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Characterisation of solid particles emitted from diesel and petrol engines as a contribution to the determination of the origin of carbonaceous particles in urban aerosol

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Abstract. Solid particles emitted from diesel and petrol engines were studied using a scanning electron microscope fitted with an energy dispersive spectrometer. The soot emitted from different engines under different operating conditions differed in particle size, and the form and size of aggregates. Identification of the soot particles emitted from diesel or petrol engines in urban aerosol based on their size and morphology was found to be impossible.

1. Introduction

The particulate matter (PM) emitted into the atmosphere together with engine exhaust gases is very difficult to define in a simple way. The complex composition of PM causes problems in determining its specific physical and chemical characteristics. Single particles are usually an irregular mixture of chemical compounds. They exhibit different shapes and sizes. The results from their study vary depending on the methodology of the measurement. In addition to the difficult determination of highly diverse chemical compositions, a major research challenge is determining the size of the individual particles. Separation of given individual size-fraction is usually made using a filter, with a pore size larger than the particle test fraction.

In engine measurements of solid particles the total content of organic or inorganic matter, both solid or liquid, which accumulates on the filter with absolute retention of 99% of solids and pore-size ≥ 0.3 μm is usually determined after passing through an exhaust gas air diluter at a temperature of 52 ± 3 °C.

The environmental hazard of particles emitted together with the engine exhaust gases is caused by their chemical activity and very small size. The atmospheric residence time of small particles of size less than 100 nm is long, and they easily penetrate into the human body via the respiratory system [1]. Respirable particles containing heavy metals, sulphur and nitrogen compounds, and heavy hydrocarbons like polycyclic aromatic hydrocarbons (PAHs) are dangerous for human health. Exposure to engine-originated PM increases human morbidity and mortality [2].

Particle emissions from road vehicles are studied extensively worldwide because of their dominant contribution towards the total airborne particle number concentrations found in the atmosphere in numerous cities [3].

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The concentration of air pollution in Krakow has been high for over fifty years [4, 5]. It is possible to note variations in the concentration of different components of air pollution, as well as variations in the dominant sources of pollution from a historical perspective. Recently, household, vehicular exhaust and industrial emissions are considered as meaningful anthropogenic sources of air pollution. The contribution of different sources is evaluated using modelling methods. Analytical data related to the share of various sources of PM in the atmosphere are limited.

Single particle analysis of aerosol in Krakow indicates that carbonaceous particles are the most common when taking into account the total number of particles, especially in PM2.5 fraction of airborne dust [6, 7]. The morphology of carbonaceous particles varies significantly. Both single particles and aggregates of different shape and size are present.

Carbonaceous particles are considered to be more harmful than mineral ones due to their small size and composition [8]. Proper assessment of their sources is crucial to undertake reasonable efforts to improve the situation in highly polluted cities. The aim of this study was to compare the morphology and composition of solid particles emitted from diesel and petrol engines with carbonaceous particles present in aerosol. Solid particles from different engines operating in different conditions were collected. The results might be important for the elaboration of a method for the determination of sources of air pollution. The results of detailed studies of exhaust particles are also useful in the modelling of the dispersion of pollution emitted from vehicles, the determination of health effects, prediction of the soiling of building facades, determination of the deterioration mechanism of building materials, the influence on chemical reaction in the atmosphere, and the modification of climatic conditions.

2. Sampling

Investigations of PM emission from different diesel and spark ignition (SI) engines were conducted on the engine test bed of the Institute of Automobiles and Internal Combustion Engines of Cracow University of Technology.

Solid particle samples were collected on a polycarbonate membrane using a personal air sampling pump, GilAir Plus. The volume of exhausts sampled was 2 dm^3 for the diesel engine and 10 dm^3 for the petrol engines. The engines' operating conditions are listed in tables 1–3.

Table 1. Operating conditions of the Volkswagen 1.9 TDI diesel engine (1900 cm^3 displacement)

	Sample D1	Sample D2	Sample D3
Engine speed [rpm]	2000	835	2000
Torque [Nm]	115	0	200
Exhaust gas opacity (^{o}B)	8	0.35	0.3
EGR* (%)	60	60	0

* Exhaust Gas Recirculation

Table 2. Operating conditions of the Fiat type 170A1 – conventional SI engine (900 cm^3 displacement)

	Sample B1 (warming-up phase)	Sample B2 (thermal stabilised phase)
Cylinder head coolant temperature [^{o}C]	30–75	87
Torque [Nm]	30–40	40

Table 3. Operating conditions of the direct injected research SI engine (different injection advance angle)

	Sample B10	Sample B11	Sample B12	Sample B13	Sample B14	Sample B15
Exhaust gas temperature [^{o}C]	500	500	500	760	900	890
Air excess number (λ)	0.875	0.875	0.875	1	1	1
Engine speed [rpm]	2480	2480	2480	2600	2600	2600
Injection advance angle [^{o} c.a.]	340	180	90	340	180	90

Samples of the aerosols were collected on Nuclepore filters over 24 hr periods. Three size fractions (<2.5 μm, 2.5–10 μm and >10 μm) were collected by an NILU Stucked Unit connected with a flowmeter and pump. The flow rate of air was equal to 30 l per min.

3. Methods

The exhaust particles and aerosols were analysed using a field emission scanning electron microscope ([SEM], HITACHI S-4700) equipped with an energy dispersive spectrometer ([EDS], NORAN) with a Nordlys detector. Both observation and chemical analyses were performed at the voltage of 15 kV. The standardless method was used for quantification of the chemical components.

Fragments of polycarbonate membranes with deposited particles were mounted on graphite holders using conductive carbon discs, and then coated with a gold conductive layer.

4. Results

Carbonaceous particles (soot) dominate in the collected engine exhaust solid particles' samples. Their characteristics (particle or aggregate size, form of aggregates, number of particles in aggregate) are presented below.

4.1. Diesel engine - Volkswagen 1.9 TDI

The size of single particles emitted from the diesel engine observed in SEM vary from 50 nm to 100 nm in samples D2 and D3 (figures 1A, 1B). Particles below 50 nm occur rarely. Determination of the single particle size in sample D1 was not possible because of the presence of a complex network of elongated aggregates composed of numerous particles (figures 1C, 1D). Elongated chain-like aggregates occur commonly in sample D2 (figure 1E); however, isometric aggregates are also present. Their size varies from 10 μm in the case of the elongated aggregates to <100 nm for the isometric ones composed of several particles. The isometric aggregates dominate in sample D3 (figure 1F). Elongated aggregates are also present in sample D3, but they are shorter compared with sample D2. Their size is between 8 μm and 200 nm. Comparison of the solid particles' samples and operating conditions of the engine suggest that exhaust gas recirculation (EGR) is an important factor. Two samples collected at EGR=60% contain elongated chain-like aggregates.

4.2. Conventional petrol engine - Fiat type 170A1

The characteristics of the solid particles collected during the warming-up phase (sample B1) and during the thermal stabilised phase (sample B2) are similar. Single particles or small aggregates composed of several particles are common; larger aggregates containing numerous particles also occur. The single particles vary in size from <20 nm to 50 nm (figures 2A–2D). Larger particles occur rarely.

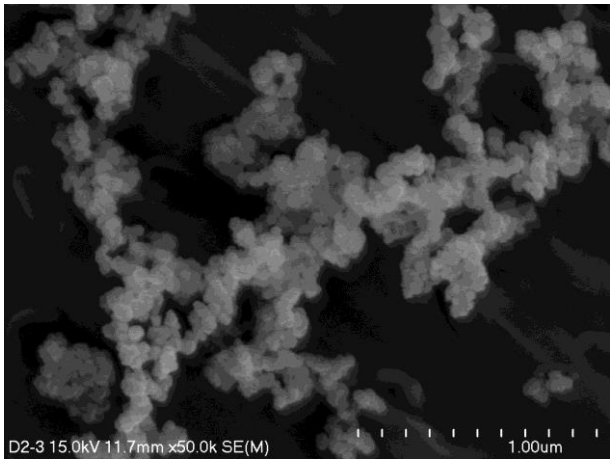

Figure 1A. Soot particles in chain-like aggregate - Sample D2.

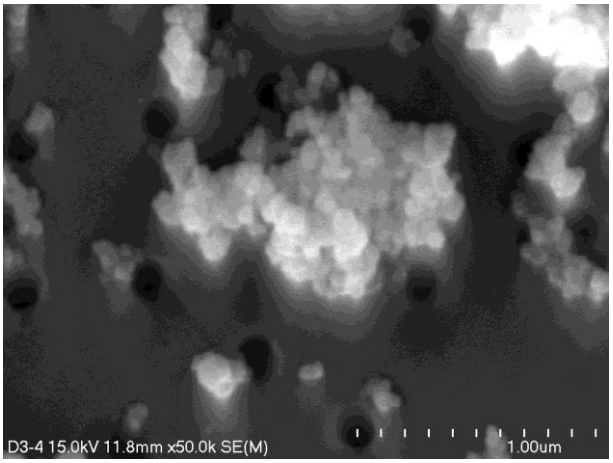

Figure 1B. Soot particles in aggregate - Sample D3.

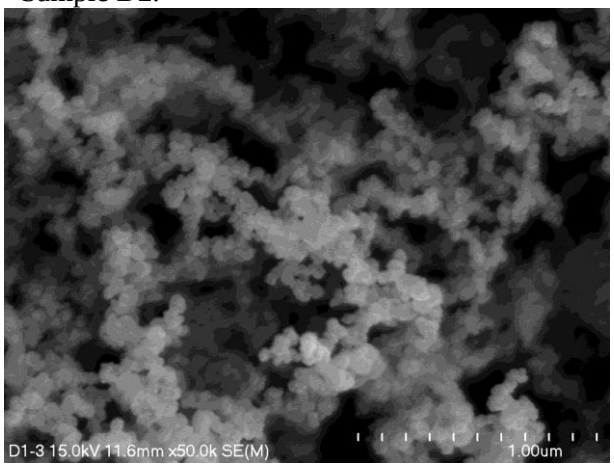

Figure 1C. Complex network of soot particles' aggregates - Sample D1.

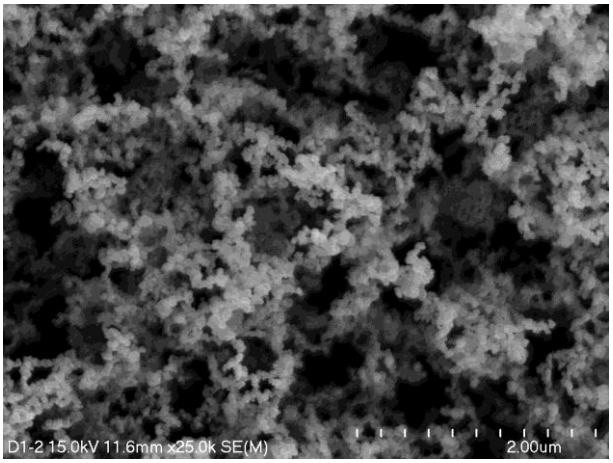

Figure 1D. Densely packed network of soot particles' aggregates - Sample D1.

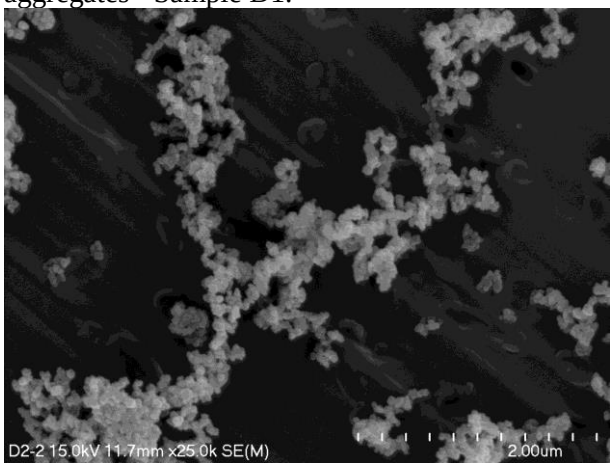

Figure 1E. Chain-like aggregates of particles - Sample D2.

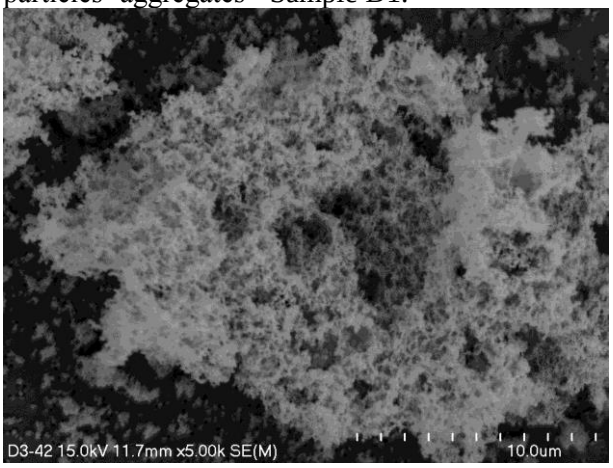

Figure 1F. Isometric aggregate of soot particles - Sample D3.

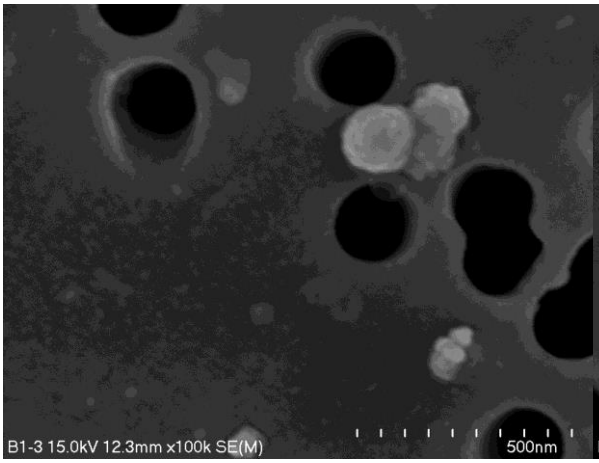

Figure 2A. Single particles of soot - Sample B1.

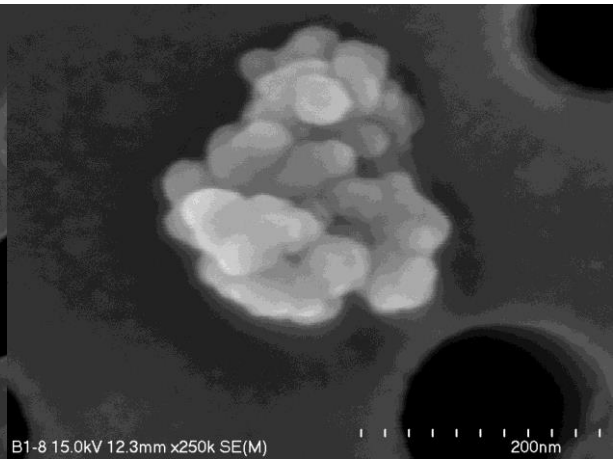

Figure 2B. Aggregate of soot particles – Sample B1.

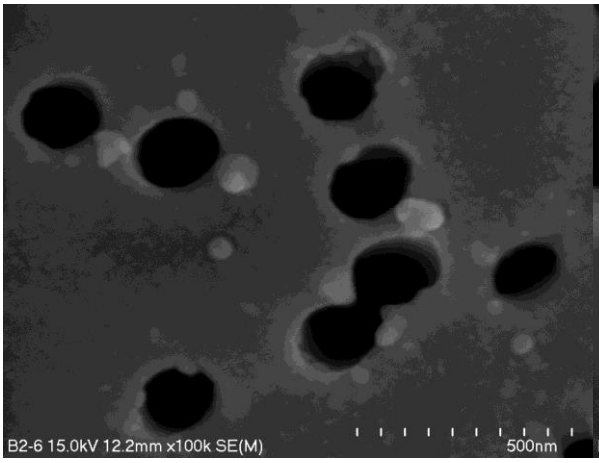

Figure 2C. Single particles of soot - Sample B2.

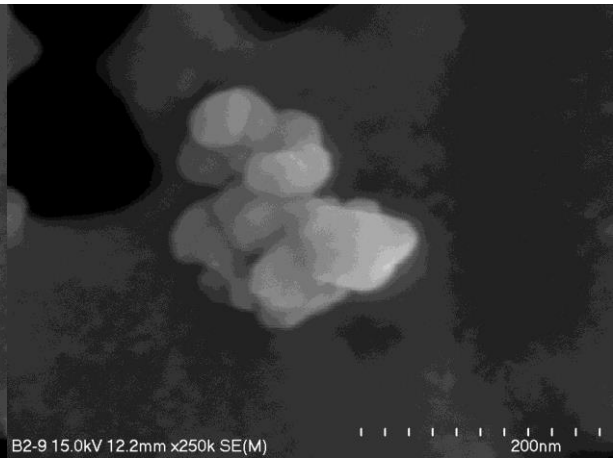

Figure 2D. Aggregate of soot particles - Sample B2.

4.3. Direct injected research SI engine

The single particles or small aggregates are common in all the samples, but a large number of particles occur in the form of very complex aggregates. The aggregates are elongated and branched. Their length is usually up to 70 μm; some chain-like aggregates reach 350 μm (figures 3A–3D). Aggregates

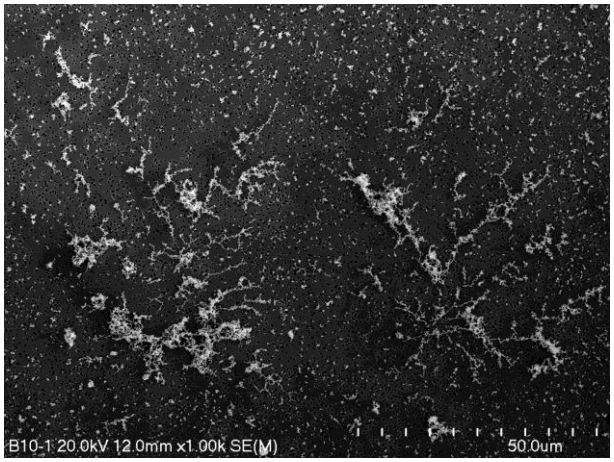

Figure 3A. Single particles and complex aggregates of soot - Sample B10.

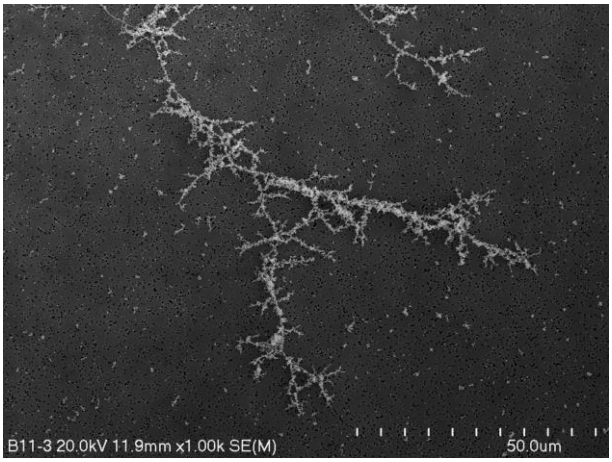

Figure 3B. Branched chain-like aggregates of soot particles - Sample B11.

forming irregular ring-like patterns are less common. The size of the single particles varies from 25 nm to 50 nm (figures 3E, 3F).

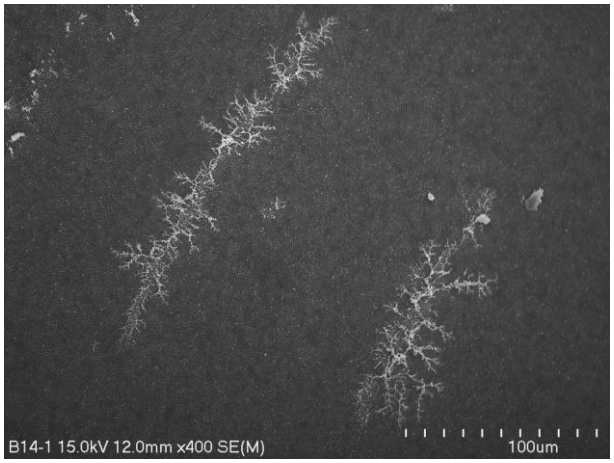

Figure 3C. Chain-like aggregates of soot particles - Sample B14.

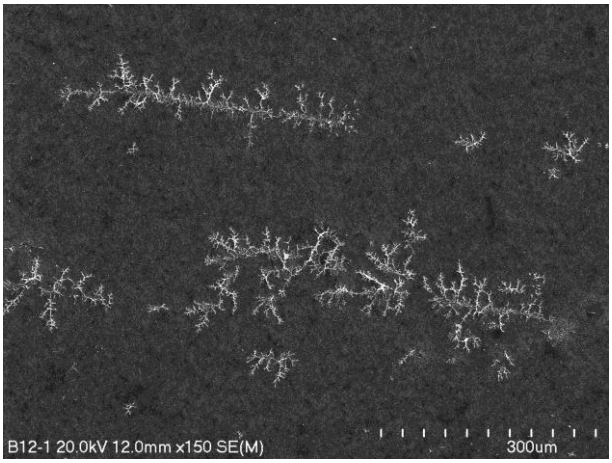

Figure 3D. Chain-like aggregates of soot particles - Sample B12.

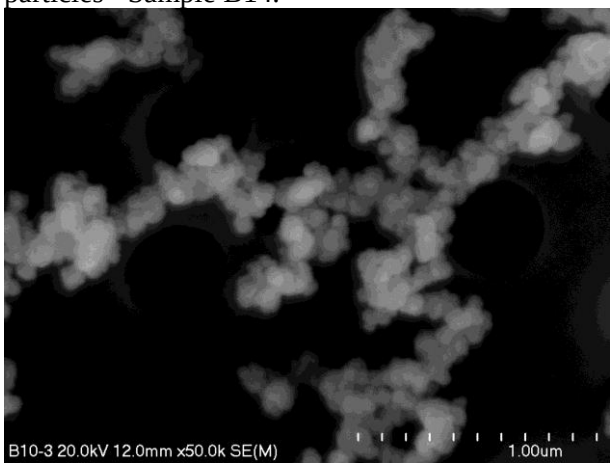

Figure 3E. Soot particles in chain-like aggregate - Sample B10.

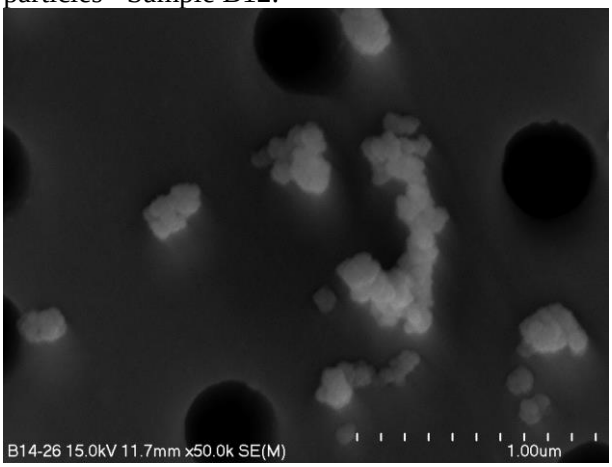

Figure 3F. Single soot particles and small aggregates - Sample B14

4.4. Metal containing particles

Metal containing particles occur rarely in the analysed samples. Their size and morphology vary within a broad range. Cr-containing particles were noted in samples collected from the diesel and conventional petrol engines (figures 4A, 4B). Other particles (e.g. containing Si, Al, Cl, K, Ca) were noted only as unique examples.

5. Discussion and conclusions

The soot emitted from different engines differs in particle size, and the form and size of aggregates. Detailed discussion of the relationships between operating conditions and soot characteristics needs more systematic study using a larger number of samples.

Identification of the soot particles emitted from diesel or petrol engines in urban aerosol based on their size and morphology is impossible. In urban aerosol, numerous carbonaceous particles similar to those identified in engine exhaust occur (figures 5A–5F) [6, 7]. Soot particles emitted from different sources (e.g. coal-powered household stoves, power plant boilers, biomass and waste combustion) could be similar in terms of the size and form of aggregates [6]. The opinion that soot particles emitted from engines are smaller in size compared with soot from other sources is not supported by our results.

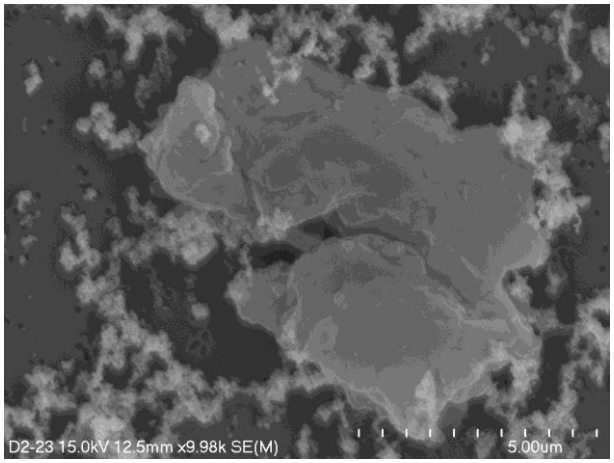

Figure 4A. Cr-rich particle - Sample D2.

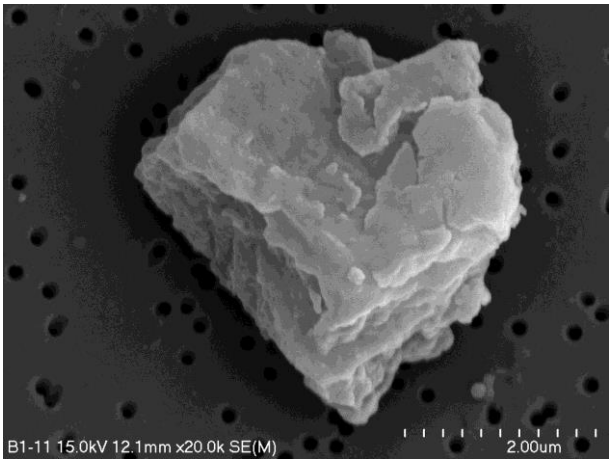

Figure 4B. Cr-rich particle - Sample B1.

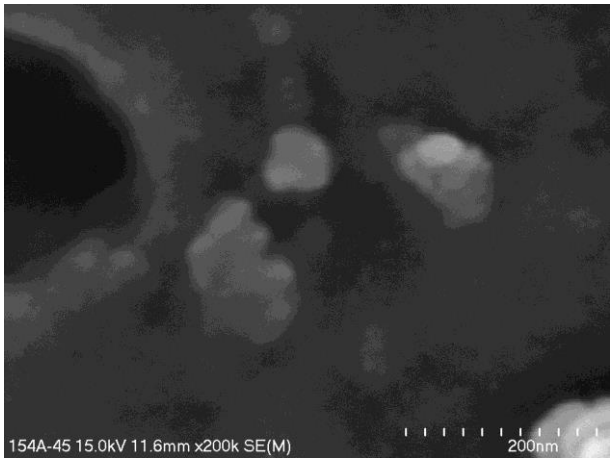

Figure 5A. Single soot particles - aerosol in Krakow.

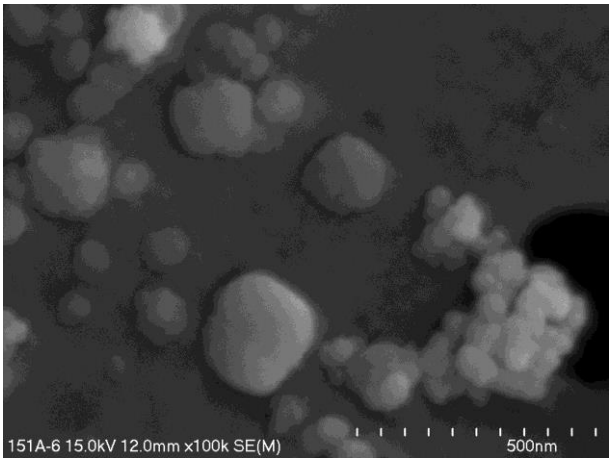

Figure 5B. Single soot particles and aerosol in Krakow.

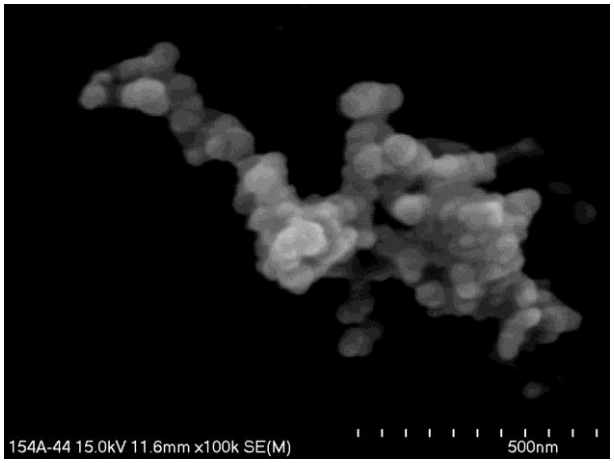

Figure 5C. Soot aggregate - aerosol in Krakow.

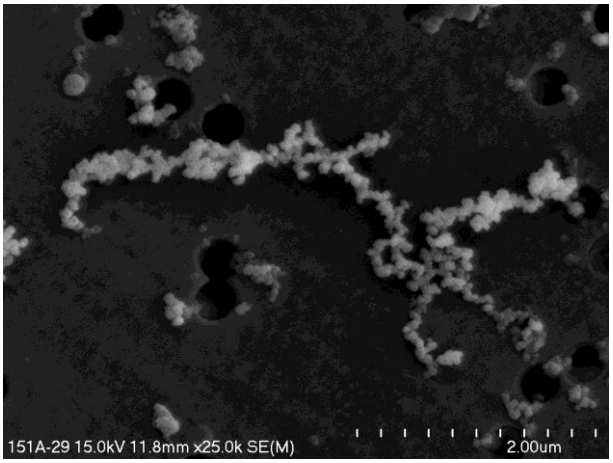

Figure 5D. Chain-like soot particles' aggregate - aerosol in Krakow.

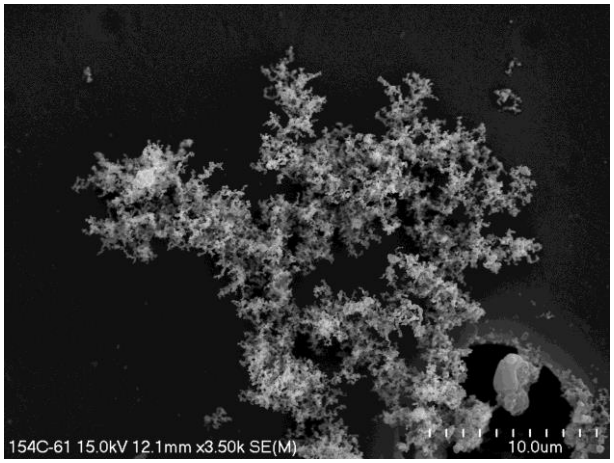

Figure 5E. Loosely packed isometric aggregate of soot particles - aerosol in Krakow.

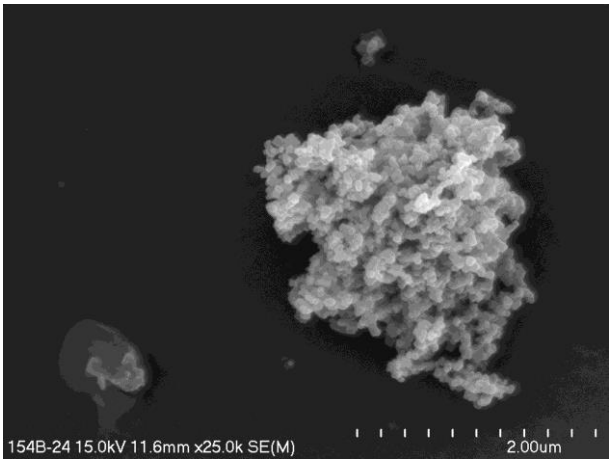

Figure 5F. Densely packed aggregate of soot particles - aerosol in Krakow.

Determination of the contribution of different sources of carbonaceous compounds in urban aerosols needs the application of detailed chemical analyses in aerosol studies [e.g. 9, 10], coupled with systematic analyses of the material from all possible sources.

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