Can migration of endocrine disruptors from plastic bottles be the cause of estrogenic burden recently determined in bottled mineral water?[1]

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Introduction

Since several years endocrine disruptors have been discussed as potential chemical contaminants in foodstuffs. For this purpose screening tests were developed and in particular drinking water and mineral water were targets for such testing due to their high consumption. In addition, water is a pure matrix with little analytical interference potential and can therefore serve as a food model matrix.

Within a study published in 2006[2] seven drinking water and 37 mineral water samples were investigated. As a result, the drinking water samples gave no endocrine activity with the applied yeast test. On the other hand, in the case of eight mineral water samples an endocrine activity was found. Based on the results, the authors came to the conclusion that the packaging materials are most likely not the source for the observed estrogenic activity because in fresh well water samples prior to be packed an endocrine activity was found also in some cases. Only for one mineral water sample packed in a glass bottle the endocrine activity increased during storage time, which gave hints that migration of packaging compounds into the mineral water might be responsible for the endocrine activity. In 2009 another study[3] found also estrogenic activity in mineral water packed in glass and PET bottles as well as in cardboard boxes and expressed in estradiol equivalents up to a maximum value of 75 ±5 ng l^{-1}. Within this publication, the authors concluded that leaching of packaging constituents from plastic materials, in particular PET, is the major source for this activity. In both studies potential compounds, however, were not identified.

The objective of this study is to examine on the scientific basis of migration theory the possibility whether migration of xeno-estrogens from PET bottles can be the reason for the endocrine activity in mineral water.

Results

The calculated results for the migration at different temperature (15 °C, 25 °C and 40 °C) after 30 d, 60 d, 90 d, 180 d and 360 d are given in Table 1. As a result, for potential endocrine active compounds with the same estrogenic activity as estradiol concentrations in the PET material which would correspond to a water concentration of 75 ±5 ng l^{-1} must be in the lower ppm range even if the samples are stored for about one year in a PET bottle at 40 °C. The inlay concentration of a potential migrant from the closure corresponding to 75 ±5 ng l^{-1} is calculated to be approximately 2 ppm for $K_{Inlay/Beverage}$ = 1. The equilibrium between the inlay material and the foodstuff is reached after a few days of storage, which means that the overall shelf life is negligible. Both results, however, does not yet consider the relative (to estriadiol) activity of the particular xeno-estrogenic substance potentially originating from the PET and the closure material. For example, the endocrine activity of 4-nonylphenol is by a factor of 5000 lower than that of estradiol. Therefore the packaging concentrations as established above would increase by a factor of 5000. For bisphenol A a factor of 15000 is reported with the corresponding consequence for the concentration in the packaging materials.

When, due to the unknown identity of the suspected xeno-estrogenic substance in the packaging material, we conservatively assume a factor 1000, than the concentrations in the packaging materials should be in the range of 1000 ppm to 4000 ppm either in the PET materials or in the closure inlays in order to explain the endocrine activity found in literature[2,3]. Such high concentrations of potential xeno-estrogens are untypical for PET and have never been found there. Moreover, if such compounds would be present in PET bottle materials at these concentrations they would have been already found and identified for a long time. It's most unlikely that they would have been remained there undiscovered. Analogous conclusions can be made for the bottle closures. In aluminium mineral water closures for glass bottles, DEHP was used since several decades as a plasticizer for the PVC inlay materials. Within the last years, this inlay material for this closure type was changed to polyolefins without using any longer DEHP. Therefore DEHP should not be found anymore in mineral water.

Table 1: Examples of calculated concentrations in the PET packaging material corresponding with a migration of 75 ±5 ng l^{-1} as a function of storage time and temperature

Storage time [days]	Concentration [mg kg^{-1} or ppm] of migrant in PET bottle wall								
	Estradiol (MW = 272 g mol^{-1})			Nonylphenol (MW = 220 g mol^{-1}) Bisphenol A (MW = 228 g mol^{-1})			Diethylhexyl phthalate (MW = 390 g mol^{-1})		
	15 °C	25 °C	40 °C	15 °C	25 °C	40 °C	15 °C	25 °C	40 °C
30	3.57	1.77	0.67	2.66	1.32	0.50	6.45	3.20	1.22
60	2.52	1.25	0.48	1.88	0.93	0.35	4.55	2.26	0.86
90	2.06	1.02	0.39	1.54	0.76	0.29	3.73	1.85	0.70
180	1.46	0.73	0.28	1.09	0.54	0.21	2.63	1.31	0.50
360	1.03	0.51	0.20	0.77	0.38	0.14	1.86	0.92	0.35

Migration calculations

The migration of nonylphenol, bisphenol A and DEHP was calculated based migration models. For theoretical reference purposes, the migration of estradiol was also calculated, being aware that it is not used for PET manufacturing. The most crucial parameter which influences migration is the molecular weight of the compound. Nonylphenol and bisphenol A have similar molecular weights being 220 and 228 g mol^{-1}, respectively. Therefore also their diffusion coefficients are very similar. Due to the fact that the diffusion coefficient decreases with increasing molecular weight, the migration for nonylphenol was calculated as a worse case compared to the others including DEHP and estradiol which have molecular weights of 390 g mol^{-1} and 272 g mol^{-1}. The migration was calculated for different temperatures (15 °C, 25 °C and 40 °C) after 30 d, 60 d, 90 d, 180 d and 360 d. A storage time of 360 d can be considered as the maximum shelf life of PET or cardboard packed mineral water.

For the calculations the PET polymer specific migration modelling parameters A'_P = 1 for consideration of the polymer diffusivity and τ = 1577 K for consideration of the diffusion activation energy were used. As a partition coefficient describing the relative solubility of a migrant between PET and the beverage a value of $K_{PET/Beverage}$ = 1 was used, which assumes good solubility of the migrant in the foodstuff (worse case). A typical bottle with a thickness of 300 µm, 660 cm^2 inner surface area and a volume of 1000 ml was used for migration modelling.

The target value for the migrants in the PET packed food was assumed to 75 ±5 ng l^{-1} which is the maximum EEQ (estradiol equivalent) value. However, according to migration theory the migration is directly proportional to the concentration in the packaging material. Therefore the results can be directly correlated with other migration target concentrations of interest. The migration of potential components from the closures was calculated with (A'_P = 11.5 and τ = 0) with a surface area of about 4.2 cm^2 and inlay mass of about 0.3 g. The volume of the bottle was assume to 1000 ml.

Conclusions

Based on the migration theoretical considerations presented in this study migration from plastics bottles cannot be the reason for the endocrine activity measured[2,3] in mineral water samples.

References

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