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# Phthalates in $PM_{2.5}$ airborne particles in the Moravian-Silesian Region, Czech Republic☆

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**Summary** Industrial area of the Moravian-Silesian Region (the Czech Republic) is highly polluted by air contaminants, especially emissions of particulate matter. Samples of $PM_{2.5}$ 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 $PM_{2.5}$ particles have the same proportion in both heating and non-heating season: di(2ethylexyl 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.


## 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 $PM_{2.5}$ 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

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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 $PM_{2.5}$ 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 (Salapasidou 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 $ng/m^3$ for DnBP and 1.4 $ng/m^3$ for DEHP), or the concentrations measured for Arctic: DEHP 543 $pg/m^3$, DnBP 139, and DEP 20 $pg/m^3$ (Xie et al., 2015). Higher concentrations (the annual average value) were measured in Paris: DEHP $17.5 \pm 7.7$, DnBP $18.4 \pm 9.9$, and for DEP $9.0 \pm 6.2$ $ng/m^3$. In Sweden, the concentrations of DEHP ranged from 0.28 to 77.7 $ng/m^3$ and those of DnBP from 0.23 to 49.9 $ng/m^3$. The research on the occurrence phthalate (DEHP) in Thessaloniki, Greece confirmed that concentration of DEHP in areas loaded by transport ($21.3 \pm 11.2$ $ng/m^3$) is higher than in urban areas ($2.86 \pm 1.81$ $ng/m^3$); Salapasidou et al. (2011).

## Materials and methods

Qualitative and quantitative determination of phthalates was monitored in $PM_{2.5}$ particles that should predominantly accumulate ''heavy'' phthalates (molecular weight >252) with demonstrable impact on human health (Wang et al., 2008b).

Samples of $PM_{2.5}$ 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 PM2.5 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 $PM_{2.5}$ (100 $\mu g$) 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 $\mu$m). 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 $PM_{2.5}$ 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