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# Phthalates in PM<sub>2.5</sub> airborne particles in the Moravian-Silesian Region, Czech Republic<sup>☆</sup>

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Received 1 October 2015; accepted 19 November 2015

Available online 10 December 2015

## KEYWORDS

Airborne particles;  
Air pollution;  
Environmental  
geochemistry;  
Moravian-Silesian  
Region;  
PM<sub>2.5</sub>;  
Phthalates

**Summary** Industrial area of the Moravian-Silesian Region (the Czech Republic) is highly polluted by air contaminants, especially emissions of particulate matter. Samples of PM<sub>2.5</sub> particles were analysed by pyrolysis gas chromatography with mass spectrometric detection. Concentrations of phthalates were determined for the winter season, transitional period and the summer season. The relative concentrations of phthalates in PM<sub>2.5</sub> particles have the same proportion in both heating and non-heating season: di(2-ethylhexyl phthalate) > di-n-butyl phthalate > diisononyl phthalate > diethyl phthalate. The most common increase in concentration in the winter season is from 5 to 10 times higher; the maximum of average concentration was 44 times higher than in the non-heating season.

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## Introduction

The Moravian-Silesian Region (the Czech Republic) has particularly high pollution of air, especially in the city of Ostrava and industrial towns Karvina and Trinec. Concentrations of phthalates bound to PM<sub>2.5</sub> particles in the air were studied at

selected localities in order to identify areas with the highest incidence in relation to the sources of pollution.

Phthalates (esters of phthalic acid) belong among endocrine disrupting compounds which have gained great attention due to their widespread environmental occurrence and possible adverse effects on reproduction and development of exposed organisms (Salapasidou et al., 2011). Important representatives of phthalates include di-n-butyl phthalate (DnBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di(2-ethylhexyl phthalate) (DEHP), and diisononyl phthalate (DINP). Phthalates have a negative impact on human health, primarily affecting the functions of

<sup>☆</sup> This article is part of a special issue entitled "Proceedings of the 1st Czech-China Scientific Conference 2015".

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endocrine and immune systems. Occurrence of phthalates in the environment is associated with the disease of the respiratory system (asthma), and a higher incidence of allergies (Bornehag et al., 2004).

Phthalates are manufactured worldwide on a large scale, mainly as plasticizers in resins and polymers, and especially as a softener in polyvinylchloride (PVC) as well as in other polymers such as polyethylene terephthalate (PET), polyvinyl acetates, cellulose, and polyurethanes. Other industrial applications include the manufacturing of cosmetics, insect repellents, insecticide carriers, and propellants (Staples et al., 1997). As plasticizers, phthalates are not physically bound to the polymer and can thus diffuse out of the plastic and leach into the environment. They can enter the environment via emissions from household and industrial products (Xie et al., 2007).

During combustion of plastics, phthalates enter the air, where they occur in the gas and solid phases. Phthalate ester distributions between the vapour and particulate phases, with values ranging from 93.8% to 64.9%, indicate that esters with alkyl chain lengths of less than 6C were primarily in the vapour state whereas compounds with longer alkyl chains were rather associated with aerosols (Teil et al., 2006). The distribution of phthalates between the gas and the solid phase depends on the molecular weight of phthalates; the vapour pressure decreases with the increasing molecular weight, and the higher the molecular weight, the more phthalates passes from the gaseous phase into the solid phase of particulate matter (PM) particles (Weschler, 1984; Weschler et al., 2008). The qualitative and quantitative determination of phthalates was tested in PM<sub>2.5</sub> particles that should accumulate predominantly "heavy" phthalates (molecular weight >252) with demonstrable effects on human health (Wang et al., 2008a). DEHP (25–85%) is bound mainly to solid phase, DEP up to 25% at maximum (Salapacidou et al., 2011). The correlation between the amount of dust particles and phthalates is presented by Fromme et al. (2013).

Phthalates have moderate long-range atmospheric transport potentials. The concentrations of phthalates (DEP, DnBP, and DEHP) varied throughout seasons and were four times lower in summer than in winter, which is affected by temperature (Teil et al., 2006). Phthalates are not covalently bound to the polymer matrices and they may increase the rate of release of their emission into the environment at elevated temperatures (Fujii et al., 2003). Behavioural mechanisms of phthalates in ambient air are complex. The main parameter that affects the decomposition of phthalates and their removal from the atmosphere is rainfall and temperature. Generally, increasing temperature accelerates the photochemical reactions of phthalates with free radicals, which leads to the formation of secondary organic compounds and to the reduction of the concentration of phthalates in the air. Phthalates tend to accumulate in urban and suburban areas of large urban and industrial agglomerations. As a background, concentrations in the isolated areas can be considered: DnBP and DEHP mean concentrations at Enewetak Atoll in the air over the North Pacific Ocean (0.9 ng/m<sup>3</sup> for DnBP and 1.4 ng/m<sup>3</sup> for DEHP), or the concentrations measured for Arctic: DEHP 543 pg/m<sup>3</sup>, DnBP 139, and DEP 20 pg/m<sup>3</sup> (Xie et al., 2015). Higher concentrations (the annual average value) were measured in Paris: DEHP

17.5 ± 7.7, DnBP 18.4 ± 9.9, and for DEP 9.0 ± 6.2 ng/m<sup>3</sup>. In Sweden, the concentrations of DEHP ranged from 0.28 to 77.7 ng/m<sup>3</sup> and those of DnBP from 0.23 to 49.9 ng/m<sup>3</sup>. The research on the occurrence phthalate (DEHP) in Thessaloniki, Greece confirmed that concentration of DEHP in areas loaded by transport (21.3 ± 11.2 ng/m<sup>3</sup>) is higher than in urban areas (2.86 ± 1.81 ng/m<sup>3</sup>); Salapacidou et al. (2011).

## Materials and methods

Qualitative and quantitative determination of phthalates was monitored in PM<sub>2.5</sub> particles that should predominantly accumulate "heavy" phthalates (molecular weight >252) with demonstrable impact on human health (Wang et al., 2008b).

Samples of PM<sub>2.5</sub> particles were collected by the Health Institute in Ostrava at the following localities: Ostrava-Marianske Hory, Ostrava-Radvanice, Karvina, Havirov, Trinec, Frydek-Mistek, Oldrichovice, Hradec nad Moravici, and Ostravice. Sampling was carried out in four stages, which include winter 2013/2014, summer 2014, the transition period 2014, and winter 2014.

Analysis of phthalates in PM<sub>2.5</sub> was performed by method of pyrolytic gas chromatography with mass spectrometry detector (Py-GC/MS). The apparatus consists of pyrolytic unit Pyroprobe 5200 (CDS Analytical Inc.) connected by interface directly with gas chromatograph (HP Agilent 7890 A) with mass spectrometric detector (5975 C). Residue samples of PM<sub>2.5</sub> (100 µg) were inserted into a quartz tube sealed at both ends by quartz wool. In order to prevent contamination by methylstyrene, the quartz wool was pyrolyzed in advance alone, at the temperature of 1200 °C, with temperature ramp 10 °C/ms during 10 s. The samples were analysed by sequential pyrolysis at the temperatures of 700 °C and 1000 °C, for the period of 20 s, the rate of temperature increase was 20 °C/ms. The interface between the pyrolytic unit and gas chromatograph was heated to the temperature of 300 °C in order to prevent condensation of pyrolytic products. The pyrolysate was then separated at the non-polar column HP5 ms (60 m × 0.25 mm × 0.25 µm). The temperature programme for separation was 40 °C (retention time 4 min), 320 °C (retention time 18 min, temperature ramp 10 °C/min). The sample was injected automatically by the pyrolytic unit into the part of chromatograph at the temperature of 290 °C in the split mode 1:10. The substances were identified and quantitatively determined using standards in the SCAN mode and SIM mode (for very low concentrations of phthalates).

## Results and discussion

Analysis of phthalates in PM<sub>2.5</sub> particles was focused on the determination of the content of di(2-ethylhexyl phthalate) (DEHP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), and diisononyl phthalate (DINP) and their seasonal behaviour. The highest sum concentrations of phthalates were detected in the winter season of 2013 and 2014 at all localities, the only exception was the town of Havirov and Frydek-Mistek, where the maximum concentrations of phthalates occurred in the transitional period (Tables 1 and 2). Minimum concentrations of phthalates were

**Table 1** Concentrations of DEHP and DnBP in PM<sub>2.5</sub>.

Locality	DEHP (ng/m <sup>3</sup> )				DnBP (ng/m <sup>3</sup> )			
	W 2013	S 2014	Trans.	W 2014	W 2013	S 2014	Trans.	W 2014
Ostrava-Radvanice	0.20	3.57	1.26	<b>5.74</b>	8.76	<b>4.57</b>	0.47	<b>0.95</b>
Ostrava-Marianske Hory	<b>1.75</b>	0.53	<b>1.36</b>	<b>6.85</b>	<b>158.90</b>	2.10	0.52	0.32
Ostrava-Poruba	0.20	4.00	0.20	0.20	1.92	0.91	<b>0.73</b>	0.40
Karvina	0.20	2.57	1.00	0.20	<0.4	2.60	<b>0.72</b>	0.36
Havirov	0.20	1.86	0.20	2.15	<0.4	<0.4	0.20	0.40
Trinec	0.20	<b>4.35</b>	1.26	0.35	18.91	1.02	<b>0.81</b>	0.14
Trinec-Oldrichovice	0.20	<b>5.64</b>	<b>1.63</b>	0.08	88.74	0.44	<0.4	0.48
Frydek – Mistek	0.20	2.58	0.20	1.43	<0.4	0.67	<0.4	0.40
Ostravice	0.20	1.52	1.14	0.21	<0.4	<0.4	<0.4	0.28
Hradec nad Moravici	0.20	1.83	0.19	<b>9.72</b>	0.44	2.35	<0.4	0.56
Mean	0.36	2.85	0.84	2.69	46.28	1.83	0.58	0.43
Standard deviation	0.47	1.46	0.55	3.30	58.75	1.29	0.21	0.20

Bold type denotes values higher than threshold of anomaly (arithmetic mean+standard deviation). W, winter; S, summer; Trans., transition.

measured in Karvina, Trinec, Ostravice, Trinec-Oldrichovice, and Ostrava-Poruba in unusually warm non-inversion winter of 2014 (this winter contained only 5 inversion days). The minimal concentrations of phthalates in the summer period were measured only in Ostrava-Marianske Hory and Havirov, which corresponds to the results published by [Teil et al. \(2006\)](#). [Tables 1 and 2](#) show the measured values with highlighted anomalous concentrations that were determined by adding the standard deviation to the arithmetical mean (standard method for determining the anomaly threshold).

Considering the shares of concentrations of the measured amounts of phthalates in the heating and non-heating season, the localities can be divided into 4 groups based on enrichment in the sum of phthalates: 44 ×: Ostrava-Marianske Hory; 10–15 ×: Ostravice, Hradec nad Moravici, Trinec-Oldrichovice; 5–10 ×: Ostrava-Radvanice, Trinec, Karvina, Havirov; <4 ×: Ostrava-Poruba, Frydek-Mistek.

The above-mentioned results show that even when the lowest measured concentration of the sum of phthalates was measured in the area of the Beskydy Mountains (Ostravice) in the non-heating season, it increased during the heating season up to 15 times. The situation is similar for the locality of Hradec nad Moravici. The present results indicate that in the heating season, the concentration of phthalates in the air is not affected by the size of residential units or industrial concentration. Increased occurrence of phthalates in the heating season is mainly related to the nature of the fuel used in local heating ([Fig. 1](#)).

From the average representation of phthalates in all the localities in the heating and non-heating seasons it follows that DEHP – about 50%, and DINP–20% have the largest share of Σphthalates. In the non-heating season, there is less DEP – 5% and twice the amount of DnBP. Comparing the share of individual phthalates considering their sum in the heating

**Table 2** Concentrations of DINP a DEP in PM<sub>2.5</sub>.

	DINP (ng/m <sup>3</sup> )				DEP (ng/m <sup>3</sup> )			
	W 2013	S 2014	Trans.	W 2014	W 2013	S 2014	Trans.	W 2014
Ostrava-Radvanice	1.30	1.3	1.3	<b>36.08</b>	0.15	<b>0.65</b>	<b>5.94</b>	0.15
Ostrava-Marianske Hory	4.92	1.3	3.16	1.3	0.15	0.15	0.2	2.19
Ostrava-Poruba	1.39	1.3	1.3	1.38	5.71	0.23	1.75	0.15
Karvina	<b>26.2</b>	1.3	1.3	1.32	<b>26.2</b>	<b>0.98</b>	1.25	0.15
Havirov	1.30	1.3	<b>10.59</b>	1.98	0.15	0.17	0.35	<b>6.46</b>
Trinec	24.4	1.3	1.3	0.16	0.15	0.36	1.24	0.15
Trinec-Oldrichovice	9.27	1.3	0.46	0.31	0.15	0.15	1.36	0.28
Frydek – Mistek	1.30	1.3	<b>8.2</b>	0.53	0.15	0.41	0.51	<b>4.99</b>
Ostravice	<b>22.02</b>	0.3	1.3	1.3	1.64	0.15	1.1	0.15
Hradec nad Moravici	1.30	1.0	1.57	1.3	<b>50.26</b>	0.15	0.15	3.43
Mean	9.34	1.17	3.05	4.57	8.47	0.34	1.38	1.81
Standard deviation	10.07	0.30	3.28	10.52	15.91	0.26	1.61	2.25

Bold type denotes values higher than threshold of anomaly (arithmetic mean+standard deviation). W, winter; S, summer; Trans., transition.

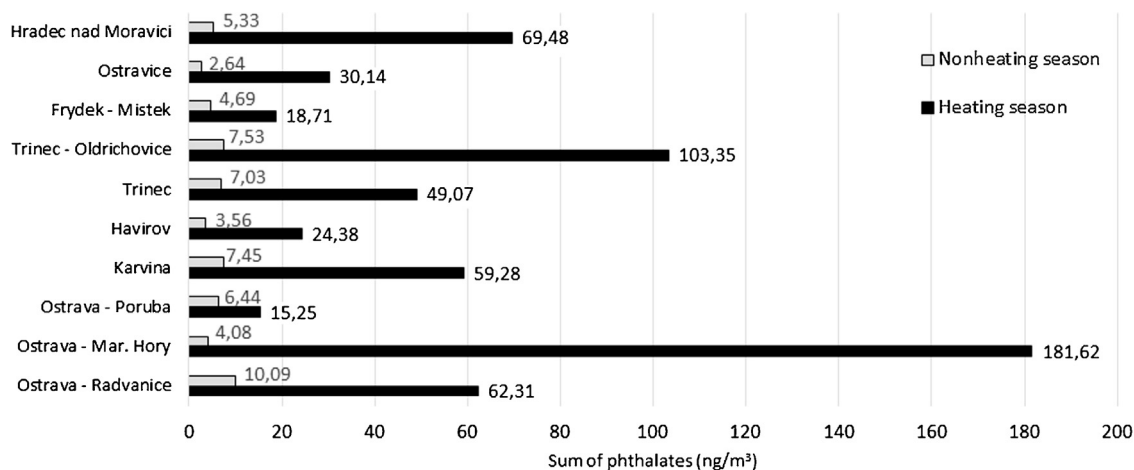


Figure 1 Occurrence of phthalates during the heating season and non-heating season.

and non-heating seasons indicates that all the monitored localities vary (Fig. 2).

Di(2-ethylhexyl phthalate) (DEHP) was identified in PM<sub>2.5</sub> particles at all localities. Heavy phthalates are bound to the fine particles in the air (Kaupp and McLachlan, 1998). More than 60% of DEHP binds to a particle size of 2.5–10 μm (Ma et al., 2014). The mean concentration of DEHP throughout the sampling period ranges from 0.77 ng/m<sup>3</sup> (Ostravice) to 2.99 ng/m<sup>3</sup> (Hradec nad Moravici).

Higher concentrations in winter (2 localities) may be the result of increased waste incineration and the reduction in photochemical reactions in the atmosphere. At the other

localities, DEHP is found in higher concentrations in the non-heating season. Among other things, the summer increase in the concentrations of DEHP may be affected by meteorological conditions. The dry period with minor precipitation allow the accumulation of DEHP in the atmosphere (Kaupp and McLachlan, 1998), rain significantly enables removal of fine particles containing DEHP from the atmosphere. Mean concentrations of DEHP detected at all the localities correspond to the concentrations reported in literature for the air in Europe and USA (Thuren and Larsson, 1990; Teil et al., 2006) – USA (Kansas, Texas 2 ng/m<sup>3</sup>), Sweden (2 ng/m<sup>3</sup>), and France (Paris 5.4 ng/m<sup>3</sup>).

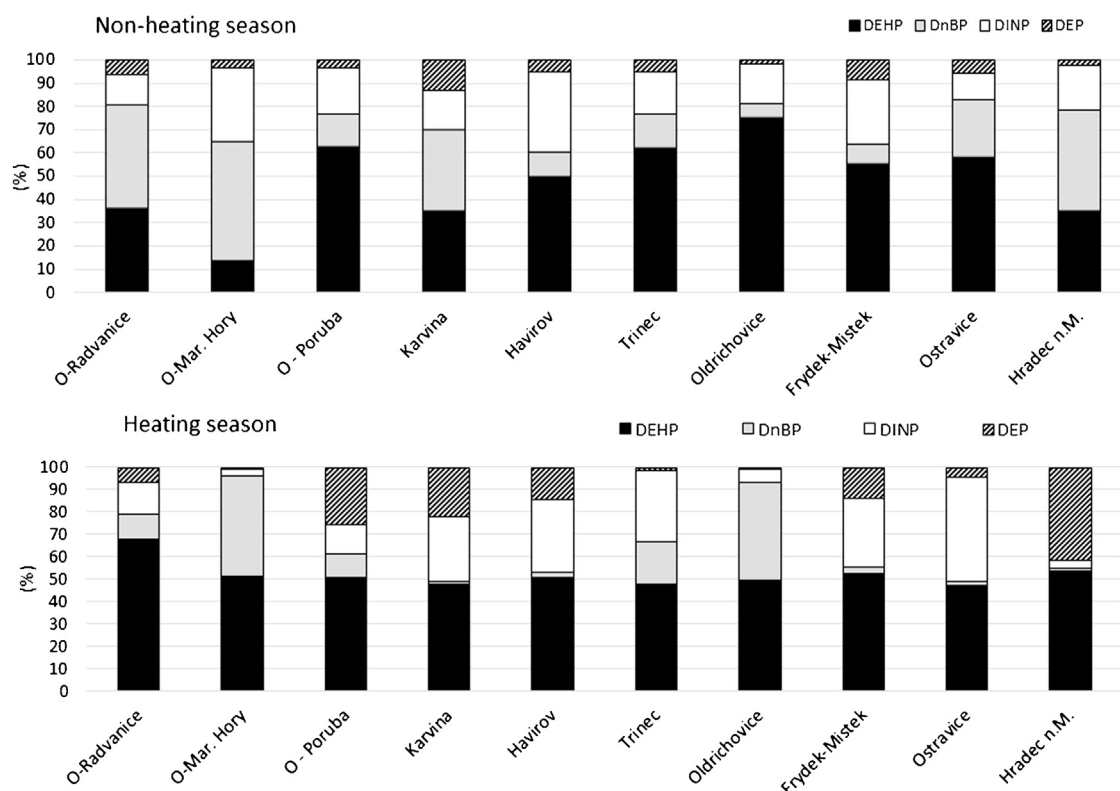


Figure 2 Percentages of phthalates in the heating and non-heating season.

Di-n-butyl phthalate (DnBP) is phthalate with a demonstrably negative effect on the hormonal system. DnBP is used in the production of epoxy resins, materials containing cellulose esters, and in special applications. The sharp reduction in the concentration of DnBP was observed at all the localities in the transitional period. In some samples of  $PM_{2.5}$  particles (Ostrava-Radvanice, Havírov, Trinec-Oldřichovice, and Hradec nad Moravíci), the minimal DnBP concentrations were identified in the transitional period. At the remaining localities, there was a significant reduction of concentrations in the transitional period, the minimal concentrations were measured in winter (Ostrava-Poruba, Ostrava-Mariánské Hory, Karvina, Trinec, Frydek-Místek, and Ostravice). At five localities, the concentration in the heating season was lower than during summer.

Diethyl phthalate (DEP) is used as a plasticizer for the production of plastics; it is a part of cosmetics and fragrances. It has been proven that the combustion of substances containing DEP produces toxic gases. DEP presence in the environment damages the nervous and reproductive systems of living organisms. The mean concentration of DEP for all the analysed localities ranges from 0.48 to 13.5 ng/m<sup>3</sup>. The highest mean concentration of DEP for the monitored period was measured in Hradec nad Moravíci, while the lowest mean concentration was at the locality of Trinec-Oldřichovice. The recreation area of Ostravice has the mean annual DEP concentration of 0.76 ng/m<sup>3</sup>. Greater concentrations of DEP in Trinec-Oldřichovice is due to increased concentration in winter 2013 (50.26 ng/m<sup>3</sup>), which is probably the result of the combustion of plastics; it was confirmed by the appearance of terephthalic and phthalic acids.

Diisononyl phthalate (DINP) is the last analysed phthalate in  $PM_{2.5}$  particles. At all the localities, the mean concentrations of DINP range from 1.29 (Hradec nad Moravíci) to 10 ng/m<sup>3</sup> (Ostrava-Radvanice). At all the localities, the concentration of DINP was lower in the non-heating season than in the heating season. The highest difference in concentrations was measured in the locality Ostravice.

## Conclusions

The presented results indicate that the profile concentration of phthalates in  $PM_{2.5}$  particles in the heating and non-heating season is the same: DEHP > DnBP > DINP > DEP. The accumulation of phthalates in Czech towns and cities is different from the accumulation of phthalates in  $PM_{2.5}$  particles reported for Chinese cities where other phthalates are more important (Wang et al., 2006; Ma et al., 2014). The differences in the accumulation of phthalates in the European and Asian continents are the result of different industrial activities and weather conditions.

The comparison of the concentrations in the heating and non-heating seasons has shown up 44 times higher increase in the concentration of phthalates (Ostrava-Mariánské Hory), where the concentration may be affected by the operation of the hazardous waste incinerator. The most common increase in the concentration in the winter season is 5–10 times higher (4 localities). The increase in the concentration in winter is caused by the combustion of plastics in local heating, as well as by lower intensity of

the photochemical conversion. The observed concentrations of phthalates in the Moravian-Silesian Region correspond to those in other cities (Paris, Thessaloniki, etc.).

## Conflict of interest

The authors declare that there is no conflict of interest.

## Acknowledgments

This paper was supported by the research project of the Ministry of Education, Youth and Sport of the Czech Republic: The National Programme for Sustainability LO1404 – TUCENET and the research project of the Czech Technological Agency: TA02020004 – The Research on the Physical and Chemical Character of Particles in Emissions.

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