MONITORING OF PHTHALATES IN MORAVIAN AGRICULTURAL SOILS IN 2011 AND IN 2012

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ABSTRACT

The aim of this study was monitoring of two phthalic acid esters, dibutyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP). The levels of DBP and DEHP were determined by high performance liquid chromatography (HPLC) with UV detection. Extraction was done using sonication and mixture of hexan/acetone (1/1). The monitoring was performed in five Moravian regions of the Czech Republic. Samples were carried out using the zig-zag pattern from topsoil. The soil samples were of arable soils and grassland. The monitoring was performed in 2011 and 2012. The concentrations of two phthalic acid esters were lower in 2012 than in 2011 in most samples.

Key words: dibutyl phthalate, di-2-ethylhexyl phthalate, soil

INTRODUCTION

Soil is a complicated system consisting of inanimate as well as animate components. It is an important feature for the life of plants, animals, but also - above all – humans. For human life, it is the agricultural soil that is especially important, from the viewpoint of breeding livestock as well as from the viewpoint of production of food of plant origin. When soil safety is threatened, it also represents a direct threat to food chain, the environment and consequently also to human health (Brimer, 2011). That is why monitoring of all foreign and harmful substances in the soil, which could represent a potential threat to human health, is so important. Pthalic acid esters enter soil through human activity. Owing to their wide usage in many areas of industry, they have become omnipresent contaminants in all components of the environment, including agricultural soil (Mankidy et al., 2013, Brimer 2011). Pthalic acid esters can be potentially harmful to human health. It was also proved that they have negative effects on the reproductive system. They also have carcinogenic and teratogenic characteristics (Piché et al., 2012, Mtibe et al., 2012, Li et al., 2012). Monitoring of these substances in agricultural soil is thus an important step to maintaining safety of food of animal as well as plant origin. So the aim of this paper was monitoring of two pthalic acid esters: dibutyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) in agricultural soil.

MATERIAL AND METHODS

Soil samples were taken in cooperation with the Central Institute for Supervising and Testing in Agriculture in 2011 and 2012. Soil samples were taken from 17 chosen areas in the region of Vysočina (3 areas) and in Moravia, in the following regions: Zlínský (3 areas). Jihomoravský (1 area), Olomoucký (2 areas) and Moravskoslezský (8 areas).

Taking of samples was carried out using the zig-zag pattern from topsoil: arable soil – 0 – 25 cm, permanent grassland – 0 – 10 cm, with the upper turf layer removed.

Approximately 0.5 kg of soil was taken from one horizon. This amount was manually homogenized right in the field. During homogenization, rough soil skeleton was removed. After homogenization was complete, the sample was put in a plastic bag, which was then tied up and inserted in a PE bag and tied up again. Packed and marked samples were transported in ice boxes, then stored in a freezer at the temperature of -18°C until it was time to take them to the laboratory.

The samples were analysed at the Department of Food Technology of Mendel University in Brno. Jarošová et al. (1999) method was used. This method was optimized for the needs of soil samples testing. The analysis of all samples was carried out duplicately, which means that the total number of analysed samples was 68. Frozen samples were defrosted and from each of them, approximately 10 g of soil was taken. Subsequently, the 10 g of soil was frozen again and then lyophilized. Then, the extraction of hexan/acetone mixture (1/1) was performed using sonication. It was carried out three times for the duration of five minutes. Joined extracts were then filtrated and subsequently evaporated in a rotating vacuum evaporator and finally dried completely using nitrogen. Then they were transferred into vials with the help of hexane. After this, they were cleaned with concentrated and then hydrated sulphuric acid. Cleaned samples were dried completely using nitrogen and supplemented with a standard addition in acetonitrile to the volume of 1 ml. The analysis of phtalates was performed with the help of HPLC and UV detection at the wavelength of 224 nm. Zorbax Eclipse colony C8 was used. The results were then evaluated with the help of calibration curve using the Agilent ChemStation software for LC and LC/MS systems.

RESULTS AND DISCUSSION

The results retrieved in 2011 and 2012 are shown in the following tables. Resulting concentrations of DBP and DEHP in 2011 are shown in table I. Resulting concentrations of DBP and DEHP from 2012 are shown in table II.

Table I Concentrations of DBP and DEHP (mg.kg^{-1} d. w.) found in agricultural soils in examined localities in 2011

S.	Region	Land registry	Culture	DBP mg.kg^{-1}	DEHP mg.kg^{-1}	∑DBP a DEHP mg.kg^{-1}
1	V	Utín	AS	0.67	0.49	1.16
2	V	Vysoké Studenice	AS	0.22	0.31	0.53
3	V	Střížov u Třebíče	AS	0.59	0.52	1.11
4	ZL	Nivnice	AS	0.19	0.47	0.66
5	ZL	Boršice u Buchlovic	AS	0.63	0.45	1.08
6	ZL	Jarcová	AS	0.73	0.42	1.15
7	JM	Chrlice	AS	0.12	0.38	0.50
8	OC	Tomíkovice	AS	0.43	0.25	0.68
9	OC	Bílá Voda u Javorníka	AS	0.38	0.19	0.57
10	MS	Stará Bělá	AS	0.36	0.16	0.52
11	MS	Šenov u Nového Jičína	AS	0.27	0.19	0.46
12	MS	Albrechtice	AS	0.42	0.33	0.75
13	MS	Raškovice	AS	0.37	0.29	0.66
14	MS	Mosty u Českého Těšína	PG	0.79	0.35	1.14
15	MS	Žilina u Nového Jičína	PG	0.57	0.41	0.98
16	MS	Žilina u Nového Jičína	PG	0.34	0.24	0.58
17	MS	Dolní Marklovice	PG	1.78	1.02	2.80

Table II Concentrations of DBP and DEHP (mg.kg^{-1} d. w.) found in agricultural soils in examined localities in 2012

S.	Region	Land registry	Culture	DBP mg.kg^{-1}	DEHP mg.kg^{-1}	∑DBP a DEHP mg.kg^{-1}
1	V	Utín	AS	0.67	0.47	1.14
2	V	Vysoké Studenice	AS	0.39	0.12	0.51
3	V	Střížov u Třebíče	AS	0.45	0.09	0.54
4	ZL	Nivnice	AS	0.23	0.11	0.34
5	ZL	Boršice u Buchlovic	AS	0.29	0.17	0.46
6	ZL	Jarcová	AS	0.67	0.14	0.81
7	JM	Chrlice	AS	0.20	0.50	0.70
8	OC	Tomíkovice	AS	0.81	0.71	1.52
9	OC	Bílá Voda u Javorníka	AS	0.59	0.24	0.83
10	MS	Stará Bělá	AS	0.28	0.10	0.38
11	MS	Šenov u Nového Jičína	AS	0.18	0.06	0.24
12	MS	Albrechtice	AS	0.48	0.19	0.67
13	MS	Raškovice	AS	0.66	0.26	0.92
14	MS	Mosty u Českého Těšína	PG	1.15	0.96	2.11
15	MS	Žilina u Nového Jičína	PG	0.67	0.27	0.94
16	MS	Žilina u Nového Jičína	PG	0.31	0.13	0.44
17	MS	Dolní Marklovice	PG	0.97	0.27	1.24

V – Vysočina, ZL – Zlínský, JM – Jihomoravský, OC – Olomoucký, MS – Moravskoslezský, AS – arable soil, PG– permanent grassland

Comparison of total concetrations of DBP and DEHP is shown in following Figure 1.

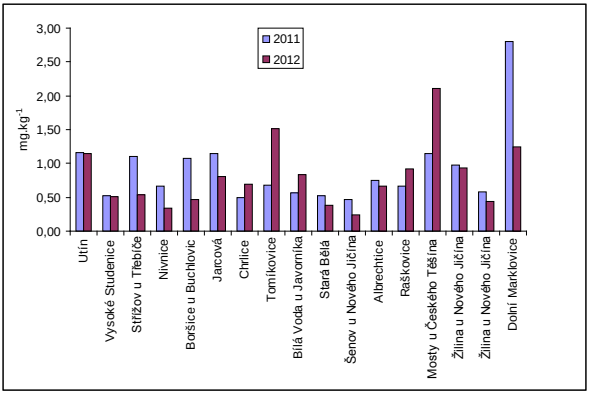

Fig. 1 Comparison of ∑DBP and DEHP concentrations (mg.kg^{-1} d. w.) in agricultural soils of examined localities in 2011 and 2012

On the basis of presented graphs, it can be concluded that the concentration of DBP and DEHP in agricultural soil is not stable. It can be said that the concentration of DBP is variable, it decreased in some localities and increased in others. In case of DEHP - with the exception of 4 localities - the concentration decreased significantly. A significant decrease in the concentration of DEHP in most samples led to the decrease of total concentration also in most samples. The most pronounced drop in the concentration of DBP and DEHP was in Dolní Marklovice, where it decreased from the value of 2.80 mg.kg^{-1} d. w. to 1.24 mg.kg^{-1} d. w. On the other hand, the concentration increased especially in two localities, namely Tomíkovice, from 0.68 mg.kg^{-1} d. w. to 1.52 mg.kg^{-1} d. w. and Mosty u Českého Těšína, from 1.14 mg.kg^{-1} d. w. to 2.11 mg.kg^{-1} d. w.

In the Czech Republic, there is no legislatively set limit on the concentration of phtalates in agricultural soils. The Ministry of the Environment issued a guideline based on the values of screening of USEPA. If these values are exceeded, there should be further research or removal of contamination. In this study, none of the values were exceeded.

CONCLUSION

This paper dealt with the determination of concentrations of dibutyl phthalate and di-2-ethylhexyl phthalate in Moravian agricultural soils. The monitoring involved five regions of the Czech Republic. Vysočina, Oloumoucký, Jihomoravský, Zlínský a Moravskoslezský. Compared to 2011, the year 2012 showed a decrease in total concentrations of DBP and DEHP. This is mainly a consequence of decreased concentration of DEHP in most samples. Values indicated in the guideline of the Ministry of the Environment were not exceeded. Increased concentrations in agricultural soils are a consequence of human activity, especially in the areas with intense industrial activity, where there is a frequent atmospheric deposition of these substances. In these areas, increased concentrations of other contaminants were detected as well, such as PCB or heavy metals. Another cause of increased concentration often is intensive agricultural activity (Zeng et al., 2009, Vikelsoe et al., 2002). Monitoring will be carried out in 2013.

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