ORGANIC COMPOUNDS IN ROAD DUST AND THEIR ASSOCIATION WITH TRAFFIC

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Abstract

Settled road dust was examined to detect the presence of organic compounds. Samples were collected from a road surface near a busy road junction in the city of Ostrava, Czech Republic, once a month from May to October. The six collected samples were analyzed by gas chromatography with mass detection. The correlation analysis divided the analyzed compounds into three distinct groups. The first group, positively correlated with the traffic count consisted of phenanthrene, acenaphthene, indenol (1,2,3-cd) pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, benzo(a)anthracene and chrysene, all positively correlated with each other. The second group of compounds, positively correlated with each other but negatively with the traffic count, consisted of dibenzo(ah)anthracene, naphthalene, anthracene, fluoranthene, acenaphthene and fluorene. The third group consisted only of pyrene, which had a positive correlation with most of the compounds from the second group apart from dibenzo(ah)anthracene and was not correlated with the traffic count in any way.

Keywords: Organic compounds, road dust, traffic, PAH

1. INTRODUCTION

The economic growth is significantly related to the increase in the number of vehicles in the Czech Republic [1], but also worldwide [2]. In the Czech Republic, the number of newly registered passenger cars has increased by approximately 2 and a half million since 1995 [1]. The daily operation of fossil fuel vehicles releases large amounts of pollutants, e.g. metal-based particles, by-products of fuel combustion, and petroleum hydrocarbons [3]. Some of these pollutants remain primarily deposited on the road surface and generate road dust. The road dust, especially in urban areas is, therefore, a mixture of particles from many sources, e.g. brake pad wear, tire wear, road wear, traffic signs, surrounding soil and vegetation, but also industry [4-6]. Naturally, the urban road dust contains a large amount of organic pollutants, especially polycyclic aromatic hydrocarbons (PAHs) [3,7]. Polycyclic aromatic hydrocarbons (PAHs) are a group of multiple compounds with two or more fused benzene rings with or without alkyl substitutes. The greatest amount of PAHs is produced by incomplete combustion of all carbon-containing substances. Pyrogenic PAHs originate from the incomplete combustion of fossil fuels and organics materials [8]. They have been characterized as ubiquitous, toxic, carcinogenic, mutagenic, teratogenic, and are typical anthropogenic pollutants [9-11]. The US Environmental Protection Agency has identified 16 PAHs as priority organic pollutants, namely naphthalene, acenaphthene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene, dibenzo(ah)anthracene, and benzo(ghi)perylene [9,12]. Of these 16 PAHs substances, Benzo(a)pyrene has been categorized as Group 1 (human carcinogen), and other six are probable

(2A)/possible (2B) human carcinogens by International Agency for Research on Cancer (IARC) [9,13]. PAHs with a larger number of benzene nuclei have low vapour pressure and practically do not occur freely in the air, but they are sorbed onto solid particles [14]. Larger and heavier particles, to which organic pollutants can bind, tend to sediment. They are whirled by traffic and weather conditions. They are often flushed with rainwater and transported to local watercourses (e.g. streams, rivers and lakes). As a result of this, they may pose a serious risk to aquatic organisms. [9]. Smaller and lighter particles are usually permanently buoyant (below 1 micrometre) and can be easily inhaled [15]. Because of their size, they pose a high risk to the living organisms; if they have organic pollutants bound to them, the risk of course increases. Some studies have shown increased lung, skin, and bladder cancer risks for employees exposed to PAHs [16-21].

The aim of the study was to determine whether there was any dependence between the detected organic pollutants in the settled road dust and the number of vehicles passing through the selected public transport hub and the sampling period (in 2015).

2. MATERIALS AND METHODS

2.1. Sample preparation

Samples were obtained from an urban crossroad surface in one of the boroughs of the Ostrava City (Czech Republic), town district Poruba. The district is a typical urban site with minimized direct influence of the steel and iron-making industrial complex or other major point sources contributing to the environmental pollution in the rest of the Ostrava City [22]. The sampling site is in the vicinity of a busy intersection and pedestrian crossing, hence, braking is common. Dust samples were collected from 1 m^2 road surface, swept using a sampling set in a glass sample container. Samples were collected once per month (from May to October = sample 1-6), between 9:00 and 10:00 in the morning. The day of the sampling was selected depending on the meteorological conditions: sampling was performed only on rainless days after at least two-day period of no wet precipitation. Six samples of 450-500 g per sample were collected. Each sample was homogenized in a rotary mill (Fritsch Pulverisette) at 250 rpm for 15 minutes and, consequently, sieved through a sieve with 200 μm mesh, the organic matter was extracted and subsequently analyzed by gas chromatography with mass detection (GC/MS).

2.2. Extraction of Organics

Dichloromethane extractions of investigated organic components were performed by pressurized solvent extraction using Speed Extractor E-916 (Büchi Labortechnik AG, Switzerland). Six 3.00 ± 0.01 g samples were extracted in dichloromethane of HPLC grade (Sigma Aldrich) in 3 cycles at 110 °C and 100 bar. The crude extracts were placed into a vacuum evaporator and concentrated to a volume of approximately 5 ml under nitrogen flow at 40 °C. The resulted extracts were cleaned through a silica gel column chromatography, evaporated to the final volume of 1 ml under nitrogen atmosphere, and immediately analyzed by GC/MS.

2.3. GC/MS analysis

A quadrupole mass spectrometer (Agilent Technologies MSD5975C) in connection with a gas chromatograph (Agilent Technologies 7890N) equipped with capillary column DB-XLB (30 m × 0.25 mm × 0.25 μm) were used for screening analysis. The GC/MS operating conditions were: the ion source operated in 230 °C, the injection port maintained at 290 °C, and the samples injected in splitless mode followed by 1.5 min purge after the injection. The program column temperature started at 40 °C for 2 min, then increased by 5 °C/min to 300 °C, and was held for 10 min at 300 °C. The scan mode was employed after additional 6 minutes of delay time. The experimental data were measured in the range of 50-550 atomic mass unit (amu).

2.4. Statistical analysis

The data on the concentrations of PAHs was transformed following the principals of Compositional Data analysis (CoDa) prior to the correlation analysis. Compositional data are non-Euclidean, their transformation into the Euclidean space is required [23], since applying correlation analysis on the raw data may result in spurious correlations [24]. The concentration data matrix was, thus, transformed using centred log-ratio (clr) transformation [25]. Transformations and analyses were performed in the R environment [26] and presented in the form of correlation plot.

3. RESULTS AND DISCUSSION

16 organic substances were detected in settled road dust samples. These substances are among the PAHs identified by the US Environmental Protection Agency as priority organic pollutants [9,12]. From the statistical database of the Statutory City of Ostrava in the Czech Republic, which is freely available, we found the average number of vehicles that passed at the place and time of collection [27].

Table 1 Overview of concentrations of polycyclic aromatic hydrocarbons found in samples of settled road dust; naphthalene NAP, acenaphtylene ACL, acenaphthene ACE, fluorene FLE, phenanthrene PHE, anthracene ANT, fluoranthene FLU, pyrene PYR, benzo[a]anthracene BaA, chrysene CHR, benzo[b]fluoranthene BpF, benzo[k]fluoranthene BkF, benzo[a]pyrene BaP, indeno[123cd]pyrene IP, dibenzo[ah]anthracene DBA, and benzo[ghi]perylene BPE. Values of concentrations in individual months are given.

ug/kg	NAP	ACL	ACE	FLE	PHE	ANT	FLU	PYR	BaA	CHR	BpF	BkF	BaP	IP	DBA	BPE
May	4.7	0.0	10.6	10.2	65.5	16.8	15.8	12.6	61.7	74.5	45.2	34.9	51.0	45.2	33.8	40.3
June	6.9	0.0	12.0	8.9	47.6	13.4	11.9	85.2	46.1	59.3	38.8	28.1	41.9	38.6	26.5	33.4
July	21.8	9.4	44.8	49.1	42.7	64.2	89.7	65.1	26.3	36.7	20.2	13.0	22.1	19.2	37.9	17.7
Aug.	48.5	10.3	53.6	52.4	44.1	67.6	76.7	55.1	24.4	31.1	19.5	11.3	21.5	18.7	40.7	17.6
Sep.	54.3	9.8	38.9	43.5	35.3	53.4	65.1	48.3	22.1	30.9	18.9	11.9	21.7	17.1	38.0	17.2
Oct.	52.6	13.2	58.7	69.4	47.3	70.1	78.9	60.6	26.2	33.3	21.3	13.3	24.3	20.7	41.0	19.2

Table 2 Number of vehicles passing through the selected public transport hub at the place and sampling period (in 2015)

Number of cars per month 10^5 (-)	May	June	July	Aug.	Sep.	Oct.
	4.65036	4.71012	5.47916	4.27332	3.0947	3.8441

The correlation analysis divided the analyzed compounds into three distinct groups. The first group, positively correlated with the traffic count consisted of phenanthrene, acenaphthene, indeno[1,2,3-cd] pyrene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, benzo[a]anthracene and chrysene, all positively correlated with each other. The second group of compounds, positively correlated with each other but negatively with the traffic count, consisted of dibenz[ah]anthracene, naphthalene, anthracene, fluoranthene, acenaphthene and fluorene. The third group consisted only of pyrene, which had a positive correlation with most of the compounds from the second group apart from dibenz[ah]anthracene and was not correlated with the traffic count in any way (**Figure 1**). The first group comprises mainly PAHs with multiple benzene nuclei

(**Table 1**). PAHs with a higher number of benzene cores have low vapour pressure and practically do not occur freely in the atmosphere, but are sorbed onto solid particles [14,28]. Their occurrence positively correlates with traffic (**Table 2**). The more cars pass through the sampling point, the more these multinucleated organic pollutants will be present in the samples of settled road dust. Conversely, the second group consists mainly of PAHs with two to four benzene nuclei. These PAHs can be sorbed to particles in the atmosphere, but can also be present in the gas phase. Only PAHs having 2-4 benzene rings may be present in the gas phase, (having high vapour pressure at normal temperature) [14,28]. This sample group negatively correlates with traffic. More volatile substances are likely to escape into the atmosphere immediately as gases. And those that bind to solid dust particles can escape again by constantly swirling road dust through traffic. The living organism is, therefore constantly exposed to organic substances originating from traffic - whether in the form of gases or in the form of contaminated solid particles of varying size and chemical composition.

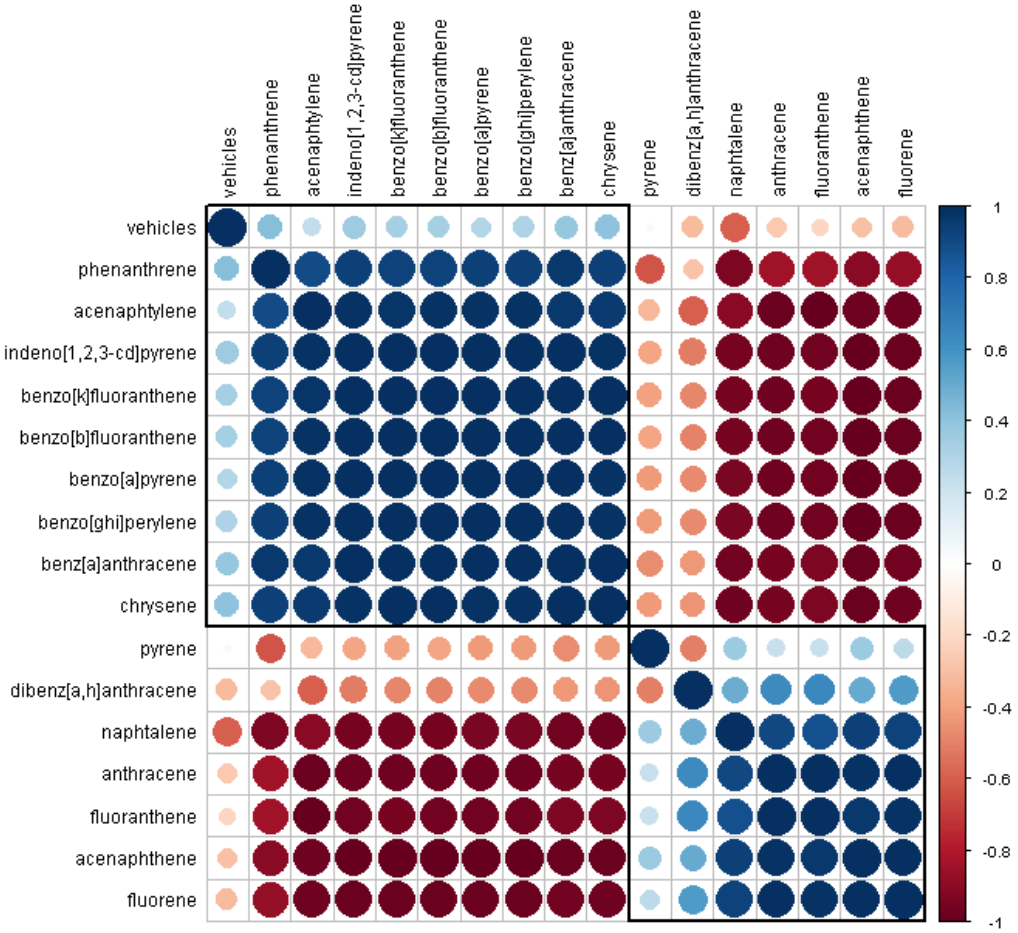

Figure 1 Correlation analysis results

4. CONCLUSION

In an industrial area such as Ostrava (Moravian-Silesian Region), there are many sources of organic pollutants. One of the most important is transport. In this study, we managed to demonstrate a certain relationship between these organic pollutants in the settled road dust and the number of vehicles passing through the selected public transport hub and the sampling period (in 2015). There was a significant correlation between the less volatile organic pollutants and traffic, and a negative correlation between more volatile organic pollutants and traffic. These data confirm that many toxic organic pollutants come from heavy traffic.

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