Characterisation of solid airborne particles in urban snow deposits from Ljubljana by means of SEM/EDS

Opredelitev trdnih zračnih delcev v snežnem depozitu iz urbanega območja Ljubljane s SEM/EDS

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Abstract: The main objective of this study was to identify and characterise solid airborne particles deposited in snow of the Ljubljana urban area over a period of 6 days, according to their morphology and chemical composition and to assess their source and genesis by means of scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM/EDS). This method enables the characterisation of submicroscopic (crystalline and amorphous) particles, present in very small quantities. Two snow samples were collected and analysed. Spherical particles, irregularly shaped fragments and agglomerates were identified according to their morphology. Geogenic and technogenic sources were assessed by considering their chemical composition and morphology. Geogenic particles are represented mostly by irregular mineral fragments of quartz, zircon and clay minerals. Technogenic particles are mostly spherically shaped carbonaceous particles, originating from combustion of coal or liquid fuel and spherical heavy metal-bearing particles, emanating from high-temperature industrial combustion and steel-melting processes. Irregular technogenic particles emanate mostly from incomplete coal combustion and road traffic emissions. Comparison of treated samples showed no significant differences in particles according to their origin. It can be concluded that the sampling location had no important influence on the distribution of particles by their origin.

Original scientific paper

Izvleček: Cilj predstavljene študije je bil prepoznati in opredeliti trdne zračne delce, ki so bili v šestih dneh odloženi v snegu na urbanem območju Ljubljane. Opredelili smo jih glede na njihovo obliko in kemijsko sestavo ter ocenili njihov izvor in nastanek z metodo vrstičnega elektronskega mikroskopa z energijsko disperzijskim spektrometrom rentgenskih žarkov (SEM/EDS). Ta metoda omogoča opredelitev submikroskopskih (kristalnih in amorfnih) delcev, ki so v vzorcih v zelo majhnih količinah. Odvzeli in analizirali smo dva vzorca snega. Po obliki smo delce razdelili v sferične, odlomke nepravilnih oblik in aglomerate. Glede na kemijsko sestavo in obliko smo ločili delce geogenega in tehnogenega izvora. Geogeni delci so večinoma nepravilni mineralni odlomki kremena, cirkona in glinenih mineralov. Med tehnogenimi delci prevladujejo votli sferični delci, ki vsebujejo večinoma ogljik in so nastali pri izgorevanju premoga ali tekočih goriv, in težke kovine vsebujoči sferični delci, ki so nastali pri visokotemperaturnih procesih industrijskega sežiga in taljenja jekla. Tehnogeni delci nepravilnih oblik nastajajo večinoma pri nepopolnem izgorevanju premoga in prometnih emisijah. Primerjava obravnavanih vzorcev ni pokazala razlik v izvoru trdnih delcev. Sklepamo lahko, da na sestavo trdnih zračnih delcev v vzorcih lokacija vzorčenja ni imela pomembnega vpliva.

Key words: solid airborne particles, snow deposit, Ljubljana urban area, source apportionment, SEM/EDS

Ključne besede: trdni zračni delci, snežni depozit, urbano območje Ljubljane, določitev izvora, SEM/EDS

Introduction

The combination of the scanning electron microscope and energy dispersive spectrometer (SEM/EDS) is a well-established analytical method across different fields of geology. It has also proved to be a very useful method world-wide in environmental geochemistry for the characterisation of particles in different environmental media. Numerous studies of solid aerosol particles and urban snow deposits attested the usefulness of SEM/EDS in terms of particle characterisation and source apportionment (Aragon et al., 2000; Sokol et al., 2002; Kemppainen et al., 2003; Trimbacher & Weiss, 2004; Umbria et al., 2004; Bernabe et al., 2005; Tasić et al., 2006; Choël et al., 2007). This method supplements other analytical methods, used in mineralogical and geochemical studies of environmental media, such as optical microscopy, X-ray diffraction and geochemical methods (ICP-MS, AAS etc.). The SEM/EDS also enables characterisation of particles, which are smaller than the resolution of an optical microscope, whose quantity is too small to be analyzed by conventional geochemical methods and when crystal structure of particles is ill-developed or amorphous and cannot be identified using X-ray diffraction. Thus, the SEM/EDS was a method of choice for identification of solid airborne particles in snow deposit from Ljubljana urban area and for the assessment of their qualitative chemical composition.

Solid airborne particles are present in all environmental media, reaching from snow to stream sediments, as a consequence of transport processes in the Earth's atmosphere and hydrosphere (Neinavaie et al., 2000). Due to erosion processes and the omnipresent geological and pedological substrata, the sources of natural mineral airborne particles are heterogeneous and well dispersed in all environmental compartments (Neinavaie et al., 2000). Compared to anthropogenic (technogenic) point sources, natural (geogenic) sources are less significant and usually represent a natural background. Solid airborne particles can be very reactive and toxic to living organisms, due to their chemical composition and large specific surface area available for interactions. For this reason it is essential to assess their chemical composition, morphology, size and source area.

Materials and methods

Snow is a natural collector and an ideal medium for observation of atmospheric constituents, which have been dry or wet deposited and are mostly well preserved in the snow (Schöner et al., 1993). Solid airborne particles in urban snow deposits are solid particles of different sizes that have been transported and deposited in the snow exclusively by air in the period between the last snowfall and the time of snow sampling. Sources of larger particles are usually located in the vicinity of sampling points; smaller particles, however, can travel between several kilometres and several tens of kilometres in the atmosphere. The average travelling distance of a particle with a diameter of 10 μm, emitted from a source 20 m above the ground, amounts to 10 km. Particles, emitted from a 100 m high source can travel as far as 60 km (Guthmann, 1958; Neinavaie et al., 2000). The content of solid airborne particles in the snow is relatively low, which is why snow samples are often prone to contamination (Telmer et al., 2004).

Two snow samples were taken at two sampling points in the urban area of

Ljubljana. The first sampling point was situated at the sports ground between the Faculty of Economics and the Chamber of Commerce and Industry of Slovenia, 250 m west of Dunajska cesta (Dunajska street) (sample SV-1; Y = 5 462 825, X = 5 103 317). The second sampling point was placed in the park between Dunajska cesta and the Chamber of Commerce and Industry of Slovenia, 13 m west of Dunajska cesta (Dunajska street) (sample SV-2; Y = 5 462 561, X = 5 103 235).

Snow samples were collected from a surface of 1 m^2 area and a depth of 1 cm, approximately 6 days after the last snowfall (20th of January 2009). Snow samples were melted at room temperature in covered glass containers and filtered through an analytical white ribbon filter paper. Filter residue was dried at 50 °C, mounted on a carbon tape and sputter-coated with a thin layer of gold. Analysis was carried out in high vacuum mode using a scanning electron microscope JEOL JSM 6490LV, coupled with an energy dispersive spectrometer Oxford INCA Energy at accelerating voltage 20 kV and working distance 10 mm. Particles were observed in BSE (backscattered electron) mode, which allows their identification by relative elemental composition (atomic number). Qualitative chemical composition of particles was measured using EDS point X-ray microanalysis with acquisition time 10 s to 30 s.

All scanning electron microscopy and energy dispersive spectrometry investigations were performed in our laboratory at Geological Survey of Slovenia.

Results and discussion

Solid airborne particles in both samples of snow deposit were successfully identified, characterised according to their morphology and elemental composition and allocated to different source categories using the SEM/EDS method. Spherical particles, irregularly shaped fragments and agglomerates were recognised according to their morphology. Particles were classified as geogenic and technogenic, considering their genesis (Table 1).

Geogenic particles

Particles of geogenic origin are mineral phases, resulting from the weathering of bedrock and erosion of soil and stream sediments (Neinavaie et al., 2000). The size of analysed solid airborne particles of geogenic origin ranges from 12 µm to 320 µm, averaging 86.2 µm (median: 70 µm). Morphologically, geogenic particles are mostly irregularly shaped sharp-edged fragments of mechanically and chemically resistant rock-forming minerals (zircon, quartz, feldspars etc.). Spherically shaped particles (some clay minerals) are also present but in smaller quantities.

Table 1. Allocation of solid airborne particles in urban snow deposits according to their source

Geogenic	Technogenic
zircon fragments (Figure 1) barite (also technogenic) pyrite (also technogenic) amphiboles pyroxenes quartz (Figure 2) K-feldspars plagioclase clay minerals carbonates	***combustion products***: low-temperature domestic combustion: hollow spherical particles (less porous) irregularly shaped soot particles irregularly shaped coal residues (coke) (Figure 2) high-temperature industrial combustion: (spherical) coal and liquid fuel combustion: hollow spherical particles (porous) (Figure 3) Ca-ferrites (Figure 4) (Ca, Al)-silicates steel-melting and processing: (Cr, Ni, Fe)-oxides (Cr, Fe)-oxides (Figure 5) (Ca, Fe)-silicates (Figure 6)
	road traffic: exhaust soot tyre fragments steel fragments

Pyrite and barite both occur as geogenic and technogenic mineral phases. The origin of geogenic pyrite and barite is most probably the weathering of bedrock in the surroundings of Ljubljana. Technogenic pyrite probably derives from inorganic mineral constituents or inclusions in parent raw coal dust or occurs as non-combustible residue in ashes produced in coal combustion (Kopcewicz & Kopcewicz, 2001; Parish & Wright, 1994).

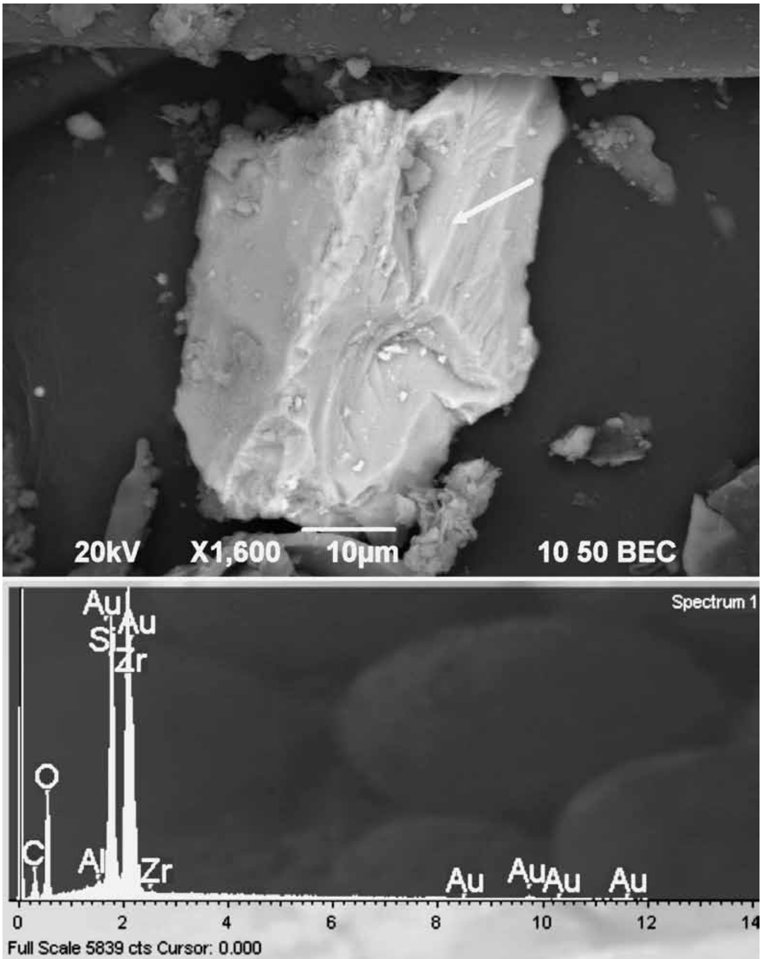

Figure 1. Geogenic zircon fragment

Technogenic barite appears as one of the basic constituents of inorganic colouring pigments (TRIMBACHER & NEINAVAIE, 2002) or as a secondary mineral phase, formed by chemical reaction of barium ions with sulphate ions, arising from high-temperature industrial coal combustion. Technogenic barite also occurs in the form of inclusions in irregularly shaped carbonaceous particles of coal residue (coke) (TRIMBACHER & NEINAVAIE, 2002).

Technogenic particles

The diameter of technogenic particles ranges from 2.5 μm to 700 μm, averaging 50 μm (median: 37.5 μm). Preva-

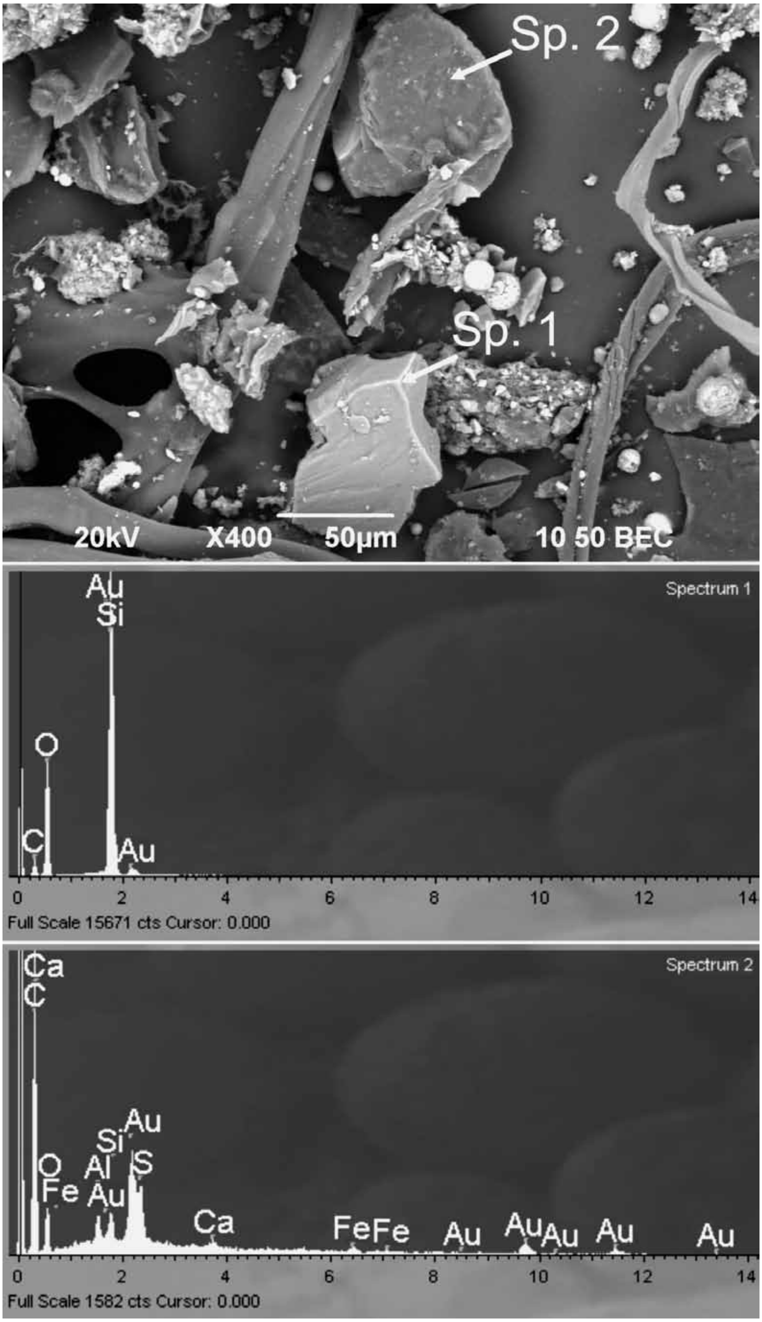

Figure 2. Geogenic quartz fragment (sp. 1 - spectrum 1) and presumably coal residue (coke) (sp. 2 - spectrum 2)

lent particle types in both samples are irregularly shaped carbonaceous technogenic particles and hollow spherical technogenic particles, as anticipated.

Irregularly shaped technogenic carbonaceous particles were interpreted as coke, originating from incomplete coal combustion, and consisting mostly of carbon, sulphur and small contents of silicon, iron, calcium and magnesium. They often contain inclusions of mineral phases such as quartz, barite and pyrite. Hollow particles have been formed during the combustion of coal (Flagan & Seinfeld, 1988) or liquid fuel (fuel oil) (Umbria et al., 2004, Massei et al., 2007). Less porous hollow spherical particles were formed during low-temperature (700–750 °C) incomplete combustion, while more porous and brittle hollow spherical particles were most probably formed during high-temperature complete combustion of coal and liquid fuel. The main constituents of these particles are carbon, sulphur and chlorine while contents of silicon, iron, calcium and magnesium depend on fuel type and manner of combustion.

The hollow spherical shape is a result of expulsion of gaseous or liquid materials from the particle interior, due to an increase in internal pressure or decrease in external pressure (Umbria et al., 2004), which is a consequence of abrupt changes in temperature during combustion processes.

Spherical particles, emanating from high-temperature industrial combustion, are mostly characterised by massive spherical shape resulting from melting processes that occur during their formation (Umbria et al., 2004; Tasić et al., 2006).

Spherical particles, consisting basically of calcium and iron, are Ca-ferrites, which are mineral phases of technogenic origin, formed during high-temperature industrial coal combustion (1400–1500 °C) and can be used as index minerals or indicators for industrial high-temperature processes (Neinavaie et al., 2000). Ca-ferrites are typical of coal-fired heating stations and thermal power plants emissions (Neinavaie et al., 2000; Sokol et al., 2002). Besides calcium and iron Ca-ferrites often contain trace contents of manganese, titanium, copper and zinc. The elemental composition of Ca-ferrites is strongly dependent upon the composition of inorganic mineral constituents in coal and different coal burning methods (Umbria et al., 2004). Considering the relatively wide range in size of analysed particles, it may be concluded that they most probably originate from local thermal power plants.

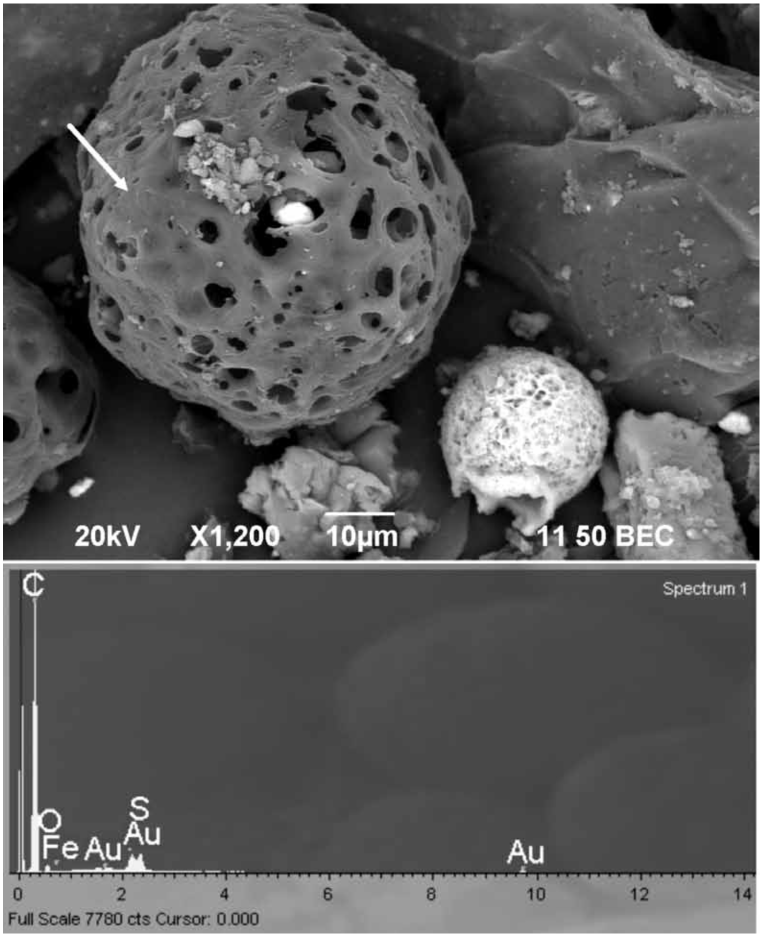

Figure 3. Porous hollow spherical particle (high-temperature coal and liquid fuel combustion)

More unusual and unexpected is the fairly high content of spherical particles, comprising compounds of iron and heavy metals, such as chromium, nickel and vanadium in variable ratios. Spherical iron oxides sometimes occur in the form of the technogenic minerals goethite, hematite and magnetite.

Particle morphology (spherical shape, dendritic and skeletal crystals in glassy matrix) suggests that they were formed during the melting of steel at very high temperatures, followed by rapid cooling (Aragon et al., 2000). According to their chemical composition these particles were most likely formed in

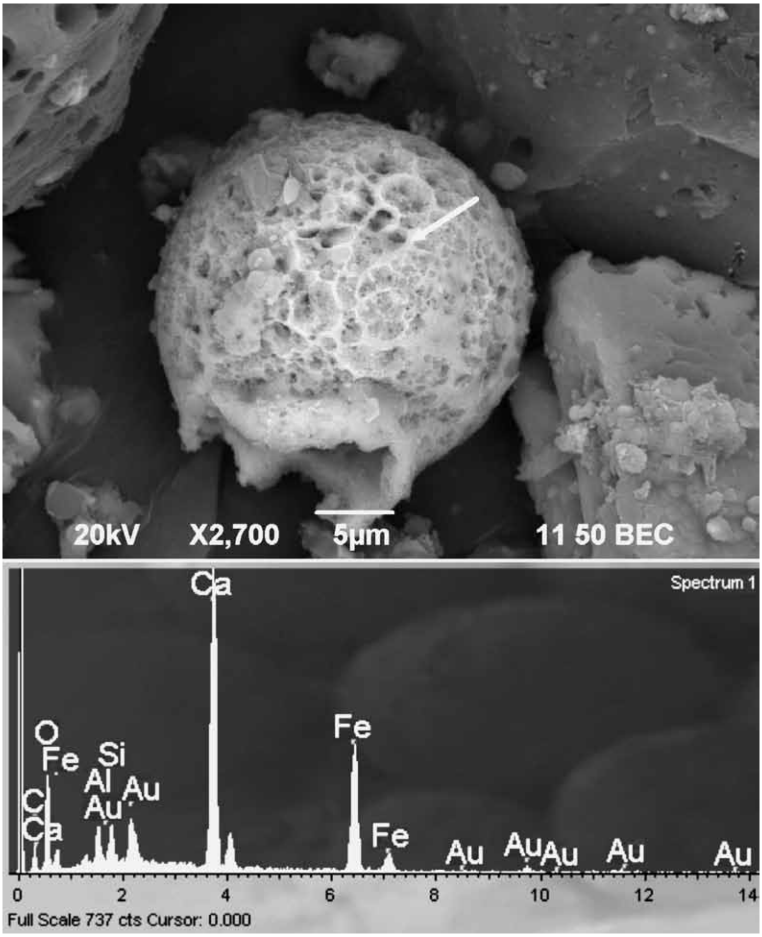

Figure 4. Spherical particle of Ca-ferrite (high-temperature industrial coal combustion)

high-temperature steel production processes or during re-melting and refining of scrap steel, containing the aforementioned heavy metals as alloy components (Seames, 2003; Zhang et al., 2005; Choël et al., 2007). Cr-Ni-V-Fe compounds are common components of different steel grades (http://www.litostroj.com/files/Materials.xls; Kaker & Glavar, 2005). In some cases, spherically shaped (Cr, Fe)-oxides contain small amounts of manganese and copper, while sharp-edged (Cr, Fe)-oxides (also chromite) often contain titanium, which replaces iron ions in the (Cr, Fe)-oxide crystal lattice. Spherical

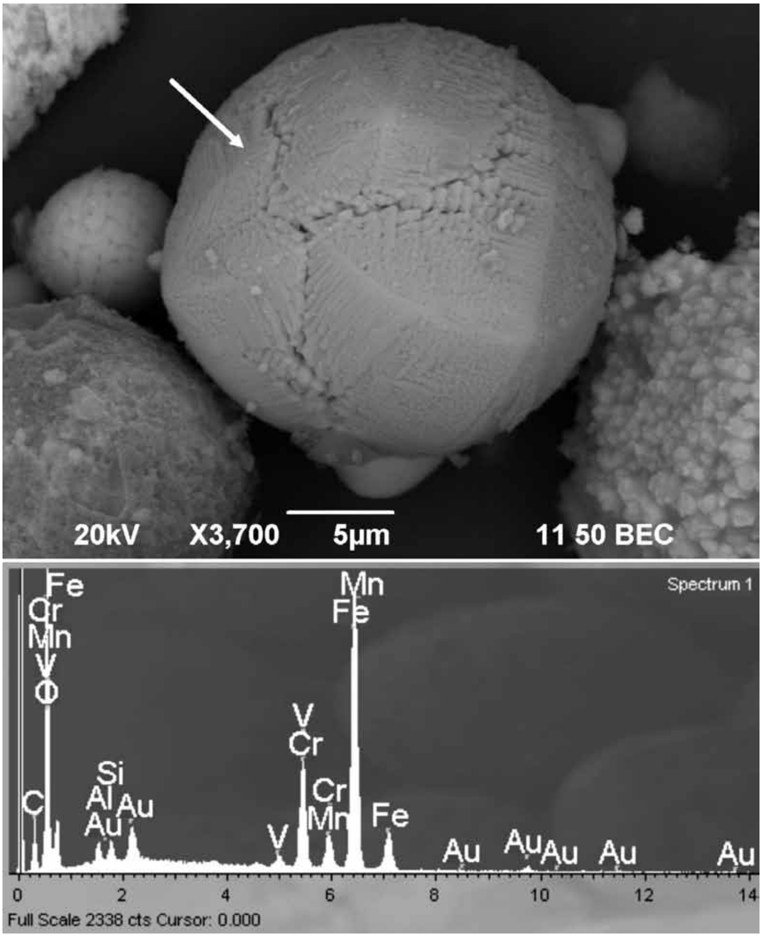

Figure 5. Spherical particle of (Cr, Fe)-oxide with V (high-temperature steel-melting processes)

(Ca, Fe)-silicates are commonly characterised by well-developed euhedral crystals of Fe-oxides (magnetite) in the glassy matrix of (Ca, Fe)-silicates (Figure 6). The euhedral form of Fe-oxide crystals suggests that they were first to crystallise from the melt, followed by (Ca, Fe)-silicates.

There are no steelworks facilities in the surroundings of Ljubljana. Two possible explanations of origin of heavy metal-bearing spherical particles or combination of both are given:

- The heavy metal-bearing spherical particles were formed during the melting and casting of steel in local steel castings production. This explanation is supported by the relatively high content of these particles in both samples and wide range in their size, ranging from 2.5 µm to 98 µm (averaging 35 µm).

- Particles emanate from a more remote source. However, it needs to be considered that a particle of 10 µm in diameter can travel over a distance of 60 km, if emitted from a source located 100 m above the ground level (GUTHMANN, 1958; NEINAVAIE et al., 2000). In our case particles have an average diameter of 35 µm (less than 11 % of particles are smaller than 10 µm) and it can be assumed that their source is either closer than 60 km or higher than 100 m.

Characteristics of samples SV-1 and SV-2 and their comparison

Sample SV-1

Irregularly shaped and sharp-edged carbonaceous technogenic particles, interpreted as coke, and geogenic particles, such as quartz, zircon and clay minerals, are the most abundant particle types among analysed particles in sample SV-1.

Heavy metal-bearing spherical technogenic particles, formed during high-temperature industrial combustion, are present in lesser quantities. The size of geogenic particles ranges from 12 µm to 320 µm, averaging 77.8 µm (median: 54.5 µm). The largest particles belong to grains of quartz and the smallest to zircon fragments, which are also the most frequently occurring particles of geogenic origin. The measured size of technogenic particles ranges from 5 µm to 181 µm, averaging 44.8 µm (median: 37 µm). The largest technogenic particles originate from low-temperature combustion processes (hollow spherical particles, coke, soot). The smallest are heavy metal-bearing particles, originating from high-temperature industrial combustion and steel-melting processes ((Cr, Fe)-oxides, (Cr, Ni, Fe)-oxides, Ca-ferrites and Fe-oxides).

Sample SV-2

Analysed particles are represented mostly by irregularly shaped flat carbonaceous particles, interpreted as coke, and geogenic particles (quartz, zircon, clay minerals). Heavy metal-bearing technogenic particles are present in smaller quantities. The size of the geogenic particles ranges from 24 µm to 173 µm, averaging 99 µm (median: 115 µm). Grains of Al-silicates and quartz are the largest and the most abundant among geogenic particles, while zircon fragments are the smallest. The technogenic particles range in size from 2.5 µm to 700 µm, averaging 57 µm (median: 38 µm). The largest technogenic particles arise from low-temperature

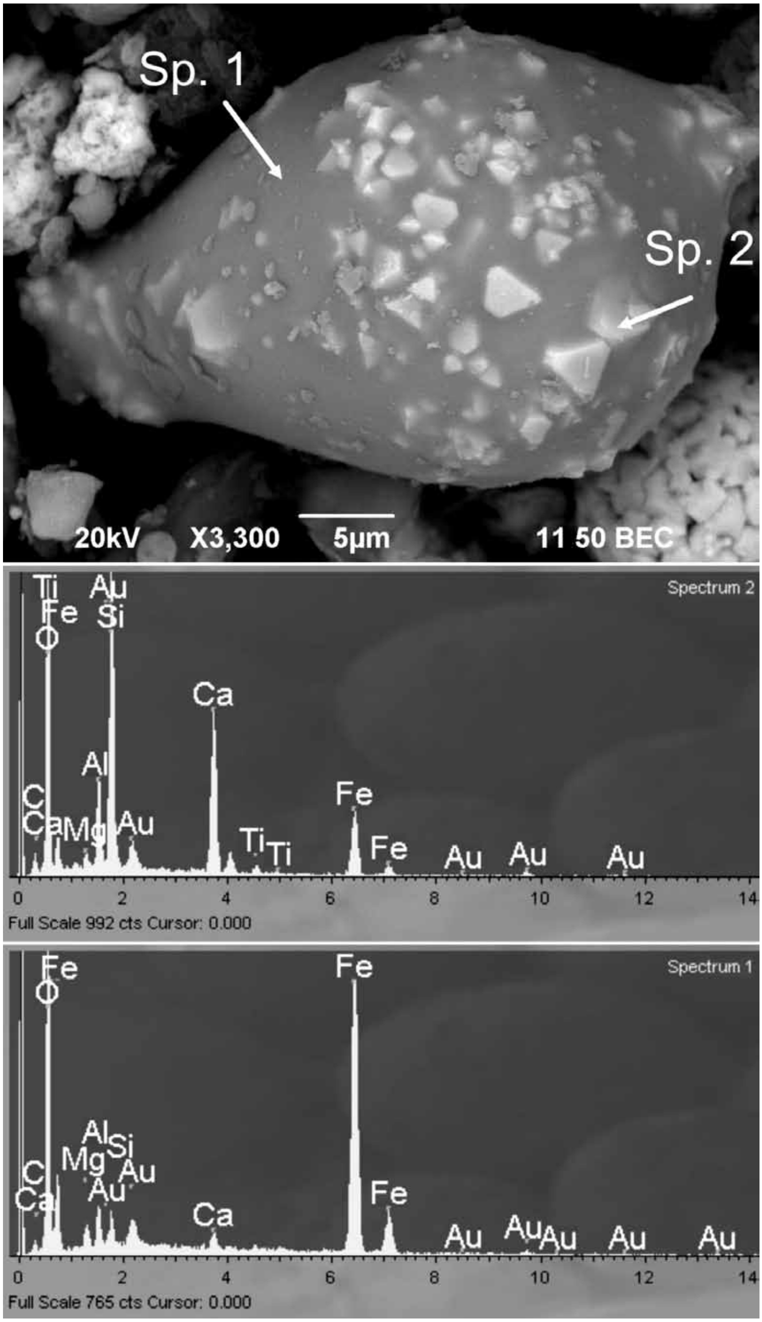

Figure 6. Particle of (Ca, Fe)-silicate with euhedral crystals of Fe-oxide (high-temperature steel-melting processes)

combustion processes (hollow spherical particles, coke, soot). The smallest in diameter are spherical Ca-ferrites, (Ca, Fe)-silicates and heavy metal-bearing (Cr, Ni, Fe)-oxides, Fe-oxides and (Cr, Fe)-oxides that are also the most numerous among heavy metal-bearing particles.

Great differences in the ratio between geogenic and technogenic particles in both samples were expected. Higher contents of technogenic particles, originating from road traffic emissions, should be present in sample SV-2, collected at sampling point close to the main road, compared to sample SV-1. But this was not the case. Comparison of both samples showed no significant differences in content of particles considering their origin. Figure 7 shows that, although absolute average particle size in the sample SV-1 differs from that in the sample SV-2, the trend of average particle size is similar in both samples.

Technogenic particles from high-temperature industrial combustion and melting processes are the smallest particle types in both samples, while the largest belong to the hollow spherical and irregularly shaped carbonaceous technogenic particles, emanating from high-temperature coal and liquid fuel combustion and low-temperature domestic combustion, respectively.

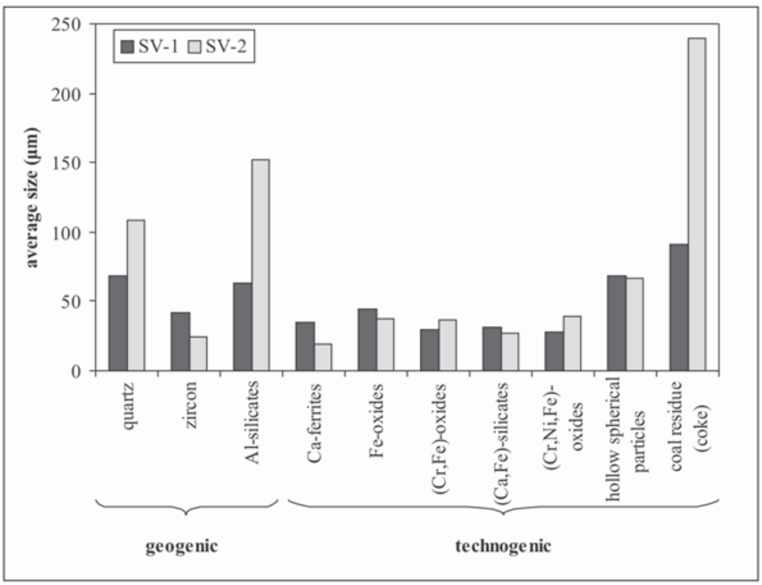

Figure 7. Comparison of average size of geogenic and technogenic particles in samples SV-1 and SV-2

Conclusions

Using the SEM/EDS method, solid airborne particles in snow deposit from the Ljubljana urban area were successfully characterised and classified according to their genesis, morphology and elemental composition. Geogenic particles are mostly sharp-edged, while technogenic particles are spherically and irregularly shaped.

It was established that irregularly shaped technogenic particles, interpreted as coke and originating from incomplete coal combustion and sharp-edged geogenic mineral particles, such as quartz, zircon and clay minerals, are the prevailing solid airborne particles in Ljubljana urban snow deposits. Spherical technogenic particles, resulting from high-temperature combustion processes, are present in smaller quantities. Considering relatively wide size range of analysed technogenic particles, formed during high-temperature industrial combustion and melting processes, it may be concluded that their source is in close vicinity of sampling points.

Comparison of both samples, SV-1 and SV-2, showed no significant differences in particles considering their origin and chemical composition. It can be concluded that sampling location had no important influence on distribution of solid airborne particles by their origin.

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