Occurrence and Fate of Organic Contaminants in Wastes

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Abstract

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This thesis deals with the determination of organic contaminants in wastes and is part of the multidisciplinary faculty programme 'Biological waste in circulation between urban and rural areas – biology and flow of energy and material' which started at SLU in 1994.

To ensure long-term sustainability of food production it is important to recycle resources such as the nutrients and organic material in organic waste. The biodegradable fraction of source separated household waste is attractive as raw material for composting and anaerobic digestion, because the products can be used in agriculture and horticulture. Quality is an important aspect on compost and anaerobically digested organic household waste, and it is important to ensure that the products are not contaminated. As the available information on organic contaminants in the biodegradable fraction of household waste and the products thereof is limited, an important goal with this work was to increase the knowledge of organic contaminants in these material as a foundation for future studies to reduce the environmental risk from these materials.

Chlorinated paraffins (CPs) were found in fresh household waste. CPs are a complex mixture of chlorinated alkanes with varying (10-30) carbon chain lengts and varying (30-70%) unspecific chlorination. The high numbers of isomers and homologues complicates the determination of CPs. We found that multivariate analysis can be used to interpret chromatographic data of CPs and this was used to characterise the CP contamination of houshold waste. It is presently impossible to pin-point the source of CP contamination using the data available, but most probably the contamination occurs during the collection of the waste. To further improve the determination of CPs an extraction method using high diffusion liquids, pressurised liquid extraction (PLE) was developed. PLE was shown to be a suitable technique for extracting CPs from complex matrices such as fresh household waste.

A source close to the collection chain is also indicated for polychlorinated biphenyls (PCB). The PCB-profile found in the fresh household waste resembles that of a low chlorinated technical product. The PCB-profile expected in this type of material would originate from waste of animal origin in which the low chlorinated congeners have been degraded and the more highly chlorinated and persistent congeners dominate. Differences in the degradation rate of PCBs between composting and anaerbically degestion of the waste were also observed.

A third indication of a contamination source in the collection chain is the presence of the n-alkanes in the fresh and anaerobically digested household waste, which suggest a petrogenic rather than a biogenic origin.

Since the major part of the organic fraction of household waste is of plant origin, much of which is treated with pesticides, it was expected to find pesticides in the waste. Many of the pesticides were not degraded during composting or anaerobic digestion, and two that were not found in the waste were found in compost or anaerobically sludge. In these cases the organic bulk material is mineralized more rapidly than the pesticides.

The anaerobic biotransformation of nonylphenol mono- and diethoxylates (NPEO1-2) was studied in sludge, landfilled sludge and landfilled municipal solid waste. The NPEO1-2 are degradation products of nonylphenol ethoxylates (heavy duty surfactants) and are further degraded to nonylphenol (NP) which is far more persistent and ecotoxic than its parental compounds.

Contents

Preface

Papers I-V

The present thesis is based on the following papers, which will be referred to by their Roman numerals.

I. Ejlertsson, J., **Nilsson, M-L.**, Kylin, H., Bergman, Å., Karlson, L., Öqvist, M., Svensson, B.H. 1999. Anaerobic degradation of nonylphenol mono- and diethoxylates in digestor sludge, landfilled municipal solid waste, and landfilled sludge. Environmental Science and Technology 33: 301-306.

II. **Nilsson, M-L.**, Kylin, H., Sundin, P. 2000. Major extractable organic compounds in the biologically degradable fraction of fresh, composted and anaerobically digested household waste. Acta Agriculturae Scandinavica. In press.

III. **Nilsson, M-L.**, Bengtsson, S., Kylin, H. Characterisation of chlorinated paraffins in the biodegradable fraction of source separated household waste using multivariate methods. Manuscript.

IV. **Nilsson, M-L.**, Waldebäck, M., Liljegren, G., Kylin, H., Markides, K. E. Pressurised liquid extraction of chlorinated paraffins from the biodegradable fraction of source separated household waste. Submitted.

V. Hellström, A., **Nilsson, M-L.**, Kylin, H. Currently used pesticides and polychlorinated biphenyls in the biodegradable fraction of source separated household waste, compost and anaerobic sludge. Manuscript.

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Introduction

Wastes are produced in most human activities. When our modern industrial and consumption-oriented society has developed the amount of waste has increased concurrently. The constant use of raw materials and increased flow of materials in society are now creating a threat due to the increasing amounts and contents of harmful compounds.

Since 1919 wastes from household and industry have been placed on landfills in Sweden (Anonymous, 1996a). During 1950-60 the waste began to be recognised as a problem, mainly because of the increased use of disposable packages. The problem was highly associated with the large amounts of waste that had to be deposited. At that time wastes were treated without much though of that the materials and substances deposited were potential resources. Today we have understood that we must decrease the use of limited resources and to a higher extent reuse, recycle, and increase the use of renewable resources.

Political decisions have led to several important steps toward "a better handling of wastes". The meaning of this is to sort the waste into fractions with different properties, so that the fractions can be directed to a treatment for the best utilisation of the resources. Regulations have led to that metal, paper, carton, cardboard, plastics and glass are diverted from landfilling and incineration and instead are reused or recycled. Economical means of control have also been used. Since 1999 a tax on waste to landfill has been implemented.

Another way to reuse resources is to recirculate the organic fraction of our household waste. There is a political goal that nutrients and organic material in organic waste should be recycled and used in agricultural and horticultural production. After the year 2005 organic waste shall not be landfilled, as stated by the Swedish Environmental Protection Agency (SEPA) (Anonymous, 1996a).

The increased demand on the recycling of organic waste has at least two important reasons. Some of the nutrients are not easily renewable, e.g. phosphorus, where the available resources are limited. There is also a decrease of organic matter in the arable soils. To ensure the long-term sustainability of food production, it is important reuse the nutrients and organic material in the organic waste from urban areas. Before utilising the organic waste in agricultural and horticultural production, however, the waste must be treated by biological methods, such as composting or anaerobic digestion, to get a more stable product. Regarding these products there are several important safety and quality aspects such as pathogens, heavy metals and organic contaminants. It is important to guarantee the quality on the products spread on the fields. Quality is also an important marketing factor for compost and sludge and it is important to ensure that unwanted organic compounds do not enter into our food chain or cause other deleterious environmental effects.

Currently, the available information on organic contaminants in organic wastes and the products thereof is very limited. Many of the European countries are implementing biological waste treatment and there is a need to create safety standards also for organic contaminants, as is the case for heavy metals. The aim with this thesis is to bring about new knowledge concerning organic contaminants and their fate in wastes.

This work has been a part of the multidisciplinary programme, 'Biological waste in circulation between urban and rural areas – Biology and flow of energy and material', initiated by the Faculty of Agriculture, Landscape Planning and Horticulture of the Swedish University of Agricultural Sciences (SLU) in 1994. The programme had the goal of generating knowledge that would enable an improved recirculation of organic materials and nutrients between the urban and agricultural systems of our society. Emphasis of the research has been basic studies of the composting and anaerobic digestion processes and the safety of the end products from a health and environmental point of view.

Objectives

The general objective of this work was to identify key organic contaminants in fresh, composted and anaerobic digested household waste. Development of improved methods for the analysis of organic contaminants in wastes, compost and anaerobically digested waste has also been a major objective. The aim of the method development has been to achieve low-cost and environmental friendly methods usable in the environmental assessment of organic contaminants in complex environmental matrices.

The specific objectives were to:

- qualitatively investigate the anaerobic biotransformation and degradation of nonylphenol mono- and diethoxylates in materials derived from 1) an anaerobic sludge digestor treating waste water from a pulp plant and industrial waste water contaminated by NPEOs, 2) a landfill site where the very same sludge is deposited and 3) a municipal waste landfill (Paper I).

- characterize the fresh, composted and anaerobically digested household waste regarding major extractable organic compounds (Paper II).

- investigate and optimize conditions for extraction of chlorinated paraffins (CP) from the biodegradable fraction of source separated household waste using pressurised liquid extraction (PLE) (Paper IV) and to characterize the CP contamination using multivariate methods (Paper III).

- improve the analytical methods for determination of pesticides and persistent organic pollutants in complex matrices and apply the method for screening of pesticides and PCB in the biodegradable fraction of fresh, composted and anaerobically digested household waste (Paper V).

Materials

Source separated household waste

Fresh source separated organic household waste, investigated in Papers II-V, was collected from Uppsala municipality, Sweden, during the last week of February 1995 (Figure 1). The waste was separated by individual households and collected in polyethylene bags according to instructions from the municipality. The following materials were allowed in the organic fraction: food remnants, vegetable peel, fruit, eggs and shellfish, coffee grounds and tea with filter or bags, small potted plants with soil, leaves and flowers (but not garden waste), uncoloured household papers and napkins, meat and fish remains (but not large bones), cat sand. The waste was transported to the municipal composting plant at Hovgården, Uppsala, in refuse lorries that were cleaned between transport of different kinds of wastes. At Hovgården the waste was sieved (< 10 cm) and visible impurities (metal, plastic, glass and textile) were removed manually. The waste was then ground (13 mm), packed in polyethylene bags and cardboard boxes (25 kg/parcel), and frozen at –24 °C until extracted, composted, or anaerobically digested. Subsamples were taken out at regular intervals during packing to get representative samples of the whole material for the characterisation studies. The waste has been thoroughly characterized regarding visible impurities/objects, major classes of organic matter (such as lipids and proteins) and contents of plant nutrients and heavy metals (Eklind et al., 1997).

Figure 1: Photo by Mikael Pell, 1995

Composted and anaerobic digested source separated household waste

Compost investigated in Paper II and Paper V was prepared from the source separated household waste described above. Composting was performed during five months in isolated bins (125 L) that were rotated once a day. Straw from winter wheat (36%) was used as litter additive and water content was held at approximately 65% during composting. The temperature reached a maximum of 61 °C after five days and then decreased to the ambient after 70 days. The compost was then stored in an open polyethylene bag at 20 °C during ten months. Preliminary analyses of compost maturity parameters (Eklind et al., manuscript) showed that the carbon to nitrogen (C/N) ratio was 11 and the ammonia to nitrate (NH_4/NO_3) ratio was 0.02. This indicated that the compost was mature (Mathur et al., 1993).

Anaerobically digested waste investigated in Paper II and Paper V was also prepared from the source separated household waste described above. The anaerobic digestion of the household waste was performed at 37 °C (mesophilic digestion) or 55 °C (thermophilic digestion) in semicontinuous anaerobic digestors (45 l). The organic loading rate for mesophilic digestion was 3 g VS L^{-1} (VS = Volatile Solids) and for thermophilic digestion 5 g VS L^{-1} with a hydraulic retention time of thirty and nineteen days, respectively. The gas yield of the digestors (0.75 L g^{-1} VS), methane content (60%) and volatile solid reduction (60-70%) were maintained on the same levels from 1995 and during the investigations reported in this thesis.

Inocula for the biotransformation study of nonylphenol mono- and diethoxylates (NPEO1-2)

To investigate the potential for anaerobic microbial transformation of NPEO1-2 (Paper I), three different microbial inocula were used. 1) Microbially active sludge was derived from a 15 000 m^3 mesopholic anaerobic digestor treating waste water from a pulp plant. The digestor was also, on a few occasions per year, fed with waste water contaminated with NPEOs. The periodic addition of NPEOs gave rise to a final concentration of approximately 2 mg L^{-1} NPEOs in the digestor, a condition that had prevailed for at least four years at the time for sludge sampling. 2) Material from a landfill, where the above described sludge had been deposited, was sampled from a depth of 1.5 m below the surface of the landfill. 3) Landfill samples were also taken from a 20 year old municipal solid waste landfill.

Methods

Experimental, extraction and chemical analyses

Biotransformation of nonylphenol mono- and diethoxylates (NPEO1-2)

The experiments were performed in glass bottles to which sludge, landfilled sludge, or landfilled municipal solid waste were added. Unlabelled NPEO1-2, or NPEO1-2 labelled with ^{14}C in the aromatic ring, and mineral medium were added to the experimental bottles, which were then incubated (Paper I). The controls, and the experimental bottles that did not receive any NPEO1-2, were also incubated. Experimental bottles with labelled NPEO1-2 were sampled every second week for $^{14}CO_2$ and $^{14}CH_4$. Experimental bottles with labelled and unlabelled NPEO1-2 were frozen during the experimental period and later thawed and analysed to determine the extent to which added compounds were transformed.

Several techniques have been used in the past to enrich nonylphenol ethoxylates (NPEOs) from solid samples. Steam-destillation/solvent-extraction with cyclohexane (Giger et al., 1985), soxhlet with methanol as solvent (Marcomini & Giger, 1987), supercritical fluid extraction (SFE) with in situ derivatization (Lee & Peart, 1995) and liquid extraction with acetone, hexane and diethylether (Wahlberg et al., 1990) are examples of techniques that have been used. The aim of this study was to follow the qualitative transformation of the NPEOs. We choose a method, liquid-liquid extraction, that will enrich the NPEOs sufficiently. The controls and samples fortified with the lower concentration of NPEO1-2 (2 mg L^{-1}) were extracted with cyclohexane and samples fortified with the higher concentrations of NPEO1-2 (60 and 308 mg L^{-1}) were extracted with diethyl-ether. The diethyl-ether extracts were injected on a GC equipped with a flame ionization detector (FID). In order to detect lower concentrations, the cyclohexane extracts were derivatizised and injected on a gas chromatograph (GC) in coupled to a mass spectrometer (MS). Wahlberg et al., (1990) came to the conclusion that the pentafluorbenzoyl (PFB) derivatives had some advantages to heptafluorobutyric (HFB) derivatives, since PFB derivatives were stable for several days and they formed molecular ions intense enough to determine NP and NPEOs. These advantages made us use the pentafluorbenzoyl chloride (PFBCl) as the derivatization agent.

Major extractable organic compounds

The advantage with rapid and solvent free extractions and high extraction efficiency and selectivity inspired us to use the supercritical fluid extraction (SFE) technique in the investigations of the household waste. SFE with carbon dioxide as supercritical fluid was selected for enrichment of the major extractable organic compounds from the organic household waste (Paper II). Extraction parameters were chosen to extract sufficient amounts of the easily extractable organic compounds from the matrix for the qualitative and semi-quantitative analyses. The fresh, composted and anaerobically digested wastes were dried to 98, 57 and 88% dry weight, respectively, before extraction. Final analysis was performed using gas chromatography with mass spectrometric detection. Full scan spectra from the major peaks in the chromatogram were manually interpreted.

Berglöf (1997) showed that it is difficult to develope general SFE methods because all new analyte-matrix combinations require an extensive method development. This made us decide to use other, more universal, total extraction techniques in the experiments described in Papers IV and V.

Chlorinated paraffins

The Soxhlet extractions (Paper III) were performed during three hours in an automatic Soxtec system with dichloromethane as solvent. The extracts were treated with concentrated sulphuric acid saturated with cyclohexane, filtered and purified using size exclusion chromatography (SEC). Using a high performance liquid chromatography (HPLC) system with n-hexane as eluent, the extracts were further cleaned-up on a nitrophenylsilica column before analysis by GC-ECD. In order to minimize thermal degradation of CP, which is known to occur at high temperatures (Bergman et al., 1984), and to obtain high sensitivity, a short (5-7 m) capillary column was used. The GC separations were optimized to obtain as high sensitivity and selectivity concerning the different CP as possible.

The Pressurized Liquid Extraction technique (PLE) is based on same principles as traditional solvent extraction. When performing the solvent extraction at a high pressure, temperatures much above the atmospheric boiling point of the solvent can be used. The possibility to carry out the extraction at an elevated temperature leads to low solvent consumption and fast extraction compared to traditional liquid extraction techniques. In order to improve the extraction of CP from the household waste with respect to shorter extraction time, reduced amount of solvent and reduced number of interferences in the extract, several PLE parameters were investigated and the conditions were optimized (Paper IV).

PLE extractions (Paper IV) were performed using an accelerated solvent extraction system. The system pressure was held constant at 10 MPa during all extractions. The extraction process and extraction cycle are described by Waldebäck et al., (1998). An extraction temperature of 190 °C and a static extraction time of 2 x 10 minutes produced the highest recovery. Different solvents, drying agents, sample particle size and adsorbents were investigated. The extracts were treated with concentrated sulphuric acid saturated with cyclohexane before analysis on GC with electron capture detection (ECD).

Pesticides & PCB

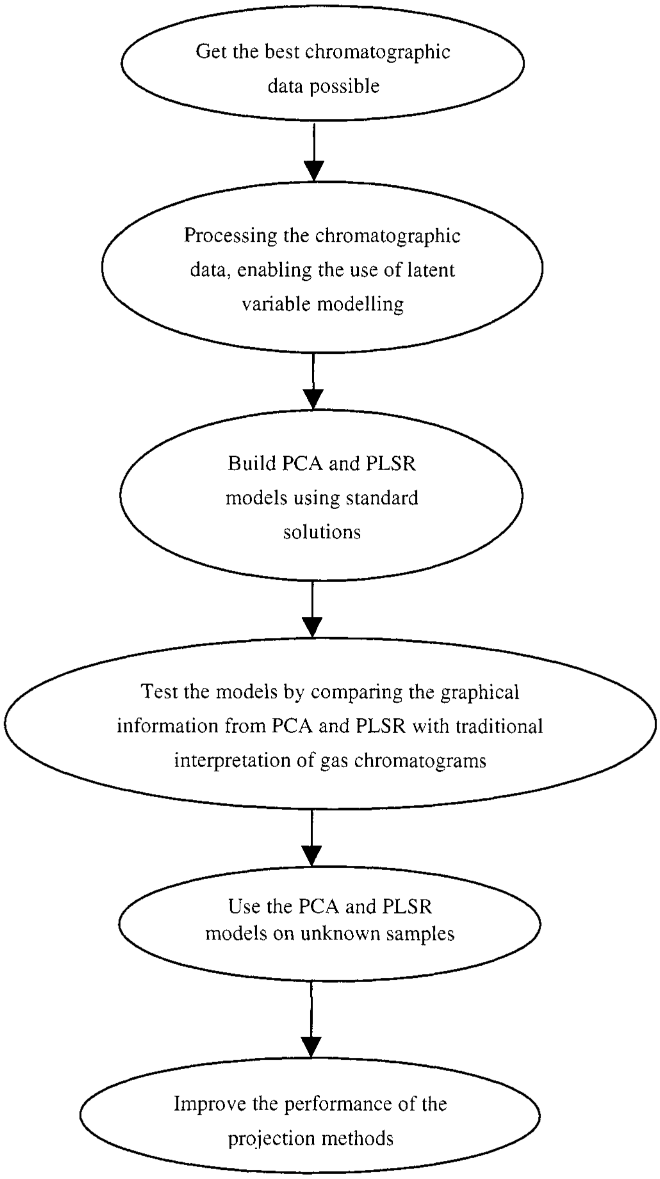
As the major part of the biodegradable fraction of the household waste is of plant origin (Nilsson et al., 1993), much of wich is treated with pesticides, it was important to investigate the presence and subsequent fate of pesticides in the fresh, composted and anaerobically digested waste. A multiresidue method was developed to enable a screening of several pesticides and PCB congeners in the waste (Paper V). The approach was described by Specht et al., (1985) for vegetables, meat, and fish. Pesticides were selected mostly from the Swedish National Food Administration (SLV) report (Andersson et al., 1995) of pesticides most frequently (based on number of findings) found in fruit, vegetables, cereals and cereal products. Pesticides included in a previous study concerning fate of pesticides under composting were also included as well as some triazines as they are active components in herbicide formulations that were available for households a few years prior to our sampling and might to an extent be used. In addition, some persistent chlorinated pesticides such as DDT and their metabolites, as well as the ubiquitously present PCB and HCB, that are industrial chemicals and incineration products respectively were included in the investigation.

The sample was mixed with a dessicant (Hydromatrix) and ground in a mortar and then extracted either in a soxhlet apparatus over night using acetone:dichloro-methane 3:1 or in a soxtec apparatus for three hours using acetone:dichloro-methane 1:1. The extract was filtered and cleaned up using SEC and silica gel fractionation. The extracts were analysed by GC-MS (EI and NCI). The persistent organohalogen pesticides, PCB and HCB were analysed in the two first silica fractions after treatment with concentrated sulphuric acid. To verify recoveries and elution profiles of pesticides and PCB, a mixture of pesticides was added to the extract. Recoveries were generally between 60 and 120% with a couple of exeptions with extremely high recoveries.

Multivariate methods

Multivariate methods have evolved rapidly over the past 10 years, largely driven by the widespread availability of powerful, inexpensive computers and implementations of multivariate tools in a number of commercially available software packages. Projection methods such as principal component analysis (PCA) and partial least squares regression (PLSR) extract systematic information from a combination of many measurement variables. They also offer a large number of interpretation features, to visualize patterns and relationships in easily interpretable graphical form. Multivariate analysis has been applied to a number of spectral and chromatographic methods in order to facilitate quantitative and qualitative analyses of complex samples. In a study performed by Andersson & Hämäläinen (1994) it was shown that pure chromatographic retention time profiles may be a source of information in latent variable projection methods from which quantitative and qualitative information can be extracted. Calibration

of overlapping chromatographic peaks (Faigle et al., 1991) and reduction of noise in data from GC-MS (Lee et al., 1991) using multivariate methods have been reported. The complex nature of CP led to difficulties with determination of them (Tomy et al., 1998). This led us to adopt a multivariate approach.
The strategy was:



The chromatographic data were pre-processed using the software ChromPro (BioTriMark, Björkkulla, Funbo, SE-75597 Uppsala, Sweden). The main steps were; noise reduction, baseline definition and subtraction, adjustment of retention times, and, finally, data reduction. The processed chromatographic data were exported to the software Unscrambler for multivariate analysis. In the multivariate datamatrix, the datapoints in chromatograms constitute the variables (x) and the object (y) is made up of the standards and samples. Latent variable projection methods, principal component analysis (PCA) and partial least square regression (PLSR) where used for the qualitative and quantitative interpretation of the chromatographic profiles. Both PCA and PLSR models were based on full cross validation. In order to give all variables the same variance they were weighed using the weighing option standardization (1/SDev). Regression models were built using standard solutions of eight different commercial CP, in order to be able to predict the concentrations of CP in the waste samples. To investigate if it was possible to increase the performance of the projection methods, variables corresponding to interferences in the waste sample extracts were excluded from the datamatrix, before the multivariate analysis. It was also investigated whether the transformation method, multiplicative scatter correction (MSC), made the variables more suitable for multivariate analysis.

Results and Discussion

Major organic compounds

Most of the organic compounds identified as major extractable organic compounds in the waste material (Paper II) are natural products. There were, however, some indications of organic contaminants among the identified compounds. The presence of equal levels of n-alkanes with odd and even numbers of carbon atoms in the chain may be an indication that the waste may have been contaminated with petroleum products. Gonzalez-Vila et al., (1982) found similar distribution in composted waste and suggest that they derive from fungi because the distribution is the same as in hydrocarbons from fungi. It seems unlikely, however, that the alkanes in the fresh household waste originate from fungi as these do not become abundant until in later stages of decomposition (Bertoldi et al., 1983).

There were also indications of bis-(2-ethylhexyl) phtalate (DEHP) in the source separated waste, in addition to the DEHP in the blanks. The presence of DEHP was expected, since DEHP is the most commonly used phthalate and ubiquitous in the environment (KemI, 1991; Heijkenskjöld, 1990).

The n-alkanes identified in the fresh household waste, indicateing a possible contamination with petroleum products, were found to be absent in the compost

(Paper I). This finding supports the investigations by Kästner et al. (1995) and Giusquiani et al. (1989) that alkanes are mineralized or decreased during composting and usually prone to oxidative degradation (Alexander, 1994). Quite contrary, Gonzalez-Vila et al. (1982) and Keeling et al. (1994) reported that alkanes are the main organic compounds in compost. Thus it seems that the composition of mature compost with respect to n-alkanes may vary. In the anaerobically digested waste n-alkanes became the major organic components when most of the more oxidized products (fatty acids and fatty acid esters) were degraded.

The results on fate of DEHP during composting and anaerobic digestion (Paper II) support previous studies on degradation of DEHP (Ejlertsson & Svensson, 1997; Staples et al., 1997), in which degradation was retarded to a higher extent under anaerobic conditions than under aerobic conditions.

Chlorinated paraffins

$C_nH_{2n+2-z}Cl_z$ (n=10-30, z=30-70%)
In the household waste quite high levels (0.5-48 µg/g dry matter) of chlorinated paraffins (CP) were found (Paper III and Paper IV). Two different types of CP were identified (Paper III), one highly chlorinated short chain and one medium chlorinated medium chain. PCA and traditional visual inspection of chromatograms were used to examine the CP in the waste.

CP have been produced since 1930 and today the total world production is approximately 300 kt/year (Tomy et al., 1998). They have found many applications and today the main uses are as flame-retardant plasticizers in vinyl plastics and as high-temperature lubricants in metal-processing industry (Tomy et al., 1998). CP are produced industrially by direct chlorination of petroleum n-alkane fractions under UV irradiation. The low positional selectivity of the reaction results in a very complex mixture of chlorinated alkanes with varying (10-30) carbon chain lengths and varying (30-70%) unspecific chlorination. CP mixtures thus fall into different categories based on the number of carbons (C_n) in the petroleum n-alkane fraction; short (C_{10}-C_{13}), medium (C_{14}-C_{17}) and long (C_{20}-C_{30}) chain CP. Carbon chain length and chlorine percentage also determine the properties of the chlorinated paraffin and their usefulness for different applications.

The determination of CP is complicated as the very high number of congeners results in that CP elute over a wide retention time when analysed with gas chromatography (GC) and there is no baseline resolution of the components. Different commercial CP can give rise to nearly the same chromatographic pattern, which leads to identification difficulties (Figure 2).

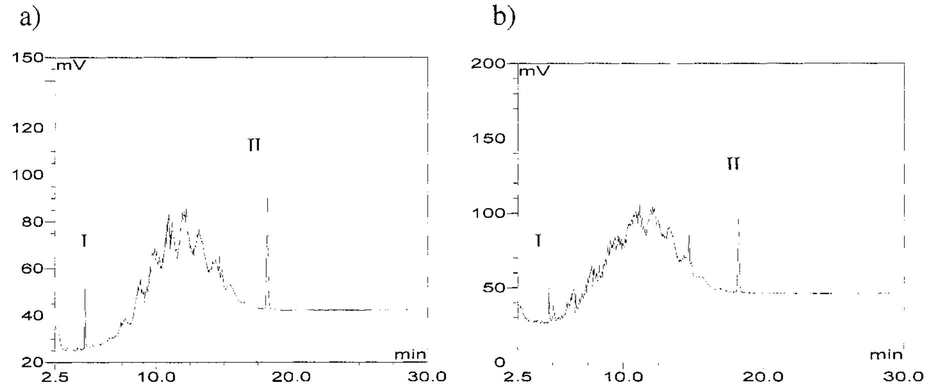


Figure 2. Electron capture detector gas chromatograms of two commercial chlorinated paraffins with different carbon chains (C) and degree of chlorination (%Cl). a) C_{10-13}, 60% Cl (4.76 µg/ml, b) C_{14-17}, 42% Cl (32 µg/ml). The standard solutions were fortified with α,α,α′,α′- tetrachloro-*o*-xylene (0.0019 ng ml^{-1}) (I) and 1,2,5,6,9,10-hexabromocyclododecane (0.185 ng ml^{-1}) (II) as internal standards.

It is obvious that it is difficult, if not impossible, to do a correct identification of CP by visual inspection of chromatograms. Using the wrong commercial CP as a standard will result in incorrect estimates of concentrations as the different mixtures are detected with considerable variation in sensitivity. The importance of a reliable identification of CP before quantifying has been stressed by Tomy et al., (1999b). The difficulty associated with the determination has resulted in limited information on levels and fate of CP in the environment (Tomy et al., 1998).

Other commonly found environmental contaminants acting as interferences make it even more difficult to perform reliable identifications as they overlap and obscure the chromatographic pattern of CP. Even if correction for interferences is made when quantifying CP (Rieger & Ballschmiter 1995; Tomy et al 1999), using methods described by Walter & Ballschmiter (1991), they obscure the CP pattern and obstruct identification. The reduced amounts of interferences in the extract when using PLE with cyclohexane as solvent show that PLE is a practicable technique for extraction of CP from such a complex matrix as household waste (Paper IV). After optimzing parameters such as extraction temperature, extraction time, solvent, drying agent, and sample particle size a mean recovery of 94% from waste samples fortified with CP was obtained.

Multivariate methods

The study presented in Paper III shows that the multivariate approach is suitable for the evaluation of chromatographic data of CP. In the PCA it was possible to distinguish between different types of CP, including those which were difficult to distinguish by visual inspection of the chromatograms. Differences between the CP seem to be more easily recognizable by PCA compared visual inspection of chromatograms, concequently the identification will be more trustworthy using PCA. However, the number of variables seems to have a lower limit. In the case with the waste samples most affected by interferences too much information was excluded which led to that the differences betweeen CP in the PCA plot were less obvious.

Since one of the principal components in the PCA was related to the concentration of CP it was possible to use the PCA for quantifying or estimating the concentration of CP in the waste. The advantage with PCA is that all chromatograms, both standards and samples, are included in the analysis and enables us to see what is information and what is noise. In principle the function of the PCA is to reduce the noise level, for which it also has been used in gas chromatography/mass spectrometry (Terrence et al., 1991).

The concentrations predicted with PLSR deviate from concentrations based on total peak area and concentrations estimated from the PCA plot. The reason for the deviation is most probably that the PLSR models do not cover all the variation in the waste sample chromatography data, because the models are built only on a "known" calibration set, in this case, the CP standards. In the literature where the theory of multivariate analysis is discussed (Kramer 1998; Martens & Naes 1989) it is stressed that the testing of the calibration model is very important in order to avoid inadequate calibration. In this study the PLSR models were not validated with waste samples with known concentrations of CP, which would have been desirable in order to provide information needed to better predict accuracy. However, cross-validation provides a certain amount of validation of a calibration, although not fully the level of information needed.

The source of contamination

Since the types of CP found in the waste have many different applications, such as additives in metalworking fluids, plasticizers for PVC and paints etc., it is impossible to point out the source based on the data currently available. The discussion about the source can only be speculative.

The samples analysed were taken out at regular intervals during packing in such a way as to be representative of the whole material. The results presented in Paper III indicate that the CP is distributed in the whole waste material, which led us to the assumption that the contamination is not caused by a particular household but rather occured during collection. The most probably candidate is hydraulic fluids leaking from the refuse lorries that transport the waste to the municipal composting plant at Hovgården. However, analysis of hydraulic fluid from one of the contractors transporting waste in Uppsala gave no positive results as no CPs were found. If the contamination arises from a particular household, the distribution in the whole material can be explained by the mixing of the material during the sampling procedure. In that case a rather high volume of for example a metalworking fluid must have been discarded into the biodegradable fraction of the household waste. The content of CP in metalworking fluids range from 2-80% or more (Tomy et al., 1998). It would therefore be possible to reach the concentrations we found in waste (Papers III and IV) if one litre of a fluid containing the higher amount of CP is discarded.

Pesticides & PCB

Currently used pesticides and persistent chlorinated pesticides as well as polychlorinated biphenyls (PCB) were identified in the fresh, composted and anaerobically digested household waste (Paper V). Most of the currently used pesticides found in the household waste are not registered for use in Sweden, but probably present in the waste due to contamination of imported fruits and vegetables. The acaricides bromopropylate and tetetradifon, the fungicides chlorothalonil (trace), diphenylamine (trace), quintozene, and vinclozoline, the herbicide; chlorpropham, the insecticides dieldrin, endrin (trace), parathion, phosalone, 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and its metabolite 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (DDE), and the insecticide and acaricide endosulfan (both the α and β isomers) and their metabolite endosulfan-sulphate were identified in the fresh household waste. Most of these pesticides, except endrin, dieldrin and quintozene were found quite frequently in fruit and vegetables by the Swedish National Food Administration (Andersson et al. 1995).

The analyses of the compost and anaerobically digested household waste show that the degradation rate of the various pesticides depend on the waste treatment processes. Some pesticides not found in the waste were found in either compost or anaerobic sludge e.g. the organophosphorous insecticides chlorpyrifos-ethyl and ethion, and the soil herbicide dichlobenil (trace) and its metabolite 2,6-dichlorobenzamide (trace). Obviously, the mineralization of the bulk material is more rapid than the degradation of these specific pesticides.

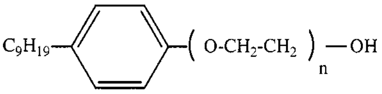
Persistent organic pollutants (POPs) include both the classical chlorinated pesticides, industrial chemicals such as polychlorinated biphenyls (PCB) and incineration products such as hexachlorobenzene (HCB). Due to their persistence in the Environment POPs are major environmental problems. Many are banned in most industrialised countries but still find use in economically less developed countries. DDT is e.g. used for malaria vector control and PCB is still used and produced in Russia. All POPs are present more or less ubiquitously since they undergo long-range atmospheric transport and may be deposited in even the most remote areas of the world. Due to their accumulation in higher trophic levels, the highest concentrations in human food are usually found in products of animal origin, such as fish, meat, and dairy products. In Sweden the main source for human intake are fish and dairy products (de Wit 1998). Therefore, we expected that the main source of POPs to the waste would fish and meat, even though approximately 70% of the material in a Swedish municipal compost is of plant origin (Nilsson et al. 1993). This may be the case for the organochlorine pesticides, but the results do not confirm this assumption for PCB. Generally, in animal tissues the most persistent congeners dominate whereas the less persistent (often those with low chlorination) are degraded much more rapidly. However, the PCB-profile in the fresh waste resembles that of the fairly low chlorinated technical product Arochlor 1242. Both the fact that so many low chlorinated congeners are present and that the profile resembles a technical mixture indicate that the source for the PCB is close to the collection chain of the household waste rather than in waste material of animal origin. Several technical applications of PCB in Sweden has left residues in various places that are very difficult to remove. Such a source within the transport chain may contribute to the PCB-contamination of the waste.

The pesticides in current use in industrial countries are generally considered to be non-persistent and are expected to degrade rapidly during composting and anaerobic digestion. However, in this study it is clear that some currently used pesticides found in the waste do not degrade fully during the processing period. Even more surprising, some pesticides that were not found in the waste appear in the compost and anaerobic sludge. This means that the relative degradation rate of the organic carbon in the waste material is more rapid than the pesticides, so that these after the composting or anaerobic degradation reaches levels above the detection limits of the respective compound. The effects of the levels reached in the compost and sludge are difficult to assess as few studies regarding the ecotoxicological consequences of currently used pesticides in these materials exist. However, for at least some compounds, such as chlorpyriphos-ethyl, the levels reached are within the range where ecotoxicological effects in soil are expected for other similar compounds in a study by Crommentuin et al., (1997).

Tetradifon is a currently used pesticide that we have found in all samples analysed. It has structural similarities to methylsulphone metabolites of PCB and DDE and most of all with bis(4-chlorophenyl)sulphone, an industrial compound recently found to contaminate all biota in the Baltic (Olsson & Bergman 1994). These sulphonated compounds often have a high tissue selectivity in living organisms (Bahrami 2000; Bergman et al. 1993; Brandt & Bergman 1987, Brandt et al. 1992), and it is possible that tetradifon in more ubiquitous in the environment than formerly realised if it accumulates in a tissue that is not normally analysed in environmental monitoring programmes.

The presence if dichlobenil and 2,6-dichlorobenzamide (BAM, a degradation product of dichlobenil) are diffucult to understand. Dichlobienil is a soil herbicide taken up via the roots and should not normally be present in any vegetables or fruits. The most plausible source is that the machines used at the composting plant also have been used to shovel soil contaminated with these compounds. Products containing dichlobenil were deregistered in Sweden around 1990, but residues of these compounds are still found in the soil and groundwater of many areas (Wallman 2000).

Biotransformation of nonylphenol mono- and diethoxylates (NPEO1-2)



n= 4-40

Nonylphenol ethoxylates (NPEOs) are mixtures of polyethoxylated monoalkylphenols, predominantly parasubstituted, with the number of ethoxy groups varying between 4-40. NPEOs are used as surfactants in industries and in households and in Sweden the major uses are in the manufacturing of paints and plastics, detergents, lubricant and pesticides (KemI 1991). The original compounds are known to degrade rather rapidly in the environment (Giger 1984; Ahel 1994b. Complete degradation of NPEOs is reported to occur under aerobic conditions (Ekelund et al., 1993; Ahel et al., 1994a) but they have been reported to be more persistent in anaerobic environments (Ekelund et al., 1993). Our own studies also show that NP is more persistent under anaerobic conditions (Paper I).

The main interest in NPEOs are, their degradation products. The degradation products nonylphenol mono- and diethoxylates (NPEO1-2) and especially nonylphenol (NP) have been shown to have ecotoxicological effects. NP is known to act as an environmental hormone and stimulate the same processes as oestradiol with the risk of being hazardous to the reproduction of living organisms (Danzo 1998). NPEO1-2 and NP have shown a considerable potential for bioaccumulation in both freshwater organisms and birds (Ahel et al., 1993). Recently, it was reported that concentrations of NP in sediment could be high enough to approach chronic effects in wild fish (Lye et al., 1999).

Anaerobic microorganisms in all inoculates included in the study in Paper I transformed parts of added NPEO1-2 to NP at a concentration of 2 mg NPEO1-2 L^{-1}. The highest degree of transformation occurred with the two landfill inocula. The background content of NP in the landfilled MSW was found to be relatively high. A transformation of NPEO1-2 would only increase the NP concentration 5-10%. Therefore, the absolute concentrations of NPEO1 and NPEO2 were presented for the landfilled MSW while relative proportions between NP, NPEO1 and NPEO2 were presented for the other inocula (Paper I). The relatively high concentration of NP in the landfilled MSW was most likely a result of previous extensive use of 4-nonylphenol polyethoxylates as nonionic surfactants in industrial and household detergents. The occurrence of high NP concentrations is not surprising, but agrees with the concentrations observed for NP (<10-107 ug L^{-1}) in landfill leachate (Öman & Hynning, 1993). Assuming that NP is adsorbed on the solids of the leachate and the dry matter content of mature landfill leachate is in the range of 0.5 to 5 g L^{-1}, the concentration of NP will be in the range of <2-214 mg NP per kg solids of leachate.

The absolute concentrations of NPEO1 and NPEO2 decreased significantly within 22 days of incubation with the landfill MSW inoculi. In bottles containing landfilled digestor sludge the relative proportion of NP increased from 0.15% to 81% during 53 days of incubation, whereafter the proportional distribution of the homologues remained constant. In the samples with 10 and 100% anaerobic digestor sludge amended with 2 mg NPEO1-2 L^{-1}, NP levels increased steadily during the experiment, at the end of which the NP level was 57% in the 100% digestor sludge sample and 31% in the 10% sludge sample.

Transformation of NPEO1-2 was also observed at a concentration of 60 mg NPEO1-2 L^{-1}, in both landfill inocula. Transformation of NPEO1-2 also occurred in 100% sludge amended with 60 mg NPEO1-2 L^{-1} where the NPEO2 was transformed to NPEO1. No transformation occurred in the diluted sludge inoculum.

At 308 mg L^{-1} less than 1% of the added NPEO1-2 was transformed into NP in the undiluted sludge and the landfilled sludge inoculum.

Transformation of NPEO1-2 or formation of NP were not observed in the autoclaved incubations which supports earlier investigations that NPEO are biotransformed. Quite recently John & White (1998) established the mechanism that the biotransformation commences at the hydrophilic part of the molecule via successive exoscission of the ethoxylate chain.

The explanation for the relatively high transformation efficiency in both landfill inocula may be by that the microorganisms in the landfills had adapted to the short-chain nonylphenol polyethoxylates. The digestor sludge landfill most probably contained short chain NPEOs as it is known that the long chain degrades fast. For landfilled MSW the same reasoning could be applied owing to the previously extensive use of 4-nonylphenol polyethoxylates. The decrease in transformation efficiency in the 10% digestor sludge compared to the 100%

digestor sludge can be explained by the dilution, resulting in a decreased microbial density.

There were several indications of absence of cleavage or further breakdown of the aromatic structure during the incubation period. No $^{14}CO_2$ or $^{14}CH_4$ could be detected in any of the experimental bottles to which labeled NPEO1-2 had been added and almost all of the labelled material was found in the organic solvent phase and on the solid particles.

The fact that a substantial fraction of the labelled material occurred in the solid phase of some inocula may have implications for the degradation process. Sorption of the compounds to the solids decreases the susceptibility of these short-chained hydrophobic compounds to microbial attack, thus promoting their persistence in contaminated systems. It has been reported earlier that the degradation of short-chained NPEOs in sewage treatment plants as well as in natural aquatic environments are affected not only by microbial activity but also by physicochemical processes (Ahel et al., 1994b; John et al., 2000).

Our observations on the degradation of NPEO1-2 are in accordance with earlier reports (Giger et al., 1984; Wahlberg et al., 1990) showing that under anaerobic NPEOs can be degraded to NP, which is far more persistent than its parental compounds.

Reflections and Future research

The results presented in this thesis show that organic contaminants are present in fresh source separated organic household waste.

It is important to increase the understanding of how the organic fraction of household waste can be contaminated with technical products such as chlorinated paraffins (CP) and polychlorinated biphenyls (PCB). The present studies have been based on fresh source separated household waste collected in February, 1995, in Uppsala, Sweden. Continous sampling during one year would give more information whether the contaminants occurring accidental or constantly.

Most of the pesticides found in the fresh, composted and anaerobically digested household waste are not registered for use in Sweden. The pesticide contents in the waste will vary during the year, depending on from which country fruits and vegetables are imported. Therefore, it would be of interest to continue the analytical work on pesticides in fresh household waste and the products thereof, on samples collected during an entire year. This will give a more complete picture of which pesticides should be selected to further elucidate the differences between the processes and to more comprehensively evaluate the impact of pesticides on composted and anaerobically digested waste.

The method development using high diffusion liquids, such as supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) have been rewarding. In the continued work on contaminants identified in the waste, it would be desirable to make use of the potential of SFE concerning selectivity. In identification of key pollutants the (PLE) technique should be preffered since it is a more universal total extraction method.

The multivariate method showed to be a very useful tool to explore information in chromatographic data. Within this study only a limited selection of methods for improvement of the performance of the projection method has been used. The method have considerable possibilites that must be investigated further. It is also important to do a more elaborate validation of the method, with samples with known concentrations, to probe in more detail the limit of the method.

References

Ahel, M., Giger, W. & Koch, M. 1994b. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment- I. Occurence and transformation in sewage treatment. *Wat. Res. 28,* 1131-1142.

Ahel, M., Giger, W. & Schaffner, C. 1994c. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment- II. Occurence and transformation in rivers. *Wat. Res. 28*, 1143-1152.

Ahel, M., Hrsal, D. & Giger, W. 1994a. Aerobic tranformation of short-chain alkylphenol polyethoxylates by mixed bacterial cultures. *Arch. Environ. Contam. Toxicol. 26,* 540-548.

Alexander, M. 1994. *Biodegradation and Bioremediation*, 302 pp. New York: Academic press.

Andersson, A., Bergh, T., Jansson, A. & Pålsheden, H. 1995. *Pesticide Residues in Food of Plant Origin 1994.* Livsmedelsverket (The Swedish National Food Administration), Rapport 20/96

Andersson, R. & Hämäläinen, M.D. 1994. Simplex focusing of retention times and latent variable projections of chromatographic profiles. *Chemomet. Intelligent Lab. Syst. 22*, 49-61.

Anonymous 1996a. *Aktionsplan avfall,* Report 4601, 138 pp. Stockholm: Swedish Environmental Protection Agency. (In Swedish).

Anonymous 1996b . *The Unscrambler 6 user's guide*, 372 pp. Trondheim: Camo AS.

Bahrami, F. 2000. Methylsulphonyl-chlorobenzenes and the olfactory system: comparative toxicity of the 2,5- and 2,6-dichlorinated isomers in mice. PhD-Thesis Uppsala University.

Berglöf, T. 1997. Supercritical fluid extraction (SFE) in environmental analysis. Total extraction and study of pesticides retention in soil. PhD Thesis, Acta Universitatis Agriculturae Sueciae, Agraria 70, Uppsala, Sweden, 33 pp.

Bergman, Å., Hagman, A., Jacobsson, S., Jansson, B. & Åhlman M. 1984. Thermal degradation of polychlorinated alkanes. *Chemosphere 13*, 2, 237-250.

Bergman, Å., Haraguchi, K., Athanasiadou, M. & Larsson, C. 1993. Selective retention of PCB methyl sulphonesin liver of mammals. Organohalogen Compounds 14, 199-203.

Bertoldi, M. de, Vallini, G. & Pera, A. 1983. The biology of composting: A review. *Waste Manage. Res. 1*, 157-176.

Brandt, I. & Bergman, Å. 1987. PCB methyl sulphones and related compounds: Identification of target cells and tissues in different species. *Chemosphere 16*, 1671-1680.

Brandt, I., Jönsson, C.-J. & Lund, B.-O. 1992. Comparative studies onadrenocorticolytic DDT-metabolites. *Ambio 21,* 602-607.

Crommentuijn, T., Kalf, D.F., Polder, M.D., Posthumus, R., van de Plassche, E.J. 1997. Maximum Permissible Concentrations and Negligible Concentrations for Pesticides. Report no. 601501 002, National Institute of Public Health and the Environment [Rijkinstitut voor Volksgezondheid en Mileu, RIVM] Bilthoven, The Netherlands).

Danzo, B.J. 1998. Review. The effects of environmental hormones on reproduction. *CMLS Cell. Mol. Life Sci.* 54, 1249-1264.

de Wit, C. 1998. in Monitor 16: *Persistent Organic Pollutants - A Swedish View of an International Problem.* Swedish Environmental Protection Agency, p 126.

Ejlertsson, J. & Svensson, B.H. 1997. Degradation of bis-(2-ethylhexyl) phthalate constituents under methanogenic conditions. *Biodegradation 7*, 501-506.

Ekelund, R., Granmo, Å., Magnusson, K., Berggren, M. & Bergman, Å., 1993. Biodegradation of 4-nonylphenolinseawater and sediment. *Environ. Pollut. 79*, 59-61.

Eklind, Y., Beck-Friis, B., Bengtsson, S., Ejlertsson, J., Kirchmann, H., Mathisen, B., Nordkvist, E., Sonesson, U., Svensson, B.H. & Torstensson, L. 1997. Chemical characterization of source-separated organic household wastes. *Swedish J. Agric. Res. 27*, 167-178.

Eklind, Y., Rämert,B & Wivstad, M. Manuscript. Propagation of lettus (*Lactuca sativa L.*) transplants using organic growing media.

Faigle, J.F., Poppi, R.J., Scarminio, I.S. & Bruns, R.E. 1991. Multi-component principal component regression and partial least-squares analyses of overlapped chromatographic peaks. *J. Chromatogr. 539*, 123-132.

Giger, G., Brunner, P.H. & Schaffner, C. 1984. 4-Nonylphenol in sewage sludge: Accumulation of toxic metabolites from nonionic surfactants. *Science 225*, 623-625.

Giusquiani, P.L., Patumi, M. & Businelli, M. 1989. Chemical composition of fresh and composted urban waste. *Plant Soil 116*, 278-282.

Gonzalez-Vila, F.J., Saiz-Jimenez, C. & Martin, F. 1982. Identification of free organic chemicals found in composted municipal refuse. *J. Environ. Qual. 11*, 2, 251-254.

Heijkenskjöld, L. 1990. Ftalater. In (KemI report 10/90) *Appendix*, 157-171. Swedish Chemical Inspectorate, Stockholm, Sweden (In Swedish).

John, D.M. & White, G.F. 1998. Mechanism forbiotransformation of nonylphenol polyethoxylates to xenoestrogens in *Pseudomonas putida. J. Bacteriol. 180, 4332-4338.*

John, D.M., House, W.A. & White, G.F. 2000. Environmental fate of nonylphenol ethoxylates: Differential adsorption of homologs to components of river sediment. *Environ. Toxicol. Chem. 19*, 2, 293-300.

Kästner, M., Lotter, S., Heerenklage, J., Breuer-Jammali, M., Stegmann, R. & Mahro, B. 1995. Fate of ^{14}C-labelled antracene and hexadecane in compost-manured soil. *Appl. Microbiol. Biotechnol. 43*, 1128-1135.

Keeling, A.A., Mullett, J.A. & Paton, I.K. 1994. GC-Mass Spectrometry of refused-derived composts. *Soil Biol. Biochem. 26*, 773-776.

KemI. 1991. Risk Reduction of Chemicals, a Government Commission Report. TheSwedish National Chemicals Inspectorate, Report No 1/91, pp 201-218.

Kramer, R 1998. *Chemometric Techniques for Quantitative Analysis*, vi + 203 pp. Marcel Dekker, New York.

Lee, T.A., Headley, L.M. & Hardy, J.K. 1991. Noise Reduction of Gas Chromatography/Mass Spectrometry Data Using Principal Component Analysis. *Anal. Chem. 63*, 357-360.

Lee, H.-B. & Peart, T.E. 1995. Determination of 4-nonylphenol in effluent and sludge from sewage treatment plants. *Anal. Chem. 67*, 1976-1980.

Lye, C.M., Frid, C.L.J., Gill, M.E., Cooper, D.W. & Jones, D.M. 1999. Estrogenic alkylphenols in fish tissues, sediments and waters from the U.K. tyne and tees estuaries. *Environ. Sci. Technol.* 33, 1009-1014.

Marcomini, A. &Giger, W. 1987.Simultaneous determination of linear alkylbenzenesulfonates, alkylphenol polyethoxylates, and nonylphenol by high-performance liquid chromatography. *Anal. Chem. 59*, 1709-1715.

Martens, H. & Naes, T. 1989. *Multivariate Calibration,* 419 pp. Wiley: New York.

Mathur, S.P., Owen, G., Dinel, H. & Schnitzer, M. 1993. Determination of compost biomaturity. I. Literature review. *Biol. Agric. Hort. 10*, 65-85.

Nilsson, P., Persson, P.-E., Schroeder, H. & Fergedahl, S. 1993. Utvärdering av källsortering och lokal hemkompostering en fallstudie i HSB BRF Tusenskönan, Västerås och västra Orminge, Nacka. Ett Reforsk-projekt FoU nr 84, 231 pp. (In Swedish).

Olsson, A. & Bergman, Å. 1994. A new persistent contaminant detected in Baltic wildlife: Bis(4-chlorophenyl)sulfone. *Ambio 24*, 119-121.

Öman, C. & Hynning, P.-Å. 1993. Identification of organic compounds in municipal landfill leachates. *Environ. Pollut. 80*, 265-271.

Rieger, R. & Ballschmiter, K. 1995. Semivolatile organic compoundspolychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), biphenyls (PCB), hexachlorobenzene (HCB), 4,4´-DDE and chlorinated paraffins (CP) - as markers in sewer films. *Fresenius' J. Anal. Chem. 352*, 715-724.

Specht, W. & Tillkes, M. 1985. Gas-chromatographische Bestimmung von Rückständen an Pflanzenbehandlungsmitteln nach Clean-up über Gelchromatographie und Mini-Kieselgel-Säulen-Chromatographie. *Fresenius' Z. Anal. Chem. 322*, 435-455. (In German)

Staples, C.A., Peterson, D.R., Parkerton, T.F. & Adams, W.J. 1997. The environmental fate of phthalate esters: A literature review. *Chemosphere 35*, 4, 667-749.

Terrence, A. L., Headley, L.M. & Hardy, J.K. 1991. Noise reduction of gas chromatography/mass spectrometry data using principal component analysis. *Anal. Chem. 63*, 357-360.

Tomy, G.T., Fisk, A.T. & Muir, D.C.G. 1998. Environmental chemistry and toxicology of polychlorinated n-alkanes. *Rev. Environ. Contam. Toxicol. 158*, 53-128.

Tomy, G.T., Westmore, J.B., Stern, G.A., Muir, D.C.G. & Fisk, A.T. 1999. Interlaboratory study on quantitative methods of analysis of C_{10}-C_{13} polychloro-n-alkanes. *Anal. Chem. 71*, 446-451.

Wahlberg, C., Renberg, L. & Wideqvist, U. 1990. Determination of nonylphenol and nonylphenol ethoxylates as their pentafluorobenzoates in water, sewage sludge and biota. *Chemosphere 20*, 179-195.

Waldebäck, M., Jansson, C., Señoráns, F.J. & Markides, K.E. 1998. Accelerated solvent extraction of the antioxidant Irganox 1076 in linear low density polyethylene (LLDPE) granules before and after γ-irradiation. *Analyst 123*, 1205-1207.

Wallman, K. (2000) Atrazine and dichlorobenxamide residues in the ground water of Uppsala: The source of the contamination. Diploma thesis, Dept. Environ. Assess., Swed. Univ. Agric. Sci. Report 2000:7.

Walter, B. & Ballschmiter, K. 1991. Quantitation of camphechlor/toxaphene in cod-liver oil by integration of the HRGC/ECD-pattern. *Fresenius' J. Anal. Chem. 340*, 245-249.

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