Scientific paper

Composition of Organic Compounds Adsorbed on PM10 in the Air Above Maribor

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Abstract

Organic compounds in atmospheric particulate matter above Maribor were analysed in 120 samples of PM10 sampled according to the EN 12341:2014 reference method. Organic compounds compositions were investigated together with the primary and secondary sources of air pollution. Silylation as derivatisation method was used for the GC-MS determination of volatile and semi-volatile polar organic compounds. Distribution of fatty acids, *n*-alkanes and iso-alkanes, phthalate esters, siloxanes, different sterols, various sugars and sugar alcohols, compounds of lignin and resin acids, dicarboxylic acids from photochemical reactions, PAHs, organic nitrogen compounds and products from secondary oxidation of monoterpenes were determined. The use of silicone grease for the purpose of lubricating the impact surface of the air sampler caused higher values of gravimetric determination. Solid particles may have been bounced from the surface of a greasy impact plate and re-entrained within the air stream and then collected on a sample filter. The carryover of siloxanes was at least from 5% up to 15% of the accumulated particles weight, depending on ambient temperature. This was the reason that the gravimetric results for determination of PM10 according to the standard EN 12341:2014 were overestimated.

Keywords: PM10, EN 12341:2014, secondary organic aerosol, volatile organic compounds

1. Introduction

Throughout the member States of Europe there is valid a uniform legislation on regulating the environmental area and the protection of human health. Member States are obliged to carry out measurements of air pollutants and keep the local public informed about the air quality. This data must be reported to the European Environmental Agency. In those cases where pollutants exceed the threshold values the state must design and implement measures to improve the conditions.[1–4] Air Quality in Slovenia is determined by local emissions and the transport of polluted air across borders.[3] In the air quality directive 2008/EC/50 the European Union has set two limit values for particulate matter with aerodynamic diameter of 10 μm or less (PM10).[1] The PM10 daily mean value may not exceed 50 μg/m^3 more than 35 times during a year and the PM10 annual mean value may not exceed 40 μg/m^3. Celje is the most polluted Slovenian town regarding the particulate matter PM10 with an average daily concentration of 45 μg/m^3 and 41 exceedances of daily concentrations limits during the year 2014. In the year 2014 Maribor exceeded the daily concentrations limits 25 times with the PM10 annual mean value of 26.5 μg/m^3.[2] Air quality is usually the worst from November to March. The daily limits are exceeded mainly in winter due to increased traffic, domestic heating, industrial processes and meteorological phenomena such as inversion or low wind speed.[1–5]

Airborne suspended particulate matter can be of natural (forests, pollen, rainfall, storm, vegetation, volcanic ash...) or anthropogenic origin (emissions of industry, transport, burning of fossil fuels, biomass, agriculture...). Primary particles are released into the atmosphere from sources on the Earth's surface.[6,7] A major fraction of organic aerosol load within the atmosphere is attributable to secondary organic aerosols (SOA) which are formed via gas phase oxidation of volatile organic compounds (VOCs) by atmospheric oxidants such as O_3, OH-radicals and NO_3-radicals and by further gas-to-particle conversion processes. Photochemical processes can affect the chemical composition of organic compounds and their physicochemical properties such as volatility, hygroscopicity or the cloud condensation activities of SOA compounds. Three types of chemical processing can occur: fragmentation, functionalisation, and oligomerisation. Fragmentation will ultimately lead to degradation of a compound to a smaller, more volatile one. Functionalisation will basically introduce more oxygen containing groups and lead to the formation of less volatile, more polar oxygenated organic aerosol. During oligomerisation compounds with higher molecular mass are formed.[7,8,9] The urban population is exposed to excessive concentrations of particulate matter, CO, NO_x, O_3 and different organic compounds. Even indoors within homes there are high concentrations of particulate matter due to internal sources (cooking, heating, smoking…) and the impact of external sources. Soot particles can carry toxic material such as polycyclic aromatic hydrocarbons (PAH) and heavy metals on their surfaces.[9]

The chemical composition of aerosols is a key factor for understanding the link between aerosols, clouds and climate. Carbonaceous aerosols are a subgroup of atmospheric aerosols, that consist of elemental carbon and organic compounds.[10] Bio aerosols are particles that originate from vegetation. Aerosols affect human health, climate and visibility (smog, fog). Chemical compounds from industry and transport react in the atmosphere with ozone, OH, NO_3 and other radicals to form SOA. Together with the primary emissions they form the photochemical smog, which could be a risk to human health.[11]

Standard EN 12341:2014 is a reference method for sampling and measurements of the suspended fraction of PM10. This method is based on collecting the suspended fraction of particles with a diameter of 10 µm or less (PM10) on a filter with a low volume sampler and gravimetric mass determination.[12] The aim of our study was that after the gravimetric determination of PM10 also the chemical composition of organic compounds adsorbed on PM10 would be determined. This can provide us with better insight in the atmosphere and the possibility to identify harmful organic substances in the air above Maribor.

2. Materials and Methods / Experimental Section

Sample Collection and Preparation: The research included 120 samples of particulate matter PM10 collected according to standard EN 12341:2014 using low-volume air samplers (TCR Tecora Skypost PM, Leckel SEQ 47/50) with a flow rate of 38.3 L/min. Silicon-Hochvakuumfett (Merck 100g, CAS Nr. 107922) was used as a coating for the impact plate. 36 samples were obtained in winter, 34 in summer, 27 in spring and 23 in autumn. 30 samples were additionally obtained using polyphenylether (Santovac 5, CAS Nr. 2455-71-2) as a coating for the impact plate. Aerosol samples were collected on quartz filters (Munktell, quartz microfiber discs, 47 mm) during the period from July 2013 to August 2014 at eight locations in Maribor and its surroundings. The sampling sites are illustrated in Fig. 1. All experimental devices including a low-volume air sampler probe and glassware were pre-extracted using dichloromethane. A reagent blank was analysed before sample analysis in each batch. Quartz filters were combusted before use at 500 °C for 6 h. The benefit of using combusted quartz filters over the non-combusted filters is the reduced contamination.

After the gravimetric weighing of PM10 particles (Standard EN 12341:2014) the collected samples were placed in a glass vial with a Teflon cap and stored at –20 °C prior to analysis. Samples were extracted three times (3 × 20 mL) using a shaker with orbital movement having a mixture of dichloromethane/methanol (2:1; *v/v*). On a rotary evaporator the combined extracts were evaporated to dryness. Dry residues of extracts were dissolved in pyridine and derivatised with MSTFA (*N*-methyl-*N*-trimethylsilyl trifluoroacetamide) for 1 h at 60 °C. Hexatriacontane (nC36) was used as a compound of the external standard. Concentrated and derivatised extracts with a final volume of 100 µL were quantitatively transferred into a glass vial and analysed using GC-MS.

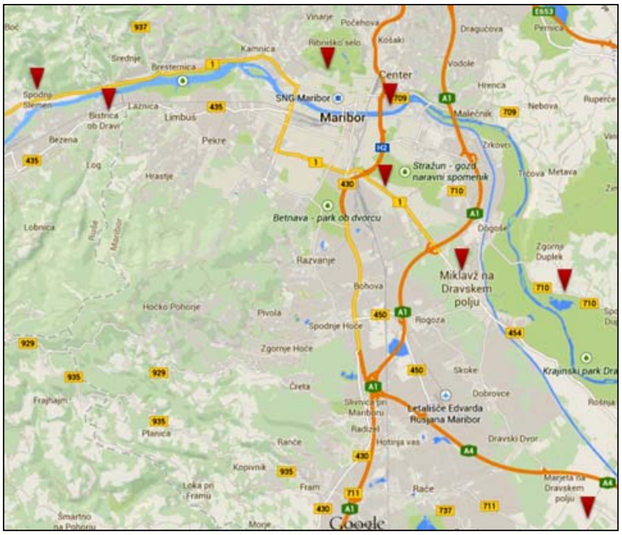

Figure 1. Sampling sites of PM10 collection in Maribor and its near surroundings (Sp. Slemen, Vrbanski plato, Bistrica ob Dravi, MB Center, MB NLZOH, Miklavž, Trniče, Duplek).

Instrumental Analysis: An Agilent (5973) mass spectrometer was used coupled to a gas chromatograph Agilent (6890) and Agilent autosampler (7683). For the chromatographic separation an Agilent DB-UI 8270 D capillary column was used (30 m × 250 µm i.d., 0.25 µm film thickness).

The temperature program was the following: 0.75 min at a temperature of 105 °C, 30 °C /min up to 120 ° C (0.1 min), 2.7 °C/min to 320 °C (5 min). The carrier gas was helium (He 6.0, Messer Austria) at a constant flow of 0.9 ml/min. The ion source temperature was 250 °C. The injection port and transfer line were kept at 290 °C. The mass spectrometer was operated in electron ionisation (EI) mode at 70 eV and scanned in full scan mode in the range 70–800 Da. Chromatograms were processed by a computer program AMDIS (Automated Mass Spectral Deconvolution And Identification System Software). Detected compounds were identified by comparing their spectra with those, reported in the Willey and NIST (W9N08) mass spectra libraries or with data from literature.

3. Results and Discussion

In the sample extracts the following compounds were detected: fatty acids, sugars, sugar alcohols and higher alkanols, compounds of lignin and wood resins, dicarboxylic acids, distribution of *n*-alkanes and iso-alkanes, phthalate esters, siloxanes, sterols, polycyclic aromatic hydrocarbons, urea as an organic nitrogen compound and products from secondary oxidation of monoterpene compounds.

Emissions from individual sources depended on the season. We detected indicators (tracer compounds) for combustion of biomass (levoglucosan), lignin and wood resins (dehydro-abietic acid and vanillic acid), secondary biogenic aerosols (pinonic acid) and fecal pollution from livestock and aeration of biological treatment plants (cholesterol). From the review of the detected compounds it could be seen that the most abundant compounds during the summer season were the derivatives of sugars, sugar alcohols and free fatty acids. The comparison between the chromatograms of all the samples' extracts showed that the composition of aerosols was very similar in warmer seasons with a predominance of biogenic compounds over anthropogenic compounds. During winter the anthropogenic organic compounds dominated on PM10 sample extracts, the source of which was the combustion of fossil fuels for heating or transport.

3. 1. Free Fatty Acids

A set of silylated derivatives of free fatty acids (FFA) from pentanoic acid up to hexacosanoic acid is shown in Figure 3. FFA had characteristic mass fragments

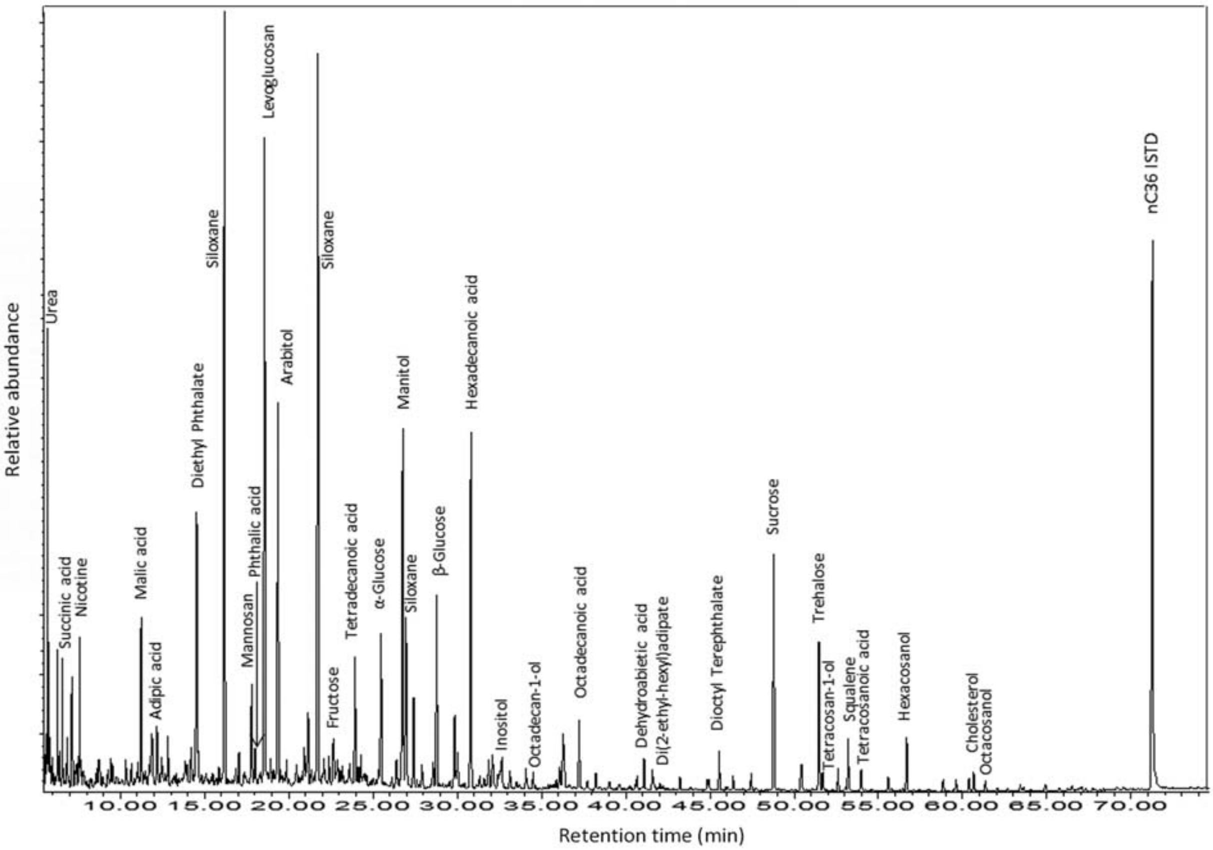

Figure 2. Typical GC/MS chromatogram of silylated PM10 sample extract from Maribor (Collected: 18.7.2014, MB NLZOH).

Table 1. Compounds detected in concentrated silylated sample extracts in the air above Maribor.

	Compound	Formula	M.W.	Major ions (m/z)	Source/tracer/ industrial use
***n*-Alkanoic acids**	Pentanoic acid	$C_5H_{10}O_2$	102	117, 159	<C20: 0 Burning of fossil fuels, microbial activity and cooking
	Hexanoic acid	$C_6H_{12}O_2$	116	117, 173	
	Heptanoic acid	$C_7H_{14}O_2$	130	117, 187	
	Octanoic acid	$C_8H_{16}O_2$	146	117, 201	
	Nonanoic acid	$C_9H_{18}O_2$	166	117, 215	
	Decanoic acid	$C_{10}H_{20}O_2$	176	117, 229	
	Undecanoic acid	$C_{11}H_{22}O_2$	190	117, 243	
	Dodecanoic acid	$C_{12}H_{24}O_2$	200	117, 257	
	Tridecanoic acid	$C_{13}H_{26}O_2$	214	117, 271	
	Tetradecanoic acid	$C_{14}H_{28}O_2$	228	117, 285	
	Pentadecanoic acid	$C_{15}H_{30}O_2$	242	117, 299	
	Hexadecanoic acid	$C_{16}H_{32}O_2$	256	117, 313	
	Heptadecanoic acid	$C_{17}H_{34}O_2$	270	117, 327	
	Octadecanoic acid	$C_{18}H_{36}O_2$	284	117, 341	
	Eicosanoic acid	$C_{20}H_{40}O_2$	312	117, 369	>C20: 0 Incineration of biomass
	Tetracosanoic acid	$C_{24}H_{48}O_2$	368	117, 425	
	Hexacosanoic acid	$C_{26}H_{52}O_2$	396	117, 453	
***n*-Alkenoic acids**	Hexadec-9-enoic acid	$C_{16}H_{30}O_2$	254	117, 311	
	9,12-Octadecadienoic acid	$C_{18}H_{32}O_2$	280	117, 337	
	Octadec-9-enoic acid	$C_{18}H_{34}O_2$	282	117, 339	
Dicarboxylic acids	Succinic acid	$C_4H_6O_4$	118	147, 247	
	Malic acid	$C_4H_6O_5$	134	147, 233	
	Glutaric acid	$C_5H_8O_4$	132	147, 349	Aliphatic olefins
	Adipic acid	$C_6H_{10}O_4$	146	147, 275	Aliphatic olefins
	Phthalic acid	$C_8H_6O_4$	166	147, 295	
	Azelaic acid	$C_9H_{16}O_4$	188	147, 317	Carboxylic acids
	Citric acid	$C_6H_8O_7$	192	147, 273	
	Quinic acid	$C_7H_{12}O_6$	192	147, 345	Polyol
	Di(2-ethyl-hexyl)adipate	$C_{22}H_{42}O_4$	370	147, 112	
***n*-Alkanols**	Hexadecanol	$C_{16}H_{34}O$	242	103, 299	Wax coatings of higher plants, deciduous and coniferous trees, biomass
	Octadecanol	$C_{18}H_{38}O$	270	103, 327	
	Docosanol	$C_{22}H_{46}O$	326	103, 383	
	Tetracosanol	$C_{24}H_{50}O$	354	103, 411	
	Hexacosanol	$C_{26}H_{54}O$	382	103, 439	
	Octacosanol	$C_{28}H_{58}O$	410	103, 467	
***n*-Alkanes**	Dodecane	$C_{12}H_{26}$	170	85, 170	
	Tridecane	$C_{13}H_{28}$	184	85, 184	
	Tetradecane	$C_{14}H_{30}$	198	85, 198	
	Pentadecane	$C_{15}H_{32}$	212	85, 212	
	Hexadecane	$C_{16}H_{34}$	226	85, 226	
	Heptadecane	$C_{17}H_{36}$	240	85, 240	
	Octadecane	$C_{18}H_{38}$	254	85, 254	
	Nonadecane	$C_{19}H_{40}$	268	85, 268	
	Eicosane	$C_{20}H_{42}$	282	85, 282	
	Heneicosane	$C_{21}H_{44}$	296	85, 296	
	Docosane	$C_{22}H_{46}$	310	85, 310	C_{15}-C_{37} (odd>even) microbial, plant waxes
	Tricosane	$C_{23}H_{48}$	324	85, 324	
	Tetracosane	$C_{24}H_{50}$	338	85, 338	
	Pentacosane	$C_{25}H_{52}$	352	85, 352	C_{16}-C_{40+} (odd<even) plastics
	Hexacosane	$C_{26}H_{54}$	366	85, 366	
	Heptacosane	$C_{27}H_{56}$	380	85, 380	
	Octacosane	$C_{28}H_{58}$	394	85, 394	C_{15}-C_{37}, carbon preference index (CPI) = 1 vehicles exhaust
	Nonacosane	$C_{29}H_{60}$	408	85, 408	
	Triacontane	$C_{30}H_{62}$	422	85, 422	
	Hentriacontane	$C_{31}H_{64}$	436	85, 436	

	Compound	Formula	M.W.	Major ions (m/z)	Source/tracer/ industrial use
	Dotriacontane	$C_{32}H_{66}$	450	85, 450	
	Tritriacontane	$C_{33}H_{68}$	464	85, 464	
	Tetratriacontane	$C_{34}H_{70}$	478	85, 478	
	Pentatriacontane	$C_{35}H_{72}$	492	85, 492	
Sugars and sugar alcohols	Galactosan	$C_6H_{10}O_5$	162	204, 217	Cellulose and Hemicellulose
	Mannosan	$C_6H_{10}O_5$	162	204, 217	
	Levoglucosan	$C_6H_{10}O_5$	162	204, 333	Biomass burning
	Arabitol	$C_5H_{12}O_5$	152	204, 217	Fungal spores
	1,6-anhydro Glukopyranose	$C_6H_{10}O_5$	162	204, 217	
	Fructose	$C_6H_{12}O_6$	180	204, 217	Soil resuspension and microbiota
	α-Glucose	$C_6H_{12}O_6$	180	204, 217	
	Mannitol	$C_6H_{14}O_6$	182	204, 217	Fungal spores
	β-Glucose	$C_6H_{12}O_6$	180	204, 217	
	Inositol	$C_6H_{12}O_6$	180	204, 217	
	Sucrose	$C_{12}H_{22}O_{11}$	342	204, 361	
	Trehalose	$C_{12}H_{22}O_{11}$	342	204, 361	
Lignin and Resin products	4-Hydoxybenzoic acid	$C_7H_6O_3$	138	267, 282	Lignin
	Vanillin	$C_8H_8O_3$	152	194, 209	Conifers
	Vanillic acid	$C_8H_8O_4$	168	297, 312	Conifers
	Syringaldehyde	$C_9H_{10}O_4$	182	224, 254	Hardwood
	Syringic acid	$C_9H_{10}O_5$	198	297, 327	Hardwood
	Dehydroabietic acid	$C_{20}H_{28}O_2$	300	239, 357	Conifers
Phthalates	Diethyl Phthalate	$C_{12}H_{14}O_4$	222	149, 177	Plasticizer, aerosol sprays
	Dibutyl Phthalate	$C_{16}H_{22}O_4$	278	149, 117	Cosmetics
	Benzylbutyl Phthalate	$C_{19}H_{20}O_4$	312	149	Plasticizer
	Diethylhexyl phthalate	$C_{24}H_{38}O_4$	390	149, 279	Plasticizer
	$(C_{10}$–$C_{21})$Alkylsulfonic phenyl (ester)			94, 293	Replacement of bis(2-ethylhexyl) phthalate
SOA products from terpenes	Sabina ketone	$C_9H_{14}O$	138	81	Sabinene
	Nopinone	$C_9H_{14}O$	138	83	β-pinene
	p-Cymene	$C_{10}H_{14}$	134	119	Monoterpenes
	Pinonaldehyde	$C_{10}H_{16}O_2$	168	83	α-Pinene
	Pinonic acid	$C_{10}H_{16}O_3$	184	83	α-Pinene
PAH	Pyrene	$C_{16}H_{10}$	202	202, 101	
	Benzo[ghi]fluoranthene	$C_{18}H_{10}$	226	226, 113	
	Benzo[a]anthracene	$C_{18}H_{12}$	228	228, 114	
	Chrysene	$C_{18}H_{12}$	228	228, 114	Fossil fuels, incomplete combustion of carbon based fuels
	7H-Benz[de]anthracen-7-one	$C_{17}H_{10}O$	230	230, 115	
	Benzo[k]fluoranthene	$C_{20}H_{12}$	252	252, 126	
	Benzo[e]pyrene	$C_{20}H_{12}$	252	252, 126	
	Benzo[a]pyrene	$C_{20}H_{12}$	252	252, 126	
	Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	276, 138	
	Benzo[ghi]perylene	$C_{22}H_{12}$	276	276, 138	
	Indeno [1,2,3-cd]fluoranthene	$C_{22}H_{12}$	276	276, 138	
	Coronene	$C_{24}H_{12}$	300	300, 150	
Other compounds	Urea	CH_4N_2O	60	189, 147	Agricultural activities, SOA
	2-methylthreitol	$C_5H_{12}O_4$	136	219, 321	Isoprene
	2-methylerythritol	$C_5H_{12}O_4$	136	219, 321	Isoprene
	Nonanal	$C_9H_{18}O$	142	98	Biogenic SOA
	Decanal	$C_{10}H_{20}O$	156	112	Biogenic SOA
	Nicotine	$C_{10}H_{14}N_2$	162	84, 161	Smoking
	Tricarballylic acid	$C_6H_8O_6$	176	217, 377	SOA
	6,10,14-trimethyl -2-pentadecanone	$C_{18}H_{36}O$	268	109, 250	Phytol
	Cholesterol	$C_{27}H_{46}O$	386	329, 353	Fecal pollution
	Squalene	$C_{30}H_{50}$	410	129	
	β-Sitosterol	$C_{29}H_{50}O$	414	357, 486	Vegetation in general

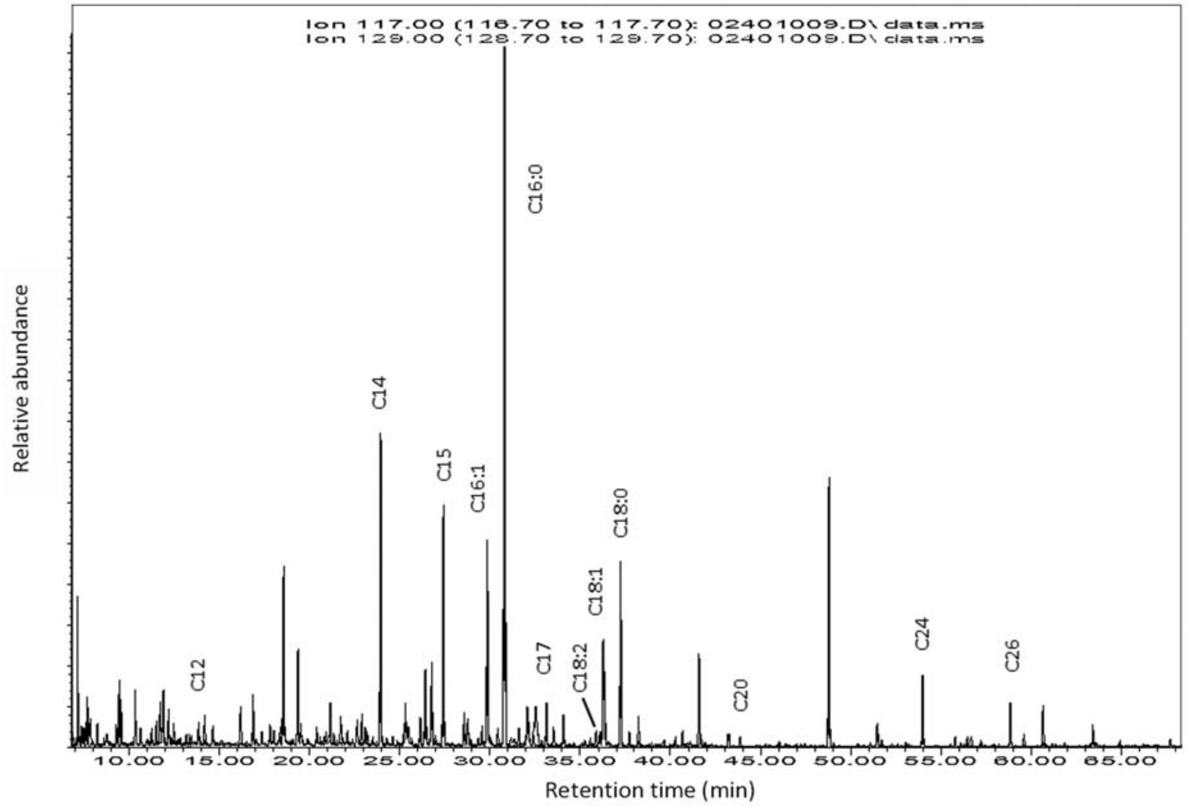

Figure 3. Chromatogram of free fatty acids distribution from sample extracts (Collected: 10.5.2014, MB VP).

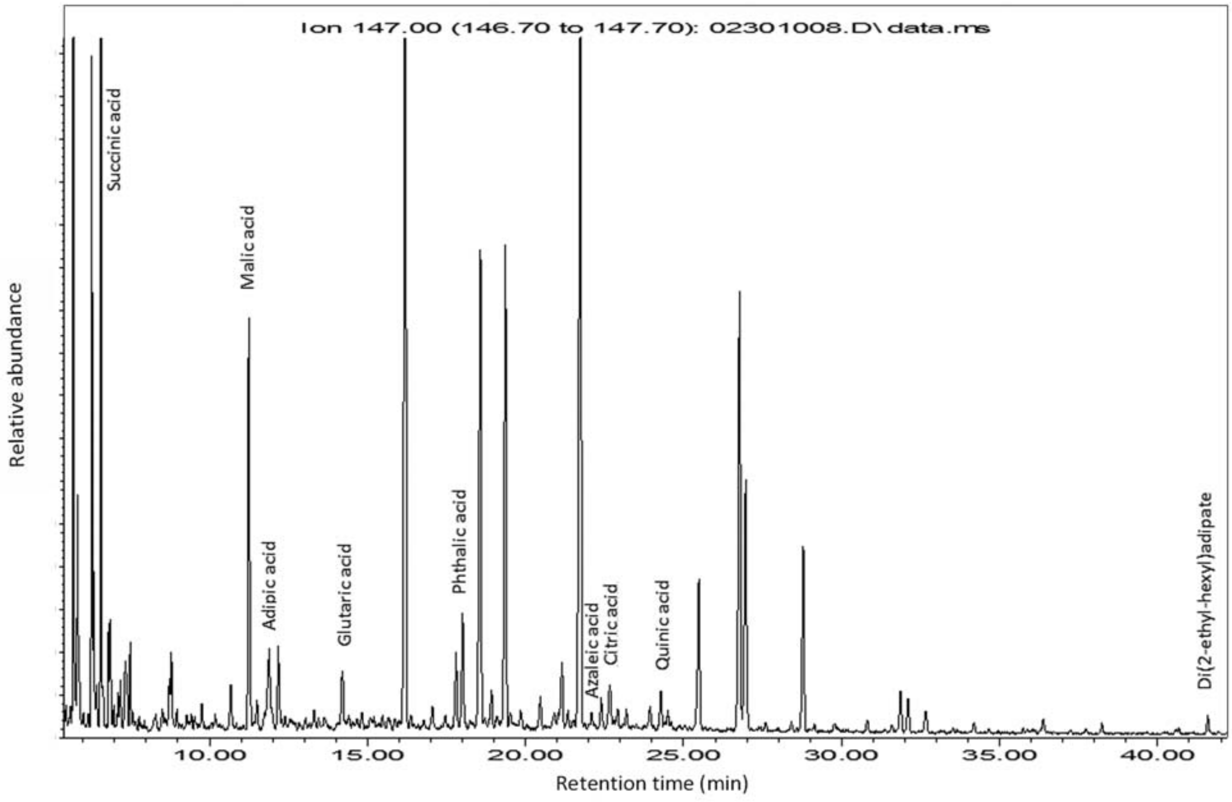

Figure 4. Typical chromatogram of dicarboxylic acids distribution from sample extracts (Collected: 10.5.2014, MB VP).

m/z 117 and *m/z* 129. Odd-numbered FFA were naturally present in trace amounts. Their presence in the sample extracts PM10 was attributed to decomposition of higher fatty acids and their photochemical transformation.[13] The presence of fatty acids with low molecular weight (<C20:0) indicated burning of fossil fuels, microbial activity, and cooking. High molecular weight fatty acids are produced by the incineration of biomass which contains plant waxes.[13,14] As anticipated palmitic (16:0) acid was the most abundant.

3. 2. Dicarboxylic Acids

Emissions from motorised vehicles, combustion of biomass and oceanic emissions are the primary sources of dicarboxylic acids. One of the main sources of dicarboxylic acids are also atmospheric photochemical reactive processes.[6,9,16] Lower dicarboxylic acids have different origins than higher dicarboxylic acids.[10] Phthalic acid is an aromatic dicarboxylic acid that is released into the environment by biomass burning, vehicle emissions or as a by-product from the photochemical oxidation of polycyclic aromatic hydrocarbons and phthalate esters. The presence of glutaric and adipic acid indicate oxidative degradation of cyclic and aliphatic olefins, and azelaic acid on the presence of unsaturated carboxylic acids.[6,13,15] Amongst anthropogenic compounds di(2-ethyl-hexyl)adipate and quinic acid as a polyol from cyclohexane and cyclohexanecarboxylic acid were also detected.[6,16]

3. 3. Alkanols

All alkanols are presented with the fragment *m/z* 75 and *m/z* 103. They range from hexadecanol up to octacosanol. Odd-alkanols were not detected. We associated the presence of alkanols with wax coatings of higher plants, deciduous and coniferous trees.[17]

3. 4. n-Alkanes

Anthropogenic and biogenic primary sources such as vegetation waxes, incineration of biomass, cooking and exhaust gases of motor vehicles were sources of *n*-alkanes and iso-alkanes which can be detected on collected PM10 samples from dodecane (nC12) to pentatriacontane (nC35).[18] The carbon preference index (CPI) is a qualitative tool to assess the influences of biogenic and anthropogenic inputs for *n*-alkanes. The equation for CPI is a sum of the odd carbon number homologs (over a range), divided by the sum of even carbon homologs (over the same range). An odd-to-even carbon number predominance was observed for biologically sources of *n*-alkanes. A CPI>3 indicated a major recent release of biological components into the air. CPI values close to unity were observed regarding the presence of anthropogenic compounds. Petroleum-derived *n*-alkanes had CPI≈1.[16,17]

The predominance of odd numbered *n*-alkanes during warmer seasons points to increased biological activity. This biological impact could be linked to the nearby Pohorje Mountain. *n*-alkanes of higher plants (nC25 to

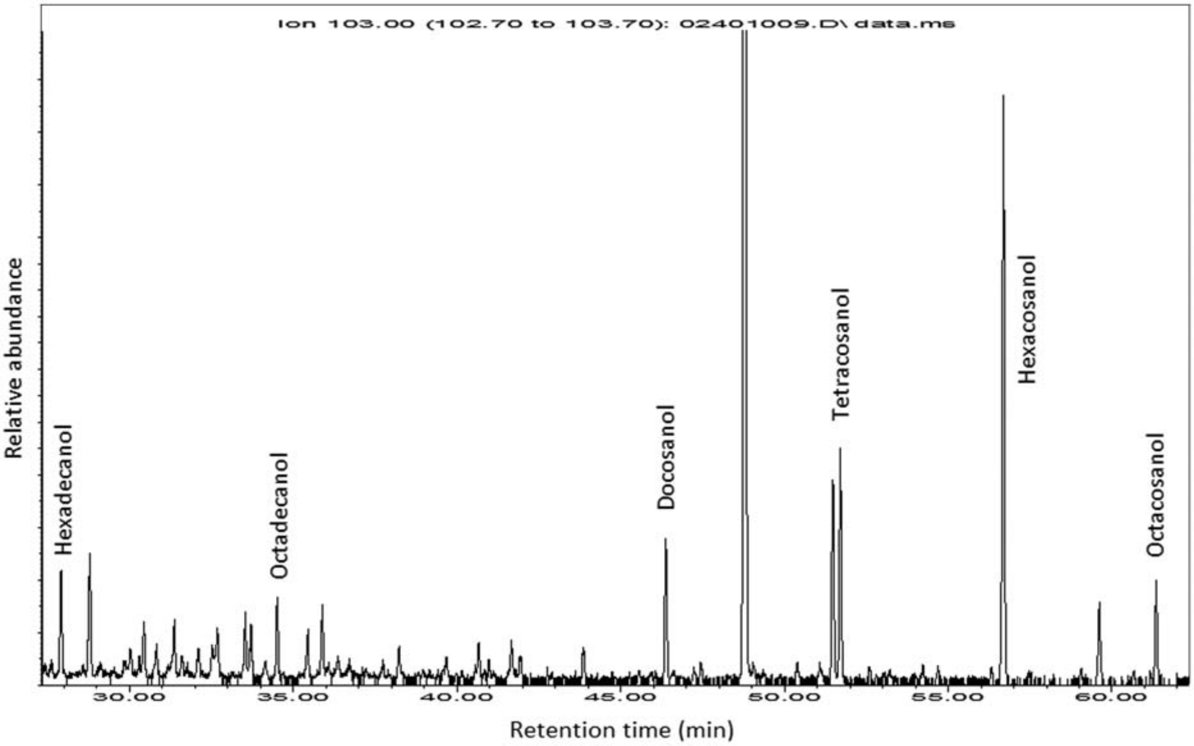

Figure 5. Chromatogram of fatty alcohols (alkanols) distribution from sample extracts (Collected: 19.7. 2014, NLZOH).

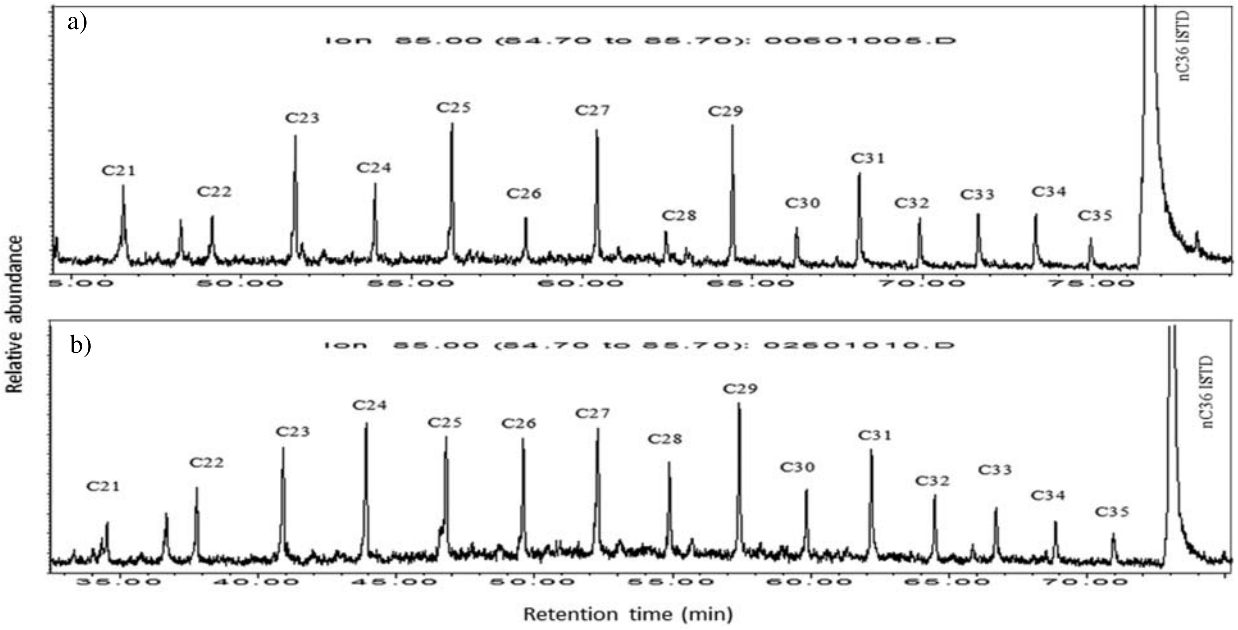

Figure 6. Typical chromatogram for distribution of n-alkanes from sample extracts collected on A) 18.7.2014 at MB NLZOH and B) 19.11.2013 at MB NLZOH.

nC35) are part of epicuticular wax layers and the waxes of needles from conifers.[19,28] *n*-alkanes with a lower molecular weight are characteristic for the car exhaust gases. The predominance of even *n*-alkanes is expected by pyrolytic decomposition of fossil fuels and burning. During the winter season we detected an increase of even numbered *n*-alkanes and a CPI close to 1 as the result of increased use of fossil fuels during the colder seasons.

3. 5. Sugars and Sugar Alcohols

All sugars and sugar alcohols are presented with fragments *m/z* 204 and *m/z* 217, sucrose and glucose have a characteristic fragment *m/z* 361. Biomass burning is a major source of atmospheric gases and particles on regional and global scales. Particles produced by biomass burning can influence the global climate.[6] Levo-

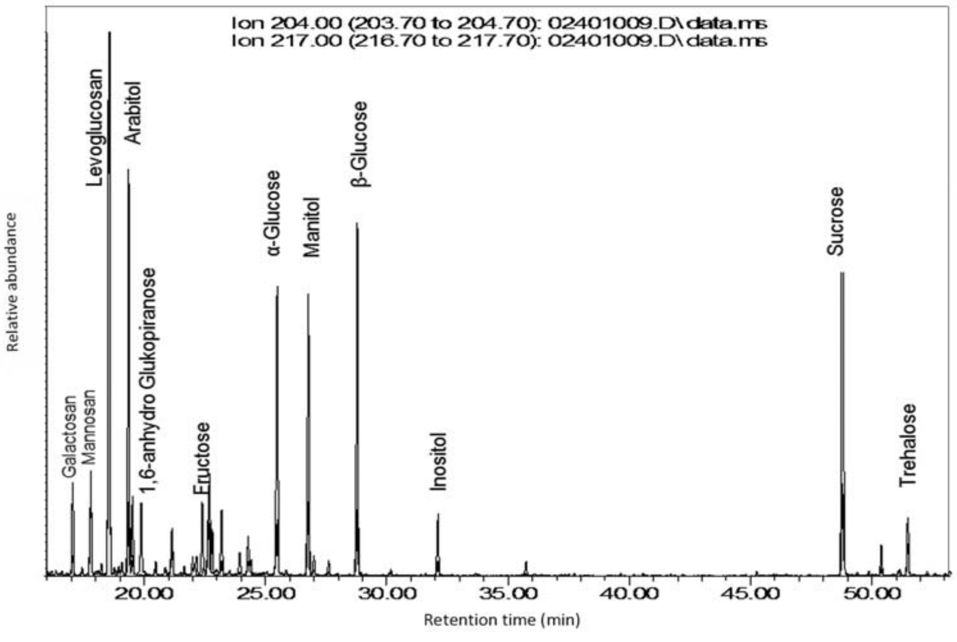

Figure 7. Total Ion current of mass fragments *m/z* 204 and *m/z* 217 characteristic for sugars and sugar alcohols silylated derivatives from sample extracts (Collected: 12.5. 2014, MB VP).

glucosan is produced by combustion of cellulose and is the key tracer compound for the incineration of biomass. Mannosan and galactosan are thermal breakdown products of cellulose and hemicellulose and were detected in all samples.[13,16] Elevated concentrations of sugars in spring and summer were observed, suggesting enhanced biological activity during warmer seasons. In all PM10 samples glucose and sucrose are the dominant sugars. Arabitol and mannitol are proposed tracer compounds of fungal spores. Plant elements such as pollen, fungal spores, fruits and their fragments are a source of fructose, glucose and sucrose. Trehalose is present in micro-organisms (fungi, bacteria and yeast), invertebrates and in some plants.[6,20] Trehalose is the most common disaccharide of earth soil and is a proposed tracer compound for re-suspension of soil particles and macadam roads.[13]

3. 6. Lignin and Resin Products

Lignin is a major biopolymer of wood and upon burning yields aromatic phenols, aldehydes, ketonic acids and alcohols.[13,17] 4-hydroxybenzoic acid is a breakdown product of lignin. Dehydroabietic acid, vanillin and vanillic acids are specific compounds of conifers.[6,14] The presence of methoxyphenols from lignin and resin acids indicates incineration of biomass.[17]

Methoxyphenols are the organic tracers for wood combustion. Direct photolysis converts vannilin or syringaldehyde into less volatile hydroxylated product such as vanillic or syringic acid. Syringaldehyde is a hardwood tracer compound, also present as minor amounts in softwood emissions.[21,22]

3. 7. Phthalate Esters

The sample extracts contained a series of the polymeric materials' additives. Di(ethyl)phthalate (DEP), di(butyl)phthalate (DBP), di(2-ethylhexyl)phthalate (DEHP), di(isononyl)phthalate (DiNP), and di(isodecyl)phthalate (DiDP) are dominating compounds. The last two are present as a mixture of several isomers. Phthalate esters have a characteristic mass fragment *m/z* 149. DEHP, DiNP and DiDP are mainly used as additives for softening PVC plastic. Evaporative releases from plastic material suggest the source for higher concentrations of phthalates during summer. Phthalates are possible carcinogens and endocrine disruptor compounds.[19]

3. 8. Secondary Organic Aerosol (SOA) Products of Terpenes

Terrestrial vegetation emits large amounts of biogenic volatile organic compounds (BVOCs) into the atmosphere. Biogenic secondary aerosols (BSOA) are a fraction of secondary organic aerosols where the constituents are emitted from biogenic sources such as vascular plant waxes, micro-organisms, pollen, isoprene, monoterpenes etc.[6] Figure 10 shows tracer compounds formed by the oxidation of cyclic monoterpene compounds. Pinonic acid and nopinone are oxidation products of monoterpenes α-pinene and β-pinene. Terpenes are large and diverse class of organic compounds, produced by a variety of plants, particularly conifers. Pohorje Mountain is highly forested with conifer trees and is a large source of terpene compounds. Sabina ketone indicates transformation of monoterpene sa-

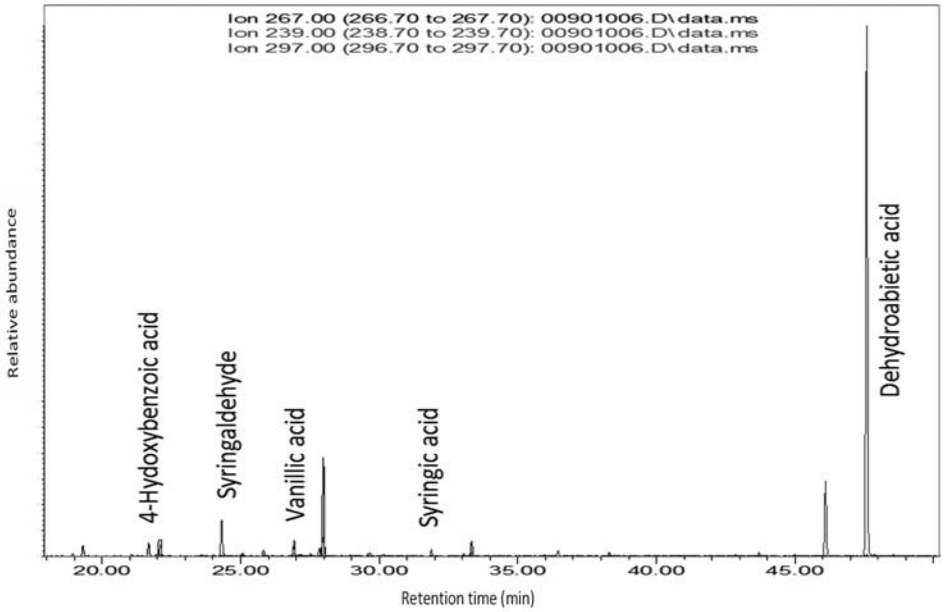

Figure 8. Selected ion chromatogram of lignin and resin acids from sample extracts (Collected: 12.5. 2014, MB VP).

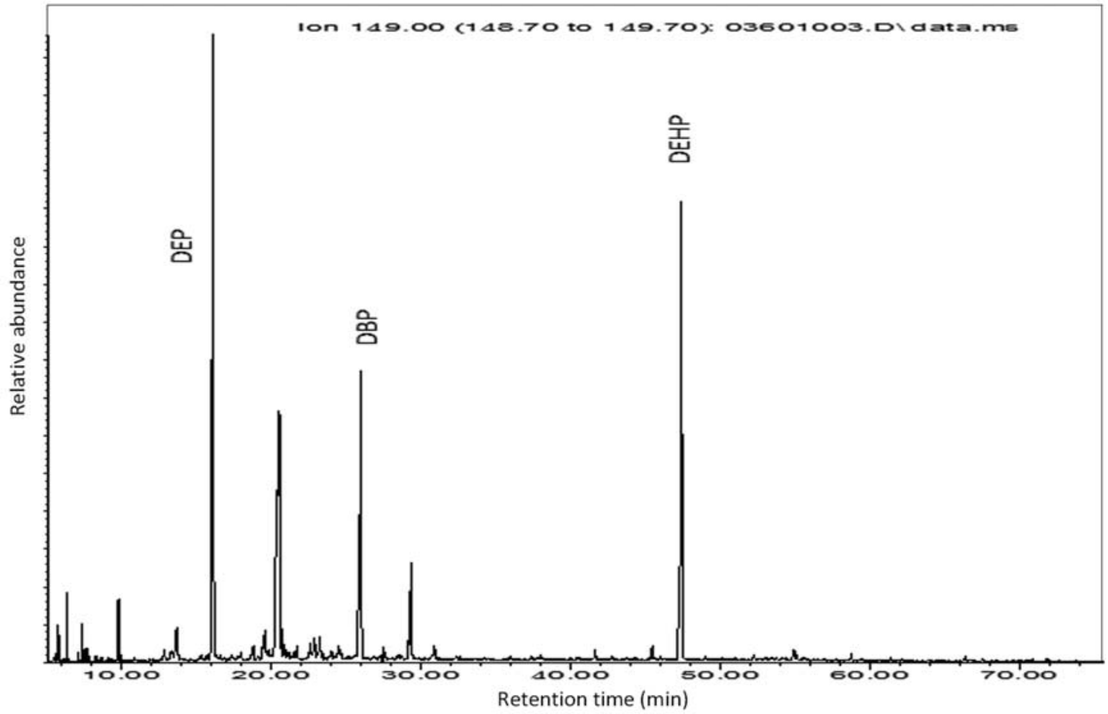

Figure 9. Chromatogram of phthalate esters from sample extracts (Collected: 18.7. 2014, MB NLZOH).

binene. Pinonaldehyde is the main product of the reaction between α-pinene, ozone and OH radicals.[6,17,23]

In the sample extracts we detected 2-methyltetrols (2-methylthreitol and 2-methylerythritol) the oxidation products of isoprene.[17] Photo-oxidation of isoprene is an important atmospheric chemical process that plays a unique role in the process of particles nucleation, contributes to the formation of SOA and causes »blue hazes« over forests.[16,17, 23]

3. 9. Unresloved Complex Mixtures

In several samples we detected unresolved complex mixtures (UCMs). UCMs appear in the chromatogram as large humps of complex mixture containing many components which are difficult to separate due to the large number of co-eluting compounds.[23,24]

It is evident from Figure 11 that the position of UCM in the chromatograms of silylated sample extract is different regarding the seasonal time. During the late

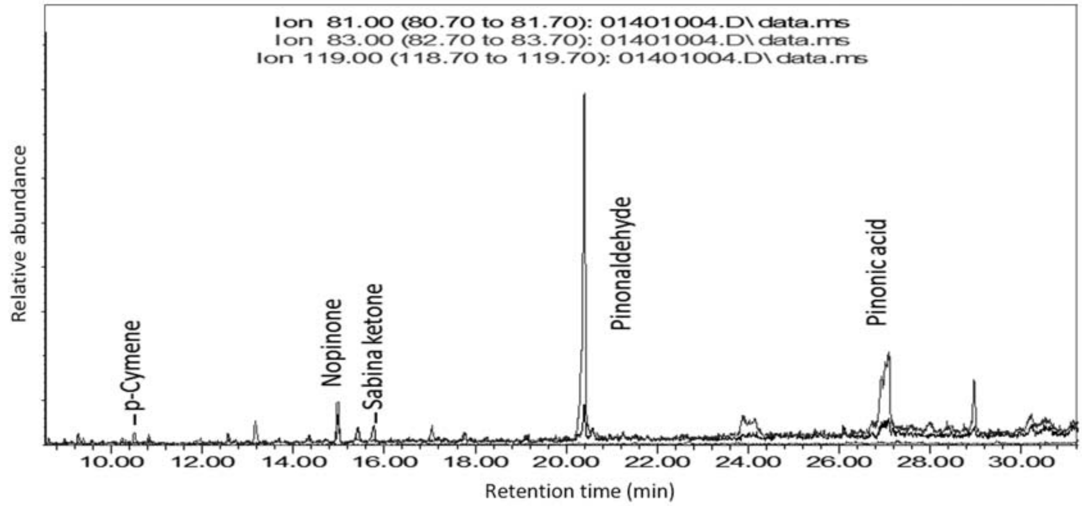

Figure 10. Ion current of selected mass fragments m/z 81, 83, 119 of monoterpenes photochemical oxidation products from sample extracts (Collected: 22.8. 2013, Miklavž).

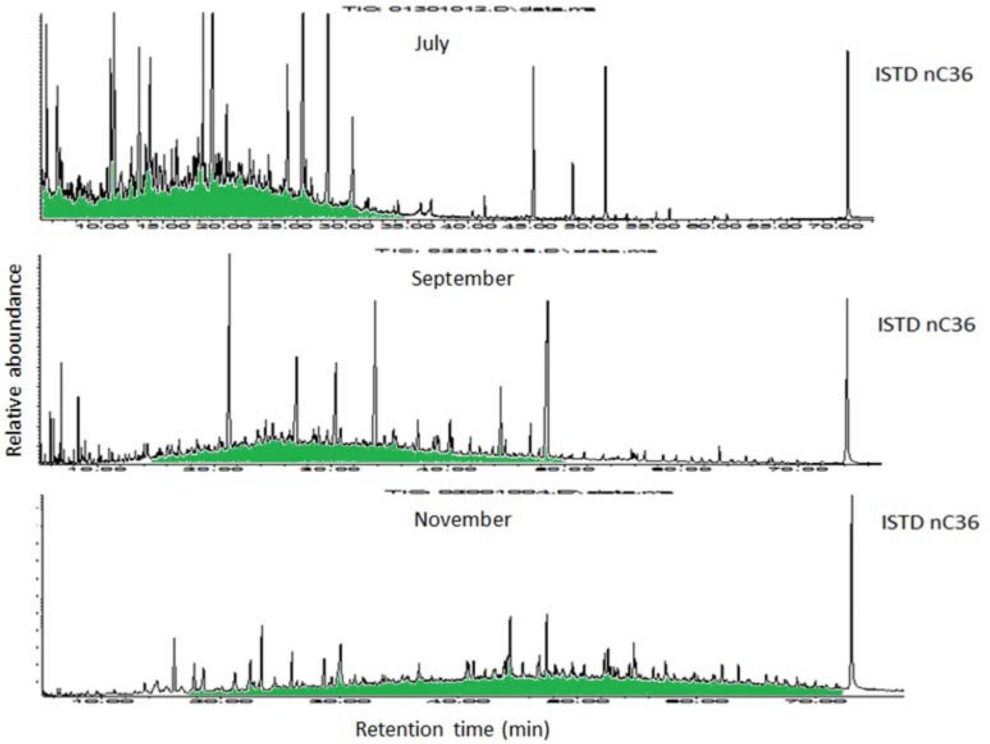

Figure 11. GC-MS chromatogram of detected UCMs from sample extracts in different seasons.

spring and summer atmospheric photo oxidation of VOCs may lead to the formation of particulate matter, also called SOA. These are polar organic compounds that are present in the air over the Maribor region. The production of biogenic precursors such as isoprene, pinene and other monoterpenes is increased in warmer seasons. This is due the influence of the Pohorje Mountain which is highly forested with coniferous trees. We used silylation, a derivatisation reaction to make polar compounds amenable for GC analysis. The formation of the silylated derivatives of SOA, namely polar polyfunctional compounds bearing labile hydrogens such as hydroxyl and carboxylic groups, provides analytes with lower polarities and better stability that enables the GC-MS identification.

During autumn and winter biogenic contribution to SOA is expected to be lower. Consequently classic UCM of branched and cyclic hydrocarbon compounds typical for fossil fuels and originating mostly from lubricating oils from vehicle engine exhausts predominate.[24,25]

3. 10. Siloxanes

Producers of air samplers prescribe different adhesive coatings used for impaction surface such as Apiezon L. grease, silicone oil or silicone grease, polyisobutene, vaseline and others materials.[32] 120 samples were obtained using Silicon-Hochvakuumfett as it is recommended in standard EN12341:2014. 30 samples were additionally obtained using polyphenylether as a coating for the impact plate. Aerosols smaller or equal to 10 μm pass through the sampler unaffected and are collected on the sampling filters. Aerosols greater than 10 μm stroke and stuck on the greasy impact plate. Solid particles may be bounced from the surface of a greasy impact plate and re-entrained into the air stream and then collected on a sample filter.[12,32] In such a way the certain part of silicones can be transferred on the sampling filter and can have an impact on the accuracy of PM10 gravimetric determination. Such "carryover" of siloxanes could disturb the gas chromatographic separation and determination of other organic compounds. In order to prevent contamination with siloxanes we experimentally used an adhesive material for the impact plate, polyphenylether (Santovac 5, diffusion pump oil is a 5-ring polyphenyl ether), with the adequate viscosity and sticky properties. This compound doesn´t interfere with the chromatographic separation of other organic compounds, because it gives only one chromatographic peak eluting at the end of the chromatogram. We haven´t detected siloxanes in sample extracts while using polyphenylether as a coating. Content of siloxanes in sample filter extracts was chromatographically quantitatively determined. The carryover of siloxanes was at least from 5% up to 15% of the accumulated particle's weight, depending on ambient temperature (from 20 °C to 30 °C during summer). This contribution of siloxanes in 50 m^3 of sampled ambient air with the daily limit value of 50 $\mu g/m^3$ for PM10 is the reason that gravimetric results for determination of PM10 sampled and measured according to the standard EN 12341:2014 were overestimated.

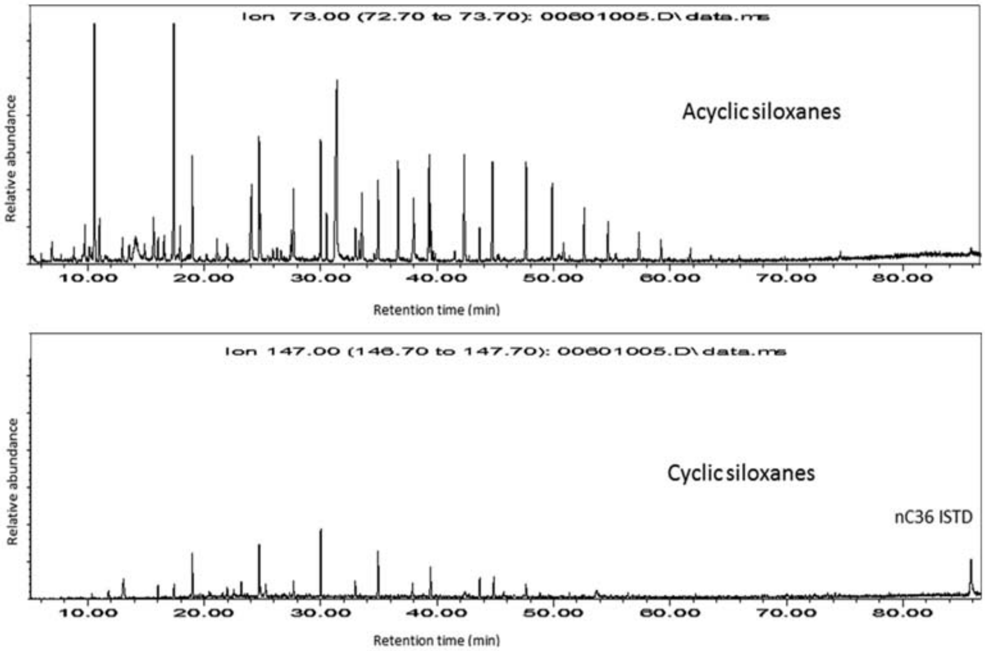

Figure 12. The chromatogram shows the distribution of anthropogenic cyclic and acyclic siloxanes from sample extracts (Collected: 22.7. 2013, MB VP).

Sample inlets should be cleaned and impact plates cleaned and greased according to the manufacturers requirements.[12] We believe that it would be better to choose only one adhesive material with unique physicochemical properties. In such a way the influence of adhesive material on gravimetric PM10 determination could be better controlled.

3. 11. PAHs

From the detected compounds and from the chromatographic data of samples gathered from Maribor district, it was evident that the presence of PAHs in comparison to other compounds was low during spring and summer but had increased concentrations during the heating season in

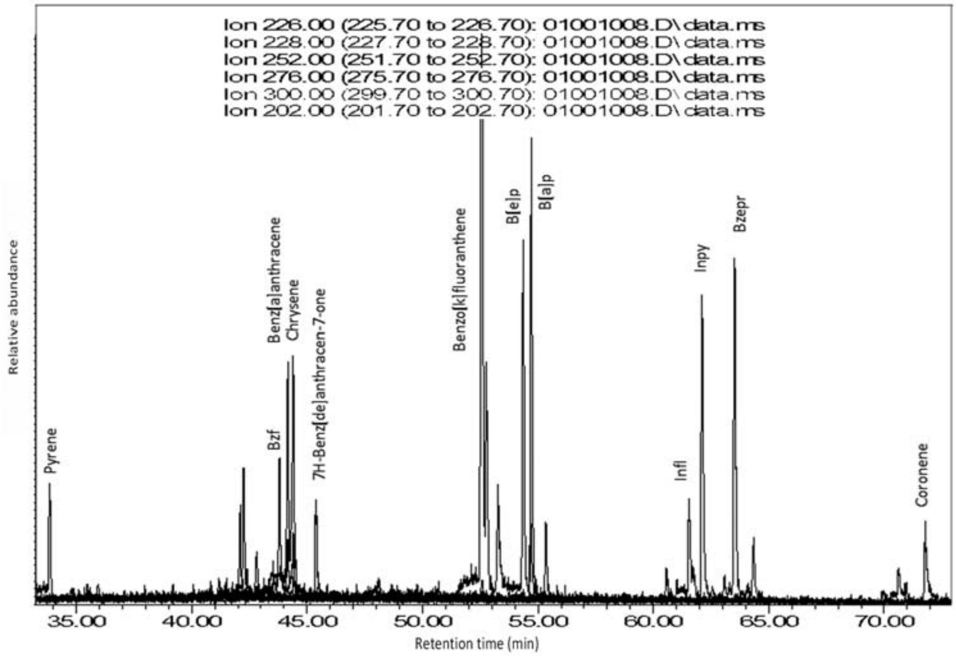

Figure 13. Chromatogram of PAHs distribution with selected ions *m/z* 202, 226, 228, 252, 276, 300 from sample extracts (Collected: 19.12. 2013, MB NLZOH).

autumn and winter with highest concentrations in December and January. Benzo[k]fluoranthene was the most abundant PAH on annual basis in the PM10 sample extracts of the city of Maribor.

PAHs are carcinogenic and mutagenic compounds naturally occurring in fossil fuels, their derived products can be formed during incomplete combustion of carbon based fuels.[13,26] Combustion of fossil fuels is the main source of PAHs in the urban atmosphere. Domestic heating, industrial processes, energy production and natural sources (biomass burning, fire and vulcanic activity) are also responsible for the release of PAHs into the atmosphere.[17]

3. 12. Other Detected Compounds

Sitosterol is an indicator for vegetation in general.[16] Cholesterol is emitted from meat cooking, fecal pollution and biological treatment plants. Nicotine is a tracer compound for tobacco smoke.[17] Urea is a nitrogen-containing organic compound that might be directly emitted from active agricultural activities, biological waste water treatment plants or is a possible product of secondary photooxidation.[6] The ketone 6,10,14-trimethylpentadecan-2-one is a SOA and can be produced by thermal alteration and oxidation of phytol emitted from plants.[17] Determination of organic compounds composition can help us to determine different local sources of air pollution. During industrial incidents air pollution in form of smoke, dust, smog or bad odour can appear. In that case air should be monitored within urban areas and in micro-environments relatively close to the emission's sources. Also the analysis of organic compounds in air should be performed. The method is suitable for the detection and tracking of local sources of pollution. In Figure 14 pollution from local industry in the city of Maribor is demonstrated, where lower molecular mass of polyoxymethylene (POM) has been detected.

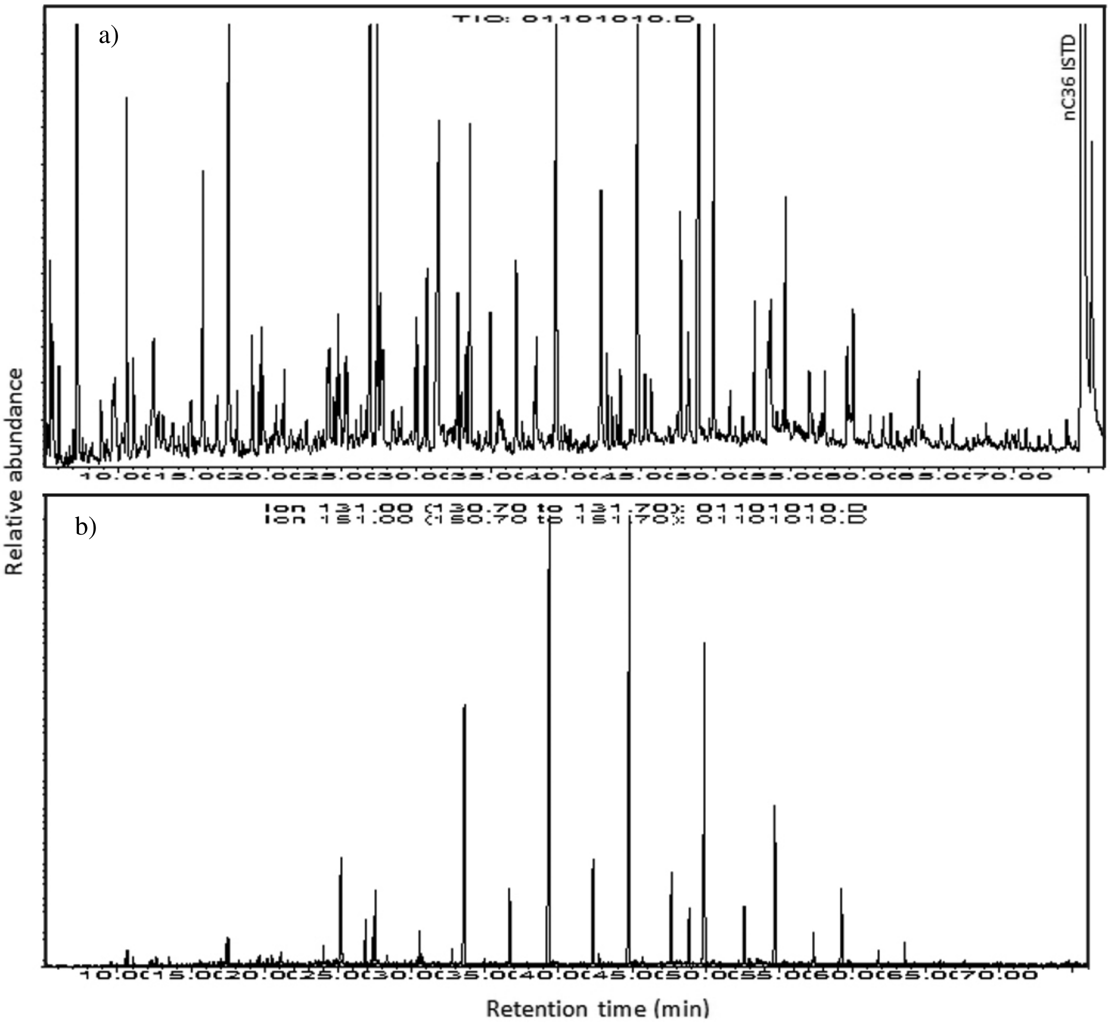

Figure 14. Chromatogram of sample PM10 extracts from an industrial zone in Maribor where impact of local industry is observed (A), characteristic selected mass fragments *m/z 131 and m/z 151 for* polyol distribution *(B).*

4. Conclusions

Using the GC-MS analytical approach the composition of organic compounds in aerosols was determined. The suspended fraction of particulate matter PM10 in the air samples was analysed according to the standard EN 12341:2014 reference method. The research included 120 samples sampled during the period from summer 2013 to summer 2014. Beside gravimetric determination of PM10, the composition of organic compounds for estimation of pollution source was performed. During determination of organic compounds composition, the primary and secondary sources of air pollution were investigated. The technique of recording the full mass spectra has allowed us to monitor the presence of many pollution tracer compounds. The detected compounds included distributions of fatty acids, *n*-alkanes and iso-alkanes, phthalate esters, siloxanes, sterols, sugars and sugar alcohols, lignin tracer compounds and resin acids, dicarboxylic acids, polycyclic organic compounds, organic nitrogen compounds and products from secondary oxidation of monoterpenes. For the determination of volatile and semi-volatile polar organic compounds, the silylation was a prerequisite for good chromatographic analysis.

It was proven that the use of silicone grease for the purpose of lubricating the impact plate of the air sampler may cause higher values of gravimetric results. Quantitative determination was performed for siloxanes, which are a source for »carry over« and consequently are the reason for overestimated gravimetric results of PM10 determination according to the EN 12341:2014 reference method.

We demonstrated that the method is suitable for detecting and tracking air pollution from local sources. The research provides us with a better insight into composition of organic compounds in the atmosphere above Maribor.

5. Acknowledgements

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Povzetek

V 120 vzorcih PM10 smo analizirali organske spojine v aerosolskih delcih v zraku nad Mariborom z uporabo metode EN 12341:2014. Proučevali smo sestavo organskih spojin ter primarne in sekundarne izvore le-teh. Za določevanje hlapnih in delno hlapnih polarnih organskih spojin z GC-MS smo uporabili sililiranje kot derivatizacijsko metodo. Določevali smo porazdelitve maščobnih kislin, *n*-alkanov in izo-alkanov, ftalatnih estrov, siloksanov, različnih sterolov, različnih sladkorjev in sladkornih alkoholov, spojine ligninov in smolnih kislin, dikarboksilnih kislin nastalih s fotokemijskimi reakcijami, policikličnih organskih ogljikovodikov, organskih dušikovih spojin in produktov nastalih pri sekundarni oksidaciji monoterpenov. Uporaba silikonske masti na površini impaktne plošče vzorčevalnika lahko povzroči višje vrednosti gravimetrijske določitve. Trdni delci se lahko odbijejo od impaktne plošče in ponovno vstopijo v zračni tok in se nato zberejo na filtru. To prenašanje siloksanov je lahko najmanj od 5% do 15% skupne mase akumuliranih delcev v odvisnosti od temperature. To je razlog, da so gravimetrijski rezultati določevanja PM10 po EN 12341:2014 standardu previsoki.

SUPPLEMENT:

The levels of detected organic compounds were expressed in relation to the injection standard hexatriacontane (HTA, n-C36) with the equation (1). We used the method of normalization in relation to the injection standard HTA.

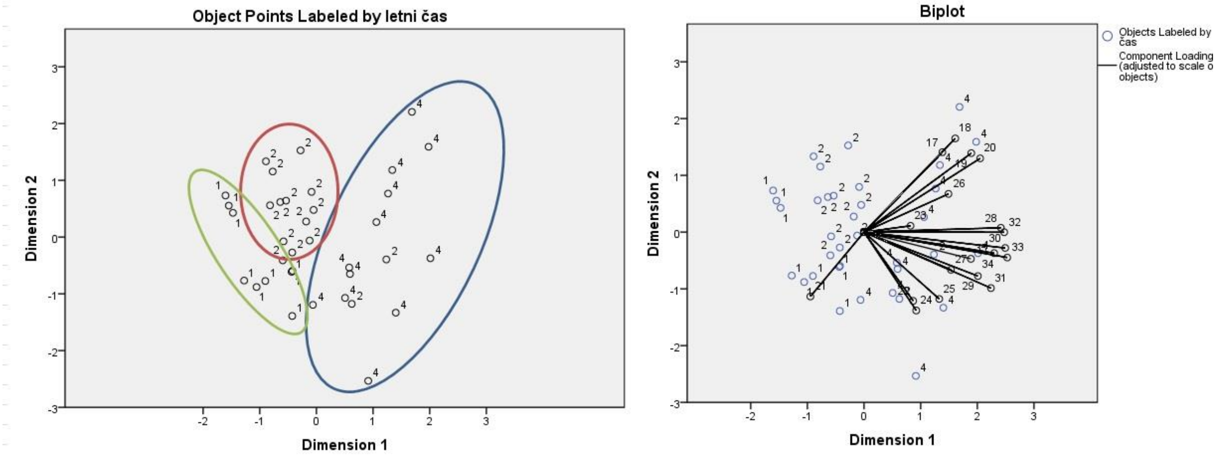
Ci = (Ai / AHTA) (1)

Ci: mass fraction of the compound i
Ai: peak area of compound i
A : peak area of hexatriacontane (HTA)

Statistical data calculations and graphical displays were performed using program IBM SPSS Statistics 21, Microsoft EXCEL was applied for the data preparation and generation of the results' outputs. The direct examination of any inter-relation between the two measured analytes was mostly realized by the correlation analysis when determining the extent to which the values of the two variables were mutually dependent. We carried out the test of normality by which we checked the assumption of the normal distribution of data. Because the data was normally distributed, we used the Pearson correlation analysis. Principal Components Analysis (PCA) is an important method for the characterization of different samples. This method was used for classifying samples of PM10 in dependence on the measured variables. We carried out the analysis of variance (ANOVA), a method used to determine whether there are any significant differences between the means of three or more groups. With ANOVA we compared the samples of PM10 in dependence of the measured variables.

1. **n-alkanes**

The homologue distribution of n-alkanes and their CPI values are useful tools to distinguish sources. We normalized chromatographic data. The peak area of individual organic compound was divided with peak area of standard compound hexatriacontane. We calculated the CPI values for n-alkanes. The sum of odd n-alkanes was divided by the sum of even n-alkanes. The average CPI in summer was 2.45 with a maximum at 8.03 pointing to increased biogenic emissions. In winter we calculated an average CPI of 1.07. These lower CPI values could be explained due to lower biogenic activity and increased use of fossil fuels because of the heating season in winter. We also observed that in winter the daily CPI was never higher than 1.5.



PCA analysis for n-alkanes labeled by season (1. summer, 2. spring, 4. winter).

From the data in figure 1 we can conclude that n-alkanes have greater concentrations in winter. From the calculated CPI (Table 1) we concluded that the main sources of n-alkanes in warmer seasons are biogenic emissions. In winter season the main source is burning of fossil fuels.

Table 1. Calculated CPI for n-alkanes

Season	Month	CPI
1	7	2,1945
1	7	1,577077
1	7	2,548057
1	7	2,11946
1	7	7,143483
1	7	8,031594
1	7	2,844191
1	7	3,941347
1	7	3,334718
2	5	1,960648
2	5	1,708324
2	5	1,499454
2	5	2,066057
2	5	1,516805
2	5	6,495399
2	5	0,722564
2	5	0,550732
2	5	0,628907
2	5	0,550643
2	4	1,825488
2	4	1,585603
2	4	1,199747
2	4	1,383403
2	4	1,412544
4	12	1,083993
4	12	1,219255
4	12	1,356668
4	12	1,70117
4	12	1,52465
4	12	1,926487
4	12	1,16167
4	12	0,629022
4	12	0,629022
4	12	0,527793
4	12	0,527793
4	12	0,595326

2. **Chromatographic determination of siloxanes**

Qualitative and quantitative analyses were performed with a GC/MS system consisting of a HP 6890 Gas Chromatograph with a 5973 Mass Selective Detector (Agilent Technologies, CA, USA). For quantitative analysis of siloxanes, the instrument was operated in selected ion monitoring (SIM) mode. The selected ions for siloxanes were *m/z* 147 and *m/z* 221. The injected volume was 2 µL and the splitless technique was used. The ion source temperature was 230 °C. The injection port and transfer line were kept at 290 °C. The temperature program was the following: 0.75 min at a temperature of 105 ºC, 30 ºC /min up to 120 º C (0.1 min), 2.7 °C/min to 320 ºC (5 min). The carrier gas was helium (He 6.0, Messer Austria) at a constant flow of 0.9 ml/min. The ion source temperature was 250 °C. The injection port and transfer line were kept at 290 °C. The standard stock solution was constructed from the same Silicon-Hochvakuumfett grease (Merck 100g, CAS Nr. 107922) with which the impact plate of the instrument was greased. We prepared a standard stock solution STD with a concentration of 2 *µg/µL.* For the quantification of siloxanes calibration curves were constructed by analyzing aliquots of stock solution. The 4 points for the calibration curve were prepared by using calibrated syringes with which we pipetted different volumes of the standard stock solution and added a known amount of the external standard hexatriacontane. We daily prepared and measured calibration solutions, using STD and InjSTD to assure method linearity and precision.

The concentration of PM10 was gravimetrically determined. Filters were weighted before and after the sampling. The difference is the weight of PM10. The concentration of PM10 is expressed as weight per volume of 1 m^3 of sampled air. The determined concentrations of siloxanes in sample extracts were divided with the volume of sampled air. Percentage of siloxanes was calculated by dividing mass of siloxanes with the mass of PM10.

Table 2. Calibration curve for siloxanes

Calibration curve points	InjSTD nC$_{36}$ *c= 0,5 µg /µL*	STD stock solution *c =2 µg/µL*
K1	5000 ng - 10 µL	2 µg - 1 µL
K2	5000 ng - 10 µL	10 µg - 5 µL
K3	5000 ng - 10 µL	20 µg - 10 µL
K4	5000 ng - 10 µL	50µg - 25 µL

Table 3. Gravimetrically weighing and PM10 calculations according to EN12341 for summer sample extracts.

Location	Filter Nr.	The mass of the filter before weighing (g)	The mass of the filter after weighing (g)	Difference (*µg*)	Volume (m^3)	C$_{PM10}$ (*µg*/ m^3)
MB VP	3611	0,11134	0,11180	460	55,14	8,3
MB VP	3612	0,11132	0,11184	520	55,13	9,4
MB VP	3613	0,10880	0,10943	630	55,14	11,4
MB VP	3614	0,11277	0,11340	630	55,13	11,4
Miklavž	3625	0,11272	0,11338	660	54,54	12,1
Miklavž	3626	0,11213	0,11338	660	57,89	11,4
Miklavž	3627	0,10992	0,11076	840	54,54	15,4
Miklavž	3628	0,11100	0,11190	900	54,54	16,5

Table 4. Calculated % of siloxanes for summer sample extracts.

Location	Filter Nr.	Calculated mass sum of siloxanes (*µg*)	∑C$_{siloxane}$ (*µg*/ m^3)	C$_{PM10}$ (*µg*/ m^3)	% siloxanes compared to C$_{PM10}$
MB VP	3611	47,03	0,94	8,3	11,34
MB VP	3612	22,52	0,45	9,4	4,79
MB VP	3613	28,84	0,58	11,6	5,09
MB VP	3614	29,30	0,59	11,4	5,14

Miklavž	3625	60,09	1,20	12,1	9,93
Miklavž	3626	48,29	0,97	11,4	8,47
Miklavž	3627	60,85	1,22	15,4	7,90
Miklavž	3628	104,45	1,92	16,5	11,64

Table 5. Calculated % of siloxanes for silicone grease and polyphenyether.

Location	Date	Coating for impaction plate	Calculated mass sum of siloxanes (μg)	$\sum C_{siloxane}$ (μg/ m^3)	C_{PM10} (μg/ m^3)	% siloxanes compared to C_{PM10}
Miklavž	20.9.2015	silicone grease	11,32	0,21	9,4	2,23
Miklavž	21.9.2015	silicone grease	19,33	0,36	11,4	3,14
Miklavž	22.9.2015	silicone grease	16,74	0,31	11,4	2,74
MB VP	20.9.2015	silicone grease	23,22	0,43	15,0	2,88
MB VP	21.9.2015	silicone grease	18,9	0,35	16,3	2,13
MB VP	22.9.2015	silicone grease	19,47	0,36	18,4	1,96
MB VP	20.9.2015	polyphenylether	0,0	0,0	15,0	0,0
MB VP	21.9.2015	polyphenylether	0,0	0,0	16,3	0,0
MB VP	22.9.2015	polyphenylether	0,0	0,0	18,4	0,0

For the comparison of coatings for impaction plate we used 3 low-volume vacuum samplers at 2 locations. On 2 samplers we used silicone grease for impaction plate and on 1 we used polyphenyether (Santovac 5). Before any measurements were done, we cleaned all the sampler parts with toluene. Table 5 demonstrates the use of polyphenylether coating compared to silicone grease. The results show, that sample extracts for using silicone grease coating had an average of 2,51 $\mu g/m^3$ of siloxanes per sample. We didn't detect any siloxanes while using polyphenylether, but we detected polyphenylether as a “carryover” contaminant.