





ABSTRACT

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Potential of municipal sewage treatment plants to remove bis(2-ethylhexyl) phthalate

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Yhteenvedo: Bis-(2-etyyliheksyyli)ftalaatin poistaminen jätevesistä yhdyskunta-jätevedenpuhdistamoilla

Diss.

The removal of bis(2-ethylhexyl) phthalate (DEHP) at municipal sewage treatment plants (STPs) was studied at full-scale plants and in experiments carried out with sewage, reject water and sludge containing native DEHP. DEHP concentration in Finnish sewages was typically at a level of 100 µg/l. Most of the DEHP was sorbed to colloidal or settleable solids, while less than 6% was in dissolved state or sorbed to soluble organic matter. Typically, more than 90% of DEHP was removed from sewage at STPs, and secondary effluent concentrations were lower than 8 µg/l. The removal was a result of both biodegradation in activated sludge stage and sorption to primary and secondary sludges. DEHP concentrations in primary and secondary sludges and anaerobically digested sludges were often higher than 100 mg/kg dw, which is the proposed maximum value for DEHP in sludges to be used in agriculture. Reject waters together with return secondary sludge are usually returned to the headworks of the STP, and give rise to an internal circulation of pollutants, which in the case of DEHP may be as high as the load in sewage. DEHP is effectively removed from reject waters by improving solids separation or in nitrogen-removing sequential batch reactors (SBRs), partly by biodegradation and partly by sorption to sludge. The results indicate that anaerobic biodegradation occurred during the digestion of sludge. Composting and aeration efficiently removed DEHP from both raw and anaerobically digested sludge. During sludge aeration, a part of the DEHP originally weakly bound to the sludge matrix became more strongly bound, but it was able to biodegrade in a later phase of the aeration. The results of the study suggest that DEHP that is sorbed to the sludge matrix is biodegraded after desorption, which is aided by the decomposition of organic sorption sites. In conclusion, if properly operated, STPs have the potential to efficiently remove DEHP from sewage and reduce its load to the environment.

Key words: Biodegradation; composting; DEHP; digestion; reject water; removal; sewage treatment plant; sludge; sorption-desorption; wastewater.

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LIST OF ORIGINAL PUBLICATIONS

This thesis summarises results presented in the following articles, which are referred to in the text by their Roman numerals I-V. The experiments and methodologies I planned together with my supervisor Professor Jukka Rintala, with the aid of Dr. Riitta Kettunen in the case of papers I and II and with the aid of Acting Professor Kari Hänninen in the case of paper IV. I performed a significant part of the experimental work in all studies. Study III was carried out in co-operation with Ms Maria Ruissalo and the practical work in study V in co-operation with Ms Riitta Ryyänen. All the materials for the papers were compiled and processed and the papers written by myself under the supervision of Professor Jukka Rintala.

- I Marttinen, S. K., Kettunen, R. H. & Rintala, J. A. 2003. Occurrence and removal of organic pollutants in sewages and landfill leachates. *Sci. Tot. Environ.* 301: 1-12.
- II Marttinen, S. K., Kettunen, R. H., Sormunen, K. M. & Rintala, J. A. 2003. Removal of bis(2-ethylhexyl) phthalate at a sewage treatment plant. *Wat. Res.* 37: 1385-1393.
- III Marttinen, S. K., Ruissalo, M. & Rintala, J. A. 2004. Removal of bis(2-ethylhexyl) phthalate from reject water in nitrogen-removing sequencing batch reactor. *J. Environ. Manage.* 73: 103-109.
- IV Marttinen, S. K., Hänninen, K. & Rintala, J. A. 2004. Removal of DEHP in composting and aeration of sewage sludge. *Chemosphere* 54: 265-272.
- V Marttinen, S. K., & Rintala, J. A. Sorption and biodegradation of bis(2-ethylhexyl) phthalate during aeration of sewage sludge determined by sequential supercritical fluid extraction. (Manuscript)

ABBREVIATIONS

amu	Atomic mass unit
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DEHP	Bis(2-ethylhexyl) phthalate
DN/N	Denitrification-nitrification process
dw	Dry weight
F/M	Food to microorganisms ratio
GC-MS	Gas chromatography with mass spectrometric detection
HRT	Hydraulic retention time
MEHP	Mono(2-ethylhexyl) phthalate
MLSS	Mixed liquor suspended solids
NH ₄ -N	Ammonium-nitrogen
NO ₃ -N	Nitrate-nitrogen
PVC	Polyvinyl chloride
SBR	Sequential batch reactor
SCOD	Soluble chemical oxygen demand
SFE	Supercritical fluid extraction
SIM	Selected ion monitoring
SRT	Sludge retention time
SS	Suspended solids
STP	Sewage treatment plant
TCOD	Total chemical oxygen demand
tot-N	Total nitrogen
TS	Total solids
v	Volume
VS	Volatile solids
VSS	Volatile suspended solids
w	Weight

1 INTRODUCTION

In this work, study was made of the occurrence and removal of bis(2-ethylhexyl) phthalate (DEHP) in different stages of municipal sewage treatment plants (STPs). The objective was to better understand the mechanisms by which DEHP is removed and provide a foundation upon which to improve plant operation and treatment methods.

1.1 Properties of DEHP

DEHP is an industrially produced organic compound belonging to a group of chemicals called phthalic acid esters or phthalates. DEHP is extensively used to plasticize polyvinylchloride (PVC), which is used in e.g. wires and cables, floorings, roofing, wall coverings, flexible film, sheeting and clothing (Anon. 2001). A minor amount of DEHP is used as an additive in non-polymer applications such as lacquers, paints, printing inks, rubber and ceramics. DEHP has been industrially synthesized since 1932 (Graham 1973). The global production of DEHP in 1994 was estimated at one to four million tonnes (Anon. 2001). Chemically, DEHP is an ester of 1,2-benzenedicarboxylic acid and 2-ethyl hexanol. Some physico-chemical properties of DEHP are given in Table 1.

Since DEHP is not bound to the PVC polymer or other matrices with covalent chemical bonds, it slowly migrates to the surface of the matrix, where it is lost during use of products or after disposal. It also may be released to the environment during production, distribution, incorporation into products and waste incineration (Anon. 2001). The widespread applications of DEHP make it a ubiquitous environmental pollutant. Part of the DEHP released to the environment ends up in wastewater and finally at STPs.

TABLE 1 Physico-chemical properties of DEHP.

Parameter	Unit	Value
CAS No.		117-81-7
Molecular formula		C ₂₄ H ₃₈ O ₄
Molecular weight	g/mol	390.6
Physical state at 20°C		Liquid
Melting point	°C	-55 (pour point)
Boiling point	°C	ca. 230
Density	g/ml	0.980–0.985
Vapour pressure at 20°C*	Pa	0.000034
Water solubility at 20°C*	mg/l	0.003
Partition coefficient; n-octanol-water (log K _{ow})*		7.5
Henry's Law constant*	Pa•m ³ /mol	4.43

*A wide range of values are available in the literature. The values here are those used in the EU risk assessment for DEHP (Anon. 2001)

DEHP has been a subject of public debate during recent years because of its possible health effects on humans or damage to the environment. The EU is currently carrying out a risk assessment of DEHP (Anon. 2001), which should be completed in 2004. DEHP is regarded as not acutely toxic to aquatic organisms at exposure levels far exceeding its apparent water solubility. It is also regarded as not harmful to soil organisms. Exposure via food, however, indicates effects on fish. The main concern with DEHP is that it is suspected of being a reproductive, developmental and teratogenic toxicant (NTP-CERHR 2000).

According to current knowledge, DEHP does not biomagnify in aquatic food-webs (Gobas et al. 2003). Bioconcentration and bioaccumulation factors of DEHP in aquatic organisms are below the bioaccumulation criterion of 5000 proposed by the United Nations Environmental Program (UNEP). Bioaccumulation in terrestrial organisms is assumed to be rather low, and in terrestrial plants it is limited by the high affinity of DEHP to organic matter (Anon. 2001).

Some recommendations for DEHP concentrations in natural and technical environments exist. The maximum concentration for DEHP in household water recommended by WHO (1996) is 8 µg/l. In a working EU document concerning sewage sludge (European Commission 2000), the proposed maximum value for DEHP in sludge destined for use in agriculture is 100 mg/kg dry sludge. In Denmark, the limit of 50 mg/kg dry sludge has been in place since 2000 (Knudsen et al. 2000).

1.2 DEHP at sewage treatment plants

1.2.1 Fate processes for organic compounds

Municipal STPs treat a variety of wastewaters including municipal sewage, industrial effluents, landfill leachates and stormwater runoffs. At conventional STPs, combined sewage treatment typically comprises primary sedimentation followed by aerobic biological treatment with secondary sedimentation (Metcalf & Eddy 1991). Primary and secondary sludges are combined, thickened, stabilized (e.g. by anaerobic digestion) and dewatered. The reject waters from thickening and dewatering are returned to the headworks of the STP. Secondary effluent is discharged to a receiving water body. The most common final destinations for sludge are agricultural use, energy production and landfilling (Matthews 2001). In Finland, the most common uses are in agriculture and green building (Paatero 2000). Tighter controls on landfilling can be expected in future, and incineration is under serious consideration in many Finnish plants. STPs act as a barrier against environment contamination with wastewater pollutants. If not removed in STP processes, organic pollutants will contaminate the water environment via secondary effluent discharges, and sludge utilization in agriculture or green building will contaminate soils.

The main alternatives for an organic compound entering the STP are sorption on sewage or sludge solids, desorption, chemical or biological degradation or transformation, volatilization or stripping, and passing through the process unchanged (Rogers 1996; Byrns 2001). The fate and removal of a compound is governed by its physico-chemical properties and the process design and operating conditions (Clark et al. 1995).

1.2.2 Biodegradation of DEHP

The most desirable fate for DEHP at an STP is mineralization or degradation to harmless by-products. The degradation of DEHP by different micro-organisms and in various media has been investigated in many studies, as reviewed by Staples et al. (1997) and in a DEHP risk assessment by the EU (Anon. 2001). There has been wide variation in the results of tests measuring the ready biodegradation of DEHP. A mineralization rate of 4 to 86% after 28 days has been reported. The marked differences in the tests results are considered to be related to the low solubility of DEHP and adaptation of the sludge to the test compound. Scholz et al. (1997) showed that DEHP meets all the criteria for ready biodegradability, including 60% degradation within the 10-day window and 80% degradation during 28 days. They used an internationally accepted test system (the modified Sturm test), where the test substance is incubated in a mineral medium and inoculated with a small amount of sewage sludge, and the amount of carbon dioxide that is generated is determined.

Another type of test used for measuring DEHP biodegradability is the primary degradation test, where decrease of the parent compound is measured.

Saeger & Tucker (1976) and O'Grady et al. (1985) reported 70–85% transformation of DEHP after 24 hours in a semicontinuous activated sludge (SCAS) test, where they used activated sludge obtained from municipal STPs.

Although laboratory studies suggest that DEHP should be readily biotransformed in STPs, high DEHP concentrations have been detected in STP sludges. Several factors may account for the different biodegradabilities obtained in laboratory experiments and field studies. In the laboratory, activated sludge typically is spiked with DEHP concentrations of several mg/l, which considerably exceeds the aqueous solubility of DEHP (0.003 mg/l, Table 1). In such high concentrations, DEHP may form a dispersion with the water phase, in which the extent and kinetics of biodegradation of DEHP are different than they are in dissolved state. Although sorption may also occur in spiking experiments, the bonds between contaminant and the sorption site are assumed to be stronger in real wastewater because of longer contact time (Hatzinger & Alexander 1995). Thus, DEHP may be much less bioavailable in real wastewater than when spiked. Furthermore, in laboratory experiments DEHP has been the sole carbon source, unlike in STPs where microbes capable of degrading DEHP may favour other substrates easier to use as a carbon source. Although laboratory studies have their place, the best way to understand the complete biodegradation behaviour of DEHP is to study native DEHP in its typical concentrations at real STPs.

Laboratory experiments indicate that under anaerobic conditions, DEHP is persistent to biodegradation in sludge (Shelton et al. 1984; Ziogou et al. 1989; Painter & Jones 1990). Anaerobic degradation of DEHP has nevertheless been reported to occur in soil matrix (Shanker et al. 1985) and in methanogenic landfill conditions (Ejlertsson, 1997).

Both aerobic and anaerobic biodegradation of DEHP are suggested to begin with ester hydrolysis and the formation of mono(2-ethylhexyl) phthalate (MEHP) and corresponding alcohol. MEHP is an active metabolite of DEHP in organisms, but little is known of the extent of direct exposure to MEHP in the environment. Further mineralization of DEHP is discussed, for example, in Staples et al. (1997).

Abiotic degradation of DEHP by hydrolysis can be regarded as negligible at the pH values prevailing in STP processes (Staples et al. 1997). Likewise, photodegradation of DEHP in water solutions is low and does not represent an important transformation process at STPs.

1.2.3 Sorption and desorption of DEHP

The high log K_{ow} and low water solubility of DEHP (Table 1) indicate hydrophobicity and high affinity to solid surfaces and dissolved organic matter. In the environment, DEHP occurs mainly sorbed to organic matter in solids, which makes it less bioavailable (Peterson & Staples 2003).

It is usually assumed that chemicals bound to solid phase are non-degradable (European Commission 1996). In their review of phthalates biodegradation data, however, Peterson & Staples (2003) conclude that DEHP

biodegradation is probably occurring in the sorbed phase, although at a lower rate than in soluble phase. The reasons they suggest for this are the sorption to organisms capable of degrading phthalates and the ability of interfacial surfaces to concentrate both the phthalate and degrading organisms.

A compound may be sorbed within a matrix in many different ways, e.g. by chemical or physical bonding or by molecular diffusion (Pignatello & Xing 1996). Sorption is also assumed to be reversible, i.e. the sorbed compound may be desorbed (Peterson & Staples 2003). Chemicals age as the contact time between compound and matrix increases, which can be seen in the stronger binding of compounds to the matrix, resulting in decreased bioavailability and lower yield in analytical extractions as well as reduced toxicity in the environment (Alexander 1995).

In activated sludge stage at an STP, particles are introduced to an environment where they may further be sorbed to sludge or the organic fraction of particles may undergo biotransformation. The sorbed pollutants may accumulate to sludge or they may be desorbed as the sorption sites decompose (Pignatello & Xing 1996). The desorbed compounds are bioavailable and may undergo biotransformation or mineralization, or they may be sorbed once again. Understanding of these mechanisms of sorption-desorption in sludge, which are poorly known at present, would help in developing better removal methods for hydrophobic organic pollutants from wastewaters.

1.2.4 Evaporation and stripping of DEHP

A Henry's Law constant of $4.43 \text{ Pa}\cdot\text{m}^3/\text{mol}$ indicates a moderate evaporation for DEHP from pure water solution and classifies it as a semi-volatile compound (Anon. 2001). An evaporation half-life of 139 days for DEHP from water (original concentration 0.35 mg/l , 22°C) has been reported (Anon. 2001). In the environment, however, sorption to organic matter will reduce the evaporation potential significantly (Cousins et al. 2003). Thus, evaporation and stripping can be assumed to be very low at an STP.

1.2.5 Concentrations of DEHP

Concentrations of DEHP in sewage, STP effluent and sludges are reported in a number of studies, whereas the overall fate of DEHP is reported in only a few papers. DEHP concentrations in incoming sewage at various STPs in the EU, Canada and the United States ranged from not detected to $370 \mu\text{g/l}$, while corresponding STP effluent concentrations ranged from not detected to $40 \mu\text{g/l}$ (Monteith 1987; Anon. 2001). Paxéus (1996) analysed effluents for MEHP, the primary degradation product of DEHP, at the three largest STPs in Sweden, but no MEHP was found.

DEHP concentrations ranging from 4 to 661 mg/kg dw have been reported in sludges at various STPs in the EU and Canada (Anon. 2001). The sludges included primary and secondary sludges, aerobically or anaerobically digested sludges and dewatered sludges. Some higher values for sewage and

sludge DEHP concentration have been reported in a review by Clark et al. (2003). The concentrations reported by different authors are not fully comparable because of the different analytical methodologies employed, but they indicate the level of typical concentrations.

1.2.6 Operating plant parameters

STP parameters affecting the removal of organic compounds have been presented in the literature. The effective removal of suspended solids (SS) is important for the removal of a highly hydrophobic compound such as DEHP when sorbed to solids (Zitomer & Speece 1993). Usually, high solids retention time (SRT > 15 d) and high mixed liquor suspended solids concentration (MLSS > 5 g/l) result in the better removal of toxic organics. High SRT results in low food to microorganisms ratio (F/M), which causes microorganisms to use food that is more difficult to degrade, like DEHP. High biomass concentration causes compounds with high K_{ow} to partition to biomass.

1.2.7 Evaluation of the potential of STPs to remove DEHP

The removal of DEHP at an STP is often expressed simply as a percentage difference between influent and effluent DEHP concentrations. The reduction of phthalates concentration at several full-scale STPs has typically been 60–100%, although some lower levels of reduction have been reported for DEHP (reviewed by Monteith 1987). In a three-year study at a Swedish STP, the removal of DEHP was in the range of 90% or greater (Paxéus et al. 1992). Even where sludge was studied as well, usually only the concentrations in different compartments were reported (Hannah et al. 1986), not mass balances which would enable calculation of the amount of biological removal. Fauser et al. (2003) measured DEHP concentrations in influent, effluent and primary and secondary sludges, applied the measured data in a computational model and concluded that 70% of DEHP in sewage was biodegraded, while 28% was sorbed to sludge. Petrasek et al. (1983) calculated mass balances in their pilot-scale study with spiked DEHP in an activated sludge process. The sum of the percentages of DEHP in secondary effluent and primary and secondary sludges in relation to input DEHP was more than 100%, showing the difficulty of this approach. The results nevertheless showed that no significant biological removal occurred.

The results from pilot-scale studies indicated 26% and 61% biotransformation of spiked DEHP during anaerobic digestion of sludge (Govind et al. 1991; Parker et al. 1994); this is in contrast to the results of laboratory studies where significant anaerobic biotransformation was not found (Shelton et al. 1984; Ziogou et al. 1989). Studies at Danish STPs have indicated poor anaerobic biodegradation of DEHP in digestion of sludge, whereas a post-aeration process reportedly resulted in 30–40% reduction in DEHP concentration in digested sludge (Knudsen et al. 2000). Monteith (1987) has

suggested that reject waters from sludge treatment could cause high internal phthalate loadings when returned to the head of an STP.

Various computational models have been used to evaluate the behaviour of DEHP at an STP. Table 2 reports the fate of DEHP in different studies. Models are based on literature values of physico-chemical and biological properties of chemicals and standard values of the plant's design and operating parameters (Clark et al. 1995; Mikkelsen et al. 1996) or on measured concentrations and real design and operating parameters at STPs (Fauser et al. 2003). The biodegradation rate constant is assumed to be the main source of error in modelling (Mikkelsen et al. 1996). The assumption that biodegradation can occur only in soluble phase explains the low level of estimated biodegradation of DEHP in some studies. Peterson & Staples (2003), however, propose that some biodegradation occurs in the sorbed phase as well. The later versions of some models (e.g. SimpleTreat) gives the possibility to take biodegradation of sorbed chemical into account (Mikkelsen et al. 1996).

TABLE 2 DEHP removal (%) at STPs by different mechanisms, as measured in a pilot-scale study and predicted with different models. Percentages are calculated with respect to the original concentration in sewage.

	Removal efficiency	Volatilized	Biodegraded	Sorbed to sludges	Discharged with effluent
Pilot ¹	-	na ⁶	0	102	21
Single bioreactor model ²	98		70	28	2
STP Model ³	91	<1	27	63	9
SimpleTreat ⁴	86	3	6	78	14
SimpleTreat ⁵	93.2	0.016	15	78	6.8

¹) Petrasek et al. 1983, based on mass balances

²) Fauser et al. 2003; process includes biological phosphorus and nitrogen removal

³) Clark et al. 1995

⁴) Mikkelsen et al. 1996

⁵) Anon. 2001

⁶) na not analyzed

2 OBJECTIVES

The overall objective of this work was to study the potential of the different treatment stages of an STP to remove DEHP. This information will assist the improvement of treatment methods and operation strategies for the removal of organic pollutants in general.

The specific aims of the work were

- To provide information on the occurrence and concentrations of DEHP and other selected pollutants in municipal sewages and in STP effluent and sludges (I)
- To evaluate the origin of the DEHP in sewage and the contribution of landfill leachates to sewage DEHP (I)
- To clarify the most important unit processes for the removal of DEHP at a full-scale STP (II)
- To evaluate the sorption of DEHP on different particle size fractions and the effectiveness of treatments currently available for solids removal for DEHP removal (I)
- To evaluate the feasibility of employing a sequencing batch reactor (SBR) to remove nitrogen and DEHP from reject water and reduce the internal circulation of pollutants at an STP (III)
- To evaluate the potential of composting and aeration of municipal sewage sludges to remove DEHP (IV, V)
- To provide information on the mechanism of the removal of DEHP during sewage sludge aeration using sequential supercritical fluid extraction (SFE), which allows the changes in binding of the native DEHP to the sludge matrix to be followed over time (V).

Native compounds at STPs were studied throughout the work to obtain information corresponding to real conditions as well as possible. Spiked compounds were used in one experiment for purposes of comparison (III). A mass balance approach was employed whenever possible. Conventional parameters were studied in addition to DEHP to evaluate the overall performance of the systems.

3 MATERIALS AND METHODS

3.1 Sewage treatment plants and landfills

Studies were carried out between 1998 and 2004 at four Finnish STPs receiving different combinations of domestic and industrial wastewater, stormwater runoff and landfill leachate (Table 3), and at 11 municipal landfills representing both operating landfills and closed ones (Table 4). All these sites were included in the wastewater characterization study reported in paper I. Study II investigating DEHP removal was performed at Espoo STP. The reject water from Jyväskylä STP was used in the reject water treatment experiments of study III. Composting and aeration experiments (IV, V) were performed with sludges from Virrat and Jyväskylä STPs.

At the Espoo and Jyväskylä STPs, sewage treatment comprises mechanical treatment (e.g. primary clarification) and biological activated sludge processes with simultaneous phosphorus precipitation; at Toivakka and Virrat, only biological treatment with phosphorus precipitation is practiced. In Espoo and Jyväskylä, sludge processing consists of prethickening, anaerobic digestion, chemical conditioning and dewatering; in Virrat prethickening, chemical conditioning and dewatering; and in Toivakka prethickening and dewatering.

TABLE 3 Characteristics of STPs and sewages (data obtained from STPs).

STP	Population served by STP	Sewage flow rate m ³ /a	Sewage type ¹	Sewage BOD/COD ² mg O ₂ /l	Sewage NH ₄ -N/tot-N ² mg/l
Espoo	257 000	28 098 900	D+I+L	210/470	39/50
Jyväskylä	118 000	14 412 300	D+R+I+L	270/590	36/46
Virrat	4400	445 300	D+R+I	160/380	na/39
Toivakka	740	76 100	D+R	200/na	na/65

¹) D Domestic wastewater, R Runoff, I Industrial wastewater, L Landfill leachate

²) Annual average based on statutory monitoring
na not analysed

TABLE 4 Characteristics of landfills and leachates.

Landfill	Established	Area ⁽¹⁾ ha	Waste volume Mm ³	Leachate volume m ³ /a	Leachate treatment method	Leachate BOD/COD ³ mgO ₂ /l
Espoo (Ämmässuo)	1987	52	5	182 500	to STP	370/1180
Jyväskylä	1963	30	5	172 400	to STP	84/440
Tampere	1977	30	3.2	109 500	to STP	130/570
Hyvinkää	1974	12	1.3	54 400	to STP	1300/2800
Iisalmi	1971	10	0.65	13 500	to STP after basins	260/710
Nurmijärvi	1993	2.5	i.n.a.	18 300	biological N/DN ⁽⁴⁾	260/590
Lahti	1952	32	2.9	105 700	evaporatio n	30/200
Joensuu	1957	20	1.5	420 000	basins and roof zone to STP	14/190
Espoo (Mankkaa, closed)	1957	50 ⁽²⁾	i.n.a.	182 500	to STP	21/300
Leppävirta (Konnus, closed)	1960	2	i.n.a.	37 800	aerated basin	i.n.a.
Jyväskylä (Palokka, closed)	1978	5.5	0.3	94 000	no treatment	i.n.a.

¹⁾ Area covered with wastes

²⁾ Landfill area where leachate is collected

³⁾ Annual average based on statutory monitoring

⁴⁾ N nitrification, DN denitrification

i.n.a. information not available

3.2 Sampling in full-scale studies (I, II)

Samplings at STPs were performed either in one-day periods (I) or during three consecutive days (II). Wastewater samples were obtained from the incoming sewage (S; I, II), primary effluent (PE; II) and secondary effluent (SE; I, II), and sludge samples were taken from secondary sludge (SeS; II), combined primary and secondary sludge (CoS; I, II), treated sludge (TrS; I, II) and combined supernatants and filtrate from sludge treatment (R; II) (Fig. 1). Samples were collected either with a programmable sampling device or by taking subsamples manually and combining them as a one-day composite. Furthermore, grab samples were taken from supernatants from pre-thickening and post-thickening and from filtrate from dewatering were taken (II). Leachate samples were also taken manually as grab samples (I).

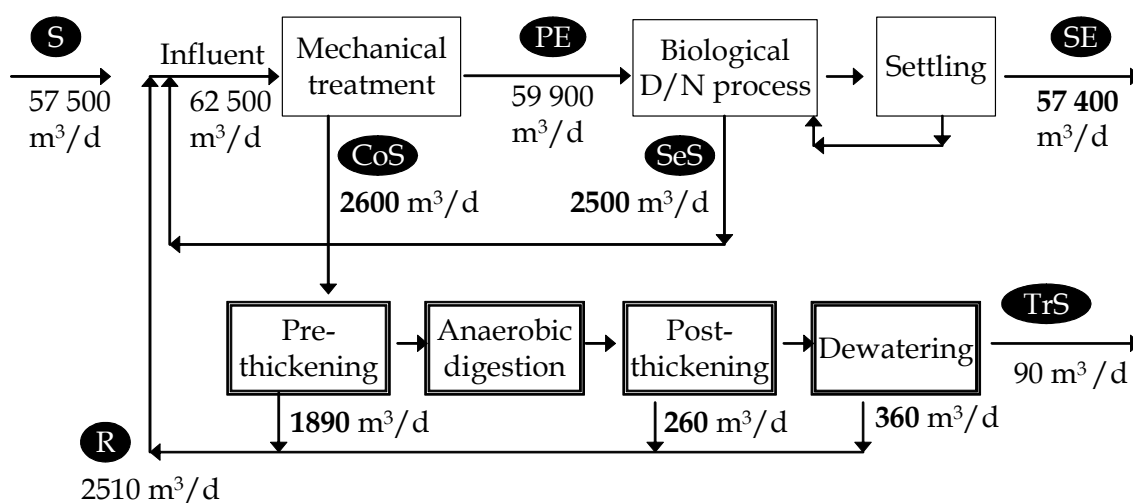


FIGURE 1 Flow chart of the Espoo STP, sampling points and average flow rates during the study period (II) (sampling points: S sewage, PE primary effluent, SE secondary effluent, SeS secondary sludge, CoS combined sludge, TrS treated sludge and R returned supernatants and filtrate; bold numbers are measured flows and nonbold are calculated values).

The tubings in the programmable sampling device were made of phthalate-free HDPE. Samples were not allowed to come in contact with any other plastics so as to avoid contamination with plasticizers. Samples for DEHP analysis were stored at -20°C until analysed, except samples for particle size distribution analysis (I), which were filtered immediately. Conventional parameters were measured immediately in separate samples.

3.3 Experimental set-up in laboratory and pilot studies

3.3.1 Particle size fractionation (I)

Particle size distribution in sewage (I) was measured immediately after sampling by serial filtration using a vacuum filtration apparatus (Schleicher & Schuell). A 100-ml sewage sample was filtered through a $41\text{-}\mu\text{m}$ filter (Nylon Net Filter, Millipore). The filtrate was further filtered through polycarbonate membranes (Isopore™ membrane filter, Millipore) with pore sizes of $1.2\ \mu\text{m}$ and $0.1\ \mu\text{m}$. Mechanical stirring of the sample was used to prevent cake filtration effect. The membranes were dried in a vacuum dessicator overnight and stored at -20°C until analysed.

3.3.2 Sedimentation tests (I, III)

Sedimentation tests for settleable solids were performed for different sewages (I) and reject waters (III). Settleable solids in sewage were determined with an

Imhoff cone as recommended by the APHA (1998). After one hour settling, the upper phase in the cone was sampled and filtered through 41 μm and 1.2 μm membranes. The amount of particles settled from each size fraction was determined by calculating TS concentration in each fraction and subtracting it from TS in the corresponding fraction of unsettled sewage.

Settleable solids in the reject mixture used as the feed for the SBRs were determined by allowing a portion of the reject water to settle in beakers for 30 min, after which the liquid and solid phases were carefully separated. The samples of unsettled reject water and the liquid fraction of settled reject water were analysed for DEHP.

3.3.3 Separate treatment of reject waters in sequential batch reactors (III)

3.3.3.1 Removal of native DEHP from reject water

Experiments were carried out at 20°C in two 5-l glass vessels (SBR1 and SBR2) with a total liquid volume of 4 l. The tubing material was polyurethane, which was first analysed to ensure that it did not contain phthalates. Reactors were operated in six-hour cycles (Fig. 2). Different aerobic and anoxic periods were used in the reactors to study the nitrogen and DEHP removal under two sets of conditions. During each cycle, 500 ml of the feed solution was pumped continuously for the 'fill' period, and the same volume of treated effluent was removed during the 'draw' period. Mixing in the reactors was done with a magnetic stirrer during the 'fill' and 'react' periods. Full aeration was provided during the 'aerobic react' periods using aquarium aerators (Rena Air 200), through ceramic stones producing fine bubbles. The activated sludge inoculum was obtained from the Jyväskylä STP.

The feed solution for both reactors consisted of supernatants from the pre-thickening and dewatering stages of the Jyväskylä STP. These reject waters were collected manually three times per week and combined in the ratio they were produced (3:1 v:v) before the experiments. The characteristics of the feed wastewater are presented in Table 5. At the beginning of the experiments, the feed was diluted with tap water to allow micro-organisms to acclimate to the reject waters. Undiluted feeding was provided on days 70–116. The pH of the feed was adjusted to 7.8 on a daily basis with 10 M NaOH or HCl solution. A portion of settled sludge was removed daily from both reactors to keep the MLSS concentration at 7 g/l. Sludge ages and other operating conditions during the experimental period are summarized in Table 6. Influent, effluent and sludge samples for phthalate analysis were collected in glass bottles on experimental days 101, 105, 108, 112 and 116. Influent samples (40 ml) were immediately centrifuged to separate the particulate matter from solution. Samples were stored at -20°C until analysis.

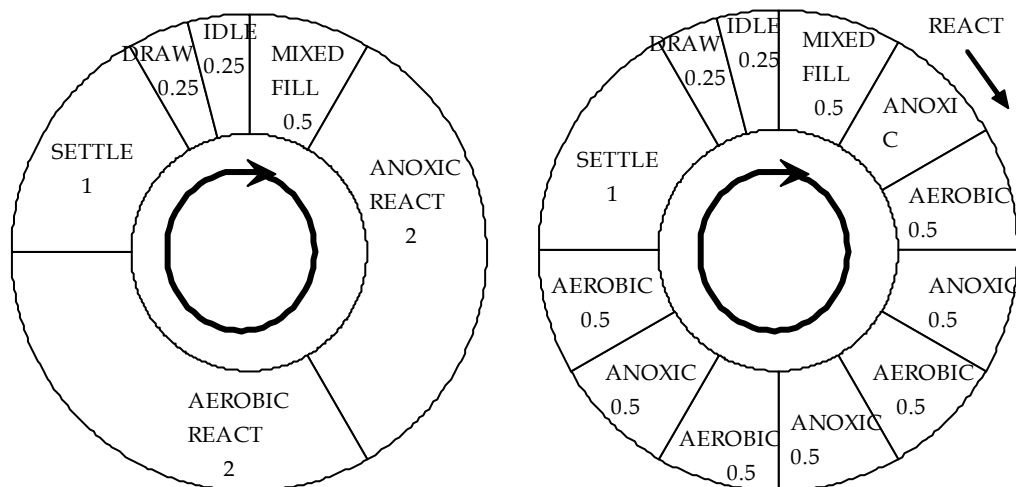


FIGURE 2 Schematic organization of the 6-hour cycle in SBR reactors SBR1 (left) and SBR2 (right).

TABLE 5 Characteristics of undiluted influent of SBRs.

Parameter	Unit	Value
NH ₄ -N	mg/l	159-190
NO ₃ -N	mg/l	0.6-1.7
tot-N	mg/l	350
TCOD	mgO ₂ /l	1300-3500
SCOD	mgO ₂ /l	240-920
Alkalinity	mmol/l	16-23
pH		7.5-8.1

TABLE 6 Operating conditions in SBR experiments.

Parameter	Unit	Days 1-69	Days 70-121
Feed dilution factor		6-1.3	1
HRT	d	2	2
Loading	mg NH ₄ -N/l d	10-75	63-95
Sludge age	d	10-20	6

3.3.3.2 Removal of spiked DEHP from reject water

Reactors were operated for 116 days, after which the influent for SBR1 was spiked with 300 µg DEHP per litre of feed and the reactor was operated for five days under similar conditions as earlier. DEHP was dissolved in methanol in a concentration of 1.2 mg/ml. A portion of this mixture was then added to the feed dropwise, while the feed was continuously stirred. The level of spiked DEHP was approximately 5 times as high as the background DEHP level. New

feed was spiked in every two days. Influent, effluent and excess sludge samples were taken daily for the five days of operation and stored at -20°C until analysed.

3.3.4 Sludge composting (IV)

Dewatered raw sludge from Virrat STP and anaerobically digested sludge from Jyväskylä STP were composted in two parallel closed compost bins (Biolan Composter 220 l, bottom area 61×61 cm, height 120 cm) for 85 days. Ventilation was provided through the adjustable air intake opening and air distribution tubes. The bin material was polyethene, which was first tested to ensure that it did not contain phthalates. A 10-cm layer of commercial amendment consisting of dried coniferous tree-bark and peat (Biolan Compost Bedding) was placed in the bottom of the bin. The same amendment was mixed with the sludge in ratio 1:2 (v:v) and the bin was filled with this mixture.

The anaerobically digested Jyväskylä sludge was additionally composted in a pilot rotary drum (Quantor, Biofacta Ltd, 5 m^3) for 28 days. The sludge feed was mixed with peat (1:1, v:v) and the drum was filled to about 65% level. The drum was rotated for 1 minute every 12 hours, and forced ventilation was provided by means of a blower that pulled air through the composting material.

Composting vessels were located indoors, except for the first 14 days in experiments with Jyväskylä sludge composting in bins, where the composting was started at outdoor temperatures of 10°C . The water-holding capacity of the Virrat composts was exceeded on day 7, when they began to produce approximately 140 ml of leachate daily. No leachate was produced by the Jyväskylä composts.

Subsamples of the composting material and leachate were taken weekly and stored at -20°C until analysed.

3.3.5 Sludge aeration (IV, V)

Two separate sludge aeration experiments were performed. First, DEHP removal during aeration was studied with raw sludge from Virrat STP and compared with the removal in composting (IV). In a later experiment the mechanism of the removal was studied more closely with a mixture of primary and secondary sludges from the Jyväskylä STP.

The sludges were first diluted with distilled water to obtain total solids concentrations of 2%. A 1500-g portion of sludges was placed in parallel 2-l glass vessels and aerated at 20°C for 28 days. The suspension was mixed with a magnetic stirrer and air was introduced to the vessel with an aquarium aerator (Rena Air 200) through a ceramic stone that produced fine bubbles. Dissolved oxygen concentration was above 2 mg/l throughout the experiment. Suspension pH was maintained at 6.5–7.5 by daily additions of NaOH or HCl.

In the experiment reported in paper IV, the amount of water evaporated during aeration was calculated from an aeration experiment carried out with

pure water, and the analysed concentrations were corrected for that amount. In study V, the decrease in reactor weights during the study was assumed to be the result of water evaporation and was compensated by daily addition of distilled water.

The suspensions were sampled on days 0, 1, 7 and 28 (IV) or on weekly basis (V), and stored at -20°C until analysed (IV), or they were subjected immediately to pretreatment for analysis (V).

3.4 Analytical procedures

3.4.1 Chemicals and materials

All solvents and chemicals were of analytical grade. The Base Neutral Extractables Mixture (BN625-1JM) used for quantitation of 44 compounds, including DEHP (I), and the anthracene- d_{10} solution were obtained from Chem Service (West Chester, USA). The phthalate esters mixture (M-8060) used for quantitation of DEHP and other phthalates (II-V) was obtained from AccuStandard Inc. (New Haven, USA). 9-Bromophenanthrene was obtained from Lancaster (Morecambe, England) and was 95% pure. Florisil (60–100 mesh; Fluka) was heated to 150°C for 8 h, cooled in a desiccator and de-activated with 3% of distilled water prior to use. Neutral alumina (Brockman activity I, 70-230 mesh; Merck) was heated to 400°C for 8 h, cooled in a desiccator and de-activated with 15% (w:w) of distilled water before use.

Special care was taken of the materials and cleanness of sampling devices and laboratory vessels and equipment to avoid laboratory contamination with DEHP or other pollutants. All the glassware was (i) rinsed with acetone, (ii) washed with detergent, (iii) rinsed with hot water, (iv) kept overnight in 10% hydrochloric acid, (v) washed in a laboratory washing machine, (vi) heated to 400°C for 8 h, (vii) capped and finally rinsed with dichloromethane prior to use. Distilled water was occasionally analysed in a similar manner to the wastewater samples, to check for the laboratory contamination.

3.4.2 Phthalate determination

In study I, the samples were screened for 44 priority pollutants, including six phthalates (dimethyl, diethyl, di-n-butyl, butyl benzyl, DEHP and di-n-octyl phthalate). In study II, six phthalates were determined, while in studies III, IV and V only DEHP was determined. Extraction procedures differed slightly in the various experiments.

3.4.2.1 Wastewater extraction

For the 44 priority pollutant analysis (I), a one-litre wastewater sample was spiked with internal standards anthracene- d_{10} and 9-bromophenanthrene, and

extraction was carried out with two lots of 50 ml dichloromethane. The combined extracts were dried over anhydrous sodium sulphate and reduced to approximately 5 ml in a rotary evaporator and further to 1 ml with nitrogen. The residue was then quantitatively transferred to a column consisting of 0.5 g anhydrous Na₂SO₄ above 1 g Florisil in a Pasteur pipette. The column was eluted with 12 ml dichloromethane previously tested to remove all compounds of interest. This fraction was evaporated to 1 ml with a stream of nitrogen for analysis by gas chromatography-mass spectrometry (GC-MS, procedure A).

For the analysis of six phthalates (II), a one-litre wastewater sample was first filtered through an acetone-washed glass fibre filter (Schleicher & Schuell GF50) and the water phase and solid fraction were analysed separately. The water phase was extracted as in the analysis for 44 priority pollutants, while the filter containing the solid fraction of wastewater was freeze-dried and placed into an acetone-washed single-walled cellulose thimble (Macherey-Nagel 645) and spiked with 10 µg of anthracene-d₁₀. The thimble was placed into a Büchi B-811 Extraction System (Büchi, Flawil, Switzerland). The sample was extracted with 40 dichloromethane cycles by the warm Soxhlet extraction method where the solvent is gently heated in the extraction chamber. After the extractions the samples were reduced to approximately 1 ml and purified in Florisil column. Instead of dichloromethane, the Florisil column was now pre-eluted with 5 ml petroleum ether (40–60°C), and phthalates were eluted with 12 ml petroleum ether/diethyl ether (1/1). This fraction was evaporated to 1 ml with a stream of nitrogen for the analysis by GC-MS (procedure B).

For the DEHP determination in the SBR experiment (III), water phases of influent samples separated by centrifugation (40 ml) and 100 ml effluent samples were extracted twice with dichloromethane. The combined extracts were reduced to approximately 10 ml in a rotary evaporator and further to 1 ml with nitrogen. The solid phases of the influent samples were dried for two days in a freeze drier (Hetosicc CD 52) and extracted with dichloromethane in an ultrasonic water bath at 35°C according to the method described by Zurmühl (1990). After extraction the samples were purified in alumina columns, spiked with internal standards 9-bromophenanthrene and anthracene-d₁₀, then evaporated and analysed by GC-MS (procedure B).

3.4.2.2 Sludge extraction

Sludge samples for DEHP analysis were dried for two to four days (I, II, III, IV) or for 24 hours (V) in a freeze drier (Hetosicc CD 52) and homogenized manually in a mortar (I, II, III) or by a mill (Fritsch pulverisette 14) to obtain particle size less than 0.2 µm (IV, V). Three different extraction methods were used for the determination of DEHP in sludge.

In modified Soxhlet extraction (II), approximately 0.5 g of freeze-dried and homogenized sludge was placed into an acetone-washed single-walled cellulose thimble (Macherey-Nagel 645) and spiked with 10 µg of anthracene-d₁₀. The thimble was placed into a Büchi B-811 Extraction System (Büchi, Flawil, Switzerland). The sample was extracted with 40 dichloromethane cycles by the

warm Soxhlet extraction method where the solvent is gently heated in the extraction chamber. After the extraction the sample was reduced to approximately 1 ml and purified in Florisil column using petroleum ether/diethyl ether (1/1) for eluting the phthalates. After evaporation to 1 ml, the extract was subjected to analysis by GC-MS (procedure B).

In ultrasonic extraction (I, IV), the freeze-dried and homogenised sludge was extracted with dichloromethane in an ultrasonic water-bath at 35°C by the method described by Zurmühl (1990). Membranes with particles from filtration experiments (I) were extracted the same way but with acetone/hexane (1:1). After the extraction the sample was reduced to approximately 1 ml and purified in Florisil (I) or alumina (III, IV) column. Compounds were eluted from Florisil column with dichloromethane and from alumina column with hexane/dichloromethane (1:1). The samples were spiked with internal standards 9-bromophenanthrene and anthracene-d₁₀, and then evaporated and analysed by GC-MS (procedure A (I); procedure B (III, IV)).

Supercritical fluid extractions (SFEs) (V) were performed using a SFE system (ISCO SFX 3560 with a 260 D syringe pump). A 0.2 g portion of sludge was placed on the bottom of the extraction cell and the cell was filled with glass beads. The instrument was run with CO₂ (5.5, 99.9995%, Messer) in the dynamic mode. Flow rate in the restrictor was 1.5 ml/min and the temperature 100°C. Analyte collection was performed at room temperature by inserting the restrictor into a vial containing 5 ml methanol and utilizing a solvent replenishment rate of 0.5 ml every 2 min. Each sample was sequentially extracted for six 30-min periods and the extract of each sequence was collected to a separate vial. The extraction conditions in six sequences were as follows: (1) 40°C and 160 bar; (2) 40°C and 450 bar; (3) 80°C and 450 bar; (4) 150°C and 450 bar; (5) 150°C and 450 bar; (6) 150°C and 450 bar. The sixth sequence was performed after opening the extraction cell and adding 0.5 ml methanol. The extraction conditions were chosen on the basis of a preliminary experiment where the effect of temperature and pressure on the extraction efficiency was studied. After the extractions, 9-bromophenanthrene was added to each extract as an internal standard. The extracts were evaporated to 1 ml with a stream of nitrogen in warm water bath and analysed by GC-MS (procedure B).

3.4.2.3 GC-MS procedures

Procedure A was used for the screening of 44 priority pollutants (I): Extracted compounds were analysed with a Hewlett Packard GC-MS equipped with a 30-m HP-5 fused silica capillary column with a film thickness of 0.25 µm and with helium as carrier gas. The following oven temperature program was used: 40°C for 6 minutes, increased by 15°C/min to 70°C, then by 4°C/min to 275°C, held for 15 min. The compounds were detected and quantitated using the SIM mode. The ions used to identify DEHP were 149, 167 and 279 amu. The standard solution used for the quantitation contained all compounds of interest and was spiked to distilled water and led through the same analytical procedure as the samples. Quantitation was then based on one-level response factors, which took

into account the differences in extractability, volatility and GC-MS response of the compounds and the internal standards. The quantitation limit was 1 µg/l for phthalates, 0.05 µg/l for PAHs and 0.1 µg/l for other compounds.

For the determination of six phthalates or of DEHP alone, procedure B was used (II, III, IV, V): The equipment was the same as in procedure A, but the oven temperature program was following: 115°C for 4 minutes, increased by 16°C/min to 275°C, held for 15 min. The compounds were detected and quantitatively analysed using the SIM mode. Quantitation was based on five-level response factors and the limit for quantitation was 0.1 µg/l.

3.4.3 Measurement of conventional parameters

Total solids (TS), volatile solids (VS), suspended solids (SS), pH and conductivity were determined according to APHA (1998). In particle size fractionation (I), TS and VS concentrations in the different particle fractions were calculated by subtracting the TS and VS concentrations of the filtered sample from the concentrations in the sample before filtration.

Total and soluble chemical oxygen demand (TCOD, SCOD, dichromate method), biochemical oxygen demand (BOD₇), ammonia nitrogen (NH₄-N), nitrate-nitrogen (NO₃-N), total nitrogen (tot-N) and alkalinity were determined according to the Finnish Standards Association (SFS 5504, SFS 5508, SFS 3012/3032, modified SFS 5752, SFS 5505/SFS-EN ISO 11905-1, SFS-EN ISO 9963-1). Before the SCOD analyses, the samples were filtered through a glass fibre filter (Whatman GF/A).

Flow rate and process temperature data at STPs were obtained from the STP automated control system (II). In composting experiments (IV), temperatures in compost bins and the rotary drum were measured with a temperature probe at 40 cm depth. Oxygen, carbon dioxide and methane were determined with a portable IR gas analyser (Geotechnical Instrument GA 94) by pumping a gas sample from the composting material at 40 cm depth. It may be relevant that methane analysis is sensitive to interference from some other hydrocarbons. For pH and electrical conductance measurements, the sample was slurried with deionized water (1:5 wet weight basis), allowed to soak for 2 h and stirred before the electrode was immersed.

3.4.4 Calculation of mass balances (II, III, IV, V)

The simplified mass balance of DEHP at an STP (II) and in the reject water treatment experiment (III) was established using the daily mass of the compound (kg/d) at each sampling point, calculated as the volumetric flow multiplied by the concentration of the DEHP. At the STP, influent (In) compound mass was calculated as sum of the mass in sewage (S), returned supernatant and filtrate from sludge treatment (R) and secondary sludge (SeS) ($In = S + R + SeS$). The portion of the compound removed in the biological DN/N process was calculated by subtracting the compound mass in the secondary effluent (SE) and secondary sludge from the mass in the primary

effluent (PE) ($PE - SE - SeS$) and the portion removed in anaerobic sludge digestion was calculated by subtracting the compound mass in the returned supernatants and filtrate (R) and treated sludge (TrS) from the mass in the combined sludge ($CoS - R - TrS$).

The mass balance approach was also used in composting and aeration experiments (IV, V). The amount of feed in the composting bins and drum was weighed at the beginning of the experiments, and the composted product was weighed at the end of the experiments. The mass of DEHP in the bins and drum was calculated by multiplying the DEHP dry weight concentration by the total solids (TS) concentration and the total weight of material in the system. Absolute removal of DEHP during the experiment was calculated as the difference between the DEHP masses at the beginning and end of the experiment. In aeration experiments, the amount of DEHP in the reactor was calculated as in the composting experiment, but separately for each sampling period.

4 RESULTS AND DISCUSSION

4.1 Concentrations and origin of DEHP in municipal sewages and STP effluents and sludges

Sewages, STP effluents and sludges and landfill leachates were analysed for DEHP and 43 other priority pollutants. DEHP was the compound occurring most often and in highest concentration in almost all samples. Its concentrations were 28–122 and 2–8 µg/l in sewage and secondary effluent of STPs, respectively, (Table 7). These concentrations lie within the range not detected to 370 µg/l reported for sewages in the EU, Canada and the United States (Monteith 1987; Anon. 2001). Because sampling was carried out in different seasons, and with peak sewage flow periods avoided, the data of this study represents the typical level of pollutant concentrations in Finnish sewages.

As in sewages, DEHP was the most common pollutant in landfill leachates, with concentrations of 1–89 µg/l (Table 7). Although pollutant concentrations in leachates may vary widely with the time of year, the large number of landfills studied made it possible to give an average concentration level for each pollutant group. DEHP concentrations were somewhat lower than in three Swedish municipal landfill leachates (97–346 µg/l) analysed by Paxéus (2000). Very low concentrations (0.09–8 µg/l) have been reported in some leachates in German landfills (Anon. 2001). In Jyväskylä and Espoo where landfill leachates were discharged to the STP, leachate was responsible for 0.3–1.0% of the total DEHP load to the STP (data not shown).

No appreciable differences were found in DEHP concentrations in the sewages, even though only domestic wastewater and stormwater runoff were discharged to the Toivakka STP, while industrial wastewaters and landfill leachates were included in sewage at other STPs. The amount of DEHP discharged per person daily (9–31 mg) was of the same order of magnitude at all STPs, a finding that supports the findings of Robinson et al. (1989, referred to by Paxéus et al. 1992) and Jacobsen & Guildal (2000) that a significant part of the DEHP in sewage originates from households. PVC pipes were still in use in

some parts of all the sewage networks. It is known that DEHP may slowly diffuse out from the PVC matrix. In the environment, however, PVC surfaces are often colonized by slow growing fungi, yeast and bacteria that are able to biodegrade the DEHP as it diffuses out (Peterson & Staples 2003). Thus, it is unclear whether PVC pipes are a source of DEHP in sewage.

TABLE 7 DEHP concentrations in STP sewages and effluents ($\mu\text{g/l}$) and dewatered sludges (mg/kg dw) and in landfill leachates ($\mu\text{g/l}$). Number of samples 1-3.

Site	Sampling site	DEHP
Espoo STP	Sewage	28-122
	Effluent	2-8
	Combined prim.+sec. sludge	99-203
	Anaerobically digested and dewatered sludge	91-179
Jyväskylä STP	Sewage	32-66
	Effluent	2
	Anaerobically digested and dewatered sludge	91
Virrat STP	Sewage	83
	Effluent	4
	Dewatered sludge	108
Toivakka STP	Sewage	59-75
	Effluent	2
Espoo landfill (Ämmässuo)	Untreated	41-60
Jyväskylä landfill	Untreated	1-6
Tampere landfill	Untreated	2
Hyvinkää landfill	Untreated	89
Iisalmi landfill	Untreated	5
	Basins treated	4
Lahti landfill ¹⁾	Untreated	3
	Treated	nd
Nurmijärvi landfill ¹⁾	Untreated	9
	Treated	1
Joensuu landfill ¹⁾	Untreated	3
	Treated	3
Leppävirta landfill (Konnus)	Untreated	2
Jyväskylä landfill (Palokka)	Untreated	1
Espoo landfill (Mankkaa)	Untreated	37

¹⁾ On-site leachate treatment, see Table 4

²⁾ nd not detected

Approximately 80-91, 96, 95, and 96% of DEHP was removed from sewage at Espoo, Jyväskylä, Virrat and Toivakka STPs, respectively. Despite efficient removal from the water phase, DEHP accumulated on sludges and was present in concentrations of 91-179 mg/kg dw even after anaerobic digestion of sludge. These concentrations were somewhat higher than those reported for Finnish sludges by Aalto (1992), but both fall in the range of 4-661 mg/kg dw reported for sludges at various STPs in the EU and Canada (reviewed in Anon. 2001).

In anaerobically digested and dewatered sludges, 37 and 35% of DEHP in the incoming sewage were found in Espoo and Jyväskylä, respectively, while in

dewatered sludge in Virrat 62% of DEHP was present. The total removal of DEHP was thus higher in Espoo and Jyväskylä STPs with anaerobic digestion of sludge (43–61%) than in the Virrat STP where there was no biological treatment of sludge (33%).

DEHP sorption on sewage solids at three STPs was studied by particle fractionation using filters with nominal size of 41 μm , 2.1 μm and 0.1 μm . A 10–27% portion of the total sewage DEHP was found in size fraction above 41 μm (Table 8), which in tests could be almost totally removed by sedimentation in Imhoff cones (data not shown). Most of the sewage DEHP was sorbed on particles 0.1–41 μm in size, of which only a small portion was sedimented in tests. Calculated DEHP removal by sedimentation in this study (17–35%) was somewhat lower than removals in primary sedimentation of the pilot STPs studied by Petrusek et al. (1983) and Hannah et al. (1986), where 63 and 37% of DEHP in the STP influent, respectively, ended up in the primary sludge. Less than 6% of the sewage DEHP was in the fraction below 0.1 μm , either in dissolved form or sorbed to dissolved matter or very small particles. This can be regarded as bioavailable DEHP. Organic matter is known to play the main role in sorption of hydrophobic organic compounds. From the measured DEHP and VS concentrations in different fractions, it would appear that DEHP preferentially sorbs to solid rather than dissolved organic matter (Table 8).

TABLE 8 TS, VS (mg/l or mg/fraction/l) and DEHP ($\mu\text{g/l}$ or $\mu\text{g/fraction/l}$) concentrations in different sewage particle size fractions (average of two analyses \pm standard deviation, percentage of total concentration in parenthesis).

	Total ¹⁾	<0.1 μm	0.1–1.2 μm	1.2–41 μm	>41 μm
TS					
Espoo	650 \pm 10	370 \pm 48 (56%)	17 \pm 1 (3%)	120 \pm 21 (18%)	150 \pm 24 (23%)
Jyväskylä	1130 \pm 20	570 \pm 9 (50%)	22 \pm 0 (2%)	210 \pm 19 (18%)	340 \pm 9 (30%)
Virrat	810 \pm 20	520 \pm 44 (64%)	19 \pm 1 (2%)	110 \pm 17 (14%)	160 \pm 27 (20%)
VS					
Espoo	390 \pm 35	120 \pm 5 (37%)	5 \pm 2 (2%)	79 \pm 25 (24%)	120 \pm 41 (37%)
Jyväskylä	570 \pm 7	190 \pm 15 (37%)	7 \pm 2.4 (1%)	150 \pm 10 (28%)	180 \pm 16 (34%)
Virrat	450 \pm 40	200 \pm 18 (46%)	11 \pm 2 (3%)	83 \pm 12 (20%)	130 \pm 35 (31%)
DEHP					
Espoo	72.7	<0.5 \pm 0.0 (<1%)	18.1 \pm 4.7 (26%)	35.2 \pm 1.6 (52%)	14.9 \pm 0.1 (22%)
Jyväskylä	66.0	1.3 \pm 0.0 (2%)	15.3 \pm 1.0 (23%)	31.8 \pm 3.4 (48%)	17.4 \pm 0.1 (27%)
Virrat	82.9	5.3 \pm 0.2 (6%)	30.8 \pm 1.3 (36%)	42.2 \pm 5.1 (48%)	9.2 \pm 5.5 (10%)

¹⁾ Measured from total sample

4.2 Removal of DEHP at a full-scale STP

The most important unit processes for DEHP removal were evaluated on the basis of samples collected on two consecutive days from different stages of a full-scale STP. Sewage DEHP concentration was, on average, 110 $\mu\text{g}/\text{l}$, of which about 88% was detected in the solids fraction. The average DEHP masses in different treatment stages and the percentages of the masses relative to sewage DEHP mass are presented in Fig. 3. The simplified mass balance shows that the external DEHP load coming to the treatment process from the sewer system was on the same level as the internal load comprising the returned supernatants and filtrate from sludge treatment and excess secondary sludge.

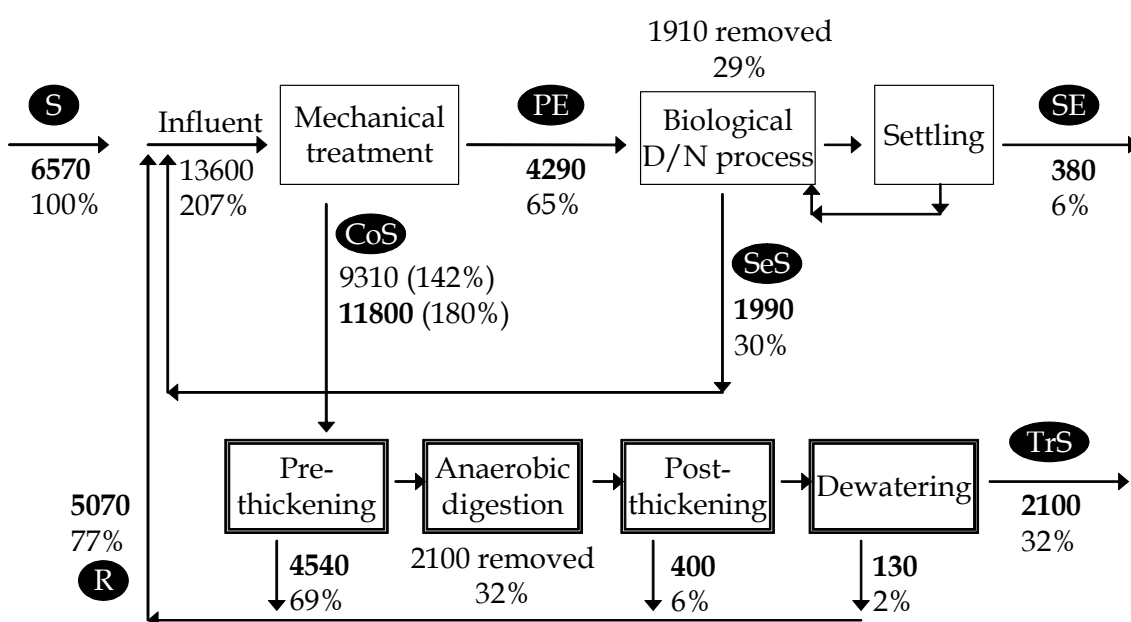


FIGURE 3 Mass balance of DEHP at Espoo STP. Bold numbers are measured masses (average of Monday and Tuesday) and nonbold are calculated masses (g/d); percentages are in respect of the mass in sewage. For explanation of symbols, see Fig. 1.

Approximately 65% of the sewage DEHP was present in the primary effluent and 6% in the secondary effluent. Most of the DEHP in sewage was sorbed in the combined primary and secondary sludges. The portion removed biologically in the activated sludge process was calculated to be on average 29%, assuming that volatilization and abiotic transformation of DEHP are negligible in an STP. This removal differs from the results of pilot studies by Petrasek et al. (1983) and Hannah et al. (1986), who found no removal of spiked DEHP in the activated sludge process. Much higher removal (70%) was reported by Fauser et al. (2003), who measured concentrations of DEHP in various stages of an alternately operated STP and calculated the fate of DEHP with a computational model.

Two values are presented for DEHP mass in combined sludge: calculated mass (mass in influent minus mass in primary effluent) and measured mass (flow multiplied by concentration). The calculated masses were 16–25% lower than the measured masses. A similar finding is reported by Petrusek et al. (1983), who calculated mass balances for various compounds at a pilot-scale plant. Because sewage treatment is a continuous process, the true steady-state requirement for mass balance analysis is not fulfilled. Possible reasons for the inaccuracy may be the variation of hydraulic retention time resulting in a timing error for sampling, difficulties in measuring the flowrates of waters with different solids concentration, and analytical problems related to differences in sample matrices. Furthermore, the solids retention time in the system is much greater than the hydraulic retention time, resulting in inaccuracy when attributing the DEHP in sludge to the DEHP removed from the water phase. Calculated mass (CoS) was used to calculate the amount of DEHP removed in anaerobic digestion of sludge.

DEHP removal in anaerobic digestion of sludge at the Espoo STP was 32% of sewage DEHP and 23% of the DEHP in combined sludge. The latter value is close to the removals measured in the pilot-scale study of Govind et al. (1991) who found 26% removal of spiked DEHP in anaerobic digestion of sludge. Much higher removal (61%) in a pilot-scale study has been reported by Parker et al. (1994), while no significant anaerobic biodegradation of DEHP has been found in laboratory studies (Shelton et al. 1984; Ziogou et al. 1989). Studies at Danish STPs suggest poor anaerobic biodegradation of DEHP in the digestion of sludge, in contrast to a post-aeration process, which resulted in 30–40% reduction in DEHP concentration in digested sludge (Knudsen et al. 2000). DEHP concentration in the treated sludge at Espoo (160–166 mg/kg dw) noticeably exceeded the maximum acceptable value (100 mg/kg dw) for sludge to be used in agriculture proposed by the European Commission (2000).

Approximately half of the DEHP introduced to sludge treatment was recirculated back to the sewage treatment process in the form of supernatants and filtrate (Fig. 3). Most of the DEHP was released from sludge pre-thickening, while sludge post-thickening and dewatering were of minor importance. The higher than normal SS concentrations of returned supernatants may have resulted from high internal DEHP load, because most of the DEHP was sorbed on solids. Concentration of DEHP on dry weight basis was slightly lower in the supernatant from post-thickening than in that from pre-thickening or in the combined sludge, indicating that anaerobic digestion did not significantly mobilize DEHP. The portion of soluble DEHP of the total DEHP was not determined, however. Since the concentration of DEHP in wastewater appears to closely follow solids concentration, the internal circulation of DEHP at STPs might be reduced by improving the solids separation in sludge treatment.

In addition to DEHP, after derivatization extracts were analysed for MEHP, but the MEHP concentrations did not exceed the detection limit (2 µg/l) in GC-MS in any sample (data not shown).

Process conditions and treatment results at Espoo STP were stable during the study period and represented well the average process performance in autumn (data not shown). BOD₇ removals (secondary effluent/sewage) of about 99% and total nitrogen removals of 76% were achieved. In the biological DN/N process approximately 33% and 23% of COD and BOD₇, respectively, disappeared. The simplified mass balances of conventional parameters were calculated in a similar way to DEHP and are presented in paper II.

4.3 Reject water treatment in SBRs

The feasibility of separate reject water treatment to reduce internal circulation of DEHP at STPs was studied in two nitrogen-removing SBRs. Influent, effluent and sludge DEHP concentrations were determined during the last 15 days of the 116-d experiment. Wide variation in the influent DEHP concentration (41–119 µg/l) resulted in wide variation in the influent DEHP load (Fig. 4). Approximately 85–98% of the influent DEHP was in the solids fraction (Table 9). Despite the variation in the amount of input DEHP, the effluent DEHP concentration usually remained below 2 µg/l. The profile and level of the sludge DEHP concentration were similar in the two reactors despite their different operating sequences (Table 9; Fig. 4).

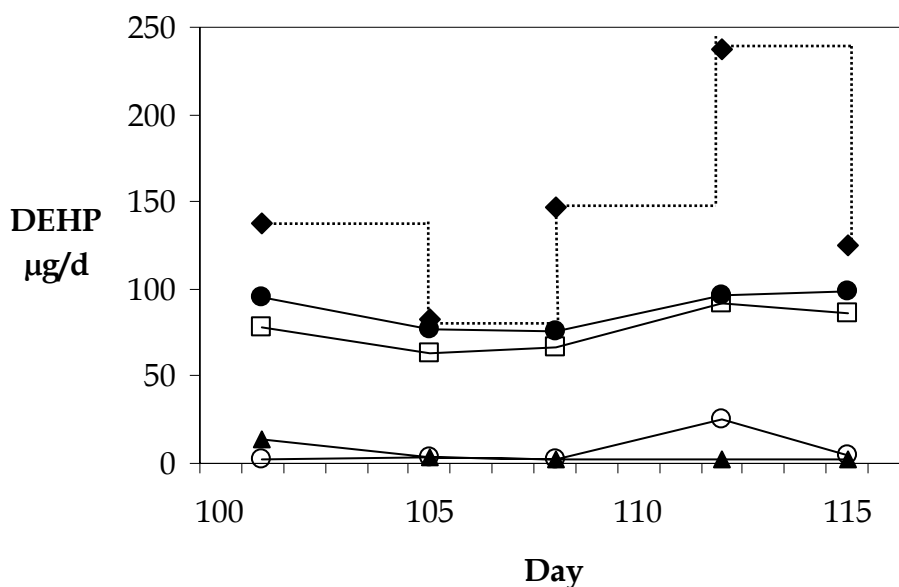


FIGURE 4 DEHP mass in SBR influent (♦), effluents of SBR1 (▲) and SBR2 (○) and sludges of SBR1 (●) and SBR2 (□) during days 101–116. The dotted line is unsmoothed because each influent sample represents reject water from a different lot.

TABLE 9 DEHP concentrations in influent (measured soluble and sorbed, calculated total), effluents and sludges in SBR1 and SBR2.

Day	Influent			Effluent	Effluent	Sludge	Sludge
	Soluble	Sorbed to particles	Total	SBR1	SBR2	SBR1	SBR2
	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{g dw}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{g dw}$	$\mu\text{g}/\text{g dw}$
101	10	113	69	7	1	49	40
105	2	68	41	2	2	40	33
108	3	82	73	1	1	39	35
112	4	75	119	1	13	50	48
116	4	75	62	1	2	51	45

Determination of DEHP removal during the study was made difficult by the wide variation in the influent DEHP concentration. As well, the hydraulic and sludge retention times caused inaccuracy in the mass balance calculations. On average, across all samples, 97 and 95% of DEHP were removed from the water phase in SBR1 and SBR2, respectively, during days 101–116. Most of this removal occurred by sorption to sludge, which is typical for hydrophobic compounds. When the amounts of DEHP determined in sludges and effluents were subtracted from those in influent, the average total removals of DEHP were found to be 36 and 42% in SBR1 and SBR2, respectively. If these removals were the result of biological degradation, some of the sorbed DEHP must have been desorbed in order to be bioavailable or else biodegradation occurred in sorbed phase. It is also possible that some of the observed removals were the result of irreversible sorption to particles.

The amounts of DEHP totally removed from the SBR systems are notable given that the reject water used in the experiments had already been through aerobic sewage and anaerobic sludge treatments, in which the bioavailable fraction of DEHP can be expected to be biotransformed. It is possible that anaerobic treatment makes DEHP more bioavailable by degrading chemical groups on sorption sites, but no evidence for this is available in the literature. As an option for biotransformation in the present study, some of the DEHP may have been converted to bound residues not extractable with the procedure employed (Alexander 1995). Distinguishing these two processes is not possible with the methods of this study.

Because most of the DEHP in reject waters is sorbed to solids, the internal circulation of DEHP could be reduced by improving the solids removal. In the present case, the sedimentation tests showed that removal of the settleable solids (21% of TS) from reject water would result in 42% DEHP removal from these waters.

Performance of the SBRs was verified by determining nitrogen removal throughout the study. $\text{NH}_4\text{-N}$ removal was efficient in both SBRs, resulting in $\text{NH}_4\text{-N}$ concentrations in the effluents below the detection limit. $\text{NO}_3\text{-N}$ concentrations were usually below 20 mg/l, but increased as the SCOD value dropped.

Spiking experiment

To evaluate the role of bioavailability in DEHP removal, at the end of the study one of the SBR systems was fed with reject spiked with a known amount of DEHP. Part of the DEHP was found to have been removed from the influent before it was fed to the reactor, indicating some microbial activity in the feed container. During the experiment the total DEHP removal, calculated as an average across the five days of the study, was 99% from the water phase and 77% in total (Fig. 5). Total DEHP removal calculated from daily values increased from 68% on day 116 to above 80% on days 119 and 120. This increase in removals was the result of a lower DEHP concentration in the sludge during the final days of the experiment. Part of the sludge in the SBR was removed daily to adjust the sludge age. The sludge DEHP concentrations during the spiking experiment indicated that spiked DEHP was sorbed onto the sludge at a lower rate than was the native DEHP in the reject water. The removal of spiked DEHP in the influent container and in the reactors indicates that DEHP is readily biodegraded in SBRs if not bound to solids.

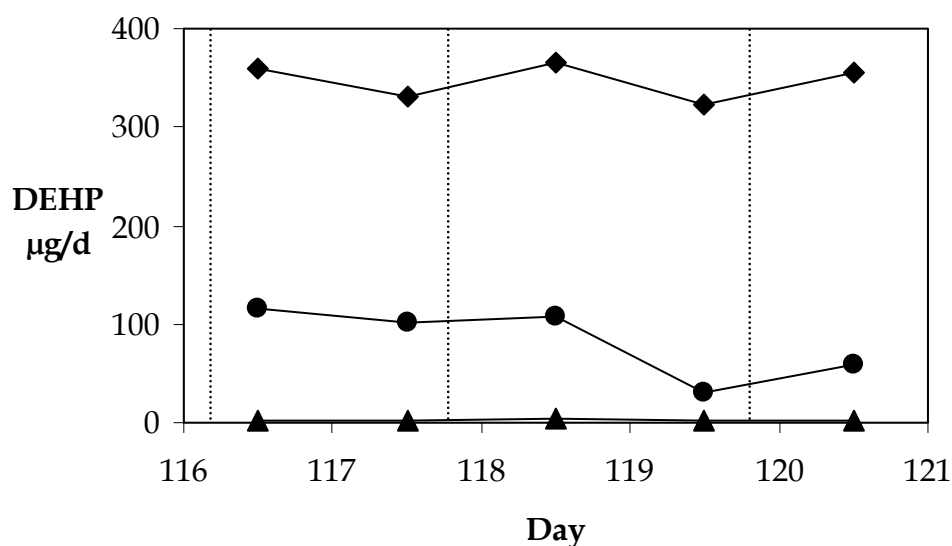


FIGURE 5 DEHP mass in spiked SBR1 influent (♦), effluent (▲) and sludge (●) during days 116-121. Dotted line shows the days of starting with a new lot of spiked reject.

4.4 Sludge treatment by composting and aeration

Because most of the DEHP entering the STP was found to end up in sludge, study was made of the potential of sludge composting and aeration to reduce sludge DEHP concentrations. Both methods were found to efficiently remove DEHP.

4.4.1 Composting

DEHP concentrations were measured during the composting of Virrat raw sludge (V1, V2) and Jyväskylä anaerobically digested sludge (J1, J2, J3). In bin composting, DEHP concentration in V1 and V2 decreased by approximately 31% and 48% in 14 and 85 days, respectively, while decreases in J1 and J2 were only 4% and 18% during 14 and 85 days (Fig. 6a). The DEHP concentrations of Jyväskylä sludge compost decreased slightly more rapidly in the rotary drum (J3) than in the compost bins.

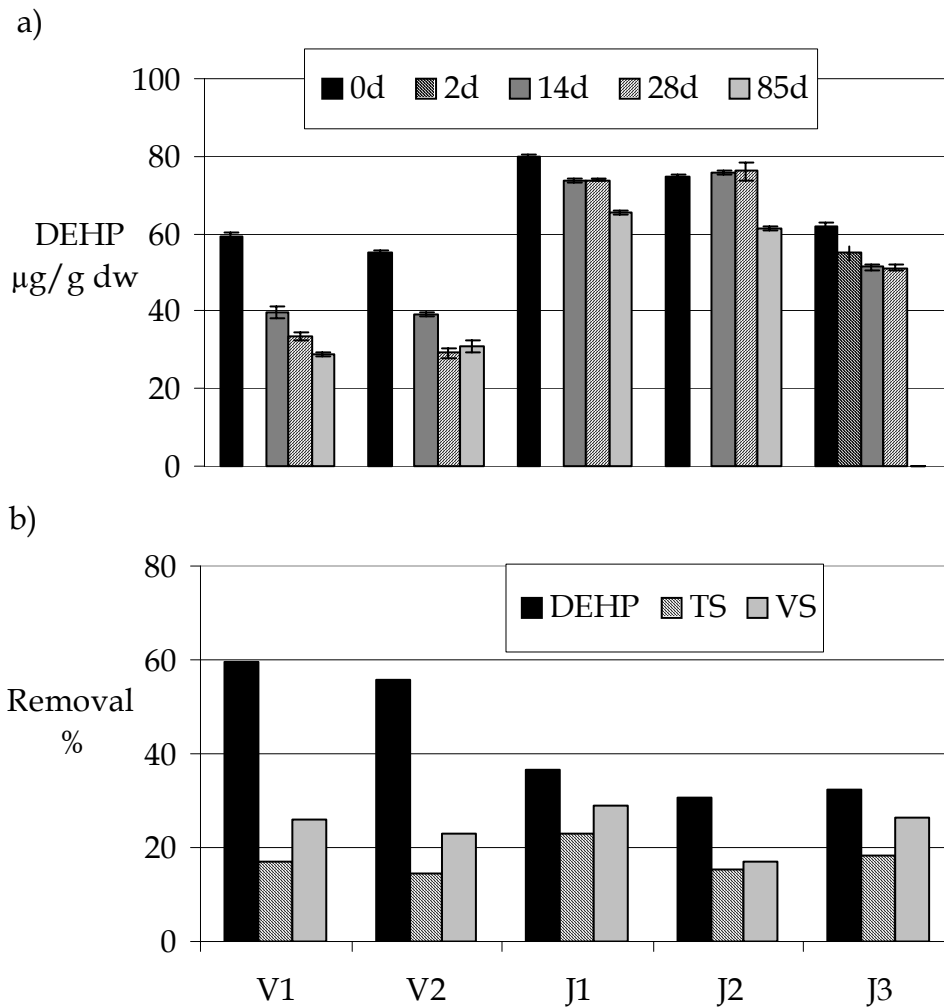


FIGURE 6 DEHP concentrations ($\mu\text{g/g dw}$) (a) and absolute removals (mass basis) of DEHP, TS and VS (b) from Virrat (V1, V2) and Jyväskylä (J1, J2) sludge composts in bins at 85 days and in rotary drum (J3) at 28 days.

The degradation rate of an organic compound tends to be higher at the beginning of the degradation process than in the late phase, as was shown by Madsen et al. (1999) for DEHP degradation in a soil system. In the present study, DEHP concentration continued to decrease in the curing phase of

composting when the temperature was low; thus it is likely that DEHP concentrations would have decreased further, though at a lower rate, if stabilisation by composting had been continued. Epstein (1997) discusses the data from a composting experiment involving removal of organic compounds, but he does not explain whether removal means decrease in concentration or mass removal. However, the reported 25% and 41% removals for DEHP in 7 and 30 days, respectively, are on the same level as the decreases in DEHP concentration for Virrat sludge in the present study.

Although often expressed in terms of changes in concentration, the DEHP removal during composting is better described by absolute removals, which take account of the decrease in solids content. On average, 58% of the DEHP content of the Virrat sludge composts was removed during 85 days composting (Fig. 6b). In the case of the Jyväskylä sludge composts, approximately 34% of the DEHP was removed in compost bins in 85 days and 32% in the rotary drum in 28 days. In all experiments, DEHP removal was somewhat higher than the TS and VS removals.

Leachate samples collected from Virrat compost bins between days 7 and 28 were combined and analysed for DEHP. Concentrations of 9 ± 1 and 24 ± 3 $\mu\text{g/l}$ were measured in V1 and V2, respectively, and were at the same level as those reported by Fromme et al. (2002) (16.8–26.1 $\mu\text{g/l}$). Based on average leachate flow (140 ml/d), the total amount of DEHP removed from composts with leachate in 85 days was approximately 100 μg in V1 and 290 μg in V2. The 56% and 60% absolute removals of DEHP from compost bins V1 and V2 shown in Fig. 6b correspond to removals of 650–950 mg. Thus, the portion of the total DEHP removed from composts in leachate was far less than 1%. At full-scale composting plants, the possible contamination of leachate with organic pollutants should be considered in assessing the leachate treatment.

The traditional parameters were measured to ensure that composting conditions prevailed in compost bins and the rotary drum. Temperature and pH profiles were typical for composting. Optimum moisture content for sludge composting was very much exceeded in the present study, especially in Virrat composts, and may have reduced the efficiency of the composting process. Oxygen was present in the matrix throughout the study, however, and carbon dioxide was generated constantly.

4.4.2 Aeration

Aeration was studied in two experiments employing different sludges. In the experiment with Virrat raw sludge described in paper IV, the effect of aeration on DEHP removal was compared with the effect of composting. The study in paper V with Jyväskylä raw sludge concentrated on the mechanism of DEHP removal during sludge aeration.

DEHP mass removal during 28 d aeration was 50–62% in Virrat sludge (data not shown) and 73–75% in Jyväskylä sludge (Fig. 7). The removal rate was highest during the first seven days, when, respectively 33–41 and 41–47% of DEHP disappeared from the system.

In the study with Jyväskylä sludge, VS and SCOD were measured to confirm that biodegradation of organic matter occurred in the reactors. In both reactors, the total removal of VS determined on mass basis was 48–49% during 28 days (Fig. 7). Similar to DEHP, the removal rate of VS was highest during the first seven days of the study. Significant correlations were obtained between amounts of DEHP and VS during sludge aeration ($r = 0.982$, $P < 0.001$). Changes in sludge SCOD content also resemble the removal rate of DEHP during the study.

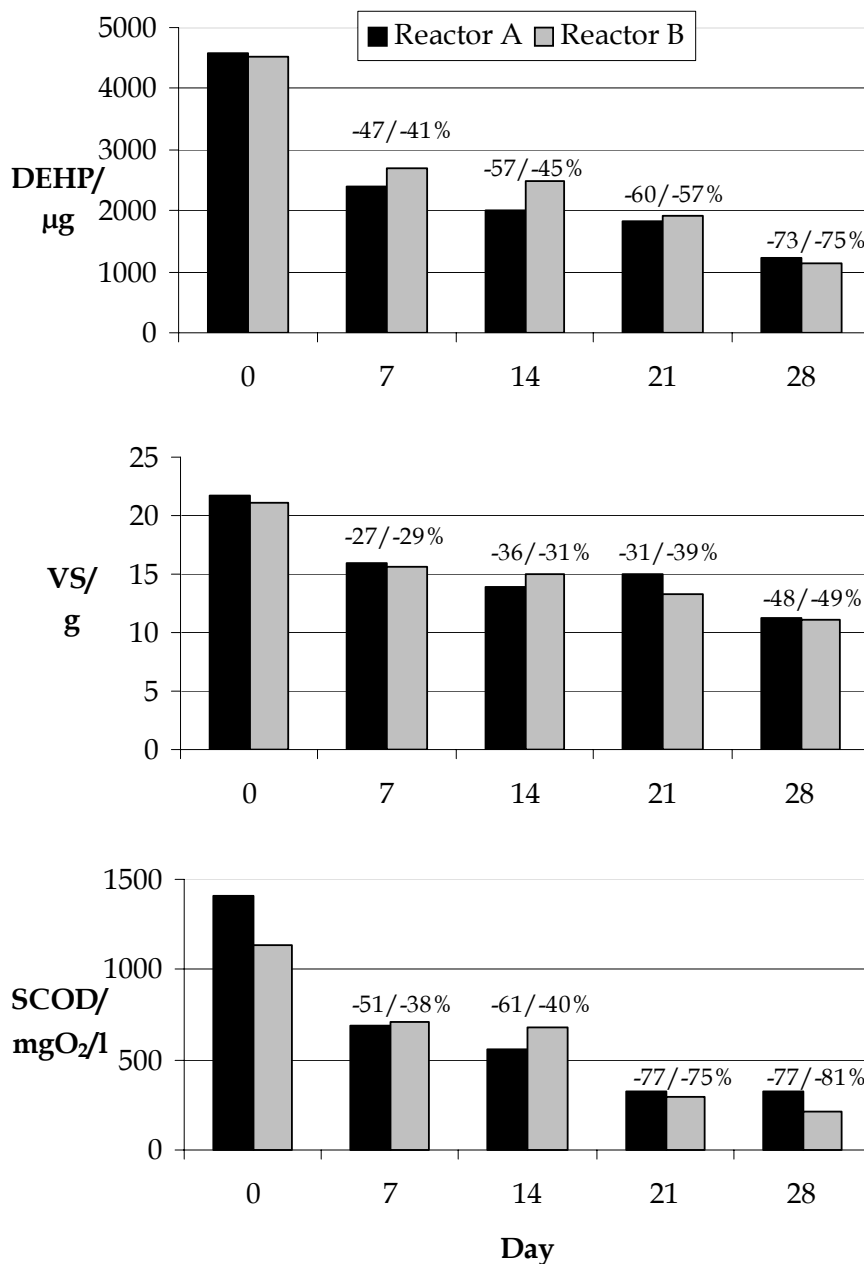


FIGURE 7 Changes in DEHP and VS masses and SCOD value in parallel reactors A and B during 28 d aeration. Percentages show the removal of DEHP in relation to day 0.

Sequential SFE was used to study the changes in binding strength of DEHP during 28 days aeration of Jyväskylä sludge. Six discrete DEHP fractions were extracted, starting with mild extraction conditions and moving towards harsher conditions. At the beginning of the study approximately 79% of the DEHP was in fractions 1-3 (Fig. 8). It was found that approximately 93% of the DEHP originally loosely bound to the matrix (fractions 1-3) was removed during the first 7 days. Altogether 41-47% of the removal was explained by biodegradation, but, interestingly, 47-51% of the DEHP that disappeared was more strongly bound to the matrix. Although sorption usually means decrease in biodegradation potential of a compound, the biodegradation continued in fractions 4 and 5 where DEHP was strongly bound to the matrix, and harsh conditions were needed to desorb it. The biodegradation rate was lower during days 8-28 than during the first 7 days, however.

DEHP in sludge mainly occurs sorbed to organic matter, though biodegradation of organic compounds is usually assumed to occur only in soluble phase (European Commission 1996). The biodegradation of DEHP observed during the study showed that biodegradation must also have occurred in sorbed phase, or that sorbed DEHP became bioavailable through desorption. In a review of the biodegradation data of phthalates, Peterson & Staples (2003) concluded that DEHP biodegradation is probably occurring in the sorbed phase, although at a lower rate than in soluble phase. This can occur, they suggest, through sorption of DEHP to organisms capable of degrading phthalates and the aid of interfacial surfaces that serve to concentrate the phthalate and its degrading organisms. They also assumed that sorption is reversible, i.e. the sorbed compound may be desorbed. Pignatello & Xing (1996) suggest that the desorption of organic pollutants is aided by decomposition of the sorption sites. The significant correlation between DEHP and VS concentrations in the present study support the idea that DEHP is made bioavailable by degradation of organic sorption sites.

After desorption, DEHP must have been quickly biodegraded, for no significant DEHP concentrations were found in fraction 1 after the study began. This result supports the findings of laboratory biodegradation studies performed with spiked compounds, which suggest that desorbed DEHP is readily biodegradable (Saeger & Tucker 1976; O'Grady et al. 1985). In further support, our spiking experiment showed DEHP to be readily biodegraded in reject water from the same origin as the sludge used in this study when bioavailability was not limited by prolonged sorption to sludge (III).

Very harsh conditions were needed to desorb the DEHP in fraction 6. The amount of DEHP in fraction 6 was low at the beginning of the study and slightly increased after 14 d. The low concentrations confirm that the DEHP removal during aeration was rather a result of biodegradation than transformation to bound residues. It is probable that the increase in DEHP concentration in fraction 6 would have continued if the experiment had lasted longer, because stronger bonding and decreased desorption potential are

typical in environmental matrices during extended contact of a compound and its sorption site (Alexander 1995).

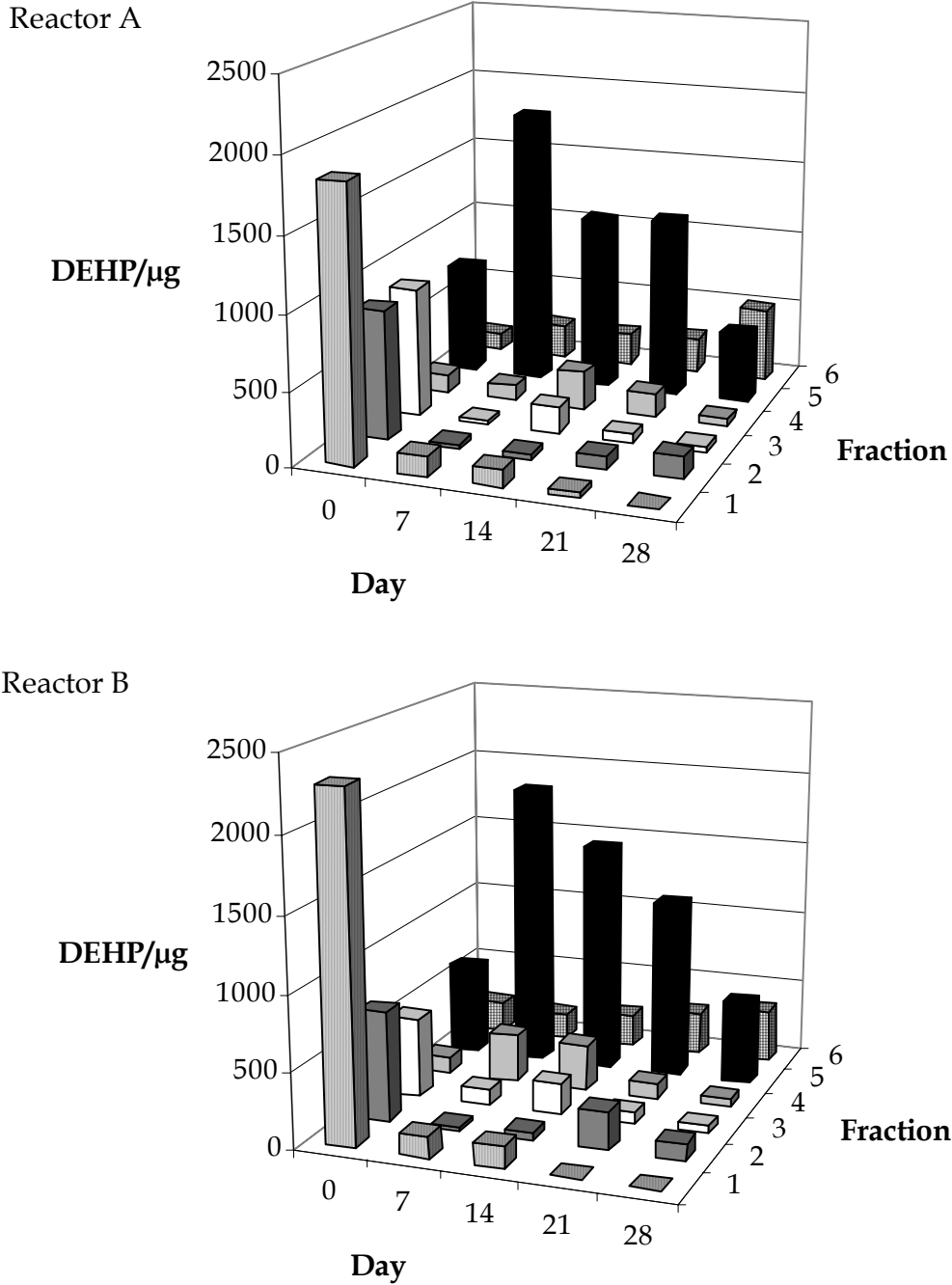


FIGURE 8 Changes in DEHP mass in parallel reactors A and B during 28 d aeration in six extraction fractions.

4.5 Overall potential of STPs to remove DEHP

DEHP concentration in Finnish sewages is typically about 100 µg/l (I, II). A major part of this originates from households (I). Because STPs probably receive only a minor part of the phthalates originating in households, any approaches to decreasing DEHP releases to the environment should focus on decreasing its use in everyday products.

In sewages, DEHP is fractionated into soluble and sorbed forms. The soluble fraction, which can be regarded as bioavailable, represents a minor part of the total DEHP load (I), while sorption to the colloidal particle fraction seems to be somewhat higher than sorption to the settleable fraction (I, II). If primary sedimentation is included at an STP, the settleable fraction is removed in that stage. The colloidal particle fraction enters the activated sludge stage, where it may undergo sorption-desorption with activated sludge flocs (Guellil et al. 2001). Furthermore, sorbed DEHP may be desorbed as its sorption sites decompose. In biological treatment, sorption makes a pollutant less available for bacteria and hinders biodegradation (Pignatello & Xing 1996). However, a large part of sorbed DEHP is biodegraded during sewage treatment in the activated sludge stage (II) and during the biological treatment of reject water (III) or sludge (IV, V). Because DEHP is mostly sorbed to solids when it enters the biological treatment stage, it has to be desorbed to be bioavailable. The present study suggests that the desorption is promoted by decomposition of organic sorption sites (IV).

Dissolved organic matter in wastewaters, in turn, may act as a carrier (Bauer & Herrmann 1998) and transport DEHP through the treatment process unaffected. The present study has indicated, however, that DEHP is preferentially sorbed on solids rather than being in dissolved form in sewages (I).

Evidently, most of the DEHP in the soluble fraction of sewage, or made soluble through desorption, is rapidly biotransformed during biological treatment of sewage or sludge (III, V). MEHP, the primary degradation product of DEHP was not detected at the STP, which indicates that MEHP is itself biodegraded at STPs. The fraction of DEHP released to receiving waters is usually small, but larger if solids separation in secondary stage is poor. DEHP concentrations detected in Finnish STP effluents have typically been lower than 8 µg/l, which is the limit for household water recommended by WHO (1996).

Abiotic degradation, volatilization or stripping of DEHP in STPs was not studied in this work, because the physico-chemical properties of the chemical indicated that these processes can be regarded as negligible in the STP environment.

At a typical STP, primary and secondary sludges are combined, thickened, stabilized (for example by anaerobic digestion or aeration), dewatered, sometimes composted and finally utilized in agriculture or otherwise disposed of. Reject waters separated in thickening and dewatering may contain high

concentrations of DEHP, especially if the solids content is high (II, III). Reject waters, together with return secondary sludge, are usually returned to the headworks of the STP where they give rise to an internal circulation of pollutants, which may be present in as high concentrations as in sewage (II). The internal load of DEHP can be reduced by improving solids separation from reject waters (III). Moreover, separate biological treatment of reject waters with the goal of nitrogen removal was shown to almost totally remove the load of DEHP through biodegradation and sorption to sludge (III). The efficient removal of solids in a separate treatment of reject waters has sometimes been considered unimportant since the effluent is circulated back to the sewage treatment process (Arnold et al. 2000). However, as noted above, the hydrophobic compounds sorbed to solids are also returned to the sewage treatment process, and the internal circulation of pollutants continues. Sludge with high DEHP concentration may need further treatment.

The results of the present study indicate that anaerobic biotransformation occurs during the digestion of sludge (II). Although anaerobic removal has seldom been observed in laboratory biodegradation studies (Shelton et al. 1984; Ziogou et al. 1989), the results of pilot-scale studies support the occurrence of anaerobic degradation of DEHP in sludge digestion (Govind et al. 1991; Parker et al. 1994). Anaerobic degradation of DEHP has been observed in the soil environment (Shanker et al. 1985), which shows the possibility of anaerobic degradation of DEHP in sludge. This subject is in need of further study.

Composting and aeration of both raw and anaerobically digested sludge were found to be efficient ways to remove DEHP (IV, V). The removal rate was highest during the first weeks of treatment but continued in later phases. DEHP removals during the first weeks are most likely the result of biodegradation, but in later phases unreversed binding of DEHP to the sludge matrix may occur.

It is important that the degradable organic matter in sludge has been minimized with a proper stabilization method before the sludge is utilized, in agriculture for example. If degradation of organic matter occurs in the environment, the DEHP or other hydrophobic pollutants sorbed to sludges may be desorbed in the environment (Barraclough et al. 2005). On the other hand, the concentrations of organic pollutants in sludge should be minimized before application. For removal of DEHP and other sorbed but biodegradable pollutants from sludge, it should be possible to develop pretreatment methods that solubilize organic matter and free the sorbed pollutants before biological treatment of the sludge.

Concentrations of DEHP in Finnish raw and anaerobically digested sludges have usually ranged from 90 to 200 mg/kg dw. If use of sludges in agriculture is to increase in future, high DEHP concentration may become a limiting factor. The proposed maximum value for DEHP in sludge to be used in agriculture is 100 mg/kg dry sludge (European Commission 2000), but lower values have already been adopted in some EU countries. Sufficiently long composting times and aeration with sufficiently long SRTs appear to result in DEHP concentrations in sludge acceptable for agricultural use.

Some ideas emerged during the study as to how operations at STPs might be improved in regarding to the removal of DEHP and other hydrophobic but biodegradable pollutants. If incineration is to be the final destination of sludge in future, it would be wise to operate the STP in such a way that most of the DEHP is removed with the sludge. Burning of DEHP does not give rise to harmful by-products, although this occurs with some other compounds. If the sludge is to be used in agriculture, on the other hand, it is important that DEHP biodegradation at STPs is improved. Biodegradation of DEHP during sludge aeration takes time, and SRTs during aeration must be long enough for efficient removal of the pollutant. The reason suggested here for the improved removal of DEHP with long SRTs is the improved decomposition of organic matter, which makes sorbed pollutants bioavailable. Treatment methods could also be developed that would solubilize the organic matter in sludge and free the sorbed pollutants before biological treatment.

5 CONCLUSIONS

- Concentration of DEHP in Finnish sewages is at a level of 100 µg/l.
- Sewage DEHP mostly originates from households, while landfill leachates represent a minor part of the sewage DEHP load.
- Most of the DEHP in sewage is sorbed to colloidal or settleable solids.
- Usually, STPs remove more than 90% of sewage DEHP. Secondary effluent concentrations are lower than 8 µg/l, which is the upper limit for household water recommended by WHO.
- DEHP removal from sewage occurs by both biodegradation and sorption to primary and secondary sludges.
- DEHP concentrations in Finnish raw and anaerobically digested sludges is often higher than 100 mg/kg dw, which is the proposed maximum value for DEHP in sludge to be used in agriculture and may become the limiting factor if the use of sludges in agriculture increases in future.
- Anaerobic biodegradation of DEHP appears to occur during sludge digestion and is in need of further study.
- Reject waters separated from sludge at STPs may contain high concentrations of DEHP if solids separation is poor.
- DEHP is effectively removed from reject waters in nitrogen-removing SBRs, partly by biodegradation and partly by sorption to sludge.
- Composting and aeration efficiently remove DEHP from both raw and anaerobically digested sludge.
- During sludge aeration, a part of the DEHP originally weakly bound to the sludge matrix becomes more strongly bound, but it is able to biodegrade in a later phase of aeration.
- DEHP sorbed to the sludge matrix is biodegraded after desorption, evidently aided by the decomposition of organic sorption sites.
- The bioavailable DEHP fraction is rapidly biodegraded.
- If properly operated, STPs have the potential to efficiently remove DEHP from sewage and reduce the load of DEHP to the environment.

Acknowledgements

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YHTEENVETO (Summary in Finnish)

Bis-(2-etyyliheksyyli)ftalaatin poistaminen jätevesistä yhdyskuntajätevedenpuhdistamoilla

Bis-(2-etyyliheksyyli)ftalaatti (DEHP) on teollisesti tuotettu kemikaali, jota käytetään pääasiassa PVC-muovin pehmentimenä. DEHP ei sitoudu kemiallisesti matriisiinsa, minkä takia se voi hitaasti irrota tuotteista, jolloin osa siitä päätyy jätevesiin esim. pesuvesien mukana. Yhdyskuntajätevedenpuhdistamolla jätevedet käsitellään yleensä sekä mekaanisesti että biologisesti. Etuselkeytyksessä erotettava primaariliete ja jälkiselkeytyksessä erotettava sekundääriliete yleensä yhdistetään, minkä jälkeen ne tiivistetään, stabiloidaan esim. anaerobikäsittelyssä ja lopuksi niistä erotetaan ylimääräinen vesi. Lietteen käsittelyssä erotetut vedet, rejektivedet, kierrätetään yleensä puhdistusprosessin alkuun. Jälkikäsiteltyä lietettä voi olla esim. kompostointi tai ilmastus. Mikäli jäteveden haitta-aineet eivät hajoa puhdistamon prosesseissa, voivat ne kulkeutua ympäristöön käsitellyssä jätevedessä sekä maataloudessa tai viherrakentamisessa käytetyn lietteen mukana. DEHP:lla on esitetty olevan haitallisia vaikutuksia eliöiden lisääntymiseen ja kehitykseen.

Tässä väitöskirjassa tutkittiin yhdyskuntajätevedenpuhdistamojen kykyä poistaa DEHP:a jätevesistä ja siten vähentää DEHP:n ympäristökuormitusta. Täydenmittakaavan jätevedenpuhdistamoilla tutkittiin DEHP:n käyttäytymistä prosessin eri vaiheissa. DEHP:n biohajoamista puhdistamojen rejektivesissä ja lietteissä tutkittiin laboratorio- ja pilotkokeilla. DEHP:n pitoisuudet suomalaisissa yhdyskuntajätevesissä olivat tyypillisesti luokkaa 100 µg/l. Suurin osa jäteveden DEHP:sta oli kolloidiseen tai laskeutuvaan kiintoaineeseen sitoutuneena, liukoisen ja liukoiseen orgaaniseen ainekseen sitoutuneen DEHP:n osuuden ollessa alle 6 %. Jäteveden DEHP:sta poistui jätevedenpuhdistamoilla tyypillisesti yli 90 %, jolloin puhdistetun jäteveden pitoisuudet olivat yleensä alle 8 µg/l, mikä on WHO:n suosittelema maksimipitoisuus juomaveden DEHP-pitoisuudelle. DEHP:n poistuma perustui osittain biohajoamiseen aktiivilieteprosessissa ja osittain sitoutumiseen primaari- ja sekundäärilietteiin. Sitoutuminen jäteveden partikkeleihin ja lietteeseen oli DEHP:n biohajoamista rajoittava tekijä.

DEHP:n pitoisuudet tutkituissa primaari- ja sekundäärilieteteissä sekä anaerobisesti käsitellyissä lietteissä olivat usein yli 100 mg/kg kuiva-ainetta, mikä on EU:n ehdottama DEHP:n maksimipitoisuus maataloudessa käytettävässä lietteessä. Tämän tutkimuksen tulokset viittasivat siihen, että DEHP:a hajosi biologisesti myös lietteen anaerobikäsittelyn aikana. Lietteen kompostointi ja ilmastus poistivat tehokkaasti DEHP:a sekä käsittelemättömästi että anaerobikäsittelystä lietteestä. Lietteen ilmastuksen aikana osa DEHP:sta, joka alun perin oli heikosti sitoutunut lietematriisiin, sitoutui vahvemmin, mutta biohajosi käsittelyn myöhemmässä vaiheessa. Biohajoamista edelsi ilmeisesti lietteeseen

sitoutuneen DEHP:n irtoaminen lietematriisistaan, mitä edesauttoi sen orgaanisen aineksen hajoaminen, johon DEHP oli sitoutunut.

Lietteenkäsittelyn rejektivedet ja ylijäämäliete aktiivilieteprosessista kierätetään yleensä puhdistamon alkupäähän, jolloin ne muodostavat haitta-aineiden sisäisen kierron puhdistamolla. DEHP:n kokonaiskuormasta puhdistusprosessiin sisäisestä kierrosta aiheutuva kuorma voi olla yhtä suuri kuin puhdistamolle tulevasta jätevedestä aiheutuva kuorma. DEHP voidaan poistaa rejektivesistä tehokkaasti sekä parantamalla kiintoaineen erotusta että tyypeä poistavassa biologisessa puolijatkuvassa panosreaktorissa, missä osa DEHP:sta biohajoaa ja osa sitoutuu lietteeseen.

Tämän tutkimuksen perusteella yhdyskuntajätevedenpuhdistamo omaa hyvät mahdollisuudet DEHP:n poistamiseen jätevesistä ja siten sen ympäristökuormituksen vähentämiseen. DEHP:n hydrofobisuus ja taipumus sitoutua lietteeseen tulee kuitenkin huomioida puhdistamon operointitapoja valittaessa.

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