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SEM-EDX IDENTIFICATION AND CHARACTERIZATION OF AIRBORNE MICROSPHERES: POTENTIAL EFFECTS ON HUMAN HEALTH

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Abstract: Airborne particulate matter (PM) are a major environmental pollutant adversely affecting human health. Exposure to atmospheric PM is correlated with significant damages to physiological systems from respiratory and circulatory level to reproductive and central nervous systems. The paper describes the elemental composition of a particular category of PM2.5 – microspheres, originate in exhaust pipes of automobiles and deposited onto vegetation planted along the roads. Microspheres were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX). Based on size and chemical composition, the hazard on human health of identified microspheres was evaluated. SEM investigation showed that microspheres size was between 3 and 0.5 µm. EDX analysis indicate that microspheres have a complex elemental structure, which concentrate mainly Si and Al in combination with Mg, Na, Fe, K, Ca and Cl, and seldom Ba and Ti. Our results showed that detected airborne microsphere are breathable and potential harmful to human health.

Keywords: air pollutants; microspheres; EDX analysis; health hazard, SEM investigation

1. INTRODUCTION

According to the latest report on air quality released by European Environment Agency (European Environment Agency, Report no. 05/2022) air pollution is still a major health concerns for Europeans. The briefing report aware that in European Union the great majority of the urban population (95%) was exposed to levels of fine particulate matter (PM2.5) above the latest health-based guideline set by the World Health Organization (WHO). For example, in Romania the annual mean for 2021 was 13µg\m3, exceeding 2.6 times the WHO annual limit, updated in 2021 at 5µg\m3.

Fine particulate matter - PM2.5 – refers to airborne particles with dimensions under 2.5 microns that originate mainly from the combustion of fossil fuels, road transport and industrial activities. These particles are considered a key air pollutant because are associated with health hazards ranging from allergies to respiratory, cardiovascular, and neurological diseases and premature death (Valavanidis et al., 2008, Wu et al., 2019, Manisalidis et al., 2020, Zhang et al., 2015, Yang et al., 2020, Sierra-Vargas et al., 2023). The latest assessment released by EEA in cooperation with European Topic Centre on Human Health and the Environment (ETC HE) showed that the exposure to PM2.5 concentration in 2020 resulted in 275 000 premature deaths (PD) across the EU countries (Soares et al., 2022). The report also ranks the countries where PM2.5 concentrations have the largest absolute health im-pacts: Italy (52 300 PD), Poland (36 500 PD), Germany (28 900 PD), Romania (21 600 PD), and Spain (17 000 PD).

A particular category of PM2.5 are microspheres. Airborne spheres and spheroids were reported worldwide being related with coal combustion. Spherical particles were isolated from fly ash samples and characterized by SEM-EDX or TEM-EDX (Shao et al., 2021, Sonwani et al., 2018, Li et al., 2016, Pachauri et al., 2013, Iordanidis et al., 2008, Zajzon et al., 2013). Currently are available many studies upon particular matter composition of vehicle exhaust (Chernyshev et al., 2018, Pallares et al., 2019, Wang et al., 2019, Chernyshev et al., 2019, Neer & Koylu, 2006) but none describes individual perfect spherical particles that originate from vehicle combustion.

Scanning electron microscopy (SEM) is a powerful tool widely used to characterize fine particles while energy-dispersive X-ray (EDX) analysis complement SEM investigations discriminating elemental composition (Li et al. 2016, Iordanidis et al., 2008, Heredia Rivera & Gerardo Rodriguez, 2016, Suzuki, 2006).

Sampling for airborne particles is usually done by conventional methods that include high-volume air sampling through a filter. In the last decade conventional methods are complemented with new ones, such as analysis of car air filters captures (Heredia Rivera & Gerardo Rodriguez, 2016, Zhang et al., 2011, Katsoyiannis, 2014) or depositions on ambient air exposed surfaces, including plant leaf. Recently, leaf epicuticular deposits analyses gained an increased attention for air pollutants assessment (Park et. al., 2022, Maria et al., 2022, Zhang et al., 2022, Sgrigna et al., 2022, Sillars-Powell et al., 2020, Kwak et al., 2020, Ristorini et al., 2020a, Ristorini et al., 2020b, Zhang et al., 2017, Liu et al., 2015).

Table 1. Plant material sampling sites.

Sample ID	Coordinates	Site name
P1	44°27'05.9"N 26°02'45.9"E	Șos.Virtuții
P2	44°26'05.4"N 25°59'07.0"E	Bd.Iuliu Maniu
P3	44°24'04.3"N 26°03'09.1"E	Intrarea Ghimeș
P4	44°24'15.1"N 26°05'46.9"E	Bd. Pieptănari
P5	44°23'36.4"N 26°07'20.2"E	Șos.Olteniței
P6	44°25'34.2"N 26°07'04.8"E	Bd.Unirii
P7	44°25'39.9"N 26°06'12.9"E	Piața Unirii
P8	44°26'13.0"N 26°06'07.3"E	Bd. Nicolae Bălcescu
P9	44°27'09.8"N 26°05'11.1"E	Piața Victoriei
P10	44°26'29.2"N 26°08'01.5"E	Piața Iancului

In present study we have analyzed microspheres originate from exhaust emissions and deposited on epicuticular surfaces of black pine (Pinus nigra J. F. Arnold) leaf, that accompany the main roads in Bucharest. Since particulate matter effects are highly correlated with the concentration, size, and chemical composition (Zhang et al., 2015) the main goal of our study was to investigate the elemental composition of airborne microspheres and to estimate their potential impact to human health.

2. MATERIALS AND METHODS

2.1. Plant material sampling

Full matured leaf samples from black pine were collected in vegetation stage (during summer 2021) from 10 different sites from metropolitan area of Bucharest (Romania). The sampling points were chosen along roadsides with intense traffic. The geographical coordinates of the sampling sites are shown in Table 1 and each site locations are pinned in a map shown in Figure 1. Needles of 1 year old, were sampled from branches about 1.5 – 2 m above ground level, which is proposed as the average height where humans breathe (Kenagy et al., 2016).

Fresh collected needle samples were closed in paper envelopes and preserved at 4ºC for further investigations.

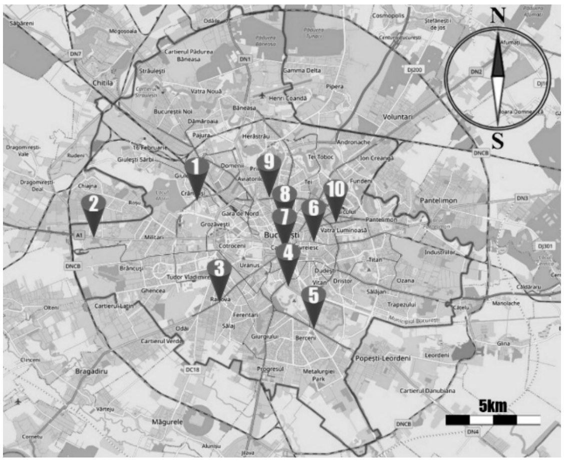

Figure 1. Location of sampling sites in Bucharest metropolitan area.

2.2. Exhaust material sampling

Solid matter depositions were collected with a spatula from the external exhaust pipe of a vehicle with petrol fuel engine, that travel daily between the most of the sites established for plant material sampling. The collected material was discarded directly to an electrically conductive tape and immediately analyzed under SEM.

2.3. SEM investigations

Fresh leaf samples were cut in 2 cm long pieces and fixed on aluminum stubs with double sided adhesive electrically conductive tape; double sided tape allowed to expose and examine both leaf surfaces.

The mounted specimens were coated with a thin layer of gold (99.9% purity) using the JEOL JFC 1300 Auto Sputter Coater. Coated samples were placed into the microscope vacuum chamber and examined under the JEOL JSM 66-10 LV scanning electron microscope at an operating voltage between 10kV and 20kV, at different magnification range from 5,000 to 14,000×.

2.4. SEM-EDX investigations

For SEM-EDX investigation needle samples were cut and gold-coated as described for SEM and analyzed under Quanta Inspect F50 Scanning Electronic Microscope equipped with field emission gun with 1.2 nm resolution and energy-dispersive X-ray spectrometer with the resolution performance of 127.5 eV at MnK. The elements present in mounted samples were both qualitatively and quantitatively evaluated. For elemental quantification, EDX spectrograms were recorded and both weight and atomic percentage of each element were displayed in the spectrum.

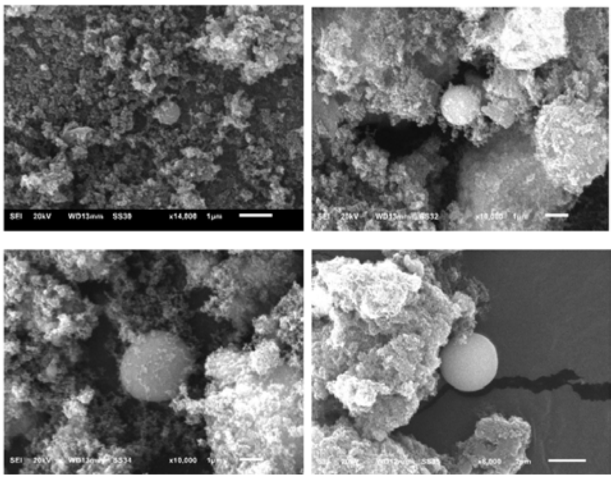

Figure 2. SEM images showing perfectly spherical particles deposited in exhaust pipe

3. RESULTS

3.1. SEM identification of spherical particles in exhaust depositions

SEM investigation of residues deposited in exhaust pipe of a vehicle that circulate in Bucharest metropolitan area clearly revealed perfectly spherical and smooth particles (Figure 2).

3.2.SEM-EDX investigation results

SEM-EDX investigation showed that identified microspheres in leaf depositions consist of different elemental composition and could be separated in 5 categories as follows:

- Microspheres with high aluminum and magnesium content as shown in Figure 3A.

Elemental quantification showed that this type of particles contains high content of aluminum and magnesium and moderate silicon, sodium and barium (Table 2).

Table 2. Elemental quantification of Al-Mg Microspheres

Element	Weight %	Atomic %
C K	25.60	35.93
O K	42.79	45.08
NaK	2.73	2.00
MgK	8.97	6.22
AlK	11.88	7.42
SiK	3.33	2.00
ClK	0.57	0.27
K K	0.15	0.07
CaK	1.18	0.49
BaL	1.82	0.22
FeK	0.98	0.30

- Microspheres with high silicon, aluminum and sodium content as shown in Figure 3B.

Elemental quantification showed high content of silicon, aluminum, and sodium with moderate iron (Table 3).

Table 3. Elemental quantification of Si-Al-Na Microspheres.

Element	Weight %	Atomic %
C K	44.85	55.82
O K	37.36	34.91
NaK	3.18	2.07
MgK	0.81	0.50
AlK	3.95	2.19
SiK	6.30	3.36
ClK	0.43	0.18
K K	0.70	0.27
CaK	0.67	0.25
FeK	1.75	0.47

- Microspheres with high silicon and sodium (sodium silicates) and moderate aluminum, iron, calcium and magnesium content as shown in Figure 3C.

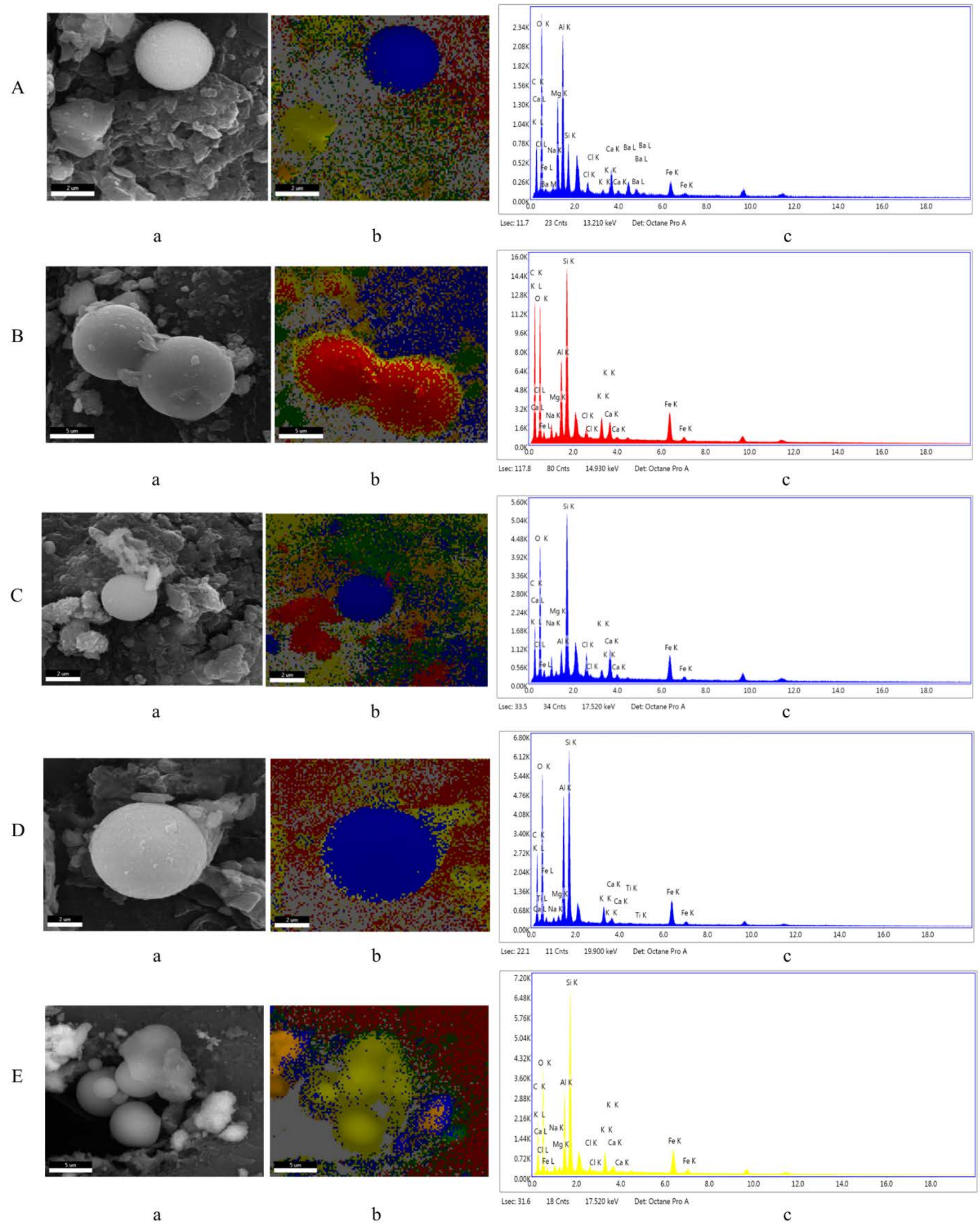

Figure 3. A - Al-Mg Microsphere, peaks indicates prevalence of metals aluminum and magnesium; **B** - Si-Al-Na-Microspheres, peaks indicates prevalence of silicon, aluminum and sodium; **C** - Si-Na -Microspheres, peaks indicates prevalence of silicon and sodium followed by aluminum and iron; D - Si-Al-Microspheres, peaks indicates prevalence of silicon and aluminum; **E** - Si-Al-Na-Fe-Microspheres, peaks indicates prevalence of silicon followed by aluminum, sodium, and iron (a - SEM image, b - EDX overall map, c - EDX spectra).

Elemental quantification showed high content of silicon and sodium with moderate aluminum, iron, calcium, magnesium and chlorine (Table 4).

• Microspheres with high silicon and aluminum (aluminosilicates), moderate sodium, iron and magnesium content as shown in Figure 3D.

Table 4. Elemental quantification of Si-Na Microspheres.

Element	Weight %	Atomic %
C K	28.35	38.69
O K	44.41	45.50
NaK	6.80	4.85
MgK	1.76	1.18
AlK	2.79	1.69
SiK	10.09	5.89
ClK	1.40	0.65
K K	0.41	0.17
CaK	1.78	0.73
FeK	2.22	0.65

Elemental quantification showed high content of silicon and aluminum with low content of sodium, iron and magnesium (Table 5).

Table 5. Elemental quantification of Si-Al Microspheres.

Element	Weight %	Atomic %
C K	34.47	45.29
O K	42.57	41.99
NaK	2.21	1.52
MgK	1.12	0.73
AlK	7.88	4.61
SiK	8.69	4.88
K K	0.75	0.30
CaK	0.27	0.11
TiK	0.09	0.03
FeK	1.93	0.55

Table 6. Elemental quantification of Si-Al-Na-Fe Microspheres.

Element	Weight %	Atomic %
C K	33.64	45.03
O K	40.28	40.47
NaK	2.80	1.96
MgK	0.86	0.57
AlK	6.31	3.76
SiK	11.73	6.71
ClK	0.32	0.15
K K	1.12	0.46
CaK	0.39	0.16
FeK	2.54	0.73

• Microspheres with high silicon and aluminum and moderate sodium, iron and potassium content as shown in Figure 3E.

Elemental quantification showed high content of silicon with moderate aluminum and low sodium, iron and potassium (Table 6).

4. DISCUSSION

Airborne spheres and spheroids, in the range of 0.5–20 µm, have been recorded, described and characterized mainly from fly ash samples (Shao et al., 2021, Sonwani & Kulshrestha, 2018, Li et al., 2016, Pachauri et al., 2013, Iordanidis et al., 2008, Zajzon et al., 2013, Suzuki, 2006). Fly ash is a waste product from using coal in electrical power generation. The described spherical particles that originate from fly ash were rich in Si, Ca, Al, K, S, Fe, Mg, C and Ti and resulted from softening, melting and vitrification of coal minerals such as clay minerals, chlorite, mica, feldspars, quartz and other phases, which have a low melting point (Iordanidis et al., 2008). Tree bark samples examined by SEM-EDX revealed deposition of spherical particles with high Fe content along with Pb and S (Suzuki, 2006).

Our SEM-EDX analysis showed that identified microspherical particles were predominantly composed by aluminosilicates with a variable mix of Mg, Na, Fe, K, Ca and Cl, and occasionally with Ba and Ti. Their elemental spectra were very similar with those of spheroids isolated from fly ash, except the presence of sulfur. In addition, SEM analysis showed that microspheres of exhaust origin were perfect spherical and very smooth, almost glassy, indicating a result of high melting temperatures, similar with those developed in engine combustion chamber. The microspheres of exhaust origin correspond to typical morphologies of the Silicon-Oxygen-Aluminum group described and characterized by Li et al., (2016). Li et al., (2016) hypothesized that these particles originally were dust that have undergone fragmentation and melting inside engines, or other burning chambers, which use dust-containing air and exhale out smaller round-shaped particles.

Even though currently are available many studies upon particulate matter from vehicle exhaust (Pallarés et al., 2019, Wang et. al., 2019, Neer & Koylu, 2006) this type of PM is described as aggregates of particulates, almost spherical (spherules). Our investigation showed that vehicle emissions contain also individual glassy spherical particulates, most of them with dimensions under 2.5 µm. This category of particulate matter was identified in all collected samples along with many other different types of PM with morphologies, ranging from prismatic and acicular crystalloids, to flakes or amorphic agglomerates (**a** section from Figure 3) often described as derived from both from natural and anthropogenic sources (Prack et al., 2016). Deposition of particular matter on plant leaf surface are favored in conifers by the sticky waxes secreted by epidermal cells, thus conifer leaves are a very good investigation material for PM deposition (Maria et al., 2022).

As part of PM2.5 category, microspheres are of potential risk for a plethora of diseases associated with airborne fine particulate, including respiratory, cardiovascular and skin diseases, and diverse neurological disorders (Valavanidis et al., 2008, Wu et al., 2019, Manisalidis et al., 2020, Zhang et al., 2015, Yang et al., 2020, Sierra-Vargas et al., 2023, Kim et al., 2020). Moreover, due to their spherical shape and glassy surface these particles have the "advantage" to be extremely mobile and once inhaled could easily disseminate through the human body via blood vessels.

Investigations upon chemical composition and physical characteristics of particulate matter are extremely important to assess health impacts since biological responses are not always related with major components, but rather with minor ones with potential hazard (Zhang et al., 2015). Our results revealed that exhausted microspheres contained significant amounts of aluminum, ranging from 11.88% to 2.79% (weight). Incorporated in small airborne particulates aluminum is breathable and due to the small size of the "carrier" (often under 1 μm) can reach the general circulation and distribute to various organs including brain. It is thought that aluminum passes through the blood–brain barrier through transferrin and accumulates in the area of the brain cortex that is rich in transferrin receptors (Inan-Eroglu & Ayaz, 2018). Currently, a plethora of studies bring evidence that aluminum is neurotoxic and associated with neuropathology including senile plaques and neurofibrillary tangles, being recognized as primary etiological factor in Alzheimer's disease (Exley, 2017, Exley & Clarkson, 2020, Dhaneesh et al., 2014).

5. CONCLUSIONS

Current work has described and characterized individual microspherical particulate that originate from vehicle exhaust emissions. The identified microspheres are included in PM 2.5 category size, are smooth glass-like and composed mainly from aluminosilicates and a variable proportion of Mg, Na, Fe, K, Ca and Cl, and seldom Ba and Ti. Due to their breathable size and high aluminum content, the identified particulates are potential harmful to human health and could be also a mean for aluminum uptake in humans; a mechanism that gain less attention in current scientific literature than aluminum ingestion. The results could raise new question about the origin of airborne microspheres, attributed until now as a result of coal combustion, but not identified in automobiles exhausted matters.

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