BEHAVIOUR OF PVC PRODUCTS IN LANDFILLED MUNICIPAL SOLID WASTE AT DIFFERENT TEMPERATURES

Modular Environmental Test System (METS) Study
in Support of the Research Project
»Long-term behaviour of PVC products
under soil-buried and landfill conditions«

Jörgen Ejlertsson[1], Maritha Hörsing[1]
& Ivo Mersiowsky[2]

[1] *Department of Water and Environmental Studies, Linköping University, Sweden*

[2] *TUHH Technologie GmbH (TuTech) – Integrated Management*
at the Technical University of Hamburg-Harburg, Germany

SUMMARY AND CONCLUSIONS

General Remarks

The *Modular Environmental Test System (METS)* provides an appropriate method for the investigation of the behaviour of PVC products in landfilled municipal solid waste at different temperatures. The experimental set-up and procedure qualify for a standardised test. The METS complements the landfill simulation in lysimeters and enables the operation of a large number of parallel assays at a range of temperatures exceeding the capacities of regular climate rooms.

In spite of the careful composition of a model waste from “pure” materials, a considerable background of the target substances was detected in both leachate and solids. In general, concentrations of both phthalic and organotin species were found to be considerably higher than observed with the landfill simulation assays in lysimeters (Mersiowsky and Ejlertsson 1999). Even values from the blank control METS units often exceed the concentration ranges exhibited by lysimeters spiked with PVC products: this demonstrates the intense leaching of ubiquitous contaminants from waste, regardless of the presence of PVC products.

The quality of the leachate differed from mature landfills and lysimeters in that the organic pollution (TOC) was rather high throughout the experimental period, implying a substantially higher carrying capacity for hydrophobic compounds (Mersiowsky and Ejlertsson 1999). The METS set-up promoted leaching effects due to the water-logged waste and the substantially higher organic pollution of the leachate. This outcome underlines the importance of the leachate matrix and its carrying capacity as a sensitive indicator of test conditions. Comparability between different tests is given for the fate of PVC products and overall budgets of target substances, but concentrations in leachate vary widely on a micro-scale.

The METS set-up allows for an assessment of the maximum emission potential. In order to derive a risk assessment, these values would need to be considered in conjunction with their respective probabilities in pertinent case studies. Predicted environmental concentrations (PEC) of the target substances have already been presented on the basis of measurements at real-world landfill sites (Mersiowsky and Ejlertsson 1999). These real-world measurements in conjunction with the lysimeter assays of the Basic Project and the present METS assays provide a comprehensive picture about the fate of PVC products and their additives under landfill conditions.

A discoloration at temperatures of 55 °C and above was observed for all of the investigated PVC products. In case of the rigid PVC foil, a discoloration occurred already at 37 °C.

The behaviour of the PVC matrix and its additives alters considerably upon glass transition which occurs at approximately 60–80 °C for unplasticised PVC. Plasticisers, particularly those for low-temperature applications, decrease this glass transition temperature to around 20 °C or even into the sub-zero range. In case of losses of plasticisers from flexible PVC products, this critical temperature increases again. Hence it is assumed that a temperature variation in the range of 20–85 °C includes the transition and thus produces non-linear effects.

Additionally, the microbial populations undergo severe alterations at changing temperatures. When progressing through the range of 20–85 °C, several local optima of microbial activity exist. The introduction of aerobic conditions microflora alters the redox state and the biochemical conditions altogether.

The non-linear causality and complex interdependencies of the processes prevent simple predictions of landfill behaviour. As a consequence, an experimental set-up cannot employ higher temperatures with the intention of accelerating landfill processes. Some extrapolation due to continuity of effects may be permissible within a narrow range of temperatures, unless glass transition takes place. Otherwise each configuration of parameters (temperature and redox state) constitutes a rather specific case of its own. The solution to this problem is a scenario analysis, in which the observed effects need to be related to their specific likelihood and relevance.

Behaviour of Plasticised PVC Products and Fate of Plasticisers

Losses of plasticisers DEHP and BBP from the PVC flooring at temperatures 20–37 °C were not observed or somewhat inconclusive (possibly a considerable loss of BBP occurred at 37 °C). Minor losses were detected at 55 °C, and considerable losses were observed at 70 °C as well as under aerobic conditions at 85 °C (significantly continuing under anaerobic conditions at 55 °C).

In case of losses of plasticisers, there was no corresponding release of phthalates into the leachate. Rather there were indications of a sorption of phthalates to the solid waste matrix (particularly DEHP) as well as of an *in-situ* biodegradation at the surface of the PVC flooring or in the waste matrix (Mersiowsky and Ejlertsson 1999).

The occurrence of degradation products (phthalic monoesters and phthalic acid) in the leachate confirmed the relevance of biodegradation for the removal of phthalates. In some cases at thermophilic temperatures, the degradation of phthalic acid may have been rate-limiting step. In general, however, a stable methanogenic microflora appears to be capable of a complete biodegradation of phthalates (particularly BBP) into biogas.

The possible loss of phthalates and their degradation products via gaseous emissions (or gas-borne condensate or aerosols) is a conjecture that cannot be supported by the present investigation.

Behaviour of Organotin-stabilised PVC Products and Fate of Organotin Stabilisers

The release of organotin stabilisers from all of the investigated PVC products was detectable at each temperature (20–85 °C). The concentrations of organotin species in the leachate increased with temperature in most cases, particularly at 70 °C and above.

The flexible butyltin-stabilised PVC flooring gave rise to the highest concentrations of butyltin species in the leachate, both in comparison to the blank control and to the butyltin-stabilised rigid PVC construction sheet. The presence of the methyltin-stabilised PVC foil caused findings of methyltin species in the leachate.

While in several cases the concentrations of organotin compounds in the leachate decreased, findings of total tin account for the tin budget: either organotin compounds were adsorbed to the waste matrix, or they were degraded to inorganic tin.

There was sufficient indication that organotin species are subject to biological or abiotic dealkylation processes: thus, di-and monoalkyltin species from stabiliser compounds (as well as TBT) are successively transformed and possibly mineralised to inorganic tin. The respective capability of microorganisms was addressed in more detail in the ORTEP Extension Project (Mersiowsky and Ejlertsson 2000).

Inorganic tin is reasonably supposed to be subject to biological methylation processes. Some findings suggest that this might be relevant. Gaseous emissions of methylated species cannot be excluded, even though the gas was screened just once, but appeared not to play a considerable role.

CONTENTS

ABBREVIATIONS

BBP — butylbenzyl phthalate

DEHP — bis(2-ethylhexyl) phthalate

ECPI — European Council for Plasticisers and Intermediates (www.ecpi.org)

ECVM — European Council of Vinyl Manufacturers (www.ecvm.org)

ESPA — European Stabilisers Producers Associations

EuPC — European Plastics Converters (www.eupc.org)

LiU — Linköping University

MSW — municipal solid waste

ORTEP — Organotin Environmental Programme Association

PA — Phthalic acid

PAE — Phthalic acid esters (here: diesters), phthalates

PME — Phthalic acid monoesters

TUHH — Technical University of Hamburg-Harburg

VFA — volatile fatty acids

VI — Vinyl Institute (USA)

1 INTRODUCTION

The present study is intended to expand the findings of the recently concluded three-year research project »Long-term behaviour of PVC products under soil-buried and landfill conditions« (Mersiowsky and Ejlertsson 1999) commissioned by *Norsk Hydro*, *ECVM*, *ECPI*, *ESPA* and *ORTEP*.

In the meantime, the *European Commission Directorate General Environment (DG XI)* had commissioned a similar study into »The behaviour of PVC in landfill« which was conducted by *ARGUS (Berlin)* in association with *Rostock University*. While this third-party project raised a number of relevant questions concerning the behaviour of PVC products in landfills in case of elevated temperatures, the experimental conditions and procedures differed considerably from those employed in the above project, resulting in a lack of comparability.

The main objective of this so-called Add-on Project is to »close this methodological gap« between the procedures established in the two studies. By specifically addressing the impact of increasing temperatures, the two projects shall be linked and complemented, putting the results into perspective and thus enabling a comparative evaluation.

The three year research project »Long-term behaviour of PVC products under soil-buried and landfill conditions« is referred to as the **Basic Project**, and the one year follow-up project »Long-term behaviour of organotin-stabilised PVC products under landfill conditions« commissioned by *ORTEP* and the *Vinyl Institute* (USA) is referred to as the ***ORTEP* Extension Project**. This additional study intended to close the gap is referred to as the **Add-on Project**. For convenience, the *European Commission* study »The behaviour of PVC in landfill« is referred to as the **ARGUS/Rostock Project**.

From the Basic Project the following conclusions were drawn:

- The most important processes affecting PVC products under landfill conditions are leaching and biodegradation. Both effects occur simultaneously, but each may take precedence over the other during certain stages of landfill development. Generally speaking, in the course of the ageing of the landfill body acidogenic leaching occurs initially for months or years, whereupon long-term methanogenic biodegradation prevails for decades or centuries.
- Some uncertainty exists with respect to aerobic conditions which may occur transiently in landfills. The experiments conducted by *Rostock University* (at temperatures around 80 °C, additionally alternating between aerobic and anaerobic conditions) are expected to constitute worst-case conditions.
- The respective additives in the formulation of the PVC compound play a significant role and differ considerably in their behaviour, as is best illustrated by the comparison of the plasticisers DIDP and DINA in the PVC cable (investigated in the Basic Project). Similarly, plasticised and rigid PVC products were found to exhibit different properties.
- Elevated temperatures are expected to increase the malleability of plastic materials and the rates of migration processes. Additionally, a decline in temperature or substantial losses of plasticisers

from flexible products may cause the polymer matrix to undergo glass transition; this altered state would bring about dissimilar physical properties. A non-linear behaviour of the plastic matrix appeared probable.

Since it is hardly feasible to operate laboratory-scale lysimeters at temperatures of 55 °C and above and at the required number of parallel assays, a supplementary small-scale assay was necessary. In contrast to lysimeters which are indispensable for the long-term simulation of landfill conditions, the auxiliary test was designed as an easily expandable series of small units to be operated at a large range of temperatures. Jörgen Ejlertsson and Ivo Mersiowsky have developed the requisite test set-up on the basis of the biocorrosion assays proposed in the Basic Project. Similar to these, the effects are magnified by increasing the contents of PVC in the waste. For validation and comparability of the assays, the PVC flooring from the earlier lysimeter assays was included as a reference product. Additionally, the revised experimental set-up was accepted for the then on-going ORTEP Extension Project instead of the originally planned biocorrosion assays.

The resulting *Modular Environmental Test System (METS)* qualifies for a standardised screening assay. The experimental set-up consists of a series of small glass reactors equipped with manual leachate recirculation and automatic gasometers. Incubation is done either in climate rooms or in small climate units. The inoculum is started up from a mixture of biologically active materials (thermophilic compost, landfill waste and soil) in order to introduce a wide range of microorganisms. The model waste is composed of pure raw materials, comprising all relevant fractions found in household waste. Both the inoculum and the model waste are designed according to a recipe which is easily reproducible.

1.1 Aim of the study

The aim of this study was to generate experimental data on the behaviour of PVC products and their additives at different temperatures, thus allowing a comparative evaluation of results from the Basic Project, the ORTEP Extension Project, and the ARGUS/Rostock Project.

The key questions are therefore:

1. Is there a correlation between temperature (20–70 °C) and the occurrence of PVC additives in landfill leachate?
2. Is there a connection between the landfill conditions – acidogenic or methanogenic – and the occurrence of PVC additives in landfill leachate?
3. If the milieu were changed to aerobic and the temperature increased to 85 °C, which impact would these extreme conditions have on the occurrence of PVC additives in landfill leachate?

1.2 Temperatures in Landfills

The ranges of temperatures vary significantly both in different locations within the same landfill body and between different landfill sites. Generally speaking, the landfill temperature depends primarily upon the ambient temperature. The waste may heat up due to exothermal biochemical or chemical processes, but these so-called »hot spots« are relatively rare. In particular, they may result from aerobic composting processes or auto-catalytic chemical reactions. An early top cover or a waterlogged bottom possibly deter the escape of heat into the surroundings.

A mean temperature around 30 °C is usually a good estimate. A recent landfill joint research programme determined the range of temperatures to be between 18 °C and 55 °C (Figure 1.1), with the statistical mean at 35 °C (Dohmann 1997, reference in Basic Project report).

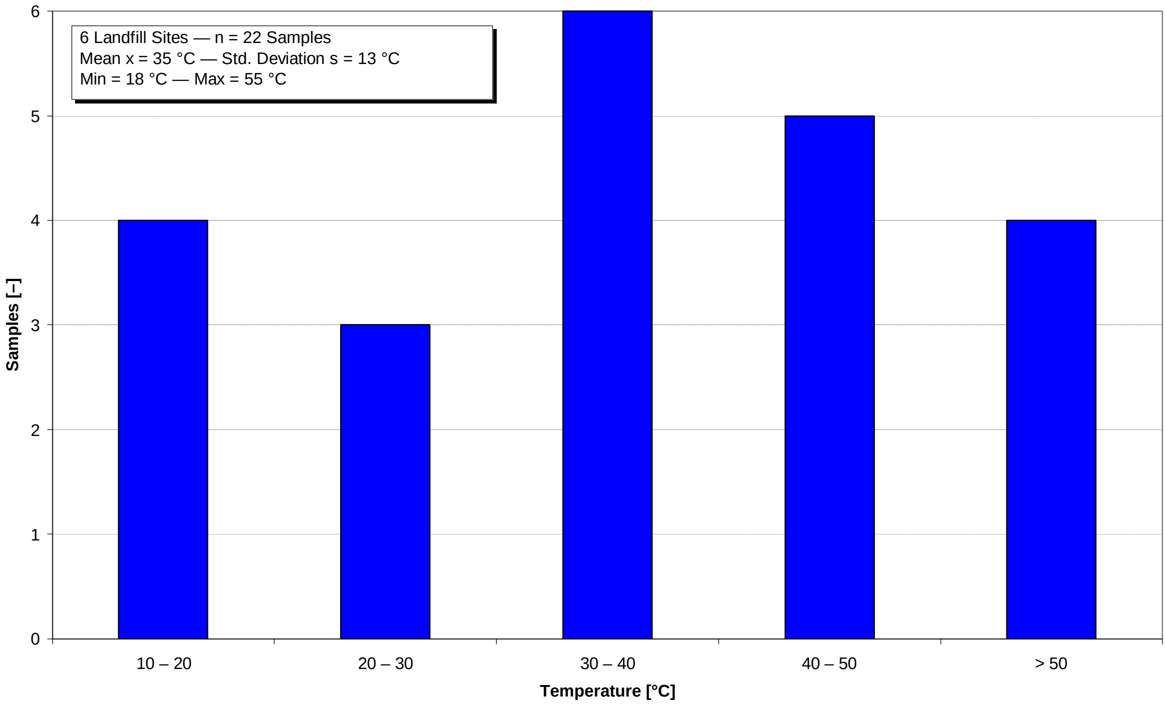


Figure 1.1 Distribution of temperatures in samples from German landfills (Dohmann 1997 cited in Mersiowsky and Ejlertsson 1999)

Temperature is one of the most important environmental factors influencing the growth and survival of organisms (Brock et al. 1994). It can affect living organisms in either of two opposing ways. As temperature rises, chemical and enzymatic reactions in the living cell proceed at higher rates and growth becomes faster. However, above a certain temperature, proteins, nucleic acids and other cellular material may be irreversible denatured. Therefore, as temperature increases within a given range, growth and metabolic function are enhanced up to a point where inactivation reactions set in. Above this point, cell functions fall sharply to zero.

Every living organism has its minimum temperature below which growth no longer occurs, an optimum temperature at which growth is most rapid, and a maximum temperature above which growth is impossible. Although there is a continuum of microbial populations occurring in nature, from those with very low temperature optima to those with high temperature optima, it is possible to distinguish four groups of organisms depending on their temperature requirements (Figure 1.2): psychrophiles with low temperature optima, mesophiles with mid-range temperature optima, thermophiles with high temperature optima, and hyperthermophiles, with very high temperature optima. These distinctions are generalised, however, and ranges should not be taken as absolutely precise temperatures.

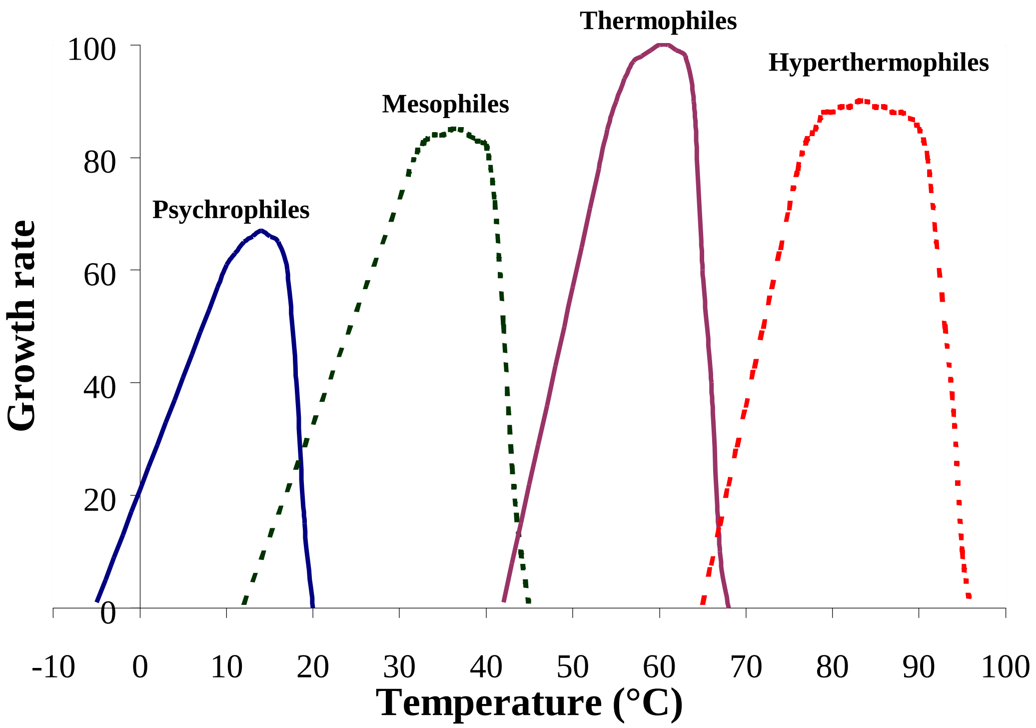


Figure 1.2 Relation of temperature and growth rates of microbial populations: temperature ranges for psychrophiles, mesophiles, thermophiles and hyperthermophiles (adopted from Brock et al. 1994)

1.3 Behaviour of the PVC Polymer Matrix and Plasticisers at Different Temperatures

Depending on the specific formulation of the PVC product, especially the blend of PVC polymer and plasticisers, the polymer matrix possesses the characteristic property of a temperature-dependent glass transition. The term glass transition denotes an alteration of the physical state of the blend from elasticity into rigidity similar to an amorphous (glass-like) compound. The higher the content of plasticisers, the lower the characteristic temperature at which the polymer matrix undergoes glass transition and becomes rigid or brittle (“freezing”). Due to this change of material properties, the polymer compound eventually becomes more inclined to break from strain upon a sufficient decrease of temperatures.

This glass transition temperature is shifted to the lower (less than zero) range by special plasticisers such as DINA which are employed to keep PVC flexible in cold climates. Conversely, the more plasticiser the compound contains the lower the upper critical temperature at which the matrix looses its consistency and the tensile strength decreases.

The glass transition temperature of rigid PVC matrices is in the range of 60–80 °C, whereas the plasticised PVC flooring should be around 20+/–20 °C. Hence, the investigated PVC flooring is assumed to be above the critical temperature in all assays, whereas the rigid PVC construction sheet and the rigid PVC foil very probably undergo glass transition (in reverse) when progressing from 55 °C to 85 °C.

2 MATERIALS AND METHODS

2.1 Investigated PVC Products

Three different PVC products were investigated: a rigid construction sheet (probably for windowframes), a rigid foil, and a flooring. All of these products have been documented and reported earlier. The two rigid products were also the subjects of the ORTEP Extension Project (Mersiowsky and Ejlertsson 1999), (Mersiowsky and Ejlertsson 2000).

The rigid construction sheet was stabilised with a mixture of mono- and dibutyl tin thioester (*Irgastab T22 M*), the composition being shown in Table 2.1. The rigid foil (Table 2.2) was stabilised with a mixture of mono- and dimethyl tin thioester (*Advastab TM-181-FS*).

The flexible PVC flooring was used in the Basic Project (Mersiowsky and Ejlertsson 1999). It was intended to be included by the ARGUS/Rostock Project as well in order to serve as a reference product. The flooring (Table 2.3) was plasticised with a mixture of 15 % bis(2-ethylhexyl) phthalate (DEHP) and 5% butylbenzyl phthalate (BBP). Furthermore, it was stabilised with a mixture of mono- and dibutyl tin thioesters (0.2%), Ca/Zn soaps (1%) and epoxidised soy bean oil (1%).

Table 2.1 Formulation of the rigid PVC construction sheet

Constituent	Amount (phr)	Amount (% wt.)	Annotation
PVC (S-PVC; K = 60)	100	85	
Stabiliser butyltin*1	1.7	1.4	
Modifier (CPE)	8	6.8	
Titanium dioxide	4	3.4	
Others (fillers etc.)	4	3.4	
Totals	117.7	100	

[*1] *Irgastab T22 M* by *Ciba*

Table 2.2 Formulation of the rigid PVC foil

Constituent	Amount (phr)	Amount (% wt.)	Annotation
PVC	100	n/a	
Stabiliser methyltin[*1]	1.1–1.2	n/a	
Others (fillers etc.)	n/a	n/a	
Totals	n/a	n/a	

[*1] *Advastab TM-181-FS* by *Morton*

Table 2.3 Formulation of the PVC flooring

Constituent	Amount (phr)	Amount (% wt.)	Annotation
PVC	100	61	
Plasticiser DEHP	25	15	Analysis by Exxon Lab: 17 % wt.
Plasticiser BBP	8	5	Analysis by Exxon Lab: 6 % wt.
Stabiliser Ca/Zn soaps	2	1.2	
Stabiliser butyltin	0.3	0.2	
Epoxidised soy bean oil	1	0.6	
Others (fillers etc.)	28	17	
Totals	164	100	

2.2 Experimental Set-up

The landfill simulation study of the Basic Project was performed at mesophilic temperatures of 30 °C and 30 °C at TUHH and LiU, respectively. In order to investigate the possible correlation of observed effects with temperature, it appeared instrumental to select a roughly equidistant series of temperature steps that centres around this mesophilic range for comparability and extends upwards to the extreme conditions of aerobic thermophilic composting. Therefore the following series of test conditions was planned: anaerobic 20 °C, 37 °C, 55 °C, 70 °C and aerobic/85 °C.

A total number of twenty METS units were equipped and set-up. For each of the investigated temperatures four units were employed (Table 2.4):

1. one control reactor with model waste only;
2. one reactor containing the rigid construction sheet plus model waste;
3. one reactor containing the rigid foil plus model waste;
4. and one reactor containing the BBP/DEHP plasticised flooring material plus model waste.

It should be noted that all reactors contained the same model waste mixture and the same inoculum (see below).

The anaerobic METS reactors underwent the characteristic landfill development: acidogenic start-up phase, then a long-term methanogenic behaviour. In addition, one set of parallel reactors was operated at aerobic thermophilic conditions by heating and aeration; this situation is comparable with a biological pre-treatment (composting) of the waste.

The conditions in the reactors were monitored by measuring gas production and pH in the leachate. The content of volatile fatty acids (VFA) occurring in the leachate was monitored weekly during the acidogenic phases and then on the sampling occasions for leachate. Samples for TOC and AOX were withdrawn every three or four months for organic leachate pollution (leachate matrix characteristics) and trace contaminants in leachate (target substances: phthalic diesters and monoesters as well as organotin compounds). The METS reactors spiked with the plasticised flooring material were also sampled intermittently for PVC plastics. The samples of flooring were then analysed in order to determine the loss of plasticisers.

Table 2.4 Overview of the METS assays at the different temperatures; spiked METS reactors contain 60 g of the respective PVC product.

METS Unit (PVC Material)	20 °C (Anaerobic)	37 °C (Anaerobic)	55 °C (Anaerobic)	70 °C (Anaerobic)	85 °C (Aerobic)
Control	x	x	x	x	x
Sheet	x	x	x	x	x
Foil	x	x	x	x	x
Flooring	x	x	x	x	x

2.3 Experimental Procedures and Test Conditions in METS

2.3.1 Preparation of Inocula

In “real” landfills inoculation may be effected by a pre-treatment of the waste (aerobic composting) or by co-disposal of different types of waste containing microorganisms (e. g. sewage sludge or soil). Also different waste fractions of the MSW, such as used diapers, flower soil, food residues etc., contain microorganisms.

The constituents of the model waste used in the METS reactors are not refuse, but rather “clean” products with low numbers of relevant microorganisms. In order to introduce a wide range of microorganisms to the fresh model waste and thus accelerate the onset of biological activity, an inoculum was necessary. Additionally, the inoculum had to provide microorganisms active at a wide range of temperatures. It should also contain little or no contamination of the target trace substances (phthalic and organotin compounds).

In order to meet the above requirements, the selected mixture of inocula originated from four different sources: thermophilic household compost, waste from a landfill simulation reactor situated at LiU (LiU-3; cf. Mersiowsky and Ejlertsson 1999), landfilled MSW from Filborna landfill (Helsingborg, Sweden), and garden soil (Table 2.5).

In the Basic Project, the landfill simulation study at LiU did not require inoculation since genuine household waste was used, and the landfill simulation study at TUHH employed the mature anaerobic sludge of a biowaste fermentation plant as an inoculum for the model waste (Mersiowsky and Ejlertsson 1999). It is important to note that the inoculum does not substantially influence the substance inventory of the assays, but first and foremost provides a starting pool of microorganisms, lest a mixed culture suitable to a certain temperature cannot develop.

Table 2.5 Composition of the inoculum for the METS assays: inocula for assays at 20 °C, 37 °C and 55 °C were incubated two months before start-up; inocula for assays at 70 °C and 85 °C were prepared a few days prior to start-up.

Fraction	Wet weight (g)	Remarks
Compost (65–70 °C)	500	
MSW from LiU-3	100	
Soil	200	Garden soil
Landfilled MSW	200	from Filborna (Helsingborg)
Tap water	2000	
Total	3000	

The ingredients were scaled, passed through a sieve (mesh 8 mm) in order to remove larger particles, and added to 5 L glass bottles. Then water was added. During this whole procedure, the vessels were flushed with nitrogen gas. In contrast to the larger bulks of waste handled for landfill simulation in lysimeters, the small amounts employed here are somewhat more sensitive to exposure to oxygen. The flushing with N_2 gas was therefore necessary to preserve an anaerobic atmosphere of the inoculum. The bottles were then closed with a silicon stopper equipped with gas drainage tubing and incubated at the respective temperatures, 20 °C, 37 °C and 55 °C. Due to the late inclusion of an assay at 70 °C in the experimental set-up, the inoculum for this assay was prepared a few days prior to start-up. The same inoculum was applied to the aerated reactors to be operated at 85 °C.

2.3.2 Preparation of the Model Waste

The model waste used in the study consisted of 20 different components (Table 2.6). The recipe closely resembles the model waste which had been employed for the lysimeter study at TUHH in the Basic Project (Mersiowsky and Ejlertsson 1999). Both total solids and moisture as well as substrates are sufficiently similar. There are a few differences in selection of raw materials and precise amounts, but these are considered inconsequential. In both cases, the model waste represents the composition of a generic household waste according to national surveys. By supplying a comparable selection of substrates and trace elements as encountered in landfilled MSW, however reducing the background contamination with the target substances (phthalic and organotin compounds), a sufficiently accurate rendition of landfill conditions is reasonably expected.

Every constituent of the model waste was prepared and then scaled separately according to Table 2.6, then transferred to a 10 L polyethylene bucket.

Apples, potatoes, carrots and bread were cut to 1 x 1 cm pieces with a knife, whereas the yellow peas were added as such. The complete metal fraction was purchased in a grocery store and was added as such, except for the beer cans which were emptied and cut into 0.5 x 1 cm pieces with a scissors (the top and bottom parts were left out). The un-printed paper for newspaper use (a gift from *Östgöta Correspondenten*, Linköping/Sweden) was cut into approximately 2 x 2 cm pieces as was the diaper (*Up & Go*, Libero). The cardboard (*Duka*, Sweden) and milk cartons (*Mellanmjölk*, Arla/Sweden) were cut into 1 x 2 cm pieces. The wood shavings (for pets' coops) were purchased in a grocery store. The plastic fraction consisted of polyethylene granules (gift from *Borealis*, Stenungsund/Sweden). The cotton sheets (ca. 5 years old and washed at least 20 times) were cut into 2 x 2 cm pieces before being mixed into the model waste. The coarse gravel (3 mm) was of the type used on frozen pavements and roads. From the garden soil, roots, leaves and gravel were removed before adding it to the mixture. The glass fraction originated from 120 serum bottles (*Duma*, Sweden) which were smashed to pieces (between dust and 1 cm) with a hammer. Due to risk of injuries, this fraction was added only during the filling of the reactors.

The PVC construction sheet (Table 2.1) was cut into 1 x 2 cm pieces using metal shears. A regular pair of scissors was used to cut both the rigid PVC foil (Table 2.2; 2 x 2 cm) and the PVC flooring (Table 2.3; 1 x 2 cm).

After all components (except glass and PVC) had been placed in the polyethylene bucket, one litre of milliQ water was added. The waste was then mixed thoroughly by hand. The PVC products were then scaled, 60 g of each, and added to the respective model waste, except for the blank control. After another thorough mixing, the waste was placed into the reactors, adding the glass.

Note that the specific amount of PVC in relation to the model waste (total solids and moisture) is approximately equal to the percentages used in the lysimeter assays of the Basic Project. Consequently, the direct comparability of the model waste composition is given. Nonetheless caution is warranted when relating the results since the scale-down from lysimeters to METS units tends to bring about somewhat different properties: lysimeters may rather develop more pronounced fixed-bed zones in the solid waste matrix and a percolation of leachate, whereas METS units will probably develop a less heterogeneous macro-structure, thus promoting an even more thorough contact of liquid and solids in suspension.

Table 2.6 Composition of the model waste used in the METS assays

Waste fraction	Share (%)	Wet weight (g)
Food wastes	**30**	**180**
Apples	6	36
Potatoes	6	36
Carrots	6	36
Yellow peas	6	36
Bread	6	36
Metals	**5**	**30**
Nails	1	6
Tacks	1	6
Paper clips	1	6
Beer can	1	6
Tin plates	1	6
Papers	**15**	**90**
News paper[1]	10	60
Milk carton	2.5	15
Cardboard	2.5	15
Diapers	**5**	**30**
Wood shavings	**10**	**60**
PE plastics[2]	**5**	**30**
Clothing[3]	**5**	**30**
Glass[4]	**10**	**60**
Coarse gravel (3mm)	**5**	**30**
Garden soil	**10**	**60**
Totals	**100**	**600**

1 Non printed newspaper was used
2 Polyethylene granules from *Borealis* (Stenungsund, Sweden)
3 Old and worn out cotton sheet
4 Non-coloured glass (120 mL serum bottles)

2.3.3 Design and Start-up of METS Reactors

Each METS unit consists of a glass reactor equipped with tubings for gas and leachate, coupled to a methanogenic leachate filter and an automatic gasometer. The METS reactors used in this study were 3.0 L glass vessels with glass lids (*Luminarc*, France) of the type used for conserving fruits or vegetables. Each reactor was equipped with a gas pipe and a leachate recirculation system (Figure 2.1). In order to attach tubes, a hole (3 cm diameter) was drilled in each lid in which a silicon stopper was placed. All tubings used inside the reactors were made of polypropylene (*Noax*, Sweden) and guaranteed to resist temperatures up to 250 °C.

In order to be able to effect a controlled conversion from the early acidogenic into stable methanogenic conditions, a so-called methanogenic filter was connected to each METS reactor. These filters consisted of one litre bottles filled with 300 mL milliQ water and 50 mL sieved inoculum. As a buffer, 10 g $NaHCO_3$ were added. By neutralising and consuming acids, the methanogenic filters thus acted as an external buffer medium, which is comparable in effect to older and more mature layers of landfilled waste. The second purpose of these filters was to constitute a leachate storage tank that allowed a restoration of the liquid volume after leachate sampling, thus equalising the amount of leachate in the METS reactor during the experimental period. Leachate exchange and pumping was done manually with a 20 mL syringe, on a daily basis during the transition period between acidogenic and methanogenic conditions, and afterwards once every week. The gas produced in the filters was fed back to each respective reactor via the polypropylene tubing and thus contributed to the integral gas volume produced in the METS.

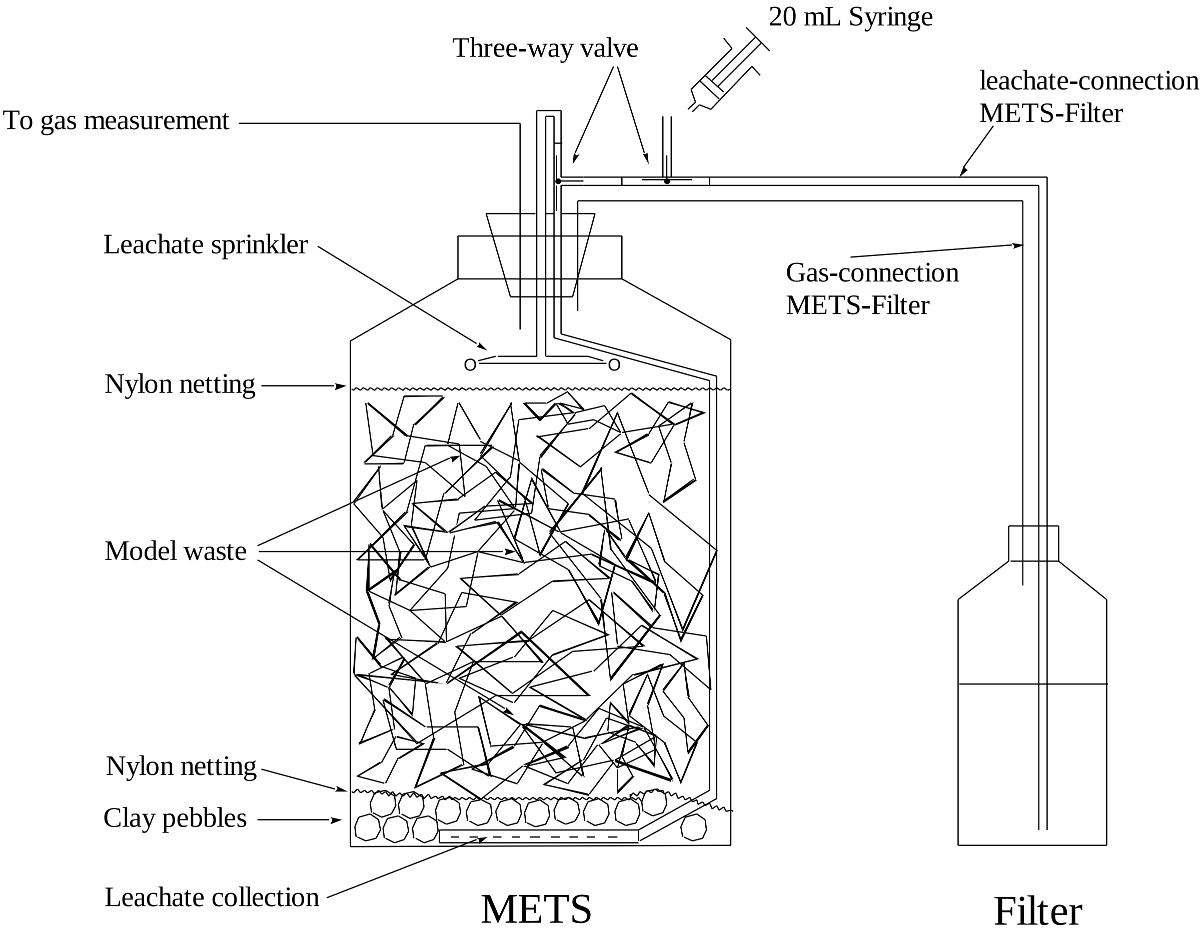


Figure 2.1 Generic set-up of a Modular Environmental Tests System (METS) unit. The arrangement consisted of a reactor containing the model waste and PVC samples as applicable, coupled to a methanogenic filter which was used as a buffer tank both for leachate storage and acid consumption in order to establish methanogenic conditions. The evolved gas is measured by an automatic gasometer (not shown).

At the bottom of each METS unit, the leachate collection tubing was covered by a 2 cm filter layer of clay pebbles (*Hasselfors Garden*, Sweden) covered by a nylon mesh, in order to avoid clogging of the leachate abstraction (cf. Figure 2.1). During filling and start-up of the METS units, the vessels were flushed with nitrogen gas during the hole procedure. First 50 mL of inoculum were added. A 2–3 cm layer of the model waste was then placed, followed by the addition of 100 mL milliQ water. Then the reactor was gradually filled with the model waste, intermittently adding the remaining inoculum (500 mL in total). The glass fraction was added in one clump after about half of the waste had been placed. Finally, another nylon mesh was placed on top of the bulk of waste and the METS reactor was closed. The METS reactors were again flushed with nitrogen gas through the leachate collection tubing and then incubated at the respective temperature.

2.4 Sampling and Analytical Procedures

2.4.1 Vinyl Chloride in the Biogas

The analysis of vinyl chloride (VC) in the biogas of the METS units was performed on a gas chromatography unit with flame ionisation detection (GC-FID) as previously described in (Ejlertsson et al. Submitted). The detection limit was 1 mg VC per m^3.

2.4.2 Leachate Sampling Plan

Since the amount of leachate in the METS reactors was limited, a sampling plan was needed. Upon start-up in June/July 1999, three samplings had been scheduled: September and December 1999, and April 2000. At these occasions, liquid samples for organotin, phthalic compounds, TOC, AOX, NH_4 and VFA, as well as samples of the PVC products were obtained (Table 2.7). In total 107 mL of leachate were taken out at each sampling. Additionally, samples for ICP-MS analysis of metal species in the leachate were obtained one month after start-up and upon termination of the assays. Since the adopted procedure for analysis of phthalic compounds requires only comparatively small volumes of leachate, these target substances were monitored at monthly intervals.

Table 2.7 Leachate sample volumes for the respective parameters: amounts withdrawn at each sampling and total volume (Liquid withdrawn) during the experimental period.

Substance(s)	1/week	1/month	1/3months	Start/termination	Liquid withdrawn
Organotin			50 mL		150 mL
PAEs		5–6 mL			50 mL
VFA[*1]	2 mL	1 mL			50 mL
TOC, NH_4			50 mL		150 mL
Metals (ICP-MS)				50 mL	100 mL
PVC flooring[*2]			X	X	—
Total					500 mL

[*1] VFA samples were taken once per week during the acidogenic phases, and afterwards once per month in the methanogenic phase.

[*2] A maximum of 2 g PVC material are retrieved at each sampling. The PVC flooring is then analysed for residual contents of its plasticisers BBP and DEHP.

2.4.3 Volatile Fatty Acids (VFA) and pH

Once a week, a sample of 1 mL leachate was abstracted by means of a 20 mL syringe from the leachate recirculation system connecting the METS reactors and the methanogenic filters. The analytical procedure employed to analyse volatile fatty acids (VFA) has previously been described in (Ejlertsson et al. Submitted). After stable methanogenic conditions had been established in all METS incubated at each respective temperature, samples for VFA were taken only once per month.

The pH value was measured during the sampling for VFA by applying a drop of leachate from each METS unit onto a pH stick (4.5–7.0, 6.5–9; MERCK).

2.4.4 TOC and NH_4^+

At the three major samplings, samples of 50 mL leachate were withdrawn from each METS unit. From these samples, 20 mL were allowed for total organic carbon (TOC) analysis and 10 mL for ammonium (NH_4), and 20 mL were saved as a reserve. The sample volume sufficed for duplicate analyses. The analytical procedures have previously been described in (Ejlertsson et al. Submitted).

2.4.5 Metal Species in the Leachate and in the Waste Matrix (ICP-MS)

At the beginning and at the termination of the experiments, leachate samples of 50 mL were transferred to 100 mL Duran bottles together with 5 mL HNO_3. The samples were then autoclaved at 121 °C for 30 minutes. Prior to semi-quantitative analysis on ICP-MS (*Perkin-Elmer Sciex Elan 6000*), the samples were diluted by a factor of ten. With respect to tin (Sn), the isotopes 118, 119 and 120 were monitored using rhodium as an internal standard. Since standards for tin were run in the same matrix the precision in the Sn quantification is ± 5 %.

At the termination of the assay, waste samples were recovered from the METS, diluted and homogenised (see section 2.4.3). For the quantification of tin, a quantity of 1 g slurry was transferred into a 100 mL Duran bottle and 5 mL of HNO_3 and 1 mL of HCl were added. The samples were then autoclaved at 121 °C for 30 minutes, and afterwards they were transferred to a Teflon chamber (*Kebo*, Sweden) and heated until dryness. After addition of HF (1 mL) and $HClO_4$ (0.5 mL) the samples were stored overnight. Again, 0.4 mL HF and 1 mL $HClO_4$ were added, and the suspension was heated until dry. Then HNO_3 (0.5 mL) was added to the samples and allowed to boil to dryness. Finally, the remaining precipitates were dissolved in 0.5 mL HCl. The sample was then transferred to a tube with milliQ water to render a final volume of ca. 10 mL. Analysis was performed on an ICP-MS (*Perkin-Elmer Sciex Elan 6000*). As above, the isotope masses 118, 119 and 120 were used to monitor tin, using rhodium as an internal standard.

2.4.6 Organotin Compounds in the Leachate

At the three major samplings, leachate samples of 50 mL each were transferred to polycarbonate bottles by means of a 20 mL syringe. The samples were then sent immediately to the *Limnological Institute Dr. Nowak*, Ottersberg/Germany. The *Limnological Institute* had also performed the organotin trace analyses in leachate matrices for the Basic Project **(Mersiowsky et al. Manuscript)**. They are an acknowledged laboratory and validated for the analysis of organotin compounds (quality assurance reports accepted by *Witco/ORTEP*).

2.4.7 Phthalic Compounds in the Leachate and in the Waste Matrix

On a monthly basis, leachate samples of 6 mL each were transferred to a 13 mL glass vial free of phthalates. The vial was then scaled and leachate was withdrawn by means of a cleaned Pasteur pipette so that the remaining amount was 5 g. The vials were closed with Teflon coated stoppers and frozen (–20 °C) until analysis. The analyses were conducted at the *Department of Water and Environmental Studies, Linköping University*, Sweden. The methods used for the determination of different phthalates and their degradation products had already successfully been established in the Basic Project (Jonsson et al. Manuscript).

Upon termination of the experiments, the waste from each METS reactor was recovered, spread on aluminium foil and homogenised manually (wearing gloves free of phthalates). The waste was then divided into two halves, one of which one half was discarded and the other half was further homogenised. In the same way, the amount of waste was reduced twice more, so that approximately 160 g of waste remained. From this remainder all PVC samples as well as all discernible pieces of glass and metal were removed. The waste was then placed in a food processor, 160 mL of milliQ water were added, and the suspension was homogenised for about 2 minutes. The slurry was transferred to a polyethylene plastic bag and stored in a refrigerator (+4 °C) overnight. From each slurry triplicates of 2 g each were transferred to 30 mL glass vials and frozen (–20 °C) for further analysis.

In order to conduct the analysis of this material for phthalic compounds, 2 mL of acidic milliQ water and internal standard (DDP 100 µg) were added and the vial was placed into an ultrasonic bath for 5 minutes. Afterwards, 5 mL of isopropanol and 5 mL of cyclohexane were added. The samples were then shaken at 145 rpm for 60 minutes, followed by centrifugation at 2000 rpm (10 min), removing the cyclohexane phase. For a second extraction, 3 mL isopropanol and 5 mL cyclohexane were added. Again the samples were shaken at 145 rpm for 60 minutes, followed by centrifugation. The cyclohexane phase was withdrawn and united with the first extract. This was flushed twice with 10 mL acidic milliQ water and 0.2 g NaCl in order to remove isopropanol from the extract. The cyclohexane extract (10 mL) was dried with Na_2SO_4 and then concentrated under a gentle stream of nitrogen to 1 mL. The concentrated extract was derivatised with a silylating agent (TMS) prior to injection on the GC-MS.

2.4.8 Residual Content of BBP and DEHP in the PVC Flooring

In order to retrieve samples of the PVC flooring, the lids of the METS reactors were opened at the three major samplings and 1–2 g of plastic pieces were collected while flushing with nitrogen. The control reactors were also opened and closed again in order to ensure equal conditions in the complete test system. The PVC samples of the rigid PVC products (construction sheet and foil) were placed in a freezer (–20°C) for later analysis, if necessary. The samples of the PVC flooring were sent to the *IKP Institute of Polymer Testing and Polymer Science*, *Stuttgart University*, Germany. The *IKP* are an acknowledged laboratory and validated for the determination of additives in polymer matrices.

3 RESULTS AND DISCUSSION

3.1 Vinyl Chloride in the Biogas of METS Units

Gas samples were withdrawn from the METS units at two occasions: in February 2000 and in April 2000 (just before the major sampling for leachate and PVC poducts). No vinyl chloride (VC) was detected in the biogas at any of the temperatures 20–70 °C. The detection limit was 1 mg VC per m^3.

It should, however, be noted that the aerated METS at 85 °C were not analysed for VC due to the late decision to include this target substance in the analytical protocol for this study.

3.2 Performance of METS Units at Temperatures 20–85 °C

3.2.1 Gas Production

The gas evolving in the anaerobic METS units at temperatures 20–70 °C during the first months originated predominantly in the methanogenic filter, since acidic conditions prevailed in the METS reactors themselves. At the first major sampling (September 1999), the pH had attained neutral levels only in the incubations at 55 °C.

Approximately 120–140 days after start-up, the METS unit running at 20 °C had turned over to methanogenic conditions, and at the second major sampling (December 1999), the pH was about neutral. The accumulated biogas formed until termination (Figure 3.1) amounts to approximately 75 L (equivalent to 125 m^3/t). This figure is comparable to the usual findings under landfill conditions, i. e. 150–200 m^3 per tonne of wet waste.

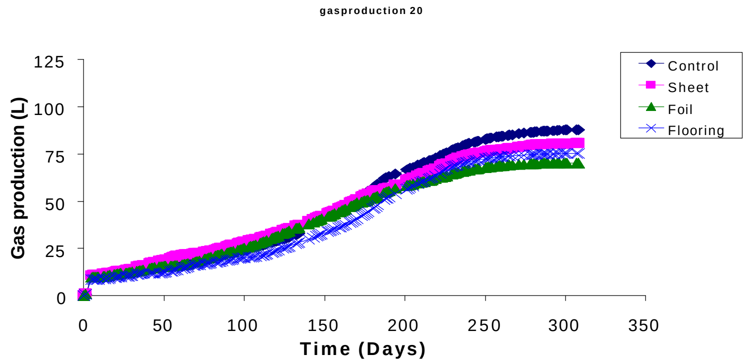


Figure 3.1 Cumulative biogas production in the METS units incubated at 20 °C

At 37 °C, the gas production from the METS units spiked with the PVC flooring and the rigid PVC sheet was found to exceed for unknown reasons the yield from the blank control unit and the METS unit spiked with the PVC foil (Figure 3.2). The accumulated biogas formed until day 180 amounts to approximately 130–180 m^3/t.

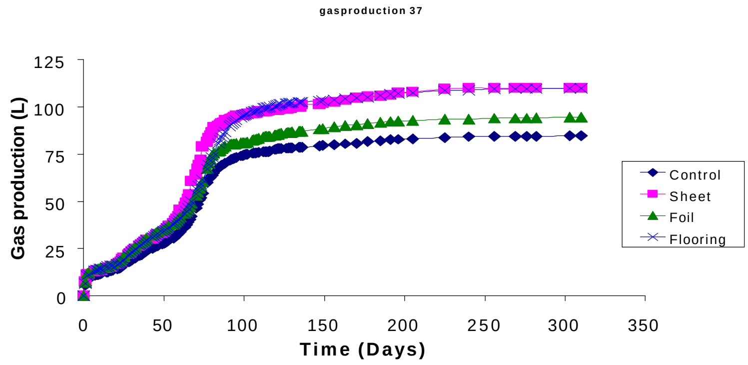


Figure 3.2 Cumulative biogas production in the METS units incubated at 37°C

At 55 °C an effect on the gas production was observed for the units containing the PVC foil and the PVC flooring (Figure 3.3). Both the blank control unit and the unit spiked with the PVC construction sheet showed increased gas production rates as soon as the conditions became methanogenic (cf. Figure 3.8). The units spiked with the PVC foil and the PVC flooring, however, showed low pH values and also little biogas production. In relation to the blank control unit and the METS unit spiked with the PVC construction sheet (140 m^3/t), the unit containing the flooring showed the least cumulative gas production (55 m^3/t) and the one with the foil 100 m^3/t.

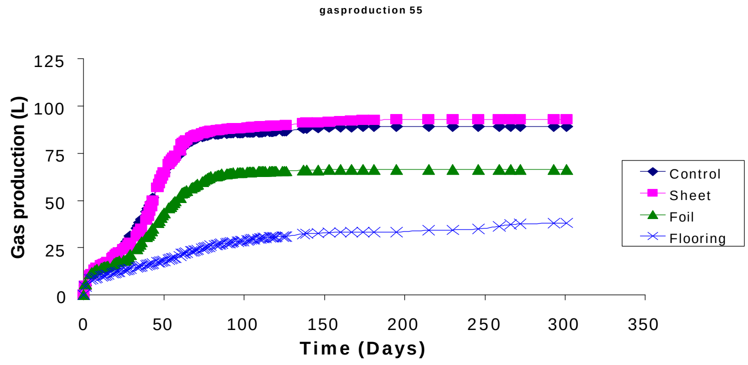


Figure 3.3 Cumulative biogas production in the METS units incubated at 55°C

During the first months, the biogas formed in the METS units running at 70 °C originated predominantly in the methanogenic filter (Figure 3.4). The volumes were rather low as compared to the units at 20 °C, 37 °C and 55 °C. At day 140 the methanogenic filters were re-inoculated using the inoculum adapted to 55 °C and then placed at 60 °C in order to promote balanced methanogenic consortia. Apparently the original inoculum was not able to sustain an anaerobic microflora adapted to 70 °C. Only towards the end of the experimental period, a personal communication became available asserting that probably temperatures 65 °C or 75 °C should have been selected due to the interface between thermophilic and hyperthermophilic microorganisms (cf. Figure 1.2).

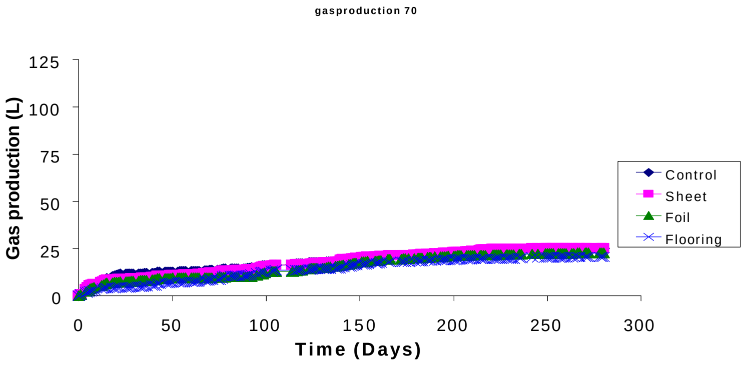


Figure 3.4 Cumulative biogas production in the METS units incubated at 70°C

The last series of METS units was initially operated under aerobic conditions and at 85 °C. The aeration was switched off at day 150, and afterwards the units were kept at 55 °C and allowed to develop under anaerobic conditions. Since the waste was somewhat dehydrated, 300 mL of milliQ water were also added on day 150. From then on, the gas production increased (Figure 3.5) and an increase in pH was observed. The highest gas production of this set was shown by the METS units spiked with the PVC foil and the PVC flooring and amounted to almost 15 L at termination whereas the blank control unit and the unit spiked with the PVC construction had produced only 3–4 L by the time of termination.

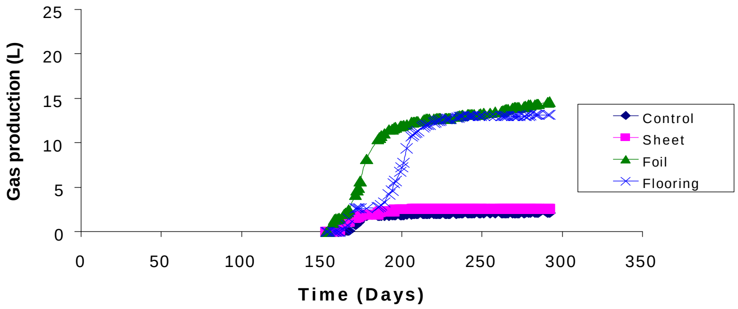
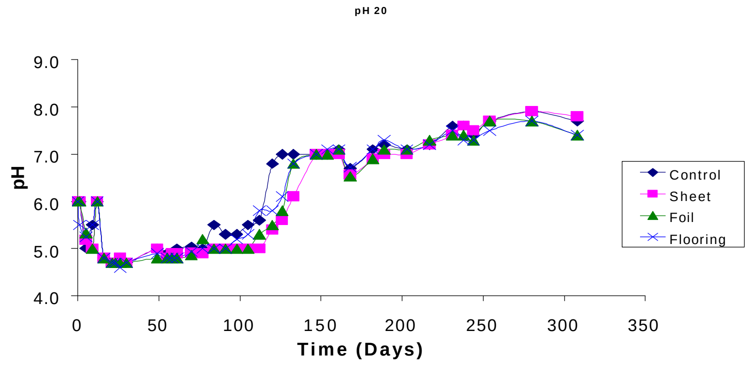


Figure 3.5 Cumulative biogas production in the METS units incubated at 85 °C (monitored after termination of the aeration period and further operation under anaerobic conditions at 55 °C).

3.2.2 Volatile Fatty Acids (VFA) and pH

All METS units incubated at 20–70 °C presently commenced to produce large amounts of volatile fatty acids (VFA) and became acidic after a few days after start-up.

At 20 °C, the pH ranged between 4.5–5 during the first 100–120 days of incubation (Figure 3.6). Due to the leachate exchange with the methanogenic filter, a consumption of VFA was achieved and this gradually brought about a neutral pH in these four METS units. The blank control reactor was the first to turn methanogenic after 110 days of incubation, whereas the unit spiked with the PVC sheet reactor became methanogenic only after 140–150 days.



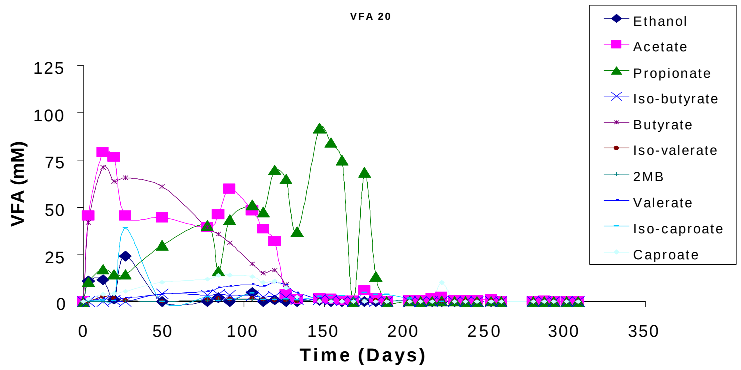
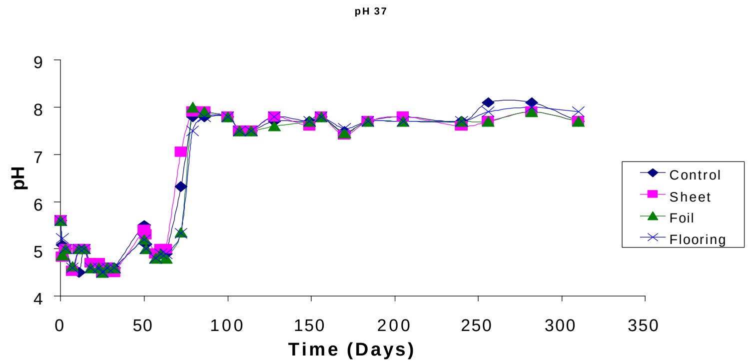


Figure 3.6 Development of pH in the METS units incubated at 20 °C and concentrations of VFA in the 20 °C blank control unit.

At 37 °C the pH ranged between 4.5–5 during the first 65 days (Figure 3.7), then increased to about 7 after 80 days of incubation. At the two major samplings, all METS units of this set were about neutral, with VFA below the detection limits of 0.05 mM (Figure 3.7). By the time of termination the pH had increased to almost 8 in these mesophilic METS units.



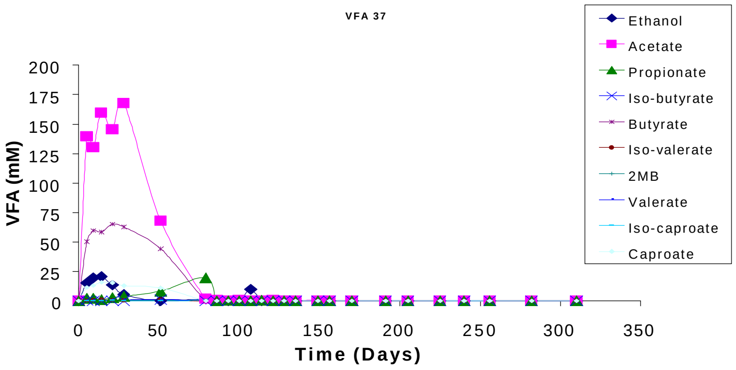


Figure 3.7 Development of pH in the METS units incubated at 37 °C and concentrations of VFA in the 37 °C blank control unit

At 55 °C the pH ranged between 4.5–5 during the first 20 days of incubation (Figure 3.8). Then the pH rose to about 7.5–8 in the blank control and the unit with the PVC construction sheet, whereas in the units containing the PVC foil and the PVC flooring it remained around 6 for another 45 days. From day 65 and onwards, the pH increased in these METS units to 7.5–8 as well. By the time of termination (day 320) the pH had increased to 8.5. It should be noted that the concentrations of VFA were still rather high (acetate ca. 25 mM) and had not decreased to below detection limit as in the 37 °C METS units.

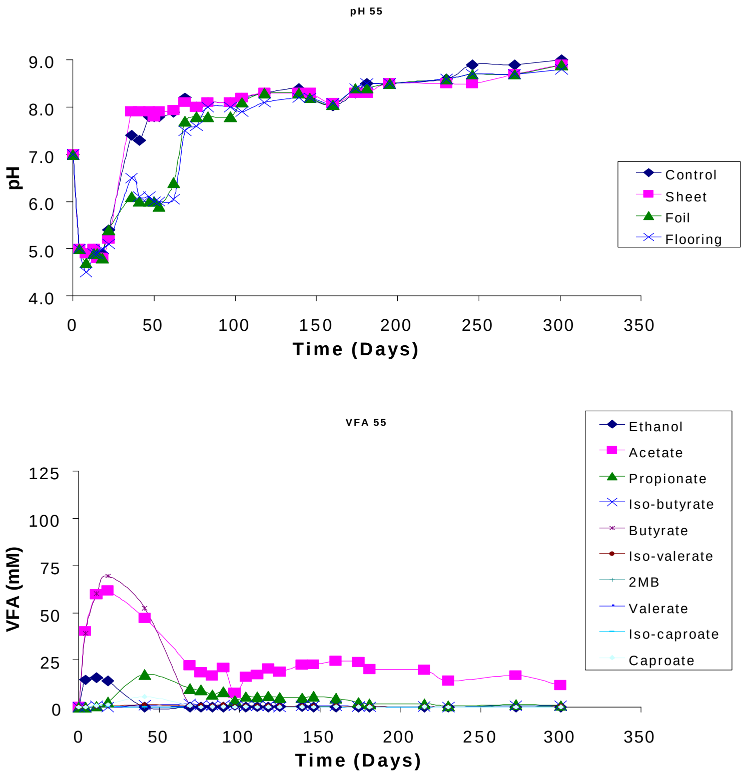


Figure 3.8 Development of pH in the METS units incubated at 55 °C and concentrations of VFA in the 55 °C blank control unit

At 70 °C the pH ranged between 4.5–5, and all four METS units started to produce large amounts of volatile fatty acids (Figure 3.9), predominantly acetate. From an initial pH of about 6, the pH value decreased to about 5 mainly in the blank control and in the unit containing the PVC construction sheet. After 40–50 days of incubation the pH started to increase again to ca. 5.5 and after 200 days of incubation the pH levelled out at 8.

It also appears noteworthy that the highest concentrations of ethanol in all METS units amounted to 75 mM and were observed in this set running at 70 °C.

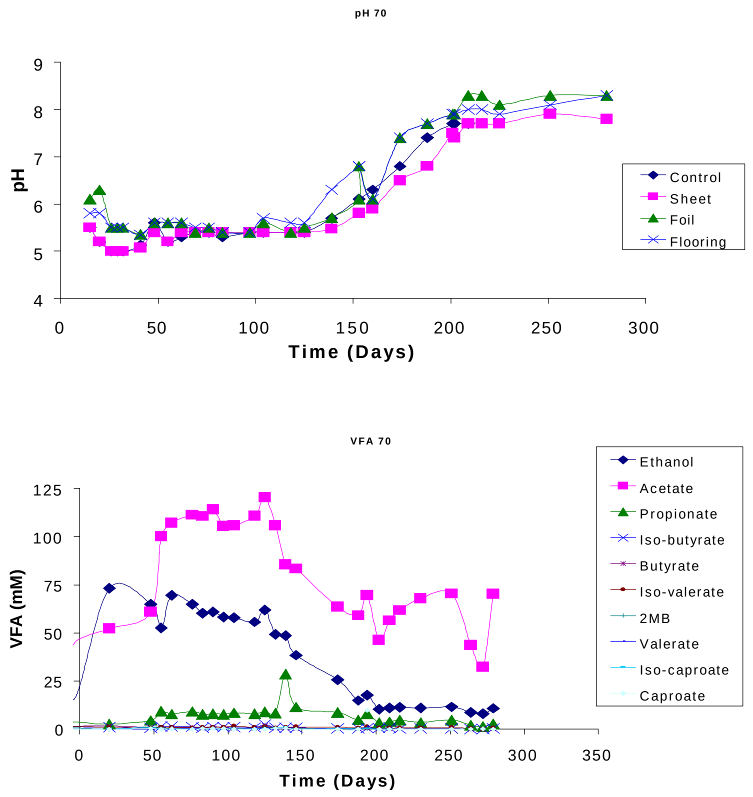


Figure 3.9 Development of pH in the METS units incubated at 70 °C and concentrations of VFA in the 70 °C blank control unit

The METS unit incubated at 85 °C was aerated for 153 days. During this period, the target temperature being 85 °C, the temperature (Figure 3.10) of the heating device was increased in steps to allow for a succession of composting microorganisms. Then the air was switched off and the temperature was lowered to 55 °C. At that time, the pH was about 6. The METS were then allowed to turn anaerobic and commenced to produce gas (see above). Concentrations of VFA were only measured at the major sampling in September, December and April and were found to be below detection limits. In September the pH was neutral; however, in December the pH had decreased to around 5.5. After the cessation of the aeration, the pH increased to approximately 8 (Figure 3.10).

It is interesting to note that the lowest pH at 4.3 was measured in the leachate from the METS unit spiked with the PVC flooring. A possible reason for this observation were the high concentrations phthalic acid present in this METS unit (600 mg/L, see below).

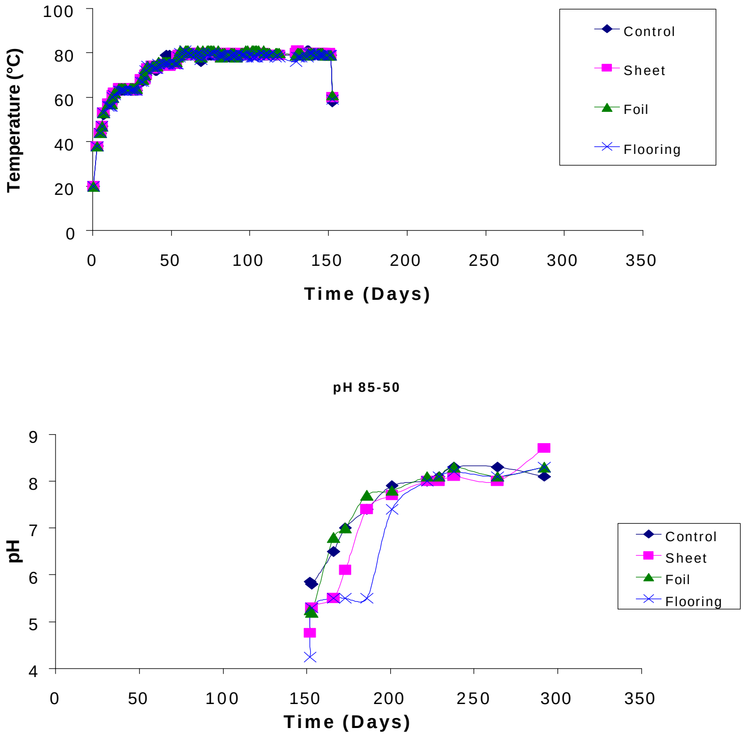


Figure 3.10 Temperature development in the METS unit with target temperature 85 °C during the aeration period (days 0–152) and development of the pH after cessation of aeration (day 152 and onwards).

3.2.3 TOC and NH_4^+

At the first sampling, the contents of total organic carbon (TOC) in all leachates was found to be in the range of 5,000–8,000 mgC/L (Table 3.1). Due to microbial transformation of the organic matter to methane and carbon dioxide the concentrations subsequently decreased with a factor of five to ten. However, in the METS units incubated at 70 °C little or no transformation occurred, as reflected by the TOC content.

The TOC values in all of the METS units are rather high (1,000–7,000 mgC/L even upon termination) in comparison to the lysimeter assays of the Basic Project (around 500 mgC/L in stable methanogenic phase). This is partly due to the geometry and operation of the METS reactors (as with the biocorrosion assays of the Basic Project): in contrast to the lysimeters, there is less volume that acts as a filter zone allowing settling, precipitation and sorption. Hence the leachate carries more suspended matter. It is noteworthy that the TOC concentrations provide an indication of the carrying capacity of the leachate for hydrophobic compounds such as phthalates and organotin compounds (Mersiowsky and Ejlertsson 1999).

Table 3.1 Concentrations of TOC in the leachate at the three major samplings.

Temperature Time (days)	Control mgC/L	Sheet mgC/L	Foil mgC/L	Flooring mgC/L
20 °C				
35	7044	7090	7028	7032
168	3364	3664	3776	3248
310	1946	2902	2126	2838
37 °C				
37	5314	6234	7652	8184
170	1920	934	845	1187
312	1123	1209	1005	1356
55 °C				
27	5990	6702	6528	6916
160	3074	3458	3538	3534
302	3974	4106	3280	3882
70 °C				
6	4526	7162	10266	7950
139	4382	4192	5106	4878
281	6422	6724	7636	7422
85 °C				
19	8908	8042	8040	8236
152	6972	7934	5774	5882
294	4630	3018	3000	3040

The concentrations of ammonium increased with time in the leachates of the METS units incubated at 20–70 °C (Table 3.2). This is due to the degradation of proteins in the waste. At 85 °C the concentrations decreased which may be due to incorporation of ammonium into microbial biomass, since the yields of biomass formation are considerably higher under aerobic conditions than under anaerobic conditions. Another possibility is the nitrification of ammonium into nitrate under aerobic conditions, followed by denitrification of formed nitrate into nitrogen gas under the subsequent anoxic conditions. Finally, a stripping of ammonia gas during the aeration period is possible. Generally speaking, the values are rather low (also compared to the lysimeter assays of the Basic Project).

Table 3.2 Concentrations of ammonium (NH_4^+) in the leachate at two of the three major samplings.

Temperature Time (days)	Control mg NH_4^+/L	Sheet mg NH_4^+/L	Foil mg NH_4^+/L	Flooring mg NH_4^+/L
20 °C				
35	132	142	165	128
310	558	534	534	534
37 °C				
37	202	229	202	202
312	507	618	581	590
55 °C				
27	313	313	271	294
302	886	839	835	867
70 °C				
6	165	165	183	165
281	396	396	220	257
85 °C				
19	599	655	590	682
294	109	109	197	119

3.3 Metal Species in the Leachate at Temperatures 20–85 °C

The findings of tin (Sn) from the semi-quantitative analysis of metal species in the leachate are shown in Table 3.3 and in Figure 3.11 rendered in logarithmic scale. Since standards were prepared in the same leachate matrix, the quantification error for tin is at maximum 5 %. The ICP-MS analysis rendered a number of other metals besides tin, with semi-quantitative determination implying a error margin of 20 %. As these findings provide additional reference values they are included in the appendices for information.

Table 3.3 Concentrations of total tin (Sn) in the leachate from the METS units.

Temperature (°C)	Control (µgSn/L)	Sheet (µgSn/L)	Foil (µgSn/L)	Flooring (µgSn/L)
20	7	5	5	64
37	4	5	4	77
55	8	20	12	238
70	17	33	1601	462
85	16	26	281	79

In general, the concentrations showed similar trends, increasing with temperatures above 37 °C. The total tin concentrations in the METS unit containing the PVC flooring lay approximately one order of magnitude above the others. The most noticeable development was observed for the METS unit with the PVC foil where concentrations differed by more than one order of magnitude when comparing the METS unit running at 55 °C with those at 70 °C and 85 °C (Figure 3.11). As this change of behaviour is corroborated by the species-selective organotin analyses (cf. chapter 3.4), it would be useful to know the precise glass transition temperature of the rigid PVC foil.

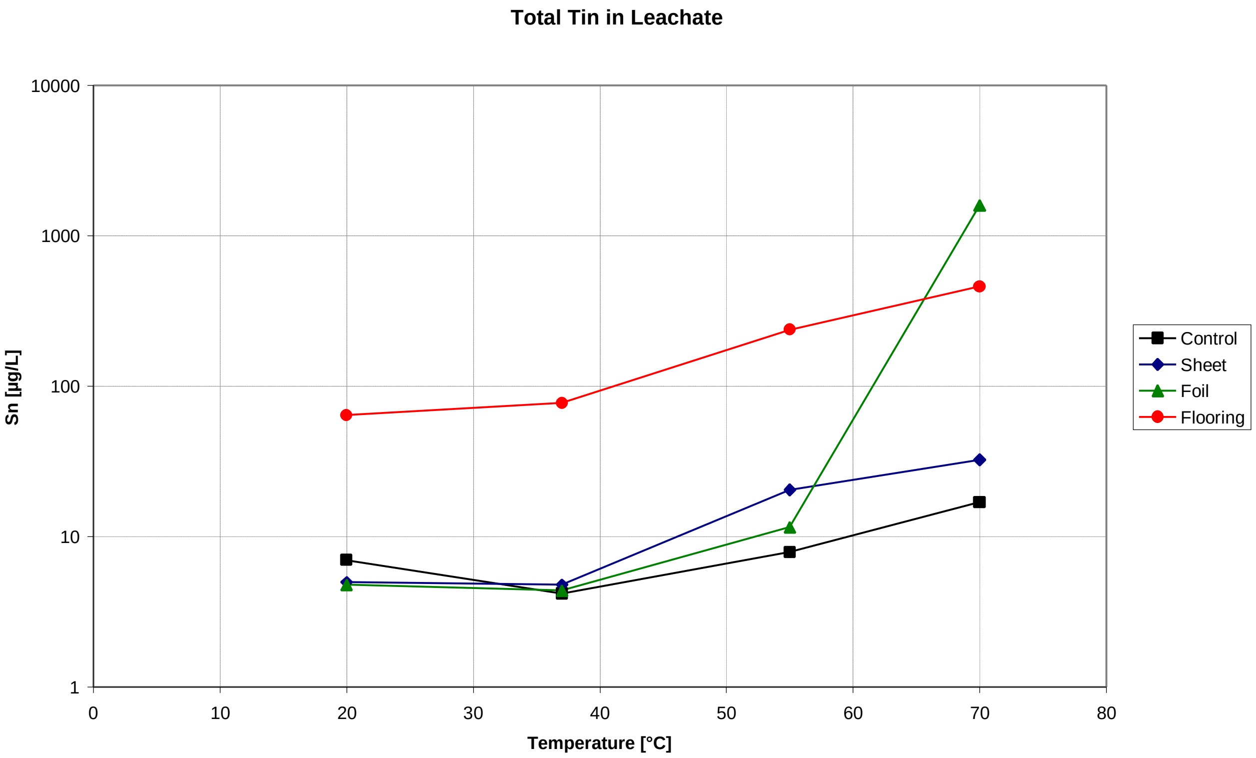


Figure 3.11 Logarithmic concentrations of total tin (Sn) in the leachate from the METS units in relation to temperatures 20–70 °C (anaerobic)

In Table 3.4 the distribution of total tin between the leachate, solid waste and clay pebbles is given for the end of the experimental period. It should be noted that the amount of total tin computed for the »solids« also includes tin from the leachate, since the wet waste used for analysis was soaked. Nevertheless, the budget given in Table 3.4 is instrumental when assessing into which media or phase the tin is allocated. Generally speaking, the greater part of tin is found on the solids, either as adsorbed organotin compounds or possibly mineralised as inorganic tin.

The highest amount of total tin (7.8 mg tin) was observed in the METS unit spiked with the PVC flooring running at 70 °C; this amount equals approximately 50 % of the butyltin stabiliser contained in the PVC flooring according to the formulation (16 mg tin). At the same temperature (70 °C) 0.5 % of the tin contained in the PVC construction sheet and 5 % of the tin contained in the PVC foil were found. At 20 °C and 37 °C, 13–19 % of the total tin contained in the PVC flooring were found in the wet waste.

Table 3.4 Distribution of total tin at termination of METS assays: budget includes leachate, wet waste (in total ca. 1.2 kg), and the clay pebbles.

Temperature METS Unit	Leachate µg Sn	Wet waste µg Sn	Clay pebbles µg Sn
20 °C			
Control	6	785	23
Sheet	5	892	20
Foil	4	472	25
Flooring	62	2,099	34
37 °C			
Control	4	359	18
Sheet	5	632	19
Foil	4	581	23
Flooring	77	2,978	47
55 °C			
Control	8	459	9
Sheet	18	590	13
Foil	11	471	14
Flooring	216	4,687	70
70 °C			
Control	16	207	21
Sheet	30	582	17
Foil	1,416	6,822	186
Flooring	411	7,786	263
85 °C			
Control	14	386	19
Sheet	24	1,466	32
Foil	215	5,656	149
Flooring	69	6,459	76

3.4 Organotin Compounds in the Leachate at Temperatures 20–85 °C

3.4.1 Overall Comments

Leachate samples to be analysed for organotin compounds had been collected from all METS units in the course of the major samplings in September 1999, December 1999 and April 2000.

The findings indicated that both the PVC flooring and the rigid PVC foil gave rise to organotin compounds in the leachate at levels increasing with temperatures. The rigid PVC sheet appeared to give rise to less organotin compounds in the leachate than the other two PVC materials investigated.

There is a reasonable possibility that tin species had been adsorbed to the solid waste matrix, since the total tin analyses did not differentiate between inorganic and organic species. It is also possible that volatile tin compounds had been vented out of the system, even though the total tin recovery more than well accounts for disappearance of organic tin species.

It should be noted that the figures given previously for total tin and those for organotin compounds in the tables below cannot directly be compared since the organotin compounds are specified in µg organotin compound (as cation) per litre. The conversion factors from 1 µg organotin compound (as cation) into µg tin are provided in Table 3.5.

Table 3.5 Conversion factors from 1 µg organotin compound (as cation) into µg tin.

Organotin species (cation)	Conversion factors [µg Sn/µg cation]
Monomethyltin (MMT)	0.89
Dimethyltin (DMT)	0.80
Monobutyltin (MBT)	0.68
Dibutyltin (DBT)	0.51

As a general conclusion, the analysis for organotin species and total tin in the leachate indicated that a dealkylation of organotin species as well as methylation processes had occurred.

3.4.2 METS Units at Temperature 20 °C

The concentrations observed at the three samplings in the leachate from the METS units running at 20 °C are shown in Table 3.6–Table 3.8; the respective graphs are included in the Appendices.

The highest organotin concentration at 52 µg/L was observed in the METS unit containing the rigid PVC foil (April 2000). However, when comparing this with the pertinent total tin analysis rendering 4.8 µgSn/L, it appears that there might be an error. The ratio between the species mono- and dimethyltin indicates that a dealkylation of dimethyltin may have occurred. The drastic increase in methyltin species observed at the last sampling occurred during the long and stable methanogenic phase; this could be due to increased microbiological activity in the vicinity of the PVC products increasing the leaching effects. A similar behaviour was observed for the PVC flooring where monobutyltin concentrations had increased by an order of magnitude since the December sampling. Again the ratio between the butyltin species indicates that a dealkylation may have occurred. The total tin mounted to 64.3 µg/L, and a complete transformation of butyltin species to inorganic tin appears possible.

Table 3.6 Concentrations of organotin compounds in leachate samples from the METS units incubated at 20 °C (sampled September 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	<0.05	<0.05	<0.05	<0.05
Dimethyltin (DMT)	<0.05	<0.05	0.25	<0.05
Monobutyltin (MBT)	<0.05	0.60	<0.05	1.20
Dibutyltin (DBT)	<0.05	1.70	<0.05	0.76
Tributyltin (TBT)	<0.05	0.10	<0.05	0.07
Monooctyltin (MOT)	<0.05	0.09	<0.05	<0.05
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.7 Concentrations of organotin compounds in leachate samples from the METS reactors units at 20 °C (sampled December 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.09	0.26	0.33	<0.05
Dimethyltin (DMT)	0.05	0.87	0.49	<0.05
Monobutyltin (MBT)	0.86	0.22	<0.05	1.50
Dibutyltin (DBT)	0.54	0.46	<0.05	2.80
Tributyltin (TBT)	0.09	0.22	0.07	0.11
Monooctyltin (MOT)	<0.05	0.13	<0.05	<0.05
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.8 Concentrations of organotin compounds and total tin in leachate samples from the METS units incubated at 20 °C (sampled April 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	1.10	0.72	52	1.10
Dimethyltin (DMT)	0.08	0.24	3.70	0.12
Monobutyltin (MBT)	0.07	1.10	0.11	31
Dibutyltin (DBT)	<0.05	0.32	<0.05	9.30
Tributyltin (TBT)	0.15	<0.05	<0.05	0.15
Monooctyltin (MOT)	<0.05	<0.05	<0.05	0.38
Dioctyltin (DOT)	<0.05	<0.05	<0.05	1.80
Total Sn[*2]	7.0	5.0	4.8	64.3

[*1] All organotin compounds are measured as cations.
[*2] Cf. Table 3.3 above. Unit is µg Sn/L.

3.4.3 METS Units at Temperature 37 °C

The concentrations observed at the three samplings in the leachate from the METS units running at 37 °C are shown in Table 3.9–Table 3.11; the respective graphs are included in the Appendices.

It is apparent that the PVC products gave rise to an increase of organotin concentrations in the leachate as compared to the blank control. The METS unit spiked with the PVC flooring showed the maximum concentration of monobutyltin at 54 µg/L (April 2000). Since the total tin is much higher than the observed mono- and dibutyltin concentrations, the results indicate that the butyltin species may have been completely transformed to inorganic tin. As discussed for METS units running at 20 °C, the observations suggest that a dealkylation of both dimethyltin and dibutyltin occurred. However, the maximum monomethyltin concentration was only 2.4 µg/L (April 2000) as compared to 52 µg/L at 20 °C; this may either imply dealkylation processes progressing to inorganic tin at 37 °C, or an analytical error in the value for 20 °C (as discussed above).

Table 3.9 Concentrations of organotin compounds in leachate samples from the METS units incubated at 37 °C (sampled September 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	<0.05	0.17	0.16	<0.05
Dimethyltin (DMT)	<0.05	0.26	0.32	<0.05
Monobutyltin (MBT)	0.17	0.11	0.07	6.6
Dibutyltin (DBT)	0.12	<0.05	<0.05	2.7
Tributyltin (TBT)	<0.05	<0.05	<0.05	0.07
Monooctyltin (MOT)	<0.05	<0.05	<0.05	<0.05
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.10 Concentrations of organotin compounds in leachate samples from the METS units incubated at 37 °C (sampled December 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.19	0.14	0.70	<0.05
Dimethyltin (DMT)	0.09	<0.05	0.37	<0.05
Monobutyltin (MBT)	0.07	0.41	0.15	34
Dibutyltin (DBT)	<0.05	0.43	<0.05	6.5
Tributyltin (TBT)	<0.05	0.06	<0.05	0.36
Monooctyltin (MOT)	<0.05	0.18	<0.05	0.97
Dioctyltin (DOT)	<0.05	0.28	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.11 Concentrations of organotin compounds and total tin in leachate samples from the METS units incubated at 37 °C (sampled April 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.48	0.21	2.40	<0.05
Dimethyltin (DMT)	0.33	<0.05	1.70	<0.05
Monobutyltin (MBT)	0.28	1.30	0.10	54
Dibutyltin (DBT)	0.18	0.49	<0.05	6.30
Tributyltin (TBT)	0.17	<0.05	<0.05	0.20
Monooctyltin (MOT)	0.07	0.08	<0.05	0.20
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05
Total Sn[*2]	4.2	4.8	4.4	77.4

[*1] All organotin compounds are measured as cations.

[*2] Cf. Table 3.3 above. Unit is µg Sn/L.

3.4.4 METS Units at Temperature 55 °C

The concentrations observed at the three samplings in the leachate from the METS units running at 55 °C are shown in Table 3.12–Table 3.14; the respective graphs are included in the Appendices.

The maximum concentration of organotin compounds was detected in the METS unit spiked with the PVC flooring: monobutyltin amounted to 240 µg/L in April 2000. The ratio between the species mono- and dibutyltin differed between the samplings in September and December, with amounts of monobutyltin increasing; this may be imply a dealkylation of the dibutyltin. From the presence of methyltin species it appeared possible that a methylation of either indigenous tin from the model waste or from mineralised organotin had taken place.

It should also be noted that methyltin species are volatile and may escape from the METS system with the biogas. Furthermore, other organotin species were detected (TBT, MOT, DOT) in the leachate of the METS unit containing the PVC flooring. This observation may be explained by a contamination of the stabiliser compound with minor amounts of tributyltin as well as octyltin species that become discernible if sufficient amounts are released (Mersiowsky and Ejlertsson 1999).

Table 3.12 Concentrations of organotin compounds in leachate samples from the METS units incubated at 55 °C (sampled September 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.09	0.19	1.00	0.16
Dimethyltin (DMT)	0.06	<0.05	1.40	0.66
Monobutyltin (MBT)	0.18	5.10	0.20	12
Dibutyltin (DBT)	<0.05	1.60	<0.05	2.50
Tributyltin (TBT)	<0.05	<0.05	<0.05	<0.05
Monooctyltin (MOT)	<0.05	<0.05	<0.05	0.28
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.13 Concentrations of organotin compounds in leachate samples from the METS units incubated at 55 °C (sampled December 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.67	0.40	3.30	<0.05
Dimethyltin (DMT)	0.21	<0.05	<0.05	<0.05
Monobutyltin (MBT)	0.14	14	0.10	49
Dibutyltin (DBT)	<0.05	1.6	<0.05	1.90
Tributyltin (TBT)	<0.05	0.07	<0.05	0.17
Monooctyltin (MOT)	<0.05	0.08	<0.05	1.20
Dioctyltin (DOT)	<0.05	<0.05	<0.05	0.66

[*1] All organotin compounds are measured as cations.

Table 3.14 Concentrations of organotin compounds and total tin in leachate samples from the METS units incubated at 55 °C (sampled April 2000).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	1.10	1.20	17	1.80
Dimethyltin (DMT)	0.20	<0.05	0.37	<0.05
Monobutyltin (MBT)	0.46	14	0.24	240
Dibutyltin (DBT)	<0.05	0.77	<0.05	2.90
Tributyltin (TBT)	<0.05	<0.05	<0.05	0.23
Monooctyltin (MOT)	<0.05	<0.05	<0.05	0.40
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05
Total Sn[*2]	7.9	20.5	11.6	238.3

[*1] All organotin compounds are measured as cations.
[*2] Cf. Table 3.3 above. Unit is µg Sn/L.

3.4.5 METS Units at Temperature 70 °C

The concentrations observed at the three samplings in the leachate from the METS units running at 70 °C are shown in Table 3.15 - Table 3.17; the respective graphs are included in the Appendices.

Also at 70 °C an influence of the PVC materials on organotin concentrations in the leachate is recognisable as compared to the control. The METS unit spiked with the PVC flooring showed the maximum concentration of butyltin species at the September sampling, but decreased almost by a factor of ten by the December sampling. Again the dibutyltin appears to be subject to dealkylation since the ratio between the species di- and monobutyltin diminished. The concentration of monomethyltin in the METS unit spiked with the PVC foil increased dramatically to 1,600 µg/L by the last sampling. As above, from the decrease in the ratio between the species di- and monomethyltin, a demethylation appears conclusive.

It is noteworthy that due to the prolonged acidogenic state of these assays at 70 °C, the leachate matrix was rather different from those METS units which had already attained a methanogenic state: in particular the high loads of solute and suspended organic matter in the leachate had probably increased its carrying capacity for organotin compounds.

Table 3.15 Concentrations of organotin compounds in leachate samples from the METS units incubated at 70 °C (sampled September 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.08	0.05	51	0.05
Dimethyltin (DMT)	0.15	0.11	120	0.06
Monobutyltin (MBT)	0.18	0.56	0.18	78
Dibutyltin (DBT)	0.09	0.72	0.08	52
Tributyltin (TBT)	<0.05	<0.05	<0.05	0.20
Monooctyltin (MOT)	<0.05	<0.05	0.08	0.72
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.16 Concentrations of organotin compounds in leachate samples from the METS units incubated at 70 °C (sampled December 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.37	0.09	40	0.37
Dimethyltin (DMT)	<0.05	<0.05	35	3.60
Monobutyltin (MBT)	<0.05	4.40	0.19	11
Dibutyltin (DBT)	<0.05	0.27	<0.05	3.90
Tributyltin (TBT)	<0.05	0.07	<0.05	<0.05
Monooctyltin (MOT)	<0.05	<0.05	<0.05	<0.05
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.17 Concentrations of organotin compounds and total tin in leachate samples from the METS units incubated at 70 °C (sampled April 2000).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	1.10	<0.05	1600	<0.05
Dimethyltin (DMT)	<0.05	<0.05	80	<0.05
Monobutyltin (MBT)	0.09	16	0.26	200
Dibutyltin (DBT)	<0.05	0.87	<0.05	6.10
Tributyltin (TBT)	<0.05	<0.05	<0.05	<0.05
Monooctyltin (MOT)	<0.05	<0.05	0.13	0.24
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05
Total Sn[*2]	17.0	32.6	1600.9	462.0

[*1] All organotin compounds are measured as cations.
[*2] Cf. Table 3.3 above. Unit is µg Sn/L.

3.4.6 METS Units at Temperatures 85 °C (Aerobic) and 55 °C (Anaerobic)

The concentrations observed at the three samplings in the leachate from the METS units running at 85 °C (aerobic) and 55 °C (anaerobic) are shown in Table 3.18–Table 3.20; the respective graphs are included in the Appendices.

At 85 °C, an influence of the PVC materials on the concentrations of organotin in the leachate as compared to the blank control was readily discernible. In the METS unit spiked with the PVC flooring, the concentrations of mono- and dibutyltin attained 170 and 120 µg/L, respectively. However, by the time of the December sampling, the butyltin concentrations had diminished to levels at the detection limit, whereas the concentrations of methyltin species had increased substantially. Similarly, the concentrations of butyltin species in the METS unit spiked with the PVC sheet had decreased by a factor of ten between these two samplings. The concentrations of methyltin species in the METS unit spiked with the PVC foil was in the same order of magnitude between the two first samplings.

When the aeration was ceased and the METS units were allowed to turn over into anaerobic conditions at 55 °C the amount of organotin compounds increased tremendously, except for the METS unit containing the PVC flooring (Table 3.20). In the METS unit with the PVC foil, the concentration of mono- and dimethyltin reached 650 µg/L and 290 µg/L, respectively. High concentrations of monomethyltin were also observed in the METS unit with the PVC sheet. This is interpreted as an indication of intense methylation processes.

Since findings of total tin in the waste amounted to around 5,000 µg (cf. Table 3.4), it appears reasonable that tin species had been adsorbed to the solid waste matrix. Another possibility is that volatile organotin species had escaped out of the METS system with the exhaust gas in the case of the METS units containing the PVC flooring and the PVC sheet. Yet it would then seem inconsistent that the concentrations of methyltin species in the METS unit with the PVC foil remained rather unchanged. Furthermore, a screening of the condensate did not render any findings of organotin species (as of December 1999). The organotin compounds may have been subject to dealkylation, but measurements of inorganic tin were not included in the analytical programme.

Beside the elevated temperature, it is essential to take into account the differences in leachate matrices (carrying capacity) as well as redox state and microflora (chemical/biochemical degradation capacity) in these aerobic METS units. Consequently, a direct comparison with the conditions in the anaerobic METS units is impaired.

Table 3.18 Concentrations of organotin compounds in leachate samples from the METS units incubated at 85 °C/aerobic (sampled September 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	1.80	2.70	24	0.39
Dimethyltin (DMT)	7.00	7.80	41	0.98
Monobutyltin (MBT)	1.20	12	0.67	170
Dibutyltin (DBT)	0.35	5.90	0.43	120
Tributyltin (TBT)	<0.05	0.26	<0.05	0.69
Monooctyltin (MOT)	0.06	0.12	0.37	1.90
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.19 Concentrations of organotin compounds in leachate samples from the METS units incubated at 85 °C/aerobic (sampled December 1999).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.80	<0.05	37	2.70
Dimethyltin (DMT)	0.65	<0.05	48	7.00
Monobutyltin (MBT)	<0.05	0.91	0.17	0.62
Dibutyltin (DBT)	<0.05	0.60	0.08	0.10
Tributyltin (TBT)	<0.05	<0.05	<0.05	<0.05
Monooctyltin (MOT)	<0.05	<0.05	<0.05	<0.05
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05

[*1] All organotin compounds are measured as cations.

Table 3.20 Concentrations of organotin compounds and total tin in leachate samples from the METS units incubated at 85°C/aerobic–55 °C/anaerobic (sampled April 2000).

Analyte[*1]	Control (µg/L)	Sheet (But-Sn stab.) (µg/L)	Foil (Met-Sn stab.) (µg/L)	Flooring (But-Sn stab.) (µg/L)
Monomethyltin (MMT)	0.80	77	650	0.48
Dimethyltin (DMT)	0.65	5.10	290	0.13
Monobutyltin (MBT)	<0.05	3.80	1.70	0.64
Dibutyltin (DBT)	<0.05	0.50	<0.05	<0.05
Tributyltin (TBT)	<0.05	<0.05	<0.05	<0.05
Monooctyltin (MOT)	<0.05	<0.05	<0.05	<0.05
Dioctyltin (DOT)	<0.05	<0.05	<0.05	<0.05
Total Sn[*2]	15.9	26.3	281.3	79.1

[*1] All organotin compounds are measured as cations.
[*2] Cf. Table 3.3 above. Unit is µg Sn/L.

3.5 Phthalic Compounds in the Leachate at Temperatures 20–85 °C

3.5.1 Overall Comments

One important observation of the experiment is that the losses of plasticisers from the PVC flooring (see chapter 3.6) substantially exceeded the findings of all phthalic compounds (i. e., phthalic diesters, monoesters, and phthalic acid) in the leachate. Two possible reasons are plausible: either the phthalic compounds were adsorbed to the solid waste matrix, or they were subject to biodegradation.

The transient appearance and disappearance of phthalic monoesters and, even more significant, phthalic acid, is an indication that an *in-situ* degradation of the phthalate plasticisers BBP and DEHP had occurred. It is noteworthy that both phthalic monoesters (PME) and phthalic acid (PA) are considerably more hydrophilic than the phthalates (PAE) themselves; therefore PME and PA are less inclined to sorption on solids.

At the termination of the METS assays, an analysis for phthalates was conducted on the wet waste residues from the reactors in order to examine the share of BBP and DEHP adsorbed to the solid waste matrix. The results are shown in Table 3.21: it follows that the greater part of the PAE were indeed adsorbed to the waste solids. It should, however, be noted that the given concentrations of BBP and DEHP in the wet waste (»solids«) also include the quantities carried in the leachate, since the recovered waste was soaked with leachate. Hence the concentration of PAE detected in the leachate ought to be less than or equal to the amounts found on the wet waste. Yet this was not the case at 55 °C and 70 °C, where the findings of BBP in the leachate exceeded the measurement for the wet waste. A possible explanation for this discrepancy is that the determination of PAE in the wet waste was performed 2 months after the last PAE analysis in the leachate: in the meantime, a considerable degradation of BBP in the wet waste may have taken place. Note that at 37 °C the findings of BBP in the leachate of the METS unit spiked with the flooring were below the detection limit, whereas the blank control showed higher findings.

Regardless of this discrepancy, these findings of the adsorbed fraction are sufficient to refute an adsorption of phthalates to the solid waste matrix as the only explanation of the observed losses (see next chapter). Furthermore, losses by volatilisation cannot be substantiated by any findings of BBP nor DEHP in the condensate of the exhaust air from the METS unit at 85 °C. As for the anaerobic METS units, the major gas production had occurred before any losses of BBP from the PVC flooring were observed. Consequently, biodegradation most probably plays a significant role, as asserted in the report of the Basic Project (Mersiowsky and Ejlertsson 1999).

Table 3.21 Amounts of BBP and DEHP in the leachate and in the wet waste of the blank control and the METS unit spiked with the PVC flooring, at the respective temperatures.

	BBP		**DEHP**	
Temperature METS unit	Leachate [µg BBP]	Wet waste [µg BBP]	Leachate [µg DEHP]	Wet waste [µg DEHP]
20 °C				
Control	179	1,679	0	339
Flooring	992	4,039	272	1,530
37 °C				
Control	355	4,748	205	2,269
Flooring	0	4,705	248	4,971
55 °C				
Control	262	586	163	366
Flooring	7,603	5,933	810	4,249
70 °C				
Control	205	520	99	367
Flooring	5,287	564	238	38,593
85 °C				
Control	106	183	78	737
Flooring	470	3,215	445	8,728

3.5.2 METS Unit at Temperature 20 °C

At 20 °C the concentration of phthalic compounds peaks after an experimental period of 220 days. The pH in the leachate at that time had been neutral for almost 100 days and concentrations of VFA were low (cf. Figure 3.6), implying that the conditions were methanogenic. The findings of phthalic compounds in the leachate from the spiked METS unit considerably exceeded the concentrations observed in the blank control and can reasonably be attributed to the PVC flooring (Figure 3.12). The concentrations of BBP increased after 200 days of incubation and reached approximately 1 mg/L by the time of termination. The concentrations of DEHP were rather stable throughout the experimental period at about 200–250 µg/L.

It is remarkable that a hypothetical release of only 1 % of the plasticiser DEHP, for instance, would equal 90 mg phthalates in the leachate or in the waste. As discussed above, much less was found. The actual losses are discussed in the following chapter 3.6.

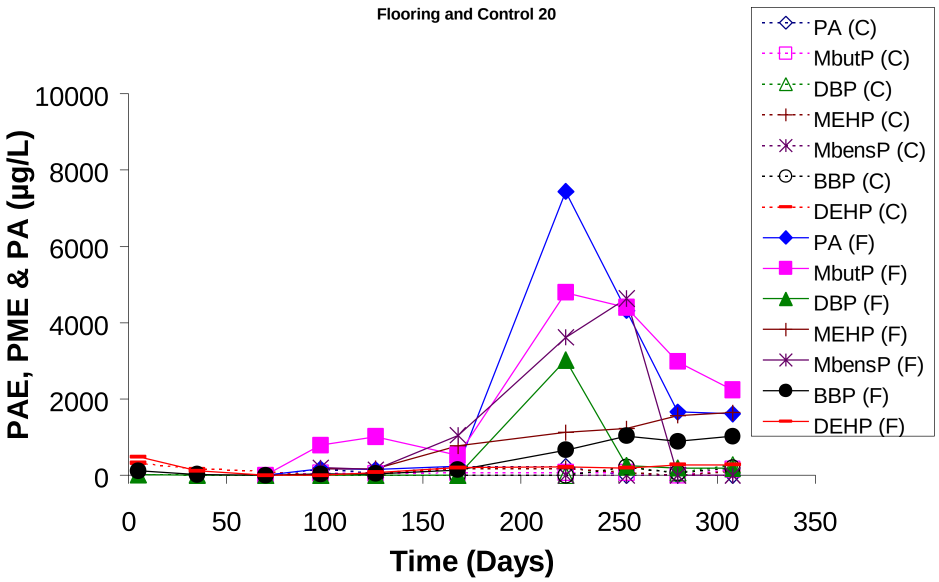


Figure 3.12 Concentrations of DBP, BBP and DEHP in leachate from the METS units incubated at 20 °C: blank control (C; dashed lines) and spiked with PVC flooring (F; black lines).

3.5.3 METS Unit at Temperature 37 °C

The concentrations of phthalic compounds in the METS units incubated at 37 °C were the lowest of the whole series, with phthalic acid (PA) prevailing (Figure 3.13). This is particularly interesting because this METS unit constitutes the baseline and reference to the lysimeter studies in the Basic Project: both the simulation of regular landfill conditions and the anaerobic biodegradation assays were conducted at this mesophilic range of temperatures (Mersiowsky and Ejlertsson 1999).

After about 170 days of incubation the concentrations of BBP decreased and were below the detection limit after day 250. During the disappearance of BBP a peak of phthalic acid was observed, indicating a transformation of BBP to PA. The levels of other phthalic compounds were in the same range as or even below the concentrations observed in the blank control (Figure 3.13). In the blank control, the concentration of BBP increased at day 200 from below detection limit to approximately 250 µg/L by the time of termination.

Taking into account the loss of BBP from the PVC flooring (cf. chapter 3.6) amounting to 1.5 g, it appears plausible, that this loss of BBP was mainly related to biodegradation instead of absorption in the waste matrix (cf. Table 3.21). This hypothesis seems conclusive, as 1) the concentrations of BBP increased in the blank control whereas it decreased in the METS unit spiked with the PVC flooring; and 2) because BBP had been shown to be degraded by landfill microorganisms at 37 °C (see Ejlertsson 1997).

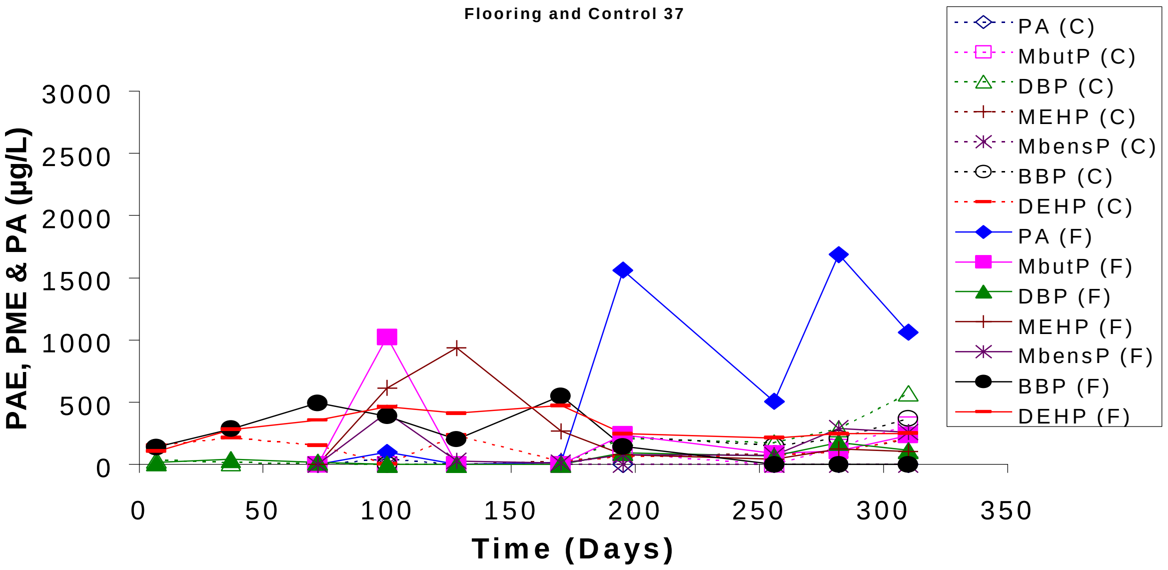


Figure 3.13 Concentrations of DBP, BBP and DEHP in leachate from the METS units incubated at 37 °C: blank control (C; dashed lines) and spiked with PVC flooring (F; black lines).

3.5.4 METS Unit at Temperature 55 °C

Similar to the METS unit running at 20 °C, the concentrations of BBP also started to increase after 200 days of incubation at 55 °C. The findings of phthalic compounds exceeded by far the concentrations detected in the blank control (Figure 3.14), implying that phthalates were lost from the PVC flooring.

According to the determination of the residual content of plasticisers in the PVC matrix (cf. chapter 3.6) approximately 240 mg of BBP were lost from the PVC flooring. This quantity dissolved in leachate would correspond to a BBP concentration of approximately 160 mg/L. This amount of BBP cannot be accounted for by the findings, neither in the leachate (5.5 mg/L at termination) nor in the wet waste (cf. Table 3.21). However, if all phthalic compounds that can be derived from BBP (i. e., MBenzP, MButP, and PA) are added together on a molar basis, the mass balance is almost 100 %. Phthalic acid constitutes approximately 60 % of this total. This observation in turn might lead to the hypothesis that the biodegradation of the aromatic structure is the rate-limiting step under thermophilic landfills conditions.

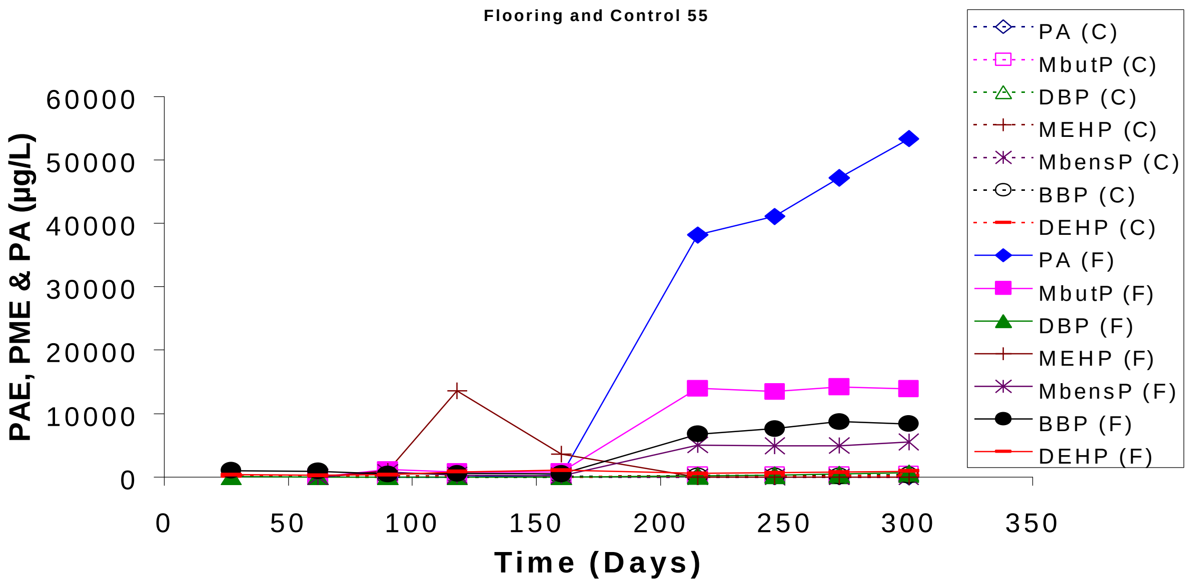


Figure 3.14 Concentrations of DBP, BBP and DEHP in leachate from the METS units incubated at 55 °C: blank control (C; dashed lines) and spiked with PVC flooring (F; black lines).

3.5.5 METS Unit at Temperature 70 °C

At 70 °C the behaviour of the phthalic compounds was observed to be similar as at 55 °C. However, the findings of PA were much higher at 70 °C (250 mg/L, Figure 3.15). The concentrations of BBP and DEHP were approximately 5 mg/L and 300 µg/L, respectively.

The yield of phthalic acid would be approximately 70 % under the premise that the greater part of the BBP lost from the PVC flooring was actually transformed to PA. Yet, this calculation does not take into account the 2.2 g of DEHP that were lost from the PVC matrix (cf. chapter 3.6). Since DEHP is the most hydrophobic phthalate, it seems plausible that in contrast to BBP the greater part of this loss is adsorbed to the waste matrix. This conjecture appears to be corroborated by the high findings of DEHP in the wet waste (cf. Table 3.21).

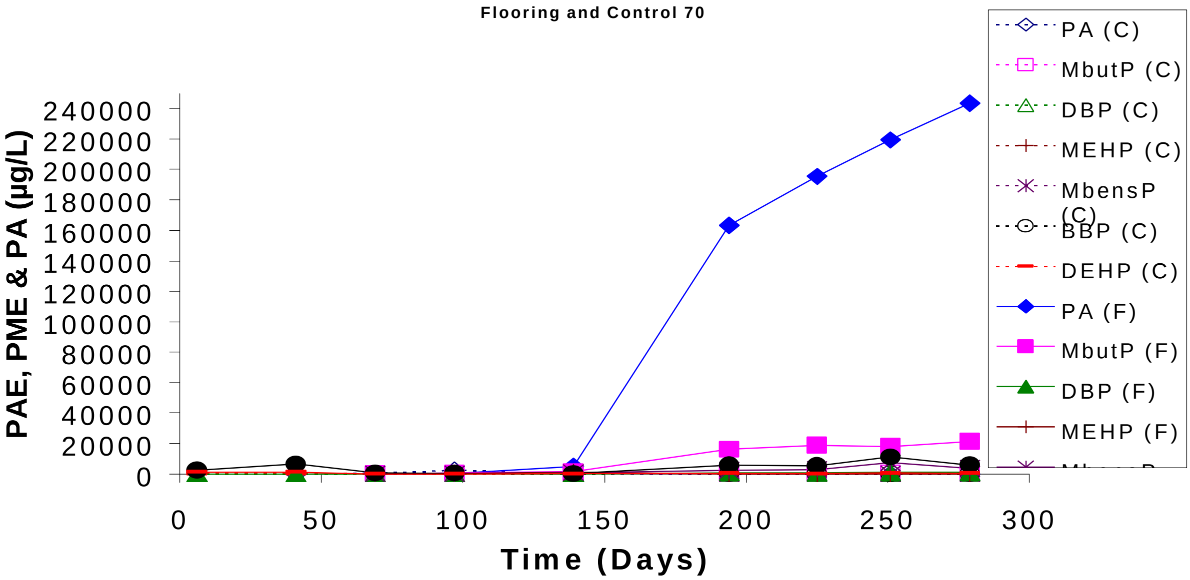


Figure 3.15 Concentrations of DBP, BBP and DEHP in leachate from the METS units incubated at 70 °C: blank control (C; dashed lines) and spiked with PVC flooring (F; black lines).

3.5.6 METS Unit at Temperatures 85 °C (Aerobic) and 55 °C (Anaerobic)

During the aeration period of ca. 150 days approximately 1.7 g of BBP were lost from the PVC flooring, whereas the loss of DEHP was within the analytical error margin (cf. chapter 3.6). During the same period an accumulation of phthalic acid was observed, growing to almost 600 mg/L (Figure 3.16). This quantity of PA would account for approximately 60 % of the BBP lost by day 150, whereas the remainder may have been either adsorbed, degraded or emitted from the METS unit with the exhaust air. A single screening investigation of the exhaust condensate, however, failed to produce any findings.

The accumulation of PA might reasonably also have caused the low pH in the METS unit spiked with the PVC flooring which had reached 4.5 by day 150 (cf. Figure 3.10). After the aeration had been switched off and 400 mL of water were added, the biological activity apparently recovered, resulting in gas production (cf. Figure 3.5) and presumably a consumption of phthalic acid. In contrast to the METS unit incubated under anaerobic conditions at 55 °C throughout the experimental period, it appears as if in this case – first aerobic conditions at 85 °C, then anaerobic conditions at 55 °C – a biodegradation of phthalic acid was indeed accomplished (Figure 3.16).

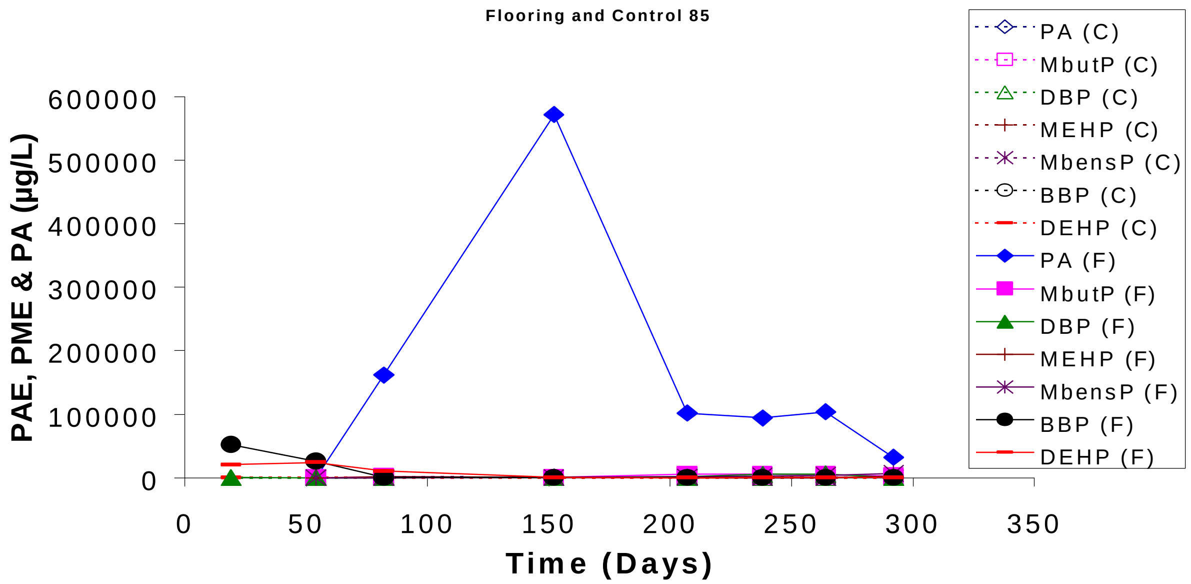


Figure 3.16 Concentrations of DBP, BBP and DEHP in leachate from the METS units incubated at 85 °C (aerobic) and 55 °C (anaerobic, after day 150): blank control (C; dashed lines) and spiked with PVC flooring (F; black lines).

3.6 Residual Contents of Plasticisers DEHP and BBP in the PVC Flooring at Temperatures 20–85 °C

3.6.1 Overall Comments

Generally speaking, substantial losses of plasticisers DEHP and BBP from the PVC flooring were observed at 70 °C under anaerobic conditions, and at 85 °C under aerobic/anaerobic conditions. At temperatures 20 °C there are no detectable losses with the analytical methodology used.

At 37 °C considerable losses of BBP were found, which may be attributed to biodegradation. This would agree with the fate of BBP and its intermediary degradation products observed in the leachate (cf. Figure 3.13). However, there is also a possibility that the measurement of BBP lost from the PVC flooring was subject to an analytical error.

At 55 °C losses are found to be minor with the analytical methodology used. Tables with the loss figures are provided in the appendices.

3.6.2 METS Unit at Temperature 20 °C

At 20 °C, the residual contents of plasticisers DEHP and BBP in the PVC flooring was found not to differ significantly from the original sample (Figure 3.17).

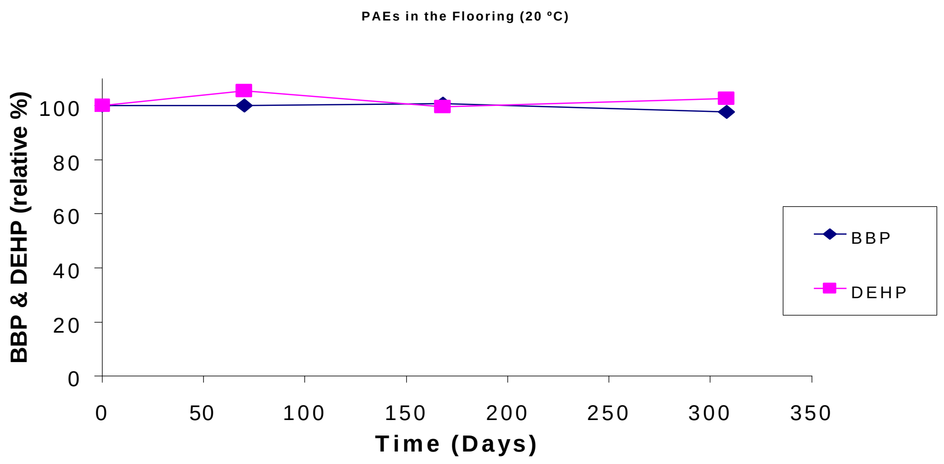


Figure 3.17 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 20 °C; amounts of DEHP and BBP are given in relation to the quantities determined in an untreated original PVC flooring sample.

3.6.3 METS Unit at Temperature 37 °C

At 37 °C the determination of BBP in the PVC flooring showed that less than 1 % of the original contents of this plasticiser had been lost from the PVC material during the first 160 days of the experiment (Figure 3.18). However, after another 140 days of incubation, a 50 % loss of BBP was observed (cf. Table 5.11 in the appendices). Since the findings of DEHP at the same measurement were somewhat higher, there is a certain possibility that this was an erroneous determination. It appears advisable to confirm this analysis by repetition.

If indeed a decrease in the contents of BBP from the original 5.6 % wt. to 3.0 % wt. occurred, this would correspond to a loss of ca. 1.6 g BBP from the original 60 g of PVC flooring that were incubated in this METS unit. Supposing that this whole quantity was dissolved in the leachate (at a total liquid volume of about 1.5 L), the concentration of BBP should be about 1 g/L. Other possible fates are adsorption to the solid waste matrix, biodegradation or evaporation. Neither the concentrations of BBP and its degradation products in the leachate nor the findings of phthalates in the wet waste showed conclusive evidence to support such a hypothesis (see previous chapter, cf. Table 3.21 and Figure 3.13).

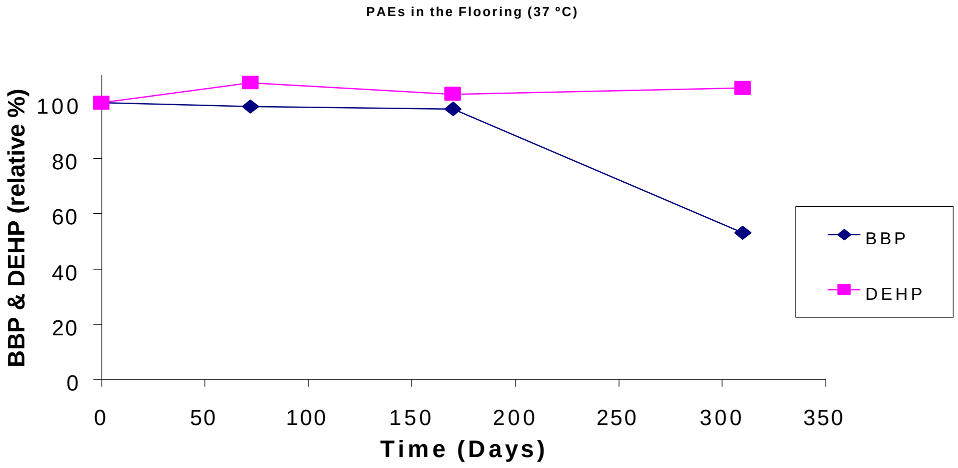


Figure 3.18 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 37 °C; amounts of DEHP and BBP are given in relation to the quantities determined in an untreated original PVC flooring sample.

3.6.4 METS Unit at Temperature 55 °C

At 55 °C the determination of BBP in the PVC flooring indicated that 6–7 % of the original contents of BBP had been lost (Figure 3.19, cf. Table 5.12–Table 5.14 in the appendices). Similar to the findings for the METS unit at 37 °C, a slight increase of DEHP in the PVC flooring was determined; this may be explained by analytical errors and therefore warrants caution.

A decrease in the contents of BBP from the original 5.6 % wt. to 5.2 % wt. would correspond to a loss of ca. 240 mg BBP from the original 60 g of PVC flooring that were incubated in this METS unit. Supposing that this quantity was completely dissolved in the leachate, the concentration of BBP would amount to approximately 160 mg/L. As shown in the previous chapter (cf. Table 3.21 and Figure 3.14), there are considerable findings of phthalates in the wet waste matrix and in the leachate which yet could not account for this loss. From the occurrence of degradation products in the leachate, however, it appears plausible to suggest a substantial biodegradation turnover.

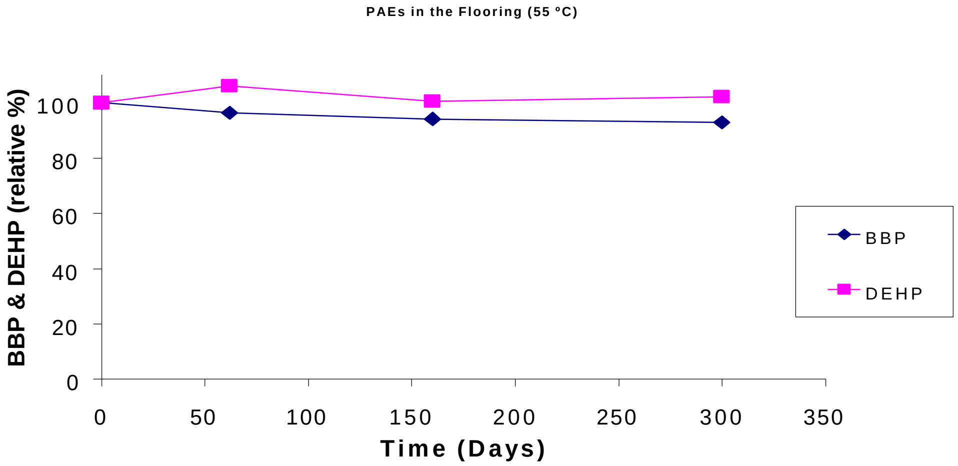


Figure 3.19 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 55 °C; amounts of DEHP and BBP are given in relation to the quantities determined in an untreated original PVC flooring sample.

3.6.5 METS Unit at Temperature 70 °C

At 70 °C there is a noticeable loss of both DEHP and BBP from the PVC flooring. The incubation period was some 25 days shorter for this assay than for the METS units at the lower temperatures for organisational reasons. Nevertheless considerable deficits were detectable of approximately 20 % and 25 % of the original contents of DEHP and BBP, respectively (Figure 3.20, cf. Table 5.15–Table 5.17 in the appendices). These losses are equivalent to ca. 2.2 g of DEHP and 1 g of BBP from the PVC flooring.

Assuming that these amounts of DEHP and BBP were dissolved in the leachate, the concentrations would attain 1500 mg/L and 720 mg/L, respectively. Yet, the greater part of DEHP was probably adsorbed to the waste matrix, whereas BBP was in all probability subject to biodegradation (cf. Table 3.21 and Figure 3.15).

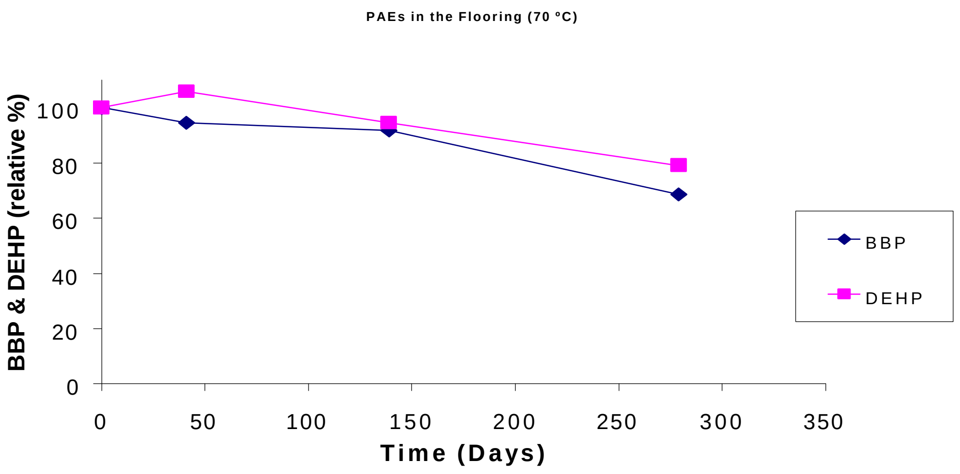


Figure 3.20 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 70 °C; amounts of DEHP and BBP are given in relation to the quantities determined in an untreated original PVC flooring sample.

3.6.6 METS Unit at Temperatures 85 °C (Aerobic) and 55 °C (Anaerobic)

During the aeration period, the PVC flooring samples from the METS unit incubated at 85 °C showed significant losses of BBP, whereas losses of DEHP were minor or not detectable with respect to the analytical error margin (Figure 3.21, cf. Table 5.18–Table 5.19). When the aeration was switched off around day 150 and the METS units were allowed to turn anaerobic, the content of BBP in the PVC flooring was found to have decreased approximately by another 20 % by the last sampling in April 2000. The contents of DEHP in the PVC flooring might have diminished at best by a few % during the total incubation period, but the findings are not conclusive.

Indeed findings indicated a presence of both DEHP and BBP originating from the PVC in the leachate and in the wet waste (cf. Table 3.21 and Figure 3.16). If the entire quantity of BBP lost from the PVC flooring were dissolved in the available leachate, the respective concentration would be 2.3 g/L. While concentrations of DEHP and BBP in the leachate could by far not account for any substantial losses, the substantial presence of phthalic acid implied that BBP, at least, was subject to biodegradation.

Losses of phthalates (or their degradation products) via the exhaust gas appear likewise possible, either by volatilisation (expected to be negligible for phthalates) or by means of condensate. As mentioned earlier, a single screening investigation of the condensate failed to produce any such findings. It should also be noted that the determination of a budget of phthalic compounds in the leachate is impaired by the unknown losses of water due to intense evaporation during the aeration period.

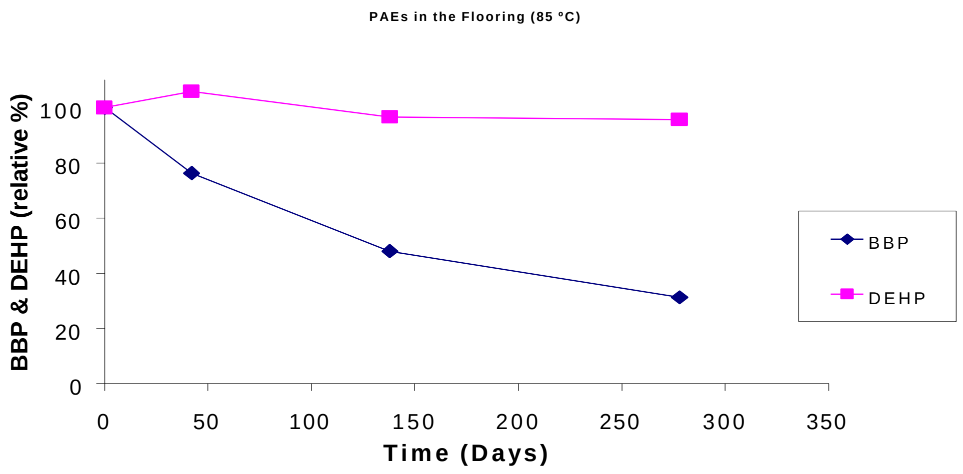


Figure 3.21 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 85 °C under aerobic conditions until day 150 and at 55 °C under anaerobic conditions afterwards; amounts of DEHP and BBP are given in relation to the quantities determined in an untreated original PVC flooring sample.

3.7 Behaviour of the PVC Products at Different Temperatures

3.7.1 Rigid PVC Construction Sheet

At temperatures of 55 °C and above, a discoloration of the rigid PVC construction sheet was observed. At 55 °C and 70 °C the originally white samples showed some tanning, and at 85 °C most of the pieces had tarnished to a brownish hue.

In comparison to the blank control, the METS unit with the butyltin stabilised construction sheet showed higher concentrations of butyltin species in the leachate, with monobutyltin substantially prevailing (Figure 3.22–Figure 3.24). There was an apparent tendency that concentrations of organotin compounds increase with temperature.

At the September sampling, methyltin species were observed in some of the METS units with the PVC construction sheet, but similar observations were also made with the blank control at the same sampling and at similar concentrations (cf. Table 3.14, Table 3.18). The occurrence of methyltin species could result from biotic or abiotic methylation processes.

It should be noted that methylated butyltin species (mixed alkylated species) were not included in the analytical programme, but would provide a good indication of the relevance of these methylation processes.

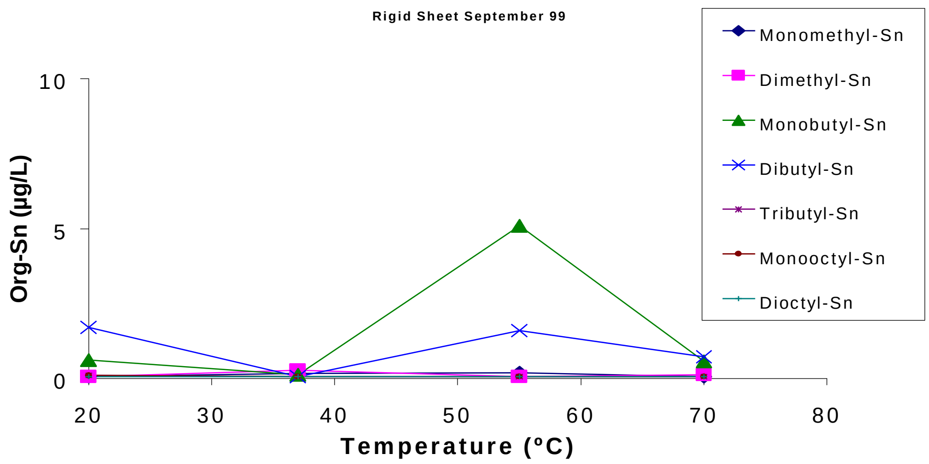


Figure 3.22 Concentrations of organotin species in the leachates from the METS units spiked with the rigid PVC construction sheet, in relation to the investigated range of temperatures 20–70 °C (sampled in September 1999).

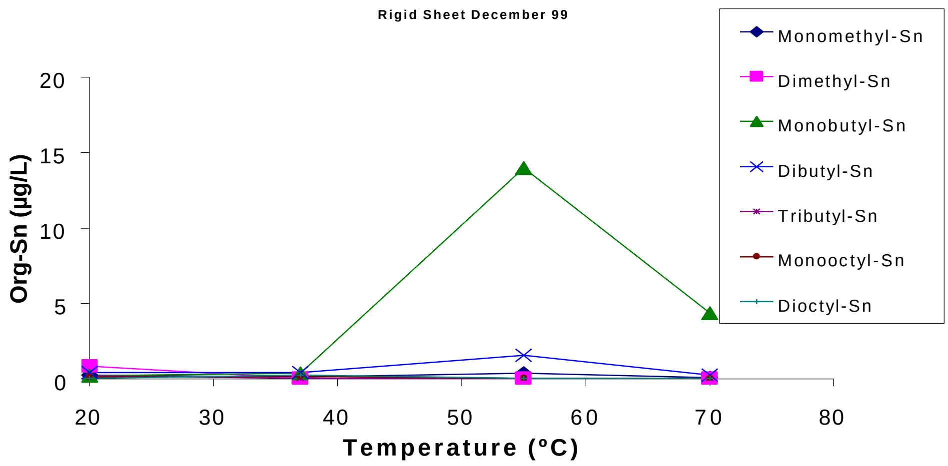


Figure 3.23 Concentrations of organotin species in the leachates from the METS units spiked with the rigid PVC construction sheet, in relation to the investigated range of temperatures 20–70 °C (sampled in December 1999).

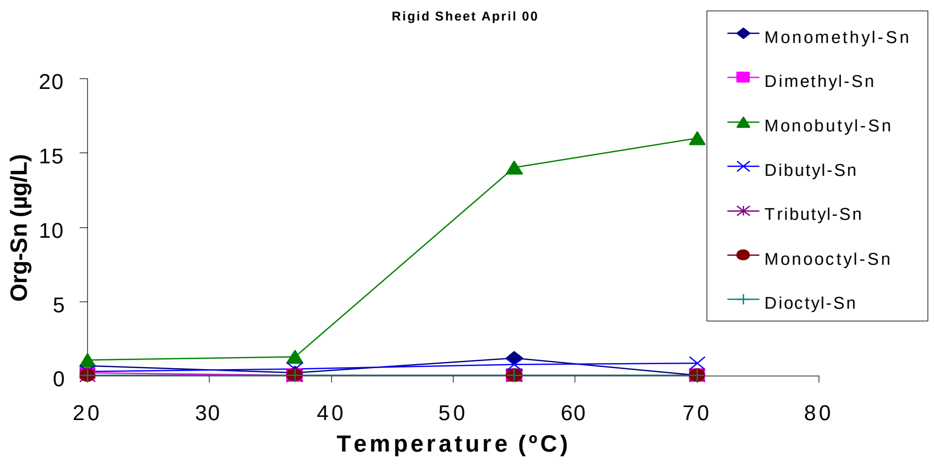


Figure 3.24 Concentrations of organotin species in the leachates from the METS units spiked with the rigid PVC construction sheet, in relation to the investigated range of temperatures 20–70 °C (sampled in April 2000).

Under aerobic conditions at 85 °C, the overall concentrations of organotin species in the METS unit containing the rigid PVC construction sheet decreased between the September and the December sampling (Figure 3.25). However, after the conditions had changed from aerobic to anaerobic at day 150, a formation of predominantly monomethyltin (77 µg/L) was observed. Further findings included dimethyltin (5.1 µg/L), monobutyltin (3.8 µg/L), and dibutyltin (0.5 µg/L).

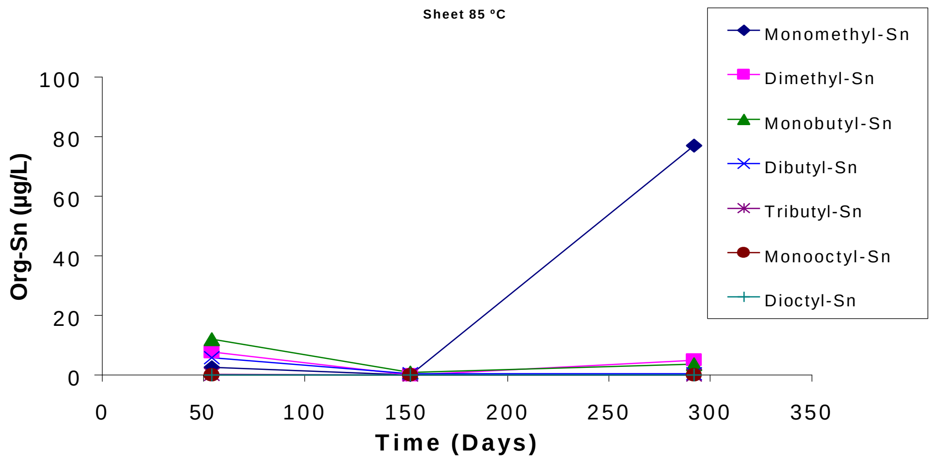


Figure 3.25 Concentrations of organotin species in the leachate from the METS unit containing the rigid PVC construction sheet, operated under aerobic conditions at temperature 85 °C until day 150 and under anaerobic conditions at 55 °C afterwards, measured at the three samplings.

3.7.2 Rigid PVC Foil

An intensifying discoloration of the rigid PVC foil was observed at temperatures of 37 °C and above. At 20 °C no such effects were visible. The foil changed from originally transparent to opaque at 37 °C, to milky at 55 °C, to brownish or milky at 70 °C, whereas under aerobic conditions at 85 °C the hue was more brownish/pinkish.

In comparison to the blank control, the METS unit with the methyltin stabilised foil showed higher concentrations of methyltin species in the leachate. There was an apparent tendency that concentrations of organotin compounds increase with temperature, with a notable increase at 70 °C (cf. Figure 3.26–Figure 3.27). But at the time of the December sampling, the concentrations of methyltin species in the spiked METS unit exceeded those of the blank control already at 20 °C and 37 °C (Figure 3.28).

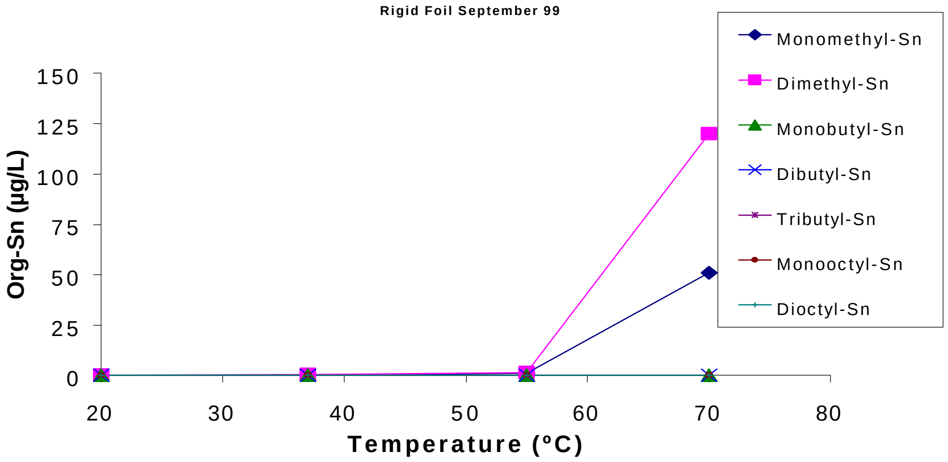


Figure 3.26 Concentrations of organotin species in the leachates from the METS units spiked with the rigid PVC foil, in relation to the investigated range of temperatures 20–70 °C (sampled in September 1999).

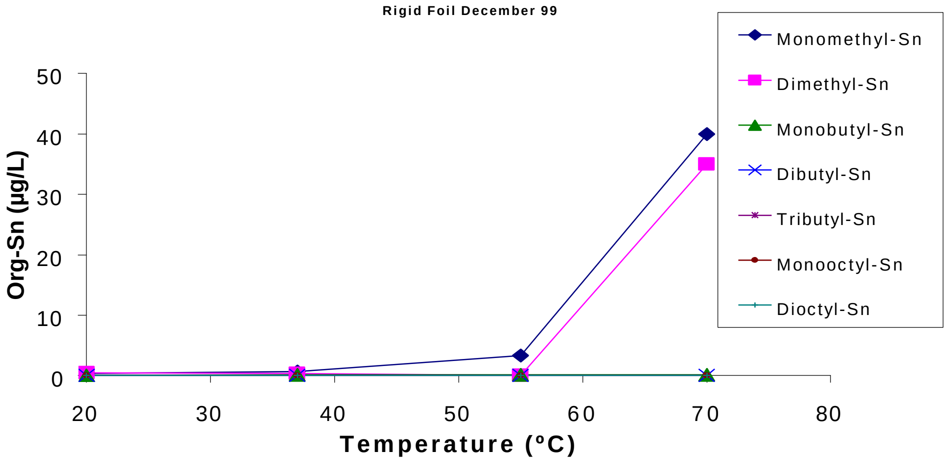
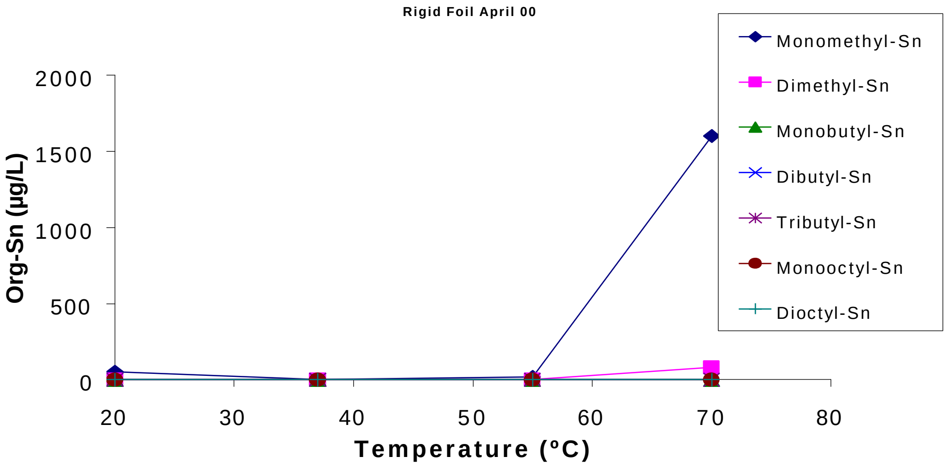


Figure 3.27 Concentrations of organotin species in the leachates from the METS units spiked with the rigid PVC foil, in relation to the investigated range of temperatures 20–70 °C (sampled in December 1999).



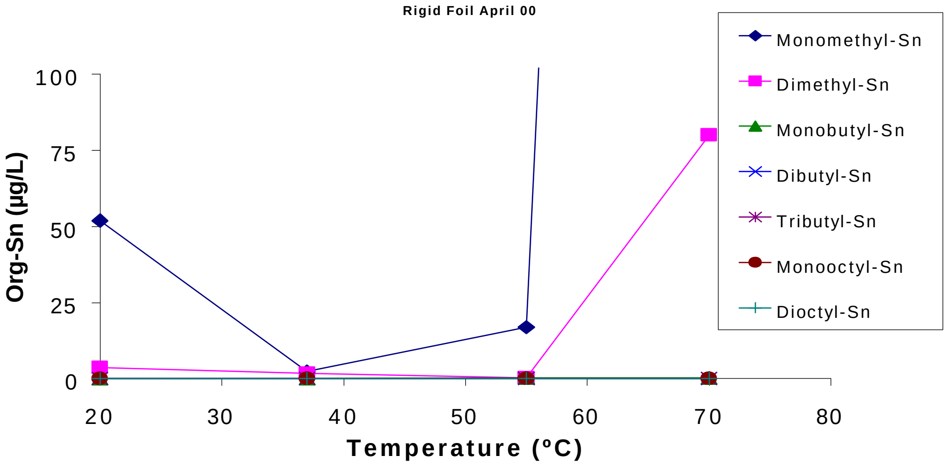


Figure 3.28 Concentrations of organotin species in the leachates from the METS units spiked with the rigid PVC foil, in relation to the investigated range of temperatures 20–70 °C (sampled in April 2000); upper graph scaled to show maximum concentration of monomethyltin, lower graph scaled to show details for demethyltin.

Under aerobic conditions at 85 °C, the ratio of species mono- and dimethyltin changed somewhat when comparing the September and the December sampling (MMT:DMT=24:41 and 37:48 [µg/L], respectively, Figure 3.25). After the conditions had changed from aerobic to anaerobic at day 150 the concentrations of both mono- and dimethyltin rose considerably with the ratio increasing further (650:290). These shifts in distribution between the species may indicate a transformation of dimethyltin into monomethyltin.

It should be noted that the waste at day 150 was rather dehydrated although the inlet air had been moisturised. Therefore it appears possible that organotin species may have been either volatilised with the exhaust gas or adsorbed to the waste matrix during the aerobic period, whereas after the end of the aeration, followed by addition of water and conversion to anaerobic conditions, they may have increasingly entered the leachate again.

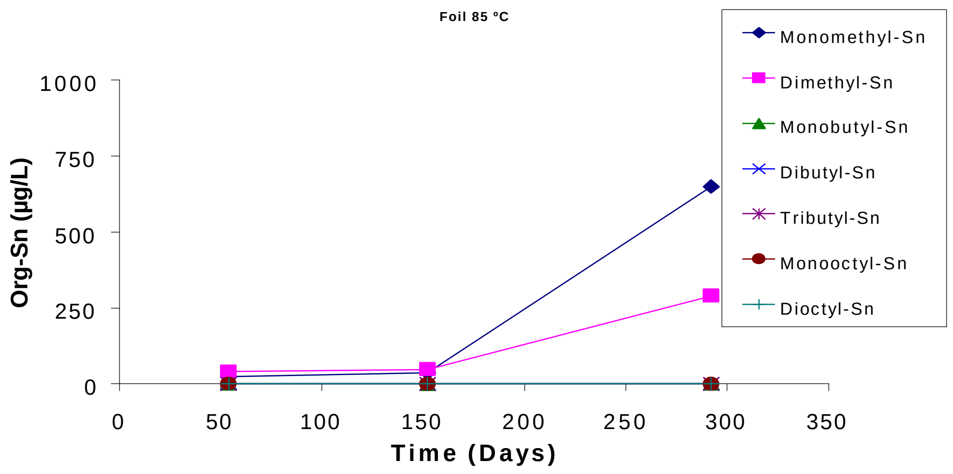


Figure 3.29 Concentrations of organotin species in the leachate from the METS unit containing the rigid PVC foil, operated under aerobic conditions at temperature 85 °C until day 150 and under anaerobic conditions at 55 °C afterwards, measured at the three samplings.

3.7.3 PVC Flooring

At temperatures of 37 °C and above, a discoloration of the PVC flooring was observed. While effects were visible at 20 °C, minor colour changes were discernible at 37 °C by the time of the last sampling in April 2000. At temperatures 55 °C and 70 °C the PVC flooring had tanned, and under aerobic conditions at 85 °C the hue was more brownish/pinkish. Similar observations were made in the Basic Project.

In comparison to the blank control as well as the METS units spiked with rigid butyltin-stabilised PVC construction sheet, the METS unit containing the PVC flooring showed substantially higher concentrations of butyltin species. There was an apparent tendency that concentrations of organotin compounds increase with temperature (Figure 3.30).

It appears plausible that organotin stabilisers in flexible PVC compounds are more inclined to migration. This observation agrees with the results of the Basic Project and the ORTEP Extension Project (Mersiowsky and Ejlertsson 1999), (Mersiowsky and Ejlertsson 2000).

The findings of tributyltin may result either from minor impurities of the butyltin stabiliser compound, or from a transalkylation. The first possibility seems more probable, since there were also findings of octyltin species that most likely originate from a contamination of the stabiliser during production which become discernible if sufficient amounts of the stabiliser are released (Figure 3.30–Figure 3.32). These observations corroborate analogous results of the Basic Project.

Additionally, there was a change of the ratio between the species mono- and dibutyltin when comparing the September and the December samplings (Figure 3.31). This may indicate that a transformation of dibutyltin had taken place; possibly there was a complete degradation to inorganic tin. Although there are substantial findings of total tin in both leachate and waste (cf. Table 3.4), a corresponding increase in inorganic tin cannot be substantiated, since analysis for inorganic tin was not included in the analytical protocol.

It should also be noted that a methylation of inorganic tin or butyltin species may occur; mixed alkylated species (for instance, methylated butyltin) were not included in the analytical programme.

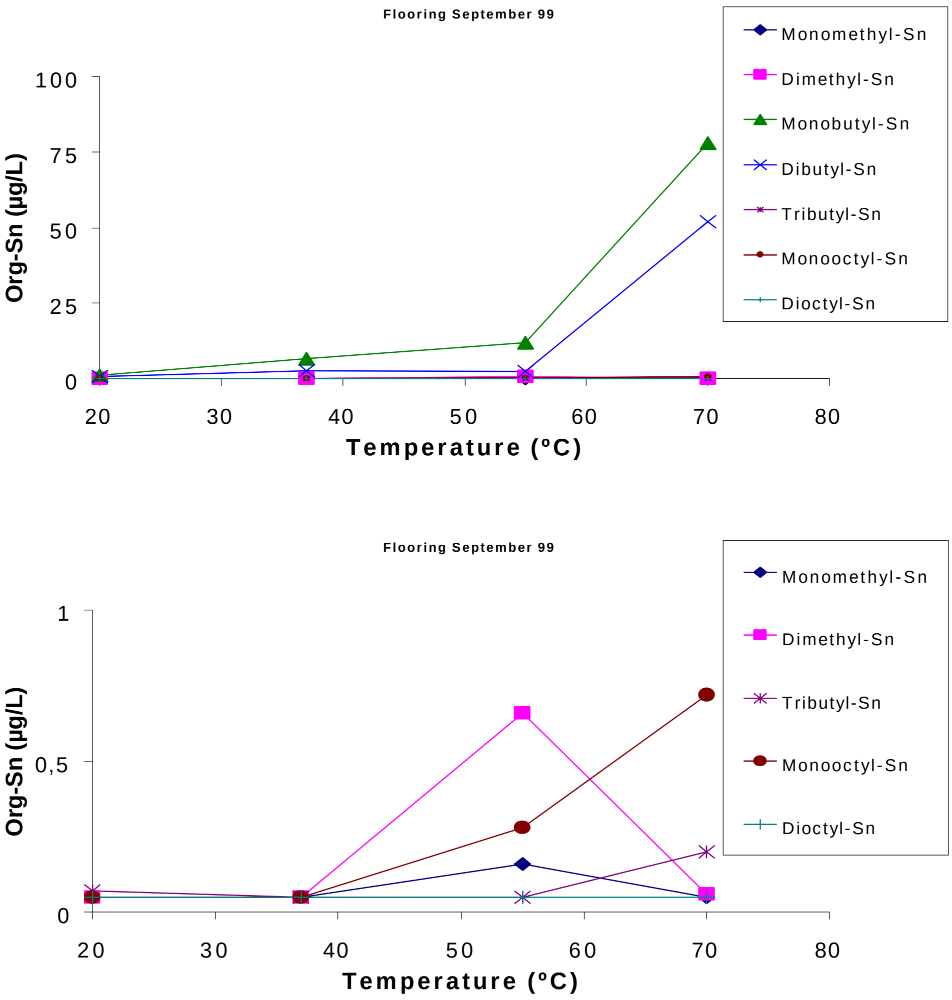
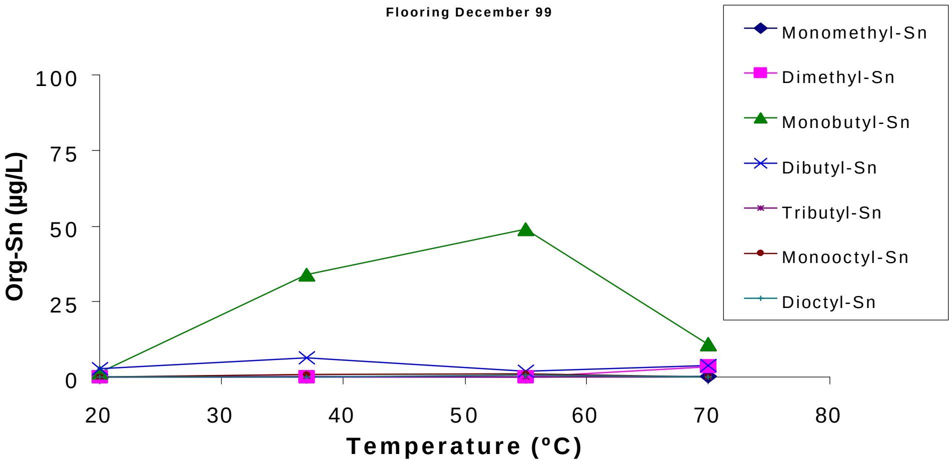


Figure 3.30 Concentrations of organotin species in the leachates from the METS units spiked with the PVC flooring, in relation to the investigated range of temperatures 20–70 °C (sampled in September 1999); upper graph scaled to show maximum concentrations of butyltin species, lower graph scaled to show details for other organotin species.



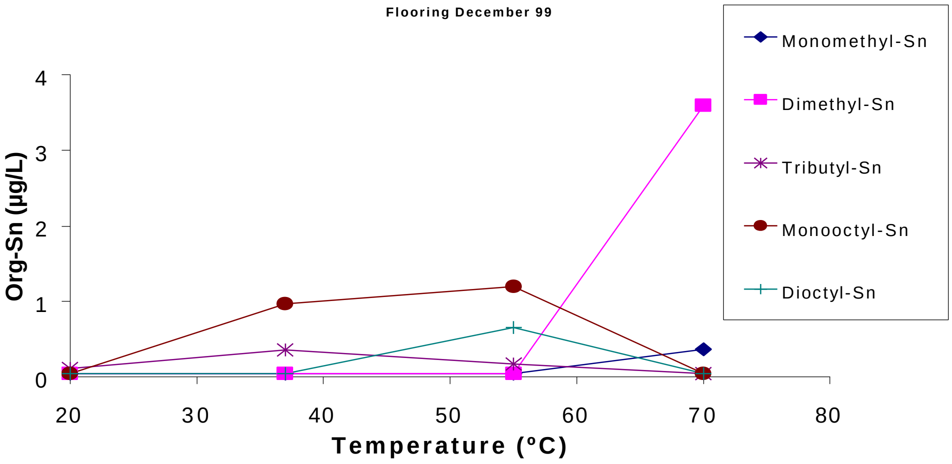
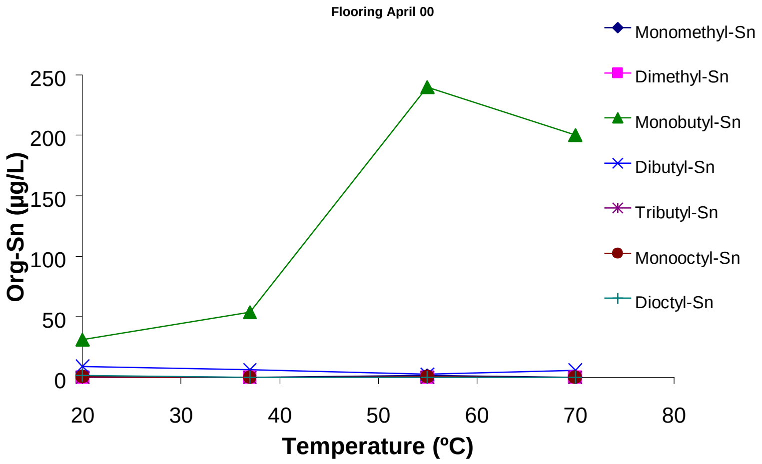


Figure 3.31 Concentrations of organotin species in the leachates from the METS units spiked with the PVC flooring, in relation to the investigated range of temperatures 20–70 °C (sampled in December 1999); upper graph scaled to show maximum concentrations of butyltin species, lower graph scaled to show details for other organotin species.



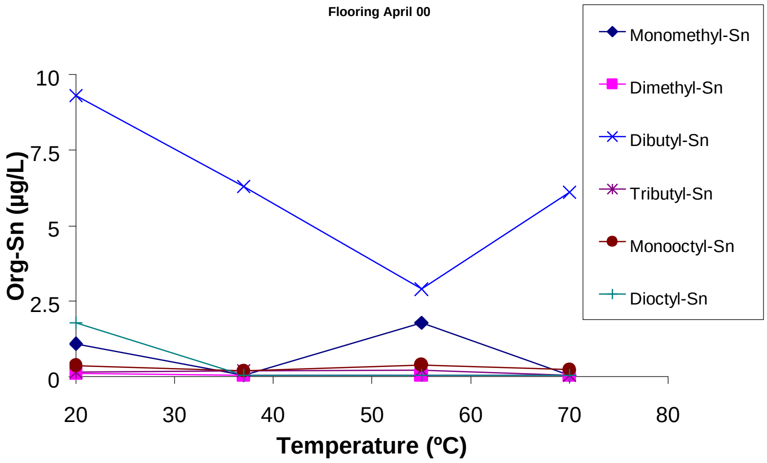


Figure 3.32 Concentrations of organotin species in the leachates from the METS units spiked with the PVC flooring, in relation to the investigated range of temperatures 20–70 °C (sampled in April 2000); upper graph scaled to show maximum concentrations of butyltin species, lower graph scaled to show details for other organotin species.

Under aerobic conditions at 85 °C, the concentrations of butyltin species decreased by two orders of magnitude (Figure 3.33). This may be attributed either to a complete dealkylation and aerobic mineralisation to inorganic tin, and/or to a stripping of volatile organotin species from the METS system.

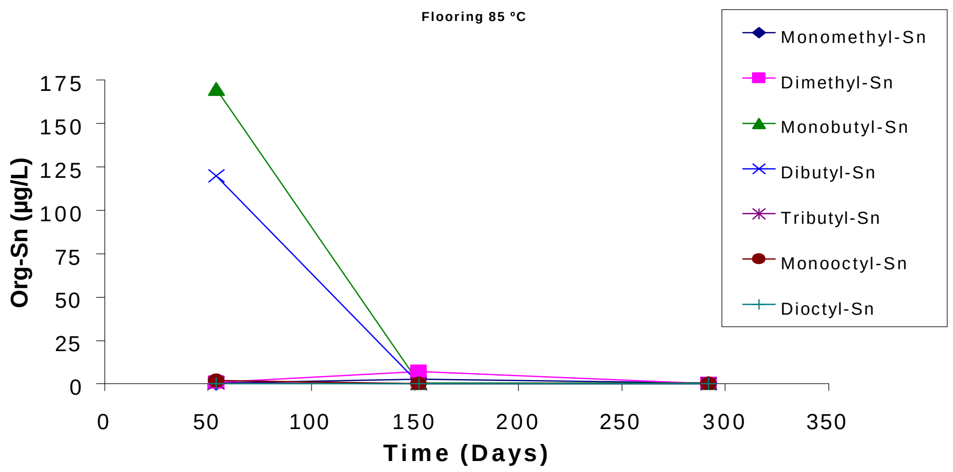


Figure 3.33 Concentrations of organotin species in the leachate from the METS unit containing the rigid PVC construction sheet, operated under aerobic conditions at temperature 85 °C until day 150 and under anaerobic conditions at 55 °C afterwards, measured at the three samplings.

A deficit of plasticisers in the PVC flooring samples was observed at 70 °C by the time of the last sampling (April 2000). Otherwise there were no detectable or no substantial losses at the earlier samplings and lower temperatures (Figure 3.34–Figure 3.36, cf. Figure 3.17–Figure 3.20). The sole exception is a somewhat uncertain measurement at 37 °C indicating a considerable loss of BBP (Figure 3.36, cf. Figure 3.18). This instance notwithstanding, it appears that elevated temperatures (beyond 70 °C) promote losses of plasticisers during extended periods (nine to eleven months in the METS assays).

The results also indicate that, besides temperature and migration, the development of a methanogenic microflora consuming phthalates is apparently a major factor driving the losses of plasticisers. If the substantial loss of BBP at 37 °C were confirmed (Figure 3.36), and taking into consideration the removal of phthalates in the leachate (cf. Figure 3.13) as well as the stable methanogenic performance of the METS unit at 37 °C (cf. chapter 3.2), this would confirm the hypothesis developed during the Basic Project that the biodegradation of phthalates commences when the easily degradable substrates have been consumed (transition phase). In the lysimeter assays of the Basic Project, the same type of PVC flooring showed no substantial losses of BBP, whereas another similar type of PVC flooring did exhibit losses of BBP (Mersiowsky and Ejlertsson 1999).

Under aerobic conditions at 85 °C more than half of the original contents of BBP from the PVC flooring was lost (cf. Figure 3.21), whereas the contents of DEHP decreased only slightly. A biodegradation of BBP at the surface of the flooring or in the vicinity may reasonably have enhanced the migration of BBP from the PVC matrix. The removal of BBP might, however, also be caused by the stripping due to the high flux of moist air through the METS during aeration. Probably both degradation (anaerobic and aerobic) and the high temperature combined with air flow (plus aerosoles) contributed to the observed losses of BBP.

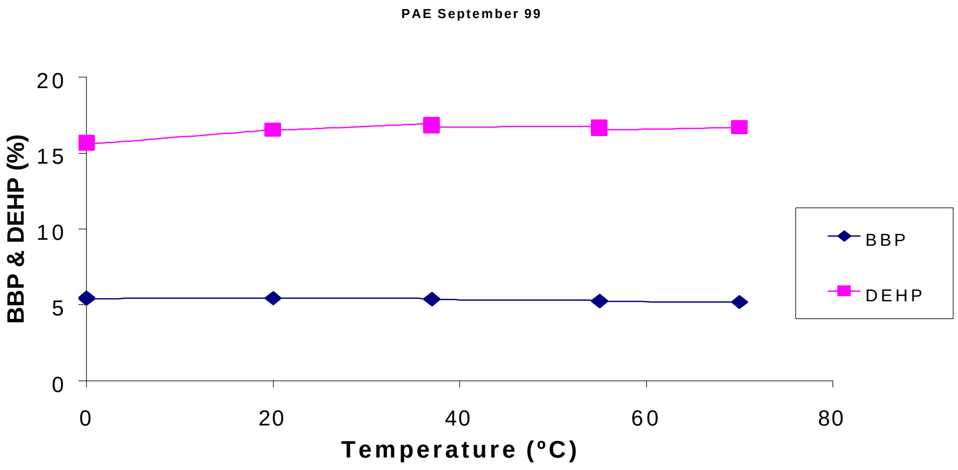


Figure 3.34 Residual contents of plasticisers DEHP and BBP [% wt.] in the PVC flooring at temperatures 20–70 °C; sampled during September 1999 (after 40–70 days of incubation).

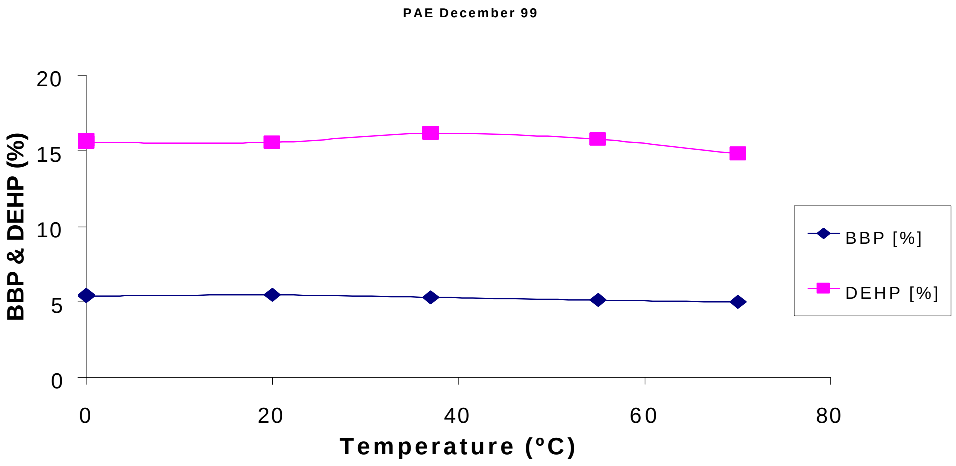


Figure 3.35 Residual contents of plasticisers DEHP and BBP [% wt.] in the PVC flooring at temperatures 20–70 °C; sampled during December 1999 (after 130–170 days of incubation).

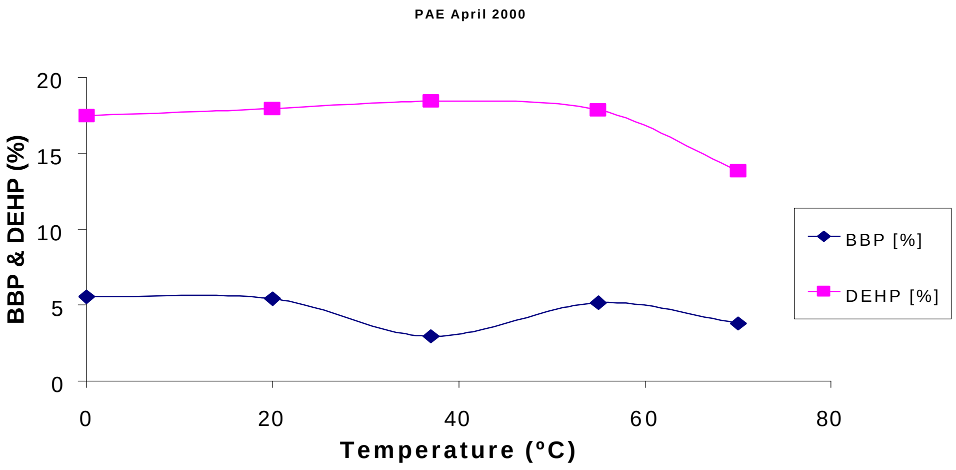


Figure 3.36 Residual contents of plasticisers DEHP and BBP [% wt.] in the PVC flooring at temperatures 20–70 °C; sampled during April 2000 (after 280–320 days of incubation).

3.7.4 Blank Control METS Units

The blank control METS units had been set up as a reference without any PVC or additives. Nonetheless, it was found that even the model waste was by no means without background contamination with the target substances.

The leachates in these blank control units contained concentrations or organotin compounds ranging from below detection limit to ca. 1 µg/L (Figure 3.37–Figure 3.39). The presence of mono- and dibutyltin in the METS unit running at 20 °C may originate from a contamination of the model waste, while possibly these compounds were transformed or degraded in the other control units.

The presence of both mono- and dimethyltin may be attributed either to a background contamination of the model waste or a formation of these compounds from indigenous inorganic tin or mineralised organotin species in the model waste (Figure 3.38–Figure 3.39).

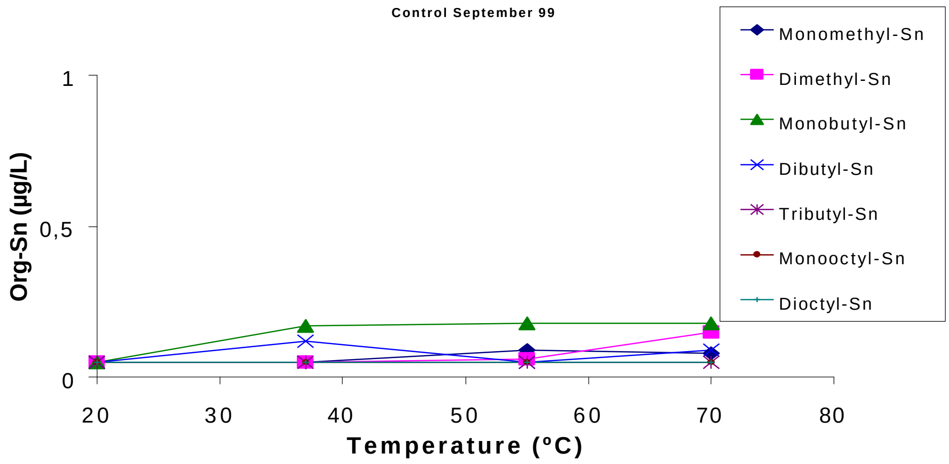


Figure 3.37 Concentrations of organotin species in the leachates from the blank control METS units, in relation to the investigated range of temperatures 20–70 °C (sampled in September 1999).

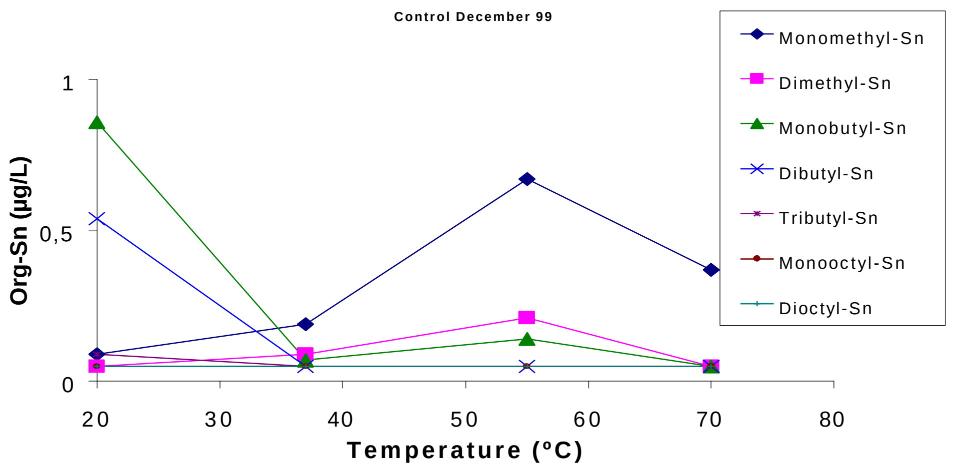


Figure 3.38 Concentrations of organotin species in the leachates from the blank control METS units, in relation to the investigated range of temperatures 20–70 °C (sampled in December 1999).

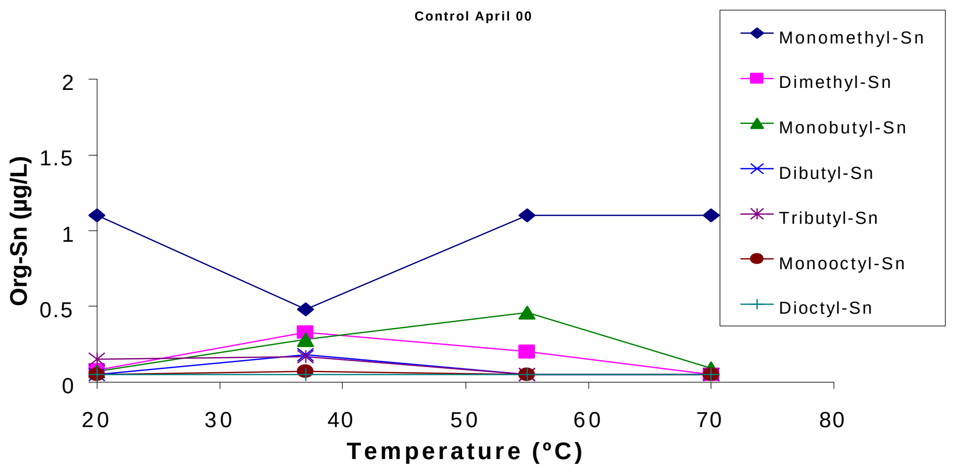


Figure 3.39 Concentrations of organotin species in the leachates from the blank control METS units, in relation to the investigated range of temperatures 20–70 °C (sampled in April 2000).

The detectable and in some cases substantial presence of phthalic compounds in the leachate and in the wet waste of the blank control METS units has already been discussed in previous chapters 3.5 and 3.6 (cf. Table 3.21, Figure 3.12–Figure 3.16).

4 CONCLUSIONS

4.1 General Remarks

The *Modular Environmental Test System (METS)* provides an appropriate method for the investigation of the behaviour of PVC products in deposited municipal solid waste at different temperatures. The experimental set-up and procedure qualify for a standardised test. The METS complements the landfill simulation in lysimeters and enables the operation of a large number of parallel assays at a range of temperatures exceeding the capacities of regular climate rooms.

In spite of the careful composition of a model waste from “pure” materials, a considerable background of the target substances was detected in both leachate and solids. In general, concentrations of both phthalic and organotin species were found to be considerably higher than observed with the landfill simulation assays in lysimeters (Mersiowsky and Ejlertsson 1999). Even values from the blank control METS units often exceed the concentration ranges exhibited by lysimeters spiked with PVC products: this demonstrates the intense leaching of ubiquitous contaminants from waste, regardless of the presence of PVC products.

The quality of the leachate differed from mature landfills and lysimeters in that the organic pollution (TOC) was rather high throughout the experimental period, implying a substantially higher carrying capacity for hydrophobic compounds (Mersiowsky and Ejlertsson 1999). The METS set-up promoted leaching effects due to the water-logged waste and the substantially higher organic pollution of the leachate. This outcome underlines the importance of the leachate matrix and its carrying capacity as a sensitive indicator of test conditions. Comparability between different tests is given for the fate of PVC products and overall budgets of target substances, but concentrations in leachate vary widely on a micro-scale.

The METS set-up allows for an assessment of the maximum emission potential. In order to derive a risk assessment, these values would need to be considered in conjunction with their respective probabilities in pertinent case studies. Predicted environmental concentrations (PEC) of the target substances have already been presented on the basis of measurements at real-world landfill sites (Mersiowsky and Ejlertsson 1999). These real-world measurements in conjunction with the lysimeter assays of the Basic Project and the present METS assays provide a comprehensive picture about the fate of PVC products and their additives under landfill conditions.

A discoloration at temperatures of 55 °C and above was observed for all of the investigated PVC products. In case of the rigid PVC foil, a discoloration occurred already at 37 °C.

The behaviour of the PVC matrix and its additives alters considerably upon glass transition which occurs at approximately 60–80 °C for unplasticised PVC. Plasticisers, particularly those for low-temperature applications, decrease this glass transition temperature to around 20 °C or even into the sub-zero range. In case of losses of plasticisers from flexible PVC products, this critical temperature increases again. Hence it is assumed that a temperature variation in the range of 20–85 °C includes the transition and thus produces non-linear effects.

Additionally, the microbial populations undergo severe alterations at changing temperatures. When progressing through the range of 20–85 °C, several local optima of microbial activity exist. The introduction of aerobic conditions microflora alters the redox state and the biochemical conditions altogether.

The non-linear causality and complex interdependencies of the processes prevent simple predictions of landfill behaviour. As a consequence, an experimental set-up cannot employ higher temperatures with the intention of accelerating landfill processes. Some extrapolation due to continuity of effects may be permissible within a narrow range of temperatures, unless glass transition takes place. Otherwise each configuration of parameters (temperature and redox state) constitutes a rather specific case of its own. The solution to this problem is a scenario analysis, in which the observed effects need to be related to their specific likelihood and relevance.

4.2 Behaviour of Plasticised PVC Products and Fate of Plasticisers

Losses of plasticisers DEHP and BBP from the PVC flooring at temperatures 20–37 °C were not observed or somewhat inconclusive (possibly a considerable loss of BBP occurred at 37 °C). Minor losses were detected at 55 °C, and considerable losses were observed at 70 °C as well as under aerobic conditions at 85 °C (significantly continuing under anaerobic conditions at 55 °C).

In case of losses of plasticisers, there was no corresponding release of phthalates into the leachate. Rather there were indications of a sorption of phthalates to the solid waste matrix (particularly DEHP) as well as of an *in-situ* biodegradation at the surface of the PVC flooring or in the waste matrix (Mersiowsky and Ejlertsson 1999).

The occurrence of degradation products (phthalic monoesters and phthalic acid) in the leachate confirmed the relevance of biodegradation for the removal of phthalates. In some cases at thermophilic temperatures, the degradation of phthalic acid may have been rate-limiting step. In general, however, a stable methanogenic microflora appears to be capable of a complete biodegradation of phthalates (particularly BBP) into biogas.

The possible loss of phthalates and their degradation products via gaseous emissions (or gas-borne condensate or aerosols) is a conjecture that cannot be supported by the present investigation.

4.3 Behaviour of Organotin-stabilised PVC Products and Fate of Organotin Stabilisers

The release of organotin stabilisers from all of the investigated PVC products was detectable at each temperature (20–85 °C). The concentrations of organotin species in the leachate increased with temperature in most cases, particularly at 70 °C and above.

The flexible butyltin-stabilised PVC flooring gave rise to the highest concentrations of butyltin species in the leachate, both in comparison to the blank control and to the butyltin-stabilised rigid PVC construction sheet. The presence of the methyltin-stabilised PVC foil caused findings of methyltin species in the leachate.

While in several cases the concentrations of organotin compounds in the leachate decreased, findings of total tin account for the tin budget: either organotin compounds were adsorbed to the waste matrix, or they were degraded to inorganic tin.

There was sufficient indication that organotin species are subject to biological or abiotic dealkylation processes: thus, di-and monoalkyltin species from stabiliser compounds (as well as TBT) are successively transformed and possibly mineralised to inorganic tin. The respective capability of microorganisms was addressed in more detail in the ORTEP Extension Project (Mersiowsky and Ejlertsson 2000).

Inorganic tin is reasonably supposed to be subject to biological methylation processes. Some findings suggest that this might be relevant. Gaseous emissions of methylated species cannot be excluded, even though the gas was screened just once, but appeared not to play a considerable role.

5 APPENDICES

5.1 Metal Species in the Leachate

Table 5.1 Concentrations of metal species in the leachate of the METS units running at 20 °C (sampled at termination).

Analyte	Control (µg/L)	Sheet (µg/L)	Foil (µg/L)	Flooring (µg/L)
Li	14.0	11.7	15.8	13.7
Be	0.3	0.2	0.3	0.3
B	1002.9	1152.8	1055.2	1306.4
C	149402.2	149367.1	119322.0	146541.0
Mg	32274.4	31313.9	33815.0	31979.9
Al	3822.3	3585.0	1982.3	2918.2
Si	7274.5	7636.2	6601.3	7185.1
P	5319.6	4974.7	4170.6	4332.9
S	42329.0	50952.4	35762.9	41115.9
K	342856.7	339608.1	367124.6	355273.2
Ca	97169.8	85927.9	98542.2	84321.2
Sc	27.8	30.2	18.0	21.8
Ti	246.5	228.6	197.8	189.9
V	0.0	0.0	0.0	0.0
Cr	0.0	0.0	0.0	0.0
Mn	1454.8	1634.9	1000.2	1083.1
Fe	141203.0	149960.9	85649.3	101663.3
Co	40.7	43.3	35.3	34.0
Ni	0.0	0.0	0.0	0.0
Cu	85.3	77.5	52.7	80.0
Zn	2076.3	1241.5	951.8	1233.1
Ga	2.2	3.0	0.0	1.1
Ge	0.0	0.0	0.0	0.0
As	0.0	0.0	0.0	0.0
Se	4.4	1.1	1.5	0.8
Br	409.6	0.0	0.0	0.0
Rb	281.5	264.2	284.2	268.1
Sr	249.0	224.6	257.3	233.6
Y	7.8	8.8	3.4	4.8
Zr	11.7	11.9	11.2	11.1
Nb	1.4	1.5	0.9	1.2
Mo	39.4	35.7	23.6	32.8
Ru	0.0	0.0	0.0	0.0
Rh	0.0	0.0	0.0	0.0
Pd	1.7	1.1	0.8	1.0

Ag	0.8	1.7	0.2	1.0
Cd	3.1	1.9	1.1	0.6
In	15.7	13.4	15.9	12.9
Sn	7.0	5.0	4.8	64.3
Sb	1.6	1.8	1.3	1.7
Te	1.2	0.7	0.3	0.2
I	13.1	14.6	14.0	13.6
Cs	0.7	0.8	0.6	0.5
Ba	166.3	148.2	110.4	141.9
La	6.2	6.9	2.9	3.8
Ce	11.6	13.0	5.7	7.4
Pr	1.8	2.0	0.9	1.1
Nd	6.2	6.5	2.9	3.6
Sm	1.1	1.1	0.5	0.6
Eu	0.2	0.2	0.1	0.1
Gd	1.1	1.2	0.5	0.7
Tb	4.1	6.3	4.3	5.2
Dy	0.9	1.0	0.4	0.6
Ho	0.2	0.2	0.1	0.1
Er	0.5	0.6	0.2	0.3
Tm	0.1	0.1	0.0	0.1
Yb	0.6	0.6	0.2	0.3
Lu	0.2	0.2	0.2	0.1
Hf	0.2	0.2	0.2	0.2
Ta	0.0	0.0	0.0	0.0
W	5.0	5.3	3.5	5.0
Re	0.0	0.0	0.0	0.0
Os	0.0	0.0	0.0	0.0
Ir	0.0	0.0	0.0	0.0
Pt	0.0	0.0	0.0	0.0
Au	0.0	0.0	0.0	0.0
Hg	2.4	1.8	1.2	1.6
Tl	0.6	0.3	0.2	0.2
Pb	49.6	33.5	22.7	28.6
Bi	0.0	0.0	0.0	0.0
Th	0.0	0.0	0.0	0.0
U	5.4	6.6	3.2	4.8

Table 5.2 Concentrations of metal species in the leachate of the METS units running at 37 °C (sampled at termination).

Analyte	Control (µg/L)	Sheet (µg/L)	Foil (µg/L)	Flooring (µg/L)
Li	24.8	28.2	28.0	23.6
Be	0.3	0.3	0.4	0.4
B	1561.3	1797.1	1548.1	1602.0
C	100814.3	104253.8	130387.8	127219.0
Mg	23756.1	25728.3	27051.0	29770.0
Al	2096.7	1669.9	4292.3	3828.6
Si	9347.7	10135.3	13613.7	10160.2
P	3622.0	3570.4	4467.5	4535.7
S	37261.4	14828.5	29417.5	30831.4
K	328054.3	345456.3	347833.9	324116.5
Ca	82808.3	83286.1	103483.3	150190.0
Sc	25.4	23.1	29.4	25.4
Ti	171.2	169.8	239.0	280.4
V	0.0	0.0	0.0	0.0
Cr	0.0	0.0	0.0	0.0
Mn	1665.4	965.1	1889.1	2621.6
Fe	43767.4	39306.9	76695.6	111866.1
Co	51.3	56.8	63.1	57.5
Ni	0.0	0.0	0.0	0.0
Cu	40.7	42.1	71.8	68.5
Zn	939.5	484.3	1422.8	1507.3
Ga	0.0	0.0	0.9	0.8
Ge	0.0	0.0	0.0	0.0
As	0.0	0.0	0.0	0.0
Se	0.1	0.1	0.2	0.0
Br	0.0	0.0	0.0	0.0
Rb	265.6	266.3	296.4	258.3
Sr	187.7	200.6	241.0	294.0
Y	9.7	7.2	15.8	21.4
Zr	5.4	4.0	6.6	10.5
Nb	0.9	1.0	1.3	1.1
Mo	27.1	23.6	33.3	36.8
Ru	0.0	0.0	0.0	0.0
Rh	0.0	0.0	0.0	0.0
Pd	0.9	0.4	0.8	1.0
Ag	0.2	0.1	0.2	0.6
Cd	2.2	1.0	1.2	3.5
In	14.3	14.5	16.1	15.4
Sn	4.2	4.8	4.4	77.4
Sb	0.6	0.5	0.7	0.7
Te	0.0	0.1	0.1	0.1

I	13.7	15.7	15.7	14.8
Cs	1.0	1.0	1.3	1.1
Ba	234.8	186.8	406.7	459.4
La	8.2	5.6	14.8	22.5
Ce	17.0	11.6	29.6	43.2
Pr	2.4	1.7	4.3	6.4
Nd	8.3	5.9	14.6	22.3
Sm	1.5	1.0	2.6	3.9
Eu	0.3	0.2	0.5	0.7
Gd	1.6	1.2	2.6	3.8
Tb	5.4	4.0	4.1	3.5
Dy	1.3	0.9	2.0	2.8
Ho	0.2	0.2	0.3	0.5
Er	0.7	0.5	1.1	1.4
Tm	0.1	0.1	0.2	0.2
Yb	0.7	0.5	1.1	1.5
Lu	0.1	0.2	0.3	0.3
Hf	0.1	0.1	0.1	0.3
Ta	0.0	0.0	0.0	0.0
W	2.1	2.3	2.3	2.4
Re	0.0	0.0	0.0	0.0
Os	0.0	0.0	0.0	0.0
Ir	0.0	0.0	0.0	0.0
Pt	0.0	0.0	0.0	0.0
Au	0.0	0.0	0.0	0.0
Hg	0.9	1.1	1.4	1.3
Tl	0.1	0.1	0.1	0.1
Pb	25.0	19.0	33.1	48.9
Bi	0.0	0.0	0.0	0.0
Th	0.0	0.0	0.0	0.0
U	6.7	5.8	9.2	9.8

Table 5.3 Concentrations of metal species in the leachate of the METS units running at 55 °C (sampled at termination).

Analyte	Control (µg/L)	Sheet (µg/L)	Foil (µg/L)	Flooring (µg/L)
Li	37.1	45.1	56.1	66.6
Be	0.8	0.4	0.5	0.8
B	2124.3	2322.7	2235.6	2691.3
C	267099.9	274437.9	271509.6	329533.5
Mg	34916.3	35660.0	34190.4	32648.6
Al	4639.4	3602.5	4041.6	2980.3
Si	7299.9	8047.0	9483.8	6522.7
P	9302.6	9961.9	7622.5	8611.9
S	79459.0	74612.6	77378.3	96515.5
K	378423.7	346921.2	-	-
Ca	206407.6	221539.7	196759.5	173877.0
Sc	27.5	3.6	25.8	18.5
Ti	495.2	486.8	370.7	381.6
V	0.0	0.0	0.0	0.0
Cr	0.0	0.0	0.0	0.0
Mn	4509.0	4299.1	4111.3	3582.5
Fe	48139.0	67546.8	55247.1	44035.6
Co	29.7	29.2	27.9	23.9
Ni	0.0	0.0	0.0	0.0
Cu	166.8	219.0	177.1	157.5
Zn	30055.0	38546.1	38591.1	31271.3
Ga	3.3	2.5	2.3	1.8
Ge	0.0	0.0	0.0	0.0
As	0.0	0.0	0.0	0.0
Se	3.9	4.4	3.6	3.6
Br	0.0	0.0	0.0	0.0
Rb	331.8	335.2	360.5	378.4
Sr	479.2	439.9	423.4	375.9
Y	73.3	61.7	59.3	47.2
Zr	15.9	14.7	12.3	38.0
Nb	3.0	2.6	2.1	2.5
Mo	130.4	103.8	130.1	146.8
Ru	0.0	0.0	0.0	0.0
Rh	0.0	0.0	0.0	0.0
Pd	1.1	1.2	0.3	2.1
Ag	1.1	1.3	0.8	0.8
Cd	4.3	3.9	3.7	1.7
In	12.3	6.6	7.3	9.5
Sn	7.9	20.5	11.6	238.3
Sb	4.1	4.6	4.6	4.4
Te	0.2	0.1	0.1	0.1

I	19.0	19.1	19.4	20.0
Cs	2.1	2.2	2.3	2.7
Ba	854.3	773.3	802.1	712.5
La	81.3	66.6	59.9	45.3
Ce	161.7	144.6	123.4	89.1
Pr	23.3	20.2	17.7	13.1
Nd	78.9	64.8	57.4	43.6
Sm	13.5	11.1	10.0	7.7
Eu	2.5	2.0	1.9	1.4
Gd	14.0	11.1	10.2	7.9
Tb	8.2	3.8	6.2	6.3
Dy	9.8	8.2	7.6	6.0
Ho	1.7	1.4	1.3	1.0
Er	4.9	3.8	3.7	3.0
Tm	0.7	0.6	0.6	0.5
Yb	5.1	3.9	3.8	3.3
Lu	0.7	0.7	0.6	0.5
Hf	0.4	0.4	0.4	0.9
Ta	0.1	0.0	0.0	0.1
W	7.8	5.9	7.3	9.9
Re	0.0	0.0	0.0	0.0
Os	0.0	0.0	0.0	0.0
Ir	0.0	0.0	0.0	0.0
Pt	0.0	0.0	0.0	0.0
Au	0.0	0.0	0.0	0.0
Hg	3.7	3.3	3.2	3.2
Tl	0.3	0.4	0.5	0.4
Pb	95.0	104.1	83.4	62.9
Bi	0.0	0.0	0.0	0.0
Th	0.0	0.0	0.0	0.1
U	30.0	22.7	24.8	27.8

Table 5.4 Concentrations of metal species in the leachate of the METS units running at 70 °C (sampled at termination).

Analyte	Control (µg/L)	Sheet (µg/L)	Foil (µg/L)	Flooring (µg/L)
Li	117.2	73.8	78.1	100.1
Be	0.3	0.2	0.3	0.3
B	2705.5	2367.1	2095.5	2737.3
C	704452.1	487958.8	481127.3	546311.3
Mg	78149.7	38005.8	41267.6	48696.6
Al	4893.4	3694.8	4487.1	5107.3
Si	26401.0	14520.5	15997.3	18467.2
P	5735.7	3326.6	6953.0	5992.1
S	130209.8	63328.9	98088.2	111754.9
K	-	-	-	-
Ca	324274.5	125513.9	131542.7	158750.5
Sc	70.2	39.5	30.1	47.7
Ti	528.0	239.7	351.0	348.2
V	0.0	0.0	0.0	0.0
Cr	0.0	0.0	0.0	0.0
Mn	16436.5	8014.8	6898.2	8332.6
Fe	161330.8	102418.5	114895.8	139127.5
Co	26.3	13.5	29.9	27.0
Ni	0.0	0.0	0.0	0.0
Cu	286.8	187.0	322.6	304.3
Zn	63467.7	53956.1	73588.1	71227.0
Ga	3.7	3.3	4.2	5.1
Ge	3.3	0.0	0.0	3.1
As	0.0	0.0	0.0	0.0
Se	5.1	2.7	3.3	3.2
Br	16.6	0.0	0.0	0.0
Rb	878.5	533.8	519.6	534.1
Sr	570.7	246.3	202.2	249.4
Y	15.9	9.8	13.6	16.0
Zr	46.3	28.2	50.8	46.5
Nb	1.8	1.0	2.0	1.6
Mo	113.6	53.1	137.1	85.3
Ru	0.0	0.0	0.0	0.0
Rh	0.0	0.0	0.0	0.0
Pd	3.5	1.6	2.1	2.4
Ag	1.2	0.7	1.5	10.1
Cd	4.3	1.7	3.3	5.3
In	17.6	12.0	6.6	14.1
Sn	17.0	32.6	1600.9	462.0
Sb	3.3	1.2	6.9	6.8
Te	0.0	0.0	0.0	0.0

I	17.1	10.5	12.5	12.3
Cs	4.4	2.8	2.4	2.8
Ba	321.5	164.9	151.7	180.6
La	10.0	6.7	7.3	8.9
Ce	20.7	13.7	16.2	19.8
Pr	3.0	2.0	2.4	2.8
Nd	10.4	7.1	8.1	10.0
Sm	1.9	1.3	1.5	1.9
Eu	0.4	0.3	0.3	0.4
Gd	2.1	1.4	1.6	2.0
Tb	5.0	3.6	3.6	4.4
Dy	1.7	1.1	1.4	1.6
Ho	0.3	0.2	0.3	0.3
Er	1.1	0.6	0.9	1.0
Tm	0.2	0.1	0.1	0.2
Yb	1.2	0.6	1.1	1.2
Lu	0.4	0.3	0.3	0.3
Hf	1.0	0.6	1.2	1.1
Ta	0.1	0.1	0.1	0.1
W	4.2	3.1	5.9	5.3
Re	0.0	0.0	0.0	0.0
Os	0.0	0.0	0.0	0.0
Ir	0.0	0.0	0.0	0.0
Pt	0.0	0.0	0.0	0.0
Au	0.0	0.0	0.0	0.0
Hg	1.3	1.2	1.5	2.2
Tl	0.6	0.3	0.7	0.4
Pb	94.2	55.8	106.6	83.2
Bi	0.0	0.0	0.0	0.0
Th	0.0	0.0	0.0	0.0
U	9.0	5.2	13.7	10.5

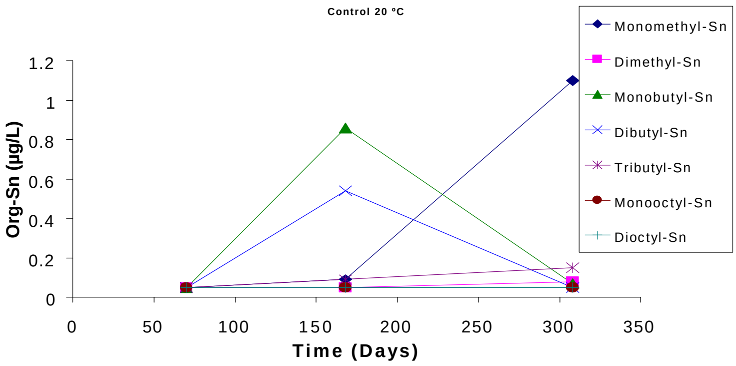
Table 5.5 Concentrations of metal species in the leachate of the aerobic/anaerobic METS units running at 85/55 °C (sampled at termination).

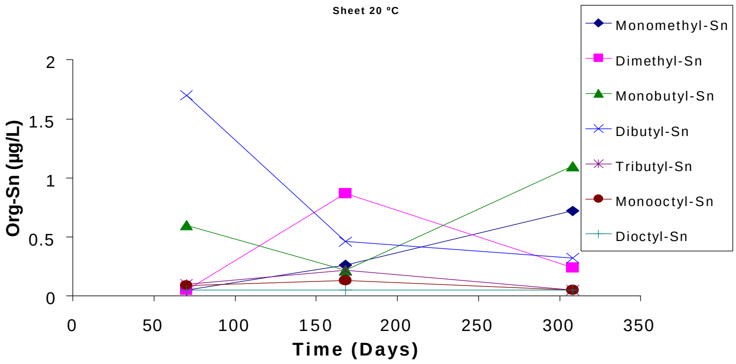
Analyte	Control (μg/L)	Sheet (μg/L)	Foil (μg/L)	Flooring (μg/L)
Li	32.9	38.6	58.0	63.7
Be	0.9	0.4	0.5	0.3
B	1426.0	752.9	1427.1	962.1
C	360992.8	257816.6	233856.9	191547.2
Mg	62728.3	42382.5	42912.3	31974.5
Al	4630.3	6391.1	9318.8	10214.0
Si	8586.2	5581.1	7383.0	3483.5
P	6369.9	5243.0	6376.6	3385.6
S	191824.9	129485.4	120698.0	77213.5
K	-	-	-	-
Ca	257634.8	156660.2	164178.6	99117.1
Sc	20.3	22.8	12.7	8.1
Ti	471.3	297.3	302.8	203.3
V	0.0	0.0	0.0	0.0
Cr	0.0	0.0	0.0	0.0
Mn	6238.7	5380.8	5066.8	2983.8
Fe	335792.5	221543.1	161819.9	115671.1
Co	53.2	43.7	30.8	25.7
Ni	0.0	0.0	0.0	0.0
Cu	1106.1	519.2	626.2	312.4
Zn	48728.7	33504.7	45769.9	19100.8
Ga	1.6	2.4	2.3	2.3
Ge	0.0	0.0	0.0	0.0
As	0.0	0.0	0.0	0.0
Se	8.5	4.8	5.4	2.3
Br	1188.5	691.7	716.4	539.0
Rb	1176.7	928.0	1055.2	944.1
Sr	531.3	336.0	333.3	209.9
Y	23.7	18.6	22.5	9.0
Zr	71.5	35.1	38.6	15.6
Nb	2.8	1.8	1.7	1.0
Mo	196.6	169.2	154.3	139.8
Ru	0.0	0.0	0.0	0.0
Rh	0.0	0.0	0.0	0.0
Pd	3.3	2.0	2.3	1.1
Ag	3.5	1.7	1.7	0.3
Cd	9.6	4.8	5.2	4.7
In	7.4	7.8	7.8	5.0
Sn	15.9	26.3	281.3	79.1
Sb	3.8	2.8	1.6	0.8
Te	0.1	0.0	0.0	0.0

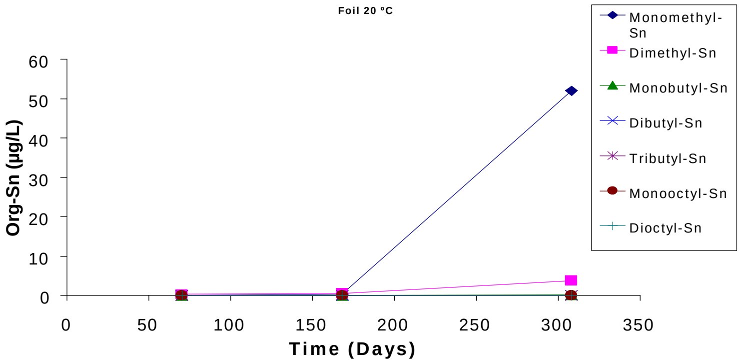
I	10.3	9.0	9.1	6.9
Cs	1.3	0.8	2.1	1.5
Ba	280.0	227.0	276.1	168.1
La	19.7	16.0	20.9	8.2
Ce	46.5	36.9	50.4	18.0
Pr	6.0	4.9	6.4	2.5
Nd	20.2	15.9	21.7	8.3
Sm	3.8	2.8	3.8	1.4
Eu	0.7	0.5	0.7	0.3
Gd	3.6	2.9	3.8	1.5
Tb	3.1	4.0	2.7	1.5
Dy	2.8	2.2	2.8	1.1
Ho	0.5	0.4	0.5	0.2
Er	1.5	1.2	1.4	0.5
Tm	0.2	0.2	0.2	0.1
Yb	1.8	1.3	1.5	0.6
Lu	0.4	0.3	0.3	0.2
Hf	1.5	0.6	0.7	0.3
Ta	0.1	0.1	0.1	0.0
W	2.3	2.2	1.7	2.1
Re	0.0	0.0	0.0	0.0
Os	0.0	0.0	0.0	0.0
Ir	0.0	0.0	0.0	0.0
Pt	0.1	0.0	0.0	0.0
Au	0.1	0.0	0.0	0.0
Hg	1.0	0.7	0.8	1.1
Tl	0.9	0.3	0.4	0.1
Pb	188.0	75.3	117.8	49.6
Bi	0.1	0.0	0.0	0.0
Th	0.0	0.0	0.1	0.0
U	21.1	15.9	19.3	9.0

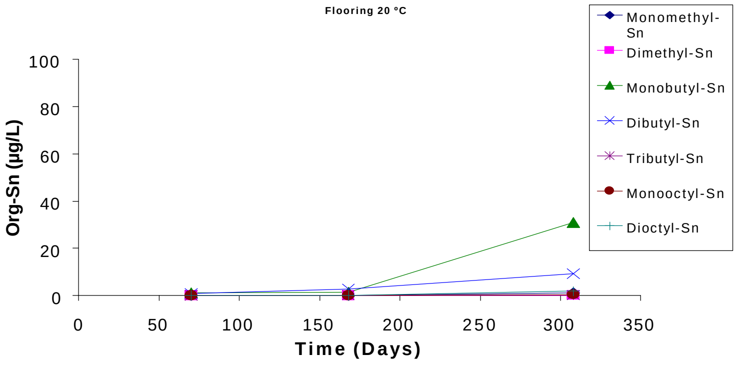
5.2 Organotin Compounds in Leachate

5.2.1 METS Units at Temperature 20 °C

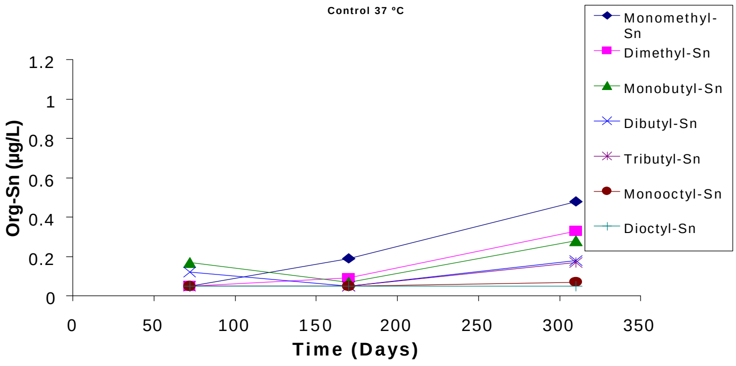


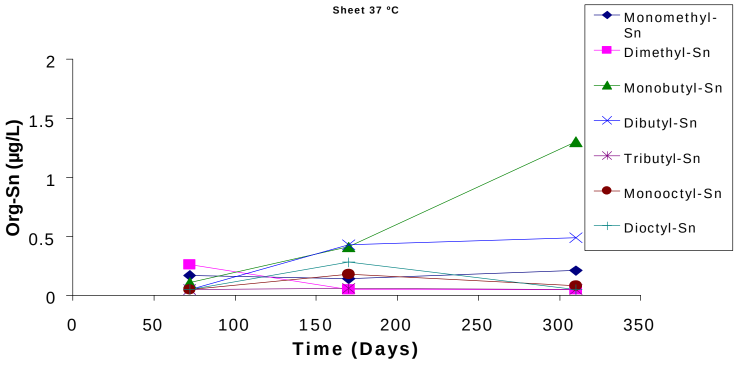


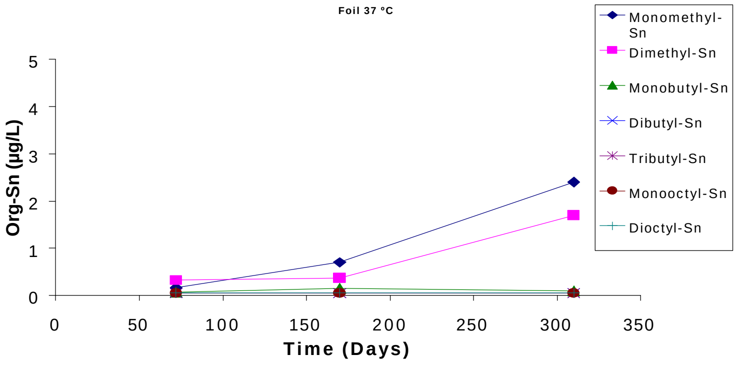


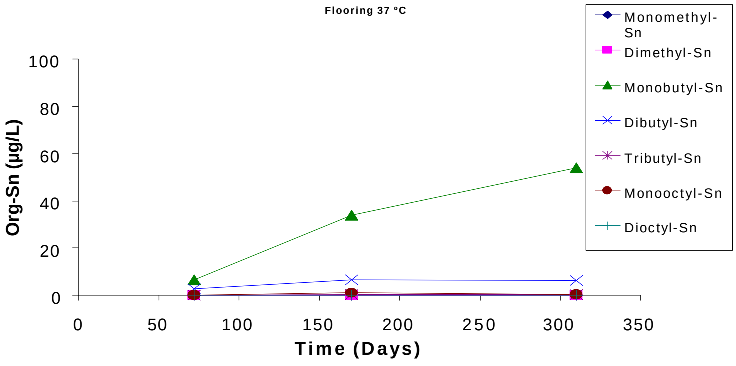


5.2.2 METS Units at Temperature 37 °C

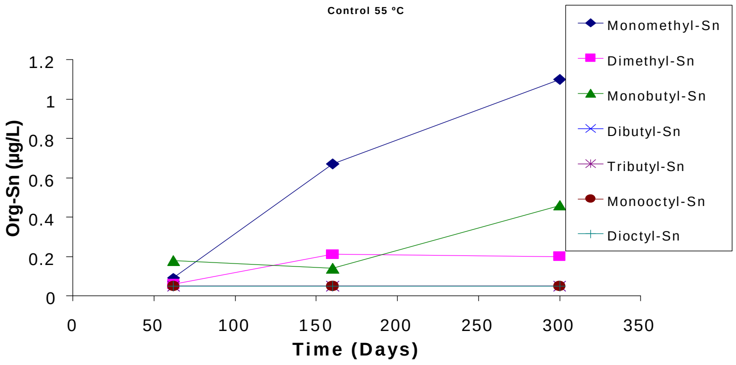


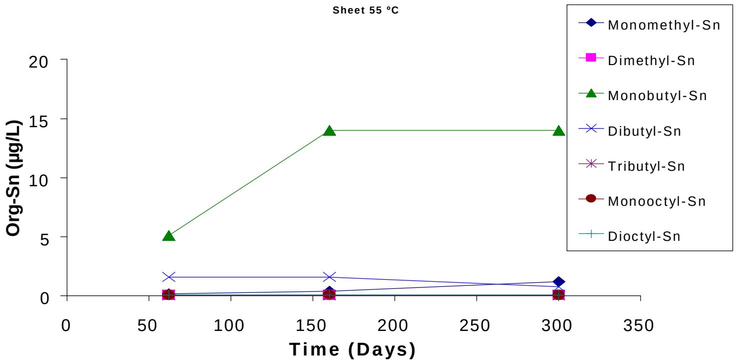


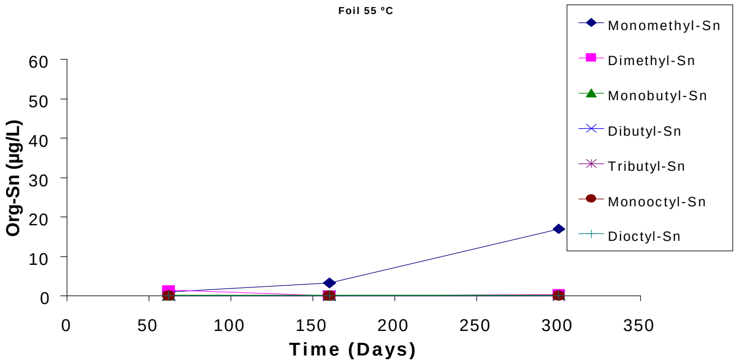


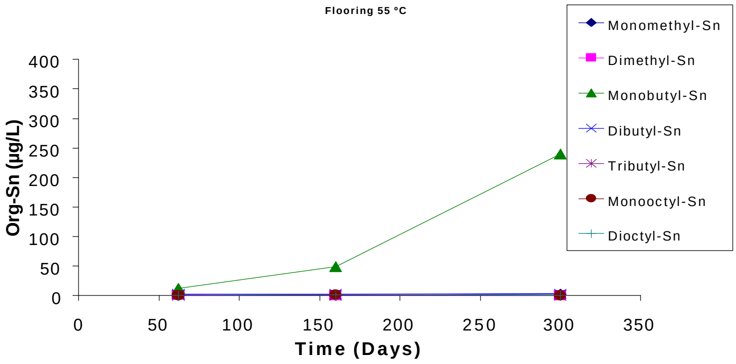


5.2.3 METS Units at Temperature 55 °C

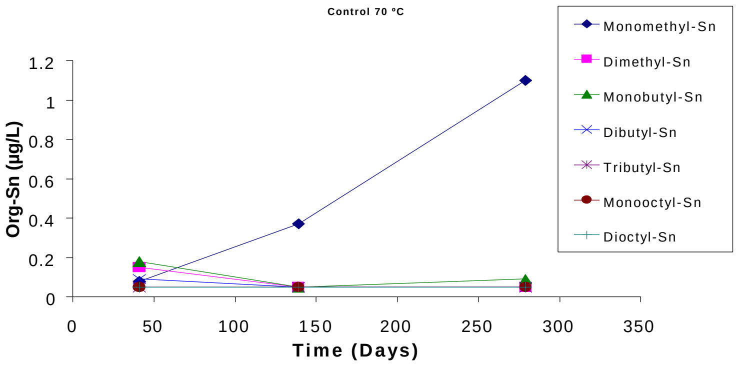


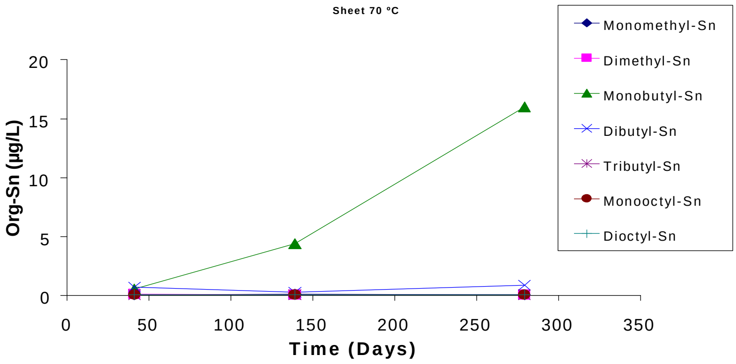


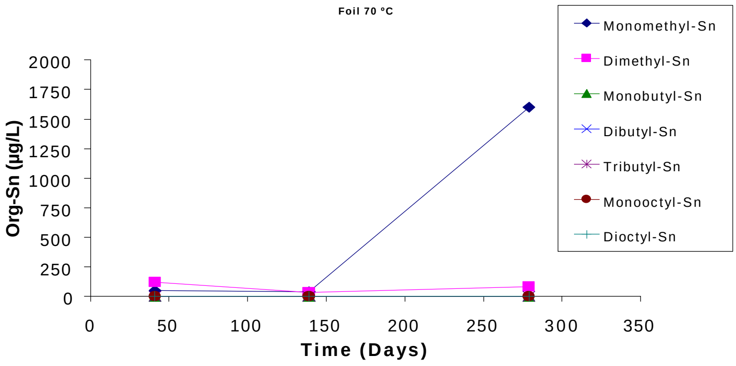


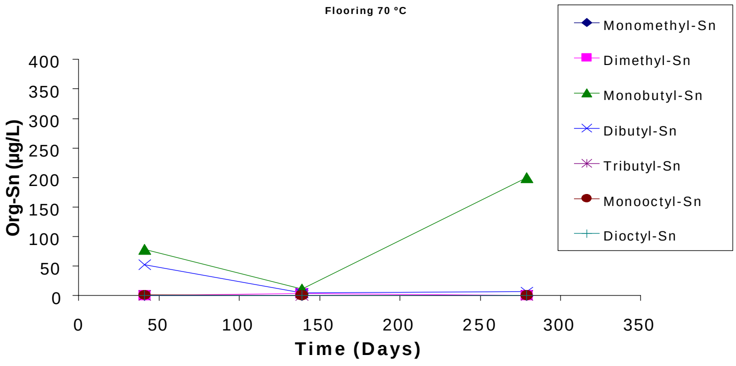


5.2.4 METS Units at Temperature 70 °C

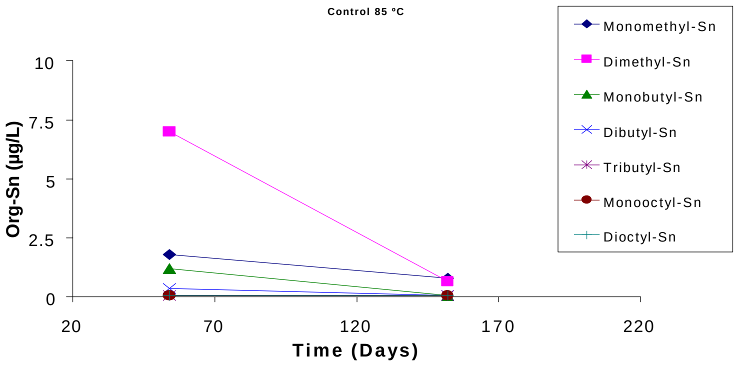


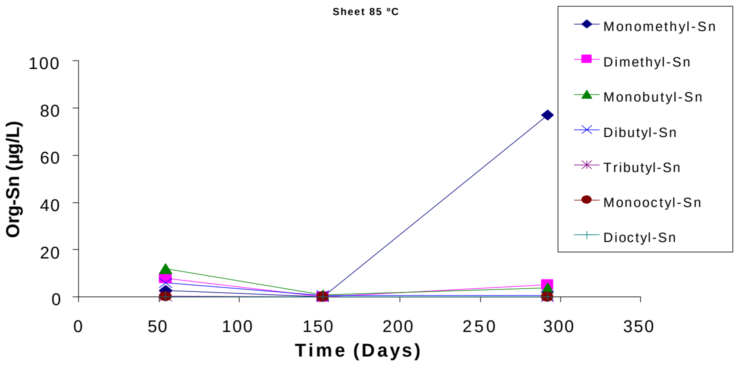


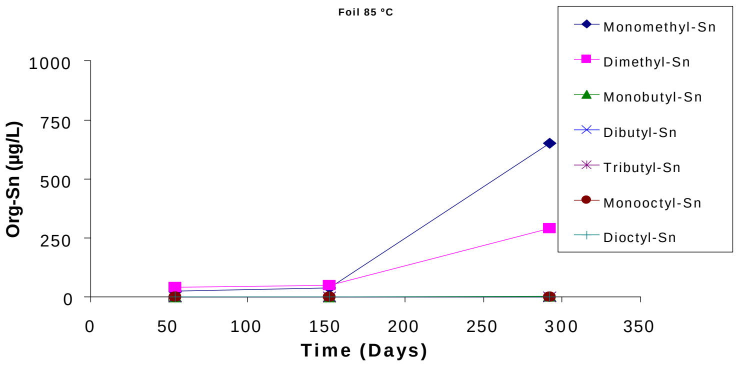


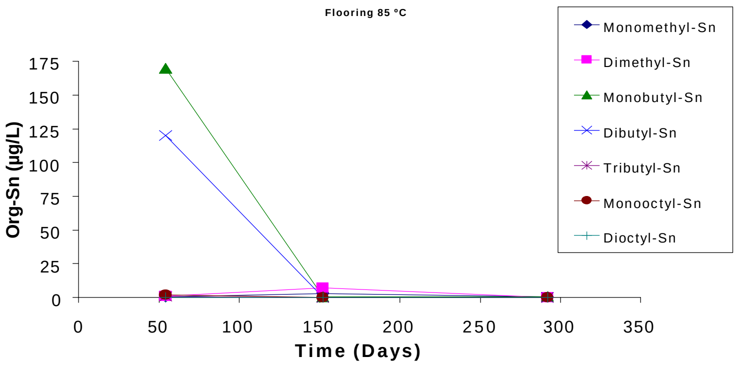


5.2.5 METS Units at Temperatures 85 °C (Aerobic) and 55 °C (Anaerobic)









5.3 Residual Contents of Plasticisers BBP and DEHP in the PVC Flooring

5.3.1 METS Unit at Temperature 20 °C

Table 5.6 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 20 °C (sampled in September 1999, day 75).

Plasticiser	Untreated (%)	Untreated (%)	20°C (day 75)	20°C (day 75)
BBP	5.5	5.5	5.5	5.4
DEHP	16.5	16.5	16.5	16.5

Table 5.7 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 20 °C (sampled in December 1999, day 168).

Plasticiser	Untreated (%)	Untreated (%)	20°C (day 168)
BBP	5.5	5.4	5.5
DEHP	15.8	15.6	15.6

Table 5.8 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 20 °C (sampled in April 2000, day 310).

Plasticiser	Untreated (%)	20°C (day 310)
BBP	5.6	5.4
DEHP	17.5	17.9

5.3.2 METS Unit at Temperature 37 °C

Table 5.9 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 37 °C (sampled in September 1999, day 75).

Plasticiser	Untreated (%)	Untreated (%)	37°C (day 75)	37°C (day 75)
BBP	5.5	5.5	5.4	5.3
DEHP	16.5	16.5	16.9	16.7

Table 5.10 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 37 °C (sampled in December 1999, day 170).

Plasticiser	Untreated (%)	Untreated (%)	37°C (day 170)
BBP	5.5	5.4	5.3
DEHP	15.8	15.6	16.2

Table 5.11 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 37 °C (sampled in April 2000, day 310).

Plasticiser	Untreated (%)	37 °C (day 310)
BBP	5.6	3.0
DEHP	17.5	18.4

5.3.3 METS Unit at Temperature 55 °C

Table 5.12 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 55 °C (sampled in September 1999, day 62).

Plasticiser	Untreated (%)	Untreated (%)	55 °C (day 62)	55°C (day 62)
BBP	5.5	5.5	5.3	5.2
DEHP	16.5	16.5	16.8	16.5

Table 5.13 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 55 °C (sampled in December 1999, day 160).

Plasticiser	Untreated (%)	Untreated (%)	55 °C (day 160)
BBP	5.5	5.4	5.1
DEHP	15.8	15.6	15.8

Table 5.14 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 55 °C (sampled in April 2000, day 290).

Plasticiser	Untreated (%)	55 °C (day 290)
BBP	5.6	5.2
DEHP	17.5	17.9

5.3.4 METS Unit at Temperature 70 °C

Table 5.15 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 70 °C (sampled in September 1999, day 41).

Plasticiser	Untreated (%)	Untreated (%)	70°C (day 41)	70°C (day 41)
BBP	5.5	5.5	5.2	5.1
DEHP	16.5	16.5	16.7	16.5

Table 5.16 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 70 °C (sampled in December 1999, day 139).

Plasticiser	Untreated (%)	Untreated (%)	70 °C (day 139)
BBP	5.5	5.4	5.0
DEHP	15.8	15.6	14.8

Table 5.17 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 70 °C (sampled in April 2000, day 280).

Plasticiser	Untreated (%)	70°C (day 280)
BBP	5.6	3.8
DEHP	17.5	13.8

5.3.5 METS Unit at Temperatures 85 °C (Aerobic) and 55 °C (Anaerobic)

Table 5.18 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 85 °C under aerobic conditions until day 150 and at 55 °C under anaerobic conditions afterwards (sampled September 1999).

Plasticiser	Untreated (%)	Untreated (%)	85°C (day)	85°C (day)
BBP	5.5	5.5	4.2	4.1
DEHP	16.5	16.5	16.6	16.5

Table 5.19 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 85 °C under aerobic conditions until day 150 and at 55 °C under anaerobic conditions afterwards (sampled December 1999).

Plasticiser	Untreated (%)	Untreated (%)	85 °C (day)
BBP	5.5	5.4	2.6
DEHP	15.8	15.6	15.2

Table 5.20 Residual contents of plasticisers DEHP and BBP in the PVC flooring samples from the METS unit incubated at 85 °C under aerobic conditions until day 150 and at 55 °C under anaerobic conditions afterwards (sampled April 2000, day 280).

Plasticiser	Untreated (%)	(day 280)
BBP	5.6	1.7
DEHP	17.5	16.7

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