Migration of Phthalates from Plastic Containers into Soft Drinks and Mineral Water

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Summary

The aim of this study was to determine the level of phthalate migration from plastic containers to soft drinks and mineral water and to identify a possible relationship between the amount and type of phthalate migration, type of preservative used, and the pH of the sample. The analysis included 45 samples of products packed in containers made from polyethylene terephthalate. The samples were divided into 5 groups: group 1 (N=9), soft drinks preserved with orthophosphoric acid; group 2 (N=14), soft drinks preserved with Na-benzoate; group 3 (N=5), soft drinks preserved with K-sorbate; group 4 (N=8), soft drinks preserved with a combination of Na-benzoate and K-sorbate; and group 5 (N=9), mineral water without preservatives. The samples were analyzed by the method of gas chromatography, with a detection limit of 0.005 μg/L. The mean pool phthalate level and mean pH value were 91.67 μg/L and 2.82±0.30 in group 1; 116.93 μg/L and 2.75±0.32 in group 2; 819.40 μg/L and 2.88±0.15 in group 3; 542.63 μg/L and 2.82±0.54 in group 4; and 20.22 μg/L and 5.82±1.26 in group 5, respectively. The highest rate of migration to soft drinks was recorded for dimethyl phthalate, ranging from 53.51 to 92.73 %, whereas dibutyl phthalate and diethylhexyl phthalate showed highest rate of migration to the mineral water (56.04 and 43.42 %, respectively). The highest level of phthalate migration from plastic containers to soft drinks was found in the products preserved with K-sorbate. The rate of phthalate migration appears to be influenced also by the drink pH, i.e. the lower the pH value, the greater the phthalate migration. Dimethyl phthalate showed highest migration to preserved drinks as an acidic medium, which might stimulate modification in the composition of plastic containers according to the type and composition of the product. Additional studies in a greater number of samples are needed. Although the phthalate levels measured in these samples pose no risk for human health, it should be borne in mind that the accumulation of small individual amounts taken with time may increase the lifelong phthalate exposure and eventually threaten the exposed person’s life.

Key words: phthalates, soft drinks, plastic containers, preservatives, pH, food safety

Introduction

Living in the modern society is hardly conceivable without the use of plastic products in everyday activities (1–3). Since 1862, when the production of plastic began, the technology of its production has considerably changed. Currently, various agents are added in plastic material processing to improve its properties, such as
softeners, plasticizers, fillings, stabilizers, and pigments. For several decades now, phthalic acid esters, phthalates, have been the most widely used plasticizers, with diethylhexyl phthalate (DEHP) accounting for 50 % of this utilization. The production of phthalates in the world has grown to 3.5 million tonnes per year (4). The proportion of phthalates in a plastic material may amount to up to 45 % of its mass, depending on the type and purpose of the product (1,2,5,6).

The use of plastic containers has been on a constant increase in all fields of human activities, resulting in the portion of plastics in total solid waste growing at a rate of 1 % per year. Plastic solid waste, especially that from plastic food containers, poses a great problem due to both its volume and relative nonbiodegradability (1,2,6–8). Recent studies have shown that plastic disposed of as solid waste and exposed to weather conditions (sun, rain, snow, etc.) undergoes degradation, although at a very slow rate, whereby plasticizers, primarily phthalates, which are most widely used to achieve the desired elasticity and softness of plastic materials, are released from the plastic. The phthalates thus released migrate to the underground layers and waterflows, and from there to the waters intended for human use (1,9,10). The problem of plastic disposal is additionally burdened by the fact that other hazardous compounds such as dioxins (dibenzodioxins and dibenzofurans) are produced by inappropriate burning of plastic materials (7,11).

The interest of both professional circles and the public in the phthalate issue has recently been aroused by the latest research demonstrating adverse effects of phthalates in experimental animals, and a variable response of human and animal hepatocytes to the action of phthalates (12–17). These studies revealed numerous adverse effects of phthalates in experimental animals, from those tentatively less harmful, such as body mass loss and slight lifespan reduction in exposed animals (18,19), to the extremely hazardous effects, e.g. spontaneous abortion, stillbirth, low birth mass of the offspring, along with toxic, carcinogenic, mutagenic and teratogenic effects of phthalates, all these correlating directly with the extremely hazardous effects, spontaneous abortion, and stillbirth, low birth mass of the offspring, along with toxic, carcinogenic, mutagenic and teratogenic effects of phthalates, all these correlating directly with the amount and length of phthalate exposure (14,17,20,21). In addition, phthalates found in the environment have been observed to mimic estrogens, thus eliciting adverse effects on the male sex glands in experimental animals (15,22,23).

There are two opposite opinions on the potential harmful effects of phthalates on human health. Those advocating reduction (in type and number) in the use of plastic materials find grounds for their standpoint in the World Health Organization’s (WHO) conclusions and recommendations, stating that phthalate exposure implies a risk for human health (4,24–29). The others believe that the human health risk associated with phthalate exposure is negligible, stating that even in humans with highest phthalate exposure the level of this exposure is several dozen or several hundred times lower than that in experimental animals, it is generally only occasional and gradual, and received over a long period of time, sometimes over decades (18,19).

In Croatia, not all issues related to the use of phthalates in daily life have been regulated by legal acts. Only the total amount of phthalates in plastic materials has been defined and it should not exceed 35 %, irrespective of the purpose of the product, length of usage, and user’s age (30).

The aim of the present study is to assess the rate of phthalate migration from plastic containers to soft drinks and mineral water and the influence of the pH of the sample and type of preservative used in the product manufacture on it.

Material and Methods

A total of 45 samples of different soft drinks and mineral water packed in plastic were sent to the Department of Ecology, Division of Food and Common Goods Chemical Testing, Zagreb Public Health Institute, Zagreb. Plastic containers were made of standard, widely used polyethylene terephthalate (PET), the composition of which was determined using infrared (IR) spectrometer. Raw materials for soft drinks and final products (both soft drinks and mineral water) are under obligatory and continuous public health validity control, which excludes possible contamination with phthalates. The samples were divided into 5 groups as follows: group 1 (N=9), soft drinks preserved with orthophosphoric acid; group 2 (N=14), soft drinks preserved with Na-benzoate; group 3 (N=5), soft drinks preserved with K-sorbate; group 4 (N=8), soft drinks preserved with a combination of Na-benzoate and K-sorbate; and group 5 (N=9), mineral water without preservatives. Total level of phthalate migration, and individual levels of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), diethylhexyl phthalate (DEHP) and dioctyl phthalate (DOP) were determined.

The samples were randomly collected during routine sanitary inspection for food and common goods safety. Samples were stored at room temperature (22 °C). The level of phthalate migration was measured 30 days from the date of the product manufacture and packing in plastic containers.

The samples were analyzed by gas chromatography with a specific electron capture detector (ECD) on a Perkin Elmer AutoSystem (Norwalk, USA). Detection limit in standard conditions ranged from 0.005 µg/L for BBP to 0.040 µg/L for DOP. The samples were extracted by using dichloromethane. Blank sample was prepared as follows: the model solution (distilled water) was put in a glass container and left there for 30 days. After that, the whole procedure of the sample preparation was made in the same way as for studying samples. The measured level of phthalates in blank sample was below the detection limit. The value of pH was measured in all samples.

Results

The mean pool phthalate level and mean pH value were 91.67 µg/L and 2.82±0.30 in group 1; 116.93 µg/L and 2.75±0.32 in group 2; 819.40 µg/L and 2.88±0.15 in group 3; 542.63 µg/L and 2.82±0.54 in group 4; and 20.22 µg/L and 5.82±1.26 in group 5 (Table 1).

The highest rate of migration to soft drinks was recorded for DMP, ranging from 53.51 % (accounting for 62.57 of 116.93 µg/L) in group 2 to as high as 92.7 % in...
Table 1. Individual and pooled mean levels of phthalate migration to soft drinks and mineral water (µg/L), according to type of preservative and pH of the drink

<table>
<thead>
<tr>
<th>Sample group</th>
<th>N*</th>
<th>pH</th>
<th>Phthalate migration, mean individual and pool levels</th>
<th>Statistical analysisa (3I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft drinks preserved with orthophosphoric acid</td>
<td>9</td>
<td>2.82 ±0.30</td>
<td>DMP 17 (0), DBP 60.56 (66.1 %), DOP 12.89 (14.0 %), DEP 0 (0 %), BBP 1.11 (1.2 %), DEHP 0 (0 %), Total 18 (100 %)</td>
<td>$\chi^2=27.401$, p&lt;0.001</td>
</tr>
<tr>
<td>Soft drinks preserved with Na-benzoate</td>
<td>14</td>
<td>2.75 ±0.32</td>
<td>DMP 0 (0), DBP 62.57 (53.5 %), DOP 21.29 (18.2 %), DEP 0 (0 %), BBP 17.14 (14.7 %), DEHP 0 (0 %), Total 91.67 (100 %)</td>
<td>$\chi^2=24.441$, p&lt;0.001</td>
</tr>
<tr>
<td>Soft drinks preserved with K-sorbate</td>
<td>5</td>
<td>2.88 ±0.15</td>
<td>DMP 0 (0), DBP 759.80 (92.7 %), DOP 9.00 (1.2 %), DEP 8.60 (1.0 %), BBP 5.40 (0.7 %), DEHP 36.60 (4.5 %), Total 819.40 (100 %)</td>
<td>$\chi^2=11.714$, p=0.020</td>
</tr>
<tr>
<td>Soft drinks preserved with Na-benzoate and K-sorbate</td>
<td>8</td>
<td>2.82 ±0.54</td>
<td>DMP 18 (0), DBP 500.88 (92.3 %), DOP 26.75 (4.9 %), DEP 0 (0 %), BBP 15.00 (2.8 %), DEHP 0 (0 %), Total 542.63 (100 %)</td>
<td>$\chi^2=28.964$, p&lt;0.001</td>
</tr>
<tr>
<td>Mineral water without preservative</td>
<td>9</td>
<td>5.82 ±1.26</td>
<td>DMP 0 (0), DBP 11.33 (56.0 %), DOP 0.11 (0.6 %), DEP 0 (0 %), BBP 8.78 (43.4 %), DEHP 0 (0 %), Total 20.22 (100 %)</td>
<td>$\chi^2=20.22$</td>
</tr>
</tbody>
</table>

*N is number of samples in each group. All analyzed samples were «positive». There was not a single sample without migration of phthalates, but final result for each group is pooled mean level of measured phthalate

**Total is sum of all single phthalates which migrated from plastic containers to soft drinks and mineral water

*Kruskal-Wallis test

Depending on the type of preservative used in product manufacture, the highest phthalate levels were measured in soft drinks with K-sorbate used as preservative (819.40 µg/L), followed by 1.5 times lower levels in drinks preserved with a combination of Na-benzoate and K-sorbate (542.63 µg/L), 7 times lower levels in drinks preserved with Na-benzoate (116.93 µg/L), and 9 times lower levels in drinks preserved with orthophosphoric acid (91.67 µg/L). The phthalate level recorded in mineral water samples free from preservatives was as low as 20.22 µg/L.

The results indicated K-sorbate as a preservative in combination with an acidic medium to favour the migration of phthalates from plastic containers into the drinks. A significant level of phthalate migration was also recorded in the same medium with K-sorbate and Na-benzoate used as preservatives. However, as the level of phthalate migration was several times lower with the use of Na-benzoate alone, this preservative appears to be less aggressive in terms of phthalate migration from plastic containers, yet with a note that all this applies to a medium of pH<3.

Irrespective of the preservative used, the highest level of phthalate migration from plastic containers into drinks was recorded for DMP, ranging from 53.5 % in group 2 to as high as 92.7 and 92.3 % in groups 3 and 4, respectively, whereas all other phthalates were measured in levels lower than 19 % (Table 1). The difference in the level of migration between DMP and other phthalates (DBP, DEP, BBP and DEHP) in each of the four

Discussion

The results of the study showed the levels of phthalate migration from plastic containers to soft drinks to be several fold (5 to 40 times) higher than those recorded in mineral water packed in identical containers. One of the possible reasons for this may lie in great pH differences between the samples, which was below 3 in all soft drinks and above 5 in all mineral water samples on average. This finding may point to the stimulating effect of an acidic medium on phthalate migration from plastic containers.

Despite the fact that phthalates present in soft drinks are in much smaller quantities than those present in mineral water, the higher levels of migration were observed in mineral water. This may be due to a number of factors, including the different pH levels of the drinks, the presence of preservatives, and the type of plastic containers used. The highest migration of phthalates was observed in mineral water packed in containers with Na-benzoate as a preservative, while the lowest was observed in soft drinks.

The results of this study highlight the importance of considering the type of preservative used in the production of drinks, as well as the pH of the drink, in determining the level of phthalate migration. Further research is needed to better understand the factors that influence phthalate migration from plastic containers into drinks.
study groups of soft drinks of comparable pH, manufactured with the use of different preservatives, was statistically significant at p<0.05 (Table 1).

In the group of mineral water samples, the highest level of migration was recorded for DBP (56.0 %), followed by DEHP (43.4 %). There was no DMP migration from plastic containers to mineral water.

The results obtained in the present study may prove useful in designing the composition of plastic containers for particular types of drinks. On planning the composition of plastic containers for low pH drinks (in this case soft drinks), care should be taken to eliminate or at least reduce the level of DMP, which is readily dissolved in the given conditions. On the other hand, plastic containers without or with a low content of DBP and DEHP should be designed for mineral water.

Man is exposed to phthalates from a variety of sources throughout his life. The presence of phthalates has been proved in baby formulae, dietary and normal foods (3,32,33). Furthermore, phthalate leaching from toys under the influence of saliva (due to keeping toys in the mouth) has been reported (6,34). Phthalates are found in house dust (4), and in tablet and capsule sheaths, thus being taken into the body (29). Since phthalates are used as softeners in various plastic medicinal products, their effect on individuals during prolonged intensive care has been emphasized (29,30,32–36). Phthalates have also been found in the atmosphere (37,38), various drinks (as well as in bottle caps) (39,40), water surfaces (sea, rivers, lakes) (41–43), and in underground and drinking water (II). Occupational exposure to phthalates, e.g. in the manufacture of phthalates and plastic materials, should also be taken into consideration (18,44–46).

The possible harmful effects of phthalates on human health have not yet been definitely demonstrated. Individuals working in the manufacture of phthalates or plastic products, where phthalates are used as plasticizers, report headache and minor neurovegetative discomforts in the form of excessive perspiration and sleep disorders (9,44–46). Studies showed no overt adverse effects of phthalates on human cell cultures in vitro (17).

The results obtained in the present study and literature data point to a conclusion that the total level of phthalates accumulated in a lifetime may reach high values. Not all issues related to daily use of phthalates have been regulated by the Croatian legislation. Only the total allowed level of phthalates in plastic common goods has been legally regulated to a maximum of 35 % (30), however, the purpose, length of usage, and the age of potential users have not been specified.

Conclusions

Considering the ever growing use of plastic containers for ever greater number and kinds of drinks, including soft drinks as well as alcoholic beverages such as beer, wine and spirits, the present study may serve as a basis in search for the most acceptable composition of particular plastic containers, and provide grounds for additional studies of human exposure to phthalates through the intake of various drinks packed in plastic containers. Along with drink pH and type of preservative used in the production of drinks, future studies should also include other potential factors and circumstances that may influence phthalate migration from plastic containers, such as the level and type of alcohol, and chemical composition of particular drinks (e.g. Coca-Cola® vs. fruit juice).

References


