Organic Compounds on PM_{10} Particles in Air Pollution

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Abstract

In Ružomberok (Slovakia) and its environs, PM10 air pollution was analysed in the winter and summer periods of 2015 in order to identify organic composition. In the winter months, a higher number of organic substances (536) was found than in summer (374); the concentrations of various organic substances were higher in winter. Organic compounds were determined in the samples of air pollution by pyrolysis chromatography with mass spectrometric detection. Analysis showed that the higher concentrations of organic compounds in PM10 are the result of fossil fuel and biomass combustion. Apart from these sources, substances from transport, combustion and volatilization of polymers based on plastics, preparation and processing of food and biogenic (natural) contamination have been identified in air pollution. Biomass combustion was demonstrated using the diagnostic ratio levoglucosan/manosan. The average proportion of pollution produced by biomass combustion for the summer months is 4% and winter months 15%.

Keywords: air pollution, markers, combustion, biomass, fossil fuels, geochemical background

Introduction

Burning fossil fuels, biofuels and a variety of waste, along with of transportation and industrial activities have led to an increase in the content of fine and ultrafine particles – PM (particulate matter) in the air. PM particles emitted by different anthropogenic processes contain various chemical compounds generated during certain combustion conditions and also depend on the chemical composition of the original fuel. The organic substances contained in the PM particles allow the identification of pollution sources, monitoring what happens with pollutants in the environment (Giri et al., 2013). This is due to "genetic" relationship between the resulting contaminant and the parent matrix from which the contaminant was released. Compounds that are distinguished by this relationship are referred to as geochemical (molecular) markers (Simoneit, 2004). Geochemical markers are released into the environment mainly through thermal processes – burning fossil fuels. In neither case they are a by-product of combustion, they must be considered to be indicators.

Pollutants produced by specific anthropic activities are referred to as anthropogenic molecular markers. They include plasticizers, flame retardants, linear alkyl benzenes, polycyclic aromatic hydrocarbons, detergents, additives, silicones (Ricking et al., 2003). Markers for the identification of biogenic (natural) materials constitute a significant proportion of organic matter contained in PM particles. Identification of the original fuel and other sources of pollution in the PM particles is performed using the above mentioned markers. The markers contained in PM particles can be divided based on the occurrence to the unique (these are typical and unique to a given fuel) and general (these are supporting and occur in more types of fuels).

This article is focused on the identification of organic compounds in PM_{10} particles and evaluation of sources of pollution in the city of Ružomberok using markers and diagnostic conditions in the summer and winter period, and the identification of the geochemical background values and anomalous concentrations.

Material and methods

The company ENVITECH collected samples of pollutants PM_{10} using low-volume samplers in Ružomberok municipal city districts and in the surrounding villages during summer and winter of 2015 (Figure 1). The sampling localities: Martinček, Hrboltová, U polikliniky, Sv. Anny, Pod Cintorinom, A. Hlinka Square, Štefana Hýroša, Klačno, Liptovská Štiavnica, Likavka, Hriadky, Nová Hrboltová, Lisková, Štiavnička, Automont complex, Karola Sidora, Road to the brickyard, Baničné, Mondi areal, Gravel Pit. To ensure a sufficient amount of sample on the filter, the collection lasted one day during the winter season and 3 days in the summer season.

Organic compounds including (the content of resistant organic material and the determination of degrada-

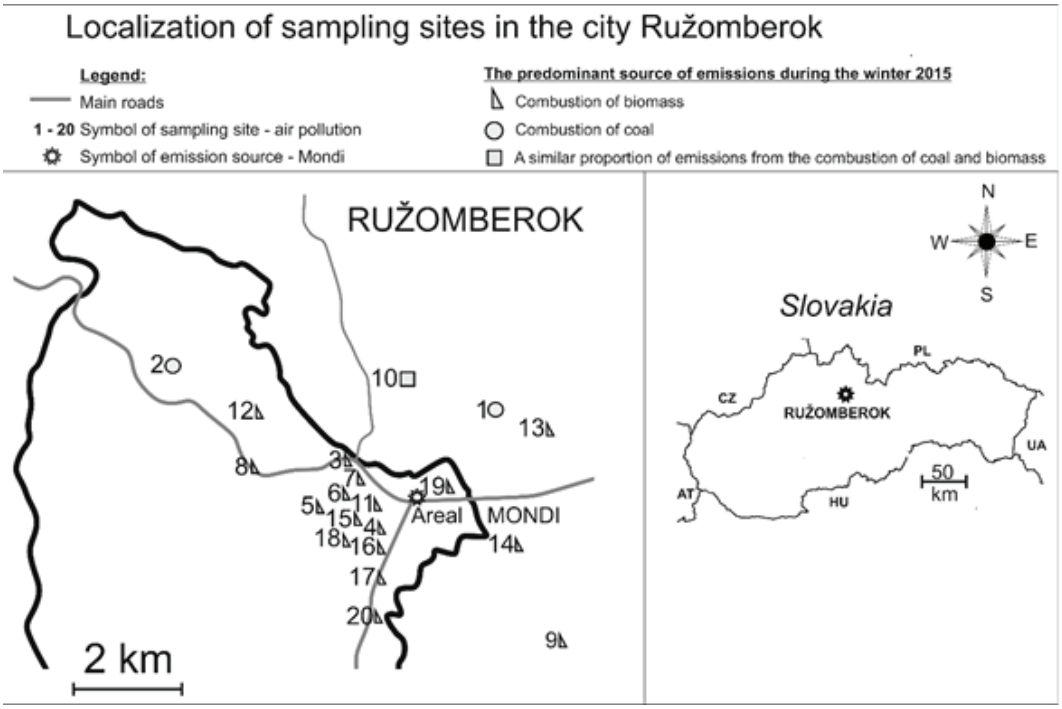

Fig. 1 Sampling localities in the city of Ružomberok.
1. Martinček, 2. Hrboltová, 3. U polikliniky, 4. Sv. Anny, 5. Pod Cintorinom, 6. A. Hlinka Square, 7. Štefana Hýroša, 8. Klačno, 9. Liptovská Štiavnica, 10. Likavka, 11. Hriadky, 12. Nová Hrboltová, 13. Lisková, 14. Štiavnička, 15. Automont complex, 16. Karola Sidora, 17. Road to the brickyard, 18. Baničné, 19. Mondi areal, 20. Gravel Pit

Rys. 1 Lokalizacja miejsc pobierania próbek:
1. Martinček, 2. Hrboltová, 3. U polikliniky, 4. Sv. Anny, 5. Pod Cintorinom, 6. Plac A. Hlinka 7. Štefana Hýroša, 8. Klačno, 9. Liptovská Štiavnica, 10. Likavka, 11. Hriadky, 12. Nová Hrboltová, 13. Lisková, 14. Štiavnička, 15. Automont complex, 16. Karola Sidora, 17. Droga do cegielni, 18. Baničné, 19. Mondi areal, 20. Żwirownia

tion products from combustion of plastics (analysis of additives and markers) were determined in the samples of air pollution by the py-GC/MS method.

Results

The following groups of organic compounds have been identified in air pollution – aromatic hydrocarbons, alkanes, alkenes, alkines, alkadienes and their cyclic analogues, aldehydes, ketones, phenols, ethers, oxiranes, carboxylic acids, nitrils, pyrans, furans, benzofurans, polycyclic aromatic hydrocarbons, anhydrosaccharides, nitrogen compounds, compounds containing sulphur, geochemical markers and additional markers. In the winter and summer seasons, the occurrence and concentration of organic compounds are different. 536 compounds were identified in winter, while in summer, there were only 374 organic compounds. Comparing the concentration for the winter and summer season it was found (Table 1), that in winter there is an increase in all groups of organic compounds. The most significant increase in the concentrations proves to be in alkanoates (50 x) anhydrosaccharides (26 x), sulphur compounds (18 x), pyrans, furans and benzofurans (17 x), aldehydes and ketones (16 x), alkanes (13 x), carboxylic acids (12 x), nitrils and polycyclic aromatic hydrocarbons (11 x), and phenols (10 x). The concentration of the remaining organic compounds, e.g. ethers and oxirane, alkenes, the BTEX chemicals, geochemical, and other markers are increased from 2.5 to 8.5 x compared to the concentrations in summer.

Figure 2 shows the number of exceedances of geochemical background values for 20 groups of organic compounds. The highest number of exceedances in both winter and summer is shown in the locality Martinček, Hrboltová and Lísková, in summer Likavka (Ružomberok satellite village).

Increase the concentration of organic substances in the winter period is related to combustion processes. Increased concentrations of anhydrosaccharides and markers such as dehydroabietic acid, methyldehydroabietate, stigmasta-3.5-diene (thermal alteration product of stigmasterol) dehydroabietine, retene indicate biomass combustion. Biomass combustion was demonstrated using the diagnostic ratio levoglucosan/manosan (Ward et al., 2006, Simoneit et al., 1999). Biomass combustion in winter was demonstrated at all localities except for the localities Štefana Hýroša, A. Hlinka Square, Sv. Anna, Pod Cintorinom, Baničné, and U polikliniky. The average percentage rate of pollution produced by biomass combustion for the summer

Tab. 1 The background values and anomalous values for organic compounds in the summer and winter season (ng/m³)

Tab. 1 Zawartości składników organicznych tła i wartości odchylen dla sezonu letniego i zimowego (ng/m³)

	Winter		Summer		
	Background	Anomaly threshold	Background	Anomaly threshold	Winter/summer
BTEX	1,590	5,370	850	1,750	1.87
Alkanes, cycloalkanes	73.88	239	5.72	13.4	13
Alkenes, cycloalkenes	36.78	111	5.3	11.6	7
Alkines	2.81	9.4	1.12	4.1	2.5
Alkadienes	5.28	18.8	1.58	4.4	3.3
ALCOHOLS	27.75	81	5.57	26	5
Alkanoates	49.5	444	BLD		50
Aldehydes and ketones	44.83	135	2.88	7.8	16
Phenols	22.81	61	2.39	6.3	10
ETHERS +OXIRANS	1.33	4	0.27	1	5
Carboxylic acids	71.78	173	5.92	13.4	12
Nitrogen containing compounds	35.07	109	3.65	9.5	10
Nitrils	13.89	60	1.2	3.5	12
Pyrans, furans, benzofurans	10.03	30.4	0.58	2.0	17
PAHs	129.24	324	11.22	26.4	12
Sulphur containing compounds	5.26	16.7	0.29	1.7	18
Markers	133.54	518	15.5	32.1	9
Geochemical biomarkers	29.72	69	19.18	35.5	1.5
ANHYDROSACCHARIDES	48.64	130	1.85	9.4	26

Explanatory notes: BLD – below detection limit

BIOMASS	Fossil fuels	**Biomass and fossil fuels**	***Biomass and fossil fuels and transport***

months is 4% and for the winter months 15%. Increase in the content of phenol-containing compounds is not associated only with biomass combustion, when phenolic compounds (e.g. methoxyphenols) are released by fragmentation of lignin and tannins (Bocchini et al., 1997), but also with the combustion of fossil fuels (coal).

Combustion of fossil fuels produces a higher concentration of organic compounds with sulphur, which are not generated by burning biomass (Song and Peng, 2010). It also produces unique geochemical markers from the group of hopanoid and isoprenoid hydrocarbons, steranes. The occurrence of fragments from coal combustion in PM particles is also associated with the occurrence of alkanoates, unique (e.g. hydroxyprene) and typical polycyclic aromatic hydrocarbons according to the US EPA, aliphatic and aromatic hydrocarbons, carboxylic acids and alkylnitrils. Verification of the origin of the above mentioned organic substances for the combustion of coal is carried out using the diagnostic ratios of geochemical markers (pristane/phytane, 22S-17α(H),21β(H)-homohopane (C_{31})/22S-17α(H),21β(H)-homohopane (C_{31}) + 22R-17α(H),21β(H)-homohopane (C_{31}) and others), and calculating the CPI index (Carbon Preference Index) for aliphatic organic substances. CPI index is a key diagnostic parameter to determine the biogenic and anthropogenic nature of n-alkane sources. Based on the calculation of the CPI index and ratios of hopanoid and isoprenoid hydrocarbons, emissions from the combustion of coal in winter were unequivocally confirmed at the localities Martinček, Likavka and Hrboltová. In other localities, based on the values of the above mentioned diagnostic ratios, emissions from the combustion of petroleum substances and products (gasoline, diesel, oil) were detected.

Increased incidence of ketones in PM_{10} air pollution in winter is generally related to the combustion

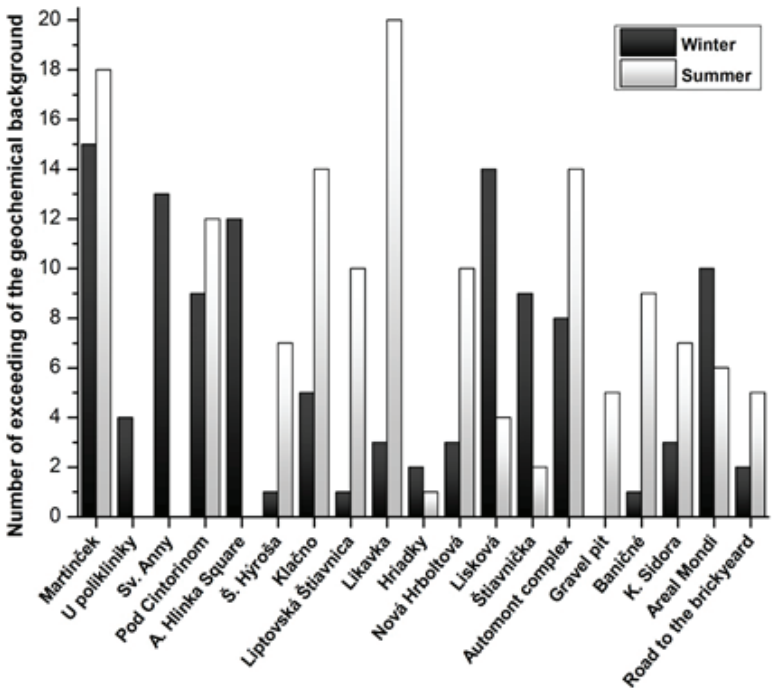

Fig. 2 The number of exceedances of the geochemical background

Rys. 2 Ilośc przekroczeń wartości geochemicznych tła

of biofuels and fossil fuels. Ketones are derived from thermal alteration products of aliphatic precursors that are oxidized by the secondary alkanols to ketones. The origin of ketones cannot be determined, their source is not specific, but they reflect combustion conditions. Similarly, increased concentrations of alkenes indicate the increased thermal processes, as alkenes are thermal decomposition product of alkanes contained in the original fuel.

An important group of organic compounds contained in PM_{10} at all localities were aromatic hydrocarbons from the BTEX group (benzene, toluene, xylens, and ethylbenzene). The occurrence of the compounds from the BTEX group in PM_{10} is mainly associated with combustion and transport. The average concentration of BTEX for the winter season ranges from 0.19 (A. Hlinka Square) to 4.31 (Nová Hrboltová) µg/m³. During summer, the average concentrations of the compounds from the BTEX group range from 0.10 (Likavka) to 2.31 (Martinček) g/m3. The average concentration of BTEX for all localities in summer is 0.82 µg/m3, while in winter it is almost 2.7 times higher (2.19 µg/m3). The identification of the origin of benzene is possible on the basis of the diagnostic ratio B/T, benzene/toluene (Barletta et al., 2005, Buczynska et al., 2009). The values of the ratio B/T>1 indicate combustion (Fabbri et al., 2012), the values ranging from 0.67 to 0.74 indicate the transport (Barletta et al., 2005).

In the summer season, at all localities except Hrboltová, the values of the ratio B/T correspond to the range stated for transportation. In the winter season, benzene emissions from combustion were confirmed at the localities Martinček and Mondi Areal. The remaining localities include emissions of benzene and toluene, especially from traffic. Higher average concentrations of BTEX in the winter season are due to increased emissions of these hydrocarbons from combustion processes (coal, biomass) and a slight increase in traffic, especially in Ružomberok municipal city districts. The average percentage rate of pollution produced by transport have been calculated using the methodology of Rushdi et al., (2014). In the summer and winter months, it is 23%. The average percentage rate of pollution produced by the combustion of coal is about 14% in winter.

Fragments characterizing combustion and volatilization of polymers based on plastics were identified in all air pollution in the winter and summer season, except for the locality U polikliniky. The identification was based on fragments of unique and general markers which, are typical of synthetic polymers. Usually these substances (markers) form additives, flame retardants, plasticizers, antioxidants, lubricants, which are added to synthetic polymers to improve their properties. The substances normally exhibit different stability in the environment, the degree of stability (persistence) depends on their chemical, physical and chemical properties. The markers that were identified include primarily phthalates (bis(2-ethylhexyl)phthalate, dibutylphthalate, diethylphthalate, diisoktylphthalate), adipates (diisooctyl adipate), phosphates (triphenyl phosphate), stearate zinc, caprolactam, 2-ethylhexylacrylate, chlorothene monomer (vinyl chloride). These fragments

were detected in the winter season in the localities Martinček and Baničné. For phthalates and adipates it can be assumed that their emissions in summer are released into the environment mainly by spontaneous volatilization due to high temperatures (Teil et al., 2006), and in winter they are released into the environment by combustion. This hypothesis was confirmed by comparing their concentrations in winter and summer. The amount of phthalates, adipates and triphenyl phosphate in summer ranges from 0.08 (Štiavnička) to 1.71 ng/m³ (Martinček) with an average value of 0.66 ng/m³. In winter they range from 0.1 to 19.8 ng/m³ with a mean value of 5.39 ng/m³. In the winter season, the concentration of phthalates and adipates increased about 8 times, their occurrence in the environment is therefore related to combustion.

Emissions from the preparation and processing of food were identified based on the occurrence of unique (specific) markers, which include carboxylic acids (octadecanoic, hexadecanoic, oleic, palmitooleic), nonanal and cholesterol. For direct indication of emissions from food preparation, we can apply the diagnostic ratio C_{18}/C_{16} (octadecanoic/hexadecanoic acid) in the range from 0.9 to 1 (Rogge et al., 1991). Emissions from food preparation were identified at all localities. In the winter season, the average contribution of emissions was 3%, in the summer season it was 2%.

In the air pollution PM10, both in summer and in winter, fragments of substances which originate from natural decomposition of biogenic (natural) mass were detected. An integral part of the biogenic material are fragments of vegetation, but also microorganisms (e.g. spores, bacteria, etc.) and small animals (e.g. insects). Biogenic matter is released into the air by various decomposition processes, volatilization and various mechanical damages, abrasion. Volatilization is among the most significant natural ways to release of certain substances (e.g. essential oil, terpenes) mainly from coniferous trees into the environment. From the fragments, simple saccharides, terpenoid substances, colourants, sterols, plant alkadienes (isoprene) were identified. Fragments of proteins were identified by the occurrence of pyrrole, pyridine and indole, and their compounds. Fragments derived from the degradation of complex saccharides and polysaccharides (cellulose, hemicellulose) were identified using simple pyrans, furans, furfural, 2.5-dimethylfuran, furancarboxaldehyde, hydroxypropanone, furanmethanol cyclopentenone and its compounds (Saiz Jimenéz and De Leeuw, 1986). Lignin fragments were identified in accordance with (Bocchini et al., 1997, Chiavari and Galletti, 1992). Microbial activity was identified by the presence of simple alcohols and lower carboxylic acid (pentadecanoic, dodecanoic, tetradecanoic) and the occurrence of ergosterol.

The quantity of biogenic materials was determined using the sum of the above mentioned markers. The amount of fragments of biogenic materials varies depending on the season. Maximum concentrations occur in summer for analysed PM_{10} particles from 27% (Sv. Anny) to 58% (Liptovská Štiavnica) when vegetation growth reaches its optimum. The average quantity of biogenic matter reaches 37% in summer and 24% in winter.

Conclusion

The analysis of PM_{10} particles in winter and in the summer season showed that the concentrations of all the groups of organic compounds are much higher in the winter season. The highest number of exceedances of the geochemical background in winter was found for the localities: Likavka, Martinček, Klačno, Automont complex, Pod Cintorinom and Nová Hrboltová. In summer, the highest exceedance of the geochemical background was found for the localities: Hrboltová, Martinček, Lísková, Sv. Anny, and A. Hlinka Square. In winter, the average pollution produced by the combustion of biomass (expressed as 100% of organic matter in PM_{10}) is 15%, in summer, it is only 4%. The contribution of the combustion of coal in winter is 16% of air pollution. The average pollution produced by transport does not differ much in both seasons (winter 23.5% and summer 24%). The average biogenic pollution in summer reaches 37%, and 24% in winter. Pollution from volatilization and combustion of polymers for the winter and summer seasons is around 2.5 and 2.6%. Emissions from food preparation are similar for both periods; they amount to 2.5% (summer) and 3% (winter).

Acknowledgement

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Związki organiczne na cząstkach PM_{10} w zanieczyszczeniu powietrza

Analizę zawartości skladnikóworganicznych w cząstkach PM_{10} w powietrzu zbadano w okresie zimowym i letnim 2015 r w Rużomberku (Słowacja) i jego okolicach. W miesiącach zimowych stwierdzono większą liczbę substancji organicznych (536) niż w lecie (374), stężenia różnych substancji organicznych były wyższe w zimie. Związki organiczne oznaczono w próbkach zanieczyszczenia powietrza metodą chromatografii pirolitycznej z detekcją spektrometrii masowej. Analiza wykazała, że wyższe stężenia związków organicznych w PM_{10} są wynikiem spalania paliw kopalnych i biomasy. Poza tymi źródłami, w zanieczyszczeniu powietrza zidentyfikowano emisję z transportu, spalania i emisję części lotnych z produkcji tworzyw sztucznych, przygotowania i przetwarzania żywności oraz zanieczyszczenia biogeniczne (naturalne). Emisję ze spalania biomasy okreslono przy użyciu wskaźnika diagnostycznego levoglucosan/manosan. Średni udział zanieczyszczeń powstających w wyniku spalania biomasy w miesiącach letnich wynosi 4%, a w miesiącach zimowych 15%.

Słowa kluczowe: zanieczyszczenie powietrza, znaczniki, spalanie, biomasa, paliwa stałe, baza geochemiczna