Behaviour of mono- and diesters of o-phthalic acid in leachates released during digestion of municipal solid waste under landfill conditions

Susanne Jonsson*, Jörgen Ejlertsson, Bo H. Svensson

Department of Water and Environmental Studies, Linköping University, S-581 83 Linköping, Sweden

Accepted 18 January 2002

Abstract

In order to investigate phthalates in landfill leachates, four landfill simulation reactors, filled with municipal solid waste from a housing area, were studied. Plasticised polyvinyl chloride (PVC) was added to two of the reactors. Two reactors, one with and one without the additional PVC, were aerated for 3 months to achieve methanogenic conditions. The other two became acidogenic a few days after filling and closing. After approximately 3 years, the acidogenic waste became methanogenic. The leachates were analysed for phthalic acid diesters and their degradation products, phthalic acid monoesters and o-phthalic acid. The occurrence of monobenzyl phthalate (MbenzP) and mono(2-ethylhexyl) phthalate (MEHP) showed that the diesters, butylbenzyl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP), released from the PVC products had been transformed, and that they were not completely sorbed to particles or to the waste material. Monoesters were observed once methanogenic conditions were established. The monoesters and phthalic acid were present in concentrations several orders of magnitude higher than the diesters themselves. Our results show that it is important to include monoesters in studies of the fate of diesters. To date, monoesters have been neglected in investigations of organic pollutants in landfill leachates.

Keywords: Acidogenic; Anaerobic; Analysis; Degradation; Leachate; Methanogenic; Phthalic acid diester; Phthalic acid monoester; Phthalate

1. Introduction

Landfills pass through four typical phases (Christensen and Kjeldsen, 1989). The initial oxic phase is characterised by aerobic degradation. The oxygen within the landfill is soon depleted and an acid fermentation takes place, during which volatile fatty acids (VFAs) and alcohols are produced. The third, methanogenic, phase is characterised by methane production, and is the longest phase in a microbiologically active landfill. When the substrates from which methane is produced are depleted, oxygen may enter the landfill, and the final oxic degradation phase is established. Management measures affect the duration of these phases and the rate of degradation. For example, older landfills were not compacted and contained more organic waste, which caused faster degradation due to rapid microbial growth and the ingress of water, from precipitation, into the landfill. Modern landfills are compacted (to reduce volume) and covered (to reduce the amount of leachate). Source-sorting of waste also influences the characteristics of a landfill and its leachate. Transformation and degradation of organic pollutants vary during the different phases. In this paper we focus on a group of
substances that are regularly disposed of in landfills, namely phthalic acid diesters. Diesters are widely used in for example cardboard, insect repellents, fragrances and paints but their main use is as plasticisers in polyvinyl chloride (PVC) plastics. The worldwide consumption of diesters in the year 2000 was $4.75 \times 10^9$ kg (Forslund, 2000). Possible chemical transformations of PVC plastics in landfills and the fate of the PVC plasticisers have been investigated previously (Mersiowski and Stegman, 1997). They found that the loss of plasticisers from the PVC polymer is enhanced by continuous removal at the product surface, either by microbial degradation or by physical–chemical wash-off effects. Furthermore, it has been suggested that monoesters are the components of diesters responsible for human hormone imbalances (Gray and Gangolli, 1986; Richburg and Boelkelheide, 1996).

The degradation pathways of diesters have been studied under oxic and anoxic conditions (Engelhardt et al., 1975; Roslev et al., 1998; Saager and Tucker III, 1973; Shelton et al., 1984). The primary hydrolysis of diesters via monoesters to phthalic acid and the esterifying alcohols is similar under both aerobic and anaerobic conditions, however, subsequent degradation of phthalic acid differs. Hence, monoesters can occur as intermediates under both aerobic and anaerobic conditions. Pathways for degradation in the presence of oxygen have been known for decades. Briefly, they involve the oxidation of the alcohols to the corresponding carboxylic acid and subsequent β-oxidation. Phthalic acid is oxidised to 4,5- or 3,4-dihydroxyphthalate (Keyser et al., 1976). The dihydroxyphthalate is converted to protocatecuate (Ribbons and Evans, 1960) and is further degraded via orto- or meta-cleavage (Eaton and Ribbons, 1982) to key intermediates in common biochemical pathways. In anaerobic conditions, phthalic acid is decarboxylated to benzoate. Benzoate is reduced; the ring structure is cleaved followed by β-oxidation, to hydrogen gas, carbon dioxide and acetate (Elder and Kelly, 1994). Methanogenic micro-organisms transform these compounds to methane and carbon dioxide.

The primary and sometimes ultimate degradation of selected diesters under landfill conditions has been reported previously (Ejlertsson, 1997; Karlsson, 2000). Organisms present in waste samples from both landfill sites and landfill simulation reactors (LSRs) have shown such activity. Waste samples containing phthalate diesters have been degraded to methane and carbon dioxide with few or no monoesters occurring transiently. However, under certain conditions, the diesters were degraded only to monoesters. Engelhardt et al. (1975) suggested that monoesters might accumulate and persist during microbial degradation. Their statement was based on degradation studies in soil, where several aerobic isolates formed monobutyl phthalate (MbutP) as the end product of growth on dibutyl phthalate. However, Ejlertsson showed that different monoesters were degraded by methanogenic enrichment cultures (Ejlertsson et al., 1996a; Ejlertsson and Svensson, 1997).

Given this background, we wanted to analyse leachates from a set of landfill simulation reactors (LSRs) to determine if the occurrence of diesters, monoesters, and phthalic acid, if any, was linked to specific landfill degradation phases, i.e. acidogenic and methanogenic. We also wanted to elucidate whether the addition of plasticised PVCs contributed to elevated concentrations of related diesters, monoesters and phthalic acid in the leachates.

2. Material and methods

2.1. Landfill simulating reactors (LSRs)

At our hand four 100-l landfill simulation reactors, called LiU1–4, were available. For details on the waste used, its distribution to the reactors, operation and LSR-performance, see Ejlertsson et al. (2002). Each of the reactors contained municipal solid waste (MSW), collected from a housing area in Porsön (Luleå, Sweden). Such waste tends to contain the phthalates we wanted to study. The reactors were set up to simulate the ageing sequence of a landfill. Water was added to give a total solids (TS) content of 35%. Two of the reactors, LiU2 and LiU4, were supplied with 3250 g extra waste material containing organic pollutants [e.g. PVC plastics (1000 g), freon-blown insulation (200 g), a seat cushion (200 g), a radio (350 g) and flame-retardant treated materials (1500 g)]. The purpose of adding extra waste material was to extend our knowledge of the behaviour of the components of these materials in landfills and to study their possible effects on the bacterial population of the landfill. To study the effects of diesters, two types of plasticised PVC floorings were added. When the floorings were added to LiU2 and LiU4, each reactor contained 14 g BBP and 174 g DEHP, according to the PVC formula (Ejlertsson et al., 2002). Leachates from LiU1 and LiU3 were analysed to determine the background levels of diesters, monoesters and phthalic acid, to assess the influence of the extra PVC plastics added to LiU2 and LiU4.

Due to rapid fermentation, acidogenic conditions were established within a few days after filling and closing the reactors. Measurements of pH, volatile fatty acids (VFAs), total organic carbon (TOC) and the volume of gas production were made continuously. The methanogenic conditions were determined by analysing the methane content of the gas produced. The reactors LiU3 and LiU4 were operated under acidogenic conditions, while LiU1 and LiU2 were methanogenic. In order to enforce methanogenic conditions and avoid acidification of the latter, they were intermit-
tently aerated from day 4 to day 117: continuously for 3 weeks and then 2 days a week. When the aeration was stopped the gas production was measured. After 117 days, when gas production stabilised, aeration was stopped and the waste became completely anaerobic and methanogenic. Leachates from the acidogenic LiU3 and LiU4 were withdrawn (3 litres per week) and replaced by tap water to simulate precipitation (100 l in total). The dilution procedure continued from day 129 to day 362 and was followed by the measurement of inorganic halides in the leachates (Ejlertsson et al., 2002). Ceasing the addition of tap water simulated covering the landfill.

After 1007 days of operation, the acidogenic reactors, LiU3 and LiU4, were slowly made methanogenic by exchanging 1 l of leachate once a week. Leachate exchange was performed between LiU1 and LiU3 from day 1007 to day 1186 and between LiU2 and LiU4 from day 1007 to day 1596. The exchange of leachate was stopped when methanogenic conditions were established and the waste produced biogas at steady rates. The transition from acidogenic to methanogenic conditions was slower for LiU4 than LiU3. This effect could probably be attributed to the addition of extra waste materials containing organic pollutants to LiU4, of which the Freon-R11 blown insulation probably had the most significant effect on the anaerobic organisms (Ejlertsson et al., 2002).

Leachate samples from the reactors were taken frequently and kept frozen in polyethylene bottles at –20°C until analysis for phthalates was undertaken. The reactors had been running for 5.5 years, when the study ended. A full description of the monitoring of the MSW is provided in Ejlertsson et al. (2002).

A basic problem in diester analysis is the ubiquitous presence of diesters in many laboratory products, reagents, solvents and supplies. To eliminate this problem, some clean-up procedures were necessary. First, the glassware was cleaned in an ordinary dishwasher, then rinsed in filtered MilliQ-water followed by 95% ethanol. After drying for 30 min at 100°C, the glassware was heated for 20 h at 450°C. All glassware that had been in contact with leachate samples, and that was to be reused in the analysis, was stored in 3 M NaOH for 6 h before washing, to hydrolyse any diesters to the more water soluble PA and corresponding alcohols. All glassware apertures were covered with aluminium foil.

2.2. Chemicals

Pro analysis (pa) quality acetone was distilled once and the diethylether (pa) twice. NaCl (pa) was washed three times in distilled acetone, dried for 30 min at 100°C, and then heated for 20 h at 450°C. The diesters and phthalic acid were of analytical grade, and the monoesters were synthesised in the laboratory (Ejlertsson et al., 1996). Other chemicals were used without further cleaning. The derivatising reagent tetramethylsilane (TMS) was prepared from chlortrimethylsilan (TMCS) and bis(trimethylsilyl)-trifluoracetamide (BSTFA), which were of gas chromatography grade. The TMS reagent was prepared in pyridine (pa) in the proportions 1:10:10. The didecyl phthalate (DDP) was a gift from Neste Oxo, Stenungsund, Sweden, and all other chemicals, except the monoesters, were purchased from Merck Eurolab, Stockholm, Sweden. Stock solutions of diesters, monoesters, phthalic acid and the internal standard were prepared in distilled acetone. Gases used for the analytical procedure were 99.9999% pure.

2.3. Analytical procedure

The analytical procedure was as follows: 5 g of leachate were transferred to a 13-ml serum bottle, then 0.1 ml of concentrated H2SO4, 0.65 g NaCl and 5 μl internal standard (DDP 5 μg μl–1) were added, followed by diethylether (3.0 ml). The serum bottle was sealed with a Teflon-coated rubber stopper (purchased from Apodan, Copenhagen, Denmark). All bottles were shaken vigorously for 2 min. If necessary, they were centrifuged until the liquid phases were separated. They were then frozen at –25°C for at least 6 h to eliminate water in the organic phase, since the derivatising agent is very sensitive to moisture and requires a water-free medium. The ether phase was withdrawn and gently evaporated with nitrogen to a volume of 100 μl. The monoesters and phthalic acid were derivatised prior to analysis by the addition of 100 μl of TMS. Derivatisation was necessary, since it made possible the simultaneous analysis of diesters, monoesters and phthalic acid.

The number of samples analysed was 33, 27, 36 and 37 for LiU1, LiU2, LiU3 and LiU4, respectively. Samples were diluted when concentrations above 5000 μg l–1 were observed for any phthalate compound. The detection limit was 1 μg l–1 for all phthalates. The phthalates analysed in this study were dimethyl, diethyl, dibutyl, butylbenzyl and di(2-ethylhexyl) phthalate (respectively designated DMP, DEP, DBP, BBP and DEHP), and their corresponding monoesters monomethyl, monoethyl, monobutyl, monobenzyl and mono(2-ethylhexyl) phthalate (MMP, MEP, MBuP, MBenP and MEHP, respectively), as well as phthalic acid (PA).

Analysis involved separation of the compounds by a capillary column (BPX5 30 m×0.25 mm, film thickness 0.17 μm) in a HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector (GC/MS) run in selected ion monitoring (SIM) mode. The extracts were introduced using a HP 6890 automatic liquid sample injector. The injected volume was 0.5 μl and a pulsed splitless-injection technique was used (splitless time 1.0 min, pulsed pressure 40 psi). The injection...
Table 1

Mass fragments (m/z) used for the identification of the phthalic acid diesters DMP, DEP, DBP, BBP, DEHP and the silylated monoesters MMP, MEP, MbutP, MbenzP, MEHP and phthalic acid

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Retention time (min)</th>
<th>m/z</th>
<th>Proportion of fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl-</td>
<td>DMP</td>
<td>10.79</td>
<td>163, 194, 133</td>
<td>100/7/6</td>
</tr>
<tr>
<td>Monomethyl-</td>
<td>MMP</td>
<td>13.28</td>
<td>237, 163, 221, 252</td>
<td>100/59/11/3</td>
</tr>
<tr>
<td>Diethyl-</td>
<td>DEP</td>
<td>13.62</td>
<td>149, 177, 222</td>
<td>100/26/2</td>
</tr>
<tr>
<td>Monoethyl-</td>
<td>MEP</td>
<td>14.47</td>
<td>251, 223, 149, 221</td>
<td>100/86/40/36</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>PA</td>
<td>15.26</td>
<td>147, 295, 221</td>
<td>100/26/7</td>
</tr>
<tr>
<td>Monobutyl-</td>
<td>MbutP</td>
<td>17.77</td>
<td>223, 221, 149, 279</td>
<td>100/47/40/10</td>
</tr>
<tr>
<td>Dibutyl-</td>
<td>DBP</td>
<td>20.31</td>
<td>149, 223, 205</td>
<td>100/5/4</td>
</tr>
<tr>
<td>Mono(2-ethylhexyl)-</td>
<td>MEHP</td>
<td>22.65</td>
<td>221, 223, 149, 239</td>
<td>100/65/47/26</td>
</tr>
<tr>
<td>Monobenzyl-</td>
<td>MbenzP</td>
<td>24.30</td>
<td>91, 179, 222</td>
<td>100/61/47</td>
</tr>
<tr>
<td>Butylbenzyl-</td>
<td>BBP</td>
<td>26.60</td>
<td>149, 91, 206, 238</td>
<td>100/56/25/4</td>
</tr>
<tr>
<td>Di(2-ethylhexyl)-</td>
<td>DEHP</td>
<td>29.08</td>
<td>149, 167, 279</td>
<td>100/29/14</td>
</tr>
<tr>
<td>Didecyl-</td>
<td>DDP (IS)</td>
<td>36.60</td>
<td>149, 307</td>
<td>100/9</td>
</tr>
</tbody>
</table>

The internal standard (IS) was DDP.

Table 1: Mass fragments (m/z) used for the identification of the phthalic acid diesters DMP, DEP, DBP, BBP, DEHP and the silylated monoesters MMP, MEP, MbutP, MbenzP, MEHP and phthalic acid.

Retention time and mass fragments (m/z) qualified all the quantified compounds in this study. The m/z used are shown in Table 1.

For quantification, the area ratio of the most abundant mass fragment and the internal standard was calculated, thus providing the concentrations from a calibration curve produced by standard addition procedures to a leachate sample from LiU4 (22 December 1997). The coefficients of determination, R², for each of the compounds were 0.98–1.00.

Blanks consisting of 5.0 g MilliQ-water were treated and analysed in the same way as the leachate samples and were always included when analysing the leachates from the reactors. The following tests were performed to confirm that the polyethylene sampling bottles did not influence the results. MilliQ-water was adjusted to pH 10.6 or 2.6, to simulate the possible extreme values in a leachate. Three test-bottles with pH-adjusted water were spiked with 20 µg l⁻¹ of each phthalate. All bottles were frozen and analysed 5 months later. The plastic material of the bottles and the treatment during the analytical procedure did not give rise to any extra phthalates, and the concentration was still 20 µg l⁻¹ in the spiked bottles.

2.4. Statistics

The statistical Mann–Whitney U-test was used (Miller and Miller, 1993) to establish whether the plasticised PVC contributed to the observed concentrations. The test is a non-parametric sign ranked test that evaluates the difference between two independent samples. In this study, the two-tailed test was used with a significance level of 5%.

3. Results

The evaluation of the data was undertaken with consideration of the following facts: each monoester originated from one specific diester, except MbutP, the source of which could be either DBP or BBP and that phthalate acid originated from all diesters. However, other possible sources for phthalic acid, such as formation from polycyclic aromatic hydrocarbons (Dean-Ross and Cerniglia, 1996; Grifoll et al., 1994) may have contributed. First, a detailed description of all diesters and their corresponding monoesters is given, i.e. Figs. 1–4, show the observed phthalate concentrations of diesters, monoesters and phthalic acid from the four reactors LiU1–4. Accumulated biogas has been included in the figures to exhibit the development of methanogenesis. Thereafter, discussions concerning aspects of adsorption mechanisms, the effects of general waste degradation, i.e. acidogenic and methanogenic conditions, and addition of extra PVC plastic are given.

3.1. Detailed results of all diesters and their corresponding monoesters and phthalic acid

3.1.1. DMP and MMP

DMP was monitored for 20 days at the beginning of the operation of LiU1 (Fig. 1a) and LiU2 (Fig. 2a). After 60 days, MMP appeared in LiU1 and it remained for a longer period and at slightly higher concentrations than the DMP. During this period, LiU2 contained...
concentrations of both DMP and MMP twice as high as in LiU1 (Fig. 2a). After the aeration period, neither DMP nor MMP was detected. DMP was observed in the acidogenic LiU3 for the first 300 days at concentrations up to 120 μg l⁻¹ (Fig. 3a). The same maximum concentration was observed at the beginning of the operation period for LiU4, but declined to below the detection limit after 63 days (Fig. 4a). No MMP was observed in either LiU3 (Fig. 3a) or LiU4 (Fig. 4a).

3.1.2. DEP and MEP

The initial concentration of 150 μg l⁻¹ DEP in LiU1 decreased rapidly (to 40 μg l⁻¹ by day 20) and it slowly disappeared when methane production commenced (Fig. 1b). Concomitantly, MEP, conversely, increased from below the detection limit to almost 3000 μg l⁻¹. When aeration ceased, on day 117, the concentration decreased until it fell below 20 μg l⁻¹ on day 500. During the leachate exchange with LiU3, both DEP and MEP concentrations increased from below the detection limit to 10 and 100 μg l⁻¹, respectively. This was most likely a result of dilution of the high DEP concentration in the LiU3 leachate and its degradation to MEP in LiU1 (Fig. 1b). The initial concentration of DEP in LiU2 was similar. After fluctuations (14–785 μg l⁻¹) during the dilution period, it stabilised at approximately 400 μg l⁻¹ and stayed at this level until the leachate exchange with LiU4 was stopped (Fig. 2b) when it dropped to 4 μg l⁻¹. MEP displayed the same pattern as in LiU1. In LiU3, DEP increased to a stable level of 600 μg l⁻¹ (Fig. 3b), which slowly decreased to 15 μg l⁻¹ when the leachate exchange had resulted in methanogenic conditions. An increase in the MEP concentrations was observed as soon as the DEP concentration decreased, indicating that a transformation had occurred in LiU3. When the gas production rate in LiU3 decreased (at approx. day 1350, Fig. 3f), the MEP concentrations (900–1000 μg l⁻¹) also declined, reaching stable levels (5–10 μg l⁻¹) on approximately day 1600 (Fig. 3b). The initial concentrations of DEP (500 μg l⁻¹) in LiU4 also stabilised but at 400 μg l⁻¹. As soon as methanogenic conditions were established, a transformation of DEP to MEP resulted in a DEP concentration of 30 μg l⁻¹ (Fig. 4b). Thus, MEP peaked as in LiU3 but at lower concentrations of approximately 450 μg l⁻¹.

3.1.3. DBP and MbutP

In LiU1 the relatively low initial concentration (30 μg l⁻¹) of DBP decreased to levels below 10 μg l⁻¹, where it remained throughout the operation period, except for samples from days 654 and 736, which contained 107 and 25 μg l⁻¹, respectively. MbutP was observed at levels up to 5000 μg l⁻¹ during the aeration of the reactors (Fig. 1c). Lower initial DBP concentrations (13 μg l⁻¹) were measured in the LiU2 leachate.

Fig. 1. Analysis of leachate from reactor LiU1. The diesters (Φ) and biogas (●) are represented by solid lines and degradation products (*) by dotted lines. Concentrations of diesters and monoesters are given in μg l⁻¹ and accumulated biogas in litres. Number 1 indicates the end of the 117 days of periodic aeration in the reactor. After day 117 the waste was methanogenic. Number 2 indicates days 1007–1186 when leachate was exchanged between LiU1 and LiU3.
Fig. 2. Analysis of leachate from reactor LiU2 (with plasticised PVC-flooring added). The diesters (•) and biogas (●) are represented by solid lines and degradation products (*) by dotted lines. Concentrations of diesters and monoesters are given in µg l⁻¹ and accumulated biogas in litres. After day 117 the waste was methanogenic. Number 2 indicates days 1007–1596 when leachate was exchanged between LiU2 and LiU4.

3.1.4. BBP and MbenzP

In the LiU1 leachate, BBP was below the detection limit during the whole operation period, except during the initial aeration period, when concentrations up to 8 µg l⁻¹ were measured. Soon after the disappearance of BBP (days 10–80), MbenzP peaked at 835 µg l⁻¹. It decreased from 835 to approximately 5 µg l⁻¹ after aeration ceased and methanogenic conditions were established, but was never below the detection limit (Fig. 1d). In LiU2, BBP was observed at a few micrograms above the detection limit in all samples and there was slightly more during aeration. The highest concentration of BBP (16 µg l⁻¹) in the LiU2 leachate was observed on day 20 after aeration for 2 weeks. MbenzP peaked (at approx. 1500 µg l⁻¹) in conjunction with the aeration and onset of methanogenesis in LiU1 and LiU2 (Fig. 1d and Fig. 2d). MbenzP was never below the detection limit in the LiU2 leachate. In LiU3 BBP and MbenzP followed the patterns of DBP and MbutP, respectively. BBP had a concentration of approximately 3 µg l⁻¹ (maximum 30 µg l⁻¹) in LiU3 and MbenzP reached a maximum level of 310 µg l⁻¹ (Fig. 3d). In LiU4, BBP was at approximately 40 µg l⁻¹ and declined to a few micrograms when MbenzP increased (Fig. 4d). The highest concentration, 16 300 µg l⁻¹, of any monoester was observed for MbenzP in LiU4.

3.1.5. DEHP and MEHP

Levels of up to 93 µg l⁻¹ of DEHP were measured during the aeration period in the LiU1 leachate and less
than 5 \mu g \text{l}^{-1} during the rest of the period (Fig. 1e). One extreme value of 710 \mu g \text{l}^{-1} was measured on day 248. MEHP behaved differently than the other monoesters in the LiU1 leachate. After 500 days, all monoesters, except MEHP, declined quickly to levels below 20 \mu g \text{l}^{-1}. Small amounts of MEHP were detected during the aeration period, but when methanogenic conditions were developing, the concentration increased to 1000 \mu g \text{l}^{-1}. Thereafter, the MEHP concentration decreased, but was still at 60 \mu g \text{l}^{-1} after almost 2000 days of operation (Fig. 1e). When the aeration ceased in LiU2 on day 117, the level of DEHP dropped from 147 to approximately 15 \mu g \text{l}^{-1} where it remained for almost 1300 days. After 1400 days of operation, the concentrations increased to 560 \mu g \text{l}^{-1} (day 1805) and then decreased again to 15 \mu g \text{l}^{-1} (Fig. 2e). The increase in DEHP coincided with the increase in gas production. MEHP increased from below the detection limit to 2200 \mu g \text{l}^{-1} when the aeration was terminated and methanogenic conditions were developing. During the rest of the operation period, the concentration ranged from 10 to 80 \mu g \text{l}^{-1}, except for the period of leachate exchange when the MEHP increased to levels between 90 and 180 \mu g \text{l}^{-1} (Fig. 2e). Except for day 6 (5 \mu g \text{l}^{-1}), the DEHP concentrations in leachate from LiU3 were below the detection limit until the gas production increased on day 1100. Then the concentration increased to 10 \mu g \text{l}^{-1} where it remained for 300 days (Fig. 3e). At approximately day 1600, the DEHP concentrations suddenly increased to 120 \mu g \text{l}^{-1}. Towards the end of the experimental period, the concentration decreased to 105 \mu g \text{l}^{-1}. MEHP followed the same pattern in LiU3 as the other monoesters, i.e. it increased in concentration when methanogenic conditions were developing (Fig. 3e). No MEHP was observed before the leachate exchange was initiated, but when the gas production started, on day 1100, the level increased to 150 \mu g \text{l}^{-1}. After 500 days of methanogenesis (day 1600), MEHP decreased to 27 \mu g \text{l}^{-1} and was still decreasing at the end of the experimental period. The concentrations of DEHP in the leachate from LiU4 ranged from below the detection limit to 70 \mu g \text{l}^{-1} during the first 1500 days (Fig. 4e). When methanogenic conditions became established due to the leachate exchange, the concentration increased to 120–310 \mu g \text{l}^{-1}. As with other monoesters, the concentration of MEHP increased when methanogenic conditions were developing in the LiU4 leachate. Concentrations up to 906 \mu g \text{l}^{-1} were observed on day 1398. At the end of the experiment, the level of MEHP was approximately 300 \mu g \text{l}^{-1} (Fig. 4e).

3.1.6. Phthalic acid

No phthalic acid was observed in leachate from LiU1 during aeration, but phthalic acid was present in all samples during the rest of the experimental period.

Fig. 3. Analysis of leachate from reactor LiU3. The diesters (△) and biogas (●) are represented by solid lines and degradation products (*) by dotted lines. Concentrations of diesters and monoesters are given in \mu g \text{l}^{-1} and accumulated biogas in litres. Number 1 indicates the end of the 117 days of periodic aeration in the reactor. Number 2 indicates days 1007–1186 when leachate was exchanged between LiU3 and LiU1, i.e. before day 1107 the waste was acidogenic and after day 1186 it was methanogenic.
Fig. 4. Analysis of leachate from the reactor LiU4 (with plasticised PVC-flooring added). The diesters (●) and biogas (●) are represented by solid lines and degradation products (∗) by dotted lines. Concentrations of diesters and monoesters are given in µg l⁻¹ and accumulated biogas in litres. Number 2 indicates days 1007–1596 when leachate was exchanged between LiU4 and LiU2, i.e. before day 1107 the waste was acidogenic and after day 1596 it was methanogenic.

Between days 111 and 325 concentrations of 4000 µg l⁻¹ were observed (Fig. 1f). Following the decline, the level varied at approximately 10 µg l⁻¹, except for the period after the leachate exchange (days 1100–1400) when concentrations were up to 6340 µg l⁻¹. In LiU2, approximately 5000 µg l⁻¹ were present from days 111 to 325, with an extreme value of 8470 µg l⁻¹ on day 262. After the decline, phthalic acid was present in all samples in concentrations ranging from 6 to 82 µg l⁻¹. During the exchange of leachate (days 1007–1186), concentrations up to 318 µg l⁻¹ were observed. Higher levels of phthalic acid (500 µg l⁻¹) were also observed on day 1805. Phthalic acid was not present during the acidogenic phases in LiU3 and LiU4, but was observed after the exchange of leachate, i.e. day 1100 in LiU3 and day 1500 in LiU4. The highest concentration observed in LiU3 was 307 µg l⁻¹ on day 1216. During the rest of the experiment, phthalic acid ranged from 50 to 91 µg l⁻¹. In leachate from LiU4, phthalic acid was present at concentrations up to 2740 µg l⁻¹ on day 1842, and was still at a concentration of 880 µg l⁻¹ at the end of the observation period.

4. Discussion

We used the same criteria as Robinson and Gronow (1998) who arbitrarily defined acidogenic leachates as having concentrations of volatile fatty acids greater than 1000 mg C l⁻¹ and the methanogenic leachates less than 200 mg C l⁻¹ of volatile fatty acids. The in situ degradation rates for the phthalates in the reactors were unknown in this study.

4.1. Occurrence of phthalates in the LSR leachates

The disappearance of a diester is followed by the generation of its corresponding monoester (Figs. 1–4). A correlation between the length of the alcohol chain of the diester and the time of appearance of its corresponding monoester was observed, i.e. the shorter the alcohol, the earlier the monoester appeared and disappeared. This was in agreement with studies done by Ejlertsson et al. (1997) who studied influence of water solubility, side-chain degradability and side-chain structure on the degradation of phthalic acid esters under methanogenic conditions. Their results showed that diesters with long hydrophobic side chains obtain a three-dimensional structure hindering the hydrolytic enzymes from binding to the phthalate and therefore hindering the hydrolysis. They also observed retarded degradation of the hydrolysed long hydrophobic alcohols and concluded that water solubility was a major factor limiting the degradation of diester. Reduced degradation of diesters with long hydrophobic side chains has also been observed in other studies (O’Con-
When the biogas production increased, the concentrations of monoesters increased and the concentrations of diesters decreased (Figs. 3 and 4), which was most clearly expressed for BBP in LiU4 (Fig. 4d,f) when acidogenic conditions slowly turned methanogenic. Thereby, our results show that the transformation of diesters to monoesters is coupled to the establishment of methanogenesis in the waste.

Diester degradation to monoester seems to be an unspecific ester-cleavage (Bauer et al., 1998; Inman et al., 1984), and coincides with general degradation of organic material. The decrease of leached TOC in the reactors (Ejlertsson et al., 2002) during degradation of diesters supports that statement. The general degradation probably changes the particulate and colloidal properties of the organic matter in the reactors and therefore changes the sorption characteristics, e.g. by degradation of existing particles, by degradation of sorption active surface structures of the waste material, or by increasing the amount of fragmented particles. All these possibilities will affect the sorption pattern of the phthalates; e.g. new surfaces will absorb diesters, while the degradation of others will release them. The diesters extracted from the waste material (e.g. PVC plastics) may be released to the surrounding media or stay adsorbed onto the newly formed particulate and colloidal fractions (Gounaris et al., 1993; Painter and Jones, 1990). Since colloids are mobile in water, the mobility of the compounds sorbed to the colloidal fraction increases. Consequently, the concentrations of adsorbed compounds will increase in the leachate. Thus, the presence of colloid-sorbed diesters may explain the presence of the hydrophobic DEHP in the leachates at concentrations far above its water solubility. A fourfold increase of DEHP in laboratory biogas reactors has also been reported by Bauer et al. (1998) during the transition to methanogenic conditions. Confirmatory, Bauer and Herrmann (1998) stated that an average of 87% of hydrophobic compounds, such as DEHP, were sorbed to dissolved organic carbon (DOC).

4.2. Effects of waste degradation state on the presence of phthalates

The reactors LiU1 and LiU2 were aerated periodically from day 1 to 117 (Figs. 1 and 2). This procedure might have enhanced the degradation of the phthalates, since aerobic phthalate diester degradation may be completed within a period of days to weeks (Sugatt et al., 1984). However, it should be noted that their conclusions were derived from studies using pure compounds and not the type of phthalate diester-containing wastes used in the present study. Their degradation rates are therefore higher than the presumable aerobic degradation of diesters in the aerated LiU1 and LiU2. Furthermore, their studies were made with materials from soil- and sewage sludge. Figs. 1 and 2 show that the monoesters were present during the aeration days 1–117, but concentrations became higher during the early methanogenic phase, i.e. soon after aeration ceased. Since most of the monoesters, and specially phthalic acid, were observed during the methanogenic phase we believe that the major degradation of diesters resulted from the adapted microflora able to produce methane rather than the effects of oxygen per se.

Although leachate was drained off between days 4 and 117 in LiU3 and LiU4, the diester concentrations remained fairly constant. Hence, diesters were continuously released from the waste. The results presented by Ejlertsson et al. (2002) show that pH also remained constant (at approx. 5.5), indicating that acid conditions persisted throughout the drainage period. The dilution is clearly demonstrated by the decrease in concentrations of inorganic halides in the leachates (Ejlertsson et al., 2002). Although diesters were released from the extra PVC plastics and diesters were present in the acid leachate, the microflora did not seem to have the capacity to degrade the diesters, since no monoesters or phthalic acid were observed in these leachates. Likewise, degradation assays with inoculum from the different degradation phases in the reactors showed that the acidogenic waste did not degrade phthalate diesters. The degradation only occurred with samples from methanogenic waste (Ejlertsson, 1997; Karlsson, 2000). However, the absence of monoesters and phthalic acid in acidogenic leachates might be due to a complete degradation without generation of monoesters or phthalic acid. Although we have not been able to verify this, we cannot rule out the possibility.

The methanogenic microflora present in the reactors had the capacity to transform not only the diesters to monoesters, but also the monoesters to phthalic acid. The more hydrophobic MEHP seems to have been more resistant than the hydrophilic and more short-chained monoesters. However, complete degradation of MEHP under methanogenic conditions has been shown (Ejlertsson and Svensson, 1997). The presence of MEHP in this study demonstrates an in situ degradation of DEHP in the reactors, which contradicts previous anoxic degradation studies on this compound (Ejlertsson et al., 1997; O’Connor et al., 1989). However, in a long-term reactor study done by Reinhart and Pohland (1991) it was reported that DEHP was completely eliminated within 4 years and argued that the disappearance was not due to adsorption to the waste. However, degradation products such as MEHP were not measured.

Comparisons of the analyses of phthalate diester content in the PVC flooring between the first (day 1122) and second (day 1640) PVC sampling in LiU4 demonstrated that methanogenic conditions generated a
larger loss of diester from the PVC plastics (Ejlertsson et al., 2002). This coincided with higher concentrations of monoesters in the leachate during the same period, showing that a transformation of PAE to PME took place during the development of methanogenic conditions. The developing microflora generating the methanogenic conditions was probably responsible for this transformation. The accumulation of monoesters observed suggests that the conversion of monoesters to phthalic acid is slower than the transformation of the released diesters to monoesters. This should also explain why the monoesters were observed in higher concentrations than the diesters. The concentrations in the leachate suggest that most of the phthalates, even the non PVC-related DMP, DEP, and DBP, were present in the form of monoesters.

The disappearance of a diester and the appearance of corresponding monoester in the leachates demonstrates the same pattern as observed for methanogenic enrichment cultures degrading diesters, although these previous studies were conducted using pure diesters (Ejlertsson, 1997; Inman et al., 1984; O’Connor et al., 1989).

4.3. Phthalates in the LSR leachates originating from plasticised PVC

The Mann–Whitney U-test showed significant differences in the concentrations of BBP, MbenzP and MEHP between LiU1 and LiU2. These differences could be attributed to the higher concentrations of the PVC-related phthalates observed in the LiU2 leachates. Higher concentrations of the non PVC-related DEP were also present in the LiU2 leachate and were significant compared with LiU1. In contrast, the significant difference observed for DBP was derived from higher concentrations in LiU1 than in LiU2.

The same tests on leachates from LiU3 and LiU4 showed significant differences for BBP, MbenzP, MbutP, DEHP, MEHP and PA. Thus, the extra PVC materials added to the waste in LiU4 seemed to have released diesters at higher concentrations than in the control. In contrast, significantly more MEP was observed in LiU3 than in LiU4. The reason for this is unknown. The statistical results were unambiguous only for the PVC-related phthalates.

The reactors LiU2 and LiU4 were opened on two occasions (days 1122 and 1640) and the PVC plastic floorings were sampled so that its diester content could be determined (Ejlertsson et al., 2002). These analyses showed that more BBP and DEHP had been lost from the PVC-plastic materials in the methanogenic LiU2 than in the acidogenic LiU4 at the time of the first sample. The changes in the concentrations of MbenzP and MEHP (Fig. 2d,e) suggest that the loss of parent compounds from the PVC plastics might have taken place just after the aeration period when methanogenesis commenced. A greater loss was observed in LiU4 between days 1122 and 1640 (Table 2) when the conditions had become methanogenic. The concentrations of the diesters used in the introduced PVC plastics (LiU2 and LiU4) were elevated in the leachates compared to the control reactors (LiU1 and LiU2). The BBP in the leachate in LiU4 on day 1640 corresponded to approximately 3% of the BBP loss from the PVC plastics analysed. However, the MbenzP corresponded to 7%, thus 10% of the BBP lost on day 1640 was present in the leachate. The remaining 90% may have been completely degraded, adsorbed onto solids in the waste, or contained within the pool of phthalic acid and other diester-related degradation products.

In a reactor, where the reactions are more intense, each phase is reinforced, and thus is completed more rapidly than in a landfill. The continuous supply of new waste on a fullscale-landfill also means that all phases will occur simultaneously. Therefore, it should be possible to observe diesters, monoesters and phthalic acid regardless of the average state of the degradation phase of a landfill, since monoester/phthalic acid-generating ‘hot-spots’ are likely to be present within the landfill body over extended periods of time. Likely, the concentrations to be observed in reactor leachates are higher than in full-scale landfills (Bauer and Herrmann, 1998).

5. Conclusions

Our results from the analysis of phthalates in leachates from landfill simulation reactors strongly support the conclusion that phthalate diesters were in situ degraded and that the degradation products, monoesters and phthalic acid, sometimes were present in the leachates to a higher extent than the diesters, in fact several orders of magnitude.

In the present study, added PVC plastics contributed to additional BBP and DEHP and their intermediate degradation products MbenzP and MEHP in the leachates from the two reactors in which PVC plastics had been added (LiU2 and LiU4). Also, the presence of the PVC-related MbenzP and MEHP indicates that the diesters released from plasticised PVC products were degraded to some extent and thus not completely sorbed to particles or to the waste material.
The degradation of phthalic acid diesters to monoesters occurred during the methanogenic degradation of the waste, or more specifically during the early phase when such conditions developed in the reactors.

Phthalic diester-containing products such as plasticised PVC in landfills will be subjected to the same ageing phases as the waste in this study. Hence, full-scale landfill leachates are expected to contain phthalates, both diesters and monoesters, in different concentrations, depending on the current phase of the landfill, type of waste and management regime.

To date monoesters have been neglected in investigations of organic pollutants in landfill leachates. Our results contradict studies suggesting that hydrophobic diesters, such as DEHP, are not degraded within the anaerobic environment of a landfill (Bauer et al., 1998), since we observed MEHP in all reactors.

Acknowledgments

The authors wish to thank Dzeneta Nezerivic (Linköping University) for assistance with the reactor performance and the VFA and TOC analyses. This project was funded by the Swedish Environmental Protection Board, contract no. 802-335-903-Fr. The organisations ECPI, ECVM, ELSA, ORTEP and Norsk Hydro supported the project ‘Long-term behaviour of PVC-products under soil-buried and landfill conditions’.

References


