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The Spatial and Temporal Behaviour of Particulate Matter and Submicron Particles in the Molise Region

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traffic
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ABSTRACT

Environmental pollution and its impact on human health has become a topic of great concern. In recent years, the scientific community has significantly increased its attention towards the protection of human health and an increasing number of analytical determinations are being carried out on food and environmental matrices to guarantee their quality. Within these determinations, the monitoring of air quality, both in indoor and outdoor environments, is of particular scientific interest. In particular, the presence of micrometric particles, atmospheric particulate matter (PM) and ultrafine particulate matter (UFP) has become a marker of air quality in recent years. The study of these substances is particularly important since the diameter of the particles is inversely proportional to their ability to penetrate the respiratory system. In places of greatest attendance and areas with high vehicular traffic, units are installed for continuously monitoring the air quality. This paper aims to bring a snapshot of the concentrations of these particles in Molise, a small region in Italy. The results obtained present rather limited PM_{10}, PM_4, $PM_{2.5}$, PM_1 and UFP ranges, especially as regards Campobasso, the regional capital.

Introduction

The terms "fine dust" or "atmospheric particulate matter" (*i.e.*, PM) refer to a series of particles suspended in the air that humans breathe daily. PM_{10} is characterised by a diameter of less than 10 μm. Its presence in the air is due to natural events or anthropic activities. PM_{10} is considered an indicator of air quality (Vahlsing & Smith, 2012; Costa et al., 2014) as well as of the entire ecosystem (Wright et al., 2018). It is well-known that atmospheric particulate persists in the air for a long time. Such persistence determines that PM could be transported over long distances (Arfin et al., 2023). Studies showed that PM had an impact on human health, particularly disorders of the respiratory system (Johannson et al., 2015; Avino et al., 2013; Marini et al., 2015; Dondi et al., 2023; Madureira et al., 2020). Organic and inorganic pollutants could adhere to the surface of fine dust, facilitating their penetration into the human body (Dongarrà et al., 2010; Turpin et al., 2000). PM_{10} is also called the thoracic fraction. It can reach the throat and trachea, located in the first part of the respiratory system. The smallest particles, characterized by a suspension

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with a particle size class < 4 μm (*i.e.* PM_4), represent the respirable fraction. Due to the effect of respiratory motions, they can reach even deeper until they reach the alveolar area, the non-ciliated part of the lung. $PM_{2.5}$ is a numerical classification given to fine particulate matter based on the average size of its particles. The term $PM_{2.5}$ encompasses all particles with dimensions equal to or smaller than 2.5 μm, where 1 μm. These tiny particles can penetrate deep into the lungs and even enter the bloodstream. $PM_{2.5}$ particles can reach the alveoli in the lungs, potentially causing serious health issues (Feng et al., 2016). Studies have shown that exposure to elevated levels of $PM_{2.5}$ is associated with an increased risk of cancer (Xing et al., 2016). Exposure to $PM_{2.5}$ has been linked to mutations in genes Egfr and Kras associated with lung cancer (Han et al., 2023; Hill et al., 2023). PM_1 consists of particles with an aerodynamic diameter of less than 1 μm. PM_1 is incredibly small and can remain suspended in the atmosphere for extended periods. PM_1 particles can penetrate deep into the lungs, potentially causing harm. PM_1 particles can originate from both natural and anthropogenic sources. Organizations like the World Health Organization (WHO) and the European Union have studied and regulated $PM_{2.5}$ and PM_{10} particles for air quality, but PM_1 remains less explored. In summary, PM represents fine particulate matter with potentially serious health implications, and efforts to reduce exposure are crucial for public health. Minimizing exposure to fine particulate matter is essential for maintaining good respiratory health. Furthermore, the air is characterized also by the presence of ultrafine particles (*i.e.*, UFP), with a diameter between 10 and 100 nm. Such small diameters can penetrate the deeper ways of the respiratory system (Donaldson et al., 2001). Their size is comparable to those of human blood cells or alveolar macrophages, which could be able to internalise UFP. UFPs remain suspended in the air for hours or days, meaning that their deposition can occur far from the point of emission (Avino & Manigrasso, 2017). It is well-known that UFPs mainly arise from vehicle emissions, as well as fuels used for heating systems (Stabile et al., 2018; Jiang et al., 2019). Furthermore, industrial processes (i.e., oil industry, waste incineration and plant treatments) contributed the most to UFPs emissions in the air (Fernández-Camacho et al., 2012; Buonanno et al., 2011; Buonanno & Morawska, 2015; Borrow et al., 2018; Wang et al., 2018; Soggiu et al., 2020). Furthermore, due to their high persistence in the air before deposition, UFPs generally tend to clot/accumulate, leading to an increase in their size (Famiyet et al., 2023; Manigrasso et al., 2020). Generally, deposition of particles > 1 μm occurs by sedimentation, whereas for those smaller than 100 nm, the deposition occurs following chaotic diffusion motions of the particles, dependent on the diffusion coefficient (Famiyeh et al., 2023; Manigrasso et al., 2020). It has been reported that PM_{10} and UFPs become the main causes of diseases, affecting both the respiratory system (*e.g.*, lungs) and the cardiovascular and nervous systems (Du et al., 2016; Heusinkveld et al., 2016; Li et al., 2003; Lodovici & Bigagli, 2011). Recently, traces of ultrafine metal particles were detected in the human brain (Maher et al., 2016). The International Agency for Research on Cancer (IARC) classified PM_{10} as carcinogenic to humans (Word Health Organization, 2010). Therefore, European Member States proposed establishing appropriate guidelines to increase the protection level of their citizens (Settimo et al., 2023).

Generally, most of the population spends most of the hours of the day (up to 90%) indoors (Kelly & Fussell, 2019), so it becomes a necessity for every person to go out into the open air and take short or long walks. Monitoring air quality becomes of fundamental importance for the health of the population (Manigrasso et al., 2017; Notardonato et al., 2019). The present paper aims to carry out a characterization of the distribution of thoracic and respirable fractions and UFP on the exposure of a person during a recreational walk-in in different areas of the Molise region.

Materials and Methods

Sampling Sites

The sampling campaign was carried out in five sites in the Molise region, Italy, about 150 km away from Rome in a southeast direction (Figure 1). The territory is predominantly hilly and there are municipalities and small towns with a population of less than 50000. The surface area of 4461 km^2 and the density of 64.81 inhabitants per km^{-2} describe the predominance of a naturalistic landscape. The sites were chosen for their differences in terms of pollution levels and they can be considered representative of Italian cities characterized by a low population density. Particular attention was paid to the regional capital, Campobasso (41°33'39.6''N 14°40'06.24''E), a city of approximately 49700 inhabitants, with a surface area of 56.11 km^2, 701 m above sea level, with a density of 838.1 inhabitants km^{-2}. Furthermore, an area of environmental whiteness has been identified, the protected natural oasis of "Montedimezzo" (41°45'28.08"N 14°12'46.44"E, approximately 6.4 km^2, between 920 and 1284 m above sea level). The oasis is one of the first natural areas, among the eight Italian ones, to be registered as a "Biosphere Reserve" for the conservation and protection of the environment. The municipality of Agnone (41°48'37.44''N 14°22'42.6''E, approximately 4600 inhabitants, 96.85 km^2, 830 m above sea level, density of 48.17 inhabitants km^{-2}) is the municipality closer to the environmental white which has a sufficient population to con-

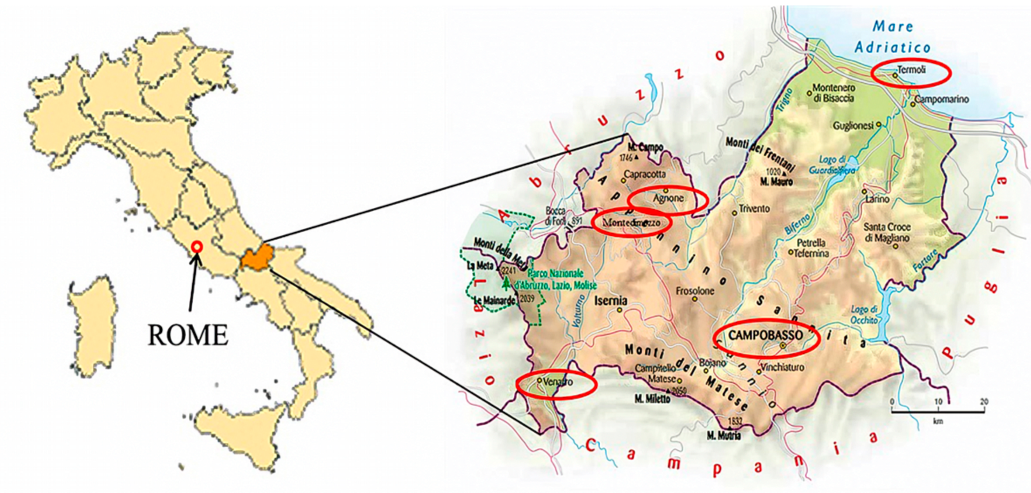

Figure 1. Geographical location of the Molise region and sampling sites

sider the significant anthropic activity. Samplings were also carried out in two municipalities that represent the access routes to the region. The municipality of Venafro (41°28'57''N 14°02'51''E, approximately 10800 inhabitants, surface area of 46.45 km^2, 222 m above sea level, density 232.85 inhabitants km^{-2}), is characterized by high heavy traffic, both cars, buses and trucks. There are two industries, a cement plant and an incinerator. The municipality of Termoli (42°00'10''N 14°59'41''E, approximately 32000 inhabitants, 55.64 km^2, 15 m above sea level, density 576.8 inhabitants km^{-2}) is characterized by the presence of a small port size and a motorway stretch that connects the south with the north of Italy. There are two medium-sized industries relating to the automotive and chemical-pharmaceutical sectors. Where possible, three different areas were identified for each sampling location. Specifically, city centre, residential and green areas were selected. To evaluate the impact of climatic conditions, a sampling campaign was conducted both during the summer and winter seasons. Each sampling activity was repeated twice within the same day at the site of Campobasso, Termoli e Venafro: in the morning between 9.30 and 11.30 AM and in the afternoon between 3.30 and 6.30 PM. In the sites of Montedimezzo and Agnone, areas with zero and low population density respectively, sampling was carried out only once per season as anthropic activity was considered null or almost null. All sampling lasted between 30 and 90 minutes.

Instrumentation

All measurements were performed with certified and appropriately calibrated portable electronic instruments from TSI Instruments (Shoreview, MN, USA). Specifically, the PM was studied under different size fractions using the DustTrak™ II Aerosol Monitor 8532, this is a handheld battery-operated, data-logging, single-channel, light-scattering laser photometer. The DustTrak™ II provides real-time aerosol mass readings using a sheath air system. This system isolates the aerosol in the optics chamber, ensuring cleaner optics for improved reliability and low maintenance. It's useful for assessing workplace air quality. It is ideal for monitoring indoor environments. The DustTrak™ II can measure aerosol concentrations corresponding to PM_1, $PM_{2.5}$, PM_4, or PM_{10} size fractions. It covers an aerosol concentration range from 0.001 to 150 mg m^{-3}. The handheld unit is lightweight and portable, making it easy to carry. The DustTrak™ II Aerosol Monitor 8532 is a versatile tool suitable for various environments, from clean office settings to harsh industrial workplaces and outdoor applications. Its real-time monitoring capabilities make it valuable for assessing aerosol contaminants such as dust, smoke, fumes, and mists. To count the number of nanoparticles (# m^{-3}) with dimensions between 10 and 365 nm, a NanoScan SMPS 3910 was used, which adopts a particle sizing technology with scanning mobility. Nanoparticles were counted in real-time at 60 s time resolutions in thirteen different size channels (11.5 nm, 15.4 nm, 20.5 nm, 27.4 nm, 36.5 nm, 48.7 nm, 64.9 nm, 86.6 nm, 115.5 nm, 154.0 nm, 205.4 nm, 273.8 nm and 365.2 nm), of these all the lower fractions smaller than 115.5 nm were examined. The SMPS NanoScan is ideal for applications requiring portability such as on-the-road measurements, field studies or workplace surveys. The internal Condensation Particle Counter (CPC) uses isopropyl alcohol as a working fluid, making the NanoScan suitable for use in various sensitive environments. The focus fell on ultrafine particles, *i.e.*, on size channels from 11.5 nm to 115.5 nm. A backpack was equipped with a portable DustTrack system, while the Nanoscan was carried by hand. The NanoScan SMPS 3910 is a revolutionary nanoparticle sizer. It opens the door to routine nanoparticle size measurements and delivers a Scanning Mobility Particle Sizer (SMPS™) spectrometer in a portable package and it is an excellent choice for researchers, students, and industrial workers alike.

Results and discussion

The results obtained are detailed and described below.

Natural oasis of Montedimezzo

Results of PM_1, $PM_{2.5}$, PM_4 and PM_{10} are reported in Table 1.

The ultrafine particles present very low values, in the winter period lower than 409 # m^{-3} and in the summer period lower than 750 # m^{-3} and prove to be in line with the concentrations of atmospheric particulates.

Table 1. Average concentrations of PM_1, $PM_{2.5}$, PM_4 and PM_{10} the (µg m^{-3}) related to the summer and winter periods; standard deviation (SD); minimum (min) and maximum (max) value; 60, 80, 95 percentiles of Montedimezzo. (*sum.* = summer; *win.* = winter)

	Concentration (µg m^{-3})							
	PM_1		$PM_{2.5}$		PM_4		PM_{10}	
	sum.	*win.*	*sum.*	*win.*	*sum.*	*win.*	*sum.*	*win.*
mean	8.7	4.9	11.2	5.4	12.5	5.5	15.8	6.0
SD	0.3	7.5	0.5	7.5	0.8	7.5	2.1	7.5
min	7.9	0.9	9.9	1.3	10.9	1.4	13.2	1.5
max	9.3	28.9	12.6	29.5	14.5	29.6	22.4	30.1
60 %	8.7	2.5	11.3	3.1	12.5	3.4	15.6	4.1
80%	8.8	4.5	11.5	5.2	13.1	5.3	17.7	6.5
95%	9.0	25.4	12.2	26.0	14.1	26.2	19.5	26.3

From Table 1 emerged that PM concentrations (µg m^{-3}) in the summer period have higher values than in the winter period. In the summer period, the delta between the minimum value and the maximum value is very narrow, both values approach the average value. In the winter period, however, the minimum and maximum values present a greater delta, which often deviates from the average value. Furthermore, the table shows the values of the eightieth percentile (80%) are in almost all cases close to the average. Such a difference could be due to the increase in recreational anthropogenic activities.

Agnone

Results obtained during the sampling campaign in Agnone are summarised in Table 2.

The average concentrations of atmospheric particulate matter are different between the summer period and the winter period. Concentrations during the winter period tend to almost triple compared to the summer period. Considering the altitude of the municipality, this increase is attributable to the use of heating systems such as methane boilers or wood-burning fireplaces, present in almost all homes in the municipality. The combustion processes influence the winter values. The minimum and maximum

Table 2. Average concentrations of PM_1, $PM_{2.5}$, PM_4 and PM_{10} the (µg m^{-3} relating to the summer and winter periods; standard deviation (SD); minimum (min) and maximum (max) value determined; 60, 80, 95 percentiles. (*sum.* = summer; *win.* = winter)

	Concentration (µg m^{-3})							
	PM_1		$PM_{2.5}$		PM_4		PM_{10}	
	sum.	*win.*	*sum.*	*win.*	*sum.*	*win.*	*sum.*	*win.*
mean	6.5	18.6	9.3	20.1	11.8	20.6	22.4	32.0
SD	0.5	13.4	2.9	13.8	7.5	13.9	58.2	14.2
min	5.7	6.8	7.7	7.9	8.2	8.0	9.1	8.3
max	8.0	75.6	21.5	78.1	44.7	78.6	291.8	79.4
60 %	6.5	16.0	8.6	17.4	9.5	18.3	12.6	20.8
80%	6.7	21.3	9.1	22.6	10.8	23.1	18.4	25.2
95%	7.6	46.8	15.5	49.1	26.5	49.5	153.8	52.2

values present a greater delta compared to the average value in the winter period. Also, in this determination, the values at the eightieth percentile are close to the averages in almost all determinations.

Campobasso

Campobasso city was monitored in different meteorological situations, to have a representativeness of the pollution level of the area.

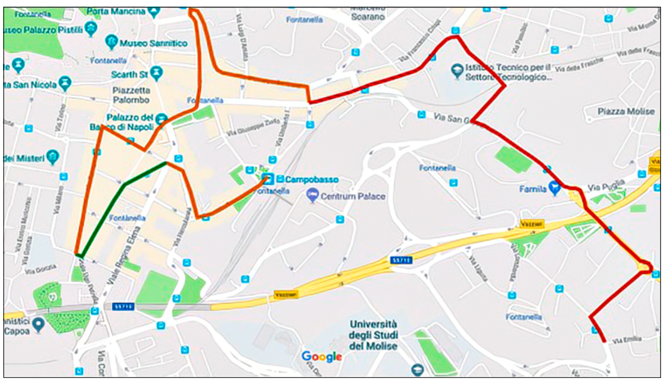

Figure 2. Route in Campobasso city: the red line indicates residential area with high traffic intensity, the orange line indicates residential area with medium traffic intensity, whilst the green line represents pedestrian area

The entire route (Figure 2), touched different areas of the city, appropriately selected based on population density, vehicular traffic and green areas. The route highlighted in red shows a peripheral road, characterized by a high population density, and heavy vehicular traffic of cars and coaches which also operate routes outside the city. In the area, there is a bus terminal located a short distance from the road examined. The route highlighted in orange indicates a road in the city centre, characterized mainly by light vehicular traffic and city buses. Finally, the route represented by the green line represents the pedestrian area closed to traffic where there is a green park used by the majority of the population for walking. The housing units are similar to those of the orange route but the park is very large, full of trees and varied vegetation. These three situations identify and characterize different practicable routes within the town centre. They simulate a different exposure to atmospheric particulates and ultrafine particles to which the pedestrian is subjected.

Table 3 shows the average results of the PMs, with the SD, MIN, MAX, 60, 80, and 95 percentiles. The average values during the summer period are between 7.2 and 11.1 ppm, while the winter values were between 8.8 and 26.8 ppm. Significant differences between the maximum values are noted. The maximum values determined during the afternoons of the summer period (401.0 - 521.0 µg m^{-3}) are far higher than the respective average values (8.8 - 11.1 µg m^{-3}). However, by comparing the maximum values with the relative values at 95% (23 – 28 µg m^{-3}), it can be noted that the maximums represent instantaneous values of little significance. Furthermore, especially in the summer sampling, the average composition of the aerosol is predominantly PM_1 (around 66.0% in the morning and 79.3% in the afternoon).

The correspondences between percentiles and averages are also different. During the summer period, considering the standard deviation, the average values are comparable to those of 95%. While in the winter period, the correspondence is 80%. In the winter period, the average values of the various particulate fractions become comparable between morning and afternoon. The data show an increase in particulate values in the winter period compared to the summer period. This could be due to an anthropic action linked to the use of heating systems. Campobasso is characterized by a fairly harsh climate during the winter period. Consequently, the use of combustion boilers leads to doubling the values of both the respirable fraction and PM_{10} compared to the values found during the summer period.

Table 3. Average concentrations of the different sizes of atmospheric particulate matter (µg m^{-3}) relating to the summer and winter periods; standard deviation (SD); minimum (min) and maximum (max) value determined; 60, 80, 95 percentiles. (*mor.* = morning; *aft.* = afternoon)

	Concentration mean (µg m^{-3})															
	Summer								Winter							
	PM_1		$PM_{2.5}$		PM_4		PM_{10}		PM_1		$PM_{2.5}$		PM_4		PM_{10}	
	mor.	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*
mean	6.8	8.8	7.2	9.1	8.2	9.7	10.3	11.1	8.8	9.6	15.2	13.9	17.9	17.0	21.9	26.8
SD	1.9	13.5	2.0	13.5	2.7	13.9	5.9	17.1	8.1	4.3	9.5	6.2	10.2	8.5	11.0	17.5
min	5.0	1.0	5.0	1.0	6.0	1.0	6.0	1.0	2.4	4.6	5.3	7.4	6.6	8.6	8.4	11.1
max	17.0	401.0	19.0	403.0	25.0	410.0	46.0	521.0	48.5	22.3	57.4	37.9	60.7	52.9	62.7	99.8
60 %	7.0	7.0	7.0	7.0	8.0	8.0	10.0	9.0	8.4	10.0	16.5	13.8	19.4	16.3	23.2	23.2
80%	7.0	10.0	7.2	10.0	9.0	11.0	11.0	14.0	10.1	11.6	18.2	16.7	22.2	20.9	27.0	34.0
95%	8.1	23.0	9.1	24.0	12.0	24.0	17.0	28.0	23.9	18.1	31.6	26.0	35.9	32.2	41.4	54.7

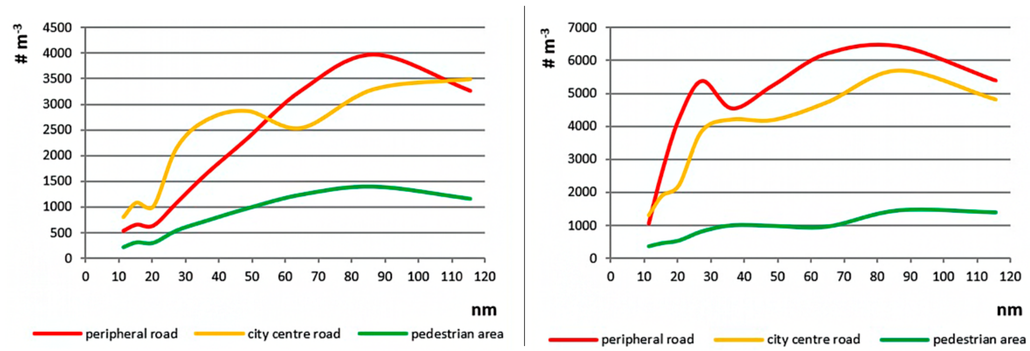

Figure 3. Comparison between the average distribution of ultrafine particles (# m^{-3}) VS the diameter of the particles (nm) between the summer and winter periods in the three types of routes

The comparison between the composition of UFPs between the summer and winter periods confirms a change in air quality (Figure 3). The number of UFPs per cubic meter (# m^{-3}) of air also tends to increase in the analyzed routes. Specifically, in the red and orange routes, the number of UFPs tends to grow in the winter period compared to the summer period, with values respectively lower than 6500 # m^{-3} and 4000 # m^{-3}. Such a trend was not observed in the green one, where the UFPs are comparable in the two periods.

Venafro

Routes carried out during the sampling campaign in Venafro are represented in Figure 4.

A route was identified that covered almost the entire country. An alasting of approximately 30 minutes was considered: two different areas can be identified on the selected stretch. The route highlighted in red develops along the "SS6" and the "SS85", the two main roads that connect Venafro with the motorways and the industrial area, characterized by a high density of heavy vehicular traffic. The route highlighted in orange is in the centre with medium traffic density, essentially local traffic.

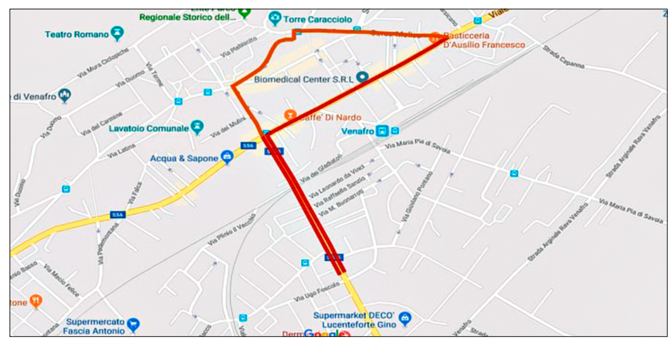

Figure 4. The city route of Venafro where the red line indicates a residential area with high traffic intensity, and the orange line indicates a residential area with medium traffic intensity

The concentrations of atmospheric particulate matter are different between the summer and winter periods, as shown in Table 4. In the summer period, PM concentrations are on average higher than those in the afternoon. This difference could be due to the heavy vehicular traffic of trucks and road transporters, which, can walk freely on urban and extra-urban roads during the night hours, and then have limitations during the daytime hours to reduce the risks for cars. This gap decreases during the

Table 4. Average concentrations of the different sizes of atmospheric particulate matter (µg m^{-3}) relating to the summer and winter periods; standard deviation (SD); minimum (min) and maximum (max) value determined; 60, 80, 95 percentiles (*mor.* = morning; *aft.* = afternoon)

	Concentration mean (µg m^{-3})															
	Summer								Winter							
	PM_1		$PM_{2.5}$		PM_4		PM_{10}		PM_1		$PM_{2.5}$		PM_4		PM_{10}	
	mor.	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*
mean	23.1	13.1	23.9	13.6	25.1	14.6	28.3	17.1	35.5	32.5	47.3	40.9	50.9	45.9	58.4	66.5
SD	39.9	35.1	40.5	35.3	43.2	36.4	57.3	43.9	20.0	23.9	20.5	25.3	20.9	33.4	31.5	125.1
min	0.0	5.0	8.0	6.0	8.0	7.0	8.0	7.0	13.9	16.9	23.7	24.5	26.3	26.3	30.1	29.4
max	1090.0	1080.0	1100.0	1090.0	1130.0	1130.0	1720.0	1430.0	135.5	155.0	147.0	165.0	149.7	170.3	215.9	738.6
60 %	20.0	10.0	21.0	11.0	22.0	12.0	24.0	13.0	35.3	28.9	47.7	35.6	50.7	37.3	54.9	39.8
80%	25.0	13.0	26.0	14.0	27.0	15.0	31.0	18.0	43.3	39.0	55.7	48.4	61.1	50.5	67.5	53.9
95%	43.8	26.0	45.0	27.0	46.8	28.0	53.0	33.0	59.4	46.6	72.5	64.4	76.0	106.5	95.1	110.0

winter period. The maximum values appear to be occasional when compared to respective 95% values. During the summer period, considering the standard deviation, the average values are comparable to those of 95%. While in the winter period, the correspondence is 80%. Furthermore, in the winter period, the concentrations between morning and afternoon become broadly comparable, since in addition to the emissions due to heavy vehicle traffic, there are also emissions linked to the use of heating systems.

Termoli

The last sampling was carried out in the municipality of Termoli, the only seaside town in the region. Four samplings were also carried out in this municipality, two during the winter period and two during the summer period.

Routes carried out during the sampling campaign in Termoli are represented in Figure 6. The route is traced based on the type of vehicular traffic and housing structures present. The red route represents the streets with intense vehicular traffic and represents the main entrance to the city,

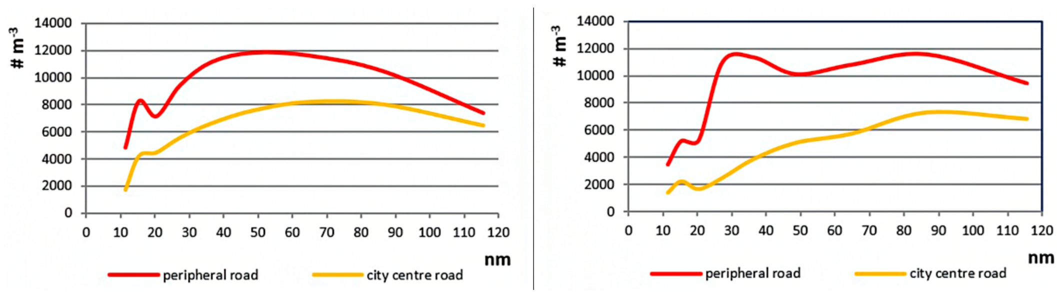

Figure 5. Comparison between the average distribution of ultrafine particles ($\# \ m^{-3}$) VS the diameter of the particles (nm) between the summer and winter periods in the two types of routes

Table 5. Pearson correlation coefficient between submicron particles in different size fractions. Values> 0.7 are highlighted

11.5	15.4	20.5	27.4	36.5	48.7	64.9	86.6	115.5	
1	0.666	0.782	0.928	0.959	0.945	0.806	0.298	0.162	**11.5**
	1	0.909	0.564	0.582	0.714	0.816	0.589	0.520	**15.4**
		1	0,802	0,782	0,815	0,792	0,576	0,456	**20.5**
			1	0,985	0,894	0,813	0,418	0,179	**27.4**
				1	0,949	0,856	0,334	0,107	**36.5**
					1	0,922	0,354	0,195	**48.7**
						1	0,609	0,614	**64.9**
							1	0,920	**86.6**
								1	**115.5**

The UFP concentrations, as shown in Figure 5, are comparable in the two periods. In both types of path, the distribution curves show similar trends and are lower than 12000 $\# \ m^{-3}$ for the path highlighted by the red line and lower than 8000 $\# \ m^{-3}$ for the path highlighted by the orange line. It was decided to carry out Pearson correlations only for this reason since the ultrafine particles present significantly higher values compared to the other sites examined.

Table 5. shows the relative Pearson correlation coefficients (r) determined for all sizes: the coefficients highlighted in blue, *i.e.*, those with a value greater than 0.7, highlight a good correlation between the two fractions considered. Correlations are good for sizes ranging from 11.5 to 64.9 nm, which means that fresh aerosol is emitted from the same sources.

while the orange route represents the city centre, characterized by larger spaces and a small limited traffic area.

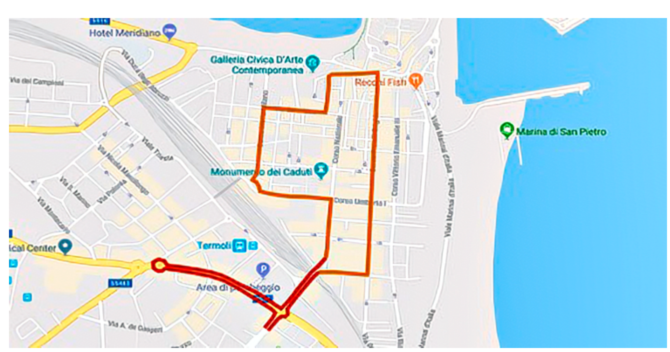

Figure 6. City route of Termoli where the red line indicates a residential area with high traffic intensity whereas the orange line indicates a residential area with medium traffic intensity

Table 6. Average concentrations of the different sizes of atmospheric particulate matter (μg m^{-3}) relating to the summer and winter periods; standard deviation (SD); minimum (min) and maximum (max) value determined; 60, 80, 95 percentiles. (*mor.* = morning; *aft.* = afternoon)

	Concentration mean (μg m^{-3})															
	Summer								Winter							
	PM_1		$PM_{2.5}$		PM_4		PM_{10}		PM_1		$PM_{2.5}$		PM_4		PM_{10}	
	mor.	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*	*mor.*	*aft.*
mean	15.1	11.4	15.6	11.8	16.6	12.5	18.7	14.1	8.8	18.5	18.5	35.5	24.0	44.9	39.5	64.0
SD	7.4	10.8	7.5	10.9	8.2	11.3	10.8	12.9	2.5	3.2	2.6	3.9	3.1	5.1	6.9	10.1
min	8.0	3.0	9.0	4.0	9.0	4.0	9.0	4.0	6.8	12.6	16.2	30.1	20.4	38.2	28.5	51.7
max	122.0	164.0	135.0	165.0	169.0	166.0	276.0	184.0	22.6	27.0	32.4	50.0	38.3	64.3	58.8	101.9
60 %	14.0	9.0	14.0	10.0	15.0	10.0	18.0	12.0	8.5	18.7	18.2	35.7	23.7	44.7	39.5	63.2
80%	17.0	14.0	18.0	14.0	19.0	15.0	22.0	18.0	9.6	20.9	19.7	37.5	25.6	47.8	44.0	67.9
95%	26.0	26.0	27.0	27.0	29.0	28.0	33.0	32.0	11.5	24.3	21.5	42.6	28.5	55.4	52.1	85.2

Table 6 shows a variation in average concentrations between the summer period and the winter period. The concentrations of atmospheric particulates in the summer period are comparable within the day, while in the winter period, an increase in the concentration of the various fractions of PM is observed in the afternoon compared to the morning. This variation could be influenced by the presence of the sea breeze, which rises in the summer period and participates in the exchange of air. During the summer period, there is a greater delta between the minimum value and maximum value in the various fractions of the particulate matter. But even in this case, these values are occasional when compared to the 95% average values. In the afternoon sampling the average values of both $PM_{2.5}$ and PM_{10} exceed the permitted limit, 35.5 μg m^{-3} and 64 μg m^{-3} respectively. However, if this value is averaged with the average morning value, 11.8 μg m^{-3} for $PM_{2.5}$ and 14.1 μg m^{-3} for PM_{10}, the average daily values are 23.7 μg m^{-3} for $PM_{2.5}$ and 39.05 μg m^{-3} for PM_{10}, values that fall within the permitted limits. As regards the winter period, it should be underlined that the municipality of Termoli is crossed by a highly travelled stretch of motorway, which connects the south with the north of Italy. It is possible to suppose that in the winter period, the colder climatic conditions limit the exchange of air linked to convective motions and consequently, there is an increase in fine dust concentrations.

Figure 7 shows the comparison between the average distribution of ultrafine particles between the summer and winter periods in the two types of routes. It could be observed that the concentrations of UFP are comparable to those of atmospheric particulates. They appear to be 2000 # m^{-3} and 6000 # m^{-3} respectively lower in the summer and winter periods. Furthermore, on this site, the trend of UFPs in both the red path and the orange path assumes a comparable trend.

This paper aimed to characterize the air quality of some sites in the Molise region with data collected experimentally. The analysis of the data collected has underlined an important influence of air quality due to vehicular traffic and the use of heating systems, highlighting significant gaps between the summer period and the winter period. The geographical and demographic characteristics of Campobasso make the city comparable in terms of quality of life to many small Italian towns. In Italy the PM_{10} evaluation parameter is the daily average: according to Legislative Decree 155/2010 this limit is equal to 50 μg m^{-3}, not to be exceeded more than 35 times per year. The same decree also establishes an average annual limit of 40 μg m^{-3}. In April 2008 the European Union definitively adopted a

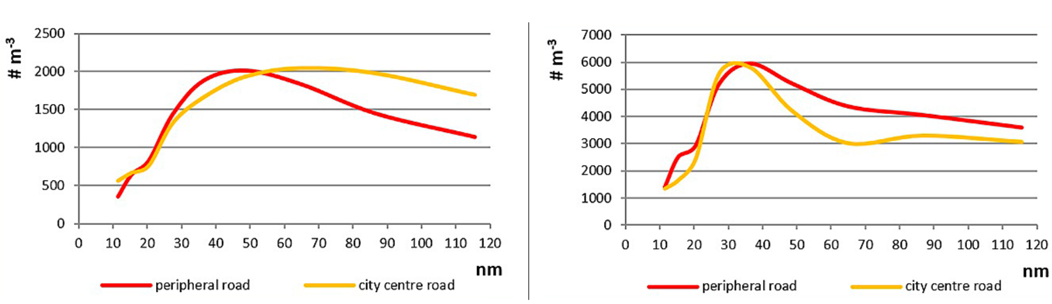

Figure 7. Comparison between the average distribution of ultrafine particles (# m^{-3}) VS the diameter of the particles (nm) between the summer and winter periods in the two types of routes

new directive (2008/50/EC) which sets air quality limits with concerning $PM_{2.5}$, considered the most dangerous for our health. As regards $PM_{2.5}$, only the average annual limit of 25 µg m^{-3} is established. There is currently no regulation on exposure limits for PM_4, PM_1 and ultrafine particles. The overall picture shows an almost ideal climatic situation, with concentrations of atmospheric particulates and ultrafine particles which in most cases are below the limit concentrations established by law. The presence of anomalous peaks is resolved over time.

The results of concentrations of $PM_{2.5}$ and PM_{10} in Campobasso were compared with those of atmospheric particulate matter in some Italian cities. There are approximately 15 common demographically comparable results, but only three present works in the literature regarding the monitoring of $PM_{2.5}$ and PM_{10} in different atmospheric and climatic conditions. The municipality of Lodi (Urso et al., 2015) is approximately 580 km from Rome in the North-West direction (45°19'N 9°30'E), approximately 44700 inhabitants, 41.38 km^2, 87 m above sea level, 1080.45 inhabitants km^{-2}. The municipality of Biella (Diana et al., 2022) is approximately 670 km from Rome in a North-West direction (45°33'59"N 8°03'12"E), approximately 42800 inhabitants, 46.69 km^2, 420 m above sea level, 917.22 inhabitants km^{-2}. Finally, the municipality of Avellino (Capozzi et al., 2022), about 250 km from Rome in a south-east direction (40°54'55"N 14°47'23"E), approximately 52100 inhabitants, 30.55 km^2, 348 m above sea level, 1,706.58 inhabitants km^{-2}. Table 7 compares the concentrations reported in the literature with those obtained experimentally with this work in the municipality of Campobasso.

In all the municipalities examined there is a variation in the concentration of the various dimensions of atmospheric particulate matter between the summer and winter periods linked to the variation in climatic conditions. The work carried out in the municipality of Biella presents concentration values relating only to PM_{10} and the reasons that explain the difference in concentrations between the summer and winter periods are widely discussed by the authors in the article [Diana et al., 2022]. It is possible to note how the concentrations of the two fractions of particulate matter, respectively the inhalable fraction (PM_{10}) and the respirable fraction ($PM_{2.5}$), present lower values in the municipality of Campobasso compared to the cities examined. Furthermore, the average concentrations obtained during the entire sampling campaign are decidedly lower when compared with those reported in the literature [Manigrasso et al., 2017] regarding large metropolises such as Rome (Table 8).

Table 7. Comparison of the average concentrations (µg m^{-3}) of $PM_{2.5}$ and PM_{10} in four comparable Italian cities. (*sum.* = summer, *win.* = winter)

	Concentration mean PM (µg m^{-3})			
	$PM_{2.5}$		PM_{10}	
	sum.	*win.*	*sum.*	*win.*
Lodi	19.8	38.3	28.3	65.2
Biella	/	/	4.0	80.0
Avellino	35.0	36.1	31.9	39.2
Campobasso	8.2	14.6	10.5	23.9

Table 8. Comparison between the average values of the three most populated areas of the entire sampling (µg m^{-3}) with the city of Rome

	Concentration mean PM (µg m^{-3})			
	PM_1	$PM_{2.5}$	PM_4	PM_{10}
Campobasso	8	11	12	16
Termoli	14	21	25	35
Venafro	26	31	40	45
Roma	129	130	131	137

Although the average concentrations of the various fractions of atmospheric particulate matter in Venafro are greater than those in Termoli or Campobasso, they become small (about a quarter) when compared to those of metropolises such as Rome.

Conclusions

In conclusion, this work began to demonstrate the quality of the air in the Molise region, starting from the measurement of the respirable and inhalable fraction of atmospheric particulate matter. The data collected is only a starting point. The authors examined the importance of respirable and non-respirable fractions and ultrafine particles for air quality monitoring. Studies on this topic are constantly updated and are not always sufficient to describe a correct public health assessment. It remains confirmed by the literature, the danger of submicron particles, which manage to reach the deepest part of the human respiratory system and are responsible for various pulmonary and cardiovascular diseases. They should represent, together with atmospheric particulate matter, the new assessment target for air quality.

References

Arfin, T., Pillai, A. M., Mathew, N., Tirpude, A., Bang, R., & Mondal, P. (2023). An overview of atmospheric aerosol and their effects on human health. *Environmental Science and Pollution Research*, 30, 125347–125369. https://doi.org/10.1007/s11356-023-29652-w

Avino, P., Casciardi, S., Fanizza, C., & Manigrasso, M. (2011). Deep Investigation of Ultrafine Particles in Urban Air. *Aerosol and Air Quality Research*, 11(6), 654–663. https://doi.org/10.4209/aaqr.2010.10.0086

Avino, P., Lopez, F., & Manigrasso, M. (2013). Regional Deposition of Submicrometer Aerosol in the Human Respiratory System Determined at 1-s Time Resolution of Particle Size Distribution Measurements. *Aerosol and Air Quality Research*, 13(6), 1702–1711. https://doi.org/10.4209/aaqr.2013.06.0189

Avino, P., & Manigrasso, M. (2017). Dynamic of submicrometer particles in urban environment. *Environmental Science and Pollution Research*, 24(16), 13908–13920. https://doi.org/10.1007/s11356-016-6752-8

Borrow, D. J., Van Netten, K., & Galvin, K. P. (2018). Ultrafine Particle Recovery Using Thin Permeable Films. *Frontiers in Chemistry*, 6, 220. https://doi.org/10.3389/fchem.2018.00220

Buonanno, G., & Morawska, L. (2015). Ultrafine particle emission of waste incinerators and comparison to the exposure of urban citizens. *Waste Management*, 37, 75–81. https://doi.org/10.1016/j.wasman.2014.03.008

Buonanno, G., Stabile, L., Avino, P., & Belluso, E. (2011). Chemical, dimensional and morphological ultrafine particle characterization from a waste-to-energy plant. *Waste Management*, 31(11), 2253–2262. https://doi.org/10.1016/j.wasman.2011.06.017

Capozzi, V., Raia, L., Cretella, V., De Vivo, C., & Cucciniello, R. (2022). The Impact of Meteorological Conditions and Agricultural Waste Burning on PM Levels: A Case Study of Avellino (Southern Italy). *International Journal of Environmental Research and Public Health*, 19(19), 12246. https://doi.org/10.3390/ijerph191912246

Costa, S., Ferreira, J., Silveira, C., Costa, C., Lopes, D., Relvas, H., Borrego, C., Roebeling, P., Miranda, A. I., & Paulo Teixeira, J. (2014). Integrating Health on Air Quality Assessment—Review Report on Health Risks of Two Major European Outdoor Air Pollutants: PM and NO_2. *Journal of Toxicology and Environmental Health*, Part B, 17(6), 307–340. https://doi.org/10.1080/10937404.2014.946164

Diana, A., Bertinetti, S., Abollino, O., Giacomino, A., Buoso, S., Favilli, L., Inaudi, P., & Malandrino, M. (2022). PM10 Element Distribution and Environmental-Sanitary Risk Analysis in Two Italian Industrial Cities. *Atmosphere*, 14(1), 48. https://doi.org/10.3390/atmos14010048

Donaldson, K., Stonea, V., Cloutera, A., Renwicka, L. & MacNee, W. (2001). Ultrafine particles. *Occupational and Environmental Medicine*, 58(3), 211–216. https://doi.org/10.1136/oem.58.3.211

Dondi, A., Carbone, C., Manieri, E., Zama, D., Del Bono, C., Betti, L., Biagi, C., & Lanari, M. (2023). Outdoor Air Pollution and Childhood Respiratory Disease: The Role of Oxidative Stress. *International Journal of Molecular Sciences*, 24(5), 4345. https://doi.org/10.3390/ijms24054345

Dongarrà, G., Manno, E., Varrica, D., Lombardo, M., & Vultaggio, M. (2010). Study on ambient concentrations of PM_{10}, $PM_{10-2.5}$, $PM_{2.5}$ and gaseous pollutants. Trace elements and chemical speciation of atmospheric particulates. *Atmospheric Environment*, 44(39), 5244–5257. https://doi.org/10.1016/j.atmosenv.2010.08.041

Du, Y., Xu, X., Chu, M., Guo, Y., Wang, J. (2016). Air particulate matter and cardiovascular disease: The epidemiological, biomedical and clinical evidence. *J. Thorac. Dis.*, 8. https://doi: 10.3978/j.issn.2072-1439.2015.11.37

Famiyeh, L., Jia, C., Chen, K., Tang, Y. T., Ji, D., He, J., & Guo, Q. (2023). Size distribution and lung-deposition of ambient particulate matter oxidative potential: A contrast between dithiothreitol and ascorbic acid assays. *Environmental Pollution*, 336, 122437. https://doi.org/10.1016/j.envpol.2023.122437

Feng, S., Gao, D., Liao, F., Zhou, F., & Wang, X. (2016). The health effects of ambient $PM_{2.5}$ and potential mechanisms. *Ecotoxicology and Environmental Safety*, 128, 67–74. https://doi.org/10.1016/j.ecoenv.2016.01.030

Fernández-Camacho, R., Rodríguez, S., De La Rosa, J., Sánchez De La Campa, A. M., Alastuey, A., Querol, X., González-Castanedo, Y., Garcia-Orellana, I., & Nava, S. (2012). Ultrafine particle and fine trace metal (As, Cd, Cu, Pb and Zn) pollution episodes induced by industrial emissions in Huelva, SW Spain. *Atmospheric Environment*, 61, 507–517. https://doi.org/10.1016/j.atmosenv.2012.08.003

Han, S. C., Wang, G. Z., & Zhou, G. B. (2023). Air pollution, EGFR mutation, and cancer initiation. *Cell Reports Medicine*, 4(5), 101046. https://doi.org/10.1016/j.xcrm.2023.101046

Heusinkveld, H. J., Wahle, T., Campbell, A., Westerink, R. H. S., Tran, L., Johnston, H., Stone, V., Cassee, F. R., & Schins, R. P. F. (2016). Neurodegenerative and neurological disorders by small inhaled particles. *NeuroToxicology*, 56, 94–106. https://doi.org/10.1016/j.neuro.2016.07.007

Hill, W., Lim, E. L., Weeden, C. E., Lee, C., Augustine, M., Chen, K., Kuan, F. C., Marongiu, F., Evans, E. J., Moore, D. A., Rodrigues, F. S., Pich, O., Bakker, B., Cha, H., Myers, R., Van Maldegem, F., Boumelha, J., Veeriah, S., Rowan, A., Lombardelli, C, N., Karasaki, T.,… Swanton, C. (2023). Lung adenocarcinoma promotion by air pollutants. *Nature*, 616(7955), 159–167. https://doi.org/10.1038/s41586-023-05874-3

Jiang, B., Xie, Y., Xia, D., & Liu, X. (2019). A potential source for PM2.5: Analysis of fine particle generation mechanism in Wet Flue Gas Desulfurization System by modeling drying and breakage of slurry droplet. *Environmental Pollution*, 246, 249–256. https://doi.org/10.1016/j.envpol.2018.12.001

Johannson, K. A., Balmes, J. R., & Collard, H. R. (2015). Air Pollution Exposure. Chest, 147(4), 1161–1167. https://doi.org/10.1378/chest.14-1299

Kelly, F. J., & Fussell, J. C. (2019). Improving indoor air quality, health and performance within environments where people live, travel, learn and work. *Atmospheric Environment*, 200, 90–109. https://doi.org/10.1016/j.atmosenv.2018.11.058

Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wang, M., Oberley, T., Froines, J., & Nel, A. (2003). Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environmental Health Perspectives*, 111(4), 455–460. https://doi.org/10.1289/ehp.6000

Lodovici, M., & Bigagli, E. (2011). Oxidative Stress and Air Pollution Exposure. *Journal of Toxicology*, 2011, 1–9. https://doi.org/10.1155/2011/487074

Madureira, J., Slezakova, K., Silva, A. I., Lage, B., Mendes, A., Aguiar, L., Pereira, M. C., Teixeira, J. P., & Costa, C. (2020). Assessment of indoor air exposure at residential homes: Inhalation dose and lung deposition of PM10, PM2.5 and ultrafine particles among newborn children and their mothers. *Science of The Total Environment*, 717, 137293. https://doi.org/10.1016/j.scitotenv.2020.137293

Maher, B. A., Ahmed, I. A. M., Karloukovski, V., MacLaren, D. A., Foulds, P. G., Allsop, D., Mann, D. M. A., Torres-Jardón, R., & Calderon-Garciduenas, L. (2016). Magnetite pollution nanoparticles in the human brain. *Proceedings of the National Academy of Sciences*, 113(39), 10797–10801. https://doi.org/10.1073/pnas.1605941113

Manigrasso, M., Costabile, F., Liberto, L. D., Gobbi, G. P., Gualtieri, M., Zanini, G., & Avino, P. (2020). Size resolved aerosol respiratory doses in a Mediterranean urban area: From PM10 to ultrafine particles. *Environment International*, 141, 105714. https://doi.org/10.1016/j.envint.2020.105714

Manigrasso, M., Natale, C., Vitali, M., Protano, C., & Avino, P. (2017). Pedestrians in Traffic Environments: Ultrafine Particle Respiratory Doses. *International Journal of Environmental Research and Public Health*, 14(3), 288. https://doi.org/10.3390/ijerph14030288

Marini, S., Buonanno, G., Stabile, L., & Avino, P. (2015). A benchmark for numerical scheme validation of airborne particle exposure in street canyons. *Environmental Science and Pollution Research*, 22(3), 2051–2063. https://doi.org/10.1007/s11356-014-3491-6

Notardonato, I., Manigrasso, M., Pierno, L., Settimo, G., Protano, C., Vitali, M., Mattei, V., Martellucci, S., Di, F., Boccia, P., & Avino, P. (2019). The importance of measuring ultrafine particles in urban air quality monitoring in small cities. *Geographica Pannonica*, 23(4), 347–358. https://doi.org/10.5937/gp23-24447

Settimo, G., Yu, Y., Gola, M., Buffoli, M., & Capolongo, S. (2023). Challenges in IAQ for Indoor Spaces: A Comparison of the Reference Guideline Values of Indoor Air Pollutants from the Governments and International Institutions. *Atmosphere*, 14(4), 633. https://doi.org/10.3390/atmos14040633

Soggiu, M. E., Inglessis, M., Gagliardi, R. V., Settimo, G., Marsili, G., Notardonato, I., & Avino, P. (2020). PM10 and PM2.5 Qualitative Source Apportionment Using Selective Wind Direction Sampling in a Port-Industrial Area in Civitavecchia, Italy. *Atmosphere*, 11(1), 94. https://doi.org/10.3390/atmos11010094

Stabile, L., Buonanno, G., Avino, P., Frattolillo, A., & Guerriero, E. (2018). Indoor exposure to particles emitted by biomass-burning heating systems and evaluation of dose and lung cancer risk received by population. *Environmental Pollution*, 235, 65–73. https://doi.org/10.1016/j.envpol.2017.12.055

Turpin, B. J., Saxena, P., & Andrews, E. (2000). Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmospheric Environment*, 34(18), 2983–3013. https://doi.org/10.1016/S1352-2310(99)00501-4

Urso, P., Cattaneo, A., Garramone, G., Peruzzo, C., Cavallo, D. M., & Carrer, P. (2015). Identification of particulate matter determinants in residential homes. *Building and Environment*, 86, 61–69. https://doi.org/10.1016/j.buildenv.2014.12.019

Vahlsing, C., & Smith, K. R. (2012). Global review of national ambient air quality standards for PM10 and SO2 (24 h). *Air Quality, Atmosphere & Health*, 5(4), 393–399. https://doi.org/10.1007/s11869-010-0131-2

Wang, G., Bai, X., Wu, C., Li, W., Liu, K., & Kiani, A. (2018). Recent advances in the beneficiation of ultrafine coal particles. *Fuel Processing Technology*, 178, 104–125. https://doi.org/10.1016/j.fuproc.2018.04.035

Word Health Organization - WHO. (2010). *Guidelines for indoor air quality: selected pollutants*. Copenhagen, Denmark.

Wright, L. P., Zhang, L., Cheng, I., Aherne, J., & Wentworth, G. R. (2018). Impacts and Effects Indicators of Atmospheric Deposition of Major Pollutants to Various Ecosystems—A Review. *Aerosol and Air Quality Research*, 18(8), 1953–1992. https://doi.org/10.4209/aaqr.2018.03.0107

Xing, Y. F., Xu, Y. H., Shi, M. H., Lian, Y. X., (2016). The impact of PM2.5 on the human respiratory system. *Journal of Thoracic Disease*, 8(1), E69 - E742016. https://doi:10.3978/j.issn.2072-1439.2016.01.19