Phthalates concentration in leachate from operating and closed municipal landfills of central Poland

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Abstract: Phthalates (PAEs) are organic esters of phthalic acid used mainly as plasticizers in the production of PVC products, but also as additives in the production of paints and varnishes. The content of plasticizers in soft PVC products may reach up to 40–60%. With the global yearly production of phthalates estimated at approx. 5–8 million tons, large amounts of PAEs had to end up on the landfills and therefore can be found in high concentrations in the municipal landfills leachate. The landfills without proper environmental protection systems may pose a threat to the environment and human health. In this research two landfills with different "history and parameters" were studied. First landfill was closed in 2011 and a remediation process started in 1996, while the second one is currently under a closing process but is still in use. Those landfills were compared in terms of phthalates concentration in raw leachate. It was found that most of the PAEs concentrations were below LOQ, with an exception of DEHP, DBP and DIBP. The highest DEHP concentrations were detected on landfill 1 in 2015, in summer, ranging from 32.2 to 38.6 µg/l, autumn <LOQ to 20.2 µg/l and winter 16.5 to 19.6 µg/l. Also in summer 2015 the highest DEHP concentrations were detected on landfill 2 (ranging from <LOQ to 19.3 µg/l). During the study no correlation between the sampling seasons and PAEs concentrations were observed. Moreover, the landfill 1 releases more DEHP than landfill 2 because it contains more than fivefold amount of waste. Interesting fact is that landfill 1 underwent remediation in 1996 and has been closed for many years (since 2011) but DEHP emissions are still present in the leachate. In 83% of studied all samples DEHP concentrations exceeded (from 2.5 to 18.7 times) the acceptable EU limits for surface water (1.3 µg/l).

Key Words: DEHP, DBP, PAE, PVC, contamination

INTRODUCTION

Phthalates (PAEs), which are organic esters of phthalic acid, are used mainly as plasticizers in the production of polyvinyl chloride (PVC) products, but they are also used as additives in the production of cellulosics, polyvinyl acetates and polyurethane resins (Sailas et al. 2015). One-third of the mass of phthalates produced is used for the production of soft PVC products (cable insulation, floor coverings, footwear, wallpaper, furniture, etc.), while the remaining two-thirds are used to manufacture the products from hard PVC (Europe Commission DGXI.E.3). Most commonly used PAEs in the production of PVC were di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) (Gao et al. 2016). The content of plasticizers in soft PVC products may reach up to 40–60% (Erythropel et al. 2014, Gao et al. 2016).

PAEs are not chemically but only physically bond to a polymer matrix, which allows them to migrate to the product surface and leach to the environment (Erythropel. et al. 2014, Sailas et al. 2015). The global production of phthalates is estimated at approx. 5-8 million tons a year (Gao and Wen 2016, Przybylińska and Wyszkowski 2016, Vaverkova and Adamcova 2018) and since the landfilling has been the most popular techniques of municipal waste disposal (Gworek et al. 2015, Koda et al. 2017), large amounts of PAEs had to end up on the landfills. Precipitated water which penetrates through the landfill body can carry many chemicals including PAEs, which can be found in high concentrations in the

municipal landfills leachate (Asakura et al. 2004, Gao and Wen 2016). The leachate migrating to ground or surface water may cause water contamination making it unfit for drinking (Koda 2012). Therefore, the landfills without proper environmental protection systems, such as leachate collection systems, may pose a threat to the environment and human health (Przybylińska and Wyszkowski 2016).

PAEs are consider as toxic (Grynkiewicz-Bylina 2011) and widespread environmental pollutants (Przybylińska and Wyszkowski 2016). PAEs are endocrine disruptors which may result in health problems including hepatomegaly, osteoporosis, feminization of boys, weight loss, and skin and breast cancer (Sailas et al. 2015). They might also have negative effects on reproduction, fertility and carcinogenicity (Net et al. 2015). For the human population, the main concern is related to bioaccumulation of PAEs over long term exposure to contaminated food or drinking water (Gao et al. 2016).

This paper presents the results of the first exhaustive study conducted on the concentration of phthalates in raw municipal leachates in Poland.

MATERIAL AND METHODS

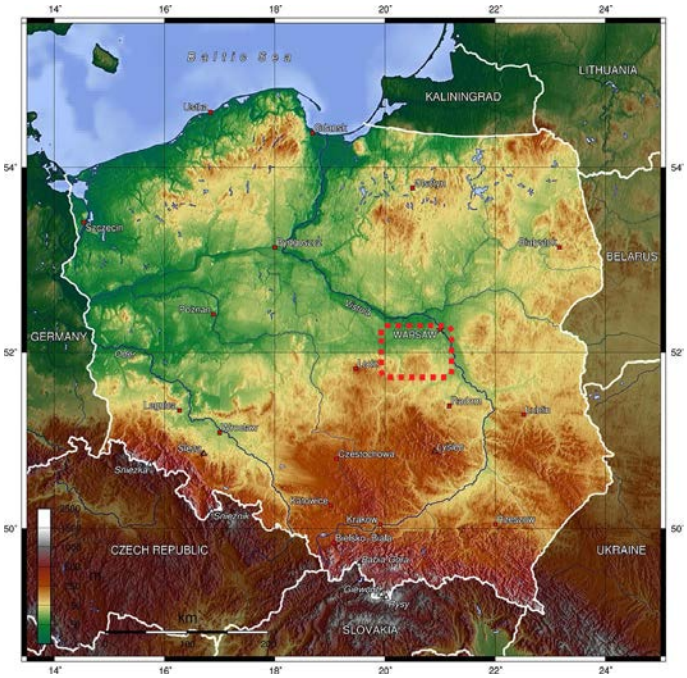
Characterization of landfills, location and technical data

Two large municipal waste landfills in a radius of up to 70 km from Warsaw were selected for the study (figure 1). During the selection of the landfills their age, size and operational status were taken into account. The first landfill was closed in 2011, and a remediation process started in 1996, while the second one is currently under a closing process but is still in use. Both landfills have vertical barriers for controlling the flow and leachates collection systems in place.

The following landfills were selected:

1. Location 1 – year of launch 1978, 5.5 million m^3 of waste and area of 21.7 ha.
2. Location 2 – year of launch 1970, 0.9 million m^3 of waste and area of 8.7 ha.

Figure 1 Landfills location map.



Characterization of analytical procedure

The research material consisted of samples of raw leachate collected from the leachate tanks. All the samples were collected according to the EPA Ireland Landfill manual. Each sample was taken in triplicate, using only phthalate-free objects (metal buckets, Teflon pump tubes, etc.). After collection, the samples were kept in glass containers and insulated with a phthalate-free layer (aluminium foil with

plastic or rubber caps). Samples were collected from two municipal waste landfills in summer, autumn, winter 2015 and spring, summer, autumn 2016.

Phthalates concentrations were determined with the W-PTHGMS01 method, based on US EPA 8061A, 3500, 3510 in the accredited laboratory (The Certificates of Accreditation no. 819/2015 and 319/2016). This method is suitable for groundwater and potable water, leachate and sewage analysis.

The following PAEs were analysed in this study: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-propyl phtalate, di-n-butyl phthalate (DBP), di-isobutyl phthalate (DIBP), di-pentyl phthalate (DPP), dutyl benzyl phthalate (BBP), di-cyclohexyl phthalate (DCP), di(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP).

RESULTS AND DISCUSSION

The results of PAEs concentrations are presented in Table 1. Most of the PAEs concentrations were below LOQ (DMP, DEP, DPP, BBP, DCP, DNOP and di-n-propyl phthalate), with an exception of DEHP, DBP and DIBP, whereas the concentration of the last two were much lower (ranging from <LOQ to 1.64 µg/l and from <LOQ to 2.83 µg/l accordingly). DEHP was the most prevalent and in the concentrations many times higher than the other PAEs, ranging from <LOQ to 38.6 µg/l. High concentrations for DEHP were expected as historically PAE was the most commonly used plasticizer and represented around half of all PAEs used in Europe in the past (Jonsson et al. 2003). Similar DEHP concentrations in the landfills leachate were reported in Japan [9.6-49 µg/l], China [n.d.-46 µg/l], Sweden [<1-9 µg/l] or Denmark [<1-3 µg/l]. The resultant DEHP concentrations were lower than those reported in Sweden (Göteborg) [97-346 µg/l], Germany [up to 240 µg/l] and Italy [88-460 µg/l] (Wowkonowicz and Kijeńska 2017). The reason for those differances could be other composition of waste in Western and Eastern Europe, but also a fact that those studies were conducted more more then 15 years ago, when DEHP was much more frequently used plastisizer then now.

The highest DEHP concentrations were detected on landfill 1 in 2015 in summer, ranging from 32.2 to 38.6 µg/l, autumn <LOQ to 20.2 µg/l and winter 16.5 to 19.6 µg/l. Also in summer 2015 the highest DEHP concentrations were detected on landfill 2 (ranging from <LOQ to 19.3 µg/l). It should be also noted that year 2015 was much drier when 2016 and summer 2015 was the driest among all the seasons with an average precipitation of 32.6 mm for this region (see Table 2).

Table 1 PAEs concentrations in municipal solid waste landfill raw leachate – summer, autumn, winter 2015 and spring, summer, autumn 2016.

PAE name	Loca-tion	Content range of phthalates (n=3) in leachate in different seasons of 2015 and 2016 [µg/l]					
		2015			2016		
		Summer	Autumn	Winter	Spring	Summer	Autumn
Di-n-butyl phthalate (DBP)	Landfill 1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Landfill 2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ-1.64	<LOQ
Di-isobutyl phthalate (DIBP)	Landfill 1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Landfill 2	<LOQ	<LOQ	<LOQ	<LOQ-1.13	<LOQ-2.83	<LOQ
Di(2-ethylhexyl) phthalate (DEHP)	Landfill 1	<LOQ-38.6	<LOQ-20.2	16.5-19.6	2.7-4.7	11.3-12.8	<LOQ
	Landfill 2	<LOQ-19.3	<LOQ	<LOQ	<LOQ-2.3	<LOQ	<LOQ

Legend: LOQ for all PAEs (except DEHP) was 0.6 µg/l, LOQ for DEHP was 1.3 µg/l. For some samples LOQ was raised due to matrix interference. Measurement uncertainty was (+/-35%).

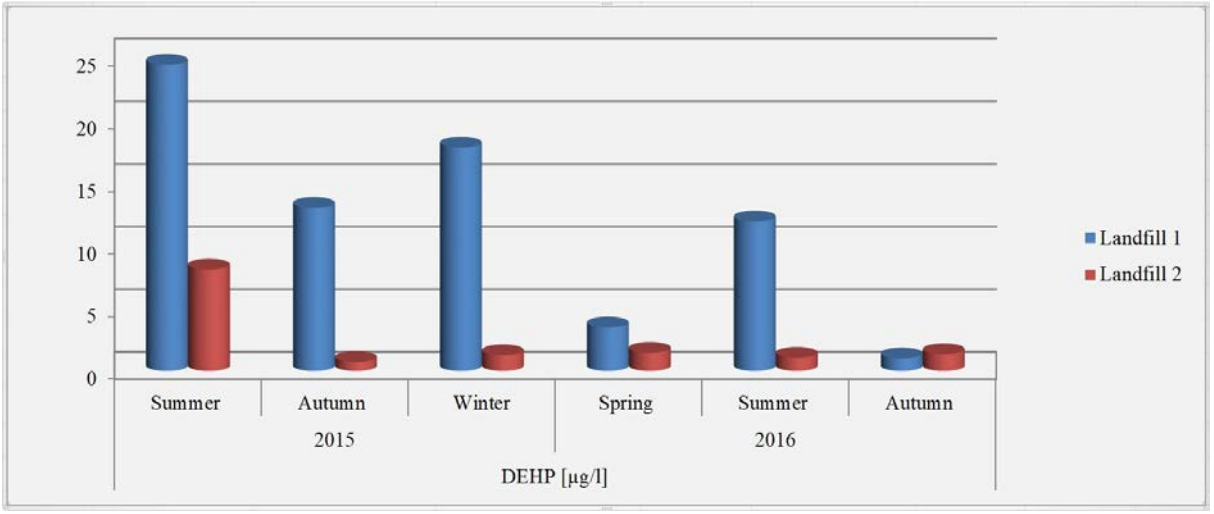
Table 2 Average precipitation in the region during sampling seasons.

Year	Season	Average precipitation in the region* [mm]
2015	Summer	32.65
	Autumn	47.65
	Winter	37.81
2016	Spring	37.20
	Summer	66.68
	Autumn	58.07

*Legend:*based on the data from meteorological stations provided by the Institute of Meteorology and Water Management—National Research Institute (IMGW-PIB).*

DEHP was the only PAE determined in the majority of samples analysed. It was observed, that mean concentrations of DEHP in leachate from landfill 1 were much higher than those determined in leachate from landfill 2 (see Figure 2).

Figure 2 Mean DEHP concentrations in municipal solid waste landfill raw leachate.



Legend: The concentrations presented on Figure 2 are average concentrations (n=3). In case a single sample concentration was <LOQ, the value 0.5LOQ was taken into average, in accordance with Commission Directive 2009/90/EC.

CONCLUSION

The research material, which consisted of the samples of raw landfills leachate, shows presence of the following PAEs in at least one sample: DEHP, DBP and DIBP. Out of all 10 analysed PAEs, DEHP was the most prevalent ranging from <LOQ to 38.6 µg/l.

There is a relationship between the landfill size and the PAE concentrations with comparable precipitations in the region. The landfill 1 releases more DEHP than landfill 2 as it contains more than fivefold amount of waste. Interesting fact is that landfill 1 underwent remediation in 1996 and has been closed for many years (since 2011) but DEHP emissions are still present in the leachate.

In 83% of samples mean DEHP concentrations exceeded (from 2.5 to 18.7 times) the acceptable EU limits for surface water (1.3 µg/l).

During the study no correlation between the sampling seasons and PAEs concentrations have been observed, which was also concluded by Asakura et al. (2004). The highest DEHP concentrations were detected on both landfills in summer 2015 (the driest of all investigated seasons).

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