

European Commission DGXI.E.3

The Behaviour of PVC in Landfill

Final Report February 2000

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STUDY INTO THE BEHAVIOUR OF PVC IN LANDFILLS

1 INTRODUCTION

1.1 The Provenance of this Report

- 1 This is the Final Report of the Study in the "Behaviour of PVC in Landfills" undertaken by ARGUS (Germany), Prof. Spillmann (University of Rostock, Germany), Carl Bro (Denmark) and Sigma Plan (Greece).
- 2 The study was carried out between October 1998 and September 1999 with the objective of evaluating the environmental impact of PVC waste after final disposal in landfills. The Terms of Reference (Technical Annex) for the study can be found in Annex I.
- 3 In the context of the preparation of an EU strategy for the management of PVC waste, four studies are being carried out on behalf of the DG XI, Environment, Nuclear Safety and Civil Protection. Apart from this study on the behaviour of PVC in landfills, the economic impact of PVC waste management is evaluated, and mechanical recycling and incineration of PVC waste is investigated. The arguments and conclusions published in the report reflect the authors' position and the Commission does not necessarily endorse every opinion and conclusion as stated in this report.

1.2 The Scope and Objective of the Study

- 4 PVC is one of the most widely used and economically relevant plastic materials, used for a large variety of applications. PVC is also one of the most controversially debated plastic materials with regard to hazardous impacts to the environment and an extensive number of studies investigating the life-cycle of PVC have been produced. The focus of these studies in respect of potential detrimental impact on the environment and human health has moved gradually from production and service life to incineration and recycling. In recently published studies, particular concern is expressed in view of the behaviour of PVC in landfills, drawing attention to several aspects which require further study since the evidence obtainable is either inconclusive or contradictory.
- 5 As PVC products contain a wide range of other substances of which some are known for their hazardous properties the question arose whether there is a release of additives from PVC products to the landfill body, to which extent does this occur, and what are the emissions to landfill gas and leachate.
- 6 Prevailing controversy refers particularly to environmental health effects resulting from the use of phthalates as plasticisers in flexible PVC, and the ultimate fate of these plasticisers and heavy metals used as stabilisers once the PVC products are disposed of in landfills.
- 7 The objective of this study is to:
 - a) provide a survey of existing analyses and research as regards the behaviour of PVC in landfills
 - b) evaluate the environmental impact of PVC waste after final disposal in landfills
 - c) perform practical analysis under simulated landfill conditions
 - d) estimate the quantities of PVC landfilled as well as costs of landfilling PVC waste, including the environmental costs.

- 8 For the purpose of this study the literature survey on PVC is limited to research reports on the behaviour of PVC in landfills, or under landfill and soil-buried conditions. Particularly addressed are the questions whether there is a possible degradation of the PVC polymer, whether there is a release of additives and what emissions may occur to landfill gas and leachate.
- 9 For the practical analysis on how PVC products behave under the specific conditions of municipal solid waste landfills, a range of PVC products were selected in agreement with DG XI of the Commission, comprising both rigid and flexible, long-life and short-life applications.
- 10 A study of one year time is extremely short for the investigation of the behaviour of PVC in landfills. With regard to task c) of the technical specifications for the study, it appeared appropriate, to investigate first possible changes and emissions of different PVC materials under landfill conditions before studies on selected landfill sites can be carried out and the influence of the various parameters (pH, temperature, geology of soil/underground, precipitation, microbial activity, availability of oxygen and light etc.) can be assessed and evaluated. It was therefore agreed with DG XI to concentrate on simulation experiments and on the literature survey.
- 11 For the practical part of the study a methodological approach consisting of various different tests and analyses was developed. Major changes or repetitions of tests were not possible within the available time, multiple measurements were only possible to a very limited extent. In our study the landfill simulation investigations (lysimeter investigations) were supported by supplementary other tests and examinations such as tests on leaching behaviour and on microbial activity, samples taken from a landfill and the examination of samples in a biological treatment plant. These supplementary experiments were carried out in order to check the results from the lysimeter studies, i.e. to verify results and to identify contradictory results, and to be able to distinguish between microbiological and physical processes.
- 12 Within the scope of the study the behaviour of PVC in landfills will be considered under normal landfill operation conditions, excluding accidental fires.

1.3 The structure of this report

- 13 This report is structured in 8 chapters.
 - In Chapter 2 general information on PVC applications, on the most commonly used additives, and to what extent these substances are used in PVC products is provided. For selected ingredients in PVC products information is given on their behaviour in the environment.
 - Chapter 3 summarises data on the PVC waste arisings and the amount of PVC being landfilled in Member States.
 - In Chapter 4 the relevant landfill processes are described.
 - Chapter 5 presents the results of the literature survey.
 - Chapter 6 sets out the analytical programme of the study
 - In Chapter 7 the results of the practical analysis are discussed in the context of findings from the literature survey
 - Chapter 8 summarises our conclusions and findings as regards the environmental impact of PVC in landfills, taking note of the emissions and additional costs resulting from the landfilling of PVC.

2 PVC APPLICATIONS AND ADDITIVES

- 1 During the fifty years following the end of World War II, PVC has become the second most widely used plastic in the world. Today more than 20 million tonnes are manufactured each year. In Europe the total consumption of PVC products was estimated at approximately 7.4 million tonnes in 1998, which corresponds to ca. 5.5 million tonnes of PVC polymer (ECVM). About one third of the total production of PVC polymer is used for the production of flexible PVC products, the remaining two thirds fall into the category of rigid PVC products.
- 2 Virgin PVC is thermally and photochemically unstable and depending on requirements and desired characteristics of the application, a number of additives are applied to reduce these problems prior to manufacture of PVC products. The quantitatively important classes of additives are heat stabilisers, plasticisers, and inert fillers, the latter generally added to reduce cost and get more volume for a given amount of polymer. Other classes of additives for specific applications include pigments, impact modifiers, lubricants, fillers, UV stabilisers, biocides (to prevent fungal growth on flexible PVC) and antistatic agents.
- 3 In the following sections an overview is provided of the main application areas of PVC and the most important classes of additives. The average quantities of these components used in PVC products are given wherever possible. It has to be borne in mind that a wide range of applications and substances are added to different PVC products, accordingly, a more detailed and quantified inventory of components applied to PVC is hardly possible within the scope of this study.

2.1 PVC Applications

- 4 The consumption of final PVC products according to application sectors in Europe and in some Member States is shown below:

Table 2-1: PVC application according to sectors

	Europe	Austria	Germany	Denmark	France
building	53 %	81 %	60 %	69 %	50 %
packaging	16 %	2 %	11 %	8 %	30 %
electronics/cable	9 %	8 %	8 %		8 %
transport/cars	3 %	4 %	4 %		6 %
furniture	3 %	2 %	3 %		
others	16 %	3 %	14 %	23 %	6 %

source: Europe, Austria, Germany (AgPU, 1997), Denmark (Moeller et al., 1996), France (PVC working Group, 1999)

- 5 Although the PVC application, according to sector, is not directly comparable in detail, it is obvious that the main application area for PVC products in Europe is the building sector and that the consumption of PVC packaging materials in particular differs between Member States. The life-span of PVC products ranges from very short service life up to 50 years and more. The majority of PVC products are designed for long-term applications. A classification of PVC according to the life-span and relevant product types is given below.

Table 2-2: Life-span of common PVC products and their share of production

Life-span	Share of production in Europe (1991)	Examples of product types
Short-term < 2 year	12 %	Packaging, medical equipment, office supplies
Medium-term 2-10 years	15 %	Wall covering, flooring, footwear
Long-term 10-20 years	28 %	Flooring, wire and cable, furniture, automobiles
Extra-long-term > 20 years	45 %	Pipe, window profile, cables, roof liners

source: APME, cited in UBA, 1999

- 6 PVC products with long and extra long service life are predominately used in the building and automotive sector, while PVC products for packaging purposes have a short service life. Except for cables, flexible PVC has a rather short to medium-term service life and the majority of rigid PVC products is in use for a long time period. PVC products with very long life-span are presently still retained in the use phase. Thus, the present PVC waste stream is not directly correlated with the current production, in particular PVC products with a comparatively long life-span used in large quantities in the building sector are just beginning to appear in the waste stream and will certainly effect future PVC waste stream composition (chapter 3 refers).

2.2 PVC Additives

- 7 All PVC products contain at the minimum a PVC polymer, a stabiliser and a lubricant. Various other components are incorporated in PVC, sometimes in large quantities with regard to the polymer. Generally, the percentage of additives varies between 10 and 25 % in weight of the resin, in the case of rigid products. Flexible PVC can contain plasticisers up to 60 % of the weight, the average content is about 30%. Although the composition of PVC products is broadly known, the actual formulation of a product differs depending on the year of production and on compounding specifics of different PVC converters, thus even in the same application (e.g. window profiles, pipes, films) the composition of the PVC material varies. In the following sections the most commonly used additives are described in brief. The effect of additives on the properties and characteristics of the product is summarised in the following overview:

Table 2-3: Effect of PVC additives on product properties

Additives	Property of PVC article affected
Stabiliser	Prevents decomposition during processing, imparts light and weather resistance
Colorant	Colour, weather resistance
Plasticiser	Mechanical properties, burning behaviour
Impact modifier	Impact strength and other mechanical properties
Lubricants	Rheology of the PVC melt, transparency, gloss, surface finish and printability
Fillers	Electrical and mechanical properties
Flame retardants	Burning behaviour
Antistatic agents	Electrical properties
Blowing agents	Processing to expanded products

source: Moeller et al, 1996

Stabilisers

- 8 Stabilisers are ingredients that are generally added to the PVC polymer in order to prevent thermal degradation and hydrogen chloride evolution during processing and to give the finished article optimum properties (heat and UV stability). Approximately 1-8 % may be added to PVC formulation depending on other components and the final application. The most important group of stabilisers are (based on Moeller et al, 1996)
- metal salts (i.e. calcium and zinc stearates, basic lead sulphate and lead phosphite)
 - organo metals (i.e. mono- and diorganotin, tin thioglycolate)
 - organo phosphites (i.e. trialkyl-phosphites)
 - epoxy compounds (i.e. epoxidised soya bean oil, sunflower oil and linseed oil)
 - antioxidants, polyols (i.e. BHT, pentaerythritol)
- 9 The tonnages of different stabiliser systems sold in the European Union Countries in 1998 representing over 98% of all suppliers are shown below.

Table 2-4: Amount of stabiliser sold in the EU in 1998

Stabiliser type	tonnes	%
Formulated lead stabilisers	112,000	70,2
Mixed metal solid stabilisers (eg Ca/Zn systems)	14,500	9.1
Organotin stabilisers	15,000	9.4
Liquid stabilisers (Ba/Zn or Ca/Zn)	18,000	11.3
Total	159,500	100.0

source: Donnelly, 1999

- 10 The dominant stabilisers used in PVC today are lead compounds, organotin compounds, barium/zinc, calcium/zinc systems. Currently, about 60-75 % of stabilisers for PVC in Europe contain lead (OSPARCOM 1997), organotin stabiliser comprise 10 –15 % with the rest being solid, liquid or paste combination of calcium, barium salts with zinc. Regulations regarding the use of lead salts as stabilisers vary throughout Europe. Lead salts are not authorised as stabilisers in France and Belgium in drinking water pipes (PVC working group, France 1999), Sweden wishes to phase out any use of lead on a voluntary basis. Also in Austria a voluntary agreement aims at phasing out lead stabiliser, whereas Denmark has notified a draft ban on the use of lead and its compounds.
- 11 Previously cadmium based stabilisers were widely used (window profiles, doors, other profiles), with a cadmium content of 0,5 to 2,5 g/kg. Due to restrictions or bans, cadmium has become less important as a stabiliser and was replaced mainly by lead. Directive 91/338/EEC limits the use of cadmium to < 0.01% in PVC for colouring and for stabilisation in most applications, except for windows and claddings.
- 12 Pigments and stabilisers combined make up some 20% (approximately 2,800 to 3,000 tonnes in 1994/95) of OECD consumption of cadmium, and ca. 85% of cadmium pigments are used in PVC. In 1995 about 30 % of the European market used cadmium in the stabiliser system (OECD Cadmium Workshop 1995). The amount of cadmium used as stabiliser for PVC in Europe is gradually reduced from 600 t in 1992 (OSPARCOM 1997) to 50 t in 1998 (espa-European Stabilisers Producers Association). Two Member States (Sweden and Austria) have received a temporary authorisation to be even more restrictive.
- 13 Liquid cadmium stabilisers generally contain from 1 to 8% cadmium expressed as metal, whilst solid cadmium stabilisers contain 4 to 12%. The cadmium content of the finished article is usually 0,1% in flexible PVC where liquid stabiliser systems are used and 0,2% in rigid PVC where solid

stabilisers are used. For flexible PVC, cadmium stabiliser has been almost completely substituted (Pohle, 1997), in new rigid products it is still applied in windows and claddings and, with regard to disposal in landfills it can be expected that cadmium containing products due to their long life period are entering the waste stream today and will be in increasing amounts in the future.

- 14 Lead stabilisers are the most widely used in terms of quantity in Europe, the lead concentration in PVC products is about 0.1-1.8 weight%. Lead stabilisers are mainly used for construction products with long life (or barium/cadmium/lead for some window profiles):

Pipes - including drinking water pipes

Windows and other building profiles

Electrical cables - lead is used here because of its good electrical properties

- 15 Solid calcium/zinc systems are mainly used for food-contact and medical applications, other stabiliser systems are under development for possible replacement of lead. Liquid barium/zinc (little barium/cadmium/zinc is used today) and liquid calcium/zinc are used for many flexible PVC applications.
- 16 Organotin systems are used in rigid packaging film, bottle, flooring, roofing and rigid clear constructional sheeting. They are little used in pipes in Europe except for small bore pipes and some drinking water pipes in France. There are various uses in flexible PVC especially where high clarity is required. The most common organotin stabilisers used for PVC in Germany are butyl- and octyltin compounds, methyltin compounds are not common in Europe but in the USA and Canada.
- 17 All the stabiliser systems will require the addition of a number of other substances such as lubricants (see below) and co-stabilisers. Co-stabilisers include various phenolic antioxidants, polyols and alkyl/aryl phosphites, which are widely used to stabilise all the main polymer types e.g. polyethylene and polypropylene. Bisphenol A is mainly used as an intermediate in the production of epoxy and polycarbonate resins, as a stabiliser for plasticisers in PVC and as an antioxidant in rubber and plastics. All stabiliser systems except organotin contain these co-stabilisers at low levels and some organotin systems do contain phenolic antioxidants. A newer sophisticated Ca/Zn stabiliser designed to replace lead does contain some other co-stabilisers which include hydrotalcites and β -diketones. These co-stabilisers often have approval for use in food-contact plastics or are very closely related to such molecules (Donnelly, 1999).

Plasticisers

- 18 The plasticisers are added to the resin in variable quantities to achieve a flexible and soft PVC. Flexible PVC can contain plasticisers at concentrations of up to 60% of the total weight. Typical amounts in selected products are shown below.

Table 2-5: Content of plasticisers in different types of PVC

Product	Content of plasticisers (%)
Cables insulation coating	23 – 33 33 - 44
Films wrapping clinical use	17 – 23 31
Floor and wall coatings calendered spread coated	23 29 – 38
Extruded profiles and tubings	17 – 47
Artificial leather	29 – 44
Rotation moulding	38 – 50
Injection moulding	38 – 58
Conveyor belts	38 – 44
Capsules	38
Protection, air-tight sealants	44 - 60

source: Christiansen, 1990, cited by UBA, 1999

- 19 The dominant group of plasticisers used are phthalic acid esters (PAE) of which bis(2-ethylhexyl)phthalate (DEHP) also known as dioctylphthalate (DOP), di-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di-isodecyl phthalate (DIDP) and di-isononyl phthalate (DINP) are most commonly used. The consumption of the most commonly used phthalates is as follows:

Table 2-6: Consumption of phthalates in Europe

Phthalate	Abbreviation	European consumption (kt/a)
Bis(2-ethylhexyl)phthalate	DEHP	400 – 500
Di-isononyl phthalate	DINP	100– 200
Di-isodecyl phthalate	DIDP	100 – 200
Butyl benzyl phthalate	BBP	20 – 50
Di-butyl phthalate	DBP	20 – 40
Di-isobutyl phthalate	DIBP	20 – 40
Di-tridecyl phthalate	DTDP	3 – 10
Di-ethyl phthalate	DEP	10– 20
Di-methyl phthalate	DMP	

source: Harris et al, 1997

- 20 In 1992/93 the total consumption of plasticisers amounted to 945,000 t/a (OSPARCOM 1997), according to Cadogen et al. (1993) about 1 million tonnes of plasticisers are used annually in Western Europe. 90% (~900,000t) of this total is used to plasticise PVC and 93% (~840,000t) of these plasticisers are phthalates. About 50% (~420,000t) of the total consumption of phthalates is covered by bis(2-ethylhexyl)phthalate DEHP and 40% (~350,000t) is covered by DINP and DIDP.
- 21 Phthalates are also used in paper coatings, cosmetics, adhesives, inks, and paints. The phthalates BBP and DBP are used in product types such as paints, lacquers, glues, printing inks, etc.

Lubricants

- 22 Lubricants are used in amounts of 1 – 4 weight %, they are added to prevent the plastic from adhering to the metal walls of the moulding machines, and to modify the properties of mixtures. Examples of such lubricants are waxes, fatty acids (stearic acid etc), fatty alcohols, etc.

Fillers

- 23 Fillers are added to improve certain properties, i.e. mechanical and electrical resistance, and may comprise 50% of a PVC formulation. In rigid PVC for building applications, no more than 5 % fillers are added. The main fillers are of mineral origin: calcium carbonate (limestone), talc, chalks etc.

Pigments

- 24 These are mainly organic pigments and colouring agents and mineral pigments (titanium oxide, iron oxide, chromium oxide, cadmium oxide, etc). Typical amounts are 0,1 weight%, but up to 15% may be used in extraordinary cases. (see para. 11 for the use of cadmium as pigment).

Flame retardants

- 25 In many applications, the presence of chlorine in PVC provides satisfactory fire performance, but the addition of flame retardants is used in particular in some flexible PVC building materials in relatively high concentrations – up to 10 – 20 weight %. Flexible PVC has a lower chlorine-content than rigid PVC and is therefore more flammable. Chlorinated paraffins are commonly used as flame-retardants, the chlorinated paraffins used are almost exclusively of medium chain length or longer (C₁₄₋₁₇) (Moeller et al. 1996). Chlorinated paraffins also have plasticising properties and therefore are also used as secondary plasticiser for PVC products such as floorings, cable insulation, garden hoses, coatings, and shoes (UBA 1999).

Other additives

- 26 Other additives are added for specific purposes, such as biocides or fungicides. Impact modifiers are used in concentrations of up to 15 weight % to improve the impact resistance of rigid PVC.

2.3 Environmental Effects of Additives (plasticiser and organotin)

- 27 The aim of this section is not to provide an in depth description of the hazardous characteristics of additives, nor to perform an environmental risk assessment with regard to emissions of the substances in question from landfills, but to give a general overview of the potential environmental effects. Within the EU framework of the evaluation and control of the risks of existing substances, risk assessments on the phthalates DBP, DEHP, DINP, DIDP and BBP, and on cadmium are currently being carried out and are already partly finalised. The focus is laid on the effects of phthalates and to a certain extent on organotin stabilisers. The hazardous properties and environmental impact of e.g. lead and cadmium are well known and described elsewhere.

DEHP

- 28 The following overview is based on WHO EHC, 1992 and on ECB (1999)¹. DEHP is environmentally ubiquitous and is found in most samples, including air, precipitation, water, sediment, soil, and biota. Determination of DEHP in different media in low concentration is difficult due to contamination from plastic equipment during sampling and analysis. Transport in the air and leaching from applications are the major routes by which DEHP enter the environment (ECB, 1999). From the atmosphere DEHP either falls or is washed out by rainfall. Analysis of rainfalls in industrial countries have shown concentrations of a few ng/l to 9,820 ng/l, in Germany deposition rate of 0.45 to 1.5 µg/m² • mm rainfall was calculated by Furtmann (1993). DEHP is detected in groundwater (max. 170 µg/l), in rivers and sediments as well as in snow and sea water samples of the Antarctic (max. 530 ng/l and 140 µg/l) (UBA 1999). The max. concentration in rivers are 10 µg/l in Rhine (Furtmann, 1993) and 9 µg/l in the river Humber (Long et al, 1998). Max sediment concentrations are 33 and 47mg/kg dw from two Swedish rivers near PVC flooring plant (Parkman and Remberger, 1995).²
- 29 DEHP has a high octanol-water partition coefficient, so the equilibrium between water and an organic-rich soil or sediment is in favour of the soil or sediment. Although the solubility of DEHP in water is low, the amount present in surface water may be higher due to adsorption onto organic particles and interaction with dissolved organic matter. Atmospheric photodegradation of DEHP is rapid, but its chemical hydrolysis in the environment is practically non-existent. Aerobic microbial degradation in the environment is slow and is temperature dependant (>10°C), anaerobic degradation is much slower and accumulation is probably occurring in low-oxygenated areas and areas of low temperature in the environment. Reports on degradation are not consistent, both are reported, rapid degradation and low degradation rate. Factors influencing degradation are temperature, acclimation, bioavailability and concentration.
- 30 Estrogenic activity was not confirmed by Harris et al. (1997). DEHP does have the tendency to bioaccumulate in aquatic organisms, BCF (bio-concentration-factor) ranging between <100 and 101.780 (UBA 1999). The acute toxicity to algae, plants, earthworms and birds appears to be low. A reduction of microbial activity in sediment at environmental levels of DEHP was reported. There are conflicting data on effects on hatching of frog eggs.

DIDP

- 31 The following overview is based on ECB (1999)³. DIDP is a mixture of isomers with mainly branched alkyl chains. The water solubility is much lower than 1 mg/l (around 0.2 µg/l). DIDP has been found in water, sediment, and fish in Japan. If released into water, DIDP would be expected to adsorb strongly to particulate matter in the water column. Due to expected lowered biodegradability at low temperatures DIDP may accumulate in sediments and soils in areas where temperatures are relatively low throughout the year.
- 32 No information on anaerobic degradation is available. DIDP is not acutely toxic towards soil organisms. No data is available on long-term effects towards soil organisms. DIDP did not induce mutagenic effects in vitro tests with bacteria. The reliable data indicates that the substance does

¹ European Chemical Bureau, personal communication

² Figures on maximum concentration of DEHP including given references are provided by European Chemical Bureau, these references are not included in the list of references of this report.

³ European Chemical Bureau, personal communication

not induce direct acute or long-term effects in aquatic or benthic organisms. DIDP showed extremely weak estrogenic activity in vitro tests (Harris et al. 1997).

DBP

- 33 The following overview is based on BUA-Report 22, 1993; on Danish EPA, Report No. 412, 1998; and the draft RAR of May 1999 prepared under the Existing substances regulation EC (No.) 793/93.⁴ The largest usage of DBP in general is as a plasticizer in resins and polymers such as polyvinyl chloride. Furthermore, DBP is used in other consumer products such as cosmetics: a perfume solvent and fixative, a suspension agent for solids in aerosols, a lubricant for aerosol valves, an antifoamer, a skin emollient and a plasticizer in nail polish, fingernail elongators and hair spray. For DBP, several aqueous solubility data are referred to in the literature ranging from 3.25 to 13.0 mg/l. In a literature review by Staples et al. (1996, cited by Danish EPA, 1998) it was concluded that a water solubility of about 11.2 mg/l was the most likely value based on available evidence. DBP is environmentally ubiquitous. More than half the emissions will be in the form of gas. DBP has been detected in soil water (rivers, estuaries and seawater) and ground water at variable concentrations. In aquatic environments, DBP concentrations of up to 623 µg/l have been measured while concentrations as high as up to 2,249 µg/l have been detected in ground water. In sediments, DBP has been found in concentrations of up to 100,000 µg/kg. In biota, DBP has been measured in concentrations of up to 11,700 µg/kg, 500 µg/kg, 1,750 µg/kg, 1,557 µg/kg and 1,900 µg/kg dry matter, in fish, aquatic invertebrates, terrestrial invertebrates, terrestrial plants and aquatic plants, respectively (Danish EPA, Report No. 412, 1998).
- 34 DBP is relatively non-persistent in air, surface waters and soil, and has a half-life in these compartments of only a few days. Aerobic biodegradation takes a few days and results in complete mineralization, anaerobic biodegradation is slower but also results in complete mineralization. Under natural conditions, hydrolysis of DBP is insignificant as a mechanism of elimination. Nothing is known about photodegradation. DBP is readily biodegradable in standard laboratory tests and, hence, the substance is expected to be mineralized rapidly in the aerobic part of a sewage treatment plant. The studies of anaerobic biodegradability indicate a potential for mineralization of DBP during anaerobic treatment of sludge (Danish EPA, Report No. 412, 1998).
- 35 DBP is bioaccumulating in aquatic biota, which is demonstrated by the experimentally derived BCF values of up to 2,125 for fish. The acute and subchronic toxicities of DBP for various organisms of the hydroflora are high (classification with R50 is warranted). The lowest NOEC in chronic toxicity tests on aquatic organisms is 100 µg/l for fish (*Oncorhynchus mykiss*) leading to a Predicted No-Effect Concentration for the aquatic compartment of 10 µg/l. PNECs for sediment and soil are 3.1 and 2.0 mg/kg dw, respectively. DBP showed weakly estrogenic activity in vitro tests (Jobling et al. 1995, Harris et al. 1997), this was not confirmed in *in vivo tests* (CSTEE opinion on phthalates in soft PVC toys, 24 April 1998). Some indications are available that DBP has phytotoxic effects at low concentrations but further testing is required to investigate this potential effect (draft RAR of May 1999).

BBP

- 36 The following overview is based on Danish EPA, Report No. 412 (1998). For BBP, several aqueous solubility data are referred to in the literature ranging from 0.70 to 40.2 mg/l. In a literature review by Staples et al. (1996, cited by Danish EPA, 1999) it was concluded that a water solubility of about 2.7 mg/l was the most likely value based on available evidence. BBP has been detected in soil and water (rivers, lakes and estuaries) at variable concentrations. In the aquatic

⁴ via European Chemical Bureau, personal communication

environment, BBP concentrations of up to 49 µg/l have been found. In sediments BBP has been detected in concentrations of up to 14,000 µg/kg and in biota BBP has been detected at concentrations of up to 39 µg/kg wet weight (fish) and up to 1,256 µg/kg dry matter (terrestrial plants). BBP seems to be efficiently removed from waste waters based on the low output concentrations compared to inlet concentrations in sewage treatment plants. However, large differences exist between different treatment plants. Degradation may account for some of the reduction seen but accumulation in sludge may be important based on the high concentrations of BBP measured in some sludge samples.

- 37 Hydrolysis and photodegradation are not significant degradation routes of BBP in the aquatic environment. BBP is readily biodegradable in standard laboratory tests and, hence, the substance is expected to be mineralized rapidly in the aerobic part of a sewage treatment plant. The studies of anaerobic biodegradability indicate a potential for mineralization of BBP during anaerobic treatment of sludge. BBP is bioaccumulative in aquatic biota, which is demonstrated by the experimentally derived BCF value of up to 663 for fish.
- 38 BBP has been shown acutely toxic (EC50 or LC50 values) to algae, crustaceans and fish in the range from 0.1 to 2.1 mg/l, in which algae seem slightly more sensitive than crustaceans and fish. BBP is thus considered very toxic to aquatic organisms. NOEC levels in chronic toxicity tests with algae, crustaceans and fish were observed in the range from 0.03 to 0.35 mg/l. BBP has shown to be estrogenic in vitro, this was not confirmed in *in vivo* tests (CSTEE opinion on phthalates in soft PVC toys, 24 April 1998).

DINP

- 39 The following overview is based on ECB (1999)⁵. DINP is a mixture of isomers with mainly branched alkyl chains. If released in air, DINP will probably be in form of an aerosol or adsorbed on particulate matter. No information on photolysis or photooxidation, or on chemical hydrolysis alone has been found. In water and soil, adsorption to sediment and particulate matter is expected. DINP is readily biodegradable under aerobic conditions but probably more slowly than DEHP, no information is available on anaerobic degradation. DINP did not induce mutagenic effects in vitro tests with bacteria. DINP is not acutely toxic towards soil organisms. The reliable data indicates that the substance does not induce direct acute or long-term effects in aquatic organisms. No data on chronic effects towards benthic organisms is available. DINP showed extremely weak estrogenic activity in vitro tests (Jobling et al. 1995, Harris et al. 1997).

Organotin

- 40 The following overview is based on Länge (1998) and UBA (1999). Various types of organotins are used as stabilisers. Butyl- and octyltin compounds are commonly used in Germany. PVC products containing methyltin compounds, which are used mainly in the USA and Canada as stabilisers, can also be found on the EU market. Organotin compounds are not persistent in the aquatic environment, a higher stability is observed when adsorbed to sediment and suspended particles. The main degradation processes are photolysis and microbial degradation. Half-life estimates vary considerably, for butyltin compounds several weeks are estimated. Although the use of methyltin is low in Europe, it has been found in sediments of the Rhine river (max. 20 µg/kg dry weight Sn as monomethyltin and 10 µg/kg dry weight Sn as dimethyltin), however this does not necessarily result from anthropogenic release (UBA, 1999). Mono – and dibutyltin has been found in rivers and sediments in a range of a few ng/l to 267 µg/l max in Germany (with the exemption of the river Elbe), octyltin has been found only in the Elbe and in samples of sewage

⁵ European Chemical Bureau, personal communication

sludge in Sweden. Butyltin compounds were found in sewage sludge in Germany in a range of 0.02 to 2.9 mg/kg TG (tributyltin), 0.02 to 2.9 mg/kg TG (dibutyltin), and 0.02 to 30 mg/kg TG (monobutyltin). Butyltin in landfill leachates was detected in the range of 20 to 240 ng/l, mainly associated with the particulate fraction, but not octyltin. Bioaccumulation of mono- and diorganotin in fish is low (BCF <100). Little is known about the ecotoxicological effects of di- and monoorganotin compared to triorganotin, which is used as antifouling agent on boats. At present it has not been clarified whether the detected amounts of di- and monobutyltin compounds in the aquatic environment, in sediments and sludges are primarily the result of the use of triorganotin or also the result of the use of organotin in PVC products (UBA, 1999).

3 PVC WASTE ARISING AND AMOUNT BEING LANDFILLED

3.1 PVC waste arisings

- 1 In general data on PVC waste arisings are not specifically compiled by Member States as a matter of routine within the context of national waste statistics. For some Member States information on PVC waste arisings and amounts of PVC waste being landfilled is available. Data was received mainly from national environmental protection agencies, data from Spain, France and Italy comes from the Report on Mechanical Recycling of PVC (Prognos, 1999). Data compilation on PVC waste arisings is based on different methodological approaches. A general distinction can be made between data compilation based on analyses of, and estimations of the content of PVC waste in different waste streams, and calculation of waste arisings based on a theoretical model considering the consumption and the different life-spans of PVC products. The collection of information on data compilation methods in Member States was not considered in this study, however it can be assumed that data on PVC arising is derived from a combination of both methods. In the Netherlands only the amount of PVC in municipal solid waste is compiled from annual waste analysis, the amounts in other waste streams are estimated. Data from Austria is calculated on the basis of consumption and life-span. Uncertainties arise from the underlying assumption of life-spans, i.e. the estimates used to predict at what time a product will enter the waste stream, and from the estimated content of PVC in different waste streams. It has further to be considered whether the calculation model is based on the consumption of PVC polymer or on PVC compound as the amount of additives in PVC products varies considerably. Estimates based on an average content of PVC in different waste streams are particularly inaccurate with regard to construction and demolition waste as data on waste arisings of this waste stream already comprises considerable uncertainties.
- 2 Data from Member States refers partly to total PVC waste arisings without further details, a distinction between post-consumer waste and waste from production (pre-consumer waste) is not always provided. Only for the data from Germany and Austria it is known that waste from production is included, for other countries it is not known whether pre-consumer waste is included or not. For the purpose of this study pre-consumer PVC waste is of minor importance, as recovery is carried out to 85% (Prognos 1999).
- 3 For some Member States national data were not available, we have used the average of per capita PVC waste arisings from reported data to calculate the amount of PVC waste for these countries. From the data reported no particular waste arisings pattern could be identified for e.g. Nordic countries or southern countries in Europe, thus an overall average of per capita waste arisings seems to be reasonable. Data reported from Greece and France (Ademe) was excluded from further consideration. Data from Greece was extremely low and thus probably not reliable. Ademe reports PVC waste arisings in France of 300,000 tons (1997), which is 2/3 of the reported PVC waste arisings by Prognos (1999). The figure provided by Ademe appears to be too low when compared on the basis of per capita arisings with reported data from other Member States. For Belgium only data from the Flanders region was available, and as this amount did not contain PVC waste from (non sorted) household waste, this figure was also not considered.
- 4 The table overleaf summarises data on PVC waste arisings reported by Member States and calculated on this basis. A more detailed overview on PVC waste arisings figures is given in Annex II.

Table 3-1: PVC waste arisings based on information by Member States (compound basis)

Member States	year	PVC waste			Population 1997 (mill)
		tonnes	kg/capita	as % of total	
Austria	1995	45,200 ¹	5.6	1.7	8.1
Belgium		66,000 ²	6.5	2.5	10.2
Denmark	1999	34,000 ¹	6.4	1.3	5.3
Finland	annually	30,000 ¹	5.9	1.1	5.1
France		450,000 ¹	7.7	16.8	58.4
Germany	1995	683,000 ¹	8.3	25.6	82.0
Greece		68,000 ²	6.5	2.5	10.5
Ireland		24,000 ²	6.5	0.9	3.7
Italy		450,000 ¹	7.8	16.8	57.5
Luxembourg		2,600 ²	6.5	0.1	0.4
Portugal		64,000 ²	6.5	3.2	9.9
Spain		250,000 ¹	6.4	2.4	39.3
Sweden	1996	40,000 ¹	4.5	9.4	8.8
The Netherlands	1996	86,000 ¹	5.5	1.5	15.6
United Kingdom		380,000 ²	6.5	14.2	58.9
Total		2,672,800 ²	6.5	100.0	374

¹ data reported, sources of data are included in Annex II

² data calculated from population x assumed per capita arisings (6.5 kg/person/yr)

- 5 EuPC (European Plastic Converters) has developed a computer model for the calculation of PVC waste arisings in Europe. The computer model is based on production data of virgin materials (PVC polymer) and of additives used for the manufacture of PVC products. Data for PVC applications is recorded and introduced in the calculation system from the first year of production for each product. National statistics on export and import of PVC intermediates and products are used to calculate the consumption of PVC products in each Member State. The life-span of different applications is taken into account in order to calculate the total PVC waste quantities. Uncertainties in waste arisings derived from this computer model may result from the underlying assumptions regarding the life-span of products and from the calculation of the national consumption according to export/import statistics in particular. The theoretical total PVC arisings is further processed using different factors for different applications to calculate the amount of PVC waste which is available for recovery purposes, i.e. which can be separated from different waste streams. These factors are expressed in percentage of the total amount and range between 30% for cable and 95% for vehicles. There are certain products such as pipes and cables for underground applications which will remain in the soil. In the following section the theoretical total PVC waste arisings according to EuPC except for underground applications is the basis for further estimates on disposal of PVC in landfills. Data on Member State basis are not yet available, European-wide data is structured according to relevant waste streams, i.e. waste streams for which legal obligations are in force or are expected to come into force in the near future.
- 6 The following table shows the amount of PVC waste arisings in Europe according to reported data from Member States, and the total and available amount of PVC waste arisings derived from the EuPC computer model. The total PVC waste arisings according to data from EuPC is distinctly higher than the amount of PVC waste extrapolated on the basis of reports from Member States. On the other hand, the so-called available PVC waste according to EuPC is comparable to the amount of PVC waste arisings reported by Member States.

Table 3-2: PVC waste arisings (compound basis) in EU based on information by Member States and according to EuPC

PVC waste arisings 1998 according to different sources (in mill t)		
Member States	available PVC waste (EuPC)	total PVC waste (EuPC)
2,7	2,6	3,5

- 7 Provided that the data derived from the computer model are accurate and that data from Member States is likewise well-founded, estimates of the comparison of reported data and so-called available PVC waste data may indicate that a considerable amount of PVC wastes remain unidentified in waste analyses and in estimates based on statistics on waste arisings in different waste streams.
- 8 EuPC has estimated the future development of PVC waste arisings to the year 2020 based on the assumption as described above, and on expected market development for the consumption of PVC products. Although prediction of PVC waste arisings is even more difficult and bears uncertainties particularly with regard to consumption patterns, the data provided by EuPC will be used as a basis for the purpose of this study. The following figure shows the predicted PVC waste development according to relevant waste streams.

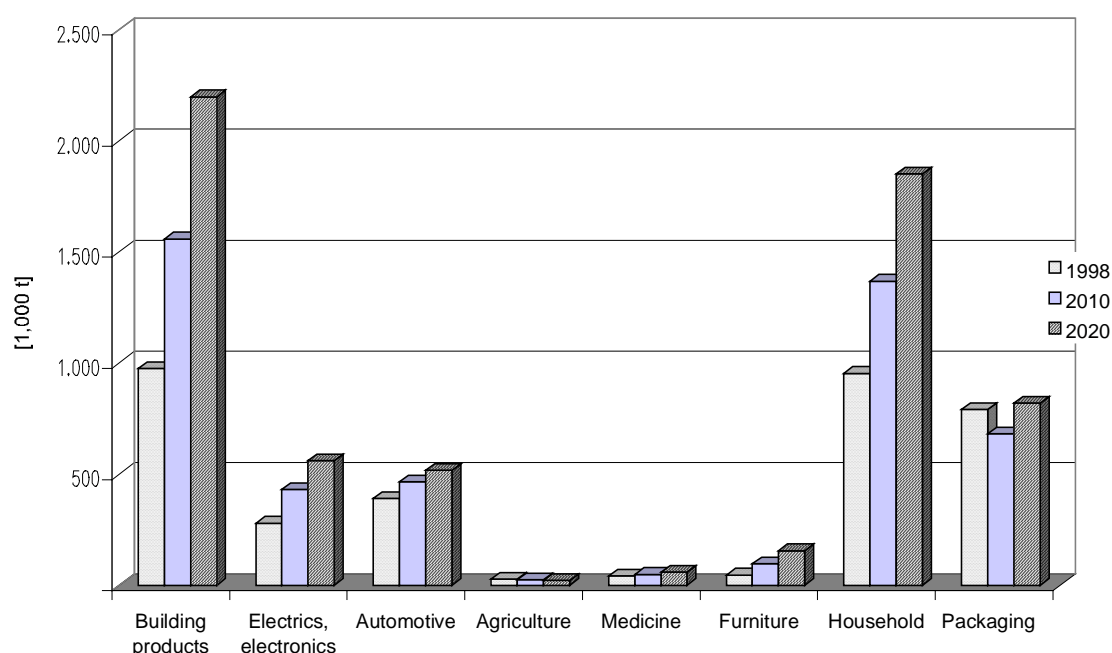


Figure 3-1: PVC waste arisings development according to EuPC

- 9 Accordingly, the most important increase in future PVC waste arisings can be expected in construction and demolition waste and in household waste, while the other waste streams are of quantitatively minor importance and/or the development of future PVC waste arisings does not show a comparable increase.

3.2 Amount of PVC being landfilled

- 10 The following assumptions regarding the destination of different PVC waste streams were made for the estimation of PVC waste being disposed of in landfills in Europe based on EuPC data. Today municipal solid waste includes PVC waste from household and trade, furniture, agriculture, electric/electronic and hospitals. Although hospital waste is, to an extent, treated separately we have assumed that it is included in municipal solid waste. In view of the small amount of medicine waste this simplification seems to be reasonable. The calculation of the share of PVC waste being landfilled is based on the development in municipal waste/household waste by the treatment method as provided by the European Topic Centre on Waste (see Annex II for details), using the ratio between incineration and landfilling in Member States only. Other treatment methods such as composting and recycling are either not applicable for PVC or irrelevant in view of the quantities. The ratio between incineration and landfilling of MSW within the European Union is 21 to 79. Accordingly, the amount of PVC which is disposed of in landfills is estimated to comprise 79% of the PCV waste arising.
- 11 PVC waste resulting from construction and demolition activities was not considered separately. Although in some Member States sorting and separate treatment schemes according to main components of construction and demolition waste exist, it is assumed that generally the non recyclable fractions of this waste stream are disposed of in incinerators or in landfills in a comparable manner as MSW and as described above.
- 12 Through the implementation of the packaging directive the amount of packaging waste being currently landfilled is reduced by 15% assuming that this amount is recycled. Although in some Member States higher recovery rates are required for plastic waste than according to the EC packaging directive, there are other countries which have not yet fully implemented the directive or which concentrate on easy to recycle plastics.
- 13 For estimates regarding future development, more differentiated assumptions are necessary, particularly because national restrictions on landfilling are coming into force for the year 2005 or earlier and due to emerging legal obligations on the recovery of used vehicles and electric/electronics. For example in France, The Netherlands, Austria and Germany, waste has to be treated before landfilling. Only almost inert waste will be allowed to be landfilled and thus PVC waste will be excluded from MSW landfills. To estimate the effect of the landfill restrictions the percentage share of PVC waste arisings in EU was calculated on the basis of the reported PVC waste arisings by Member States. Accordingly, France, The Netherlands, Austria and Germany contribute 47% of the total PVC waste arisings. For the year 2010 and 2020 the amount of PVC being landfilled is thus reduced to 53%. The ratio of incineration to landfill in the remaining countries is at present 10% to 90% respectively.
- 14 The main objective of the landfill directive is to ensure high standards for the disposal of waste in the European Union and to stimulate waste prevention via recycling and recovery of waste. The directive stipulates rates by which biodegradable waste going to landfills must be reduced. The cost of the landfill of waste is to cover all the costs involved in the setting up and operation of the landfill, including the aftercare and site closure costs. As a result the rates fixed should reflect the true cost for the whole life-time of a landfill. The Directive requires that landfill installations comply with a number of technical standards. General environmental requirements are set out with respect to the location of a landfill, the water control and leachate management, the protection of soil and water including leachate collection, bottom sealing and gas control. Collected contaminated water and leachate has to be treated according to appropriate standards required for their discharge, the treatment of collected gas is to be carried out in a manner which minimises damage to or deterioration of the environment and risk to human health. Any existing landfill shall comply with the requirements of the directive within eight years after transposition into national law.

- 15 The landfill directive will have an indirect influence on the management of PVC waste by encouraging alternative treatment schemes to final disposal in landfills due to an expected increase in landfill costs in some Member States. Although this influence cannot be estimated in quantitative terms it is very likely that incineration with or without energy recovery will become more important. As mentioned in para 13 in some member states restrictions on landfilling are introduced with effect of 2005. The estimated ratio of incineration to landfill in Member States except these countries (Austria, France, Germany and The Netherlands) is at present 10% to 90% respectively. Although detailed information on planning's of alternative waste treatment capacities, such as incineration of waste, is not available to the project group, it can be expected that such capacities will be increased mainly in those countries where landfilling is currently the principal disposal route for waste. We assume that landfilling of MSW in these countries will gradually be reduced from 90% landfilling today to 85% in 2010 and 80% in 2020.
- 16 The proposed directive on end of life vehicles⁶ stipulates recovery rates of 85% and recycling rates of 80% for the year 2005 and 95% recovery and 85% recycling for 2015, the draft directive on electric and electronic equipment sets out recovery obligations for separate collected waste electrical and electronic equipment, e.g. large household appliances of 90% and other electrical and electronic equipment of 70% in 2004. The following assumption are made to estimate the effect of the directive on end of life vehicles. PVC materials from automobiles are not mechanically recycled, these materials are part of 5% being recovered. 80% of end of life vehicles will have to be recycled in 2005, from the remaining 20% of the vehicle one quarter will have to be recovered to reach the recovery rate of 85% and in 2015 two third will have to be recovered to reach the recovery rate of 95%. Thus, we assume that PVC waste from vehicles being recovered amount to 25% in 2005 and 67% in 2015. With regard to the effect of the draft EEE directive⁷ it is assumed that 80% of PVC content will be recovered. From the year 2010 ongoing we thus assume 40% landfilling for packaging PVC materials. Mechanical recycling is not particularly addressed in our assumptions on the future development of PVC waste being landfilled.

⁶ Amended proposal for a Council Directive on end of life vehicles. The amended Proposal takes account of a number of amendments from the European Parliament which were adopted at its Plenary Session on 8-12 February 1999.

⁷ Draft proposal of 05.07.1999 for a European Parliament and Council Directive of on Waste Electrical and Electronic Equipment amending Directive 76/769/EEC.

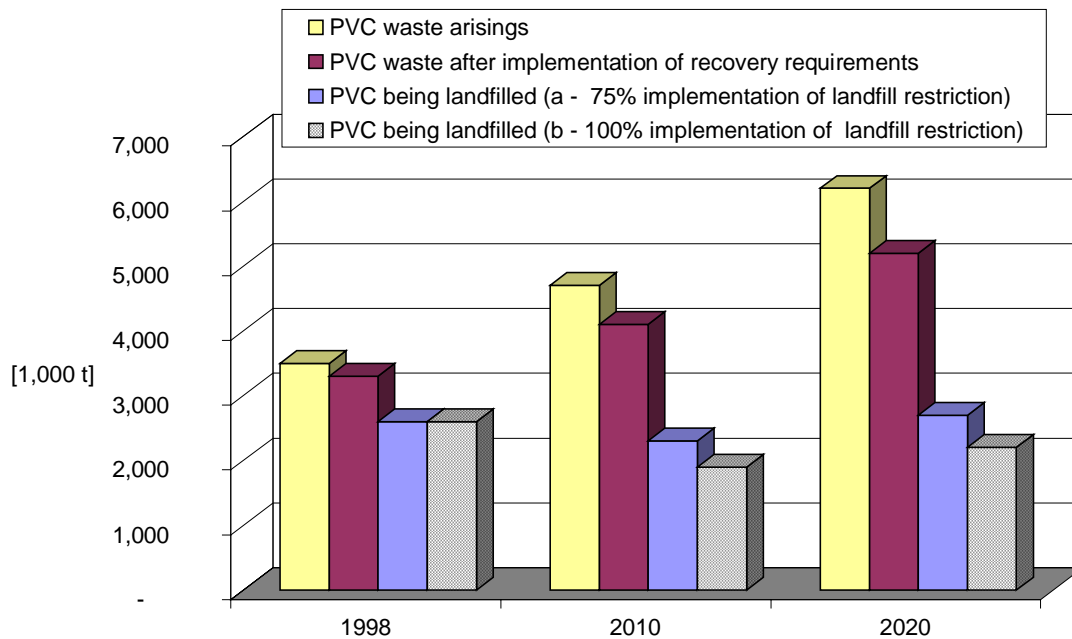


Figure 3-2: Estimated development of landfiling PVC

- 17 In figure 3-2 the development of the PVC waste arisings in Europe in comparison to the assumed development of landfiling PVC waste is shown. The amount of PVC arisings will increase from 3.5 mill tons in 1998 to 4.7 mill tons in 2010 and to 6.2 mill tons in 2020. These amounts are estimated to be reduced following the implementation of directives on packaging waste, on end of life vehicles and on waste from electrics and electronics from 3.3 mill tons in 1998 to 4.1 mill tons in 2010 and to 5.2 mill tons in 2020. Currently approximately 2.6 mill tons of PVC waste arisings is landfilled in Europe. With regard to the effects following the restrictions on landfiling in some Member States (Germany, Austria, France and the Netherlands) and the indirect influence of the landfill directive we considered in our estimation a) the implementation of landfill restriction to 75% and b) 100% implementation of landfill restriction. Accordingly, the landfilled amount of PVC waste in EU can be expected to range between 1.9 mill tons and 2.3 mill tons in 2010. Without further actions the amount of PVC waste being landfilled will increase again in 2020 with 2.2 to 2.7 mill tons landfiling. The estimated direct and indirect influence of the directives on packaging waste, on end of life-vehicles, on wastes from electric/electronic and on landfills is of minor importance compared with the general restriction on waste being accepted for landfills.

3.3 Estimated amount of additives

- 18 The content of additives varies widely between different PVC applications, with the main general difference between rigid PVC and flexible PVC, but also within the same PVC product types the content of additives is dependent on the specific formulation of PVC converters and on the time of production. About 2/3 of the PVC waste arisings consist of flexible PVC, the remaining 1/3 being rigid products. As PVC products being landfilled are expected to release additives we have estimated the amounts of selected additives being landfilled along with the products. These estimates are based on assumptions of the composition of PVC products, the necessary information for these assumptions are primarily provided by industry. The applied percentages are used in the computer model from EuPC for the calculation of PVC waste arisings.

- 19 Three groups are distinguished in the computer model, which are partly a sum of different constituents: the content of stabilisers, lubricants and others substances are estimated to amount to 2.1% in relation to the total of PVC products of which presumably 2/3 (1.4%) are stabilisers. Pigments and fillers make up 11.2%. The average content of phthalates in flexible products amount to 29.4%.
- 20 To estimate the quantities of heavy metals (lead and cadmium) some further assumptions are necessary. Presumably 80% of stabilisers are lead stabiliser formulations. The lead content in these formulations varies widely according to specific applications. We assume that the average lead content in lead stabiliser formulation amounts to 50%. So, as a result an average content of lead in PVC waste of about 0.5% is estimated.
- 21 A finished cadmium stabilised product contains ~ 0.2 to 0.3% of cadmium. In the following estimation we can consider only the cadmium content of window frames because the present data is not detailed enough to also consider other applications. We assume that 80% of window frames becoming waste today are stabilised with a cadmium containing stabiliser.

Table 3-2: Estimated amount of additives in landfilled PVC waste (in tons) in 1998

	landfilled PVC waste in EU			landfilled MSW in EU	Contribution of PVC waste to landfilled MSW in %
	total	flexible PVC	rigid PVC	total	
	2,600,000	1,800,000	800,000	103,713,000	2,5%
containing:					
lead content	13,000			47.643 ⁸	28%
plasticiser		537,000	-		
cadmium (window frames waste)			60 to 90	751 ⁹	~ 10%

- 22 It has to be stressed that the quantities of additives disposed of in landfills along with PVC products depict only the dimension of these amounts in landfills. It was envisaged to provide more substantial estimates, due to lacking information this is not possible at the moment, but respective estimates will be made available by the Industry in the near future.
- 23 Furthermore, it's arguable whether the given amount of total lead in MSW accurately reflects the lead load in MSW landfills. Presumably a co-disposal of industrial waste and slags from incinerators are not considered in the average element composition of MSW in landfills and therefore the total lead may be underestimated.

⁸ Lead content is approx. 647 mg/kg dry solids, 103,713 mill tons wet MSW = 71% equivalent to 73.636 mill tons ds. (TNO 1996, modified and expanded by Mersiowski et al. 1999)

⁹ Cadmium content is approx. 10.2mg/kg dry solids (TNO 1996, modified and expanded by Mersiowski et al. 1999)

4 LANDFILL PROCESSES

- 1 In the following section an overview of landfill processes and their influences on waste materials is provided.

4.1 Degradation processes in landfills

- 2 Municipal waste landfills are very heterogeneous in terms of waste composition and the disposed materials are subject to a wide range of physical, biological and chemical processes. The microbiological processes can be described according to the ageing process of the landfill:
- 3 Phase I (initial aerobic phase): Aerobic conditions prevail until the oxygen contained in the fresh waste is consumed by aerobic micro-organisms and transformed to carbon dioxide. This phase is rather short, approximately 14 days, depending on the operation techniques applied. The organic content of the leachate (BOD_5 , COD) increases.
- 4 Phase II (anaerobic acidogenic phase): As the oxygen level decreases, acetogenic and fermentative bacteria decompose the easily degradable material of the waste. High organic acid content during the acetic phase results in decreasing pH-values with the increasing solubility of some anorganic substances. High organic pollution of the leachate is shown with high values of COD and BOD_5 , a BOD_5/COD relationship greater than 0.4 indicates good biodegradability (Ehrig and Scheelhase 1993). Due to the low pH, heavy metals are more likely to be dissolved. No prediction on the time span of this phase is possible, however this phase is longer than the initial aerobic phase.
- 5 Phase III (anaerobic methanogenic phase): This phase is characterised by the proliferation and activity of the methanogenic bacteria. Increasing methane production is typical at the beginning of this phase until a stable level of methane and carbon dioxide production is reached. Fatty acids are gradually consumed and pH will increase. With the change to the methanogenic phase, the BOD_5 to COD-ratio decreases to below 0.1, with low biodegradability of organic contents. Estimates of the time span of the methanogenic phase vary considerable and a time span of up to several centuries can be expected.
- 6 Phase IV (final aerobic phase): This phase is expected to follow after the methanogenic phase, however, current landfills have hardly reached this phase and therefore only assumptions can be made regarding the processes which may happen. During the methanogenic phase the production of methane will decrease concurrent to microbiological degradation and with diminishing gas pressure to the end of this phase oxygen will be able to diffuse into the landfill body. The result is a change from anaerobic to aerobic conditions. The change to the aerobic condition may lead to mobilisation of heavy metals (Ehrig and Scheelhase 1993).

4.2 Water and substance inventory

- 7 With regard to emissions of toxic substances characteristic phases can be distinguished which occur parallel to and after the above mentioned phases. The behaviour of emissions of soluble materials is decisively affected by the hydraulic interaction, which has to be subdivided into the following three phases¹⁰:

¹⁰ German Research Association (DFG, Deutsche Forschungsgemeinschaft), Water and material budget of landfills and its impact on water bodies, not yet published

- storage phase
 - mobilisation phase
 - consolidated phase
- 8 The storage phase is characterised by the retention of precipitation water in the capillaries of the waste matrix. During the storage phase only the non storable share of the percolating precipitation drains of through coarse hollows. In case of high precipitation this can amount to 30% of the input. Substances being in contact with these hollows are washed out and high emission peaks occur.
 - 9 The mobilisation phase starts when the capillary stores are saturated. In this phase precipitation water causes a drain off of long stored contaminated capillary water and likewise causes a so-called seeping front. This hydraulic effect is strengthened by biological anaerobic degradation leading to a decline of the storage capacity of the waste matrix. Up to 50 % of the stored capillary water is released in addition to the percolating precipitation during the mobilisation phase.
 - 10 Intensive emissions from soluble waste contents are expected only at the beginning of the mobilisation phase. The probable beginning can be estimated by means of the climatic water balance, the total storage capacity, the speed of its building up and the course of its decline. Under ideal conditions (short acid phase, slow build up) and in the climate of North Germany the consolidation phase would begin in a 50m high landfill about 50 years after landfill operation started. If the conditions are worse or the landfills are higher, the relevant emissions are expected after about one century. From prevailing low emissions today the potential emission in the future cannot be predicted. Nowadays the technical guarantee for long-term buildings is restricted to 80 years. So, the relevant emissions are to be expected at the end of the guarantee of the technical barrier.
 - 11 The consolidated phase starts after the biological release of the seeping water has finished. The weight of the waste body causes a compression of the capillary stores. This state reflects a long-term balance between seeping water input and draining off.
 - 12 A slow aerobic stabilisation starts, as soon as the inner gas pressure has diminished and the oxygen of the air is able to re-enter the landfill by diffusion. It is estimated that a 5 metres high landfill takes about 100 years and a 50 metres high landfill about 10.000 years to reach a state where no further degradation takes place. These estimations are confirmed by calculations by Belevi and Baccini (1989) who have calculated that it may take up to 1700 years before the content of organic carbon in the leachate from a traditional MSW landfill is reduced to a low level of 20 mg/l.

4.3 Energy budget

- 13 Since more than 50 % of solid municipal waste consists of organic matter, there is a huge capacity for microbiological digestion processes. From aerobic composting processes it is known that these processes result in the production of energy. Pöpel (1968) determined by means of composting experiments an energy production of 34 - 42 kJ for each gram of decomposed organic carbon. In case of anaerobic decomposition the heat production is smaller (Collins 1993).
- 14 The small amount of energy suggests that the temperature inside landfills remains low. This, however, is not correct. The increase in temperature of a defined mass depends upon the difference in energy leading to, and away from this mass. In case of sanitary landfills the heat is produced through degradation processes while energy loss takes place at the surface through air cooling and via the bottom structure into the ground. Because of the high pore space of dumped refuse the heat conductivity of air will govern the energy release through the surface. Therefore it can be expected that the temperature in the landfill will be higher than in the surrounding area.

- 15 This situation of heat production and heat transfer lasts as long as organic matter for decomposition is available in the landfill. The latter depends on the origin and constituents of the waste as well as on climatic conditions. A certain moisture level is required for these microbiological activities. Therefore the landfill may remain uncomposted and consequently cool in arid and even semiarid regions. Here the temperature may rise if water is added to the dumped refuse. In humid areas water is sufficiently available so that microbiological activity is not hampered.
- 16 Measurements by Collins and Münnich (1993) have confirmed these assumptions. The landfill of the City of Hannover, Germany, operated and built up to a height of 60 m between 1936 and 1980, has been out of operation for 15 years. In spite of this, temperatures of up to 65 °C have been measured in the core and in the lower part of the landfill body where only anaerobic processes took place. It was proved, by means of further measurements, that only anaerobic processes were taking place in the waste body.
- 17 This corresponds to findings in literature. Calculations by Knez (1993) confirm the theoretical observations as well as the measurements with temperature values of 81°C inside the landfill body. Houi et al. (1997) report that temperature of wastes in the landfill varies a lot (between 15°C to 75°C) and presents a great spatial dispersion. Yoshida et al. (1997) observe higher temperature at the bottom of landfills than at the surface with up to 70°C under anaerobic conditions.

4.4 Technical status of MSW landfills and leachate management in EU

- 18 In Member States new landfills are designed with bottom liners and with leachate and gas collection and treatment systems. A broad overview of the technical status of landfill sites and leachate management in EU is given by Hjelmar et al (1995) and can be summarised as follows. In 1994 uncontrolled dumps were still very common in some countries, and numerically, the majority of existing landfills had no leachate control at all. Some Member States allowed co-disposal of certain types of hazardous waste with MSW, in sites with active leachate management. Low permeability top cover was specified for MSW landfills in many Member States to minimise leachate production. There was, however, a growing realisation that the presence of moisture and leaching is necessary to reach final storage quality and that minimising leachate production simply prolongs the period of active leachate management. The most common form of active leachate management was collection and discharge to sewer, usually without pre-treatment. The greatest use of this route was for MSW landfills and in some countries as much as 60-80% of such sites discharge to sewer. The number of sites with on-site leachate treatment plants is increasing rapidly but at present relatively few landfills in the EU have on-site treatment. Most are at MSW landfills and very little treatment is carried out at non-hazardous and low organic waste landfills, and none is known at inert waste landfills. The most widespread active leachate management strategy is containment and collection. The major components of the management systems at such sites are: leachate containment; collection, recirculation of leachate and other landfill management techniques, treatment, and discharge. Treatment of leachate most commonly consists of aerobic biological treatment to remove organics, but may also include physical-chemical pre- and post-treatment processes to remove trace organics, colour, residual COD or dissolved solids.

5 RESULTS OF LITERATURE SURVEY

- 1 Depending on the required properties of applications, PVC products contain a wide range of substances, some of which are known for their hazardous impact on the environment. Little is known to what extent these substances are mobilised once the PVC products have been disposed of in landfills and whether there is a significant contribution of the respective substances to their occurrence in landfill leachate and landfill gas. The literature survey focuses on studies into the behaviour of PVC under landfill and soil buried conditions, special attention is paid to the behaviour of environmentally relevant additives such as plasticisers and stabilisers.
- 2 Other aspects of the complex material stream of PVC such as environmental risks resulting from production, service life, recycling and incineration are not addressed in this study. Although the issue of landfill fires and the adverse environmental effects resulting from the presence of PVC is beyond the scope of this study some information is included. However, this issue is not followed up in detail.
- 3 Because of the very limited number of reports concerning the behaviour of PVC in landfills, the literature survey was extended. A comprehensive online search of protected databases via STN International (Scientific and Technical Information Network) was carried out including not only the search for studies on the impact of PVC waste in landfills, but to a certain extent also on the behaviour of relevant additives, plasticisers and stabilisers in particular, in environmental media such as soil, sediment, water and the atmosphere.
- 4 Details from the online-search, e.g. the search profile and the databases searched are given in Annex V as well as a selection of relevant references, including abstracts as supplied by databases. Not all references were available in full text format, the discussion will therefore only partly reflect the contents of abstracts.
- 5 With regard to the methodological approaches applied in studies for the evaluation of landfilled PVC products, a general distinction has to be made between leaching tests, soil-burial tests and the simulation of landfill conditions in laboratory scale. Results from leaching tests and soil-burial tests are not as such transferable to landfill conditions, however they provide indications of what could happen. An evaluation on the basis of simulated landfill condition in laboratory-scale is much closer to reality, and results are assumed to allow an assessment of long periods of landfill disposal. Wherever it is possible the applied methodological approach is briefly described, however not all articles contained a detailed description of the test conditions.
- 6 The review of literature is structured to reflect the following aspects:
 - Observation of the behaviour of PVC polymer,
 - Loss of stabilisers
 - Loss of plasticisers
 - Degradation of plasticisers
 - Phthalate in landfill leachate
 - Landfill fires
 - Environmental impact
 - Summary of results

5.1 Observation of the behaviour of PVC polymer

- 7 Degradation of PVC products in soil buried tests (Plate, 1997; Yabannavar *et al*, 1994; Yabannavar *et al*, 1993), after long-term underground application (Hjertberg and Grevert 1995), and under simulated landfill conditions (Mersiowski *et al*, 1999; Hagan *et al*, 1995;) has been evaluated but no effect is observed on the PVC polymer itself.
- 8 Lysimeter studies into the long-term behaviour of PVC waste under landfill conditions have been carried out by the Technical University Hamburg-Harburg. In order to identify and observe effects, PVC products were incubated under controlled laboratory conditions over a period of several years. Elution and biodegradation processes were accelerated by leachate recirculation. PVC samples were investigated and both leachate and landfill gas from lysimeters were monitored. Genuine household waste as well as model waste mixtures were used as mediums in the lysimeter assays. To cover the relevant degradation processes of real landfills, acidogenic and methanogenic conditions were simulated in the lysimeters.
In the gas of the lysimeter no vinyl chloride was detected. The concentrations of adsorbable organic halogenated compounds (AOX) in the leachate were not raised compared to blank controls. Further, the examination of samples retrieved from the lysimeter for molecular weight distribution in the PVC polymer matrix revealed no changes in the aged samples. (Mersiowski *et al*. 1999)
- 9 Hjertberg and Grevert (1995) did not observe any sign of degradation of the PVC polymer in PVC samples after 25 years of application in soil. In a theoretical study on the degradation of PVC, they assumed that rigid PVC will not degrade at a practically relevant rate, and plasticised PVC will degrade slowly with the PVC chain remaining intact. This corresponds to observations on the PVC polymer reported by Plate (1997) and Yabannavar (1993 and 1994).
- 10 The common statement throughout the literature review is that PVC products are probably not environmentally significant sources of vinyl chloride (VC) monomer which can be found in landfill leachate. PVC does not depolymerize to VC and/or other degradation products unless placed under extreme thermal, chemical or photolytic conditions. The PVC polymer is therefore regarded as resistant under landfill conditions. More likely primary sources of VC are chlorinated solvents, VC aerosol propellants and PVC sludge waste (Mersiowski *et al*, 1999; Hagan *et al*, 1995).

5.2 Stabiliser

Heavy metals, organotin

- 11 There are only a very limited number of studies on losses of stabilisers of PVC products disposed of in landfills. The leaching of cadmium from pigmented plastics was studied by Wilson *et al*. (1982). Leaching tests were carried out using acetic acid buffered to pH 5 with sodium hydroxide under test conditions which corresponds to about 20 to 30 years of landfill condition. Test results indicated that the contribution of all plastics (including PVC stabilised with cadmium) to the cadmium content of landfill leachate is unlikely to exceed that from trace contaminants in food and paper (1-2µg/l).
- 12 Brederick (1983) reports on leaching experiments involving cadmium stabilised window frames during which a 10 kg window frame was exposed to 3% acetic acid for one year. Subsequent extraction measurements revealed that from 25 mg cadmium contained in the sample the total amount of cadmium leaching was 1.2 mg, thus, 4.8% of the cadmium content.

- 13 Griebenow et al. (1992) investigated the leaching behaviour of four differently composed window and shutter profiles containing lead phosphite and barium/cadmium as stabilisers. The samples were ground in order to increase the surface area of the material and exposed to three different test solutions: distilled water with 3 weight% of active carbon, diluted aqueous acetic acid pH 3 and aqueous alkaline solution with soda pH 10. Results show that PVC containing Pb, Cd, and Ba as stabilisers hardly bleeds in distilled water with 3% active carbon as a test medium. The least dissolving ones are Pb phosphite and mixtures of Pb phosphite and Pb stearates, the same is true for Ba/Cd laurate. The Ba/Cd soaps pass somewhat more easily into this test medium. In an acidic test medium considerable amounts of stabilisers did dissolve but a pH of 3 in the percolating water of a landfill is very unlikely. It is concluded that under landfill conditions, PVC moulded parts in building debris exhibit almost no bleeding of the heavy metal stabilisers, and that they have very little effect on landfill leachate.
- 14 The behaviour of flexible PVC containing Ca/Zn, organotin and lead stearate as stabilisers was investigated in soil-buried tests over 1 ½ years by Plate (1997). Three different solutions were used for percolation, buffered at pH of 4.5 and 8.5, and distilled water. Losses of organotin and Ca/Zn stabilisers were observed but examination of the soil did not result in detectable amounts of stabilisers.
- 15 Hjertberg and Grevert (1995) analysed the content of lead in pipes and in the surrounding soil after ca. 25 years of application. An elevated level of lead was detected in the surrounding soil, but no difference in lead content for the pipe samples taken from the outer surface, the interior or the inner surface was observed. A possible explanation for the higher lead concentration in the soil close to the pipe could be that the virgin pipe had a thin layer of stabiliser on the surface and that this layer with time was transferred to the soil. However, it has to be pointed out that the original concentrations of the samples were not known and thus, estimates with regard to the loss of lead are less reliable.
- 16 The study into the long-term behaviour of PVC waste under landfill condition showed a release of lead stabiliser from PVC cable of about 10% (Mersiowski *et al.* 1999), though this loss was observed only after an incubation time of more than one year under methanogenic conditions. The investigated cable contained DINA as plasticiser which is not a typical formulation for Europe but is commonly used in Scandinavian countries. It is noted that the release of lead occurs in conjunction with the loss of the plasticiser DINA. As an explanation for the loss of lead from the investigated cable it was assumed that the particular formulation containing DINA as plasticiser is more inclined to release lead than usual blends without DINA. Any elevated concentrations of lead in the leachate were recognisable only if the background contamination was very low and if rather large amounts of PVC cable were introduced to the waste. No long-term release of lead is expected to occur, the leaching effect is explained as a superficial wash-off from the surface of the material.

Elevated concentrations of lead in the leachate were also observed in the early acidogenic phase of the landfill simulator incubated with PVC pipe. The acidic properties in combination with the high content of organic carbon in the leachate enhance the leaching processes considerably. There was no sustained release of lead and concentrations subsequently decreased below detection limits. It is concluded that particularly the acidogenic conditions of early landfill development constitute the critical stage regarding emissions of heavy metals from the PVC products. A preliminary assessment of the environmental impact indicated that the investigated PVC products do not significantly contribute to the concentrations of heavy metals in landfills and are not assessed as constituting a risk to the environment.
- 17 Other PVC products investigated in the above study are flooring, pipe, rigid foil and rigid sheet. The loss of the calcium/zinc stabiliser from the flooring was too small to be quantified. The presence of organotin stabiliser in the leachate was observed with concentrations of monobutyl and dibutyltin ranging between 1 µg/l and 10 µg/l and around 1µg/l, respectively. The leachates of rigid blister foil stabilised with octyltins did generally contain organotin concentrations <0.03 µg/l.

Elevated concentrations of zinc in the leachate were observed during the early acidogenic phase, but no long-term release of zinc was detectable. Migration of stabilisers from rigid foil and rigid sheet was considered as not significant.

- 18 The general view expressed in studies investigating the release of stabilisers from PVC products is that as the stabilisers are encapsulated in the PVC matrix, the migration rate is expected to be extremely low and would only affect the surface of the PVC but not the bulk of the material. The mobility of organotin stabilisers in flexible PVC is higher than in rigid PVC due to the plasticiser, the release of organotin in landfills can be expected, however available data is insufficient.

Other substances, co-stabilisers

- 19 The leachability of bisphenol A, used as co-stabiliser and antioxidant for many types of plastics including PVC is reported by Yamamoto *et al.* (1999). The amount of bisphenol A leached from the plastic wastes, exposed to distilled water for two weeks at room temperature in the dark, ranged from undetectable to 139 µg/g. Polyvinyl chloride products yielded the highest concentrations with 1.98 to 139 µg/g. Waste plastics belonging to the group with high leaching rates, such as polyvinyl chloride may be one of the most important sources of bisphenol A found in landfill leachate samples. Bisphenol A may serve as an endocrine disrupter at environmental concentrations well below acutely toxic levels. The author concluded that more attention should be paid to the use of bisphenol A as co-stabiliser for polyvinyl chloride and the possible environmental consequences of this use. No other information has been found on the leachability of bisphenol A from PVC.
- 20 Tris (nonyl and dinonylphenol) phosphite is used in liquid stabiliser systems for flexible PVC. Although the content in flexible PVC is limited, it is expected that nonylphenol can be released from the PVC products through hydrolysis. (UBA, 1999) No studies have been found on the release of nonylphenol from PVC. Ejlerthsson *et al.* (1997) have investigated the anaerobic degradation of nonylphenol mono- and di-ethoxylates in municipal solid waste and landfilled sludge and observed that nonylphenol was not further degraded and thus, appeared to be resistant to microbial transformations under methanogenic conditions.

5.3 Loss of plasticisers

- 21 In general, and with regard to organic substances in particular, it has to be considered that landfills are very heterogeneous in terms of waste composition and physico-chemical characteristics - not only between landfills but also within a single landfill. Organic compounds inside the landfill are subjected to spatially and temporally changing processes. Examples of these processes are given by Öman *et al.* (1997): i) the initial release of the compounds from the waste (the PVC product), ii) sorption of the compounds to stationary and mobile matrices, iii) transport of dissolved compounds, iv) transport of the compounds, with or as, colloids or particles, v) transformations of compounds by for example microbial degradation, abiotic hydrolysis, or abiotic redox transformations, vi) aggregations to humic-like material, and vii) evaporation and transport of compounds in the gas phase. The processes affecting organic compounds inside the landfills interact with each other and the processes vary with time as the waste changes and the environment inside the landfill changes.
- 22 Microbiological attack of plastified polyvinyl chloride under modified soil buried conditions was gravimetrically, electron optically and chemically investigated by Pantke (1970). 7 different PVC formulations were used for the tests. Phthalic acid esters (PAEs) with chain lengths of C8 and C9 were added to the basic polymer substance as primary plasticisers (bis(2-ethylhexyl) phthalate and di-isodecyl phthalate). After a test period of 48 weeks the original amounts of primary and

secondary plasticisers were reduced to 70-75% and 20-40%, respectively. No PAEs or metabolites could be detected in the soil.

- 23 Hjertberg and Grevert (1995) identified a loss of plasticisers from cables after 25 years of underground application. The measured content of plasticiser was 20% in the inner layer and 17% in the outer layer of the cable. A typical plasticiser content for cable insulation would mean 26-28%. The obvious conclusion is that the plasticiser migrates out from the material. This is confirmed by the observation that the content of plasticiser is lower in the outer layer compared to the interior and the inner layers. As mentioned above (para. 9 refers) the original compositions and the type of plasticisers were not known. The release of different plasticisers of PVC under soil buried test conditions and after long-term underground application is also reported in a number of studies, but without determination of the quantities of losses (Plate, 1997; Yabannavar 1994; Ohtake, 1993; Svetov, 1982)
- 24 Results from the investigation into the long-term behaviour of PVC (Mersiowski *et al*, 1999; see para. 16) also revealed losses of plasticisers. For the investigated PVC cable containing DINA/DIDP a loss of the plasticisers of up to 40% was detected, though this loss was observed only after an incubation period of more than one year. From PVC flooring subjected to methanogenic conditions, a loss of the plasticisers DEHP and BBP was observed, losses being in the range of 10 to 15%. Two other samples of PVC floorings investigated in the above mentioned project, a homogeneous flooring material and a two layer flooring were incubated in a laboratory-scale landfill simulator for over 4 years, samples of the material were retrieved after 36 months and after 55 months. The results after 36 months incubation time show that the homogeneous flooring material remained more or less intact during the experimental period under both acidogenic and methanogenic conditions, while the two layer flooring showed in its upper layer a loss of almost 20% of BBP and 12% of the DEHP under methanogenic conditions. After 55 months under methanogenic conditions the homogeneous flooring had lost 26% of its total BBP content and 4% of DEHP.
- 25 The losses of plasticisers in the landfill simulation study during the acidogenic stage were found to be low or not detectable. Instead, anaerobic biodegradation at or near the surface of the PVC product seems to be an important determinant for the possible loss of plasticisers from the PVC matrix (Mersiowski *et al*. 1999). Findings of these compounds released from the PVC materials in the leachate did, however, not correspond to the amounts expected if only dissolution were taken into account. Further investigation on whether anaerobic microorganisms developing in acidogenic and methanogenic landfill environments have the potential to degrade phthalic acid esters (PAEs) and what kinds of intermediates may be formed was carried out by Ejlerstsson (1997), para. 27refers.

5.4 Degradation of plasticisers

- 26 Adams, William J. et. al., (1988) conducted a 30-day freshwater microcosm study to measure the biodegradability of butyl benzyl phthalate in water and sediment. The results indicated that BBP was readily degraded in water and sediment. The estimated half-life in water for primary degradation was typically 2 days. The collective data indicate that BBP should not be persistent chemically in freshwater environments.
- 27 The results of the investigation on degradability of PAEs (Ejlerstsson 1997) showed that the microorganisms present in the MSW-samples were able to transform almost all PAEs investigated. However, it was observed that the degradation of PAEs may give rise to compounds which are more chemically inert than the parental compounds. As an example bis(2-ethylhexyl) phthalate (DEHP) was observed to be degraded to mono(2-ethylhexyl) phthalate during 300 days of incubation. Monoesters of PAEs were detected in leachate from methanogenic landfill

lysimeters in concentrations up to 12 mg per litre during MSW degradation. PVC-plastics subjected to methanogenic conditions were shown to be leached of PAEs, which did not occur for samples under acidogenic conditions. The results imply that microbial degradation enhanced the loss of PAEs from the PVC-plastics incubated under methanogenic conditions.

- 28 In an earlier study Ejlertsson *et al.*, (1996) investigated anaerobic microorganisms in municipal solid waste samples from laboratory-scale landfill reactors and a pilot-plant biogas digester with the aim of assessing their ability to transform four commonly used phthalic acid esters (DEP, BBP, DBP, and DEHP) and phthalic acid (PA). No biological transformation of DEHP could be detected in any of the experiments. Together with waste samples from the simulated landfilling conditions, the PAEs (except DEHP) were hydrolytically transformed to their corresponding monoesters. These accumulated as end products, and in most cases they were not further degraded. During incubation with waste from the biogas digester, the PAEs (except DEHP) were completely degraded to methane and carbon dioxide. It was concluded that microorganisms developing in a methanogenic landfill environment have a substantially lower potential to degrade PAEs than those developing in a biogas reactor.

- 29 O'Connor (1989) evaluated DMP, DEP, DBP and DEHP for their anaerobic biodegradability and toxicity to methanogenesis. Bis(2-ethylhexyl)phthalate showed little mineralization at any concentration, although biotransformation of this substrate was indicated. Acclimation for most of the compounds took several days to weeks before degradation commenced. Generally, increased incubation led to increased levels of methane production above active control levels. Thus, many of these compounds were metabolized completely under methanogenic conditions and were observed to produce little inhibition of methane production. Their fate, therefore, may be significantly influenced by their concentration and residence time in methanogenic habitats.

- 30 The fate and behaviour of phthalic acid esters during anaerobic conditions in municipal solid waste landfills was investigated in laboratory scale bioreactors under conditions of anaerobic digestion by Bauer (1997). DMP, being very water soluble, could be biologically transformed during the anaerobic degradation sequence of the municipal waste regardless of the length of incubation. A primary degradation of DEHP during the hydrolytic and acidogenic phases of anaerobic digestion could not be precluded. However, there was no evidence of a transformation of DBP and BBP. During methanogenesis all the phthalic acid esters except DMP turned out to be persistent. DEHP could not be decomposed abiotically at pH 9. It is concluded that in the biochemical environments of municipal landfills, short chain PAEs can be degraded by base-catalyzed hydrolysis or by microorganisms which enzymically split the side chains. However, there is no cleavage of the aromatic ring. Long chain PAEs like di-(2-ethylhexyl) phthalate are neither degraded abiotically nor by microorganisms.

- 31 In the bioreactors' leachates investigated in the above study, there was more phthalic acid ester in the solution with higher water solubility of the respective PAE. The presence of dissolved organic substances in the leachate resulted in a solubility enhancement of the PAE. Increased concentrations of DEP, DBP and BBP could be observed during the acidogenic phase. Nevertheless, volatile fatty acids could be ruled out as the cause of this phenomenon. Fractionation experiments using ultrafiltration techniques showed that DBP could be transported via macromolecular substances (>3000 Da) in the leachate. In most cases, the DEHP concentration in the leachate did not increase until the transition phase to methanogenesis was reached. Substances with a molecular weight > 50000 Da were the reason for this enhancement of the PAE's water solubility. It is assumed that these macromolecules changed their shape with decreasing concentration of dissolved organic carbon (DOC), thereby increasing the molecular surface required for the adsorptive binding of DEHP. The results of the investigation of several leachates from municipal solid landfills indicate that humic and fulvic acids were acting as the solubilizing macromolecular agents.

- 32 The leachate transports PAEs either adsorbed on particulate matter or in dissolved phase. Dissolved organic macromolecules, mainly humic-like substances, enhance the solubility of PAEs. In the course of the municipal waste digestion sequence DEHP accumulated at suspended solids. As a result, only about a quarter of the overall load with DEHP could be found in solution. The concentration of DEHP in solution was significantly dependent on the amount of humic substances.

5.5 Plasticisers in landfill leachate

- 33 Mersiowski *et al.* (1999) have analysed leachates from landfills in Sweden, Italy and Germany for their content of monoesters (MMP, MEP, MBUTP, MbenzP and MEHP), of phthalic acid and the following phthalic acid esters: DMP, DEP, DBP, BBP, and DEHP. The occurrence of phthalic acid and phthalic monoesters in the leachates is seen as a strong indication that an *in situ* degradation of PAEs occurs (see results from lysimeter studies, para. 24 and 25). In several of the analysed leachates, both PAEs and their metabolites were detected. The detected concentrations of these analytes were generally in the range of 1 to 30 µg/l. The highest concentrations observed in leachate samples were phthalic acid at 18,900 µg/l, DEP at a level of 540 µg/l, and DMP at a level of 300 µg/l. High concentrations of DEHP were also detected in the leachates of a Swedish landfill and two Italian landfills (75, 49, and 460 µg/l) which far exceeded the water solubility of DEHP.
- 34 Greenpeace has analysed leachates from landfills in Sweden and detected concentrations of PAEs at the following levels: DMP <2 µg/l, DEP <29 µg/l, DBP <2 µg/l, DEHP 42 µg/l, BBP <2µg/l. Öman and Hynning (1993, cited by Moeller *et al.* 1996) found concentrations of DEHP between 2 and 9.7 mg/l in the leachate of Swedish landfills. The highest concentration of DEHP detected in effluent water samples from various types of UK based landfills was 30µg/l (Cadogen *et al.* 1994, cited by Moeller *et al.* 1996)
- 35 Bauer has examined landfill leachates of different origin in order to verify the results obtained in the laboratory (see para. 30 - 32, Bauer, 1997). The concentrations of phthalates detected in the liquid phase of landfill leachates in Germany (Bavaria) ranged between from 0.1–62.7 µg/l for DBP and 0.6-235.9 µg/l for DEHP, the concentration of phthalates in suspended solids of leachates analysed after ultracentrifugation ranged between 3.5-126 µg/l for DBP and 0.4-187.6 µg/l for DEHP. In addition, 5 landfills with different leachate treatment plants were investigated: biological treatment, reverse osmosis, UV/ozone oxidation, evaporation, and precipitation (Bauer *et al* 1998). Usually landfill leachate is treated by an activated sludge process. This treatment was found to efficiently and rapidly degrade short chain PAEs, however, long-chain PAEs, such as DEHP, were only partly degraded and at the same time they were enriched on suspended particles. Bauer concluded that only a combined UV radiation/ozonation treatment is capable of fully destroying PAEs.
- 36 Investigations of the load and reduction of a number of organic xenobiotics including DEHP in waste water treatment plants were carried out in Denmark and Austria. Results from Denmark indicate that 10 to 50% of the DEHP in concentrations of about 2 to 20 µg/l (Denmark) and <4µg/l (Austria) passes the water treatment plant to the aquatic environment. An elimination of DEHP of 43 –99 % in sewage treatment plants is reported from Germany, however the rate of primary degradation varies between 0 – 70%. It appears that below a certain limit no further degradation of DEHP occurs (UBA 1999). Furtmann (1993) observed that the concentration of DEHP in the effluent of sewage treatment plants did not fall below ca. 5µg/l.

5.6 Landfill fires

- 37 Ettala et al (1996) have investigated landfill fires in Finland. On average, there are 633 sanitary landfills in operation in Finland. In the period of 1987-92 between 360 and 380 landfill fires occurred annually. One-quarter were deep fires at a depth of more than 2m and a maximum depth of 8m. Deep fires are difficult to extinguish and last longer than surface fires. The most severe deep fires lasted for 2 months. Only four fires occurred in waste older than 2 years. In 400 sanitary landfills in Sweden, 200-250 fires have been reported. According to international experts¹¹, landfill fires are common in Iceland because of arson. Other replies considered that landfill fires are very uncommon but reliable statistics were lacking. Disposal of ash, deliberate fire starting and insufficient covering or compacting were reported to be the most common causes for landfill fires. Possible air flow through drainage pipes has been one reason for landfill fires in the U.K.
- 38 Temperatures in waste bodies are expected to be low during landfill fires, although direct measurements are lacking. In order to determine the occurrences and circumstances of landfill fires, a 10m high, 35,000 m³ large experimental bank of waste was built, instrumented and set on fire from a 7m deep well located at the centre of the area. The highest temperature of about 700°C was measured in the centre of the fire, depth 5m. In a distance of 5m from the centre the temperature ranges about 200-300°C. The wide range of refuse temperatures during the landfill fires promotes the generation of hazardous combustion gases. During the fires, the concentrations of PCDD/PCDF in the air of the landfills were high. The limit value for waste incineration plants in many European countries, 0,1ng/m³, was exceeded during the active fire. The toxic congener distributions in the air samples were the same as have already been detected in pilot tests and MSW incinerators. The greatest contribution to the toxic equivalent was made by the same toxic congeners as detected in the landfill fire tests and MSW flue gas (Ruokojärvi et al, 1995).
- 39 The fire performance properties differ from rigid to flexible PVC. Rigid PVC is difficult to ignite and burns only with the continuous addition of heat from other sources. The flash ignition temperature for PVC is 346°C. Flexible PVC can easier ignite than rigid PVC dependent on the amount and type of plasticiser, e.g. with more than 40% phthalate plasticiser the material will burn after the external heat source has been removed. When burning, PVC yields a number of combustion products of which carbon dioxide, carbon monoxide, water and hydrogen chloride make up the largest part. Hydrogen chloride is converted to hydrochloric acid. The presence of chlorine in the material gives the potential for contribution to the formation of polychlorinated dioxins and furans. The amount will depend on the fire conditions such as oxygen available, temperature, catalyst available such as copper and the amount of chlorinated material. Worst case is expected at low oxygen concentration and lower temperature (500 – 700°C). Laboratory tests with different types of PVC products report formation of PCDD/PCDF in the level of microgram per kilo. The dioxin formation is starting at low temperatures at 250-300°C (Moeller et al, 1996).
- 40 PVC products disposed of in landfills will certainly contribute to the formation of PCDD/PCDF, but the quantitative contribution cannot be estimated.

¹¹ Questionnaires were send out to 12 international experts involved in landfilling. Replies where received from United Kingdom, the Netherlands, Hong Kong, Iceland and Italy.

5.7 Environmental impact

- 41 The conclusions drawn in the studies differ with regard to the detrimental effects on the environment of different constituents of PVC. Generally, the view is held that rigid PVC products do not constitute an environmental risks in landfills due to the low concentrations of contaminants released from PVC which could be found. The observed releases of stabilisers are in the range of hardly detectable and these losses would only occur from the surface of products but not from bulk of the material.
- 42 Mersiowski *et al.* (1999) have calculated the quantitative relevance of lead (cadmium was excluded from the scope of the study) released from PVC products investigated in their study. Based on the average lead content of MSW (TNO 1996) of 647 mg/kg dry solids, the total lead content of MSW being landfilled in EU amounts to 42,500 tons. The contribution of lead introduced in landfills along with PVC cables and pipes is about 1,425 tons and represents 3% of the total MSW lead content. The contribution of zinc is exceedingly small (0.4%) at 3 mg/kg ds (dry solids) of the average amount of zinc of MSW (844 mg/kg ds). It is concluded that PVC products do not contribute significantly to the amounts of heavy metals stored in the landfill body – irrespective of any possibility for release.
- 43 The exposure and effects of mono- and diorganotin stabilisers were assessed by Länge (1998). Mono- and diorganotin stabilisers do not persist in the aquatic environment, however degradation mainly by micro-organisms is relatively slow. Half-life estimates for butyltin compounds range from a few days to three months under environmental conditions. In waste water treatment plants the butyl- and octyltin stabilisers are effectively eliminated. Adsorption to sewage sludge was observed for butyl- and octyltin compounds. Methyltin compounds were not found. Leachates from landfills contained organotin stabilisers at concentrations which were much below the predicted no-effect concentration. The author concluded that there is no indication that the manufacture and use of organotin stabilisers presents a risk for the aquatic environment. (Note: tri-organotin is not used in PVC but as anti-fouling application for ships)
- 44 The German Protection Agency concluded, that the use of organotin as a stabiliser for PVC applications represents a potential environmental risk, however further investigation would be necessary before final conclusions can be drawn. At present it has not been clarified whether the detected amounts of di- and monobutyltin compounds in the aquatic environment, in sediments and sludges are primarily the result of the use of tributyltin or also the result of the use of organotin in PVC products. Further research is required with regard to e.g. ecotoxicological effects of organotin, degradation and bioaccumulation (UBA, 1999).
- 45 While for lead, other sources for the contamination of MSW are considered to be more relevant than PVC products, this is not the case for phthalates, other sources than PVC are negligible. No total releases of phthalates from a PVC product under soil-buried and landfilled conditions has been reported, however in the long-term a total loss of all phthalates introduced in the MSW stream and landfills through PVC products and the contamination of environmental media (soil, water, groundwater) via leachate cannot be excluded (Bauer, 1997). Although the majority of phthalates appear to be ultimately biodegradable in environmental compartments, this is not true of DEHP, which is the most important plasticiser in terms of quantities.
- 46 Cadogen *et al.* (1993) have estimated the emissions of phthalates considering the entire life-cycle. In order to quantify the emissions which occur, information was obtained from the Western European plasticiser manufacturers, their hauliers and customers regarding losses during plasticiser production and distribution and on the use of exhaust air purification equipment in processing plants. Total emissions of phthalates amount to 7,740 tons/a, of which the most important emission path constitutes the service-life and exterior use in particular of flexible PVC applications with 5,600 tons/a (72% of total emissions). Emissions from disposal are estimated to

be 250 tons/a (3% of total emissions). Although the estimated emissions of phthalates from disposal in landfills may be too low, the dimension of emissions corresponds to the general view, that emission via the atmosphere is presumably the main reason for the ubiquitous distribution of phthalates in environmental media (UBA 1999, WHO EHC, 1992).

- 47 The environmental impact of DEHP was assessed by the environmental protection agency of Germany (UBA, 1999). The model of sustainable development, linked with and complemented by the precautionary principle, was used as the basis for the derivation of environmental quality and environmental action targets, taking current developments in substance control policy into account. The criteria for a precautionary and sustainable substance control policy are briefly summarised below:
- a) The release of xenobiotics (including metabolites) with persistent, bioaccumulative and/or toxic/ecotoxic properties into the environment has to be avoided.
 - b) The irreversible release of xenobiotics (including metabolites) with persistent and/or bioaccumulative properties into the environment has to be avoided irrespective of their toxicity.
 - c) Natural background contamination of substances with persistent, bioaccumulative and/or toxic/ecotoxic properties in the environment shall not be increased through anthropogenic release.
 - d) The release of other toxic/ecotoxic substances not covered by these categories has to be limited to the amount technically unavoidable.
- 48 A number of substances used as additives in PVC products become environmentally relevant and would require preventative measures when considered according to the above precautionary criteria. With regard to the behaviour of PVC products under landfill condition it can be concluded that although the reported releases of cadmium, lead, organotin and phthalates are considered to be of minor relevance either in terms of quantities introduced and released in landfills or because of the retention capacity of the waste matrix and biodegradation in landfills they are only controllable if landfills are equipped with adequate liner and leachate treatment, which is for old landfills in particular not the case. However, even in controlled landfills uncertainties remain with regard to long-term behaviour.

5.8 Summary of results

- 49 The PVC polymer is regarded as being resistant under soil-buried and landfill conditions. Changes of the PVC polymer are not reported in the literature reviewed.
- 50 The general view expressed in the literature with regard to the potential release of stabilisers from PVC products under landfill conditions is that because stabilisers are encapsulated in the PVC matrix, the migration rate is expected to be extremely low and would only affect the surface of the PVC but not the bulk of the material. However, losses of stabilisers at a rather low range have been detected. With regard to heavy metals, particularly in acidic medium, elevated concentrations in the leachates were detectable. Thus, the early acidogenic stage of the landfill development seems to constitute the critical stage regarding emissions of heavy metals from the PVC. Compared to the total load of lead and zinc in MSW the contribution of PVC is considered to be negligible.
- 51 The release of plasticisers from PVC products under soil-buried and landfill conditions as well as during the use of PVC products is widely recognised in the literature. Phthalates, with 93% the most important plasticisers, are not chemically bound to the product and may therefore leach into the surrounding medium. Results differ with respect to the quantities of phthalates released from products and detected in soil, landfill leachates, sediments etc., and with respect to microbial biodegradability of phthalates.

- 52 The degradation of phthalates from PVC under methanogenic conditions is observed to be higher than under acidogenic conditions. Results from studies on the degradability of phthalates under landfill conditions show that degradation of PAEs occur, however, the rate of degradation does appear to be influenced by the length of their side chain. Both, PAEs and phthalic monoesters can be detected in landfill leachate, which indicates that these substances are not completely degraded. Long-chain PAEs, like DEHP, are only partly degraded in landfills and sewage treatment plants. Thus, emissions of phthalates to landfill leachates and to the aquatic environment cannot be excluded. DEHP in particular is considered to be persistent and to accumulate in sediments. Apparently DEHP is not further degraded below a certain background contamination in the range of few µg/l.
- 53 Apart from the study undertaken by Yamamoto (1999) on the release of bisphenol A from PVC products, no other study was found on this issue. Bisphenol A may be an endocrine disrupter at environmental concentrations well below acutely toxic levels, estrogenic activity is reported (Harris *et al.* 1997, Feldmann *et al.* 1995, Nordic Council of Ministers 1996). The amount of bisphenol A used in PVC products is not known to the project group, however more attention should be paid to the use of bisphenol A as a co-stabiliser for polyvinyl chloride in particular, and for other plastics and the possible environmental consequences of this use.
- 54 Nonylphenol which may be released in the long term through hydrolysis from PVC products is not further degraded under methanogenic conditions. Because of its ecotoxicity, low degradability and the expected estrogenic effect, nonylphenol is regarded as environmentally problematic substance to which special attention should be paid (UBA 1999).

6 THE BEHAVIOUR OF PVC UNDER SIMULATED LANDFILL CONDITIONS

6.1 Methodological approach

- 1 All investigations into the impact of landfill conditions on different materials or substances have to take two major factors into consideration: time and scale. To evaluate the behaviour of PVC in landfills suitable methods had to be developed to overcome these factors. Any long term attack in landfill is characterised by slow processes in the rather large landfill body. Within the scope of study the size scale was decreased by step from real landfill to container size and further to laboratory lysimeters and finally to detailed laboratory investigations as depicted in Figure 6 - 1.

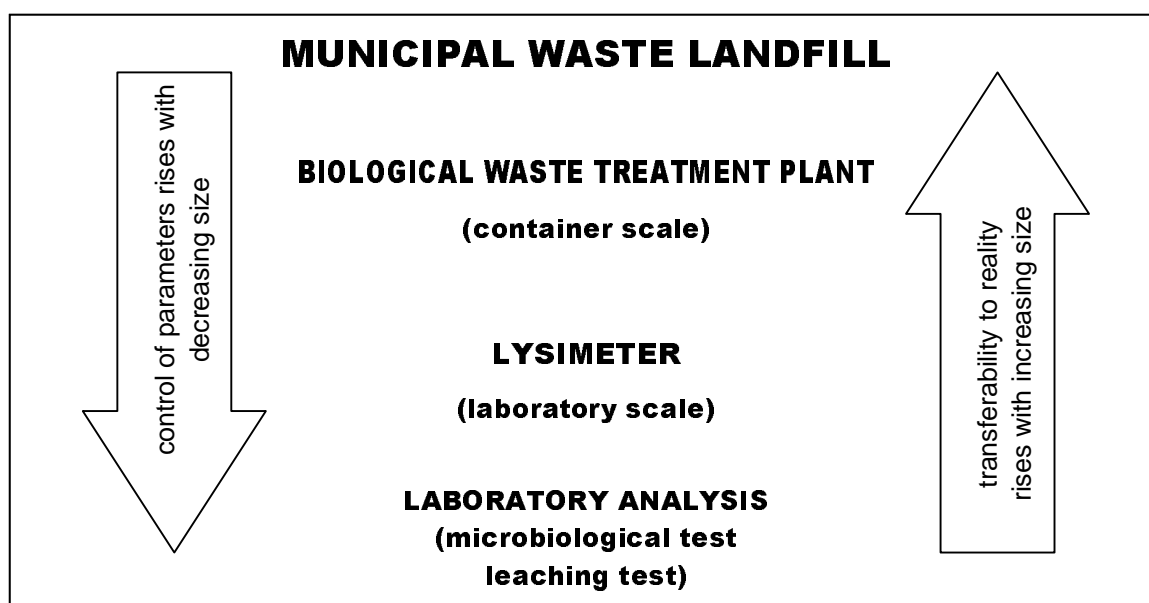


Figure 6 - 1: Size scale of the experiments to examine the behaviour of PVC in landfill

- 2 With the reduction of the experiment's size, the ability to control and to characterise processes increases. Further, changes within the PVC as well as emissions from the material become measurable. On the other hand, the influence of slight differences in border conditions rises and the results deviate from reality. To reach results within the time frame of the study, deviations were controlled by comparisons between the different size scales. On the basis of similarities results are assumed to be transferable to reality. To overcome the time problem maximum attack on the PVC materials under conditions comparable to landfills were examined. Maximum attack on organic matter is known from aerobic thermophilic decomposition¹². Investigations in earlier studies showed that the final state of organic substances in a staunch free landfill is always the same: an aerobic stabilised humic-like substance, nearly water insoluble. The same result can be reached by aerobic degradation within a much shorter time span.
- 3 To achieve comparability between tests and the real behaviour of PVC in landfill, PVC samples from a landfill were analysed. At the second stage, examinations were carried out at container

¹² In biological waste treatment plants under aerobic thermophilic decomposition temperatures up to 80°C develop and the degradation rate of organic matter is highest in comparison to other biological processes.

size under aerobic thermophilic conditions at a biological waste treatment plant. In laboratory scale the samples were exposed to aerobic thermophilic conditions, to anaerobic thermophilic conditions and to alternating aerobic-anaerobic conditions. Aerobic thermophilic conditions are usual in landfills during the initial phase and are considered to be rather aggressive to materials. Anaerobic thermophilic conditions also occur commonly in landfills, this condition is expected to be less aggressive to PVC although it shows better comparability to the long term behaviour of landfills. From remediation of contaminated sites it is known that aerobic-anaerobic treatment is most aggressive to chlorinated compounds. Laboratory studies of microbial attack on PVC and its additives as well as leaching tests were examined to investigate PVC-influencing processes in detail.

- 4 In this study great emphasis was put on the diversity of the investigations. This approach was chosen in order to achieve comparability and confirmation between observed effects. Therefore, most of the numerous experiments were carried out only one time. Similar effects resulting from different tests increase the reliability of results. In contrast, effects which occurred only in a single investigation are easy to identify as failures. However, conclusions of the analytical programme have to be seen as hints and have to be compared with results from other studies on the behaviour of PVC in landfill.

6.2 Analytical programme

- 5 Based on the considerations presented in the section above the analytical programme was developed. The chemical, physical and biological influences of landfill conditions differ considerably. Hence different influences on the behaviour of PVC in landfill were examined. The investigations as conducted in the study are outlined below.
 - Identification and investigation of PVC from landfill
 - Investigation of the behaviour of PVC in a waste treatment plant in technical scale¹³
 - Investigation of the behaviour of PVC in lysimeter studies
 - Investigation of the behaviour of PVC in a leaching test
 - Investigation of microbial degradation of PVC
 - Investigation of carcinogenic effects of emissions resulting from PVC in landfill
- 6 To give an overview about follow-up and dependencies between the investigations the analytical programme is shown overleaf in figure 6 - 2.

¹³ See chapter 6.5

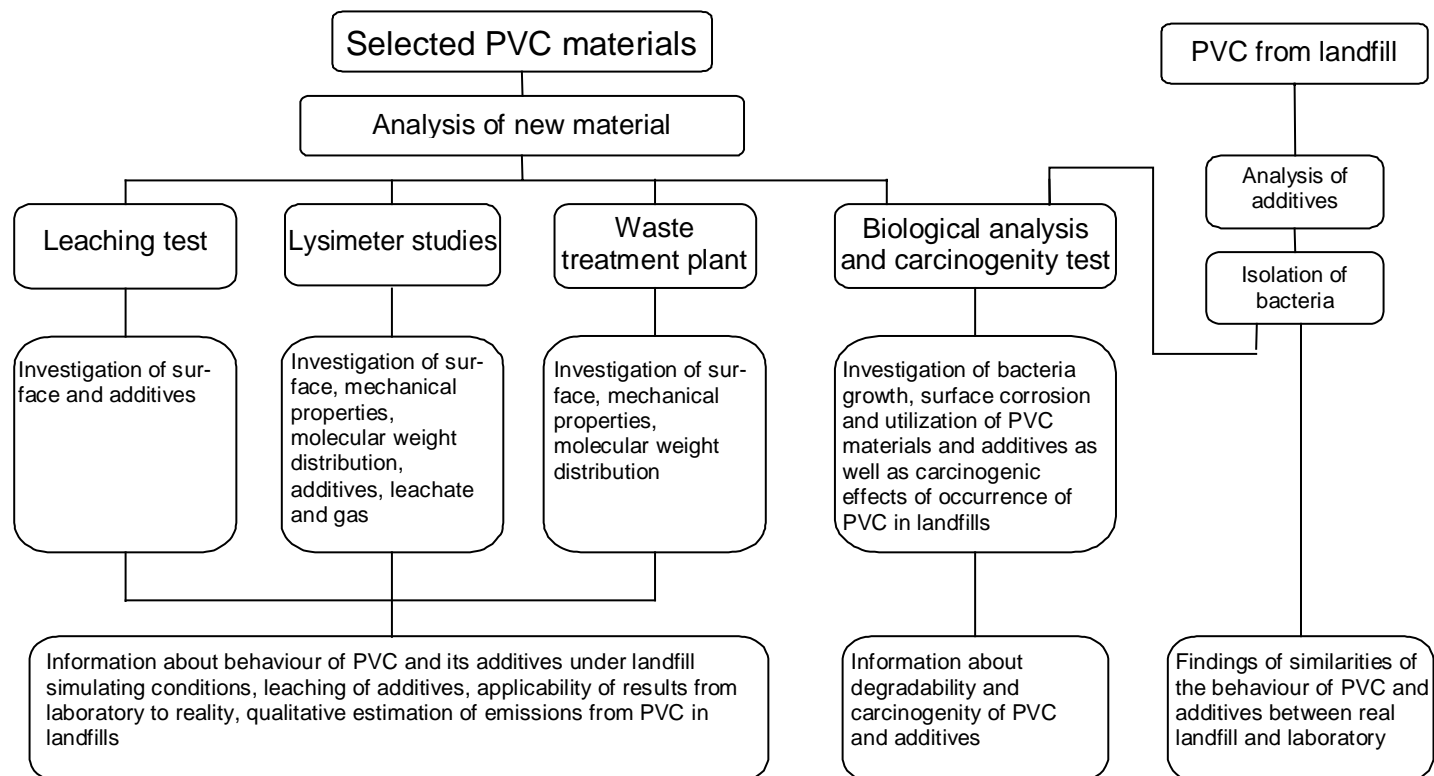
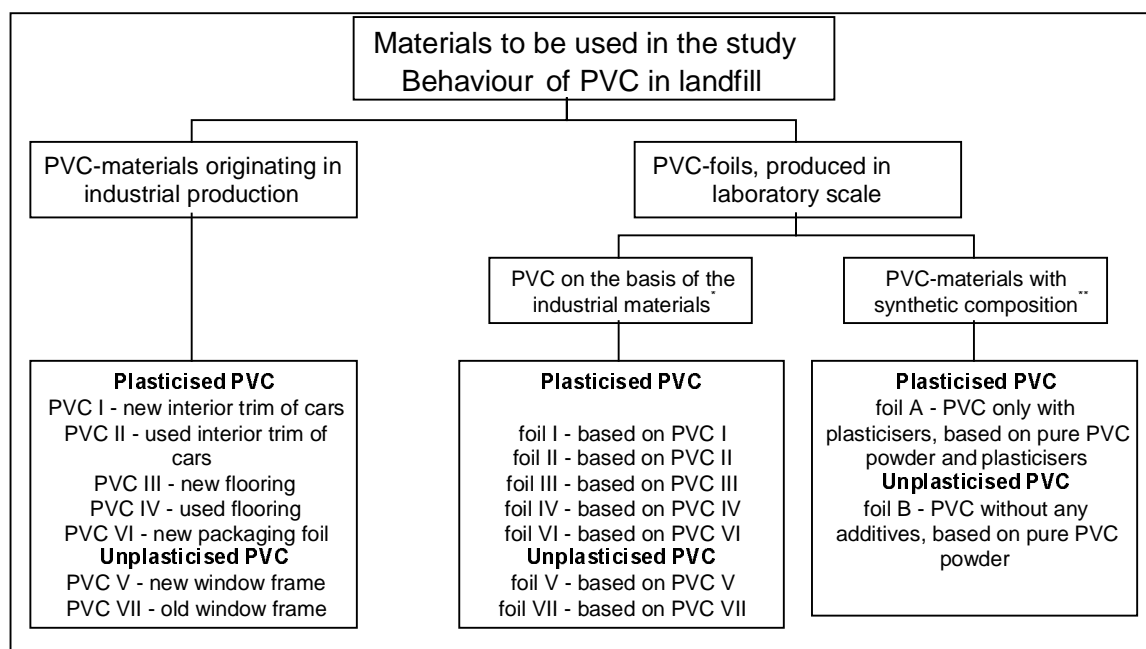


Figure 6 - 2: Analytical programme

6.3 Investigated PVC-products

- 7 PVC is used for a broad spectrum of products. For the purpose of this study the sampling of the PVC-materials to be examined should take into account:
 - a) the already known potential of toxicological and ecotoxicological effect of PVC-components
 - b) the diversity of additives
 - c) the difference between shortlife and longlife PVC-applications and their relevance in landfill
 - d) differences between the behaviour of new and used PVC-products in landfill
- 8 Considering a) and b), it is necessary to know the composition of the samples. Due to the information policy on the part of the PVC producers, it was not possible to analyse in detail but a broad spectrum of additives contained in the PVC-samples was discovered. Within the framework of the study it was not possible to distinguish effects of each additive or the interactions between different additives. The items c) and d) were considered in the analytical programme as short-life and long-life PVC products and new and used samples were included in the study.
- 9 In the investigations two different kinds of PVC-materials were used. For maximum comparability of the study, results relating to the behaviour of PVC in real landfill, materials were initially chosen which are produced industrially in great quantities. These materials are of crucial importance for landfilled PVC.
- 10 The second kind of PVC is produced in laboratory scale for detailed studies. An overview is given in figure 6 - 3.



* transformation of the industrial materials to standardised thin foils was carried out, the method is described in annex III

** PVC-foils were produced from pure PVC-powder and plasticiser to investigate influences of further additives which are not present in the synthetic foils but in the foils from industrial materials

Figure 6 - 3: PVC-materials investigated

6.3.1 PVC-materials originating in industrial production

- 11 The following PVC-materials from industrial production were established for use in investigations relating to behaviour of PVC in landfills:
 - Plasticised PVC-car interior trim, used and new material
 - Plasticised PVC-flooring, used and new material
 - Plasticised PVC-packaging foil
 - Window frame rigid PVC, stabilised with cadmium, used and new material
- 12 The specific PVC products selected for the purpose of this study and their compositions are described in Table 6 -1 on the following pages. Analysis of the different constituents of the samples before incubation was carried out by the companies Bärlocher, Oxeno, NORDUM and Vestolit. The content of heavy metals were analysed by two different laboratories. The variation of measured contents cannot be explained, but may result from different analytical methods. Optical and mechanical properties of the raw materials are depicted in section 6.6 where the changes of these parameters during the different examinations are discussed.

Table 6 - 1: Summary of examined PVC materials originating in industrial production

Type of PVC	Description and Analysis Results			
PVC I <ul style="list-style-type: none"> plasticised PVC film laminated with polyurethane foam - new (recently produced) material 	Description	<ul style="list-style-type: none"> the material was provided by Benecke-Kaliko AG and used in DaimlerChrysler 202 series as ceiling no information supplied about the composition 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> C7/C9/C11-phthalate ester could not be identified precisely the content of plasticiser was measured at 38,6 %^A 	Stabiliser <ul style="list-style-type: none"> significant heavy metal stabiliser was not identified the stabiliser system consisted of heavy metal free components^B 	Further Additives <ul style="list-style-type: none"> the content of other additives was measured with 30.6% traces of other unknown compounds 0.4 % of the metal Antimony identified as compounded with a flame retardant^A
PVC II <ul style="list-style-type: none"> plasticised PVC film laminated with unknown textiles, used as interior trim of cars - used material 	Description	<ul style="list-style-type: none"> the material was taken from a car Opel Corsa A-CC manufactured in 1993 applied as ceiling information about composition was not provided 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> was identified as DEHP/Dioctyladipate in a ratio of 2:1 the content of plasticiser was measured at 38,3 %^A 	Stabiliser <ul style="list-style-type: none"> the stabiliser system was identified as Barium / Zinc Barium as pure heavy metal was measured at 0.1 % Zinc was detected as trace^B 	Further Additives <ul style="list-style-type: none"> the content of other additives was measured with 24.9% traces of other unknown compounds 0.4 % of the metal Antimony identified as compounded with a flame retardant^A
PVC III <ul style="list-style-type: none"> plasticised flooring material armoured with glass fibre and laminated with polyurethane at the bottom - new material 	Description	<ul style="list-style-type: none"> the material was provided by Tarkett AB it was used in the investigations of STEGMANN and MERSIOWSKY (1999) at the University of Hamburg-Harburg^D 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> the contents including other additives was measured at 47.1%^A the type was identified as DIDP 	Stabiliser <ul style="list-style-type: none"> the stabiliser system was identified as Barium / Zinc pure Barium metal was measured at 0.14 % Zinc was detected as trace^B 	---
PVC IV <ul style="list-style-type: none"> plasticised flooring material armoured with glass fibre - used material 	Description	<ul style="list-style-type: none"> the material was taken from a recycling centre 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> the type was identified as DIDP the plasticiser content including other additives was measured at 55.9 %^C the result has to be taken carefully, because the sample was very inhomogeneous and the layers were made from different compositions 	Stabiliser <ul style="list-style-type: none"> the stabiliser system was identified as Lead the pure heavy metal lead was measured at 2.1%^B the result has to be taken carefully, because the sample was very inhomogeneous and the layers were made from different compositions 	----

Type of PVC	Description and Analysis Results			
PVC V <ul style="list-style-type: none"> cadmium-stabilised window-frame rigid PVC - new material^E 	Description	<ul style="list-style-type: none"> the material was provided by Vestolit GmbH sample of the total cadmium content was declared as 0.34 % 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> no plasticiser was found^C 	Stabiliser <ul style="list-style-type: none"> the stabiliser system was identified as Barium / Cadmium the pure heavy metal Cadmium was measured at 0.33 % Barium at 0.17 %^B 	Further Additives ---
PVC VI <ul style="list-style-type: none"> plasticised packaging foil - new material 	Description	<ul style="list-style-type: none"> the material was provided by Krüger GmbH Solingen information was not provided about the material 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> the type of plasticiser was identified as DEHP the plasticiser content including other additives was measured at 26.3%^C another result is measured at 29.5 %^A 	Stabiliser <ul style="list-style-type: none"> the stabiliser system was identified as Barium / Zinc the pure heavy metal component Barium was measured at 0.16 % and Zinc was detected as trace^B 	Further Additives ---
PVC VII^F <ul style="list-style-type: none"> cadmium-stabilised window-frame rigid PVC - used material 	Description	<ul style="list-style-type: none"> the window was produced by TROCAL in 1977 the material was stabilised with Barium / Cadmium as only stabiliser system (ratio 2:1) and announced with about 2 % at production time the total metal content was estimated to be less than 0.5 % the PVC material contained calculated on that basis less than 0.15 %^G pure cadmium in 1977 		
	Analysis Result	Plasticiser <ul style="list-style-type: none"> no plasticiser was found^C 	Stabiliser <ul style="list-style-type: none"> the stabiliser was identified as Barium / Cadmium system the pure heavy metal component Cadmium was measured at 0.35%^G Barium was measured at 0.17 %^B 	Further Additives ---

^A analysed by Vestolit GmbH company

^B analysed by Bärlocher company

^C analysed by Oxeno company

^D unfortunately a change in product composition took place since they began with their analysis. Our own analysis shows great differences in plasticisers (DIDP in spite of BBP/DEHP) and in stabilisers only Calcium / Zinc. No Antimony was detected

^E this material was produced only for purposes of this study to include a cadmium-stabilised material. Its composition is based on an old receipt for cadmium-stabilised window frames.

^F The material PVC VII was introduced to the study while the investigations were still running. Therefore the material could not be used in all examinations. The material was provided by H-Tetroplast GmbH. The old windows were taken from a district of Karlsruhe in a project of "facelifting" in 1996. The project included environmentally friendly recycling methods, among them recycling of 4300 old PVC-windows.

^G the difference in the cadmium content cannot be explained exactly but the provided information bases on an estimation of the producers, the exact composition of the material is not known

6.3.2 PVC-materials from production at University of Rostock

- 13 For detailed investigations into the behaviour of PVC materials a method had to be developed to observe effects of corrosion and attack on PVC in the short time of the study. In fact, the processes to be investigated during the study were surface processes. According to that a PVC sample with similar composition to the original PVC products and a maximum of surface to volume ratio would be the best suitable material to investigate effects. Therefore a method to get a very thin foil was developed. The original PVC products were dissolved in tetrahydrofurane and transformed to foils being 20 to 40 µm in thickness. Additionally, foils with a defined composition can be produced when necessary. The method is described in detail in annex III.
- 14 The self-produced foils are mainly made from materials PVC I – VII. For the leaching test and microbiological investigations slightly different foils were produced. Exact definition of the foils composition is to be found in the relevant sections of the report.
- 15 It is not guaranteed that the dissolution and precipitation of the material does not lead to a major change in the distribution of the various compounds throughout the membrane in comparison to the original material. However, within the available time for the study this method appeared appropriate to gain visible and measurable results. It was expected that the method could show whether effects can be expected or not and whether an attack can occur or not.

6.4 Identification and investigation of PVC from landfill

- 16 In the waste taken from the landfill of Schwäbisch-Hall, four different PVC-materials (further called PVC A, B, C and D) were found. The positive result of the Beilstein-method¹⁴ guaranteed the identification of the plastics samples as PVC. Before landfilling the waste was pre-treated biologically. The pre-treatment was carried out with the Kaminzug-method¹⁵. This method is based on aeration of the waste pit through drain pipes. A natural air stream is induced by warm air rising in the pit through pipes. It supplies the pit continuously with fresh air. The municipal waste was mixed with sludge and was dumped in 1977 at the landfill of Schwäbisch-Hall. The samples were analysed to get information about composition of long-landfilled PVC.
- 17 The contents of plasticisers and heavy metals of the materials were analysed using the methods described in annex III. Further analysis has to be considered as not meaningful because of the small amounts of samples available. On the basis of performed analysis it is to conclude that PVC-additives during staying for more than 20 years in a landfill will neither degrade completely or release completely from PVC products.

Plasticisers

- 18 Only one of the investigated materials contained plasticiser. DEHP was identified in PVC D. The content of the plasticiser was calculated as difference to the content of PVC-polymer by using X-ray-fluorescence-analysis. The value was quantified to 31.9 % by weight but partly included stabilisers, fillers and other additives. Only the heavy metals were known by weight, at 2.35 %. The plasticiser content was within the lower bounds of the new materials if there were no high share of fillers in PVC D. No plasticiser was analysed in the materials PVC A-C. Therefore, they seem to be unplasticised PVC. New materials originating from the same production as the PVC-

¹⁴ for a description of the method see annex III

¹⁵ this kind of pre-treatment can be seen as a common example for waste management in Germany

materials from the landfill were not available. By this reason no comparison is possible and nothing about degradation can be concluded.

Stabilisers

- 19 The stabilisers are measured by analysing the heavy metals. Table 6 - 2 shows the content of heavy metals in PVC A-D.

Table 6 - 2: content of heavy metals in PVC A-D taken from a landfill

	Sn	Al	Ba	Ca	Cd	Mg	Pb	Zn	type of stabiliser
	% weight	% weight	% weight	% weight	% weight	% weight	% weight	% weight	
PVC A	2.0	-	-	trace	-	-	-	-	Sn
PVC B	2.0	trace	-	trace	-	-	-	-	Sn
PVC C	1.7	trace	trace	0.13	-	trace	-	trace	Sn
PVC D	trace	trace	0.16	1.6	0.07	trace	0.52	trace	Ba/Zn ¹

¹ The laboratory announced that lead and cadmium in this product can be attributed to lead containing gliders and cadmium containing pigments . Normally this kind of product was stabilised with Ba/Zn

- 20 In this investigation, a comparison to new materials is not available. It can be concluded that in 20 years of landfilling with preceding biological pre-treatment, stabilisers and plasticisers are not completely leached.

6.5 Investigation of the behaviour of PVC in a biological waste treatment plant in technical scale

- 21 Due to time constraints resulting from the very short time allocated for the study, PVC I - VI were stored in organic municipal waste in a biological waste treatment plant during the phase of intense aerobic decomposition as described in annex III. This results in an acceleration of the landfill degradation processes with the same final result as achieved in a landfill [SPILLMANN 1999]. However, this method should not only be considered as a simulation method. Such waste treatment methods operating at high temperatures under aerobic conditions at landfill sites have to be taken into account with view of future development of landfilling and waste pre-treatment.
- 22 During the waste treatment only temperatures in the waste are measured. Figure 6 - 4 depicts the conditions the PVC samples were exposed to.

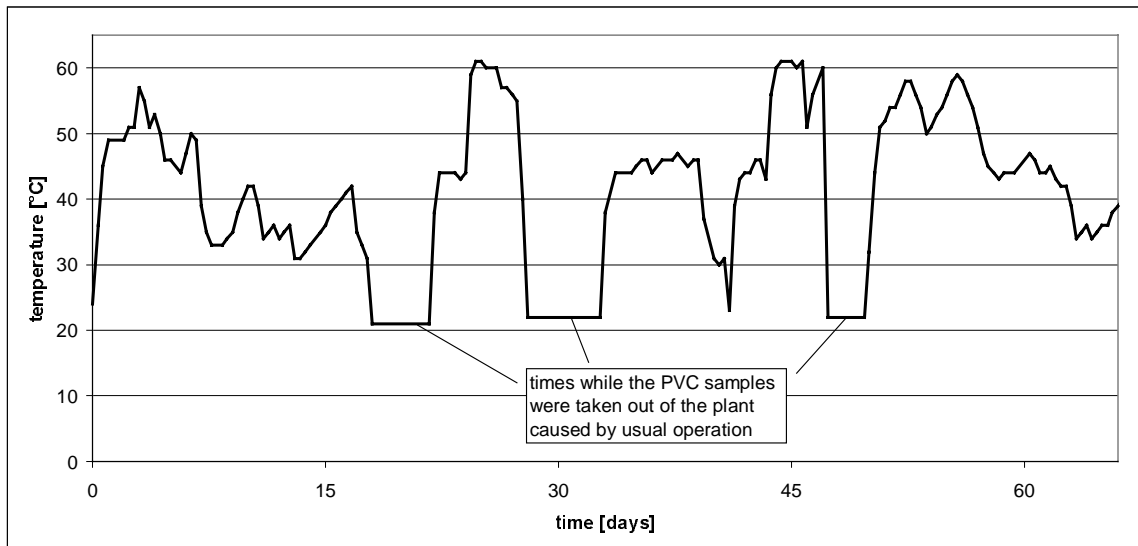


Figure 6 - 4: Development of temperature during exposition of PVC samples in a waste treatment plant

- 23 Due to operation control of the plant the heat production which causes high temperature during aerobic degradation processes was restricted. Therefore the temperatures were generally lower than in lysimeter investigations. The intensive degradation phase in the waste treatment plant usually takes about 12 days dependent on the amount of waste to be treated. This phase is carried out in containers which will be emptied after that time. Therefore the PVC samples could not be stored in the waste continuously. The intervals of temperature of about 20°C in figure 6 - 4 show the times the PVC was stored while waiting for the next run of waste treatment.
- 24 The PVC-materials changed during the incubation in the biological waste treatment plant. Both, optically and mechanically they showed differences to the raw materials. Analysis of the materials was carried out similarly to investigations during the lysimeter tests. Changes in materials were examined by electron scanning microscopy, tensibility tests, analysis of molecular weight distribution and analysis of the contents of additives. Detailed description of the behaviour of the material samples investigated in the biological waste treatment plant follows in section 6.6.
- 25 Investigations on the behaviour of PVC products in the biological waste treatment plant showed clearly recognisable effects on the PVC. An attack on the surface of the materials is confirmed by electron scanning microscopy. Chemical analysis indicated a reduction of plasticiser contents. The mechanical behaviour of the materials changed according to tensibility tests. Investigated effects on PVC under conditions of the biological waste treatment plant are comparable to effects caused by treatment in the aerobic lysimeter but were much lower. That is caused by duration of the investigations and the lower temperatures reached in the plant. Therefore, it is assumed that PVC will be affected in biological waste treatment plants at the same level as found under lysimeter conditions but the time until effects become observable is dependent on the prevailing parameters, in particular the temperature.

6.6 Investigation of the behaviour of PVC in lysimeter studies

26 The lysimeter studies were carried out to examine the conditions considered as most important for the attack on PVC products. The investigated conditions were outlined as follows:

- intensive aerobic degradation, beginning at 70 – 80°C¹⁶ with a reduction of temperature according to microbiological activity within the study period to standard landfill conditions
- alternate anaerobic / aerobic degradation, temperature and final phase similar to aerobic degradation
- thermophilic anaerobic degradation, at a steady temperature of 60°C which would occur in large landfills.

27 The analytical programme for lysimeter studies was as illustrated in figure 6 - 5 Figure 6 - 5.

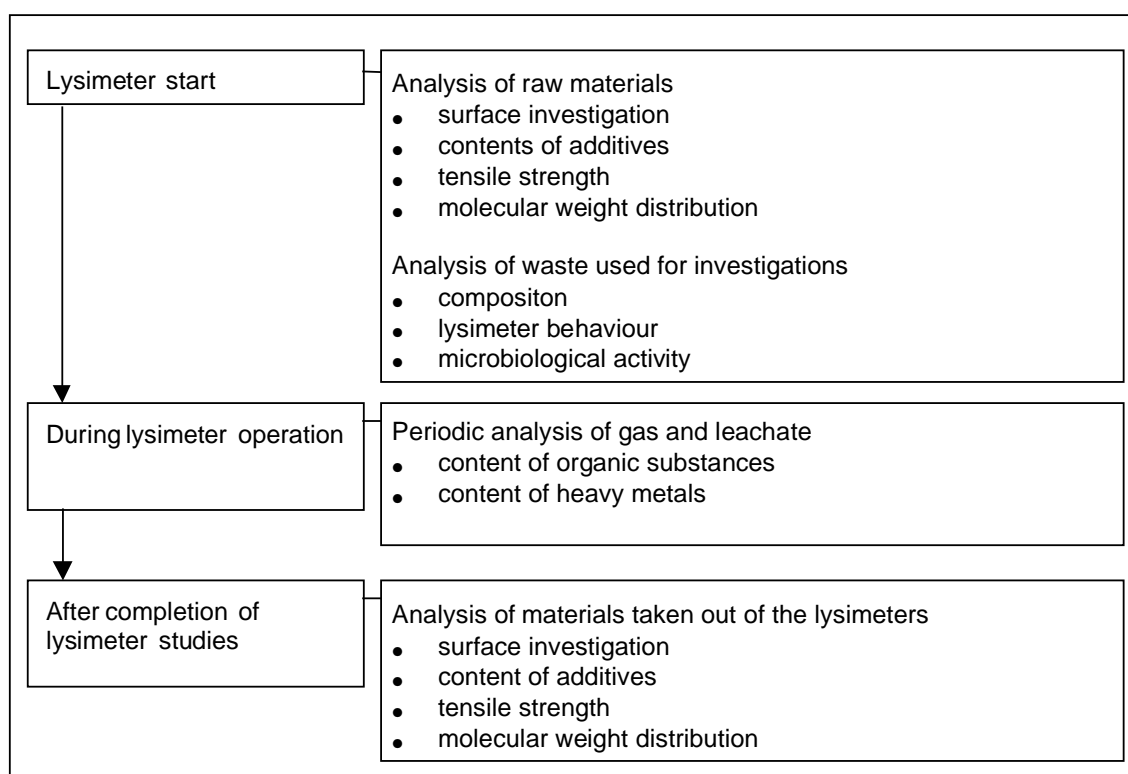


Figure 6 - 5: Analytical programme for lysimeter studies

¹⁶ these temperatures occur during intensive aerobic waste treatment under optimised conditions

6.6.1 Characterisation of the degradation processes under simulated landfill conditions

- 28 The degradation processes of biological utilisable waste are characterised through changes of temperature due to microbial activity expressed in carbon dioxide production, mass balance during the examination and pH in the leachate.
- 29 The aerobic and anaerobic lysimeters were controlled by the methods described in annex III. In this way the accurate simulation of heat balance was guaranteed. Under anaerobic conditions the temperature was fixed at 60°C which is likely to occur in landfills. The degradation parameters are compared to distinguish between the aggressiveness of the investigated lysimeter conditions.
- 30 The degradation of organic matter to carbon dioxide leads to a reduction of material from the lysimeters. Table 6 - 3 summarises the determination of loss of material measured as a reduction of dry weight. Results show the reduction of the pure waste. Added PVC is not included in calculations.

Table 6 - 3: Reduction of material in lysimeters due to degradation processes, calculated as reduction of dry weight; PVC is not included in the calculations

lysimeter	lysimeter running time [days]	reduction of material in lysimeters [% of dry waste inserted in the lysimeter]
1 (aerobic without PVC)	124	25
2 (aerobic with PVC)	124	22
3 (aerobic-anaerobic without PVC)	105	28
4 (aerobic-anaerobic with PVC)	105	27
5 (anaerobic without PVC)	118	16
6 (anaerobic with PVC)	118	14

- 31 The results of the analysis show a slight difference in the degradation rate depending on the share of PVC in the lysimeters. A clear difference could be recognised according to the different lysimeter conditions. Degradation processes could be disturbed by the presence of PVC in high concentrations. Changes in the waste structure caused by the PVC sample pieces have occurred and an influence on degradation processes caused by that is probable. However, the differences in material reduction indicate that the PVC and/or its additives influenced the degradation process in the lysimeters negatively. This result cannot be applied to a landfill because of the much smaller share of PVC in the waste in the landfill. The share of PVC in the lysimeters was about 8%.
- 32 Further the aggressiveness of the lysimeter conditions to the waste in the lysimeters has to be taken into consideration. As shown in table 6 - 3 the lowest degradation effect is visible under anaerobic conditions. The aerobic-anaerobic conditions are most aggressive. Comparison between the lysimeter conditions results in the fact that under alternating aerobic-anaerobic conditions the waste degradation is the highest in the lysimeter studies.
- 33 In aerobic and aerobic-anaerobic lysimeters a constant gas flow through the waste was caused by aeration and the carbon dioxide concentrations were measured and evaluated. Gas flow from anaerobic lysimeters can not be assumed as constant and no analysis was undertaken. The courses of temperatures as well as carbon dioxide production in the aerobic and anaerobic lysimeters are to be found in annex IV. Figure 6 - 6 demonstrates the effects.

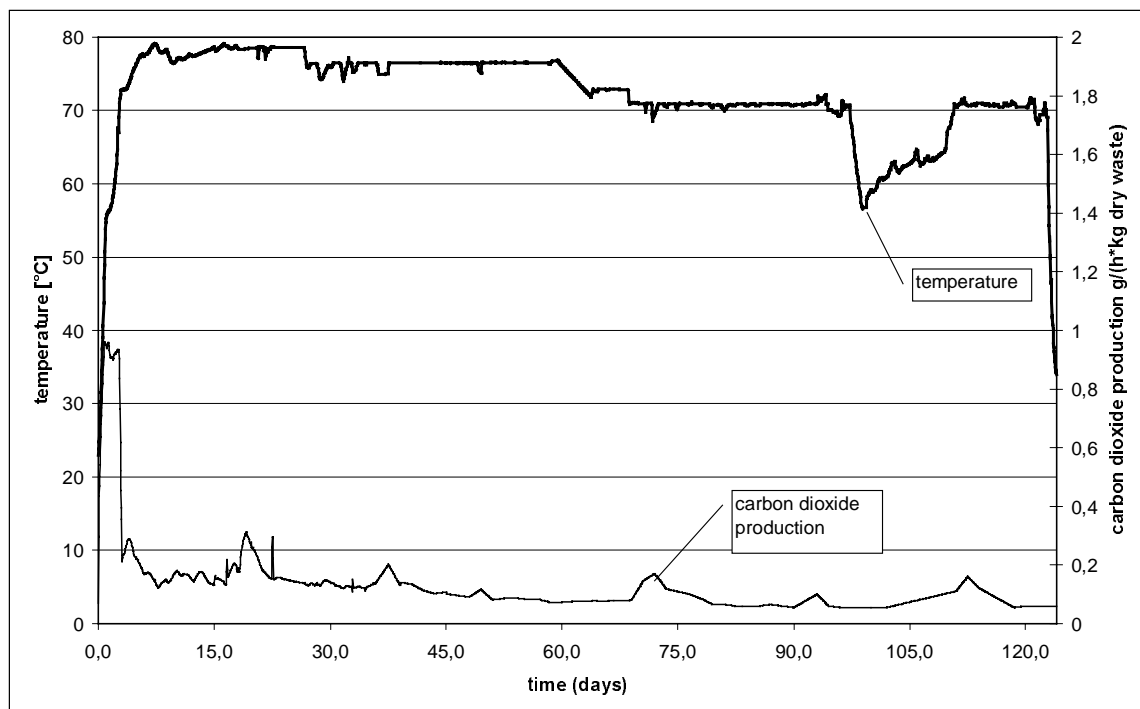


Figure 6 - 6: Course of temperature and carbon dioxide production in lysimeter 1 (aerobic, without added PVC)

- 34 No specific differences were found between the behaviour of lysimeters containing PVC and lysimeters without PVC. Throughout the study, almost stable conditions were reached in the lysimeters. Variations in the courses can be attributed to some malfunctions of the equipment. Temperatures of up to 79°C were reached in both aerobic lysimeters. The inclining temperatures are attributed to decreasing microbial activity confirmed by the course of carbon dioxide production. Degradation processes in both aerobic lysimeters with and without PVC appear to be similar. Under aerobic-anaerobic conditions temperatures reached (up to a maximum of 70°C) are lower than under aerobic conditions. The varying course of temperature and carbon dioxide production depends on alternating aeration. Under anaerobic conditions microbial activity is lower and the temperature decreases. The carbon dioxide produced was not displaced in the lysimeter and its share in the lysimeters atmosphere increased. When aeration starts again the carbon dioxide content running through the measuring device rises heavily for a short interval. During the aerobic period, the temperature rises again and carbon dioxide production reaches a stable level. The behaviour of both aerobic-anaerobic lysimeters with and without PVC is considered as similar. In anaerobic lysimeters, methane production started after about 12 days and reached a steady level. Methane concentration was detected as more than 30% during the lysimeter studies.
- 35 The pH of the six lysimeters during their operation is depicted in figure 6 - 7. The values and their course are considered as normal. Similar behaviour is concluded for corresponding lysimeters.

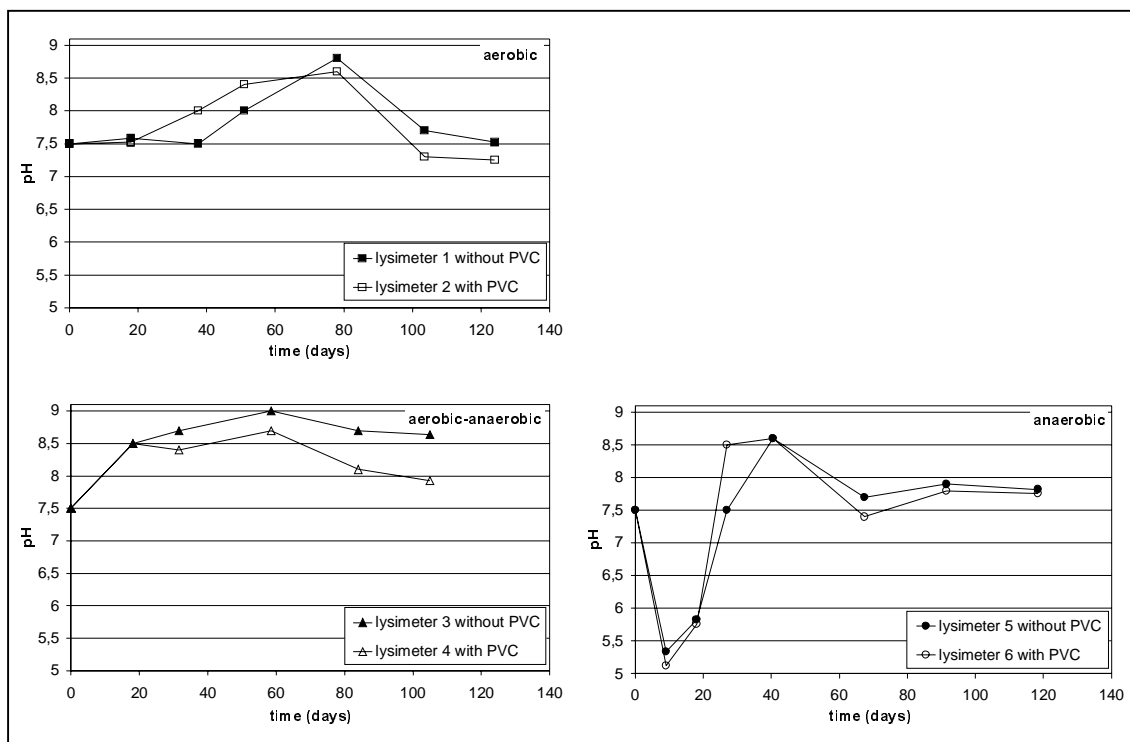


Figure 6 - 7: Course of pH in leachate from the lysimeters running under different conditions

- 36 Due to the low precision of the determination method (indicator paper was used) no difference between lysimeters with and without PVC was found. Differences in the aggressiveness of the investigated conditions cannot be determined.
- 37 Based on the results of analysis degradation and reduction of waste in lysimeters aerobic-anaerobic conditions have to be considered as the most aggressive to the waste matrix followed by aerobic conditions. Anaerobic conditions show by far the lowest degradation. The physical influence on PVC has to be considered as the most aggressive under aerobic conditions due to the higher temperatures reached during the lysimeter studies.

6.6.2 Behaviour of the PVC-materials under simulated landfill conditions

Optically visible changes to the PVC-materials during landfill simulation

- 38 The PVC-material changes were clearly visible during the lysimeter study. Both optically and mechanically they showed enormous differences to the raw materials. Changes could be observed on every sample from the three lysimeters. However there were certain differences in the extent of the change according to the lysimeter. The samples which were in the aerobic lysimeter showed the strongest change. The following photograph illustrates this using PVC VI as an example. Photographs of the other six materials can be found in annex IV.



Figure 6 - 8: Changes in PVC-material VI, the packaging foil, caused by the different kinds of treatment; from left to right: 1. raw material, 2. PVC VI from lysimeter 2 (aerobic), 3. PVC VI from lysimeter 4 (aerobic-anaerobic), 4. PVC VI from lysimeter 6 (anaerobic), 5. PVC VI from biological waste treatment plant

- 39 Generally, a strong deformation and brittleness of the plasticised PVC occurred. As was concluded, the brittleness occurred due to the reduction in suppleness. Furthermore, clear changes in colour were noticed, too. The features did not appear consistent on all of the materials. Inhomogeneities in colouring and hardness were observed within the samples. These inhomogeneities resulted from the storage of the samples. According to the surrounding material seeping water flows might have been different or materials might have stuck together. A table containing a characterisation of the materials taken out of the lysimeters is to be found in annex IV.

Influence of simulated landfill conditions on the surface of the materials

- 40 Any attack on a material starts at its surface. Because of this, the commencement of changes in the PVC-material was investigated by examining its surfaces by microscopy. The scanning electron microscope PHILIPS XL 30 ESEM was used for examinations. To see any differences in the appearance of the PVC-materials taken from the lysimeters and the biological waste treatment plant, the raw materials were first examined under the scanning electron microscope. After completion of the lysimeter studies, the materials from the lysimeters were investigated using the same methods.
- 41 For scanning electron microscopical examinations only those samples which showed major differences to the raw material were selected. Therefore the materials used to examine the differences between all the different lysimeters were PVC I, PVC II, PVC IV and PVC VI. The samples PVC III and PVC V were analysed only from lysimeter 2 and 6. PVC VII was not investigated because of the delay in including it in the study.
- 42 The following investigated differences will be explained using the examples of some microscopic pictures. A characterisation of the materials appearance in each lysimeter and other photographs can be found in annex IV. The following figures illustrate the material's surface.
- 43 Figure 6 – 9 shows the raw material PVC VI and Figure 6 - 9 depicts PVC VI being treated in lysimeter 2 under aerobic thermophilic conditions.

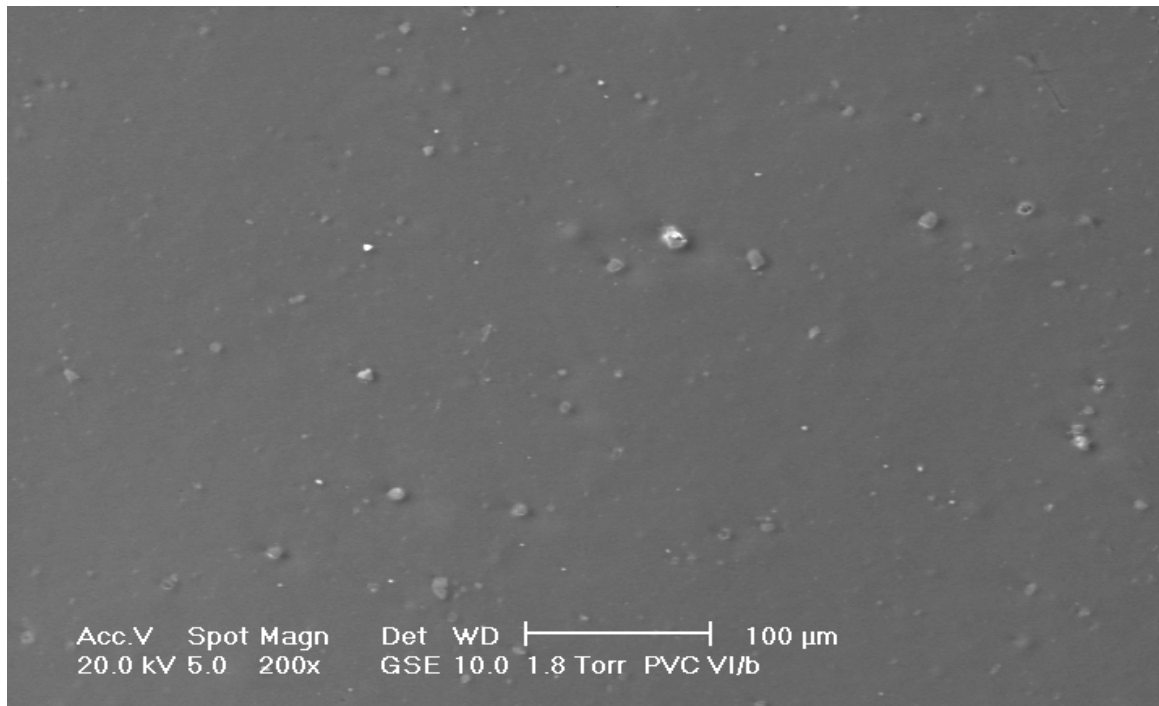


Figure 6 - 9: Photograph from scanning electron microscopy of the raw material PVC VI; the light spots are dust and the material shows a very homogenous surface

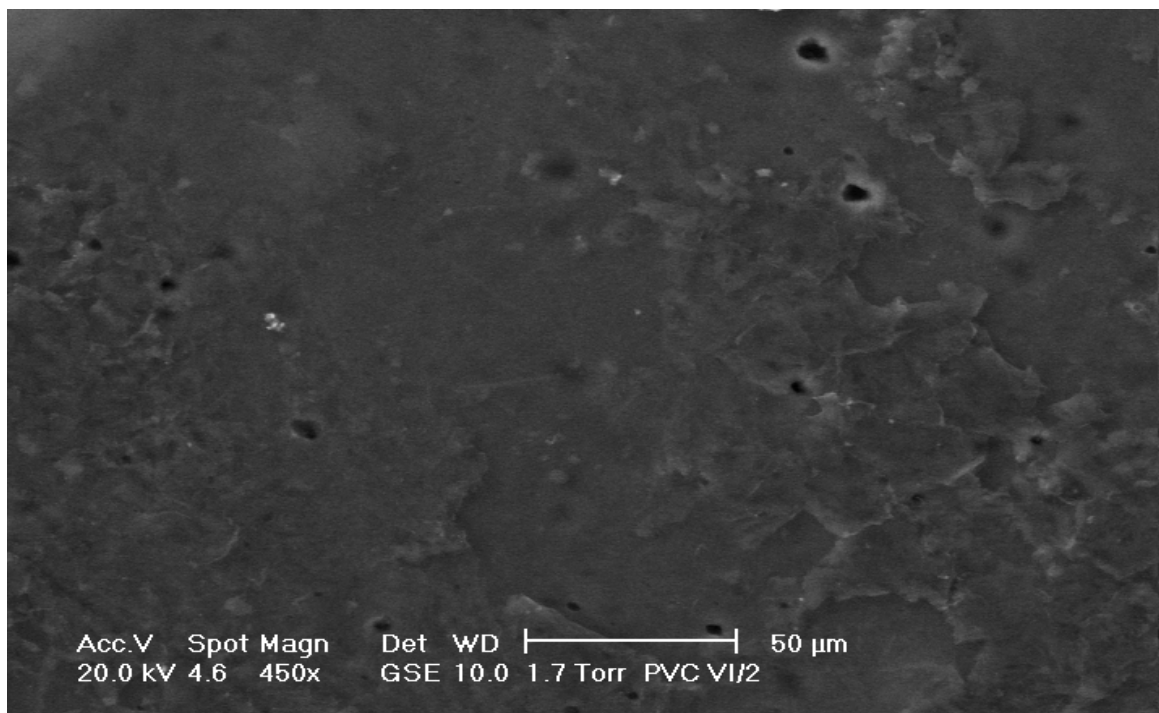


Figure 6 - 10: Photograph from scanning electron microscopy of PVC VI, taken from the lysimeter 2 (aerobic decomposition); the dark spots are craters of erosion or burst blisters caused by migration of additives, very probable plasticisers and the areas resembling scales lying on the surface are microbial populations which cling tightly to the material.

- 44 It can be concluded from the microscopic investigations that the aerobic thermophilic conditions in lysimeter 2 have the most aggressive character on PVC. All plasticised materials show clear signs of erosion. The photographs are to be found in annex IV. Compared to that, lysimeter 4 (aerobic-

anaerobic conditions) shows no attack on the materials and lysimeter 6 (anaerobic conditions) as well as the biological treatment plant shows only slight signs of attack. The erosion processes were running at a much slower speed than under aerobic conditions. No attack was found on the unplasticised material. Either there was no visible surface reaction under the investigated conditions the incubation was too short for erosion processes on unplasticised PVC.

- 45 The examined corrosion effects show clearly an attack on the plasticised material. The apparent craters and holes show a loss of material from the surfaces. That loss is probably transported with the leachate or the gas through the waste material but due to its very low quantity it is not necessarily detectable. There are three possibilities for its remaining. It can be degraded partly or completely and causes emissions to leachate or gas, it can be moved directly as emission to leachate or gas, or it can be retained by the waste matrix in the lysimeter. The identification of specific degradation products was not possible within the scope of the study.

Influence of simulated landfill conditions on mechanical properties

- 46 The changes of the mechanical characteristics of the PVC materials during the lysimeter studies were realised by the tensibility test and the behaviour of the material during this test. To guarantee high comparability, the mechanical features of the PVC materials, which were incubated into the composting plant Parkentin, were considered here, too. The parameters maximum tensile strength¹⁷ and tensile strain limit¹⁸ show changes according to the different conditions within the lysimeters. Changes in the composition of the materials are indicated.
- 47 Plastics including PVC are regarded as a considerable part of the „friction mooring“ of a landfill being responsible for the steadiness of the landfill body. The PVC quantity in relation to the total synthetic material content is rather small in comparison to the mass of the plastic materials polyethylene and polystyrene, its share in the armouring of the landfill however, is noticeable. The decrease in tensile strength of the PVC products diminishes the tensile-strength relevant friction-part and causes decreasing sturdiness. Decreased sturdiness can cause e.g. sliding downhill of parts of elevated landfills or landfills situated on a slope as has been reported from some landfill sites. The contribution of PVC degradation to such effects cannot be estimated but has to be considered in future design policy for landfill bodies.
- 48 The best visualisation of changes in the different PVC-materials allows a comparison of the course of tension and dependent tensile strain under the tensibility test. In addition the behaviour of plasticised PVC can be differentiated very well from unplasticised PVC. A very good example of unplasticised PVC's behaviour is shown by the new window frame material. The courses of the raw material and the material after different kinds of treatment are shown in the following figures.

¹⁷ The tensile strength describes the ability of the material to take up tensile force. The maximum tensile strength is the force value which will be maximum tolerated by the material before it breaks.

¹⁸ The limit of tensile strain describes the maximum stretch during the tensibility test in percent of the length at the start of the test.

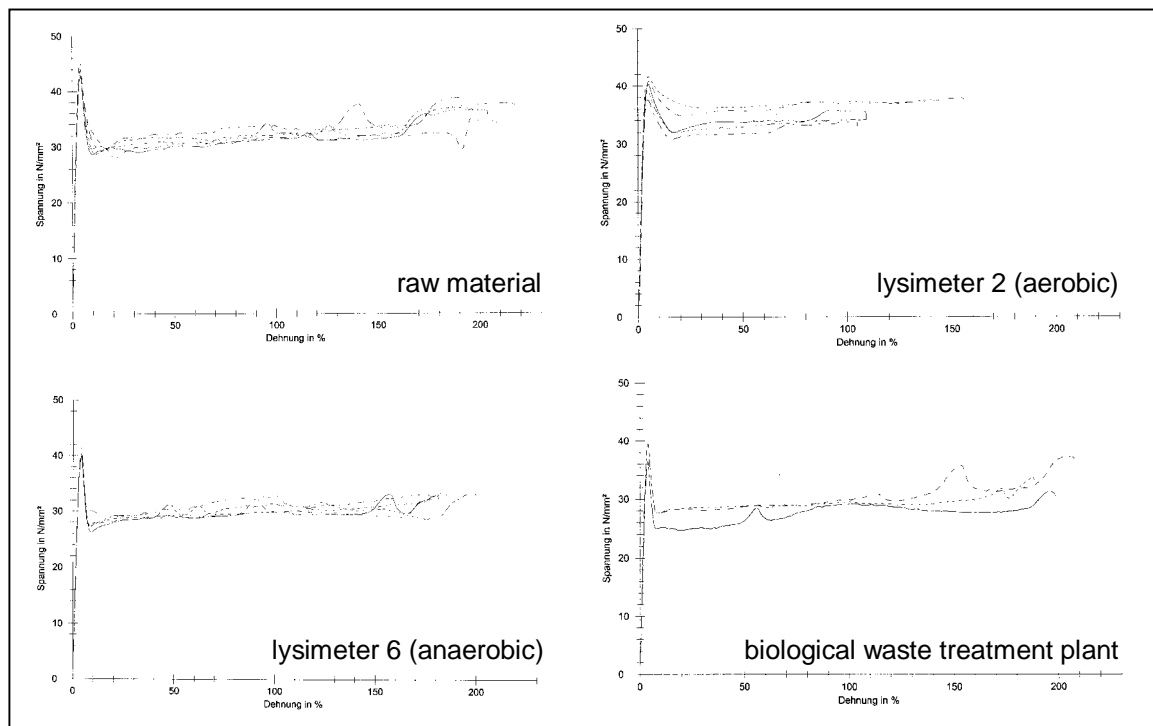


Figure 6 - 11: Courses¹⁹ of the tensibility test of the unplastified new window frame

- 49 Typical for unplasticised PVC is that the tensile strength shows a steep increase followed by a rapid decrease and a stable value until the test specimen breaks during the tensibility test. That can be seen in the course of the raw material. Properties of the new window frame changed due to storage in the lysimeters and the biological waste treatment plant. The maximum tensile strength (maximum height of the courses) as well as the tensile strain limit (maximum length of the courses to the right) decreased. The decline of the tensile strength is visible after all kinds of treatment, the decrease of the tensile strain limit is most obvious in the tensibility test of the material taken from lysimeter 2, the aerobic lysimeter. Changes in the PVC polymer could have occurred at the same time but this is not necessarily the case. Another reason for the decreased limit of tensile strain could be damage or corrosion on the materials surface which causes the PVC to break earlier. The attack of the aerobic treatment on the materials in lysimeter 2 was the strongest. Under the other conditions investigated, changes in the PVC material had occurred but the effects were a lot less clear.
- 50 Plasticised PVC seems to be much more susceptible to the attack which occurred in the lysimeters and the biological waste treatment plant. The following figures show the courses of the tensibility tests of the plasticised packaging foil, first the raw material and then the materials from the different treatments.

¹⁹ The different courses in each diagram represent the tensibility tests of the single tension test specimen, several tests have to be performed to get representative results. The variations are normal. Variations were low during measurement of the raw materials but increased with the treatment. This was the result of the different attack on parts of the materials caused by uneven leachate flow and uneven waste distribution around the material.; „Spannung“ is tensile strength and „Dehnung“ is strain

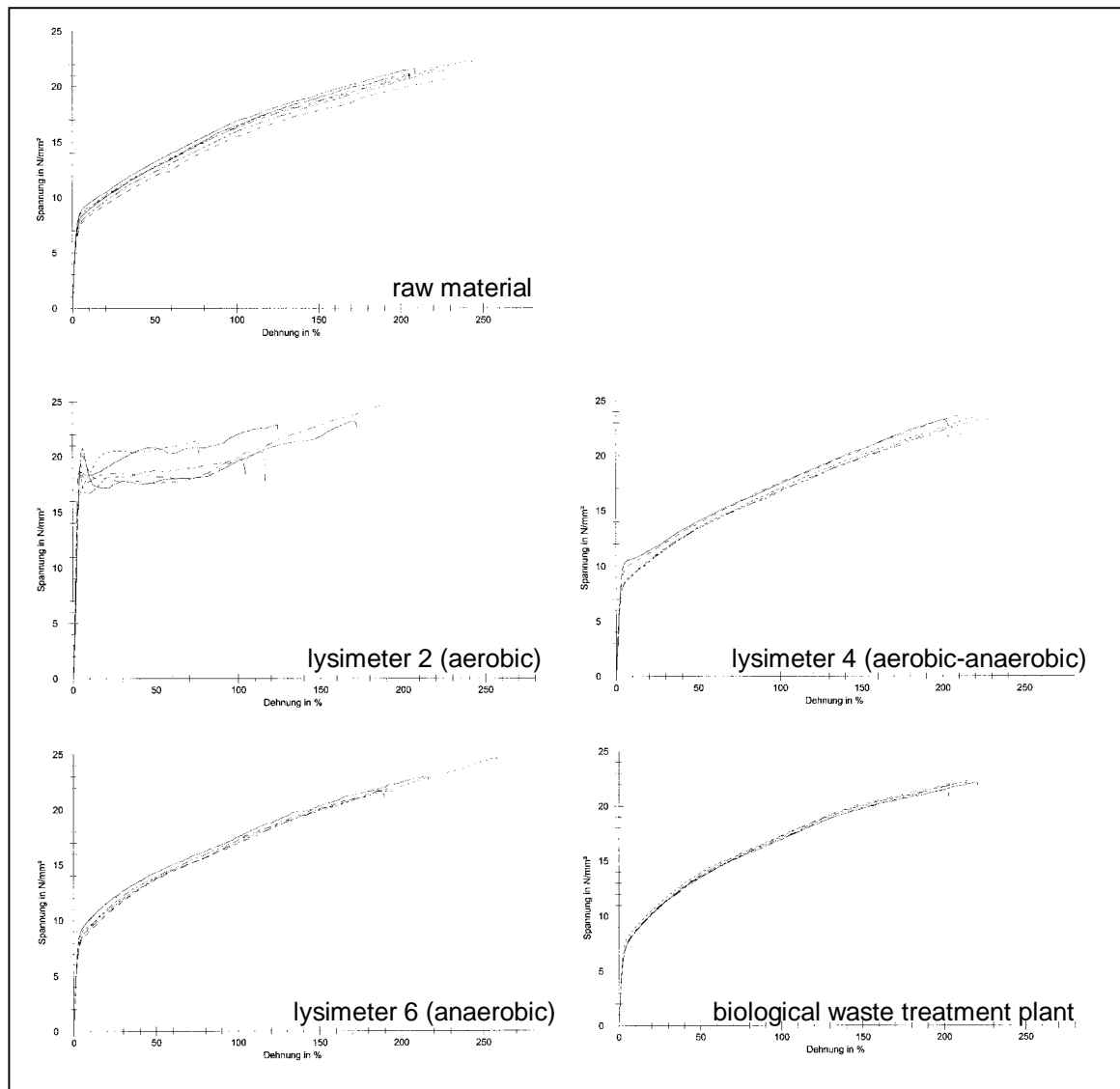


Figure 6 - 12: Courses²⁰ of the tensibility test of the plasticised new packaging foil

- 51 The behaviour of plasticised PVC in the tensibility test is very different from unplasticised PVC. It is typical that the tensile strength shows a first short but steep increase followed by a low further increase which will get lower until the test specimen breaks. That can be seen in the course of the raw material. Caused by the storage of the plasticised packaging foil in the lysimeters and the biological waste treatment plant properties changed. The tensile strain limit (maximum length of the courses to the right) decreased and the behaviour of the material during the test changed. The decrease of the tensile strain limit is most obvious in the tensibility test of the material taken from lysimeter 2, the aerobic lysimeter. The best indicator for the attack on the material is the change in behaviour during the test. In lysimeters 2 and 4 the first increase of tensile strength becomes steeper than in the raw material. This behaviour is not clearly visible in the materials from the biological waste treatment plant and lysimeter 6. In particular the material incubated in lysimeter 2

²⁰ The different courses in each diagram represent the tensibility tests of the single tension test specimen, several tests have to be performed to get representative results. The variations are usual. Variations were low during measurement of the raw materials but increased with the treatment. This was the result of the different attack on parts of the materials caused by uneven leachate flow and uneven waste distribution around the material; „Spannung“ is tensile strength and „Dehnung“ is strain

(aerobic) shows the strongest change and shows that under these condition the attack on plasticised PVC is the highest. Under the other conditions investigated, changes in the PVC had occurred but the effects were a lot less clear. During the storage of the plasticised packaging foil in the aerobic lysimeter, properties changed so that the tensibility test definitely shows an unplasticised material. The typical increase in tensile strength during the initial stretching and the further stretching without a clear rise in tension are typical for unplasticised PVC as shown above. A notable loss of plasticiser is the only cause which can be responsible for this behaviour. Changes in the PVC polymer could have occurred at the same time but this is not necessarily the case. Another reason for the decreased limit of tensile strain could be damage or corrosion on the materials surface which causes the PVC to break earlier.

- 52 All the other materials show a plain decrease of the tensile strain limit during any kind of treatment whether the material was used or not. Therefore, the conclusions drawn from the behaviour of the plasticised packaging foil have to be seen as valid for the behaviour of all plasticised PVC in landfills. The courses of the other investigated materials are to be found in annex IV.

Influence of simulated landfill conditions to molecular weight distribution

- 53 One of the favourite methods of determining the polymer degradation is the analysis of the molecular weight distribution (Hjertberg 1995). Each polymer shows a specific distribution of the molecular weight. This is directly linked to the polymers chain length. Every shortening of the chain length indicates an attack on the polymer. The weight of the polymer molecules depends directly on the polymer molecules chain length. In case of chain shortening the molecular weight of the sample decreases and its distribution spreads. Analysis was carried out with the samples PVC V and PVC VI, one rigid and one plasticised PVC. The rigid PVC shows no significant changes in the polymer molecules. The variation in figure 6 - 13 can be attributed to normal tolerance of the determination method.

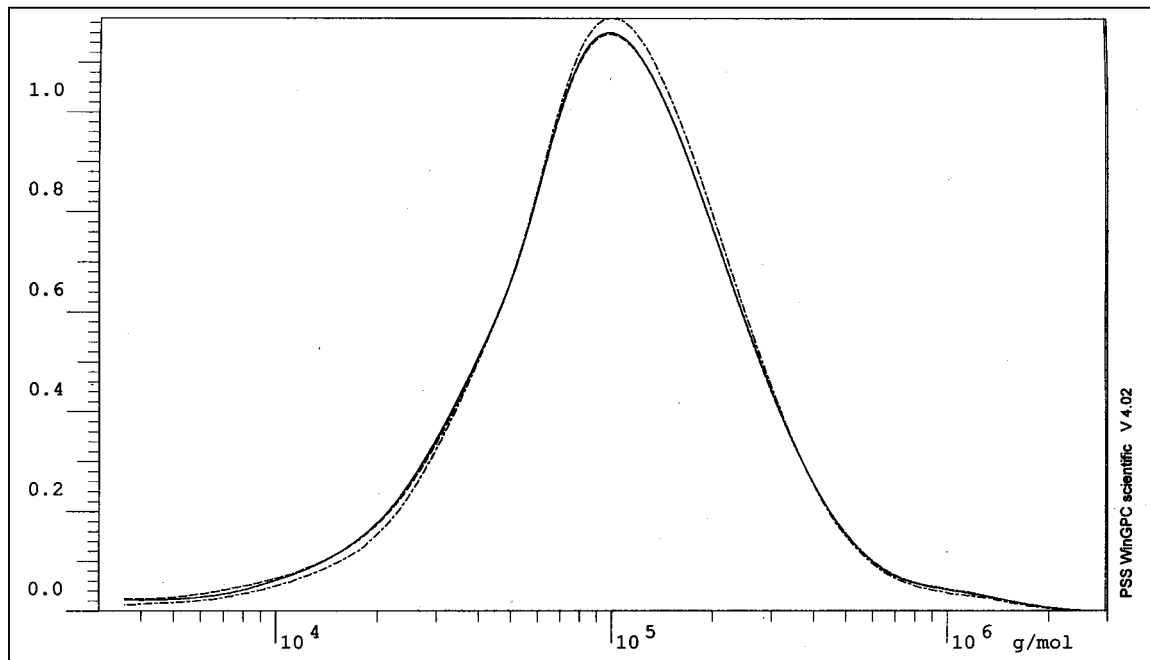


Figure 6 - 13: Molecular weight distribution of PVC V before and after exposition to different kinds of landfill simulation

54 More interesting seems the analysis of PVC VI depicted in figure 6 - 14.

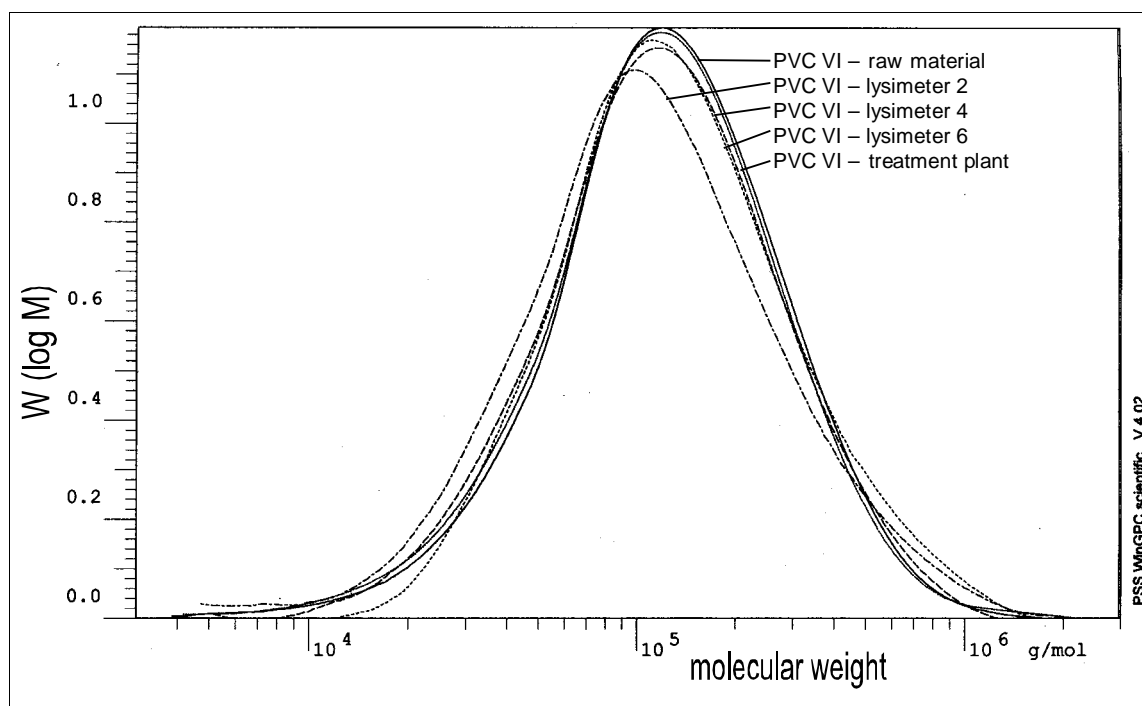


Figure 6 - 14: Molecular weight distribution of PVC VI before and after exposition to different kinds of landfill simulation

- 55 The flexible transparent packaging foil shows clear signs of attack on the PVC polymer. The decreased height and the increased spread of the molecular weight distribution indicates clear degradation of the PVC polymer. Additionally, an slight incline to the left is determined at PVC VI from the lysimeter 2 with aerobic thermophilic treatment. This indicates a decreased molecular weight indicating a shortening of the polymer chains. Therefore an attack on the polymer has taken place in that lysimeter.
- 56 The material from the other lysimeters 4 and 6 show very slight changes in the molecular weight distribution. The lowest deviation in the range of the normal tolerance of the determination method shows the material which was inserted in the biological decomposition plant in Parkentin. However these deviations are in the range of failure due to the measuring method described in annex III and will not be interpreted. So the attack on the PVC-polymer is highest under aerobic thermophilic conditions. Anaerobic as well as alternating anaerobic-aerobic conditions show less aggressiveness to PVC. The indications found during this analysis are confirmed by the tensibility tests as described above.
- 57 The differences between the two materials may be a result of varying composition and thickness. Every attack on the PVC is a surface reaction. The higher thickness of PVC V leads to a much thicker layer in the material before changes in the PVC polymer occur. Therefore, a longer treatment would be necessary to identify if an attack occurs or not.
- 58 PVC V is made for a application with a very long life time (window frame). PVC VI is, on the other hand, a material designated for short term use. These facts cause differences in stabilisation of the materials. PVC V will be stabilised much more than PVC VI. This stabilisation acts against the attack on the PVC material. Additionally, the contents of plasticiser in the packaging foil could

raise the susceptibility of PVC to the attack. Therefore PVC V shows no detectable attack under the same conditions and degradation times. However, it is not certain which effect would have the highest influence on the intensity of the polymer's degradation.

Influence of simulated landfill conditions on chemical properties

PLASTICISER

- 59 Any loss of plasticiser leads to emissions as either leachate or gas. To identify release of phthalates the plasticiser content was investigated before and after storing the PVC-materials in the lysimeters. The investigation method is extraction with acidic acid ethyl ether and gas chromatographical analysis (see annex III) The investigated materials were stored all together for nearly the same time in the lysimeters. Therefore the results of the analysis of the materials taken from the lysimeters are comparable among themselves. The analysed concentrations are not absolute certain caused by a margin of error of 30% of this method.²¹
- 60 The materials used to examine the differences between all the different lysimeters were PVC II, PVC III, PVC IV and PVC VI. PVC I was not investigated because of its unidentifiable plasticiser. The results are depicted in figure 6 – 15 and figure 6 - 16.

²¹ The 30% margin of error of the results from analysis of the phthalate content of the PVC-samples was estimated taking into account the following sources of error:

1. precession (in thickness) of the production of the self-made PVC-foils and the industrial produced materials
2. precession (in measures) of the samples which were cut out of the foils and materials
3. precession of the amounts of solvents and the sample which was injected into the gas chromatograph

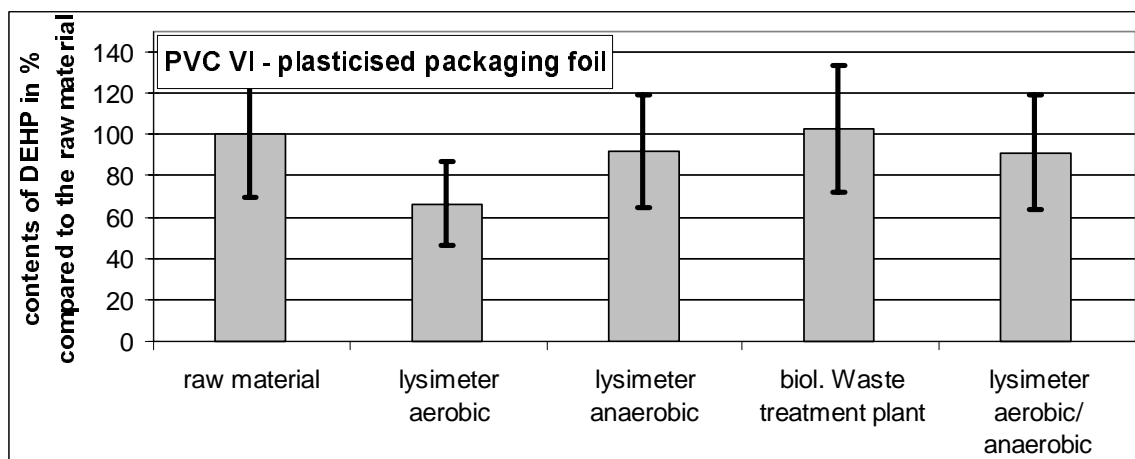
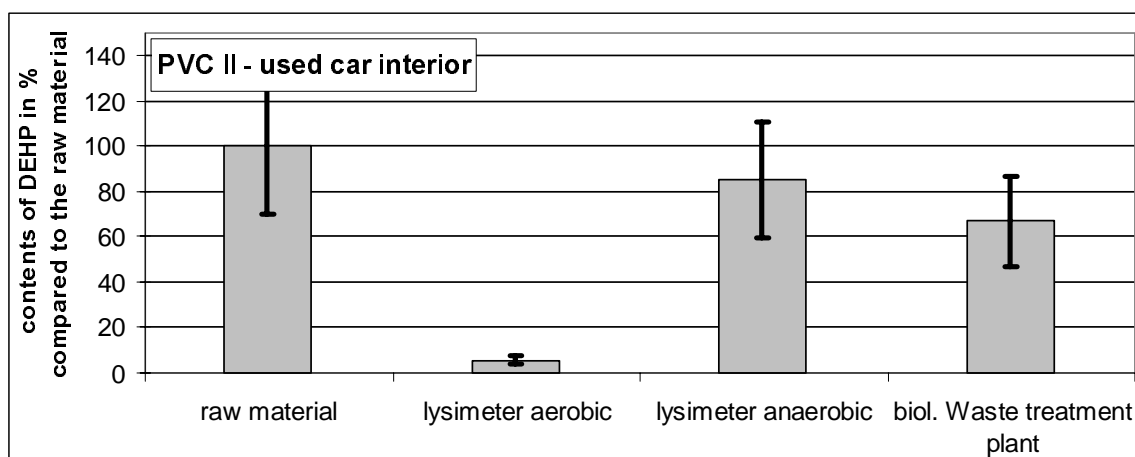


Figure 6 - 15: Examined values of DEHP content in the PVC-materials used car interior and plasticised packaging foil after storing them in the lysimeters in comparison to the plasticiser content of the raw materials (100 %); vertical lines indicate the tolerance of the determination method

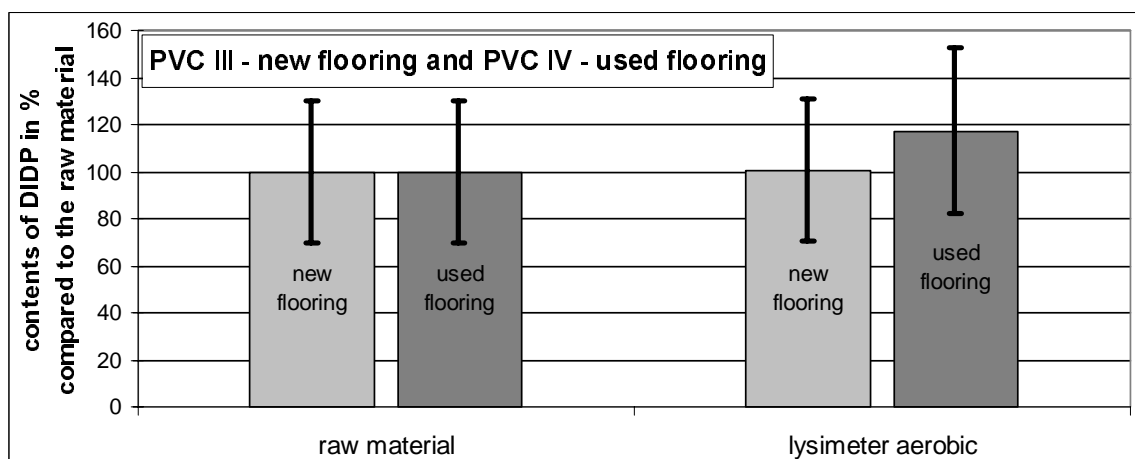


Figure 6 - 16: Examined values of DIDP content in used and new flooring after storing them in the lysimeters in comparison to the plasticiser content of the raw materials (100 %); vertical lines indicate the tolerance of the determination method

- 61 Analysis of the contents of plasticisers show that DEHP is partly lost from plasticised PVC under aerobic thermophilic conditions in lysimeter 2. The difference in the percentage of the loss of plasticiser between the materials used car interior and plasticised packaging foil is caused by the thickness of the PVC. The car interior consists of a much thinner layer of plasticised PVC than the packaging foil.
- 62 Any loss of plasticiser is a leaching process from the surface of the material. During such loss the concentration gradient inside the material increases and causes internal diffusion. The diffusion processes are very slow and on that basis it could be concluded that the loss of plasticiser related to the materials surface from the car interior is nearly the same as from the packaging foil but a higher stock of plasticiser is retained inside this foil. Furthermore the car interior was corroded already at the beginning of the examinations and so the active surface was higher than that of the packaging foil from the beginning. The surface reactions could start at a higher level.
- 63 The results show a clear loss of plasticiser during the lysimeter studies under aerobic thermophilic conditions within the short time of examinations. Measured losses from the materials taken from the lysimeters 4 and 6 are within the tolerance of the determination method. The trend towards a decreasing content of plasticiser is probable. A clear loss of plasticiser has occurred to the car interior material in the aerobic biological treatment plant supporting the results from lysimeter 2. The theory to explain the differences between the losses of plasticiser between the used car interior and the packaging foil with the dependence on the thickness of the material are strengthened by the results from lysimeter 6 and the biological treatment plant. In these investigations too the percentage of loss of plasticiser is higher from the thin material.
- 64 The content of the plasticiser DIDP in both flooring materials shows no decrease following the aerobic treatment in lysimeter 2. On the one hand it could be explained with the fact that DIDP will leach much slower than DEHP or it would not leach out. On the other hand the flooring materials are much thicker than the materials containing DEHP. Further analysis of flooring materials was not carried out because of the fact that lysimeter 2 showed the highest aggressiveness and no loss was detected. Therefore, no effects are expected from the conditions in lysimeter 4 and 6. Within the investigations no loss of DIDP from PVC was measured.

STABILISER

- 65 Any loss of stabiliser leads to emissions in leachate. The stabiliser content was investigated by analysis of the heavy metal contents before and after storing the PVC-materials in the lysimeters. In this investigation only the samples containing stabilisers based on heavy metals were tested. These are PVC II, PVC VI, PVC V, PVC VI and PVC VII. In spite of its content of Ba/Zn-stabiliser PVC III was not investigated because PVC II contains the same elements. The results are summarised in table 6 - 4.

Table 6 - 4: Stabiliser contents of the PVC-materials during lysimeter study; analysis performed by NORDUM Umwelt + Analytik

Material	Examined condition	Contents of heavy metals in % by weight			
		Pb	Ba	Zn	Cd
PVC II	raw material	-	0,01	0,02	-
	lysimeter 2; aerobic	-	0,09	0,02	-
	lysimeter 6; anaerobic	-	0,03	0,01	-
PVC IV	raw material	2,8	-	-	-
	lysimeter 2; aerobic	1,2	-	-	-
	lysimeter 6; anaerobic	1,8	-	-	-
PVC V	raw material	-	0,18	-	0,33
	lysimeter 2; aerobic	-	0,13	-	0,33
	lysimeter 6; anaerobic	-	0,16	-	0,33
	biol. waste treatment plant	-	0,16	-	0,31
PVC VI	raw material	-	<0,01	0,01	-
	lysimeter 2; aerobic	-	0,15	0,04	-
	lysimeter 6; anaerobic	-	0,04	0,05	-
	biol. waste treatment plant	-	0,16	0,05	-
PVC VII	raw material	-	0,14	-	0,39
	lysimeter 2; aerobic	-	0,13	-	0,38

- 66 On the basis of the analysis of heavy metal content, no clear interpretation of the behaviour of stabilisers in PVC under landfill simulating conditions is possible. Analysis of the samples before incubation in lysimeters was carried out by the companies Bärlocher and NORDUM. The variation of measured contents cannot be explained, but may result from different analytical methods. Therefore only preliminary interpretation of the results is possible.
- 67 Only indications of the behaviour of cadmium and lead stabilisers are visible. In cadmium content no change was found between raw materials and materials from lysimeters. No loss of cadmium from rigid cadmium-stabilised PVC was determined. The lead content indicated a decreased content in samples taken from aerobic as well as anaerobic lysimeters. However, due to the uncertainties of the analyses these results have to be checked.
- 68 The behaviour of barium and zinc contents in the materials can only be explained by the influence of the surrounding waste in the lysimeters. Organics and even plastics are known for their ability to adsorb heavy metals and on that basis it has to be considered as possible that this process has affected the results shown.

6.6.3 Behaviour of gaseous emissions from landfill simulation

- 69 To examine gaseous emissions from PVC the condensate from lysimeter gas and the gas, enriched on charcoal, from the lysimeters were analysed to identify differences in composition and possible detrimental substances in gas from waste not contaminated with PVC and waste enriched with PVC. Only aerobic and aerobic-anaerobic lysimeters were included in the investigation because of the constant gas flow through the waste. This flow was caused by aeration of the lysimeters. Gas flow from anaerobic lysimeters can not be assumed as constant and no analysis was undertaken. Comparison of the results from anaerobic lysimeters would not be feasible. Sampling times were once at the beginning and once at the end of the studies. To investigate emissions different gaschromatographical analyses were carried out.

- 70 Analysis of the gas from the lysimeters was performed as gaschromatographical fingerprint. The scope of the examination was not to identify substances but to recognise differences between the gases. Therefore only the gases of the corresponding lysimeters running under similar conditions but distinguished by contents of PVC are comparable. Figure 6 - 2 depicts the difference in gas composition from aerobic-anaerobic lysimeters 3 and 4 at the start of lysimeter studies.

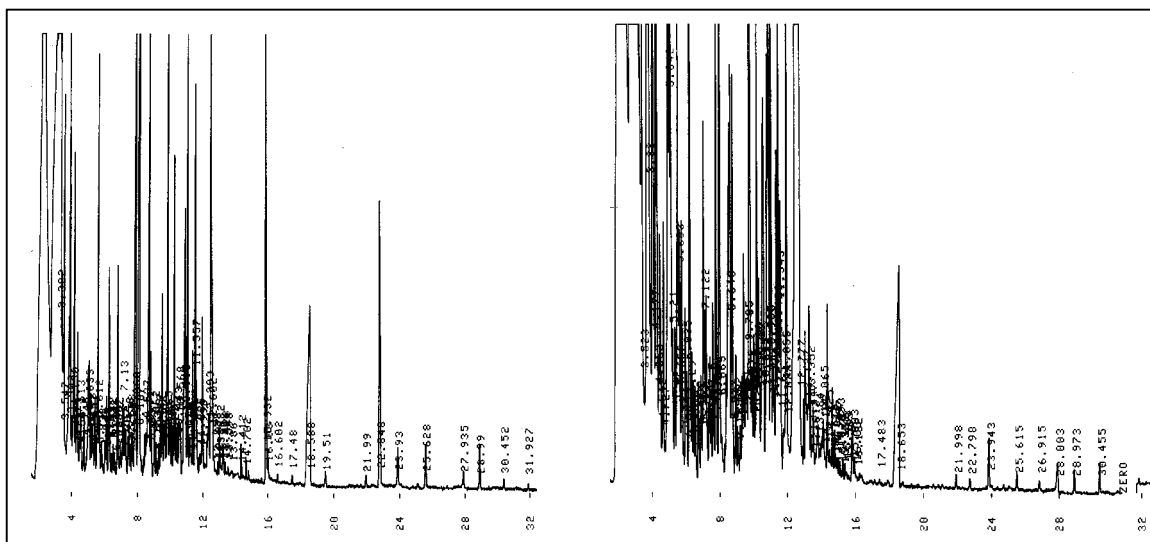


Figure 6 - 2: Chromatogram of gas enriched on charcoal from aerobic-anaerobic lysimeters 3 (left, without PVC) and 4 (right, with PVC) at the start of lysimeter studies; every peak characterises a single substance, the height its quantity; numbers at the bottom and at the peaks characterise the retention time, every detected substance appears at a specific retention time

- 71 Every peak in a chromatogram characterises a single substance, the height its quantity. Changes in the number of substances and its quantity in landfill gases indicates degraded materials and degradation processes. Degradation processes in both presented lysimeters can be considered as largely similar. Clear differences in gas composition are very likely caused by the presence of PVC samples in the lysimeters, however possible differences in the waste matrix will also influence the gas composition.
- 72 The chromatogram belonging to lysimeter 4 (aerobic-anaerobic with PVC) contains more and higher peaks than the chromatogram on the left from lysimeter 3 (without PVC). The same observation is detectable at other chromatograms from aerobic lysimeters 1 and 2, depicted in annex IV. That result indicates that volatile substances are released in case of the presence of PVC in degrading waste. The determined emissions are likely to result from degradation of substances contained in the PVC samples in the lysimeters. Differences consist in the composition of the substances as well as in the quantity of some substances. It should be mentioned in this context that some of the investigated PVC samples were laminated with polyurethane (samples I and III) and unknown textiles (sample II), which could have influenced the chromatogram. Identification of the gaseous emission compounds would be necessary before any conclusion could be drawn, though it was not carried out during the study. The results found are confirmed by investigation of waste gas at the end of lysimeter studies using similar methodology but another gas chromatograph because of new acquisition of the equipment. Results are shown in figure 6 - 18.

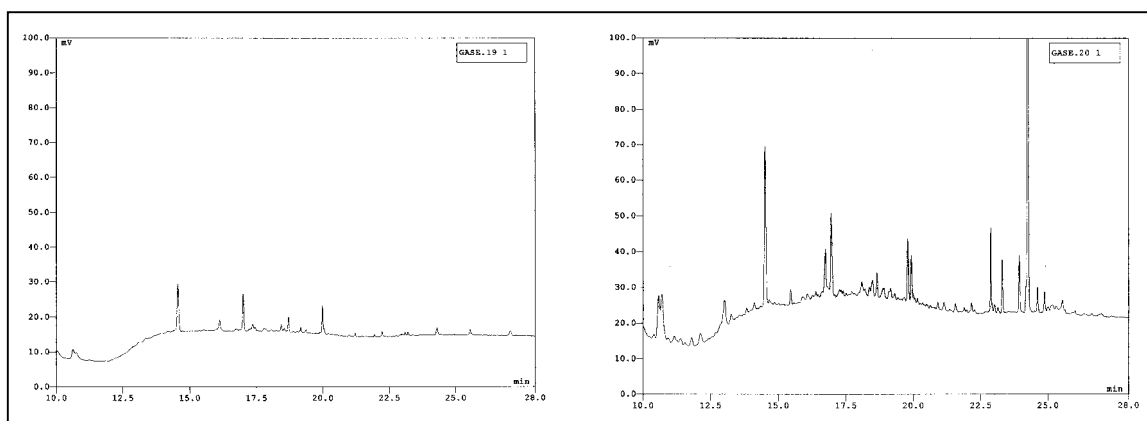


Figure 6 - 18: Chromatogram of gas composition from aerobic lysimeters 1 (left, without PVC) and 2 (right, with PVC) at the end of investigations; every peak characterises a single substance, the height its quantity

- 73 The sample from the lysimeter containing PVC shows more and higher peaks similar to analysis described above. Gaseous emissions from the lysimeter 2 are increased by number of substances and their quantity. Summarising the results it is probable that the raised emissions caused by PVC in waste are likely to occur during a long time span.
- 74 The condensate collected would contain mainly volatile substances with high condensation point which condensate at a temperature of 6°C. Analysis by gas chromatography and connected mass spectrometry resulted in chromatograms and a list of identified substances. Some results are depicted in figure 6 - 19.

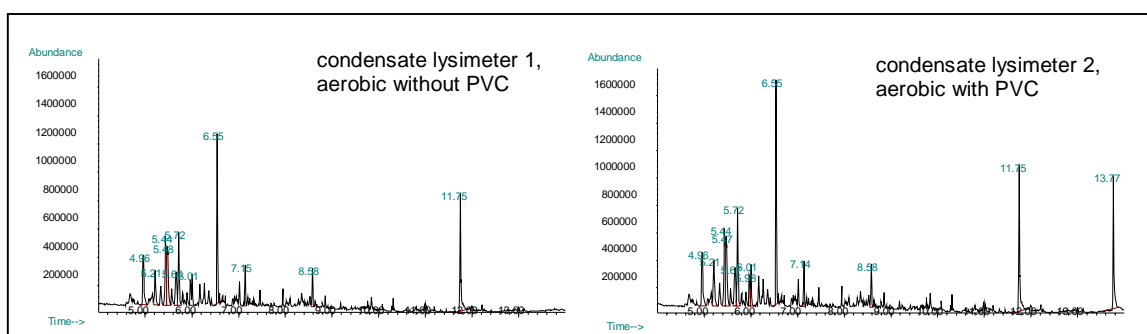


Figure 6 - 19: Chromatogram of condensate composition from aerobic lysimeters 1 (left, without PVC) and 2 (right, with PVC) at the end of investigations; every peak characterises a single substance, the height its quantity; numbers at the peaks characterise the retention time, every detected substance appears at a specific retention time

- 75 No certain differences in composition from condensed lysimeter gas from waste with and waste without PVC were determined. In condensate from two lysimeters with PVC and one lysimeter without PVC DEHP was found. DEHP has been found in the condensate from lysimeters 2,3 and 4. This indicates a release of DEHP from waste to gas phase which results in gaseous emissions. The positive result for DEHP from the lysimeter without added PVC may be caused by PVC which was not sorted out during preparation of the waste.
- 76 No clear conclusions about gaseous emissions of defined substances caused by PVC in waste during lysimeter studies can be drawn, but the behaviour of the gas composition emitted from lysimeters with and without PVC shows differences, which are likely to result from the incubated PVC samples. This conclusion can only be drawn for plasticised and unplasticised PVC together

because they were always stored together in the lysimeters. Resulting emissions cannot be attributed to plasticised or unplasticised PVC without further research.

6.6.4 Behaviour of emissions from landfill simulation to leachate

- 77 To examine emissions from PVC, the leachate from the lysimeters was analysed to investigate differences in composition and pollution of leachate from waste not contaminated with PVC and waste enriched with PVC. The samples were taken from the lysimeters half-way through and at the end of the studies. To investigate emissions caused by degradation of the polymer or plasticisers, gaschromatographical analysis was carried out. Possible effects of the heavy metals containing stabilisers were examined through atom absorption spectroscopy.

Analysis of organic emissions

- 78 To evaluate emissions caused by the PVC polymer or additives excluding stabilisers the leachate from the lysimeters was analysed by gas chromatography as described in annex III. The results show no certain differences between the lysimeters containing PVC and the lysimeters without PVC. There are normal differences between the three conditions aerobic, aerobic-anaerobic and anaerobic, but there is no connection to the PVC materials. The results of the analysis are added in annex IV. Slight differences have to be seen as inconclusive.
- 79 Despite of the indicated release of plasticiser from the PVC samples no emissions were detected in leachate. The way of the emissions depends on e.g. the solubility of the substances and on the retention capacity of the waste matrix. There is not a direct correlation between the release and the contamination of leachate. Additionally, the background contamination of the leachate could be too high to identify emissions in the leachate attributed to PVC.

Analysis of heavy metals

- 80 To evaluate emissions of heavy metals caused by the PVC stabilisers, the leachate from the lysimeters was analysed by atom absorption spectroscopy. The results are shown in table 6 - 5.

Table 6 - 5: Results from the analysis of heavy metals in the leachate of the lysimeters

Lysimeter	Cadmium [mg/l]		Lead [mg/l]		Zinc [mg/l]	
	after 45 days	after 90 days	after 45 days	after 90 days	after 45 days	after 90 days
1 (aerobic without PVC)	0.08	0.08	0.77	0.50	17.1	5.18
2 (aerobic with PVC)	0.04	0.04	0.25	0.27	1.38	1.32
3 (aerobic-anaerobic without PVC)	0.03	0.03	0.33	0.66	33.0	20.8
4 (aerobic-anaerobic with PVC)	0.01	0.05	0.37	0.50	1.30	3.48
5 (anaerobic without PVC)	0.02	0.02	0.23	0.12	0.21	0.16
6 (anaerobic with PVC)	0.05	0.02	0.40	0.12	0.23	0.18

- 81 The measured values of heavy metals in the leachate show no clear differences between the lysimeters connected to the PVC and the stabiliser content of the waste. Moreover the lysimeters running under the same conditions show very strong varying values. For example both aerobic lysimeters show zinc contents varying in the area of one order of magnitude. That difference can reasonably be explained by the different composition of the waste. In spite of the very careful

preparation of the waste samples used in the lysimeters, pieces contaminated with the heavy metals must have been included which were not equally distributed in the waste matrix.

- 82 There was a release of lead from the waste matrix of the various lysimeters, but no increase of lead concentrations in the leachate from the lysimeters with PVC was found. Regarding the contamination of leachate with lead from PVC we have to emphasise that released substances are not necessarily to be found immediately in leachate. Substances can be retained by the waste matrix caused by adsorption or concentration gradients. Thus, the contamination of leachate occurs with a time-lag. There is not a direct correlation between the release and the contamination of leachate.

6.7 Investigation of the influence of leaching processes on PVC

- 83 In the leaching test, the release of additives without any microbial influence on the plasticised PVC was examined in order to distinguish between physical and microbiological influences on PVC. After and during the test the contents of plasticiser were analysed. This investigation is supporting the interpretation of lysimeter results.
- 84 In this test the behaviour of a number of self-made foils and a PVC product as used during lysimeter tests was investigated. Due to the expected low leaching effect mainly the thin laboratory produced foils were applied in this test. It is assumed that any release of plasticiser will be easier to detect. This method was used for the first time and therefore all results are only indicative.
- 85 The tests using self-produced foils bear some uncertainties caused by the distribution of the various components throughout the membrane in comparison to original materials (see chapter 6.3.2) and regarding the determination method of the phthalate contents. Therefore this approach did not produce very convincing results and does not necessarily allow conclusions about the leaching behaviour of plasticised PVC-products. Despite of this, the test method and results are presented below.
- 86 The laboratory-produced foils are made from materials PVC I – VII and were manufactured as described in annex III with a thickness of 20 µm. Additionally a PVC-material in original form, the plasticised packaging foil (PVC VI) was investigated in order to ensure comparability to the lysimeter studies. Two further self-made PVC foils were included in the examination: a) an unplasticised foil (foil A) made from pure PVC powder as blank control. Using this foil possible adsorption effects of phthalates, which might be found in the freshwater, to the PVC foils was observed. No such effects were found at the end of analysis. b) A plasticised foil (foil B) made from pure PVC powder and the plasticisers BBP (5 % by weight) and DEHP (15 % by weight) was added to the investigations. To detect hampering effects of other additives in the foils made from the PVC products this foil was added to the leaching test. The composition was chosen similar to the sample PVC III, flooring material. This sample and information about the composition was provided by the University Hamburg-Harburg at an early stage of the study. The sample should have the same composition as the flooring material used in their investigation and was used in order to allow comparison with their study. Unfortunately, it turned out later that the flooring material as used in our lysimeter studies had a different composition. The investigations could not be repeated.
- 87 The investigated foils were stored for 32 days under percolation with 40 – 45°C warm water. For reasons of the low solubility of phthalate-plasticisers it is necessary to use percolating water to avoid saturation of the leachate and to arrest the leaching process. In this way, the maximum loss of plasticiser for physical reasons shall be determined. Further specification of the method is described in annex III. Therefore samples were taken at the beginning and at the end of the

period. Analysis of the content of plasticiser by gas chromatography was carried out according to annex III.

- 88 The measured plasticiser content shows differences during the leaching test. This is shown in figure 6 - 20. The values in figures 6-20 and 6-21 are the amounts of extracted plasticiser from the foils during analyses. The authors indicate with 'extracted plasticiser' the quantity of plasticiser that could be extracted from the samples, after having been exposed to percolating water for x days. It was observed that not all plasticiser contained in the samples was extracted by the used method.

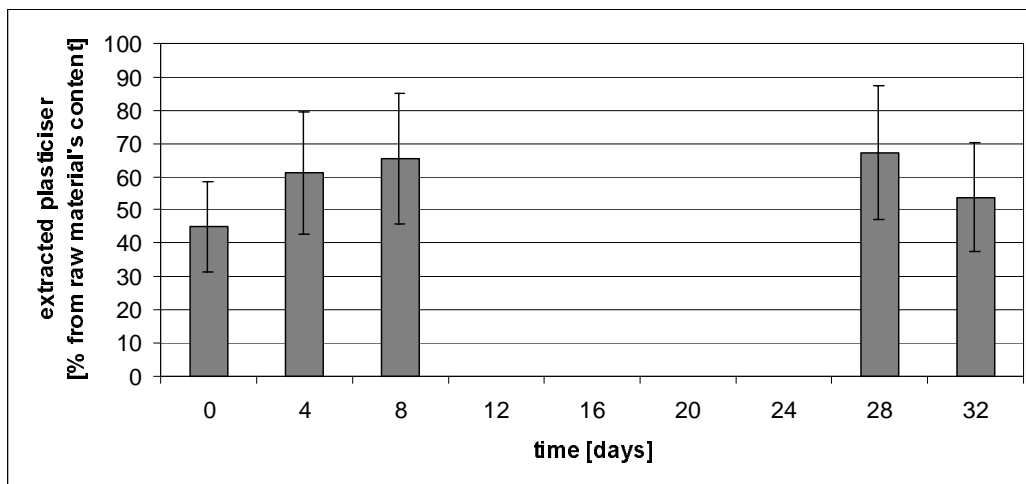


Figure 6 - 20: Extracted²² plasticiser DIDP measured from the laboratory produced foil IV during the leaching test; the vertical lines indicate the tolerance of the determination method

- 89 The measured content of DIDP in the dry new foil was determined much lower than the calculated value, in the figure equal to 100 %. After some days of leaching the measured content of DIDP in the material rose unexpectedly. A decrease first occurred after 28 days. This effect can be explained by the used extraction method. From dry foil the extractability of plasticisers in acidic acid ester is reduced in comparison to foils being exposed to water. While storing in water PVC takes up water and the extractability increased up to a maximum dependent on to the water uptake. Any effect of leaching of plasticisers can be measured with this method after the maximum is reached. The behaviour of foil IV shows that this maximum for DIDP was reached at the end of the investigation at about 28 days. The behaviour of DEHP is illustrated in figure 6 - 21.

²² see the description of the method in annex III

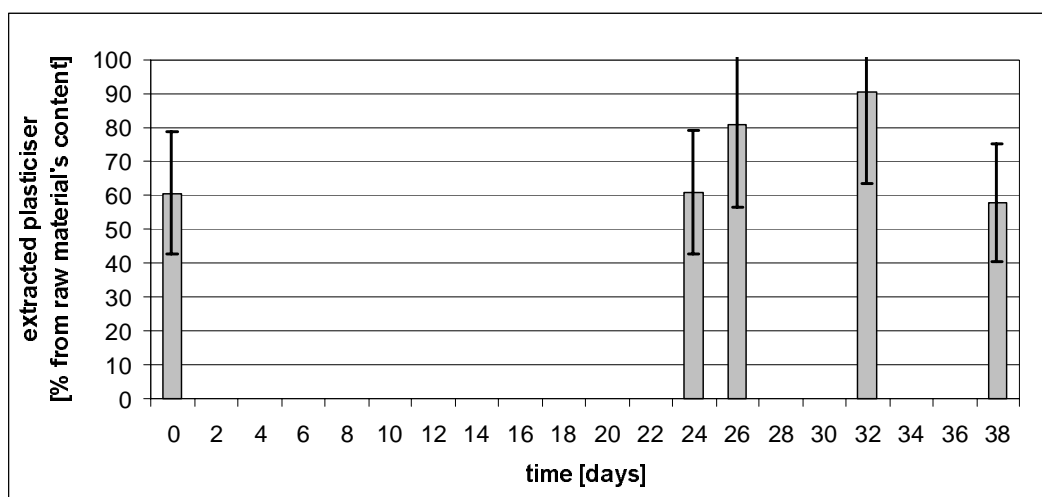


Figure 6 - 21: Measured extracted contents of plasticiser DEHP from the self produced foil B during the leaching test; the vertical lines indicate the tolerance of the determination method

90 The extractable amount of DEHP from foil B increases similarly to DIDP from foil IV with the investigation time. The maximum of extractable amount of plasticiser seems to occur later. Comparison with the thick original PVC product plasticised packaging foil shows similar effects but the increasing extractability of DEHP reaches no maximum within the examination time. It is indicated that the extractability of plasticisers depends on the kind of plasticiser in the material and the thickness of the material. From the courses of contents of plasticiser in the PVC materials no conclusion about the leaching behaviour of plasticisers in PVC is possible.

6.8 The influence of micro-organisms from landfills on PVC

91 In this test the microbial attack on a number of laboratory-made foils²³ was investigated. The choice of materials is the same as investigated in the leaching test (see section 6.7) with the difference that the foils were made 40 µm in thickness because increased stability was necessary. Falsifications caused by the foil production (see chapter 6.3.2) have to be considered in this test too. Despite the fact that the distribution of the various components throughout the membrane in the foils containing additives may be different in comparison to original materials all microbiological effects on the foils have to be seen as clear indications for a microbiological attack. However, the PVC foil prepared of pure PVC is not affected by the varying additives distribution.

92 To characterise any attack on the PVC foils the following parameters were observed:

- (a) Changes in the surface structure of the PVC foil, investigated by scanning electron microscopy
- (b) Development of bacteria cultures utilising PVC foils as source of carbon, investigated by counting cell numbers.
- (c) Reduction of the content of plasticisers in the PVC foils, investigated by gas chromatography

²³ production of the laboratory-made PVC foils is described in annex III

93 To investigate the attack on PVC three different parallel test series were carried out at 60°C which is, according to pre-tests the best suited temperature for the growth of the micro-organism cultures and a usual temperature in landfills. A detailed description of the methods is to be found in annex III. First a blank control without any inoculation with bacteria but exposed to mineral medium was prepared. In the second series the PVC foils were inoculated with mineral medium and the bacteria cultures described above. In this incubation test series the only source of carbon were the PVC polymer and the additives, so that any growth of the micro-organism population can be attributed to an attack on PVC and its additives. In the third series additionally 0,5 % glucose was added to the inoculation of incubation test series two. This glucose should support the micro-organisms acclimatisation to the PVC as food for the start phase. Due to experiments on microbial attack on glass this action is known to have a positive effect on the aggressiveness.

6.8.1 Investigation of the foils by scanning electron microscopy

94 The following investigated differences will be explained using the examples of some microscopic pictures. Further pictures are to be found in annex IV. The following figures will illustrate the materials behaviour. Figure 6 - 22 show foil A made from pure PVC-powder and figure 6 - 23 depicts the same material being inoculated with mineral medium and micro-organism culture without glucose.

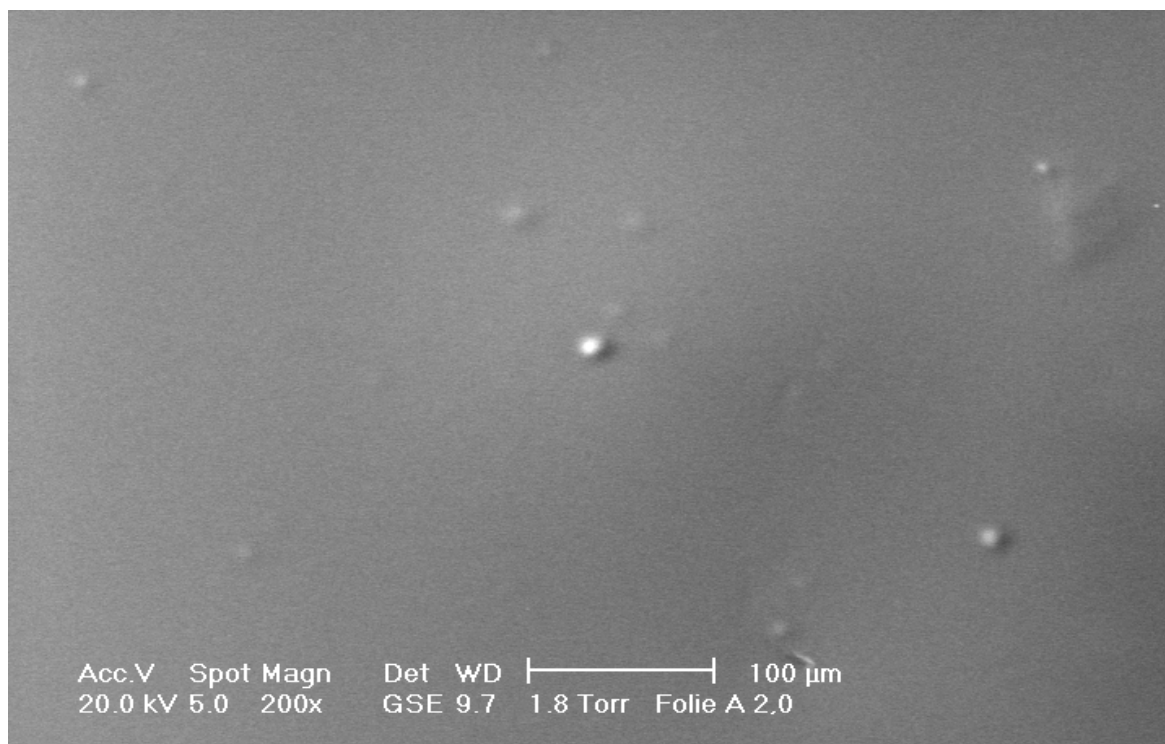


Figure 6 - 22: Photograph from scanning electron microscopy of foil A (made from pure PVC powder) after production; the light spots are dust and the material shows a very homogenous surface

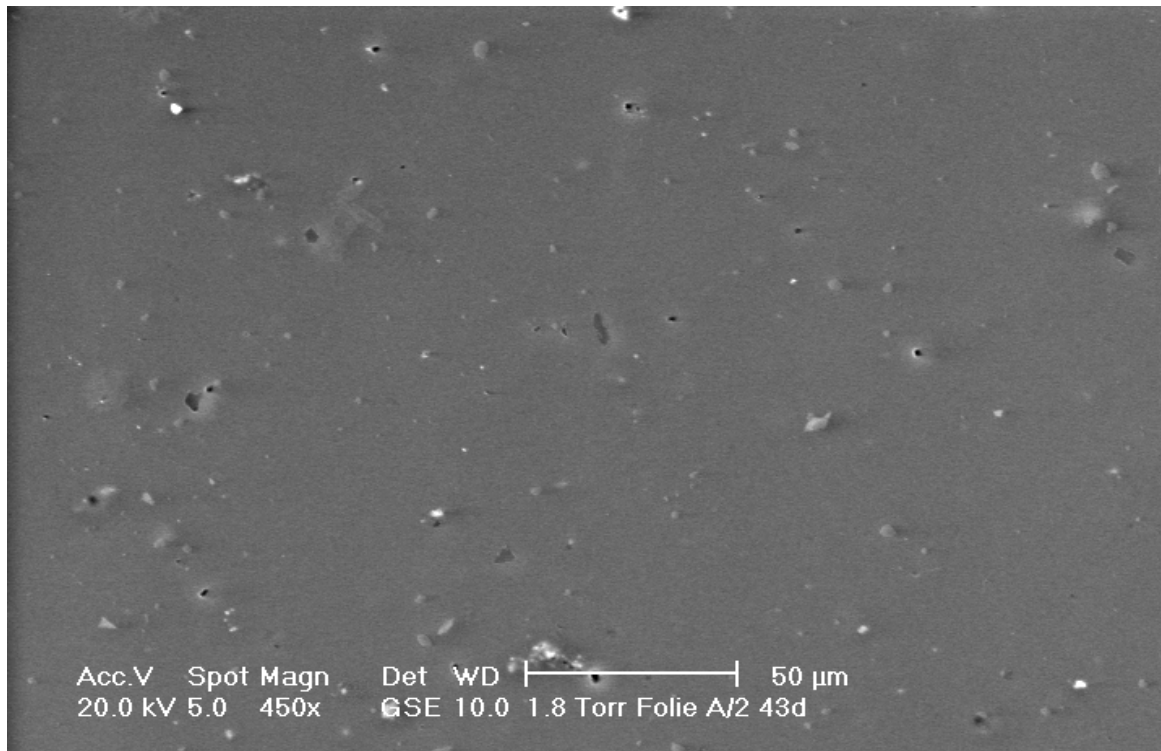


Figure 6 - 23: Photograph from scanning electron microscopy of foil A (made from pure PVC powder) after 43 days of incubation in mineral medium without added glucose at 60°C); the dark irregular spots are holes of erosion what means that parts of the material are lost; the light spots are dust

- 95 All foils from the incubation test series without added glucose indicate different levels of attack. During the series with added glucose in contrast almost no attack has occurred. The presence of glucose restricts the micro-organisms utilising the PVC. In comparison to that, during the first incubation test series without micro-organisms, no effects were visible in the microscopic pictures. A negative influence of the mineral medium is excluded. Indicated by corrosion effects on both plasticised and unplasticised PVC it appeared likely that additives as well as the PVC polymer were utilised. To clarify whether an attack has occurred to PVC polymer or not the molecular weight distribution of the pure PVC sample before and after the microbiological test was analysed. The results showed no differences, thus the PVC polymer was obviously not affected (see para 100).

6.8.2 Investigation of the microbial growth on the PVC foils

- 96 Due to the cell counts a microbial growth based on utilising additives and PVC results of the microscopically investigations are proved. An example of growth representative for all investigated samples is shown in figure 6 - 24.

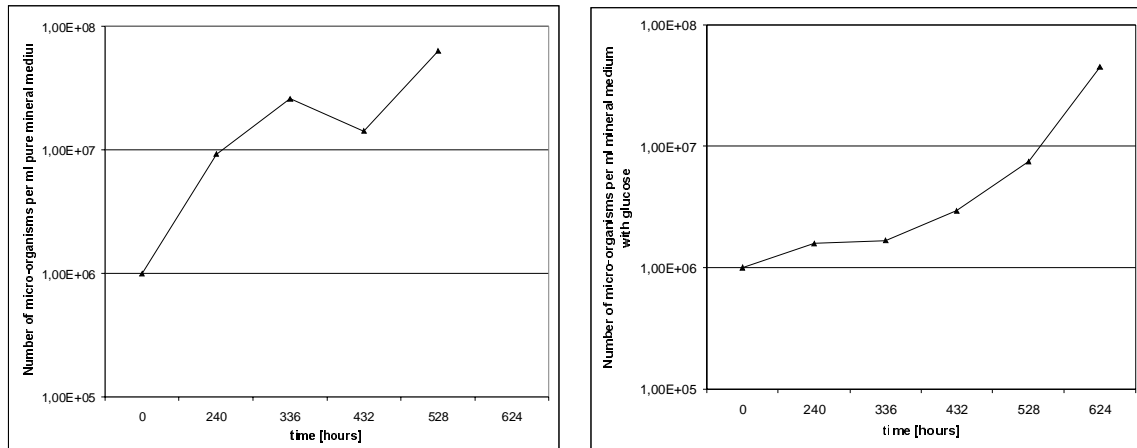


Figure 6 - 24: microbial growth on foil I, made from the new car interior, incubated without (on the left) and with glucose (on the right)

- 97 The presence of glucose seems to hamper the cultures being acclimatised to PVC. Microbial growth in the incubation test series without glucose starts much faster than in the parallel series with added glucose. This result can be seen as representative for all observations during this investigation. Additionally the growth of the microbiological populations was detected on unplasticised PVC in comparable order as on plasticised PVC as shown in figure 6 - 25.

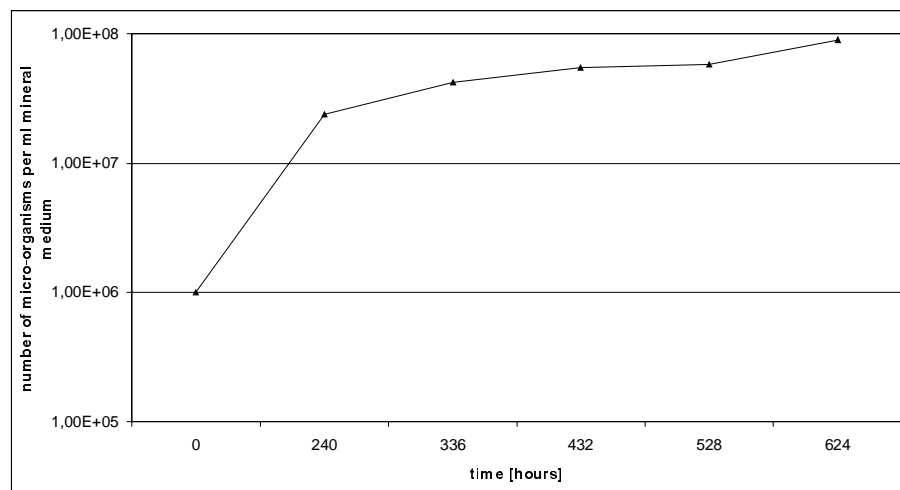


Figure 6 - 25: microbial growth on foil A, made from pure PVC-powder without plasticisers, incubated without glucose

- 98 Due to the microbial growth an attack on PVC-polymer and its additives could be concluded. Another observed effect is shown in figure 6 - 26.

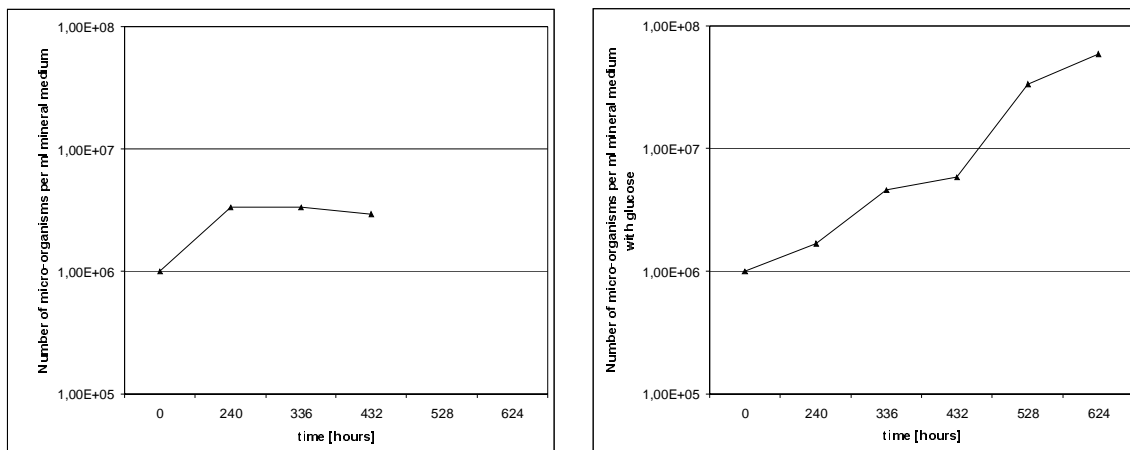


Figure 6 - 26: microbial growth on foil B, made from PVC-powder and the plasticisers BBP and DEHP, incubated without (on the left) and with glucose (on the right)

- 99 The growth on that material is clearly hampered compared to the other materials. During similar investigations on materials containing DEHP no decreased growth is recognised. Due to the presence of BBP, DEHP and no other additives, a hampering of microbial activity caused by the presence of BBP is concluded from the poor growth.
- 100 The observed microbiological growth on PVC samples containing plasticisers as well as on PVC without any additives provides an indication that both PVC polymer and additives are utilisable by microorganisms. To clarify whether an attack has occurred to PVC polymer or not the molecular weight distribution of the pure PVC sample before and after the microbiological test was analysed. The result of this analysis shows no difference of molecular weight distribution between the raw material and the PVC sample which has shown a microbiological growth. Some impurities were detected, probably caused by the production of PVC powder, which are likely to be the reason for the observed microbiological growth.

6.8.3 Investigation of the content of plasticisers in PVC foils

- 101 The microbiological tests focussed on corrosion effects on the material's surface and microbial growth. The content of plasticiser in the foils which were exposed to microorganisms was analysed to get information about the loss of plasticiser during the microbiological tests. The method is described in annex III. The tests using self-produced foils bear some uncertainties caused by the distribution of the various components throughout the membrane in comparison to original materials (see chapter 6.7) and regarding the determination method of the phthalate contents. Therefore this approach did not produce very convincing results and does not necessarily allow conclusions about the microbiological attack on plasticised PVC-products.
- 102 For interpretation of the results the fact that the extractable amount of plasticiser is depending on the water uptake of the material is to be taken into account. Therefore the remaining plasticiser in the material at the end of the investigation has to be compared with the values from the leaching tests after similar storing time in liquids.
- 103 Results of analysis of the contents of plasticisers in foils investigated in leaching tests and microbiological tests show approximately the same order of release. Leaching effects during microbiological tests are assumed as much lower because dissolved substances were not removed from the liquid surrounding the PVC samples. It seems possible that micro-organisms growth is based on consuming plasticisers.

6.8.4 Identification of the micro-organisms responsible for the attack on PVC materials

104 For purposes of collecting data about the micro-organisms which seem to be responsible for the indicated attack on PVC materials the species contained in the bacteria cultures used during the investigations were examined. Using common methods as described in annex III single strains were isolated. After first microscopic characterisation ten strains appeared to be different to one another but representative for the cultures. These ten strains were identified using the test systems API 20 E and API 50 CH. Results are summarised in table 6 - 6.

Table 6 - 6: Identification of strains from microbiological investigations identified using the test systems API 20 E and API 50 CH; identification at probabilities higher than 75 % are considered as certain identification

strain code	identification (% probability)	similarities to:
D 2	<i>Bacillus sphaericus</i> at 85,8 %	<i>Bacillus firmus</i> <i>Bacillus brevis</i>
D 5	<i>Bacillus sphaericus</i> at 96,0 %	<i>Bacillus stearothermophilus</i> <i>Bacillus laterosporus</i>
D 12	<i>Bacillus stearothermophilus</i> at 99,9 %	-
D 16	<i>Bacillus stearothermophilus</i> at 99,6 %	<i>Bacillus pumilus</i>
D 17	<i>Bacillus brevis</i> at 99,6 %	<i>Bacillus sphaericus</i> <i>Bacillus stearothermophilus</i>
D 20	Bacillus spec. (possibly <i>Bacillus circulans</i>)	-
D 23	<i>Bacillus brevis</i> at 68,7 %	<i>Bacillus sphaericus</i>
D 25	<i>Bacillus brevis</i> at 98,1 %	-
D 26	<i>Bacillus sphaericus</i> at 68,0 %	<i>Bacillus brevis</i> <i>Bacillus laterosporus</i>
D 28	<i>Bacillus brevis</i> at 94,0 %	<i>Bacillus firmus</i> <i>Bacillus stearothermophilus</i>

105 All identified strains are species of the genus *Bacillus*. This genus is usually involved in biological degradation processes. Almost similar strains were identified though they showed different growth behaviour during microscopic characterisation. It can be concluded that only the three strains *Bacillus brevis*, *Bacillus sphaericus* and *Bacillus stearothermophilus* are involved in the indicated attack on PVC materials under aerobic thermophilic conditions.

6.9 Investigation of carcinogenic effects of leachates and condensates

106 In co-operation with Prof. Schiffmann from the Institute of Animal Physiology, Cytopathophysiology Unit at University of Rostock, the carcinogenic effects of PVC-degradation products in liquid phase (condensate and leachate) was investigated. The intended method called "Syrian hamster embryo (SHE) micronucleus test in vitro" is described in annex III in brief.

107 The results of the micronucleus tests of the condensate from the aerobic and aerobic-anaerobic lysimeters is shown in figure 6 - 27. The test is carried out with different concentrations of condensate in the test medium. The pure test medium was used as blank control.

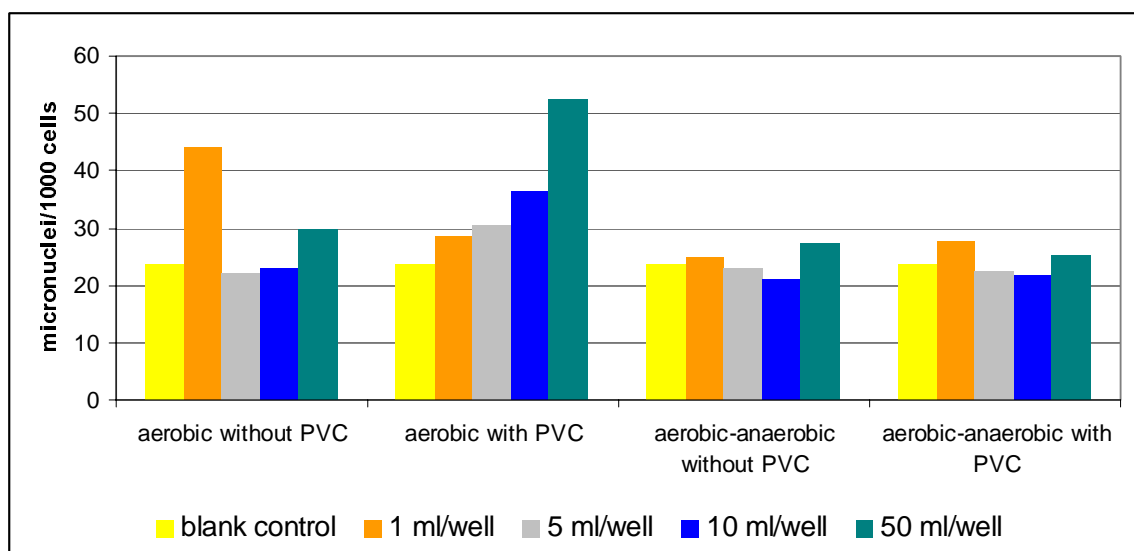


figure 6 - 27: Numbers of micronuclei in different concentrations of condensate from the lysimeters

108 The numbers of micronuclei being counted in the tests show no clear carcinogenic activity in the condensates, with exception of the condensate from the aerobic lysimeter with incubated PVC sample. A clearly increasing tendency of the number of micronuclei with increasing condensate-concentration in the test medium is shown only in the sample from the aerobic lysimeter. This corresponds to the chemical analysis of the condensate of this lysimeter where DEHP was detected. A repetition of this test is currently carried out, but the result will not be available in due time to be taken into account in the Final Report. However, earlier studies confirm carcinogenic activity caused by DEHP (Schiffmann et al. 1993). The result may also be a hint to the pollution of the non-condensing gas stream from the lysimeters as determined in the chapter about the chemical composition of the gaseous emissions. An investigation of the carcinogenic activity of these gaseous emissions seems to be of high interest.

109 The values of the other single tests are not clearly different to the values of the blank control. No indication for carcinogenic effects of the condensate from the gas stream of the other lysimeters is given. There are no clear differences recognisable between lysimeters which contain PVC and the lysimeters without PVC.

110 The results of the micronucleus tests of the leachate from the aerobic, aerobic-anaerobic and anaerobic lysimeters is shown in figure 6 - 28. The test conditions are equal to the investigation of the carcinogenic activity of the condensate.

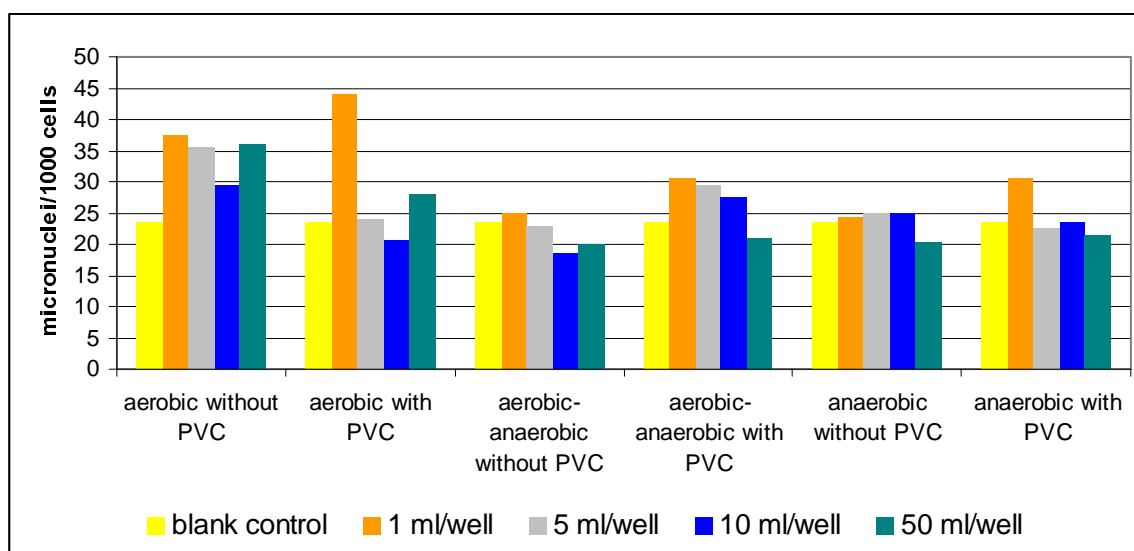


figure 6 - 28: Numbers of micronuclei in presence of leachates from the lysimeters in different concentrations

111 The numbers of micronuclei being counted in the tests indicate no clear carcinogenic activity in the leachates. The values of the single tests are not clearly different to the values of the blank control. No indication for carcinogenic effects of the leachate from all the lysimeters is given. There are no differences recognisable between lysimeters which contain PVC and the lysimeters without PVC.

112 The investigation of carcinogenic activity in the condensate and in the leachate from the lysimeters confirms the results of the chemical analysis of condensates and leachates, where DEHP was detected in the condensate of gaseous emissions from the aerobic lysimeter with incubated PVC. However, DEHP was also detected in the blank control, therefore no direct relation to the PVC content in lysimeters can be drawn. The leachates of lysimeters did not show an increased carcinogenic activity, this is probably due to the fact that the phthalates were still retained in the waste matrix and have not been found in the leachates.

7 SUMMARY OF THE ANALYTICAL PROGRAMME AND RESULTS

7.1 Comparability of the results to landfill conditions

- 1 The investigation into the behaviour of PVC consisting of a) examination in different size scales and b) an acceleration of certain processes occurring in landfills, resulted in observable effects within the short time available to this study. An acceleration of landfill processes can be achieved through aerobic thermophilic degradation. This condition causes the main attack on waste and is considered to provoke a degradation level, similar to the final aerobic landfill phase, within a rather short time. As assumed, the effects resulting from test conditions considered as the most aggressive were quite clear and were to a certain extent measurable, while effects became less distinguishable with increasing size and under simulated anaerobic conditions representing the prevailing condition in landfills.
- 2 For example, the examination of PVC samples incubated in the biological waste treatment plant implied possible changes of their mechanical properties and chemical composition, however, results could reasonably only be interpreted as hints. The same applies to the examination of PVC materials extracted from landfill. Under different lysimeter conditions the effects became more observable and could be related to aerobic and anaerobic conditions. In all lysimeters and the biological waste treatment plant similar effects were observed, however with different intensities. Recognised effects from microbiological tests and examination of leaching behaviour support the interpretation of results, in particular when biological and physical effects are to be differentiated. Therefore it is assumed that PVC materials will be affected in landfills, but the time until effects become observable is dependent on the prevailing parameters (temperature, moisture, presence of oxygen, activity of micro-organisms) and interactions between parameters.

7.2 Behaviour of PVC under simulated landfill conditions

- 3 The influence of test conditions in lysimeters as well as in the biological treatment plant on PVC samples was clearly recognisable. Examinations showed differences between the raw materials and the incubated materials. The extracted samples showed inhomogeneities in colouring and hardness between and within samples, changes of the surface structure was confirmed by scanning electron microscopy. Different effects between samples result from specific material composition, the history (used or new material) and the test conditions. Inhomogeneities within one sample are caused by the surrounding material in contact with the sample and by seeping water flows. This fact causes variations in the results in all investigations, therefore certain deviations within single examinations have to be seen as normal.
- 4 A general distinction can be made according to material composition and between old and new PVC samples. Used plasticised materials show a higher susceptibility to landfill processes. That could be attributed to commencement of corrosion, water uptake and stresses during life time. New plasticised materials show lower degradation effects. Between used and new rigid PVC almost no differences were detectable. Long term PVC applications can be considered as more resistant to simulated landfill conditions than short term applications like the investigated plasticised packaging foil.

PVC polymer

- 5 The investigations of the mechanical properties of the materials incubated in lysimeters result in more or less obvious changes of these properties for both plasticised and rigid PVC samples. While the decline of limit of tensile strain with respect to flexible PVC could have been explained

by the loss of plasticiser this could not be the reason for the slight but visible change in mechanical properties of rigid PVC. We therefore examined a rigid and a flexible PVC sample (window frame and packaging foil) through analysis of molecular weight distribution for possible affected polymer structure of the PVC polymer. The window frame material shows no difference between raw material and material taken out of the lysimeters. But the thin plasticised packaging foil designed for short service life indicates an attack on the polymer, which was most obvious under aerobic thermophilic conditions. The decreased height and the increased width of the molecular weight distribution as well as a slight reduction of molecular weight are probable results of a shortening of the polymer chains. It has to be considered that the test conditions causing the most obvious results are rather extreme due to the high temperature of 80°C. Such temperatures are not very likely to occur in old and small landfills but with the increasing height of a landfill such temperatures do occur. Additionally, waste treatment methods operating at high temperatures under aerobic conditions at landfill sites have to be taken into account considering the future development of landfilling, e.g. biological-mechanical pretreatment of waste before landfilling.

- 6 Through our microbiological tests at a lower incubation temperature (60°C, aerobic condition) the investigation of a PVC sample without any additives has shown microbial activity. However, the molecular weight distribution showed no difference between raw pure PVC foil and the PVC foil after microbiological tests. Therefore, a potential attack on the PVC polymer is likely to be provoked by the physical effects of high temperature in combination with the waste and leachate in the lysimeter. However, an indication is given for an attack on the PVC polymer from one type of application (packaging foil) at 80° C and the effect observed should be further scrutinised considering the following aspects:

- Influence of temperature
- Influence of stabilisers
- Interdependence between parameters and additives

Additives

Plasticiser

- 7 The release of plasticiser from the PVC samples was detected. The PVC materials taken from the lysimeters and from the biological waste treatment plant respectively showed both optically and mechanically clear differences to the raw materials. Changes could be recognised in each sample from the lysimeters, with the greatest effect caused by aerobic conditions and the least effect caused by anaerobic and aerobic-anaerobic conditions. Changes in the mechanical properties of the materials from lysimeters and the biological waste treatment plant indicated a loss of plasticiser from all flexible materials examined. The elasticity module as well as the elasticity limit decreases. The course of tension and related stretching in the tension-stretching-diagram of materials from lysimeters in comparison to the raw materials showed a clear increase in brittleness.
- 8 Analysis of the contents of plasticisers show that DEHP is lost from plasticised PVC under aerobic thermophilic conditions as well as in the biological treatment plant. Differences in total release between materials are caused by the thickness of the PVC. The release is a surface reaction and therefore the loss of plasticiser was more recognisable from thin material because of the higher surface to volume ratio. A loss from the materials taken from aerobic-anaerobic and anaerobic lysimeters cannot be determined with certainty. The trend towards a decreasing contents of plasticiser under these conditions is apparent but due to low extent of release analytical results are not conclusive.

- 9 The contents of the plasticiser DIDP in old and new PVC flooring showed no decrease after treatment under aerobic thermophilic conditions within the time of the study. Within the investigations no loss of DIDP from PVC was measured.
- 10 However, the behaviour of plasticisers in PVC should be further scrutinised considering the following aspects:
- Influence of temperature, moisture
 - Influence of microbiological processes (aerobic / anaerobic conditions)
 - Behaviour of different plasticisers under landfill conditions

Stabiliser

- 11 An analysis of the samples before incubation in lysimeters was carried out by two different companies resulting in varying contents of heavy metals. The variations cannot be fully explained, but may result from different analytical methods. One laboratory analysed both, the heavy metal content of the samples before incubation and after incubation, and results are expected to be comparable. Nevertheless, due to inconsistent results regarding the content of heavy metals in the raw material, the reliability of the results may be questionable.
- 12 The examinations of the behaviour of cadmium and lead stabilisers are interpretable in terms of indication. The cadmium content in the materials did not change during the incubation in the lysimeters. No loss of cadmium from rigid cadmium-stabilised PVC was detected but cadmium was detected in leachate. As mentioned above, results of analysed incubated samples are not very reliable, therefore no conclusion can be drawn regarding the source of cadmium found in the leachate. The possibility of a release of lead is reported in the literature in the acidogenic phase. Thus, although the indicated release of lead from samples taken from aerobic as well as anaerobic lysimeters is inconsistent, it cannot be excluded that a release has taken place.
- 13 The varying and slightly increased content of barium and zinc in the materials after incubation can only be explained by the influence of the surrounding waste in the lysimeters. Organics and plastics are known for their ability to adsorb heavy metals which have been found in the leachate from lysimeters, and the increase must be attributed to contamination of waste used for the lysimeter studies. Further research is necessary to explain the stabiliser's behaviour and its share in landfill emissions.

7.3 Emissions resulting from PVC in landfills

- 14 Due to the determined releases of additives from PVC samples emissions to the environment via gas and/or leachate are likely. Analysis results of gas and leachate from the lysimeters are summarised in the following.
- 15 Examinations of gaseous emissions reveal variations in gas composition between lysimeter serving as blank control and lysimeters containing PVC samples. Gas chromatographical analysis show several not identified substances in most gas samples from lysimeters incubated with PVC which were not found in lysimeters without PVC²⁴. The continuous tendency covering most single gas analyses indicates that PVC materials are likely to contribute to gaseous emissions from landfills. Further research is needed to determine components and its share to landfill emissions.

²⁴ some substances found in the blank control have disappeared

- 16 The condensate from the lysimeter would contain all volatile substances which condensate at 6°C. Analysis showed no indication of volatile emittents with high condensation point caused by PVC in landfills. No clear difference between lysimeter gas condensate from waste with and without PVC was determined. DEHP was found in condensate from two lysimeters with PVC and one lysimeter without PVC. That indicates a loss of DEHP from waste in the gaseous emissions. The positive result for DEHP from the lysimeter without added PVC could be caused by very small pieces of PVC which were not sorted out during preparation of the waste.
- 17 The investigation of the condensate of gaseous emissions by the cell test method called "Syrian hamster embryo (SHE) micronucleus test in vitro" revealed a carcinogenic activity of the condensate from one lysimeter (aerobic) out of four, which could be caused by the presence of DEHP. This testing method provides information about whether there is a risk of a carcinogenic effect or not without any specification.
- 18 No emissions of plasticisers in leachate of the lysimeters caused by the PVC samples were found within the study. The retention capacity of the waste matrix may be a reason for this result as well as biodegradation of phthalates. Heavy metals (lead, zinc, cadmium) were found in the leachates of all lysimeters in highly varying concentrations regardless of whether PVC was included or not. These results are not coherent and due to the high background contamination no conclusion regarding a contribution of PVC to this contamination is possible. No carcinogenic activity caused by PVC in landfilled waste is indicated.
- 19 Contaminants detected in leachate and in gas which are likely to result from the presence of PVC in the waste cannot definitely be attributed to PVC. Plasticisers were not found in the leachate and DEHP in the condensate of gas was also detected in a lysimeter without PVC samples. The background contamination of the waste with heavy metals varied in concentrations so that the effect of incubated PVC samples could not be identified. Thus, the release of additives, determined through analysis of the material itself, does not correspond to emissions to leachate and gas. Possible reasons are adsorption to the waste matrix of released additives, degradation of plasticisers and high background contamination of both heavy metals and DEHP. Further investigation is suggested considering the following aspects:
- Determination of composition and carcinogenic effects of gaseous emissions caused by PVC in landfills
 - Contribution of plasticisers and their degradation products to gas emissions
 - Effects of gaseous emissions caused by PVC in landfills to the environment

7.4 Processes causing the attack on PVC materials

- 20 To distinguish between the processes causing the changes in the investigated PVC, leaching tests and microbiological tests were carried out. The tests using self-produced foils were carried out the first time and bear some uncertainties caused by the distribution of the various components throughout the membrane in comparison to original materials (see chapter 6.7) and regarding the determination method of the phthalate contents. Therefore this approach did not produce very convincing results and does not necessarily allow conclusions about the leaching behaviour of plasticised PVC-products.
- 21 During the microbiological tests under aerobic conditions the investigated PVC foils were evidently attacked. That was confirmed by scanning electron microscopy and a decrease in the content of plasticiser. A growth of the bacteria population was observed on plasticised as well as on unplasticised PVC foils without any further source of carbon. This effect appeared in all tests, though in different intensities. However, the molecular weight distribution showed no difference between raw pure PVC foil and the PVC foil after microbiological tests. Due to the different

composition of investigated PVC samples and the short time span of the studies no prediction about the share of micro-organisms activity in the potential attack on PVC materials can be made.

- 22 Indicated plasticiser-leaching effects during microbiological tests are assumed as very low because the dissolved substances in the liquid surrounding the PVC samples are not removed. Therefore it seems possible that micro-organisms growth is based on consuming plasticisers. During microbiological tests there was no growth on PVC foil containing the plasticiser BBP and on the foil made from new car interior. That could be explained by hampering compounds, e.g. biocides or toxic plasticiser in the PVC. Due to inconclusive results from the leaching tests, it is not possible to distinguish between the share of physical and biological influences on PVC within the study.

7.5 Effects on the sturdiness of the landfill body

- 23 The investigation of the mechanical properties of the materials from lysimeters results in more or less obvious changes in these properties for both plasticised and rigid PVC samples. Plastics including PVC are regarded as a considerable part of the „friction mooring" of a landfill being responsible for the sturdiness of the landfill body. The PVC quantity in relation to the total synthetic material content is rather small in comparison to the mass of the plastic materials polyethylene and polystyrene, its share on account of the average maturity however, is considerable. The decrease in elasticity module as well as in tensile strength of the PVC products investigated, diminishes the tensile-strength relevant friction-part and results in decreasing steadiness. Decreased steadiness can cause e.g. downhill slippage of parts of elevated landfills or landfills situated on a slope as reported at some landfill sites. The contribution of PVC degradation to such effects cannot be estimated but has to be considered in future design policy for landfill bodies.

8 CONCLUSIONS

- 1 The following chapter is structured in three parts. Part 1 summarises the findings from our own analyses and from the literature survey with regard to the behaviour of PVC in landfills. In part 2 these results are discussed in the context of emissions to the environment and in part three areas for further investigation are identified.

Findings from lysimeter assays and literature survey

- 2 The aerobic thermophilic condition is considered to accelerate landfill degradation processes and to provoke a state of degradation, which is similar to the state of degradation in the final aerobic landfill phase. In our analytical test programme this condition was the most aggressive one to PVC. The observed effects provide indications on what is likely to occur in real landfills, however in unpredictable time spans. The change of the PVC polymer weight distribution was observed with certainty only under this condition and only in the thin plasticised packaging foil designed for short service life. Within the scope of this study it was not possible to distinguish definitely between physical and microbiological effect, however it is very likely that the attack to the PVC polymer is provoked only by the high temperature under the aerobic thermophilic condition. All other results from the aerobic thermophilic lysimeter were observable also under the other test conditions but somewhat less clear.
- 3 Landfills are very heterogeneous in terms of waste composition and physico-chemical characteristics not only between landfills but also within a single landfill. PVC products are subjected to different degradation processes in landfills which are determined by the parameters temperature, moisture, presence of oxygen, activity of micro-organisms and the interactions between parameters at different stages of the ageing development of landfills. During the initial stage of the landfill aerobic and facultative anaerobic micro-organisms oxidise the easily degradable fractions contained in fresh waste. This process is accompanied with an increase of temperature. The acidogenic stage of early landfill development shows the highest leaching efficiency. Due to the acidity of fermentation products occurring in the water phase, the pH (pH at 5,5 to 6,5) of the leachate will be low and heavy metals may be dissolved during this phase. The methanogenic phase is characterised by anaerobic conditions and with increased consumption of fatty acids, pH and alkalinity will increase (pH at ~7,5 to 8,5).
- 4 Changes in the PVC products are reported from aerobic as well as from anaerobic conditions. In real landfills aerobic conditions prevails in the initial stage, which is rather short. Losses of phthalates from PVC materials under soil-buried (aerobic) conditions are reported to amount to 30-35% of the total content. In these studies no phthalates were detected in the soil, aerobic degradation of phthalates is a possible reason. However, the initial stage of the landfill is a very short period in comparison to the following phases and its duration depends on landfill operation methods as well as on the composition of the landfilled waste. Therefore, it cannot be estimated to what extent PVC materials are affected during this phase.
- 5 During the anaerobic phases of the landfill, degradation of PVC products appears to be slower than under aerobic thermophilic conditions but the release of phthalates in particular, will probably continue and an attack on the PVC polymer, at least caused by high temperatures which may occur in large landfill sites, cannot be excluded. Results from the analytical programme indicate that the same effects as discovered under aerobic conditions may occur during the anaerobic phases of a landfill, but the time until similar effects to aerobic conditions are reached is fairly prolonged. The analysis of materials being disposed of in a landfill more than 20 years ago still showed considerable amounts of plasticisers and stabilisers. A release of phthalates under methanogenic conditions is reported in the literature in a range of 4 to 40 %.

- 6 A further broad distinction can be made regarding the effects on additives. Heavy metals are more likely to be released under acidogenic conditions while phthalates are particularly released during aerobic and methanogenic stages of landfill development. With regard to the release of phthalates again different processes are to be distinguished, i.e. physical, hydrolytic and biological effects occur concurrently. The fate of released additives is in case of phthalates depending on hydrolytic and biological effects, on the retention capacity of the waste matrix, on adsorption to particulate matter and co-transport. In case of heavy metals, particularly acidity, the retention capacity of the waste matrix and hydraulic effects determine emissions.
- 7 Microbial primary and ultimately degradation of phthalates under aerobic and anaerobic conditions are reported from other studies. The degradation of phthalates from PVC under methanogenic conditions is observed to be higher than under acidogenic conditions. Results from studies on the degradability of phthalates under landfill conditions show that degradation of PAEs occur, however, the rate of degradation does appear to be influenced by the length of their side chain. Both, PAEs and phthalic monoesters can be detected in landfill leachate, which indicates that these substances are not completely degraded. One further factor influencing the degradation of phthalates is the time of acclimation. Therefore, although degradation of phthalates under aerobic conditions is known to occur, the acclimation time may be too short during the initial aerobic stage of landfill development for complete degradation. Thus, emissions of phthalates to landfill leachates and to the aquatic environment cannot be excluded. DEHP in particular is considered to be persistent and to accumulate in sediments.
- 8 There is no evidence that the release of additives will come to a standstill. Thus, it is expected that this process will last for a very long time which cannot be estimated at a probably steady decreasing level. Nowadays the technical guarantee for landfill bottom liners and pipes for leachate collection is restricted to 80 years. Emissions resulting from the presence of PVC in landfills are likely to last longer than the guarantee of the technical barrier.

Landfill emissions

- 9 In Member States new landfills are designed with bottom liners and with leachate and gas collection and treatment systems. But, in 1994 uncontrolled dumps were still very common in some countries, and numerically, the majority of existing landfills had no leachate control at all. The most common form of active leachate management is collection and discharge to sewer, usually without pre-treatment. The greatest use of this route is for MSW landfills and in some countries as much as 60-80% of such sites discharge to sewer. Treatment of leachate most commonly consists of aerobic biological treatment, but may also include physical-chemical pre- and post-treatment processes to remove trace organics, residual COD or dissolved solids.
- 10 According to the findings from the literature survey and from our own analysis with regard to emissions resulting from the disposal of PVC in landfills, a contribution to the contamination of leachate and to gas occurs. The occurrence of phthalates in leachates and gas emissions is however not necessarily a direct result of the presence of PVC products in landfills. The presence of phthalates was detected in blank controls in our study and the same effect is reported from another study. Thus, disposed of materials may already be contaminated during the use-phase. Other substances, i.e. heavy metals and organotin cannot directly be attributed to the presence of PVC in landfills. Reported releases of these substances from PVC range at rather low levels. The results of our study with regard to losses of lead and cadmium from PVC products are not conclusive and cannot be quantified. The general view expressed in studies investigating the release of stabilisers from PVC products is that stabilisers are rather fixed in the PVC matrix and thus, the migration rate and mobility of lead from PVC is low. Nevertheless, the contribution to the contamination of leachate from the presence of PVC in landfills should not be neglected. Considering the very long time spans the materials will be exposed to landfill conditions also a very slow process will contribute to landfill emissions.

- 11 Emissions to environmental media such as air, soil and groundwater is to be expected particularly from landfills without active environmental protection measures (old landfills). Furthermore, as there is evidence that phthalates, DEHP mainly, are not fully eliminated through current leachate treatment, even from landfill sites equipped with leachate collection system and treatment of leachate either on-site or off-site, emissions to aquatic ecosystems cannot be excluded. Regarding the contribution to contaminants of gaseous emissions and possible elimination through gas treatment no conclusions can be drawn at present. Traces of DEHP have been detected in condensates of gas emissions of lysimeters containing PVC samples, but also in lysimeters without PVC, other substances found could not be identified within the scope of this project.
- 12 PVC waste is generally being disposed of in landfills as part of the municipal solid waste stream or together with commercial waste. The costs for landfilling in Member States are those for landfilling municipal solid waste and show a wide range of tariffs. There are a number of factors which influence the prices or tariffs for landfills amongst which the standard of the landfill, competition between different disposal routes, type and nature of waste being accepted are the important ones. Generally, no influence on prices or tariffs could be related or is expected due to the presence of PVC in municipal solid waste being landfilled. The quantity of PVC materials represents approximately 2.5% of landfilled MSW. The broadly estimated amount of lead introduced in landfills along with PVC products has shown a share of 28% of the total load of lead in MSW. According to literature lead stabilisers are rather fixed in the PVC matrix and thus, the migration rate and mobility of lead from PVC is low. No estimation about the contribution from PVC to lead contamination of leachate is possible. Leachate collection and treatment is generally necessary to eliminate heavy metals and no specific additional treatment measures attributed to the presence of PVC in landfills can be suggested.
- 13 With regard to the phthalate load introduced in landfills together with flexible PVC products and the expected long-term emissions of these substances more general considerations appear to be appropriate. Based on the findings about gaseous emissions caused by PVC treatment of landfill gas would be necessary. Due to unidentified composition of the emissions no prediction about its fate and possible treatment methods can be concluded. The elimination of phthalates in leachates from landfills is, as outlined above, not completely possible with current usually applied leachate treatment methods. Technical solutions for leachate treatment are feasible, in Germany costs amount to ca. 25– 50 Euro/m³. However, due to the expected long time span of occurring emissions resulting from PVC in landfills and the technical guarantee for landfill liners the life span of the liner system needs to be prolonged and the leachate has to be monitored for long time when emissions of PVC to leachate should be eliminated completely.
- 14 Considering the entire life-cycle of flexible PVC applications, short- and medium term emissions from landfills do not appear to be the most relevant source. Much more quantitatively important are short- and medium term emissions resulting from service-life and exterior use in particular. In general, emission via the atmosphere is quoted to be the main reason for the ubiquitous distribution of phthalates in environmental media.
- 15 However, essential information is still lacking for an assessment of quantitative phthalate emissions from landfills. Data on accumulated amounts of PVC and phthalates in landfills were not available for this study. Furthermore, phthalate emissions in landfill gas are, according to our findings, likely to occur. As a consequence, although the extent of phthalate emissions from landfills is not predictable, they may be underestimated as a percentage of total phthalate emissions from flexible PVC.

Further investigations

- 16 The study has raised a lot of questions which have not been considered in this detail in earlier investigations. According to findings from the literature survey and the lysimeter studies the following aspects should be further investigated:
- the PVC polymer of a thin flexible packaging foil has changed under thermophilic aerobic condition. This effect needs to be further investigated in order to identify the influence of temperature and microbial activity and possible interdependencies (interaction, synergy).
 - the influence of different stabilisers and plasticisers on the attack on PVC in landfill
 - identification and investigation of the carcinogenic effects of the gaseous emissions (additives and metabolites)
 - the quantitative load of PVC additives in landfilled MSW
 - accumulated quantities of PVC and PVC additives in landfills
 - identification of all additives used in PVC products, including those not previously investigated, and their behaviour in landfills (i.e. bisphenol A, chlorinated paraffins).

Abstract

The behaviour of plasticised and rigid PVC in landfill was investigated through literature survey and in landfill simulation studies. Plasticised and rigid PVC was incubated in lysimeters under aerobic thermophilic (up to 80°C), anaerobic thermophilic (60°C) and alternating aerobic-anaerobic conditions. The samples were also incubated in a biological waste treatment plant under aerobic condition. Specific processes, microbiological attack on PVC materials and the leaching behaviour were examined. The main results are summarised as follow:

- Phthalates are released from PVC material under landfill and under soil buried condition
- DEHP was detected in the condensate of gaseous emission from lysimeters with and without incubated PVC
- Fingerprint analysis from gaseous emissions from lysimeters indicate differences between those with incubated PVC and blank control
- Microbial growth was discernible on plasticised PVC
- Mechanical properties of plasticised and rigid PVC samples, investigated through tensibility tests, have changed during incubation conditions
- Molecular weight distribution of the PVC polymer of a thin flexible packaging foil has changed under thermophilic aerobic condition

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