Mono- and diesters of *o*-phthalic acid in leachates from young landfills in early degradation phases

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Background

All members of the chemical group of phthalates are salts of phthalic acid and in the international literature dealing with phthalates, the chemical group seems to have been regarded as phthalic acid diesters (PDEs) only, although, the diesters might be degraded to phthalic acid monoesters (PMEs) and *o*-phthalic acid (PA). PDEs are widely used in a range of different products such as in, cardboard, paint, ink, adhesives, perfumes, but mainly as plasticisers in polyvinyl chloride (PVC) plastics. They are not chemically bound to the products and are therefore able to migrate to the aquatic environment when disposed of in landfills. Emissions to air are negligible due to their high boiling points (dimethyl phthalate 284ºC). The fate of PDEs in landfills has been investigated with respect of adsorption [6] and the degree of release from industrial products to the leachate [7]. Biodegradation is considered to be the most significant process affecting PDEs [1] and degradation of phthalate diesters to monoesters has been shown to occur in both aerobic [2,3] and anaerobic [4] laboratory studies. The amount of diesters presented as monoesters and PA in landfill leachates has rarely been considered. The degradation capacity decreases with the length of the phthalate ester chain and the most common PDE, di(2-ethylhexyl phthalate (DEHP), was degraded first after several a few months studies under methanogenic conditions. However, co-disposed DEHP with municipal solid waste in a 4-m^3 lysimeter simulating the conditions prevailing in landfills showed complete disappearance after four years [8], although no degradation products were analyzed to confirm degradation as being the reason for its disappearance. However, the monoesters (including the monoester of DEHP) and PA has been found in leachates from old methanogenic landfills collected from different European landfills [5]. Even though the toxicity of the degradation products of PDEs are less acute (data not published) and perhaps also less chronic than that of the PDEs themselves, it is of great importance to map their fate and longtime behavior, if not but to rule them out of the list of hazardous compounds.

Research questions

Since the anaerobic processes in landfills stay on for under several decades, their equivalence are sometimes very hard to achieve under laboratory conditions. Leachates collected during 7 years from 100-L landfill simulating reactors with extra co-disposed PDE-containing products offered a unique opportunity for long-term degradation studies. The aim was to follow the development of the different degradation phases and relate the observed phthalate concentrations to the specific degradation conditions. To confirm the results, leachates from three newly constructed full-scale landfill cells (10.000 metric tons of compacted but not grained municipal solid waste) were sampled at eight occasions during a period of two years

(1998-2000). The well-defined starting period of the cells (1995, 1996 and 1997) made it possible to study the development from acidogenic to methanogenic stage.

Analysis

The analyses were performed with either liquid/liquid extraction with ether as the organic solvent, or with solid phase extraction (polystyrene-divinylbenzene) with ethyl acetate as the desorbing solvent. The extracts were silylated and analyzed with GC-MS in selective ion monitoring (SIM) mode.
The phthalates included were the monoesters monomethyl, monoethyl, monobutyl, monobenzyl and mono(2-ethylhexyl) (respectively designated MMP, MEP, MbutP, MbenzP and MEHP) and the diesters dimethyl, diethyl, dibutyl, butylbenzyl, and di(2-ethylhexyl) phthalate (respectively designated DMP, DEP, DBP, BBP, and DEHP), as well as phthalic acid (PA).

Conclusions

The lysimeter study showed several orders of magnitude higher concentrations of the monoesters than the diesters originating from the extra PDE-containing products added, which indeed confirmed the potential of landfill organisms to degrade even high molecular weight PDEs [9]. The study also showed that the more hydrophilic diesters were observed in the leachates earlier than the hydrophobic. Furthermore, the concentrations of the monoesters increased when the diesters decreased occurring most probably due to degradation. With the exception of some aerobic degradation in the very early beginning of a landfill's construction, the most potent degradation seemed to exist during the transitional development of the methanogenic micro-flora, i.e. when the acidogenic phase converts to stable methanogenic conditions. The analyses of the leachates from the full-scale landfill cells confirmed this behavior of the phthalates. The concentrations of PA (mg/L) showed that accumulation of PA was the limiting factor concerning degradation of PDEs, or/and that PA might have other origin than PDEs.

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