

Research Article

Chemical Analysis of Air Particulate Matter Trapped by a Porous Material, Synthesized from Silica Fume and Sodium Alginate

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This work shows the ability of a new porous material (SUNSPACE), obtained by industrial by-products, to sequester air particulate matter (PM). This activity allows introducing the azure chemistry approach, devoted to better link new remediation strategies and sustainability. In particular, SUNSPACE is synthesized from silica fume and sodium alginate; it can be shaped in a porous solid, and it looks promising for environmental application as nanoparticle sequestration. Studies to evaluate the sequestration capability of SUNSPACE are performed in different environments, with and without anthropogenic sources of PM. Solid SUNSPACE disc samples are used as passive samplers and exposed for one and two months, in vertical and horizontal positions, indoor, and outdoor. Total reflection X-ray fluorescence technique is employed to perform elemental chemical analysis of the entrapped PM. Two sample preparation strategies to evaluate the composition of PM are considered: sample sonication in Milli-Q water and total sample mineralization by microwave acid digestion. These two options are proposed to analyse different PM fractions: in particular, sonication allows removing the coarse PM, entrapped on external material surface pores; on the contrary, digestion can offer information on fine and ultrafine PM, trapped in internal pores. Results confirm the ability of the porous material to sequester air PM and the differences in the sample preparation, supported by elemental analysis, and show the difference in the coarse and fine air particulate matter composition. In summary, the new material results as very promising for applications requiring nanoparticle sequestration.

1. Introduction

Air pollution is becoming an important issue worldwide. The presence of solid components in air is referred to particulate matter (PM) or dust. The main sources for air PM presence in the environment are tyre emissions, vehicle exhausts, brake water, resuspension of soils, road dust [1], biomass combustion such as wood [2, 3], and pellet stoves [4]. PM identification and characterization are challenging due to several issues such as the low concentration, small particle size, and variable composition [5]. The most problematic PM are fine and ultrafine PM (PM with aerodynamic diameter less than 2.5 and 0.1 μm , respectively) that mainly originate from transport, combustions, and photochemical reactions in the atmosphere [6]. The potentially adverse

health effects due to PM inhalation can be related not only to particle dimensions (they are often nanoparticles) but also to their physicochemical characteristics, which vary significantly in urban, industrial, and rural areas [7].

Furthermore, air PM depends on meteorological conditions, such as humidity, rainfall, and wind speed. The chemical composition of air PM is complex and heterogeneous, and it may change with time [8]. Elements commonly present in PM, such as V, Fe, Ni, Al, Si, Zn, Cu, and Pb, may be dangerous for human health. In literature, different studies have shown the relationship between Pb in blood and cardiovascular mortality and morbidity [9, 10] or role of Cu smelter strike on monthly mortality [11]. The presence of Al and Si is often associated with resuspended soil. There is high interest about the relationships between indoor and outdoor air, with

the aim in assessing the air quality in houses [12, 13]. Several source apportionment studies report the distribution of heavy metals on PM collected on air filtering membranes [14–16] and biological indicators such as lichens [17], tree barks [18], and tree leaves [19, 20].

In addition to the studies dedicated to environmental assessment and emission reduction, the European Commission (EC) welcomes and encourages innovative ways to reduce the amount of PM suspended in air, with particular emphasis to nanoparticles. In this paper, an innovative and sustainable porous material is designed and proposed to sequester PM from air. SUNSPACE (sustainable materials synthesized from by-products and alginates for clean air and better environment) material is made with silica fume, an industrial by-product of ferrosilicon and/or silicon metal alloy processing. Silica fume is made up of amorphous silicon dioxide (85–95%) and soluble heavy metals, like Zn, Pb, and As. It consists of spherical-like particles with diameters generally ranging from 20 to 500 nm. Being an industrial by-product, several impurities are present in variable amount, such as carbon, silicon carbide, and alkaline metal oxides (5–15%). Silica fume is a pozzolanic material that may react with calcium hydroxide to form calcium silicate hydrate, known as a binder compound in concrete [21, 22]. A porous solid can be obtained by gel casting and heating, at about 70–80°C, a mixture of silica fume, alginate, as gelifying agent, and sodium bicarbonate, as the pore maker. This new material was developed in response to the EC request to obtain affordable, sustainable, and innovative design-driven material solution that can reduce the concentration of air PM in urban areas [23]. A very recent work showed that the material pore size distributions calculated from the desorption branch of the isotherms range from 20 to 60 nm. The pore sizes calculated from the corresponding adsorption branch are generally larger than 100–150 nm [24]. This suggests that ink bottle-shaped pores are present. SUNSPACE was designed to sequester PM; then, it should be used as a coating (as a plaster on a wall or roof tiles). Moreover, to optimize air trapping efficiency, it should be fundamental to promote SUNSPACE diffusion on all the available building surfaces [25].

The new material sustainability was demonstrated by embodied energy (EE) and CO₂ footprint (CF) calculations [26], where EE is defined as the energy required to produce 1 kg of the new material and CF corresponds to the equivalent mass of greenhouse gases produced and released into the atmosphere as a consequence of the production of the same mass [27]. In a recent published paper, the new porous material ability in fine PM trapping was presented in comparison to a leaf. Indeed, currently, foliage represents the most efficient and sustainable method to reduce PM in urban areas [25]. Results show that SUNSPACE appears to be more efficient compared to leaves in PM sequestration. Indeed, mainly due to the ink bottle-shaped pores, it was shown that new material can accumulate to about 24 (±6) g/m² of air PM, with dimensions lower than 2.5 μm [28]. The aim of this study is to evaluate the ability of the aforementioned new material to collect air PM, with great attentions to nanoparticles. For this reason, several porous solid samples are realized

and used as passive samplers in deposition tests performed in different indoor and outdoor environments. The amount of collected PM is estimated from elemental chemical analysis made by TXRF.

2. Materials and Methods

2.1. Reagents and Materials. Calcium iodate (Ca(IO₃)₂, CAS number: 7789-80-2), sodium alginate (SA, CAS number: 9005-38-3, viscosity $c = 1\%$ water @ 25°C 5.0–40.0 cps), sodium bicarbonate (NaHCO₃, CAS number 14455-8, ≥99.8% w/w), nitric acid (≥65%), hydrofluoric acid (48%), and hydrochloric acid (37%) were purchased from Sigma-Aldrich. Silica fume provided by Metalleghe S.P.A., Brescia, Italy, was used to prepare the porous material. Ultrapure deionized water was obtained from a Milli-Q purifier system (Millipore Direct Q™). Silicon solution in isopropanol (Serva Electrophoresis, Heidelberg, Germany) was deposited on quartz reflectors for surface hydrophobization. Reagents such as NaHCO₃, Na₂CO₃, H₂SO₄, and HNO₃ (Fluka) were used for ion chromatography analysis.

2.2. Synthesis of Porous Material. A slurry is prepared according to the following steps: 0.6 g of sodium alginate (SA) was mixed vigorously with 25 mL of Milli-Q water at room temperature; 1 g of Ca(IO₃)₂ was rapidly added to the SA solution under continuous stirring, and a gel rapidly formed; 17.88 g of silica fume (72% w/w of solid content, respectively) was transferred into the mixture; 5 g of sodium bicarbonate was thoroughly mixed into the slurry. A volume of 2 mL of the formed paste was deposited in the aluminium sample holder, having the shape of a disc with 2.5 cm diameter, and placed over the heating plate at 70–80°C for 1 h, to obtain a porous solid disc. The solubility of Ca(IO₃)₂ increases at high temperature, and the release of Ca²⁺ ions speeds up the paste solidification. Simultaneously, sodium bicarbonate thermally decomposed and CO₂ release induces pore formation. Porous disc samples with 2.3 cm diameter and 5 mm thickness were obtained.

2.3. Air PM Indoor and Outdoor Sampling. Deposition studies were performed indoor and outdoor in five environments: in a steel making industry, in the laboratory, in a gateway, in the highway, and in the courtyard area of Brescia (Italy). Samples were exposed in vertical and horizontal position for one and two consecutive months from April to June 2017. The back side of the sampler was covered with a plastic cap, to expose only one face. The calculated geometrical area is 4.15 ± 0.01 cm². Indoor samples were placed in different sites far from people and living places. Outdoor samples were covered by a weather proof cabinet and placed near a house roof in the highway area and in a balcony in the courtyard. The weather proof cabinet was used only for the sampler exposed to the outdoor environments, with the aim of protecting them from rainfall events. Indeed, SUNSPACE, if used as a plaster in the urban area, can be regenerated by rainfall; then, PM can be washed out. Information about the indoor ongoing activities and weather conditions, such as rainfall and wind, were noted. Collected samples were

transferred to the laboratory in clean plastic envelopes and cut in halves. One half was grinded and the powder mineralized, while the other half was sonicated.

2.4. Sample Preparation for Digestion. About 0.25 g of the powder obtained from one half of one sample was put in a Teflon vessel and added with 4 mL of HNO₃ (≥65%), 2 mL of HCl (37%), and 2 mL of HF (48%) according to the EPA method 3052 for siliceous matrices [29]. Each vessel was capped and individually processed by the CEM SP-D microwave system, equipped with a 24-place autosampler, for microwave digestion. The following automatic five-step procedure was performed to achieve complete digestion: 3 min at 160°C, 5 min at 180°C, 3 min at 200°C, 5 min at 205°C, and 10 min at 210°C. After cooling, the volume of each sample was adjusted to 50 mL adding ultrapure water. The other entire half of the sample, about 0.75 g, was put in 10 mL of Milli-Q water and sonicated in ultrasonic bath (UESSETT 2000, UST model) for 5 min. The liquid was filtered through 0.45 μm pore membranes.

2.5. Total Reflection X-Ray Fluorescence (TXRF) Analysis. Ga was added to the prepared liquid samples, as internal standard (IS) element, in concentration equal to 1 mg L⁻¹, from a nitric acid standard solution (1000 mg L⁻¹, Sigma-Aldrich). A drop of 10 μL was deposited in the center of a siliconized quartz sample carrier and dried on a hot plate at 50°C under laminar hood. Plexiglass reflectors were used for digested samples because of the presence of HF. Three trials were prepared.

A commercial benchtop TXRF spectrometer equipped with Mo anode (S2 PICOFOX, Bruker AXS Microanalysis GmbH, Berlin, Germany) was employed for TXRF analysis. It is equipped with air-cooled low-power X-ray tubes operating at 750 μA and 50 kV and a Peltier-cooled silicon drift detector (SDD), and thus, no cooling media and gas consumption are required. Spectrum evaluation and calculation of the analyte net peak area were performed using the provided software (Spectra Plus 5.3, Bruker AXS Microanalysis GmbH, Berlin, Germany). For the peak integration, the software applies a deconvolution routine which uses measured element profiles for the evaluation of peak areas. Trials were measured for 600 s live time.

2.6. Ion Chromatography Analysis. Four anions (Cl⁻, NO₂⁻, NO₃⁻, and SO₄²⁻) and one cation (NH₄⁺) were analysed by ion chromatography (883 Basic IC Plus, Metrohm, Switzerland) equipped with separate columns for anions (Metrostep A Supp 4-250/4.0) and cations (Metrostep C4-100/4.0), conductivity detector, peristaltic pump, injection valve, and suppressor module. The gradient weak base eluent (NaHCO₃+Na₂CO₃+Milli-Q) was used for anion and weak acid (3.5 mM HNO₃) for cation determination. Instrument calibration was performed according to EPA 300.0 for anions [30] and EPA 300.7 for cations [31]. Qualitative analysis of chromatograms is performed based on retention time, while their concentrations were evaluated by algorithms taking into account the area under the peak.

3. Results and Discussion

The preliminary SUNSPACE ability to entrap air PM in its porous structure has been shown exposing the samples to exhaust from a diesel car at a short distance. It was observed a visible colour change and entrapment of a significant amount of C (more than 23% in weight) [28]. In addition, it was shown that the new material can trap incense smoke PM [28]. Moreover, the capacity of SUNSPACE to capture PM is already showed through two different model tests in controlled conditions using (1) TiO₂ nanoparticles [25] and (2) monodisperse Fe₃O₄ nanoparticles [32]. Indeed, TEM images clearly allow distinguishing titania nanoparticles, with 25 nm mean size diameter, significantly lower than that of SUNSPACE particles.

The present study serves to evaluate the capability of collecting air PM in different indoor and outdoor environments where a significant change in SUNSPACE mass cannot be measured. It was reported that porous structure of SUNSPACE is similar to a sponge with micro and macro pores, mostly interconnected [24]. The new material contains ink bottle-shaped pores, with dimension in the order of some hundreds of nanometers. Due to the pore morphology and dimensions, SUNSPACE appears to be suitable to entrap fine and ultrafine PM [24]. For this reason, elemental analysis of digested samples is compared to sonication to evaluate if some particles are entrapped permanently in the SUNSPACE matrix. Indeed, it is possible to suppose that sonication allows extracting entrapped particles. On the contrary, digestion has the ability to solubilize all the PM, then also fine and ultrafine particles that may trap in pores. In particular, acid digestion is still one of the most common sample pretreatment approaches to analyse composition of air PM collected on filters [33]. Samples were sonicated to have the possibility to wash the material, with the aim of simulating a rainfall event. Moreover, rainfall can happen at different intensities, and it was shown that increased rainfall intensity caused less PM retention by foliage [34]. However, this is hard to simulate in laboratory. Literature also shows that simulated rainfall events can remove large quantities of PM depending on its dimensions [35]. In particular, the largest PM fraction (10-100 μm) was most easily removed by simulated precipitation (33-42%), followed by the coarse fraction (2.5-10 μm) that is removed for 25-36%. On contrary, the fine fraction (0.2-2.5 μm) appears to adhere most strongly to the foliage, with a loss of only 21-30%, when exposed to simulated rainfall.

Figure 1 shows the TXRF spectra of the digested and sonicated halves of the blank. The following elements are present in both spectra: Cl, K, Ca, I, Ba, As, Se, Br, Rb, and Sr, while Mn, Fe, Ni, Cu, Zn, and Pb are clearly identified only in the digested one. The intensity of all the elements, normalized to that of the IS, is higher for the digested sample, except for Cl and I, that may be lost during the mineralization, due to their volatility [36]. The fluorescence intensity of the digested sample is higher due to the total matrix decomposition, and considering the origin of the new material components, most of the heavy metals may belong to the industrial by-products, silica fume.

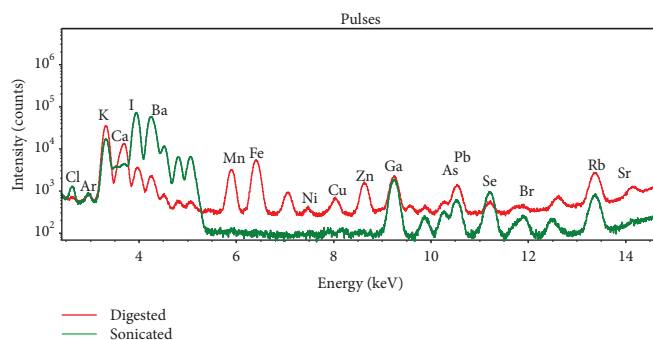


FIGURE 1: TXRF raw spectra of the digested (red) and sonicated (green) blank sample.

Samples exposed in horizontal and vertical positions for one and two months were analysed to evaluate the capability in coarse PM trapping.

Results obtained by TXRF analysis of sonicated samples exposed in vertical and horizontal positions in the highway for two months are reported in Figure 2 in comparison with the blank, whose results are the average of three tested samples.

The concentration of As, Se, Br, Rb, and Ba in all samples is almost one order of magnitude higher with respect to trace elements such as Mn, Fe, Zn, and Sr. The reproducibility of the three tested blank samples is estimated in terms of relative standard deviations that vary from 3.8 to 54 with the highest values for Ba and Mn. Nevertheless, the difference of exposed samples with respect to the blank is significant for most of the elements, with the exception of Mn. In particular, it is worth noting the Ni presence in the exposed samples, completely absent in the blank. The estimated composition of PM is consistent with that from vehicle emissions that could be the main source of PM in this area. The content of heavy metals is higher, even if not always significantly, in the samples exposed horizontally. This may be due to a more effective exposure of the sample surface to the flow of air PM present in the area. On this basis, the following comparison was performed between samples exposed horizontally.

Table 1 reports the elemental concentration of sonicated samples exposed in the five studied areas for 1 and 2 months, normalized with respect to the geometrical surface area. All the elements show an increasing content with time, suggesting an increasing contribution of the entrapped PM. In particular, the industry shows the highest amount of Mn, Ni, Zn, and Rb, probably related to the steel and iron treatment activities performed indoor, that may affect the concentration of heavy metals in the environment [37]. The lowest and highest concentrations of Fe were found in samples exposed in the laboratory and the highway, respectively. This result may depend on the influence of vehicular emission on the heavy metal content in PM, being the highway, an area with heavy traffic [38–41]. As and Se have a behaviour similar to Fe. Samples exposed in the gateway have the highest concentration for Ba and Br. In this case, their origin may be related to the cement building works performed during the weekdays in the warehouse. K and Sr, known as crustal elements, dominated in the courtyard area, and their source is

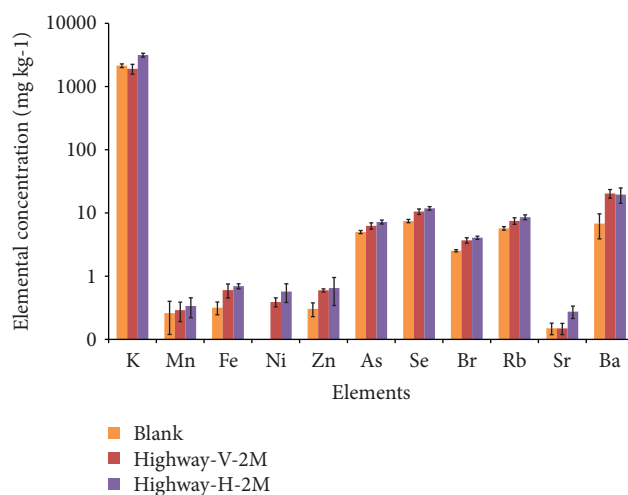


FIGURE 2: Effect of vertical (V) and horizontal (H) position during deposition study of the sample exposed for 2 months in the highway. Results are reported as the average and standard deviation (error bars). Three measurements are performed on each sample sonication solution. Three blank samples are tested.

probably soil or resuspended road dust [42]. The lowest concentrations are found in the samples exposed in the laboratory. On this basis, K, Fe, As, Se, and Sr may come from outdoor sources, while Mn, Zn, Ni, Rb, Br, and Ba may have both indoor and outdoor origin. Based on these preliminary results of this pilot study, it is possible to observe that the content of heavy metals can be correlated with anthropogenic emission sources, such as vehicle emissions, and industrial activities, in accordance with literature results. However, further studies are necessary for a better characterization of PM collected in different environments.

Determination of elements with atomic number less than 19 by means of the TXRF spectrometer working in air is a critical issue because of their low fluorescence yield [43]. Therefore, analysis of Cl, N, and S was performed based on their ionic state by ion chromatography (IC). The concentration of SO_4^{2-} , NH_4^+ , Cl^- , NO_2^- , and NO_3^- measured in samples exposed for 2 months in the industry, in the laboratory, and in the highway is presented in Figure 3. Sulphate, known as involatile species [12], gives the highest contribution to the total ionic mass. The highest

TABLE 1: Elemental concentration normalized per geometrical surface area (ng m^{-2}) of sonicated samples exposed in the five studied environments for 1 and 2 months. Values are expressed as the average \pm standard deviation of three TXRF measurements.

Samples	Time (month)	Industry (ng m^{-2})	Laboratory (ng m^{-2})	Gateway (ng m^{-2})	Highway (ng m^{-2})	Courtyard (ng m^{-2})
K ($\times 10^3$)	1	47 ± 21	92 ± 20	155 ± 17	67 ± 7	133 ± 50
	2	215 ± 32	146 ± 18	273 ± 53	242 ± 18	341 ± 97
Ba ($\times 10^3$)	1	3.7 ± 0.1	2.4 ± 0.4	2.9 ± 0.5	1.51 ± 0.04	0.68 ± 0.04
	2	4 ± 1	3.56 ± 0.01	6 ± 3	3.1 ± 0.6	1.8 ± 0.9
Mn	1	40 ± 16	8 ± 3	21 ± 17	9 ± 7	8 ± 1
	2	53 ± 35	33 ± 6	32 ± 24	39 ± 26	22 ± 6
Fe	1	14 ± 6	<LOD	6.5 ± 4.3	9 ± 3	4 ± 1
	2	51 ± 17	19 ± 6	29 ± 17	91 ± 2	23 ± 8
Ni	1	143 ± 106	87 ± 67	71.4 ± 0.2	85 ± 69	69 ± 25
	2	167 ± 77	159 ± 22	151 ± 80	138 ± 45	88 ± 26
Zn	1	94 ± 48	29 ± 19	38 ± 20	35 ± 6	7 ± 2
	2	119 ± 95	101 ± 25	92 ± 24	83 ± 55	12 ± 1
As	1	146 ± 121	142 ± 60	36 ± 4	48 ± 6	33 ± 7
	2	414 ± 17	163 ± 27	397 ± 108	531 ± 54	297 ± 140
Se	1	441 ± 167	106 ± 72	248 ± 110	156 ± 55	137 ± 26
	2	873 ± 19	284 ± 25	771 ± 223	1056 ± 77	708 ± 323
Br	1	175 ± 18	210 ± 85	236 ± 85	22 ± 10	444 ± 231
	2	357 ± 5	284 ± 52	1291 ± 216	370 ± 30	590 ± 358
Rb	1	400 ± 89	169 ± 25	457 ± 119	205 ± 7	418 ± 299
	2	756 ± 22	450 ± 24	653 ± 174	691 ± 97	696 ± 248
Sr	1	9 ± 2	<LOD	<LOD	<LOD	<LOD
	2	17 ± 4	13 ± 5	14 ± 5	30 ± 12	53 ± 5

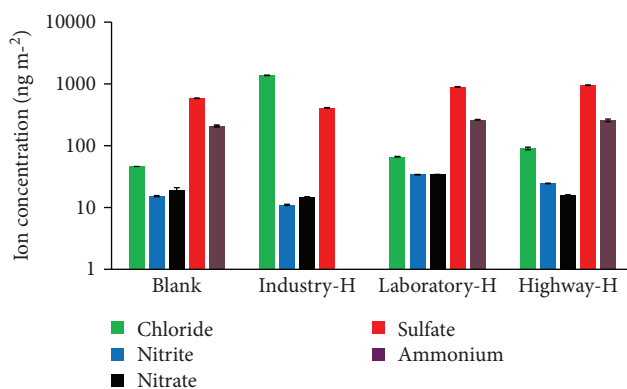


FIGURE 3: Ion concentration in blank and exposed samples for 2 months horizontally in the industry, in the highway, and in the laboratory. Results are reported as the average of three measurements and standard deviation (error bars).

sulphate amounts are found in samples exposed in the highway and in the industry for two months. The origin of sulphate could be related to emissions of SO_2 from fuel combustion and the industrial activities [44]. The highest

concentration of ammonium was found in samples exposed in the highway, where it may be found as ammonium nitrate (NH_4NO_3), and fuel combustion, mainly from road transport, may be the major contributor [44]. The content of chloride in the sample exposed in the industry is the highest. This may be related to some chemical cleaning activities performed during the second month in the industrial plant of alloy [45].

Table 2 shows the linear correlation matrix between the TXRF and IC datasets of blanks and exposed samples. Significant correlation ($r^2 = 0.8-0.9$) is present among As-Se-Rb, K-Br, and Ni-Zn, suggesting that they could have the same origin, probably traffic emission, soil resuspension, and industrial activities, respectively. Lower correlation ($r^2 = 0.6-0.7$) is observed among Cl^- - NO_3^- , Rb-Ni-Ba, Mn-Ni-Zn, and Zn-Ba. Poor correlation ($r^2 = 0.5$) is observed for Fe-As, Fe-Se, and Ni-Ba. It is interesting to note a negative poor correlation ($r^2 = -0.583$) between NH_4^+ and NO_2^- and no correlation between NO_2^- and NO_3^- . Indeed, depending on environment conditions, nitrites may be oxidated or reduced, and they are known as intermediate in the nitrogen cycle [46]. However, considering the basic solution pH and the low correlation, probably the SUNSPACE matrix plays an important role.

TABLE 2: Matrix correlation coefficients among concentration of ions and heavy metals for sonicated samples.

	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	K	Mn	Fe	Ni	Zn	As	Se	Br	Rb	Sr	Ba
Cl ⁻	1															
NO ₂ ⁻	0.192	1														
NO ₃ ⁻	0.641	-0.137	1													
SO ₄ ²⁻	-0.774	-0.019	-0.452	1												
NH ₄ ⁺	-0.095	-0.583	0.182	0.190	1											
K	-0.088	-0.035	0.086	0.148	0.079	1										
Mn	0.231	-0.226	0.070	0.074	0.379	0.062	1									
Fe	-0.006	-0.237	0.232	0.076	-0.192	-0.295	0.153	1								
Ni	0.316	0.188	0.142	0.238	0.325	0.081	0.659	0.003	1							
Zn	0.243	-0.047	0.159	0.146	0.429	-0.115	0.637	0.103	0.822	1						
As	0.340	0.013	0.288	0.147	-0.004	-0.217	0.365	0.557	0.605	0.462	1					
Se	0.333	0.006	0.288	0.151	-0.035	-0.234	0.356	0.578	0.588	0.448	0.998	1				
Br	-0.067	-0.129	0.094	0.177	0.134	0.953	0.153	-0.263	0.079	-0.052	-0.162	-0.171	1			
Rb	0.365	-0.083	0.206	0.161	0.273	-0.087	0.550	0.339	0.786	0.661	0.922	0.910	-0.015	1		
Sr	-0.016	-0.470	0.300	-0.231	0.282	0.440	-0.008	-0.425	-0.279	-0.244	-0.523	-0.525	0.410	-0.436	1	
Ba	0.216	-0.193	0.096	0.273	0.418	-0.007	0.425	-0.047	0.568	0.623	0.534	0.529	0.186	0.705	-0.195	1

To investigate the composition of fine- and ultrafine-trapped particles, digested samples can be considered. In this case, it is important to highlight that the presence of metals in blank SUNSPACE samples has a big influence on the total measured elemental concentration in mineralized samples compared to sonication, where only the particles entrapped on the external surface or part of soluble sample compounds should be determined (see Figure 1). The significant contribution of the blank must be carefully considered and subtracted when estimating the amount and composition of air PM collected in the samples.

PM emissions from exhaust vehicle emissions contribute predominantly to fine and ultrafine PM [47]. When measurements close to sources are considered, the contribution from road vehicles can be up to 90% of total particle number concentration [48]. For this reason, samples exposed for 2 months in the highway were measured after digestion and sonication for comparison. Results of quantitative TXRF analysis are reported in Figure 4.

Elements found in both sample typologies are K, Mn, Fe, Ni, Zn, As, Se, Br, Rb, Sr, and Ba. In addition, Cu and Pb were detected only in the digested solutions; then, they cannot be reported in Figure 4. Concentrations of Br, As, and Se are comparable, while all the others, with the exception of Ba, are higher in the digested samples. It was already reported that Ba, which generally has a crustal origin, is present in coarser PM [47]. Then, it is possible to suppose that it was mainly deposited on the external surface of the porous material and thus, more easily removed by sonication. On the contrary, Mn, Ni, Fe, and Zn are mainly contained in fine particles; then, they may be trapped in the internal pores, may be not transferred into the water during sonication. Then, it is possible to hypothesize that Mn, Ni, Fe, and Zn are mainly contained in fine and ultrafine PM.

These results are in good agreement with literatures [47, 49] showing that traffic-related fine and ultrafine PM

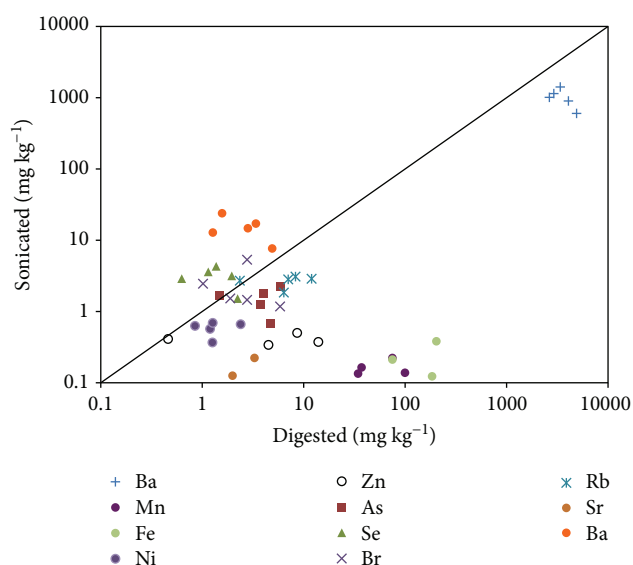


FIGURE 4: Comparison of the elemental content in digested and sonicated samples exposed for 2 months in the highway.

contains concentration of Mn, Zn, Fe, Ni, Cu, Sr, and Pb. Concerning PM dimensions, Zn is found in particles with a maximum in the interval 0.03-0.17 μm [49] and Ni in the interval 0.02-0.05 μm [50]. Then, trace elements are used as source markers for vehicle emissions. Ni, for example, has been reported to be present in emissions due to oil combustion [51]; Zn has been reported to be strongly associated with diesel fuel, whereas Mn, Sr, and Cu in the particles < 0.1 μm have been found to be associated with gasoline [47].

It is interesting to highlight that Cu (concentration in the range of 53-853 ng m^{-2}) and Pb (concentration in the range of 174-1093 ng m^{-2}) can be detected only in digested solutions, strongly suggesting that these elements can be found only

in ultrafine particles. In particular, Pb, derived from road traffic, was found not only in ultrafine but also in nanomode particles [50]. Concerning Cu, it was observed in high quantities also in nanoparticles derived from brake materials [47]. Finally, also Fe (that is a typical crustal element) was associated to diesel emissions [50] and tyre wear [47].

In summary, the results of this first study about characterization of air PM trapped in SUNSPACE show that it is possible to evaluate the composition of coarse particles in the porous solid material realized sonicating samples exposed in different environments during deposition studies. The composition of entrapped PM is consistent with that estimated from the most relevant emission sources of the studied environments. Digestion procedure is able to provide information also about fine and ultrafine PM, but it is affected more by the entrapping sample matrix contribution.

4. Conclusions

The aim of this study is to evaluate the ability of a new sustainable porous material, called SUNSPACE, to entrap air PM. The preparation procedure is based on environmentally friendly gel-casting procedure, starting from a mixture of industrial by-products, including silica fume and sodium alginate, to obtain a porous solid, whose ability to entrap carbon-based PM is already demonstrated. Samples are exposed in five different environments during deposition studies and sonicated or completely digested. Even though it is very difficult to differentiate the contribution of the SUNSPACE matrix, especially after digesting the whole samples, results show that it is possible to find some correlations with the main emission sources of each environment. In particular, important anthropogenic contributions may be identified, in the highway and industry sampling environments. The comparison among sonicated and digested samples allows making some considerations about composition of fine- and ultrafine-trapped PM.

Data Availability

All data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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References

- [1] B. Srimuruganandam and S. M. Shiva Nagendra, “Analysis and interpretation of particulate matter – PM₁₀, PM_{2.5} and PM₁ emissions from the heterogeneous traffic near an urban roadway,” *Atmospheric Pollution Research*, vol. 1, no. 3, pp. 184–194, 2010.
- [2] N. Kantová, M. Holubčík, J. Jandačka, and A. Čaja, “Comparison of particulate matters properties from combustion of wood biomass and brown coal,” *Procedia Engineering*, vol. 192, pp. 416–420, 2017.
- [3] T. Nussbaumer, “Aerosols from biomass combustion,” *IEA Bioenergy Task*, vol. 32, 2017.
- [4] A. T. Zosima, L. A. V. Tsakanika, and M. T. Ochsenkühn-Petropoulou, “Particulate matter emissions, and metals and toxic elements in airborne particulates emitted from biomass combustion: the importance of biomass type and combustion conditions,” *Journal of Environmental Science and Health Part A*, vol. 52, no. 6, pp. 497–506, 2017.
- [5] I. Araújo, D. Costa, and R. de Moraes, “Identification and characterization of particulate matter concentrations at construction jobsites,” *Sustainability*, vol. 6, no. 11, pp. 7666–7688, 2014.
- [6] J. C. Chow, J. G. Watson, J. L. Mauderly et al., “Health effects of fine particulate air pollution: lines that connect,” *Journal of the Air & Waste Management Association*, vol. 56, no. 10, pp. 1368–1380, 2012.
- [7] L. Borgese, M. Salmistraro, A. Gianoncelli et al., “Airborne particulate matter (PM) filter analysis and modeling by total reflection X-ray fluorescence (TXRF) and X-ray standing wave (XSW),” *Talanta*, vol. 89, pp. 99–104, 2012.
- [8] F. J. Kelly and J. C. Fussell, “Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter,” *Atmospheric Environment*, vol. 60, pp. 504–526, 2012.
- [9] A. Menke, P. Muntner, V. Batuman, E. K. Silbergeld, and E. Guallar, “Blood lead below 0.48 micromol/L (10 microg/dL) and mortality among US adults,” *Circulation*, vol. 114, no. 13, pp. 1388–1394, 2006.
- [10] S. E. Schober, L. B. Mirel, B. I. Graubard, D. J. Brody, and K. M. Flegal, “Blood lead levels and death from all causes, cardiovascular disease, and cancer: results from the NHANES III mortality study,” *Environmental Health Perspectives*, vol. 114, no. 10, pp. 1538–1541, 2006.
- [11] C. A. Pope III, D. L. Rodermund, and M. M. Gee, “Mortality effects of a copper smelter strike and reduced ambient sulfate particulate matter air pollution,” *Environmental Health Perspectives*, vol. 115, no. 5, pp. 679–683, 2007.
- [12] N. C. Jones, C. A. Thornton, D. Mark, and R. M. Harrison, “Indoor/outdoor relationships of particulate matter in domestic homes with roadside, urban and rural locations,” *Atmospheric Environment*, vol. 34, no. 16, pp. 2603–2612, 2000.
- [13] H. S. Lee, B. W. Kang, J. P. Cheong, and S. K. Lee, “Relationships between indoor and outdoor air quality during the summer season in Korea,” *Atmospheric Environment*, vol. 31, no. 11, pp. 1689–1693, 1997.
- [14] A. G. Allen, E. Nemitz, J. P. Shi, R. M. Harrison, and J. C. Greenwood, “Size distributions of trace metals in atmospheric aerosols in the United Kingdom,” *Atmospheric Environment*, vol. 35, no. 27, pp. 4581–4591, 2001.
- [15] F. Amato, M. Pandolfi, M. Viana, X. Querol, A. Alastuey, and T. Moreno, “Spatial and chemical patterns of PM₁₀ in road dust deposited in urban environment,” *Atmospheric Environment*, vol. 43, no. 9, pp. 1650–1659, 2009.
- [16] L. Borgese, A. Zacco, S. Pal et al., “A new non-destructive method for chemical analysis of particulate matter filters: the case of manganese air pollution in Vallecamonica (Italy),” *Talanta*, vol. 84, no. 1, pp. 192–198, 2011.

- [17] L. Borgese, A. Zacco, E. Bontempi et al., "Total reflection of X-ray fluorescence (TXRF): a mature technique for environmental chemical nanoscale metrology," *Measurement Science and Technology*, vol. 20, no. 8, article 84027, 2009.
- [18] J. M. Santamaria and A. Martin, "Tree bark as a bioindicator of air pollution in Navarra, Spain," *Water, Air and Soil Pollution*, vol. 98, no. 3-4, pp. 381-387, 1997.
- [19] F. Bilo, L. Borgese, R. Dalipi et al., "Elemental analysis of tree leaves by total reflection X-ray fluorescence: new approaches for air quality monitoring," *Chemosphere*, vol. 178, pp. 504-512, 2017.
- [20] R. S. Mansour, "The pollution of tree leaves with heavy metal in Syria," *International Journal of Chem Tech Research*, vol. 6, no. 4, pp. 2283-2290, 2014.
- [21] B. J. Christensen, T. O. Mason, and H. M. Jennings, "Influence of silica fume on the early hydration of portland cements using impedance spectroscopy," *Journal of the American Ceramic Society*, vol. 75, no. 4, pp. 939-945, 1992.
- [22] M. Mazloom, A. A. Ramezani-pour, and J. J. Brooks, "Effect of silica fume on mechanical properties of high-strength concrete," *Cement and Concrete Composites*, vol. 26, no. 4, pp. 347-357, 2004.
- [23] European Commission, "Horizon prize - materials for clean air - call for proposal: Up2Europe," 2017, https://www.up2europe.eu/calls/topic-horizon-prize-materials-for-clean-air_700.html.
- [24] A. Zanoletti, I. Vassura, E. Venturini et al., "A new porous hybrid material derived from silica fume and alginate for sustainable pollutants reduction," *Frontiers in Chemistry*, vol. 6, no. 60, 2018.
- [25] A. Zanoletti, F. Bilo, L. Borgese et al., "SUNSPACE, a porous material to reduce air particulate matter (PM)," *Frontiers in Chemistry*, vol. 6, 2018.
- [26] E. Bontempi, "A new approach for evaluating the sustainability of raw materials substitution based on embodied energy and the CO₂ footprint," *Journal of Cleaner Production*, vol. 162, pp. 162-169, 2017.
- [27] M. F. Ashby, *Materials and the Environment: Eco-Informed Material Choice*, Elsevier Science, 2012.
- [28] A. Zanoletti, F. Bilo, L. E. Depero, D. Zappa, and E. Bontempi, "The first sustainable material designed for air particulate matter capture: an introduction to Azure Chemistry," *Journal of Environmental Management*, vol. 218, pp. 355-362, 2018.
- [29] US-EPA, "Method 3052-microwave assisted acid digestion of siliceous and organically based matrices," 1996.
- [30] J. D. Pfaff, "Method 300.0 determination of inorganic anions by ion chromatography," *Standard Methods*, vol. 28, 1993.
- [31] S. R. Bachman, J. E. Rothert, and M. E. Peden, *Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography*, Standard Methods, 1986.
- [32] A. Zanoletti, F. Bilo, S. Federici et al., "The First Material-Based Solution Able to Sequester Fine and Ultrafine Air Particulate Matter," *Journal of Hazardous Materials*, 2018, Submitted.
- [33] I. De La Calle, N. Cabaleiro, V. Romero, I. Lavilla, and C. Bendicho, "Sample pretreatment strategies for total reflection X-ray fluorescence analysis: a tutorial review," *Spectrochimica Acta - Part B Atomic Spectroscopy*, vol. 90, pp. 23-54, 2013.
- [34] X. Xu, Z. Zhang, L. Bao et al., "Influence of rainfall duration and intensity on particulate matter removal from plant leaves," *Science of the Total Environment*, vol. 609, pp. 11-16, 2017.
- [35] A. Przybysz, A. Sæbø, H. M. Hanslin, and S. W. Gawroński, "Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time," *Science of the Total Environment*, vol. 481, pp. 360-369, 2014.
- [36] F. Bilo, L. Borgese, A. Zacco, P. Lazo, and C. Zoani, "Total reflection X-ray fluorescence spectroscopy to evaluate heavy metals accumulation in legumes," *Journal of Analytical & Bioanalytical Techniques*, vol. 7, no. 1, pp. 1-7, 2015.
- [37] B. Pekey, Z. B. Bozkurt, H. Pekey et al., "Indoor/outdoor concentrations and elemental composition of PM₁₀/PM_{2.5} in urban/industrial areas of Kocaeli City, Turkey," *Indoor Air*, vol. 20, no. 2, pp. 112-125, 2010.
- [38] O. A. Al-Khashman, "Heavy metal distribution in dust, street dust and soils from the work place in Karak Industrial Estate, Jordan," *Atmospheric Environment*, vol. 38, no. 39, pp. 6803-6812, 2004.
- [39] T. T. T. Duong and B. K. Lee, "Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics," *Journal of Environmental Management*, vol. 92, no. 3, pp. 554-562, 2011.
- [40] M. Thakur, M. Kanti Deb, S. Imai, Y. Suzuki, K. Ueki, and A. Hasegawa, "Load of heavy metals in the airborne dust particulates of an urban city of Central India," *Environmental Monitoring and Assessment*, vol. 95, no. 1-3, pp. 257-268, 2004.
- [41] M.-Y. Tsai, G. Hoek, M. Eeftens et al., "Spatial variation of PM elemental composition between and within 20 European study areas—results of the ESCAPE project," *Environment International*, vol. 84, pp. 181-192, 2015.
- [42] W. Rogula-Kozłowska, G. Majewski, and P. O. Czechowski, "The size distribution and origin of elements bound to ambient particles: a case study of a Polish urban area," *Environmental Monitoring and Assessment*, vol. 187, no. 5, 2015.
- [43] R. Klockenkämper and A. von Bohlen, *Total-Reflection X-Ray Fluorescence Analysis and Related Methods*, Wiley, 2nd edition, 2015.
- [44] S. Kundu and E. A. Stone, "Composition and sources of fine particulate matter across urban and rural sites in the Midwestern United States," *Environmental Science, Processes & Impacts*, vol. 16, no. 6, pp. 1360-1370, 2014.
- [45] Ö. Işıldak, "Determination of ion concentrations and heavy metals in the air particulates of an industrial area," *Karal-mas Science and Engineering Journal*, vol. 1, no. 2, pp. 49-54, 2011.
- [46] R. Michalski and I. Kurzyca, "Determination of nitrogen species (nitrate, nitrite and ammonia ions) in environmental samples by ion chromatography," *Polish Journal of Environmental Studies*, vol. 15, no. 1, pp. 5-18, 2006.
- [47] P. Pant and R. M. Harrison, "Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: a review," *Atmospheric Environment*, vol. 77, pp. 78-97, 2013.
- [48] P. Kumar, L. Pirjola, M. Ketznel, and R. M. Harrison, "Nanoparticle emissions from 11 non-vehicle exhaust sources - a review," *Atmospheric Environment*, vol. 67, pp. 252-277, 2013.

- [49] W. Rogula-Kozłowska, "Traffic-generated changes in the chemical characteristics of size-segregated urban aerosols," *Bulletin of Environmental Contamination and Toxicology*, vol. 93, no. 4, pp. 493–502, 2014.
- [50] C.-C. Lin, S.-J. Chen, K.-L. Huang, W.-I. Hwang, G.-P. Chang-Chien, and W.-Y. Lin, "Characteristics of metals in nano/ultrafine/fine/coarse particles collected beside a heavily trafficked road," *Environmental Science and Technology*, vol. 39, no. 21, pp. 8113–8122, 2005.
- [51] J. Pey, X. Querol, and A. Alastuey, "Discriminating the regional and urban contributions in the North-Western Mediterranean: PM levels and composition," *Atmospheric Environment*, vol. 44, no. 13, pp. 1587–1596, 2010.



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