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Organic compounds in the urban dusts in Celje area

Organske spojine v urbanih prahovih na območju Celja

Gorazd ŽIBRET

Geological survey of Slovenia, Dimičeva ulica 14, SI – 1000 Ljubljana, Slovenia;
e-mail:gorazd.zibret@geo-zs.si

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Abstract

This paper presents the results of the analysis of organic chemicals in different urban dusts. The aim of the research is preliminary evaluation of the presence of organic contaminants in household dust, attic dust and street sediment. Celje area has been chosen as a pilot study site due to availability of sampling materials from previous sampling campaigns. Samples have been tested to the presence of 120 organic compounds. Attic dust contains 98 different organic compounds or 82 % of all measured. Terpenoids, alkylbenzenes and different Polycyclic Aromatic Hydrocarbons (PAH's), as well as plasticizers, halogenated compounds (among them also PCB's) and pesticides (DDT and degradation products) can be found there. It also contains all of the in this study analysed US-EPA priority pollutants. Street dust contained 70 different organic chemicals (58 %), among them 14 priority pollutants. Traces of aliphatic organic compounds, PAH's, aldehydes and ketones, esters, and plasticizers are found there. House dust contains lowest number of organic compounds. Among 45 detected (38 % of total measured), 8 are priority pollutants. Aliphatic compounds, alkylbenzenes, aldehides, ketones, acids and PAH's can be found there. Current number of analysed samples, as well as only qualitative evaluations were made does not allow making any solid interpretation of obtained results in regarding to the potential sources of chemicals or potential environmental hazards. This study can thus be used only as a guideline for future studies of organic chemicals in urban dusts.

Izvleček

Na območju Celja je bilo do sedaj opravljenih veliko raziskav onesnaženja s strupenimi kovinami. Vendar pa je bilo opravljenih premalo raziskav v povezavi s tematiko onesnaženja z organskimi spojinami na tem območju. Zato je namen te raziskave preliminarno ugotoviti, katere organske spojine so prisotne v prahovih na tem območju. Zaradi bremen iz preteklosti lahko pričakujemo tudi obremenjenost okolja na področju onesnaženja z organskimi spojinami. Vzrokov je več, izpostavimo pa lahko poleg rastlinstva in mikrobnega delovanja, ki je naravni vir organskih spojin, potencialne antropogene vire, ki so: izhlapevanje spojin iz deponij katrana na območju stare Cinkarne (zaradi proizvodnje tehničnega plina iz premoga v preteklosti), delovanje današnje kemične, papirne in lesno-predelovalne industrije, promet in drugo izgorevanje fosilnih goriv, izhlapevanje spojin iz asfaltiranih površin in gradbenih materialov ter druge vire. V gospodinjstvih pa lahko k prej naštetim virom dodamo tudi uporabo kemikalij (barvila, laki, topila ipd.) in proizvodov, ki vsebujejo kemikalije (pohištvo, gradbeni materiali, tekstil, plastični izdelki ipd.), kajenje, kuhanje na plinu in ostale vire. V tej raziskavi smo analizirali vzorec podstrešnega prahu, ki kaže na „zgodovinsko" onesnaženje zraka, vzorec cestnega prahu, ki kaže na današnje stanje zraka in vzorec hišnega prahu, ki kaže na morebitno izpostavljenost ljudi. Analiziranih je bilo 120 različnih organskih spojin po metodi plinske kromatografije in masne spektroskopije, od tega jih 17 spojin spada pod t.i. prioritetna onesnažila, ki so na seznamu ameriške agencije za okolje. Podstrešni prah vsebuje največ različnih spojin (82 % od vseh analiziranih), od katerih so zastopane skoraj vse skupine (tabeli 1 in 2) organskih spojin. Najbolj značilne skupine so: terpenoidi, alkilbenzeni in policiklični aromatski ogljikovodiki in produkti delnega razpada le-teh. Zanimivo je tudi, da podstrešni prah vsebuje sledi DDT-ja (uporaba v kmetijstvu) in PCB-ja (industrija), ki sta oba že več kot 40 let prepovedana, a njihove ostanke še vedno lahko najdemo v njem. Cestni prah vsebuje 58 % vseh analiziranih spojin, od katerih so značilne skupine: policiklični aromatski ogljikovodiki, aldehidi in ketoni, etri, amini in plastifikatorji. Hišni prah vsebuje najmanj različnih spojin (38 % vseh analiziranih). V njem najdemo terpenoide, alkilbenzene, policiklične aromatske ogljikovodike, aldehide in ketone ter organske kisline. Od 17-ih analiziranih US-EPA prioritetnih polutantov, v podstrešnem prahu najdemo sledi prav vseh, v cestnem prahu 14 in v hišnem prahu 8 različnih. Ker v tej raziskavi ne razpolagamo s koncentracijami, ampak le s prisotnostjo snovi, prav tako pa je vzorcev malo, pa še ti so bili odvzeti zgolj na območju, kjer pričakujemo najvišjo stopnjo onesnaženja, ne moremo delati prav nobenih ocen, kakšni so morebitni viri spojin in ali predstavljajo prisotnosti rakotvornih spojin tveganje za okolje in zdravje ljudi. Analiz organskih spojin je draga metoda, zato je dodana vrednost te raziskave v tem, da lahko sedaj bolje načrtujemo morebitne nove raziskave organskih onesnažil v prahovih in okolju in ne „zapravljamo" denarja za analize spojin, katerih ne najdemo. S tem lahko zmanjšamo morebitne stroške. Avtor se zahvaljuje Radim Lána, ki je opravil analize, in Evi Franců (oba iz Češkega geološkega zavoda, izpostava Brno), ki je kot vodja laboratorija omogočila kemijsko analizo.

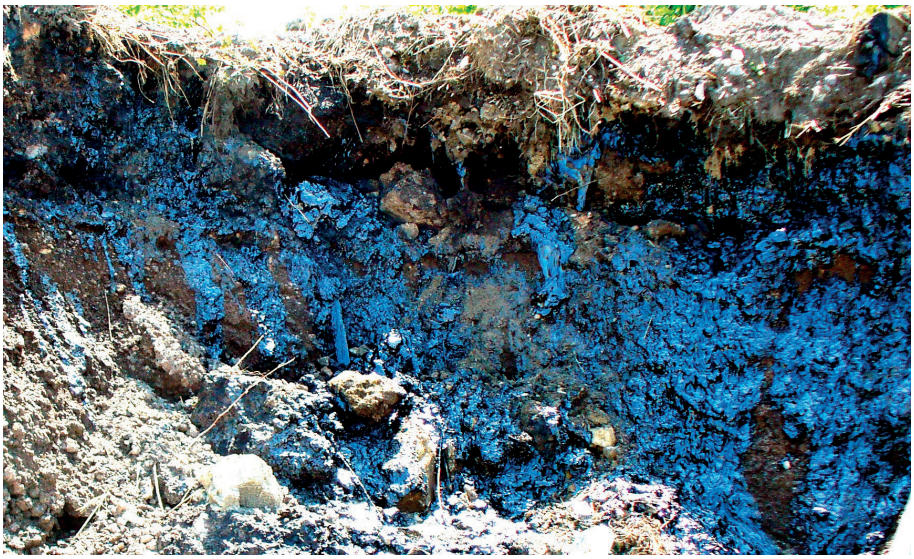

Fig. 1. Pyrometallurgical waste deposit and tar creosote around past Zn smelting furnaces in Celje.

Introduction

Celje area is well known for its environmental contamination. In the past studies main focus has been put on the evaluation of toxic metals contamination in soil due to past smelting and ironworking activities (Frančiškovič-Bilinski et al., 2006; Leštan et al., 2003; Lobnik et al., 1989; Šajn, 2005; Zupan et al., 2000; Žibret, 2002, 2008; Žibret & Šajn, 2008). But few researches have been done regarding the evaluation of organic pollutant contamination in the area, and even existing studies are focused mainly on the presence of very limited list of organic pollutants in drinking water.

This article presents the results of the chemical analyses of urban dusts in the Celje area by the means of gas chromatography / mass spectrometry. The focus has been put on the detection of the presence of 120 different organic substances. Description of the research area gives the main reason why the Celje area needs such pilot study. Materials and methods chapter describes the sampled materials, samples preparation, samples handling and chemical analyses. In the Results chapter results are presented and evaluated in the Discussion chapter. Main conclusions are presented in the Summary chapter.

Description of the research area

Celje, the third biggest town in Slovenia with the inhabitants around 50.000, lies in Celje basin in central Slovenia. It is surrounded with the Sava folds hills on the south (up to 1200 m above sea level) and with the Periadriatic lineament hill range on the north (1100 m above sea level). On the east side there is Voglajna River valley and on the west side the open space of Savinja River valley dominates.

Mayor pollution from the past was caused by zinc smelting by Cinkarna Celje plant. In its 100-year history of operation (between 1870 and 1970) approximately 500.000 tons of raw zinc has been produced (Žibret, 2008). On the peak of the production there has been 12 pyrometalurgical furnaces operating. This resulted in high rate of environmental pollution, caused by airborne particle sedimentation on the wider area of Celje basin. The Zn smelting process required highly caloric burning material, which was produced by coal gasification process. Formation of brownfield, containing highly toxic pyrometallurgical waste and coal tar creosote (Fig. 1) around past furnaces is a direct follow-up of zinc production. There were also other possible sources of organic chemicals, like Štore ironworks, traffic, small furnaces for heating of houses, chemical, paper and wood processing industry, metal manufacturing, domestic use of chemicals and products containing chemicals. Taking into account organic pollutants in Celje area several possible sources can thus be identified:

- Evaporation of volatile organic compounds from tar creosote in Celje brownfield area;
- Emissions from traffic;
- Past and present coal and other fossil fuel combustion for heating of houses and other purposes, including cooking with natural gas;
- Intensive hop and other crops farming west from Celje area and substantial use of phytopharmaceuticals;
- Emissions from Celje industry, including chemical industry, as well as wood processing, paper industry and others;
- Vaporisation of compounds from asphalt (tarred) surfaces and other construction materials;
- Domestic indoor and outdoor uses of chemical products or products containing chemicals.

Since atmospheric dust particles can travel distances of several hundred km from their source to their deposition, regional influences to the composition of the urban dusts might also be mentioned here. Two coal-powered power stations exist in the vicinity of Celje. The first one is Šoštanj power station, located 21 km NW and the other one is Trbovlje-Hrastnik power station,

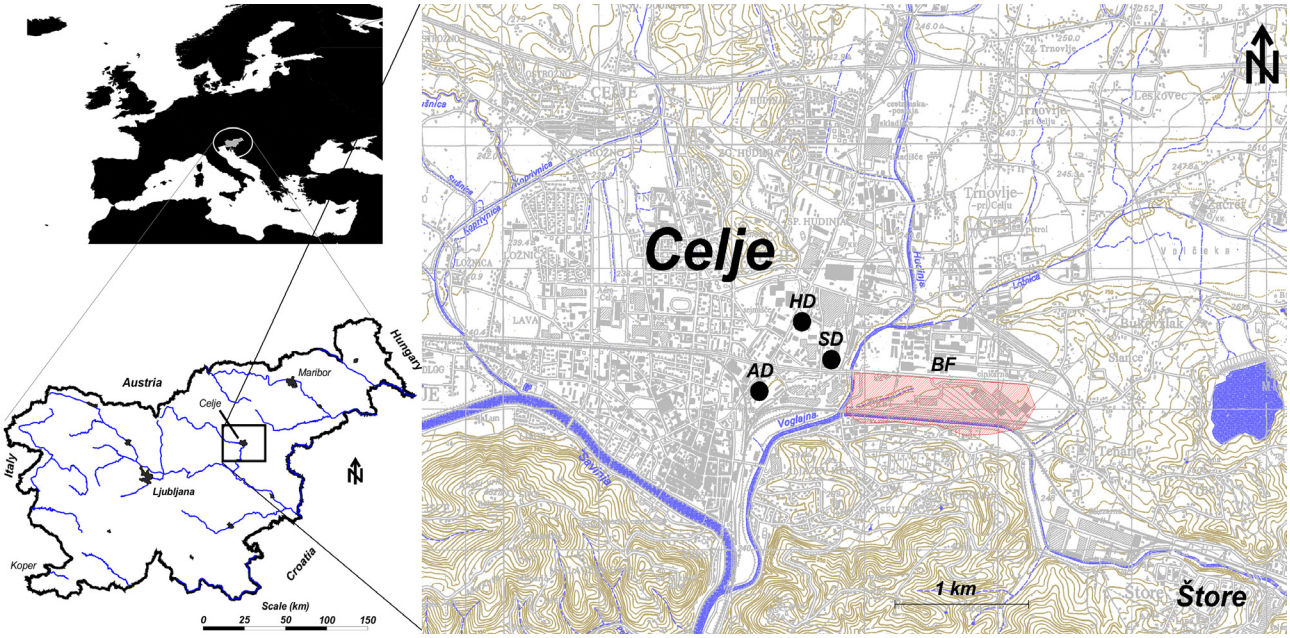

Fig. 2. The map of Celje area indicating the position of sampling points. HD - house dust sampling point; AD - attic dust sampling point; SD - street dust sampling point; BF - approximate area of pyrometallurgical slag and coal creosote deposit.

located 20 km SW. Cement factory is also located next to the aforementioned power plant. Mayor wind direction is SW wind. During the winter period, temperature inversion with fog is an important factor which influences the transportation of atmospheric particles.

Materials and methods

Three sampling materials have been chosen: attic dust, household dust and street sediment because of their availability from past studies (Žibret, 2002; Žibret & Rokavec, 2010). Positions of the samples are shown on Figure 2.

Attic dust has been sampled in the attics of old house in the vicinity of past Cinkarna Celje smelting plant and Celje brownfield where the highest Zn-Cd-Pb contamination has been detected (Šajn, 2005) and there is clear influence of Cinkarna Celje to the chemical composition of soil and attic dust detected. This sampling point also lies next to the busiest road in Celje (Mariborska Street). Attic dust is formed by the deposition of airborne particles. Being situated under the roof it is preserved from rain, heavy winds or sun's radiation, so it contains the record of past atmospheric pollution from the time the house was build. Its composition is not influenced by everyday activities of the inhabitants of the house (Balbanova et al., 2011; Bačeva et al., 2011; Šajn, 2006 and others). Sample was taken from the wooden roof bearing trams using plastic brush. Special attention was put not to sample possible roof tiling dust, sand from walls or possible plant remains. Sample in this study was collected in September 2001 in a building constructed in the beginning of 20 century, as a part of the other project, which aim was to evaluate the extent of toxic metal contamination in Celje area (Žibret, 2002; Šajn, 2005).

Street dust is regarded as a sink of atmospheric dust in urban environments (AYRAULT et al., 2013). It shows the contamination with particulate matter in the period of past 6 - 12 months. The reason for this is that storm events remove only a minority of the particles, deposited on the road surface (Chiew et al., 1997; Malmquist, 1978) and during rain events its composition is changed in the sense that larger particles are washed up so smaller particles prevail (Vaze & Chiew, 2002). Such dust cannot be removed by street sweeping, since street sweeper machines efficiently remove only particles larger than 0.25 mm, but they do not affect much of the particles below that size (Bender & Tarstreip, 1984). Therefore atmospheric deposit and pollutants build-up occurs on dry days and electrostatically bound to the pores in the asphalt or concrete in the form of street dust. Sample of street dust was brushed from the road surface with the hard plastic brush (Fig. 3) prior sweeping the road with the soft broom to remove sand particles. Approximately of 2 m^2 of road has to be brushed to collect enough atmospheric deposit. Road was brushed on 10-15 places in the radius of 20 m around sampling point to eliminate possible small-scale sample composition fluctuations. Importance of studying the street dust lies in the fact, that re-mobilised street dust by traffic is a dominant source of inhalable particles in urban environments (Amato et al. 2009; Piña et al. 2000; Sutherland, 2003).

Household dust reflects ambient air pollution and pollution from other sources, indoor and outdoor (ABT et al., 2000; TONG, 1998). The importance of studying house dust lies in the fact that this is the material we are exposed daily. Its latency is between 1 to 3 months. Its composition depends on the size of the house, dwelling habits of the inhabit-

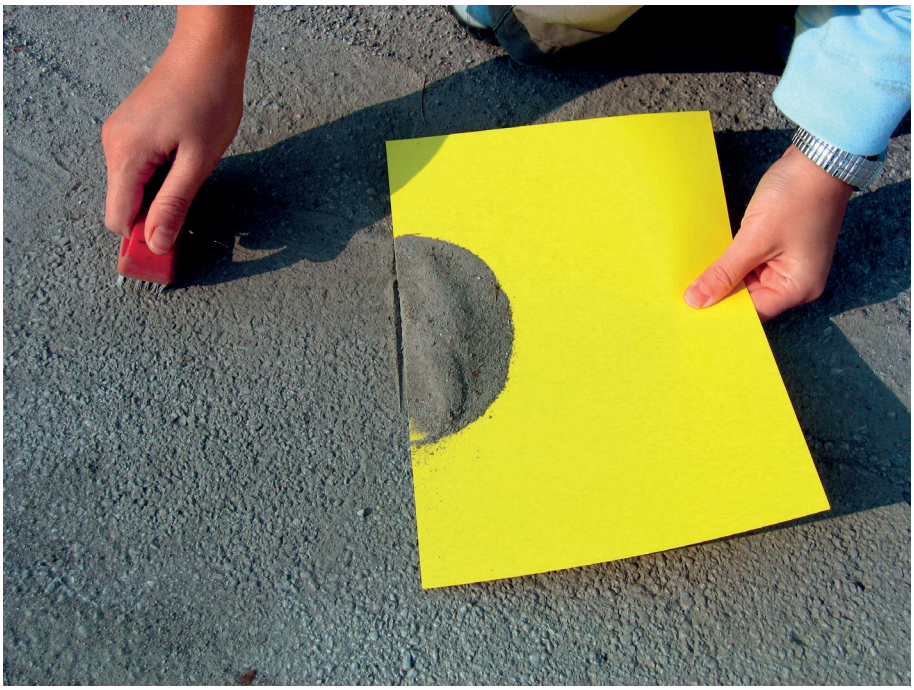

Fig. 3. Sampling of street dust sediment. After sweeping the surface with the soft broom to remove coarse particles, fine-grained dust were extracted from pores with the hard plastic brush.

ants, pet presence etc. Household dust sample was represented by three full vacuum cleaner bags from dwellings next to the sampling point. We sampled only bags, which were used for cleaning the interior of the houses or apartments. Bags, used for vacuuming of any construction works, paint jobs, pet droppings, cars or workshops were avoided. Conversation with the owner of the house helped to identify good samples. Samples of household dust and street sediment were taken in dry weather condition in the early spring 2009, as a part of the study of Žibret & Rokavec (2010).

Laboratory preparation of the samples included drying on 303K until no weight loss is observed, and sieving. When particles coagulated into clods due to the presence of humidity, the aggregates were softly crushed in the ceramic mortar. Fraction under 0.125 mm represented material for chemical analysis. Special procedure was applied to household dust sample preparation to remove as much fibres as possible. The contest of the vacuum cleaner bag (coagulates of hair, dirt, fibres etc...) was rubbed on the 1 mm sieve to extract finer particles (Fig. 4). Hair and other fibres and coarse particles were discarded. The remains were sieved with quick and strong hand shaking on 0.5 mm sieve, and after that the procedure was repeated with the 0.125 mm sieve. During this procedure majority of fibres were removed and only dry air deposit and possible soil particles remained.

Samples were stored in the dark and dry place in the air-sealed plastic containers prior chemical analyses, which were done in the Czech Geological survey, using gas chromatography and mass spectrometry. Only qualitative measurements were made for screening purposes for 120 different organic compounds. Extraction, fractionation and analysis were done according to Czech geological survey procedures (Franců et al., 2010). The presence of certain chemicals was evaluated according to the presence of the peak on the chromatogram. However, no evaluation of the peak significance was made.

Fig. 4. Household dust preparation. Material was rubbed on the 1 mm sieve. Fibres (right) were discarded, remains (left) were sieved several times on 0.5 and 0.125 mm sieves to remove as much smaller fibres as possible.

Results

Table 1 shows the aggregated results - presence of chemicals among different groups of organic compounds. The presence of the peak on chromatograph, representing a specific substance, is indicated in table 2. Unfortunately, chromatography data system for the identification of the substances, as well as identification of their sources, was unavailable to the author of this article. This is why extensive literature search was performed in order to try to interpret results. Special emphasis was put on the identification of possible origin of a certain substance, and to determine possible industrial or domestic use of it. We did not provide data sources for each of the chemicals separately, because table 2 would be too large and would loose its clarity. Therefore we provide a list of data sources for uses and occurrence for chemicals in table 2, which are:

1. Scientific books, chemical atlases and articles (Bryant et al., 2007; CCME, 2008; Harvey et al., 1991; Kavouras et al., 1998; Kingsbury et al., 1979; Melber, 2004; Tsapakis et al., 2002; U.S. EPA, 2006; US Public Health Service, 1995; Weschler & Nazaroff, 2008);
2. Chemical safety information factsheets (Internet 1 and 2),
3. Data from search engines of suppliers of chemicals (Internet 3 and 4)
4. Information from on-line chemical databases (Internet 5 and 6) and for fragrance and food additives (Internet 7);
5. If aforementioned information sources did not provided enough information for specific chemical, a search at google.com and duckduckgo.com search engines were performed.

Since there is not much scientific information about many of the analyzed organic chemicals in world literature, and even that is scattered in a vast amount of publications, also non-scientific sources of information were used to search for the specific chemical. Therefore provided information about the occurrence and use of chemicals can be incorrect or incomplete and this information must be therefore taken into account by knowing aforementioned fact.

A special emphasis was put on US-EPA priority pollutants list (Internet 8), which are regarded as high threat to the humans and environment. However, some studies revealed that also other chemicals can also be a similar environmental threat as US-EPA priority pollutants. When such study was found during literature search it is noted in the table 2, despite not indicated as being a priority pollutant.

Table 1 shows that attic dust is the most diverse "cocktail" of organic substances, containing 98 organic substances out of 120 analysed (82 %). It also contains all of the analysed priority pollutants and representatives of almost all of the analysed groups of organic chemicals. Among them the most abundant are terpenoids, alkylbenzenes and polycyclic aromatic hydrocarbons (PAH's). Street dust contains 70 of different organic compounds out of 120 analysed (58 %). PAH, aldehydes, ketones, ethers, amines and plasticizers are the most characteristic. Among 17 analysed priority pollutants, 14 were detected in street dust. House dust contains the fewest different organic compounds among three types of dusts - 45 compounds out of 120 analysed, which means 28 % of all analyzed. Terpenoids, alkylbenzenes, PAH's, aldehides and ketones, organic acids and other compounds can be found there. 8 out of 17 analysed priority pollutants were detected in house dust.

Table 1. Analysed groups of organic compounds. Table shows total number of different compounds analysed in a specific group (TOT) and detected in attic dust (AD), household dust (HD) and street dust (SD).

groups of chemicals	TOT. ANAL.	AD	HD	SD
Aliphatic compounds	5	3	3	3
Terpenoids and degradation products	17	16	6	5
Alkylbenzenes	8	8	4	2
Polycyclic aromatic hydrocarbons (PAH)s	51	49	21	38
Sulphur containing PAHs	7	5	3	2
Oxygen containing PAHs	4	4	1	3
Nitrogen containing PAHs	2	2	0	1
Oxygenated aromatic compounds	3	1	0	2
Alcohols and phenols	2	0	1	1
Aldehydes and ketones	3	1	2	3
Ethers	1	0	0	1
Amines	1	0	0	1
Acids	2	0	2	0
Esters	2	0	0	2
Plasticizers	5	3	1	4
Fragrances	3	1	1	1
Halogenated compounds	2	2	0	1
Pesticides and degradation products	1	1	0	0
Other compounds	1	1	0	0
TOTAL	120	98	45	70
%		82	38	58
PRORITY POLLUTANTS ANALYSED	**17**	**17**	**8**	**14**

Discussion

With only few data available, the interpretation of the results certainly contains the speculations, at some extent. From the number of different chemicals present in dusts it can be concluded, that diversity of organic molecules is decreasing in the following order: attic dust > street dust > house dust. The same order is also when we take into account priority pollutants. Lower number of different chemicals found in street dust in comparison with attic dust can be attributed to the fact that street dust is exposed in comparison to attic dust is exposed to

Table 2. Organic compounds identified in environmental samples from Celje (Slovenia). AD – attic dust; HD – household dust; SS - street dust. US-EPA priority pollutants are indicated with italic underline letters.

	occurrence & use	AD	HD	SS
Aliphatic compounds				
Homologues series of n-alkanes (C10 to C30)[a]		+	+	+
Series of various methylated n-alkanes[b]		+	+	+
n-alkylcyclohexanes with side chains[b]	intermediate in industrial processes, unstable	+		
n-alkylcyclohexenes[b,c]	intermediate in industrial processes, unstable		+	
Misc. alkyl cycloalkanes[b,c]	naturally occurring molecules; chrysanthemic acid, prostoglandins, steroids			+
Terpenoids and degradation products				
D-Limonene[b]	citrus, detergents, cosmetics, orange juice	+	+	+
Cymenes[b,c]	cosmetic, food, medicine	+	+	+
3-Methoxy-p-cymene[b]	wood industry, plant gradient, cumin, thyme	+		
(+)-4-Carene[b]	wood turpentine; paints, solvent, volatile oil	+	+	
Octahydro-4b,8-dimethyl-2-isopropylphenanthrene[b]	cigarette smoke, coal burning	+		
Cadalene[b]	essential oil of high plants	+		
Calamenene[b]	essential oil	+		+
a-Cedrene[b]	cedar oil, spices	+	+	
a-Muurolene	essential oil, perfumes, medicines		+	
Longicyclene[b]	essential oil (*Orchidacaea, Asparagales*)	+		
Junipene[b]	essential oil (*Abies cilicica*)	+		+
Ferruginol[b]	essential oil (*Sequoia sempervirens*), anti-tumour, anti-bacterial activity	+		
Squalene[b]	lipid, produced by plants, animals, incl. humans, olive oil, cosmetics, vaccines	+	+	+
Selinane[b]	enzymes, found in algae, plants and insects	+		
Isophyllocladene[b]	essential oil of *Araucaria excelsa*	+		
Aromadendran ('2')	flavonoid (Pinus sibirica)	+		
ß-Patchoulane	terpene, extracted from *Pogostemon cablin*	+		
Alkylbenzenes				
5-Ethyl-m-xylene[b]	wood, petrochemical, coke fuel, additive in gasoline	+		
Trimethylbenzenes[b,c]	coal tar, petroleum, mineral oils, gasoline additive, dyes, perfumes, scintilators	+	+	+
Tetramethylbenzenes[b,c]	toxic, curing agents, plastics, cross-linking agents, alkyd resins	+	+	+
Dimethylstyrenes[b,c]	flavour and fragrance agent; orchids Catasetum.	+		
Linear alkylbenzenes (Cx-benzenes)[b,c]	surfactants, detergents	+	+	
1-Methyl-4(1-methylpropyl)benzene[b]	-	+		
2,4-diphenyl-4-methyl-2(E)-pentene	-	+		
4,4'-Diacetyldiphenylmethane[b]	polyurethane foams	+	+	
Polycyclic aromatic hydrocarbons, PAH				
Naphtalene[a]	coal tar, heavy petroleum fractions, petroleum based fuels, coal, burning of wood and tobacco, indoor air pollutant	+	+	+
Ethylnaphthalene[b]	coal tar, heavy petroleum fractions (oil spills)			+
1-Methylnaphtalene[b]	coal tar, heavy petroleum fractions (oil spills)	+	+	+
2-Methylnaphtalene[b]	coal tar, heavy petroleum fractions (oil spills)	+	+	+
C2-Naphthalenes[b,c]	coal tar, heavy petroleum fractions (oil spills)	+	+	+
C3-Naphthalenes	coal tar, heavy petroleum fractions (oil spills)	+	+	+
C4-Naphthalenes	coal tar, heavy petroleum fractions (oil spills)	+		+
2-Phenylnaphthalene[b]	occurrence with PAH in sediments, decomposition of plastics, coal	+		+
Phenylmethylnephtalenes[b,c]	-	+		+
2,6-Diisopropylnaphthalene[b]	pesticides, natural plant growth regulator	+	+	+
Biphenyl[b]	organic compounds, plastics, coal tar, oil, natural gas, preservative (E230)	+	+	+
3- and 4-methylbiphenyl[b]	naturally occurrence in cocoa, spicy odour, flavouring agent	+		+
C2-Biphenyls[b,c]	organic compounds, plastics, emulsifiers, naturally occurrence in coal, crude oil and natural gas	+	+	+
1-Phenyl-1,3,3-trimethylindan	fragrance agent	+		+
Acenaphthylene[a]	coal tar	+		+
Acenaphtene[a]	coal tar	+		+
Fluorene[a]	coal tar	+	+	+
Methylfluorenes[b,c]	coal liquefaction by-product	+		+
Dimethylfluorene[b]	organic electroluminescent elements			+
1- and 2-phenylnaphthalenes[b,c]	plant lignans, found in organic sediments	+		+
Phenanthrene[a]	combustion by-product, cigarette smoke, coal burning	+	+	+
Anthracene[a]	coal tar, dyes, plastics, incomplete combustion of coal, gas or garbage	+		
2-Ethylanthracene	toxic to aquatic organisms	+		+
9-Phenylanthracene	component in crude oil, final stage of oil generation	+		
Methylphenanthrenes[b,c]	natural oil, coal-derived liquids, tar, traffic	+	+	+
Methylanthracenes[b,c]	diesel engines exhaust, crude oil component	+	+	+
Dimethylphenanthrenes[b,c]	wood combustion, motor vehicle exhaust, tars, coal-derived liquids, oxidation of resins	+	+	+

C3-Phenanthrenes[b,c]	cigarette smoke, coal burning, dyes, plastics, pesticides, garbage incineration, oil, oil marker	+	+	+
4H-Cyclopenta(def)phenanthrene[b]	pyrolysis product of catechol (precursor chemical of pesticides, flavours and fragrances), fuel component	+		
Retene[b]	coal tar fraction, resinous wood distillation	+		
Fluoranthene[a]	low-temperature combustion by-product, carcinogen	+	+	+
Pyrene[a]	incomplete combustion of organic compounds, coal tar	+	+	+
Methylfluoranthenes/-pyrenes[b,c]	?	+		+
o,p,m-Terphenyls[b,c]	fungus and mould growth prevention, sunscreen lotion component, pharmaceuticals, intermediate for many other chemicals	+		+
Benzo(ghi)fluoranthene[b]	tobacco smoke, fuel combustion	+		+
Chrysenea/Triphenylene[b]	coal tar, electronic and optic cables, wood preservative, stable	+	+	+
Benzo(a)anthracene[a]	coal tar, roasted coffee, smoked foods, automobile exhaust, intermediate for other chemicals, carcinogen	+		+
Methylbenz(a)anthracenes[b,c]	?	+		
Cyclopenta(cd)pyrene[b]	gasoline engine exhaust	+		
Methylchrysenes[b,c]	tobacco smoke, diesel engine emissions, carcinogen	+		+
1,2'- and 2,2'-Binaphthyl[b]	?	+		
Benzo(x)fluoranthene (x=j,b,k)[b,c]	tobacco smoke, incomplete combustion of fossil fuel, carcinogen	+	+	+
Benzo(a)pyrene[a]	coal tar, diesel engine exhaust, wood combustion, highly carcinogenic	+	+	+
Perylene[b]	tobacco smoke, Rylene dyes, in-situ biogenic origin from organic matter	+		
Indeno(1,2,3-cd)pyrene[a]	coal slurry, coal tar, tobacco smoke, gasoline engine exhaust	+	+	+
Dibenzo(a,h)anthracene[a]	automobile exhaust, cigarette smoke, carcinogenic	+		
Benzo(g,h,i)perylene[a]	incomplete combustion or pyrolysis of organic matter, fossil fuels combustion, cigarette smoke	+	+	+
Benzo(b)chrysene[b]	coal tar, airborne pollution (traffic)	+		
Coronene[b]	hydrothermal mineral carpathite, gasoline exhaust	+		
Dibenzopyrenes[b,c]	coal tar, forest fires, cigarette smoke	+		
Indeno(1,2,3-fg)naphthacene	tobacco smoke	+		
Oxygenated aromatic compounds				
Benzanthrone[b]	dyes, pyrotechnics industry-green and yellow colour smokes	+		
Sulphur containing PAHs				
Dibenzothiophene[b]	heavier fractions of petroleum	+	+	
Methyldibenzothiophene(s)	component of crude oil, occurrence in sedimentary rocks	+	+	
Dimethylbenzothiophene[b]	component of crude oil, occurrence in sedimentary rocks, coal-derived liquids		+	
C2-Dibenzothiophenes[b,c]	component of crude oil	+		
Benzo(b)naphtho(1,2 or 2,1-d) thiophene[b]	product of crude-oil microbial degradation	+		+
Mono- and dimethylbenzonaphthothiophenes[b,c]	product of crude-oil microbial degradation			+
Benzothieno(4,5-b)benzothiophene	?	+		
Oxygen containing PAHs				
Dibenzofuran[b]	coal tar, oil, insecticide, production of PVC, industrial bleaching and incineration	+	+	+
Methylbenzofuranes[b,c]	occurrence in coffee, flavouring agent	+		+
Benzonaphthofuran[b,c]	burning of residential waste, coal tar	+		+
Benzobisbenzofuranes[b,c]	oled diodes	+		
Nitrogen containing PAHs				
Carbazole[b]	coal tar; intermediate in synthesis of pharmaceuticals, agrochemicals, dyes, pigments, optoelectronics...	+		
Methylcarbazoles[b,c]	coal tar, crude oil;	+		+
Oxygenated aromatic compounds				
9-Fluorenol[b]	substance in coal	+		
Ditertbutylquinone	oxidant, polymerization catalyst			+
Benzanthrone[b]	dyes, pyrotechnics			+
Alcohols and phenols				
Butylated hydroxytoluene (BHT)[b]	antioxidant (=E321), fuel additive, hydraulic fluid, jet fuel, rubber		+	
Di-tert-butylphenol	antioxidant in petrochemicals and plastics, aviation fuel			+
Aldehydes and ketones				
Misc. n-aldehydes[b,c]	polyurethane and other construction materials production, plastics, essential oils	+	+	+
Misc. x-alkanones[b,c]	solvent, polymer precursor, pharmaceuticals, natural molecules		+	+
Diisobutyl ketone[b]	solvent (leather, cleaning, paint, lack...)			+
Ethers				
Dioctyl ether	lubricant , anti-static agent, electrical insulator, water repellent			+
Amines				
Diphenylamine[b]	food			+
Acids				
Misc. n-alkanoic acids[b,c]	soap, food, drugs, rubber, dyes, perfumes		+	
Benzoic acid	food preservative (E210), pharmaceutics, sunscreen, body wash...		+	
Esters				
Isopropyl myristate[b]	cosmetics			+
Methylpalmitate	detergents, resins, plastics, lubricants, food			+

Plasticizers				
Diethylphthalate[b]	cosmetics, detergents, sprays	+		+
Dibutyl phthalate (DBP)[b]	solvent, additive to pesticides, repellents, adhesive, ink	+		+
Di-iso-butylphthalate[b]	PVC, PVC copolymers, footwear, jackets			+
Bis(2-ethylhexyl)phthalate (DEHP)[b]	PVC, capacitors, hydraulic fluid	+		+
Phthalic anhydride	plastics, paints, urethane polyester, insect repellent		+	
Fragrances				
?-, ?-Muurolene[b]	herbs, spices, wood	+		
Geranylacetone[b]	perfumery, food (chocolate, marzipan)		+	
Hexahydrofarnesyl acetone	long-lasting fresh jasmine, celery odour			+
Halogenated compounds				
Mixture of di- to hexachlorinated biphenyls (PCB's)[a,b]	heat-transfer fluids, dielectric fluid, persistent pollutant, carcinogenic	+		
Tetrachloro-m-xylene[b]	pesticides & metabolites	+		+
Pesticides and degradation products				
o,p- and p,p-DDT	phytopharmaceutical, pollutant	+		
Other compounds				
Octasulfur	yellow sulphur powder	+		

[a] Identified by comparison of GC and MS data with those of reference compounds
[b] Identified by comparison of MS data with those of MS data bases (NIST98)
[c] Mixtures of isomers/homologues

the ultraviolet light from sun produce photo degradation and oxidation of many of the compounds. Also other weather influences might change the composition of street dust. As the retention time of the street dust is estimated to be between 6 to 12 months, certain chemicals, which are banned today, are no longer found there, but they are preserved in attic dust (such as DDT and PCB for example). Lowest number of compounds in house dust can be explained that certain chemicals can be effectively removed by regular cleaning of homes in contaminated environments.

First group of organic chemicals of interest are terpenoids, which are dominantly the compounds, found in plants. Their origin is from wood remains, pollen and other plant remains. Majority of terpenoids are of natural origin. They are most abundant in attic dust, most probably because attic dust contains a lot of pollen or similar windblown organic material. Alkylbenzenes are also abundant in all types of dusts. Since alkylbenzenes are usually biodegradable, we assume that their presence in dusts do not pose increased long-term environmental or health risk.

But the focus of future studies might be on PAH's and other aromatic compounds, since the occurrence of this group of chemicals has the major potential to pose a health or environmental risk. Some of them are regarded also as priority pollutants. Literature search points out the source of PAH's are dominantly coal tar and by-products of incomplete combustion of all types of burning materials. From current dataset it is impossible to determine the source of PAH's in Celje. Traffic and burning of fossil fuels can be suspected to be responsible for their presence. But it can be speculated that vaporisation from tar at the Celje brownfield can also be an important source of PAH's in the attic and street dust, and to some extent also in house dust. It is interesting, that also short-lived PAH's are present in attic dust. Thus it can be suspected that a continuous source of such compounds exists in Celje. Regarding the the occurrence of PAH's indoors, it must be denoted that beside outdoor sources also smoking, grilling of food, wood burning for heating (like fireplace indoors), vaporisation of petroleum products and burning of natural gas can all be possible indoor sources.

Aldehides and ketones, ethers, amines, organic acids, esters and fragrances are abundant natural molecules and usually do not pose increased risk at exposure to small quantities, so their occurrence will not be discussed here.

Another group which contains priority pollutants are plasticizers, and this group of chemicals might also be a focus of future studies. Street dust contains 4 among 5 chemicals from this group, attic dust 3 and house dust 1 representative. It can be speculated, that additives to construction materials can be a reason for plasticizer occurrences in urban atmosphere. House dust, contrary, contains no priority pollutant plasticizers. Among environmentally dangerous and carcinogenic pollutants, PCB's were found in attic dust, but not in street and house dust, which might indicate that PCB's are no longer emitted in Celje any more, but they were used at some point in the past. Last priority pollutant chemical is pesticide DDT and its degradation products. As at PCB case, they can be found only in attic dust, but not in street or house dust. This can be explained by the possible use of DDT containing insecticides for the hop and other crops production in the Celje area in the past, thus proving that attic dust is really a museum for atmospheric contamination in the area of interest, as being expressed by Davis & Gulson (2005). Our results also points out that no sources of DDT exist in Celje area today.

Conclusions

Attic dust, house dust and street dust samples from Celje area were analysed for the presence of 120 different organic substances using gas chromatography and mass spectrometry. Attic dust contains 82 % of organic substances, among them all of the US-EPA priority pollutants. Terpenoids,

alkylbenzenes and PAH's are the most abundant. Street dust contains 58% of analysed organic chemicals. Most abundant groups of compounds are PAH's, aldehydes, ketones, ethers, amines and plasticizers. House dust contains the least different organic compounds – 38 % of all analysed. Terpenoids, alkylbenzenes, PAH's, aldehides, ketones and organic acids can be found there. Among 17 analysed priority pollutants, all were detected in attic dust, 14 of them in street dust and 8 of them in house dust. Evaporation of organic compounds from Cinkarna brownfield, traffic and other types of fossil fuel combustion, use of certain chemical and natural products, construction, evaporation from tarred road surfaces, wood-processing and chemical industry, wood burning, as well as natural gas burning for cooking, smoking or food grilling can be suspected anthropogenical sources of detected organic chemicals.

Since no quantitative evaluation was made, this study must be used only as a guideline for possible further studies. Its main added value is that certain groups of chemicals are evaluated in street, attic and house dust, thus the results can point to the direction of future interests. Since analyses of organic compounds are expensive, this study can be very useful for reducing possible costs of future studies of organic pollutants. Moreover, an analysis of groundwater in the area around industrial waste deposit might be useful. Author recommendation is, that the most interesting groups of organic chemicals for the future studies of ambient dusts in Celje, as well as also in the other places, might be PAH's and plasticizers. Measuring actual concentrations of such organic compounds in different natural and anthropogenical materials in Celje area might be an useful follow-up of this study.

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