

## **Chemical and biotic processes affecting the fate and transport of trace organic contaminants in municipal landfills: a discussion**

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### **Abstract**

During sequential anaerobic digestion of municipal wastes, distinct biogeochemical phases occur which show different capabilities for transforming halogenated hydrocarbons and phthalic acid esters (PAE). Halogenated hydrocarbons within the municipal waste are reductively dehalogenated during methanogenetic conditions. For example Lindane, a chlorinated hydrocarbon, is degraded during acidogenesis, although slowly, as well as during methanogenesis. The observed transformation capabilities are a pertinent feature of methanogenetic leachate, probably due to prevailing low redox potential and/or microbial activities. In this biochemical environment short-chain PAEs can be degraded by base-catalysed hydrolysis or by microorganisms that enzymatically split the side chains. However, there is no cleavage of aromatic rings. Long-chain PAEs are neither degraded abiotically nor by microorganisms. Leachate transports halogenated hydrocarbons and PAEs, either adsorbed on particulate matter or in a dissolved phase. Dissolved organic macromolecules or colloids, mainly humic-like substances, enhance the solubility of hydrophobic PAEs and halogenated hydrocarbons. Anaerobic conditions in landfills may inhibit extensive sorption of polar phenols, thus enhancing their mobility. Chlorofluorocarbons (CFCs) are model substances representing the vapour phase mobility of volatile organic carbons in landfills. By means of model calculations using one-dimensional diffusion models, we were able to estimate the amount and rate of outgassing of CFCs. The model was validated with measured vertical CFC-concentration profiles.

### **Keywords**

Phthalic acid esters; halogenated hydrocarbons; municipal waste; sequential anaerobic digestion; chemical and biological transformation; chemodynamics.

## Introduction

The debate about the long-term ecological risks associated with municipal landfills needs—amid all the acrimony—an understanding of the basic chemodynamics and transport processes of pollutants. Therefore, I here describe the results of investigations into the behaviour of organic trace pollutants in municipal landfills, which function as biogeochemical reactors.

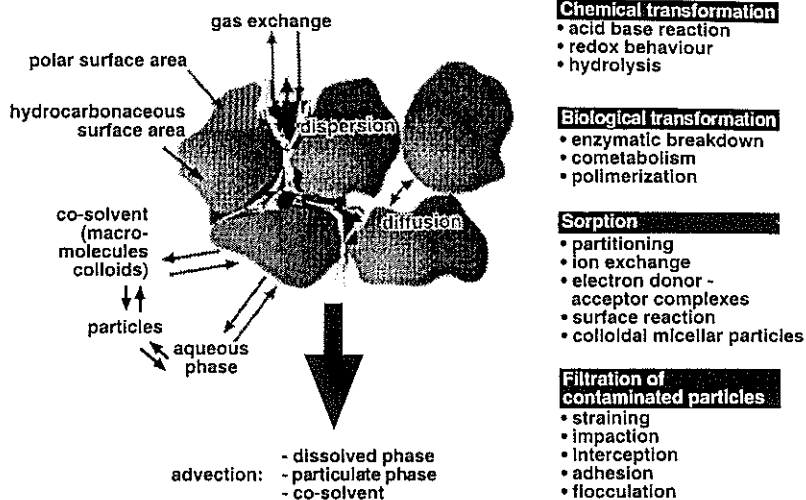
Figure 1 shows a summary of the exchange and transformation processes of trace organic pollutants in municipal landfills. A number of important transport and chemodynamic processes affect the behaviour of trace organic pollutants within the landfill. However, since at any time no single process acts alone, the behaviour of the organic chemicals cannot definitely be attributed to a single contributing chemical process.

Chiou *et al.* (1985) described the sorption of non-ionic organic compounds onto soil humus and minerals: I will transfer their reasoning to the chemodynamic behaviour of non-ionic organic pollutants on waste material, and further to hydrophobic ionizable organic chemicals (e.g. phenols) and mixtures of water and organic solvents (e.g. DOC) (Sawhney, 1989; Rao *et al.* 1989). Wet surfaces of waste material that has undergone varying diagenetic development and is coated with organic material should linearly, and without competition between different solutes, take up non-ionic organic compounds from water into the waste organic matter by means of solute partitioning. However, decreasing with increasing dipole interaction of water with minerals, non-ionic organics will be adsorbed on the minerals' surfaces by entropy-driven processes. This process leads to competition between the various adsorbates in a mixture.

Sawhney (1989) discussed the sorptive behaviour of phenols as an example of hydrophobic ionizable hydrocarbons. Partition coefficients predicted from water solubility or water-octanol partitioning are lower than those measured in sediment-water systems. He explained this discrepancy by sorption processes of phenols on soil and sediment surfaces, which are related to specific interactions, such as by H-bonds, rather than by general hydrophobic mechanisms. Furthermore, phenolic compounds with a  $pK_a$  lower than the pH of waste leachate will dissociate, and the resulting phenolate has a much greater solubility than the protonated form.

Colloidal and macromolecular compounds in landfill leachate enhance the solubility of trace organic pollutants e.g. by forming colloidal unicles, which provide hydrocarbon-like regions in the water and act as co-solvents (Totsche *et al.* 1996).

In municipal landfills the prevalent biodegradation is under anaerobic conditions. Following the oxidation potential, there is a progressive series of alternative electron acceptors in the landfill environment (Atlas and Bartha,



**Figure 1** – Exchange and transformation processes of trace organic pollutants in municipal landfills.

1993). Anaerobic degradation pathways in municipal landfills have not been as extensively studied as the pathways for aerobic degradation of trace organic pollutants (Pecher *et al.* 1995; Pohland *et al.* 1998; Bauer *et al.* 1998). Many trace organic pollutants that are easily degraded aerobically, such as polycyclic aromatic hydrocarbons, are difficult to break down anaerobically. However, in at least the chlorinated hydrocarbons, the chlorine substituents are removed more rapidly under anaerobic conditions.

Kromann and Christensen (1998) studied the degradability of organic chemicals in landfill environments. Under stabilized anaerobic conditions with low methane production, they found no degradation of tetrachloroethene, BTX, naphthalene and anilines, but 1,1,1-trichloroethane (1,1,1 TCA), tetrachloromethane (TeCM), nitrobenzene, 2-methylnitrobenzene, 4-methylnitrobenzene, o-dinitrobenzene and m-dinitrobenzene were transformed. They observed partial transformation of ethylbenzene. Further, abiotic processes seemed to be important for the transformation of 1,1,1 TCA, TeCM and important in part for nitroaromatic compounds. The authors point to the fact that leachate with very low methanogenic activity may result in a low degradability of the organic chemicals.

The results of the Danish study are deduced from intensive field site investigations. In contrast, the understanding of pollutant behaviour presented

in this study is predominantly derived from an experiment-based approach, which draws together the results of a wide range of laboratory work in Bayreuth, Germany. The two approaches, of course, have their pros and cons.

During sequential anaerobic digestion of municipal wastes, distinct biogeochemical phases occur, with different capabilities of transforming trace organic pollutants.

### Chemical breakdown: hydrolysis

Hydrolysis is an abiotic decomposition process. For example, in a reducing environment in landfills, organic substances with ester bonds, such as phthalic acid esters (PAE), can be hydrolytically decomposed without the influence of microorganisms. The hydrolysis rate of esters is dependent on the pH, which differs at different stages of fermentation. We can assume (see Figs. 2 and 3) that the decomposition of dimethyl phthalate (DMP) is caused by base-catalyzed hydrolysis (Schwarzenbach *et al.*, 1993). We performed these experiments strictly abiotically (Figs. 2 and 3; Bauer *et al.* 1998). Long-chain PAEs are not hydrolysed at pH 9. This indicates that abiotic hydrolysis further depends on the length of the side chain (cf. Wolfe *et al.*, 1980).

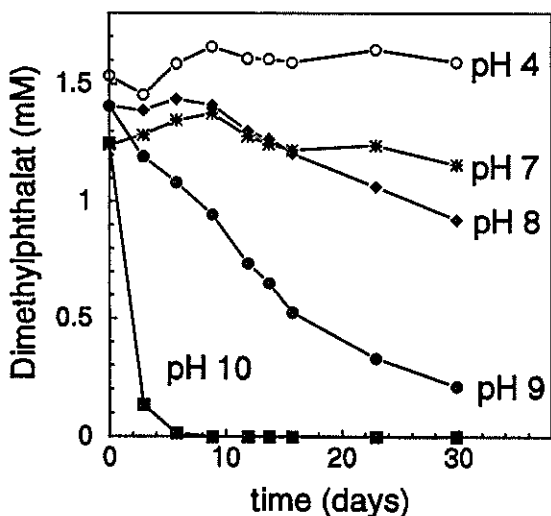
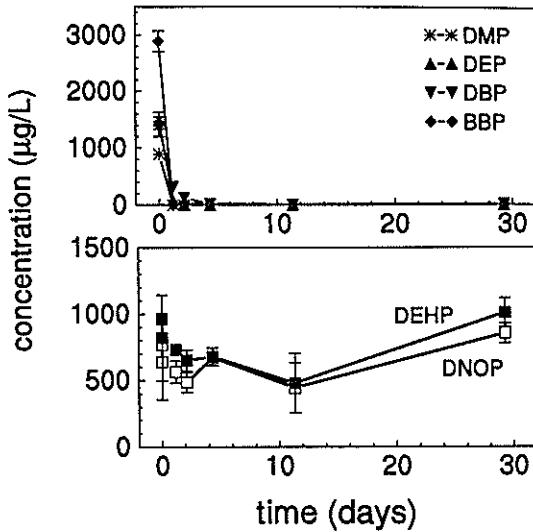


Figure 2 – Hydrolysis of DMP at various pH values, (Bauer *et al.* 1998).

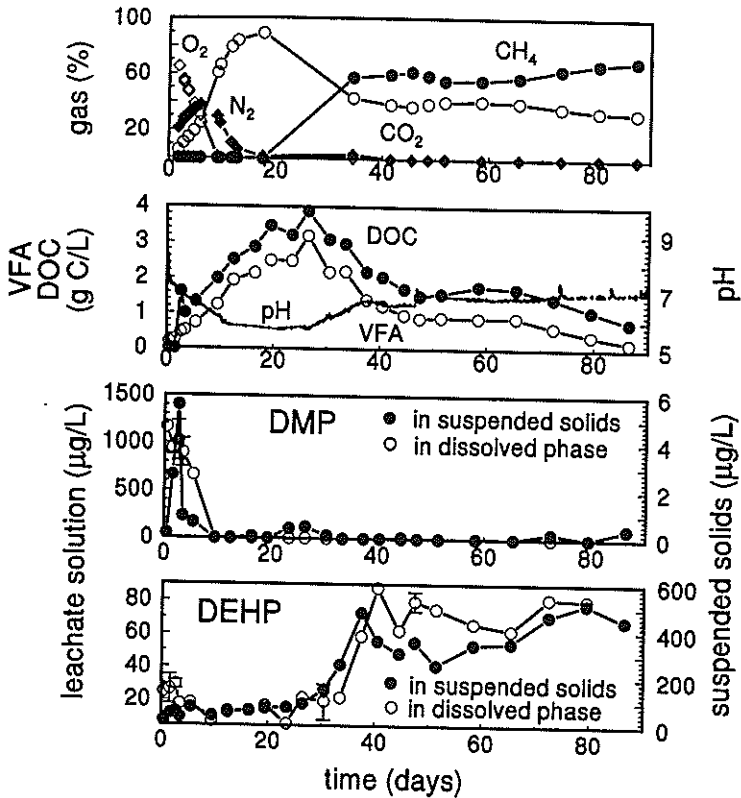


**Figure 3** – Hydrolysis of various PAEs at pH 9 (DMP = dimethyl phthalate, DEP = diethyl p., DBP = dibutyl p., BBP = benzyl butyl p., DEHP = (2-ethyl-hexyl) p., DNOP = di-n-octyl p.), (Bauer *et al.*, 1998).

## Biological breakdown

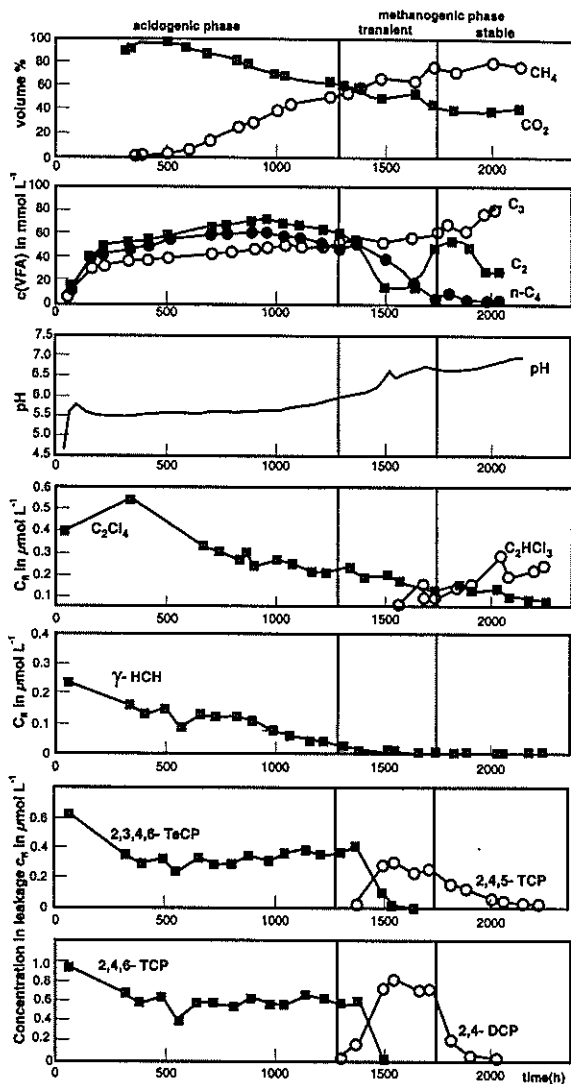
During sequential anaerobic digestion of municipal wastes, there are distinct biogeochemical phases, which show different capabilities for transforming halogenated hydrocarbons or PAE. We selected these two groups of compounds to explain some pathways of biological breakdown in municipal waste. We performed our experiments in a laboratory waste lysimeter filled with shredded household waste and saturated with water, which was circulated at a constant flow rate. We explained the operation, condition, and analyses in detail elsewhere (Pecher *et al.* 1995; Bauer, 1997).

In both experiments (Figs. 4 and 5) we observed an acidogenic phase with low pH, within which organic substrates were hydrolysed and were fermented to volatile fatty acids (VFA). The transition from the acidogenic to the methanogenic phase was indicated by a marked decrease of the sum of volatile fatty acids, with a resulting increase in pH and alkalinity. This leads to an improvement in the environmental conditions for methanogenic bacteria and an increase of methane production. Within the final methanogenic phase, the characteristic biogas composition of municipal landfills (60 % CH<sub>4</sub>, 30 – 40 % CO<sub>2</sub>) can be observed.



**Figure 4** – Variation of DMP and DEHP in leachate during the fermentation sequences in bioreactors (Bauer *et al.*, 1998).

Chlorophenols and tetrachloroethylene (Fig. 5) within organic-rich waste substrates are reductively dehalogenated during methanogenic conditions. Lindane, a chlorinated hydrocarbon commonly used in households and gardens, is degraded during acidogenesis as well as during methanogenesis. However, its degradation in methanogenic leachates is faster by a factor of 10. The poor transformation potential during acidogenesis, compared to that during the subsequent transient methanogenic and stable methanogenic phases, cannot be explained by inadequate acclimation of prevailing microorganisms to the organochlorines. The observed transformation capabilities are a pertinent feature of methanogenic leachates, probably due to the prevailing low redox potential and/or microbial activities (not necessarily methanogenic).

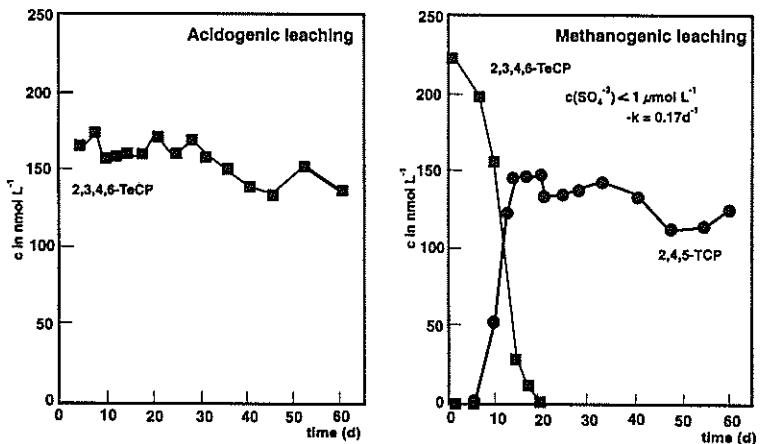


**Figure 5** – Synoptic representation of process variables for separation of sequential degradation phases during the reactor experiment. Concentrations of VFA ( $\text{C}_2$  = acetate  $\text{C}_3$  = propionate,  $n\text{-C}_4$  = n-butyrate),  $\text{C}_2\text{Cl}_4$ , lindane, 2,3,4,6-TeCP, 2,4,6-TCP and pertaining metabolites are plotted as a function of time, (Pecher *et al.*, 1995).

The fate of two PAEs with different properties during the fermentation sequence of domestic waste in bioreactors is shown in Figure 4. DMP ( $\log k_{\text{ow}} = 1.53$ ) rapidly disappeared from both the dissolved and adsorbed phases of leachate, whereas the concentrations of DEHP increased fourfold at the transition period of volatile fatty acid (VFA) production to methanogenesis. In the bioreactor leachates DEHP was predominantly transported adsorbed onto suspended matter. I will explain this particular transport mechanism in the section on Water/solid waste partitioning.

### Dehalogenation potential

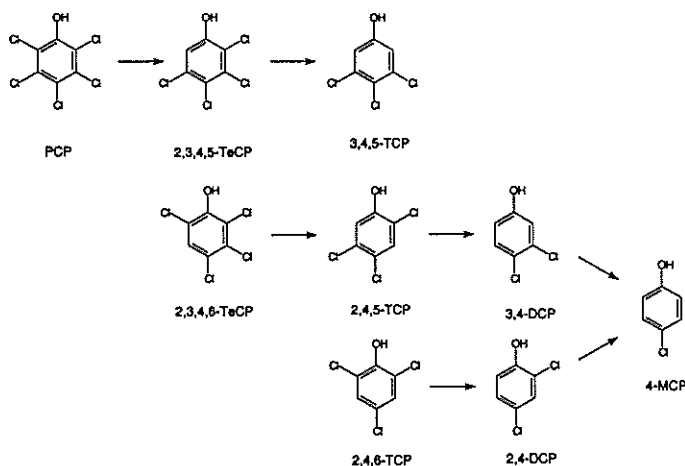
In Figure 6 we (Pecher *et al.* 1995) show changes in the concentration of 2,3,4,6 TeCP (tetrachlorophenol) vs. time in leachate of the acidogenic and the methanogenic phases in closed bottle tests. In acidogenic leachate we did not observe any significant transformation, whereas in methanogenic leachate a rapid decrease with no lag phase occurred. Equally we did not observe any significant breakdown of other chlorinated aromatic hydrocarbons (PCP, lindane, 2,4,6-TCP (trichlorophenol), 2,3,4,5-tetrachloro-anilin (TeCA, not shown) within the first 40 days of incubation in acidogenic leachate. In methanogenic leachate lindane was broken down rapidly, but not 2,3,4,5 TeCA. 2,3,4 TeCA appeared in methanogenic leachate as a metabolite only after 50 days.



**Figure 6** – Concentrations of 2,3,4,6-TeCP (parent substrate) and 2,4,5-TCP (metabolite) vs. time in leachates originating from acidogenic and methanogenic stabilisation phases (closed-bottle test), (Pecher *et al.*, 1995).



Figure 7 shows the pattern of stepwise reductive dehalogenation of three chlorophenols. The phenols are preferably dehalogenated in the ortho-position. Pecher *et al.* (1995) explain in more detail the transformation reaction of 2,3,4,6-TeCP to 2,4,5-TCP where only position 2 is dechlorinated.



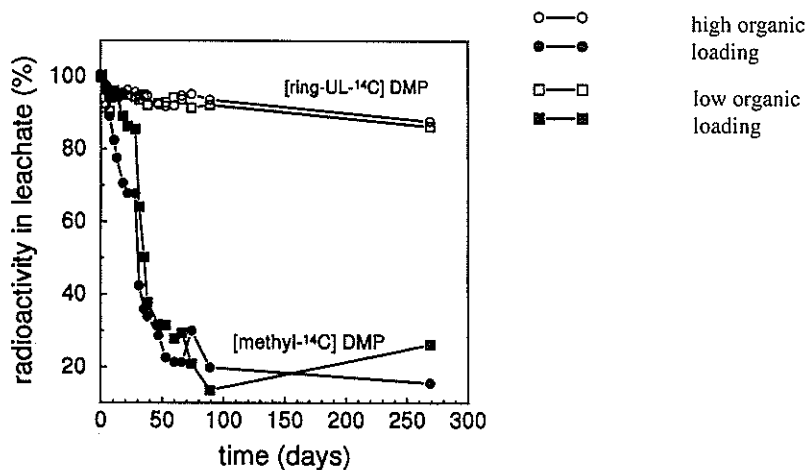
**Figure 7** – Pattern of stepwise reductive dehalogenation of pentachlorophenol (PCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and 2,4,6-trichlorophenol (2,4,6-TCP) in methanogenic leachate, (Pecher *et al.*, 1995).

## Can microorganisms degrade PAEs in anaerobic landfill environments?

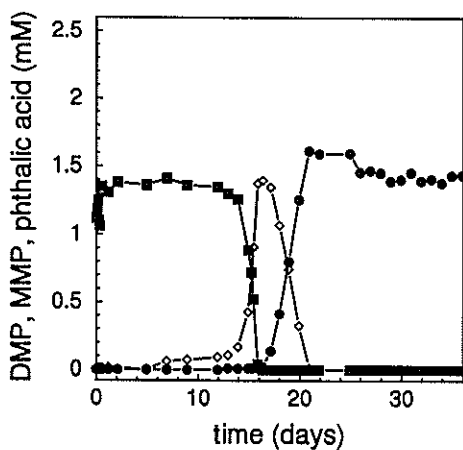
We spiked leachates from bioreactors with DMP of which, in one experiment, both rings were  $^{14}\text{C}$ -labelled and, in another experiment, both side chains were labelled (Fig. 8). After 270 days the ring-labelled DMP still showed 90 % of the initial radioactivity, in contrast to the DMP with labelled side chains, which was transformed in about 100 days. We deduce from this experiment that, under anaerobic conditions, there is no cleavage of the aromatic ring, only the side chain (in this case -  $\text{CH}_3$ ) is split off (cf. Nozawa and Maruyama, 1988).

### Side chain split off

The anaerobic biotransformation of DMP produces monomethyl phthalate (MMP) in a first step and phthalate acid (Fig. 9) in a succeeding step. These



**Figure 8** – Anaerobic transformation of differently labelled DMP (Bauer *et al.*, 1998).



**Figure 9** – Anaerobic transformation sequence of DMP ■: DMP, ◇: MMP, • phthalic acid (Bauer *et al.*, 1998).

reactions are carried out by enzymes that are located within the bacteria cells or are extruded into the surrounding leachate. By separating the bacteria from the leachate, we observed that only one side chain was split off by extracellular enzymatic hydrolysis. The second side chain was split off only in the presence of bacteria.

## Phase distribution

### Water/atmosphere partitioning

Pecher *et al.* (1995) measured the abundance of  $C_a$  in air and of  $C_w$  in leachate equally as moles per litre for two volatile chlorinated hydrocarbons. They obtained the dimensionless Henry's Law constants  $k_H' = C_a/C_w$  ( $k_H' (C_2Cl_4) = 0.59$  and  $k_H' (C_2HCl_3) = 0.37$ ), which are in agreement with data in the literature (Thibodeaux, 1979). This leads to the assumption that these compounds were in equilibrium between the gas phase and the liquid phase and that  $V_w \ll V_a k_H'$ , resulting in  $V_{tot} \sim V_w$ . This indicates that the transfer is dominated by the water boundary layer ( $V_w, V_a, V_{tot}$  = water, air and total transfer velocities respectively.)

However, the following balance of  $C_2Cl_4$  (Pecher *et al.* 1995) points to the assumption that the transfer of volatile chlorohydrocarbons in a three-phase system (i.e., including solids) can be considerably slowed down by adsorption into the solid waste matrix. For example, after 98 days we found in the vapour phase:  $m(C_2HCl_3) = 1.6\%$ , in the leachate remained:  $m(C_2Cl_4) = 0.2\%$ ,  $m(C_2HCl_3) = 0.7\%$ . Assuming that we detected all metabolites (we did not find other chlorohydrocarbons in the atmosphere) the rest must have been adsorbed. We, however, did not check this analytically.

### Water/solid waste partitioning

Leachates contain dissolved organic matter (DOC) that can enhance the solubility of trace organics and thus facilitate their transport in the liquid phase (cf. Kile and Chiou, 1989). The fraction of humic substances in leachates of our experiments reached 10% per weight of the DOC present. These macromolecules are well suited to adsorb, for example, PAEs such as DEHP, which are otherwise only slightly soluble, and which, as a result, are then co-transported along with the leachate.

By means of laboratory experiments we demonstrated that DEHP can only be washed out of solid waste by landfill leachate, but not by distilled water or solutions of inorganic ions or volatile fatty acids. Humic-like substances seem to be responsible for the mobility of hydrophobic phthalic acid esters, as there is a significant positive correlation between PAEs and humic acids (Bauer and Herrmann, 1998). This hypothesis was confirmed by an experiment where landfill leachates were spiked with  $^{14}C$ -labelled

DEHP. After ultrafiltration, 90–98% of  $^{14}\text{C}$ -DEHP was found associated with the highest molecular masses (50 k – 100 k Dalton). Thus, soluble macromolecular organic substances in the leachate are able to mobilize organic pollutants with very high octanol/water partition coefficients, such as DEHP ( $\log k_{ow} = 7.48$ ), from the solid waste matrix.

### Chemodynamics of polar trace organic pollutants

Sawhney (1989) summarizes his and other work on the behaviour of phenols, out of the group of ionizable hydrophobic hydrocarbons, in soils and landfills. He points out that, despite their extensive sorption and polymerization by soils, sediments, and clays, phenols are present in large amounts in landfill leachate. He suggests that the anaerobic environment within a landfill hinders their sorption and polymerization and, as a result, leads to higher mobility. Sawhney (1985) showed that uptake and polymerization of phenols were inhibited in an  $\text{N}_2$  environment.

### Vapour phase transport

As an example of vapour phase transport of volatile trace organic pollutants, I present the results of a study on mobility of chlorofluorocarbons (CFC) in and out of a landfill site by Haderlein and Pecher (1988 a, b). They sampled two vertical profiles from a shredder waste area with high CFC-contamination, one immediately after deposition of the waste and the other five days later (Fig. 10). The steep increase of  $\text{CF}_2\text{Cl}_2$  with depth compared with the lower concentration and weak increase 5 days later are strong evidence for a rapid emission of CFC into the atmosphere.

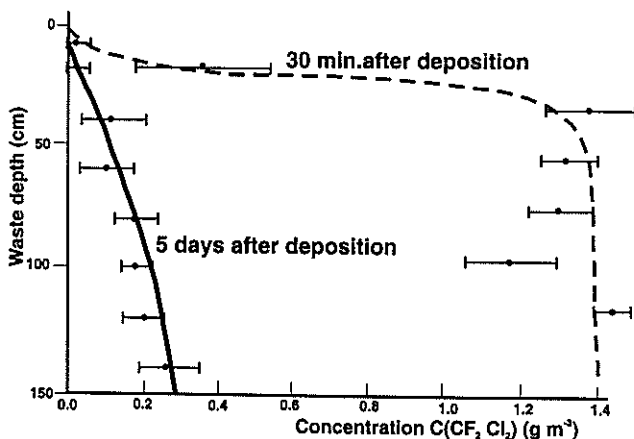
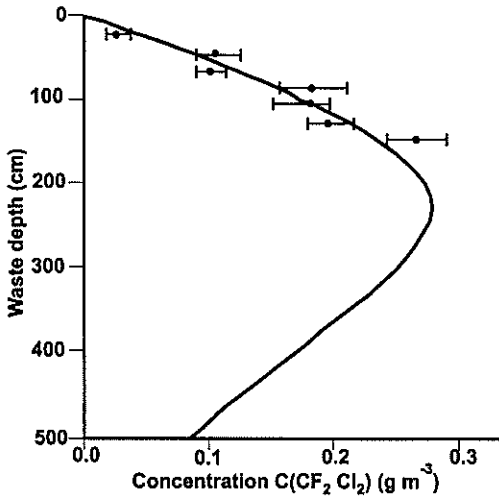


Figure 10 – Measured vertical concentration profiles of  $\text{CF}_2\text{Cl}_2$  in landfill air of shredder wastes (Haderlein and Pecher, 1988 b).

In order to estimate the amount and rate of outgassing CFCs, Haderlein and Pecher (1988 a, b) used several one-dimensional diffusion models with different boundary conditions.

Figure 11 compares a measured depth profile five days after waste deposition with model calculations.



**Figure 11** – Comparison of measured and calculated landfill air concentration profiles five days after waste deposition (Haderlein and Pecher, 1988 b).

Their calculations show that two days after waste deposition, more than 50% of the supply of  $\text{HCF}_2\text{Cl}_2$  in landfill gas is lost due to diffusion into the atmosphere. As  $\text{HCF}_2\text{Cl}_2$  is a chlorofluorocarbon in a medium range with respect to molecular weight, we expect other chlorofluorocarbons to behave in a similar way.

## Conclusion

Diagenetic processes cause a sequential anaerobic digestion of municipal waste, with distinct biochemical phases. Biochemical transformation of trace organic pollutants is dependent on redox potential, acid-base reactions, and microbial activities. Within a landfill, the location of a pollutant molecule with respect to available exoenzymes (and co-factors which may or may not be washed away) decides its biochemical fate. The mobility is dependent on Henry's Law constant and the water-octanol partition coefficient of the pollutant and the sorbent-sorbate-solvent-co-solvent system, which changes

during waste diagenesis, and finally the saturated and unsaturated flow within the landfill, which may substantially affect the transport behaviour of conservative and sorbing solutes (Fesch *et al.*, 1998).

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