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Phthalates in Underground Waters of the Zagreb Area

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Aim. To determine whether and in what concentrations the underground waters, stream waters, spring water, and tap water from the Zagreb area contain phthalates – compounds used as plastic softeners, which have recently been ascribed carcinogenic, mutagenic, and teratogenic effects.

Method. The presence of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), diethylhexyl phthalate (DEHP), and dioctyl phthalate (DOP) was determined in a total of 96 samples of underground waters, stream waters, and tap water from the Zagreb area between February and June 1998. Identification and quantification of phthalates were performed by the method of gas chromatography (GC-ECD), with a detection limit of 0.005 μg/L.

Results. The presence of one or more phthalates was demonstrated in 93 out of 96 (97%) water samples. The measured values ranged from 0.005 to 18.157 μg/L. Phthalates were detected in 76 out of 77 (98%) underground water samples. The mean level of all phthalates present in the water samples was 4.879 μg/L. Median test yielded a significantly increased level of phthalates in the underground waters from Jakuševac (sampled in February 1998) and Trebež, which are Zagreb and Samobor city waste dumps, as compared with other sites in the study (overall median = 3.785; chi/square = 22.682; $p < 0.001$). Phthalates were found at a mean concentration of 3.363 μg/L in all 10 water samples from the Sava river, the major source of the Zagreb alluvium underground waters. In case of drinking water, phthalates were detected in 7 out of 9 (78%) samples, at a mean concentration of 0.887 μg/L. As expected, DEHP was the most commonly detected phthalate, found in 78 (81%) water samples.

Conclusion. The highest phthalate concentrations were recorded in underground waters directly related to the proximity of a waste dump. The levels of phthalates recorded in this study were lower than those reported from other countries and did not present a threat to human health. Environmental phthalate monitoring should be continued and their maximum allowed concentrations should be prescribed by regulations.

Key words: *chromatography, gas; Croatia; diethylhexyl phthalate; refuse disposal; water pollutants*

The main shortcomings of initial plastics were their hardness, fragility, and rigidity. Today, these shortcomings are eliminated by adding various agents to plastic products, such as fillings, softeners-plasticizers, stabilizers, and pigments. The most commonly used softeners are phthalates. Their production amounts to 2.7 million tons per year. Di(2-ethylhexyl) phthalate (DEHP) accounts for almost 50% of overall phthalate production. The weight proportion of phthalate in a plastic material may reach 50% (1-3).

Environmental effects of phthalates may occur during the technological process, manufacture, and use of plastic materials, or on their disposal after use (1-3). The main route of phthalates entering the environment is atmosphere, wherefrom they are washed out by precipitation. Phthalates are partially dissolved in water in the form of residues, and partially adsorbed to organic substances in the soil and sediment, like the long-chained, lipophilic portion of DEHP (1,4,5). Subsequently, they reach underground waters through continuous soil filtration, where certain amount of phthalates undergoes slow-process disintegration, whereas the rest accumulates in the plants, fish, amphibians, birds, and eventually humans (1-4). The presence of phthalates has been demonstrated in the atmosphere (6-10), food (11-15), rivers, lakes and sea (3,16-21), underground waters (5,22-24), and drinking water (25).

At present, it is quite difficult to conceive any human activity free from the use of plastic materials, their production exceeding 25 million tons per year (1,3). The proportion of plastics in solid waste increases by 1% a year, and poses a considerable problem because of its volume and nondegradability (1,3). Uncontrolled disposal of plastic materials and packaging containers can contaminate both the soil and underground water streams (1,4,5), whereas inappropriate incineration of plastics can trigger the formation of highly noxious compounds known as dioxins (dibenzodioxins and dibenzofurans) (26).

Studies in experimental animals have pointed to the possible toxic, carcinogenic, mutagenic, and teratogenic effects of phthalates (27-37), but evidence about harmful influence of phthalates on human health is still doubtful. Accordingly, there is still no international agreement on maximally allowed concentration of phthalates in the environment. On the other hand, effects of the environmental presence of phthalates have been paid ever more attention in industrialized countries, and World Health Organization advises systematic phthalate control and monitoring (1). However, respective recommendations and regulations still lack in most countries, including Croatia.

The city of Zagreb has been virtually built on water springs. Unfortunately, many of these springs are out of function today because of contamination, primarily due to poor control of industrial wastewater release to the underground. Also, the quality of underground waters has been found to deteriorate to some extent because of uncontrolled city waste disposal (38-40).

The aim of the study was to provide an insight into the level of contamination of underground waters and the currently exploited and other potential sources of drinking water in the Zagreb area. Although the previous investigations of phthalate concentrations in underground waters of some parts of the Zagreb alluvium suggested the presence of these substances, only their overall presence was assessed, whereas studies of individual phthalates have not been performed (38-40). We wanted to find out whether and to what extent the underground water phthalate load could be related to uncontrolled waste disposal in the vicinity of water springs. The main purpose of our analysis was to assess the residents' exposure to these contaminants through the use of drinking water.

Material and Methods

We analyzed a total of 96 water samples divided into three groups. Most samples (group 1) were obtained from underground waters of the Sava river alluvium (n = 77). Water samples were collected from pipeline bores (piezometers) at four sites (Fig. 1), according to potential phthalate exposure, technical possibilities, and available data on the water concentration of phthalates. The four sites of water sampling were Jakuševac (Zagreb city dump), Kosnica, Petruševec, and Trebež (Samobor city dump). Petruševec and Strmec are currently used as water sources for the Zagreb water supply, and Kosnica is planned to be used for the same purpose in the near future. The aim of water sampling at Jakuševac was to show the impact of city waste dump on the quality of underground waters, not only at the location of Jakuševac, but also at the location of Kosnica, situated several hundred meters from Jakuševac. Similarly, water sampling was performed at the Samobor waste dump, Trebež, and at the nearby pump site Strmec. Samobor is a small town near Zagreb, a part of Zagreb city district. Pumping from the bores-piezometers was done by a Grundfos MP-1 type pump, maximal capacity of 0.5 L/s. Water samples were collected one meter below the measured level after pumping 5 water volumes from the bore, to obtain representative water samples. On the location of the city waste dump Jakuševac, water sampling was performed twice, ie, in February and in June, to assess the impact of phthalate filtration through the soil via precipitation.

Group 2 samples included 10 water samples from the Sava river as the main source supplying water to the Sava alluvium, whereas group 3 consisted of nine drinking water samples collected from the water supply network and captages.

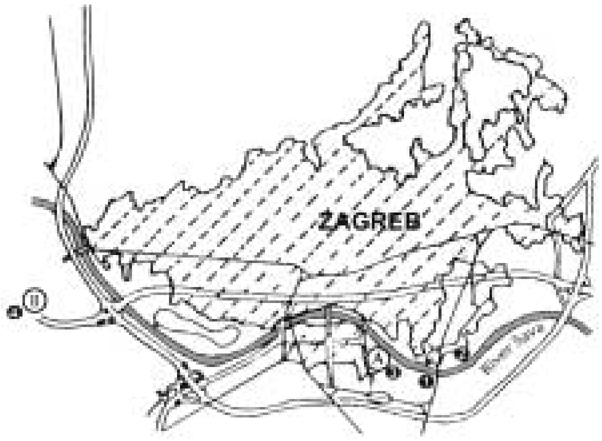

Figure 1. Underground water sampling sites and locations of solid waste disposal in the Zagreb area. Full circle – underground water sampling sites: 1 – Kosnica, 2 – Petruševec, 3 – Jakuševac, 4 – Trebež; open circle – locations of solid waste disposal: A – Jakuševac, B – Trebež.

The property of phthalates to readily dissolve in organic solvents was used for their concentration and separation from water samples. Extraction with the organic solvent dichloromethane was performed from neutral and acidic samples, with a modification using a high rpm mixer on extraction instead of regular extraction in separation funnel. Phthalate identification was done by the method of gas chromatography with a specific electron capture detector (ECD). A Perkin Elmer PE AutoSystem XL supplied with ECD with ^{63}Ni (Norwalk, CT, USA) gas chromatograph was employed (41,42). Under standard gas chromatography conditions, detection limits of 0.005 and 0.040 μg/L for BBP and DOP, respectively, were achieved.

Results

The presence of one or more phthalates was demonstrated in 93 of 96 (96.9%) water samples. The measured levels ranged from 0.005 to 18.157 μg/L. Among underground water samples, phthalates were found in 76 of 77 (97.8%) samples (Table 1). The mean overall concentration of phthalates in water samples was of 4.879 μg/L. Among the underground water sampling sites, the highest mean phthalate concentration was recorded in the water from Trebež (5.934 μg/L), followed by the water from Jakuševac sampled in June (5.184 μg/L) and February (3.720 μg/L). The mean concentration of phthalates was lower at the other two sites that have no known communication with waste dumps (2.570 μg/L at Kosnica and 1.655 μg/L at Petruševec). Considering each individual water sample, median test showed a significantly higher phthalate concentration in the water from Trebež and Jakuševac sampled in February, as compared with other study locations (pooled median = 3.785; chi-square = 22.682; $p < 0.001$). In the water from Jakuševac sampled in June, however, the concentration of phthalates did not significantly exceed the concentrations measured at the sites of Kosnica and Petruševec.

Phthalates were found to be present in all 10 samples from the Sava river. The mean concentration of all phthalates was 3.363 μg/L (Table 1).

Table 1. Pooled results on the presence of phthalates in 77 underground water samples from the Zagreb area (Sava river alluvium), 10 water samples from Sava river in the Zagreb area, and 9 drinking water samples from the Zagreb water supply in 1998

	Type of phthalate[a]						
Water source	DMP	DEP	DBP	BBP	DEHP	DOP	total
Underground water							
Positive samples (n)	36	17	58	47	65	18	76
Positive samples (%)	46.8	22.1	75.3	61.0	84.4	23.4	98.7
Minimal value (mg/L)	ND[b]	ND	ND	ND	ND	ND	ND
Maximal value (mg/L)	3.603	14.886	18.157	7.001	5.344	2.817	18.157
Mean value (mg/L)	0.501	0.574	1.864	0.699	0.222	0.222	4.879
Sava river							
Positive samples (n)	2	8	0	9	10	0	10
Positive samples (%)	20.0	80.0	0	90.0	100	0	100
Minimal value (mg/L)	ND	ND	ND	ND	0.023	ND	ND
Maximal value (mg/L)	0.033	6.255	0	0.664	1.270	0	6.255
Mean value (mg/L)	0.005	2.324	0	0.370	0.664	0	3.363
Drinking water							
Positive samples (n)	5	4	0	7	3	0	7
Positive samples (%)	55.6	44.4	0	77.8	33.3	0	77.8
Minimal value (mg/L)	0.041	ND	ND	0.096	ND	ND	ND
Maximal value (mg/L)	0.255	0.409	0	0.672	0.798	0	0.798
Mean value (mg/L)	0.135	0.195	0	0.322	0.247	0	0.887

[a]Abbreviations: DMP – dimethyl phthalate; DEP – diethyl phthalate; DBP – dibutyl phthalate; BBP – benzylbutyl phthalate; DEHP – diethylhexyl phthalate; DOP – dioctyl phthalate.
[b]Not determined.

Table 2. Proportion of underground water, Sava river water, and drinking water samples from the Zagreb area positive for particular phthalates in 1998

	Water sample (n, %)								
	underground waters								
Phthalate[a]	Kosnica	Petruševec	Jakuševac (Feb)	Jakuševac (Jun)	Trebež	total	Sava river	drinking water	total
DEHP	12 (63.2)	3 (75.0)	24 (92.3)	19 (90.5)	7 (100)	65 (84.4)	10 (100)	3 (33.3)	78 (81.3)
BBP	3 (15.8)	0	25 (96.2)	18 (85.7)	1 (14.3)	47 (61.0)	9 (90.0)	7 (77.7)	63 (65.6)
DBP	14 (73.7)	3 (75.0)	19 (73.1)	16 (76.2)	6 (85.7)	58 (75.3)	0	0	58 (60.4)
DMP	15 (78.9)	4 (100)	8 (30.8)	5 (23.8)	4 (57.1)	36 (46.8)	2 (20.0)	5 (55.5)	43 (44.8)
DEP	0	0	9 (34.6)	7 (33.3)	0	16 (20.8)	8 (80.0)	4 (44.4)	28 (29.2)
DOP	0	0	9 (34.6)	7 (33.3)	1 (14.3)	17 (22.1)	0	0	17 (17.7)

[a]Abbreviations: DEHP – diethylhexyl phthalate; BBP – benzylbutyl phthalate; DBP – dibutyl phthalate; DMP – dimethyl phthalate; DEP – diethyl phthalate; DOP – dioctyl phthalate.

Phthalates were also demonstrated in 7 of 9 (77.8%) drinking water samples, at a mean concentration of 0.887 μg/L (Table 1).

Analysis of particular phthalate frequency revealed DEHP to be by far most common. DEHP was detected in 78 (81.3%) water samples, followed by benzylbutyl phthalate (BBP) and dibutyl phthalate (DBP), which were found in 63 (65.5%) and 58 (60.4%) of 96 water samples, respectively (Table 2).

Discussion

Since uncontrolled waste dumps can definitely influence the quality of underground waters, various studies were conducted to define the level of their impact (20,43). The present study was similarly designed. Of the four underground water locations, Petruševec is currently used as a source of drinking water for Zagreb, and Kosnica is planned to serve as another water supply source in the near future. Unfortunately, the potential water pump plant Kosnica has been located near the city waste dump Jakuševac for more than 30 years. Another such example of poor environmental management is the waste dump Trebež, close to the Strmec water pump, near Samobor. Considering the long-lasting waste disposal at Jakuševac, its impact on the underground water quality was assessed in two hydrologic periods during the year, ie, in the period rich in precipitation (February) and in the dry period (June) after due time had elapsed for the effect of phthalate filtration and penetration from the surface waste to the underground. Our results pointed to the role of phthalate filtration from the surface during the period rich in precipitation. In conjunction with the depth of sampling (about 7 meters), they also indicated that very little phthalates reached the underground during the dry period of the year. The results obtained so far suggest the presence of phthalates in underground waters is most probably associated with the vicinity and impact of waste dump.

Although the river of Sava contributes most to the underground waters of the Zagreb alluvium, the total amount of phthalates in the Sava river was lower than in the underground waters, whereas the lowest phthalate levels were measured in drinking water (upon processing), as expected. This is consistent with literature reports on low river levels of phthalates (comparable to ours or even lower) (16,17,19), unless being directly endangered by wastewater release from a plastics factory (18). Due to their lipophilic properties, considerably higher levels of phthalates are found in the sediment and suspended particles (6,17,19). In the United States and Japan, DEHP concentrations in drinking water ranged from 1.2 to 1.8 μg/L and 0.05 to 11 μg/L, respectively (25), ie, significantly higher than the values recorded in our study (total phthalates, 0.887 μg/L), especially considering the fact that in our study DEHP accounted for 20-30% of total phthalates, irrespective of the water origin. DEHP was by far the most common phthalate detected (1-3), especially in underground waters, proving that phthalates had reached them by soil filtration from the surface plastic waste, which is in concordance with findings of other studies (22,23,25,43).

Rough estimates based on this study would imply a mean phthalate intake of less than 2 μg/day in drinking water, which is not expected to exert any significant toxicological effect on human health, especially as it is several-fold lower than the amounts of phthalates found in drinking water in some other countries, where no effects of phthalate intake on human health have yet been positively demonstrated (25). However, phthalates are lipophilic substances showing the effect of bioaccumulation, which may manifest in the conditions characterized by body fat reserve activation (starvation or disease). Also, the additional intake of phthalates from other sources, such as food (11-15), cosmetics (44), plastic medical accessories (44-48), or toys (49) should not be neglected either.

In conclusion, the levels of phthalates in the Zagreb area waters are not high and not likely to present a threat to human health in the long run. The study clearly demonstrated the association between the presence of phthalates in the waters and uncontrolled city waste disposal, pointing to the need of a general strategy of waste disposal at both local and national levels. Considering the data of the World Health Organization on the possible carcinogenic effect of phthalates in humans (50), a prolonged, lifetime exposure to low amounts of phthalates should not be ignored.

In addition, the study points to the need of international co-ordination and standardization of maximum allowed environmental levels of phthalates (in the atmosphere, food, water, etc.) to which people can be exposed during the lifetime, in accordance with the World Health Organization recommendations.

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