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Geochemical investigations of potentially toxic trace elements in urban sediments of Idrija

Geokemične raziskave potencialno strupenih slednih elementov v urbanih sedimentih Idrije

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Abstract

Urban areas and associated human activities (industry, traffic, processes of mining and ore extracting, etc.) have induced anthropogenic emissions of potentially toxic trace elements (PTTE), which can present risk to living organisms and ecosystems in case of enriched levels. An example of such area in Slovenia is the Idrija town, the central part of the second largest Hg mining district in the world, which is heavily contaminated with Hg in all environmental compartments. The knowledge about levels and distribution of other PTTE in Idrija is very limited due to the outstanding Hg related problems. In this study the geochemical investigation of PTTE (As, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn) was performed in urban stream and road sediments of Idrija town for the first time. In addition, solid phases of PTTE were observed using SEM/EDS and their potential sources were assessed. The results show that the levels of PTTE in urban stream and road sediments are mostly below international guidelines, except for Cu some high values were measured in road sediments. The highest Cu level was determined in the vicinity of a commutator production industry. The associations of Cu with other elements in solid phases are very diverse, which is why the analyses could not reveal the specific source of high Cu levels.

Izvleček

Urbana območja in z njim povezane antropogene aktivnosti (industrija, promet, procesi rudarjenja in predelave rude, itn.) so pospešile antropogene emisije potencialno strupenih slednih elementov, ki lahko v primeru povišanih vrednosti predstavljajo tveganje za žive organizme in ekosisteme. Primer takega območja v Sloveniji je Idrija, osrednji del drugega največjega živosrebrovega rudarskega območja na svetu, ki je močno onesnažen s Hg v vseh segmentih okolja. Zaradi izjemnih problemov v povezavi s Hg je znanje o vsebnostih in porazdelitvi ostalih potencialno strupenih slednih elementov zelo omejeno. V tej študiji smo izvedli geokemično raziskavo potencialno strupenih slednih elementov (As, Cd, Co, Cr, Cu, Mo, Ni, Pb in Zn) v urbanih potočnih in cestnih sedimentih. Poleg tega smo z SEM/EDS metodo opazovali trdne faze potencialno strupenih slednih elementov in ugotavljali njihove potencialne izvore. Rezultati so pokazali, da so vrednosti potencialno strupenih slednih elementov v urbanih potočnih in cestnih sedimentih večinoma pod mednarodnimi smernicami, z izjemo visokih vrednosti Cu v cestnih sedimentih. Najvišja vrednost Cu je bila določena v bližini industrijskega obrata, v katerem proizvajajo komutatorje. Združbe Cu z drugimi elementi v trdnih fazah so zelo pestre, zato z analizo ni bilo možno oceniti specifičnega izvora visokih vrednosti Cu.

Introduction

Trace elements are chemical elements that occur in natural and perturbed systems in small amounts and among others include arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn) (Adriano, 1986) that were investigated in this study. All investigated trace elements are metals, except As, which is a metalloid (Adriano, 1986). Co, Cu, Mo and Zn are essential for the nutrition of higher plants, while Co, Cr, Cu, Mo, Ni and Zn are essential for animal nutrition (Adriano, 1986; Addiscott, 2006). The essential trace elements are those which cannot be substituted by others in their specific biochemical roles and they have a direct negative influence on the organism, if their supply is inadequate (Adriano, 1986; Kabata Pendias & Pendias, 2001). An inadequate supply of trace elements can affect the living organism in two ways: either there is a lack of a trace element in the living organism (deficiency) or an excess of a trace element in the living organism (toxicity). In both cases, the growth of a plant or an animal is abnormal, so it can neither grow nor complete some metabolic cycle (Adriano, 1986; Kabata Pendias & Pendias, 2001). As, Cd and Pb are non-essential, which means that no beneficial function to the living organisms has been recognized yet for them and furthermore, when these elements are present in sufficient concentrations they become toxic (Adriano, 1986; Kabata Pendias & Pendias, 2001; Addiscott, 2006). As explained above, all investigated elements can potentially cause harm to living beings in explicit conditions, this is why they are also called potentially toxic trace elements (PTTE). The sources of trace elements are primarily natural, such as soil parent materials (rocks) (Adriano, 1986). However, with urban development and associated human activities the anthropogenic sources of trace elements emerged, such as mining, industries and energy production, traffic, agriculture, construction- building materials, landfills and illegal waste dumps, etc. (Wong et al., 2006; Zupan et al., 2008). Anthropogenic influences induced PTTE emissions that often accumulate in earth materials of urban areas (urban materials) (Thornton et al., 2008; Johnson et al., 2011).

An example of contaminated urban materials are urban sediments of Idrija town (Slovenia), in which mercury (Hg) levels are several hundred times increased regarding to the European median for stream sediments due to the past Hg mining and ore processing activities (Bavec et al., 2014). Several natural and anthropogenic identified Hg sources (Čar, 1998; Čar & Terpin, 2005; Gosar & Čar, 2006; Mlakar & Čar, 2009, 2010; Kavčič, 2008) were recognised as sources of Hg in investigated sediments, such as outcrop of rocks containing Hg ore, former ore roasting sites, ore residue dumps and mine ventilation shafts (Bavec et al., 2014). After the Hg production was stopped in 1995, a commutator production industry evolved. In addition, Idrija is nowadays amongst higher urbanized areas in Slovenia that raised new scientific questions about accumulation of other PTTE in urban area of Idrija.

Therefore, in this study the levels of PTTE (As, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn) in the urban sediments of Idrija were determined and evaluated regarding to the European background for stream sediments and international guidelines. In addition, the solid phases of PTTE were observed and their potential sources were assessed.

Materials and methods

Site description and potential PTTE sources

Idrija town (Fig. 1), where past Hg mining district is situated, consists of a small densely populated centre with highly developed urban infrastructure along the rivers. The main river Idrijca flows through the district in the direction from south to north and has several tributaries (local streams). Another major stream, named Nikova, flows from the west and joins the river Idrijca in the centre of the town. The detailed surface water flow is presented in Fig. 1. For the majority of streams, regulation of natural waterways took place during the development of the town and consequently artificial channels were constructed. In addition, an urban drainage system has been established and runoff is discharged directly into the river Idrijca without any pre-

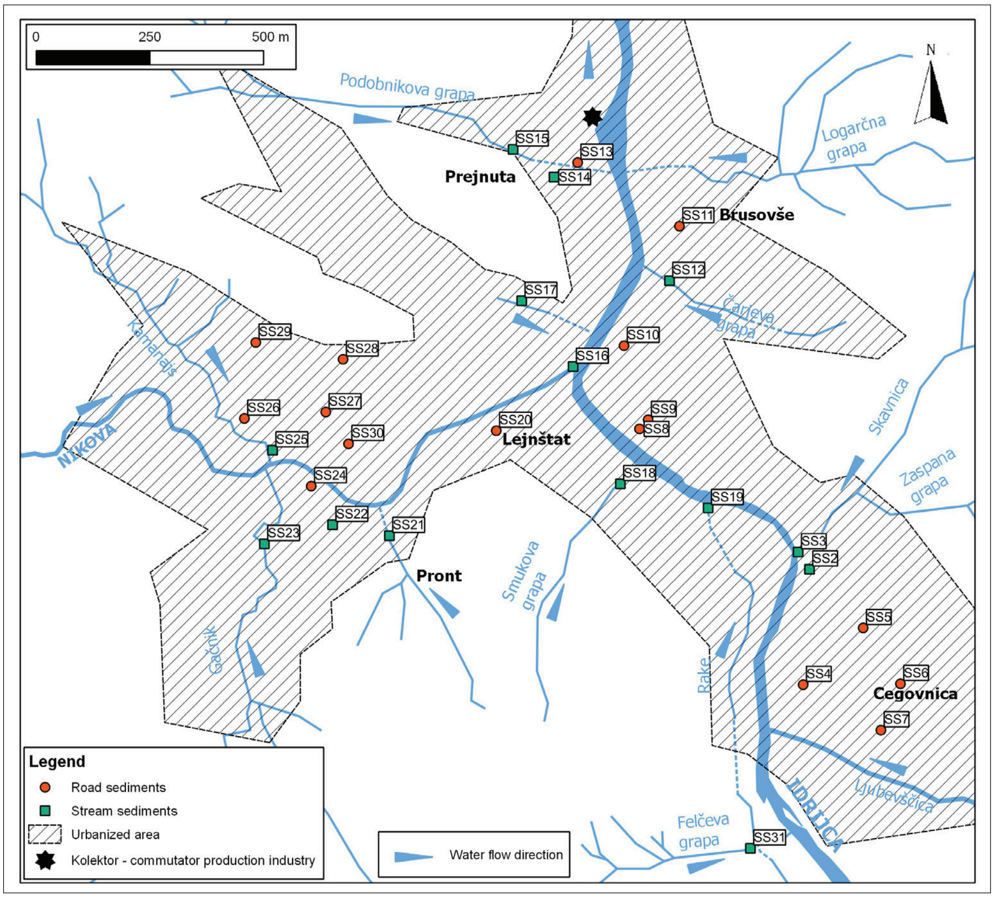

Fig. 1. Sediment sampling locations in the Idrija urban area and near surroundings (modified after Bavec et al., 2014).

treatment (Bavec et al., 2014). In Idrija town, the following trace element sources are recognised, besides local bedrock. There are two main roads following the rivers Idrijca and Nikova, where traffic is denser mostly during rush hours, while in the surroundings traffic is scarce. Ore deposit is monometallic, therefore Hg is the only mineral found in economically important quantities, while other elements occur only in traces or insignificant quantities (Čar, 1998). A commutator production industry is situated in the northern part of the town, where former Hg roasting facilities used to be. The industry started in the year 1963 as a small factory, but developed into a worldwide successful company as it is today (Kolektor, 2014). The biggest wastes in their manufacturing process are plastic and non-ferrous metals, primarily copper (Benčina, 2007).

Urban sediments

In the urban areas the major sites of sediment deposition are: street surfaces, gully pots and storm sewers, rivers, canals, docks and lakes (Fig. 2) (Taylor, 2007). Deposition and storage on street surfaces, gully pots and storm sewers is short term (in the order of days and month), while in canals, docks and on floodplains is longer term (in the order of years to decades, although they are not necessarily permanent due to erosion of floodplain banks and dredging of channels, canals and docks) (Taylor, 2007; Taylor & Owens, 2009).

Road-deposited sediment is the accumulation of particulate matter on street surfaces and it has received considerable attention in recent years, because it can be used to define current diffuse or local deposition of contaminants (Taylor, 2007; Johnson & Demetriades, 2011). Contaminated road sediment affects urban air quality and urban runoff. Gully pots are the first entry point of road runoff into the urban drainage network and are designed to trap some of the sediment carried by the runoff (Taylor & Owens, 2009). The processes acting within gully pots are complex. During runoff events (wet weather processes), denser particles in the water will settle under gravity. However, there is usually a high degree of turbulence within the gully pot, which not only limits the amount of sediment that will settle down, but may also lead to the erosion and resuspension of existing sediment in the pot. Biochemical changes also take place within the gully pot. Most biochemical changes take place during periods between runoff events (dry weather processes) (Taylor & Owens, 2009). Sediments within gully pots are neither wholly subaerial nor subaqueous, but experience both conditions episodically dependent on weather conditions (Taylor, 2007). The sources of road deposited sediments include vehicle exhaust emissions, vehicle tyre and body wear, break lining material, building and construction material, road salt, road paint and pedestrian debris, soil material, plant and leaf litter and atmospheric deposition (Taylor, 2007).

River bottom sediment is a mixture of mineral as well as organic material that is deposited on the bottoms of river channels (Taylor et al., 2008). In case of constant water flow, bottom sediment is often eroded or re-suspended within a channel by flowing water, so the composition of sediment is constantly changing. The sources of river sediments have much larger background than road sediments and include mainly weathering of rock by physical, chemical and biological processes and the actions of wind and rain as mobilizing and transporting agents. The main natural sources of sediment to river are atmospheric dust deposition and wind erosion, mass movement events (landslides, debris flows, etc.) and erosion of soils by water. Within the river corridor, also

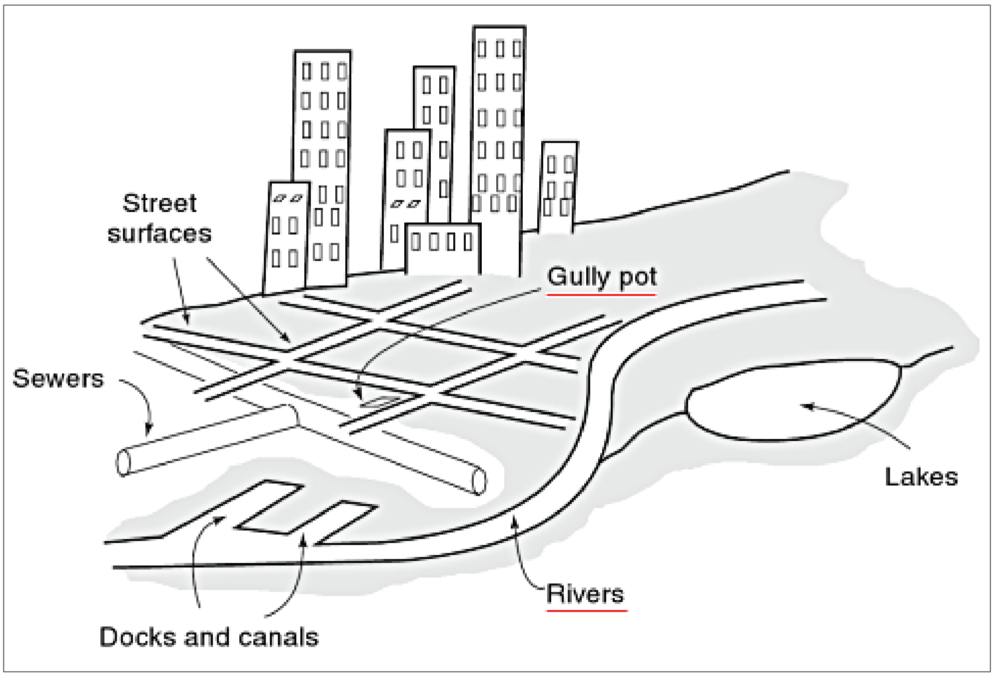

Fig. 2. Sites of sediment deposition in urban areas (after Taylor, 2007). In our study, sediments from gully pots and river channel beds (underlined with red) from Idrija urban area were investigated.

erosion of channel banks, floodplain deposits and resuspension of channel bed sediments contribute to sediment loads. Anthropogenic sources are mines, construction sites, urban road network and mineral and organic material from point sources and industrial sites (Taylor et al., 2008).

Sample collection

On 2.06.2011 two different types of urban sediments were collected - road sediments from gully pots of the urban drainage system (n=16) and active bottom stream sediments from the local streams flowing through the urban area (n=14). Altogether 30 samples were collected and sampling locations (Fig. 1) were spatially defined by a GPS device. The weather was sunny and windy and the last rain event (24-hour rainfall at 7 a.m. = 32.1 mm) was on 28.05.2011 (NMS, 2012). Approximately 1 kg of urban sediment was collected at each sampling site with a scoop and stored in polyethylene bags.

Sample preparation

In the laboratory, dry sieving was performed to collect two grain size fractions (<0.125 and <0.04 mm) for chemical analyses after aqua regia digestion. The preparation of samples for SEM/EDS analysis was performed according to Miler (2012). The sieved samples (n=5), (SS11 (<0.04 mm), SS13 (<0.04 mm & <0.125 mm), SS15 (<0.04 mm) and SS21 (<0.04 mm)) were mounted on a double-sided carbon tape with the surface of 25 mm^2 (the excess was blown off with compressed air) and sputter-coated with a thin layer of gold to achieve conductivity. Samples were analysed in a high vacuum using BSE mode on JEOL JSM 6490LV SEM coupled with Oxford INCA EDS system, comprising Oxford INCA PentaFET3 Si(Li) detector and INCA Energy 350 processing software at accelerating voltage 20 kV and working distance 10 mm. This instrument was used for qualitative chemical point analysis and for microphotographs in backscattered and secondary electron modes. Each analysed metal particle was characterized by its size, morphology and qualitative chemical composition measured by the EDS X-ray point analysis with an acquisition time 60 s. The particle size was determined by measuring their longest dimension using a measuring tool included in the JEOL SEM software.

Chemical analysis after aqua regia digestion

Pseudo-total levels of PTTE were determined with inductively coupled plasma (ICP) mass spectrometry (MS) after aqua regia digestion at AcmeLabs, Canada-Vancouver (accredited under ISO 9001:2008). Certified reference materials (CRM) and replicate samples were used to control the quality analysis and detailed description is provided in Bavec and co-workers (2015).

Scanning Electron Microscopy with Energy Dispersive Spectrometer

Solid phases of PTTE were investigated using the combination of scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). SEM/EDS analysis is useful to observe the morphology, chemical and mineral composition of individual solid particles on the micron level and thus serves as a complementary method to the conventional mineralogical and geochemical methods (Miler & Gosar, 2009a, 2009b, 2012, 2013; Teršič, 2011; Miler, 2012). Backscattered electron (BSE) images in the SEM display compositional contrast that results from different atomic number of elements and their distribution in solid particles, while the EDS enables qualitative and semi-quantitative chemical analyses and it allows to identify the elements that are present in the investigated samples as well as their relative proportions (atomic % for example) (Beane, 2004). The method is particularly effective for investigation of metals due to their chemical properties: metals are electron dense elements with high atomic numbers (Z) and effective electron backscatterers. Consequently they appear visibly bright in a low-Z matrix (Aragon et al., 2000; Bernaus et al., 2005; Miler, 2012). In this study the SEM/EDS analysis was used as a complementary method for investigation of PTTE asscociations in urban sediment particles.

Results and discussion

PTTE levels

The basic statistics of PTTE levels in the road sediment samples and stream sediment samples are presented in Table 1 and Fig. 3. To evaluate the PTTE levels in the studied sediments, the results were compared to the European background median levels (determined after aqua regia) of stream sediments (<0.15 mm) (Salminen et al., 2005) and to The New Dutchlist action values for sediments (MHSPE, 2014) (Table 1, Fig. 3). Median values were selected for comparison, because strong positive skewness, kurtosis (Table 1) and histogram inspection showed that the bulk of values for all elements were clustered around the median on the left side of the histogram.

Box and whisker plots of PTTE levels in urban sediments (Fig. 3) show that for elements As, Cd, Cr, Mo and Zn the ranges of levels are wider and the medians are lower in the stream sediments in comparison to the road sediments for both grain size fractions. For Cu, the ranges of levels are narrower and the medians are lower in the stream sediments in comparison to the road sediments for both grain size fractions. For Ni and Co the ranges of levels and their medians are similar in both types of sediments (road and stream). The differences in basic statistical distribution (As, Cd, Cr, Mo, Zn and Cu) in road and stream sediments suggest that their

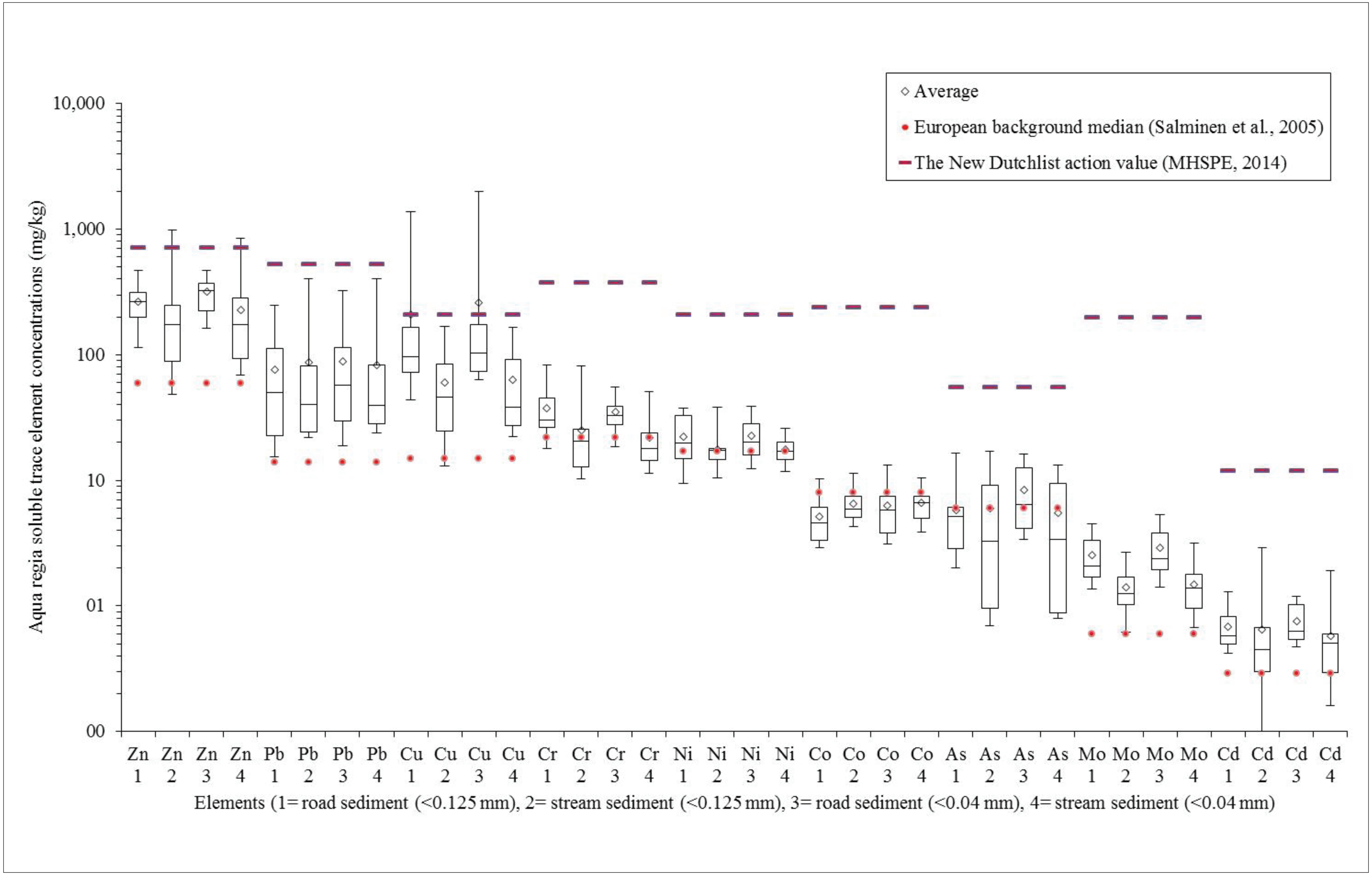

Fig. 3. Box and whisker plots of PTTE levels in urban road sediments (<0.125 mm and <0.04 mm) and stream sediments (<0.125 mm and <0.04 mm) of Idrija together with the European median background concentrations (determined after aqua regia) for sediments (SALMINEN et al., 2005) and The New Dutchlist action values for sediments (MHSPE, 2014)

Table 1. Basic statistics of PTTE levels in road (n=16) and stream sediments (n=16) for grain size fractions <0.125 and <0.04 mm

Element	Unit	LoD	Fraction	Type	x	Md	Ave	Min	Max	s	Skew	Kurt	
As	mg/kg	0.1	<0.125 mm	ROAD	0	5.2	5.7	2	16.5	3.6	1.9	4	6* 55**
				STREAM	0	3.3	5.9	0.7	17.1	5.7	0.9	-0.3	
			<0.04 mm	ROAD	0	6.4	8.3	3.4	16.3	3.4	0.6	-1.2	
				STREAM	0	3.4	5.4	0.8	13.2	4.8	0.4	-1.6	
Cd	mg/kg	0.01	<0.125 mm	ROAD	0	0.6	0.7	0.4	1.3	0.2	1.4	1.5	0.29* 12**
				STREAM	0	0.4	0.6	0.1	2.9	0.7	3.1	10.5	
			<0.04 mm	ROAD	0	0.6	0.7	0.5	1.2	0.5	0.7	-1.1	
				STREAM	0	0.5	0.6	0.2	1.9	0.4	2.5	7.7	
Co	mg/kg	0.1	<0.125 mm	ROAD	0	4.6	5.1	2.9	10.3	2.2	1.3	0.7	8* 240**
				STREAM	0	5.9	6.4	4.3	11.4	1.9	1.3	1.8	
			<0.04 mm	ROAD	0	5.8	6.2	3.1	13.3	3.1	1.1	1.1	
				STREAM	0	6.7	6.5	3.9	10.5	1.9	0.6	-0.2	
Cr	mg/kg	0.5	<0.125 mm	ROAD	0	30.4	37.1	17.9	82.9	17.6	1.4	1.7	22* 380**
				STREAM	0	20.4	24.8	10.3	81.7	18	2.5	7.1	
			<0.04 mm	ROAD	0	32.7	34.7	18.5	55.5	18.5	0.7	0.1	
				STREAM	0	18	21.4	11.4	50.5	10.6	1.9	3.4	
Cu	mg/kg	0.01	<0.125 mm	ROAD	0	96.5	206.8	43.9	1369.5	315.9	3.4	12.4	15* 210**
				STREAM	0	45.8	59.1	13	166.6	40.8	1.4	1.9	
			<0.04 mm	ROAD	0	102.4	254.7	63.8	1988.4	63.8	3.7	14.2	
				STREAM	0	38.2	62.5	22.3	166	43.8	1.3	0.7	
Mo	mg/kg	0.01	<0.125 mm	ROAD	0	2.1	2.5	1.4	4.5	0.9	0.7	-0.7	0.6* 200**
				STREAM	0	1.3	1.4	0.6	2.7	0.6	1	0.7	
			<0.04 mm	ROAD	0	2.4	2.9	1.4	5.3	1.4	0.8	-0.3	
				STREAM	0	1.4	1.5	0.7	3.2	0.6	1.4	2.6	
Ni	mg/kg	0.1	<0.125 mm	ROAD	0	19.9	22	9.4	37.4	9.3	0.6	-1	17* 210**
				STREAM	0	17.2	17.5	10.5	38	6.2	2.7	9	
			<0.04 mm	ROAD	0	20.1	22.2	12.4	39.1	12.4	0.7	-0.2	
				STREAM	0	17.1	17.3	11.8	25.9	3.6	0.7	0.6	
Pb	mg/kg	0.01	<0.125 mm	ROAD	0	50	75	15.4	246.7	65.6	1.6	1.8	14* 530**
				STREAM	0	39.9	85.2	22.1	402.8	104.5	2.4	5.8	
			<0.04 mm	ROAD	0	57.1	87	19	326.4	19	1.9	3.2	
				STREAM	0	39.3	82.1	23.8	401.8	100	2.7	7.5	
Zn	mg/kg	0.1	<0.125 mm	ROAD	0	266.7	258.7	114.4	471.8	86.2	0.5	1	59.5* 720**
				STREAM	0	172.4	222.7	48.1	984.5	228.5	2.9	9.3	
			<0.04 mm	ROAD	0	326.4	313	162.8	471.9	162.8	0.1	-0.8	
				STREAM	0	172.5	224	68.7	848.4	195.9	2.5	7.2	

Md= median; Ave= average; Min= minimum; Max= maximum; s= standard deviation; Skew= skewness; Kurt= Kurtosis; LoD = Limit of detection; x = Number of samples below lower LoD;* the European background median concentration (determined after aqua regia) for stream sediments (<0.15 mm) (Salminen et al., 2005); **The New Dutchlist action value for sediments (MHSPE, 2014) geochemical distribution is potentially impacted by anthropogenic activities, while not for Ni and Co. The ranges and the medians of levels in different grain size fractions of road and of stream sediments are similar for all investigated PTTE (Fig. 3), which indicates that different grain size fraction (<0.125 mm and <0.04 mm) does not affect the geochemical distribution of PTTE in urban sediments of Idrija.

In comparison to the European background medians for stream sediments (Table 1, Figure 3), As, Co, Cr and Ni levels are not enriched, Mo levels are enriched up to 9 times, Cd levels up to 10 times, Zn levels up to 17 times, Pb levels up to 29 times and Cu levels up to 133 times in urban sediments of Idrija. For these enrichments again anthropogenic influences are possible due to the urban settlement of the investigated area.

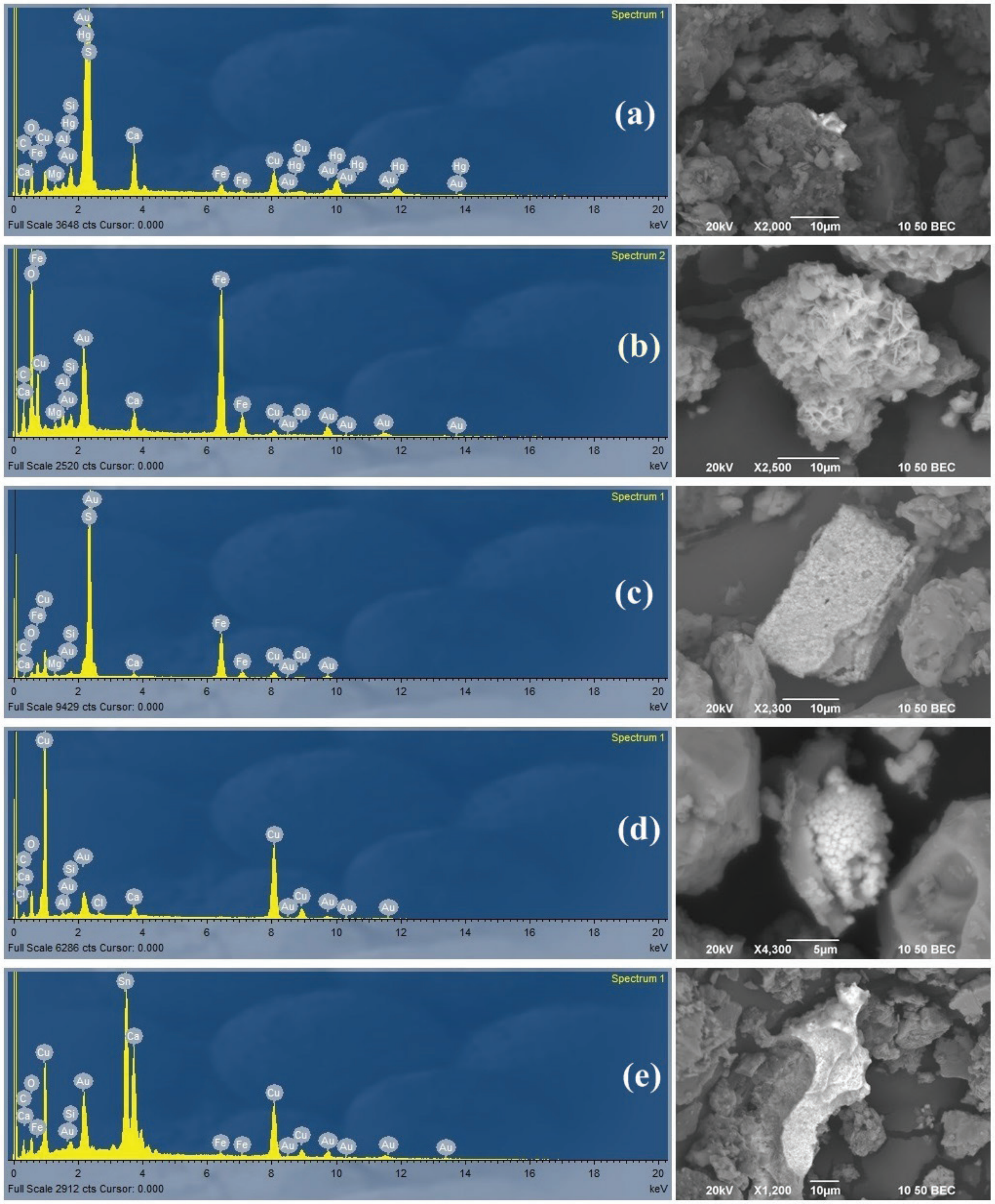

Fig. 4. Particles containing Cu in associations with the following elements: (a) Hg-S-Cu, (b) Fe-O-Cu, (c) Cu-Fe-S, (d) pure Cu (e) Sn-Cu

In comparison to The New Dutchlist action values (MHSPE, 2014) (Table 1, Fig. 3), almost all investigated PTTE are below it, except Cu and Zn. In case of Cu the levels exceed The New Dutchlist action value (210 mg/kg; MHSPE, 2014) in 3 road sediments (SS8, SS13 and SS29). The sample SS8 contains 305 mg/kg of Cu in the grain size fraction <0.125 and 350 mg/kg in the grain size fraction <0.04 mm. The sample SS13 contains 1370 mg/kg of Cu in the grain size fraction <0.125 and 1989 mg/kg of Cu in the grain size fraction <0.04 mm. The sample SS29 contains 434 mg/kg of Cu in the grain size fraction <0.125 and 415 mg/kg of Cu in the grain size fraction <0.04 mm. For the extra high Cu levels that were determined in the sample SS13 (<0.125 & <0.04 mm), two potential sources were observed. First is the vicinity of the manufacturing facilities of the company Kolektor. As already mentioned, the company Kolektor is a commutator production industry, which started in 1963 as a small factory, but developed into a worldwide successful company as it is today. Its manufacturing facilities are located on the right and on the left bank of the river Idrijca in the northern part of Idrija, where Hg ore roasting facilities used to be. Benčina (2007) also mentions that the company uses three types of water: sanitary, cooling and technology. The cooling water that is used for the cooling of the machinery from the production process is collected from the river Idrijca and after use it is returned back into the river Idrijca. The exhaust of cooling water that is released back into the river Idrijca is constantly monitored (Benčina, 2007). Second possible source of Cu is the Hotel Jožef that is situated near the road shaft. The cladding of the hotel consists mainly of an alloy of iron with the addition of copper (Hotel Jožef, 2015). The reason for high Cu enrichments in the samples SS8 and SS29 are unknown. It is possible that there was some current local source of Cu spilled in the road shaft prior to the sampling. In the rest of the road samples Cu levels were low and in the stream sediment samples even lower. Copper enrichments are very local, but this indicates an obvious anthropogenic disturbance. In need of a special attention are sediments from the location SS13, because the concentrations are extremely high. In case the Cu loadings are constant, this could potentially cause negative local disturbance, since the sediments are discharged directly into the river Idrijca without any pre-treatment. In case of Zn the levels exceed The New Dutchlist action value (720 mg/kg; MHSPE, 2014) in one stream sediment (SS22) that contains 984.5 mg/kg of Zn in the grain size fraction <0.125 and 848.4 mg/kg of Zn in the grain size fraction <0.04 mm. The source for high Zn value in the sample SS22 could not have been recognized.

Solid phases of PTTE regarding to SEM-EDS

Using SEM/EDS Cu was the only element abundantly recognized among the investigated elements in PTTE bearing phases, and even Cu particles were abundant in only one sample - SS13, which contained the highest Cu level. Some very interesting Cu associations with elements were observed (Fig. 4). Because of the diversity of Cu mineral phases, both grain size fractions (<0.125 and <0.04 mm) were inspected. Following element associations were recognised:

- Cu with Hg and S in atomic ratio Hg : Cu : S = 4.07 : 4.72 : 8.30 (Fig. 4 example (a)). The size of the particle is 6 μm. This particle is not recognised as any known mineral Hg phase. However, we propose two possible origins of the element associations Hg-Cu-S. Firstly, based on the assumptions that Cu ore is not present in Idrija Hg ore deposit, that current industry (Kolektor) uses Cu-based alloy for the production of commutators for electrical motors (Ule et al., 1994) and that the biggest waste in the manufacturing process of commutator production is primarily copper (Benčina, 2007), it is possible that Hg-Cu-S associations are of secondary origin (anthropogenic). It should be noted that the Hg-Cu-S associations were found in the sediment collected in a gully pot that is situated in the immediate vicinity of the Kolektor manufacturing facilities. Secondly, Drovenik and co-workers (1980) performed spectrochemical analyses of cinnabar and metacinnabar from Idrija ore deposit and found out that they contain from 1 to 200 mg/kg of Cu. Therefore, it is possible that Cu was concentrated in secondary metacinnabar during roasting of cinnabar ore.
- Cu with Fe and O in atomic ratio Cu : Fe : O = 0.50 : 10.35 : 55.52 (Fig. 4 example (b)). This particle is a secondary authigenic (crystalized in situ) iron oxyhydroxide that has a rosette like morphology, which most probably entrapped traces of Cu into the crystals during growth (Cu partially substitutes for Fe in iron oxyhydroxide). Cu has a high tendency to bound to iron oxyhydroxides during low pH conditions. The size of the particle is 32 μm.
- Cu with Fe and S in atomic ratio Cu : Fe : O: S = 2.81 : 12.97 : 14.09 : 29.78 (Fig. 4 example (c)). This mineral phase is probably a product of iron sulfide oxidation and the mineral phase is recognised as an oxyhydroxy sulphate containing Cu (Cu partially substitutes for Fe in partially oxidised pyrite (iron oxyhydroxy sulphate)). The particle size is 32 μm.
- Metallic Cu in atomic ratio Cu = 28.53 (Fig. 4 example (d)). This is a pure copper particle and it is undoubtedly anthropogenic, which is shown by its morphology. The shape of a particle is partialy rounded, composed of micron-sized crystals and it appears hollow. The size of the particle is 14 μm.
- Cu with Sn in atomic ratio Sn : Cu = 13.3 : 13.51 (Fig. 4 example (e)). This is an anthropogenic particle (Sn-Cu alloy), known as bronze. The size of the particle is 82 μm.

A diversity of Cu mineral phases was observed in the sample SS13 and some particles are obviously of anthropogenic origin.

Conclusions

The investigation of levels of potentially toxic trace elements (As, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn) in urban stream and road sediments revealed that they are mainly within European background and below The New Dutchlist action values, only for Cu local enrichments were discovered in road sediments. Particularly in one road sediment an extremely high Cu level (1989 mg/kg) was determined in the vicinity of a commutator production industry. The Cu particles were inspected by SEM/EDS analysis that revealed a diversity of Cu associations with other elements in solid phases.

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