



Priority pollutants behaviour in end of pipe wastewater treatment plants

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ScorePP



Priority pollutants behaviour in end of pipe wastewater treatment plants

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Abstract (max. 200 words)

The following report is a review of the behaviour and fate of priority pollutants in urban municipal conventional waste water treatment plants (activated sludge process). The report has been divided into five parts. The first part gives a brief overview of the pollutant removal mechanisms involved in conventional waste water treatment plants. This part solely involves activated sludge as this is the most common process found in urban waste water treatment plants. The second part is a literature review of fate and behaviour of priority pollutants in activated sludge processes. The third part deals with models used to predict the fate and behaviour of priority pollutants in the absence of experimental data. Countries within the European Union are expected to reduce emissions of priority pollutants, therefore in the fourth part examples of concentrations in influent and effluent waste water treatment plant streams are discussed for two countries (Denmark and Slovenia). It appears that within the European Union important inequalities exist in research on these PPs within waste water treatment plants, implying that much needs to be done concerning PPs in urban municipal waste water treatment plants where different mixtures and combinations of these pollutants are possible. The final part focuses on possible alternative processes that are being studied to remove priority pollutants from waste water.

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LIST OF ABBREVIATIONS AND SYMBOLS

AS	Activated Sludge
BOD	Biochemical Oxygen Demand
HCH	Hexachlorocyclohexane
HRT	Hydraulic Retention Time
MBR	Membrane Bioreactor
NP	Nonylphenols
OECD	Organisation for Economic Cooperation and Development
OP	Octylphenols
PAH	Polycyclic Aromatic Hydrocarbons
PBDE	Pentabromodiphenylether
PP	Priority Pollutant
PST	Primary Sedimentation Tank
RAS	Return Activated Sludge
SD	Standard Deviation
SRT	Solids Retention Time
SSS	Secondary Sedimentation Stage
TOC	Total Organic Content
US-EPA	United States - Environmental Protection Agency
UV	Ultraviolet
VCHC	Volatile Chlorinated Hydrocarbon
VOC	Volatile Organic Compound
MLVSS	Mixed Liquor Volatile Suspended Solids
WAS	Waste Activated Sludge
WFD	Water Framework Directive
WW	Wastewater
WWTP	Wastewater Treatment Plant
F_{OC}	Fraction of organic carbon in the adsorbent (g C/g).
K_a	Air-side mass transfer coefficient
K_{aw}	Water-side mass transfer coefficient
K_h	Henry constant ($\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$)
K_{ow}	Octanol-water partition coefficient
K_p	Partition coefficient
R	Gas constant $R = 8.026\cdot 10^{-5} (\text{m}^3\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
R_{biode}	Removal rate of each pollutant due to degradation ($\text{g}\cdot\text{d}^{-1}$)

R_{sorpt}	Removal rate of each pollutant due to sorption on to organic solids ($\text{g}\cdot\text{d}^{-1}$)
R_{volat}	Removal rate of each pollutant due to volatilisation ($\text{g}\cdot\text{d}^{-1}$)
$T_{1/2}$	Half-life (days)
T	Temperature (K)

1. Introduction

This report was conducted within the scope of the project Source Control Option for Reducing Emissions of Priority Pollutants (ScorePP). The objective is to develop comprehensive and appropriate source control strategies that authorities, cities, water utilities and chemical industries can use to reduce priority pollutants emissions to urban waterways. The project focuses on the 33 priority pollutants initially identified in the Water Framework Directive (WFD) and more precisely on the 11 hazardous compounds.

The ScorePP project is organized in a set of 10 work packages that each has a specific objective. This report is part of the fifth work package (WP5) that aims at investigating the treatment options for priority pollutants. This report addresses Task 5.4 which focuses on assessing the fate of the 33 priority pollutants in the conventional waste water treatment plant (WWTP) processe (activated sludge treatment), as all European case cities in ScorePP have adopted this type of waste water treatment.

Previous tasks in work package 5 have focused on the behaviour of priority pollutants in storm water best management practices (Task 5.1), in treatment and reuse systems for household waste water (Task 5.2) and in on-site treatment systems for industrial waste water (Task 5.3). All former tasks have focussed on specific waste water streams and thus have concentrated their research on technologies that remove pollutants specifically from these waste water streams. Task 5.4 aims at investigating the behaviour of priority pollutants in municipal waste water treatment plants, that most of the time receive waste water from all of the above waste water streams. The fates of priority pollutants found in literature for pre-treatment, primary and secondary treatment steps are addressed in this report. Data on tertiary treatment will also be mentioned when available.

Influent water in municipal waste water treatment plants comes from domestic and industrial sources, and from land and impermeable surface runoff. This wide range of polluted water sources results in a broad spectrum and concentration range of pollutants arriving at the plant. Municipal WWTPs have often been identified as point pollution sources discharging into water bodies. Nowadays, WWTPs have to comply with more and more restrictive discharge limits to water bodies. With an increasing number of pollutants to be removed from conventional WWTP effluents, it is important to understand the behaviour of such compounds during different treatment processes. This will provide information on to what extent priority pollutants are removed and what additional technologies are needed to enable WWTPs to discharge priority pollutants below acceptable limits.

This report is organised into five sections. The first section describes the different waste water treatment stages and the main mechanisms involved in the removal of pollutants in conventional WWTPs. The second part of the report investigates the fate and behaviour of priority pollutants in municipal WWTPs in pre-treatment, primary and secondary treatment stages through a comprehensive literature review. The third part uses models to assess the fate and behaviour of priority pollutants for which no experimental data were found. The fourth section discusses the removal efficiencies of some priority pollutants in waste water treatment plants in Denmark and Slovenia. The last section identifies other possible municipal waste water treatment options that remove priority pollutants from municipal waste water.

2. Removal of pollutants in conventional wastewater treatment plants

2.1 Description of treatment processes in the waste water treatment plants of the case cities

Figure 1 describes the different treatment stages in the WWTPs chosen as case cities in the project. Treatment steps are divided into primary and secondary treatment stages. Primary treatment involves a sequence of physical processes including screening, grinding, and separating debris in mechanical and sedimentation stages. Secondary treatment consists of aerobic biological treatment, known as activated sludge process, followed by a sedimentation stage in which solid particles are removed by skimming or gravitation (Metcalf&Eddy, 1994).

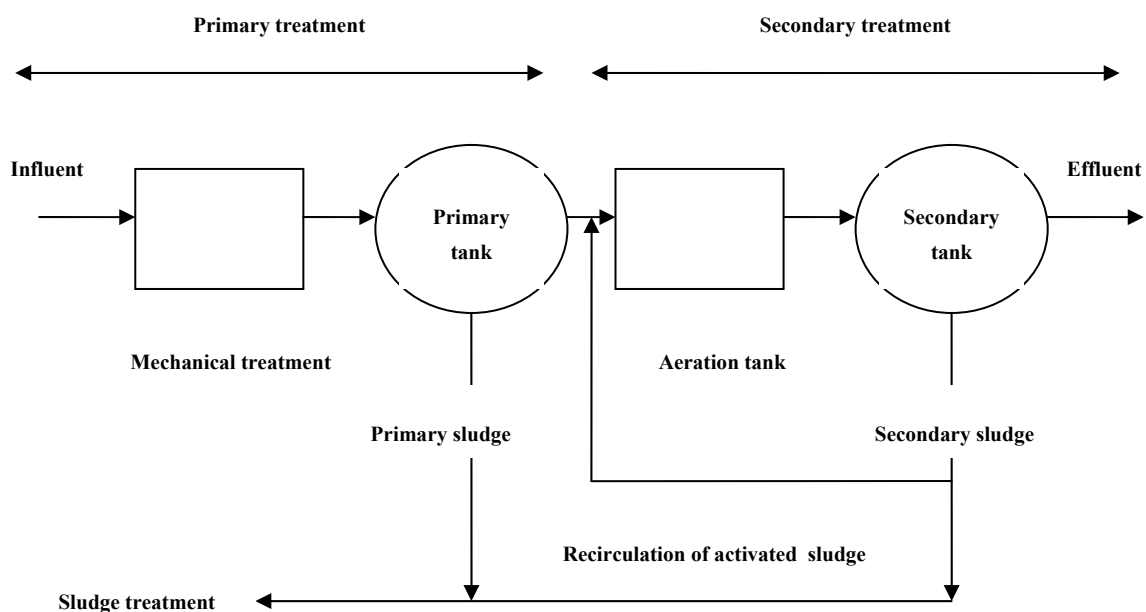


Figure 1: Representation of a conventional activated sludge waste water treatment plant

2.1.1 Primary treatment

The primary treatment stage is divided into two sections consisting of mechanical treatment and primary sedimentation. The mechanical process consists of using differently sized grids to remove large particles, gravels and other unwanted particles that could damage the plant machinery. The sedimentation process produces a homogeneous water mixture for the secondary treatment stage. During this process, particles that have not been intercepted during the mechanical process due to their small diameter (such as sand, faecal matter, grease and oil) are removed. Water is fed to the tank at a low velocity which enables either the flotation of particles to the surface or their sinking to the bottom of the tank. Unwanted particles are either skimmed off from the surface with scrapers or gathered at the bottom and discharged for primary sludge treatment.

2.1.2 Secondary treatment

The activated sludge process is widely used in Europe (and worldwide) as a biological treatment. The effluent stream from the primary treatment stage is directed to an aeration tank where oxygen is introduced either at the bottom by plate or pipe diffusers or at the surface by propellers or jet diffusers to increase bacterial activity. The bacterial activity results in a decrease of the organic and nutrients

content in the waste water. The effluent is directed to a secondary sedimentation tank to allow the removal of aggregates. Part of the sludge obtained from the sedimentation tank is re-circulated to seed the sewage entering the aeration tank and part sent for sludge treatment and disposal. Effluent streams from the sedimentation tank are either sent for tertiary treatment, for disinfection purposes (which is not the case in the ScorePP case cities) or directly discharged into a stream.

2.2 Mechanisms of pollutant removal in waste water treatment plants

Organic pollutants can be removed by different processes such as sorption, volatilization, biodegradation, hydrolysis, photolysis, photo-oxidation, and electrochemical-oxidation (Rogers, 1996). In waste water treatment four mechanisms are of particular importance with regard to pollutant removal (Figure 2):

- Sorption
- Volatilisation
- Biodegradation
- Air stripping

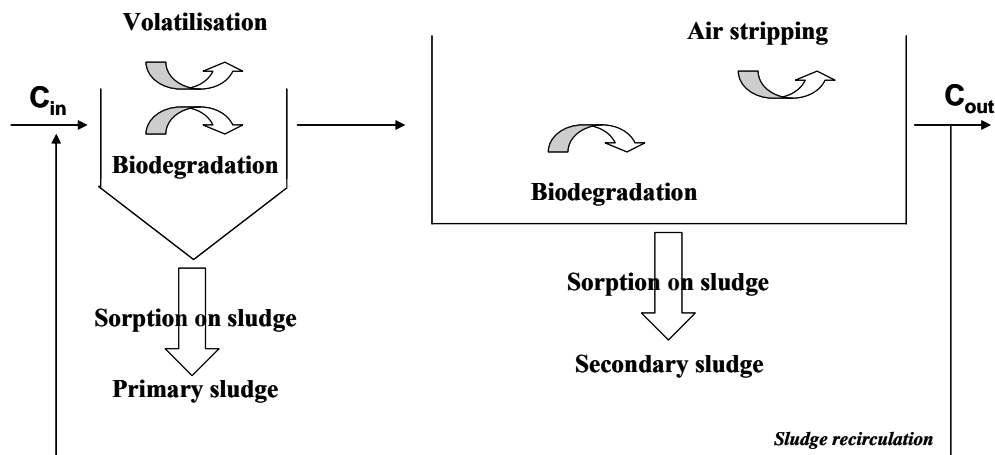


Figure 2: Major pollutant removal pathways in conventional activated sludge waste water treatment

2.2.1 Sorption

Sorption is an important physical process in which removal of specific contaminants can be predicted using the physico-chemical characteristics. During primary or secondary sedimentation stages, hydrophobic contaminants may partition onto settled sludge solids. This tendency to accumulate on sewage sludge solids is related to the octanol-water partition coefficient (K_{ow}) of the compound (Rogers, 1996). This coefficient is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. Octanol is used because it simulates the uptake of a pollutant by lipids and it relates to bioaccumulation. Another coefficient used is the K_{oc} , used to indicate the capacity of a compound to adsorb to organic particles. It represents the retention potential of a compound by organic matter. This parameter is used in many environmental studies to help determine the fate of chemicals in the environment. According to Rogers (1996), the following guide to the importance of sorption can be used:

- | | |
|-----------------------------|---------------------------|
| • $\log K_{ow} < 2.5$ | Low sorption potential |
| • $2.5 < \log K_{ow} < 4.0$ | Medium sorption potential |
| • $\log K_{ow} > 4.0$ | High sorption potential |

2.2.2 Volatilization

Volatilization is also a physical process that can be predicted using the physico-chemical characteristics of contaminants. Volatilization losses are influenced by the partitioning or sorption behaviour of organic compounds. For instance, it is generally considered that volatilization losses from the aqueous phase are only attributed to the fraction of chemical in the dissolved state which is then transferred through the water–air interface in accordance with basic chemo-dynamic properties of the system. The fraction that is sorbed to particulate matter is not directly available, under equilibrium conditions, for mass transfer across the water/air interface (Byrns, 2001). According to Rogers (1996), the significance of volatilization losses of specific organic compounds during sewage treatment can be estimated using the following empirically defined categories based on Henry's Law constant (K_h) and K_{ow} :

- $K_h > 1 \cdot 10^{-4}$ and $K_h / \log K_{ow} > 1 \cdot 10^{-9}$ High volatilization potential
- $K_h < 1 \cdot 10^{-4}$ and $K_h / \log K_{ow} < 1 \cdot 10^{-9}$ Low volatilization potential

2.2.3 Biodegradation

Since biodegradation of organic compounds can occur under both aerobic and anaerobic conditions, both processes could be involved in WWTPs. However, the complete mineralization of xenobiotic compounds in treatment systems is rare and the term biotransformation more accurately describes the potential changes to the composition and molecular structure of such compounds (Byrns, 2001). Biodegradation can be measured in a number of ways. The US-EPA and OECD have developed a series of laboratory screening tests that can be used to determine the "ready" and "inherent" biodegradability of organic compounds. Ready biodegradability is determined under the most stringent test condition, using a very small amount of microbial inoculum, and where the test chemical is present as the sole carbon source at low concentrations. Inherent biodegradability tests are intended to provide more favorable conditions for biodegradation to occur. Such tests are often conducted using higher microbial inoculum concentrations, higher test chemical concentrations, and are conducted under conditions which allow for acclimation of the micro-organisms. Chemicals that pass an inherent biodegradability test are considered non-persistent, although the breakdown of the chemical in the environment may be slow.

Table 1 shows the physico-chemical data for solubility, octanol-water partition coefficient (K_{ow}), Henry's law constant (K_h) and the half life of priority pollutants ($T_{1/2}$) found in literature. These data enable to predict in which media priority pollutants are expected to be found and also enable an understanding of their behaviour during waste water treatment (for complimentary data on physico-chemical characteristics see Task 3.1 report).

2.2.4 Air stripping

In the activated sludge process, air is forced into waste water which can induce the removal of volatile organic compounds. During air stripping, volatile pollutants are removed from waste water and are transferred into air. The percentage of compounds to be stripped depends on the air flow rate in the aeration basin and on the type of aeration equipment

Table 1: Priority pollutants characteristics (SCOREPP database; HSDB; INERIS; EPI suite)

CAS number	Compound	Solubility (mg·l ⁻¹)		K _{ow}		K _h (atm·m ³ ·mol ⁻¹)		T _{1/2} (days)*	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
71-43-2	Benzene	1,790-1,880	1,835	**	135	4.4E ⁻³ -5.7E ⁻³	5.3E ⁻³	2-28	10.9
91-20-3	Naphthalene	**	31	1,023-3,467	2,046	4.2E ⁻⁴ -7.9E ⁻⁴	5.2E ⁻⁴	1-31	12.4
120-12-7	Anthracene	**	0.04	28,184-35,481	31,572	1.8E ⁻⁶ -6.5E ⁻⁵	4.1E ⁻⁵	3.3-210	80
206-44-0	Fluoranthene	**	0.3	89,125-316,228	170,096	6.4E ⁻⁶ -1.6E ⁻⁵	1.0E ⁻⁵	2-440	153
50-32-8	² Benzo(a)pyrene	**	0.0016	933,254-1,348,963	1,203,200	4.5E ⁻⁷ -1.1E ⁻⁶	6.2E ⁻⁷	54-830	326
191-24-2	Benzo(g,h,i)perylene	**	2.6 E ⁻⁴	3,160,000-6,025,596	4,250,333	5.3E ⁻⁸ -3.3E ⁻⁷	2.0E ⁻⁷	173-865	521
193-39-5	Indeno(1,2,3-cd)pyrene	**	1.9 E ⁻⁴	1,995,262-12,589,254	4,990,125	6.9E ⁻⁸ -1.6E ⁻⁶	5.2E ⁻⁷	58-790	334
207-08-9	Benzo(k)fluoranthene	**	8 E ⁻⁴	1,000,000-6,918,310	2,256,250	4.3E ⁻⁷ -8.2E ⁻⁷	6.4E ⁻⁷	65-1400	451
205-99-2	Benzo(b)fluoranthene	**	1.5 E ⁻³	602,560-3,715,352	1,731,196	5.1E ⁻⁷ -1.1E ⁻⁴	3.1E ⁻⁵	87-610	285.6
75-09-2	Methylene chloride (Dichloromethane)	13,000-28,488	20,774	17.8-17.8	17.8	1.1E ⁻³ -3.2E ⁻³	1.9E ⁻³	1-704	333
67-66-3	Chloroform	3,810-7,950	6,393	83.2-93.3	91.3	1.7E ⁻³ -4.8E ⁻³	3.4E ⁻³	2-180	91.5
107-06-2	Ethylene chloride (1,2 Dichloroethane)	8,600-12,035	10,318	29.5-30.2	30.1	8.8E ⁻⁴ -1E ⁻³	9.9E ⁻⁴	9-365	131.5
85535-84-8	C10-C13 chloroalkane	0.15-0.47	0.31	24,547-1,000,000	451,596	1.2E ⁻⁷ -7.5E ⁻⁴	1.9E ⁻⁴	**	No Value

CAS number	Compound	Solubility (mg·l ⁻¹)		K _{ow}		K _h (atm·m ³ ·mol ⁻¹)		T _{1/2} (days)*	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
12002-48-1	Trichlorobenzenes	**	30	7,943-15,849	11,793	1.3E ⁻³ -3.7E ⁻³	2.3E ⁻³	194-1380	723
120-82-1	1,2,4-Trichlorobenzene	**	49	7,943-15,849	11,793	1.8E ⁻³ -1.4E ⁻²	1.7E ⁻³	2.1-150	51.6
118-74-1	Hexachlorobenzene	**	0.0062	147,911-776,247	401,476	4.9E ⁻⁴ -1.7E ⁻³	1E ⁻³	41-4161	1676
608-93-5	Pentachlorobenzene	**	0.831	63,096-181,970	134,360	7E ⁻⁴ -9.9E ⁻²	3.4E ⁻³	2.1-150	43
87-86-5	Pentachlorophenol	14-80	47	100,000-141,254	125,823	2.4E ⁻⁸ -3.4E ⁻⁶	1.4E ⁻⁶	10-48	24.25
608-73-1	Hexachlorocyclohexane	**	8	5,012-18,197	9,396	2.8E ⁻⁷ -6.8E ⁻⁶	2.1E ⁻⁶	23.4-184	84.1
58-89-9	Lindane	**	7	4,074-6,310	5,262	1.8E ⁻⁶ -7.4E ⁻⁵	1.6E ⁻⁵	4-365	126.1
330-54-1	Diuron	**	42.0	398-479	418.3	5E ⁻⁴ -5.1E ⁻⁵	1E ⁻⁵	70-372	236.3
34123-59-6	Isoproturon	65-70	67.5	316-741	457.7	1.4E ⁻¹⁰ -4.7E ⁻⁹	1.7E ⁻⁹	6.5-61	30.2
15972-60-8	Alachlor	140-240	190	427-3,388	1,687	8.3E ⁻⁹ -3.2E ⁻⁸	2.2E ⁻⁸	7-808	224
122-34-9	Simazine	**	6.2	87.1-182.0	143	9.4E ⁻¹⁰ -3.5E ⁻⁹	1.1E ⁻⁸	30-110	69
1912-24-9	Atrazine	34.7-70	52.4	218.8-562.3	425	15.2E ⁻⁹ -5.E ⁻⁸	1.2E ⁻⁸	30-231	102.1
470-90-6	Chlorfenvinphos	124-145	134.5	4,786-14,125	7,811	2.4E ⁻⁵ -2.5E ⁻³	1.0E ⁻³	4-161	62.3
2921-88-2	Chlorpyrifos	1.12-2.0	1.56	16,982-128,825	76,944	2.3E ⁻⁸ -1.1E ⁻⁵	5.8E ⁻⁶	1.2-34	24.5
959-98-8	α-Endosulphan	0.325-0.51	0.42	3,311-12,589	7,243	5.4E ⁻⁶ -6E ⁻⁵	1.89E ⁻⁵	8-60	31.2
115-29-7	Endosulfan (Endosulfan-thiosulphate)	0.325-0.51	0.42	3,981-12,589	8,018	1E ⁻⁵ -6.5E ⁻⁵	2.45E ⁻⁵	2-42	22.9

CAS number	Compound	Solubility (mg·l ⁻¹)		K _{ow}		K _h (atm·m ³ ·mol ⁻¹)		T _{1/2} (days)*	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
87-68-3	Hexachlorobutadiene	3.2-50	26.6	19,953-79,433	56,743	8.1E ⁻³ -5.4E ⁻²	2.2E ⁻²	28-300	97
1582-09-8	Trifluralin	0.184-24	12.09	117,490-218,776	168,133	1.0E ⁻⁴ -6.2E ⁻³	1.3E ⁻³	21-405	152
1806-26-4	Octylphenols	**	12.6	**	12,589	7E ⁻⁶ -8.6E ⁻⁶	7.6E ⁻⁶	5-50	20.7
140-66-9	para-tert-Octylphenol	5-12.6	8.8	9,120-199,526	88,800	3.3E ⁻⁷ -3.4E ⁻⁵	1E ⁻⁵	**	5
25154-52-3	Nonylphenols	**	6	15,849-575,440	237,178	2.4E ⁻⁹ -3.7E ⁻⁵	1.3E ⁻⁵	5-20	11.4
104-40-5	4-para-Nonylphenol	**	6.6	15,849-575,440	237,178	7E ⁻⁶ -3.4E ⁻⁵	2E ⁻⁵	**	12
117-81-7	DEHP	**	0.278	74,131-39,810,717	17,107,756	1.6E ⁻⁸ -1.7E ⁻⁵	3.5E ⁻⁶	3-54	21.9
	Brominated diphenylether	**	9 E ⁻⁷	3,715,352-79,432,823	32,675,830	6E ⁻⁷ -8.7E ⁻⁶	3.5E ⁻⁶	150-600	300
7440-43-9	Cadmium and its compound	Insoluble to 1.4E ⁻⁷	-	NA	NA	NA	NA	NA	NA
7439-92-1	Lead and its compounds	Insoluble to 4.43E ⁵	-	NA	NA	NA	NA	NA	NA
7439-97-6	Mercury and its compounds	Insoluble to 6000	-	NA	NA	NA	NA	NA	NA
7440-02-0	Nickel and its compounds	Insoluble to 6000	-	NA	NA	NA	NA	NA	NA
688-73-3	Tributyltin	18-61.4	-	3.1-3.8	-				

*half-lives under aerobic condition; ** only one value was found in the literature; N.A. Not Applicable

3. Fate of priority pollutants in different treatment stages in conventional waste water treatment plants

3.1 Parameters influencing the removal of priority pollutants from waste water

Several parameters can influence the removal of priority pollutants from waste water:

- Hydraulic Retention Time (HRT); this is the average time waste water remains in the reactors. Increasing the HRT in an activated sludge plant has been reported in literature to contribute to improving pollutant removal (e.g COD, BOD, xenobiotics,...) (Barr, 1996; Ritchelita, 1999; Rempel, 1992). Higher HRT enable longer contact time between the degrading organisms and pollutants and also increase the pollutant sorption on to sludge.
- Solids Retention Time (SRT); this is the average time that sludge remains in the reactors. Depending on the pollutants to be removed, decrease change in SRT influences the sorption of pollutants to sludge and the adaptation and specialisation of micro-organisms. It was found in literature that long SRTs in biological treatment processes favour the biodegradation of many xenobiotic compounds but not all potentially hazardous organic substances (Byrns, 2001; Clara *et al.*, 2005; Jacobsen *et al.*, 2004).
- Mixed Liquor Volatile Suspended Solids (MLVSS); this is the microbial suspension in the aeration tank of an activated sludge wastewater treatment plant. MLVSS is the combination of influent waste water going into the reactor with the recycled sludge taken from the same reactor and from the secondary settling tank.
- Airflow rate; this is the injection of diffused air into the aeration vessel and strongly influences the volatilization of priority pollutants.

3.2 Fate of priority pollutants during waste water treatment in conventional waste water treatment plants

3.2.1 Benzene and Polyaromatic Hydrocarbons

Benzene is a mono-aromatic hydrocarbon compound found in petrol and also used as a solvent. The compound is classified as carcinogenic for humans. Compared to other hydrocarbons, benzene is highly soluble which makes its removal from water more complex. The compound has a low sorption potential ($\log K_{ow} = 2.13$) but a high volatilisation potential ($K_h = 5.35 \cdot 10^{-3}$). Benzene removal efficiencies in conventional activated sludge treatment are found to be from 83 to 96 % (Table 2).

Polycyclic aromatic hydrocarbons (PAHs) are widely studied substances in surfactants, dyeing processes, pigmentation and solvents. These compounds are also emitted during partial combustion and are known for their persistency, low biodegradability and their hydrophobic characteristics. PAH are also a serious problem due to their high toxicity, mutagenicity and carcinogenicity to mammals and aquatic organisms (Zheng, 2007; Martinez, 2007).

PAHs have sorption potentials ranging from medium to high (naphthalene: $\log K_{ow} = 3.31$; indeno(1,2,3-cd)pyrene: $\log K_{ow} = 6.69$) and most of the them demonstrate low volatilisation (ranging from $5.26 \cdot 10^{-4}$ to $6.49 \cdot 10^{-7}$). Several studies have documented PAH removal (Bressy, 2006; Bussetti, 2006, Katsoyiannis, 2004). The following removal percentages have been found in conventional activated sludge WWTPs, 69 to 95 % for naphthalene, 32 to 80 % for anthracene, 66 to 97 % for fluoranthene, from above 50 to 78 % for benzo(a)pyrene, 56 to 62 % for benzo(ghi)perylene and 59 to 76 % for benzo(b)fluoranthene (Table 2).

Table 2: Removal percentage of benzene and PAH in conventional activated sludge treatment plants

Compounds	Reference	Removal (%)
Benzene	Escalas <i>et al.</i> (2003)	83
	Barbosa <i>et al.</i> (2007)	> 99
	Parkerton (2001)	92-96
Naphthalene	Escalas <i>et al.</i> (2003)	95
	Busetti <i>et al.</i> (2006)	69
	RDSE (2006)	> 93
	Clark <i>et al.</i> (1995)	85
Anthracene	Busetti <i>et al.</i> (2006)	59
	RDSE (2006)	32-78
	Clark <i>et al.</i> (1995)	80
Fluoranthene	Busetti <i>et al.</i> (2006)	66-80
	RDSE report (2006)	90-97
Benzo(a)pyrene	Busetti <i>et al.</i> 2006	78
	RDSE (2006)	> 50
Benzo(ghi)perylene	RDSE (2006)	56-62
Benzo(b)fluoranthene	RDSE (2006)	59-76

3.2.2 Chlorinated aliphatics

Methylene chloride (dichloromethane) is used in the pharmaceutical industry, paint cleansing, grease removal for metallic parts and chemical analysis in laboratories. Chloroform is mainly used as an intermediate in the production of a solvent, chlorodifluoromethane. Ethylene chloride (1-2 dichloroethane) is mainly used as an intermediate in the production of vinyl chloride or for production of solvents.

These three chlorinated hydrocarbons have low sorption potentials (log K_{ow} values of 1.25, 1.96 and 1.47 respectively) and are particularly volatile as suggested by their K_h values (ranging from $9.96 \cdot 10^{-4}$ to $1.96 \cdot 10^{-3}$). According to literature references, removal of these priority pollutants from conventional activated sludge waste water treatment plants are up to 59 % for methylene chloride, 51 to >99 % for chloroform and 94% for ethylene chloride (Table 3).

Studies of the fate of volatile organic compounds (VOCs) in the activated sludge process have shown that stripping, biodegradation and adsorption all occur. Adsorption is however not as important as stripping and biodegradation (Hsieh, 2000). Melcer *et al.* (1994) indicated that the sorption process prevailed in the pre-treatment and primary clarifier steps. In the secondary treatment step, volatilization, sorption and biodegradation have been identified as the main mechanisms involved (EPA, 1994). In the case of the removal of non chlorinated VOCs, biodegradation is the major mechanism, while in the case of chlorinated VOCs, air stripping dominates the mechanical removal processes.

Table 3: Removal percentages of chlorinated aliphatics in conventional activated sludge treatment

Compounds	Reference	Removal (%)
Methylene chloride (Dichloromethane)	RDSE (2006)	59
Chloroform	Escalas <i>et al.</i> (2003)	> 99
	RDSE (2006)	51-93
Ethylene chloride (1,2 Dichloroethane)	Freitas dos Santos and Livingston (1995)	94

3.2.3 Chlorobenzenes

Trichlorobenzenes are mainly used as intermediates for the production of different products as herbicides, pigments, solvents, lubricants and dyes. Pentachlorobenzene is no longer used nor produced in Europe; previously they were by-products from pesticide production but are still emitted during the incineration of solid waste. Trichlorobenzenes have a high sorption potential ($\log K_{ow} = 4.1$) and a high volatilization potential ($K_h = 2.3 \cdot 10^{-3}$ and $1.73 \cdot 10^{-3}$). Removal efficiency found in the literature for such compounds in the activated sludge process are 98 % for 1,2,5-Trichlorobenzene (Escalas, 2003).

Hexachlorobenzene (HCB) is neither commercialized nor produced in Europe (Denier van der Gon, 2007). HCB was used in fungicides, soil treatments, in industrial processes such as aluminum fusion, in the production of military products and wood preservation. HCB is a hydrophobic compound known for its bioaccumulation, impact on organisms and persistence in the natural environment. It possesses a high sorption potential ($\log K_{ow} = 5.6$) and a high volatilization potential ($K_h = 1.08 \times 10^{-3}$). HCB removal efficiencies during the activated sludge process are between 88 % and 91 % (Table 4).

The compounds considered in this section have high sorption and high volatilization potentials suggesting that sorption and volatilization are the main removal mechanisms. No data relating to pentachlorobenzene and 1,2,4 trichlorobenzene removals were found in literature.

Table 4: Removal percentages of chlorobenzenes in conventional activated sludge treatment

Compounds	Reference	Type of treatment	Removal (%)
1,2,5-Trichlorobenzene	Escalas <i>et al.</i> (2003)	Conventional AS - WWTP	98
		Primary treatment	70 (\pm 23)
Hexachlorobenzene	Katsoyiannis and Samara (2004)	Secondary treatment (AS)	72 (\pm 24)
		Conventional AS - WWTP	90 (\pm 15)

3.2.4 Chlorophenols

Use of pentachlorophenol (PCP) has been restricted to professional use. It is a synthetic chlorinated organic compound found in fungicides, bactericides and the wood preserving industry. Uncontrolled releases of this compound have been reported due to its widespread use. Pentachlorophenol is known to be a toxic compound and to be persistent in the environment. The compound is recognized as causing adverse long term effects to people exposed to levels over 1 $\mu\text{g/L}$ for a short period of time (Visvanathan *et al.*, 2005).

With a $\log K_{ow}$ value of approximately 5, PCP is considered to have a high sorption potential. The compound has a low K_h value ($1.45 \cdot 10^{-6}$) indicating a low volatilization potential. According to Clark *et al.* (1995), removal of pentachlorophenol in activated sludge process can reach up to 85 % (Table

5). Pentachlorophenol has been found to degrade in both aerobic and anaerobic conditions, but anaerobic conditions were identified as having higher removal efficiencies (Moos, 1983; Guthrie, 1984). Jacobsen *et al.* (1993) studied the removal of micro-pollutants using laboratory scale activated sludge reactors and observed that under low solid retention times, PCP removal was mainly due to sorption and with negligible biodegradation occurring.

Table 5: Removal percentage of pentachlorophenol in conventional activated sludge treatment

Compounds	Reference	Removal (%)
Pentachlorophenol	Clark <i>et al.</i> (1995)	85

3.2.5 Hexachlorocyclohexanes and lindane

Hexachlorocyclohexane (HCH) has 7 isomers. The most encountered ones are α -HCH and γ -HCH, also known as lindane. Derogations within the EU had to be issued for the use of HCH as an intermediate for the production of chemical substances and for uses in products restricted to public health applications and in veterinary products until the end of 2007 (European Parliament, 2004). Former uses of HCH include wood and construction treatment and internal industrial and residential applications. HCH has a medium sorption potential ($\log K_{ow} = 3.9$) and a low volatilization potential ($K_h = 2.1 \times 10^{-6}$). Katsoyiannis and Samara (2004) reported overall removal efficiency for α -HCH and δ -HCH within a conventional activated sludge treatment plant of 79 % with the primary treatment slightly more efficient (55 %) than the secondary treatment process (40 %) (Table 6).

Lindane is a widely used insecticide in creams and powders for humans and animals due to its anti parasitic properties. Lindane is lipophilic, with a moderate sorption potential ($\log K_{ow} = 3.7$), a low volatilization potential ($K_h = 2.1 \cdot 10^{-3}$) and is resistant to biodegradation. According to Hill and McCarty (1967) (cited in Rogers, 1996), lindane is degraded much more rapidly under anaerobic than aerobic conditions. Both authors suggest that effective degradation of lindane occurs with an increased biological activity (in the activated sludge process) which has also been corroborated by Callahan (1979) (cited by Nyholm, 1992). Petrsek *et al.* (1983) and Katsoyiannis and Samara (2004) reported lindane removal efficiencies in a conventional activated sludge process of 45 % and 70 to 90 % respectively (Table 6). According to Petrsek *et al.* (1983), lindane is hardly volatilized and sorption on sludge would remove up to 91%. Harper *et al.* (1977) and Garcia-Gutierrez *et al.* (1984) reported similar values for lindane removal in the primary treatment step while Kipopoulou *et al.* (2004) reported a value two times larger (Table 6), suggesting that the major removal mechanism of lindane in the primary treatment step is sorption whereas the dominant mechanism for the secondary treatment step is biodegradation.

Table 6: Removal percentages of hexachlorocyclohexane and lindane in primary, secondary treatment and the entire conventional activated sludge treatment plant

Compounds	Reference	Type of treatment	Removal (%)
Hexachlorocyclohexane	Katsoyiannis and Samara (2004)	Primary treatment	55 (\pm 27)
		Secondary treatment (AS)	40 (\pm 20)
	Katsoyiannis and Samara (2007)	Conventional AS - WWTP	79 (\pm 19)
		Conventional AS - WWTP	84
Lindane	Garcia-Gutierrez <i>et al.</i> (1984)	Primary treatment	14-49 (mean=32)
	Harper <i>et al.</i> (1977)	Primary treatment	44
	Petrasek <i>et al.</i> (1983)	Conventional AS - WWTP	45
	Katsoyiannis and Samara (2004)	Conventional AS - WWTP	80 (\pm 10)
	Katsoyiannis and Samara (2007)	Conventional AS - WWTP	59
	Kipopoulu <i>et al.</i> (2004)	Primary treatment	94.3 (\pm 1.9))
Kipopoulu <i>et al.</i> (2004)	Secondary treatment (AS)	67.1 (\pm 10.3)	

3.2.6 Phenyl urea compounds

Diuron is an herbicide that has been widely used to control weeds as well as mosses along roads, garden pathways, railway lines, and within crops such as fruits, alfalfa and wheat. Diuron is a pollutant in the aquatic environment as it is used as an antifouling paint biocide. Diuron is slightly toxic to mammals, birds and to aquatic invertebrates. It is highly persistent (remaining up to one year) with a medium sorption potential ($\log K_{ow} = 2.6$) and a low volatilisation potential ($K_h = 1.07 \cdot 10^{-4}$) (Giacomazzi *et al.*, 2004).

Isoproturon has also been widely used as an herbicide and has been shown to be the most prevalent herbicide in groundwater (Böttcher *et al.*, 2007). It has a medium sorption potential ($\log K_{ow} = 2.6$) and very low volatility ($K_h = 1 \cdot 10^{-9}$). Nitschke *et al.* (1999) investigating the biodegradation of isoproturon in a laboratory scale activated sludge plant under nitrogen removing conditions and after an experimental period of 6 weeks, found that the compound was poorly (4 %) biodegraded (Table 7).

Lapertot and Pulgarin (2006) performed biodegradation tests on diuron and isoproturon using the Zhan-Welles test (similar to activated sludge process) and found that neither of the compounds were biodegraded. Singh and Ward (2004) indicated that during activated sludge treatment, microbial processes may lead to a minor reduction of such persistent polar pollutants, whereas sorption can be neglected. Seel *et al.* (1994) cited by Bernhard *et al.* (2006), performed isoproturon spiking in a wastewater treatment plant and also found that no significant isoproturon removal occurred.

Table 7: Removal percentage of isoproturon in conventional waste water treatment plants

Compound	Reference	Type of treatment	Removal (%)
Isoproturon	Nitschke <i>et al.</i> (1999)	Pre-nitrification +Conventional AS - WWTP	< 10
Diuron	Lapertot <i>et al.</i> (2006)	Zhan-Welles test	< 10

3.2.7 Anilide compounds

Alachlor is a common agricultural herbicide which is also known to cause cancer, have toxic and genotoxic effects and to be mutagen. Alachlor has also been recognized as being able to disrupt endocrine systems (Zhu *et al.*, 2006). Alachlor has a medium sorption potential ($\log K_{ow} = 3.2$) and a low volatilisation potential ($K_h = 2.29 \cdot 10^{-8}$). Zhu *et al.* (2006) conducted biodegradability tests on alachlor using activated sludge. The results showed that poor biodegradability occurred and that alachlor affected removal of other pollutants during the process. He concluded that the biodegradation of alachlor using the activated sludge process was not efficient (Table 8). Lapertot *et al.* (2007) also indicated that alachlor had low degradability when using conventional wastewater treatment which was corroborated by Martín *et al.* (2007).

Table 8: Removal percentage of alachlor in conventional waste water treatment plant

Compound	Reference	Type of treatment	Removal (%)
Alachlor	Zhu <i>et al.</i> (2006)	Conventional AS - WWTP	< 10

3.2.8 Triazine compounds

Triazines are mostly used as herbicides for crop protection in agriculture. Atrazine and simazine have been applied on large scales in the past decades. Atrazine is suspected as being an endocrine disrupter and has been reported as causing different types of cancers, birth defects, reproductive tumors (Zhou *et al.*, 2006). Atrazine and simazine have moderate sorption potentials ($\log K_{ow}$ values of 2.6 and 2.1, respectively) and a low volatilisation potential (K_h values of $1.20 \cdot 10^{-8}$ and $1.12 \cdot 10^{-8}$ respectively).

These herbicides have high aqueous solubilities and moderate abilities to adsorb onto soils, which during rainfall events induces important wash off of the substances into municipal waste water treatment plants. It has been shown that conventional wastewater treatment plants are ineffective in reducing the concentrations of triazine compounds from waste waters (Bratby, 2004, Meakins *et al.*, 1994) with removal efficiencies consistently less 40 % (Table 9). According to Wang *et al.* (1994) (cited by Meakins *et al.*, 1994) the removal was suspected to be due to two processes:

- Adsorption from bulk liquid onto solid surfaces,
- Partitioning between the aqueous phase and the organic matter in sludge.

Meakins *et al.* (1994) explained that negligible adsorption onto primary waste solids may have occurred during the primary treatment step and that triazine partition into the lipid structures of biological flocs or the chemical binding to bacterial proteins and nucleic acids in activated sludge may have occurred during the secondary treatment.

Table 9: Removal percentages of simazine and atrazine in conventional waste water treatment plant

Compound	Reference	Type of treatment	Removal (%)
Simazine	Bratby <i>et al.</i> (2004)	Conventional AS - WWTP	< 40 %
	Meakins <i>et al.</i> (1994)	Primary treatment	<10 %
	Meakins <i>et al.</i> (1994)	Secondary treatment (AS)	< 40 %
Atrazine	Bratby <i>et al.</i> (2004)	Conventional AS - WWTP	< 40 %
	Lapertot <i>et al.</i> (2007)	Biological treatment (AS)	No-biodegraded
	Meakins <i>et al.</i> (1994)	Primary treatment	<10 %
	Meakins <i>et al.</i> (1994)	Secondary treatment (AS)	< 40 %

3.2.9 Organophosphate esters

Chlorpyrifos has been widely used as an insecticide for both agricultural and residential purposes. Evidence has shown that the compound has negative impacts on human health and affects fresh water fishes, aquatic invertebrates and estuarine species. The compound has a low solubility in water, a high sorption potential ($\log K_{ow} = 4.88$) and a low volatilisation potential ($K_h = 5.8 \cdot 10^{-8}$) which suggests that the compound would more readily be found associated with organic particulate matter. Studies have been carried out on chlorpyrifos degrading bacteria found in activated sludge and soil. Singh *et al.* (2004) isolated the Enterobacter strain from soil and showed that the bacteria were capable of complete chlorpyrifos degradation at a concentration > 250 mg/L in two days. Ghanem *et al.* (2007) isolated the Klebsiella bacteria from activated sludge and found that the bacteria were capable of complete chlorpyrifos degradation at a concentration > 2 g/L in two days.

Chlorfenvinphos is also used as an agricultural and domestic insecticide. It has a high solubility in water, a low sorption potential ($\log K_{ow} = 0.89$) and a high volatilization potential ($K_h = 1.09 \cdot 10^{-3}$). Gómez *et al.* (2007) found that a conventional waste water treatment plant could achieve 83 % removal of chlorfenvinphos but did not mention the mechanism of removal (biodegradation, absorption or stripping). However, Lapertot *et al.* (2007) conducted a biodegradation test using the Zahn-Wellens test and concluded the chlorfenvinphos was not biodegradable by activated sludge (Table 10).

Table 10: Removal percentages of chlorpyrifos and chlorfenvinphos in conventional waste water treatment plants

Compound	Reference	Type of treatment	Removal (%)
Chlorpyrifos	Lapertot <i>et al.</i> (2007)	Biological treatment (AS)	Not biodegraded
Chlorfenvinphos	Gomez <i>et al.</i> (2007)	Conventional AS - WWTP	83
	Lapertot <i>et al.</i> (2007)	Biological assay (AS)	Not biodegraded

3.2.10 Other pesticides

Endosulfan, a sulphur and oxygen containing derivative of the cyclodiene family of pesticides, is a mixture of alpha and beta isomers (ratio 7:3). Prior to its banning by the European Commission in 2005 it was used as an insecticide. Endosulfan is highly insoluble in water and is mostly associated with soil. The compound has a medium sorption potential ($\log K_{ow} = 3.85$) and a low volatilisation potential ($K_h = 1.89 \cdot 10^{-5}$). Katsoyiannis and Samara (2004) found that α -Endosulfan could be removed at levels up to 95 % by the conventional activated sludge process (Table 11). Taking into

account its properties, it is likely that endosulfan is adsorbed to sludge particles during conventional waste water treatment.

Table 11: Removal percentage of α -Endosulfan in conventional waste water treatment plants

Compound	Reference	Type of treatment	Removal (%)
α -Endosulfan	Katsoyiannis and Samara (2004)	Primary treatment	78 (\pm 17)
		Secondary treatment (AS)	46 (\pm 27)
	Katsoyiannis and Samara (2007)	Conventional AS - WWTP	84 (\pm 17)
		Conventional AS - WWTP	95

3.2.11 Endocrine disrupters

Nonylphenol and octylphenol both belong to the group of non-ionic surfactants known as alkyl phenolic compounds and remain widespread despite the European Union's ban on the use of nonylphenol ethoxylates in domestic detergents, cosmetic products and textiles (Clara *et al.*, 2007; Stasinakis, 2007). These compounds are known to have endocrine disruptive effects on aquatic species. Removal of these compounds in conventional waste water treatment plants has proved to be efficient (Table 12). Nonylphenol and octylphenol have low solubilities, high sorption potentials ($\log K_{ow} = 5.37$ and 4.1 respectively) and low volatilisation potentials ($K_h = 1.35 \cdot 10^{-5}$ and $7.66 \cdot 10^{-6}$). Calculations made by Stasinakis (2007) showed that degradation and sorption in sewage sludge are the main mechanisms involved in the removal of these compounds. Huyard *et al.* (2006) showed removal efficiencies from the water phase in 14 WWTP to be higher than 95%, although more than 75 % of the total concentration in influents was transferred to sludge.

The spread of di-(2-ethylhexyl) phthalate (DEHP) in the environment is a consequence of the wide use of phthalate esters. Phthalate esters are used as additives in plastics, in the production of paint, glues, lubricants, pharmaceuticals, cosmetics and pesticides. Several studies have suggested that phthalates bioaccumulate in aquatic organisms, have endocrine disruptive effects, and may result in carcinogenic and teratogenic effects (Roslev *et al.*, 2007). DEHP has a high sorption potential ($\log K_{ow} = 5.37$) and a low volatilisation ($K_h = 3.52 \cdot 10^{-6}$). According to Marttinen *et al.* (2003), the DEHP removal efficiency from the water phase during the sewage treatment process was on average 94% with the main removal process being sorption to primary and secondary sludge (Table 12). Monoethylhexylphthalate, the primary biotransformation product of DEHP, was not detected at any stage in the treatment process. Fauser *et al.* (2003) indicated that about 15% of DEHP was degraded and 78% was absorbed on sludge.

Brominated diphenylethers (BDE) are flame retardants used in conjunction with textiles, foams and plastics. They are highly lipophilic and easily bioaccumulate in the food chain. Studies have shown that BDE affect motor and learning skills, disrupt thyroid hormone transportation and act as endocrine disruptor (Anderson *et al.*, 2006). BDE is not soluble in water, has a high sorption potential ($\log K_{ow} = 7.5$) and a low volatilisation ($K_h = 3.54 \cdot 10^{-6}$). It has been shown that BDE can be removed from conventional waste water treatment plants at efficiencies up to 93 % (Table 12).

Table 12: Removal percentages of endocrine disruptive compounds in conventional activated sludge waste water treatment plants

Compound	Reference	Type of treatment	Removal (%)
Octylphenols (OP)	Isobe <i>et al.</i> (2001)	Conventional AS - WWTP	84
	Clara <i>et al.</i> (2005b); (2007)	Conventional AS - WWTP	80-95
	Nakada <i>et al.</i> (2006)	Conventional AS - WWTP	32-65
	Huyard <i>et al.</i> (2006)	Extended Aeration Activated Sludge	95
Nonylphenols (NP)	Huyard <i>et al.</i> (2006)	Extended Aeration Activated Sludge	69-98
		Biofilter	92
	Clara <i>et al.</i> (2007)	Conventional AS - WWTP	23-90
	Isobe <i>et al.</i> (2001)	Conventional AS - WWTP	93
	Nakada <i>et al.</i> (2006)	Conventional AS - WWTP	61-75
	Vogelsang <i>et al.</i> (2006)	Primary treatment	< 20
DEHP	RDSE (2006)	Conventional AS - WWTP	92
	Fausser <i>et al.</i> (2003)	Alternately operated WWTP	93-98
	RDSE report (2006)	Conventional AS - WWTP	95
	Clark <i>et al.</i> (1995)	Conventional AS - WWTP	50
	Marttinen <i>et al.</i> (2003)	Conventional AS - WWTP	94
BDE	Rayne and Ikonomou (2005)	Conventional AS +WWTP + UV	93

3.2.12 Metals

Cadmium is used in the production of stabilisation compounds, pigments, battery production, zinc extraction etc.. It is classified as a highly toxic and dangerous chemical within the environment. It is suspected of causing cancer, causing infertility problems and posing risks to unborn children. The literature data available for cadmium show that it can be removed in significant proportions by the sewage treatment process, with removal being mainly due to sorption or to chemical-physical processes (e.g. coagulants, membranes) (Table 13).

Lead has been used in water pipes, in paint and in petrol. Currently, lead can still be found in low concentrations in batteries or in electric and electronic equipment. It has neurological disorder effects, birth defects or can cause cancer. Lead is similar to cadmium in that it appears to be efficiently removed from conventional waste water treatment plants (Table 13).

Mercury is found in electrical and electronical equipment, batteries, amalgams and is also released through solid waste incineration. It is a neurotoxic and nephrotoxic agent known to cause damage to the respiratory, cardiovascular and gastrointestinal systems. It can be effectively removed by the conventional activated sludge. Mercury has affinities with organic and inorganic particulate matter through adsorption process. Most studies have indicated that mercury removal is more than 50 % during primary sedimentation with higher mercury removals occurring during the activated sludge process (Table 13). Volatilisation of elemental mercury is a process that has also been observed (Goldstone *et al.*, 1990). Filby and Blomquist (1984) found that up to 30 % of the mercury could be

volatized as elemental mercury. Wu and Hilger feed an activated sludge system with dosed concentrations of mercury. They noted that reduction and volatilisation processed occurred, but on the long run adsorption to the biomass was more important and therefore that volatilization of elemental mercury was unlikely to occur in a operating full-size sewage treatment plant (Wu & Hilger, 1985).

Although nickel is found naturally in the environment, several products contain this metal such as jewellery, coins and eating utensils. Nickel is also released by burning fossil fuels in power plants and automobiles, and in cigarette smoke. Nickel exposure can lead to lung fibrosis, cardiovascular and kidney diseases and is also suspected of having carcinogenic effects (Kasprzak *et al.*, 2003). Nickel is the metal that has shown the lowest removal efficiencies in literature (Table 13).

Table 13: Removal percentages of metals in conventional waste water treatment plants

Compound	Reference	Type of treatment	Removal (%)
Cadmium and its compounds	Buzier <i>et al.</i> (2006)	Conventional AS - WWTP	50
	Buzier <i>et al.</i> (2006)	Conventional AS – WWTP + disinfection	58
	Jeppe <i>et al.</i> (1983)	Primary treatment	0-87
	Jeppe <i>et al.</i> (1983)	Conventional AS - WWTP	83-96
	Oliver <i>et al.</i> (1973)	Primary treatment	50
	Oliver <i>et al.</i> (1973)	Secondary treatment (AS)	67
Lead and its compounds	Oliver <i>et al.</i> (1973)	Conventional AS - WWTP	83
	Buzier <i>et al.</i> (2006)	Conventional AS - WWTP	70
	Buzier <i>et al.</i> (2006)	Conventional AS – WWTP + disinfection	89
	Oliver <i>et al.</i> (1973)	Primary treatment	61
	Oliver <i>et al.</i> (1973)	Secondary treatment (AS)	83
Mercury and its compounds	Oliver <i>et al.</i> (1973)	Conventional AS - WWTP	93
	Oliver <i>et al.</i> (1973)	Primary treatment	57
	Oliver <i>et al.</i> (1973)	Secondary treatment (AS)	> 67
Nickel and its compounds	Oliver <i>et al.</i> (1973)	Conventional AS - WWTP	> 86
	Buzier <i>et al.</i> (2006)	Conventional AS - WWTP	50
	Jeppe <i>et al.</i> (1983)	Primary treatment	0-81
	Jeppe <i>et al.</i> (1983)	Conventional AS - WWTP	0-80
	Oliver <i>et al.</i> (1973)	Primary treatment	15
	Oliver <i>et al.</i> (1973)	Secondary treatment (AS)	4
	Oliver <i>et al.</i> (1973)	Conventional AS - WWTP	18

3.2.13 Tributyltin

Tributyltin (TBT) is a widely used organometallic chemical through its application in antifouling paints, agrochemicals, wood preservatives and general biocides. TBT is known as being one of the most toxic compounds to the aquatic ecosystems. Organotin compounds are primarily associated with suspended solids in untreated wastewater and consequently most of the TBT is typically removed during the first sedimentation step (Table 14).

Table 14: Removal percentage of tributyltin in conventional waste water treatment

Compound	Reference	Type of treatment	Removal (%)
Tributyltin	Fent (1996)	Primary treatment	66
		Secondary treatment (AS)	64
		Conventional AS - WWTP	88
		Conventional AS + WWTP + filtration	99
	Zingg <i>et al.</i> (1985)	Conventional AS - WWTP	70-80

4. Tools to predict priority pollutants removals and fates in WWTPs

One of the objectives of this report was to identify the fate and behaviour of PPs in conventional WWTPs. Of the 49 organic compounds considered in this study, no data was found in the literature for 16 substances and only a single reference was found for 14 substances. Furthermore, most references relating to the removal of PPs do not specify the predominant removal mechanisms (biodegradation, sorption or volatilization). Modelling is an appropriate alternative to fill the missing data gap. Based on the research describing the distribution and fate of pollutants in conventional biological wastewater treatment plants (Namkung and Rittmann, 1987; Cowan *et al.*, 1993; Clark *et al.*, 1995; Byrns, 2001), generalized models incorporating both the physico-chemical properties of the xenobiotic compounds and the WWTP operational conditions have been established. In this study, three models are examined:

- Byrns' model
- FATE model
- STPWIN model (or STP model)

4.1 Description of the selected models

4.1.1 Byrns' model

The model is conceptually based on a steady state mass balance around the primary treatment process (primary sedimentation tank) and the secondary treatment process (a diffused air activated sludge bioreactor followed by a secondary sedimentation tank) (Byrns, 2001). The total concentration of the xenobiotic chemicals leaving primary treatment is used as input to the biological stage in order to combine together the two treatment components. The removal mechanisms considered for a xenobiotic chemical are:

- Advection (applicable to the dissolved and adsorbed phases)
- Sorption on removed sludge (primary sludge and surplus activated sludge)
- Volatilization
- Air stripping
- Biotransformation

A crucial aspect is the solid/liquid partitioning behaviour of the xenobiotic chemicals. In this regard, the sorption of hydrophobic non-polar organic molecules (such as many xenobiotic chemicals) is commonly described by the partition coefficient $K_p = C_s/C_a$ (ratio between the concentration of adsorbed chemical in organic phase (C_s) and the concentration of chemical in aqueous phase (C_a)). For most hydrophobic non-polar organic molecules: $K_p = (6.3 \cdot 10^{-7}) \cdot F_{OC} \cdot K_{OW}$, where F_{OC} is the fraction of organic carbon in the adsorbent (Byrns, 2001). Table 15 summarizes the assumptions used in the Byrns' model.

Table 15: Assumptions in Byrns' model

Parameter	Assumption
Fraction of organic carbon (Foc)	$F_{oc} = 0.531 \text{ g C} \cdot \text{g}^{-1}$
Sorption on sludge (Kp)	$K_p \text{ bioreactor} = K_p \text{ in primary tank}$
Water mass transfer coefficient (Ka)	$K_a = 2 \text{ m} \cdot \text{h}^{-1}$
Air-side mass transfer coefficient (Kw)	$K_w = 0.02$
Sedimentation rate (Ksed)	$K_{sed} = 0.4 \text{ m} \cdot \text{h}^{-1}$
Biodegradation rate (k1 and k2)	$k_1 = k_2$

4.1.2 FATE model

The fate and treatability estimator (FATE) model was developed by the US-EPA in the early 1980's to estimate the removal efficiencies of several inorganic and organic contaminants in conventional WWTPs. The model is composed of two sub-models: the organic component including 346 organic compounds and the inorganic component including 14 inorganic elements. The organic sub-model, applied in this study, uses a steady-state mass balance around the primary sedimentation and biological reactor by considering the major removal mechanisms. Sorption is the single removal mechanism assumed to remove significant amounts of organic chemicals in primary clarifiers. Sorption, volatilization (by air stripping) and biodegradation are the major removal mechanisms considered in aeration basins and secondary clarifiers (Harrington *et al.*, 1993). For the application of the model, the required inputs are:

- The daily concentrations of individual compounds in raw wastewater (S_{in})
- The daily flow rate of the incoming waste water (Q) in $\text{m}^3 \text{ d}^{-1}$
- The daily flow rate of the effluent waste water (Q_0) in $\text{m}^3 \text{ d}^{-1}$
- The daily flow rate of effluent of the secondary treatment (Q_e) in $\text{m}^3 \text{ d}^{-1}$
- The concentration of the primary sludge suspended solids (X_p) in g m^{-3}
- The daily flow rate of waste water entering the aeration basin (Q_e) in $\text{m}^3 \text{ d}^{-1}$
- The daily flow rate of primary sludge (Q_p) in $\text{m}^3 \text{ d}^{-1}$
- The daily flow rate of secondary sludge (Q_w) in $\text{m}^3 \text{ d}^{-1}$
- The concentration of the secondary sludge suspended solids (X_v) in mg l^{-1}
- The volume of the aeration basin (V) in m^3
- The airflow in the aeration tank (G) in $\text{m}^3 \text{ d}^{-1}$
- The concentration of active cell in the bioreactor (X_a) equal to 0.64 of the MLSS
- The physical properties of the target compound: K_{ow} , K_h and biodegradation rate (k_1) in d^{-1}

Table 16 provides the equations and assumptions used in the FATE model to estimate the concentrations of an organic pollutant exiting the primary and the secondary clarifiers of a WWTP.

Table 16: Equations and assumptions used in the FATE model

Compartment	Equation	Assumption
Primary clarifier	$S_0 = (QS_m) / [Q + Q_p X_p (4.1 \cdot 10^{-5} \cdot K_{ow}^{0.35})]$	$Q = Q_0$ $R_{sorp} = Q_p \cdot X_p \cdot K \cdot S_0$
Secondary clarifier	$S = (QS_0) / [Q + GKh/RT + Q_w X_v (3.06 \cdot 10^{-6} \cdot K_{ow}^{0.67}) + k_1 X_a V]$	$Q_0 = Q_e + Q_w$ $R_{bio} = k_1 \cdot X_a \cdot S_v$ $R_{sorp} = Q_w \cdot X_v \cdot K \cdot S$ $R_{vol} = G \cdot Kh \cdot S / RT$

K: $0.000059 \cdot K_{ow}$, S_0 : concentration of the pollutant in the effluent of the primary treatment (mg l^{-1}), S: concentration of the pollutant in the effluent of the secondary treatment (mg l^{-1}), R: $8.206 \cdot 10^{-5}$ ($\text{m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$), T: temperature in the aeration basin (K)

4.1.3 STP and STPWIN model

The STPWIN program (in the EPI Suite) is a version of the Toronto STP model originally developed by Mackay and colleagues at the University of Toronto (Clark *et al.*, 1995). The STWINP model estimates the fate of a chemical present in the influent stream of a conventional activated sludge plant as it becomes subject to evaporation, biodegradation, sorption to sludge and to loss in the final effluent. The most critical and uncertain variable is the biodegradation rate constant and its dependence on biomass concentration. In prior versions of EPIWIN, half-life values for the primary clarifier (Bio P), aeration vessel (Bio A) and settling tank (Bio S) were available on the main EPIWIN data entry screen. In the latest version EPIWIN v3.12, the following options are now available for selecting the STP half-lives:

- Bio P, Bio A and Bio S are equal to 10,000 hours for the primary clarifier, aeration vessel and settling tank. These values are used to signify no biodegradation, or a worst case scenario.
- Bio P, Bio A and Bio S are determined using the ultimate biodegradation expert survey model of the BIOWIN estimation program (Biowin3) (Boethling *et al.*, 1994), in combination with the linear MITI model (Biowin5) (Tunkel *et al.*, 2000).
- The user enters the half-lives for the primary clarifier, aeration vessel and settling tank, if the Bio P, Bio A and Bio S half-lives are known.

Biowin3 provides an indication of an environmental biodegradation rate of a chemical in terms of relative time periods such as hours, hours to days, days, days to weeks, etc. These values represent the approximate amount of time needed for degradation to be "complete". Biowin5 provides the estimated probability that a substance will pass the Japanese Ministry of International Trade and Industry (MITI) I test protocol. This test is a screening test for ready biodegradability and has been described by the Organization for Economic Cooperation and Development (OECD) test guideline 301 C and European Union (EU) test guideline C4E. However, these outputs cannot be used directly by the STPWIN model. Instead, Bio P, A and S half-lives are assigned to model output as described in Table 17.

Table 17: Assignment of the half-lives in the primary clarifier (Bio P) and the aeration vessel (Bio A)

Biowin result	Bio P	Bio A	Bio S
Biowin3 <= weeks and Biowin5 > 0.5	10	1	1
Biowin3 <= weeks	30	3	3
Biowin5 >0.5	100	10	10
Biowin3 = weeks - months	300	30	30
Biowin3 = months	1,000	100	100
Biowin3 = recalcitrant	10,000	10,000	10,000

Except for the STPWIN model for which operational parameters could be not changed, a similar WWTP configuration was applied for the FATE and Byrns' models. The operational parameters retained in this study correspond to those described in Byrns (2001). Table 18 summarizes the operational parameters in question.

Table 18: Operational parameters for the tested waste water treatment plant

Parameter	Symbols	Value
Influent flow rate	Q_i ($m^3 d^{-1}$)	4 000
Volume of primary sedimentation tank	V_{pst} (m^3)	1 000
Depth of primary sedimentation tank	Hw (m)	2.5
Volume of biological reactor	V_b (m^3)	100
Influent suspended solids	SS_{in} ($g m^{-3}$)	300
Effluent suspended solids	SS_{out} ($g m^{-3}$)	20
Mixed liquor solids	MLVSS ($g m^{-3}$)	2 500
Solids retention time	SRT (d)	5
Sludge wastage rate	Q_w ($m^3 d^{-1}$)	800
Air flow rate	AFR ($m^3 d^{-1}$)	30 000
Chemical concentration	C_{in} ($mg m^{-3}$)	1

4.2 Comparison of model predictions with literature data

4.2.1 Primary sedimentation stage

The model predictions are compared to the literature data during the primary sedimentation stages for a range of different pollutants in Figure 3. The three different models predict similar removal efficiencies for the considered PPs ($3.72 < \log K_{ow} < 6.70$). A difference exists for compounds with higher K_{ow} values between the Byrns and the STPWIN models on one hand and the FATE model on the other hand. The predicted removals in the PST are generally in good agreement with those reported in different studies, except in the case of α -endosulfan and to a lesser extent for hexachlorocyclohexane (HCH).

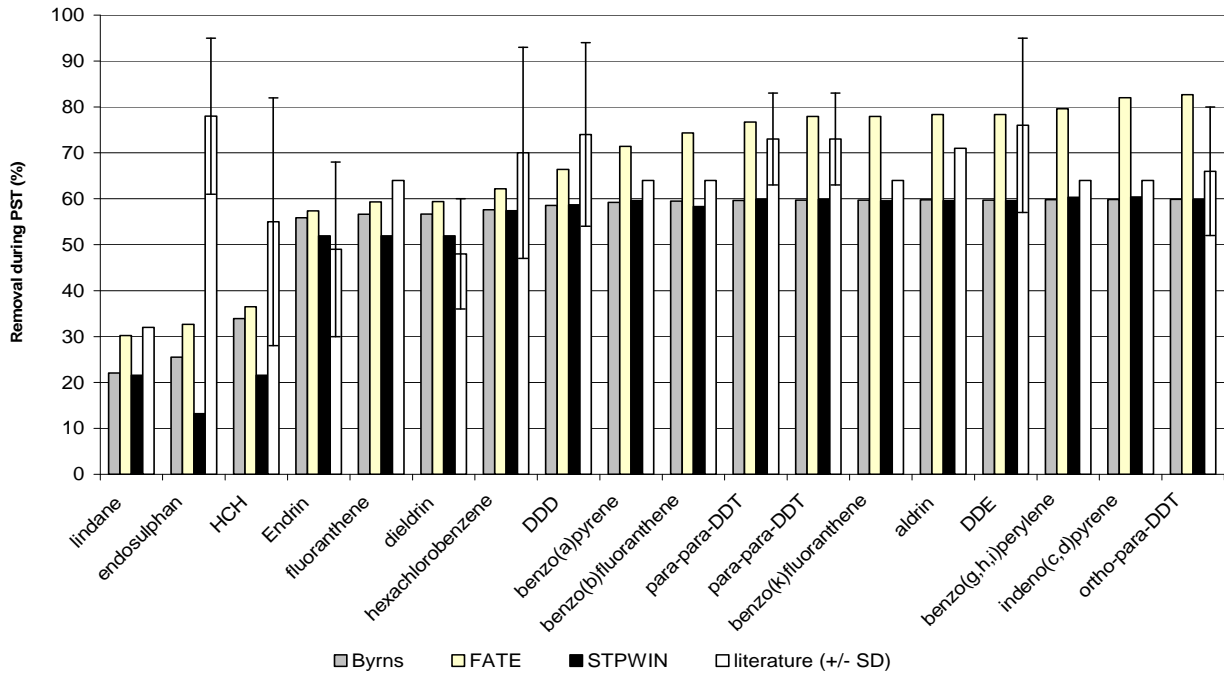


Figure 3: Model predictions compared with literature data for PP removal during the primary sedimentation stage

4.2.2 Secondary treatment stage

Figure 4 illustrates how the model predictions compare with literature during the secondary treatment stage. Pollutants with log K_{ow} values less than 4.5 are represented in Figure 4a and those having log K_{ow} values greater than 4.5 are shown in Figure 4b.

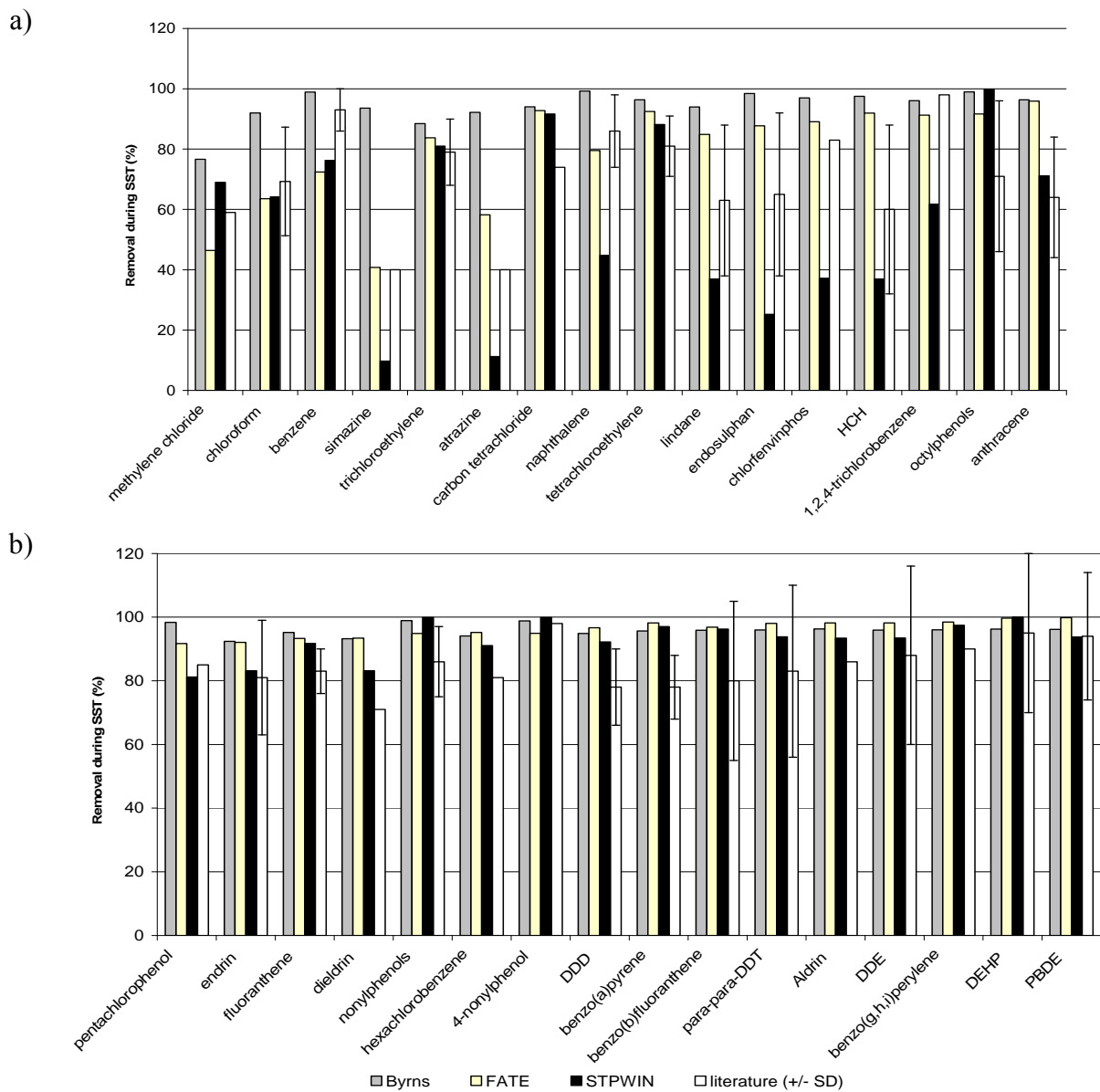


Figure 4: Model predictions compared with literature data for PP removal during the secondary treatment stage (a) pollutants with $\log K_{ow} < 4.5$, (b) pollutants with $\log K_{ow} > 4.5$

Compounds with $\log K_{ow} < 4.5$, Figure 4a:

- Out of the 16 compounds in this category, the three models predicted similar removal efficiencies for four compounds (trichloroethylene, carbon tetrachloride, tetrachloroethylene and octylphenols). These predicted values are in good agreement with those reported in literature.
- A similar trend is observed between the model predictions and the reported literature values for 8 further compounds (simazine, atrazine, naphthalene, lindane, endosulphan, chlorfenvinphos, HCH, and 1,2,4-trichlorobenzene). As illustrated in Figure 4 a and in comparison to the available data, there is evidence for under-prediction by STPWIn and over-prediction for the Byrns model. Globally, the FATE model predictions, which are generally intermediate between the STPWIn and Byrns model, appear to predict removals more consistently with the literature removals.

- For the four remaining compounds (methylene chloride, chloroform, benzene and anthracene), no specific trend was observed. Overall, the FATE model over-predicted the removal of these pollutants, whereas Byrns and STPWIN models seem to be in better agreement.

Compounds with $\log K_{ow} > 4.5$, Figure 4b:

- No marked differences between all model predictions were obvious.
- Furthermore, the model predictions were in good agreement with the literature removals (\pm SD), except for dieldrin. The prediction for dieldrin was higher than the literature value but this comparison has to be carefully considered as only one reference was found for dieldrin removal in the conventional WWTP (Katsoyiannis and Samara, 2004).

Figure 5 illustrates the percentage removal predicted to be achieved by each process (volatilization, sorption on sludge and biodegradation) during the primary sedimentation stage by the three tested models. Sorption on sludge clearly constitutes the predominant removal mechanism. The different models show similar trends for the different pollutants but the STPWIN and Byrns models appear to be the most conservative in predicting removal efficiencies in PST due to their consideration of volatilization and sorption as potential mechanisms of removal (contrary to the FATE model).

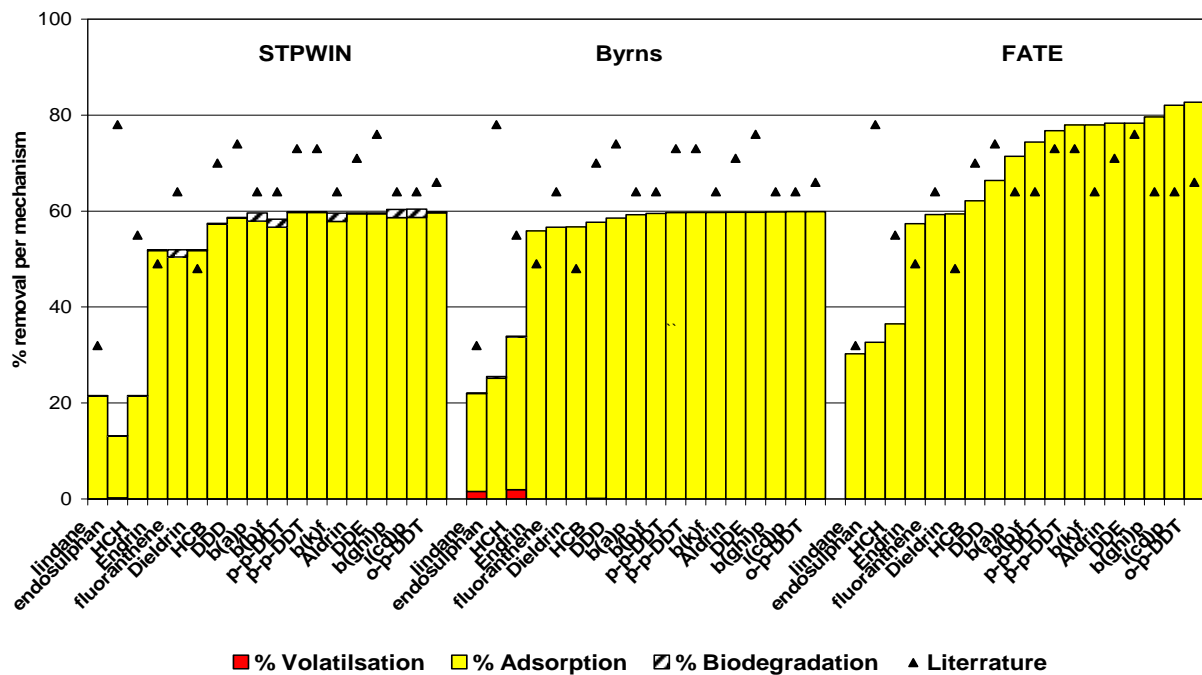


Figure 5: Percentage removal during PST according to the three tested models

Figure 6 shows the percentage removals per mechanism during secondary treatment (SST) according to the three tested models. Figure 6a includes those pollutants with $\log K_{ow} < 4.5$, while figure 6b focuses on pollutants with $\log K_{ow} > 4.5$. Although both models agree well regarding the contributions of the dominant processes during this stage, there were significant differences, particularly with regard to biodegradation, which is more predominant for the less hydrophobic organics in the Byrns model. For some compounds with $\log K_{ow} < 4.5$, the STPWIN model predicts volatilization losses from between 5 to 90% of the total removal.

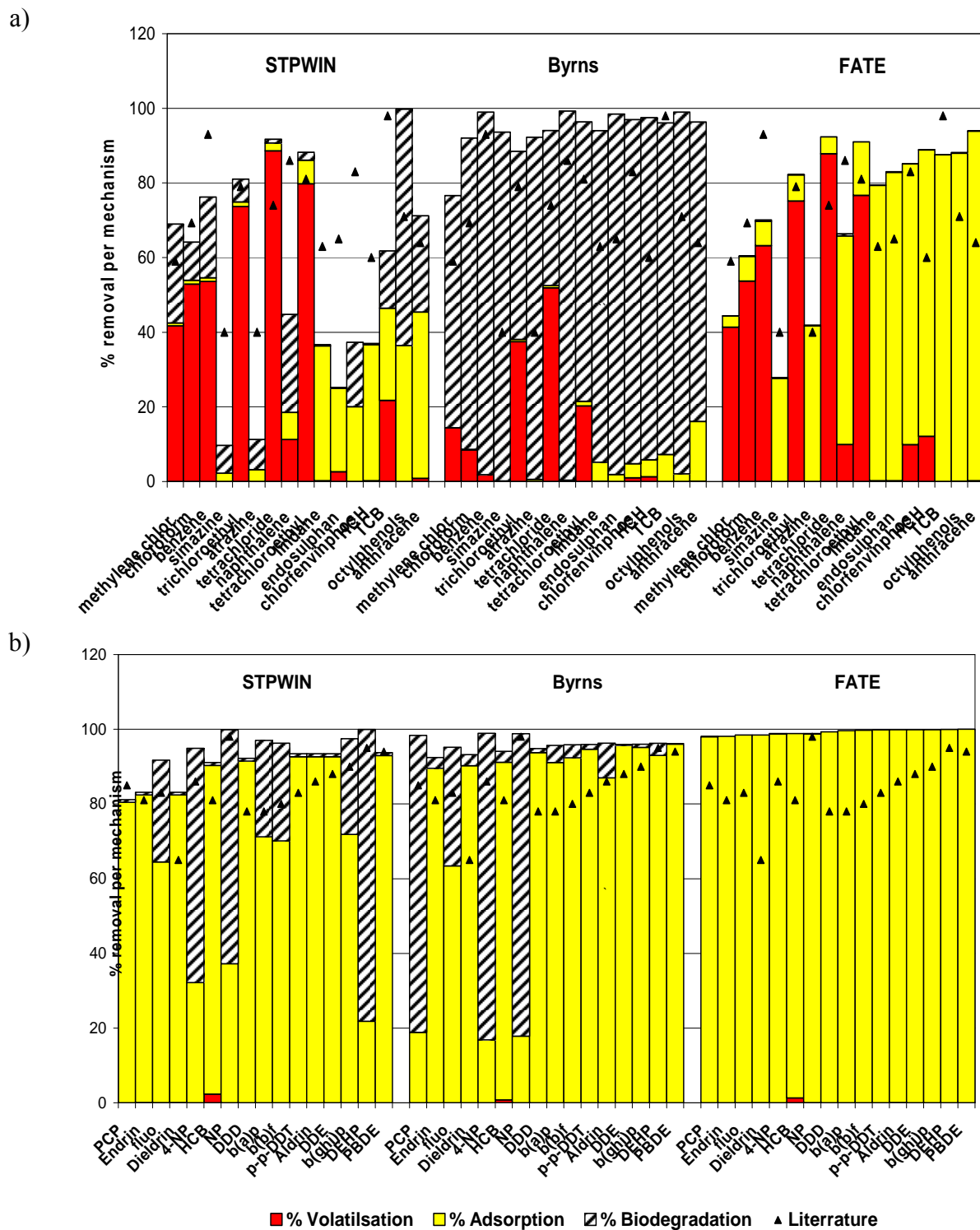


Figure 6: Percentage removal during SST according to the three tested models
 (a) pollutants with $\log K_{ow} < 4.5$, (b) pollutants with $\log K_{ow} > 4.5$

4.3 Fate and behaviour of priority pollutants

4.3.1 Total removal

Table 19 compares the removals predicted by the three tested models (Byrns, STPWIN and FATE models) for different PPs with the values derived from the literature survey.

Table19: Total priority pollutants removal in conventional WWTPs using models and literature data

Compound	Log K_{ow}	Model prediction			Literature survey		
		Byrns	STPWIN	FATE	Data	n	± SD
Methylene chloride	1.25	76.6	57.0	44.4	59.0	1	-
Ethylene chloride	1.48	87.7	34.0	33.9	-	-	-
Chloroform	1.96	92.0	60.0	60.4	69.3	-	18
Benzene	2.13	98.9	68.9	70.0	93.0	4	7
Simazine	2.16	93.6	2.5	27.8	< 40.0	1	
Trichloroethylene	2.51	88.4	79.6	82.2	79.0	4	11
Diuron	2.62	83.7	3.7	41.8	-	-	-
Atrazine	2.63	92.2	3.5	41.9	< 40.0	-	-
Isoproturon	2.66	97.6	4.7	43.1	-	-	-
Carbon tetrachloride	2.75	94.0	91.5	92.3	74.0	-	-
Alachlor	3.17	87.9	13.5	61.4	-	-	-
Naphthalene	3.23	99.2	23.6	66.4	86.0	4	12
Tetrachloroethylene	3.31	96.4	87.9	91.0	81.0	4	10
Lindane	3.72	94.0	37.0	79.4	63.0	2	25
α-endosulphan	3.86	98.4	25.2	83.0	65.0	2	27
Chlorfenvinphos	3.89	97.0	22.2	85.1	83.0	1	
Endosulphan thio	3.90	98.8	25.0	84.0	-	-	-
Trichlorobenzene	3.97	82.7	61.4	87.8	-	-	-
Hexachlorocyclohexane	4.07	97.5	37.0	88.9	60.0	2	28
1,2,4-trichlorobenzene	4.07	96.1	53.1	87.6	98.0	1	
Octylphenols	4.10	98.9	88.3	88.1	71.0	5	25
Anthracene	4.50	96.3	54.2	93.9	64.0	3	20
Hexachlorobutadiene	4.75	96.6	88.9	97.7	-	-	-
Chlorpyrifos	4.89	98.5	76.4	97.0	-	-	-
				97.4			
Para-tert-octylphenol	4.95	99.6	85.0		-	-	-

Compound	Log K _{ow}	Model prediction			Literature survey		
		Byrns	STPWIN	FATE	Data	n	± SD
Pentachlorophenol	5.10	98.4	81.1	98.0	85.0	1	-
Endrin	5.13	92.4	83.1	98.1	81.0	1	-
Trifluralin	5.16	95.2	86.0	98.3	-	-	-
Fluoranthene	5.23	95.2	82.2	98.5	83.0	-	13
Dieldrin	5.23	93.2	88.1	98.5	65.0	1	28
Nonylphenols	5.37	98.9	90.8	98.9	86.0	4	10
Hexachlorobenzene	5.38	94.1	91.1	98.9	81.0	2	13
4-para-nonylphenol	5.38	98.8	91.0	98.9	98.0		
DDD	5.60	94.9	92.2	99.3	78.0	1	18
Chloroalkane	5.65	97.3	98.2	99.4	-	-	-
Benzo(a)pyrene	5.90	95.7	92.6	99.6	78.0	-	
Benzo(b)fluoranthene	6.08	95.8	90.9	99.7	80.0	2	16
Para-para-DDT	6.24	95.8	93.8	99.8	-		-
Para-para-DDT	6.32	95.9	93.8	99.9	83.0	1	
Benzo(k)fluoranthene	6.32	95.9	92.6	99.9	-	-	-
Aldrin	6.35	96.3	93.4	99.9	86.0	-	
DDE	6.35	95.9	93.5	99.9	88.0	1	9
Benzo(g,h,i)perylene	6.45	96.0	93.6	99.9	90.0	2	4
Isodrin	6.63	96.0	93.4	99.9	-	-	-
Indeno(1,2,3-cd)pyrene	6.64	96.1	93.6	99.9	-	-	-
Ortho-para-DDT	6.70	96.1	93.7	99.9	83.0	1	-
Pentachlorobenzene	6.79	96.2	83.6	99.9	-		-
DEHP	7.23	96.2	94.0	100.0	95.0	3	2
PBDE	7.51	96.1	93.8	100.0	94.0	2	1

Based on the literature survey, the removal efficiencies of 33 substances have been reported:

- 19 of the 33 **PPs** presented removals higher than 80% (benzene, naphthalene, tetrachloroethylene, chlorfenvinphos, 1,2,4-trichlorobenzene, pentachlorophenol, endrin, p-p-DDT, fluoranthene, nonylphenols, hexachlorobenzene, 4-para-nonylphenol, benzo(b)fluoranthene, aldrin, benzo(g,h,i)perylene, o-p-DDT, DDE, DEHP and PBDE),
- 12 **PPs** exhibited removals between 50 and 80% (methylene chloride, chloroform, trichloroethylene, carbon tetrachloride, lindane, α -endosulphan, hexachlorocyclohexane, octylphenols, anthracene, Dieldrin, DDD and benzo(a)pyrene),
- 2 **PPs** (simazine and atrazine) presented removals lower than 40%.

Model predictions are highlighted below for the 16 compounds for which no removal data was found in the literature:

- For **10 PPs** with $\log K_{ow} > 4.5$ the predicted removals were around 90% (hexachlorobutadiene, chlorpyrifos, para-tert-octylphenol, trifluralin, chloroalkane, p-p-DDT, benzo(k)fluoranthene, isodrin, indeno(1,2,3-cd)pyrene and pentachlorobenzene).
- Model predictions differed significantly for **6 PPs** (ethylene chloride, diuron, isoproturon, alachlor, endosulphan thiosulfan and trichlorobenzene), all of which possess $\log K_{ow}$ values less than 4.5. The highest differences observed between all three model predictions concerned diuron, isoproturon and alachlor.

4.3.2 Behaviour and removal mechanisms of pollutants during the primary sedimentation stage

Figure 7 illustrates the percentage of each removal mechanism (volatilization, biodegradation and sorption) for a total of 49 PPs during the primary sedimentation stage according to the Byrns (a) and the STPWIN (b) models.

As expected according to the literature surveys, compounds with $\log K_{ow} < 3.5$ were not efficiently removed during primary treatment with removals consistently below 10%. On the contrary, removals around 60% could be generally expected for substances with $\log K_{ow} > 3.5$. Whatever the model considered, sorption was consistently the predominant removal mechanism.

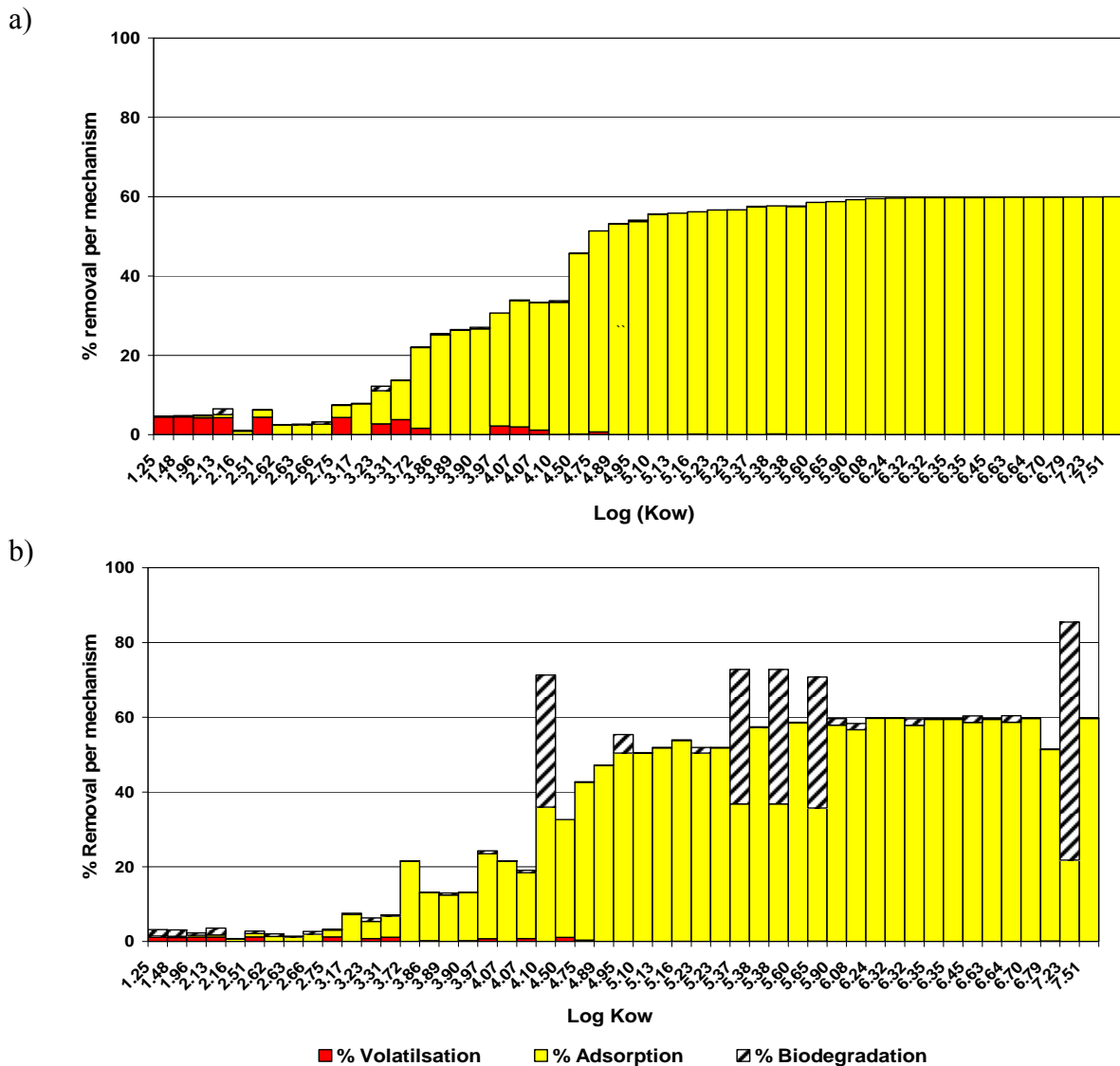


Figure 7: Percentage of each removal mechanism during primary sedimentation stage according the Byrns (a) and the STPWIN (b) models

Volatilization losses were particularly low during the primary treatment typically reaching only 2% for both models, except for some VOCs (methylene chloride, ethylene chloride, chloroform and benzene) for which the Byrns’s model predicted values approaching 5%.

Biodegradation occurred for some PPs during the primary sedimentation stage with octylphenols, nonylphenols, 4-para-nonylphenol, chloroalkane and DEHP being predominantly affected. Biodegradation losses for octylphenols, nonylphenols, 4-para-nonylphenol and chloroalkane were about 35% and reached 65% for DEHP. The high biodegradation rates for these compounds induced high PST removals (from 70 to 80%).

4.3.3 Behaviour and removal mechanisms of pollutants during secondary sedimentation stage

Figure 8 identifies the percentage contribution for each removal mechanism (volatilization, biodegradation and sorption) for 49 PPs during the secondary sedimentation stage according to the Byrns (a) and STPWIN (b) models. Both models predict quite similar tendencies for volatilization and sorption for the different PPs considered but biodegradation predictions differed significantly between the models (Figures 8a and 8b).

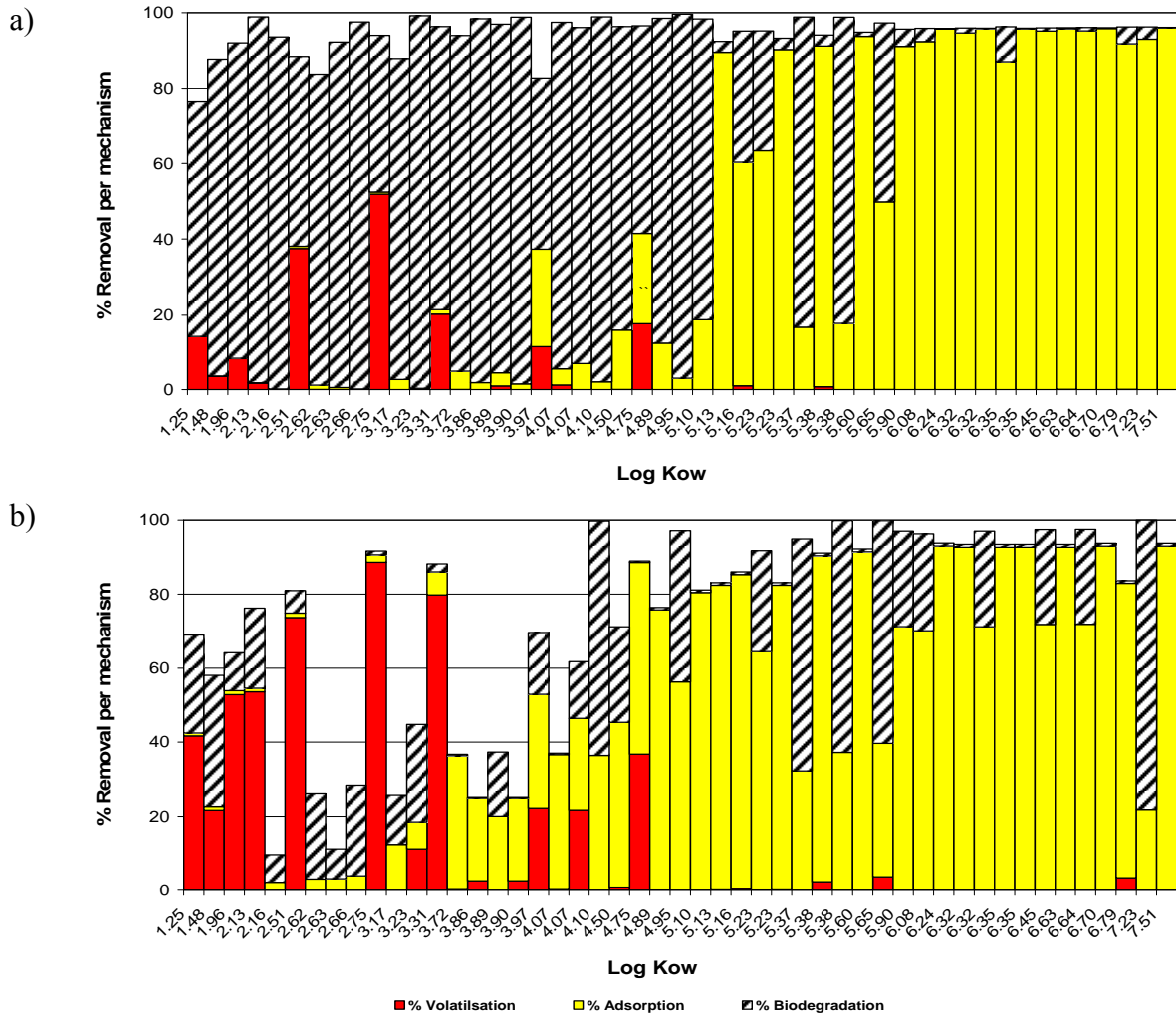


Figure 8: Percentage of each removal mechanism during the secondary sedimentation stage according to the Byrns (a) and the STPWIN (b) models

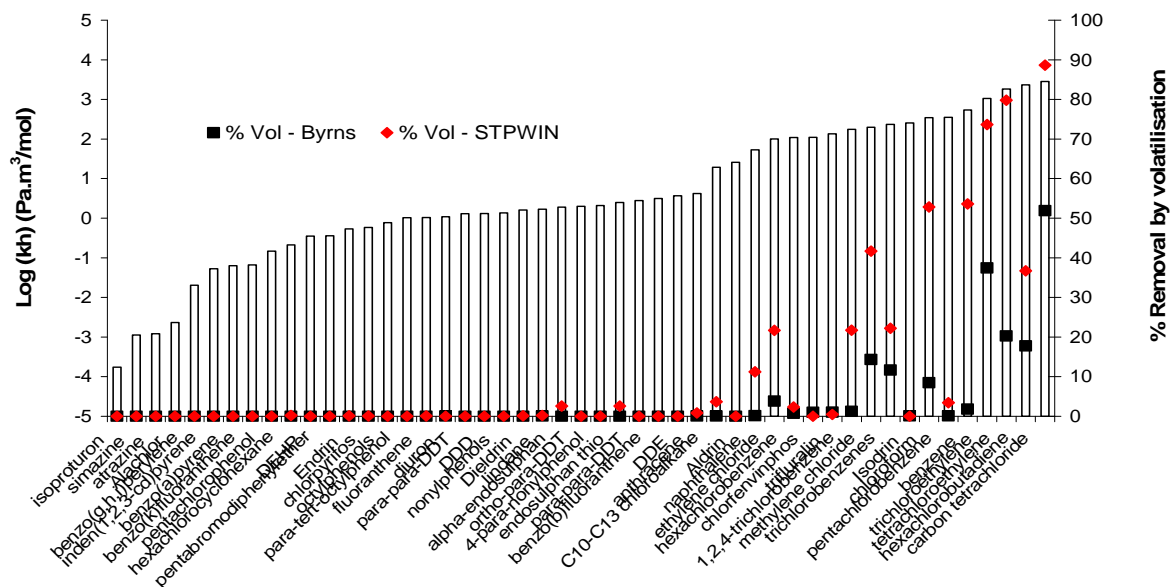


Figure 9: Percentage removal via volatilization during secondary sedimentation stage

Volatilization

Volatilization appears to be more important for compounds with $\log K_{ow} < 4.5$ than for compounds with higher $\log K_{ow}$ and constitutes in some cases the predominant removal mechanism. To better visualize the importance of the volatilization process, volatilization losses were plotted on figure 9 according to increasing $\log K_h$ values.

As expected, the results of the literature survey showed that volatilization losses increased with increasing K_h . For compounds with $\log K_h < 1.41$ (e.g. 33 compounds of the 49 considered), both models predicted a negligible volatilization ($< 1\%$ of the total secondary removal). For compounds with $\log K_h$ values above 1.41, volatilization losses varied between 4 and 52% and 9 and 83% according to the Byrns and STPWIn models, respectively. Ten PPs (ethylene chloride, 1,2,4-trichlorobenzene, methylene chloride, trichlorobenzene, chloroform, benzene, trichloroethylene, tetrachloroethylene, hexachlorobutadiene and carbon tetrachloride) presented non-negligible losses by volatilization. For the most volatile compounds ($2.73 < \log K_h < 3.45$), volatilization was the predominant mechanism contributing between 57% and 83% to the removal.

Sorption on sludge

Both models predicted that the removal via sorption globally increased with increasing $\log K_{ow}$. Furthermore, sorption constituted the predominant mechanism of removal for 17 PPs (lindane, hexachlorocyclohexane, chlorpyrifos, pentachlorophenol, endrin, trifluralin, dieldrin, HCB, DDD, DDT, aldrin, DDE, isodrin, pentachlorobenzene and PBDE) with 95 to 99% of the removal occurring by this process. In order to better visualize the dependence of sorption on $\log K_{ow}$, figure 10 illustrates the predicted removal by sorption according to the $\log K_{ow}$ value of each compound. This figure reveals that the sorption is a minor mechanism of removal for compounds with $\log K_{ow} < 3.31$. For these substances, removals did not exceed 2% and 7% according to the Byrns and STPWIn models, respectively. For compounds with $\log K_{ow} > 5.31$, sorption was the predominant removal mechanism, contributing from 50% to 90% of the removal during secondary treatment. Finally, the percentage removal via sorption was highly variable for compounds with $\log K_{ow}$ values between 3.31 and 5.31.

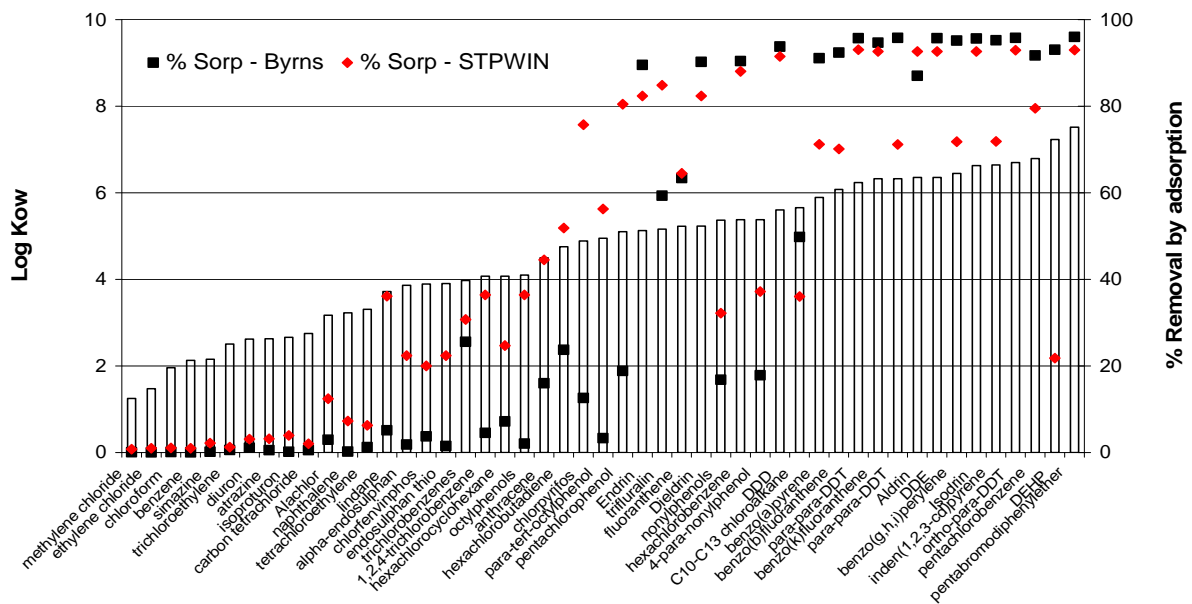


Figure 10: Percentage removal via sorption during secondary sedimentation stage

Biodegradation

As underlined by the literature survey, biodegradation constituted the most critical and uncertain variable. Nevertheless, in regard to the reported literature pollutant removals, the STPWIN prediction appeared to be in better agreement and consequently the most reliable model for predicting the percentage removal as a result of biodegradation. According to the STPWIN model predictions:

- 24 PPs (simazine, atrazine, carbon tetrachloride, tetrachloroethylene, lindane, endosulphan, hexachlorocyclohexane, hexachlorobutadiene, chlorpyrifos, pentachlorophenol, Endrin, trifluralin, hexachlorobenzene, DDD, DDT, benzo(k)fluoranthene, aldrin, DDE, isodrin, pentachlorobenzene and PBDE) exhibited biodegradation removal efficiencies of less than 10%. The low biodegradation removal found for these pollutants resulted either from the inherent biodegradability or from high level of volatilization and sorption.
- 4 PPs (octylphenols, nonylphenols, chloroalkane and DEHP) showed high biodegradation removals in excess of 50%.
- The remaining 21 compounds (out of the 49 PPs considered) exhibited biodegradation removal potentials between 15% and 40%. 10 PPs (methylene chloride, diuron, naphthalene, anthracene, fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(cd)pyrene) demonstrated losses due to biodegradation of about 25%.

5. Fate of priority pollutants in conventional waste water treatment plants in Denmark and Slovenia

5.1 The removal of priority pollutants in Denmark

A national programme for the surveillance of the aquatic environment was conducted in Denmark between 1997 and 2003 (NOVA). This project aimed at studying the presence of nutrients, metals and selected organic substances in surface and ground waters, the sea, atmospheric deposition, rainfall and point sources such as waste water treatment plants. During this project, some of the substances present in Annexe X of the Water framework Directive (2000/60/EC) were also monitored. This programme was followed by the National Monitoring and Assessment Programme for Aquatic and Terrestrial Environments in 2003, in which chemical and biological statuses were included. NOVANA surveyed 38 WWTPs across Denmark in which compounds present in the European directives were included (pesticides, PAH, DEHP). Data collected from the NOVA and NOVANA programmes are shown in Table 20. Despite the fact that no specific study on the priority pollutants identified within the Water Framework Directive has been carried out in Denmark, an increased awareness and focus on pollution has resulted from the NOVA and NOVANA programmes. No studies on the removal efficiencies of priority pollutants have yet been conducted or made available to the general public. So far, studies have focused on three stages of the waste water treatment plant process: inlet, outlet and sludge.

Studies in Denmark have mainly focused on activated sludge processes as these are widely used. As can be seen from Table 20, pesticides are poorly removed from waste water which was also noticed in Section 3. Further details on this campaign can be found in Appendix A.

Table 20: Removal of priority pollutants within Danish waste water treatment plants

<i>Priority substances</i>	<i>Mechanical treatment removal (%)</i>	<i>Biorotor removal (%)</i>	<i>Biological sand filter removal (%)</i>	<i>Root zone bed removal (%)</i>	<i>MBNDC removal (%)</i>
Anthracene					90
Benzene					92 - 98
PAH	30				
Benzo(a)pyrene					90
Benzo(b)fluoranthene					90
Benzo(g,h,i)perylene					10
Indeno(1,2,3-cd)pyrene					75
Nonylphenol	10	75	90		92
DEHP		75	85	50	96
Lead					78
Nickel					29
Fluoranthene					83 - 98
Naphthalene					95 - 96
Pentachlorophenol					> 10 - 50
Trichloromethane					88 - 92
Isoproturon					< 10
Atrazine					< 10
Simazine					< 10
Diuron					< 10

MBNDC: Mechanical, Biological, nitrifying/denitrifying, chemical treatment, Biorotor: Rotating Biological Contactor Root zone bed: Type of constructed wetland

5.2 The removal of priority pollutants in Slovenia

National Slovenian regulations Ur.l. 35/96 and Ur.l.47/05 (Slovenian Government, 1996) require municipal waste water treatment plants of more than 100,000 people equivalent to regularly perform measurements on metals (Al, As, Cu, Ba, B, Zn, Cd, Co, Sn, Cr, Ni, Ag, Pb, Hg), BTEX, AOX, VCHC, tensides (surfactants), phenols and polar organic solvents. Data on metal removals from an activated sludge treatment plant in Slovenia were collected between 2000 and 2006. Some of the removal percentages are shown in Table 21. Some measured values were below quantification limits and therefore the removal efficiencies for these metals could not be assessed. In some cases values of metals in the effluent were higher than those in the influent streams. This could be due sampling discrepancies or to the fact that sludge was releasing metals at times sampling occurred. Full details of the measured values are given in Appendix B.

Table 21: Priority pollutants in Slovenian wastewater treatment plant

<i>Priority substances</i>	<i>Removal 2000 (%)</i>	<i>Removal 2001 (%)</i>	<i>Removal 2002 (%)</i>	<i>Removal 2003 (%)</i>	<i>Removal 2004 (%)</i>	<i>Removal 2005 (%)</i>	<i>Removal 2006 (%)</i>
Cadmium	-	-	-	-	-	-	-
Nickel	Negative	> 77	Negative	25	Negative	Negative	-
Lead	50	23	-	-	-	-	-
Mercury	>94	27	91	Negative	90	Negative	-
Tributyltin	81	-	-	-	-	-	-

- Below quantification limits

6. Fate of priority pollutants in alternative waste water treatment plants

The ScorePP project focuses on reducing the emission of priority pollutants from urban waste water treatment plants. As mentioned in Section 3, several types of influent streams enter municipal waste water treatment plants giving a wide range of pollution. The characteristics of an urban catchment greatly influence the type of pollution, including the catchment size, the type and number of industries, the extent of residential housing, and the type of sewer network. Hence, a waste water treatment plant is unlikely to receive all 33 priority pollutants in high concentrations. Few studies have focused on the type of priority pollutants present in urban catchments and Table 22 summarizes the list of pollutants found in European cities or waste water treatment plants. Some pollutants, including metals and pesticides are resistant to biodegradation and are mainly removed by adsorbing into sludge. Pesticides have been reported to cause inhibition or death of bacterial activities (Maldonado *et al.*, 2007). Biological wastewater treatments are referred as been ineffective (Maldonado *et al.*, 2006; 2007) making alternative treatments possible options. The following section describes alternative waste water treatment technologies for the removal of priority pollutants.

6.1 Alternative technologies

Some technologies can be added before the activated sludge process as a pre-treatment step to increase biodegradation of pollutants during the biological process, while others necessitate a complete change of process. Table 23 contains information relating to the different treatment technologies known to be able to remove identified priority pollutants. The following groups of alternatives exist:

- Advance oxidation processes (AOPs): several techniques, employing different oxidation conditions, are available (e.g. $\text{H}_2\text{O}_2 + \text{UV}$, $\text{H}_2\text{O}_2 + \text{O}_3$, Photo-Fenton, $\text{TiO}_2\text{-UV}$, O_3) all with the aim of converting harmful or hardly biodegradable contaminants to less harmful compounds.
- Natural processes: these involve the use of constructed wetlands planted with specific types of vegetation (usually native species). The presence of vegetation increases pollutant removal from waste water through uptake by associated microbiota and humic contributions.
- Membranes: these include membrane bioreactors (a combination of the activated sludge process and membrane filtration), nanofiltration or reverse osmosis processes that are membrane technologies employing very small pore sizes. Membrane technologies (with the exception of membrane bioreactors) would represent an efficient post-treatment following the activated sludge process.

Pesticides in urban areas are mainly used as herbicides and insecticides. Both compounds are usually used within private and public gardens (including green spaces or trees along roadsides). Nitschke *et al.* (1999) found that urban waste water effluents discharged greater quantities of pesticides to surface waters than rural waste water treatment plants. In rural areas, pesticide inputs are reported to be mainly due to farm equipment washing. Waste water treatment plants in urban areas receive storm water which has, in many cases, washed off surfaces where pesticides have been applied. Table 23 shows alternative treatments found in literature for pesticides that belong to the priority pollutant list. All technologies appear to have advantages and disadvantages. Depending on the expectations, budget, space and population size, most pesticides can be removed from waste water either by sorption or “assisted” biodegradation.

Table 22: Sources of priority pollutants in urban areas

Category	CAS Number	Compound name	Waste water stream	Suspected sources	Reference
PAH	91-20-3	Naphthalene	Domestic	Incomplete combustion (wood or mineral oil), oily dirt on vehicles from asphalt and exhaust particles, traffic.	Rule <i>et al.</i> (2006a) Blanchard <i>et al.</i> (2004)
			Industrial	Food preparation, discharge of certain petroleum products, fuel stations, vehicle washing, degreasing solvent, oily dirt on vehicles from asphalt and exhaust particles.	Rule <i>et al.</i> (2006a)
	206-44-0	Fluoranthene	Domestic	Incomplete combustion (wood or mineral oil), oily dirt on vehicles from asphalt and exhaust particles.	Rule <i>et al.</i> (2006a) Blanchard <i>et al.</i> (2004)
			Industrial	Food preparation, discharge of certain petroleum products, fuel stations, vehicle washing, degreasing solvent, oily dirt on vehicles from asphalt and exhaust particles.	Rule <i>et al.</i> (2006a)
		Brominated Diphenylethers	Domestic	Upholstery and furniture.	Rule <i>et al.</i> (2006a)
Phthalate	117-81-7	Di(2-ethylhexyl)phthalate	Domestic	Leaching of PVC pipes, floor and wall covering and textiles .	Rule <i>et al.</i> (2006)
			Industrial	Vehicle washing, oily dirt and traffic grime.	Rule <i>et al.</i> (2006)
Endocrine disrupters	25154-52-3	Nonylphenol	Domestic		Rule <i>et al.</i> (2006a) Ghanem <i>et al.</i> (2007)
			Industrial	Car wash detergent, degradation of Nonylphenol Ethoxylates in products used by hairdressers, restaurants.	Rule <i>et al.</i> (2006a)

Category	CAS Number	Compound name	Waste water stream	Suspected sources	Reference
Metals	7440-43-9	Cadmium	Run off	Traffic.	Rule <i>et al.</i> (2006b)
	7439-92-1	Lead	Domestic	Washing machine.	Rule <i>et al.</i> (2006b)
			Industrial	Traffic.	
	7439-97-6	Mercury	Industrial	Dental practices, traffic.	Rule <i>et al.</i> (2006b)
7440-02-0	Nickel	Domestic	Stainless steel, pipes, fittings and surface finishing, washing machine, dishwashers, food processing, sanitary installations, protective coating, faeces.	Rule <i>et al.</i> (2006b)	
		Industrial	Metal finishing process, traffic.		
Pesticides	330-54-1	Diuron	Domestic & municipal	Herbicides	Nitschke <i>et al.</i> (1997), Ghanem <i>et al.</i> (2007)
	34123-59-6	Isoproturon	Domestic & municipal	Herbicides	Nitschke <i>et al.</i> (1997)
Solvent	67-66-3	Chloroform	Domestic	Reaction between sewerage and chlorine in drinking water (or disinfecting product).	Rule <i>et al.</i> (2006a)
			Industrial	Products for engine cleaning and degreasing.	Rule <i>et al.</i> (2006a)
	75-09-2	Dichloromethane	Industrial	Products for engine cleaning and degreasing.	Rule <i>et al.</i> (2006a)

Table 23: Priority pollutants removal using different treatment technologies

Treatment option	Compound	Removal efficiency %	Advantage	Disadvantage
Sub-surface flow constructed wetland	Alachlor	80	No use of chemicals, Best management practice Low energy consumption.	Need land space, Technology for small population, Long HRT (5 to 7 days).
	Chlorpyrifos	83 and 98		
	Pentachlorobenzene	> 99		
	Pentachlorophenol	94		
	Endosulfan	>99		
	Lindane	>99		
	Simazine	25, 64 and 95		
Solar photo-Fenton	Alachlor	50	Can be a pre-treatment to Activated Sludge, Short photo-Fenton treatment, Good results with low iron concentrations, Cheap Energy source.	Can only be used during day light, Price.
	Atrazine	70		
	Diuron	70		
	Isoproturon	70		

			photo-Fenton treatment, Good results with low iron concentration	or need UV lights
	Chlorfenvinphos	70	Pre-treatment to Activated Sludge, Short photo-Fenton treatment, Good results with low iron concentration.	Can only be used during day light or UV lights.
Ozonation	Atrazine	N.D.		
	Alachlor	N.D.	Partial to complete degradation can be achieved.	High consumption of ozone, Complete degradation over 2 hours, Needs to be tested with waste water, High electricity consumption, Total mineralization not achieved.
	Diuron	N.D.		
	Isoproturon	N.D.		
	Chlorfenvinphos	N.D.		
Membrane bioreactor	Pentachlorophenol	99	Higher quality of effluent, Less sludge production.	Membrane fouling, High energy costs, High cost maintenance.
	Atrazine	9	Higher quality of effluent, Less sludge production.	Membrane fouling, High cost maintenance High energy cost.
	Isoproturon	25	Higher quality of effluent, Less sludge production.	Membrane fouling, High cost maintenance High energy costs, Low removal.
	Nonylphenol	55	Higher quality of effluent, Less sludge production.	Membrane fouling

Photocatalysis + ultrasonic	Lindane	99	Can be a pre-treatment to Activated Sludge, Partial or complete degradation of EDC.	Not tested on large scale.
Photocatalysis + ultrasonic	Atrazine	68 to 99	Can be a pre-treatment to Activated Sludge.	
Ponded wetland	Diuron	27-55	No use of chemicals, Best management practice Low energy consumption,	Need of land space, Technology for small population, Long HRT (5 to 7 days).
Biodenitrification reactor	Alachlor	50		
Nanofiltration	Nonylphenol	74	Higher quality of effluent (removal of dissolved salt), Less sludge production, Low operation pressure, Low operation and maintenance costs.	Membrane fouling
Reverse osmosis	Nonylphenol	83	Highest effluent quality (removal of dissolved salts or particles), Resistant to biologic attacks, High water fluxes, Can be used a pH 3 to 11.	Membrane fouling, High energy costs.
Mechanical pre-treatment + biological treatment + chemical precipitation (Iron sulphate)	Naphthalene	85 to 100	High removal efficiencies of macro pollutants.	Use of chemical products.
	Nonylphenol	>90	Increase of pollutant removal thanks to chemical and biological processes.	
	PAH	94- 100	High removal efficiencies of macro pollutants.	Use of chemical products.
Mechanical pre-treatment + chemical treatment :	DEHP			Use of chemical products, Low macro pollutant removal.

with Magnafloc 155	80 to 90
with Pax 18	70

N.D: No Data

7. Conclusions

This report was conducted within the project Source Control Options for Reducing Emissions of Priority Pollutants (ScorePP). One of the aims of this task was to gather knowledge on the behaviour and fate of priority pollutants in end of pipe waste water treatment plants with the objective of producing a “guidance manual” describing the best options for PP removal in waste water treatment plants. The limited amount of data available on the behaviour of priority pollutants in conventional waste water treatment plants makes the production of a general guidance manual difficult.

The literature survey carried out for this report has provided information on the removal of the 33 PPs through monitoring data obtained from existing conventional waste water treatment plants, through laboratory experimental data and through models describing the behaviour and fate of PPs in conventional waste water treatment plants. The data collected on the 33 PPs can be summarised as follows:

- 19 PPs presented a removal efficiency higher than 80% (benzene, naphthalene, tetrachloroethylene, chlorfenvinphos, 1,2,4-trichlorobenzene, pentachlorophenol, endrin, p-p-DDT, fluoranthene, nonylphenols, hexachlorobenzene, 4-para-nonylphenol, benzo(b)fluoranthene, aldrin, benzo(g,h,i)perylene, o-p-DDT, DDE, DEHP and PBDE),
- 12 PPs exhibited removal efficiencies between 50 and 80% (methylene chloride, chloroform, trichloroethylene, carbon tetrachloride, lindane, α -endosulphan, HCH, octylphenols, anthracene, Dieldrin, DDD and benzo(a)pyrene),
- 2PPs (Atrazine and simazine) demonstrated removal efficiencies lower than 40%
- For other compounds removal efficiencies were below 10 %

Data gathered on the removal of PPs during the primary and secondary treatment steps did not allow an accurate judgment on PP removal during each treatment stage. A lack of monitoring results for PPs during the primary treatment stage has been especially observed for PPs with $1.25 < \log K_{ow} < 5.1$. For PPs with $K_{ow} > 5.3$, the primary sedimentation appeared to produce removals of 60-70%. For secondary treatment, more data was available and PP removal rates are between 60 and 90%.

For 19 PPs, no experimental field data was available and therefore modelling was used as an alternative approach to investigate their fate and behaviour in conventional waste water treatment plants. Three models were used: the one proposed by Byrns (2001), the FATE and the STPWIN models to investigate the removal efficiencies of these PPs in conventional activated sludge processes. All three models predict high (about 90%) and consistent removal for 10 PPs with $\log K_{ow} > 4.5$ (hexachlorobutadiene, chlorpyrifos, para-tert-octylphenol, trifluralin, chloroalkane, p-p-DDT, benzo(k)fluoranthene, isodrin, indeno(cd)pyrene and pentachlorobenzene). Since model predictions differed significantly for the six remaining PPs (ethylene chloride, diuron, isoproturon, alachlor, endosulphan thiosulfan and trichlorobenzene), the removal of these PPs could be not accurately estimated.

Although significant differences appeared between Byrns and STPWIN models for predicting the impact of the dominant process (volatilization, biodegradation and sorption on sludge) during secondary treatment stage, with regard to biodegradation, the Byrns and STPWIN models appeared to be the most reliable models. During primary treatment, 13 PPs with $\log K_{ow} < 3.5$ were hardly removed. Generally, removals for such compounds did not exceed 10%. For 36 compounds with $\log K_{ow} > 3.5$ removal efficiencies ranged from 30% to 60% with sorption on sludge appearing to be the predominant removal mechanism. Volatilization losses were less than 2% in primary treatment, except for four PPs (methylene chloride, ethylene chloride, chloroform and benzene) for which this process reached up to 5% with the Byrns model. Finally, biodegradation was predicted to occur for 5 PPs

(octylphenols, nonylphenols, 4-para-nonylphenol, chloroalkane and DEHP). Degradation ranged from 35% for octylphenols, nonylphenols, 4-para-nonylphenol and chloroalkane to 65% for DEHP. The biodegradation losses for these PPs induced a particular high PST removal (from 70% to 80%).

During the secondary treatment stage, the Byrns and STPWIN models predicted similar tendencies for volatilization and sorption, but differed significantly for biodegradation. Overall, 33 PPs with $\log K_h < 1.41$ presented negligible volatilization losses ($< 1\%$) whereas compounds with $\log K_h > 1.41$ exhibited volatilization losses up to 83%. For the most volatile compounds ($\log K_h > 2.43$, for 4 PPs), the volatilization represented the predominant mechanism contributing to between 57% and 83% of the removal. For 13 PPs with $\log K_{ow} < 3.31$, sorption was a minor removal mechanism (from 2% to 7%), whereas this process constituted the predominant removal mechanism for substances with $\log K_{ow} > 5.31$ (for 17 PPs), representing removal efficiencies of 50 to 90% during the secondary treatment. For compounds with $3.31 < \log K_{ow} < 5.37$, the sorption removal varied over a large range. Finally, biodegradation did not seem to constitute the predominant mechanism of removal for most of the PPs. Indeed, according to the STPWIN predictions, 24 PPs presented a removal by biodegradation of less than 10%, and 10 PPs (methylene chloride, diuron, naphthalene, anthracene, fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(cd)pyrene) revealed biodegradation removal rates of the order of 25%. Only 4 PPs (nonylphenols, chloroalkane and DEHP) showed a biodegradation removal higher than 50%.

When comparing the cases in Slovenia and Denmark, it was noticed that research, work and legislations made on priority pollutants greatly differed from a country to another one. Indeed, while some countries have well established national programmes to identify priority pollutants, others are just starting surveillance programs on a limited number of priority pollutants. Work on priority pollutants at a global European scale remains limited, making the comparison of waste water treatment technologies difficult as not enough data was found. Research on different municipal wastewater treatment processes and combination of processes needs to be conducted to assess treatment efficiencies and economic viability of treatment combination.

It appears that biological treatment of waste water is not sufficient for pollutants such as pesticides. Alternative technologies, such as advance oxidation process, seem to be promising technologies not only for pesticides present in wastewater but also for endocrine disruptors, phthalates and hydrocarbons compounds. When dealing with innovative wastewater treatment, literature found mainly focused on pesticides, while common pollution in urban wastewater was found to be compounds such as PAH, phthalates, nonylphenol, metals and solvents. Several articles dealing with conventional waste water treatment for these compounds were found, but cannot be used when comparing technologies because wide ranges were found when dealing with the same technology and no literature was found for other technologies. In a first place, further work on PPs present in conventional activated sludge needs to be done to assess ranges of PPs removal for different wastewater strength. Second work on PP and PP mixtures that are found in urban catchments needs to be done on conventional and alternative technologies to allow proper technology comparison. The oxidation process seems to be promising, having the advantage of reducing several recalcitrant compounds but also was identified to create in some cases compounds that are more dangerous than those initially present in wastewater.

8. References

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Appendix A

Contribution of Danish-specific data and evaluation of the behaviour of Priority Substances in Wastewater treatment plants

Sub-report in ScorePP T5.4

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Abstract

Wastewater may contain a vast array of different substances including the priority substances (PS) defined by the European Water Framework Directive. In Denmark, wastewater treatment plants are legally directed to remove organic matter and nutrients but emission limit values for micropollutants exist. Less than 0.1% of the wastewater is untreated and 90% of the wastewater flow in Denmark is subjected to intense treatment including mechanical, biological, nitrification/denitrification and chemical treatment (MBNDC).

In the national surveying programmes many of the PS are analysed in inlets, outlets and the sludge fractions but data are generally only available collectedly, thus hampering the potential evaluation of individual wastewater treatment plants (WWTPs). Advanced oxidation processes (AOP) for removal of steroid hormones and endocrine disrupting substances are being tested in Denmark and several studies focussing on sludge treatment optimization were found. However, no investigation of PS removal in various steps in a full-scale plant could be obtained and generally have only a few PS been studied on a wider scale (nonylphenol, di (2-ethylhexyl) phthalate and the polycyclic aromatic hydrocarbons).

The removal efficacy data from MBNDC were compared with modelled WWTP efficiencies and it was found that 3 PS were removed in lesser extent than estimated, 5 PS were found to be removed with a higher efficiency than estimated and for 6 PS were the MBNDC removal efficiencies close to those estimated in the modelling.

Introduction

All substances we humans use in our daily life have a potential to end up in our wastewater, for example, pharmaceuticals, personal care products, food remnants, substances from wear and tear of

indoor materials, human residues, laundry and cleaning detergents are discharged into the sewer system. The Danish WWTPs are designed and legally required to remove organic matter (summary parameters) and nutrients (nitrogen and phosphorous) [Guide 11058, 1999] and not micropollutants. However, Denmark has emission limit values for discharge of certain micropollutants in watercourses, lakes and the sea [Statutory order 1669, 2006], which also affect the operation of the WWTPs. Hence, the WWTPs act as barriers reducing urban pollution entering the recipients.

In the ScorePP project focus is set on the priority substances (PS) listed on the European Water Framework directive (WFD; European Commission, 2000) and the supplementing substances for which there are environmental quality standards (EQS; European Commission, 2006). Treatment barriers such as WWTPs are to be compared with source control options in order to find the optimal way to manage PS on an urban scale. Thus, it is vital to know the efficacy of PS removal in existing WWTPs.

The specific aim here was to contribute with data on PS removal in Danish WWTPs and to evaluate their behaviour.

Methodology

Literature review

The literature study focused on the PS defined in the WFD and was limited to a time period of 15 years (1992 to 2007) as it is expected that the concentrations of PS and well as the available treatment technologies were substantially different in older studies and thus not representative for the present day Denmark. Literature was searched on selected homepages and in international literature.

Homepages: Danish Environmental Protection Agency (Miljøstyrelsen, MST)

National Environmental Research Institute (Miljøundersøgelser, DMU)

Agency for Spatial and Environmental Planning (By- og Landskabsstyrelsen, BLST)

International: Technical Information Center of Denmark (Danmarks Tekniske Informationscenter)

Additionally, environmental managers representing the two water service companies in Copenhagen were contacted (Avedøre Wastewater Services (Spildevandscenter Avedøre I/S) and Lynettefællesskabet I/S).

Modeling

A modelling application with EPI Suite v3.20 (US EPA, 2007) was used to predict the fate of the PSs in a conventional activated sludge sewage treatment plant (STPWIN).

Results

Wastewater treatment in Denmark

In Denmark, wastewater treatment is common both in urban and rural areas. According to the Danish statistics [Statistics Denmark, 2007] less than 0.1 percent of all wastewater is untreated (Figure 1).

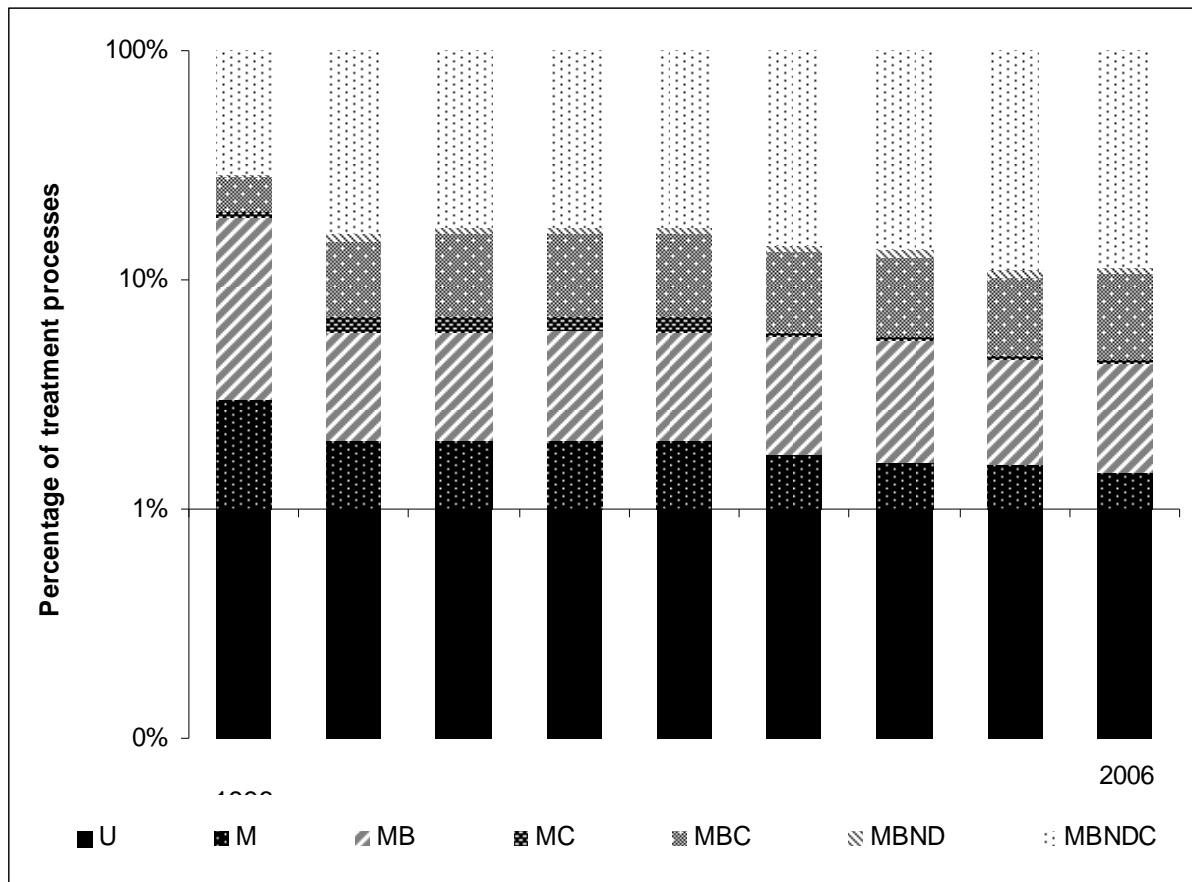


Figure 1. Processes applied in Danish wastewater treatment plants

(U = untreated, M = mechanical treatment, B = biological treatment, MB = mechanical-biological, MC = mechanical-chemical, MBND = mechanical, biological, nitrifying/denitrifying, and MBNDC = mechanical, biological, nitrifying/denitrifying, chemical)

The majority of the water flow, 89.6 % in 2006, was subjected to a treatment train including mechanical treatment (grid, sand and grease removal), biological treatment, nitrification/denitrification for nitrogen removal and chemical treatment for phosphorous removal, MBNDC.

National surveillance programmes

Denmark has a strong tradition of surveying the national waters. In 1997-2003 the “National programme for the surveillance of the aquatic environment”, abbreviated NOVA 2003, studied the presence of nutrients, metals and some selected organic substances in groundwater, surface waters (water courses and lakes), the sea, atmospheric deposition and rainfall as well as discharges from point sources such as WWTPs. NOVA 2003 was succeeded by NOVANA “National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments” in which the EU WFD [European Commission, 2000] was reflected as both chemical and biological status were included.

In NOVANA, discharges from 38 WWTPs were sampled on a monthly basis (Figure 2). [Boutrup et al., 2006]. These WWTPs represent 45% of the total wastewater flow and on average contain 31% of industrial wastewater, which is smaller than the national average of 37% [Danish Environmental Protection Agency & Agency for Spatial and Environmental Planning, 2005a].

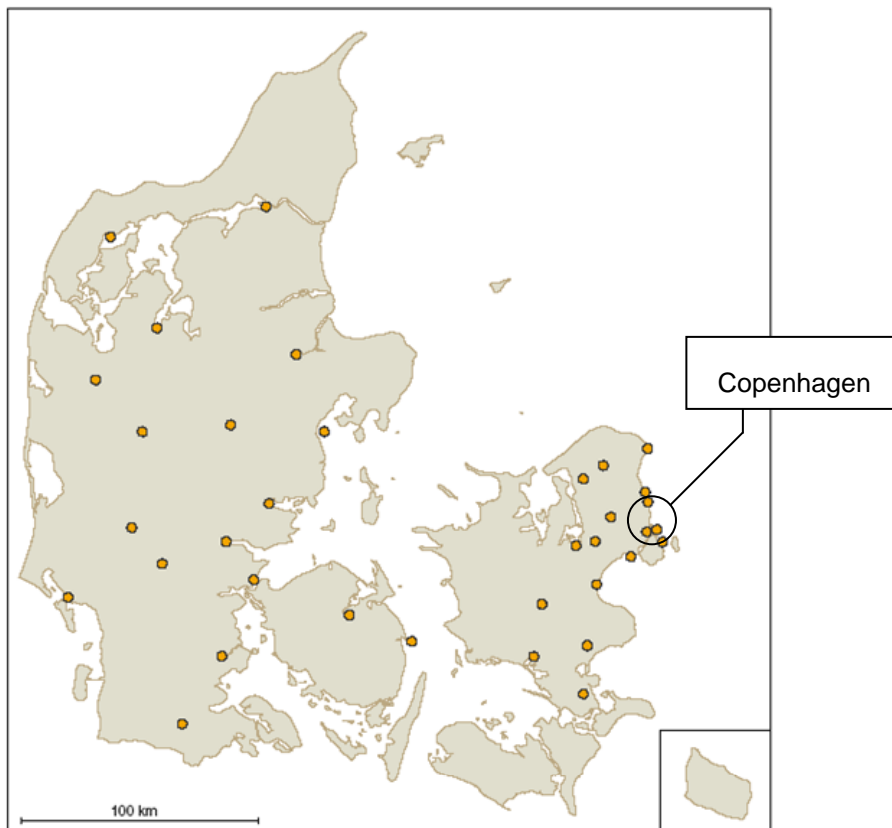


Figure 2. Location of the 38 WWTPs included in the national surveillance programme (NOVANA) [Boutrup *et al.*, 2006]

A major benefit is the large number of substances included in the monitoring programme and although the WFD PS have not been specifically addressed, a large portion of them are included (Table 1 and 2), particularly PAHs and pesticides. The major drawback with the data set is the lack of specificity as we cannot know if the data originate from dry or wet weather; the hydraulic retention time (HRT) or the sludge age (sludge retention time, SRT), thus severely hampering the applicability of the data for evaluating removal efficiencies.

Data from more recent national studies from 2005 have not been published yet. In all the tables PS are presented in an alphabetical order

Collated results from the NOVA 2003 study 1998-2003 [Danish Environmental Protection Agency & Agency for Spatial and Environmental Planning, 2005a]

Table 1. Inlet, outlet and sludge data from the national surveying programme (1998-2003)

Priority substances	Inlet ($\mu\text{g/l}$)						Outlet ($\mu\text{g/l}$)						Sludge $\mu\text{g/kg dm}$					
	average	5%	95%	% > LOD	no. of WWTPs	no. of samples	average	5%	95%	% > LOD	no. of WWTPs	no. of samples	average	5%	95%	% > LOD	no. of WWTPs	no. of samples
1,2-Dichloroethane 107-06-2		<0.02	>0.3	8	33	129			<0.3	0	33	128				0	31	31
Alachlor 15972-60-8																		
Aldrin 309-00-2	<0.3			0	32	199			<0.2	0	38	200			<LOQ	0	35	43
Anthracene 120-12-7	0.04	0.01	0.1	77	38	209		<0.01	>0.1	8	38	209	101	16	320	98	36	58
Atrazine 1912-24-9																		
Benzene 71-43-2	0.4	<0.01	2	48	23	90	0.01	<0.01	0.03	10	23	91	46	<10	237	37	34	35
Benzo(a)pyrene 50-32-8	0.05	0.01	0.1	80	36	204		<0.01	>0.05	4	36	200	289	58	480	96	36	67
Benzo(b)fluoranthene 205-99-2	0.1	0.02	0.2	87	38	215		<0.01	>1	9	38	205	546	98	910	97	36	65
Benzo(g,h,i)perylene 191-24-2	0.04	0.005	0.1	52	38	204		<0.01	>0.1	3	38	207	213	5	432	90	37	70
Benzo(k)fluoranthene 207-08-9																		
C10-13 Chloroalkanes 85535-84-8																		
Cadmium and its compounds 7440-43-9	0.5	0.09	1.4		38	281	0.09	<0.005	0.5		38	265	1700	600	3800			
Carbontetrachloride 56-23-5																		
Chlorfenvinphos 470-90-6																		
Chlorpyrifos 2921-88-2																		
DDT total																		
Di(2-ethylhexyl)phthalate (DEHP)	17	8.1	31	100	38	212	1.8	0.3	6.1	57	38	213	22700	3460	40600	96	37	71

117-81-7																				
Dichloromethane 75-09-2	3.5	<0.1	19	25	27	104		<0.1	>10	6	26	96	512	<2	1870	31	32	32		
Dieldrin 60-57-1		<0.01	>1	2	38	190			<0.1	0	38	195			<LOQ	0	35	43		
Diuron 330-54-1																				
Endosulfan 115-29-7																				
Endrin 72-20-8		<0.01	>0.7	1	38	194			<0.2	0	38	195			<LOQ	0	35	43		
Fluoranthene 206-44-0	0.1	0.03	0.2	98	38	218	0.002	<0.01	0.01	11	38	210	805	102	1,380	100	37	69		
Hexachlorobenzene 118-74-1		<0.005	>0.05	6	30	124		<0.005	>0.05	1	30	125	1.6	<5	12	21	35	42		
Hexachlorobutadiene 87-68-3																				
Hexachlorocyclohexane 608-73-1			<1	0	38	194			<0.1	0	38	195			<LOQ	0	35	43		
Indeno(1,2,3-cd)pyrene 193-39-5	0.08	0.005	0.3	54	38	185		<0.01	>0.1	5	38	206	241	23	712	96	37	69		
Isodrin 465-73-6		<0.01	>0.4	1	38	195			<0.2	0	38	196			<LOQ	0	35	43		
Isoproturon 34123-59-6																				
Lead and its compounds 7439-92-1	16	4.7	37		38	290	1.9	0.3	5.3		38	276	64000	29000	1E+05					
Mercury and its compounds 7439-97-6	0.4	0.08	1.5		38	280	0.09	<0.01	0.3		38	265	1300	200	4300					
Naphthalene 91-20-3	0.5	0.06	1.3	94	31	185	0.02	<0.01	0.06	26	31	184	3E+05	16000	1E+06	93	36	58		
Nickel and its compounds 7440-02-0	11	3.2	26		38	292	6.4	1.6	16		38	284	26000	12000	50000					
Nonylphenol 25154-52-3	3.2	1.1	8.4	97	38	211	0.3	0.05	0.6	68	38	211	17300	195	46200	95	37	74		
Octylphenol 1806-26-4			<0.5	8	38	190		<0.1	>0.5	1	38	191	49	<0.02	354	20	33	45		
para-para-DDT 50-29-3																				
Pentabromodiphenylether23 32534-81-9																				
Pentachlorobenzene 608-93-5			<0.01	34	2	7			<0.01		2	8			<5		2	8		

Pentachlorophenol 87-86-5	0.02	<0.01	0.05	34	38	158	0.01	<0.01	0.03	18	38	159	26	<0.01	116	27	23	30
Polyaromatic hydrocarbons (PAH)																		
Simazine 122-34-9																		
Tetrachloroethylene 127-18-4	0.1	<0.02	0.5	46	30	117	0.01	<0.02	0.08	13	31	120		>5	3	32	32	
Tributyltin compounds 688-73-3																		
Trichlorobenzenes (all isomers) 12002-48-1		<0.01	>0.05	1	30	124			<0.02	0	31	126		>5	<500	2	35	42
Trichloroethylene 79-01-6	0.1	<0.1	0.7	47	30	117	0.01	<0.02	0.07	10	30	117		<100	0	32	32	
Trichloromethane 67-66-3	0.6	0.06	2.4	79	27	105	0.05	<0.02	0.1	50	28	105		<1000	5	32	32	
Trifluralin 1582-09-8																		

The average refers to the average measured values during the study whereas 5% and 95% are the percentile of the lowest and highest value measured. Not all wastewater treatment plants analysed all substances, thus, the number of actually participating WWTPs and how many samples that were taken are reported. The term percentage over LOD refer to the number of sample (in %) what were found to have concentrations above the limit of detection. NB. For some have instead limit of quantification been reported (LOQ) by no justification of their difference were found in the reference.

Conclusions regarding the removal efficiencies: *"The investigation of the presence and content of XOCs and heavy metals showed that the content was substantially reduced between inlet and outlet. For some substances an actual degradation occurs, whereas others such as PAHs, chlorophenols and plasticizers sorb to the sludge"* [Danish Environmental Protection Agency & Agency for Spatial and Environmental Planning, 2005a].

Results from the NOVANA study 2004 [Danish Environmental Protection Agency & Agency for Spatial and Environmental Planning, 2005b]

Table 2. Inlet, outlet and sludge data from the national surveying programme (2004 years campaign)

Priority substances	Inlet ($\mu\text{g/l}$)						Outlet ($\mu\text{g/l}$)						Sludge $\mu\text{g/kg dm}$						
	average	5%	95%	% > LOD	no. of WWTPs	no. of samples	average	5%	95%	% > LOD	no. of WWTPs	no. of samples	average	5%	95%	% > LOD	no. of WWTPs	no. of samples	
1,2-Dichloroethane 107-06-2																			
Alachlor 15972-60-8																			
Aldrin 309-00-2																			
Anthracene 120-12-7	0.02	0.01	0.03	53%	9	36	0.002	<0.002	0.01	14%	9	36	0.06	0.02	0.11	100%	7	7	
Atrazine 1912-24-9																			
Benzene 71-43-2	0.37	0.03	1.48	63%	7	35	0.03	<0.02	0.11	27%	9	33	0.07	0.03	0.11	29%	7	7	
Benzo(a)pyrene 50-32-8	0.02	0.01	0.05	50%	9	36	0.002	<0.002	0.01	14%	9	36	0.15	0.02	0.25	100%	7	7	
Benzo(b)fluoranthene 205-99-2	0.04	0.01	0.08	78%	9	36	0.004	<0.01	0.02	17%	9	36	0.35	0.06	0.55	100%	7	7	
Benzo(g,h,i)perylene 191-24-2	0.01	<0.01	0.02	36%	9	36	0.009			11%	9	35	0.13	0.06	0.24	86%	7	7	
Benzo(k)fluoranthene 207-08-9																			
C10-13 Chloroalkanes 85535-84-8																			
Cadmium and its compounds 7440-43-9	0.56	0.07	2.14	83%	9	36	0.1	0.03	0.25	53%	9	36	1.91	0.52	5.76	100%	7	7	
Carbontetrachloride 56-23-5																			
Chlorfenvinphos 470-90-6																			
Chlorpyrifos 2921-88-2																			
DDT total																			
Di(2-ethylhexyl)phthalate (DEHP)	9.03	0.38	16.69	81%	7	32	1.93	0.25	5.21	59%	8	32	20.97	11.36	34.2	100%	7	7	

117-81-7																			
Dichloromethane 75-09-2	0.09	<0.1	0.47	10%	9	42			0.3	3%	9	34	0.13	0.06	0.19	29%	7	7	
Dieldrin 60-57-1																			
Diuron 330-54-1																			
Endosulfan 115-29-7																			
Endrin 72-20-8																			
Fluoranthene 206-44-0	0.06	0.01	0.1	75%	9	36	0.01	<0.01	0.03	25%	9	36	0.43	0.1	0.97	100%	7	7	
Hexachlorobenzene 118-74-1																			
Hexachlorobutadiene 87-68-3																			
Hexachlorocyclohexane 608-73-1																			
Indeno(1,2,3-cd)pyrene 193-39-5	0.04	0.01	0.19	39%	9	36	<0.01		0.01	11%	9	36	0.014	0.06	0.19	86%	7	7	
Isodrin 465-73-6																			
Isoproturon 34123-59-6																			
Lead and its compounds 7439-92-1	8.39	0.5	14.77	75%	9	36	2.55	0.3	8.63	56%	9	36	44.66	17.88	73.2	100%	7	7	
Mercury and its compounds 7439-97-6	0.6	0.05	1.94	64%	9	36	0.59	0.01	2.01	31%	9	36	0.85	0.33	1.69	100%	7	7	
Naphthalene 91-20-3	0.39	0.03	1.29	72%	8	32	0.02	<0.02	0.08	22%	8	32	0.14	0.07	0.28	67%	6	6	
Nickel and its compounds 7440-02-0	10.58	7.21	13.6	100%	9	36	16.72	3.12	70.36	100%	9	36	24.06	15.3	34.52	100%	7	7	
Nonylphenol 25154-52-3	1.35	0.08	2.35	86%	9	36	0.52	0.06	1.6	69%	9	36	9.93	1.45	27.25	86%	7	7	
Octylphenol 1806-26-4																			
para-para-DDT 50-29-3																			
Pentabromodiphenylether23 32534-81-9	0.01	0.01	0.01	50%	8	4			<0.01	0%	2	8			<0.02	0%	1	1	
Pentachlorobenzene 608-93-5			<0.01	0%	9	36			<0.01	0%	9	36			<0.02	0%	7	7	

Pentachlorophenol 87-86-5	0.01	<0.01	0.03	8%	9	36	<0.01	0.004	8%	9	36	0.03	0.02	0.03	29%	7	7	
Polyaromatic hydrocarbons (PAH)																		
Simazine 122-34-9																		
Tetrachloroethylene 127-18-4	0.21	0.05	0.6	57%	9	44	0.02	<0.02	0.09	28%	9	36	0.01	0.01	0.01	43%	7	7
Tributyltin compounds 688-73-3																		
Trichlorobenzenes (all isomers) 12002-48-1		0.01	0.01	25%	2	16		<0.01	25%	2	16			<0.02	0%	1	2	
Trichloroethylene 79-01-6	0.21	0.03	0.67	52%	9	44	0.01	<0.02	0.05	14%	9	36	0.01	0.01	0.01	57%	7	7
Trichloromethane 67-66-3	0.32	0.05	0.85	77%	9	44	0.04	<0.02	0.12	28%	9	36			<0.02	0%	7	7
Trifluralin 1582-09-8																		

Dm: Dry matter

See comments for Table 1.

Monitoring programmes carried out on a County level

Small municipalities generally have limited resources to monitor pollutants on a larger scale and thus they cooperate with each other and with the local County. A report from one county (Århus amt) was found, and in this report the inlet concentrations (grab sampling) of 12 WWTPs were investigated (1 to 6 samples per WWTP) and for four WWTPs were the outlet concentrations investigated [Boutrup and Pelsner, 2001]. Here, inlet and outlet concentrations from the four WWTPs are presented in Tables 3 to 6. The studied plants are small, 11 to 219 person equivalents (PE) and they have no harmonized treatment train as the treatment technique vary from site to site. Furthermore, no sludge concentrations were reported.

Table 3. Tåstrup WWTP (11 PE; mechanical treatment; 2 m³/d)

	Inlet (µg/l)			Outlet (µg/l)			
	min	max	no. of samples	average	min	max	no. of samples
1,2,4-trichlorobenzene	<0.01	<0.01	6		<0.01		
anthracene	<0.02	0.015	6	0.003	<0.01	0.005	
benzene	<0.05	0.21	6	0.17	<0.05	0.69	
Benzo(b+j+k)fluoranthene	<0.02	0.079	6	0.011	<0.01	0.03	
Benzo(g,h,i)perylene	<0.02	0.042	6	0.001	<0.01	0.005	
benzo[a]pyrene	<0.02	0.023	6	0.004	<0.01	0.015	
Carbontetrachloride	<0.05	<0.05	6		<0.05		
chloroform	<0.05	<0.05	6		<0.1		
DEHP	6.9	18	6	8.2	6.6	9.8	
fluoranthene	<0.02	0.046	6	0.008	0.005	0.014	
hexachlorobenzene	<0.01	<0.01	6		<0.01		
Indeno(1,2,3-cd)pyrene	<0.02	<0.02	6		<0.02		
naphthalene	<0.02	0.078	6	0.005	<0.02	0.025	6
NP	0.87	10	6	2.8	0.83	3.6	
NP 1-2 EO	2	23	6	5.83	1.83	7.62	
NP 1EO	0.8	12	6	2.9	1	4.2	
NP 2EO	<0.2	1.1	6	0.18	<0.1	0.39	
NP 3-15 EO	<20	<20	6		<20		
OP	<0.1	<0.1	6		<0.1		
OP 3-15 EO	<20	<20	6		<20		
pentachlorobenzene	<0.01	<0.01	6		<0.01		
pentachlorophenol	<0.04	<0.04	6		<0.04		
Tetrachloroethylene	<0.05	<0.05	6		<0.05		
Trichloroethylene	<0.05	<0.05	6		<0.05		

Mechanical treatment: the removal of PAHs is limited to about 30% and the removal of NP and its mono- and di-ethoxylates is about 10%.

Table 4 Lyngby WWTP (219 PE; biological bio rotor; 46 m³/d)

	Inlet (µg/l)			Outlet (µg/l)			
	min	max	no. of samples	average	min	max	no. of samples
1,2,4-trichlorobenzene	<0.01	<0.01	6		<0.01		6
anthracene	<0.02	0.057	6	0.004	<0.02	0.01	6
benzene	<0.05	0.39	6	0.028	<0.05	0.093	6
Benzo(b+j+k)fluoranthene	0.029	0.44	6	0.021	0.005	0.063	6
Benzo(g,h,i)perylene	<0.02	0.22	6	0.005	<0.01	0.012	6
benzo[a]pyrene	0.011	0.22	6	0.008	0.005	0.011	6
Carbontetrachloride	<0.05	<0.05	6		<0.05		6
chloroform	<0.05	0.11	6	0.008	<0.1	0.05	6
DEHP	10	38	6	4.7	2.1	7.3	6
fluoranthene	<0.02	0.41	6	0.018	0.005	0.033	6
hexachlorobenzene	<0.01	<0.01	6		<0.01		6
Indeno(1,2,3-cd)pyrene	<0.02	0.012	6	0.002	<0.01	0.01	6
naphthalene	<0.02	0.076	6	0.01	<0.02	0.025	6
NP	1.5	3.2	6	0.5	0.14	1.2	6
NP 1-2 EO	2.8	8.7	6	1.09	0.53	2.13	6
NP 1EO	0.97	4.9	6	0.4	0.17	0.72	6
NP 2EO	0.11	2.2	6	0.2	<0.1	0.42	6
NP 3-15 EO	<20	51	6	8.3	<10	10	6
OP	<0.01	<0.01	6		<0.1		6
OP 3-15 EO	<20	<20	6		<20		6
pentachlorobenzene	<0.01	<0.01	6		<0.01		6
pentachlorophenol	<0.01	0.08	6	0.04	<0.05	0.08	6
Tetrachloroethylene	<0.05	<0.05	6		<0.05		6
Trichloroethylene	<0.05	<0.05	6		<0.05		6

Bio rotor: here breakthrough of both small and heavy PAHs can be seen, but DEHP and the NPs (NP+ 1 & 2 ethoxylates) are removed about 75%.

Table 5 Jeksen WWTP (103 PE; biological sandfilter; 51 m³/d)

	Inlet (µg/l)			Outlet (µg/l)			
	min	max	no. of	average	min	max	no. of

	samples			samples			
	min	max	no. of samples	average	min	max	no. of samples
1,2,4-trichlorobenzene	<0.01	0.068	6		<0.01		6
anthracene	<0.02	0.035	6	0.003	<0.02	0.05	6
benzene	<0.05	0.059	6		<0.02	0.025	6
Benzo(b+j+k)fluoranthene	<0.02	0.12	6	0.004	<0.02	0.005	6
Benzo(g,h,i)perylene	<0.02	0.048	6	0.002	<0.02	0.005	6
benzo[a]pyrene	<0.02	0.035	6	0.03	<0.02	0.005	6
Carbontetrachloride	<0.05	<0.05	6		<0.05	<0.05	6
chloroform	<0.05	0.072	6		<0.1	0.025	6
DEHP	6.2	35	6	2.7	1.1	5.1	6
fluoranthene	<0.02	0.076	6	0.04	<0.02	0.05	6
hexachlorobenzene	<0.01	<0.01	6		<0.01		6
Indeno(1,2,3-cd)pyrene	<0.02	0.19	6	0.001	<0.02	0.005	6
naphthalene	<0.02	0.23	6	0.017	<0.02	0.025	6
NP	1.5	3.2	6	0.35	0.13	0.6	6
NP 1-2 EO	3.6	9.8	6	0.6	0.23	1.02	6
NP 1EO	1.2	5.3	6	0.15	0.05	0.25	6
NP 2EO	0.37	2	6	0.1	0.05	0.22	6
NP 3-15 EO		36	6	8.3	<20	10	6
OP	<0.1	<0.1	6	<0.01	<0.1	0.05	6
OP 3-15 EO	<20	30	6	1.67	<20	10	6
pentachlorobenzene	<0.01	<0.01	6		<0.01		6
pentachlorophenol	<0.01	0.07	6	0.008	<0.04	0.025	6
Tetrachloroethylene	<0.05	<0.05	6		<0.05	<0.05	6
Trichloroethylene	<0.05	<0.05	6		<0.05	<0.05	6

Biological sand filter: here the small PAHs can be detected in the effluent whereas the heavy PAHs are removed. DEHP is removed by 85% and correspondingly, for the NPs 90%.

Table 6 Ormslev WWTP (30 PE; root zone bed; 39 m³/d)

	Inlet (µg/l)			Outlet (µg/l)			
	min	max	no. of samples	average	min	max	no. of samples

1,2,4-trichlorobenzene	<0.01		6		<0.01		6
anthracene	<0.02	0.015	6	0.003	<0.01	0.011	6
benzene	<0.05	<0.05	6		<0.05		6
Benzo(b+j+k)fluoranthene	0.011	0.14	6	0.018	<0.01	0.049	6
Benzo(g,h,i)perylene	<0.02	0.05	6	0.003	<0.01	0.005	6
benzo[a]pyrene	<0.02	0.047	6	0.004	<0.01	0.01	6
Carbontetrachloride	<0.05	<0.05	6				6
chloroform	<0.05	<0.05	6		<0.1		6
DEHP	<0.5	0.69	6	3.5	0.57	8	6
fluoranthene	<0.02	0.077	6	0.007	<0.01	0.011	6
hexachlorobenzene	<0.01		6		<0.01		6
Indeno(1,2,3-cd)pyrene	<0.02	0.055	6	0.003	<0.01	0.005	6
naphthalene	<0.02	0.02	6	0.027	0.01	0.15	6
NP	0.38	1.1	6	0.017	<0.1	0.05	6
NP 1-2 EO	<0.2	<0.2	6	0.18	0.1	0.28	6
NP 1EO	<0.2	0.54	6	0.12	0.1	0.18	6
NP 2EO	0.39	2.3	6	0.04	<0.1	0.05	6
NP 3-15 EO	<20	<20	6		<20		6
OP	<0.1	<0.2	6		<0.1		6
OP 3-15 EO	<20	<20	6		<20		6
pentachlorobenzene	<0.01		6		<0.01		6
pentachlorophenol	<0.01		6		<0.05		6
Tetrachloroethylene	<0.05	<0.05	6				6
Trichloroethylene	<0.05	<0.05	6				6

Root zone bed: due to low PAH and NPs loading this system could not be evaluated based of their removal. Approximately 50% of DEHP is removed.

Case studies

Treatment by MBNDC

Avedøre WWTP

Avedøre WWTP is located in Southern Copenhagen and serves about 350,000 PE. The treatment is a so-called MBNDC and consists of i) a grid, ii) a sand and grease trap, iii) settling tank, iv) biological treatment, v) chemical treatment and vi) a settling tank. The sludge retention time is 15-25 days [Jacobsen et al., 2004]. The hydraulic load is 73,000 m³/day [Kjølholt et al., 2003]. In a study combining chemical analyses and biomonitoring two metals and three XOCs classified as PPs were included, see Table 7.

Table 7. Inlet and outlet concentrations from Avedøre WWTP

	Inlet (µg/l)		Outlet (µg/l)	
	average	no. of samples	average	no. of samples
DEHP	34	4	1.28	4
Dichloromethane	27	4	"-"	4
Ni	19	4	13.5	4
Nonylphenol	4	4	0.32	4
Pb	13	4	2.8	4

In this limited study, only four samples of each wastewater flow, it was found that for the metals Pb was removed (78%) from the water phase whereas Ni only partly (29%). For the XOCs both NP and DEHP were removed significantly, 92 and 96% respectively from the water phase. However, no sludge information was included.

In a subsequent study focussing on endocrine disrupting XOCs, the inlet and outlet concentrations of nonylphenols, short-chain nonylphenol ethoxylates, octylphenol and DEHP were studied [Kjølholt et al., 2003], Table 8.

Table 8. Substance included in a screening of endocrine disrupting substances

	Inlet (µg/l)		Outlet (µg/l)	
	average	no. of samples	average	no. of samples
NPs	4.2	3	0.21	3
NP 1-2 EO	4.9	3	<0.1	3
Octylphenol	<0.1	3	<0.1	3
DEHP	46	3	<0.5	3

The results were only based on a single sample of both inlet and outlet and thus the uncertainty is large but the data indicate that NPs and DEHP were removed considerably from the water phase.

Lynetten WWTP and pilot plant

Lynetten, like Avedøre, is located in the outskirts of Copenhagen. It is a scaled down pilot plant which is used to test optimization strategies and was used in-depth in a recent PhD-thesis work by K. Press-Kristensen. He analysed nonylphenol and bisphenol-A in the inlet (which corresponds to the inlet of the full-scale plant and the outlet of the pilot plant, Table 9).

During the tests, the flow was 10 m³/d, the HRT 0.5 d, the SRT 27 d and the temperature 13-16 °C [Press-Kristensen, 2007]. A major drawback with the study is that the nonylphenol ethoxylates were not measured and thus potential NP contribution due to degradation of the ethoxylates cannot be assessed. The thesis includes an optimisation of the pilot scale plant using high (spiked) concentrations of NP. NP was reduced 10-65% during standard operation of the pilot plant but with an increased aerobic phase time, the reduction yield changed to 70->80% [Press-Kristensen, 2007].

Table 9. Nonylphenol in a pilot plant of Lynetten [Press-Kristensen, 2007]

NP	Median	Average	Min	Max
influent	4.2	6.7	1.9	34.5
effluent	4.2	5.8	1 (<LOQ)	24.5

Advanced oxidation processes (AOP) for removal of estrogens and estrogenic substances

Due to a report from the Danish EPA on steroid hormones and estrogenic effects in Danish WWTPs [Andersen et al., 2004] the interest for using advanced oxidation processes as a tertiary treatment for removal of estrogenicity in wastewater discharges has increased in Denmark. The focus has primarily been on the natural and artificial steroid hormones (estradiol, ethynyl estradiol and estrone) but some studies have also included XOCs with known estrogenic effects.

Ozone

Kalundborg WWTP consists of mechanical and biological treatment (MB) and plans for an AOP exist. The load is corresponding to 25,000 PE and 12,600 m³/d [Kjølholt et al., 2003]. One test was made by adding three levels of ozone to the MB treated wastewater, using only one replicate. Already the initial MB treatment removed NP 1-2 EO and DEHP below the limit of detection (LOD). Hence, only nonylphenols could be tested in the ozone treatment. The first concentration of ozone (21.5) were all XOCs below the limit of detection, thus no clear conclusions on the applicability of ozone in this study can be drawn due to the vicinity of the LOD.

Table 10. Application of ozone for removal of endocrine disrupting substances

	Inlet (µg/l)	Outlet (MB-treatment) µg/l	MB+ozone (21.5 mg/l)	MB+ozone (53.5 mg/l)	MB+ozone (88.4 mg/l)
NPs	6.1	0.21	<0.1	<0.1	<0.1
NP 1-2 EO	1.2	<0.1	<0.1	<0.1	<0.1
Octylphenol	<0.1	<0.1	<0.1	<0.1	<0.1
DEHP	9.5	<0.5	<0.5	<0.5	<0.5

Photolysis (Ultraviolet light and hydrogen peroxide)

Photolysis as tertiary treatment has been tested on a laboratory (bench) scale with treated wastewater from Usserød WWTP and tap water that was spiked with 4-NP and octylphenols [Hansen et al., 2007]. The removal efficiency was higher in the tap water than the treated wastewater due to the absence of organic matter and solids but nonetheless 60-80% of NP and 70-90% of OP was removed from the treated wastewater [Hansen et al., 2007].

Focus on sludge treatment

Usserød WWTP

Usserød is an MBNDC treatment plant, which receives 30,000-50,000 PE and a flow of 11,000 m³/d [Kjølholt et al., 2003; Knudsen et al., 2000]. Two studies, besides the above-mentioned AOP tests, were found focusing on this treatment plant. Firstly, the aqueous phase with inlet and outlet concentrations of NP ethoxylates, OP and DEHP was studied and then post-treatment of anaerobic sludge was studied for PAHs, NPs and DEHP.

Three samples of the inlet and three of the outlet were investigated for NP and NP short-chain ethoxylates, where it could be seen that the latter were removed >98% whereas NP 96%. Also DEHP was removed from the water phase (>98%) [Kjølholt et al., 2003].

Table 11. PS in the water phase, inlet and outlet concentrations.

	Inlet (µg/l)	Outlet (µg/l)
NPs	2.7	0.12
NP 1-2 EO	6.4	<0.1
Octylphenol	<0.1	<0.1
DEHP	22	<0.5

In a sludge optimization test performed on full-scale and on a laboratory scale, the post-aeration process was tested with a modification; a semi-continuous process where anaerobic sludge was aerated in separate tanks with varying hydraulic retention times. [Knudsen et al., 2000]. An existing sludge-holding tank with an active volume of 225 m³ was used as post-aeration tank. As it can be seen in Table 11, the post-aeration achieved an improved PS removal compared to the traditionally treated anaerobic sludge.

The dry solids content was typically in the range of 23.4–26.7 g DS/kg, and 16.8–20.3 g/kg for the anaerobic and the post-aerated sludge, respectively.

Table 11. Post-aeration of anaerobic sludge

Concentrations in mg/kg DS	Anaerobic	No of samples	Post-aeration	No of samples
PAHs (acenaphthene, phenanthrene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene and fluorene)	2.5-5	14	1-3	14
NPEs (nonylphenol and nonylphenol ethoxylates with 1 and 2 ethoxy-groups)	25-55	14	<10-14	14
DEHP	20-100	14	10-40	14

For the PAHs, a reduction of 30–50% was achieved and DEHP 30-40% compared to the anaerobic sludge. For the NPE the removal efficacy reached 75–95% by means of the post-aeration process.

Roskilde WWTP (MBND; removal of NPs and DEHP and PBDEs in sludge)

Roskilde WWTP is located on the island of Zealand west of Copenhagen and discharges into the fiord of Roskilde. It receives 80,000 PE and has a dry weather flow of 50,400 m³/d and a rain flow of 79,500 m³/d [Fauser et al., 2001]. HRT is 46 h and SRT ca. 20 d.

Phthalate concentrations at the inlet were measured in the range 30-270 µg phthalates/l of which DEHP contributed with 13-44 µg/l (Table 12). Measurements from the inlet also showed concentrations of approximately 5 and 100 µg/l for NP and nonylphenol di-ethoxylate, respectively [Fauser et al., 2001] (Tables 13 and 14). Inlet and outlet concentrations in µg/l and sludge concentrations in mg/kg DW and the standard deviations refer to results originating from duplicate or triplicate samples [Fauser et al., 2001]

DEHP in the inlet was primarily found in the particulate fraction (settled). The outlet concentrations indicate that 97% of the DEHP is removed from the water phase during the treatment. Although the sludge only was samples one day, it can be seen that the DEHP largely accumulate in the primary sludge, Table 12.

Table 13. DEHP in inlet and outlet as well as sludge (liquid samples in µg/l and sludge in mg/kg DW)

Date (May 1999)	Inlet total	Inlet supernat	Inlet settled	Outlet	Primary sludge	Secondary sludge
15	13.1 ± 0.52	2.37	17.8			
16				0.11		
17	34.5 ± 1.52	7.83	31.6	0.2		
18	36.6 ± 0.00	5.89	35.8	0.27	61.11 ± 3.20	3.51 ± 0.03
19	39.5 ± 4.10	5.58	39.5	0.76		
20	44.3 ± 0.62	3.87	47.4	1.72		
21	43.9 ± 6.44	4.31	43	1.01		

22	36.1 ± 10.74	6.61	24.7			
23				2.65		

Table 14. NPs in inlet and outlet as well as sludge (liquid samples in µg/l and sludge in mg/kg DW)

Date (May 1999)	Inlet total	Inlet supernat	Inlet settled	Outlet	Primary sludge	Secondary sludge
15	2.75 ± 0.15	3.42	2.45			
16				0.14		
17	7.38 ± 1.12	3.71	3.99	0.18		
18	6.18 ± 0.98	3.47	4	0.37	11.95 ± 1.85	0.19 ± 0.01
19	10.2 ± 2.29	4.75	6.46	0.32		
20	6.62 ± 0.47	3.16	3.64	0.29		
21	9.65 ± 0.21	3.24	3.46	0.31		
22	7.28 ± 1.29	3.32	2.5			
23				0.69		

The NPs phase distribute relatively evenly between dissolved and settled fractions, although some samples indicate a preference towards the settled fraction. 95% of the NPs are removed from the water phase during the treatment and the NPs accumulate predominantly in the primary sludge, Table 13.

Table 14. NP ethoxylates in inlet and outlet as well as sludge (liquid samples in µg/l and sludge in mg/kg DW)

Date (May 1999)	Inlet total	Inlet supernat	Inlet settled	Outlet	Primary sludge	Secondary sludge
15	37.1 ± 1.17	13.9	30.6			
16				0.68		
17	155.4 ± 16.65	62.2	84.1	1.2		
18	60.0 ± 0.80	16.6	33.6	2.95	39.12 ± 3.81	1.28 ± 0.12
19	157.1 ± 53.64	63.5	113.2	2.59		
20	113.2 ± 17.25	19.7	60.4	2.29		
21	216.8 ± 15.41	42.3	93.7	1.85		
22	82.6 ± 2.89	24	25			

23				2.54		
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98% of the NP ethoxylates are removed from the inlet to the outlet. From the inlet samples it is clear that the NP ethoxylates phase distribute into the particulate fraction, e.g., by sorption to organic matter and particles (Table 14). In addition, here the levels are higher in the primary sludge compared to the secondary sludge [Fauser et al., 2001]

In another study in Roskilde, brominated flame-retardants including three congeners of pentabromobiphenyl ether were studied [Christensen et al., 2003] in the inlet and in sludge. No removal was calculated but the data may potentially be used for calculating phase distribution.

Table 15. Pentabromobiphenyl ethers congeners

	Wastewater inlet (ng/l)	Sewage sludge (µg/kg dw)
BDE-85 (2,2',3,4,4'-pentabromodiphenylether)	< 0.05	3.1 (±1.4)
BDE-99 (2,2',4,4',5-pentabromodiphenylether)	0.25 (±0.11)	86.2 (±7.7)
BDE-100 (2,2',4,4',6-pentabromodiphenylether)	0.06 (±0.03)	19.1 (±1.7)

Dw: Dry weight

Aalborg (DEHP in sludge treatment)

Aalborg East WWTP is a full-scale activated sludge WWTP (MBNDC). The wastewater at originates from households (80%) and local industries (20%) and corresponds to 100,000 PE [Roslev et al., 2007]. The HRT is about 1 day, the, the SRT is 21–28 days, and the aerobic sludge age is 6–8 days. Flow proportional wastewater samples (24h) were collected from the inlet and outlet of the treatment plant in dry weather conditions [Roslev et al., 2007]. Based on the average values, 93% of the DEHP is removed from the water phase during treatment, Table 16.

Table 17 DEHP in wastewater and sludge

	Average	Min	Max	No of samples
Inlet (µg/l)	71.89	53.23	84.1	3 to 5
Outlet (µg/l)	4.92	2.08	9.93	3 to 5
Dewatered sludge (mg/kg dw)	67.18	61.37	77.88	3 to 5

Herning and Hillerød WWTPs (sludge treatment)

Both Herning and Hillerød digest primary sludge and bio-sludge but in Herning the system is mesophilic (ca. 35°C) and in Hillerød termofilic (ca. 55°C) [Mose Pedersen and Bøwadt, 2002]. Herning serves 110,000 PE and receives 32,000 m³/d whereas Hillerød serves 48,700 and receives 20,400 m³/d. The load from the industry is 50% in Herning and 5% in Hillerød [Mose Pedersen and Bøwadt, 2002].

Alkyl phenol ethoxylates, nonylphenol ethoxylates and NPs (nonylphenol and mono- and di-ethoxylates) as well as DEHP were included in the study, Table 17 and 18.

Table 18. Alkyl phenols and DEHP in sludge from Herning

	$\mu\text{g/l}$	mg/kg dw			
	Inlet	Primary sludge	Bio sludge	Mixed sludge	Undigested sludge
NP + NPEO1-2	0.64		3	29	160
NPEOn	40		0.68	11	0.45
AEOOn	580	250	3.6	110	15
DEHP	32		78	100	84

AEOOn is a summary parameter covering all alkylphenols, of which the nonylphenol ethoxylates is a part. Here it can be seen that in Herning the distribution between the groups are 1:60:900, indicating that NPs only make a small fraction of the total load of AEOs.

Table 19 Alkyl phenols and DEHP in sludge from Hillerød

	$\mu\text{g/l}$	mg/kg dw			
	Inlet	Primary sludge	Bio sludge	Mixed sludge	Undigested sludge
NP + NPEO1-2	<0.1	0.93	1.3	3.9	8.4
NPEOn	<20	2.3	<0.05	0.37	<0.05
AEOOn	110		<1	21	13
DEHP	32	86	52	57	85

Two major problems were that most studies did not include i) all types of samples (inlet, outlet, sludge) and phases (dissolved and particulate) and ii) information regarding the sampling procedure and the previous dry periods.

MBNDC data compared to modeling

The EPI Suite modelling tool contains a sub-model STPWIN that model the fate of substances in WWTPs [US EPA, 2007]. Here removal efficiencies were estimated using this tool and subsequently compared with the actual removal efficiencies seen for the MBNDC WWTPs, Table 19. This type of WWTP was chosen because it represents treatment for 90% of the wastewater flow. “T number” refers to the table number from which the data have been obtained. Metals and summary parameters are not included.

Table 19. Comparison of MBNDC and estimated removal efficiencies (in %)

Priority substances	MBNDC	Removal in WWTP	Biodegradation	Sludge adsorption	To air
1,2-Dichloroethane		34.0	0.1	1.4	32.6
Alachlor		13.5	0.2	13.3	0.0
Aldrin		93.4	0.8	92.7	0.0
Anthracene	90 (T1)	54.2	0.5	52.5	1.3
Atrazine		3.5	0.1	3.3	0.0
Benzene	92-98 (T1,2)	68.9	0.0	1.1	67.8
Benzo(a)pyrene	90 (T2)	92.6	0.8	91.7	0.0
Benzo(b)fluoranthene	90 (T2)	90.9	0.8	90.2	
Benzo(g,h,i)perylene	10 (T2)	93.6	0.8	92.8	
Benzo(k)fluoranthene		92.6	0.8	91.8	
C10-13 Chloroalkanes		98.2	0.2	59.2	38.7
Carbontetrachloride		91.6	0.0	2.0	89.5
Chlorfenvinphos		22.2	0.3	21.9	
Chlorpyrifos		76.4	0.7	75.7	0.0
DEHP	79-99(T1,2,7,8,10,16)	94.0	0.8	93.2	0.0
Dichloromethane		56.9	0.1	1.0	55.9
Dieldrin		83.1	0.7	82.4	0.1
Diuron		3.7	0.1	3.6	0.0
Endosulfan		25.2	0.3	22.4	2.6
Endrin		83.1	0.7	82.4	0.1
Fluoranthene	83-98 (T1,2)	82.2	0.7	82.4	0.1
Hexachlorobenzene		91.1	0.7	88.0	2.3
Hexachlorobutadiene		88.9	0.3	51.9	36.7
Hexachlorocyclohexane		37.0	0.4	36.4	0.2
Indeno(1,2,3-cd)pyrene	75 (T2)	93.7	0.8	92.9	0.0
Isodrin		93.4	0.8	92.7	0.0
Isoproturon		4.7	0.1	4.6	0.0
Naphthalene	95-96 (T1,2)	23.6	0.1	8.3	15.1

Nonylphenol	61-98 (T1,2,7,8,10)	90.8	0.8	90.0	0.1
Octylphenol		88.3	0.8	87.5	0.0
para-para-DDT		93.8	0.8	93.0	0.0
Pentabromodiphenylether		93.8	0.8	93.0	0.0
Pentachlorobenzene		83.6	0.7	79.5	3.4
Pentachlorophenol	>10-50 (T1,2)	81.2	0.7	80.5	
Simazine		2.5	0.1	2.4	0.0
Tetrachloroethylene	90 (T1,2)	87.9	0.1	6.3	81.5
Tributyltin compounds		97.3	0.4	74.6	22.3
Trichlorobenzenes (all isomers)		61.4	0.3	33.1	28.0
Trichloroethylene	90-95 (T1,2)	79.6	0.0	1.3	78.3
Trichloromethane	88-92 (T1,2)	59.8	0.1	1.1	58.6
Trifluralin		86.0	0.7	84.9	0.5

Benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene and pentachlorophenol were removed in MBNDC in a lesser extent than estimated by STPWIN. Anthracene, benzene, naphthalene, trichloroethylene and trichloromethane were removed with a higher efficacy than estimated by STPWIN. For benzo[a]pyrene, benzo[b]fluoranthene, DEHP, fluoranthene, nonylphenol and tetrachloroethylene the MBNDC removal efficiencies were close to those estimated in the modelling. However, a bigger MBNDC data set would be needed to thoroughly evaluate the applicability of the STPWIN model for estimating removal efficiencies for MBNDC.

It is noteworthy that atrazine, diuron, isoproturon and simazine all received an estimated removal efficiency of less than 10% and that all the substances have an estimated biodegradation of less than 1%. Hence, sludge adsorption and stripping will be the dominating removal processes for these substances in WWTPs.

Conclusions

- There is awareness and focus on pollution in Denmark.
- Not all PSs are included in the national surveillance programme.
- Data from the national surveillance programme are not easily. No study specifically targeting the WFD PS was found.
- Only few studies include several fractions (e.g. inlet, outlet and sludge) thus the removal from the water phase can indicate both adsorption to sludge and biodegradation.
- No study focussing on PS flow through a WWTP in order to determine which processes that are most efficient to remove PS using background concentrations was found.
- Modelling can be used to estimate removal efficiencies in MBNDC.

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Appendix B



ScorePP is a Specific Targeted Research Project (STREP) funded by the European Commission under the Sixth Framework Programme

Source Control Options for Reducing Emissions of Priority Pollutants (ScorePP)



Report on parameters measured in Slovenian municipal wastewater treatment plant Domžale-Kamnik

Covering legislation: Slovenian national law Ur.l. 35/96 (valid until 2005) and Ur.l. 47/05 (valid since 2005). The national law on emissions from wastewater treatment plants is following E-PRTR (European Pollutant Release and Transfer Register). By that law, only the municipal wastewater treatment plants with capacity > 100.000 PE are required to regularly perform measurements on the following pollutants: metals (Al, As, Cu, Ba, B, Zn, Cd, Co, Sn, Cr and Cr⁶⁺, Ni, Ag, Pb, Fe and Hg), BTEX, AOX, VCHC, tenzides, phenols, polar organic solvents.

In the attached report the concentrations of PPs are given, which were measured during a 6-year period of sampling in a municipal wastewater treatment plant with >100.000 PE. Most of the parameters are reported as “lower than ... concentration”, which was typically well below the maximum concentrations allowed by the Regulation. Though, in three cases the measured parameters exceeded the max allowed concentrations:

- Hg in influent and effluent, both sampled by time-proportional procedure. 88% removal of Hg was shown for the specific wastewater treatment; however, that was due to the especially high conc. of Hg in the influent (139µg/L) not sufficient to satisfactorily remove the compound.
- Ni in influent of one sample, whereas the compound was sufficiently removed by the treatment.

SAMPLING and ANALYSES

Type of emissions: routine releases

Sampling: from 2000 to 2006, 1-3 times per year, randomly

Determined PP (included in “ScorePP list of priority chemicals”):

- Metals: Cadmium, Mercury, Nickel, Lead

- Benzene (expressed as BTEX: volatile aromatic hydrocarbons)
- Tributyltin compounds (expressed as Sn)
- AOX (adsorbable organic halogens) = the amount of organic halogenated compounds, adsorbable on activated carbon, determined as chloride
- Trichloroethylene and methylenechloride (expressed as VCHC: volatile chlorinated hydrocarbons)

Priority pollutants concentrations in a Slovenian influent waste water treatment plant

date of sampling	15.5.2000	12.6.2001	2.10.2001	5.11.2001	2.7.2002	15.10.2002	16.6.2003
time of sampling	7am	not given	not given	not given	8am	8am	8am
sampling: type	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)
sample name	2000	2001-A	2001-B	2001-C	2002-A	2002-B	2003
Cd (mg/L)	0,005	0,0004	0,002	0,002	0,002	0,002	0,002
Ni (mg/L)	0,012	0,1482	0,0970	0,1340	0,08	0,03	0,04
Pb (mg/L)	0,016	0,0419	0,02	0,0260	0,02	0,02	0,02
Hg (µg/L)	1	0,8700	2,1100	0,4850	0,36	0,58	0,02
BTEX (mg/L)	0,05	0,2	0,05	0,03	0,03	0,03	0,03
Sn (mg/L)	0,350	0,05	0,5	0,1	0,1	0,1	0,01
AOX (mg/L)	0,2	0,3	0,1	0,3	0,2	0,2	0,16
VCHC (mg/L)	0,0	0,02	0,02	0,02	0,02	0,02	0,02

	8.6.2004	21.9.2004	1.6.2005	27.9.2005	13.6.2006	national regulation*: maximum allowed value
date of sampling	8.6.2004	21.9.2004	1.6.2005	27.9.2005	13.6.2006	
time of sampling	8.15am	8am	8am	8am	8am	
sampling: type	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	
sample name	2004-A	2004-B	2005-A	2005-B	2006	
Cd (mg/L)	0,02	0,002	0,05	0,005	0,005	0,1
Ni (mg/L)	0,046	0,0373	0,08	1,80	0,05	0,5
Pb (mg/L)	0,02	0,02	0,02	0,05	0,05	0,5
Hg (µg/L)	139	0,344	0,12	0,03	0,001	10,0
BTEX (mg/L)	0,05	0,05	0,03	0,03	0,03	1,0
Sn (mg/L)	0,1	0,1	0,1	0,1	0,02	2,0
AOX (mg/L)	0,05	0,04	0,1	0,1	0,1	0,5
VCHC (mg/L)	0,02	0,02	0,02	0,020	0,02	0,1

blue fields: conc. is less than ... (< xy mg/L)

red fields: higher than max allowed value

Priority pollutants concentrations in a Slovenian effluent waste water treatment plant

date of sampling	15.5.2000	12.6.2001	2.10.2001	5.11.2001	2.7.2002	15.10.2002	16.6.2003
time of sampling	23pm	not given	not given	not given	23pm	23pm	23pm
sampling: type	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)
sample name	2000	2001-A	2001-B	2001-C	2002-A	2002-B	2003
Cd (mg/L)	0,005	0,002	0,002	0,002	0,002	0,002	-
Ni (mg/L)	0,019	0,0410	0,0690	0,03	0,09	0,05	0,03
Pb (mg/L)	0,008	0,02	0,02	0,02	0,02	0,02	0,02
Hg (µg/L)	0,062	0,3900	0,1670	0,3520	0,02	0,05	0,06
BTEX (mg/L)	0,05	0,2	0,05	0,03	0,03	0,03	0,03
Sn (mg/L)	0,065	0,05	0,05	0,1	0,1	0,1	0,1
AOX (mg/L)	0,1	0,2	0,1	0,1	0,1	0,1	0,09
VCHC (mg/L)	0,01	0,02	0,02	0,02	0,02	0,02	0,02

	9.6.2004	21.9.2004	2.6.2005	28.9.2005	14.6.2006	national regulation*: maximum allowed value
date of sampling	9.6.2004	21.9.2004	2.6.2005	28.9.2005	14.6.2006	
time of sampling	5am	5am	5am	5am	5am	
sampling: type	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	time proportional (24hrs)	
sample name	2004-A	2004-B	2005-A	2005-B	2006	
Cd (mg/L)	0,02	0,002	0,05	0,005	0,005	0,1
Ni (mg/L)	0,03	0,03	0,03	0,33	0,05	0,5
Pb (mg/L)	0,02	0,02	0,02	0,05	0,05	0,5
Hg (µg/L)	16,8	0,033	0,03	0,02	0,001	10,0
BTEX (mg/L)	0,05	0,05	0,03	0,03	0,03	0,1
Sn (mg/L)	0,1	0,1	0,1	0,1	0,02	2,0
AOX (mg/L)	0,05	0,06	0,03	0,02	0,07	0,5
VCHC (mg/L)	0,02	0,02	0,02	0,020	0,02	0,1

blue fields: conc. is less than ... (< xy mg/L)

red fields: higher than max allowed value