Phthalate hydrolysis under landfill conditions

S. Jonsson*, V.A. Vavilin** and B.H. Svensson*

*Department of Water and Environmental Studies, Linköping University, SE-581 83 Linköping, Sweden
(E-mail: susjo@tema.liu.se; bosseh@tema.liu.se)

**Water Problems Institute of the Russian Academy of Sciences, Gubkina 3, Moscow 119991, Russia
(E-mail: vavilin@aqua.laser.ru)

Abstract Experimental data from a study using a landfill simulation reactor were used to develop and calibrate a one-dimensional distributed model of co-digestion of municipal solid waste and three phthalic acid diesters with different water solubilities. The three diesters were diethyl phthalate, dibutyl phthalate, and di-2-ethylhexyl phthalate. Two types of municipal solid wastes were assumed, easily degradable and recalcitrant. The model considered inhibition of hydrolysis of the recalcitrant fraction and phthalic acid esters, and also methanogenesis at acidic pH. The results indicated that the prolonged steady-state concentrations of the diesters in the leachates could be explained by equilibrium between physicochemical desorption and sorption processes for the three diesters. When methanogenic conditions were induced in the acidogenic landfill simulation reactor, inhibition of both hydrolysis of recalcitrant MSW and of phthalic acid esters ceased.

Keywords Biodegradation; dibutyl phthalate; diethyl phthalate; di-2-ethylhexyl phthalate; landfill modeling; phthalates

Introduction Phthalic acid diesters (PDs) are ubiquitous in the chemosphere, because they are widely used in various commercial products, mainly as plasticizers in polyvinyl chloride (PVC; Staples et al., 1997). Many products are eventually disposed of on landfills, where they are usually exposed to microbiologically driven (anaerobic) degrading environments, in other words acidogenic and methanogenic conditions (Christensen and Kjeldsen, 1989). Mersiowsky and Stegmann (1997) concluded that loss of plasticizers from landfilled PVC polymer products is enhanced in anaerobic landfill environments, because these substances are continuously removed from the surface of the products by microbial transformation and/or physicochemical wash-off effects. Several studies have shown that phthalic acid esters (PE) resist transformation under acidic landfill conditions, whereas it is enhanced under methanogenic conditions (Ejlertsson et al., 1996a, b; Bauer and Herrmann, 1998; Jonsson et al., 2003). Wolfe et al. (1980) have reported that chemical hydrolysis of phthalates is probably negligible under landfill conditions; thus the breakdown of these compounds in such waste depositories must be due to microbial activity. The degradability of phthalates in a water solution is strongly related to the water solubility of these substances (Shelton et al., 1984; Ejlertzsson et al., 1997).

The ultimate anaerobic degradation of phthalic acid diesters is a complex process, but, despite that, modified first-order kinetics is traditionally used to describe the course of this transformation (Madsen et al., 1999; Gavala et al., 2003; Vavilin et al., 2005a). A model of the degradation includes hydrolysis of a diester (PD) to its corresponding monoester (PM), followed by hydrolysis of the PM to phthalic acid. Vavilin et al. (2005b) were successful in using Monod kinetics to analyze the enzymatic hydrolysis of
some phthalates, assuming that di- and monoesters were hydrolyzed by the same type of microorganisms (i.e. only the kinetic coefficients differed in the Monod kinetics).

In the present study, dynamic modeling was used to study the behavior of phthalic acid diesters and monoesters in landfill leachates in order to extend the existing knowledge of the processes of physico-chemical exchange in this context. To arrive at quantitative and semi-quantitative estimates, we developed a distributed one-dimensional (1-D) model that accounts for a vertical water flow. This model was employed to show how the release and transformation of three phthalic acid diesters with different water solubilities depend on the sequence of the phases that occur in a landfill (i.e., under acidogenic and methanogenic conditions); the three diesters were diethyl phthalate (DEP), n-dibutyl phthalate (DBP), and di(2-ethylhexyl) phthalate (DEHP). Data from a 100-L landfill-simulation reactor (Ejlertsson et al., 2003; Jonsson et al., 2003) were used to develop and calibrate the 1-D model. We have previously applied this modeling concept to describe degradation of municipal solid waste (MSW) under landfill conditions (Vavilin et al., 2005a), and the results of that study revealed that both hydrolysis and methanogenesis were inhibited during the acidogenic period. In the present investigation, we used that finding to model the dynamic occurrence of phthalates in landfilled waste.

Methods

Experimental studies used for modeling

The reactor (designated LiU3) filled with 40 kg of MSW was shown to contain the phthalates DEP, DBP, and DEHP (Jonsson et al., 2003). Water was added to give a moisture content of 65% (wet weight). Rapid fermentation induced acidogenic conditions (pH 5.5) and high concentrations of volatile fatty acids (VFA) within a few days of filling and closing the reactor. The experiment was conducted in five sequential stages (cf., equations 3–5). During weeks 18–52, water was regularly added to the top of the reactor to simulate precipitation, and the corresponding volume was withdrawn from the bottom of the reactor, which led to dilution of the leachate. The reactor was operated under acid conditions for approximately three years, after when leachate was subsequently (weeks 144–169) exchanged with a parallel reactor (LiU1) that had developed stable methanogenic conditions. The leachate recirculation led to establishment of methanogenic conditions and consumption of the VFAs present in LiU3. Previous reports have provided detailed descriptions of the waste used and the operation and performance of the reactors (Ejlertsson et al., 2003), as well as measurements of the phthalates (Jonsson et al., 2003).

The model

A simplified kinetic scheme was used in the distributed 1-D batch reactor model to describe anaerobic digestion (Figure 1), which is the basis for modeling the occurrence of phthalates in the leachate. In Figure 1, hydrolysis/acidogenesis and methanogenesis are the rate-limiting steps of the overall anaerobic digestion of MSW, a process that is considered to proceed in two stages (first acidogenic and then methanogenic), with a single group of intermediate fermentation products (VFA) serving as the precursors for methane production in the model (Vavilin et al., 2003).

An important finding was that the modeling of MSW degradation was possible only when the waste was divided into a readily degradable and a recalcitrant fraction (Vavilin et al., 2005a), which was also applied in the present study. This time, however, two types of microorganisms (phthalate degraders of each PE and methanogens) were included in the model (equation 1). Methanogenesis was the driving force for ultimate degradation of the waste. When modeling the hydrolysis of a MSW-related PD, the phthalate must be exposed to the hydrolytic agents in the liquid phase. Accordingly, the present model...
(equation 1) included release of the PD from the waste matrix induced by a desorption/sorption factor, which accounts for the hydrophobicity of the PD. The PM was assumed to be completely soluble (Jonsson and Baun, 2003); thus no sorption factor was introduced for the monoesters. For the dissolved PD, PM, VFA, protons, and also methanogens and phthalate degraders, an advection occurred due to the vertical water flow in the reactor. The model structure is described as follows:

\[
\begin{align*}
\frac{dW_1}{dt} &= -k_{h1}W_1 \\
\frac{dW_2}{dt} &= -k_{h2}W_2f_1(HVFA) \\
\frac{dVFA}{dt} &= D_{VFA}\frac{\partial^2VFA}{\partial Z^2} - \frac{\partial VFA}{\partial Z} + \chi_1k_{h1}W_1 + \chi_2k_{h2}W_2f_1(HVFA) - \rho_{m1f_2(HVFA)} \frac{B_{M}VFA}{K_{VFA} + VFA} \\
\frac{dB_M}{dt} &= D_{B_M}\frac{\partial^2B_M}{\partial Z^2} - q \frac{\partial B_M}{\partial Z} + Y_1\rho_{m1f_2(HVFA)} \frac{B_{MF}VFA}{K_{VFA} + VFA} - k_{d1}B_M \\
\frac{dCH_4}{dt} &= (1 - Y_1)\rho_{m1f_2(HVFA)} \frac{B_{MF}VFA}{K_{VFA} + VFA} \\
\frac{dH}{dt} &= D_H\frac{\partial^2H}{\partial Z^2} - q \frac{\partial H}{\partial Z} - bf_2(HVFA) \frac{B_{MF}VFA}{K_{VFA} + VFA} \\
\frac{dPD_s}{dt} &= -k_{r1}PD_s + k_{r2}PD \\
\frac{dPD}{dt} &= D_{PD}\frac{\partial^2PD}{\partial Z^2} - q \frac{\partial PD}{\partial Z} - k_2PD + k_1PD_s - \rho_{m2f_3(HVFA)} \frac{B_{PE}PD}{K_{DP} + PD} \\
\frac{dPM}{dt} &= D_{PM}\frac{\partial^2PM}{\partial Z^2} - q \frac{\partial PM}{\partial Z} + (1 - Y_2)\rho_{m2f_3(HVFA)} \frac{B_{PE}PD}{K_{PD} + PD} - \rho_{m3f_3(HVFA)} \frac{B_{PE}PM}{K_{PM} + PM} \\
\frac{dB_{PE}}{dt} &= D_{B_{PE}}\frac{\partial^2B_{PE}}{\partial Z^2} - q \frac{\partial B_{PE}}{\partial Z} + B_{PE}f_3(HVFA) \left\{ \frac{\rho_{m2PD}PM}{K_{DP} + PD} + \frac{\rho_{m3PM}}{K_{MP} + PM} \right\} - k_{d2}B_{PE}
\end{align*}
\]

where \( W_1, W_2, VFA, \) and \( H \) are the readily degradable and recalcitrant MSW, total VFA, and proton concentrations, respectively; \( CH_4 \) is the methane production; \( PD \) and \( PM \) are the soluble di- and monoester concentrations; \( PD_s \) is the sorbed diester; \( B_M \) and \( B_{PE} \) are the biomass concentrations of the methanogens and phthalate ester (PE) degraders; \( f_1(HVFA), f_2(HVFA), \) and \( f_3(HVFA) \) are the hydrolysis and inhibition factors for the various reactions.
and $f_3(HVFA)$ are the dimensionless inhibiting functions (see equation 2) of non-ionized VFA; $t$ is time $(0 \leq t \leq +\infty)$; $k_{d1}$ and $k_{d2}$ are the corresponding first-order hydrolysis rate constants of easily degradable and recalcitrant waste; $\rho_{m1}$, $\rho_{m2}$, and $\rho_{m3}$ are the maximum specific rates of VFA utilization and PD, and PM disappearance, respectively; $k_{d1}$ and $k_{d2}$ are the specific biomass decay coefficients for methanogens and PE degraders; $k_1$ and $k_2$ are the desorption and sorption rate constants for PD; $\chi_1$ and $\chi_2$ are the stoichiometric coefficients of readily degradable and recalcitrant waste; $b$ is the rate constant for the decrease of proton concentration during methanogenesis; $K_{VFA}$, $K_{PD}$, and $K_{PM}$ are the half-saturation constants for utilization of VFAs, PD, and PM, respectively; $Y_1$ and $Y_2$ are the corresponding biomass yield coefficients of methanogens and PE degraders; $q$ is the volumetric liquid flow rate per unit surface area (specific liquid flow rate); $D_{VFA}$, $D_H$, $D_{PD}$, and $D_{PM}$ are the diffusion coefficients for VFA, proton, PD, and PM, respectively; $D_{BM}$ and $D_{BPE}$ are the diffusion coefficients for methanogens and PE degraders; $L$ is the reactor height. Methane formation resulting from phthalate transformation was not taken into account (because the total amount of phthalate was negligible compared to the initial amount of MSW), nor was the initial formation of carbon dioxide during the hydrolysis/acidogenesis.

**Inhibition.** Vavilin et al. (2005a) have suggested that the inhibition of hydrolysis and methanogenesis is directly or indirectly caused by pH, and they assumed that non-ionized VFAs play a major role in this inhibition. The dimensionless function of inhibition $f(HVFA)$ is illustrated in equation 2 and Figure 2.

$$f_i(HVFA) = \frac{1}{1 + \left(\frac{VFA}{K_{i} + K_{d}H}\right)^2}$$

(2)

where $K_d = 2.0 \times 10^{-5}$ is the dissociation constant for VFA. $K_i$ is the inhibition coefficient ($i = 1, 2, 3$ corresponds to hydrolysis of recalcitrant waste, methanogenesis, and phthalate transformation, respectively).

**Boundary conditions.** Due to the different managements applied and the processes occurring in the reactor, the following boundary conditions were used in the model: changes in concentrations of the variables throughout the study due to the progress of
normal events (equation 3), due to dilution (equation 4), and due to leachate exchange between the reactors (equation 5).

\[
\frac{\partial c}{\partial Z} = 0 (z = 0); \quad \frac{\partial c}{\partial Z} = 0 (z = L) \text{ weeks: } 1 - 17, 53 - 143, 170 - 250 \quad (3)
\]

\[
\frac{\partial c}{\partial Z} = \frac{q_1}{D} (0 - c)(z = 0); \quad \frac{\partial c}{\partial Z} = 0 (z = L) \text{ weeks: } 18 - 52 \quad (4)
\]

\[
\frac{\partial c}{\partial Z} = \frac{q_2}{D} (c - c)(z = 0); \quad \frac{\partial c}{\partial Z} = 0 (z = L) \text{ weeks: } 144 - 169 \quad (5)
\]

where \( q_1 \) and \( q_2 \) are the volumetric liquid flow rate per unit surface area during the periods of water addition and leachate recirculation, respectively. In equation (3) \( c \) represents all variables in the model (equation 1); in equation 4 \( c \) stands for the VFAs, PD, PM, BM and BPE concentrations; in equation 5 \( c \) and \( c* \) are the VFA, H, DP, MP, BM and BPE concentrations in the reactor and incoming leachate during recirculation, respectively; for other variables the conditions in equation 3 were used.

Under the initial conditions, all variables were assumed to be uniformly distributed over the vertical coordinate \( Z \). All final values for the variables in the previous stage were used as the initial values in the forthcoming stage. Numerical simulations were performed using MATLAB software. Visual comparison between experimental data and the simulations made it possible to attain values of coefficients at which the sum of the differences between the observed and predicted values of model variables were near a minimum (Table 1). Since the complexity of the model made it extremely difficult to perform an identifiable study, it was not possible to ensure the uniqueness of the set of estimated parameters. However, satisfactory results could be obtained, provided that the simulations were performed after trying many sets of parameters, choosing values with physical and biological sense, and ensuring that, if there were other sets of parameter values, they were of the same order of magnitude.

**Results and discussion**

**Simulation of MSW transformation to methane**

The dynamics of the MSW in the model is shown in Figure 3. Before dilution was started (week 18), VFA accumulated in the leachate due to hydrolysis/fermentation. During dilution of the leachate (weeks 18–52), the concentration of VFA decreased in accordance with the rate of dilution. After termination of the dilution (week 52), the VFA concentration rose slightly as a result of hydrolysis and fermentation activity. When leachate

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Basic set of parameters of the model (equation 1). Asterisks indicate parameters in the incoming leachate during recirculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{M} )</td>
<td>1.16 week(^{-1} ), ( k_{S} ) = 0.049 week(^{-1} ), ( r_{p} ) = 15.4 week(^{-1} ) g g(^{-1} ), ( r_{p2DEP} ) = 6.3 week(^{-1} ) mg mg(^{-1} ),</td>
</tr>
<tr>
<td>( r_{MHz} )</td>
<td>= 0.31 week(^{-1} ) mg mg(^{-1} ), ( r_{Hz} ) = 7.0 week(^{-1} ) mg mg(^{-1} ), ( r_{M2DEP} ) = 0.28 week(^{-1} ) mg mg(^{-1} ),</td>
</tr>
<tr>
<td>( r_{M2DEP} )</td>
<td>49 week(^{-1} ) mg mg(^{-1} ), ( r_{M3MEP} ) = 0.31 week(^{-1} ) mg mg(^{-1} ),</td>
</tr>
<tr>
<td>( k_{S1} )</td>
<td>= 0.05 week(^{-1} ), ( k_{1DEP} ) = 0.15 week(^{-1} ), ( k_{2DEP} ) = 0.5 week(^{-1} ), ( k_{1DP} ) = 0.035 week(^{-1} ),</td>
</tr>
<tr>
<td>( k_{2DP} )</td>
<td>12 week(^{-1} ), ( k_{1DEHP} ) = 0.005 week(^{-1} ), ( k_{2DEHP} ) = 60 week(^{-1} ), ( x_{1} ) = 0.4, ( x_{2} ) = 0.6,</td>
</tr>
<tr>
<td>( k_{VFA} )</td>
<td>= 3.5 g l(^{-1} ), ( K_{DEP} ) = 0.2 mg l(^{-1} ), ( K_{MEP} ) = 0.15 mg l(^{-1} ), ( K_{DBP} ) = 0.005 mg l(^{-1} ),</td>
</tr>
<tr>
<td>( K_{MBP} )</td>
<td>= 0.005 mg l(^{-1} ), ( K_{DEHP} ) = 0.001 mg l(^{-1} ), ( K_{M2MEP} ) = 0.001 mg l(^{-1} ), ( Y_{1} ) = 0.1 g g(^{-1} ),</td>
</tr>
<tr>
<td>( Y_{2} )</td>
<td>= 0.1 mg mg(^{-1} ), ( K_{1} ) = 0.04 g l(^{-1} ), ( K_{2} ) = 0.065 g l(^{-1} ), ( b ) = 0.23 week(^{-1} ) g l(^{-1} ),</td>
</tr>
<tr>
<td>( q_{1} )</td>
<td>= 0.09 L week(^{-1} ), ( q_{2} ) = 0.03 L week(^{-1} ),</td>
</tr>
<tr>
<td>( D_{VFA} )</td>
<td>= 0.7 week(^{-1} ), ( H^{<em>} ) = 10(^{-7} ) g l(^{-1} ), ( B_{U}^{</em>} ) = 0.5 g l(^{-1} ),</td>
</tr>
<tr>
<td>( VFA^{*} )</td>
<td>= 0.001 g l(^{-1} ), ( B_{VFA}^{<em>} ) = 0.0001 mg l(^{-1} ), ( DP^{</em>} ) = 0.001 mg l(^{-1} ), ( MP^{*} ) = 0.001 mg l(^{-1} ), ( L ) = 80 cm</td>
</tr>
</tbody>
</table>
exchange was applied (week 144), methanogenesis commenced in the acid reactor, which enhanced the hydrolysis of the recalcitrant MSW and phthalates. This scenario gives the framework, which governs the possible patterns of phthalate hydrolysis in the model.

**Simulation of phthalate hydrolysis**

The following subsections and Figure 4 illustrate the dynamics of phthalate hydrolysis occurring in the model during co-digestion of MSW over time.

**Initial acidogenesis and dilution period.** DEP, DBP, and DEHP initially accumulated in the leachate at concentrations of about 1,500, 40, and 1 µg l⁻¹, respectively, as a result of the differences in initial sorbed concentrations and desorption rate constants \((k_j)\) of the diesters. According to the model, DEHP and DBP desorbed 6 and 24 times more slowly than DEP. The differences in sorption rate constants for the diesters were even larger. More precisely, DEHP and DBP were respectively sorbed 120 and 24 times more effectively than DEP. This gives that the rate constant was much higher for sorption than for desorption of the diesters, i.e. approx. 4, 300 and 10,000 times for DEP, DBP and DEHP respectively. Most probably, the differences in desorption and sorption are synergetic effects of the fact that DEP, compared to DEHP, is more soluble (approx. 1 g l⁻¹ compared to 3 µg l⁻¹; Staples et al., 1977) and is desorbed from more easily degraded matrices (e.g. plastic cellulose polymers and fragrances) than DEHP (PVC plastics). These differences generated a decrease of initially accumulated DEP concentration during the dilution period, while DBP remained at a stable and low level. At the end of the dilution period (week 52), the concentrations of DEPs and DEP had decreased 3.5 and 3 times, respectively, whereas the DBP concentration was essentially unchanged because desorption of this phthalate had compensated for the dilution. Regarding DEHP, dilution had no effect on the levels of either sorbed or soluble concentrations.

![Figure 3](https://iwaponline.com/wst/article-pdf/53/8/119/432796/119.pdf)

**Figure 3** Time profiles of VFA concentrations, pH levels, methanogenic biomass concentrations in the leachate averaged over the reactor volume, and the total biogas volume released. The circles represent values measured in the actual reactor and the lines are results obtained using the model.
Acidogenic conditions. After termination of the dilution, a new equilibrium was established between DEPs and DEP at lower concentrations (2,000 and 500 μg/L, respectively). However, the DEP concentration increased slightly as a result of further desorption of DEPs, whereas the levels of the other diesters remained constant. Worthy to note: during the stable acidogenic phase, the desorption/sorption equilibria remained constant for all three diesters. This indicates that the release of the diester from the matrices is strongly dependent on scavenging mechanism such as dilution or degradation (see discussion further down).

Methanogenic conditions. Initiation of leachate exchange (week 144) enhanced the hydrolytic activity associated with the recalcitrant waste and phthalate diesters (Figure 3). Compared to the acidogenic conditions, significant reduction of sorbed diesters first occurred when degradation of the recalcitrant waste began and methanogenic conditions were established (Figure 4). As a result, the concentrations of sorbed diesters, DEP, and DBP were lowered due to hydrolysis which generated monoesters. The desorption process became more intense and continued until the pool of sorbed diesters was emptied (DEPs) or substantially decreased (DBPs and DEHPs). Under the initial methanogenic conditions, the model generated higher concentrations of monoesters (MEP, MBP, and MEHP approx. 1,000, 3,000, and 350 μg/L, respectively) than diesters (DEP, DBP, and DEHP approx. 600, 40, and 1 μg/L, respectively). This was due to the relatively high initial concentrations of co-existing sorbed diesters (DEPs, DBPs, and DEHPs 7,000, 14,000, and 7,000 μg/L, respectively) and a substantially higher maximum specific rate of utilization of diesters than monoesters (ρm2 ≫ ρm1), giving ratios of 20, 25, and 158 ρm2/ρm1 for the ethyl, butyl, and 2-ethylhexyl esters, respectively. At the end of the

Figure 4 Time profiles of concentrations of sorbed diesters (PDs), soluble phthalic acid diesters (PD), phthalic acid monoesters (PM), and phthalic acid ester (PE) degrader biomass in the leachate averaged over the reactor volume. Circles are measured values and the lines are the model results.
experimental period, all the DEP seemed to have been degraded, leaving residual DBP, and the main part of the DEHP, in the bulk waste. A relatively high level of DEHP was observed in the leachate in the later stage of the experiment, but the model could not describe this phenomenon, probably because the DEHP in the leachate occurred on colloids or particles (cf. Jonsson et al., 2003), and not as a soluble in the liquid phase, as was assumed in the model setup.

**Kinetic coefficients of phthalate transformation.** The 1-D model resulted in prolonged steady-state concentration values for soluble diesters during the acidogenic phase (up to week 144) due to the equilibria between the physico-chemical desorption and sorption processes. During the acidogenic phase, only physico-chemical processes (i.e., desorption/sorption and dilution) affected the levels of diesters. The maximum coefficient of the rate of utilization of DEHP ($r_{m2DEHP} = 49 \text{ week}^{-1} \text{mg mg}^{-1}$) was much higher than the corresponding coefficients of DEP and DBP (6.3 and 7.0 week$^{-1}$mg mg$^{-1}$, respectively). This was probably due to the effect of the higher level of microbial, and thus hydrolytic, activity occurring later in the methanogenic phase, as compared to earlier in that stage when DEP and DBP were already under attack.

**Conclusions**

The ratio between desorption and sorption kinetic constants, as well as the initial value of sorbed diesters, generated an equilibrium of the sorbed and soluble diesters. The 1-D model showed that steady-state concentrations of soluble diesters existed under acidogenic conditions, when only physico-chemical desorption and sorption processes acted on the compounds. When methanogenic conditions were induced in the acidogenic landfill simulation reactor, the hydrolytic inhibition of both recalcitrant waste and phthalates ceased. The hydrolysis of diesters significantly decreased the concentrations of these compounds and enhanced the process of physical-chemical desorption from the matrix, where most of the diesters were bound. In a landfill perspective, the release of phthalate diesters from the waste depends on: (i) the nature of the diester, (ii) the degradability of its original matrix, and (iii) the overall degradation phase of the landfill. Furthermore, the released diesters are not hydrolysed to their corresponding monoesters until methanogenic conditions establish. Therefore, from the perspective of landfill management, it is essential to ensure that the organic wastes disposed of as soon as possible reach neutral methanogenic conditions e.g. by the recirculation of leachates. Such an approach would make it possible to avoid the desorption-derived leaching of anthropogenic compounds like phthalates from landfills. Precautions should also be taken to circumvent the potential release of toxic and often more soluble intermediates during the degradation.

**Acknowledgements**

Patricia Ödman is gratefully acknowledged for linguistic correction of the manuscript.

**References**


