THE LOAD ON THE SOILS IN THE CZECH REPUBLIC BY PHTHALIC ACID ESTERS

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*Abstract:*The aim of the study was to monitor two esters of the phthalic acid, dibutyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) in agricultural soils in the Czech Republic in 2014. The concentration of DBP and DEHP was determined using a high-performance liquid chromatography (HPLC) with UV detection. The extraction was performed ultrasonically by a mixture of acetone:hexane (1:1). DBP and DEHP monitoring was performed in 12 regions of the Czech Republic. The DBP values ranged from 0.08 (Hlízov) to 1.78 $mg.kg^{-1}$ (Chrlice) of dry matter. The DEHP values ranged from 0.01 (Hlízov) to 2.32 (Malenovice u Zlína) $mg.kg^{-1}$ of dry matter. The sum of the concentrations of DBP and DEHP ranged from 0.09 (Hlízov) to 3.21 $mg.kg^{-1}$ of dry matter (Chrlice).

KeyWords: soil, di-2-ethylhexyl phthalate, dibutyl phthalate, region, dry matter

INTRODUCTION

Phthalic acid esters belong to the group of plasticizers, which cause gelling in polymeric materials and improve flexibility, elasticity, expansiveness and workability of plastics materials (Rahman, Brazel 2004). Due to their exceptional properties, they find use in many manufacturing sectors, from plasticizers to solvents, films and cosmetics, to the pharmaceutical industry (Huber et al. 1996). It has been proven that the elution of phthalates from plastics releases products into the environment. They are thus widely spread into the ecosystem and are ranked among the most common substances polluting the environment (Koch et al. 2003). They can enter the body by inhalation, food consumption or absorption through the skin. People can be exposed to phthalates from construction materials, medical equipment, household equipment, soil and dust (Pan et al. 2014). Phthalic acid esters (PAEs) are considered hazardous polluting substances due to their mutagenicity and carcinogenicity, they are also classified as endocrinal disruptors. PAEs are colourless, odourless and with a high boiling point, they are insoluble in water, but soluble in fats (Barreca et al. 2014). The toxicity of phthalates applies especially to the male reproductive system and embryo fetal development (Saillenfait, Laudet-Hesbert 2005). Phthalic acid esters are biologically active compounds. They are metabolised by the body into toxic metabolites which react with biologically active substances and can negatively affect vital bodily functions. These substances are lipophilic in nature and thus accumulate in the fatty tissue. PAEs have a negative impact on human health and pose a serious global problem for the environment (Jarosova 2006).

MATERIAL AND METHODS

Samples of agricultural soil were gathered in cooperation with the Central Institute for Supervising and Testing in Agriculture in Brno. The samples were taken from 12 regions of the Czech Republic: Central Bohemian Region, Plzeň R., Karlovy Vary R., Ústí nad Labem R., Liberec R., Pardubice R., South Bohemian R., Vysočina R., Zlín R., South Moravian R., Olomouc R. and Moravian-Slezian R. The samples were taken from arable land (n = 33), permanent grasslands (n = 6) and hop fields (n = 1). Sampling was performed in a polygonal chain. Approximately 0.5 kg of soil was taken from one horizon. This amount was manually homogenized directly in the field, and the rougher skeleton was removed from the sample.

After homogenizing, the sample was placed in a polypropylene bag. The wrapped and labelled samples were then transported in cooling boxes, after which they were placed into a freezer at a temperature of -18°C until they were passed on to the laboratory.

The analysis of the samples was carried out duplicately according to the method by Dankova and Jarosova (2012). The frozen samples were defrosted and approximately 10 g of soil was retrieved from each one. These 10 g samples were then frozen again and lyophilised. Afterwards, extraction using a mixture of acetone:hexane at a ratio of 1:1 using ultrasound was performed three times for 5 minutes. The combined extracts were filtered and subsequently vaporized on a vacuum rotary evaporator and dried off with nitrogen. The extracts were then transferred into vials using hexane (3 ml). This was followed by repurification using concentrated sulphuric acid (96%) and hydrated sulphuric acid (65%). The repurified samples were then fully dried off with nitrogen and supplemented with acetonitrile to a volume of 1 ml for the HPLC determination. The phthalate analysis was performed using HPLC with UV detection at a wavelength of 224 nm. All the samples were injected twice. The injection volume of the sample was 10 µl. The analysis used a Zorbax Eclipse C8 column. The results were evaluated via a calibration curve using Agilent ChemStation software for LC and LC/MS systems.

RESULTS AND DISCUSSSION

The measured concentrations of phthalates are listed in Table 1. The highest concentrations of phthalates were measured in soil samples from "Malenovice u Zlína" – DEHP 2.32 $mg.kg^{-1}$ and DBP 0.83 $mg.kg^{-1}$ – and in "Chrlice" – DEHP 1.43 $mg.kg^{-1}$ and DBP 1.78 $mg.kg^{-1}$ of dry matter.

The higher phthalate levels in the samples from Malenovice u Zlína and Chrlice when compared to other samples are likely caused by the industrial activities in these areas (production of rubber components, manufacturing of hydraulic devices). If we compare these values with the values set out in the Methodical Instruction issued by the Ministry of the Environment, which is based on the RSL (Regional Screening Levels) issued by the United States Environmental Protection Agency (USEPA), then none of the limits were exceeded in this study (DEHP values for industrial areas: 120 $mg.kg^{-1}$ of dry matter, other areas: 35 $mg.kg^{-1}$ of dry matter, values for DBP: 62.000 $mg.kg^{-1}$ of dry matter for industrial areas and 6.100 $mg.kg^{-1}$ of dry matter for other areas) (Methodical instruction online, 2015).

Table 1 Concentration of DBP, DEHP and Σ of DBP and DEHP ($mg.kg^{-1}$ of dry matter) in soil samples

Cadastral area	DBP	DEHP	∑ DBP a DEHP	Culture
		$mg.kg^{-1}$		
Sedlec u Líbeznic	0.67	0.55	1.22	arableland
Filipov u Čáslavi	0.75	0.18	0.93	arableland
Příbram	0.64	0.66	1.30	arableland
Lhota u Příbramě	0.19	0.04	0.23	arableland
Kutná Hora 1	0.84	0.15	0.99	arableland
Hlízov	0.08	0.01	0.09	arableland
Kutná Hora 2	0.34	0.39	0.73	arableland
Dražíc	0.15	0.27	0.42	arableland
Dolní Hořice	0.18	0.10	0.28	arableland
Vysoké Studenice	0.33	0.33	0.66	arableland
Střížov u Třebíče	0.16	0.25	0.41	arableland
Utín	0.19	0.16	0.35	arableland
Žirovnice	0.34	0.02	0.36	arableland
Červený hrádek u Plzně	0.47	0.25	0.72	arableland
Zruč	0.36	0.21	0.57	arableland
Křimice	0.41	0.20	0.61	arableland
Sytno	0.18	0.04	0.22	arableland

Jenišov	0.28	0.61	0.89	permanent grassland
Panenský Týnec	0.15	0.28	0.43	arableland
Žatec	0.27	0.59	0.86	hop field
Lubenec	0.11	0.16	0.27	permanent grassland
Louny	0.24	0.36	0.60	arableland
Rádlo	0.47	0.39	0.86	permanent grassland
Újezd u Sezemic	0.18	0.19	0.37	arableland
Záhraď	0.23	0.17	0.40	arableland
Nivnice	0.18	0.06	0.24	arableland
Boršice u Buchlovic	0.44	0.45	0.89	arableland
Malenovice u Zlína	**0.83**	**2.32**	**3.15**	arableland
Jarcová	0.56	0.62	1.18	arableland
Chrlice	**1.78**	**1.43**	**3.21**	arableland
Stará Bělá	0.31	0.42	0.73	arableland
Šenov u Nového Jičína	0.21	0.35	0.56	arableland
Mosty u Českého Těšína	0.68	0.49	1.17	permanent grassland
Město Albrechtice	0.69	0.44	1.13	arableland
Žilina u Nového Jičína 1	0.51	0.54	1.10	permanent grassland
Žilina u Nového Jičína 2	0.49	0.37	0.86	permanent grassland
Raškovice	0.63	0.40	1.10	arableland
Dolní Marklovice	0.50	0.43	0.93	arableland
Tomíkovice	0.32	0.39	0.71	arableland
Bílá Voda u Javorníka	0.61	0.39	1.00	arableland

Hongjun et al. (2013) have studied the concentration of phthalates in the vicinity of the Yellow River, which is one of the typical agricultural and petrochemical industrial areas of China. Phthalates were detected in all the analysed samples of topsoil, which indicates that phthalates are a ubiquitous contaminant of the environment. Higher concentrations of phthalates were found in samples taken from the vicinity of roads, as well as in areas with high anthropogenic activities (urbanization and industrialization) and agriculture. The concentrations of DEHP and DBP were the most dominant in the above mentioned samples, reaching average values of 0.735 and 1.915 $\mu g.g^{-1}$ of dry matter.

The soil may be contaminated by high concentrations of phthalic acid esters as a result of industrial activities and intensive agricultural activity. Phthalate content was also studied in samples of urban soil in Beijing by Xia et al. (2011). The phthalate values ranged from 1.9 to 3.141.7 $\mu g.g^{-1}$ of dry matter with an average of 1.139.6 ± 727.6 $\mu g.g^{-1}$ of dry matter. Of all the phthalates, DEHP and DBP were the most common. The increased amount of DBP was caused by the presence of several factories in these areas, which manufacture chemical products and materials. Agricultural crops grown on the contaminated soil can then be a source of contamination in the human food chain.

In 2014, Ji et al. (2014) conducted a study in which 448 samples of food (rice, vegetables, meat, poultry, fish, milk and fruit) were subjected to analysis of the occurrence of phthalates. In addition, the analysis also included drinking water, soil and dust from inner and outer walls of houses. The results have shown that DBP and DEHP were detected in all the above mentioned samples. The PAEs concentrations in the environment were higher than in food.

A study conducted by Wu et al. (2015) examined samples of soil which were taken from the vicinity of roads, agricultural land, residential areas and non-cultivated areas. The highest concentration of PAEs was detected in agricultural land and subsequently (in descending order) in samples from roads, residential areas, and non-cultivated soil. PAEs levels were the highest in the soil in the vicinity of roads, residential areas, agricultural land, and non-cultivated soils. The concentrations of dimethyl phthalate

(DMP), diethyl phthalate (DEP) and di-n-butyl-phthalate (DNBP) differ significantly ($P < 0.01$) among industrial areas.

CONCLUSION

The phthalate concentrations detected were within low concentration levels in all regions of the Czech Republic. High values were measured in samples of soil collected in the area of Chrlice and Malenovice u Zlína. The higher phthalate concentrations were caused by industrial activities in these areas, such as the production of rubber components and manufacturing of hydraulic equipment. The average DBP values were 0.83 $mg.kg^{-1}$, with the DEHP values being higher, at 2.32 $mg.kg^{-1}$ of dry matter (Malenovice u Zlína). The Chrlice area reached values of DBP = 1.78 $mg.kg^{-1}$ and DEHP = 1.43 $mg.kg^{-1}$ of dry matter. The values in these two regions were higher, but did not exceed the recommended limit for phthalates as set by USEPA.

In other regions, the values of the DBP ranged from 0.08 (Hlízov) to 1.78 $mg.kg^{-1}$ (Chrlice). The DEHP values ranged from 0.01 (Hlízov) to 2.32 (Malenovice u Zlína) $mg.kg^{-1}$. It is important to constantly monitor the phthalate content in soils in order to determine the phthalate load on the environment of the Czech Republic.

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