

Article

Comparison Study between Indoor and Outdoor Chemical Composition of PM_{2.5} in Two Italian Areas

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Abstract: Outdoor air quality guidelines have been constantly implemented during the last decades. Nonetheless, no international regulations have been put into action in terms of indoor air quality standards and standardized procedures for indoor pollution measurements. In this study, we investigated the chemical composition of PM_{2.5} collected outdoors and indoors at six dwellings located in two Italian areas. The selected sites concerned inland/central and southern Italy, including urban, peri-urban, rural and coastal settings. The seasonal and site-specific particulate matter (PM) variations were analyzed outdoors and indoors, by estimating the impact of the main macro-sources and the contribution of the macro- and micro-components. Outdoors, organic matter represented the main contribution at inland and coastal sites, respectively during winter and summer. A clear, seasonal variation was also observed for secondary inorganic species. A site-specific dependence was exhibited by traffic-related components. Indoors, organic and soil-related species were influenced by the presence of the inhabitants. Some specific tracers allowed to identify additional local source contributions and indoor activities. Although the sampling season and site location defined the outdoor air quality, the higher PM concentrations and the chemical composition indoors were influenced by the infiltration of outdoor air and by the indoor activities carried out by its inhabitants.

Keywords: domestic environment; PM macro-sources; PM macro-components; extracted-elements; residual elements; infiltration; indoor air quality

1. Introduction

During the last decades, outdoor air pollution regulations have been extensively improved both in North America and Europe. These enhancements were aimed at establishing new health-based concentration standards and at improving the pre-existing legislations, providing new air quality objectives. The new regulations included both new limit values and exposure concentrations, as well as more cogent reduction targets in order to set an appropriate margin of safety to protect human health and the environment from harmful species [1,2].

Indeed, outdoor air pollution is considered by the World Health Organization (WHO) as one of the key determinants of health. The WHO published the document Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide (Global update 2005, Summary of risk assessment) to inform about the health risks related to environmental exposure and to guide policy-makers towards the implementation of appropriate air quality targets [3]. In 2013, the specialized cancer agency of WHO, the International Agency for Research on Cancer (IARC), classified outdoor air pollution and particulate matter (PM) as carcinogenic of Group 1 [4]. In the same year, the REVIHAAP report (Review of Evidence on Health Aspects of Air Pollution) was also published, with a full review and

discussion of the scientific evidences about the adverse health effects of air pollution. This technical paper highlights that several components contribute to the health effects of PM, but that there is not enough evidence to associate the health outcomes to specific emission sources. The report underlines that most of the evidences are accumulated on cardiovascular and respiratory outcomes, that are generally related to traffic emissions, coal and oil combustion and biomass combustion, particularly in indoor environments located in low-income countries [5].

Although scientific literature demonstrated that people spend more than 90% of their time in indoor environments, notably in dwellings, schools, offices and means of transport, no supranational legislation has been implemented in order to encompass indoor air quality standards [6,7]. In addition, no standard procedures have been introduced yet, in order to monitor indoor contaminants.

Indeed, the evaluation of the exposure to indoor pollutants is far from being a simple task. The concentration and chemical composition of indoor air, in fact, depends on the release of contaminants from indoor sources as well as on their penetration from outdoors. As far as PM is concerned, the few studies whose focus was set on the chemical properties of particles suspended in indoor environments have required remarkable efforts. For this reason, they mostly concerned specific group of hazardous components such as elements, carbonaceous compounds or classes of species like polycyclic aromatic hydrocarbons [8–15].

A more robust approach for a simultaneous study of outdoor and indoor suspended particles would require a detailed speciation of PM. Given the huge number of chemical species characterizing the atmospheric particles, a complete speciation could be effectively substituted by a pragmatic determination of macro-components (i.e., species individually constituting more than 1% of the PM mass), as well as of micro- and trace-components that are considered to be particularly hazardous to human health.

This study aims at giving an overview of the differences, in terms of concentration and chemical composition, of PM_{2.5} collected in the indoor and outdoor atmosphere of several dwellings in two Italian areas (inland/central and southern Italy). The selection of the sampling sites was made according to their location (urban, peri-urban, rural, coastal), considering the variety of the emission sources in the two areas.

The study design also allows evaluating how the different outdoor compositions reflect in the chemical characteristics of indoor particles. In order to obtain an accurate evaluation of the chemical properties of outdoor and indoor PM_{2.5} and to identify the most important PM sources, long-time filter-based particle collections were performed on site, in the presence of the inhabitants and during their daily activities.

The differences between outdoor and indoor particle concentrations and compositions were evaluated according to location (inland or coastal sites), sampling season and variety of sources. The indoor-to-outdoor concentration ratios (I/O), as an indicator of outdoor particle infiltration and/or the presence of indoor sources, were also investigated.

2. Materials and Methods

2.1. Sampling Sites

Sampling sites selected for the present study are located as specified in Figure 1: two urban sites (Rome), a peri-urban and a rural site in the vicinity of Rome (respectively 30 km and 40 km from the city center), two sites at a coastal location (Gela, Sicily).

The dwellings were monitored indoors and outdoors, during long-time period campaigns (at least 2 weeks), as summarized in Table 1. In some cases, simultaneous samplings at two sites were performed. The sampling sites are identified as follows: location (Urban; Peri-urban; Coastal; Rural); number of dwellings in case of multiple sites monitored in the same area (1 or 2); season (W = winter; S = summer). The subscript “sim” indicates simultaneous samplings.



Figure 1. Inland and coastal locations of the six apartments under study.

Table 1. Site identifying code, location and study period; details of the duration of each campaign.

Site Code	Location	Study Period	Duration
Urban1-W	Rome, urban	January 2012	24 h, Daily; 14 days
Urban1-S	Rome, urban	July 2012	24 h, Daily; 19 days
Urban1-Wsim	Rome, urban	December 2012	24 h, Daily; 17 days
Urban2-Wsim	Rome, urban	December 2012	24 h, Daily; 17 days
Peri-W	Monterotondo, peri-urban	February–March 2013	24 h, Daily; 18 days
Coast1-Ssim	Gela, industrial	July 2013	24 h, Daily; 14 days
Coast2-Ssim	Gela, industrial	July 2013	24 h, Daily; 14 days
Coast1-Wsim	Gela, industrial	February 2014	24 h, Daily; 14 days
Coast2-Wsim	Gela, industrial	February 2014	24 h, Daily; 14 days
Rural-W	Rural	March 2014	24 h, Daily; 15 days

Specifically, the study has taken into consideration the following sampling sites:

- Rome urban site (Urban1-W and Urban1-S; Google co-ordinates: 41°51'27.22" N, 12°25'2.93" E): two campaigns were conducted in the same dwelling in the city of Rome, during the winter and the summer period. The study was conducted in an apartment located on the fourth floor, in Rome's southwest outskirts, in an area characterized by low traffic intensity. The detailed chemical composition of PM collected during the two campaigns has already been investigated in a previous publication [16].

- Rome urban sites, simultaneous samplings (Urban1-Wsim and Urban2-Wsim; Google co-ordinates: 41°53'45.63" N, 12°29'37.86" E): the previous apartment was monitored simultaneously with another apartment located on the first floor in Rome's city center, in an area characterized by a crowded neighborhood and traffic congestion deriving from an important road nearby. A customary smoker and a pet were present during the sampling period.

- Peri-urban site (Peri-W; Google co-ordinates: 42°4'3.77" N, 12°35'41.56" E): the study was conducted inside and outside a detached house located at the edge of the urban area of Monterotondo, 30 km NE of Rome. The area is characterized by several PM sources, including: vehicular traffic (i.e., there is a major road close to the household, therefore implying a major traffic congestion during the peak hours, especially in the early morning and late afternoon), industry (i.e., the area is characterized by the presence of some small companies specialized in the production of bricks, tiles and ceramics),

and agriculture. The apartment is equipped with a wood-fueled fireplace: during the winter period many households in this specific area use biomass fireplaces and pellet stoves as domestic heating. A smoker was also present in the apartment.

- Coastal locations (Coast1-Ssim, Coast2-Ssim; Google co-ordinates: 37°4′21.22″ N, 14°15′7.10″ E and Coast1-Wsim; Coast2-Wsim, Google co-ordinates: 37°4′46.95″ N, 14°14′13.43″ E): the study was carried out simultaneously during summer and winter in two apartments located in the city of Gela (south coast of Sicily), respectively on the fifth and second floor. The city is surrounded by an area devoted to agricultural activities. A refinery adjacent to the east of town represents the most important industrial source. The plant deals both with oil-refining and power production and is provided with a pier for the transportation of raw and refined oil products with oil tankers. Vehicular traffic contribution is of local origin. A customary smoker was present at site Coast1 and Coast2 during both campaigns.

- Rural site (Rural-W; Google co-ordinates: 42°9′54.25″ N, 12°42′34.20″ E): the study was performed in a detached house located 40 km NE of Rome in a rural area characterized by extensive agricultural activities. A pellet stove was used for domestic heating: pellet stoves and fireplaces are the most popular domestic heating system in the area. A pet was present in the apartment.

2.2. Sampling Equipment

In order to minimize the noise impact on the residents, very quiet samplers (<35 dB), specifically designed for indoor use (*SILENT* Sequential Air Sampler, FAI Instruments, Fonte Nuova, Rome - Italy) were employed. These samplers, operating at a flow rate of 10 L/min, were used both indoors and outdoors at each location: for indoor use, the samplers were placed in the living room or in the most frequented area of the house, and were installed so as to avoid any restrictions to the inhabitants' daily activities. For outside use, the sampling devices were placed on the adjacent balcony and equipped with a rain cover protecting the sampling heads.

To minimize the operators' intervention, all the sampling devices were equipped with a sequential sampling unit which is capable of managing four unattended consecutive samplings by switching the sampling line every 24 h. The sampling heads were supplied with size selective inlets for PM_{2.5} and loaded with Teflon or quartz fiber filters (TEFLO, 47 mm, 2.0 µm pore size, PALL Life Sciences; Tissuquartz 2500QAT, 47 mm, PALL Life Sciences). Teflon and quartz fiber membranes were employed in parallel at all campaigns. Before use, all quartz filters were conditioned at 600 °C for 3 h in order to remove adsorbed organic compounds. Teflon filters were weighted before and after sampling by using a 1 µg sensitivity automated microbalance (mod. ME5, Sartorius AG), after conditioning at 50% R.H. and 20 °C for 24 h.

During all campaigns, the volunteers were asked to keep a daily journal, indicating the activities carried out during the day deemed as potentially affecting the concentration and the chemical characteristics of suspended particles (e.g., number of people inside the environment, cooking activities, cleaning operations, presence of smokers, etc.). In all cases, during the study period, the air exchange through natural ventilation was provided.

2.3. Chemical Characterization

The chemical characterization of PM_{2.5} included the analysis of ions, macro-elements, micro- and trace elements on Teflon fiber filters and of organic carbon (OC) and elemental carbon (EC) on quartz filters (Table 2). Briefly, after the gravimetric analysis, Teflon filters were analyzed for the elemental content (Al, Ca, Cl, Fe, K, Mg, Na, Si, S) by using X-Ray fluorescence (X-Lab2000, SPECTRO Analytical Instruments, Kleve, Germany) and then extracted in deionized water for the evaluation of ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, Mg²⁺, Ca²⁺) by ion chromatography (ICS1000, Dionex Co., CA, USA), and of the soluble fraction of micro- and trace-elements (As, B, Ba, Be, Bi, Cd, Cr, Cs, Cu, Co, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V) by ICP-MS (ICP-MS, Varian 820, Varian, PAESE). The residual solid was then digested and analyzed by ICP-MS for the same elements. OC and EC were detected

on quartz filters by thermo-optical analysis (OCEC Carbon Aerosol Analyzer, Sunset Laboratory, OR, USA) applying the NIOSH-quartz temperature protocol [17]. More details about the entire analytical procedure and quality controls are published in a previous publication [18].

Table 2. Analytical determinations carried out on Teflon and quartz membrane filters sampled at each sampling site.

Site Code	PM _{2.5} Mass	XRF	IC	ICP-MS	OC/EC
Urban1-W	x	x	x	x	x
Urban1-S	x	x	x	-	x
Urban1-Wsim	x	x	x	-	x
Urban2-Wsim	x	x	x	-	x
Peri-W	x	x	x	x	x
Coast1-Ssim	x	x	x	x	x
Coast2-Ssim	x	x	x	x	x
Coast1-Wsim	x	x	x	x	x
Coast2-Wsim	x	x	x	x	x
Rural-W	x	x	x	x	x

The mass concentration of PM_{2.5} was calculated by dividing the weight of the particles collected onto each Teflon filter by the corresponding sampling volume.

The determination of ions, macro-elements, EC and OC allowed the grouping of these species into five macro-sources of PM: *Soil*, *Sea*, *Secondary inorganics*, *Traffic* and *Organics*. The algorithm used to estimate these five macro-sources has been extensively discussed in previous publications [19,20]. Briefly, *Soil* contribution, originated by both soil erosion or road dust re-suspension is calculated by summing the concentrations of crustal elements as metal oxides (Al, Si, Fe, insoluble K, Mg and Ca, magnesium and calcium carbonates). Depending on the location and season, *Sea* is calculated by summing Cl[−] and Na⁺ multiplied by 1.176 or by multiplying Na⁺ concentration by 3.27, in order to include other sea-salt components. *Secondary inorganic* species are determined as the sum of NH₄⁺, NO₃[−] and non-sea-salt SO₄^{2−}; road *Traffic* is calculated as the sum of elemental carbon plus an equivalent amount (multiplied by 1.1) of organic carbon that includes the contribution of primary organic carbon adsorbed on particles' surface. *Organics*, which include both secondary and primary organic components, are constituted by the remaining organic matter.

3. Results

3.1. Outdoor and Indoor Average Concentration of PM_{2.5}

The comparison between the mass concentrations of PM_{2.5} measured outdoors and indoors are provided in Figure 2. In addition to the single campaigns reported with a squared pattern, also the Urban Winter (Urban-W), Coastal Summer (Coast-S) and Coastal Winter (Coast-W) data are provided as the average value calculated between multiple campaigns (respectively Urban1-W, Urban1-Wsim and Urban2-Wsim; Coast1-Ssim and Coast2-Ssim; Coast1-Wsim and Coast2-Wsim).

The average PM concentrations measured outdoors during the winter campaigns were higher at inland locations in comparison to coastal sites, resulting specifically in the range 26–34 µg/m³ (sites Urban-W, Peri-W, Rural-W) and 16 µg/m³ (sites Coast-W). During the summer season, on the contrary, higher average concentrations were observed at the two coastal locations, respectively 26 µg/m³ at Coast1-Ssim and 34 µg/m³ at Coast2-Ssim, compared to the 13 µg/m³ measured at the urban site Urban1-S.

By comparing the site-specific concentrations (squared histograms), it can be observed that the simultaneous measurements (flagged as “sim”) made at urban and coastal sites during winter, resulted in very similar concentrations (21 and 24 µg/m³ at Urban1-Wsim and Urban2-Wsim; 17 and 15 µg/m³

at Coast1-Wsim and Coast2-Wsim), while a slightly higher difference was observed in the case of simultaneous summer sites (respectively 26 and 34 $\mu\text{g}/\text{m}^3$ at Coast1-Ssim and Coast2-Ssim).

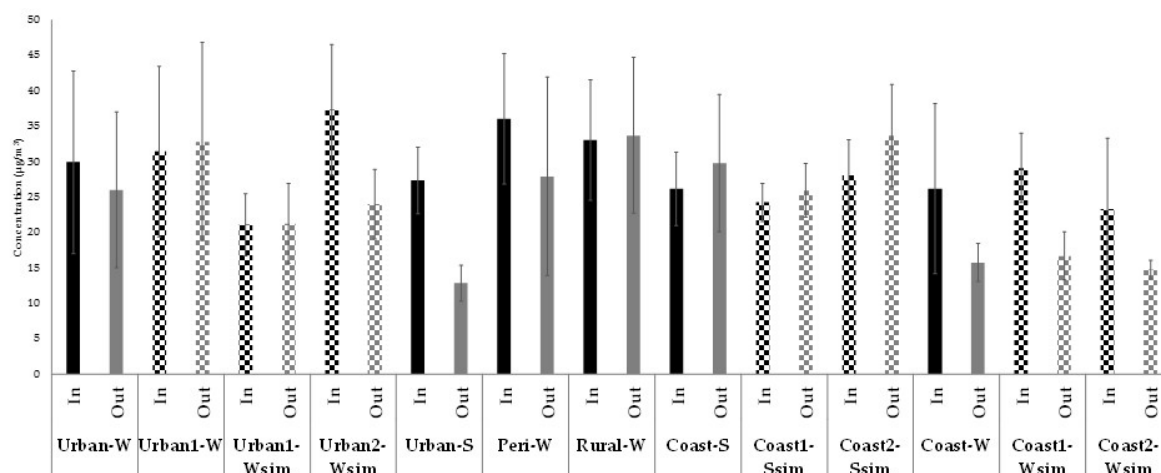


Figure 2. $\text{PM}_{2.5}$ concentrations and relative standard deviations (error bars) measured indoors and outdoors (in $\mu\text{g}/\text{m}^3$): solid histograms refer to average values calculated between multiple campaigns; single campaigns are reported with a squared pattern.

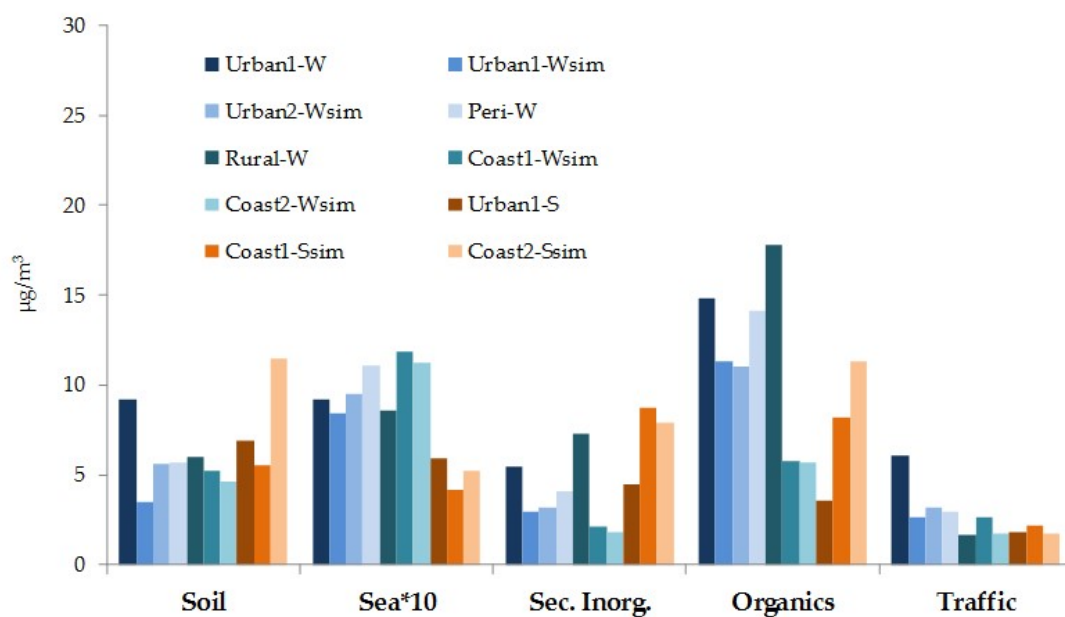
Indoors, the average $\text{PM}_{2.5}$ data result higher than outdoors at Urban-W, Urban-S, Peri-W and Coast-W sites, and quite similar at Rural-W and Coast-S sites.

In the case of sites Urban1-S, Urban2-Wsim, Peri-W, Coast1-Wsim and Coast2-Wsim, indoor PM concentrations were as higher as 15 $\mu\text{g}/\text{m}^3$ than the corresponding outdoor value, thus indicating a non-negligible effect of indoor sources.

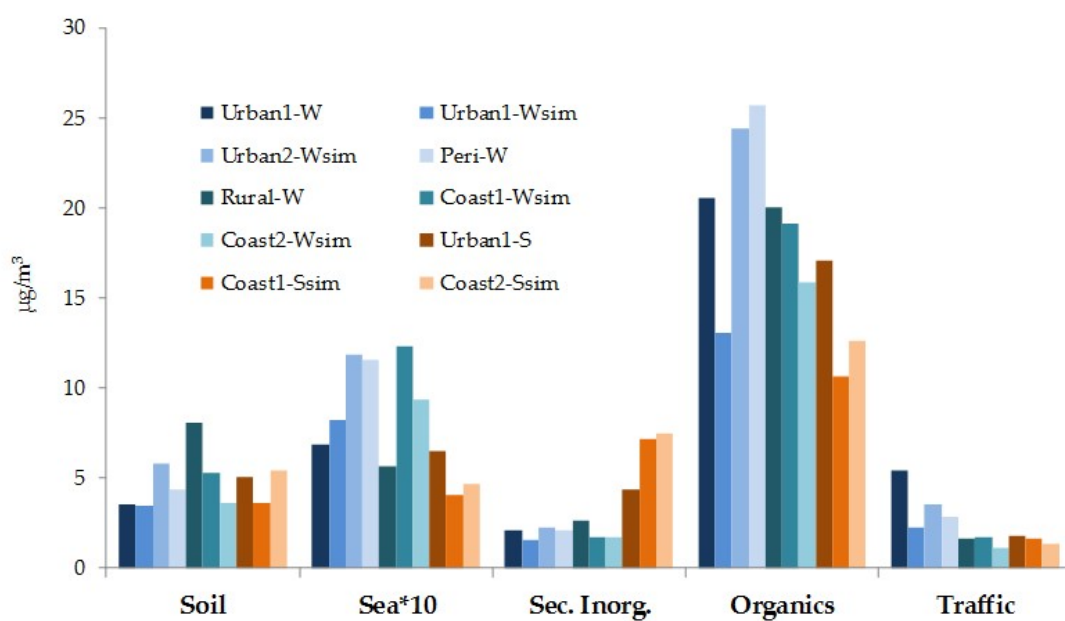
The different impact of site-specific indoor PM sources is clear at the two urban sites sampled simultaneously (Urban1-Wsim and Urban2-Wsim), thus reporting a significant discrepancy between the mass concentrations measured indoor, respectively 21 and 37 $\mu\text{g}/\text{m}^3$.

3.2. Outdoor and Indoor Average Composition of $\text{PM}_{2.5}$

The above results can be better understood by comparing the absolute ($\mu\text{g}/\text{m}^3$) and relative (%) mass contribution attributed outdoors and indoors to the main macro-sources, as shown respectively in Figure 3a,b and Table 3. For an easier interpretation, the sites considered in the study are separately displayed between the winter and the summer campaign, respectively blue/green and brown/orange shaded histograms.



(a)



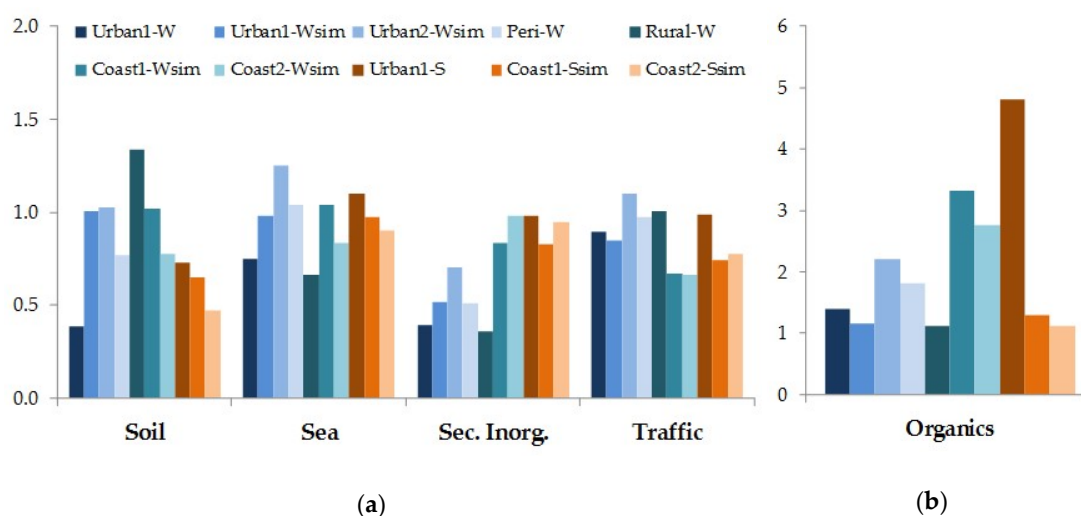
(b)

Figure 3. Outdoor (a) and indoor (b) average contribution of the five macro-sources, in $\mu\text{g}/\text{m}^3$; * sea macro-source values are multiplied by ten.

Table 3. Outdoor and indoor particulate matter (PM) composition expressed in terms of the five macro-sources average contribution (in %).

Macro-Source (%)	Urban-W		Urban-S		Peri-W		Rural-W		Coast-W		Coast-S	
	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In
Soil	22	14	40	18	20	12	18	24	31	17	29	18
Sea	3	3	3	2	4	3	2	2	7	4	1	1
Secondary Inorganics	14	7	26	15	15	6	22	8	12	7	29	29
Organics	46	64	20	59	50	71	53	61	36	67	34	46
Traffic	15	12	11	6	11	8	5	5	14	5	7	6

Furthermore, in order to evaluate the combined contribution to PM_{2.5} mass concentrations from infiltration processes and/or the impact of indoor sources, Figure 4a,b reports the indoor-to-outdoor concentration ratios (I/O) for the five macro-sources.

**Figure 4.** Average indoor-to-outdoor concentration ratios calculated for *Soil*, *Sea*, *Secondary Inorganics*, *Traffic* (a) and *Organics* (b).

The data show that *Organics* represent, in general, the most important contribution to the total outdoor PM mass. The relative share varies between 36% and 53% during winter and is below 34% during summer. The highest concentrations were registered outdoors at inland sites during winter: 18 $\mu\text{g}/\text{m}^3$ at Rural-W, 15 $\mu\text{g}/\text{m}^3$ at Urban1-W and 14 $\mu\text{g}/\text{m}^3$ at Peri-W; lower values were calculated for Coast1 and Coast2 sites in the cold season, respectively 5.8 and 5.7 $\mu\text{g}/\text{m}^3$.

Conversely, during summer, Urban1-S, Coast1 and Coast2 consisted in 3.5, 8.2 and 11 $\mu\text{g}/\text{m}^3$ respectively.

It is worth mentioning that indoors the organic components always represent the most important contribution, with a range of 46%–71% of the total mass. The mass concentration was always above outdoor data and varied between 11 and 26 $\mu\text{g}/\text{m}^3$.

Soil source represents on average the second mass contribution, showing a strong variability among sites, particularly in the range 18%–40%, with higher values during summer at urban site and at coastal locations. Indoors, it is in the range 12%–24% and mostly abundant at rural site.

More thoroughly, this macro-source shows, during winter, outdoor average concentrations ranging from 9.2 $\mu\text{g}/\text{m}^3$ at site Urban1-Wsim and 3.5 $\mu\text{g}/\text{m}^3$ at site Urban1-W. This variability within the same site during two different campaigns has been addressed to the presence of a construction site nearby the apartment only during the Urban1-W campaign. The same effect has been observed also at site Coast2-Ssim, where outdoor building renovation activities were responsible for the strong increase of soil-related components (11 $\mu\text{g}/\text{m}^3$), when compared to the simultaneous site Coast1-Ssim (5.5 $\mu\text{g}/\text{m}^3$).

Outdoor and indoor *Secondary Inorganics* result in a range between 12%–29% and 6%–29% respectively, showing a clear seasonal dependence.

During summer, the highest concentrations were registered at the two coastal sites (8.7 and 7.9 $\mu\text{g}/\text{m}^3$ respectively at Coast1-Ssim and Coast2-Ssim) while during winter were measured at inland sites (3.8 $\mu\text{g}/\text{m}^3$ on average compared to the average concentration measured at coastal sites, 1.9 $\mu\text{g}/\text{m}^3$).

The relative share calculated for *Traffic* varies outdoors at inland locations from a minimum of 5% up to 15%, respectively during winter at rural and urban sites. Indoors, we can observe the same modulation, in the range between 5%–6% (rural/coastal sites) and 12% (urban sites).

The same data expressed in mass concentrations shows higher concentrations at site Urban1-W (6.1 $\mu\text{g}/\text{m}^3$) and a lower contribution at rural (1.7 $\mu\text{g}/\text{m}^3$) and coastal sites where, during summer, the variability appears to be low and the concentrations comprised in the range 1.7–2.2 $\mu\text{g}/\text{m}^3$.

The *Sea* source contribution always results below 7%, with its maximum registered at coastal locations during winter. The contribution to the total amount of $\text{PM}_{2.5}$ was quite low compared to the other source contributions both during summer and winter campaigns and was included in the range 0.42–0.59 $\mu\text{g}/\text{m}^3$ and 0.84–1.2 $\mu\text{g}/\text{m}^3$ respectively.

As far as I/O concentration ratios are concerned, they result always higher than one for *Organics*, specifically in the range 1.1–4.8 (respectively at Rural-W and Urban-S).

A great variability is also observed for *Soil*, ranging from 0.4 (Urban1-W) up to 1.3 (Rural-W).

On the contrary, I/O for *Traffic* results very close or slightly below one for all sites and during all seasons.

A seasonal dependence is reported by *Secondary Inorganics* and *Sea* sources, that show I/O ratios always above 0.8 during summer in comparison to those obtained during winter; an exception is represented by the two winter-coastal sites, that show I/O values for secondary species of about 0.9.

3.3. Outdoor Components

The average mass concentrations and the relative standard deviations for the outdoor and indoor macro-components of $\text{PM}_{2.5}$ are reported in Table 4 (macro-elements) and Table 5 (ions, OC and EC). In addition, Tables 6 and 7 report the outdoor average mass concentrations of the elements (in ng/m^3), divided into the two different fractions, extracted and residual respectively. It is important to note that, for the urban sites Urban1-Wsim, Urban2-Wsim and Urban1-S, the analysis of the micro- and trace-elements concentrations were not provided.

3.3.1. Inland/Coastal Variations

Organic carbon (OC) results the most abundant component at almost all outdoor sites, ranging from a minimum value at the urban site during summer (Urban1-S) to a maximum value at the rural site (Rural-W).

More thoroughly, OC concentrations are distinctively higher during winter at inland locations in comparison to the coastal sites, with the highest values observed at Urban1-W and Rural-W (10 and 12 $\mu\text{g}/\text{m}^3$). The values are comprised in the range 8.7–9.3 $\mu\text{g}/\text{m}^3$ at simultaneous urban (Urban-Wsim) and peri-urban (Peri-W) sites. An important difference is then observed for OC average concentrations between the summer and winter seasons at coastal sites (6.7 $\mu\text{g}/\text{m}^3$ on average during summer, 4.3 $\mu\text{g}/\text{m}^3$ during winter).

A clear geographical difference is also observed for winter NO_3^- concentrations, resulting in 3.2 $\mu\text{g}/\text{m}^3$ at site Urban1-W, 1.7 $\mu\text{g}/\text{m}^3$ at site Urban1-Wsim, 2.0 $\mu\text{g}/\text{m}^3$ at sites Urban2-Wsim and Rural-W and 2.2 $\mu\text{g}/\text{m}^3$ at site Peri-W. The concentrations are always below 1.0 $\mu\text{g}/\text{m}^3$ at coastal sites during both seasons.

Particularly high outdoor average levels are then registered for extracted Rb and Cs during the winter period at the inland sites Urban1-W, Peri-W and Rural-W, resulting respectively in 2.6, 1.6 and 1.5 ng/m^3 for Rb and 0.081, 0.048 and 0.044 ng/m^3 for Cs. The concentrations measured for the same species at the two coastal sites Coast1-Wsim and Coast2-Wsim are 0.098 ng/m^3 for Rb and included in the range 0.0053–0.0046 ng/m^3 for Cs.

Table 4. Average mass concentrations (M) and standard deviations (σ) (in $\mu\text{g}/\text{m}^3$) of the macro-elements measured outdoors and indoors.

Site		Na		Mg		Al		Si		S		K		Cl		Ca		Fe	
		Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In
Urban1-W	M	0.30	0.20	0.040	0.036	0.12	0.047	0.26	0.081	0.47	0.36	0.64	0.49	0.45	0.22	0.33	0.22	0.036	0.011
	σ	0.13	0.16	0.030	0.023	0.045	0.011	0.14	0.041	0.15	0.095	0.26	0.20	0.27	0.17	0.11	0.073	0.022	0.0083
Urban1-S	M	0.44	0.42	0.080	0.075	0.20	0.20	0.44	0.43	1.1	1.1	1.0	1.0	0.12	0.13	1.4	1.3	0.057	0.062
	σ	0.29	0.31	0.048	0.036	0.026	0.031	0.087	0.11	0.65	0.66	0.32	0.31	0.080	0.064	0.40	0.32	0.035	0.042
Urban1-Wsim	M	0.37	0.37	0.078	0.087	0.19	0.19	0.48	0.52	0.23	0.22	0.35	0.30	0.35	0.26	0.47	0.53	0.043	0.011
	σ	0.22	0.18	0.040	0.049	0.028	0.040	0.14	0.21	0.10	0.063	0.16	0.12	0.25	0.20	0.31	0.32	0.080	0.026
Urban2-Wsim	M	0.37	0.44	0.12	0.15	0.22	0.22	0.61	0.66	0.24	0.25	0.37	0.57	0.33	0.45	0.92	0.91	0.12	0.078
	σ	0.21	0.19	0.058	0.036	0.028	0.020	0.14	0.11	0.076	0.056	0.15	0.17	0.23	0.22	0.48	0.35	0.080	0.063
Peri-W	M	0.36	0.31	0.13	0.11	0.18	0.18	0.63	0.51	0.37	0.23	0.45	0.45	0.30	0.31	1.0	0.72	0.75	0.69
	σ	0.24	0.19	0.026	0.049	0.12	0.099	0.31	0.19	0.31	0.21	0.31	0.25	0.19	0.22	0.77	0.32	0.17	0.093
Rural-W	M	0.23	0.21	0.073	0.11	0.16	0.22	0.39	0.58	0.73	0.49	0.45	0.47	0.17	0.14	0.63	0.98	0.008	0.011
	σ	0.13	0.069	0.018	0.059	0.026	0.056	0.12	0.15	0.63	0.37	0.18	0.24	0.078	0.048	0.061	0.52	0.003	0.0035
Coast1-Ssim	M	0.27	0.23	0.088	0.078	0.15	0.13	0.55	0.41	2.0	1.8	0.41	0.38	0.074	0.065	1.3	0.64	0.38	0.29
	σ	0.078	0.11	0.022	0.014	0.024	0.014	0.13	0.058	0.43	0.40	0.15	0.13	0.012	0.013	0.42	0.087	0.044	0.011
Coast2-Ssim	M	0.28	0.29	0.13	0.12	0.23	0.16	0.97	0.62	2.1	1.7	0.43	0.37	0.13	0.12	3.6	1.2	0.48	0.34
	σ	0.085	0.075	0.064	0.030	0.14	0.057	0.61	0.18	0.38	0.37	0.15	0.097	0.066	0.045	3.1	0.65	0.25	0.11
Coast1-Wsim	M	0.57	0.49	0.13	0.15	0.19	0.20	0.53	0.60	0.49	0.45	0.23	0.42	0.45	0.50	1.4	1.4	0.088	0.063
	σ	0.29	0.21	0.071	0.032	0.074	0.031	0.27	0.087	0.39	0.36	0.074	0.10	0.32	0.22	0.30	0.22	0.052	0.018
Coast2-Wsim	M	0.56	0.36	0.14	0.12	0.18	0.15	0.49	0.44	0.46	0.095	0.22	0.23	0.38	0.17	1.2	0.96	0.064	0.029
	σ	0.25	0.15	0.035	0.024	0.062	0.026	0.27	0.097	0.36	1.1	0.032	0.085	0.30	0.13	0.35	0.084	0.052	0.015

Table 5. Average mass concentrations (M) and standard deviations (σ) (in $\mu\text{g}/\text{m}^3$) of the ions, OC and EC measured outdoors and indoors.

Site		Cl ⁻		NO ₃ ⁻		SO ₄ ²⁻		Na ⁺		NH ₄ ⁺		Mg ²⁺		Ca ²⁺		EC		OC	
		Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In
Urban1-W	M	0.47	0.23	3.2	0.97	1.3	0.99	0.28	0.21	0.47	0.26	0.029	0.025	0.22	0.15	2.9	2.6	10	13
	σ	0.19	0.12	1.8	0.51	0.44	0.38	0.13	0.16	0.15	0.13	0.016	0.025	0.07	0.082	1.3	1.2	3.9	6.8
Urban1-S	M	0.12	0.14	0.38	0.33	3.2	3.2	0.38	0.41	1.1	1.1	0.10	0.10	0.57	0.47	0.87	0.86	2.5	10
	σ	0.073	0.076	0.24	0.25	1.5	1.4	0.20	0.21	0.65	0.59	0.044	0.048	0.15	0.090	0.29	0.26	0.81	1.7
Urban1-Wsim	M	0.27	0.21	1.7	0.64	0.75	0.75	0.26	0.25	0.23	0.23	0.056	0.057	0.58	0.62	1.2	1.1	8.7	10
	σ	0.18	0.19	0.89	0.28	0.48	0.38	0.18	0.15	0.10	0.11	0.037	0.034	0.30	0.31	0.60	0.40	3.1	2.0
Urban2-Wsim	M	0.25	0.38	2.0	1.4	0.76	0.81	0.29	0.36	0.24	0.14	0.10	0.091	1.2	1.3	1.5	1.6	9.3	17
	σ	0.16	0.19	0.83	0.42	0.41	0.30	0.21	0.19	0.076	0.076	0.073	0.037	0.51	0.40	0.69	0.83	3.0	6.7
Peri-W	M	0.16	0.17	2.2	1.1	1.2	0.82	0.34	0.35	0.37	0.26	0.025	0.024	0.81	0.47	1.4	1.4	8.7	19
	σ	0.094	0.13	2.1	0.73	0.91	0.50	0.12	0.13	0.31	0.17	0.020	0.021	0.53	0.18	0.54	0.55	4.2	5.1
Rural-W	M	0.071	0.049	2.0	0.57	1.8	1.5	0.22	0.19	0.73	0.37	0.014	0.020	0.17	0.41	0.79	0.79	12	13
	σ	0.047	0.017	1.6	0.26	1.4	0.86	0.061	0.053	0.63	0.27	0.009	0.022	0.071	0.23	0.29	0.59	3.1	3.7
Coast1-Ssim	M	0.053	0.051	0.44	0.32	6.9	5.7	0.30	0.30	2.0	1.6	0.047	0.036	2.1	0.67	1.1	0.78	5.9	7.2
	σ	0.015	0.019	0.13	0.12	1.7	1.1	0.08	0.097	0.43	0.43	0.016	0.011	0.39	0.17	0.25	0.24	0.72	1.3
Coast2-Ssim	M	0.11	0.076	0.56	0.32	6.3	6.0	0.33	0.33	2.1	1.6	0.073	0.042	2.9	1.1	0.82	0.63	7.6	8.3
	σ	0.069	0.032	0.20	0.093	0.96	1.4	0.088	0.041	0.38	0.47	0.047	0.006	2.6	0.39	0.18	0.11	2.3	2.1
Coast1-Wsim	M	0.30	0.33	0.62	0.49	1.3	1.2	0.36	0.38	0.49	0.15	0.025	0.036	0.90	0.90	1.0	0.69	4.5	13
	σ	0.24	0.20	0.18	0.34	0.59	0.65	0.21	0.19	0.39	0.26	0.021	0.020	0.30	0.21	0.48	0.23	1.5	3.4
Coast2-Wsim	M	0.22	0.29	0.49	0.37	1.1	1.1	0.34	0.29	0.46	0.13	0.032	0.019	0.76	0.52	0.89	0.83	4.2	10
	σ	0.23	0.29	0.15	0.34	0.50	0.66	0.17	0.13	0.36	1.1	0.015	0.013	0.35	0.056	0.21	0.094	0.41	6.1

Table 6. Average mass concentrations (M) and standard deviations (σ) (in ng/m³) of the extracted micro- and trace-components measured outdoors. * <LOD indicates a value below the limit of detection.

	Urban1-W		Peri-W		Rural-W		Coast1-Ssim		Coast2-Ssim		Coast1-Wsim		Coast2-Wsim	
	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ
Li	0.059	0.030	0.43	0.082	0.035	0.012	0.14	0.016	0.18	0.065	0.036	0.0044	0.031	0.0067
Be	<LOD	0.0009	0.0027	0.0021	0.0047	0.0013	0.0015	0.0002	0.0020	0.0010	0.0008	0.0007	0.0006	0.0005
B	2.0	2.1	3.5	2.3	3.4	2.6	3.3	1.3	3.8	1.4	1.6	0.68	1.5	0.56
Ti	<LOD	0.023	0.072	0.10	0.054	0.047	0.18	0.046	0.36	0.17	0.051	0.03	0.05	0.044
V	0.52	0.26	0.33	0.34	1.9	1.8	7.6	3.4	6.9	2.8	2.0	0.89	1.8	0.74
Cr	0.28	0.27	0.46	0.44	0.18	0.16	0.34	0.051	0.44	0.15	0.066	0.016	0.077	0.068
Mn	1.7	0.88	2.6	2.0	1.1	0.65	2.6	0.68	4.2	2.2	1.8	0.71	1.1	0.49
Co	0.047	0.030	0.027	0.016	0.039	0.042	0.055	0.010	0.062	0.019	0.028	0.0054	0.026	0.0089
Ni	1.2	0.82	0.87	0.97	0.71	0.57	2.5	0.86	2.4	0.68	0.86	0.33	0.71	0.27
Cu	3.1	1.9	2.5	1.2	1.4	1.1	2.5	0.51	2.6	1.0	1.3	0.40	0.80	0.27
As	0.42	0.090	0.29	0.15	0.52	0.15	0.48	0.12	0.58	0.16	0.19	0.054	0.17	0.044
Se	0.79	0.49	0.49	0.40	1.4	0.29	0.61	0.19	0.55	0.20	0.31	0.10	0.27	0.097
Rb	2.6	1.4	1.6	1.4	1.5	0.92	<LOD	0.00	<LOD	0.00	0.098	0.053	0.098	0.028
Sr	0.71	0.18	1.7	0.84	0.45	0.19	7.5	2.2	22	29	6.4	2.2	5.6	3.6
Mo	0.38	0.39	0.22	0.28	0.35	0.51	0.18	0.031	0.18	0.042	0.080	0.023	0.058	0.015
Cd	0.43	0.38	0.099	0.093	0.12	0.059	0.13	0.070	0.13	0.032	0.081	0.020	0.086	0.051
Sn	<LOD	0.028	0.036	0.043	0.31	0.097	0.30	0.07	0.23	0.053	0.018	0.013	0.0087	0.0082
Sb	1.7	1.7	0.51	0.37	0.75	0.45	0.87	0.41	0.95	0.46	0.52	0.28	0.37	0.20
Cs	0.081	0.036	0.048	0.035	0.044	0.018	0.023	0.0060	0.022	0.0040	0.0053	0.0019	0.0046	0.0018
Ba	1.6	0.61	1.3	0.77	0.65	0.42	1.6	0.47	1.7	1.2	1.2	0.37	0.83	0.36
Tl	0.13	0.062	0.050	0.039	0.054	0.018	0.058	0.025	0.052	0.019	0.0082	0.0022	0.0073	0.0011
Pb	3.7	1.9	1.0	0.83	1.7	1.2	2.4	0.72	2.3	0.48	1.00	0.35	0.94	0.46
Bi	0.018	0.0095	0.0077	0.011	0.011	0.0095	0.024	0.0055	0.021	0.0064	0.0027	0.0014	0.0018	0.0016
U	0.0019	0.0008	0.0020	0.0011	0.0009	0.0006	0.0040	0.0014	0.0094	0.010	0.0018	0.0006	0.0016	0.0010

Table 7. Average mass concentrations (M) and standard deviations (σ) (in ng/m³) of the residual micro- and trace-components measured outdoors. * <LOD indicates a value below the limit of detection.

	Urban1-W		Peri-W		Rural-W		Coast1-Ssim		Coast2-Ssim		Coast1-Wsim		Coast2-Wsim	
	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ
Li	0.052	0.046	0.76	0.20	0.079	0.078	0.11	0.059	0.15	0.082	0.072	0.053	0.064	0.040
Be	0.0092	0.019	0.011	0.0083	0.0020	0.0016	0.0023	0.0015	0.0062	0.0052	0.0032	0.0036	0.0018	0.0014
B	<LOD	2.6	2.3	0.92	1.4	0.83	0.77	0.26	0.79	0.25	0.37	0.11	0.62	0.16
Ti	1.7	1.3	7.6	6.1	1.6	0.82	4.1	1.6	11	8.7	3.3	2.0	2.8	1.5
V	0.57	0.88	1.5	0.73	0.77	0.58	2.1	0.64	2.9	1.5	1.1	0.46	1.2	0.48
Cr	13	13	10	3.5	3.5	0.78	4.7	0.51	4.8	1.6	1.8	0.29	2.3	0.41
Mn	5.9	11	5.4	2.5	0.97	0.51	2.3	0.50	4.2	2.2	1.8	0.66	1.2	0.37
Co	0.099	0.13	0.024	0.012	0.043	0.028	0.0049	0.0026	0.010	0.0065	0.044	0.016	0.038	0.012
Ni	4.9	4.1	3.1	1.7	0.91	0.45	1.8	0.30	2.3	0.66	1.0	0.26	0.8	0.18
Cu	6.5	7.5	8.9	3.8	2.5	0.79	3.3	0.82	4.0	1.1	4.2	3.6	2.2	0.51
As	0.40	0.19	0.24	0.19	0.090	0.10	0.49	0.43	0.46	0.30	0.10	0.082	0.081	0.073
Se	0.75	1.2	2.2	1.1	1.2	0.96	0.36	0.19	0.37	0.14	0.47	0.30	0.57	0.18
Rb	0.34	0.30	0.82	0.43	0.30	0.29	0.14	0.026	0.24	0.10	0.15	0.11	0.11	0.062
Sr	3.9	4.6	0.62	0.48	0.42	0.15	0.39	0.25	0.94	0.60	1.6	0.86	1.6	0.70
Mo	0.12	0.52	0.65	0.58	0.22	0.16	0.058	0.038	0.051	0.032	0.15	0.038	0.11	0.040
Cd	0.20	0.12	0.11	0.12	0.052	0.033	0.013	0.011	0.041	0.047	0.028	0.008	0.031	0.014
Sn	0.54	0.44	1.5	0.86	0.61	0.36	0.67	0.083	0.64	0.15	0.49	0.16	0.31	0.048
Sb	1.3	1.8	1.2	0.72	0.46	0.18	0.36	0.15	0.36	0.38	0.53	0.24	0.29	0.10
Cs	<LOD	0.0091	0.066	0.043	0.015	0.011	0.0049	0.0037	0.014	0.010	0.0088	0.0058	0.0078	0.0038
Ba	2.4	3.1	5.7	3.1	0.85	0.44	2.4	0.88	3.1	1.2	1.8	0.78	1.4	0.41
Tl	0.0065	0.0075	0.0077	0.0047	0.012	0.0068	0.0008	0.0004	0.0012	0.0015	0.0035	0.0012	0.0031	0.0013
Pb	4.1	3.5	13	27	2.8	1.7	3.2	0.82	4.7	1.6	2.2	0.81	1.9	0.63
Bi	0.012	0.14	0.15	0.10	0.076	0.056	0.012	0.011	0.020	0.012	0.057	0.042	0.22	0.42
U	0.018	0.029	0.017	0.010	0.0033	0.0027	0.0034	0.0021	0.011	0.0092	0.0064	0.0031	0.0051	0.0023

3.3.2. Seasonal variations

A clear summer/winter variation is exhibited by SO_4^{2-} : it shows higher concentrations during summer periods, with maxima at the two coastal sites ($6.9 \mu\text{g}/\text{m}^3$ at Coast1-Ssim and $6.3 \mu\text{g}/\text{m}^3$ at Coast2-Ssim respectively) and at the urban location Urban1-S ($3.2 \mu\text{g}/\text{m}^3$). During winter, the difference in mass contribution among sites is less significant, spanning from 0.75 up to $1.8 \mu\text{g}/\text{m}^3$.

For the sites that were monitored during both seasons, winter averages for Cl^- were distinctly higher than the corresponding obtained in summer, ranging from 0.071 up to $0.47 \mu\text{g}/\text{m}^3$ during the cold season and in the interval 0.053 – $0.12 \mu\text{g}/\text{m}^3$ during the hot season.

Furthermore, it is important to highlight that the comparison between the values measured at the inland locations shows a decreasing trend in concentrations with the increase of distance from the shoreline.

Another significant result is the particularly high-average concentration for extracted Ni and V measured at coastal locations during summer. The two elements also show a good spatial distribution between the sites, resulting in 2.5 and $2.4 \text{ ng}/\text{m}^3$ for Ni and 7.6 and $6.9 \text{ ng}/\text{m}^3$ for V, respectively at sites Coast1-Ssim and Coast2-Ssim.

3.3.3. Site Specific Variations

The differences observed between those species related to local emission sources and those that do not show any relevant correlation with the sampling area or the season are also of great interest.

In the case of Elemental carbon (EC), a reliable tracer for exhaust-traffic emissions, the highest values are measured at winter urban (Urban1-W, Urban1-Wsim and Urban2-Wsim, $2.9 \mu\text{g}/\text{m}^3$, $1.2 \mu\text{g}/\text{m}^3$ and $1.5 \mu\text{g}/\text{m}^3$ respectively) and peri-urban (Peri-W, $1.4 \mu\text{g}/\text{m}^3$) sites and the lowest at urban-summer (Urban1-S, $0.87 \mu\text{g}/\text{m}^3$) and rural sites (Rural-W, $0.79 \mu\text{g}/\text{m}^3$).

Additionally, Urban1-W and Peri-W sites also show an increase of the average concentrations for non-exhaust traffic (residual Sb, Sn, Mo, Pb, Zn and Cu) and soil-related components (residual U, Ba, Rb, Cs and Ti).

The only urban site Urban1-W is also characterized by a more consistent contribution of extracted Sb, Pb, Cd and Mo, that were nearly two-fold higher than the other sites (the latter also at site Rural-W).

As far as the coastal sites are concerned, they are characterized by particularly higher levels of extracted As, Sn, Bi and Co compared to the other sites. It is interesting to notice that EC results are homogeneously distributed over the urban area, showing only slightly higher values at site Coast1 during both seasons ($1.1 \mu\text{g}/\text{m}^3$ at Coast1-Ssim and $1.0 \mu\text{g}/\text{m}^3$ at Coast1-Wsim; $0.82 \mu\text{g}/\text{m}^3$ at Coast2-Ssim and $0.89 \mu\text{g}/\text{m}^3$ at Coast2-Wsim sites).

3.4. Indoor-to-Outdoor Concentration Ratios (I/O)

For an easier interpretation of the indoor results, the average indoor-to-outdoor concentration ratios calculated for the macro-components are reported in Table 8 (macro-elements) and Table 9 (ions, OC and EC). The relative indoor concentrations have been previously reported in Tables 4 and 5.

In general, the analysis of the I/O values shows, as expected, a clear seasonal difference: during summer, the average values are very close to unity for almost all macro-components at all sites (the only exception is OC at Urban1-S). On the contrary, a great variability is observed during winter, also among sites that were monitored simultaneously.

OC results as the main contributor to the total PM mass concentration also in indoor environments, and it is the only macro-component that shows higher average indoor concentration at all sites. Depending on the location, the I/O concentration ratios are very different, between 1.1 (at sites Coast2-Ssim and Rural-W) and 4.0 (site Urban1-S). In a previous study [16], where the detailed comparison between chemical composition at sites Urban1-W and Urban1-S was described, the effect of the seasonal variability in indoor OC production was found to be strongly dependent of the degree of attendance of people inside the house. This is the case of the two coastal sites Coast1 and Coast2,

where relatively similar OC concentrations measured outdoors during summer and winter results in very different I/O ratios between the seasons, with an average value of respectively 1.2–1.1 during summer and 2.8–2.5 during winter.

Table 8. Average indoor-to-outdoor concentration ratios calculated for macro-elements.

Site	Na	Mg	Al	Si	S	K	Cl	Ca	Fe
Urban1-W	0.67	0.90	0.39	0.31	0.77	0.77	0.49	0.67	0.31
Urban1-S	0.95	0.94	1.0	0.98	1.0	1.0	1.1	0.95	1.1
Urban1-Wsim	1.0	1.1	1.0	1.1	0.96	0.87	0.75	1.1	0.25
Urban2-Wsim	1.2	1.3	1.0	1.1	1.0	1.5	1.4	0.99	0.67
Peri-W	0.86	0.87	0.96	0.81	0.62	1.0	1.0	0.69	0.92
Rural-W	0.94	1.5	1.4	1.5	0.67	1.0	0.83	1.6	1.5
Coast1-Ssim	0.85	0.89	0.84	0.74	0.91	0.94	0.88	0.51	0.78
Coast2-Ssim	1.0	0.94	0.70	0.64	0.83	0.87	0.93	0.32	0.71
Coast1-Wsim	0.87	1.1	1.0	1.1	0.91	1.8	1.1	1.0	0.71
Coast2-Wsim	0.64	0.86	0.87	0.90	0.78	1.0	1.2	0.82	0.46

Table 9. Average indoor-to-outdoor concentration ratios calculated for ions, organic carbon (OC) and elemental carbon (EC).

Site	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}	Na ⁺	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	EC	OC
Urban1-W	0.49	0.30	0.76	0.75	0.25	0.86	0.68	0.90	1.3
Urban1-S	1.2	0.87	1.0	1.1	0.96	1.0	0.82	0.99	4.0
Urban1-Wsim	0.77	0.37	1.0	0.98	0.38	1.0	1.1	0.88	1.2
Urban2-Wsim	1.5	0.67	1.1	1.2	0.29	0.90	1.0	1.1	1.9
Peri-W	1.0	0.50	0.66	1.0	0.34	0.96	0.58	0.97	2.2
Rural-W	0.68	0.29	0.82	0.85	0.38	1.3	2.4	1.0	1.1
Coast1-Ssim	0.95	0.74	0.83	0.98	0.82	0.75	0.32	0.74	1.2
Coast2-Ssim	0.68	0.58	0.96	0.98	1.0	0.57	0.36	0.77	1.1
Coast1-Wsim	1.1	0.79	0.89	1.0	0.53	1.4	1.0	0.67	2.8
Coast2-Wsim	1.3	0.75	0.98	0.83	0.60	0.60	0.68	0.93	2.5

The I/O ratios for inorganic species of secondary origin, SO₄^{2−}, NO₃[−] and NH₄⁺, that mainly originate from the same secondary reactions, show a great variability: I/O values calculated for sulfate during summer are always very close or equal to unity (always > 0.83) and slightly lower only during winter period at site Peri-W (0.66); the same behavior is not observed for nitrate and ammonium. These two species both show I/O ratios very close to one in all summer campaigns with values always below 0.67 during winter periods, with the exception of sites Coast1-Wsim and Coast2-Wsim, (that showed I/O ratios similar to the summer period, respectively 0.79 and 0.75).

I/O ratios for typical crustal components (Al, Si, Ca and Fe) are above 0.6 at almost all sites and related to the presence of local outdoor or indoor sources.

The presence of a construction site nearby the apartment Urban1-W increased the local outdoor emissions of crustal species, thus resulting in particularly lower I/O ratios (respectively 0.39, 0.31, 0.67 and 0.31) compared to the other sites. It is worth mentioning that the absence of the construction site during the subsequent sampling campaign (Urban1-Wsim) resulted in higher I/O ratios.

The same effect is observed by comparing the I/O ratios between the two coastal locations during the summer season (Coast1-Ssim and Coast2-Ssim) that show lower values at Coast2 site for the presence of building renovation activities nearby.

These species do not show any correlation between indoor and outdoor data also at site Rural-W, showing I/O ratios in the range 1.4–1.6 for all components.

Finally, elemental carbon (EC), as already observed for sulfate, shows high infiltration rates for all the sites considered in the study, resulting in I/O always higher than 0.7.

In Tables 10 and 11, the I/O ratios for the extracted and residual micro- and trace-elements are also calculated. The relative indoor concentrations are respectively reported in Tables A1 and A2 (see Appendix A).

Table 10. Average indoor-to-outdoor concentration ratios calculated for the extracted micro- and trace-elements.

	Urban1-W	Peri-W	Rural-W	Coast1-S _{sim}	Coast2-S _{sim}	Coast1-W _{sim}	Coast2-W _{sim}
Li	0.61	0.99	1.5	1.0	0.91	2.6	1.2
Be	-	0.44	1.2	0.72	0.63	1.2	0.78
B	1.6	1.1	1.5	1.5	1.8	1.5	1.5
Ti	-	0.20	0.67	0.58	0.53	0.33	0.85
V	0.28	0.31	0.49	0.76	0.88	0.31	0.69
Cr	0.47	0.64	1.1	1.0	0.87	1.3	2.6
Mn	0.61	0.75	4.9	0.59	0.49	0.79	0.76
Co	0.53	0.91	0.64	0.80	0.72	0.63	0.83
Ni	0.47	0.54	0.77	0.80	0.92	0.58	1.1
Cu	0.68	0.86	13	0.54	1.5	0.74	5.6
As	0.56	0.62	1.0	0.90	0.78	0.99	1.4
Se	5.7	1.0	1.2	0.93	0.87	0.57	0.75
Rb	0.61	0.74	0.82	-	-	2.5	1.4
Sr	0.78	0.63	1.6	0.43	0.31	0.91	0.66
Mo	0.42	0.23	0.98	0.69	0.76	0.16	0.62
Cd	0.71	1.8	1.0	1.3	1.2	3.3	1.7
Sn	-	1.2	1.7	0.69	1.9	4.5	7.7
Sb	0.57	0.56	0.72	0.78	0.92	0.75	0.58
Cs	0.61	0.68	0.81	0.91	0.86	0.88	0.90
Ba	0.78	0.56	1.6	0.55	0.61	0.71	0.83
Tl	0.55	0.82	0.74	0.94	0.90	3.8	1.9
Pb	0.59	1.2	0.64	0.96	1.0	1.2	0.88
Bi	0.21	0.58	0.57	0.67	0.71	0.71	0.84
U	0.34	0.43	1.5	0.41	0.35	0.24	0.66

Table 11. Average indoor-to-outdoor concentration ratios calculated for the residual micro- and trace-elements.

	Urban1-W	Peri-W	Rural-W	Coast1-S _{sim}	Coast2-S _{sim}	Coast1-W _{sim}	Coast2-W _{sim}
Li	1.4	0.98	3.1	0.51	3.8	1.2	3.0
Be	0.30	0.26	2.8	1.6	0.46	0.81	1.0
B	-	1.8	1.0	1.6	1.1	3.7	2.0
Ti	2.5	0.72	1.8	0.54	0.35	1.1	0.85
V	0.89	0.81	0.99	1.1	0.59	2.1	0.88
Cr	0.36	1.0	1.4	0.72	0.91	1.4	0.82
Mn	0.50	0.76	1.9	0.73	0.59	1.1	0.93
Co	0.69	0.89	0.94	0.93	0.36	1.2	0.90
Ni	0.68	1.1	1.1	1.1	0.74	1.7	1.1
Cu	0.80	1.4	13	0.63	2.2	1.3	4.0
As	0.22	0.81	1.0	0.41	0.67	1.3	0.93
Se	0.11	1.1	0.92	0.81	0.77	1.6	0.81
Rb	1.4	0.65	1.4	0.81	0.53	1.2	1.0
Sr	0.34	0.53	1.4	0.39	0.32	1.1	0.57
Mo	3.0	0.88	1.7	0.60	1.0	1.1	0.94
Cd	0.53	1.3	0.98	2.3	3.6	4.0	1.2
Sn	3.0	0.95	1.4	0.79	1.1	1.2	1.1
Sb	1.2	0.86	0.90	0.70	0.67	1.2	1.2
Cs	-	0.47	2.1	0.70	0.23	1.1	1.0
Ba	0.73	0.72	1.4	0.67	0.51	1.07	0.95
Tl	4.0	0.84	1.0	2.4	0.93	3.0	0.81
Pb	0.94	1.0	0.88	0.77	0.69	1.4	0.79
Bi	4.2	0.95	0.70	0.69	0.77	0.94	0.15
U	0.29	0.51	2.1	0.78	0.35	1.2	1.0

Among the extracted micro-components, Co, Ni, As, Sb and Cs show I/O ratios close to one, with slightly lower values at urban and peri-urban sites. In the case of the two coastal sites, quite similar values are observed only during summer (comprised in the range 0.72–0.92), while, on the contrary, more discrepancies are obtained during winter (I/O ratios in the range 0.58–1.4).

Extracted Cd results in higher concentrations in indoor particles where at least one active smoker was present during the sampling period (Peri-W, Coast1 and Coast2 sites). In the case of the Coast1 and Coast2 sites the comparison shows very different I/O ratios between seasons, with distinctly higher values calculated during winter (respectively 3.3 and 1.7).

It is worth mentioning that a similar behavior in terms of I/O variations between the coastal sites is observed also for extracted Sn, whose concentrations clearly depends on the presence of a strong unknown indoor source, particularly at Coast2 site.

Finally, both extracted and residual Cu and Mn are characterized by particularly high I/O ratios only at the rural site (respectively 13 and 4.9 for Cu and 13 and 1.9 for Mn) compared to the lower variable values (from 0.54 up to 5.6) obtained for the other sites.

4. Discussion

In this study, we compared the concentrations and the chemical compositions of PM_{2.5} collected outdoors and indoors at several dwellings located in inland/central and southern/coastal Italy.

The chemical analysis of the single components, whose concentration mainly explain the total mass of PM_{2.5} (macro-components), allowed to highlight the main differences in terms of chemical composition between outdoor sites and between indoor and outdoor each site.

In addition, the chemical fractionation and the analytical determination of the micro- and trace-elements into soluble- and residual-fractions let enhanced the selectivity of the analytical method in the identification of indoor and outdoor PM source tracers. In fact, the chemical form of an element, that can be addressed to a specific emission source can present a different chemical behavior in terms of solubility.

Although this comparative study is mainly focused on the results obtained at different temporal intervals and at specific locations, a great variability among outdoor PM_{2.5} mass concentrations is also reported in other long-term studies conducted in central and southern Italy, where higher concentrations were noticed in winter compared to summer periods. More in particular, average values as high as 50 µg/m³ under more stable atmospheric conditions were reported, with concentrations below 20 µg/m³ during the warmest months. [21–24].

Indoors, the average PM_{2.5} data do not show any systematic dependence on the season or location. The higher concentrations measured indoors, when compared to outdoor levels, are ascribed to several sources, including activities such as cooking, smoking, the use of cleaning detergents, as well as the use of indoor heating during the winter and infiltration of ambient air into indoor areas [25].

Noticeably, the indoor PM_{2.5} mass concentrations frequently exceed the international WHO Indoor Air Quality standards, whose recommended limit is set at 25 µg/m³ over a 24-hour sampling [26]. Additionally, it is important to highlight that the observed values are likely to violate the target values for ambient air PM_{2.5} established for the European Union Countries (annual average of 25 µg/m³) [27].

Recent studies stated that the switch-on of the most common winter combustion sources is considered as the most likely contributor to fine PM and to the total emission of organic components in the European region [16,21,28]. This aspect is particularly significant in inland/central and northern Italy (in peri-urban, rural and mountain areas), where the extensive use of biomass fueled domestic heating appliances has been addressed as a leading contributor for the increase of organic matter [29]. Nonetheless, it is worth mentioning that this increase has also been observed in the surrounding urban areas, where the use of biomass is less widespread [30].

On the other hand, in the Italian southern regions and at coastal locations the use of residential biomass combustion is estimated to be a less frequent practice. [31].

In our study, the increased summer concentrations observed at coastal sites can be addressed to the combination of two factors that have been estimated to be a non-negligible source of organic components: firstly, the enhanced production of secondary organic aerosols via photochemical reactions (due to the typically uniform stable anticyclonic conditions that characterize the insular Italian areas during summertime) [32]; secondly, the peaking of typical seasonal anthropogenic sources, such as vehicular traffic and maritime transport emissions during the touristic season. [33].

Soil-related components represent the second most important contribution to PM mass concentrations, particularly in summer at urban and coastal sites in agreement with soil aridity and consequently with a more intense resuspension. Additionally, the observed outdoor variability was influenced in two cases by the presence of a construction site (Urban1-W) and building renovation activities (Coast2-Ssim).

Outdoor contribution to PM from secondary inorganic components shows a clear seasonal dependence and is chemically linked to the emission of its gaseous precursors: during winter is characterized by the predominance of ammonium nitrate while during summer the contribution is constituted almost exclusively by ammonium sulfate.

NO_3^- increase in the inland sites likely depends on the switch-on of seasonal emission sources, notably on the use of heat production systems, and/or vehicular traffic emissions. At the same time, the combination of lower temperatures, higher relative humidity (which are typical of winter in the central region of Italy, in comparison to insular/southern regions), together with the aging of the air masses when more stable atmospheric conditions occurred, indeed promoted the shift in the dissociation of equilibrium of ammonium salts toward the particulate phase [34,35].

Higher concentrations of SO_4^{2-} during summer are ascribed to the enhanced production of secondary ammonium sulfate by photochemical reactions and the discrepancies between urban and coastal sites to the additional emission of gaseous precursors from the harbor area [16,36,37].

Cl^- concentrations, together with soluble sodium and magnesium, are mainly related to sea-spray emissions and generally influenced by the prevalent wind directions and their intensity. Nonetheless, its spatial distribution is also altered by the occurrence of secondary processes. The calculated Cl^-/Na^+ ratios (maximum of 1.5 at Urban1-W and minimum of 0.32 at Rural-W) suggest that sea-spray reaching the most remote sites during winter likely undergoes secondary reactions, that resulted in lower ratios than the typical value calculated for sea-water (1.8). The lower Cl^-/Na^+ ratios observed during the hot season was also driven by a higher depletion rate for chloride. [22,38].

Elemental carbon (EC), a reliable tracer for combustion sources, is a primary carbonaceous component directly related to the use of fossil fuels (exhaust emissions) in urban settings [39]. Nonetheless, at the other inland sites is also connected to the emissions of biomass combustion for heat production purposes [40].

In this study, the concentration of this component seems to be dependent of the sampling site and is mainly linked to the impact of traffic congestion. The variations show a clear decreasing trend from the urban to the rural sites: in fact, the concentrations are more significant at the Urban2-Wsim and at the Peri-W sites (respectively located in the Rome city-center and close to a congested road during the rush hours) in comparison to the Urban1-Wsim and the other non-urban site (Rural-W).

The analysis of micro- and trace-components shows that vehicular traffic is also considered in the most congested sites as the leading source of some elements typically related to non-exhaust emissions (residual Sb, Sn, Mo, Pb, Zn and Cu), such as brakes friction, tires or asphalt abrasion, and/or derived from soil-dust resuspension (residual U, Ba, Rb, Cs and Ti) [19,41].

The two coastal sites were instead characterized by a strong increase in extracted Ni and V concentrations. These species are commonly associated to the combustion of low refined oils, typically used in marine engines, and thus linked to the operations in the harbor areas and dependent of the intensity of maritime traffic [42,43]. A good spatial distribution was observed for the two elements between the sites during both seasons confirming that they were affected by a common diffused source.

The higher levels of extracted As, Sn, Bi and Co at the same coastal sites, compared to the others, cannot exclude also a specific contribution from the combustion-related refinery activities to the outdoor air quality of the surrounding area.

Combustion processes associated to industrial activities and/or solid waste incinerators are likely responsible for the observed concentrations of extracted Sb, Pb, Cd and Mo in the urban/inland area. Nonetheless, the absence of any intense hot spots in the urban surroundings suggests the effect on the measured concentrations of a remote contribution diffused on a regional scale [44,45].

As for organic components, the use of biomass for domestic heating at the inland sites also triggered an increase in the average concentrations observed for extracted Rb and Cs, considered in literature as reliable tracers for biomass burning [46–48].

Regarding the indoor-to-outdoor concentration ratios (I/O), a great variability is observed between the different species which is influenced by both the infiltration of outdoor air as well as by the presence of specific indoor emission sources.

Among the macro-components, the high indoor mass contribution of organic species results in I/O ratios always above the unity. According to the information reported in the daily reports completed by the inhabitants, the most significant indoor sources of OC were inferred in the presence of people inside the apartments and to the direct emission from cooking and cleaning activities. The former source is responsible for the release of primary biogenic material (e.g., textile fibers from clothes, skin flakes, hairs and other biogenic fragments) [49], while the emissions from cooking and cleaning activities can be also responsible for the indirect formation of secondary organic products from volatile organic precursors [50]. Two additional indoor OC sources were also deducted and addressed to the presence of customary smokers at sites Urban2-Wsim, Peri-W, Coast1 and Coast2 and pets at sites Urban1, Urban2, Peri-W and Rural-W.

The observed variability is linked to the type and intensity of indoor sources and with a less extent to the infiltration processes, even during summer periods, when a constant air exchange rate through open windows would result in I/O ratios very close to one.

Furthermore, soil-related species do not show any correlation between indoor and outdoor data. Given that the I/O ratios calculated for those components related to soil erosion and/or resuspension (Al, Si, Ca, Fe) are expected to be low due to the poor infiltration capacity of coarsest particles of PM [51], the obtained values suggest that a non-negligible effect of strong outdoor (local hot spots) and/or indoor sources (the rate of occupancy of the house) occurred in some sites.

By analyzing the daily reports, particularly high I/O ratios at rural sites were mainly ascribed to the constant presence of people and of a pet inside the apartment, therefore leading to a more intense resuspension of settled particles.

The differences observed in the comparison among winter coastal sites, that showed very similar outdoor concentrations, were linked to a different resuspension rate of deposited particles inside the apartment.

Although secondary inorganic species (SO_4^{2-} , NO_3^- , NH_4^+ , and Cl^-) share the same secondary processes and are therefore characterized by a good ability to penetrate the indoor environments [15], their I/O ratios show a great variability depending on the species as well as between seasons and sites.

More thoroughly, I/O concentration ratios calculated for sulfate suggest that during all campaigns an effective penetration of fine particles occurs indoors. This species is, in fact, considered as a good proxy for the estimation of infiltration factor in indoor environments, since it has no indoor sources and is thermally stable over time in both outdoor and indoor environments [52–54].

Conversely, for nitrate and ammonium, low I/O ratios have been already observed in other studies and ascribed to the alteration of the depletion equilibrium of ammonium salts (mainly ammonium nitrate) that is moved towards the gas phase [55]. This alteration is more evident in indoor environments during winter, and it is activated by the increase in temperature when the domestic heating is switched on [56]. An exception was represented by the high average I/O ratios calculated in winter only for coastal sites; this could be explained with a lower temperature gap between indoor and outdoor

environments, due to the outdoor warmer temperatures and a more limited use of indoor domestic heating that characterized the area.

Thanks to the fact that EC is contained in the finest fraction of PM [51,57,58], this species can easily infiltrate in the indoor environments through building cracks and envelopes. Its behavior is driven by the physical properties of fine combustion-generated particles and resulted in I/O ratios very close to unity for all the sites considered in the study.

The contribution from sea species, exclusively of outdoor origin, resulted in variable I/O ratios during winter campaigns: this is probably linked to the effect of building characteristics on the penetration efficiency of coarser particles. During summer, as expected, the I/O ratios resulted very close to one, as a consequence of a more intense air exchange rate.

Among the extracted micro- and trace-elements, the infiltration of traffic components (notably residual Mo, Sn, Sb and Pb) showed a clear dependence from the sampling site and presented I/O ratios which are consistent with the results obtained for sulfur, thus indicating a good ability to penetrate indoors through the building shell. The same values are not observed at Coast1-Wsim and at the urban and rural sites. This result is presumably influenced by a combined effect of a lower air changes and/or by the contribution from resuspension of household dust [59].

A similar infiltration behavior was observed for some combustion species of outdoor origin (extracted Co, Ni, As, Sb and Cs) with I/O ratios close to one, resulting in a good correlation with the outdoor average values also during the winter period, characterized by less frequent air changes.

Considering that combustion origin species are generally homogeneously diffused over wide areas, in the two coastal sites the high ventilation rate during summer samplings explained the similarly observed I/O ratios. On the contrary, the moderate discrepancies observed during winter are ascribed to the effect of the different ventilation rate adopted within the apartments.

A clear relationship between indoor activities and I/O concentration ratios was found for some crustal-related elements (residual Rb, Sr, Cs, Ba, U) at the Rural-W site, where the resuspension operated by the inhabitants led to a particularly high I/O ratios.

Additionally, residual Ni and Cd resulted in higher-than-one I/O ratios at almost all sites, suggesting that routinely cleaning activities carried out in domestic environments are accountable for the deposition and the subsequent re-suspension of outdoor and indoor-originated particles [60,61].

The strong increase of indoor extracted Cd observed in some sites was related to indoor smoking practice, as also observed in other studies conducted in Italian dwellings [62,63]. Observing the daily reports of the two simultaneous coastal sites, the indoor concentration values seem to be influenced by the frequency of the air changes and by the number of smoked cigarettes [64]. The role of the former variable resulted in very different I/O ratios between seasons, since the residents reported to regularly ventilate the house through windows openings during the summer period and only occasionally during the cold period. Given that the average number of cigarettes smoked inside the apartments was the same between seasons, the different air changes could explain the distinctly higher ratios calculated during winter.

Finally, as already evidenced in a previous study conducted at the Rural-W site, both extracted and residual Cu and Mn are characterized by particularly high I/O ratios and linked to the ash removal from the pellet stove used in the apartment [46]. Conversely, the observed lower Cu I/O ratios calculated at the other sites are probably related to the different use in each site of electrical and electronic devices equipped with copper field coils, notably personal computers, hairdryers, vacuum cleaners [65].

5. Conclusions

In this study we analyzed the chemical characterization of PM_{2.5} collected outdoors and indoors at six households located in two Italian areas.

The analysis of the average concentrations of outdoor macro-, micro- and trace-components permitted to evaluate the differences between air quality at inland and coastal sites also between

summer and winter campaigns. Moreover, the comparison of indoor PM chemical compositions highlighted the strong effect of indoor sources' contribution and the infiltration of outdoor components.

Particularly during winter, indoor PM_{2.5} concentrations resulted as higher as 15 µg/m³ than the corresponding outdoor mean value, indicating a non-negligible effect of indoor sources.

The main contributor to the outdoor and indoor PM concentrations was organic carbon, particularly when the switch-on of domestic heating at inland sites occurred. The additional OC contribution measured indoors was related to the presence of inhabitants and then to the rate of occupancy of the apartment.

The second most important contribution to the PM mass concentrations was estimated for crustal components (Mg, Al, Si, Ca, Fe), whose concentrations were related outdoors to vehicular traffic and, in two cases, to the building renovation activities in a construction site. The indoor contribution was mainly due to the resuspension of settled dust and, in general, to the activities carried out by the inhabitants.

Regarding the outdoor concentrations of secondary inorganic species, a seasonal trend was observed outdoors, showing the predominance of NO₃[−] at inland sites during winter and of SO₄^{2−} at coastal sites during summer. Indoors, the nitrate (and ammonium) concentrations showed a strong decrease with the increase of temperature, consequently to the switch-on of domestic heating.

The components emitted from exhaust emissions (EC and Ni/V associated respectively to vehicular and maritime traffic) and from other combustion processes (Rb/Cs and Sb associated respectively to biomass burning and industrial activities) showed average concentrations that were clearly dependent of the sampling site and of the presence of local/regional emission sources. According to the fact that combustion-related species are contained in the finer fraction of PM, the indoor average concentrations always resulted very similar to the data collected outdoors, thus indicating an effective penetration through the buildings shell.

By comparing the corresponding average outdoor values, the presence of smokers resulted in particularly high indoor Cd concentrations. Furthermore, the use of electronic appliances and cleaning operations were responsible for the strong increase of Cu and Mn concentrations.

The results obtained in this study demonstrate that in naturally ventilated apartments the penetration of many PM_{2.5} components is scarcely impaired by the building characteristics, since an easy penetration of outdoor components was registered during both the warm and the cold season. Indeed, independently from the outdoor air quality, the inhabitant's habits and customs can significantly alter the indoor air quality and determine the indoor concentrations of several hazardous contaminants.

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Appendix A

Table A1. Average mass concentrations (M) and standard deviations (σ) (in ng/m³) of the extracted micro- and trace-components measured indoors. * <LOD indicates a value below the limit of detection.

	Urban1-W		Peri-W		Rural-W		Coast1-Ssim		Coast2-Ssim		Coast1-Wsim		Coast2-Wsim	
	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ
Li	0.036	0.017	0.42	0.043	0.054	0.019	0.15	0.017	0.16	0.036	0.095	0.029	0.038	0.018
Be	<LOD	0.0005	0.0012	0.0008	0.0058	0.0017	0.0011	0.0005	0.0013	0.0004	0.0010	0.0003	0.0005	0.0004
B	3.3	2.4	3.8	2.3	5.2	3.1	5.0	1.1	6.8	1.7	2.4	0.69	2.2	0.79
Ti	<LOD	0.0086	0.014	0.011	0.037	0.029	0.11	0.026	0.19	0.077	0.017	0.0072	0.043	0.037
V	0.14	0.097	0.10	0.078	0.96	0.87	5.8	2.3	6.0	2.3	0.63	0.28	1.2	0.56
Cr	0.13	0.13	0.29	0.24	0.20	0.14	0.35	0.039	0.38	0.13	0.088	0.019	0.20	0.28
Mn	1.0	0.46	1.9	1.3	5.4	11	1.5	0.30	2.1	0.48	1.4	0.34	0.86	0.24
Co	0.025	0.014	0.024	0.034	0.025	0.011	0.044	0.0052	0.045	0.011	0.018	0.0025	0.021	0.0060
Ni	0.57	0.41	0.48	0.22	0.55	0.29	2.0	0.49	2.2	0.67	0.50	0.11	0.76	0.18
Cu	2.1	1.2	2.2	1.5	18	39	1.3	0.26	3.8	1.1	0.99	0.50	4.5	6.0
As	0.24	0.088	0.18	0.077	0.54	0.18	0.43	0.10	0.46	0.10	0.19	0.056	0.23	0.088
Se	4.5	1.8	0.49	0.32	1.6	0.71	0.57	0.22	0.48	0.19	0.18	0.10	0.20	0.10
Rb	1.6	0.89	1.2	1.1	1.2	0.79	<LOD	0.00	<LOD	0.00	0.25	0.12	0.14	0.065
Sr	0.56	0.18	1.1	0.46	0.73	0.63	3.2	0.98	6.9	5.3	5.9	2.1	3.7	0.68
Mo	0.16	0.17	0.050	0.065	0.34	0.34	0.12	0.027	0.13	0.021	0.013	0.0055	0.036	0.025
Cd	0.31	0.28	0.17	0.11	0.13	0.091	0.17	0.077	0.16	0.11	0.27	0.13	0.15	0.13
Sn	0.068	0.057	0.044	0.024	0.53	0.22	0.20	0.053	0.42	0.10	0.083	0.045	0.067	0.040
Sb	0.94	0.85	0.29	0.24	0.54	0.28	0.68	0.28	0.87	0.65	0.39	0.32	0.22	0.058
Cs	0.050	0.024	0.033	0.026	0.036	0.017	0.020	0.0055	0.019	0.0040	0.0047	0.0008	0.0041	0.0015
Ba	1.2	0.64	0.70	0.35	1.0	1.2	0.90	0.34	1.1	0.23	0.86	0.18	0.68	0.15
Tl	0.071	0.038	0.041	0.028	0.040	0.017	0.054	0.020	0.047	0.018	0.032	0.012	0.014	0.012
Pb	2.2	1.5	1.2	1.1	1.1	0.65	2.3	0.65	2.3	0.77	1.2	0.63	0.83	0.29
Bi	0.0039	0.0025	0.0045	0.0070	0.0062	0.0041	0.016	0.0043	0.015	0.0034	0.0019	0.0011	0.0015	0.0008
U	0.0006	0.0002	0.0009	0.0004	0.0013	0.0004	0.0017	0.0006	0.0033	0.0018	0.0004	0.0002	0.0011	0.0005

Table A2. Average mass concentrations (M) and standard deviations (σ) (in ng/m³) of the residual micro- and trace-components measured indoors. * <LOD indicates a value below the limit of detection.

	Urban1-W		Peri-W		Rural-W		Coast1-Ssim		Coast2-Ssim		Coast1-Wsim		Coast2-Wsim	
	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ	M	σ
Li	0.073	0.12	0.75	0.13	0.24	0.17	0.054	0.030	0.59	0.43	0.086	0.035	0.20	0.090
Be	0.0028	0.0036	0.0029	0.0022	0.0056	0.0023	0.0035	0.0020	0.0028	0.0016	0.0026	0.0013	0.0019	0.0013
B	5.7	12	4.1	2.3	1.4	0.45	1.3	0.34	0.91	0.55	1.4	0.29	1.2	1.1
Ti	4.3	4.3	5.5	9.3	3.0	0.64	2.2	0.77	3.7	1.1	3.8	1.4	2.4	0.60
V	0.50	0.26	1.2	1.0	0.76	0.43	2.4	1.3	1.7	1.4	2.2	0.84	1.0	0.68
Cr	4.6	1.4	11	3.1	4.8	1.8	3.4	0.6	4.3	1.0	2.5	0.5	1.9	0.3
Mn	2.9	3.6	4.1	1.6	1.9	2.1	1.7	0.28	2.5	0.69	2.0	0.84	1.2	0.44
Co	0.068	0.033	0.021	0.012	0.040	0.0078	0.0046	0.0032	0.0036	0.0016	0.052	0.011	0.035	0.0049
Ni	3.3	3.5	3.4	2.0	1.0	0.38	2.0	0.77	1.7	0.57	1.6	0.92	0.93	0.27
Cu	5.3	2.5	12	7.8	33	62	2.0	0.5	8.9	3.7	5.4	2.0	8.8	7.8
As	0.088	0.092	0.20	0.30	0.090	0.054	0.20	0.19	0.31	0.15	0.12	0.05	0.075	0.061
Se	0.081	0.50	2.5	1.2	1.1	0.42	0.30	0.20	0.28	0.15	0.77	0.33	0.46	0.28
Rb	0.47	0.28	0.53	0.27	0.41	0.074	0.11	0.038	0.13	0.059	0.17	0.057	0.11	0.045
Sr	1.3	0.42	0.33	0.094	0.57	0.29	0.15	0.080	0.30	0.51	1.8	0.94	0.89	0.41
Mo	0.37	0.35	0.57	0.56	0.37	0.24	0.035	0.020	0.052	0.046	0.18	0.033	0.10	0.070
Cd	0.11	0.17	0.15	0.094	0.051	0.022	0.030	0.034	0.15	0.38	0.11	0.047	0.037	0.029
Sn	1.6	1.8	1.4	0.67	0.82	0.27	0.53	0.081	0.69	0.14	0.59	0.13	0.33	0.075
Sb	1.5	1.5	1.1	0.69	0.41	0.15	0.25	0.19	0.24	0.31	0.63	0.39	0.33	0.15
Cs	0.021	0.017	0.031	0.015	0.032	0.0077	0.0034	0.0020	0.0033	0.0020	0.010	0.0040	0.0078	0.0020
Ba	1.7	0.75	4.2	2.9	1.2	0.71	1.6	0.33	1.6	0.50	2.0	0.84	1.3	0.27
Tl	0.026	0.010	0.0065	0.0041	0.013	0.0041	0.0021	0.0011	0.0011	0.0015	0.011	0.0020	0.0025	0.0014
Pb	3.8	1.3	13	33	2.5	1.0	2.4	0.77	3.2	0.80	2.9	1.3	1.5	0.41
Bi	0.050	0.062	0.14	0.099	0.053	0.021	0.0080	0.013	0.015	0.010	0.054	0.011	0.033	0.0042
U	0.0052	0.0045	0.0089	0.0021	0.0071	0.0027	0.0026	0.0011	0.0039	0.0027	0.0074	0.0024	0.0052	0.00091

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