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Summary

Treatment of municipal wastewater produces large quantities of sludge that represents a cost for the individual wastewater treatment plant. Proper sludge treatment enables reuse of sludge, possibly as fertilizers. Fertilizer application of sludge is desirable since it improves the organic material reconstitution of the soil and implies recycling of nutrients. Negative aspects of sludge reuse are accumulation of persistent organic pollutants (POPs) in the sludge, and fertilizers based on sludge can therefore be a source of pollution. At present, there are only regulations regarding heavy metals (HMs) for sludge reuse in Norway, however, more stringent requirements is inevitable as the European Union is currently working on a document on sludge and sludge utilization where maximum levels of other pollutants in fertilizers, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), will be determined.

In this thesis, fate of POPs during the processes leading to bio pellets production at the municipal wastewater treatment plant *Sentralrenseanlegg Nord-Jæren* (SNJ) was examined. Fate of POPs and HMs in anaerobic digesters was determined based on modeling of PAH's partitioning between sludge particles and water phase using the software AQUASIM. An experiment was conducted to evaluate the distribution of POPs and HMs in the processes of centrifugation and drying. Analyses of samples of spiked sludge, dewatered sludge, reject water, and dried sludge were done externally by Eurofins.

Modeling of partitioning of PAHs between sludge and surrounding aqueous phase showed an approximate setting of equilibrium within the first 10 hours after which almost all of the PAHs were found sorbed to the sludge. Experimental work showed that during the processes of dewatering THC (total hydrocarbon), PAH, PCB, and HM were all tightly bound to sludge whereas BTEX (benzene, toluene, ethylbenzene, and xylene) was found to follow the reject water. During drying almost all remaining BTEX evaporated whereas THC, PAH, PCB, and HM were found in elevated quantities in the dried sludge, i.e. bio pellets.

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Abbreviation list

Acen	Acenaphthene
Acenyl	Acenaphthylene
Anth	Anthracene
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BghiP	Benzo(g,h,i)perylene
BTEX	Benzene, toluene, ethylbenzene, and xylenes
Chry	Chrysene
DBahA	Dibenzo(a,h)anthracene
DCM	Dissolved/colloidal matter
EPA	US Environmental Protection Agency
Fluanth	Fluoranthene
Fluo	Fluorene
HM	Heavy metal
I123cdP	Indeno(1,2,3-cd)pyrene
K _{oc}	Organic carbon partitioning coefficient
K _{ow}	Octanol-water partitioning coefficient
Naph	Naphthalene
NPE	Nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
Phen	Phenanthrene
POP	Persistent organic pollutant
Pyr	Pyrene
rpm	Rotations per minute
SNJ	Sentralrenseanlegg Nord-Jæren
SS	Suspended solids
TS	Total solids
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

1. Introduction

Wastewater treatment processes lead to production of sludge. Stabilization of the sludge by anaerobic treatment results in reduced amount of sludge in addition to energy production in the form of methane gas. The stabilized sludge can be used as basis for fertilizers production. Utilization of sludge is desirable since it improves the organic material reconstitution of the soil and has a positive effect on recycling of nutrients [1]. The downside to this usage is that persistent organic pollutants (POPs) tend to accumulate, and fertilizers based on sludge can therefore be a source of pollution [2]. The quality of the fertilizer needs to meet certain criteria put forward by the country's legislation. Until today's date, the only compounds underlying restriction of distribution through fertilizers in Norway are the following heavy metals (HMs): cadmium, lead, mercury, nickel, zinc, copper, and chromium. With regard to the future and the ever evolving knowledge around "old" and "new" pollutants new criteria for fertilizers produced from industrial processes will most likely be put forward. As an example, the European Union (EU) is preparing a document on sludge and sludge utilization whereby maximum levels of other pollutants in fertilizers, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) will be determined [3].

The purpose of this study was to predict fate of POPs and HMs during anaerobic digestion, centrifugation, and drying at *Sentralreanlegg Nord-Jæren* (SNJ), a municipal wastewater treatment plant in Stavanger, Norway. Fate of POPs and HMs in anaerobic digesters was determined based on modeling of PAH's partitioning between sludge particles and water phase using the software AQUASIM. In addition, an experiment was conducted to predict the distribution of POPs and HMs during centrifugation and drying.

2. Background

If treated properly sludge can be used as soil conditioners. However, presence of POPs or other pollutants can render the sludge unsuitable for usage on farmlands or other green areas. Anaerobic treatment can be one way of stabilizing the sludge, whereas processes such as volatilization and sorption determine the extent of POPs in the produced fertilizers.

2.1 Anaerobic digestion

Treatment by anaerobic digestion holds some distinct advantages over aerobic treatment, where lower biomass yield and production of energy in the form of methane are among the most significant. Anaerobic digestion is also used for stabilizing sludge obtained in treatment processes of wastewater, and it is this utilization of anaerobic treatment that will be emphasized here. The process is similar for both wastewater treatment and sludge stabilization, but the wanted end products, clean water and stabilized sludge, are different respectively [4].

Anaerobic digestion consists of a complex system of microorganisms completing different processes utilizing various compounds as their substrates. The end product of one process is the substrate for another, and the inhibition of only one of the processes can lead to failure of the entire system. The figure below (figure 2.1) shows the intricate relationship between the different processes executed by various microorganisms. As can be seen from the figure 2.1, methane is the end product of the anaerobic digestion, and as long as the process functions optimally it is energy yielding. This is may be the single most important advantage of anaerobic stabilization of sludge.

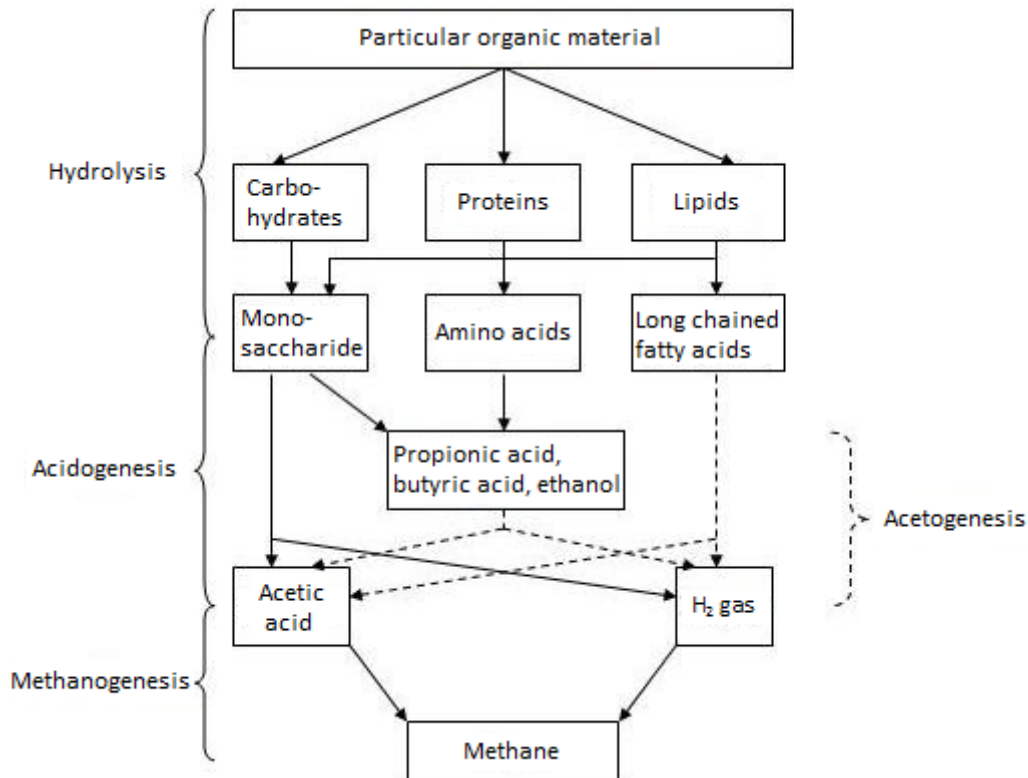


Figure 2.1: The main reactions during anaerobic digestion .The acetogenesis is indicated by the dashed lines [5].

Anaerobic digestion is a process working best under mesophilic or thermophilic conditions at temperatures of 30-38 °C or 50-57 °C, respectively. In order to obtain such temperatures, heating is necessary and is regarded as an extra cost for the operation and hence a disadvantage to anaerobic treatment. Although heating consumes energy, the amount of energy produced during anaerobic digestion is usually more than enough for the heating of the reactor, and a net production of energy is the result in most cases [4].

During wastewater treatment sludge is produced, and if not further treated this sludge represents a cost for the treatment plant due to need of processing and disposal of it. By treating the sludge anaerobically the total mass of the sludge is greatly reduced and costs related to disposal of this are therefore also lowered. With further treatment of the anaerobically stabilized sludge production of soil conditioners is a possibility.

2.2 Sludge as soil conditioner

In Europe, increasing amount of wastewater sludge produced and its environmental impact have made the traditional alternatives for sludge disposal, e.g. landfills and incineration, less viable than earlier. An alternative to these options of disposal is the use of sludge as soil conditioner in agriculture [6]. In Norway (2005) approximately 50 % of sewage sludge is used as soil improving components in agriculture. Other application areas are as cover material, in forestry, and as fertilizer and soil conditioner in parks [7].

In 2003 a new law concerning the applications of sludge in Norway came into force [8]. It comprises all fertilizers and soil conditioners and includes requirements for seven HMs. In addition to specify requirements for HMs distribution, it includes maximum volumes allowed to use of different quality classes and also what type of area they can be spread onto [7]. Table 2.1 shows the HMs underlying restrictions for distribution through soil conditioners.

Table 2.1: HMs included in regulations of soil conditioners. Classes (0, I, II, and III) indicates the quality of the soil conditioner, with class 0 being the best and class III the worst. If concentrations of any of the HMs exceed those in class III, the soil conditioner cannot be distributed [8].

Quality classes:	0	I	II	III
	mg/kg TS			
Cadmium (Cd)	0.4	0.8	2	5
Chromium (Cr)	50	60	100	150
Copper (Cu)	50	150	650	1 000
Lead (Pb)	40	60	80	200
Mercury (Hg)	0.2	0.6	3	5
Nickel (Ni)	20	30	50	80
Zink (Zn)	150	400	800	1 500

In addition HMs requirements, the law states that: *“The one producing or trading the product according to this regulation shall demonstrate caution and take reasonable measures to restrict and prevent that the product contains organic environmental pollutants, pesticides, antibiotics/chemotherapeutics, or other organic xenobiotic compounds in quantities that may cause harm to health or the environment when used”* [8]. The regulation

also requires that the product must be stabilized so that it does not cause odor nuisance or other environmentally related problems when stored or used. Anaerobic digestion is, as previously stated, a stabilization method that can be applied to sludge [7].

A working document on sludge and application of sludge as soil conditioner has been made by EU [3]. In this document limit values of heavy metals and organic compounds and dioxins have been proposed, and the following two tables (table 2.2 and 2.3) give an overview of the proposed values.

Table 2.2: Limit values for HMs in sludge and the already established maximum concentration allowed in sludge for use on land (Directive 86/278/EEC) [3].

Heavy metal	Proposed limit value (mg/kg TS)	Established limit value (mg/kg TS) (Directive 86/278/EEC)
Cadmium (Cd)	10	20 – 40
Chromium (Cr)	1 000	-
Copper (Cu)	1 000	1 000 – 1 750
Lead (Pb)	750	750 – 1 200
Mercury (Hg)	10	16 – 25
Nickel (Ni)	300	300 – 400
Zinc (Zn)	2 500	2 500 – 4 000

Table 2.3: Proposed limits for organic compounds and dioxins in sludge for use on land [3].

Organic compound	Proposed limit value (mg/kg TS)
AOX ¹	500
LAS ²	2 600
DEHP	100
NPE	50
PAH ³	6
PCB ⁴	0.8
Dioxins	Proposed limit values (ng TE/kg TS)
PCDD/F ⁵	100

- 1) Sum of halogenated organic compounds
- 2) Linear alkylbenzene sulphonates
- 3) Sum of following PAHs: Acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b,j,k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene
- 4) Sum of PCBs with following components number: 28, 52, 101, 118, 138, 153, 180.
- 5) Polychlorinated dibenzodioxins/dibenzofuranes

When comparing maximum concentrations for HMs in sludge proposed in the working document on sludge with the limit concentrations in quality class III given by the Norwegian law it becomes clear that Norwegian regulations for distribution of sludge are stricter than those proposed by EU. On the other hand, Norwegian laws do not contain specific regulations for other compounds than HMs, and are in that way less strict than regulations proposed by EU.

The production of energy along with the production of fertilizers from wastewater sludge is of importance for the future, with a growing demand for both energy and land. If not used for fertilizers the sludge will most likely end up as landfill, taking up space and also being a potential environmental risk to the site and the surrounding environment. As long as possible, anaerobic stabilization of sludge, and further production of fertilizers should be preferred over disposal.

2.3 Pollutants in wastewater

The term pollutant can be defined in many different ways. Although the variations between the definitions are often insignificant, two slightly different definitions will be given here. One is found in Walker (2006) and states that pollutants are: *“... chemicals that exist at levels judged to be above those that would normally occur in any particular component of the environment”* [9]. A different definition of the term pollutant is given in Kiely (1997), which includes an anthropogenic origin: *“A substance that occurs in the environment, at least in part, as a result of human activities, and which has a deleterious effect on the environment”* [10]. Wastewaters from urban areas often include pollutants such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, heavy metals, hydrocarbons and volatile hydrocarbons, surfactants, endocrine disrupters, and plastic softeners [11]. Some of these pollutants are unwanted because of their high resistance to biodegradation [9].

2.3.1 BTEX

The acronym BTEX stands for benzene, toluene, ethylbenzene, and xylenes. They are all aromatic hydrocarbons differing from each other by dissimilar side groups, or the lack thereof. Benzene is only an aromatic ring without any side groups and hence the simplest of them all. Toluene has a methyl side group whereas ethylbenzene has an ethyl side group. The xylenes consist of an aromatic ring with two methyl side groups, which yield a total of three isomers of xylene, *o*-xylene, *m*-xylene, and *p*-xylene [12]. The following table gives some properties for BTEX.

Table 2.4: Properties for benzene, toluene, ethylbenzene, and xylene isomers [13].

Compound	Molecular weight (g/mol)	Solubility (mg/l)	Vapor pressure (Pa)	log K _{ow}	log K _{oc}
Benzene	78.12	1.78×10^2 (25 °C)	12.3×10^3 (25 °C)	2.12	1.92
Toluene	92.15	5.15×10^2	2.9×10^3	2.73	2.48
Ethylbenzene	106.18	1.52×10^2	0.93×10^3	3.15	0.04
<i>m</i> -Xylene	106.18	1.75×10^2	1.3×10^3	2.95	-
<i>o</i> -Xylene	106.18	1.30×10^2	1.3×10^3	3.26	-
<i>p</i> -Xylene	106.18	1.98×10^2	1.3×10^3	3.15	-

BTEX is found in gasoline where between 22 and 54 percent of the compounds are aromatic. Out of the BTEX compounds toluene tends to be the prevalent followed by the xylene isomers, whereas benzene and ethylbenzene are often found in the same quantities [14]. Among the compounds, benzene is classified as an 'A' carcinogen (human carcinogen) in the categories presented by US Environmental Protection Agency (EPA). The others are also toxins and all of them are considered environmental pollutants [12]. In addition to their toxic effects the BTEX compounds are more water soluble than other hydrocarbons present in gasoline. After a spill of gasoline it is important to remove these contaminants before they enter aquifers, especially if surrounding waters are used as drinking water supplies [14].

2.3.2 Hydrocarbons

Hydrocarbons are organic chemicals consisting of only hydrogen and carbon atoms. They can be present as gasses, liquids, or solids in room temperature depending on their molecular weight. Low molecular weight hydrocarbons have higher vapor pressures and higher

solubilities than the heavier hydrocarbons [9]. Thousands of different hydrocarbons exist and the main sources to anthropogenic hydrocarbon contamination are from the processing of crude oil, transport and traffic, distribution of natural gas, and organic chemical production [10]. Natural hydrocarbon contamination is mostly due to seeps from petroleum reservoirs, and annual input of crude oil from natural leakages into the sea has been estimated to about 7×10^8 liters, which accounts for approximately 45 % of the total input [12].

2.3.3 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants that result from incomplete combustion of organic material and come from both natural incidents, such as eruptions from volcanoes, and human activities (such as combustion of coal) [14]. Two or more aromatic rings fused together at two carbon sites makes up a PAH, and the number of rings give an indication of some of the properties the PAH possesses. When increasing the number of aromatic rings the water solubility generally decreases, and the heavier PAHs tend to have a great affinity for the organic compartments of the environment. With increasing number of rings an increase in persistence follows, which could be either a result of decreasing bioavailability or decreasing biodegradation potential [13]. Some of the PAHs are known carcinogens and these should not be distributed in the environment [9].

PAHs are often used as model compounds in biodegradation studies [6, 15, 16] because of their high hydrophobicity and stable structures. This is the case in this thesis as well as where PAHs have been used to model partitioning of highly hydrophobic compounds between the different phases in an anaerobic digestion reactor. Table 2.2 below gives an overview over some parameters for different PAHs and how they vary with molecular weight.

Table 2.5: List of PAHs (EPA 16) and appurtenant parameters organized according to increasing molecular weight [11].

Compound	Molecular weight (g/mol)	Solubility (mg/l)	Vapor pressure (Pa)	log K _{OW}	log K _{OC}
Naphthalene	128	31	10.9	3.37	3.08
Acenaphthylene	152	3.42	0.6	4.07	3.4
Acenaphthene	154	4.24	0.6	3.98	3.66
Fluorene	166	1.98	0.09	4.18	3.86
Phenanthrene	178	1.1	0.02	4.46	4.15
Anthracene	178	0.05	0.0002	4.54	4.15
Fluoranthene	202	0.26	0.25	4.9	4.58
Pyrene	202	0.13	0.0009	5.18	4.58
Benzo(a)anthracene	228	0.011	0.000007	5.66	5.3
Chrysene	228	0.002	0.0000006	5.86	5.3
Benzo(b,j,k)fluoranthene	252	0.001	0.00001	6.1	-
Benzo(a)pyrene	252	0.0038	0.0000008	6.04	5.74
Indeno(123-cd)pyrene	276	0.0002	<0.000000000	7.66	7.18
Dibenzo(a,h)anthracene	278	0.0005	<0.000000001	6.86	6.52
Benzo(ghi)perylene	278	0.00026	0.00000006	7.1	6.5

As can be seen from the table above, increasing molecular weight leads to increasing octanol-water partitioning coefficient and increasing organic carbon partitioning coefficient, but to decreasing water solubility. Given the overall low water solubilities of the PAHs they are mostly considered soil contaminants in the environment, although naphthalene is frequently found as a groundwater polluter [13].

2.3.4 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a group of related compounds that all consist of biphenyl as the structures backbone and a different number of chlorine atoms attached to any of the carbons [13]. As a total, 209 different PCB congeners are possible with about 120 of them being used in commercial products, such as different Aroclor mixtures [9].

PCBs were first introduced to the industry in the 1930s and their use became more prevalent through the 1950s until they were banned from use in 1976. Up till that point, PCBs were used in hydraulic fluids and pump oils, as coolant-insulation fluids in transformers, and as plasticizers in paint. The reason for the prohibition of PCBs came with the knowledge of the

group's almost complete resistance to both chemical and biological attack. Although biological degradation of PCBs is possible given the right conditions and microorganisms, they are said to be non-biodegradable. In addition to being non-biodegradable, PCBs are lipophilic, and the combination results in PCBs being subject to bioaccumulation and biomagnification [14]. Table 2.6 gives some properties of PCBs.

Table 2.6: Properties for different PCBs [13].

Compound	Molecular weight (g/mol)	Solubility (mg/l)	Vapor pressure (Pa)	log K _{ow}	log K _{oc}
PCB 28	258	0.03	0.04	5.67	4.98
PCB 52	293	0.003	0.02	5.84	5.1
PCB 101	327	0.004	0.002	6.23	5.78
PCB 118	327	0.002	0.001	6.74	5.99
PCB 138	361	-	0.0007	6.83	6.2
PCB 153	361	0.03	0.0007	6.92	6.19
PCB 180	395	0.0013	0.0001	7.36	6.37

2.3.5 Heavy metals

Heavy metals (HMs) are inorganic pollutants that consist of those metals which have a density higher than 5 g/cm³ [12]. They originate from both natural and anthropogenic sources where direct processes resulting in anthropogenic HM contamination are mining, smelting, and refining processes [10]. Table 2.7 shows some properties for HMs.

Table 2.7: Properties for eight HMs [13].

Compound	Molecular weight (g/mol)	Solubility (mg/l)	Vapor pressure (Pa)	log K _{ow}	log K _{oc}
Arsenic	74.92	-	0.13 × 10 ³ (372 °C)	-	-
Lead	207.19	-	1.3 × 10 ³ (1160 °C)	-	-
Copper	63.55	-	1.3 × 10 ³ (1628 °C)	-	-
Chromium	52	-	1.3 × 10 ³ (1840 °C)	-	-
Nickel	58.71	-	0.13 × 10 ³ (1810 °C)	-	-
Zinc	65.37	-	0.00	-	-
Cadmium	112.4	-	0.13 × 10 ³ (394 °C)	-	-
Mercury	200.59	-	0.27 (25 °C)	-	-

Some of the HMs have biological functions, e.g., copper, zinc, and cobalt, and are only toxic when they exceed normal concentrations. Other HMs, such as lead, mercury, and arsenic,

are merely toxins no matter the concentration [12]. HMs are non-biodegradable but can be transferred to less toxic oxidation states by various microorganisms. This does not remove them from the environment and as long as they are present they will exert a toxic risk upon the environment. Some plants bioaccumulate HMs, and thus remove them from the soil, which is a promising area of remediation called phytoremediation [12].

2.3.6 Other pollutants

In addition to aforementioned compounds other pollutants exist in wastewater. Endocrine disruptors, such as bisphenol A, surfactants (e.g., nonylphenol, nonylphenol-monoethoxylates, and nonylphenol-diethoxylates), and plastic softeners, such as di(2-ethylhexyl)phthalate, are present in Norwegian wastewaters [11].

Endocrine disruptors, e.g., bisphenol A, are compounds that imitate naturally occurring hormones [13]. They are exogenous substances that have a disruptive and negative effect on the hormonal control system in organisms. By binding to the hormone receptor an endocrine disruptor can induce the hormonal processes by stimulating the transcription activity. However, if binding strongly to the receptor it can block the effects of endogenous hormones, thus reducing the hormonal processes [9]. Based upon their endpoints, three different classes of endocrine disruptors are known. The first class constitutes estrogenic chemicals that mimic or block natural estrogens. The second class consists of compounds having androgenic activities which mimic or block natural testosterone. The third class is made up of those substances that directly or indirectly cause effects to the thyroidal gland, named thyroidal compounds [9, 17]. The monomer bisphenol A belong to the first class and is widely used in the industry (estimated production volume in U.S. in 2007 was 2.4 billion pounds). It is used in the manufacturing of polycarbonate plastics, epoxy resins, and also as flame retardants. In addition to food-related uses, materials containing bisphenol A are used in transportation equipment, optical media, electrical equipment, construction, linings inside drinking water pipes, and elsewhere [18].

Nonylphenol, nonylphenol monoethoxylates, and nonylphenol diethoxylates (NPE) are pollutants found in wastewater and are degradation products of non-ionic alkylphenol polyethoxylate surfactants [11, 19]. NPE can often be found in relatively big quantities, because the parent surfactants are commonly used in detergents due to their rapid biodegradability. Nonylphenol, though, will degrade slowly under anaerobic conditions which will lead to increased concentrations in the digested sludge [19].

Di(2-ethylhexyl)phthalate (DEHP) is a compound affiliated the group phthalic acid esters (PAE) which are chemicals of industrial usage. The main application of these compounds is as additives to different industrially produced materials including polyvinylchloride, polyvinylacetate, and cellulosic and polyurethane resins. Characteristic features common for all PAEs are low water solubility and high octanol-water partitioning coefficients. Because of these features, PAEs tend to end up in the sludge and the concentrations can be several orders of magnitude higher than in the influent. If the sludge is used for soil improvement its content of PAEs should be noticed. Not all PAEs are easily degraded and some are even harmful to the environment. One good example of this is DEHP which is one of the most recalcitrant PAEs. In addition, DEHP has been found to have carcinogenic, mutagenic, and xeno-estrogenic effects [20].

2.4 Partitioning and its importance for removal of pollutants

When present in an environment consisting of more than one phase a compound can partition between the different phases depending on its properties. Examples of processes leading to partitioning are sorption, volatilization, and precipitation, all of which will be described more in detail later.

Digesters in wastewater treatment processes contain sludge and an overlying gas phase making up two distinct compartments or phases. In addition, sludge can be divided into three different compartments; an aqueous phase, a dissolved/colloidal matter (DCM) phase, and a solid phase (particles). This system was proposed by Delgadillo-Mirquez et al. (2011) and implies that POPs (or other chemicals) can partition between four phases within a sludge digester. The POP subject to partitioning can be found either in the gas phase (c_g), as freely dissolved in the aqueous phase (c_f), as sorbed to DCM (c_{DCM}), or as sorbed to particles (c_p) depending on its properties. Figure 2.2 depicts the four compartments and the equilibrium coefficients belonging to the different partitioning processes [21].

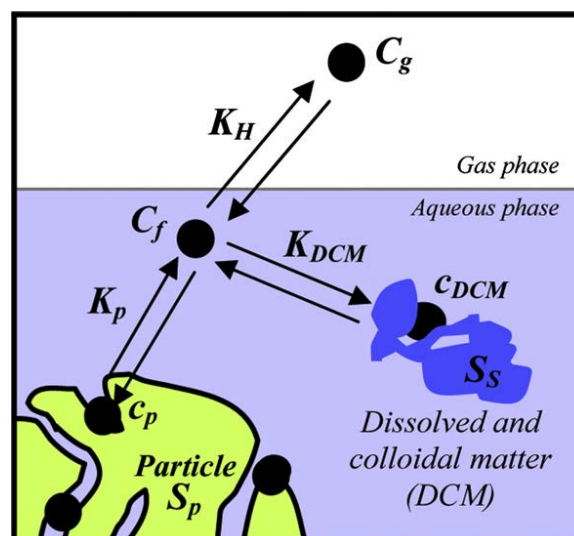


Figure 2.2: Depiction of the four different compartments and equilibrium constants for the partitioning processes. K_H is Henry's dimensionless coefficient for equilibrium between gas and water phase, K_{DCM} is the equilibrium constant for sorption to DCM, S_s is the concentration of soluble substrate (dissolved and colloidal concentration), K_p is the equilibrium constant for sorption to particles, and S_p is the concentration of particulate substrate (particulate concentration) [21].

When all compartments in a system are described the necessary partitioning coefficients can be determined. Only then can equilibrium concentrations of chemicals in the different compartments be predicted. The state of the POP is of great importance, because it determines whether or not it can be subject to biodegradation [21]. Although partitioning is of huge importance regarding bioavailability, it is not to any great extent responsible for removal of POPs. Elimination of POPs is mainly due to biodegradation [22].

2.4.1 Biodegradation and bioavailability

Biodegradation is the conversion of a compound due to biological activity and is one of the most common ways for compounds to be removed from a system. Compounds are defined as either biodegradable or non-biodegradable depending on how easily they are degraded by organisms. Even though a substance is said to be biodegradable certain circumstances might render it persistent. Maybe the most important reason for a compound's resistance to biodegradation is its availability. Partitioning is of huge importance, because it can render a biodegradable substance not bioavailable, meaning that the substance is not available for microorganisms to utilize [23]. POPs are compounds that should be removed from wastewater and sludge, but are in many cases found to be rather resistant to biodegradation. Because of high hydrophobicity of many POPs, they are mostly found in connection with organic fractions, either organic particles or DCM. In general, POPs are assumed to be bioavailable when present in the aqueous phase and not bioavailable when sorbed to particles. This implies that also POPs sorbed to DCM are not bioavailable [22]. A good example of how partitioning can influence bioavailability is the experiments conducted by Chang et al. (2003). Degradation rates for five PAHs were determined for two different concentrations of suspended solids (SS); 5 mg/l and 10 mg/l. The SS concentration of 10 mg/l resulted in lower degradation rates than that of 5 mg/l. Since PAHs are generally hydrophobic and tend to associate with solid fractions of wastewater, these findings indicate that elevated SS concentrations leads to PAHs being less bioavailable due to sorption [16].

2.5 Sorption – absorption and adsorption

Sorption is an appellation for the two processes absorption and adsorption. The processes are alike in the way that both retain solutes (originally in solution) in the solid phase. The difference is that while absorption refers to the incorporation of solute into the solid compartment, adsorption refers to solute adhering to the surface of the solid compartment [23]. Despite the differences, the literature very often refers to the processes only as sorption where the compound being sorbed is referred to as the sorbate and the substance it sorbs into/onto is called the sorbent [13].

A sorbate's affinity for the sorbent is one of the driving forces behind sorption and electrical attraction, Van der Waal forces, covalent bonds, and hydrogen bonds are all examples of such forces. Also, a sorbate with low solubility will most likely induce sorption [13].

Municipal wastewater contains organic solids that are a major constituent of the sludge produced during the treatment process. The tendency of a compound to sorb to the sludge fraction is largely determined by the hydrophobicity of the compound. Hydrophobicity can be indicated by different parameters such as K_{OW} and K_{OC} . Removal of organic toxic compounds from the liquid phase of wastewater is often controlled by sorption. This leads to concentration of such compounds being many orders of magnitude greater in the sludge than in the inlet wastewater [24].

2.5.1 K_{OW} and K_{OC}

Two parameters indicating a compound's tendency to associate with organic compartments are the octanol-water partitioning coefficient (K_{OW}) and the organic carbon partitioning coefficient (K_{OC}). The former is much used in ecotoxicology studies and is used to indicate a compound's affinity for an organic phase. In addition, it has been correlated with toxicity and is widely used for predicting the fate of a pollutant in the environment [12].

In a two-phase system consisting of octanol and water the K_{OW} is defined as the ratio between a compounds concentration in the octanol phase to its concentration in the water phase at equilibrium. Equation 2-1 gives the ratio [13]:

$$K_{OW} = C_o / C_w \quad (2-1)$$

where C_o = concentration of compound in octanol phase (mg/l_o)

C_w = concentration of compound in aqueous phase (mg/l_w)

As can be seen from the above definition, K_{OW} is a dimensionless coefficient. A given ratio tells whether the compound is hydrophobic or not, and the higher the ratio the more hydrophobic the compound. In cases involving extremely hydrophobic substances the ratio becomes very high and a more suitable value to use is $\log K_{OW}$.

The coefficient K_{OC} is a key environmental fate parameter and is defined by a compounds concentration in the organic fraction of soil to its concentration in surrounding waters at equilibrium. The ratio is given in equation 2-2 [13]:

$$K_{OC} = C_{soil} / C_{water} \quad (2-2)$$

where C_{soil} = concentration of compound in the organic carbon component of soil (mg/kg_{OC})

C_{water} = concentration of compound in water (mg/l)

Since the coefficient is based on a chemicals concentration in connection with the organic fraction of the solid compartment, it can also be used for solid material other than soil (e.g., sludge). This coefficient is not dimensionless, and from the information above it is clear that the dimension for K_{OC} is l/kg_{OC} (volume of chemical per mass of organic carbon in the solid) [25].

Another coefficient worth mentioning is the distribution coefficient, K_D . It is the ratio of a compounds sorbed concentration to its dissolved concentration in the surrounding water at equilibrium. The coefficient can be connected to K_{OC} and the following two equations give the definition of K_D (equation 2-3) and the correlation between K_D and K_{OC} (equation 2-4).

$$K_D = C_{\text{sorbed}} / C_{\text{dissolved}} \quad (2-3)$$

where K_D = distribution coefficient between solid compartment and water (l/kg)

C_{sorbed} = concentration of sorbed compound (mg/kg)

$C_{\text{dissolved}}$ = concentration of dissolved compound (mg/l)

$$K_D = f_{OC} K_{OC} \quad (2-4)$$

where f_{OC} = fraction of organic carbon in solid compartment ($\text{kg}_{OC}/\text{kg}_{\text{solid}}$)

Literature normally does not report values for K_D but extended lists for K_{OW} and K_{OC} values exist. Due to K_{OW} values being more common than K_{OC} values, correlation between these two has been subjected to many studies and a wide variety of equations have been suggested. The general equation for deriving K_{OC} from K_{OW} is as follows [25]:

$$\log K_{OC} = a \log K_{OW} + b \quad (2-5)$$

where a and b are constants estimated from empirical data

A concrete example of this correlation is given in Atlas and Philip (2005) and is shown in equation 2-6 [12].

$$K_{OC} = 6.3 \times 10^{-7} f_{OC} \times K_{OW} \quad (2-6)$$

In this equation f_{OC} has been incorporated as a part of the constant a while constant b is set to zero.

2.6 Volatilization

Volatilization is the escape of a compound from one compartment into the surrounding gas phase. Boiling, sublimation, and evaporation are all processes leading to volatilization of a compound. Of these, evaporation is the most interesting with regards to wastewater treatment processes, and will be the one representing volatilization here. Evaporation is the phase transfer of a compound from the liquid phase into the surrounding gas phase and is a diffusive transport process.

A driving force behind diffusive evaporation is setting of equilibrium between an aqueous phase and a gas phase. There is not necessarily a difference in chemical concentration between the two phases that leads to evaporation, but rather a difference in fugacity among the phases [26]. A compound's fugacity is its escaping tendency from the compartment where it currently exists [9]. Compounds are said to be volatile if they easily evaporate and are usually found on their gaseous form at room temperature.

Vapor pressure is the main driving force behind volatilization, but is not always a good way to indicate a compound's escaping tendency. A high vapor pressure normally refers to a great escaping tendency into the gaseous phase, while a low vapor pressure usually indicates a low escaping tendency. This all depends on the compounds solubility in the water phase. A compound with a low vapor pressure can still escape easily if the water solubility is low [12]. One constant taking this into account is the Henry's law constant (H). The constant is the ratio of a compounds equilibrium concentration in air to its equilibrium concentration in water. It is considered as the partitioning coefficient between gas and water phase as shown in figure 2.2. Henry's law constant can be expressed as:

$$H = P/S \quad (2-7)$$

where H = Henry's law constant (atm × m³/mol)

P = vapor pressure (atm)

S = water solubility (mol/m³)

A dimensionless version of Henry's constant can be derived from the equilibrium concentrations of the compound in the gas and water phases:

$$K_H = C_{aq} / C_{gas} \quad (2-8)$$

where K_H = Henry's dimensionless constant

C_{aq} = concentration in water phase (mol/l)

C_{gas} = concentration in gas phase (mol/l)

Other forms of Henry's constant with different dimensions are also available, which can be useful under other circumstances [12].

When a compound is lost from the system due to other ways than through biodegradation, the loss is said to be abiotic and some studies show that abiotic losses are mainly due to volatilization. In experiments conducted on anaerobic biodegradation of 13 PAHs Trably et al. (2003) found that the three lightest PAHs (fluorene, phenanthrene, and anthracene) were subject to abiotic losses. It was further shown that the highest percentage losses were found in the reactor operated under the highest temperature (55 °C) indicating that volatilization would be the main process behind the abiotic losses [27].

2.7 Precipitation

Precipitation is the crystallization or aggregation of compounds forming a solid phase within the aqueous compartment. Precipitation occurs in three steps: 1) nucleation, the formation of a fine particle on which precipitation can occur, 2) crystal growth, the adhering of precipitate components onto nuclei, and 3) agglomeration and ripening, the formation of more stable structures over time, usually with lower solubility than initial structures leading to additional precipitation and increasing size of the crystals [28].

HMs present in wastewater can be removed through precipitation. Hydroxide (OH^-) and sulfide (S^{2-}) are commonly used precipitants that form structures of low water solubility with HMs. The following table gives an overview of the solubility products for heavy metals in equilibrium with hydroxides and sulfides.

Table 2.8: Solubility products for free heavy metal ion concentrations in equilibrium with hydroxides and sulfides [4].

Heavy metal hydroxide/sulfide	Half reaction	pK_{sp}
Cadmium hydroxide	$\text{Cd}(\text{OH})_2 \leftrightarrow \text{Cd}^{2+} + 2\text{OH}^-$	13.93
Cadmium sulfide	$\text{CdS} \leftrightarrow \text{Cd}^{2+} + \text{S}^{2-}$	28
Chromium hydroxide	$\text{Cr}(\text{OH})_3 \leftrightarrow \text{Cr}^{3+} + 3\text{OH}^-$	30.2
Copper hydroxide	$\text{Cu}(\text{OH})_2 \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^-$	19.66
Copper sulfide	$\text{CuS} \leftrightarrow \text{Cu}^{2+} + \text{S}^{2-}$	35.2
Lead hydroxide	$\text{Pb}(\text{OH})_2 \leftrightarrow \text{Pb}^{2+} + 2\text{OH}^-$	14.93
Lead sulfide	$\text{PbS} \leftrightarrow \text{Pb}^{2+} + \text{S}^{2-}$	28.15
Mercury hydroxide	$\text{Hg}(\text{OH})_2 \leftrightarrow \text{Hg}^{2+} + 2\text{OH}^-$	23
Mercury sulfide	$\text{HgS} \leftrightarrow \text{Hg}^{2+} + \text{S}^{2-}$	52
Nickel hydroxide	$\text{Ni}(\text{OH})_2 \leftrightarrow \text{Ni}^{2+} + 2\text{OH}^-$	15
Nickel sulfide	$\text{NiS} \leftrightarrow \text{Ni}^{2+} + \text{S}^{2-}$	24
Silver hydroxide	$\text{AgOH} \leftrightarrow \text{Ag}^+ + \text{OH}^-$	14.93
Silver sulfide	$(\text{Ag})_2\text{S} \leftrightarrow 2\text{Ag}^+ + \text{S}^{2-}$	28.15
Zinc hydroxide	$\text{Zn}(\text{OH})_2 \leftrightarrow \text{Zn}^{2+} + 2\text{OH}^-$	16.7
Zinc sulfide	$\text{ZnS} \leftrightarrow \text{Zn}^{2+} + \text{S}^{2-}$	22.8

Although the table above indicates that HM hydroxides and sulfides have low water solubility, the solubility depends on pH. The following figure gives an illustration of this dependency for metal hydroxides [4].

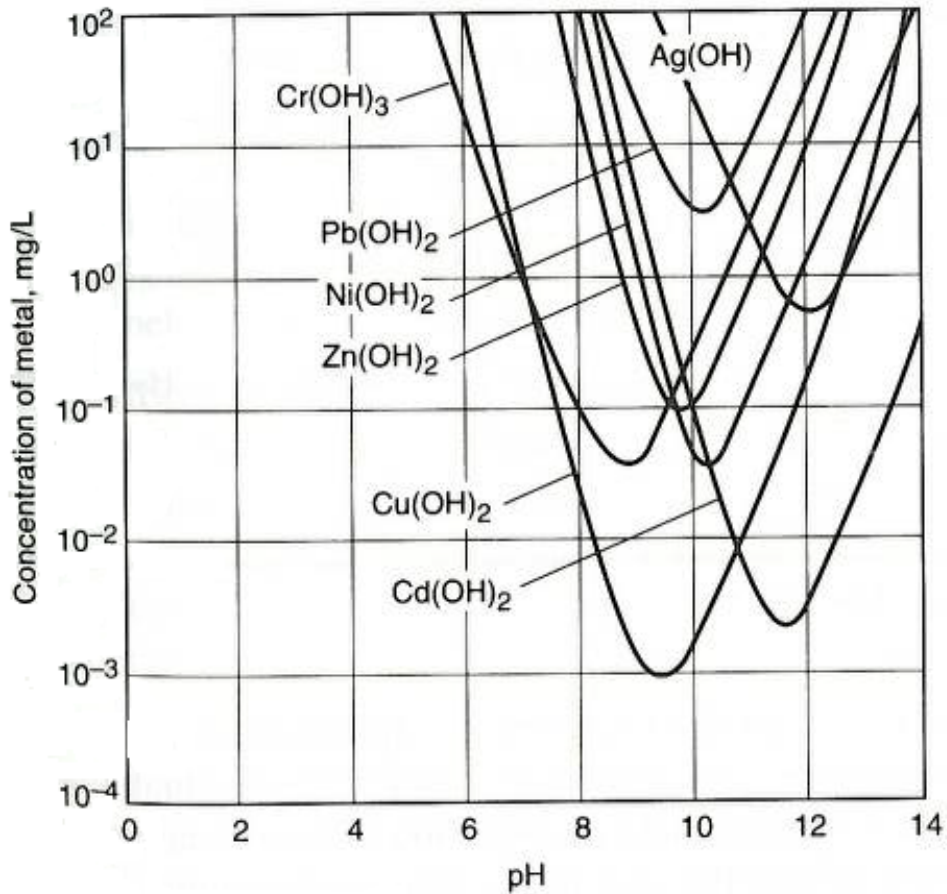
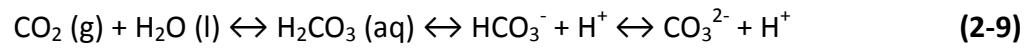


Figure 2.3: Illustration of dependency on pH for the solubility of HM hydroxides [4].

As can be seen from figure 2.3 all of the metal hydroxides have lowest solubilities at alkaline pH in the range 8-12. It should be noted that lowest solubility of such hydroxides varies depending on other constituents in the wastewater [4].

HMs can also precipitate with carbonate (CO_3^{2-}) and carbonate has in some special cases been used as precipitant [4]. Carbonate is almost always present in waters because of the bicarbonate system. The system is in equilibrium with atmospheric carbon dioxide and is defined as follows:



As seen from equation 2-9, so does concentration of carbonate depend on pH in the water and high pH will shift the equilibrium towards the right. This will lead to conditions where HMs can precipitate with carbonate [29].

3. Materials and Methods

3.1 AQUASIM

Modeling was done using the software AQUASIM 2.1 and methods used for simulation are described in Reichert (1998) [30]. Anaerobic Digestion Model No.1 (ADM1) was used as base for modeling of partitioning of PAHs, and the description of ADM1 can be found in Batstone et al. 2002 [31]. The additions made to this model are presented in the process matrix on the next side (table 3.1) and a detailed list of all parameters can be found in appendix. Initial concentrations of PAHs were based on those presented by Kommedal et al. 2008 [11] and The rate coefficients have been derived from the K_{OC} values based on the following:

$$C_f + X_p \leftrightarrow C_p \quad (3-1)$$

where C_f = concentration of compound on its freely dissolved form

X_p = concentration of organic matter the compound can sorb towards

C_p = concentration of compound sorbed to organic matter

Equation 3-1 is based on equilibrium conditions and the forward rate leading to sorption is named k_1 whereas the rate leading to desorption is called k_{-1} . The equilibrium coefficient is equal to the K_{OC} value for the compound in question which yields the following relation between the rates of sorption and desorption:

$$K_{OC} = k_1/k_{-1} \quad (3-2)$$

This results in the following:

$$\text{sorption} = C_f \times X_p \times k_1 \quad (3-3)$$

$$\text{desorption} = C_p \times k_{-1} \quad (3-4)$$

The overall rate for sorption becomes:

$$k_1 \times C_f \times X_p - \frac{k_{-1} \times C_p}{K_{OC}} \quad (3-5)$$

Table 3.1: Process matrix for the additional partitioning processes of different PAHs. k_{PAH} is the specific PAH's adsorption rate towards organic material, X_p is the concentration of particles with adsorptive capacity, and $K_{OC,PAH}$ is the organic carbon partitioning coefficient for the given PAH.

Components →		1	2	Rate	
Process ↓		C_p	C_f		
1	Sorption of acenaphthene	1	-1	$k_{Acen} \cdot C_{f,Acen} \cdot X_p - \frac{k_{Acen} \cdot C_{p,Acen}}{K_{OC,Acen} \cdot OC_{VSS}}$	mg/d·m ³
2	Sorption of acenaphthylene	1	-1	$k_{Acenyl} \cdot C_{f,Acenyl} \cdot X_p - \frac{k_{Acenyl} \cdot C_{p,Acenyl}}{K_{OC,Acenyl} \cdot OC_{VSS}}$	
3	sorption of anthracene	1	-1	$k_{Anth} \cdot C_{f,Anth} \cdot X_p - \frac{k_{Anth} \cdot C_{p,Anth}}{K_{OC,Anth} \cdot OC_{VSS}}$	
4	Sorption of benzo(a)anthracene	1	-1	$k_{BaA} \cdot C_{f,BaA} \cdot X_p - \frac{k_{BaA} \cdot C_{p,BaA}}{K_{OC,BaA} \cdot OC_{VSS}}$	
5	Sorption of benzo(a)pyrene	1	-1	$k_{BaP} \cdot C_{f,BaP} \cdot X_p - \frac{k_{BaP} \cdot C_{p,BaP}}{K_{OC,BaP} \cdot OC_{VSS}}$	
6	Sorption of benzo(ghi)perylene	1	-1	$k_{BghiP} \cdot C_{f,BghiP} \cdot X_p - \frac{k_{BghiP} \cdot C_{p,BghiP}}{K_{OC,BghiP} \cdot OC_{VSS}}$	
7	Sorption of chrysene	1	-1	$k_{Chry} \cdot C_{f,Chry} \cdot X_p - \frac{k_{Chry} \cdot C_{p,Chry}}{K_{OC,Chry} \cdot OC_{VSS}}$	
8	Sorption of dibenzo(a,h)anthracene	1	-1	$k_{DBaHA} \cdot C_{f,DBaHA} \cdot X_p - \frac{k_{DBaHA} \cdot C_{p,DBaHA}}{K_{OC,DBaHA} \cdot OC_{VSS}}$	
9	Sorption of fluoranthene	1	-1	$k_{Fluanth} \cdot C_{f,Fluanth} \cdot X_p - \frac{k_{Fluanth} \cdot C_{p,Fluanth}}{K_{OC,Fluanth} \cdot OC_{VSS}}$	
10	Sorption of fluorene	1	-1	$k_{Fluo} \cdot C_{f,Fluo} \cdot X_p - \frac{k_{Fluo} \cdot C_{p,Fluo}}{K_{OC,Fluo} \cdot OC_{VSS}}$	
11	Sorption of indeno(1,2,3-cd)pyrene	1	-1	$k_{I123cdP} \cdot C_{f,I123cdP} \cdot X_p - \frac{k_{I123cdP} \cdot C_{p,I123cdP}}{K_{OC,I123cdP} \cdot OC_{VSS}}$	
12	Sorption of naphthalene	1	-1	$k_{Naph} \cdot C_{f,Naph} \cdot X_p - \frac{k_{Naph} \cdot C_{p,Naph}}{K_{OC,Naph} \cdot OC_{VSS}}$	
13	Sorption of phenanthrene	1	-1	$k_{Phen} \cdot C_{f,Phen} \cdot X_p - \frac{k_{Phen} \cdot C_{p,Phen}}{K_{OC,Phen} \cdot OC_{VSS}}$	
14	Sorption of pyrene	1	-1	$k_{Pyr} \cdot C_{f,Pyr} \cdot X_p - \frac{k_{Pyr} \cdot C_{p,Pyr}}{K_{OC,Pyr} \cdot OC_{VSS}}$	
		Concentration of PAH sorbed to particles (mg/m ³)	Concentration of freely dissolved PAH (mg/m ³)		

3.2 Experiment

An experiment was conducted to predict the fate of five different classes of pollutants during the processes leading to production of bio pellets at SNJ. PAHs, PCBs, HMs, BTEX, and a mixture of diesel and crude oil were added to anaerobically digested sludge, mixed, centrifuged, and dried to simulate the processes the sludge undergoes.

Approximately 15 liters of secondary sludge was collected from the anaerobic digester at SNJ and transferred to a 20 liters glass flask. The sludge was magnetically stirred during the whole experiment. Two samples of approximately 1.5 liters total were collected for determination of background concentrations of the pollutants. Amount of each fraction of sludge used for the different processes are given in table 3.2. The rest of the sludge was spiked with environmental pollutants and amount of each compound added is given in table 3.3. After addition of pollutants the sludge was stirred for 7 hours. Almost 2.5 liters of spiked sludge was collected for centrifugation. Each centrifugation tube was filled with 30 ml spiked sludge and 6 ± 0.1 g polymer of 0.1 % TS. The mixture was centrifuged for 1 min at 4 125 rpm (equal to 1 140 G). Afterwards, the supernatant (reject water) was decanted off and 5 ml of tap water was added to the dewatered sludge to make it easier to collect from the tube. A second round of centrifugation was conducted to get dewatered sludge for drying. The dewatered sludge (0.904 kg) was distributed between four porcelain bowls and dried in a heating cabinet at 105 °C until it contained about 95 % TS. More sludge was centrifuged and approximately 900 g of dewatered sludge was distributed between four porcelain bowls and dried in a heating cabinet at 95 °C for 3 hours before the temperature was raised to 105 °C for 4.5 hours. The dried sludge contained approximately 95 % TS. Prior to analyses the dried sludge was dissolved in 1 l tap water.

All analyses were conducted by Eurofins Environment Testing Norway AS (Moss). The method used for determination of BTEX, THC, PAH, and PCB in the sludge samples (raw sludge, spiked sludge, dewatered sludge, and dried sludge) was ISO/DIS 16703-Mod. Determination of TS in the same samples was by method NS 4763. Most of the HMs (As, Pb, Cu, Cr, Ni, and Zn) were determined through method NS EN ISO 11885, while concentration of Cd was set by method NS EN ISO 17294-2, and Hg by method NS 4768. Same method was

used for determination of Hg in reject water, whereas concentrations of remaining HMs were set by method NS EN ISO 17294-2. Determination of BTEX, THC, PAH, and PCB in reject water were all through internal methods of Eurofins.

Table 3.2: Weight of each fraction of sludge used for the different processes.

Fraction	Weight
Entire amount of sludge used for the whole experiment	14.994 kg
Sludge used for background concentrations	1.793 kg
Sludge spiked with environmental pollutants	13.201 kg
Sludge used for centrifugation	2.483 kg
Dewatered sludge	0.929 kg
Reject water	1.954 kg
Dried sludge	0.0866 kg

Table 3.3: Amount of each compound added to digested sludge (continues on the next page).

Compound	Amount added	Compound	Amount added
Acenaphthene	1 000 µg	Aroclor 1016	200 µg
Acenaphthylene	2 000 µg	Aroclor 1232	200 µg
Anthracene	600 µg	Aroclor 1248	200 µg
Benzo(a)anthracene	600 µg	Aroclor 1260	200 µg
Benzo(b)fluoranthene	200 µg	Arsenic	3 mg
Benzo(k)fluoranthene	100 µg	Cadmium	3 mg
Benzo(ghi)perylene	200 µg	Chromium	26 mg
Benzo(a)pyrene	600 µg	Copper	237 mg
Benzo(e)pyrene	500 µg	Lead	26 mg
Chrysene	600 µg	Mercury	1.5 mg
Dibenzo(a,h)anthracene	200 µg	Nickel	26 mg
Fluoranthene	700 µg	Zinc	680 mg
Fluorene	200 µg	Benzene	176 mg
Indeno(1,2,3-cd)pyrene	100 µg	Toluene	867 mg
Naphthalene	1 000 µg	Ethylbenzene	173 mg
Perylene	500 µg	<i>m</i> -xylene	86 mg
Phenanthrene	600 µg	<i>p</i> -xylene	88 mg
Pyrene	600 µg	<i>o</i> -xylene	87 mg
Triphenylene	500 µg	Diesel/crude oil	1 ml

The PAHs and PCBs were added as mixtures produced by Supelco (Polynuclear Aromatic Hydrocarbons Mix; 4-9155, EPA 610 Polynuclear Aromatic Hydrocarbons Mix; 4-8743, and Aroclor Mix 1; 4-8861). Arsenic and nickel were Atomic Spectroscopy Standard Solutions produced by Fluka Chemika (product number 11082 and 72223, respectively). Cadmium,

chromium, lead, and mercury were standard solutions for atomic absorption spectrometry produced by BDH Chemicals Ltd (product number 14135, 14137, 14036, and 14145, respectively). Copper (copper(II)chloride dihydrate) and zinc (zinc oxide) were both dissolved in acetic acid (0.1017 M), in 1 ml and 15 ml, respectively, before added. Both compounds were produced by Laboglass. The acetic acid used was made at the laboratory at the University in Stavanger. Benzene, ethylbenzene, *m*-xylene, and *o*-xylene were all of more than 99 % purity and produced by Fluka Chemika (product number 12552, 03080, 95672, and 95662, respectively). *P*-xylene of more than 99 % purity was purchased from Aldrich. Toluene was used as solvent for PAHs in the Polynuclear Aromatic Hydrocarbon Mix (4-9155) and no extra toluene was added. The diesel/crude oil is an unknown mixture of diesel and crude oil.

4. Results and Discussion

4.1 AQUASIM

AQUASIM was used to predict distribution of PAHs between organic particles in sludge and surrounding aqueous phase (see table A.1 for details concerning parameters used in the modeling). No continuous input of PAHs was modeled, only a spiked input at time 0. This leads to a washout process where the PAHs will be totally removed after some time. Stabilization of equilibrium between aqueous phase and solid phase was quite rapid. The following five figures show setting of equilibrium for 14 PAHs.

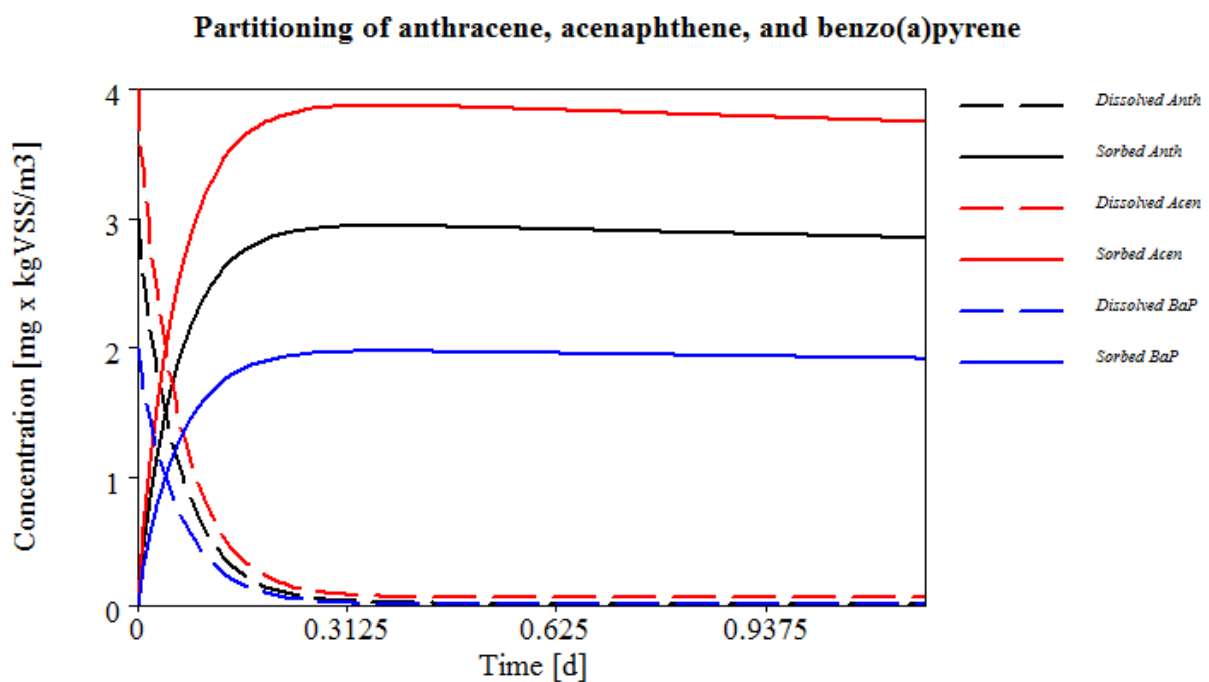


Figure 4.1: Concentrations of anthracene, acenaphthene, and benzo(a)pyrene as a function of time. Solid lines represent concentration of PAH sorbed to organic particles and dashed lines represent concentration of PAH freely dissolved in the aqueous phase.

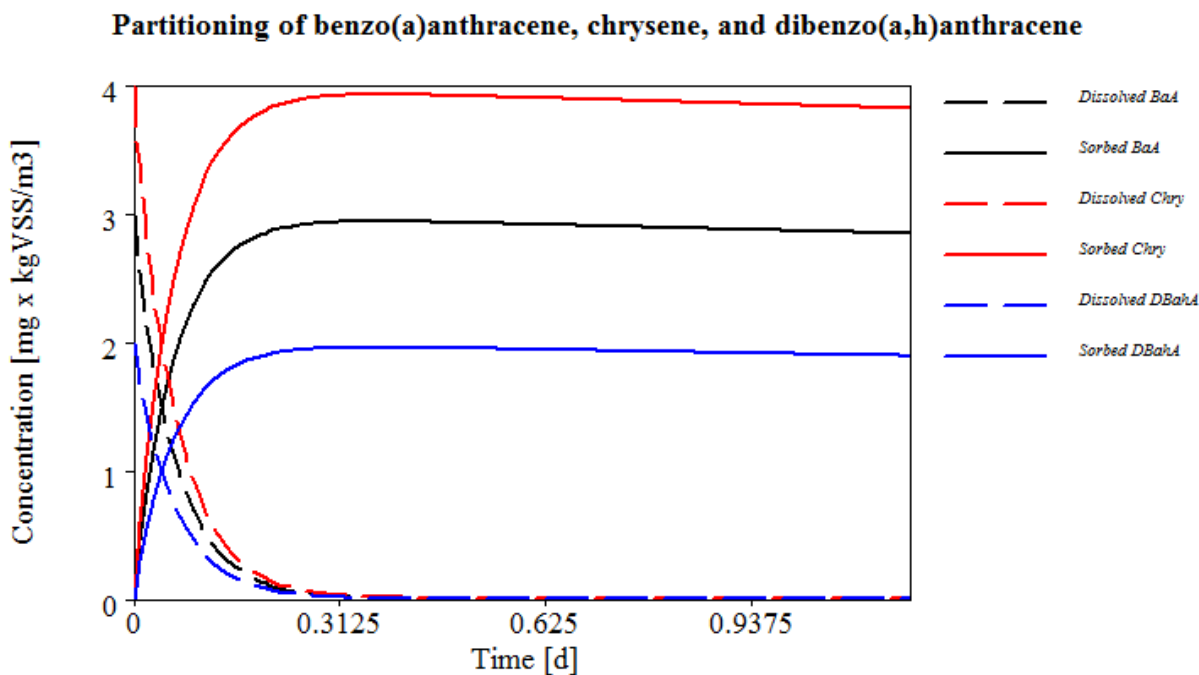


Figure 4.2: Concentration of benzo(a)anthracene, chrysene, and dibenzo(a,h)anthracene as a function of time. Solid lines represent concentration of PAH sorbed to organic particles and dashed lines represent concentration of PAH freely dissolved in the aqueous phase.

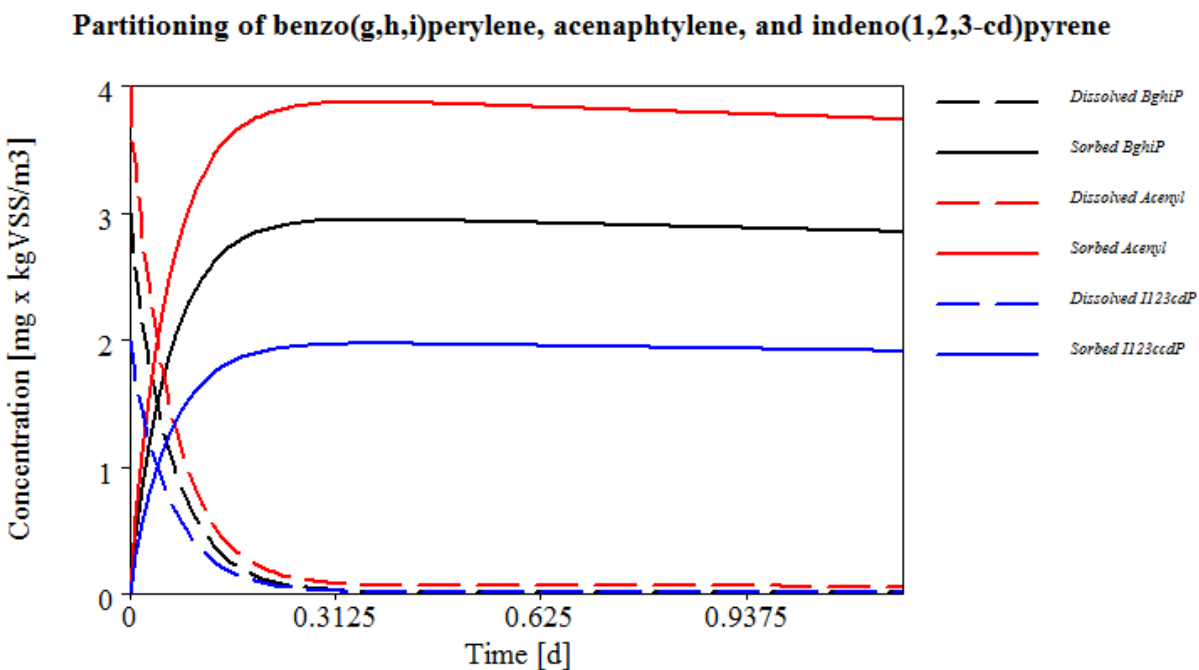


Figure 4.3: Concentration of benzo(g,h,i)perylene, acenaphthylene, and indeno(1,2,3-cd)pyrene as a function of time. Solid lines represent concentration of PAH sorbed to organic particles and dashed lines represent concentration of PAH freely dissolved in the aqueous phase.

Partitioning of fluoranthene, fluorene, and naphthalene

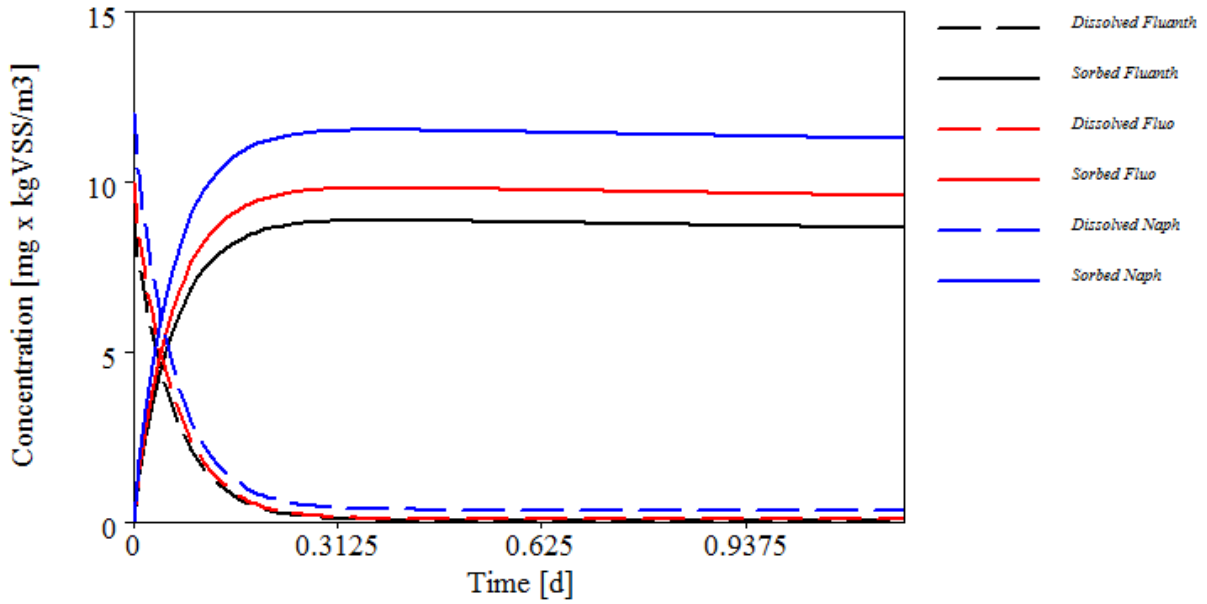


Figure 4.4: Concentration of fluoranthene, fluorene, and naphthalene as a function of time.

Solid lines represent concentration of PAH sorbed to organic particles and dashed lines represent concentration of PAH freely dissolved in the aqueous phase.

Partitioning of phenanthrene and pyrene

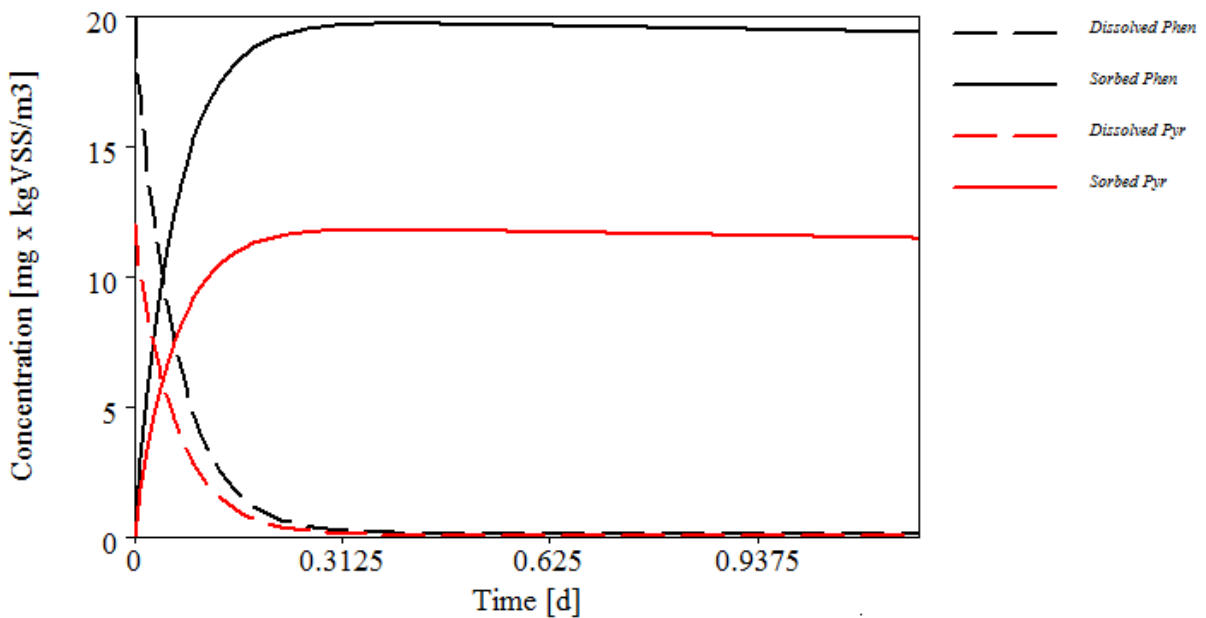


Figure 4.5: Concentration of phenanthrene and pyrene as a function of time. Solid lines represent concentration of PAH sorbed to organic particles and dashed lines represent concentration of PAH freely dissolved in the aqueous phase.

With regard to chosen kinetic coefficients, partitioning of PAHs between aqueous phase and sludge is a quick process. Just within the first 10 hours was equilibrium of partitioning set and concentration of the spike does not seem to influence the time it takes for equilibrium to be established. Barret et al. (2010) showed a similar setting of equilibrium of fluorene and benzo(a)pyrene within one hour. Compared to this, kinetic coefficients chosen for the modeling in this thesis are not overestimated but rather conservative.

Total input of PAHs in the modeling was 154 140 mg. At equilibrium 2 578 mg of the PAHs were found in the water phase. This is approximately 1.7 % of the total input, which gives that more than 98 % of input PAHs are sorbed to sludge after setting of equilibrium. Naphthalene, being the most water soluble of the PAHs, has a slightly different distribution. About 5.4 % of input naphthalene is found in the water phase and the rest (about 94.6 %) is associated with the sludge fraction. The PAHs range over a variety of water solubilities, vapor pressures, and K_{OW} and K_{OC} and it is expected that compounds with similar properties will distribute in the same way with comparable rates of setting of equilibrium.

The retention time for sludge in the anaerobic reactor at SNJ is about 15 days. When setting of equilibrium of partitioning is only 10 hours or less, this is not limited by the process, and almost everything of such pollutants will be associated with the sludge, not the aqueous phase, when leaving the reactor.

4.2 Experiment

Analysis of the different sludge samples were done externally by Eurofins. Two parallels were analyzed for all samples. The results obtained from the experiment are presented in table 4.1 and given as the average value of the two parallels. In addition, standard error is included (standard deviation divided by the square root of number of parallels).

Table 4.1: Results from the analysis done externally by Eurofins laboratories. The results given in this table are average values including standard error of two parallels.

	Digested sludge without POP mg/kg TS	Digested sludge with POP mg/kg TS	Dewatered sludge mg/kg TS	Reject water µg/l	Dried sludge (pellet) mg/kg TS
TS (%)	3.95 ± 0.05	4.0 ± 0.0	9.05 ± 0.05		0.69 ± 0.01
BTEX					
Benzene	0.265 ± 0.005	310 ± 30	56 ± 2	3 000 ± 100	0.8 ± 0.6
Toluene	1.3 ± 0.0	1 500 ± 0.0	590 ± 20	14 500 ± 500	11 ± 10
Ethylbenzene	0.098 ± 0.012	240 ± 0.0	135 ± 5	1 750 ± 50	3.2 ± 2.5
<i>m,p</i> -Xylene	2 ± 0.2	260 ± 0.0	155 ± 5	1 750 ± 50	4.1 ± 3.0
<i>o</i> -Xylene	0.145 ± 0.005	120 ± 0.0	76 ± 5	1 050 ± 50	1.8 ± 1.3
Total hydrocarbons (THC)					
THC > C5-C8	<10	1 550 ± 50	660 ± 20	10 300 ± 700	<400
THC > C8-C10	22 ± 0.0*	785 ± 5	545 ± 20	3 600 ± 100	<400
THC > C10-C12	935 ± 5	1 100 ± 0.0	916 ± 30	1 850 ± 50	<400
THC > C12-C16	1 350 ± 50	2 050 ± 50	1 850 ± 50	2 000 ± 0.0	<400
THC > C16-C35	7 150 ± 1 500	7 050 ± 150	6 350 ± 250	9 900 ± 100	4 550 ± 600
SUM THC (>C5-C35)	9 500 ± 1 500	12 500 ± 500	10 500 ± 500	27 500 ± 500	5 100 ± 600
PAH 16 EPA					
Naphthalene	0.3 ± 0.0	2.6 ± 0.0	2.45 ± 0.05	12 ± 0.0	0.09 ± 0.04
Acenaphthylene	<0.02	4.95 ± 0.05	3.95 ± 0.05	13.5 ± 0.5	0.2 ± 0.1
Acenaphthene	0.305 ± 0.005	2.6 ± 0.1	2.65 ± 0.05	5.55 ± 0.05	0.25 ± 0.07
Fluorene	0.2 ± 0.0	0.84 ± 0.0	0.91 ± 0.02	2.15 ± 0.05	0.10 ± 0.03
Phenanthrene	0.30 ± 0.01	1.8 ± 0.0	1.85 ± 0.05	4.55 ± 0.05	0.36 ± 0.09
Anthracene	0.0275 ± 0.0005	1.15 ± 0.05	1.2 ± 0.0	3.55 ± 0.05	0.22 ± 0.06
Fluoranthene	0.20 ± 0.03	1.5 ± 0.0	1.65 ± 0.05	3.3 ± 0.0	0.39 ± 0.09
Pyrene	0.25 ± 0.03	1.35 ± 0.05	1.45 ± 0.05	3.15 ± 0.05	0.35 ± 0.07
Benzo(a)anthracene	0.102 ± 0.008	2.75 ± 0.05	2.95 ± 0.05	3.25 ± 0.05	0.69 ± 0.09
Chrysene	0.235 ± 0.005	4.8 ± 0.1	4.95 ± 0.15	2.5 ± 0.2	1.4 ± 0.2
Benzo(b)fluoranthene	0.078 ± 0.001	0.485 ± 0.005	0.55 ± 0.02	1.0 ± 0.0	0.14 ± 0.05
Benzo(k)fluoranthene	0.053 ± 0.005	0.29 ± 0.01	0.31 ± 0.02	0.45 ± 0.05	0.09 ± 0.02
Benzo(a)pyrene	0.04 ± 0.01	1.1 ± 0.1	1.25 ± 0.05	2.6 ± 0.0	0.20 ± 0.08
Indeno(1,2,3-cd)pyrene	0.04 ± 0.01	0.30 ± 0.02	0.27 ± 0.03	2.55 ± 0.05	0.06 ± 0.0*
Dibenzo(a,h)anthracene	0.033 ± 0.008	0.63 ± 0.05	0.525 ± 0.005	0.12 ± 0.0	0.13 ± 0.0*
Benzo(g,h,i)perylene	0.055 ± 0.001	0.525 ± 0.005	0.54 ± 0.0	0.34 ± 0.02	0.13 ± 0.02
Sum PAH 16 EPA	2.15 ± 0.05	27 ± 0.5	27.5 ± 0.5	61 ± 0.0	4.7 ± 0.9

Table 4.1: Continues.

	Digested sludge without POP mg/kg TS	Digested sludge with POP mg/kg TS	Dewatered sludge mg/kg TS	Reject water µg/l	Dried sludge (pellet) mg/kg TS
PCB 7					
PCB 28	0.004 ± 0.002	0.068 ± 0.008	0.063 ± 0.003	0.28 ± 0.02	0.007 ± 0.004
PCB 52	0.017 ± 0.002	0.12 ± 0.01	0.099 ± 0.002	0.20 ± 0.02	0.023 ± 0.003
PCB 101	0.007 ± 0.001	0.030 ± 0.002	0.027 ± 0.001	<0.06	0.014 ± 0.009
PCB 118	0.03 ± 0.03	0.092 ± 0.008	0.038 ± 0.007	0.17 ± 0.01	0.023 ± 0.006
PCB 138	0.011 ± 0.001	0.105 ± 0.005	0.090 ± 0.004	<0.06	0.03 ± 0.01
PCB 153	0.012 ± 0.003	0.13 ± 0.01	0.105 ± 0.005	<0.06	0.040 ± 0.005
PCB 180	0.006 ± 0.001	0.078 ± 0.003	0.0615 ± 0.0005	<0.06	0.0195 ± 0.0005
Sum PCB 7	0.09 ± 0.03	0.63 ± 0.0	0.485 ± 0.005	0.66 ± 0.04	0.15 ± 0.03
Heavy metals					
Arsenic	<13	<13	7.3 ± 0.2	49.5 ± 0.5	<72
Lead	31 ± 7	78 ± 1	85 ± 0.0	78 ± 2	<43
Copper	135 ± 5	505 ± 5	570 ± 10	1 045 ± 55	365 ± 25
Chromium	18 ± 2	59 ± 1	64.5 ± 0.5	155 ± 5	34.5 ± 0.5
Nickel	14 ± 0.0	52 ± 1	48 ± 0.0	420 ± 0.0	235 ± 5
Zinc	440 ± 20	1 500 ± 0.0	1 700 ± 0.0	1 150 ± 50	950 ± 50
Cadmium	0.67 ± 0.02	6.8 ± 0.1	7.9 ± 0.3	11.5 ± 0.5	3.4 ± 0.1
Mercury	0.292 ± 0.006	3.23 ± 0.37	3.57 ± 0.03	11.2 ± 0.2	1.41 ± 0.09

*Only one parallel above limit of quantification.

The results above are those reported by Eurofins and most of them are acceptable with one exception; the results from the samples of dried sludge. TS reported by Eurofins for the dried sludge sample is more than 10 times less of its actual value (calculated based on given results and own results). For following calculations reported TS for dewatered sludge will be used (9.05 %). A sample of 905 g dewatered sludge was used for drying. This gives a total of 81.9 g TS in this sample (90.5 g TS/kg slam × 0.905 kg slam = 81.9 g TS). Weight of the sample after drying was 86.6 g, which gives a TS content of 94.6 % in the dried sludge sample (81.9 g TS/86.6 g sludge × 100% = 94.6 %). The dried sludge was dissolved in 1 000 g tap water making the total weight of submitted sample 1086.6 g. TS in submitted sludge sample should therefore be 7.5 % ((86.6 g sludge × 94.6 % TS)/1086.6 g sludge = 7.5 % TS), not 0.7 % TS as reported by Eurofins. A TS of 7.5 % will be used in all further calculations.

All other results are given as mg/kg TS and therefore depend on TS in the sample. Because of this, it is most likely that all other results from the dried sludge sample are erroneous.

Nonetheless, reported values for all results, except TS, have been used in calculations since “true” results are not obtainable without redoing the analysis.

Based on the results, mass balances have been made for each compound during dewatering and drying. Results from these calculations are graphically displayed in following figures. The first set of compounds displayed is BTEX.

4.2.1 BTEX

Figures 4.6 and 4.7 below show the mass balance of BTEX during dewatering and drying. As can be seen from the figures, BTEX is present in both dewatered sludge and reject water after dewatering. Also, it is notable that some is lost during this process. On average, approximately 40 % of the BTEX compounds are lost during dewatering. The two extreme points are benzene and *o*-xylene which have a loss of 66 % and 29 %, respectively. As can be seen in table 2.4, BTEX are volatile compounds that easily evaporate at room temperature (especially benzene and toluene), and the loss is therefore most likely due to volatilization. After dewatering, the ratio of BTEX in reject water to BTEX in dewatered sludge is 1:2. None of the other groups of compounds hold a ratio as high as this. The reason for this becomes quite evident when comparing solubilities of the compounds listed in table 2.4, 2.5, 2.6, and 2.7. BTEX is by far the most water soluble group, and it is therefore not surprising to find BTEX in such high levels in the reject water.

The process of drying leads to further loss of BTEX. Almost all BTEX is lost during this process and less than 1 % of BTEX present in spiked sludge is left in the dried sludge sample. This is, again, because of the volatility of BTEX and also due to temperatures ranging between 95 and 105 °C during the process. Such high temperatures in connection with volatile compounds will undoubtedly lead to evaporation of these, which is the case with BTEX.

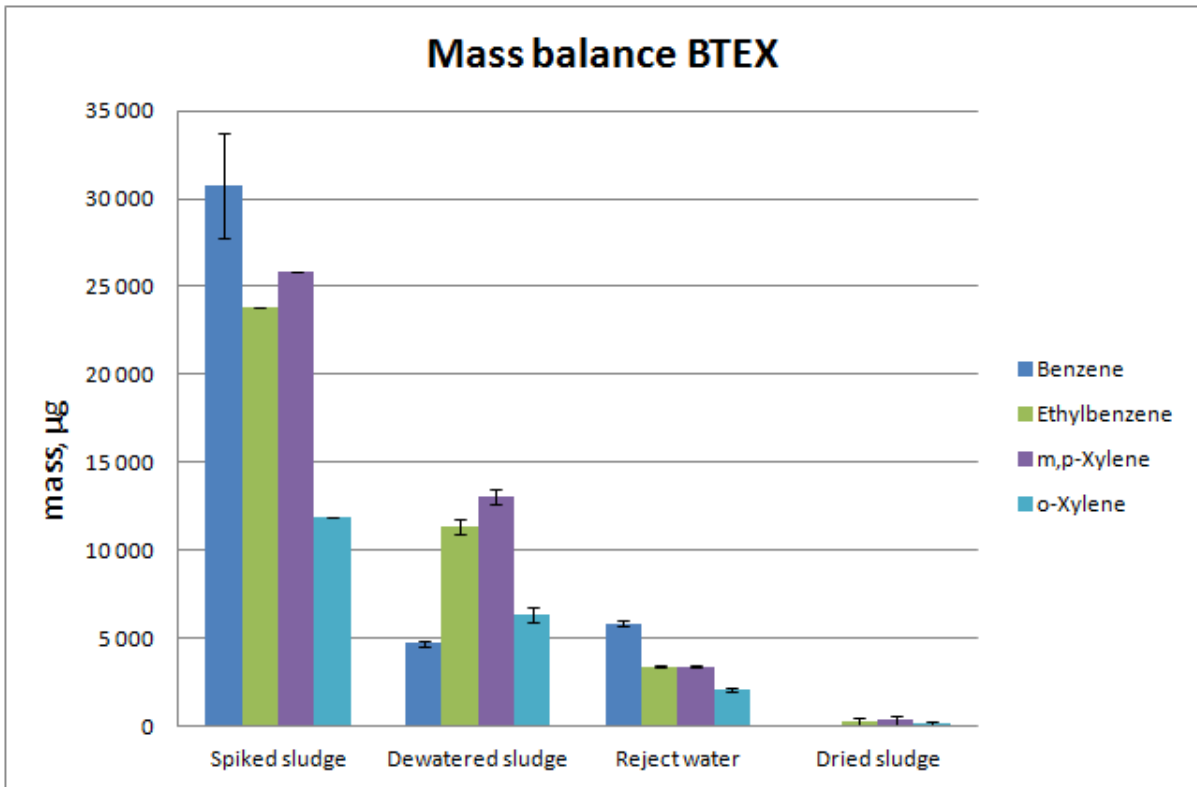


Figure 4.6: Mass balance of BTEX over the processes. Standard errors are included.

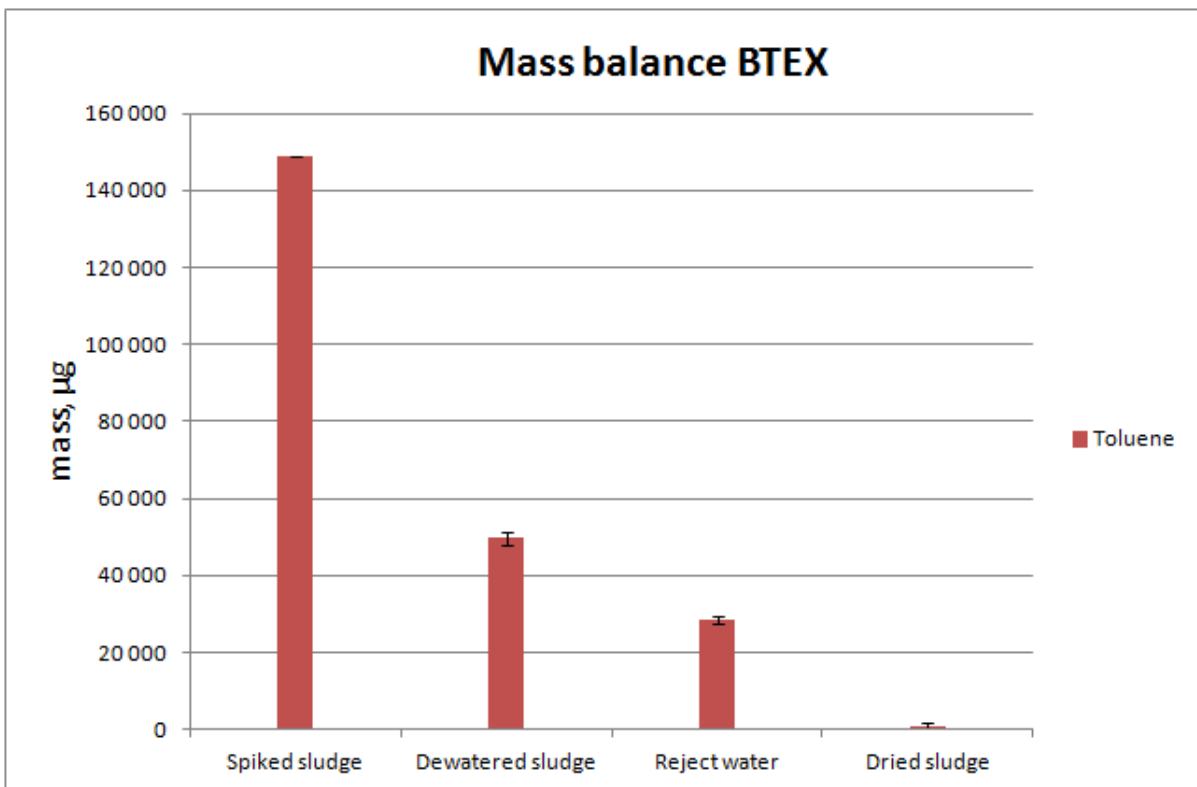


Figure 4.7: Mass balance of BTEX over the processes. Standard errors are included.

4.2.2 THC

Normal alkanes represented by THC span from low molecular weight hydrocarbons to heavier fractions and are divided into five groups. Figure 4.8 and 4.9 gives the mass balance of THC over the processes.

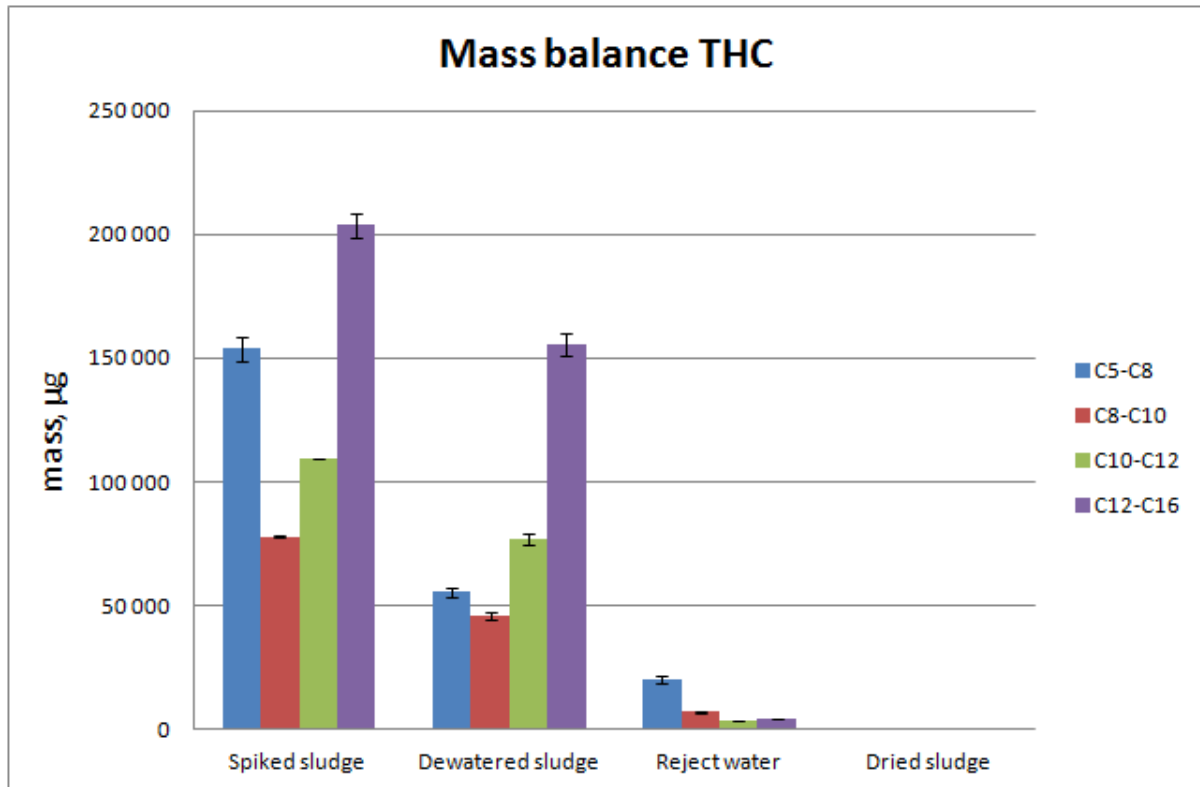


Figure 4.8: Mass balance of THC over the processes. Standard errors are included.

As was the case with BTEX, so is some of THC lost in the process of dewatering. On average about 30 % is lost. The biggest loss is found for the fraction C5-C8 with a loss of approximately 50 %, whereas the lowest loss is found for the fraction C16-C35 with a loss of about 20 %. If the fraction C16-C35 could be further divided into smaller sections, it would most likely be even less than 20 % evaporating from the sections containing the heaviest hydrocarbons. The loss of THC during the dewatering is most likely due to volatilization, because of high vapor pressures for hydrocarbon and would be expected to occur, especially for the low molecular weight compounds. The average ratio of THC in reject water to THC in dewatered sludge is around 6:100. The fraction containing the lightest hydrocarbons has a somewhat higher ratio (4:10) due to these compounds having a higher water solubility than the rest.

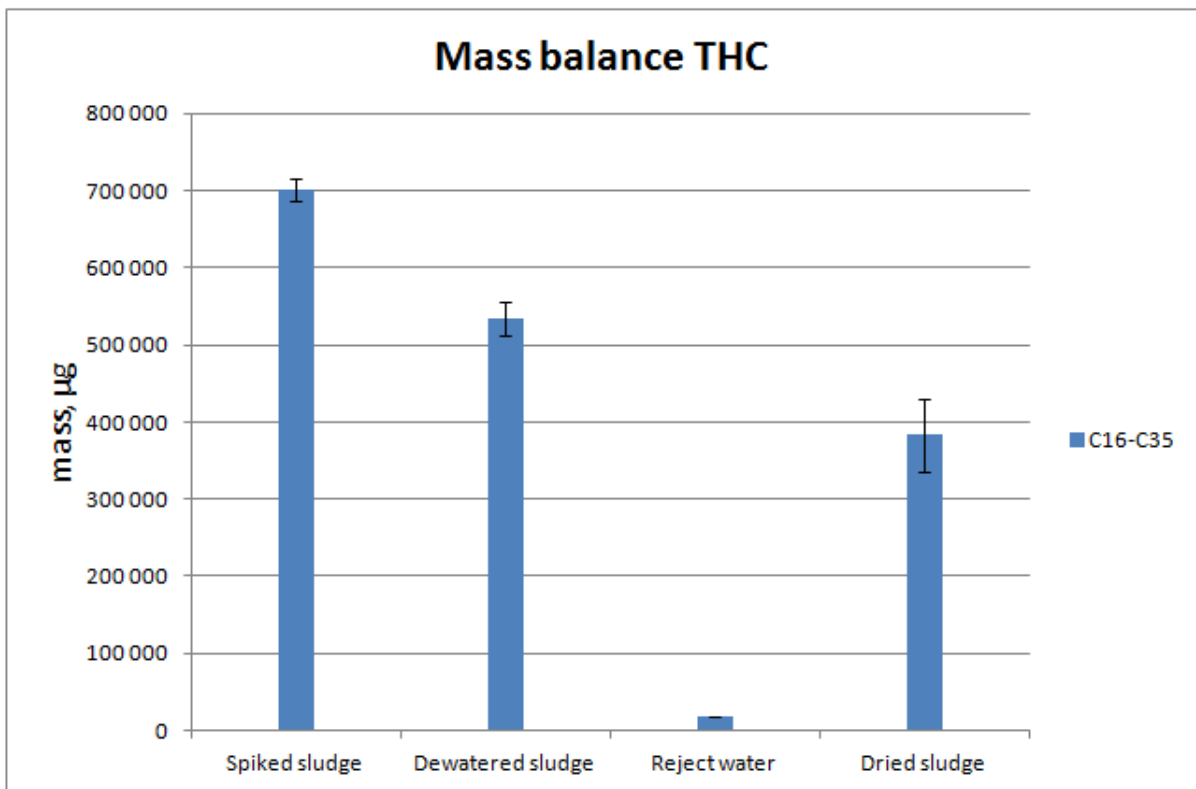


Figure 4.9: Mass balance of THC over the processes. Standard errors are included.

No THC could be detected in the sample dried sludge for fractions containing hydrocarbons with less than 16 C atoms. This was said to be because of the low TS content in the sample increasing the limit of quantification. Results were obtained for the fraction C16-C35, however, and it shows a loss of about 30 % during drying. With a loss this big for the heavier compounds in the group THC, it is reasonable to think that a higher loss will occur for the lighter hydrocarbons in this group.

4.2.3 PAHs

The group containing most compounds is PAH with a total of 17 different chemicals. These compounds span over solubilities from 0.0002-31 mg/l, from relatively high to low vapor pressures, and also big differences in K_{OW} and K_{OC} values. Figures 4.10, 4.11, and 4.12 all show mass balances of the different PAHs during dewatering and drying. The PAHs have been grouped according to input concentration.

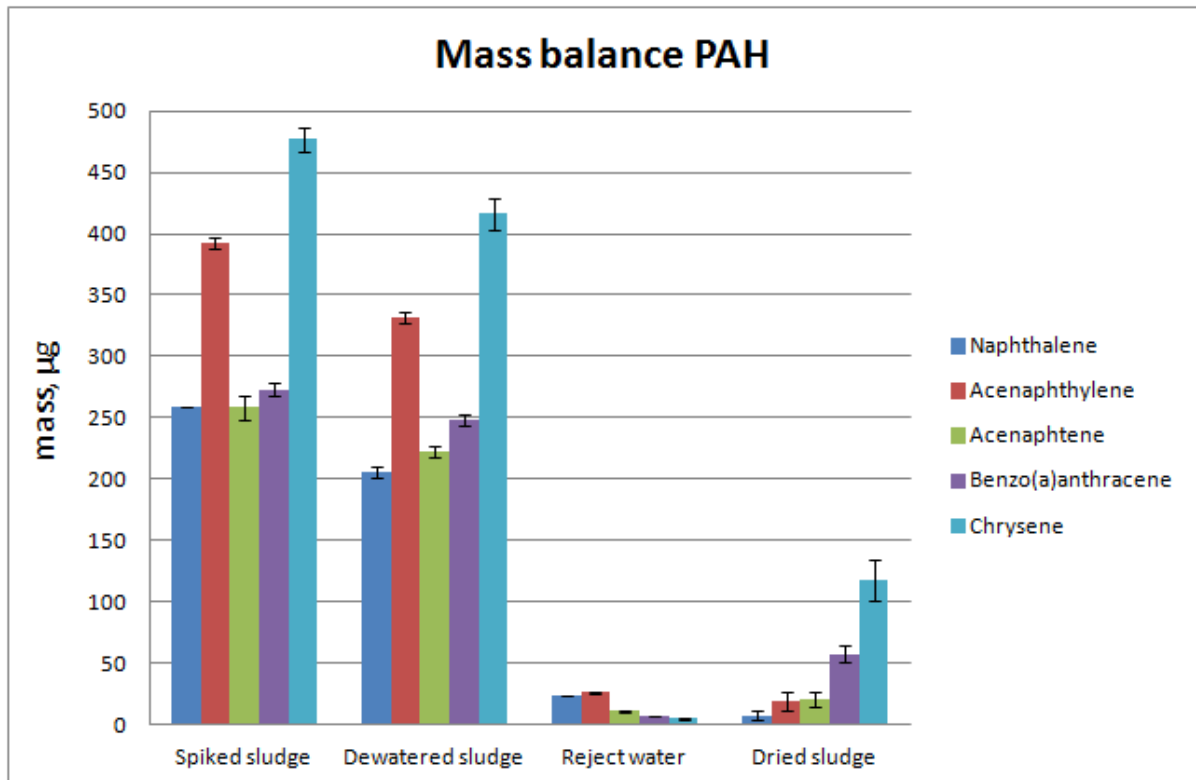


Figure 4.10: Mass balance of PAH over the processes. Standard errors are included.

PAHs are in most cases associated with organic fractions, hence their high K_{OW} and K_{OC} values, and it was predicted that they would follow the sludge during dewatering. As can be seen from the figures 4.10, 4.11, and 4.12, this is the general trend and very little of the PAHs follow the reject water. In fact, about only 5 % of the PAHs were found in samples of reject water. Again, some variations are found between the different compounds but they are not as distinctive as for BTEX and THC. Also, there is a small loss of PAHs during dewatering of about 8 %. Some of the lighter PAHs, especially naphthalene, have quite high vapor pressures and some of the loss can be due to volatilization of these. Although this could be the case, the loss is more likely due to analytical uncertainties since it is so small.

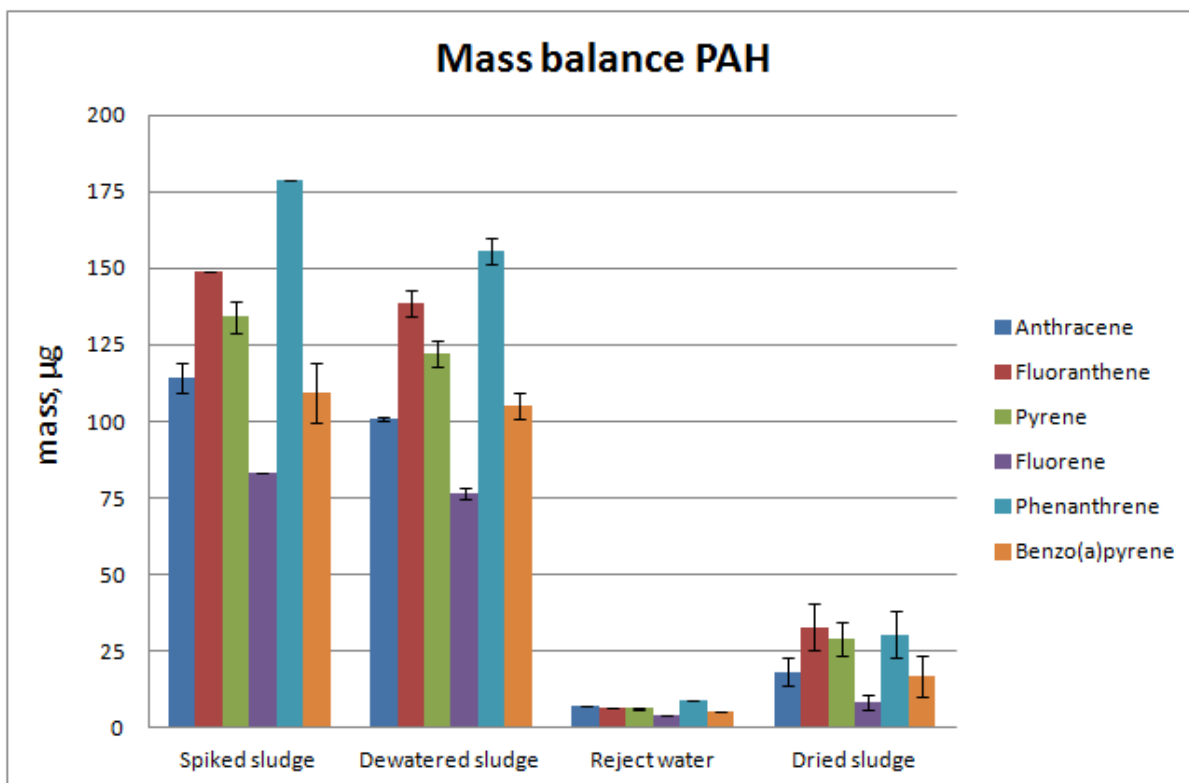


Figure 4.11: Mass balance of PAH over the processes. Standard errors are included.

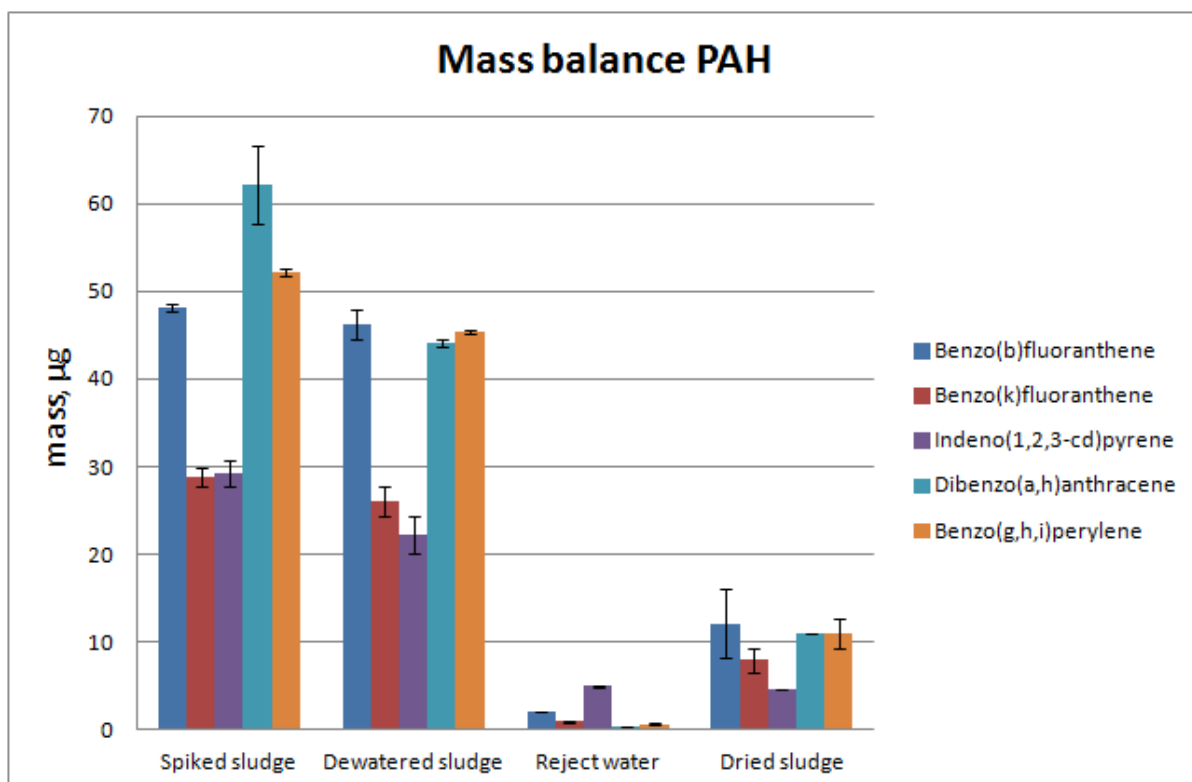


Figure 4.12: Mass balance of PAH over the processes. Standard errors are included.

Over the next process, however, the loss is somewhat bigger. About 80 % of the PAHs are lost. Although the temperature in the drier is quite high, a loss this size was not expected. Most of the PAHs have low vapor pressures and would therefore not be expected to evaporate at this temperature. Nonetheless, this could be the case, but it should be kept in mind that the reported values for dried sludge are questionable and that they might not represent the entire truth.

4.2.4 PCB

The PCBs are quite like PAHs regarding properties and a similar distribution over the processes would therefore be expected. The following figure gives mass balance of PCBs during dewatering and drying.

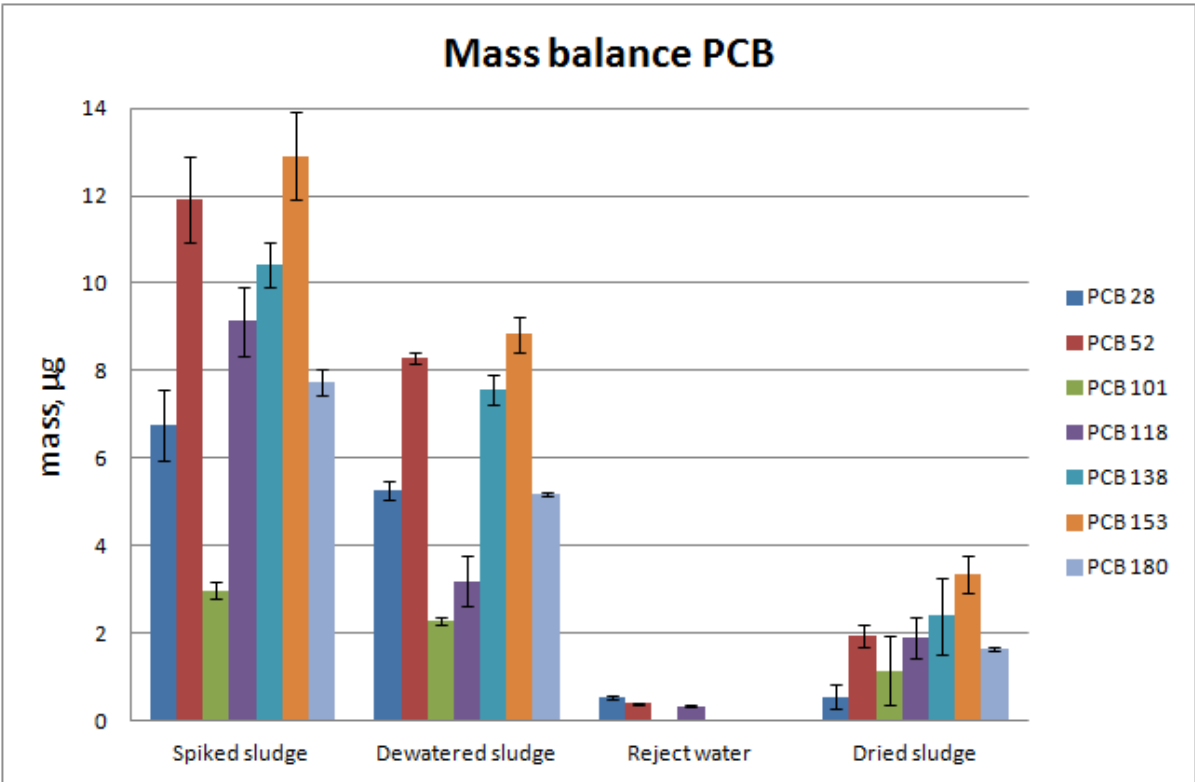


Figure 4.13: Mass balance of PCB over the processes. Standard errors are included.

Figure 4.13 resembles the figures depicting mass balances of PAHs which indicates that PCBs, as PAHs, follow the sludge through the processes. Although the PCBs resemble the

PAHs in distribution a bigger loss is found for PCBs during dewatering. About 30 % of PCBs originally preset in the spiked sludge is lost in the first process. PCBs have low vapor pressures, so loss due to volatilization seems unlikely.

The same problem occurs during drying. On average, the loss is about 70 % over this process. Some loss due to volatilization would not be unlikely since the temperature is quite high in the drier, but 70 % is maybe too much. Standard errors for measurements of the dried sludge are quite big making it difficult to predict the real loss.

4.2.5 Heavy metals

HMs have low vapor pressures (except mercury) and low water solubilities. These properties combined indicate that most of the HMs will end up in the sludge fraction. Figure 4.14, 4.15, and 4.16 shows the mass balances for the different HMs during dewatering and drying.

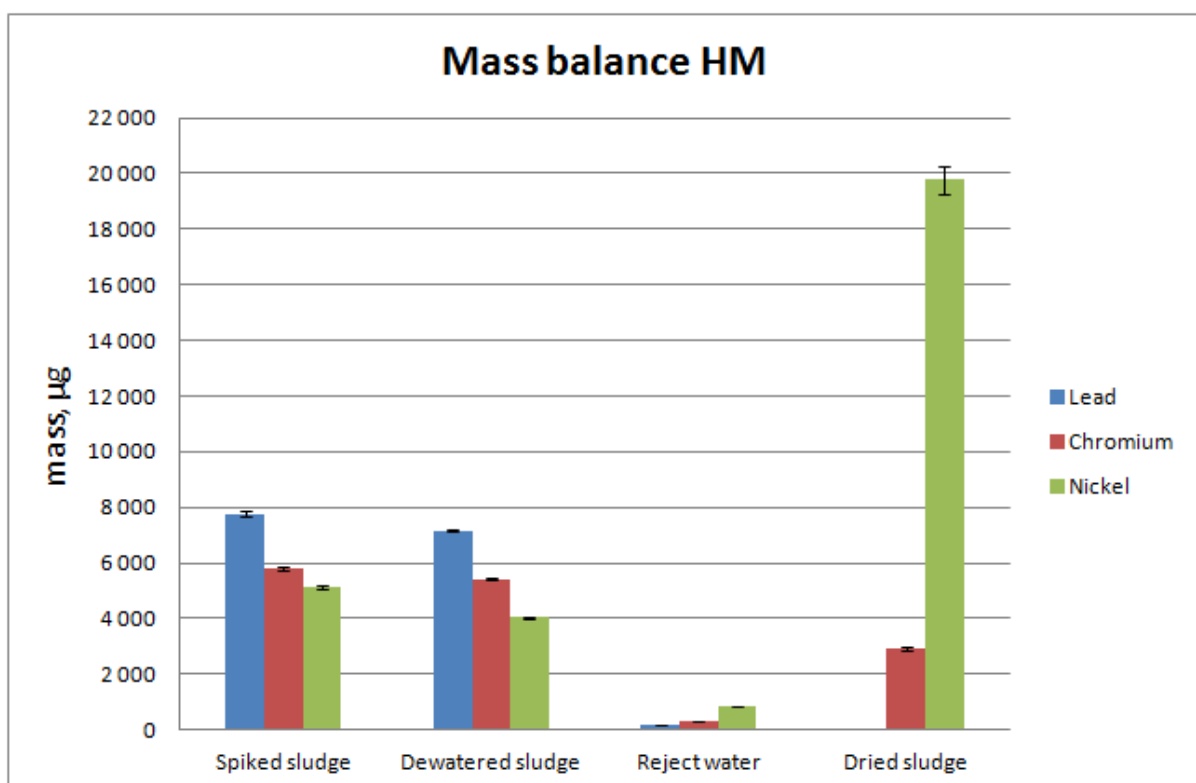


Figure 4.14: Mass balance of HM over the processes. Standard errors are included.

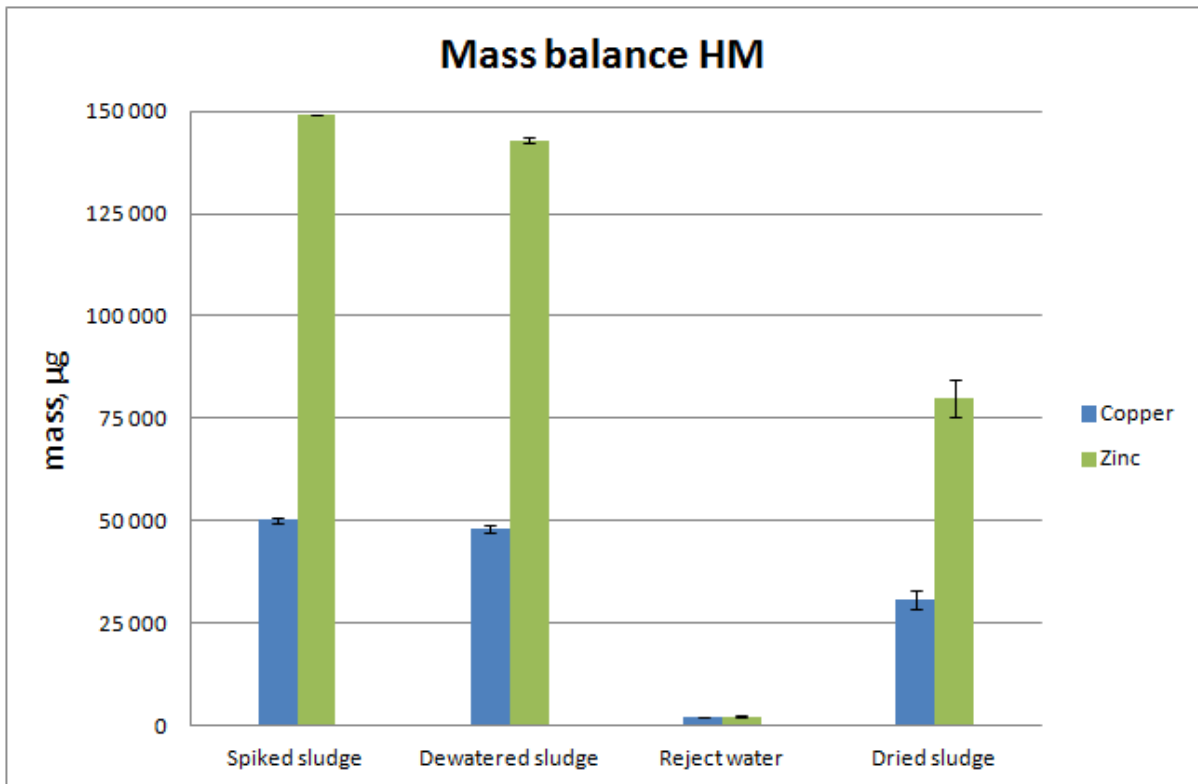


Figure 4.15: Mass balance of HM over the processes. Standard errors are included.

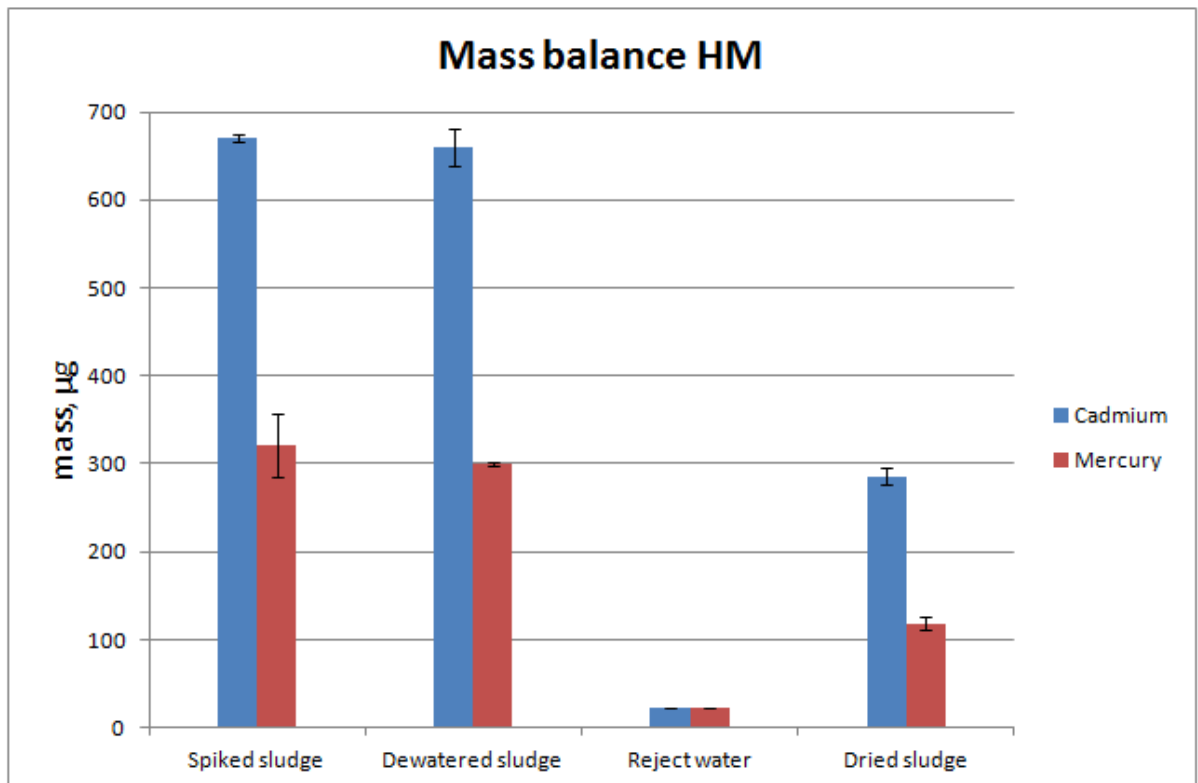


Figure 4.16: Mass balance of HM over the processes. Standard errors are included.

The most striking when looking at the previous three figures is the mass of nickel in dried sludge (figure 4.14). The mass in the dried sludge sample is approximately four times that in spiked sludge. A known amount of nickel was added (26 000 µg) and background amount of nickel in the digested sludge was analyzed to around 8 000 µg. Analysis of spiked sludge shows a quantity of approximately 27 000 µg in the sludge. Based on this, it is very unlikely that given amount of nickel in spiked sludge should be more than four times higher. Most likely the reported value of nickel in dried sludge is overestimated and can therefore not be regarded as a valid result. For further calculations of trends based on average values, nickel will be excluded.

Looking at HM concentrations in dewatered sludge and reject water it is not difficult to see the trend; HMs sticks to sludge rather than water. Moreover, little is lost during dewatering so that it can be regarded as zero loss of HMs in this process.

During drying a more noticeable loss occur. On average, about 50 % of HMs are lost in this process. This result was not anticipated and is difficult to explain, especially when taking into consideration that mercury, being the most volatile of all the HMs, is not completely lost through volatilization. Again, this can be due to uncertainties regarding reported values in dried sludge sample. Table 2.7 shows low vapor pressures for all the other HMs, making it hard to believe that as much as 50 % is lost through volatilization. Also, the standard errors for HMs are far from large enough to cover this up.

4.2.6 All groups

To get a better overview and making it easier to compare the different groups of chemicals, a flow chart of the distribution during the processes has been made and it is rendered in figure 4.17.

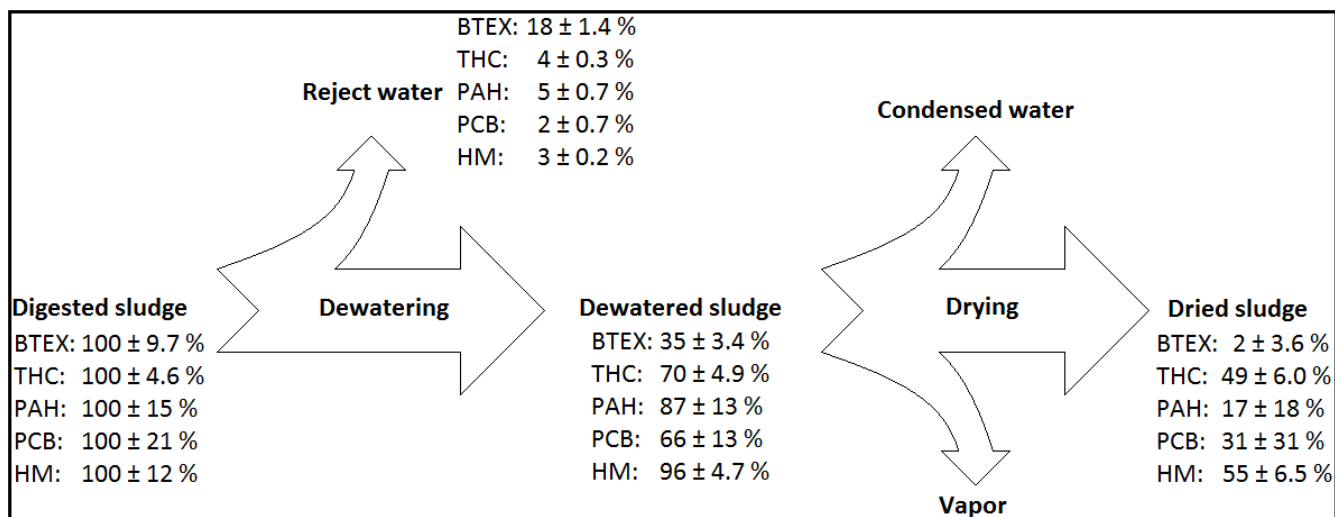


Figure 4.17: Flow chart describing the distribution of the different groups after dewatering and drying. Percentage of the different groups in dried sludge is based on values in dewatered sludge.

As expected, the majority of the compounds are associated with the sludge after dewatering. The only exception is BTEX that because of high vapor pressures and water solubilities are lost in big amounts during the process. The same trend, only some more volatilization, was anticipated to be observed during drying. This agrees with BTEX but not the other groups that all experience higher losses than expected. Due to erroneous result of TS in dried sludge, the rest of the results in this sample are probably incorrect as well, which must be taken into account.

BTEX is by far the most water soluble group and, not unexpectedly, it is found in larger quantities than THC, PAH, PCB, and HM in reject water. THC, PAH, PCB, and HM all have low water solubilities and are more or less found in similar small amounts in reject water. During dewatering BTEX, THC, and PCB all experience losses. On average, BTEX has the highest loss whereas THC and PCB experience a loss about the same size. A reason for these losses can be volatilization. This, at least, holds for BTEX where all compounds are volatile, especially

benzene and toluene. THC is also composed of compounds where some are volatile, and loss through volatilization is therefore valid for this group as well. PCB, on the other hand, is not very volatile and an average loss of about 30 % for this group is much more than expected.

Drying at temperatures between 95 and 105 °C gives rise to further volatilization of groups containing volatile compounds. Not unexpectedly, almost no BTEX is left in the sludge after drying. Much of the THC is also lost during drying, but due to heavier fractions with lower vapor pressures within this group, about 50 % THC remain in dried sludge. PAH experience a loss of about 80 %, PCB a loss of about 70 %, and approximately 45 % of HM is lost during drying. These losses exceed those expected, and it seems unlikely that these groups should experience losses this size taking into account their low vapor pressures. Losses this size is probably due to erroneous results originating from incorrect determination of TS in dried sludge.

The results obtained in the study “Overvåkning og potensiell omdanning av utvalgte organiske miljøgifter i renseanlegg på Nord-Jæren” by Kommedal et al. (2008) show similar trends. Values that are comparable with figure 4.17 can be obtained for PAH and PCB. Digested sludge contained 100 ± 24 % PAH and 100 ± 17 % PCB. After dewatering 92 ± 20 % of the PAHs were found in dewatered sludge whereas 7 ± 2 % followed the reject water. As for PCB, 83 ± 17 % were found in dried sludge and 33 ± 5 % were found in reject water. Out of that present in dewatered sludge 57 ± 9 % and 78 ± 4 % of PAHs and PCBs, respectively, remained in the sludge fraction after drying. Comparing these results with those in figure 4.17 show a similarity between the studies in the distribution of PAH and PCB in dewatered sludge. In both cases, PAH is found in larger amounts than PCB in dewatered sludge. However, in reject water PCB is found in bigger quantities than PAH only in the study by Kommedal et al. (2008). Also, the result in this thesis indicates a big loss of PCB during dewatering, which does not occur in the study by Kommedal et al. (2008). It is hard to explain a loss of PCB during dewatering. PCBs are not very volatile and loss due to volatilization is therefore unlikely. This group is not particularly water soluble either. Even so, Kommedal et al. (2008) reported that a big fraction of PCB is following the reject water. The loss experienced in this thesis can therefore be due to analytical uncertainties regarding analysis of reject water. A similarity can be seen between the two studies regarding dried sludge;

PCB is present to a bigger extent than PAH in dried sludge. However, there is a difference in amount retained in dried sludge. The study from 2008 shows a larger percentage of PAH and PCB in dried sludge than that found in this thesis. Results on dried sludge obtained in this thesis are most likely erroneous. Results given in Kommedal et al. (2008) seems more reasonable and probably gives a more correct picture of the distribution of POPs, especially during drying.

Kommedal et al. (2008) reports values of PAH and PCB in biopellets (dried sludge) during normal operation of SNJ. Average values for PAH and PCB in biopellets was found to be 1.6 mg/kg TS and 0.04 mg/kg TS, respectively. Proposed limit values for same groups are 8 mg/kg TS and 0.8 mg/kg TS for PAH and PCB, respectively (table 2.3). For now, biopellets produced at SNJ meets the proposed requirements for PAH and PCB in soil conditioners produced from sludge, and no additional treatment will be needed for these two groups. The study also includes data on DEHP and NPE, which both are subject to prospective regulations. Reported average values of DEHP and NPE are 52.0 mg/kg TS and 15.9 mg/kg TS, respectively. These values are within those proposed (100 mg/kg TS for DEHP and 50 mg/kg TS for NPE) and further treatment will therefore not be needed. Data on the other groups (AOX, LAS, and PCDD/F) presented in table 2.3 has not been provided and similar studies as those done by Kommedal et al. (2008) should be conducted for remaining groups. Only then can one be sure if SNJ needs additional treatment or not to maintain today's production of biopellets.

5. Conclusion

Both modeling and experimental work verified the affinity POPs hold for organic fractions such as sludge. Modeling of partitioning of PAHs between sludge and surrounding aqueous phase showed that about 98 % of the PAHs are found sorbed to sludge, whereas remaining PAHs are associated with the water phase. Other compounds with similar properties will behave in the same way and most POPs will be found sorbed to sludge.

Experiment work showed that during dewatering THC, PAH, PCB, and HM were all tightly bound to sludge whereas BTEX was also found to follow the reject water. Some loss during the process was experienced by BTEX, THC, and PCB. During drying all of the groups experienced losses, only to different extends. Those POPs not evaporating during drying will end up in the dried sludge, i.e. biopellets. This is of concern due to the application of such fertilizers on farmlands and other green areas. Kommedal et al. (2008) reported values of PAH, PCB, DEHP, and NPE in biopellets during normal operation at SNJ. None of these exceeds those requirements proposed for future production of soil conditioners from sludge. When similar results are obtained for AOX, LAS, and PCDD/F it can be determined whether or not additional treatment is necessary to maintain today's production of biopellets at SNJ.

Due to erroneous results from the dried sludge samples a new experiment should be conducted. Both to verify the results obtained from the other samples, but most of all to obtain more reliable results from the drying process. If possible, an experiment using a setup that captures and condenses all gas and vapor produced during the drying should be executed. By doing this it will be possible to get the whole picture and entire fate of the POPs in the processes.

References

1. El-Hadj, T.B., J. Dosta, and J. Mata-Alvarez, *Biodegradation of PAH and DEHP micro-pollutants in mesophilic and thermophilic anaerobic sewage sludge digestion*. Water Science and Technology, 2006. **53**(8): p. 99-107.
2. Jones, K.C. and P. de Voogt, *Persistent organic pollutants (POPs): state of the science*. Environmental Pollution, 1999. **100**(1-3): p. 209-221.
3. EU, *Working document on sludge 3rd draft*, 27th April 2000: Brussels, ENV.E.3/LM.
4. Tchobanoglous, G., F.L. Burton, and H.D. Stensel, *Wastewater engineering: treatment and reuse*. 2003, Boston: McGraw-Hill. XXVIII, 1819 s.
5. Jevne, A., A.N. Bynes, and C.G. Overgaard, *Anaerob behandling av slufatholdig industrielt avløpsvann*, in *Det teknisk-naturvitenskaplige fakultet* 2010, Universitetet i Stavanger: Stavanger.
6. Christensen, N., et al., *Removal of polycyclic aromatic hydrocarbons (PAHs) from sewage sludge by anaerobic degradation*. Water Science and Technology, 2004. **50**(9): p. 237-244.
7. Nedland, K.T. and B. Paulsrud, *Statusrapport for bruk av avløpsslam - endringer siden år 2000*, 2005, Aquateam: Oslo.
8. LMD, MD, and HOD, *Forskrift om gjødselvarer m.v. av organisk opphav*, 4th July 2003 nr. 951.
9. Walker, C.H., *Principles of ecotoxicology*. 2006, Boca Raton, Fla.: CRC Taylor & Francis. XXIII, 315 s.
10. Kiely, G., *Environmental engineering*. 1997, London: McGraw-Hill. XX, 979 s.
11. Kommedal, R., L. Ydstebø, and T. Bilstad, *Overvåkning og potensiell omdanning av utvalgte organiske miljøgifter i renseanlegg på Nord-Jæren*, 2008, University of Stavanger: Stavanger.
12. Atlas, R.M. and J. Philp, *Bioremediation: applied microbial solutions for real-world environmental cleanup*. 2005, Washington, D.C.: ASM Press. XI, 366 s.
13. LaGrega, M.D., P.L. Buckingham, and J.C. Evans, *Hazardous waste management*. 2001, Boston, Mass: McGraw-Hill. XXVI, 1202 s.
14. Rittmann, B.E. and P.L. McCarthy, *Environmental biotechnology: principles and applications*. 2001, Boston, Mass.: McGraw-Hill. XIV, 754 s.
15. Bernal-Martinez, A., et al., *Combining anaerobic digestion and ozonation to remove PAH from urban sludge*. Process Biochemistry, 2005. **40**(10): p. 3244-3250.
16. Chang, B.V., S.W. Chang, and S.Y. Yuan, *Anaerobic degradation of polycyclic aromatic hydrocarbons in sludge*. Advances in Environmental Research, 2003. **7**(3): p. 623-628.
17. Drewes, J.E., et al., *An Assessment of Endocrine Disrupting Activity Changes during Wastewater Treatment through the Use of Bioassays and Chemical Measurements*. Water Environment Research, 2005. **77**(1): p. 12-23.
18. EPA, *Bisphenol A Action Plan*. U.S. Environmental Protection Agency, 2010.
19. Abad, E., et al., *Priority organic pollutant assessment of sludges for agricultural purposes*. Chemosphere, 2005. **61**: p. 1358-1369.
20. Gavala, H.N., et al., *Biodegradation of phthalate esters during the mesophilic anaerobic digestion of sludge*. Chemosphere, 2003. **52**: p. 673-682.

21. Delgadillo-Mirquez, L., et al., *A new dynamic model for bioavailability and cometabolism of micropollutants during anaerobic digestion*. *Water Research*, 2011. **45**(15): p. 4511-4521.
22. Barret, M., et al., *A three-compartment model for micropollutants sorption in sludge: Methodological approach and insights*. *Water Research*, 2010. **44**(2): p. 616-624.
23. Alexander, M., *Biodegradation and bioremediation*. 1999, San Diego, Calif.: Academic Press. XIV, 453 s.
24. Dobbs, R.A., L.P. Wang, and R. Govind, *SORPTION OF TOXIC ORGANIC-COMPOUNDS ON WASTE-WATER SOLIDS - CORRELATION WITH FUNDAMENTAL PROPERTIES*. *Environmental Science & Technology*, 1989. **23**(9): p. 1092-1097.
25. Stevens-Garmon, J., et al., *Sorption of emerging trace organic compounds onto wastewater sludge solids*. *Water Research*, 2011. **45**(11): p. 3417-3426.
26. Wania, F., J. Axelman, and D. Broman, *A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface*. *Environmental Pollution*, 1998. **102**(1): p. 3-23.
27. Trably, E., D. Patureau, and J.P. Delgenes, *Enhancement of polycyclic aromatic hydrocarbons removal during anaerobic treatment of urban sludge*. *Water Science & Technology*, 2003. **48**(4): p. 53-60.
28. Snoeyink, V.L. and D. Jenkins, *Water chemistry*. 1980, New York: Wiley. 463 s.
29. Stumm, W. and J.J. Murga, *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*. 1996, New York, NY: John Wiley & Sons, Inc. XVI, 1022 p.
30. Reichert, P., *AQUASIM 2.0 - User Manual, Computer Program for the Identification and Simulation of Aquatic Systems*. 1998, Dübendorf, Switzerland: Swiss Federal Institute for Environmental Science and Technology.
31. Batstone, D.J., et al., *Anaerobic Digestion Model No.1 (ADM1) 2002*, London: IWA Publishing.

A. Appendix

The following table gives a description of all additions made to ADM1 for the modeling of partitioning of PAHs in digested sludge.

Table A.1: Detailed description of all parameters added to ADM1 (continues over 4 pages).

Abbreviation	Description	Unit	Value/Expression	Type of parameter
input_S_Acen	Input concentration of acenaphthene	mg/m ³	1.31	Constant variable
input_S_Acenyl	Input concentration of acenaphthylene	mg/m ³	1.17	Constant variable
input_S_Anth	Input concentration of anthracene	mg/m ³	1.07	Constant variable
input_S_BaA	Input concentration of benzo(a)anthracene	mg/m ³	1.06	Constant variable
input_S_BaP	Input concentration of benzo(a)pyrene	mg/m ³	0.84	Constant variable
input_S_BghiP	Input concentration of benzo(ghi)perylene	mg/m ³	1.04	Constant variable
input_S_Chry	Input concentration of chrysene	mg/m ³	1.77	Constant variable
input_S_DBahA	Input concentration of dibenzo(a,h)anthracene	mg/m ³	0.66	Constant variable
input_S_Fluanth	Input concentration of fluoranthene	mg/m ³	4.42	Constant variable
input_S_Fluo	Input concentration of fluorene	mg/m ³	5.19	Constant variable
input_S_I123cdP	Input concentration of indeno(1,2,3-cd)pyrene	mg/m ³	0.81	Constant variable
input_S_Naph	Input concentration of naphthalene	mg/m ³	6.39	Constant variable
input_S_Phen	Input concentration of phenanthrene	mg/m ³	13.03	Constant variable
input_S_Pyr	Input concentration of pyrene	mg/m ³	5.28	Constant variable
k_ads_Acen	Adsorption rate to organic particles, acenaphthene	1/d	1 000	Formula variable
k_ads_Acenyl	Adsorption rate to organic particles, acenaphthylene	1/d	1 000	Formula variable
k_ads_Anth	Adsorption rate to organic particles, anthracene	1/d	1 000	Formula variable
k_ads_BaA	Adsorption rate to organic particles, benzo(a)anthracene	1/d	1 000	Formula variable
k_ads_BaP	Adsorption rate to organic particles, benzo(a)pyrene	1/d	1 000	Formula variable
k_ads_BghiP	Adsorption rate to organic particles, benzo(ghi)perylene	1/d	1 000	Formula variable
k_ads_Chry	Adsorption rate to organic particles, chrysene	1/d	1 000	Formula variable

Abbreviation	Description	Unit	Value/Expression	Type of parameter
k_ads_DBahA	Adsorption rate to organic particles, dibenzo(a,h)anthracene	1/d	1 000	Formula variable
k_ads_Fluanth	Adsorption rate to organic particles, fluoranthene	1/d	1 000	Formula variable
k_ads_Fluo	Adsorption rate to organic particles, fluorene	1/d	1 000	Formula variable
k_ads_I123cdP	Adsorption rate to organic particles, indeno(1,2,3-cd)pyrene	1/d	1 000	Formula variable
k_ads_Naph	Adsorption rate to organic particles, naphthalene	1/d	1 000	Formula variable
k_ads_Phen	Adsorption rate to organic particles, phenanthrene	1/d	1 000	Formula variable
k_ads_Pyr	Adsorption rate to organic particles, pyrene	1/d	1 000	Formula variable
K_oc_Acen	Equilibrium coefficient for adsorption of acenaphthene to OM	-	4 571	Formula variable
K_oc_Acenyl	Equilibrium coefficient for adsorption of acenaphthylene to OM	-	2 512	Formula variable
K_oc_Anth	Equilibrium coefficient for adsorption of anthracene to OM	-	14 125	Formula variable
K_oc_BaA	Equilibrium coefficient for adsorption of benzo(a)anthracene to OM	-	199 526	Formula variable
K_oc_BaP	Equilibrium coefficient for adsorption of benzo(a)pyrene to OM	-	549 541	Formula variable
K_oc_BghiP	Equilibrium coefficient for adsorption of benzo(ghi)perylene to OM	-	3.16×10^6	Formula variable
K_oc_Chry	Equilibrium coefficient for adsorption of chrysene to OM	-	199 526	Formula variable
K_oc_DBahA	Equilibrium coefficient for adsorption of dibenzo(a,h)anthracene to OM	-	3.31×10^6	Formula variable
K_oc_Fluanth	Equilibrium coefficient for adsorption of fluoranthene to OM	-	38 019	Formula variable
K_oc_Fluo	Equilibrium coefficient for adsorption of fluorene to OM	-	7 244	Formula variable
K_oc_I123cdP	Equilibrium coefficient for adsorption of indeno(1,2,3-cd)pyrene to OM	-	1.51×10^7	Formula variable

Abbreviation	Description	Unit	Value/Expression	Type of parameter
K_oc_Naph	Equilibrium coefficient for adsorption of naphthalene to OM	-	1 202	Formula variable
K_oc_Phen	Equilibrium coefficient for adsorption of phenanthrene to OM	-	14 125	Formula variable
K_oc_Pyr	Equilibrium coefficient for adsorption of pyrene to OM	-	38 019	Formula variable
OC_VSS	Ratio of organic carbon to VSS in sewage sludge	gOC/gVSS	0.537	Formula variable
S_Acen	Freely dissolved acenaphthene	mg/m ³	-	Dynamic volume state variable
S_Acenyl	Freely dissolved acenaphthylene	mg/m ³	-	Dynamic volume state variable
S_Anth	Freely dissolved anthracene	mg/m ³	-	Dynamic volume state variable
S_BaA	Freely dissolved benzo(a)anthracene	mg/m ³	-	Dynamic volume state variable
S_BaP	Freely dissolved benzo(a)pyrene	mg/m ³	-	Dynamic volume state variable
S_BghiP	Freely dissolved benzo(ghi)perylene	mg/m ³	-	Dynamic volume state variable
S_Chry	Freely dissolved chrysene	mg/m ³	-	Dynamic volume state variable
S_DBaHA	Freely dissolved dibenzo(a,h)anthracene	mg/m ³	-	Dynamic volume state variable
S_Fluanth	Freely dissolved fluoranthene	mg/m ³	-	Dynamic volume state variable
S_Fluo	Freely dissolved fluorene	mg/m ³	-	Dynamic volume state variable
S_I123cdP	Freely dissolved indeno(1,2,3-cd)pyrene	mg/m ³	-	Dynamic volume state variable
S_Naph	Freely dissolved naphthalene	mg/m ³	-	Dynamic volume state variable
S_Phen	Freely dissolved phenanthrene	mg/m ³	-	Dynamic volume state variable
S_Pyr	Freely dissolved pyrene	mg/m ³	-	Dynamic volume state variable
S_Acen_ads	Sorbed acenaphthene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Acenyl_ads	Sorbed acenaphthylene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Anth_ads	Sorbed anthracene to organic particles	mg/m ³	-	Dynamic volume state variable
S_BaA_ads	Sorbed benzo(a)anthracene to organic particles	mg/m ³	-	Dynamic volume state variable

Abbreviation	Description	Unit	Value/Expression	Type of parameter
S_BaP_ads	Sorbed benzo(a)pyrene to organic particles	mg/m ³	-	Dynamic volume state variable
S_BghiP_ads	Sorbed benzo(ghi)perylene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Chry_ads	Sorbed chrysene to organic particles	mg/m ³	-	Dynamic volume state variable
S_DBaHA_ads	Sorbed dibenzo(a,h)anthracene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Fluanth_ads	Sorbed fluoranthene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Fluo_ads	Sorbed fluorene to organic particles	mg/m ³	-	Dynamic volume state variable
S_I123cdP_ads	Sorbed indeno(1,2,3-cd)pyrene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Naph_ads	Sorbed naphthalene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Phen_ads	Sorbed phenanthrene to organic particles	mg/m ³	-	Dynamic volume state variable
S_Pyr_ads	Sorbed pyrene to organic particles	mg/m ³	-	Dynamic volume state variable
X_Particles_ads	Particles with adsorptive capacity	kg VSS/m ³	(Biomass+X _I +X _c)/1.42	Formula variable