Phthalic acid esters found in municipal organic waste:
enhanced anaerobic degradation under hyper-thermophilic conditions

H. Hartmann and B.K. Ahring
The Environmental Microbiology/Biotechnology Research Group, BioCentrum-DTU, Building 227,
The Technical University of Denmark, DK-2800 Lyngby, Denmark
(E-mail: hwh@biocentrum.dtu.dk; bka@biocentrum.dtu.dk)

Abstract Contamination of the organic fraction of municipal solid waste (OFMSW) with xenobiotic
compounds and their fate during anaerobic digestion was investigated. The phthalic acid ester di-(2-
ethylhexyl)phthalate (DEHP) was identified as the main contaminant in OFMSW in concentrations more than
half of the threshold value for the use as fertilizer on agricultural soil in Denmark. Analysis of DEHP in
samples before and after large-scale anaerobic digesters revealed higher concentrations of DEHP per kg
dry matter in the effluent than in the influent. The concentration of DEHP and DBP (dibutylphthalate) in
OFMSW was monitored in the influent and effluent of anaerobic thermophilic (55°C) and hyper-thermophilic
(68°C) laboratory-scale reactor systems. In the thermophilic reactors with a hydraulic retention time (HRT) of
15 days 38–70% of DBP was removed, but no consistent removal of DEHP was observed. However, after
treatment of the effluent from the thermophilic reactor in a hyper-thermophilic digester (HRT: 5 days)
34–53% of the DEHP content was removed and the DBP removal was increased to further 62–74%.
Removal rates ($k_h$) of DEHP and DBP were found to be 0.11–0.32 d$^{-1}$ and 0.41–0.79 d$^{-1}$, which is much
higher than in previous investigations. It can be concluded that the higher removal rates are due to the higher
temperature and higher initial concentrations per kg dry matter. These results suggest that the limiting factor
for DEHP degradation is the bioavailability, which is enhanced at higher temperature and higher degradation
of solid organic matter, to which the highly hydrophobic DEHP is adsorbed. The investigated reactor
configuration with a thermophilic and a hyper-thermophilic treatment is, therefore, a good option for
combining high rate degradation of organic matter with high biogas yields and efficient reduction of the
phthalic acid ester contamination.

Keywords Anaerobic digestion; bioavailability; DEHP; hyper-thermophilic; organic fraction of municipal
solid waste; phthalic acid esters

Introduction
Biological waste treatment concepts need to compete with incineration. The extra costs for
separation of the organic fraction of municipal solid waste (OFMSW) for biological treatment
can only be justified if a more sustainable concept can be realized by the biological treatment. Consequently, the energy gain should be higher and emission of pollutants
should be lower than by incineration. Anaerobic digestion of OFMSW offers the advantage
of a higher net energy gain than by incineration from the production of methane.
Furthermore, the end product of the process can be used as fertilizer. However, for using the
effluent of the process as fertilizer it has to be ensured that the content of xenobiotics and
heavy metals is below the levels found to be of environmental risk.

The Danish government has set the aim to treat 150,000 tons of OFMSW (40–42% of the
total amount of municipal solid waste) biologically by the year 2004. Here, anaerobic
digestion is the major choice. Since the effluent of the biogas plants should be used as a fertil-
izer, OFMSW has to comply with thresholds for heavy metals and xenobiotics. The
threshold values for xenobiotics compounds are listed in Table 1.

Previous investigations identified the concentration of DEHP as the major concern in
OFMSW in Denmark (Kjølholt et al., 1998; Møller, 1999). This is suspected to be due to a widespread collecting system using plastic bags followed by insufficient plastics separation. The DEHP concentration in the collected waste has often been close to the threshold value (50 mg/kg-TS). Since the organic matter (VS) and thus the total solids (TS) content decrease during anaerobic digestion, the concentration of DEHP per kg dry matter of fertilizer product would exceed the permitted level if no removal of DEHP occurs.

In the development of a new treatment concept for the anaerobic digestion of OFMSW (Hartmann et al., 2001) the present work had two aims with respect to xenobiotic contamination of OFMSW: first, to identify the level of xenobiotic contamination in OFMSW of different origin in Denmark and its variation over time and second to determine the fate of phthalic acid esters contamination in OFMSW throughout the anaerobic treatment process.

The contamination of OFMSW with phthalic acid esters (PAEs) and its fate during anaerobic digestion processes is only rarely investigated (Ejlertsson et al., 1996). Most investigations concerning the degradation of PAEs are based on aerobic and anaerobic sludge treatment and their fate on sludge-amended soil (for example Roslev et al., 1998; Madsen et al., 1999; Banat et al., 1999; Merkel and Appuhn, 1996). From these studies it is well known that among all PAEs DEHP is one of the compounds that is most recalcitrant towards both aerobic and anaerobic degradation (Staples et al., 1997). The recalcitrant characteristics of DEHP are suspected to be due to two physical properties: (1) its low water solubility and (2) its three-dimensional branched structure which prevents hydrolytic enzymes from binding (Ejlertsson et al., 1997). Ejlertsson and co-workers (1997) suspected the water solubility was the major limiting factor for degradation of hydrophobic PAEs. Most reliable measurements indicate that the water solubility of DEHP and DBP is in the range of 0.0006–0.0026 mg/l and 1.5–13.0 mg/l, respectively, with a log $K_{OW}$ in the range of 7.0–7.8 and between 3.74 and 5.15, respectively (Staples et al., 1997). The difference in water solubility could explain why degradation of lower molecular weight phthalates like DBP is also relatively rapid under anaerobic conditions, while experiments with DEHP show little or no degradation (Staples et al., 1997; Ejlertsson et al., 1997). Investigations of the degradation of PAEs show furthermore a higher variability in anaerobic biodegradation suggesting that the nature of the inoculum influences test results (Ejlertsson et al., 1997). Several investigations have also shown that the degradation of DEHP is temperature dependent (Madsen et al., 1999; Banat et al., 1999). The hypothesis for the present investigation was therefore that a higher degradation efficiency could be established at higher temperatures due to enhanced water solubility and hence a higher bioavailability and biodegradability.

**Methods**

**Sampling.** For analysis of xenobiotic contamination of OFMSW from different collection sites, samples were taken from the wastewater treatment plant in Grindsted, the biogas...
plant in Studsgård, and the composting plant Noveren near Holbæk. In Grindsted and Studsgård samples were taken of untreated OFMSW and from different stages of the treatment process to follow the xenobiotic contaminants. At Noveren only the collected OFMSW was analyzed. In Grindsted OFMSW is source sorted, collected in paper bags and treated in a mesophilic anaerobic digester in co-digestion with sewage sludge. The effluent is dewatered by a ribbon press after addition of a polymer solution. The solid fraction is sold as fertilizer. In Studsgård OFMSW is collected in plastic bags, plastic is removed by mechanical separation on roller sieves and the organic waste fraction is treated in the biogas plant in co-digestion with manure under thermophilic conditions. The solids in the effluent are removed using a separator consisting of a brush sieve and a screw press. The solid fraction is incinerated. For representative sampling 20 kg untreated OFMSW was collected from each of the three sites. In Grindsted and Studsgård 1 l of mixture with the co-substrate was collected over a period of 7 days and of the effluent of the process after the hydraulic retention time of the reactor.

**Reactor set-up.** OFMSW collected for the co-digestion plant in Grindsted was used as substrate for the laboratory reactor set-up. The waste was homogenized using a meat-mincer and diluted to a slurry of 6% TS (w/w) by addition of tap water, cow manure or liquid fraction of the reactor effluent, respectively. A thermophilic (55°C) continuous stirred tank reactor (CSTR) R1 with an active volume of 3 l was operated solely on OFMSW in a wet digestion process after acclimation from cow manure to a successive higher ratio of OFMSW. A second thermophilic reactor R2 (3 l active volume) was stabilized to a (50:50%VS) co-digestion process of OFMSW and cow manure. The hydraulic retention time (HRT) was 15 days for R1 and R2. Influent for both reactors was prepared as described with the same portions of OFMSW; 200 g OFMSW was used per litre of influent for R1 and 100 g OFMSW per litre for influent of R2. Both reactors were fed every 8 hours with an organic loading rate (OLR) of 4 gVS l⁻¹ d⁻¹. After day 140 the liquid fraction of the effluent from R1 was recycled for dilution of OFMSW used for influent of R1. Due to a volume loss by sampling additional tap water was used for dilution of OFMSW. The ratio between recycled liquid effluent and tap water was on average 49% (v/v). Effluent from R1 was in a second experimental phase after day 340 treated in a subsequent hyper-thermophilic (68°C) CSTR R68 with an active volume of 1 l and a HRT of 5 days. The inoculum for start-up of R68 originated from a laboratory-scale hyper-thermophilic reactor treating cow manure. In this experimental phase, the liquid fraction of the effluent from R68 was used for dilution of influent OFMSW for R1. Process performance was monitored by VS-reduction, methane production, VFA (volatile fatty acids) concentration, ammonia formation and concentration of PAEs in the reactor influent and effluent. It has to be pointed out that OFMSW was not spiked with phthalic acid esters, so only the original contamination was measured.

**Analytical procedure.** For chemical analysis the untreated OFMSW collected from the three treatment plants was homogenized using a meat mincer. Xenobiotics were analyzed according to a method recommended by the Danish Environmental Protection Agency. A sample amount equivalent to 10 g-TS was transferred to 500 ml serum bottles. 10 µg deuterium-labeled phenanthrene d10, fluoranthene d10, benzo(a)pyrene d12 and 25 µg DEHP d4, all dissolved in 10 ml dichloromethane (DCM), was added as internal standard prior to extraction. After adjusting the pH to 10–12 using NaOH, 150 ml DCM was added as extracting agent. The serum bottles were sonicated for 5 min and shaken for 2 h at 250 rpm at room temperature. The DCM phase was harvested after centrifugation and DCM was evaporated at 70°C. The residue was dissolved in 10 ml DCM and analyzed by GC-MS.
equipped with a HP-5 column (25 m × 0.2 mm × 0.3 µm). Helium was used as carrier gas with a flow of 0.8 ml/min. GC oven temperature was 50°C for 2 min, increased with 12°C/min up to a final temperature of 310°C, which was held for 10 min. Injector temperature was 280°C, and 270°C of the MS interface. Detection limit for DEHP was 0.005 mg/l.

For analysis of PAEs in the influent and effluent samples of the laboratory reactor set-up a sample amount of 40–60 ml was taken, 60 µg DEHP d4 was added as internal standard dissolved in 3 ml DCM and the amount of DCM used for extraction was reduced to 100 ml. After extraction and evaporation of the DCM phase as described above, the residue was dissolved in 3 ml DCM. GC-MS analysis was performed as previously described.

Results and discussion

Xenobiotic contamination of OFMSW at different treatment sites. Analysis of xenobiotic compounds in the OFMSW samples from the different sites revealed concentrations of NPE and LAS below detection limits at all sites. PAH concentration (as sum of PAHs listed in Table 1) in OFMSW was below detection limits at Studsgård and Grindsted while OFMSW from Noveren contained 2.6 mg/kg-TS. The DEHP concentration, however, revealed a significant level of 10–28 mg/kg-TS in all OFMSW samples and, therefore, the present investigation focused on the fate of DEHP during anaerobic treatment processes (Figure 1). At Studsgård, the DEHP concentration per kg dry matter decreased significantly in the mixture with manure (from 25 mg/kg-TS to 2 mg/kg-TS) while the sewage sludge in Grindsted (36 mg/kg-TS) contributed to an increase of the DEHP concentration from OFMSW (10.4 mg/kg-TS) to 26 mg/kg-TS. In the effluent of both plants the concentration per kg-TS increased, at Studsgård by a factor of 11 (from 2 to 23 mg/kg-TS) and at Grindsted by a factor of 2 (from 26 to 50 mg/kg-TS). For the samples at Grindsted, this corresponds to the reduction of the TS concentration of 50% (from 4.1% to 1.9%). The increase of the DEHP concentration per kg-TS measured in the effluent from Studsgård is, however, higher than the TS reduction, which is about 80% (from 12.7% to 2.5%). This means that the concentration in mg per litre was higher in the effluent than in the influent, which suggests a higher extractability of DEHP in the effluent than in the influent sample. This is in accordance with previous investigations. Møller (1999) found DEHP concentrations of 28 mg/kg-TS in OFMSW collected in Zealand, Denmark, and levels of up to 160

![Figure 1](https://iwaponline.com/wst/article-pdf/48/4/175/423377/175.pdf)

This figure shows the DEHP and TS ratio in OFMSW from Studsgård biogas plant, Grindsted wastewater treatment plant, Noveren composting plant and in co-substrates and along the different stages of the biogas process at Studsgård and Grindsted; the concentration of DEHP in OFMSW from Grindsted was calculated from a mass balance based on the DEHP and TS values found in sewage sludge and the mixture of sewage sludge and OFMSW.
mgDEHP/kg-TS in the effluent after treatment in a biogas plant near Ålborg (Møller, 1999). It is, therefore, impossible to state whether DEHP degradation occurred in the anaerobic digesters or not. In fact, the DEHP concentration in the effluent from the digester in Grindsted was as high as the threshold value. The lower value at Studsgård was only due to the OFMSW being diluted with manure. Analysis of the effluent samples from Studsgård show, furthermore, that DEHP was efficiently separated with the solid fraction of the effluent.

Phthalic acid esters in laboratory-scale reactor experiments. The phthalic acid esters DEHP and DBP were chosen as model compounds to monitor the fate of high and low molecular weight phthalic acid esters during the anaerobic degradation process. DEHP and DBP were both found in significant concentrations, but we decided to focus on DEHP since its concentration was generally higher and its degradation is reported to be restricted during anaerobic processes. The origin of the phthalate contamination in OFMSW remained unclear since the waste showed only low content of plastic material and analysis of phthalates in the paper bags used for collection of the waste revealed low values of 0.4 mg/kg-TS and 0.9 mg/kg-TS for DEHP and DBP, respectively.

Concentrations of DEHP and DBP in the influent and effluent of R1 are given in Figure 2, of R2 in Figure 3 and of R68 in Figure 4. The concentrations are given in mg/l for a better comparison of the total in- and output of phthalic acid esters of the reactors. The threshold

![Figure 2](https://iwaponline.com/wst/article-pdf/48/4/175/423377/175.pdf)

**Figure 2** DEHP (left) and DBP (right) in influent and effluent of thermophilic reactor R1 (100% OFMSW) and threshold concentrations for influent (3 mg/l) and effluent (1.5 mg/l) for use as fertilizer

![Figure 3](https://iwaponline.com/wst/article-pdf/48/4/175/423377/175.pdf)

**Figure 3** DEHP (left) and DBP (right) in influent and effluent of thermophilic reactor R2 (50%(VS/VS) OFMSW in co-digestion with manure) and threshold concentrations for influent (3 mg/l) and effluent (1.7 mg/l) for use as fertilizer
value of 50 mg/kg-TS corresponds to 3.0 mg/l in the influent (with a TS average of 6%), to 1.5 mg/l in the effluent of R1 (with a TS average of 3%), to 1.7 mg/l in the effluent of R2 (with a TS average of 3.5%) and 0.75 mg/l in the effluent of R68 (with a TS average of 1.5%).

The concentration of DEHP in the influent of R1 showed high fluctuations (Figure 2) while the DEHP concentration in the mixture with manure in the influent of R2 was, except for the measurements around day 200, generally below the threshold value of 3 mg/l (Figure 3). DBP concentration of the influent to both reactors was except for one measurement on day 182 (R1) lower than 0.6 mg/l. Thus the reactor results confirm DEHP as the main contaminant of interest compared to DBP. High DEHP concentrations in both reactors around day 200, more than 10 mg/l in the influent of R1 and more than 5 mg/l in the influent of R2, are suspected to be due to a higher DEHP contamination of the OFMSW used in this period. The higher contamination could, however, not be visually estimated by an obvious appearance of plastic material. In the period of recycling the liquid fraction of the effluent of R1 (between days 140 and 340) the concentration of DEHP and DBP in the influent of R1 was more than twice the concentration of the influent to R2. This indicates that both PAEs were partly recycled with the liquid fraction of the effluent of R1. When the effluent of R68 was recycled as part of the influent of R1 after day 340, the influent DEHP and DBP concentration of R1 was not more than twice the concentration in R2, suggesting that recycling the liquid fraction of the effluent of R68 did not increase the DEHP and DBP concentration. After day 440 the influent DEHP concentration of R1 was again higher, which is suspected to be due to a higher level of DEHP in a new batch of OFMSW.

The fluctuation pattern of the DEHP and DBP concentration in the influent to both reactors was generally well reflected in the effluent concentration of DEHP, when comparing the concentrations after one hydraulic retention time (15 days). This can be seen, for example, in the high concentration peaks around day 200 in both reactors followed by high concentration peaks in the effluent and the dynamics in influent concentrations of R1 in the period between days 200 and 300 followed by the same pattern in the effluent concentrations of R1. In the effluent of reactor R2 the concentration in mg/l was, except for two measurements around day 200, roughly the same as in the influent (Figure 3). In the effluent of reactor R1 the measured DEHP concentration was even higher than in the influent (Figure 2). This was still true when taking into account the volume loss in R1 due to evaporation and mineralization, assuming that DEHP was not part of this loss. The reason for the higher value in the effluent than the influent is, therefore, suspected to be a higher extractability of DEHP after biological degradation of particulate organic matter in the anaerobic digester. In both reactors the effluent concentration was, except for the period between days 350 and 440 for R1 and days 330 to 440 for R2, above the threshold values of 1.5 mg/l for R1 and 1.7 mg/l for R2. DBP concentration was lower in the effluent than in the influent for both R1 and R2. Assuming first order kinetics and steady state conditions for the removal of DEHP and DBP, the kinetic constant for removal by hydrolysis $k_h$ was calculated according to Eq. (1).

$$k_h = \frac{1}{HRT} \cdot \left( \frac{C_{in} - C_{out}}{C_{out}} \right)$$

(1)

where $C_{in}$ is the influent concentration (mg/l), $C_{out}$ the effluent concentration (mg/l) and HRT the hydraulic retention time (d$^{-1}$).

$k_h$ values are shown in Table 2. DEHP removal in the thermophilic reactors could only be detected for reactor R2 in the period between days 340 and 442. The concentration was on average 9.6% lower in the effluent and the calculated $k_h$ value was 0.009 d$^{-1}$. Removal of DBP was observed in both reactors, with a range of 38–49% and 46–70% for R1 and R2,
respectively. Removal rates for DBP in the range of 0.044–0.112 d\(^{-1}\) and 0.065–0.163 d\(^{-1}\) for R1 and R2, respectively, were about 10 times higher than the observed DEHP removal rate in reactor R2.

After treatment of the effluent from reactor R1 in the hyper-thermophilic reactor R68 the effluent concentration of DEHP and DBP was consistently lower than the influent concentration (Figure 4). The reduction was 34–53% for DEHP and 62–74% for DBP. In the period between days 400 and 450 the effluent concentration was below the respective threshold value of 0.75 mg/L. \(k_h\) values reveal removal rates in the range of 0.21–0.47 d\(^{-1}\) and 0.55–1.09 d\(^{-1}\) for DEHP and DBP, respectively (Table 2). In this calculation accumulation of DBP and DEHP was considered. Accumulation was determined by extraction of the phthalic acid esters from the residue found in R68 at the end of the experiment. The accumulated amount per total volume of influent throughout the whole experimental period accounted for an accumulation of 0.029 mg/l DEHP and 0.002 mg/l DBP. Thus the accumulation was negligible considering the influent concentrations of 1.25–3.45 mg/l DEHP and 0.10–0.15 mg/l DBP.

The consistently lower effluent concentrations of both DEHP and DBP after the hyper-thermophilic treatment revealed high-rate removal of both phthalic acid esters during biological anaerobic treatment at 68°C. The benefit of DEHP reduction was, furthermore, proved in the significantly lower DEHP concentration in the influent of R1 when recycling the liquid fraction of the effluent of R68 (Figure 2).

Relatively rapid degradation of lower molecular weight phthalates like DBP under anaerobic conditions has been demonstrated before, but the reduction of DEHP in the range

---

### Table 2: Removal rates of DEHP and DBP in thermophilic reactors R1 and R2 and in hyper-thermophilic reactor R68

<table>
<thead>
<tr>
<th>Period Day</th>
<th>Reactor</th>
<th>DEHP</th>
<th>DBP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial conc.</td>
<td>Reduction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mg (kg-TS)(^{-1})</td>
<td>mg l(^{-1})</td>
</tr>
<tr>
<td>0–140</td>
<td>R1</td>
<td>20.6</td>
<td>0.98</td>
</tr>
<tr>
<td>141–339</td>
<td>R1</td>
<td>121.7</td>
<td>7.51</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>48.7</td>
<td>3.16</td>
</tr>
<tr>
<td>340–442</td>
<td>R1</td>
<td>13.3</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>16.2</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>R68</td>
<td>53.1</td>
<td>1.25</td>
</tr>
<tr>
<td>443–490</td>
<td>R1</td>
<td>35.0</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>R68</td>
<td>183.6</td>
<td>3.45</td>
</tr>
</tbody>
</table>

n.o.: not observed

---

**Figure 4**: DEHP (left) and DBP (right) in influent and effluent of hyper-thermophilic reactor R68 and threshold concentrations for influent (1.5 mg/l) and effluent (0.75 mg/l) for use as fertilizer.
of up to 53% during the hydraulic retention time of 5 days in reactor R68 is much faster than in most previous anaerobic degradation experiments where this high degradation efficiency was reached in a batch test after a duration of 100 days (Staples et al., 1997). Accordingly, $k_h$ values of the observed DEHP removal are quite high and can be compared to aerobic removal rates (Madsen et al., 1999). Madsen and co-workers (1999) investigated the kinetics of DEHP mineralization mainly under aerobic conditions at temperatures ranging from 5–20°C and with initial concentrations of 1.6–35.1 mg/kg-TS. For sludge amended soil with an initial concentration of 1.6 mg/kg-TS the $k_h$ value at 20°C was 0.0127 d$^{-1}$ in the initial degradation phase. In the temperature range of 5–20°C the results showed linear correlation between temperature and removal rate ($k_h$). Furthermore, the initial mineralization rate was increasing with higher initial DEHP concentration and $k_h$ was for an initial concentration of 35.1 mg/kg-TS 10 times higher than at 9.9 mg/kg-TS. Taken into account that in the present hyper-thermophilic treatment the temperature and the initial DEHP concentration were, respectively, 3.5 times and 2–4 times higher than reported by Madsen and co-workers (1999), the removal rates found in the present investigation are in the range of extrapolated aerobic kinetic values at higher temperature and higher initial concentrations. The benefit of high temperature treatment for DEHP reduction was also shown by Banat and co-workers (1999), who demonstrated 70% DEHP reduction within 3 days in aerobic thermophilic treatment of sewage sludge at 68°C (Banat et al., 1999). The present work reveals that this effect can also almost be reached under anaerobic conditions.

The high-rate removal of DEHP observed in the present study indicates that degradation potential under anaerobic conditions can be in the same range as under aerobic conditions. Since the initial phase of biodegradation of phthalic acid esters is expected to be both under aerobic and anaerobic conditions an enzymatic ester hydrolysis to form phthalic acid (Staples et al., 1997), this does not explain why DEHP is less biodegradable than DBP under anaerobic degradation. It can be speculated that the low degradation of DEHP rather is a result of its low water solubility and thus its lower bioavailability compared to DBP. The present results suggest that bioavailability is significantly enhanced at hyper-thermophilic conditions and at higher concentrations per kg dry matter. They indicate that a higher concentration per kg dry matter is achieved during degradation of organic matter and the bioavailability is enhanced since DEHP adsorbed to solids is released. Therefore, the high degradation of DEHP in the hyper-thermophilic reactor can be suspected to also be a result of the lower TS content of the effluent from the thermophilic reactor R1 that is treated in reactor R68. This means that the high removal rates of DEHP in the investigated reactor system are a result of the combination of thermophilic and hyper-thermophilic treatment. It is likely that no or much lower degradation of DEHP was observed in the thermophilic treatment of R1 and R2 compared to the hyper-thermophilic treatment due to two phenomena: first, the initial concentration of DEHP per kg dry matter was lower in the influent to R1 and R2 than to R68; second, the higher extractability of DEHP in the effluent concealed the degradation of DEHP in the thermophilic reactors. It can be assumed that the observed high rate degradation of highly hydrophobic phthalic acid esters like DEHP is also limited down to a certain concentration per kg-TS in the effluent for higher temperatures. This can be seen in the lowest concentrations of DEHP in the effluent of R1 and R68, which are in the same range of 40 mg/kg-TS. Further degradation below this concentration will be much slower since a certain amount of DEHP will be bound strongly to the particulate matter and will not be available for enzymatic attack.

**Conclusions**

The present study reveals that among organic contaminants found in the organic fraction of municipal solid waste (OFMSW) in Denmark phthalic acid esters, especially DEHP, is the...
most critical. In conventional anaerobic digesters treating solely OFMSW the concentration per kg-TS will exceed the threshold value for the use as fertilizer on agricultural soil in Denmark if no removal of DEHP occurs. In thermophilic laboratory-scale reactors treating OFMSW at 15 days hydraulic retention time no significant degradation of DEHP was observed while removal of DBP was between 38% and 70%. However, after treatment of the effluent from the thermophilic treatment in a hyper-thermophilic reactor at 5 days hydraulic retention time 34–53% of the DEHP content could be removed and further 62–74% of DBP. High removal rates are obviously due to the high treatment temperature and high degradation of organic matter, which both enhance the bioavailability of DEHP. The results suggest that under anaerobic conditions enzymes are present for the degradation of DEHP as well as for DBP and that it is the low water solubility of DEHP that limits its degradation. DEHP made bioavailable by the treatment is obviously degraded. For treatment of 100% OFMSW the DEHP per kg dry matter will, therefore, be in the same range as in the influent concentration and the combination of a thermophilic and a hyper-thermophilic treatment will comply with the threshold values for use as fertilizer for OFMSW that shows DEHP contents below 50 mg/kg-TS.

Acknowledgements
We would like to thank Thomas Andersen for excellent technical assistance. This project was supported by grants from the research program of The Danish Energy Council, no. 1383/99-0009 and 1713/00-0024.

References