Towards a holistic approach to the geochemistry of solid inorganic particles in the urban environment

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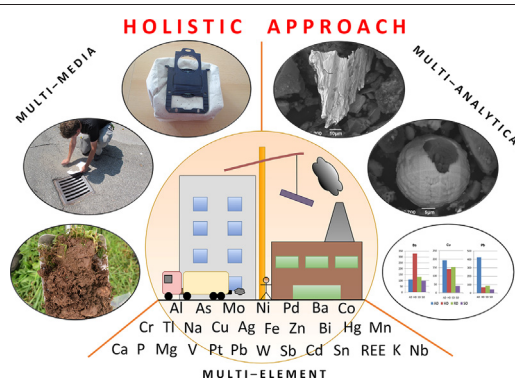
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HIGHLIGHTS

- Application of holistic approach: multi-media, multi-analytical and multi-elemental.
- Understanding geochemical fingerprint of various environmental media is important.
- SEM/EDS analysis of individual particles is useful tool for source identification.
- Minerals of geogenic origin are present in all media.
- High levels of PTEs are typical for industrial zones, except for household dust.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Airborne particulate matter (PM) has a major impact on the biogeochemical cycles of chemical elements in the urban environment. Anthropogenic-derived PM emissions are the cause of some of the most severe environmental and health problems. The presented study aims to improve our knowledge of PM dynamics by introducing a multi-media, multi-analytical and multi-elemental holistic approach to geochemical studies of inorganic PM in the urban environment. The importance of the holistic approach is highlighted and its application in a case study of Maribor (Slovenia) is presented. The chemical composition and individual particulate characteristics of street, attic and household dust were determined and compared with the characteristics of airborne PM, and PM deposited in snow, together with the chemical composition of the soil. We found that the mineralogical and chemical composition and the individual solid particle characteristics of the studied media differ considerably. Nevertheless, minerals of geogenic origin are present in all media. The highest levels of potentially toxic elements (PTEs) in all media, except household dust, are typical for industrial areas. Street dust primarily reflects the influence of winter road maintenance and industrial activities, while characteristics of household dust are predominantly influenced by indoor activities and properties of dwellings. The comparison of the chemical composition of attic and street dust indicates that emissions of As, Cd, Pb, S and Zn were higher in the past. The characterisation of airborne PM and PM deposited in snow is essential for the identification of the most recent sources of PTE-bearing particles. Several industrial sources and the fate of some particle types in the environment have been determined based on the findings of the SEM/EDS analyses. This study confirms that various environmental media are carriers of diverse geochemical information and highlights the importance of a holistic approach in geochemistry of PM in urban areas.

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1. Introduction

Urban environments have become the predominant type of human settlement in recent decades. Worldwide, 55% of people (4.2 billion) live in urban settlements, and this figure is expected to rise to 68% by 2050 (United Nations, 2019). Progressive urbanisation has significantly altered the physical, chemical and biological characteristics of natural ecosystems (Wong et al., 2006; Taylor, 2007). Complex infrastructures, high population densities and particularly intensive human activities lead to pronounced changes in the biogeochemical cycles of chemical elements (Wong et al., 2006; Taylor, 2007; Lyons and Harmon, 2012; Sobrova et al., 2012; Chambers et al., 2016). Urban biogeochemical cycles are influenced by the introduction of non-native materials (e.g. concrete) and the release of chemical elements and compounds in concentrations that are orders of magnitude higher than in their natural state (Chambers et al., 2016). One of the most severe environmental and health issues connected with the urban environment is emissions of particulate matter (PM) (Karagulian et al., 2015), including particles consisting of potentially toxic elements (PTE-bearing particles). As a result of the interaction between the geosphere, atmosphere and anthroposphere, the dynamics of PM are very complex. Inorganic PM results from the synchronous and combined action of natural driving forces, historical and ongoing human activities (Thornton et al., 2008; Chambers et al., 2016). Particulate matter is continuously released into the urban environment from numerous natural (soil erosion, volcanic activity, forest fires, sea salt and biological material (Calvo et al., 2013; Miler, 2014; Karagulian et al., 2015)) and anthropogenic sources (e.g. traffic, industry, metallurgical activities, combustion processes, mining (Thorpe and Harrison, 2008; Tack, 2010; Žibret and Rokavec, 2010; Lyons and Harmon, 2012; Karagulian et al., 2015; Žibret, 2018; Ali et al., 2019; Jabłońska and Janeczek, 2019; Miler and Gosar, 2019; Gaberšek and Gosar, 2020; Jeong et al., 2020; Miler, 2020; Teran et al., 2020)). Eventually, PM are deposited and become part of various environmental media, which act as their sinks, namely soil and different types of dust. Soil is considered the most important PTEs sink in the terrestrial ecosystem (Wong et al., 2006). Environmental media are in constant interaction with each other, with PTEs and their solid phases migrating from one medium to another (by sedimentation, resuspension, etc.). Due to different physico-chemical conditions and various natural and anthropogenic processes, several chemical and physical changes occur in the solid phase of PTEs, as well as in the environmental media during the migration process.

Because of the complex biogeochemical cycles of chemical elements and the dynamics of the interactions between different environmental media, we believe that a holistic approach to the geochemical studies of inorganic solid particles in the urban environment is required. A holistic approach can be defined as the simultaneous study of various solid environmental media using a combination of diverse analytical methods. In addition to the conventional chemical multi-element analytical methods used to determine total element levels, specific chemical and analytical methods (e.g. leaching tests) and complementary methods (to study the characteristics of individual particles, e.g. electron microscopy) should be used. The described holistic approach is necessary to adequately define the quality of the urban environment or the level of contamination, to distinguish between different sources of contamination, to define processes and transport routes, contaminant receptors and interactions, and to assess potential negative impacts on human health. Such a broad view is the exception rather than the rule in the field of environmental geochemistry (and its younger sub-field of urban geochemistry), although Fortescue (1980) already emphasised the importance of a holistic approach to environmental geochemistry a full four decades ago.

The aims of our study were the following: to apply the theoretical foundations of the holistic approach to the geochemistry of solid inorganic particles in an urban area case study by studying the chemical composition and individual particle characteristics of street, attic and household dust, by studying the characteristics of airborne PM and by comparing the results with the chemical composition of soil; to determine the similarities and differences between studied urban media; to highlight the importance of the holistic approach in urban areas; and to encourage the scientific community to apply the holistic approach more frequently in urban areas worldwide and to further develop and improve said approach.

2. Materials and methods

2.1. Study area

The presented study was performed in the town of Maribor, Slovenia (European Union) (46°32′ N, 15°39′ E, 275 m above sea level; Fig. 1). It is a comparatively small urban area with 95,000 inhabitants. Nevertheless, it was one of the most important industrial centres in both Slovenia and the former Yugoslavia. The most important industrial sectors were textile and metal industries (e.g. foundry, automotive and battery factories). Although the importance of industry in Maribor has tapered off over the last 30–35 years owing to various political and economic factors, it still plays an important role in the town's economy. Today's industrial facilities are mainly concentrated in the town's two industrial zones, Melje and Tezno. The foundry, which manufactures products from Cu-alloys and various steel tools, and a metal furniture factory are located in Melje; and automotive and metal processing factories and waste treatment plants are located in the Tezno area. The urban area of Maribor is surrounded by intensively agricultural areas: Vineyards dot the steep slopes and corn and wheat fields predominate in flatter areas. The climate of the area is continental, characterised by considerable differences in weather conditions between the different seasons. The average annual temperature over the period 1981–2010 was 10.5 °C and the average precipitation 1015 mm (Nadbath, 2019). The average winter temperature during the same period was 0.8 °C, with the lowest absolute temperature of −21 °C and the highest of 21.5 °C. The average summer temperature was 20.1 °C, with a maximum of 40.6 °C. The coldest month is January with the average temperature of −0.1 °C and the warmest month is July with an average temperature of 21 °C. On average, the most precipitation falls in summer (356 mm) and the least in winter (150 mm). The snow cover averages 50 days per year. Its depth can vary from few cm to 0.5 m (Nadbath, 2019). The prevailing wind direction is northwest and the average wind speed is 1.8 m/s (Bertalanič, 2007).

The town of Maribor developed on the Drava River alluvial plain, which is represented by Quaternary glacio-fluvial and fluvial sediments five to some twenty metres thick (Žlebnik, 1982; Mioč and Žnidarčič, 1989; Trajanova, 2002). The sediments consist mainly of metamorphic and igneous rock fragments containing quartz, garnet, rutile, epidote, amphibole, zircon, staurolite, kyanite, monazite, xenotime, ilmenite and some other minerals (Mioč and Žnidarčič, 1989; Šoster et al., 2017; Mencin Gale et al., 2019). The surroundings of the town are dominated by the hilly area of Slovenske Gorice to the east and north and by the Pohorje and Kozjak Mountains to the southwest and northwest, respectively. The first area consists of Miocene sedimentary rocks of which siliciclastic rocks (conglomerate, sandstone and sandy marlstone) and unconsolidated sediments (quartz gravel, sand and clay) predominate over carbonate rocks (lithothamnium limestone) (Mioč and Žnidarčič, 1989). The Pohorje and Kozjak Mountains area consists of a variety of metamorphic (phyllite, schist, mica schist, amphibolite, gneiss, marble, eclogite, quartzite) and igneous (granodiorite, dacite) rocks (Hinterlechner Ravnik, 1971; Mioč, 1978; Zupančič, 1994).

More detailed information about the historical industrial development of Maribor, the geological setting and soil types in the wider surroundings can be found in Gaberšek and Gosar (2018).
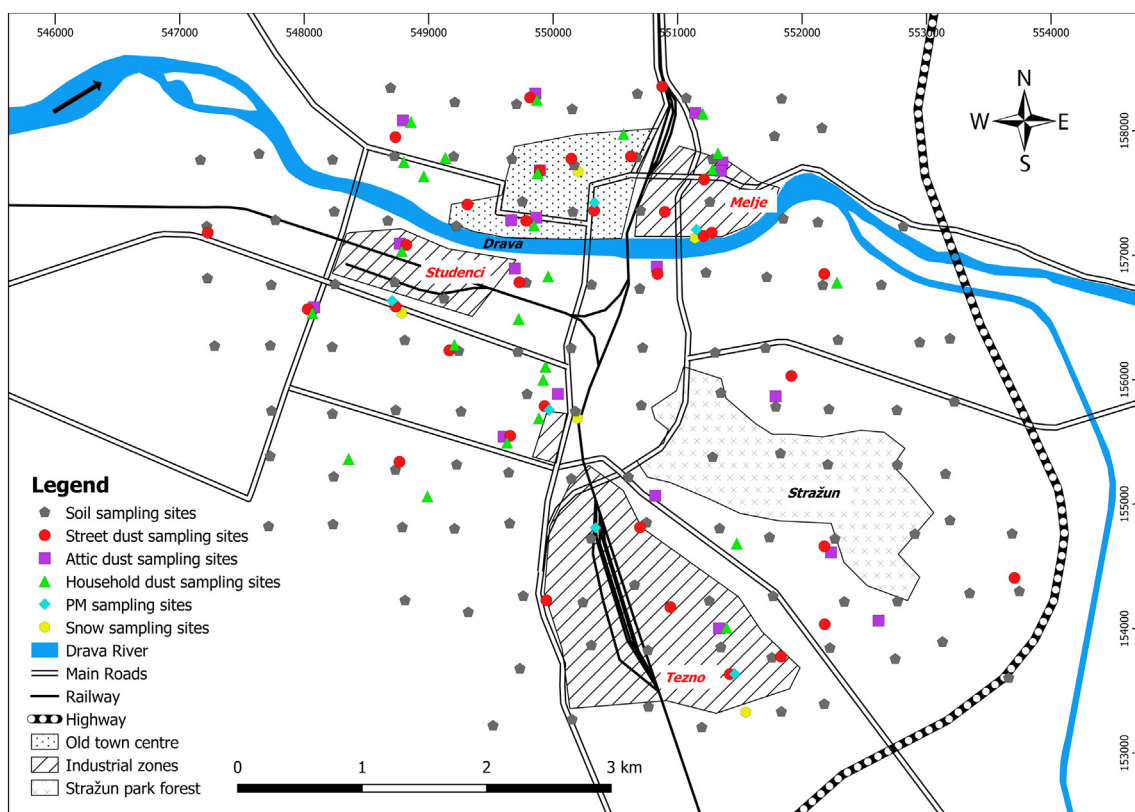
Fig. 1. Sampling sites of studied environmental media on schematic map of Maribor.

2.2. Sampling media

2.2.1. Urban soil

As a result of anthropogenic activities, the physical, chemical and bi-ological characteristics of urban soil can differ significantly from natural or undisturbed soil. Urban soil usually consists of a mixture of in situ natural weathering products and material transported from other, mostly unidentified locations (Wong et al., 2006), industrial, construc-tion and household waste, particles of plastic, wood, slag and glass, metal particles and other anthropogenic products (Craul, 1985; Howard and Orlicki, 2016). The soil horizons in urban areas have been mixed, destroyed or removed, soil is vertically and spatially heteroge-neous, it is compacted or sealed beneath urban infrastructure, it can be enriched or contaminated with various inorganic (e.g. PTE) and or-ganic substances, the circulation of water, air and nutrient is highly dis-turbed (Craul, 1985; Wong et al., 2006; Lehmann and Stahr, 2007; Yang and Zhang, 2015). A neutral to slightly or strongly alkaline soil pH values are also typical for urban soil, regardless of geological setting (Yang and Zhang, 2015).

2.2.2. Street dust

Street dust is a heterogeneous mixture of solid particles that are de-posited on paved outdoor surfaces (Gunawardana et al., 2012; Denby et al., 2018). It consists of particles of natural origin (rock fragments, soil particles, sea salt, biogenic material (e.g. seeds, pollen), particles emitted by volcanic eruptions and forest fires) (Taylor, 2007; Amato et al., 2009; Gunawardana et al., 2012; Žibret et al., 2013; Ali et al., 2019), and those of anthropogenic origin. The anthropogenic sources differ among different urban areas; some of the most important consist in the abrasion of paved surfaces, road traffic (exhaust and non-exhaust emissions, such as tyre and brake wear) (Smichowski et al., 2008; Thorpe and Harrison, 2008; Amato et al., 2009; Grigoratos and Martini, 2015; Hwang et al., 2016; Ali et al., 2019), industry, mining

and metallurgical processes, fossil fuel combustion (e.g. in thermal power plants), the degradation of construction materials, agriculture, winter road maintenance (sand gritting and salting), bulk cargo trans-port, degradation of road surface markings, such as yellow traffic paint, road signs and other road infrastructure, etc. (Fergusson and Kim, 1991; Charlesworth et al., 2003; Taylor, 2007; Amato et al., 2009; Gunawardana et al., 2012; Žibret et al., 2013; Bavec, 2015; Denby et al., 2018; Žibret, 2018; Teran et al., 2020; O'Shea et al., 2020; O'Shea et al., 2021). The deposition and persistence of street dust depends con-siderably on weather conditions (e.g. precipitation, wind) and surface properties (e.g. presence of pores where particles can accumulate). Allott et al. (1990) estimated the persistence or residence time of street dust at 150–250 days. In general, its residence time is relatively short, such that the chemical composition of street dust reflects and is the re-sult of recent natural and anthropogenic sources.

2.2.3. Attic dust

Attic dust is a type of dust that is deposited in uninhabited and unin-sulated attics. The particles largely originate from natural and anthropo-genic external sources (Cizdziel and Hodge, 2000; Šajn, 2003; Gosar et al., 2006; Davis and Gulson, 2005). The chemical composition of attic dust is therefore influenced more by external anthropogenic activ-ities than by household activities. Airborne particulate matter that en-ters attics through various cracks and openings, as the result of the lower air pressure in attics than outside (Cizdziel and Hodge, 2000; Davis and Gulson, 2005) accumulates and persists because it is not under the direct influence of weather conditions or occupant activities. The continuous, undisturbed deposition and long-lasting stability of the attic dust over a long period of time allows for indirect assessment of historical air pollution with PTEs going back to the time the building was constructed up to the present day (Gosar and Šajn, 2001; Ilacqua et al., 2003; Šajn, 2003; Davis and Gulson, 2005; Gosar et al., 2006; Völgyesi et al., 2014; Miler and Gosar, 2019). Attic dust can also be a

source of contamination when old buildings are renovated or demolished (Davis and Gulson, 2005).

2.2.4. Household dust

Household dust is a type of dust that is deposited on the indoor surfaces (e.g. floor, furniture) in residential buildings. It originates mainly from indoor sources and to a lesser extent from the outdoors. Indoor sources vary greatly from dwelling to dwelling depending on the activities and habits of the occupants and characteristics of the dwellings. The main indoor sources include residents, pets, cooking, heating, smoking, degradation of construction materials, plaster and wall paint, degradation of furniture and carpets, use of cosmetics and cleaning products and other activities (Morawska and Salthammer, 2003; Turner and Ip, 2007). As a result of these many sources, household dust consists of highly heterogeneous particles: skin, human and animal hair, dandruff, bacteria, pollen, viruses, fibres from carpets and clothing, particles of plaster, paint, paper, food, plastics, building materials, metal particles, and various particles from the outdoor environment, namely soil particles, street dust, particles from anthropogenic sources, etc. (Morawska and Salthammer, 2003; Rasmussen, 2004; Turner and Ip, 2007). One of the main characteristics of household dust is its far higher content of organic matter than other media (Rasmussen et al., 2008; Bavec et al., 2017).

2.2.5. Airborne particulate matter (PM)

As already described in the Introduction, airborne particulate matter (PM) can originate from numerous natural and anthropogenic sources. Particles released directly from source into the atmosphere are known as primary particles, while those formed within the atmosphere from the precursor gases (e.g. SO_2, NO, NO_2, NH_3) are called secondary particles (Gieré and Querol, 2010; Karagulian et al., 2015). The individual particles differ from each other in size, morphology, chemical and mineralogical composition (Turner and Colbeck, 2008). They are exposed to complex physical and chemical processes in the atmosphere, namely oxidation, nucleation, condensation, coagulation, evaporation, absorption, photochemical reactions, etc. (Turner and Colbeck, 2008; Gieré and Querol, 2010). In contrast to other environmental media, airborne PM reflect their most recent sources and may pose a direct health hazard. For this reason, it is important to include PM in geochemical studies of urban areas, especially detailed analyses of individual particles.

2.2.6. PM deposited in snow

Snow is a highly effective natural collector of airborne PM and as such a suitable medium for an indirect sampling of airborne PM and determination of organic and inorganic pollutant loadings (Engelhard et al., 2007; Kuoppamäki et al., 2014; Talovskaya et al., 2017; Miler and Gosar, 2013, 2015; Gaberšek and Gosar, 2020). It has some specific properties and advantages over other geochemical sampling media in contributing to the identification of PM sources: the effectiveness of PM collection, which is a result of the large surface area and slow fall velocity of snowflakes (Engelhard et al., 2007; Kuoppamäki et al., 2014), its sampling is far cheaper and easier than sampling of PM directly from the atmosphere, PM deposit in a definite time (during the snowfall and in the period between the end of the last snowfall and the time of sampling). These properties allow for a more accurate identification of the individual PM sources.

2.3. Sampling and sample preparation

The protocol of soil and dust sampling mostly followed the procedures outlined in the EuroGeoSurveys Urban Geochemical Mapping Manual (Demetriades and Birke, 2015). The sampling of **soil** was done in May 2016. Sampling sites were located at the centres of equal 500 × 500 m squares. A total of 118 samples were collected from the top 10 cm of soil in parks, lawns and other green areas (Fig. 1).

Samples were oven dried at 35 °C, soil aggregates were then gently disaggregated in a mortar with a ceramic pestle, homogenised, passed through a 2 mm nylon sieve and pulverized in an agate ball mill to obtain analytical grain size. More details are given in Gaberšek and Gosar (2018).

The sampling of dusts and airborne PM was carried out in summer 2017. **Street dust** was sampled at 33 sampling sites throughout the town (Fig. 1). Sampling was done 3 days after the last rain event (only light summer showers). The samples were collected by brushing the paved areas along the curbs with plastic brushes. Each sample consisted of several subsamples. The sampling of dust, which was identified as the result of soil erosion and degraded building materials by visual inspection of sampling points, was avoided. **Attic dust** was sampled by brushing the dust off the surfaces of wooden building elements in uninhabited and uninsulated attics. Samples were taken from 19 buildings (Fig. 1), most of which were more than 80 years old. **Household dust** was sampled by collecting vacuum cleaner bags that had been used for one to three months. Participating residents also completed a questionnaire on their lifestyle, habits and the characteristics of the dwellings that could influence the chemical composition of the household dust there (e.g. smoking, frequency and type of cleaning, type of heating and cooking, presence of pets, etc.). We collected 27 samples of household dust (Fig. 1), twelve of which were sampled in the same buildings as those sampled for attic dust. In two cases we collected the household dust samples from two different apartments in the same residential building. Spatial distribution of the attic and household dust sampling sites is contingent on the availability of suitable attics and the willingness of the residents to take part in the study. All dust samples were oven-dried at 35 °C and sieved at <0.063 mm using nylon sieves.

Airborne particulate matter (PM) was collected using simple passive sampling technique. Aluminium SEM/EDS specimen stubs covered with double-sided adhesive carbon tape were used as passive samplers. They were attached to six road signs throughout the town (Fig. 1) for one week, which allowed us to collect the particles that deposited gravitationally from the atmosphere. The idea to employ the passive sampling method came from the work of Wagner and Leith (2001a, 2001b), as it is an inexpensive and simple method for the simultaneous collection of PM in several town districts.

Snow was sampled in January 2017, 11 days after the last snowfall event. Four sampling sites close to or in the industrial zones and one in the old town centre were chosen (Fig. 1). Each sample was collected with a plastic trowel from a surface of 0.5 m² and a depth of 3 cm. Snow samples were melted at room temperature, and meltwater (on average 3.3 l) was filtrated (<0.6 μm) using polycarbonate filters to trap particulate matter (PM), which was analysed with SEM/EDS (Gaberšek and Gosar, 2020).

2.4. X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) was used to determine the mineral composition of two samples of street dust (MBSD14-A, MBSD24) and two samples of attic dust (MBAD02, MBAD14). The XRD analysis was performed at the University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology. The XRD measurements were performed using a PHILIPS PW 3710 X-ray diffractometer, producing CuKα radiation at 40 kV and 20 mA, using the following settings: angle range 3° ≤ 2θ ≤ 70°, step size 0.02° 2θ and time per step 0.4 s. The diffraction patterns were analysed using the X'Pert HighScore Plus 4.6 program, and minerals were determined using the ICSD database. Semi-quantitative analysis was employed to assess the levels of individual minerals in the sample, which was done by adjusting the measured diffraction intensities to the reference intensities of each mineral. The mineral composition of household dust was only assessed with SEM/EDS.

2.5. Chemical analysis

Levels of the following 65 elements were determined in all samples of soil, street, attic and household dust: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. The chemical analysis was performed by ICP-MS after a modified aqua regia digestion (HCl:HNO$_3$:H$_2$O, 1:1:1) at 95 °C. 15 g per soil and street dust sample and 0.5 g per attic and household dust sample were used. Total organic carbon (TOC) was determined using a LECO analyser in all soil samples and the 11 selected samples of attic and 12 samples of household dust. The analytical work was performed at Bureau Veritas Mineral Laboratories, Vancouver, Canada.

2.5.1. Quality control

Quality control of the chemical analyses was ensured using several steps. The sample numbers were randomised in order to evenly distribute potential analytical errors between the samples. Samples of four Certified Reference Materials (BCR 146R (4×), OREAS 45D (2×), OREAS 45E (4×), OREAS 151 B (4×)), and replicates of five samples of each dust type were randomly included in the sample batch to estimate the accuracy and precision of the analyses. In addition, the following three internal standards were included by the laboratory: OREAS 45EA (5×), DS11 (7×) and OXC129 (2×). Accuracy was estimated by calculating the relative error (RE; in %), and precision by calculating the Relative Percent Difference (RPD; in %) (Gaberšek and Gosar, 2018). Elements for which more than 20% of the measurements were below their detection limits (DL), calculated RE was >20% and/or RPD >30%, were excluded from further statistical treatment. These are: Ge, In, Re, Ta, and Te in street dust samples; Ge, In, Pd, Pt, Re, and Ta in attic dust samples; B, Ge, Hf, In, Pd, Pt, Re, Ta and Te in household dust samples. Levels below DL were substituted with half of the respective DL before statistical analysis for elements that had <20% measurements below their DL. Gold expressed a rather high RPD (40%) in attic dust samples but was nevertheless retained for statistical treatment for comparison with the other two types of dust.

2.6. SEM/EDS analysis

The detailed characterisation of the individual particles in different sampling media followed a method established and described by Miler and Gosar (2013, 2015) and Gaberšek and Gosar (2020). Four samples of each dust type and all six samples of PM (18 samples in total) were analysed with the SEM/EDS. Samples selected for the SEM/EDS analysis were taken in the old town centre, in two industrial zones (Melje and Tezno) and in a residential area. Attic and household dust samples were taken from the same buildings. The analysis was performed with a JEOL JSM 6490LV SEM coupled with an Oxford INCA EDS system consisting of an Oxford INCA PentaFET3 Si(Li) detector and INCA Energy 350 processing software with the following settings: high vacuum, accelerating voltage of 20 kV, spot size 50, working distance of 10 mm, EDS acquisition time of 60 s, backscattered electrons mode (BSE). The samples were placed on double-sided carbon tape with a surface area of about 25 mm^2 and carbon-coated to obtain the conductivity of the samples. Five fields-of-view at a magnification of 300× were randomly selected for each sample (total area about 0.7 mm^2/sample). First, a surface EDS analysis (mapping) of each field was performed. The results served as the basis for an assessment of the relative mineral and other phase abundance, which complement the XRD results. Next, a detailed semi-quantitative and qualitative analysis of the individual PTE-bearing particles was performed. The size (length of the longest axis of the particle), morphology and chemical composition of each PTE-bearing particle and other particles whose morphology indicated their anthropogenic origin (such as Si-rich spherules) were determined. PTE-bearing particles were classified into nine groups, which were

established based on the results. The chemical composition of the particles served as the primary classification factor, namely the predominant constituent elements, with the presence or absence of Fe, O, S and Si representing one of the most important factors. Analysed PTE-bearing particles are simply given as a combination of constituent elements. Those elements, whose concentrations are at least 10-times lower than the concentrations of the predominant element (according to the atomic percentages of the elements acquired with EDS) appear in brackets. Where appropriate, possible natural mineral equivalents of PTE-bearing particles are given. In addition, morphological characteristics have also been used as a classification factor for spherical particles. In this way the following groups were formed: *Fe-oxides* (particles consisting mainly of Fe and O), *Spherical Fe-oxides* (spherical particles consisting mainly of Fe and O), *Fe-alloys* (particles consisting mainly of Fe and smaller concentrations of other PTEs, without O), *Fe-silicates* (particles consisting mainly of Fe, Si and O), *Sulphates/Sulphides* (particles in which one of the main constituents is S), *Other metal oxides* (metal oxides excluding Fe), *Other metal alloys* (alloys of various metals, without Fe and O), *Spherical Si-particles* (spherical oxide particles consisting mainly of Si and/or other elements, such as Al, Ca, K, Mg) and *Other particles* (mainly mineral particles of geogenic origin, such as ilmenite, rutile, zircon and monazite). As the samples were placed on carbon tape and carbon-coated, the presence of C in individual PTE-bearing particles could not be determined; therefore, some of the oxides could actually be carbonates (Gaberšek and Gosar, 2020).

2.7. Statistical treatment

Statistical treatment of the analytical data was performed using STATISTICA 13.5 software. The statistical distribution of the data was determined by a visual inspection of the histograms, by calculating skewness and kurtosis, and by applying the Shapiro-Wilk test. Close to normal distribution in street dust includes 17 elements (Al, Be, Ca, Co, Dy, Er, Ga, Ho, Lu, P, Sb, Sc, Ti, Tm, V, Y, Yb), in attic dust 23 elements (Ag, Al, Be, Bi, Ca, Er, Ga, Hf, Li, Mn, Na, Nb, S, Sb, Se, Tb, Ti, Tl, Tm, U, V, Yb, Zr) and in household dust 23 elements (Al, As, Ba, Ca, Er, Eu, Gd, Ho, Li, Lu, Mg, Nb, Sc, Sm, Sr, Tb, Ti, Tl, Tm, U, V, Y, Yb). Since the majority of the data is not normally distributed and due to the relatively small sample number, non-parametric statistical tools were used. The Spearman rank correlation coefficient was calculated to identify correlations between elements in individual media. Based on their high mutual correlations (≥0.7) and statistical significance at *p* <0.01, the elements were organised into several groups. The differences in the chemical compositions of the various media were identified by comparing the determined levels of the elements and by using a Kruskal-Wallis non-parametric test (p <0.01; only the elements with satisfactory analysis quality in all media were included in the test).

3. Results and discussion

3.1. Mineral composition of the media

The mineral composition of soil, street, attic and household dust in the town of Maribor differs according to the type of predominant mineral and its sources. Minerals of geogenic origin (weathering of igneous, metamorphic and siliciclastic rocks) were determined in the soil. Quartz predominates in all of the samples, followed by plagioclase, muscovite/illite, chlorite and dolomite; in addition, K-feldspar, calcite and amphiboles were also determined in some soil samples (Gaberšek et al., 2020). The minerals in the street and attic dust originate from both natural (mainly quartz, plagioclase, muscovite/illite, chlorite) and anthropogenic sources. The dolomite, which is predominant in street dust originates from the application of carbonate gritting sand for winter road maintenance. The importance of winter road maintenance for the mineral composition of particulate matter in the town of Maribor was also demonstrated by the SEM/EDS study of particles deposited in the

snow; silicates of mainly natural origin and carbonates, originating mainly from gritting sand predominated (35% and 31% of the sample surface studied by SEM/EDS, respectively), while the rest of the surface was covered with C-rich particles (e.g. soot, animal hairs) and PTE-bearing particles (Gaberšek and Gosar, 2020). The predominant mineral in the attic dust is gypsum, which is probably of secondary origin, formed in situ by a reaction of SO_2 gas from the atmosphere and carbonate particles in the dust. Secondary sulphate minerals, especially gypsum, glauberite ($Na_2Ca(SO_4)_2$) and thenardite (Na_2SO_4) have also been discovered in some previous studies of attic dust (Šajn, 1999; Baricza et al., 2016). The mineral composition of household dust was not determined by XRD, but only assessed using surface EDS analysis (mapping). On average, 50% of the sample surface is covered with C-rich particles (organic matter). A high content of organic matter is typical for this type of dust (Rasmussen et al., 2008; Bavec et al., 2017). The predominant mineral groups are silicates (24%) and carbonates (17%; with calcite predominating over dolomite).

3.2. Chemical composition of the media

The chemical composition of soil, street, attic and household dust differs considerably. The Kruskal-Wallis test was applied to statistically evaluate the differences among all four media. Result showed statistically significant differences in the levels of all 42 elements, that were included in the test. The medians of the majority of the elements are the lowest in soil (Table 1), which is the result of differences in the physico-chemical characteristics of the soil and dusts and their different formation/origin. The most important factors affecting soil formation, a slow and complex process, are the weathering of the parent rock material, climate, topography, living organism and time while dusts form by deposition of airborne PM. Several physical, chemical and biological processes take place in the soil that do not occur in dusts. While PTEs accumulate in the dust, the dilution effect occurs in the soil because of the predominance of mineral component and the process of vertical displacement of the particles. The differences in the resident time and the level of exposure to weather conditions can also influence the chemical composition of the media. The residence time of soil can be several thousand years, the residence time of attic dust is several decades to centuries, while street dust remains in the same place for only a few weeks or months. Similarly, soil and street dust are directly exposed to weather conditions (e.g. precipitation, wind) while the influence of weather on household dust chemistry is negligible. The only exceptions with the highest medians in soil are Al, Be, Li, Mn and REE. Their maximum levels were also determined in soil, with the exception of Ce and La, which maximums were identified in household dust samples. Based on the calculated Spearman correlations ≥0.7, the elements in the soil were grouped into five groups (Fig. 2): (1) Al-Co-Cr-Fe-Ga-Li-Mn-Ni-V-REE, (2) Ag-Ba-Cd-Cu-Hg-Pb-Sb-Sn-Zn, (3) Ca-Mg-Sr-B, (4) Cs-Rb-Tl and (5) S-TOC-TC (Gaberšek and Gosar, 2018). The elements of the first, third, fourth and fifth groups mainly originate from the weathering of the parent material. The highest levels of some (e.g. Co, Cr, Fe, V) are clustered at the foot of the metamorphic-igneous Pohorje Mountains. The elements of the second group are considered to be of both geogenic and anthropogenic origin. In particular, the levels of Cu, Pb and Zn (with medians of 40 mg/kg, 44 mg/kg and 131 mg/kg, respectively) (Gaberšek and Gosar, 2018) are considerably higher than the medians of Slovenian soil (20, 34 and 72 mg/kg, respectively) (Gosar et al., 2019) and the European grazing land soil (15, 18 and 46 mg/kg, respectively) (Reimann et al., 2014). Their highest levels are typical for the industrial zones (especially Melje) and the old town centre, and are probably the result of industrial activities and traffic, as well as agriculture on the periphery of the urban area (Gaberšek and Gosar, 2018).

The levels of most chemical elements in street, attic and household dust is typically much higher than in soil (Table 1). As a result of an extended and undisturbed depositions of particulate matter in attics, the

Table 1
Median levels of 62 elements in soil, street, attic and household dust in the town of Maribor (minimums and maximums are given in brackets; all levels are in mg/kg, except for Al, Ca, Fe, K, Mg, Na, P, S and Ti are in %).

	Soil (N = 118)[1]	Street dust (N = 33)	Attic dust (N = 19)	Household dust (N = 27)
Ag	0.093 (0.035–1.73)	0.437 (0.068–13.4)	0.662 (0.383–1.22)	1.51 (0.369–6.88)
Al	1.64 (0.77–3.02)	1.19 (0.56–1.67)	1.16 (0.96–1.52)	0.74 (0.39–1.22)
As	10.1 (5.2–17)	5.6 (4.0–18)	24 (13–52)	4.1 (1.8–8.6)
Au	0.005 (0.001–0.315)	0.050 (0.003–2.882)	0.055 (0.016–0.649)	0.326 (0.049–4.614)
B	4 (0.5–19)	7 (4–45)	25 (10–290)	–
Ba	97 (41–613)	129 (64–765)	109 (54–198)	329 (107–815)
Be	0.7 (0.2–1.6)	0.4 (0.2–0.6)	0.6 (0.3–0.9)	0.2 (0.05–0.7)
Bi	0.3 (0.2–1.3)	1.6 (0.3–17)	1.8 (1.1–3.1)	1.9 (0.8–50)
Ca	1.10 (0.15–6.89)	8.0 (2.86–13)	6.35 (4.35–9.18)	5.75 (3.09–13.5)
Cd	0.32 (0.14–2.28)	1.32 (0.31–7.16)	2.97 (1.62–7.81)	1.12 (0.51–5.51)
Ce	28 (12–59)	18 (12–39)	20 (18–34)	14 (8–94)
Co	10.2 (5.5–32)	11.7 (6.0–22)	8.9 (5.8–19)	6.2 (3.1–22)
Cr	31 (16–74)	89 (26–1721)	61 (40–184)	65 (28–843)
Cs	1.56 (0.78–2.94)	0.81 (0.50–1.65)	1.84 (1.44–2.97)	0.69 (0.32–1.51)
Cu	40 (18–1347)	152 (51–105,240)	193 (80–2115)	140 (77–448)
Dy	1.81 (0.95–3.34)	1.39 (0.70–2.23)	1.60 (1.38–2.16)	0.72 (0.34–1.64)
Er	0.94 (0.49–1.64)	0.73 (0.41–1.14)	0.88 (0.67–1.17)	0.39 (0.15–0.64)
Eu	0.55 (0.31–1.03)	0.45 (0.23–0.76)	0.48 (0.35–0.76)	0.21 (0.12–0.33)
Fe	2.58 (1.34–4.54)	2.61 (1.74–6.85)	2.30 (1.79–4.28)	1.27 (0.71–3.84)
Ga	4.5 (2.1–9.5)	3.6 (2.6–4.9)	5.6 (4.6–7.5)	2.6 (1.0–7.3)
Gd	2.19 (1.18–4.26)	1.81 (0.93–3.34)	1.91 (1.47–2.97)	0.85 (0.40–1.41)
Hf	–	0.06 (0.01–0.20)	0.09 (0.01–0.17)	–
Hg	0.095 (0.032–0.807)	0.100 (0.043–1.837)	0.316 (0.168–4.647)	0.316 (0.089–5.462)
Ho	0.32 (0.18–0.55)	0.26 (0.16–0.38)	0.34 (0.27–0.49)	0.14 (0.06–0.24)
K	0.13 (0.07–0.25)	0.09 (0.03–0.28)	0.29 (0.22–0.54)	0.40 (0.12–1.75)
La	13.5 (5.8–29)	9.6 (6.4–21)	11.0 (9.6–23)	8.6 (4.9–84)
Li	19 (9.8–34)	12 (5.4–25)	18 (14.6–28)	9.2 (3.9–13)
Lu	0.10 (0.05–0.19)	0.09 (0.04–0.12)	0.11 (0.09–0.15)	0.05 (0.01–0.08)
Mg	0.79 (0.48–3.01)	4.09 (1.48–6.50)	1.30 (0.79–2.59)	1.21 (0.69–1.88)
Mn	613 (345–1483)	509 (335–1272)	474 (332–754)	306 (164–802)
Mo	0.9 (0.4–2.8)	5.7 (0.9–41)	5.5 (3.8–36)	2.9 (1.4–14)
Na	0.010 (0.006–0.105)	0.072 (0.039–0.279)	0.110 (0.070–0.200)	0.759 (0.352–2.426)
Nb	0.69 (0.32–1.39)	1.37 (0.80–4.70)	2.06 (1.44–2.99)	0.73 (0.34–1.08)
Nd	12.0 (5.8–27)	8.1 (4.8–18)	8.8 (7.7–18)	5.0 (2.23–15)
Ni	28 (15–63)	44 (22–221)	42 (25–104)	38 (26–142)
P	0.090 (0.049–0.328)	0.090 (0.053–0.139)	0.140 (0.100–0.450)	0.122 (0.073–0.349)
Pb	44 (19–626)	87 (32–2266)	424 (207–1208)	69 (32–573)
Pd	–	0.100 (0.005–4.788)	–	–
Pr	3.13 (1.46–7.32)	2.05 (1.39–4.73)	2.51 (2.04–5.09)	1.40 (0.57–3.39)
Pt	–	0.024 (0.006–0.214)	–	–
Rb	19 (11–34)	8.6 (5.2–21)	21 (18–34)	11 (6.8–22)
S	0.04 (0.01–0.27)	0.09 (0.02–0.51)	4.17 (1.93–6.90)	0.56 (0.25–1.87)
Sb	0.9 (0.38–12)	7.6 (0.71–17)	9.3 (4.9–16)	3.9 (2.7–18)
Sc	3.1 (1.8–8.6)	3.8 (1.6–5.5)	3.2 (1.7–3.9)	1.4 (0.7–2.4)
Se	0.4 (0.05–0.9)	0.2 (0.05–1.7)	1.9 (0.6–2.8)	0.3 (0.1–4.0)
Sm	2.48 (1.33–4.96)	1.71 (0.83–3.21)	1.93 (1.58–2.91)	0.88 (0.42–1.72)
Sn	2.3 (0.7–7)	26 (4–280)	23 (15–74)	23 (11–170)
Sr	20 (8.4–172)	62 (45–135)	126 (99–213)	100 (48–220)
Tb	0.33 (0.18–0.61)	0.24 (0.12–0.42)	0.31 (0.24–0.45)	0.14 (0.06–0.24)
Te	–	–	0.06 (0.03–0.12)	–
Th	2.0 (0.9–6.0)	2.2 (1.3–7.1)	2.3 (0.4–2.9)	0.4 (0.1–1.6)
Ti	0.026 (0.006–0.074)	0.110 (0.039–0.246)	0.050 (0.030–0.080)	0.023 (0.013–0.050)
Tl	0.17 (0.09–0.37)	0.09 (0.06–0.23)	0.27 (0.18–0.33)	0.07 (0.03–0.12)
Tm	0.12 (0.06–0.21)	0.10 (0.05–0.16)	0.12 (0.09–0.17)	0.04 (0.01–0.09)
U	1.1 (0.6–4.2)	0.9 (0.6–1.8)	2.4 (1.4–3.8)	0.7 (0.4–1.3)
V	32 (20–104)	43 (22–62)	69 (50–95)	17 (9–25)
W	–	1.4 (0.1–7.3)	2.6 (1.3–41)	1.4 (0.6–68)
Y	8.9 (5.2–15)	6.9 (4.2–10)	8.9 (7.1–13)	4.0 (1.9–6.2)
Yb	0.80 (0.43–1.40)	0.66 (0.34–0.98)	0.74 (0.57–0.91)	0.35 (0.15–0.55)
Zn	131 (54–1202)	509 (103–63,000)	1478 (597–6269)	716 (410–1517)
Zr	0.3 (0.05–2.5)	3.0 (1.2–11)	5.4 (1.2–9.2)	1.1 (0.3–19)
TOC	3.1 (1.2–12)	–	5.9 (5.0–9.4)	25 (12–37)

N = number of samples; [1]Gaberšek & Gosar (2018; sieved <2 mm, pulverized, HCl-HNO₃ digestion, ICP-MS).

following 17 elements have their highest medians in attic dust: As, Cd, Cs, Cu, Ga, Nb, P, Pb, S, Sb, Se, Sr, Tl, U, V, Zn and Zr. The medians of As (24 mg/kg), Cd (2.97 mg/kg), Pb (424 mg/kg), S (4.17%) and Zn (1478 mg/kg) in particular stand out in comparison with levels in other media, which indicate their higher emissions in the past and/or their long-term emissions. In contrast, only six elements (Ca, Co, Cr, Mg, Sc and Ti) have their highest medians in street dust and five in household dust (Ag, Au, Ba, K and Na). The medians of Bi, Ni and Sn in different types of dust are very similar and are all well above the soil median. The medians of the remaining elements are far higher in two of the four media: Fe in soil and street dust, Hg in attic and household dust, and Mo in street and attic dust (Table 1). The range of individual PTEs levels in different types of dust is usually quite wide, indicating

the influence of anthropogenic activities. By examining the spatial distribution of the elements' levels and using Spearman correlations of ≥0.7 we assessed the origin of the elements, focusing on PTEs.

Several groups of elements of at least partially anthropogenic origin were identified in the street dust samples: Ag-Au-Hg-Pd-Pt; Cd-Pb-Zn; Bi-Co-Cr-Cu-Fe-Mn-Mo-Ni-Sb-Sn-W; Ca-Mg (Fig. 2). The first and second groups are connected by the correlation between Ag and Cd, and the second and third by the correlation between Zn and Cu. The elements of the first group likely originate in part from dentistry, since their highest levels have been identified near the local dental practice and are regularly used in dentistry (Givan, 2014). It is well known that Pd and Pt also largely originate from the degradation of car exhaust catalysts (Sobrova et al., 2012). The highest levels of the majority of the
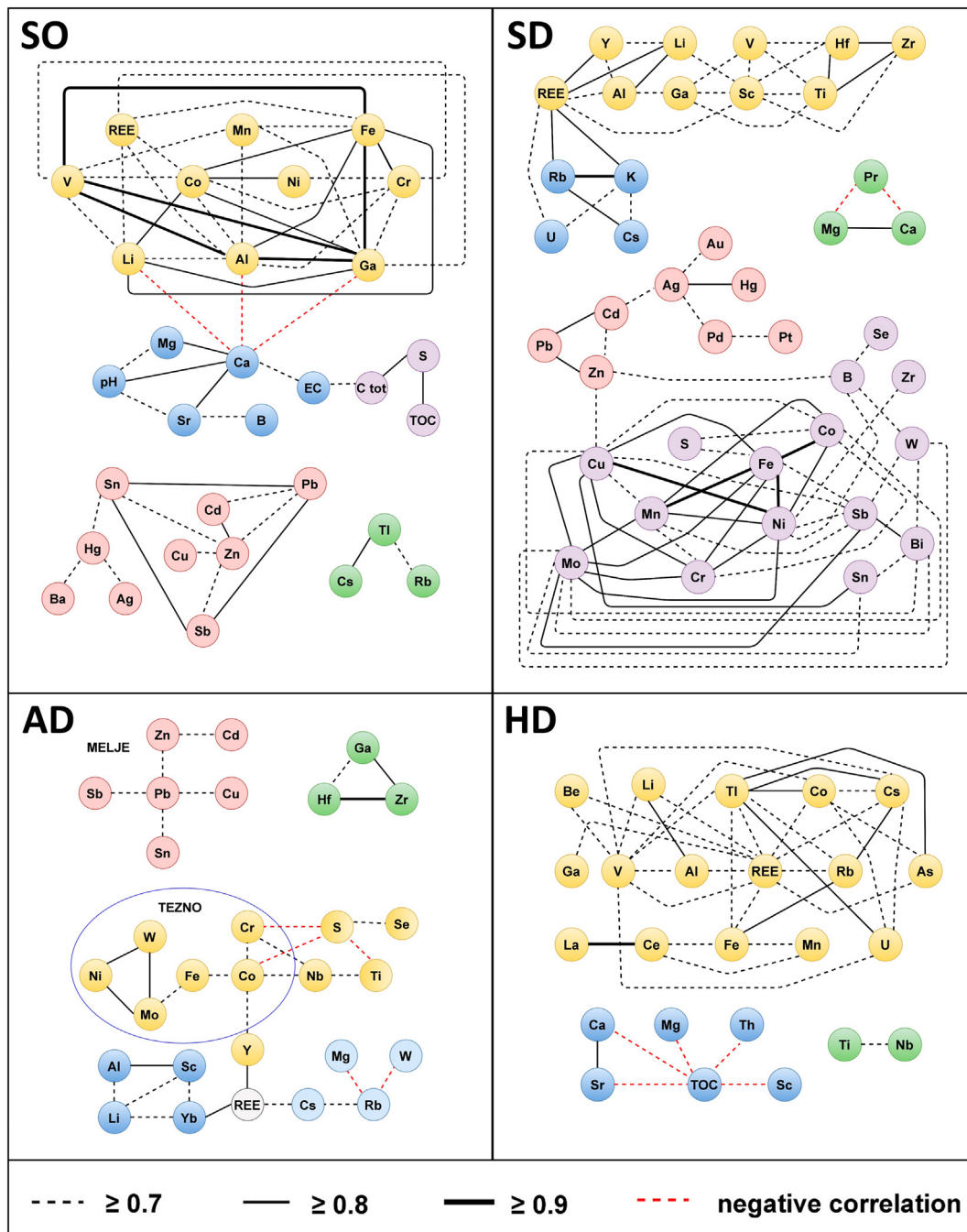

Fig. 2. A correlation diagrams showing Spearman rank correlations ≥0.7 of chemical elements in soil (SO) (Gaberšek and Gosar, 2018), street (SD), attic (AD) and household (HD) dust.

PTEs from the second and third groups were found in the two largest industrial zones (Melje and Tezno). This indicates that they predominantly originate from various metal-processing industries, which mask the traffic-related emissions of PTEs, which are generally one of the main sources of PTEs in street dust (Smichowski et al., 2008; Thorpe and Harrison, 2008; Amato et al., 2009; Grigoratos and Martini, 2015; Hwang et al., 2016; Ali et al., 2019). However, there are several differences between the two zones: the levels of Bi, Fe, Mn, Mo and W are much higher in Tezno and levels of Cr higher in Melje. The elements of predominantly geogenic origin in street dust are similar to those in soil and attic dust: Al-Ga-Hf-Li-Ti-Sc-V-Y-Zr-REE-Cs-K-Rb-U.

Two groups of PTEs of anthropogenic origin were identified in the attic dust. The first group consists of Cd-Cu-Sb-Sn-Pb-Zn (Fig. 2). Their highest levels are typical for the three sampling sites in or near the Melje industrial zone, where a foundry and a metal furniture factory have been operating since the early 20th century, and where a battery factory was once located. The determined levels of Cu in attic dust in this area (2115, 1908 and 726 mg/kg) are considerably higher than the median for the entire group of attic dust samples (193 mg/kg). The second group of PTEs of anthropogenic origin consists of Co-Cr-Fe-Mo-Ni-W, partially also Ba, Bi and Nb. Their highest levels were identified at the Tezno industrial zone, where several automotive and metal processing plants are located. The strongest correlations in this group have Mo-Ni-W (0.8–0.9), which are elements that are commonly associated with the ironworks and steel industry (Alijagić and Šajn, 2006; Teran et al., 2020). The elements of predominantly geogenic origin in attic dust were identified as Al-Cs-Li-Rb-Sc-REE and Ga-Hf-Zr (Fig. 2).

Interpreting household dust chemistry is more complex. It varies greatly from one dwelling to another, most probably as a result of differences in the habits and activities of the residents and the specific characteristics of the dwellings. High correlations (≥0.7) were found between the following elements: Al-As-Be-Ce-Co-Cs-Fe-Ga-La-Li-Mn-Rb-Ti-U-V-REE; Nb-Ti; Ca-Sr (Fig. 2). They are probably of predominantly geogenic origin. A group of elements of anthropogenic origin could not be identified using statistical methods. The only exceptions are Ce-Fe-La, which were associated with lighter use in dwellings where residents frequently smoke (this is discussed later). The anthropogenic origin of Ce and La is also confirmed by the fact that they do not show statistically significant correlations with other REEs. There are also some individual elements that can be associated with anthropogenic activities, such as Na with the use of table salt and Ba with the degradation of white wall paint, in which Ba-compounds are used as white pigments (van Alphen, 1998).

3.3. Characteristics and origins of PTE-bearing particles

The size, morphology and chemical composition of a total of 4195 PTE-bearing particles were analysed in all three types of dusts and PM. A comparison with the results of the SEM/EDS analysis of 4415 PTE-bearing particles deposited in snow in the same urban area (following the same procedure as described here) (Gaberšek and Gosar, 2020) was also made. The average sizes of the analysed particles are quite similar in all media: 7.1 μm, 4.3 μm, 6.3 μm, 4.5 μm, 5.2 μm in street, attic and household dust, PM and snow, respectively (Table 2). Based on the determined characteristics, the PTE-bearing particles were grouped into 9 larger groups. The proportions of these groups vary considerably between the different media (Table 2). Nevertheless, angular or irregularly shaped **Fe-oxide** particles predominate in all media (from 47.5% in AD to 72.6% in particles deposited in snow). They can originate from geogenic and anthropogenic sources, e.g. traffic (Slezakova et al., 2008; Miler, 2020). Spherical particles consisting mainly of iron and oxygen with lower levels of other PTEs were classified separately into the **Spherical Fe-oxides** group. Taken together, the particles of these two groups are the most numerous in all media (except household dust) in the Tezno industrial zone. Besides angular particles, particles with morphological

characteristics indicating their anthropogenic origin (probably from the metal industry), are also typical for this area. These are: spherical particles (full or hollow (Fig. 3a), with glassy, porous, skeletal-dendritic or plated surfaces, often containing Mn), thin sharp-edged shavings, partially melted particles, irregularly shaped particles with smooth, glassy or porous surface and various fragments. Smooth particle surfaces indicate partial melting during their formation, and cavities could have formed due to the expulsion of gas (Umbria et al., 2004; Miler and Gosar, 2015). These two groups of particles have the highest proportions in household dust next to the other industrial zone, Melje. Spherical particles of Fe-Ce-La-O (Fig. 3b) were found in this dwelling as well as other locations where residents smoke. Their occurrence coincides with the highest total Ce and La levels. Powell et al. (2002) discovered identical particles in household dust, but were unable to determine their origin. Since high Ce and La levels in household dust have been associated with the use of lighters (Rasmussen et al., 2017) and on the basis of our results we assume that Fe-Ce-La-O spheres originate from the use of lighters in smoker's homes.

In terms of media, *Spherical Fe-oxides* have the highest mean proportion in attic dust (12.1%), particles deposited in snow (8.8%), and street dust (7.5%). Their presence in PM is the exception rather than the rule. Similarly, another group of spherical particles **Spherical Si-particles** also has the highest mean proportion in attic dust (9.8%) followed by particles deposited in snow (3.5%), and household dust (2.1%). *Spherical Fe-particles* are more numerous in industrial areas, especially in Tezno, and *Spherical Si-particles* in residential areas in all media, except in household dust. Spherical particles composed of Fe, Si and various other elements and PTEs in urban areas originate from high-temperature processes, like the steel industry, metallurgical processes and the combustion of fossil fuels (Sokol et al., 2002; Umbria et al., 2004; Miler and Gosar, 2015; Ebert et al., 2012; Talovskaya et al., 2017).

The mean proportions of the group of **Sulphates/Sulphides** vary greatly between media. The highest mean percentages are found in household (20.4%) and attic dust (16.3%), where it is mainly represented by the irregularly shaped Ba-Zn-S-O (Fig. 3c) and Ba-S-O particles. This type of particle most likely originates from the degradation of white wall paint, where barite and lithopone (a mixture of barium sulphate and zinc sulphide) are used as white pigments (van Alphen, 1998). The Pb-particles (Pb-S-O (Cu, Zn) and K-Pb-S-O (Cu, Zn)-possible mineral: palmierite) are also quite numerous in attic dust in industrial areas. Particles of Fe-S are quite common in attic and street dust.

The group of **Other metal oxides** consists mainly of Cu and Zn oxides/carbonates, while some Pb and other oxides/carbonates are present. Their proportions are very similar among different media. Their origin is not precisely defined, as they can originate from both geogenic and anthropogenic sources. One of the exceptions is a thin, sharp-edged shaving composed of Ag-Pd-Cu-O (Au, U) (Fig. 3d), found in a street dust sample, taken outside of a dental clinic. The presence of this particle coincides with the highest total levels of these elements, which has already been described.

Particles of the groups of **Fe-silicates** and **Other particles** largely originate from geogenic sources. Their proportions are quite similar between media, with some exceptions (Table 2). The group of *Other particles* is mainly represented by the following particles: Ti-O (mineral rutile), Fe-Ti-O (often with Mn; mineral ilmenite), Zr-Si-O (mineral zircon), Ce-La-P-O (mineral monazite; Fig. 3e) and Y-P-O (mineral xenotime). All of these originate from the weathering of igneous and metamorphic rocks. Their presence in all media confirms the influence of geological sources on the composition of various media in urban areas.

The groups of **Fe-alloys** and **Other metal alloys** do not represent high proportions but are important for the identification and understanding of the anthropogenic sources of particulate matter and their fate in the environment. Particles of *Fe-alloys* have the highest mean proportions in PM (10.1%) and snow (6.8%), followed by street, attic and household dust (1.6–2.3%). This distribution structure indicates

Table 2
Mean proportions of groups (as %) of PTE-bearing particles and their average sizes in μm (in brackets ± standard deviation) in street (SD), attic (AD) and household (HD) dust, in airborne particulate matter (PM) and in PM deposited in snow.

	SD (N = 1419)	AD (N = 1294)	HD (N = 750)	PM (N = 732)	PM deposited in snow (N = 4415)[a]
Fe-oxides	68.8%	47.5%	55.5%	63.1%	72.6%
	(5.8 ± 9.6)	(4.2 ± 5.5)	(6.9 ± 10.4)	(3.8 ± 5.0)	(4.5 ± 8.1)
Spherical Fe-oxides	7.5%	12.1%	4.1%	2.3%	8.8%
	(6.7 ± 8.6)	(3.5 ± 5.5)	(4.3 ± 6.2)	(2.2 ± 2.1)	(3.2 ± 6.1)
Fe-alloys	2.3%	2.2%	1.6%	10.1%	6.8%
	(30.5 ± 27.1)	(14.1 ± 28.7)	(19.8 ± 18.5)	(10.1 ± 13.0)	(11.8 ± 11.1)
Fe-silicates	0.92%	0.23%	3.1%	5.2%	0.95%
	(28.0 ± 20.4)	(16.7 ± 4.7)	(21.9 ± 25.0)	(5.6 ± 5.9)	(10.7 ± 11.3)
Sulphates/Sulphides	7.0%	16.3%	20.4%	4.5%	2.2%
	(6.7 ± 11.8)	(3.0 ± 5.2)	(2.4 ± 6.4)	(2.3 ± 2.4)	(3.7 ± 5.4)
Other metal oxides	2.6%	3.0%	3.6%	2.2%	0.59%
	(5.6 ± 9.4)	(3.1 ± 2.5)	(3.9 ± 5.5)	(1.9 ± 0.7)	(6.1 ± 7.9)
Other metal alloys	0.63%	0.54%	0.13%	0.41%	0.09%
	(17.1 ± 21.4)	(18.2 ± 19.3)	(5 ± /)	(18.0 ± 13.6)	(19.6 ± 10.8)
Spherical Si-particles	0.92%	9.8%	2.1%	0.82%	3.5%
	(8.1 ± 10.7)	(4.8 ± 5.9)	(3.6 ± 1.1)	(2.1 ± 1.2)	(6.9 ± 4.8)
Other particles	9.3%	8.4%	9.5%	11.3%	4.4%
	(8.7 ± 13.0)	(4.6 ± 5.8)	(6.4 ± 10.7)	(3.3 ± 2.8)	(6.4 ± 5.8)
Average size of all PTE-bearing particles	(7.1 ± 11.9)	(4.3 ± 7.1)	(6.3 ± 10.9)	(4.5 ± 6.7)	(5.2 ± 8.3)

N = number of analysed PTE-bearing particles.
[a] Gaberšek and Gosar, 2020.

that their current emissions levels are higher than in the past. They are typically found in industrial zones and surroundings. Typical for the Tezno industrial zone are fragments, spheres, shavings and angular particles composed of Fe and Fe with other PTEs, especially Mn (Fig. 3f), originating from the metal processing industry. Overall, the most numerous particles in this group are thin, sharp-edged shavings made of Fe-Cr (Cu, Mn, Ni) and Fe-Cr-Ni (Cu, Mn), which is a type of stainless steel (Bell, 2014). Their shape indicates that they were formed during low-temperature mechanical processes. They are by far the most abundant in the Melje industrial zone and immediate surroundings, especially in PM (23% of all PTE-bearing particles in sampling site close to Melje), snow (21% of all PTE-bearing particles in sample from Melje; Gaberšek and Gosar, 2020), and street dust (5.1% of all PTE-bearing particles). Individual particles have also been found in attic and household dust in this area and elsewhere throughout the town. Their chemical and morphological characteristics are practically the same in all media (Fig. 3g, h), which indicates their physico-chemical stability. Their possible origins are the foundry and the metal furniture factory, which are located in this industrial zone.

On average, the group of *Other metal alloys* represents less than 1% of the PTE-bearing particles in all media and consists only of the Cu-Zn particles, mostly shavings (Fig. 4). They were identified only in the Melje industrial zone, near the foundry, which manufactures various products from Cu-Zn alloys. They occur in all media, with the exception of household dust. Along with Cu and Zn, they usually contain smaller levels of Pb, Cl and Fe, sometimes also Si, Al, S. Particles in street dust are often partially oxidised. Their morphological characteristics vary slightly among media. Cu-S-Cl crystals have crystallised on the surface of a Cu-Zn-Cl shaving in attic dust (Fig. 4a), most likely as the result of the reaction of atmospheric SO₂ and Cu in previously deposited particles. The Cu-Zn particles in street dust are somewhat more angular with a visually and chemically non-homogenous and partially porous surface (Fig. 4c, d). Particles with similar characteristics were also deposited in snow in the area (Gaberšek and Gosar, 2020; Fig. 4e). The Cu-Zn particles in PM samples are clearly different from those in other media: they do not have as many impurities as the same particles in other media and their surface structure (ribs, brighter areas enriched with Pb) is clearly visible (Fig. 4f, g, h). Certain described morphological and partial chemical differences can already occur during their formation or latter in the environment. The latter would indicate that

the Cu-Zn particles are not physico-chemically stable in the environment. Cu-Zn alloys (brass) can be exposed to various corrosion processes, such as dezincification (Zhang and Edwards, 2011). Even at 90% relative air humidity and an air temperature of 19.5 °C, some corrosion products (Cu₂O, ZnO) can form on brass surfaces (Qiu and Leygraf, 2011).

3.4. Summary

By applying principles associated with a holistic approach to the geochemistry of solid inorganic particles in the Maribor case study, we determined the following: (1) the mineralogical and chemical composition and individual solid particle characteristics of the studied media differ considerably; some differences are the result of differences in the processes to which they are exposed during their formation and later in the environment, while some are due to the influence of anthropogenic activities; (2) there are also some similarities between media: minerals of geogenic origin (e.g. monazite, rutile, quartz) are present in all media, which indicates the influence of natural sources on the composition of all media in urban areas and the fact that it is important to consider geological and pedological conditions in geochemical studies; (3) the highest levels of PTEs in all media, with the exception of household dust, are typical for the two main industrial zones; (4) street dust mainly reflects the influence of winter road maintenance and industrial activities, while traffic-related and other emissions are less pronounced; (5) comparison of the chemical composition of attic and street dust indicates that emissions of As, Cd, Pb, S and Zn were higher in the past; (6) comparison of the chemical composition of soil and street dust indicates that recent emissions of some PTEs have not yet particularly influenced the chemical composition of the soil; (7) the characteristics of household dust are mainly influenced by indoor activities and the properties of individual dwellings; the influence of smoking, salt use and degradation of white wall colour has been identified; (8) the study of the characteristics of airborne particulate matter and of particles deposited in snow is essential to identify the most recent sources of PTE-bearing particles; a particularly promising medium for the geochemical study of the urban environment is snow, which is an effective natural collector of airborne PM; (9) by comparing the results of the SEM/EDS analyses, several industrial sources of PTE-bearing particles and for some the fate of particles in the environment have been
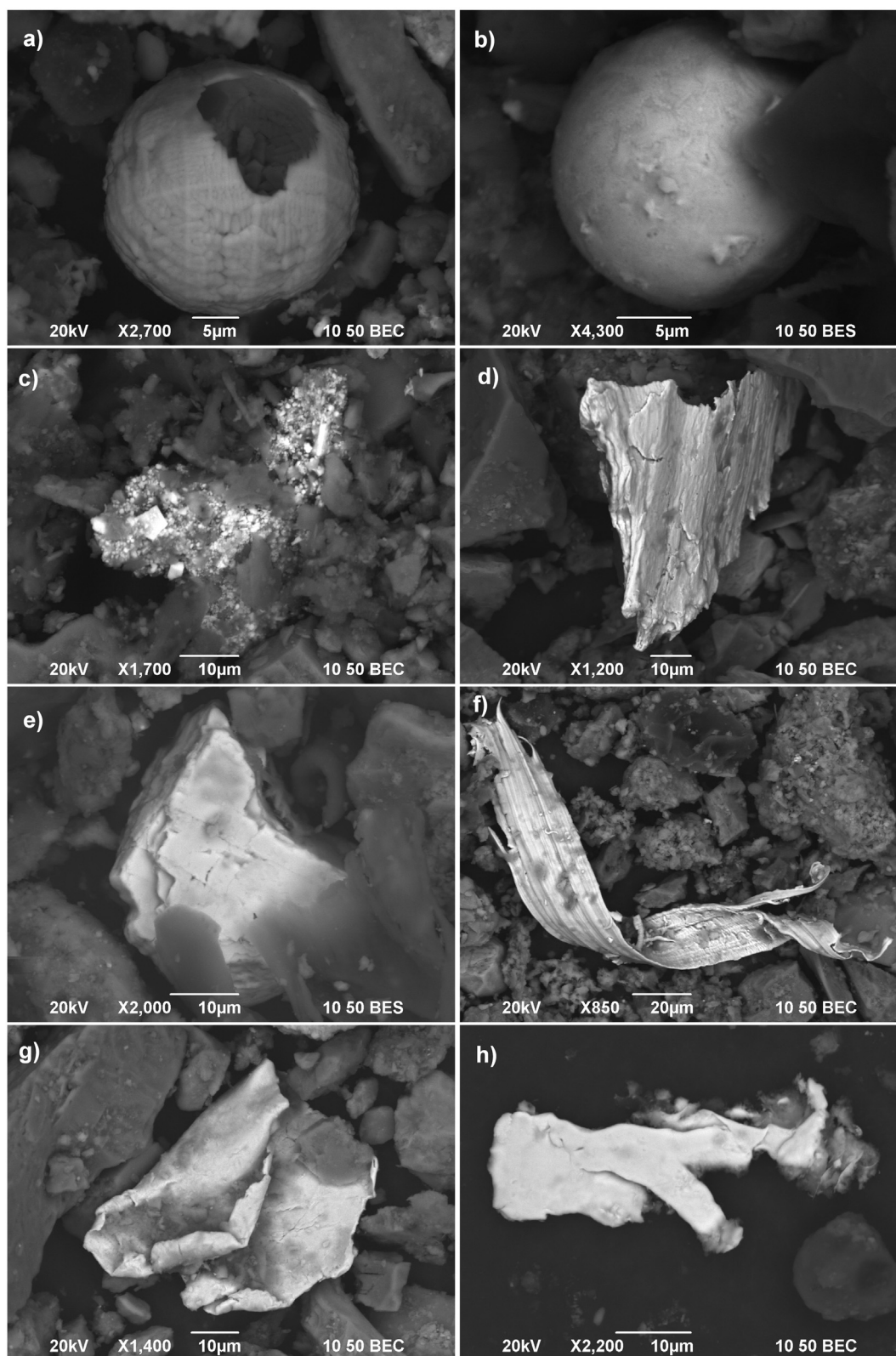
Fig. 3. SEM images of (a) skeletal-dendritic hollow Fe-O (Mn) sphere (AD); (b) Fe-Ce-La-O (Nd, Pr) sphere with smooth surface, probably originating from lighter usage (HD); (c) irregularly shaped Ba-Zn-S-O agglomerate with non-homogenous composition, probably originating from white wall paint (HD); (d) sheeted Ag-Pd-Cu-O (Au, U) shaving, probably originating from dental practice (SD); (e) angular Ce-La-Nd-P-O particle – mineral monazite (HD); (f) Fe (Cr, Cu, Mn) shaving (AD); (g, h) Fe-Cr (Cu, Mn, Ni) shavings, which probably originate from foundry and metal furniture factory in Melje, in snow and PM, respectively.

identified: the foundry in the Melje industrial zone is a source of Cu-Zn (Pb, Cl, Fe) airborne particles, which can react with atmospheric SO_2, and other corrosion processes may occur; the foundry and the metal furniture factory are the most likely sources of Fe-Cr (Cu, Mn, Ni) shavings, which appear to be physico-chemically stable in the environment; spherical Fe-O particles are typical for the Tezno industrial zone.

Fig. 4. Comparison of SEM images of morphologically different Cu-Zn particles, mostly shavings, which originate from a foundry in the Melje industrial zone: in attic dust (a, b), street dust (c, d), snow (e) and PM (f, g, h).

4. Conclusion

The presented study highlights the importance as well as some shortcomings of using a holistic approach to determine and analyse the geochemistry of solid inorganic particles in the urban environment.

We have confirmed that various environmental media are carriers of diverse geochemical information and that only the simultaneous study of as many of them as possible produces a satisfactory understanding of the biogeochemical cycles of chemical elements in environments as particular as urban areas. In addition to bulk chemical analyses, the analysis

of individual solid particles is of great importance in determining their characteristics, sources, dissemination, the processes to which they are exposed in the environment, and finally in successfully managing their anthropogenic emissions. The main drawbacks to using the holistic approach consist in the fact that it is time-consuming and requires substantial financial resources.

The results of these kinds of studies can benefit various groups of people, from environmental scientists to planning authorities and billions of individual citizens. The identification of areas with strong negative anthropogenic impacts and specific sources of PTE-bearing particles is essential for sound spatial planning and ensuring a healthy living environment. The presented study is not intended as an instructive call for holistic geochemical studies of urban areas, but as a driver for the further development of such studies and their increased application, the implementation of additional analytical methods (chemical and complementary) and studying a wide range of media.

CRediT authorship contribution statement

Martin Gaberšek: Conceptualization, Data curation, Methodology, Formal analysis, Investigation, Resources, Writing – original draft, Visualization. **Mateja Gosar:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that may have influenced the work reported in this paper.

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