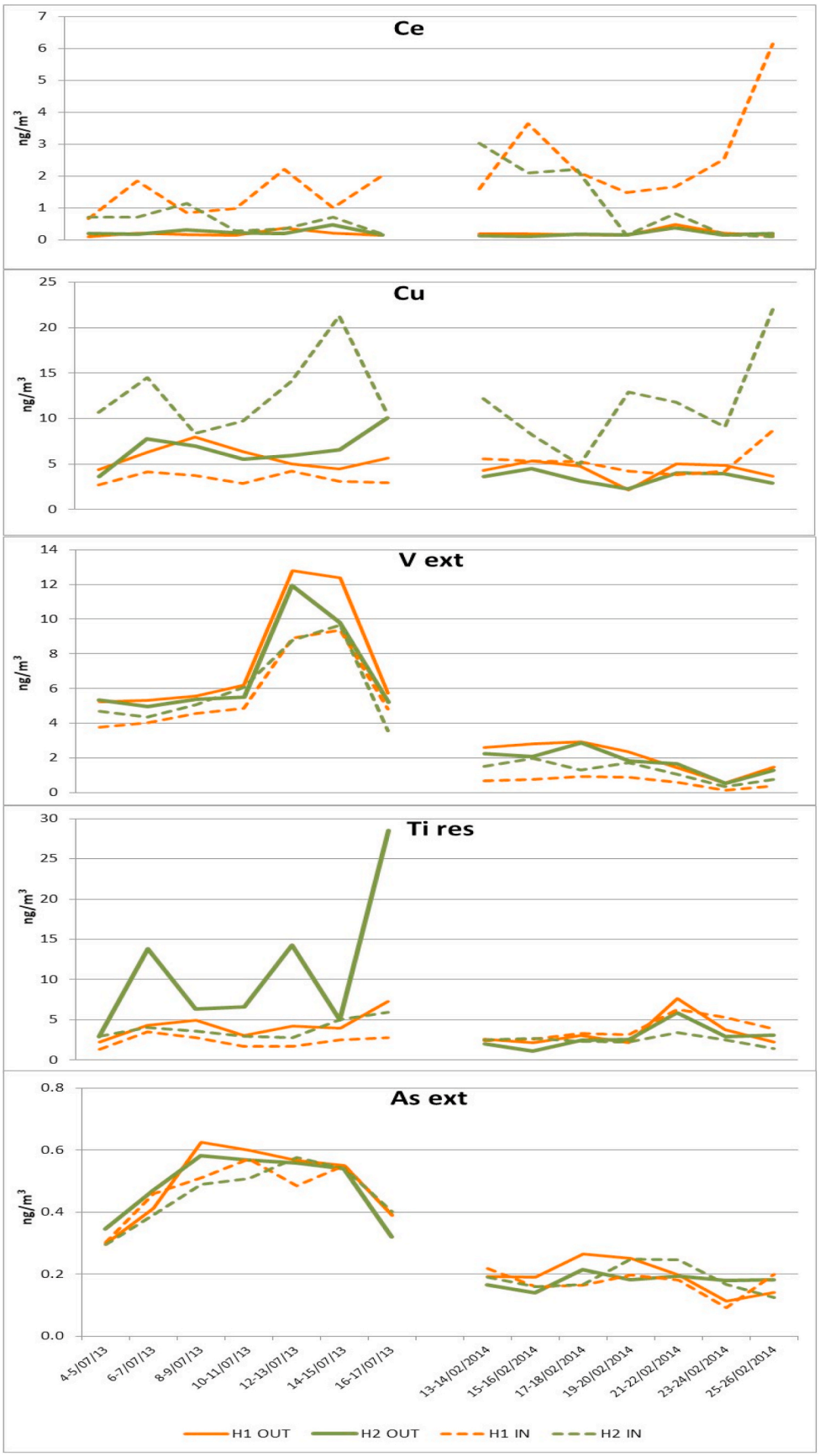

Fig. 5. Simultaneous measurements of the five source tracers at apartments H1 and H2.

Table 4
Descriptive information relevant to the subjects' sample.

Variables	Subjects (No. = 72)
Male/Female (No.)	37/35
Age (years, mean ± SD)	12.1 ± 1.2
Allergic Sensitization (No., %)	33 (45.8%)
Doctor diagnosed Asthma (No., %)	17 (23.6%)
Episode of wheezing in the last 12 months (No. %)	34 (47.2%)

extractable and the residual mineralised fraction of the elements contained in atmospheric PM. The chemical fractionation of a wide range of elements, including some uncommon rare-earth elements, has been applied for the first time to indoor $PM_{2.5}$ samples. This approach has allowed the identification of much more selective source tracers, leading to a detailed study of the behaviour of some relevant indoor and outdoor PM sources. Robust source tracers have been identified for cigarette smoke (La and Ce), use of electrical appliances equipped with brush motors (Cu and Mo), soil (insoluble fraction of Ti, Mg and Rb), industrial sources (soluble fraction of As and residual fraction of Sn), and heavy oil combustion (soluble fraction of V, Ni and S). The first two sources had an exclusively indoor origin, soil had a mixed origin, while industrial sources and heavy oil combustion were almost exclusively introduced from outdoors, with excellent infiltration capacity. The results of this study have confirmed that outdoor industrial pollution has a strong influence on the indoor air quality of domestic environments in the areas surrounding the industrial plants. Our results have also highlighted that the considered respiratory outcomes were influenced by a combination of both indoor and outdoor sources of emission.

The characterization of PM components and the identification of their sources are a fundamental step for the estimation of their impact on human health and environment and for the identification of efficient control measures. This becomes particularly relevant in highly contaminated areas, where the activities aimed at harm mitigation must

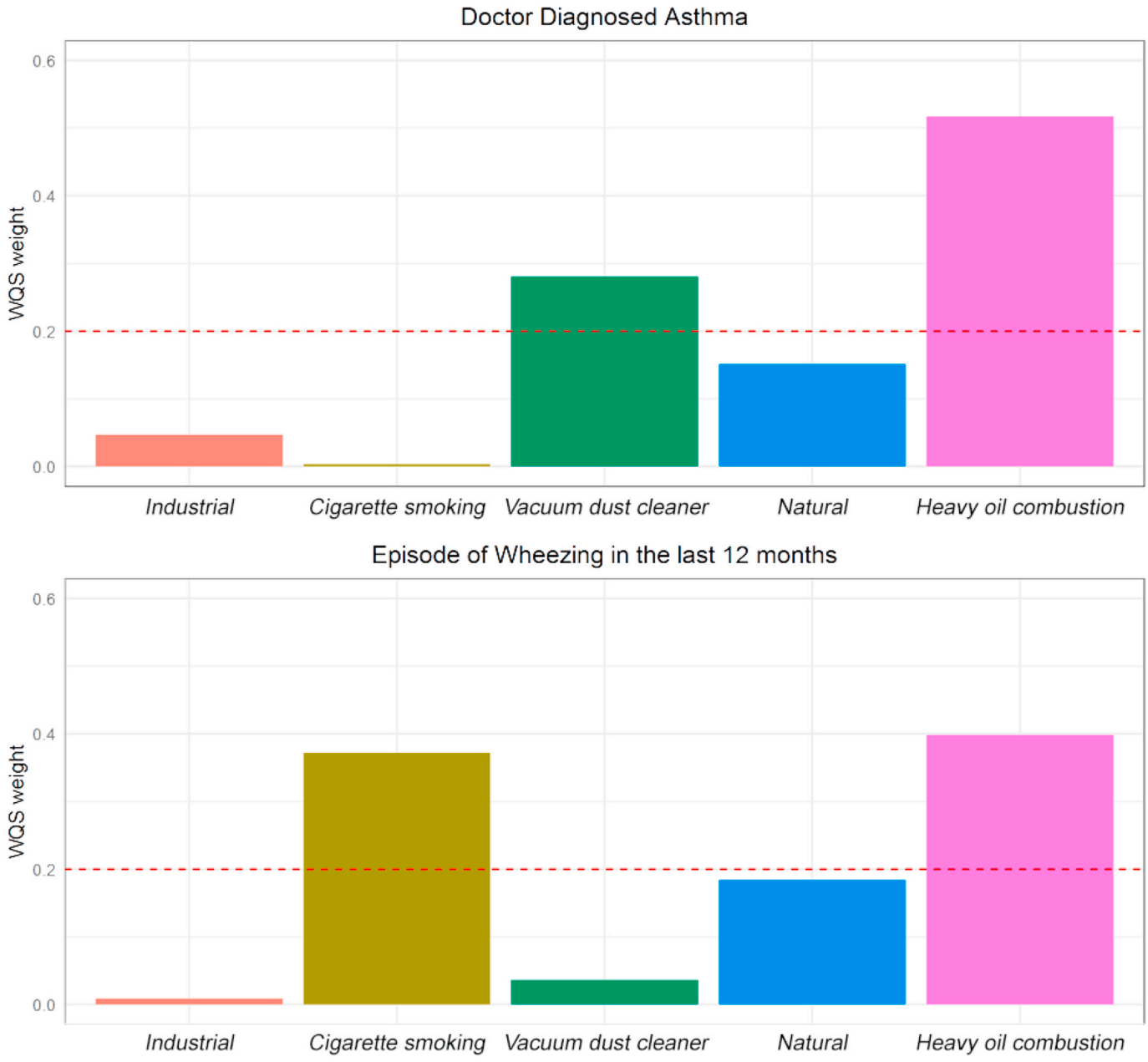

Fig. 6. Association between exposure levels and Doctor Diagnosed Asthma (A) and Episode of Wheezing in the last 12 months (B) based on weighted quantile sum (WQS) regression analysis.

include not only interventions on the outdoor environment but also promotion of good practices for individual behaviours in domestic environments.

Future directions of this study include the application of multivariate source apportionment techniques to quantify the weight of the individual sources in PM mass. This information could also be useful for the assessment of carcinogenic and non-carcinogenic health risk.

Credit author statement

S. Canepari: Data curation, Methodology, Resources, Validation, Writing – original draft; Writing – review & editing, Supervision **M.L. Astolfi:** Investigation, Validation **G. Drago:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing; **S. Ruggieri:** Data curation, Investigation, Validation, Visualization, Writing – review & editing; **E.E. Tavormina:** Formal analysis, Methodology, Software, Visualization; **F. Cibella:** Funding acquisition, Investigation, Project administration, Resources, Supervision; **C. Perrino:** Data curation, Formal analysis, Methodology, Resources, Supervision, Writing – original draft, Writing – review & editing.

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Ethics approval

The study was approved by the local Ethical Committees: the Ethics Committee of the Local Health Agency of Caltanissetta on December 15, 2011. The parents of all children signed an informed consent form. Respect of individual privacy and clinical data was granted.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2022.114630.

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