

# The Importance of Measuring Ultrafine Particles in Urban Air Quality Monitoring in Small Cities

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## Abstract

The air quality monitoring is based on the determination of some gaseous pollutants and PM<sub>10</sub> and PM<sub>2.5</sub>. Recent studies have reported the importance of the determination aerosol fraction below 1 μm both for the dynamic of the airborne and for the public health issue. This paper would like to investigate the importance of this fraction in the air quality monitoring. Further, a particular focus will be devoted the role of the Ultrafine Particles, i.e. particles below 100 nm, in the aerosol formation and in the human exposure. Two case studies will be presented and discussed on how the submicron particles can be determined and interpreted their role. In the first case, the measurements will be performed in downtown Rieti, city located in central Italy, 100 km North from Rome, with the scope to draw the behavior in relationship to the emission flexes. In the second scenario, the personal exposure of pedestrians will be investigated in Venafrò, a small city located 150 km South-East Rome, by means of measuring PM<sub>x</sub>, total submicron fraction, different aerosol dimensional sizes in the range 5-360 nm along with the total Volatile Compounds. The different sources and contributions affecting the aerosol levels in the two areas will be investigated and extensively discussed as well as the role of the such particles in the aerosols science.

**Keywords:** Aerosol; Particulate Matter; Ultrafine particles; Level; Dynamic; Instrumentation; Source; Urban; Air Quality; Monitoring; Exposure; Health effects

## Introduction

Air pollution exposure represents a well-known risk to human health (Johannson et al., 2015) and ecosystems (Wright et al., 2018; Ssebugere et al., 2019). A strong focus on atmospheric air pollution has been developed worldwide which has led to a significant reduction of some contaminants in the atmospheric environment. The starting point of this approach is that

the population, especially in urban areas, spends most of the time (up to 90 %) indoors (Carrer et al., 2000; Avino et al., 2003; Kelly & Fussell, 2019).

Studies indicate that indoor air quality is influenced by outdoor air and confirm the importance of outdoor air in determining indoor air quality (WHO, 2013a; WHO, 2013b; Lia et al., 2019). Ventilation has

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a strong influence on both indoor particulate matter and indoor gas concentrations. The lower indoor/outdoor (I/O) particle ratios were found under closed window conditions, whereas higher I/O ratios were achieved in well-ventilated environments (Leung, 2015). In addition, indoor and outdoor pollutant concentrations were correlated, and more than 75% of daily indoor variations are explained by outdoor ones (Cyrus et al., 2004).

The importance of the topic is demonstrated by some data:

- a person breathes about 15 kg of air per day, while he consumes about 1 kg of food per day, 2.5 kg of liquids per day;
- the indoor environment can be 50 times more polluted than outdoor;
- population spend about 90 % of their life in indoor environments;
- the PM<sub>1</sub> transports mutagenic chemical elements inside the buildings;
- each person inhales more than 25 million particles by each breath;
- patients in hospital healthcare settings benefit from improved air quality;
- particles smaller than 1 µm can reach the pulmonary alveoli;
- ultrafine metal particles have been found in the brain (Maher et al., 2016; Manigrasso et al., 2019a);
- particles less than 0.1 µm can reach all the human organs through the blood.

Particles of different sizes can show different characteristics during the interaction between indoor and outdoor air. Monn et al. (1997), for example, studied the indoor-outdoor relationship of particulate matter (PM) with different aerosol sizes in 17 houses in Switzerland with natural ventilation. In houses without indoor sources and with low anthropogenic activities, the I/O ratio of PM<sub>10</sub> was about 0.7. Among indoor sources, smoking is the most dominant factor and can increase the I/O ratio to > 1.8. On the other hand, human activities are an important factor contributing to high I/O ratios. Jones et al. (2000) found that I/O ratios are greater for fine particles than coarse particles, indicating greater penetration of fine particles or greater internal deposition of coarse particles. Diapouli et al. (2008) measured indoor and outdoor particulates in schools with ventilation and found I/O ratios close to or greater than 1 for PM<sub>10</sub> and PM<sub>2.5</sub>, but smaller than 1 for ultrafine particles (UFPs). However, similarly to other research results, they also observed very high I/O ratios (> 2.5) when there were intense indoor activities such as human movement, smoke, etc. Massey et al. (2009) determined the indoor/out-

door ratio of fine particles smaller than 2.5 µm in residential homes located in central India and found that average I/O ratios for PM<sub>2.5</sub>, PM<sub>1.0</sub>, PM<sub>0.5</sub> and PM<sub>0.25</sub> were near or above 1 in houses on the roadsides and in rural areas, while they were found to be lower than 1 in urban areas. Chen & Zhao (2011) examined the relationship between indoor and outdoor particles in the literature and found that very high PM<sub>2.5</sub> I/O ratios (i.e. > 3.0) occur in the presence of smoke and internal combustion sources like a fireplace, whereas the low I/O ratios (i.e. < 1) are strongly correlated to fewer internal sources, to the use of air filtration devices or to buildings with good insulation gaskets, particularly doors and windows.

The most recent studies reported in the scientific literature define, as more appropriate, the measurements for detecting lower particle size fractions. The term Ultrafine Particles (UFPs) refers to particles with an aerodynamic diameter of less than 0.1 µm (100 nm). This particle size is comparable to those of biological molecules, while such particles are larger than atoms and considerably lower than human red blood cells or human alveolar macrophages.

An important issue, connected to the physical UFP characteristics, is related to their size. In fact, the larger particles, due to gravity, are deposited on the ground in the immediate vicinity and within a short time, with respect to the emission point and time; on the contrary, the UFPs can travel long distances and remain suspended in the air for hours or days after the emission. However, they are unlikely to maintain their starting sizes, due to the high tendency to coagulate/accumulate. UFPs can derive from automotive traffic emissions (Avino et al., 2011; Marini et al., 2015), from the use of fuels used in different types of heating systems (Stabile et al., 2018; Jiang et al., 2019), as well as from the oil industry and other industrial processes (Fernández-Camacho et al., 2012; Borrow et al., 2018; Wang et al., 2018), including incineration and waste treatment plants (Buonanno et al., 2010, 2011; Buonanno & Morawska, 2015;). In recent years, a growing number of studies have reported UFP concentration values expressed as the number of particles per cubic centimeter; in most cases, where the aerosol size distribution was reported, it was found that UFPs represented the most conspicuous part in terms of numerical concentration (Manigrasso & Avino, 2012; Manigrasso et al., 2013). In a survey performed in Erfurt, Germany, the particle number counted was 73 % of the UFPs, although they contributed only 1 % of the mass concentration (Wichmann et al., 2009).

In general, aerodynamic factors predominate for particulates with diameters > 1 µm and the relative deposition occurs by sedimentation (depending on

gravity) or impact (direct collision of a particle with the epithelial surface), which in turn are influenced by characteristics of particle size and density. On the contrary, for particles with diameter less than 100 nm (0.1  $\mu\text{m}$ ), the deposition occurs as a result of chaotic particle diffusion motions (Brownian motion) dependent only on the diffusion coefficient. Finally, aerodynamic and thermodynamic factors are relevant for diameters between 0.1  $\mu\text{m}$  and 1  $\mu\text{m}$ . Studies show

that the main UFP determinants are the number and the surface area and not the weight (Manigrasso et al., 2019b). This paper would like to point out the importance of an emerging pollutant, i.e. the Ultrafine Particles (UFPs), in urban air quality monitoring: for evidencing such issue the authors will discuss the data collected in two different sites located in Central Italy and characterized by different environmental conditions.

## Materials and Methods

### Sampling sites

Two different sampling sites have been considered in this study, both of them located in central Italy: the two sites are different for extension and population number, but they can be representative of the Italian leaving areas, over the big cities.

The first sampling has been performed in Rieti, a town stands on a small hilltop, commanding from the southern edge the wide Rieti valley, at the bottom of the Sabine hills and of Monti Reatini, including Mount Terminillo, with a population of 47,700 inhabitants (coordinates 42°24'N 12°52'E; area 207 km<sup>2</sup>; elevation 405 m a.s.l.). The sampling site is located in downtown and is characterized by autovehicular traffic, i.e. cars and buses.

The second sampling has been performed across Venafro, a town in the province of Isernia, region of Molise (coordinates 41°29'4"N 14°2'45"E; area 45 km<sup>2</sup>; elevation 222 m a.s.l.). It has a population of around 11,000, having expanded quickly in the post-war period. The site is characterized by high heavy traffic, i.e. both cars, buses and trucks, and in its surroundings two main plants, i.e. a cement plant and an incinerator, are present over a large industrial area.

### Measurements

According to both the sites and the scope, two different approaches were carried out.

In downtown Rieti a Fast Mobility Particle Sizer (FMPS, model 3091, TSI, Shoreview, MN, USA) was used (Figure 1). This instrument allows the particle determination and classification at high time-resolution (1 s) in the range 5.6-560 nm by means of the electrical mobility diameter. This equipment, operating at 10 L·min<sup>-1</sup> for minimizing the UFP loss by diffusion, counts and classifies the particles in 32 size channels. The combination of features makes the FMPS spectrometer ideal for measuring the dynamic behavior of submicrometer particles over a wide range of applications, including particle formation and growth studies, indoor air-quality measurements, environmental research, urban canyon studies, and transient emission studies of stacks,

boilers, wood burners, and much more. The measurements were carried out in July.



**Figure 1.** Equipment used in the Rieti campaign: Fast Mobility Particle Sizer, counting and size dimensional classification (electrical mobility diameter) 5.6-560 nm. Temporal resolution: 1 second

In the other site, Venafro town, the approach was totally different: the methodology was addressed for evaluating the exposure of a pedestrian walking through the town. For this aim a footpath covering almost the whole town was identified. A 30-min walking path was considered: in particular, four different areas can be identified on the selected path. The first and forth sections are along “SS6” and “SS85”, the two main roads that connect Venafro with the highways and the industrial area, characterized by high heavy vehicular traffic density (cars, buses, trucks); the second one is in downtown at medium traffic density, basically local traffic, and the third section is a low vehicular traffic density. These paths allow to give an idea about the exposure of a pedestrian overall the town. In this site the approach was set up for taking different information respect the other scenario: portable instruments were used for determining particulate matter (PM), submicron particles, ultrafine particles along with the measure of total Volatile Organic



**Figure 2.** Mobile instruments used in the Venafro campaign: Nanoscan (left), DustTrak<sup>TM</sup> II aerosol monitor (middle) and Q-Trak<sup>TM</sup> Indoor Air Quality Monitors (right)

Compounds (VOCs), considered an index of the anthropogenic activities in an area (Manigrasso & Avino, 2008) (Figure 2).

In particular, a DustTrak<sup>TM</sup> II Aerosol Monitor (model 8532, TSI), a handheld battery-operated, data-logging, light-scattering laser photometer, allowed a simultaneous measurement of PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>4</sub>, or respirable fraction, PM<sub>10</sub>, and Total PM size fractions.

On the other hand, a NanoScan SMPS (model 3910, TSI), was also used for measuring particle number concentrations in the range 10–365 nm (divided in

in thirteen size channels) by means of a scanning mobility particle sizing technology with 60 s time resolutions (Manigrasso et al., 2017a). The NanoScan SMPS is ideal for applications that demand portability like on-road measurements, workplace surveys, field studies, and point source identification. Once again, also in this case, the attention was focused on UFPs, i.e., on size channels from 11.5 nm to 115.5 nm (and the first three modes, which are important in the accumulation mode). Further, a Condensation Particle Counter (CPC, model 3007, TSI) was used for measuring particle concentrations in the range 0.01–1 µm. The particles present in the sample serve as condensation sites for alcohol vapor: after the condensation starts, the particles quickly grow, and an optical detector manages to count the. Finally, a Q-Trak<sup>TM</sup> Indoor Air Quality Monitors (model 7575, TSI) was used for determining total VOCs second-by-second. For a better personal exposure evaluation, the probes (anti-electrostatic tubes) were placed on the jacket lapel, on opposite sides for avoiding air vortices that could affect the measurement. A backpack was equipped with all this equipment. This sampling was also performed in July.

## Results and Discussion

Even if the air quality monitoring is a well-known issue and the atmospheric pollutants are well-defined according to the regulations, the dynamic of aerosols is still an interesting and important task. About the inorganic and/or organic composition of PM<sub>10</sub> and PM<sub>2.5</sub> there are a lot of literature, also by the authors of this paper; on the other hand, about the sub-micron fraction and their relevance for the human health data are still scares due to the difficulties to investigate it. In fact, dedicated equipment is necessary both for monitoring stations and for personal exposure. Further, the dynamic of such fraction is not easy to understand, because of the peculiarity of these particles, as well to effectively understand how the UFPs affect the human health, over the respiratory diseases.

In this way the authors would like to show two different scenarios of sampling and evaluation of sub-micron fractions and UFPs, particularly. Both scenarios are investigated and discussed according to the number concentration and the behavior of the relative size fractions.

### *First case study: sampling in downtown Rieti*

Table 1 shows the levels of particles in the range 9–340 nm determined in downtown Rieti along with some statistical information that complete the evaluation. First, the mean total particles of 85470 # cm<sup>-3</sup> can be

determined overall the range and the measurements as well. The 95 % percentile is a more interesting information: 68 % of measures of each channel are averagely below the this value with peaks regarding the channel size at 143 nm, where only the 33.5 % of the total measures are below the 95 % percentile, and at 69,8 nm, where 98.8 % of the entire data are below the 95 % percentile. This preliminary information is important for evidencing the different role of particles in such granulometric size. Particles between 5–100 nm are considered in nucleation Aitken modes and are generally formed by carbon compounds, they come from both fuel engine combustion and lubricating diesel or petrol oils: they show long atmospheric lifetime, are subjected to coagulation processes. The times are short because the particles coagulate easily with other particles to give larger particles; consequently, these particles can better be observed close their sources. On the other hand, particles above 100 nm (up to 2.5 µm) are in the accumulation mode, generally explain most of the surface area of the aerosol and a substantial part of their mass. The particles of this mode derive mainly from coagulation and aggregation of UFPs, from vapor condensation on particles and from chemical-physical breakdown of larger particles. This mode is important because the particle removal mechanisms are less effective in the relative size range, so that the particles accumulate in the air.

**Table 1.** Levels (# cm<sup>-3</sup>) of particles in the range 9-340 nm in Rieti town. Variability (%) is calculated as coefficient of variation (cv%)

Size (nm)	9.31	10.8	12.4	14.3	16.5	19.1	22.1	25.5	29.4	34.0	39.2	45.3	52.3	60.4	69.8	80.6	93.1	107	124	143	165	191	220	255	294	340
mean	1598	3096	3348	3108	2373	2320	2060	2424	4033	5761	7015	7874	8340	8126	7233	5853	3985	2521	1459	750	393	333	252	516	370	329
min	130	126	225	343	180	543	142	137	700	2935	4313	5264	5930	6119	5750	4594	3128	1974	1012	419	164	65	25	124	28	68
max	11161	14644	11664	9414	7894	6619	5590	6821	10311	12600	13688	14087	13797	12313	9733	9763	9392	7872	5202	3093	1546	981	1000	974	886	775
60% perc.	987	3639	3729	3276	2424	2219	2258	2844	4590	6197	7248	8157	8332	8301	7246	5769	3844	2395	1410	723	397	233	182	605	465	311
80% perc.	1373	4444	4786	4372	3413	3118	2882	3618	5551	6949	7876	8842	9372	8956	7932	6313	4195	2667	1558	828	446	568	396	718	572	418
95% perc.	4908	7373	7084	6265	5240	5277	4383	4606	6613	8217	9333	10279	11106	10408	9618	7804	5175	3180	1820	1036	585	885	743	912	695	763
st. dev.	2473	2855	2284	1942	1775	1484	1314	1593	1965	1841	1706	1676	1552	1322	1068	1001	1046	972	676	429	225	269	228	248	229	224
variability	154.8	92.2	68.2	62.5	74.8	64.0	63.8	65.7	48.7	32.0	24.3	21.3	18.6	16.3	14.8	17.1	26.2	38.5	46.3	57.1	57.1	80.9	90.5	48.0	61.8	68.3

**Table 2.** Pearson's correlation coefficients (r) among particles in the range 9-340 nm in Rieti town. Values > 0.7 are reported in italic.

9.3	10.8	12.4	14.3	16.5	19.1	22.1	25.5	29.4	34.0	39.2	45.3	52.3	60.4	69.8	80.6	93.1	107	124	143	165	191	220	255	294	340	
1	0.95	0.91	0.83	0.80	0.76	0.66	0.63	0.69	0.75	0.77	0.77	0.77	0.72	0.45	0.17	0.04	-0.01	0.00	0.02	0.06	-0.20	-0.07	-0.07	-0.57	-0.04	9.3
	1	0.99	0.96	0.92	0.87	0.80	0.80	0.84	0.81	0.67	0.52	0.44	0.37	0.27	0.17	0.14	0.12	0.13	0.14	0.14	0.09	-0.01	-0.07	-0.11	-0.34	10.8
		1	0.99	0.96	0.92	0.84	0.83	0.87	0.85	0.77	0.56	0.46	0.37	0.26	0.16	0.14	0.13	0.15	0.17	0.19	0.04	0.09	-0.13	0.02	-0.31	12.4
			1	0.98	0.96	0.86	0.83	0.88	0.86	0.73	0.57	0.47	0.37	0.25	0.15	0.12	0.11	0.14	0.16	0.17	0.05	0.09	-0.13	0.06	-0.30	14.3
				1	0.99	0.85	0.82	0.85	0.83	0.69	0.54	0.45	0.35	0.20	0.09	0.07	0.07	0.09	0.12	0.13	0.10	-0.06	0.04	0.02	-0.28	16.5
					1	0.92	0.84	0.84	0.80	0.66	0.51	0.41	0.27	0.02	-0.11	-0.08	-0.05	-0.02	0.01	0.02	0.17	0.03	-0.19	-0.20	0.51	19.1
						1	0.98	0.93	0.83	0.57	0.39	0.28	0.15	-0.03	-0.09	-0.01	0.04	0.07	0.10	0.07	0.26	-0.11	-0.14	-0.12	0.61	22.1
							1	0.97	0.88	0.60	0.39	0.28	0.20	0.10	0.07	0.13	0.16	0.20	0.22	0.22	0.29	-0.16	-0.04	-0.10	0.16	25.5
								1	0.97	0.80	0.61	0.51	0.43	0.35	0.27	0.24	0.22	0.23	0.24	0.24	0.12	-0.07	-0.10	0.14	-0.28	29.4
									1	0.91	0.78	0.68	0.60	0.48	0.32	0.23	0.18	0.18	0.19	0.20	0.04	-0.03	-0.15	0.07	-0.22	34.0
										1	0.96	0.91	0.83	0.65	0.39	0.19	0.09	0.08	0.08	0.10	-0.13	0.09	-0.23	-0.06	-0.10	39.2
											1	0.98	0.93	0.74	0.44	0.18	0.05	0.04	0.03	0.06	-0.23	0.14	-0.27	-0.16	-0.01	45.3
												1	0.98	0.87	0.52	0.24	0.09	0.07	0.06	0.09	-0.25	0.15	-0.28	-0.24	0.05	52.3
													1	0.91	0.67	0.39	0.24	0.21	0.19	0.22	-0.26	0.13	-0.27	-0.30	0.06	60.4
														1	0.91	0.70	0.57	0.53	0.49	0.51	-0.21	0.06	-0.22	-0.37	0.01	69.8
															1	0.93	0.84	0.80	0.77	0.77	-0.10	-0.02	-0.13	-0.42	-0.05	80.6
																1	0.98	0.97	0.94	0.92	0.02	-0.08	-0.00	-0.42	-0.15	93.1
																	1	0.99	0.98	0.95	0.07	-0.11	0.12	-0.34	-0.25	107
																		1	0.99	0.97	0.06	-0.11	0.18	-0.30	-0.29	124
																			1	0.99	0.04	-0.12	0.24	-0.25	-0.23	143
																				1	-0.03	-0.14	0.32	-0.25	-0.13	165
																					1	0.02	-0.32	0.03	-0.08	191
																						1	-0.57	-0.03	-0.16	220
																							1	0.31	-0.02	255
																								1	-0.21	294
																									1	340



As a result, residence time is longer than for previous mode as well as for particles above 2.5  $\mu\text{m}$  (also in the order of days) and these particles manage to be transported to greater distances (up to kilometers of kilometers). Another important parameter is the variability (calculated as coefficient of variation,  $cv\%$ ): it should be noted that it varies from 155 % for lowest particles, below 10 nm, whereas it decreases up to 16 % for particles between 50-90 nm. This occurrence is also important: the high variability of the particles below 12 nm means fresh aerosol continuously present in the atmosphere, basically anthropogenic sources, like combustion processes, operating in that area. The low levels found in the range 50-90 nm are a further confirmation about the beginning of the coagulation process with formation of larger and more stable particles.

A comparison with Rome data (Manigrasso et al, 2019c) collected in downtown (10183 $\pm$ 3810 #  $\text{cm}^{-3}$ ), highlights a less UFP number in downtown Rieti (4,500 $\pm$ 2353 #  $\text{cm}^{-3}$ ) whereas the particles between 110-560 nm are higher in Rieti (4402 $\pm$ 398 #  $\text{cm}^{-3}$ ) than those determined in Rome (1722 $\pm$ 698 #  $\text{cm}^{-3}$ ). This occurrence could be explained with the different orographic and meteorological conditions of the two sites where the samplings were performed: Rome shows favor conditions for the pollutant dispersion (e.g., more open spaces, wind direction), Rieti is characterized by a small downtown where the buildings are very close between them.

Table 2 shows the relative Pearson's correlation ( $r$ ) coefficients determined for all the channel sizes: the coefficients reported in italic, i.e. those above 0.7, evidence a good correlation between the two fractions considered. Still in this case, the correlations are good

for nearby dimensional size below 34 nm, meaning that the fresh aerosol is emitted by the same sources, e.g. the automotive traffic, and this is the main source affecting the area.

Figure 3 shows the behavior of each aerosol dimensional size in the range 5-107 nm. As it can be seen, the trends are almost similar, confirming the good correlation between the particles in the nucleation mode ("fresh" aerosol). Some peaks are present in correspondence of particles formation due to presence of high automotive traffic, for instance.

The authors focused the attention on some characteristic points: particularly, we highlighted three different situations, characterized by highest (times 11:28 and 11:49) and minimum (time 11:56) peaks. Figure 4 shows these three size profiles along with the profile (named "average") obtained by the average of the particle number of each channel size overall the measurements. The profiles evidence a bimodal behavior: a high peak below 10 nm and another peak pointed out at around 50 nm.

These two peaks are indicators of two different occurrences. The particles below 10 nm are index of a strong emission located just close the sampling point: particles generated by combustion process, basically. Once formed and suspended in the atmosphere, the particles in the nucleation mode are characterized by Brownian motions: the collisions generated aggregation processes, increasing the particles in the nucleation mode up to the accumulation mode, reaching a maximum around 50-70 nm. These profiles are similar to ones recorded in downtown Rome, even if, of course, the quantitative levels are really different (Avino & Manigrasso, 2017). Such typical profiles confirm

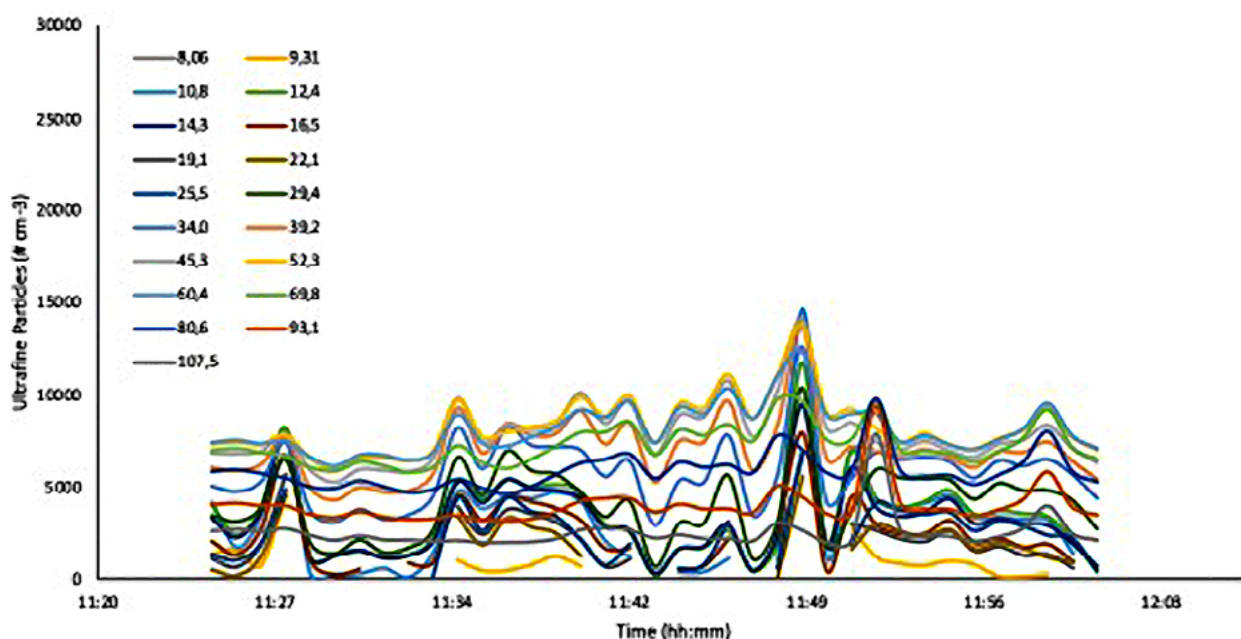


Figure 3. Typical particle distribution profiles ( $\# \text{cm}^{-3}$ ) in the range below 107 nm in downtown Rieti in the morning

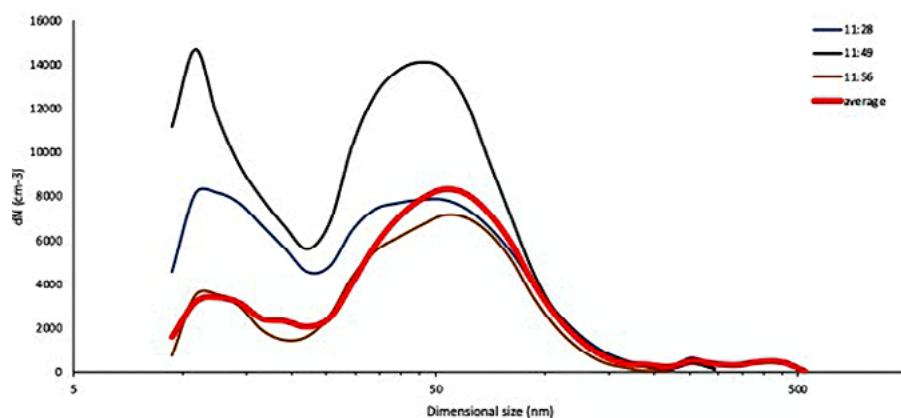


Figure 4. Typical size distribution measured in downtown Rieti at different morning times

that the autovehicular traffic is still the main problem in both big and small cities and it represents an important issue to be solved for improving the air quality. In fact, it should be underlined that this task concerns not only gaseous pollutants but also aerosols, specifically the submicron fraction and Ultrafine Particles as well, which indeed are the new target to be measured.

#### Second case study: walking and breathing around a small city

The second approach the authors would like to present regards the study of the personal exposure of a person walking along a small town, Venafro, during workdays. Table 3 shows all the levels ( $\mu\text{g}\cdot\text{m}^{-3}$ ) of  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ ,  $\text{PM}_4$ ,  $\text{PM}_1$  and Total PM.

The lines reporting the 95 % percentile and the variability are quite interesting. The first one shows that the 95 % (3196) of the all data (# samples 3364) are below 44, 45, 47 and 53  $\mu\text{g}\cdot\text{m}^{-3}$  for the four PM fractions, respectively, whereas only 168 measures (not: second-by-second) range between 44 and 1090  $\mu\text{g}\cdot\text{m}^{-3}$  for  $\text{PM}_{10}$ , for instance. The variability is quite high, ranging from 172 % for  $\text{PM}_1$  to 202 % for  $\text{PM}_{10}$ , meaning a continuous and novel particle contribution of these fractions. On the other hand, it should be noted that the

$\text{PM}_{2.5}$  fraction is 86 % of  $\text{PM}_{10}$  whereas that 83 % of  $\text{PM}_{10}$  is composed by  $\text{PM}_1$ . So, it is more interesting to investigate the submicron fraction which is the most meaningful constituent of  $\text{PM}_{10}$ . For this aim, preliminarily the particles in the range 10-1000 nm were counted. Table 3 shows the total particle number recorded during the entire footpath: the submicron particle number ranges between  $3.7\cdot 10^3 \# \text{cm}^{-3}$  and  $1.03\cdot 10^8 \# \text{cm}^{-3}$  but only the 5 % of the overall data are above  $44\cdot 10^3 \# \text{cm}^{-3}$ . For a comparison, during a similar period, i.e. June/July, in Rome levels ranging between  $3.90\cdot 10^6$  and  $5.37\cdot 10^8$  were recorded (Avino et al., 2011; Manigrasso et al., 2013; Costabile et al., 2017). Figure 5 shows the submicron fraction trend during the entire path: it could be observed the presence of three maximum peaks between 10:45 and 10:54 a.m. meaning a presence of intense instantaneous emission sources, whereas two similar occurrences, less intense but longer, are evident both at the beginning and at the end of the footpath, meaning a presence of continuous particle emission, i.e. autovehicular traffic.

Following these considerations, the authors approached the analysis of the submicron fraction, especially in the range 5-365 nm, using the Nanoscan instrumentation.

Table 3.  $\text{PM}_x$  levels (as  $\mu\text{g}\cdot\text{m}^{-3}$ ; # samples 3364) and particle numbers (as submicron fraction) measured using portable instrument during the footpath in Venafro during workdays. Variability (%) is calculated as coefficient of variation (cv%).

	Particles	$\text{PM}_1$	$\text{PM}_{2.5}$	$\text{PM}_4$	$\text{PM}_{10}$	Total PM
mean	15293 <sup>a</sup>	23	24	25	28	31
minimum	3743 <sup>a</sup>	7	8	8	8	8
maximum	103607051 <sup>a</sup>	1090	1100	1130	1720	2660
60 % percentile	11550 <sup>a</sup>	20	21	22	24	24
80 % percentile	20240 <sup>a</sup>	25	26	27	31	33
95 % percentile	43972 <sup>a</sup>	44	45	47	53	59
standard deviation	17661 <sup>a</sup>	40	40	43	57	74
variability (%)	115 <sup>a</sup>	172	170	172	202	239

<sup>a</sup> calculated as  $\# \text{cm}^{-3}$

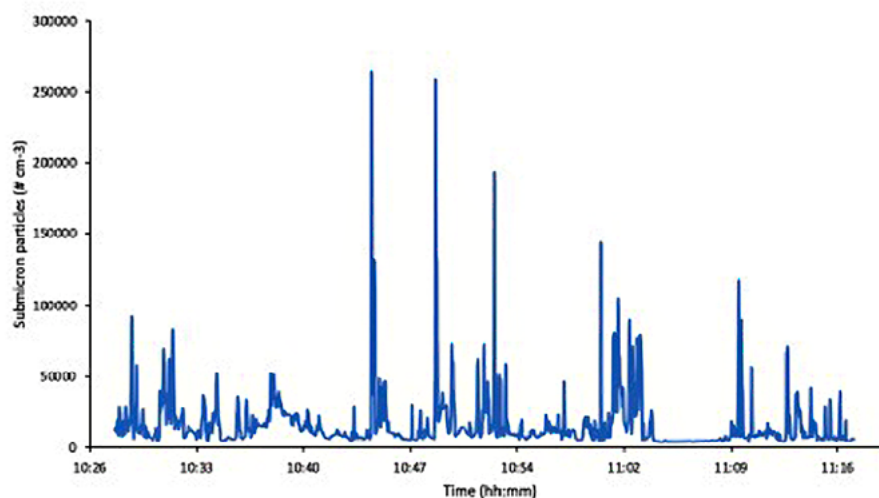


Figure 5. Submicron particles number ( $\# \text{ cm}^{-3}$ ) measure during the entire footpath in downtown Venafrò

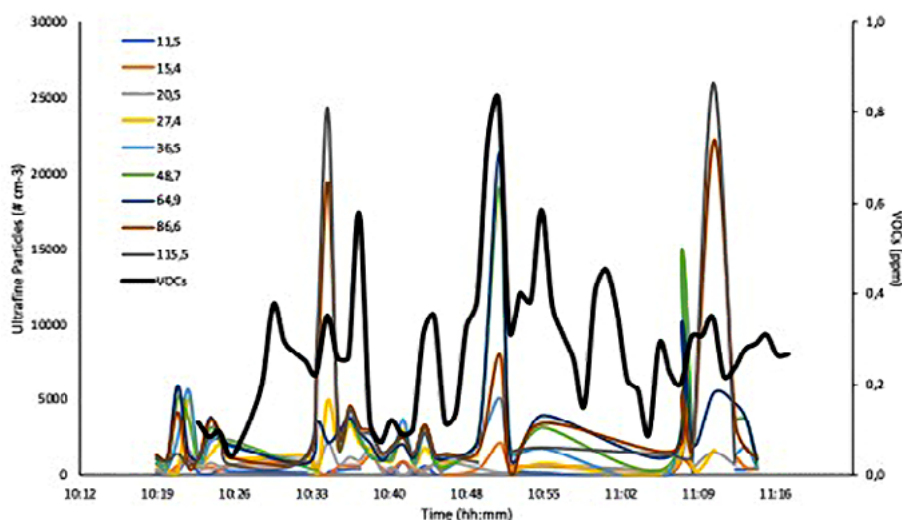


Figure 6. UFP profile ( $\# \text{ cm}^{-3}$ ) along with the total VOC (ppm) trend during the entire footpath in Venafrò town

Table 4 shows the data collected during the entire sampling, trying to evaluate the personal exposure of a pedestrian around the entire town whereas Table 5 reports the Pearson's correlation coefficients determined between two close sizes (also in this case, the  $r > 0.7$  are in italic).

A very high variability (215 %) is recorded for the particles in the size channel 11.5 nm, it means a fresh aerosol continuously emitted by sources but, different from what reported in previous study (Manigrasso et al., 2017a), the variability is always over 101 %, except in two cases (71 % at 15.4 nm and 75 % at 20.5 nm),

**Table 4.** Levels ( $\# \text{ cm}^{-3}$ ) of particles in the range 5–365 nm in Venafrò town. Variability (%) is calculated as coefficient of variation (cv%).

size (nm)	11.5	15.4	20.5	27.4	36.5	48.7	64.9	86.6	115.5	154.0	205.4	273.8	365.2
mean	467	584	696	1563	2272	3015	3180	3636	3407	2181	709	1066	750
min	25	6	2	55	441	357	746	100	639	126	100	71	8
max	5475	2111	2138	6651	14455	1895	21244	22152	25867	13241	4698	3152	4187
60% perc.	310	578	671	1307	2019	2616	2440	2763	1797	1091	320	771	394
80% perc.	400	843	996	2039	2557	3605	3791	3936	2733	1820	574	2237	532
95% perc.	917	1243	1722	5032	5394	10033	7589	12503	16741	10824	3749	2968	2922
st. dev.	1005	414	523	1588	2651	3956	3763	4756	5992	3356	1225	1270	1403
variability	215.3	70.9	75.1	101.6	116.7	131.2	118.4	130.8	175.9	153.8	172.8	119.1	186.9



**Table 5.** Pearson's correlation coefficients (*r*) among particles in the range 5-365 nm in Venafro town. Values > 0.7 are reported in italic.

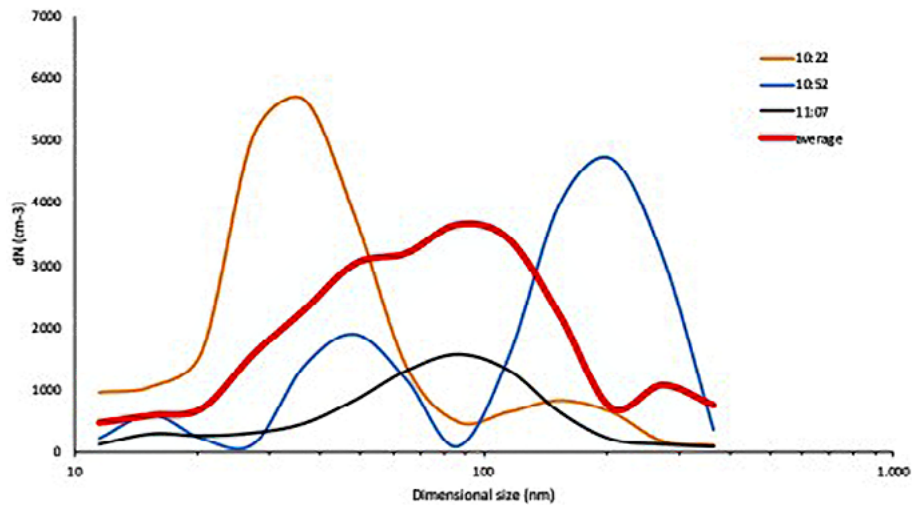
11.5	15.4	20.5	27.4	36.5	48.7	64.9	86.6	115.5	154.0	205.4	273.8	365.2	
1	0.44	0.11	<i>0.71</i>	<i>0.95</i>	<i>0.92</i>	<i>0.75</i>	0.12	-0.06	0.04	0.01	-0.18	-0.15	11.5
	1	0.08	0.41	0.45	<i>0.72</i>	<i>0.71</i>	0.01	-0.34	-0.29	0.01	0.52	0.83	15.4
		1	0.65	0.17	-0.14	-0.11	0.51	0.57	0.50	-0.14	-0.48	-0.36	20.5
			1	<i>0.90</i>	<i>0.77</i>	0.49	0.33	0.27	0.33	-0.25	-0.37	-0.30	27.4
				1	<i>0.76</i>	0.55	0.53	0.06	0.28	0.05	0.18	0.54	36.5
					1	<i>0.95</i>	0.65	-0.12	-0.10	-0.04	0.49	<i>0.98</i>	48.7
						1	0.33	0.21	0.45	0.19	0.49	<i>0.98</i>	64.9
							1	<i>0.98</i>	<i>0.94</i>	0.24	0.36	<i>0.97</i>	86.6
								1	0.97	0.49	0.37	0.08	115.5
									1	<i>0.82</i>	<i>0.94</i>	0.53	154.0
										1	<i>0.98</i>	0.53	205.4
											1	0.52	273.8
												1	365.2

showing a presence of possible different contributions over the combustion processes.

Figure 6 shows the behavior of the UFPs at different sizes related to the total VOCs trend in the same period. As it can be seen, the UFPs, especially in the range 80-110 nm, follows the same tendency of VOCs: these

related only to combustion processes: this high correlation is important because it shows how the transportation is one of the main contribution affecting the air quality in that area.

Figure 7 confirms what reported above: the aerosol size distributions determined during the maximum



**Figure 7.** Typical size distribution measured in downtown Venafro at different morning times

compounds are associated with the presence of anthropogenic sources in the area. This statement is also confirmed by the CO trend measured simultaneously (and reported in the plot), which is an index directly

related only to combustion processes: this high correlation is important because it shows how the transportation is one of the main contribution affecting the air quality in that area. Figure 7 confirms what reported above: the aerosol size distributions determined during the maximum

## Conclusions

The paper would like to review the importance of the submicron fraction, especially the ultrafine particles, in the air quality monitoring. The studies on this task based on the determination of gaseous pol-

lutants and on PM<sub>10</sub> and PM<sub>2.5</sub>, prove themselves to be not sufficient for describing the entire saturation as well as for a correct evaluation of the public health. The submicron particles, which manage to reach the

deepest part of the human respiratory system (Avino et al., 2013; Manigrasso et al., 2017b), are responsible of different pulmonary, cardiovascular diseases: they should represent the new target in the evaluation of the air quality. In this study the authors re-

port two different methodological approach for determining and evaluating the contribution of these fractions to the air quality and the correlation with the anthropogenic sources, first of all, the combustion processes.

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