

Microplastics and Harmful Substances in Urban Runoffs and Landfill Leachates

Possible Emission
Sources to Marine
Environment

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Juho Kilponen

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Mikromuovien ja eräiden haitallisten aineiden esiintymistä hulevesissä sekä suotovesissä on tutkittu melko vähän. Tämän pilottitutkimuksen tarkoituksena oli selvittää muovien ja niihin liittyvien haitallisten aineiden yhtäaikaista esiintymistä hulevesissä ja yhden vanhan suljetun kaatopaikan suotovesissä. Lisäksi työssä pyrittiin arvioimaan mikromuovien ja näiden haitallisten yhdisteiden mahdollista kulkeutumista meriympäristöön.

Haitallisten aineiden ja mikromuovien määrän selvittämiseksi näytteitä otettiin kahdesta näytteenottopisteestä Länsi-Helsingissä joulukuussa 2015 ja huhtikuussa 2016. Ensimmäinen edusti ainoastaan hulevettä ja toinen pääasiassa vanhan suljetun kaatopaikan suotovettä. Molemmat vedet purkautuvat suoraan ympäristöön. Näytteistä analysoitiin mikromuovien sekä eräiden PAH-, PCB-, PBDE- ja PFAS-yhdisteiden sekä ftalaattien pitoisuudet.

Mikromuoveja ja haitallisia aineita löytyi jokaisesta tutkitusta näytteestä. Mikromuoveista kuituja havaittiin enemmän hulevedestä kuin suljetun kaatopaikan viereisestä Mätäjoesta, kun taas synteettisiä partikkeleita oli enemmän Mätäjoessa. Suljettu kaatopaikka osoittautui PAH-, PFAS- ja PCB-yhdisteiden lähteeksi. Korkeimmat PBDE- ja ftalaatti-pitoisuudet havaittiin puolestaan Mätäjoessa.

Orgaanisen aineksen ja kiintoaineen määrä voi vaikuttaa joidenkin huonosti veteen liukenevien haitallisten yhdisteiden pitoisuuksiin erityisesti hulevesissä. Lisäksi sateen vaikutus erityisesti suljetulta kaatopaikalta huuhtoutuvien yhdisteiden pitoisuuksiin voi olla merkittävä. Eräät PAH-yhdisteet ylittivät kaatopaikan viereisessä Mätäjoessa sekä Haagan hulevedessä niille asetetut raja-arvot.

Asiasanat: PAH, ftalaatit, PCB, PBDE, PFAS, hulevedet, suotovedet, mikromuovit

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ABSTRACT

Knowledge and studies on the occurrence of microplastics and certain harmful substances in urban runoffs and landfill leachates is still scarce. The aim of this pilot study was to estimate the simultaneous occurrence of plastics and plastic related pollutants in urban runoffs and leachates in an old and closed landfill located close to the shoreline. In addition, the role of urban runoffs and landfill leachates as an emission source to marine environment was estimated.

Samples were taken from two locations in western Helsinki in December 2015 and in April 2016. The first sampling point represented urban runoff alone and the second sampling point mainly leachates from a former landfill. The urban runoff and leachates are discharged directly into the environment. Microplastics as well as certain PAHs, PCBs, phthalates, PBDEs and PFASs were analyzed from these samples.

Microplastics and harmful substances were detected in all the samples. Considering microplastics, fibres were found more in the urban runoff samples than in the Mätäjoki brook next to the former landfill, where, on the other hand, the concentration of synthetic particles was higher. The former landfill turned out as a source of PAHs, PCBs and PFASs to the environment, whereas PBDEs and phthalates were detected with higher concentrations in the Mätäjoki brook.

The amount of organic and solid material may affect on the concentrations of certain substances of lower water solubility especially in the runoffs. Moreover, the influence of heavy rain especially to the concentrations of leachates can be significant. Certain PAH compounds exceeded certain limit values in the urban runoff of Haaga and the Mätäjoki brook next to the former landfill.

Key words: PAH, phthalates, PCB, PBDE, PFAS, urban runoffs, landfill leachates, microplastics

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LIST OF ABBREVIATIONS

GC-MS	Gas chromatograph-mass spectrometer
K_{ow}	Octanol-water partition coefficient
MP	Microplastic
OCP	Organochlorine pesticide
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
PE	Polyethylene
PET	Polyethylene terephthalate
PFAS	Perfluorinated alkylated substance
POP	Persistent organic pollutant
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride

1 INTRODUCTION

Plastic has become an essential material for the present, modern living. Its cost-effectiveness with unique properties such as resistance in terms of temperature, light and chemicals as well as mouldability with strength makes it suitable for a wide range of uses. The uses of plastic cover products from the packaging and construction industry to a large variety of household products. (Andrady & Neal 2009.)

Due to the above, plastic also poses some serious problems to the environment, especially in the marine environment. Plastics are able to fragment to smaller pieces in the environment but complete natural biodegradation does not take place within any reasonable time scale. (Rios, Moore & Jones 2007.) Plastic can end up to the oceans via various routes. Land-based sources have been approximated to account up to 80% of the total litter in the oceans whereas the remaining part originates from sea based activities such as fishing, transportation and aquaculture. (Andrady 2011.) The most important land-based sources are insufficiently managed landfills, waste dumping, littering and transportation via waste water treatment plants, urban runoffs and rivers (UNEP 2005). Plastic can end up to the environment as larger items and fragments called mega- and macroplastics as well as smaller particles called microplastics (Barnes, Galgani, Thompson & Barlaz 2009).

In the marine environment, in addition to physical harm such as entanglement and ingestion, plastics are able to transport pathogens, alien species and even hazardous substances for long ranges. It is assumed that plastics can also enhance the bioaccumulation of certain hazardous substances via animal ingestion. (Munne 2016.)

Many plastic polymers often require additives to improve their properties. Additives can be used as plasticizers, stabilizers, colouring agents and flame retardants. Phthalates are an example of one widely used plasticizer whereas polybrominated diphenyl ethers (PBDE) were commonly used as flame retardants in plastics. (Andrady & Neal 2009; Darnerud, Eriksen,

Jóhannesson, Larsen & Viluksela 2001.) Moreover, perfluorinated alkylated substances (PFAS) are used as additives in plastic products which require stain, water and grease repellent properties (Miljødirektoratet 2013). In addition, plastic may contain other undesirable substances such as polycyclic aromatic hydrocarbons (PAH), which can be generated during plastic production as a byproduct (Bergmann, Gutow & Klages 2015).

In addition to additives, the tendency of plastics to adsorb contaminants on surfaces has created a new kind of concern (Bergmann et al. 2015.) Many hydrophobic, hazardous substances belonging to the group of organo chlorine pesticides (OCP), polychlorinated biphenyls (PCB) and PAHs have been discovered to be adsorbed on plastics. These compounds may eventually end up into the food webs via plastic ingestion (Rios et al. 2007). However, the recent findings have given only few answers on the actual harm of plastic related contaminants, and actually raised more very basic questions. For example, the knowledge on the simultaneous occurrence of microplastics and harmful substances related to them in the urban runoffs and landfill leachates still remains scarce.

This first pilot study contributes to Finnish national research on the occurrence of plastic particles and hazardous substances in the urban environment. The aim of the study is to clarify the simultaneous occurrence of plastics and certain plastic related pollutants as well as the significance of urban runoffs and leachates as a source and a pathway to marine environment.

2 PRODUCTION OF PLASTIC

2.1 Production and lifespan of plastic

The production of existing plastic began in the nineteenth century as the development of modern thermoplastics started (Andrady & Neal 2009). In the time period from 1950 to 2009, the global production of plastic has increased annually approximately 9 per cent (PlasticsEurope 2010). In 2014, the global plastic production reached 311 million tonnes. The trend of production is expected to grow even more in the future. (PlasticsEurope 2015; Statista 2016.)

In 2013, the largest sectors of plastic use of the total European demand were packaging (39.6%) and building/construction (20.3%) together with a sector which includes household and consumer appliances, furniture, sport, safety and health (21.7%). The remaining share is comprised of automotive (8.5%), electrical/electronics (5.6%) and agriculture (4.3%). In 2012, 62 % out of 25.2 million tonnes of post-consumer plastics in Europe was either recycled or utilized as energy whereas the remaining 38 % was landfilled. (PlasticsEurope 2015.)

It has to be taken into account that there are some challenges regarding the recycling of plastic due to some additives considered as persistent organic pollutants (POP) in certain articles. Incineration is the only way to handle and destroy the POP content when certain limit values are exceeded. Compounds classified as POPs, such as some of the flame retardants (polybrominated diphenyl ethers, PBDE) and perfluorinated alcyated substances (perfluorooctanesulfonic acid, PFOS), have been used earlier in surface finishing chemicals and as additives in plastic-based polymers. These compounds can be found for instance in furniture, electronics and building materials. (Moliis & Myllymaa 2013.)

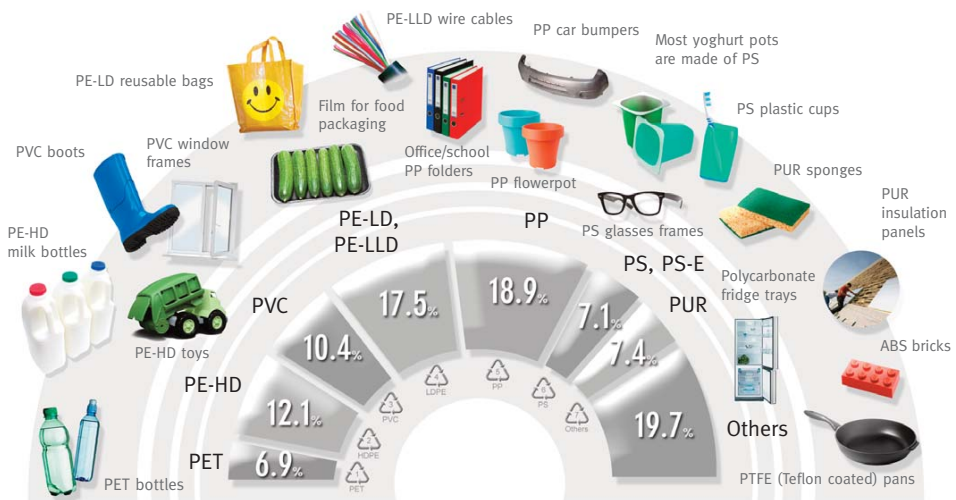
The global estimates of marine litter entering the ocean vary from 6.4 to 8 million tonnes annually. The role of proper waste management is a major

part of the problem as plastic can be carried by wind, rivers and runoffs among the waste due to insufficient waste collection and landfill maintenance. (UNEP 2005.)

2.2 Commodity plastics

Regardless of the great amount of plastic materials available on the market, due to relatively low price and high volume, nearly 90 % of the global plastic demand by weight is covered by low-density (LDPE) and high-density (HDPE) polyethylene, polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) and polyvinyl chloride (PVC) (Andrady & Neal 2009). Figure 1 presents demand of plastics in Europe by polymer type in 2013.

Different plastics for different needs



European plastics demand* by polymer type 2013
 Source: PlasticsEurope (PEMRG) / Consultic / ECEBD
 * EU-27+NO/CH

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FIGURE 1. European demand of plastics by polymer type in 2013 (PlasticsEurope 2015)

2.2.1 Polyethylene

Polyethylene (PE) is the most common plastic resin class globally. Considering the average densities of polyethylene, it is categorized in different grades such as linear low density polyethylene (LLDPE), low density polyethylene (LDPE), medium density polyethylene (MDPE) and high density polyethylene (HDPE). The latter and LDPE are the most commonly used. (Andrady & Neal 2009.) The average density of polyethylene varies from 0.92 to 0.96 g/cm³ (Tripathi 2002). Nearly half of the produced polyethylene resin is used in plastic film products, such as carrier and freezer bags, cling wrap and irrigation hoses. Other common applications include containers with a wide range of volume from detergent and milk bottles to water and chemical barrels hundreds of litres in size. It is also used in electrical cables as insulant. (Andrady & Neal 2009.) Additives are not common in polyethylene as products made of polyethylene are very flexible, especially LLDPE and LDPE which are commonly used in packaging. In a few applications demanding fire resistant properties, such as cable insulations, flame retardants are added. Also colorants are used. (Hansen, Nilsson, Lithner & Lassen 2013.)

2.2.2 Polypropylene

Polypropylene (PP) is the second most widely used thermoplastic due to its cost-effectiveness as well as diversity in terms of mouldability and formability. It is used especially in food industry as thin-walled containers, barrier film pouches and stackable crates. It can be found in building applications, for example as water pipes and geomembranes, and widely in household and personal goods as bowls, kettles and combs. (Andrady & Neal 2009.) The average density of PP is 0.90 g/cm³ and therefore it is the lightest of the commonly used thermoplastics (Tripathi 2002). As polypropylene is not oxidation resistant, it is usually stabilized with antioxidants. Other additives used are colorants and flame retardants. (Hansen et al. 2013.)

2.2.3 Polyvinyl chloride

Polyvinyl chloride (PVC) is an exceptional plastic resin type due to its chlorine content. Hence it is non-combustible and used only in long-lasting products in buildings and furniture for example as piping and upholstery. It differs from the other common plastic resins by its production process as it is in the form of white powder which is afterwards blended with other ingredients. (Andrady & Neal 2009.) The average density of polyvinyl chloride is 1.4 g/cm^3 (Tripathi 2002). Polyvinyl chloride has flame retardant properties and therefore flame retardants are not usually added. Other additives used are colorants, stabilizers and plasticizers. (Hansen et al. 2013.)

2.2.4 Polystyrene

Polystyrene (PS) is mainly used as two different grades; for general purpose and high-impact (HIPS) grade reinforced by polybutadiene for more heavy-duty usage. Due to its mouldability and insulating capability expanded polystyrene (EPS) is commonly used in consumer goods as cups and trays as well as in buildings in insulation panels and industrial packaging for example for TVs and washing machines. (Andrady & Neal 2009; Climate and Pollution Agency 2011.) The average density of polystyrene varies from 1.04 g/cm^3 to 1.07 g/cm^3 (Hansen et al. 2013). Colorants are used as additives in polystyrene. For example in building insulation applications, flame retardants are added into expanded and high-impact polystyrene. (Hansen et al. 2013.)

2.2.5 Polyethylene terephthalate

A few exceptional properties, such as transparency, lightweight and carbon dioxide permeation makes polyethylene terephthalate (PET) potentially suitable for bottles, and therefore it is the prevalent plastic resin type in bottle production. In comparison to other common plastic resin types its oxygen and carbon dioxide permeation ability is considerable. (Andrady & Neal 2009.) The average density of polyethylene terephthalate

varies from 1.33 g/cm^3 to 1.4 g/cm^3 (Hansen et al 2013). Having high chemical resistance only colorants are common additives in polyethylene terephthalate (Hansen et al. 2013).

3 PLASTICS IN THE ENVIRONMENT

3.1 Degradability of plastics

Degradation of plastics is defined as any kind of deterioration of properties. In practice, degradation of plastics is seen as fragmentation into smaller particles and as weathering. In general, weathering occurs especially in polymers which are used in outdoor applications when exposed to high temperature conditions, UV radiation and oxygen. Therefore, in order to obtain resistance against environmental impacts such as light, heat and oxygen, stabilizers are used as additives in nearly all polymers. (Yousif & Haddad 2013.) Consequently, the complete natural biodegradation of plastic is a very slow process as commonly used plastics are not particularly designed to naturally degrade in the environment but conversely to be persistent (Webb, Arnott, Crawford & Ivanova 2012).

Degradation of plastic is known to take at least 20 years in landfill environment. As thermo-oxidative degradation is the prevalent mechanism of degradation in landfills the limited oxygen availability retards the process. (Webb et al. 2012.) However, other circumstances of landfill such as elevated temperatures, pH and physical compacting are factors which contribute to more rapid plastic degradation (Sundt et al. 2014).

By the time a plastic object has fragmented into smaller particles it may have undergone several different degradation mechanisms. Depending on the circumstances, different degradation mechanisms may take place simultaneously, and, therefore, affect considerably on the rate of degradation. In the case of common polymers, the natural degradation generally starts with photodegradation leading to thermo-oxidative degradation. (Andrady 2011.) The resulting fragile particles continue fragmenting until the molecular mass of the particles is low enough for micro-organisms to metabolize (Gnanavel et al. 2012). In the marine environment hydrolysis is not considered as a significant mechanism of degradation (Andrady 2011). In fact, it has been shown that the

degradation process is retarded in the sea water in comparison to land environment (Andrady, Pegram & Song 1993 as cited in Andrady 2011).

3.2 Degradation mechanisms of plastics

In photodegradation photons with wavelengths occurring in sunlight such as visible light, UV light and infrared radiation, are being absorbed into photodegradable molecule resulting polymer break down, free radicals and decrease in molecular weight. This causes deterioration of mechanical properties in polymers. In the presence of oxygen and elevated temperatures photodegradative process may proceed as photo-oxidative and thermo-oxidative degradation. (Yousif & Haddad 2013.)

Oxidation occurs at high temperatures for most polymers. Primary products of oxidation of polyalkenes such as polyethylene and polypropylene are hydroperoxides which with the presence of radicals cause cleavage in the polymer chain. Thermo-oxidative degradation is highly dependent on the plastic structure and therefore it differs between plastic types. For example low-pressure polyethylene loses whole mechanical strength when exposed to 100 °C for 48 h in the presence of air whereas polypropylene film degrades completely after short-term heating at 100 °C. (Crompton 2010.)

In biodegradation polymers are decomposed biologically and the process is initiated by enzymes of micro-organisms, mostly by bacteria. In biodegradation the micro-organism attaches to the polymers surface and it follows growth when micro-organism utilizes the polymer as a carbon source. Eventually mineralization takes place as the polymer is degraded. Biodegradation is dependent on the chemical structure of the polymer and former degradation conditions and therefore the rate of degradation varies on different polymer types. (Gnanavel, Mohana Jeya Valli & Thirumarimurugan 2012.)

3.3 Emissions and effects of plastics in the environment

3.3.1 Size classification of environmental plastics

Plastics in the marine environment can be coarsely classified in two main groups based on their size: microplastics and macroplastics. The definition of microplastics varies among researchers but according to a workshop convened by the National Oceanic and Atmospheric Administration (Arthur, Baker & Bamford 2009) they are defined as plastic particles less than 5 mm in size. Consequently plastic pieces above 5 mm are considered as macroplastics. (Arthur et al. 2009.) However, depending on the researcher plastic particles less than the defined size are occasionally referred as microplastics (Andrady 2011). To be specific, the smaller classified group of plastic particles are characterized smaller than 1 μm in size and termed as nanoplastics (Bergmann et al. 2015).

3.3.2 Origins and occurrence

Microplastics can be divided as primary and secondary microplastics. Primary microplastics are intentionally produced microbeads or microspheres used in consumer products for example in exfoliating personal care products or in commercial or industrial products and processes as abrasive media as well as in specialty chemicals and medical applications. Also resin pellets used in plastic production are classified as primary microplastics. Secondary microplastics cover fragments of larger particles as well as fibres originated from textiles. (Sundt et al. 2014.)

Considering urban runoffs, sources include plastic dust emissions originating cities such as abrasion of tires, road paint and other paints weathering from exterior surfaces. Moreover waste handling and recycling creates microplastics. (Sundt et al. 2014.) Microsized particles easily end up into the aquatic environments via runoffs and some cases even via landfill leachates (Andrady 2011; Sundt et al. 2014).

3.3.3 Effects in the marine environment

In general, the polymer types of smaller density than the seawater are buoyant. The sea water density is mainly result from temperature and salinity of the sea water, increasing with both of these variables. The average seawater density is 1.03 g/cm^3 . (Wright & Colling 1995.) Average densities of common polymers are shown in Table 1. However, plastic may sink when its density increases due to waterlogging or in adsorbition of epibiota and consequently plastic has been found globally on the seabed. (Barnes et al. 2009.) It is estimated that only 15 % of the marine litter that enters the sea floats, 15 % ends up to beaches and the remaining 70 % sinks to the seabed (UNEP 2005).

TABLE 1. Average densities of common polymers (Tripathi 2002; Hansen et al. 2013)

Polymer type	Average density
Polyethylene (PE)	$0.92\text{-}0.96 \text{ g/cm}^3$
Polypropylene (PP)	0.90 g/cm^3
Polyvinyl chloride (PVC)	1.4 g/cm^3
Polystyrene (PS)	$1.04\text{-}1.07 \text{ g/cm}^3$
Polyethylene terephthalate (PET)	$1.33\text{-}1.4 \text{ g/cm}^3$

Hundreds of marine species are affected by marine debris, mainly plastics. Main problems arising from encounter of plastic and marine organisms are ingestion and entanglement. (Secretariat of the Convention on Biological Diversity 2012.) The species affected by plastic covers all trophic levels including invertebrates, fishes, reptiles, birds and marine mammals. (NOAA 2014a.)

Entanglement causes physical troubles by disrupting feeding, decreasing moving ability which may lead to serious injuries and eventually death (NOAA 2014b). It has been reported that approximately 136 species suffer from engtangement worldwide, including sea turtles, marine mammals, sea birds, fishes, crustaceans and squids (Laist 1997). On the contrary,

ingestion of plastic by marine species is a problem which impacts are not well enough known so far (NOAA 2014a). The rates of which plastic ingestion has been reported to occur are relatively high: for example 86% of sea turtle species (6 out of 7), 36% of sea birds and 23% of marine mammals with total number of 177 species have been evinced to ingest marine plastic. (Laist 1997.)

It is still being studied how contaminants attached to plastic really affect organisms as a consequence of the plastic ingestion. There are some species which have the ability to excrete debris from their system in a way it passes not through their digestive system. However, regarding some species plastic has been reported to pass through their digestive system with extended time periods. (NOAA 2014a.) This may cause for example reduction in food intake and gastrointestinal blockages (Barnes et al. 2009; Teuten, Saquing, Knappe, Barlaz, Jonsson, Björn, Rowland, Thompson, Galloway, Yamashita, Ochi, Watanuki, Moore, Viet, Tana, Prudente, Boonyatumanond, Zakaria, Akkhavong, Ogata, Hirai, Iwasa, Mizukava, Hagino, Imamura, Saha, & Takada 2009). It has been shown that for example in some invertebrates transference through guts epithelial lining into body tissues may occur (Browne, Dissanayake, Galloway, Lowe & Thompson 2008). This arises major concern with regard to the hazardous substances that plastic particle may transport inside the organisms.

Research on effects of different plastic and contaminant mixtures is required. It has been found that for example the duration of microbial degradation of a certain PAH compound, phenantrene, differs between polyethylene and polypropylene polymers. (Hatzinger & Alexander 1997). Therefore it is difficult to study interactions between different contaminant and plastic mixtures due to their complexity. Plastic can have an increasing effect, among other things, on the environmental persistence of the contaminants besides their transport abilities (Teuten et al. 2009). Plastic related pollutants determined in the study are shown in Figure 2.

Plastic related pollutants

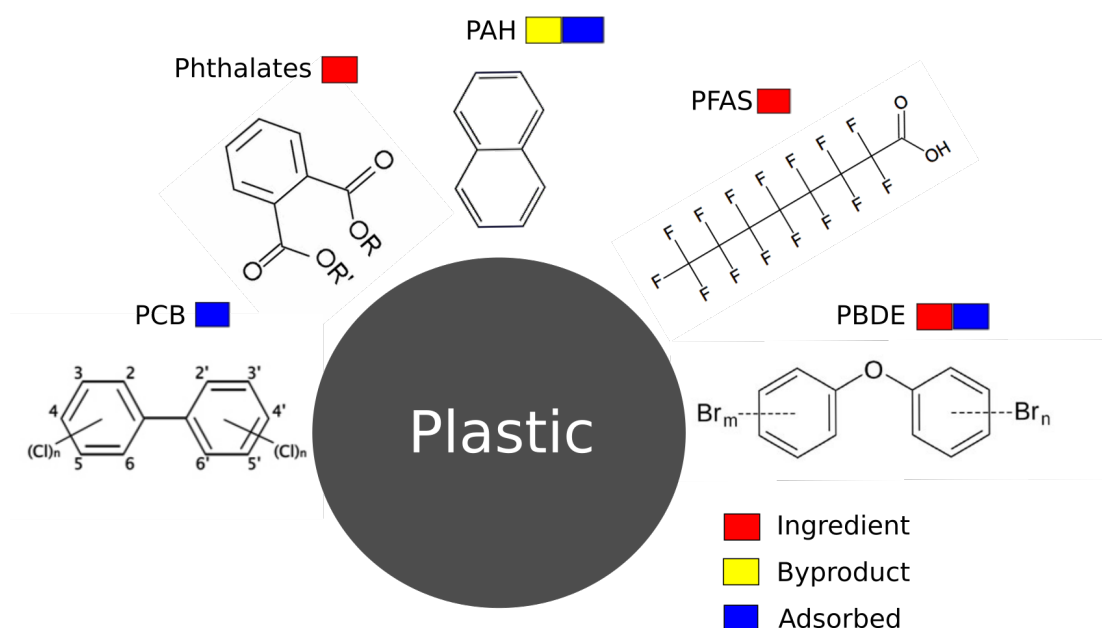


FIGURE 2. Adsorbed (PCB), ingredients (phthalates, PFAS, PBDE) and byproduct (PAH) pollutants related to plastic determined in the study.

(Modified from the original figure from Bergmann et al. 2015; Kallenborn, Berger & Järnberg 2005; Barcelò, Al-Harbi, Karapanagioti, Ginebreda, Llorca & Sanchis 2012)

4 HAZARDOUS SUBSTANCES RELATED TO PLASTICS

4.1 Polycyclic aromatic hydrocarbons

Fundamentally hydrocarbons consist purely of hydrogen and carbon. Hydrocarbons occur naturally in two forms: either nonaromatic or aromatic with regard to its structure. Aromatic hydrocarbons are often composed of multiple fused rings. (Walker 2009.) Phenantrene that belongs to the group of polyaromatic hydrocarbons (PAH) is shown in Figure 3. Known PAH compounds are more than 100 but Environmental Protection Agency (EPA, US) has prioritized 16 PAH compounds based on their importance (Lassen, Hoffmann & Thomsen 2011). These compounds are determined in the study and they are listed in Table 2.

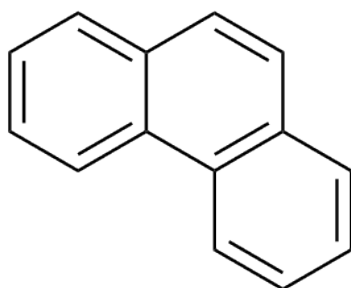


FIGURE 3. Chemical structure of phenantrene (ChemWiki 2016)

The main sources of PAHs to environment are incomplete combustion of organic compounds and crude oil discharges. The atmospheric PAH emissions caused by combustion eventually ends up in surface waters due to precipitation or diffusion of particles. (Walker 2009.) PAHs can be found in plastic itself as byproduced for example in extender oils and carbon black to improve a number of the properties of plastic (Bergmann et al. 2015; Lassen et al. 2011). Products known to contain PAHs include

for example tyres and other products which contain rubber as well as variety of toys (Lassen et al 2011). Therefore, in addition to the direct leaching, the disposal of waste containing PAHs might be a possible emission source via leachates to marine environment as well.

The harmfulness of aromatic hydrocarbons to environment as well as human health is due to their carcinogenic and mutagenic properties. (Walker 2009.) As having low water solubility and high octanol-water partition coefficients (K_{ow}) PAHs are hydrophobic and therefore tend to become adsorbed to aquatic organisms, and as recent studies (Fisner, Taniguchi, Moreira, Bicego & Turra 2013; Rios et al. 2007) evinces, to microplastics. (Walker 2009; Stogiannidis & Laane 2015.) The water solubility, among other properties, is dependent on the molecular weight of the compound and therefore lower molecular weight PAHs, such as naphthalene (NAP), are more water soluble than PAHs with higher molecular weight. On the contrary, the carcinogenic and mutagenic properties occur mainly in the higher molecular mass PAHs, such as benzo[a]pyrene (BaP). (Stogiannidis & Laane 2015.) As being ingested, some of the aquatic invertebrates biomagnify PAHs. However, higher in the food chain organisms are able to metabolize them and therefore biomagnification does not extend up the food chain. As having no functional groups PAHs are chemically quite nonreactive but in the presence of oxygen and UV radiation photodecomposition may occur resulting oxidative products such as endoperoxines and quinones, which can show significant toxicity to marine species, especially to fish. (Walker 2009.)

TABLE 2. 16 PAH compounds determined in the study

Name	Abbreviation	Molecular formula	CAS-number
Naphthalene	NAP	C ₁₀ H ₈	91-20-3
Acenaphthylene	ACY	C ₁₂ H ₈	208-96-8
Acenaphthene	ACP	C ₁₂ H ₁₀	83-32-9
Fluorene	FLR	C ₁₃ H ₁₀	86-73-7
Phenanthrene	PHE	C ₁₄ H ₁₀	85-01-8
Anthracene	ANT	C ₁₄ H ₁₀	120-12-7
Fluoranthene	FLT	C ₁₆ H ₁₀	206-44-0
Pyrene	PYR	C ₁₆ H ₁₀	129-00-0
Benzo[a]anthracene	BaA	C ₁₈ H ₁₂	56-55-3
Chrysene	CHR	C ₁₈ H ₁₂	218-01-9
Benzo[b]fluoranthene	BbF	C ₂₀ H ₁₂	205-99-2
Benzo[k]fluoranthene	BkF	C ₂₀ H ₁₂	207-08-9
Benzo[a]pyrene	BaP	C ₂₀ H ₁₂	50-32-8
Indeno[1,2,3-cd]pyrene	IcP	C ₂₂ H ₁₂	193-39-5
Dibenzo[a,h]anthracene	DhA	C ₂₂ H ₁₄	53-07-3
Benzo[ghi]perylene	BgP	C ₂₂ H ₁₂	191-24-2

4.2 Polychlorinated biphenyls

Polychlorinated biphenyls (PCB) are a group of synthetic compounds used widely in industry. In commercial use PCBs occur in various mixtures of congeners manufactured by chlorinating biphenyls. (Walker 2009.)

Fundamentally PCBs consist of two phenyl rings with delocalized electrons. This is shown in Figure 4.

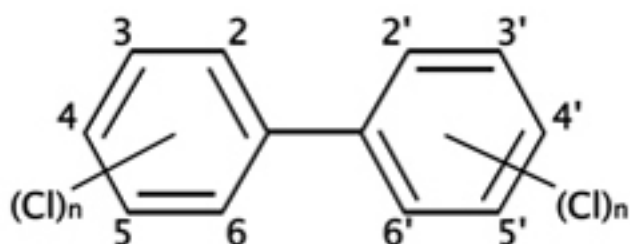


FIGURE 4. The fundamental structure of polychlorinated biphenyls (Trèdi 2016)

Chlorine substitutes some of the hydrogens of the phenyl rings. The resulting formation is called congener. If considering all the possible variations of chlorine substitution, in theory PCBs has 209 different congeners. Approximately 130 congeners have been found in commercial products. The amount of chlorinated congeners indicates the chlorination level of a PCB compound. (Walker 2009.)

The uses of PCBs are diverse: they are used for example in electronics as insulators in capacitors and transformers, in transferring heat, in oil production and as plastizicers mainly in paints (Walker 2009). In general PCBs occur in mixtures of different congeners. In the present PCBs are not produced due to their harmfulness but they are still released to the environment via hazardous waste from landfills and irregular hazardous waste sites as well as from PCB containing waste incineration. (U.S. Department of Health and Human Services 2000.)

PCBs are chemically low reactive and stable compounds occurring in quite high densities. In general PCBs are of low water solubility and high lipophilicity. The water solubility decreases and octanol-water partition coefficient (K_{ow}) increases as the level of chlorination increases. (Walker 2009.) As being easily volatile PCBs may drift long distances from the

original releasing point via air (U.S. Department of Health and Human Services 2000). Consequently PCBs have been found widely in the environment, including sea water and sediment. As being hydrophobic they tend to become adsorbed to solid particles in the sea. Adsorption on plastic has been found to occur for example in the case of plastic resin pellets. (Endo, Takizawa, Okuda, Takada, Chiba, Kanehiro, Ogi, Yamashita & Date 2005.) PCBs are listed as persistent organic pollutants (POP) to the Stockholm Convention. They have been found toxic especially to fish, and in addition they have been found to have harmful effects on reproduction and immune system of various species. (Stockholm Convention 2016.) They are found to bioaccumulate especially in marine mammals and fish and therefore they extend up in the food chain. (U.S. Department of Health and Human Services 2000.) PCB congeners determined in the study are shown in Table 3.

TABLE 3. PCB congeners determined in the study

Name	Abbreviation	CAS-number
2,2',4,5,5'-Pentachlorobiphenyl	PCB-101	37680-73-2
2,3,3',4,4'-Pentachlorobiphenyl	PCB-105	32598-14-4
2,3,3',4',6-Pentachlorobiphenyl	PCB-110	38380-03-9
2,3',4,4',5-Pentachlorobiphenyl	PCB-118	31508-00-6
2,2',3,4,4',5'-Hexachlorobiphenyl	PCB-138	35065-28-2
2,2',3,4',5',6-Hexachlorobiphenyl	PCB-149	38380-04-0
2,2',4,4',5,5'-Hexachlorobiphenyl	PCB-153	57465-28-8
2,3,3',4,4',5-Hexachlorobiphenyl	PCB-156	38380-08-4
2,2',3,3',4,4',5-Heptachlorobiphenyl	PCB-170	35065-30-6
2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB-180	35065-29-3
2,2',3,4',5,5',6-Heptachlorobiphenyl	PCB-187	52663-68-0
2,4,4'-Trichlorobiphenyl	PCB-28	7012-37-5
2,4',5-Trichlorobiphenyl	PCB-31	16606-02-3
2,2',5,5'-Tetrachlorobiphenyl	PCB-52	35693-99-3
2,3',4,4'-Tetrachlorobiphenyl	PCB-66	32598-10-0

4.3 Phthalates

Phthalates are a group of substances consisting of phthalate esters produced from oil by alcohol esterification. Phthalates are used in the plastic production as additives, in general termed as plasticizers. (Cousins, Remberger, Kaj, Ekheden, Dusan & Brorström-Lundén 2007.) The function of plasticizers in plastics is to improve their workability and flexibility (European Chemicals Bureau 2008). In the basic structure another ring of the two original fused phenyl rings is occupied by four oxygens of which two is bounded by double bonds. The structure is shown in Figure 5.

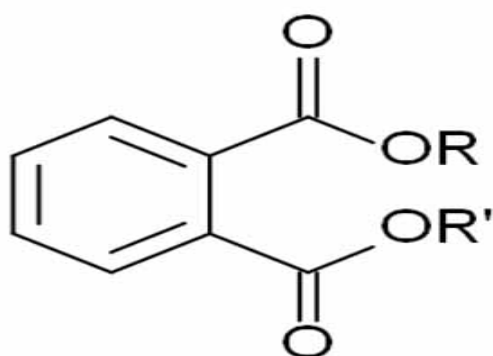


FIGURE 5. Fundamental structure of phthalate ester (Markes International 2013)

With regard to their prevalent additive usage in flexible PVC products phthalates are very widespread. These products are produced for industrial and consumer uses including a large amount of building insulation products such as wires and cables, flooring, roof and wall covering and sealants as well as clothing, car products, for example under coatings and car seats, shower curtains and prints on textiles among other products. (Hansen et al. 2013.) Especially, previously the most common plasticizer, di(2-ethylhexyl) phthalate (DEHP), is known to be used in polymers, mainly in polyvinyl chloride (European Chemicals Bureau 2008).

It has been found that DEHP percentage by weight in flexible PVC-products is typically 30 % (Kroschwitz 1998 according to European Chemicals Bureau 2008). For example DEHP is assumed to remain persistent during its attachment in the matrix. However, as plasticizers are not chemically attached to the matrix of the polymer leaching occurs, in addition to manufacturing, during usage and after the disposal of the product. During the disposal the largest DEHP emissions originate from landfills via leachates. (European Chemicals Bureau 2008.)

It has been shown that phthalates are not as biodegradative as was previously understood (Beauchesne, Barnabè, Cooper & Nicell 2007). Consequently bioaccumulation in organisms have emerged a new kind of concern. The bioaccumulation appears to vary between the species and depending on the plasticizer. Especially regarding DEHP, bioaccumulation occurs seemingly more in invertebrates than vertebrates. In general, DEHP is considered to be not very water soluble. (Oehlmann, Shulte-Oehlmann, Kloas, Jagnytsch, Lutz, Kusk, Wollenberger, Santos, Paull, Van Look & Tyler 2009.) However, the water solubility and octanol-water partition coefficients (K_{ow}) of DEHP have been reported to range widely. (European Chemicals Bureau 2008). It has been shown that phthalates affect on a large variety of species in marine environment including annelids, molluscs, crustaceans and fishes. The effects are mostly disturbances regarding development and reproduction such as larval development disruption and reduction in offspring production. The species have shown clear altering sensitivity to plasticizers such as DEHP, dimethyl phthalate (DMP), dibutyl phthalate (DBP) and diisononyl phthalate (DINP) with respect to the concentrations in the water. For example the most effects of the named compounds for molluscs and crustaceans occurred in the concentration range of ng/L to µg/L whereas for fish the respective range was from µg/L to mg/L. (Oehlmann et al. 2009.) The determined phthalate compounds in the study are shown in Table 4.

TABLE 4. Phthalate compounds determined in the study

Name	Abbreviation	CAS-number
Dimethyl phthalate	DMP	131-11-3
Diethyl phthalate	DEP	84-66-2
Diisobutyl phthalate	DiBP	84-69-5
Dibutyl phthalate	DBP	84-74-2
Dipentyl phthalate	DPP	131-18-0
Dihexyl phthalate	DHP	84-75-3
Di-2-ethylhexyl phthalate	DEHP	117-81-7
Benzyl butyl phthalate	BBP	85-68-7
Diocetyl phthalate	DOP	117-84-0
Diisononyl phthalate	DINP	68515-48-0
Diisodecyl phthalate	DIDP	68515-49-1

4.4 Polybrominated diphenyl ethers

Polybrominated diphenyl ethers (PBDE) are a group of substances, mostly associated as plastic additives called brominated flame retardants which were formerly used widely in the plastic production (Darnerud et al. 2001). PBDEs are produced by brominating diphenyl ether. The fundamental structure consists of two phenyl rings attached to each other via oxygen bridge (Ministry for the Environment 2010). The structure is shown in Figure 6.

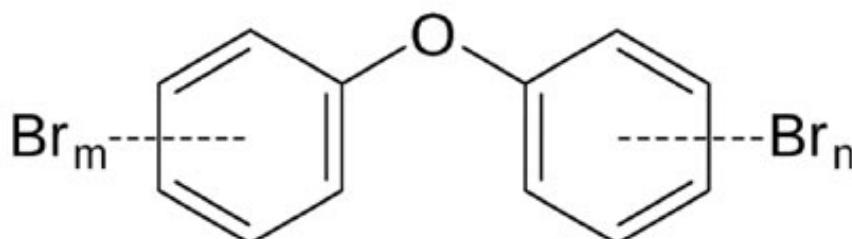


FIGURE 6. Fundamental structure of polybrominated diphenyl ethers (Ministry for the Environment 2010)

Similar to PCBs, PBDEs occur in different congeners depending on the amount and location of bromine atoms on the phenyl rings. In theory, the possible amount of different congeners of PBDEs is 209. (Ministry for the Environment 2010.) Congeners are further divided into 10 congener groups called mono- to decabromodiphenyl ethers. Despite the large theoretical number of congeners, the amount used in commercial products is relatively small. (Darnerud et al. 2001.) The production of commercially the most widely used pentaBDE and octaBDE has been banned in the EU and the United States whereas decaBDE is still in use to a certain extent (Axelrad 2009).

The flame retardant ability of PBDEs is based on chemical reduction and retardation by thermal decomposition of the bromo-organic compound. Therefore the higher bromination level indicates better flame retardant properties. The typical concentrations added varies between 5-30% in products, being commonly used for example in high impact polystyrene (HIPS). Products containing PBDEs include circuit boards and cabinets in televisions and computers, other electronics such as switches, capacitors and cables, textiles and building materials. It has been found that PBDEs leach out from the products during their use. (Darnerud et al. 2001.)

With regard to PBDEs use they are quite resistant in terms of physical, chemical and biologic degradability. In general, PBDEs are lipophilic and of low water solubility which is dependent on the amount of bromine congeners in the mixture. The higher bromination rate of the compound indicates smaller water solubility. High lipophilic ability and degradation resistance follow up the detected accumulation of PBDEs in aquatic organisms and habitats. The extent of accumulation is found to be inverse in relation to the rate of bromination of the PBDE congener. Moreover, PBDEs biomagnify in the food chain of various species. (Darnerud et al. 2001.) Hexa-, hepta-, tetra- and pentaBDEs are classified as POP compounds by the Stockholm Convention. They are the main components

of the commercial octa- and pentaBDEs and especially pentaBDEs have been found to have toxic effects in species. (Stockholm Convention 2016.) PBDEs have been found in several species including marine mammals, fishes and invertebrates (Boon, Lewis, Tjoen-A-Choy, Allchin, Law, de Boer, Tennhällers-Tjabbes & Zegers 2002). PBDEs determined in the study are shown in Table 5.

TABLE 5. PBDEs determined in the study

Name	Abbreviation	CAS-number
2,2',4,4',6-Pentabromodiphenylether	BDE-100	189084-64-8
2,2',4,4',5,5'-Hexabromodiphenylether	BDE-153	68631-49-2
2,2',4,4',5,6'-Hexabromodiphenylether	BDE-154	207122-15-4
2,2',3,4,4',5',6-Heptabromodiphenylether	BDE-183	207122-16-5
2,2',3,3',4,4',5,5',6,6'- Decabromodiphenylether	BDE-209	145538-74-5
2,4,4'-Tribromodiphenylether	BDE-28	41318-75-6
2,2',4,4'-Tetrabromodiphenylether	BDE-47	5436-43-1
2,3',4,4'-Tetrabromodiphenylether	BDE-66	189084-61-5
2,2',3,4,4'-Pentabromodiphenylether	BDE-85	182346-21-0
2,2',4,4',5-Pentabromodiphenylether	BDE-99	60348-60-9

4.5 Perfluoroalkyl substances

Per- and polyfluoroalkyl substances (PFAS) are compounds where fluorine atoms are covalently bonded to carbon chains with various lengths.

Polyfluorinated compounds refer to a compound where fluorine atom has replaced at least one of the hydrogen atoms whereas a compound is perfluorinated when fluorine atoms have replaced all of the hydrogens attached to carbon. (Buck, Franklin, Berger, Conder, Cousins, de Voogt, Jensen, Kannan, Mabury & van Leeuwen 2011.) The structure of a typical compound belonging to PFASs called perfluoro-octanoic acid (PFOA) is shown in Figure 7. Due to the strong C-F bond, PFASs were initially considered biologically inert until the late 1990s when increasing number

of scientific publications showed their potential environmental hazard. (Kallenborn et al. 2005.)

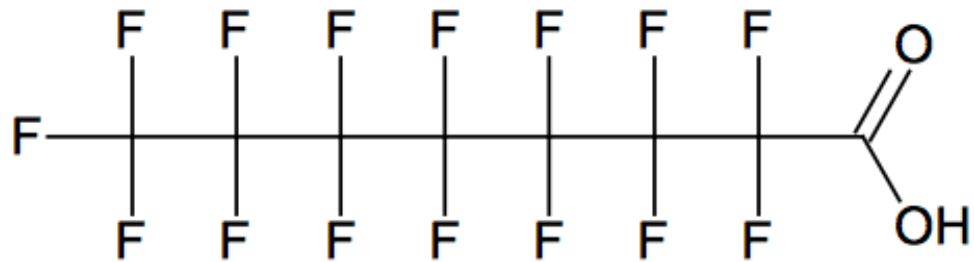


FIGURE 7. Chemical structure of perfluoro-octanoic acid (Barcelò et al. 2012)

Before the concerns on the hazardous nature of PFASs, especially PFOA and perfluorooctanesulfonic acid (PFOS) were widely used in industrial and household products, mainly in surfactants and polymers. In polymers the uses include food-contact papers and materials in cooking, water repellents, grease-proofs and textile stains. Surfactant uses include aqueous film-forming foams (AFFFs) and a number of coatings for example in water-proof purposes in textiles. (Miljødirektoratet 2013.) There are some regulations regarding PFASs, for example perfluorooctane sulfonate (PFOS) is included to the Stockholm Convention and its use in fire fighting foams has been widely banned due to its harmfulness to the environment (Regulation on persistent organic pollutants and amending Directive 79/117/EEC 850/2004). Due to the hazardous nature and wide use of especially longer chain PFASs such as PFOA and PFOS, they have been started to replace by shorter chain PFASs (Biomonitoring California 2015).

Due to their high persistency and wide use, PFASs have been found in the environment, wildlife and humans (Miljødirektoratet 2013). In the marine environment PFASs have been detected in plastic pellets (Barceló et al. 2012). PFASs are both hydrophobic and lipophobic. (Kallenborn et al. 2005). Unlike other conventional persistent compounds PFASs are not sufficiently assessable by risk assessment tools such as octanol-water partitioning coefficient (K_{ow}) due to their strong surface-active properties. Some of the compounds in PFAS group have turned out to be so toxic and persistent that it has raised concerns among scientists and governments on the possibility they might never completely degrade in the environment (Kallenborn et al. 2005). PFASs determined in the study are shown in Table 6.

TABLE 6. PFASs determined in the study

Name	Abbreviation	Carbon chain length	CAS-number
Perfluorobutyric acid	PFBA	4	375-22-4
Perfluoropentanoic acid	PFPeA	5	2706-90-3
Perfluorohexanoic acid	PFHxA	6	307-24-4
Perfluoroheptanoic acid	PFHpA	7	375-85-9
Perfluorooctanoic acid	PFOA	8	335-67-1
Perfluorononanoic acid	PFNA	9	375-95-1
Perfluorodecanoic acid	PFDA	10	335-76-2
Perfluoroundecanoic acid	PFUDA	11	2058-94-8
Perfluorododecanoic acid	PFDoA	12	307-55-1
Perfluorotridecanoic acid	PFTrDA	13	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	14	376-06-7
Perfluorohexadecanoic acid	PFHxDA	16	67905-19-5
Perfluorooctadecanoic acid	PFODA	18	16517-11-6
Perfluorobutanesulfonic acid	PFBS	4	29420-49-3
Perfluorohexanesulfonic acid	PFHxS	6	3871-99-6
Perfluoroheptanesulfonate acid	PFHpS	7	335-77-3
Perfluorooctanesulfonic acid	PFOS	8	1763-23-1
Perfluorodecanesulfonic acid	PFDS	10	13419-61-9

5 SAMPLING

5.1 Sampling method and materials

5.1.1 Microplastics

Microplastic samples were collected by using a specific sampling device. The device was built from three transparent tubes made of plastic (diameter 60 mm) which were attached to one another by screwable plastic connectors. To ensure strong attachment, O-rings made of rubber were used between the connectors. Round shape filters (diameter 80 mm) made of plankton net were placed between the connectors, the largest mesh size on the top and the smallest at the bottom of the device. The mesh sizes of the filters were 300 μm , 100 μm and 20 μm . Motor-driven pump (HondaWX15) was used to pump the water into the filter device from the water stream. To measure the volume of the sample flow meter attached to the pump was used. (Talvitie, Heinonen, Pääkkönen Vahtera, Mikola, Setälä & Vahala 2015.) The sampling device is shown in Figure 8.



FIGURE 8. The sampling device for microplastics

5.1.2 Water samples for the determination of hazardous substances

Samples were collected into glass jars directly from the urban runoff sewer and leachate by placing the bottle opening against the stream. Sample size was 1 liter excluding phthalate sample which required sample size of 2 liters. Phthalate sample jar was covered with aluminum foil in order to prevent loss due to UV radiation. All samples were kept cold during transportation.

5.2 Description and background of the sampling points

The samples were taken at two different locations in the western part of Helsinki which are shown in Appendix 8. In Southern Haaga samples were collected on the opening of an urban runoff sewer pipe. In the other sampling site, the former landfill of Tali, the samples were taken from two points close to each other: from the Mätäjoki brook and directly from the landfill leachate running into the Mätäjoki brook from the former landfill of Tali. The first samples for the determination of hazardous substances were taken from both the Mätäjoki brook and from the leachate. PCBs were not included in the runoff samples of Haaga. Collected samples by sampling points and dates are described in Table 7.

TABLE 7. Sampling dates and collected samples by sampling points.

Sampling date	Haaga (runoff) 60°12'41.5"N 24°53'59.8"E	Mätäjoki (brook) 60°12'47.6"N 24°51'03.6"E	Tali (leachate) 60°12'47.6"N 24°51'03.6"E
18.12.2015	PAH, PHTH, PBDE, PFAS, MP	PAH, PHTH, PCB, PBDE, PFAS	
21.12.2015		MP	PAH, PHTH, PCB, PBDE, PFAS
18.4.2016	PAH, PHTH, PBDE, PFAS, MP	MP	PAH, PHTH, PCB, PBDE, PFAS

5.2.1 Sampling point in southern Haaga

The samples were collected directly from the runoff water on the opening of the sewer pipe where the rainwater system discharges into the Haaganpuro brook. The location of the sampling point is shown in Figure 9.

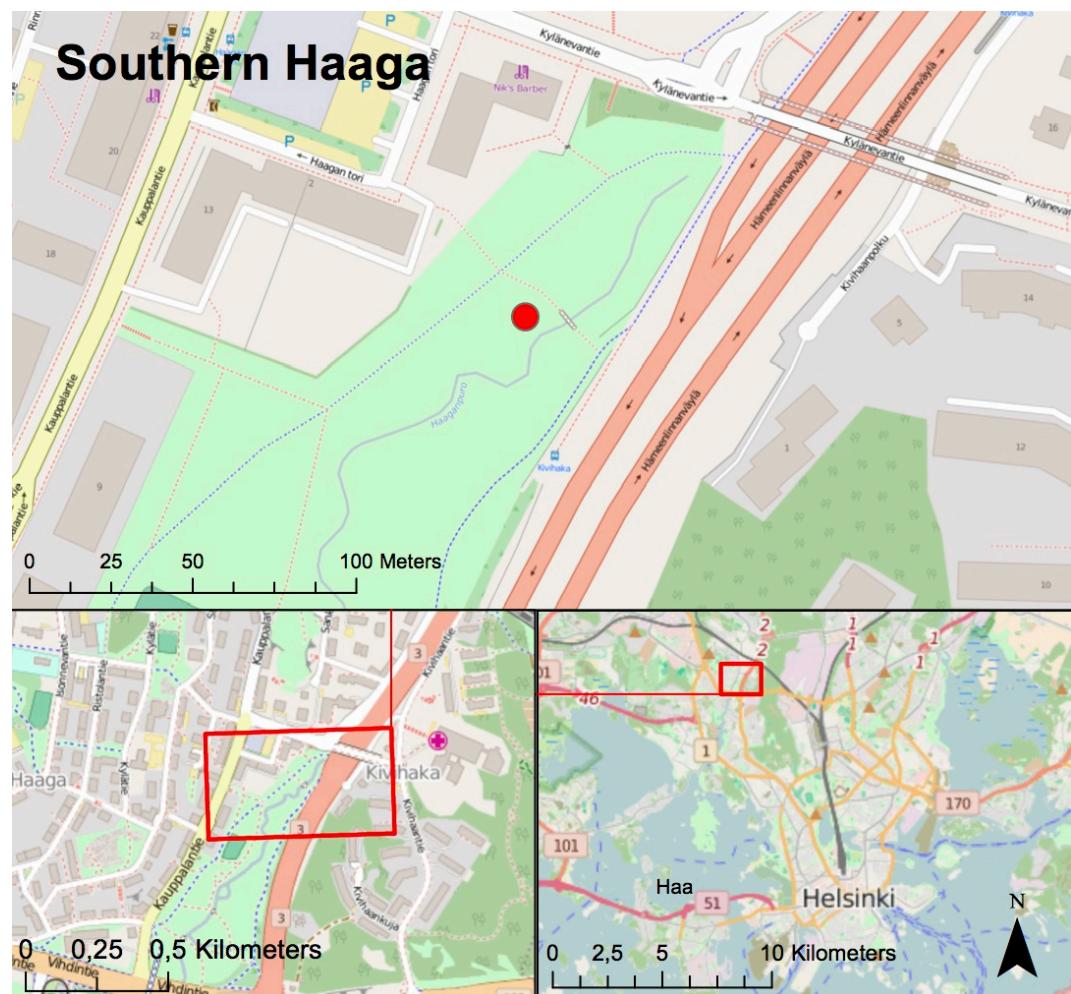


FIGURE 9. Location of the sampling point of southern Haaga in western Helsinki

Urban runoffs in Haaga district are collected to a rainwater system which discharges into the Haaganpuro (former Mätäpuro) brook in southern Haaga. The drainage area of the urban runoff system covers apartment house areas, day care centers and schools, and the runoffs originate from

paved areas such as streets, car parks and courtyards. The area includes also a part of a railway zone. The areas in between the buildings consist mainly of urban forests. (Airola, Nurmi & Pellikka 2014.) The drainage area of the rainwater system is shown in Figure 10.



FIGURE 10. Map of the drainage area of the rainwater system (Airola et al. 2014)

The Haaganpuro brook is a 11.6 km long urban brooke originating from Maununneva in north-eastern of Helsinki. The drainage basin covers an area of 10.7 km². The Haaganpuro brooke discharges eventually into the bay of Pikku-Huopalahti, Baltic Sea. (Saikku 2016.)



FIGURE 11. The discharge pipe of the urban runoff system of Southern Haaga

5.2.2 Sampling points in Tali

The sampling point was nearby the river mouth of the Mätäjoki brook, approximately 400 meters away from the bay of Iso Huopalahti. The samples were taken from the Mätäjoki brook and directly from the landfill leachate discharged into the brook. The latter is seen in Figure 14. It is known that there are several other leachate discharge points running into the Mätäjoki brook from the landfill. Because microplastic analysis required high volume of water to be filtered the samples were taken from the Mätäjoki brook instead of straight from the leachate. The Mätäjoki brook sample is therefore a mix of different waters from leachates, brook water, urban runoffs to possibly sea water. The location of the sampling point is shown in Figure 12.

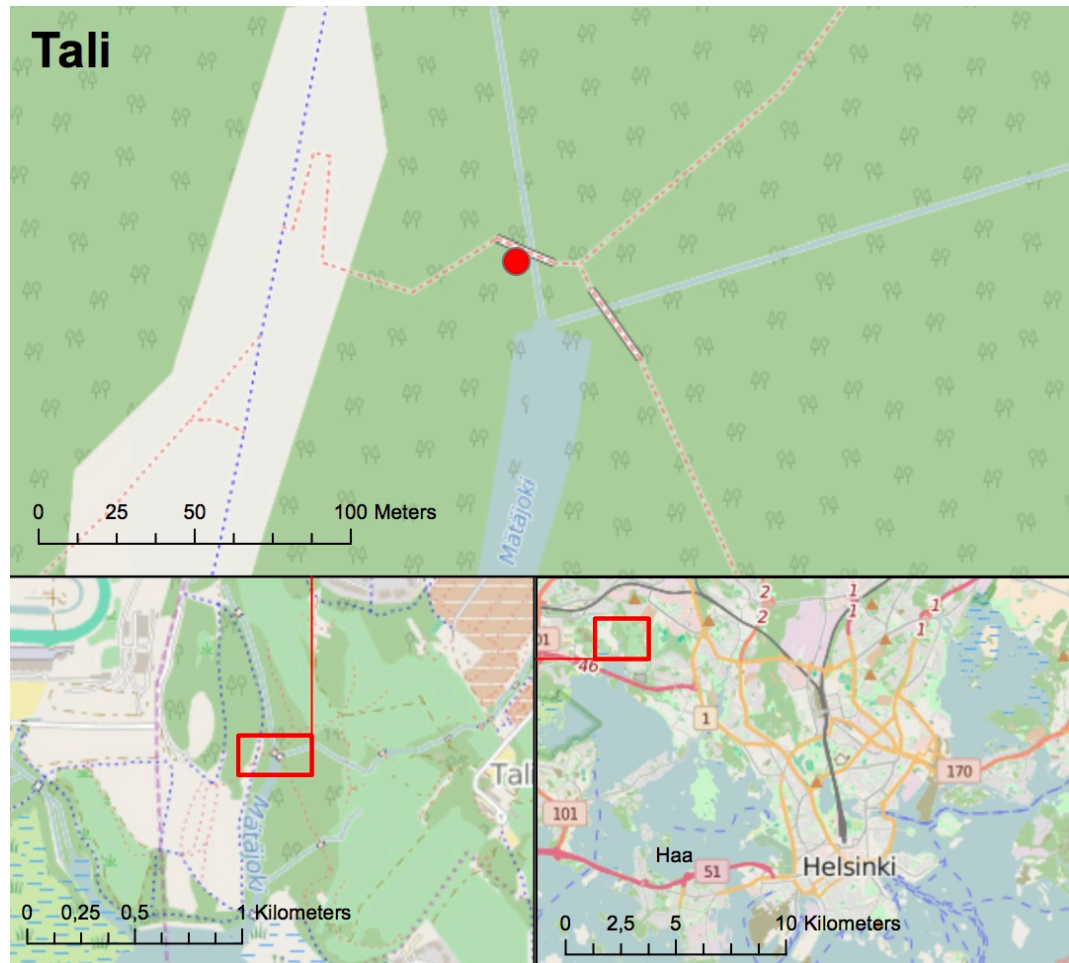


FIGURE 12. Location of the sampling point of Tali in western Helsinki

The landfill of Tali (formerly landfill of Iso-Huopalahti) was in use during 1963-1979 and it was nearest the sea of the three large landfills in Helsinki at the time. The landfill was not supervised but the fill is known to consist of municipal, industrial and hazardous waste. Consequently PAHs and heavy metals have been found on the site. (Toivola 2001 according to Hovi 2013.) Moreover, it is known that while the landfill was in use the industry in Helsinki has produced, among other types of waste, paint, lacquer and solvent waste as well as PCBs, heavy metals, insecticides and organic waste (Aluehallintovirasto 2015). Between the landfill and the sea there is a construction waste and blasted stone zone as insulation. The load capacity of the clay base beneath the landfill was exceeded and therefore the oldest waste landfilled during 1960s has submerged below the sea level. (Toivola 2001 according to Hovi 2013.) The amount of waste

on the landfill is approximately 3.5 million m³ within an area of 24 ha. Currently there is no gas production on the site (Aluehallintovirasto 2015). The location of the landfill with respect to the sampling point is shown in Figure 13.



FIGURE 13. Locations of the landfill and the sampling point in Tali

The Mätäjoki brook locates in both sites Helsinki and Vantaa. The total drainage basin of the brook covers 24.4 km² and the area is inhabited by

nearly 72,000 inhabitants. The brook originates from a marshy riverbed located in Kaivoksela in Western Vantaa. Due to its large drainage basin area, the brook floods easily during heavy rains. The main ditches of the brook are Pajamäenoja, Malminkartanoja, Hakuninmaanoja, Lassilanoja and Konalanoja. (Helsingin kaupungin rakennusvirasto 2014.) Near its rivermouth the Mätäjoki brook runs right next to the former landfill of Tali where the samples were collected.



FIGURE 14. Sampling from the landfill leachate running into the Mätäjoki brook

5.3 Sampling dates and weather conditions

The first sampling was conducted on 18th and 21st of December in 2015. During the sampling the precipitation was highest on 17th (9.7 mm) and 18th (3.0 mm) which was the first sampling day. On 20th the rainfall was 0.8 mm and on 21st which was the second sampling day, there was no rain. The temperature varied approximately from 2 to 8 °C during the sampling

days. The precipitation and the daily highest and lowest temperatures around the sampling days are illustrated in Figure 15.

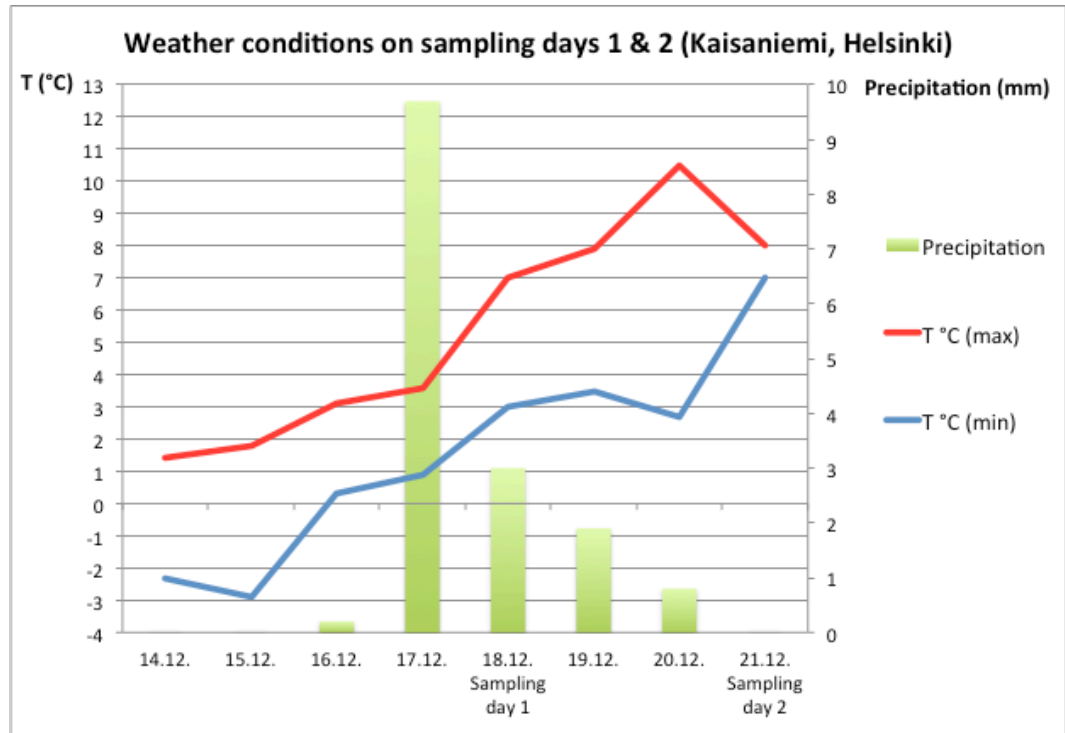


FIGURE 15. Weather conditions on sampling days 1 and 2 on December 2015 (Ilmatieteen laitos 2016)

The second sampling was conducted on April 18th in 2016. The precipitation was highest on 17th (4.2 mm) and 18th (2.4 mm) which was the sampling day. The temperature varied from 3.2 to 7.6 °C during the sampling day. The precipitation and the daily highest and lowest temperatures around the sampling day are illustrated in Figure 16.

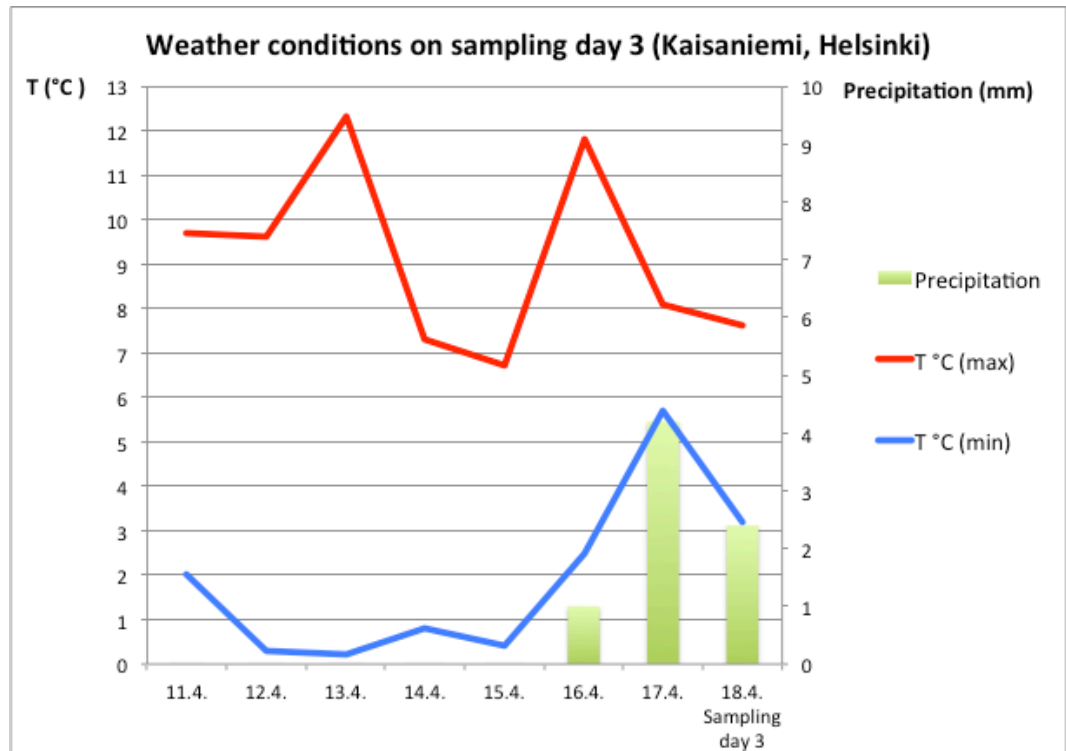


FIGURE 16. Weather conditions on sampling day 3 on April 2016 (Ilmatieteen laitos 2016)

The aim was to take the samples after the heavy rain event in order to collect as much of the washed contaminants in the urban runoff water as possible. However, different sampling times for urban runoffs and landfill leachates has to be taken into consideration in the results as well as timing of the sampling with respect to the beginning of the rain event.

6 ANALYSIS

6.1 Microplastics

Microplastics were analyzed by Julia Talvitie. Stereomicroscope (Fiberoptic – Heim LQ 1100, magnification ×50) was used to identify and count the microlitter. The analysis covered synthetic particles and fibres. In order to avoid contamination, all the used equipment was rinsed using tap water before the sampling. As room dust and fibres from the clothing are potential contamination sources during transport and analyzing, three blank samples were included in sampling in April 2016. In the case of contamination, all the filters were rinsed and inspected with a microscope before use. During the sampling, all the filters were kept in carefully sealed petri dishes. (Talvitie 2016.) The characterization of the plastics was defaulted and will be carried out afterwards. In order to obtain reliable identification between synthetic and organic particles, FTIR (Fourier transform infrared spectroscopy) is required but experienced microscope user is able to identify general particles.

6.2 Polycyclic aromatic hydrocarbons

Concentrations of 16 PAH compounds were determined applying an experiment report conducted by Brum et al. (2008). The samples were extracted by liquid-liquid extraction method and analyzed using gas chromatograph-mass spectrometer. The chemical structures of the analyzed compounds are shown in Appendix 1.

6.2.1 Pretreatment of samples

All glassware was rinsed using acetone in order to remove organic contaminants and residues. After removing the solvent, all glassware was rinsed with extraction solvent hexane. Approximately 900 mL of ultra pure water was analyzed among the samples at both analyzing times. All jars with the samples and a blank sample of ultra-pure water were weighed

and the weights were noted to determine the sample size accurately. 25 mL of hexane and 100 μ L of internal standard were added into each sample jar (Perkola 2016a). Therefore, the resulting internal standard concentration was 400 ng/ μ L per sample. The samples were extracted in the sample jars under magnetic stirring for 2 hours. After the extraction, water and hexane phases were separated using a separating funnel, and hexane was placed into erlenmeyer flasks.

In order to run the samples by gas chromatograph, the concentration of the samples was to be decreased. Small water content in hexane was removed using sodium sulfate. Water was absorbed into sodium sulfate, and hexane was transferred into Kimax bottles for the following evaporation. The original sample size being approximately 900 mL, the samples were concentrated using nitrogen evaporator to the final concentration of 0.9 mL and transferred into gas chromatograph bottles. Samples were stored in freezer until the gas chromatographic analysis was carried out. Pretreatment dates and sample weights are shown in Table 8.

TABLE 8. Sample weights and pretreatment dates

Sample and sampling date	Sample code	Date of pretreatment	Bottle with sample (g)	Empty bottle (g)	Sample (g)
Runoff 18.12.2015	HP1	16.-18.3.2016	1473.6	572.8	900.8
Brooke 18.12.2015	HP2	16.-18.3.2016	1446.3	572.7	873.6
Leachate 21.12.2015	HP2.1	16.-18.3.2016	1499.4	572.2	927.2
Runoff 18.4.2016	HP3	20.-22.4.2016	1548.4	583.9	964.5
Leachate 18.4.2016	HP4	20.-22.4.2016	1527.0	496.1	1030.9
Blank	0-2	20.-22.4.2016	1460.1	504.1	956.0

6.2.2 Gas chromatograph-mass spectrometer analysis

Gas chromatograph with mass spectrometer (GC-MS) was used in the analysis. Based on mass spectra, the method allows reliable and fast determination of compounds separated by gas chromatograph. The method applies for compounds which can withstand the elevated

temperatures of gas chromatograph and are able to evaporate sufficiently. (Jaarinen & Niiranen 2005.)

Shimadzu GCMS-QP2010 Ultra gas chromatography-mass spectrometry with Shimadzu AOC-20i Auto injector was used in analysis. GC-MS analysis conditions are shown in Table 9.

TABLE 9. GC-MS analysis conditions

GC-MS analysis conditions	
Column	Zebron ZB-5, 30m x 0.25mm x 0.25 μ m
Injection	1 μ L splitless for 1 min at 280 °C
Carrier gas	Constant flow helium at 0.91ml/min
Oven	80°C to 320°C at 10°C/min, hold for 5min
Detector	QMS, source:200°C, Interface:280°C

A calibration solution series was prepared for the calibration (Rantalainen 2016). The series consists of solutions of desirable analytes in various concentrations covering the calibration area and internal standard in constant concentration. In the calibration signal values for the desirable concentration areas of the analyte and internal standard are determined. The obtained values are plotted by a relation of each concentration of analyte and concentration of internal standard as a calibration curve. (Jaarinen & Niiranen 2005.) An example of a calibration curve obtained from the analysis is shown in Figure 17.

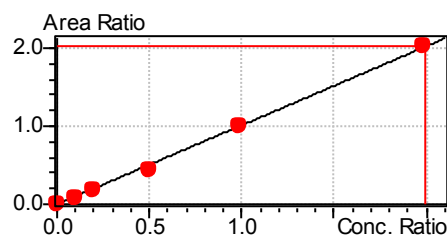


FIGURE 17. Calibration curve of naphthalene

The compounds separated by gas chromatography based on their retention time are ionized in an ionization chamber of mass spectrometer. Single ion monitoring (SIM) mode was used to acquire data for selected masses characteristic to each analyte. The correct retention time verified the existence of the analyte. (Jaarinen & Niiranen 2005.) The chromatogram of analyzed PAH compounds is shown in Appendix 2 and retention times and mass-to-charge ratios in Table 9.

TABLE 9. Retention times and mass-to-charge ratios (m/z) of analyzed PAHs

Compound	Retention time	m/z
Naphthalene	5,48	128
Acenaphthylene	8,96	152
Acenaphthene	9,38	153
Fluorene	10,61	166
Phenanthrene	12,86	178
Anthracene	12,98	178
Fluoranthene	15,70	202
Pyrene	16,22	202
Benzo[a]anthracene	19,17	228
Chrysene	19,25	228
Benzo[b]fluoranthene	21,93	252
Benzo[k]fluoranthene	22,00	252
Benzo[a]pyrene	22,70	252
Indeno[1,2,3-cd]pyrene	24,64	276
Dibenzo[a,h]anthracene	24,69	278
Benzo[ghi]perylene	25,04	276

Blank sample of the pretreatment carried out in March 2016 was distorted and therefore excluded because internal standard was not visible. The blank sample of the pretreatment carried out in April 2016 was used in all calculations. (Rantalainen 2016.)

6.3 Polychlorinated biphenyls

The analysis of PCBs was based on SFS-EN ISO 6468 standard (Nuutinen 2016). The analysis was conducted in the laboratory of the Finnish Environment Institute.

6.4 Phthalates

Phthalates were analyzed by Ramboll Analytics. The analysis was carried out modifying SFS-EN ISO 18856 standard (Vainio 2016).

6.5 Polybrominated diphenyl ethers

The analysis of PBDEs was carried out in the laboratory of the Finnish Environment Institute. The used method is developed by the laboratory. The extraction of the PBDE compounds was done by liquid-liquid extraction. Hexane and dichloromethane were used as extraction solvents and the duration of the extraction was 1 hour by using a magnetic stirrer. Sodium chloride was added into the sample. After evaporation to smaller volume the extract was cleaned up by using silica-H₂SO₄ and analyzed according to LP-GC-EI-MS/MS method (Low-Pressure Gas Chromatograph Electron Ionization Tandem Mass Spectrometer). Gas chromatograph tandem mass spectrometer was used in analyzing the extract. The quantitation is based on the use of ¹³C labeled internal standards. The identification of the compounds is based on retention time and monitoring of MS/MS reactions that are characteristic for the compounds (Multiple Reaction Monitoring). (Nuutinen 2016.)

6.6 Perfluorinated alkylated compounds

The analysis of PFASs was based on the ISO 25101 standard (Perkola 2016b). The analysis was carried out in the laboratory of the Finnish Environment Institute.

7 RESULTS AND DISCUSSION

7.1 Microplastics

Fibres and synthetic particles were analyzed from the samples. The results are shown in Figure 18.

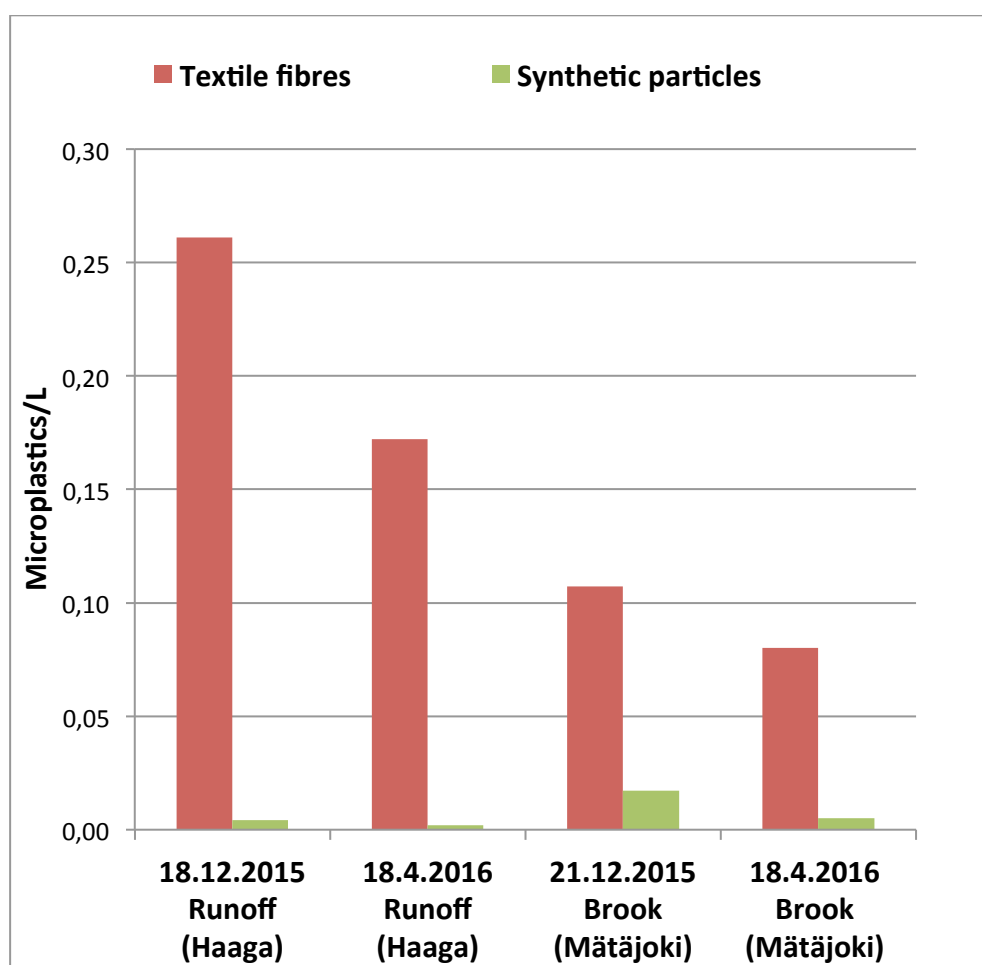


FIGURE 18. The concentrations of microplastics by samples

Microplastics were found in all the samples. In general, fibres were more prevalent than particles in all the samples. The concentrations of fibres varied from 0.080 and 0.261 fibres/L, whereas the range of particles was between 0.002 and 0.017 particles/L.

Regarding the sampling times, the concentration of both microplastic types was higher in the samples taken in December 2015. The heavy rain event prior to the sampling in December 2015 contributes to the larger amount of microplastics found in the samples in comparison to April 2016.

Considering fibres, they were found more in the runoff samples compared to the Mätäjoki brook samples, whereas the amount of particles occurred conversely.

As it has already been shown, the urban runoff waters can be quite a significant pathway of microplastics to the marine environment and the shoreline. In this case, the sampling times were not the most favourable ones but still those fibers and particles could be detected. In the case of Tali's sampling point, some of the particles may assumably originate from the leachates discharging from the landfill to the brook. In fact, in the brook banks can also be seen a lot of old waste including plastic items, so the formation of microplastic via weathering is definitely happening to some extent, and those particles are flushed into the Mätäjoki brook.

7.2 Polycyclic aromatic hydrocarbons

Concentrations of 16 PAH compounds were determined from the water samples. The results are shown in Figure 19.

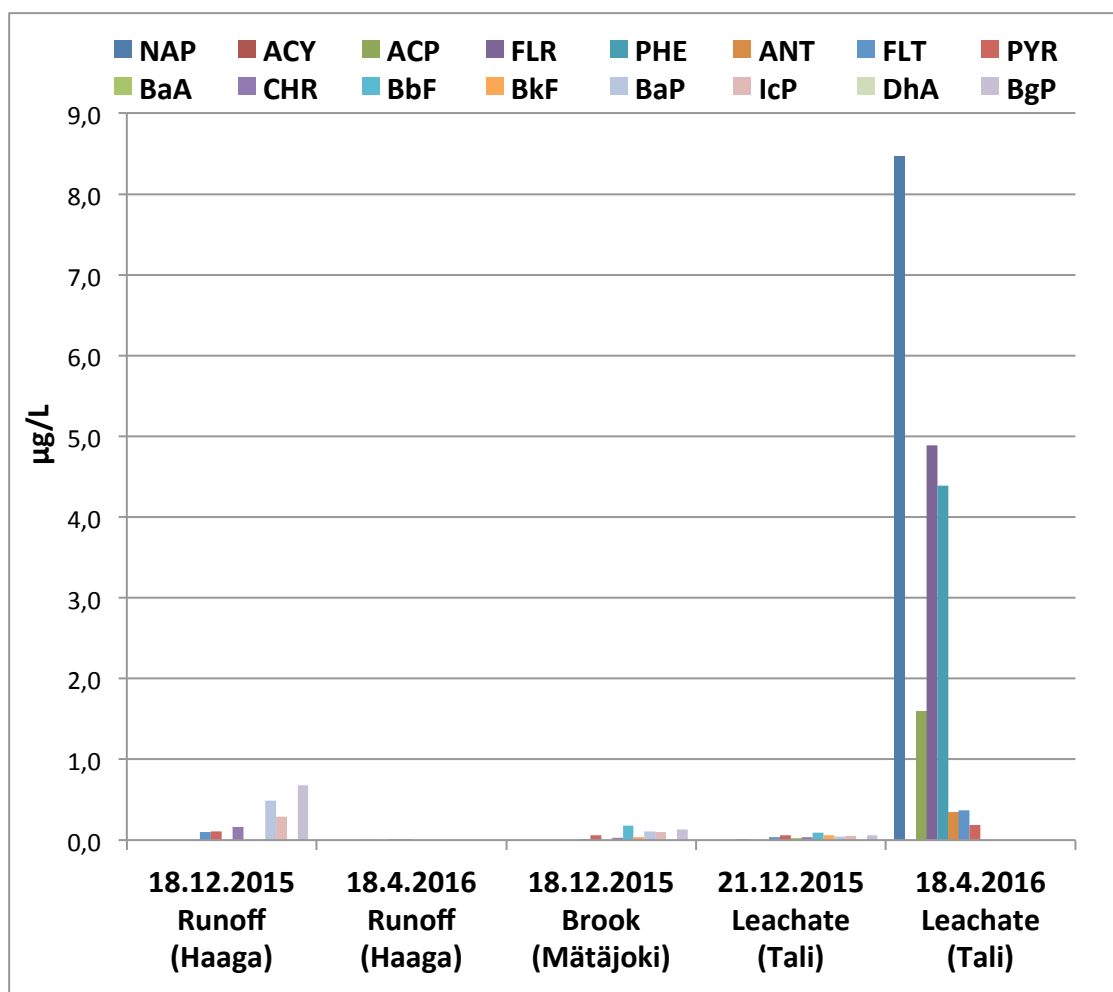


FIGURE 19. Determined PAH concentrations by samples

Among 16 analyzed compounds, 14 were detected in the samples. Acenaphthylene (ACY) and dibenzo[a,h]anthracene (DhA) were not present in any of the samples. The total PAH concentration in the leachate sample taken in April 2016 was 20.241 µg/L. Naphthalene (NAP, 8.472 µg/L), fluorene (FLR, 4.889 µg/L), phenantrene (PHE, 4.392 µg/L) and acenaphthene (ACP, 1.591 µg/L) showed the highest concentrations in that sample considering all the samples. The second highest concentrations between the samples occurred in the Haaga runoff sample taken in December 2015 where the total PAH concentration was 1.816 µg/L. The highest concentrations were detected to benzo[ghi]perylene (BgP, 0.678 µg/L), benzo[a]pyrene (BaP, 0.489 µg/L) and indeno[1,2,3-cd]pyrene (IcP 0.286 µg/L) in that sample. The concentrations are

tabulated in Appendix 3. Similar quantities to the leachate sample taken in April 2016 have been detected in October 2015 for fluoranthene (FLT), pyrene (PYR) and NAP on the same site but other concentrations, which were analyzed mainly for lower molecular mass PAHs, were considerably lower in comparison to the sample taken in April 2016 (FCG, 2016). This is most likely due to variation in the volume of the leachate discharging from the landfill, which may be seen in comparison to the leachate sample taken in December 2015 as well.

During the concentration of the samples taken in December 2015, the colour of the samples altered from transparent to yellowish, whereas the samples taken in April 2016 retained their transparency. The yellowish colour may indicate a larger quantity of organic material in these samples (Rantalainen 2016). The variation in the amounts of organic and other solid material in the samples might be a result of different sampling times, duration of rain event as well as seasonal changes.

This difference in the amounts of organic material may be seen in the detected PAH compounds. The compounds with lower molecular mass, as NAP, PHE and FLR are more water soluble, and, therefore may occur more in the water phase, which can be seen in the samples taken in April 2016. The larger volume of the more concentrated leachate filtered from the landfill due to heavy rain event after long dry period may contribute to this. On the other hand, higher molecular mass PAHs, as BgP, IcP and BaP were not detected in neither of the samples taken in April 2016 but they were found in the samples taken in December 2015. This may contribute to the higher amount of organic and solid material in the samples in comparison to the samples taken in April 2016.

The concentrations of PAHs and microplastics in the runoff samples taken in December 2015 were higher than in the samples taken April 2016. The higher concentrations in the runoff samples may contribute to the larger emissions of organic and other solid material in the runoff waters due to a longer rain period before the sampling time.

The Water Framework Directive (2013/39/EU) sets environmental quality standards (EQS) which include maximum allowable concentrations (MAC) for six PAH compounds (Valtioneuvoston asetus vesiympäristölle vaarallisista ja haitallisista aineista annetun valtioneuvoston asetuksen muuttamisesta 868/2010, 12 §; 1308/2015, 10 §). In the brook sample benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), BaP and BgP exceeded MAC-EQS values set for sea and other surface waters. In addition, MAC-EQS values set for BaP and BgP were exceeded in the runoff sample taken in December 2015. Some PAH concentrations in the leachate sample taken in December 2015 exceeded MAC-EQS values as well, but it has to be taken into account that leachates are not completely comparable to these EQS values due to their origin and nature. MAC-EQS values and concentrations of the samples are shown in Table 10.

TABLE 10. Maximum allowable concentrations of sea and other surface waters for six PAH compounds set in the Water Framework Directive

PAH	Concentration µg/L					MAC (µg/L)
	18.12.2015 Runoff (Haaga)	18.4.2016 Runoff (Haaga)	18.12.2015 Brook (Mätäjoki)	21.12.2015 Leachate (Tali)	18.4.2016 Leachate (Tali)	
NAP	<0.005	<0.005	<0.005	<0.005	8.472	130
FLT	0.097	0.016	0.012	0.036	0.371	0.12
BbF	<0.021	<0.021	0.177	0.09	<0.021	0.017
BkF	<0.021	<0.021	0.035	0.062	<0.021	0.017
BaP	0.489	<0.021	0.107	0.043	<0.021	0.027
BgP	0.678	<0.021	0.129	0.062	<0.021	0.00082

In addition, the Water Framework Directive classifies anthracene (ANT), BaP, BbF, BgP, BkF and IcP as harmful and hazardous substances for aquatic environment.

7.3 Polychlorinated biphenyls

The concentrations of 15 PCBs were determined from the water samples. The results are shown in Figure 20.

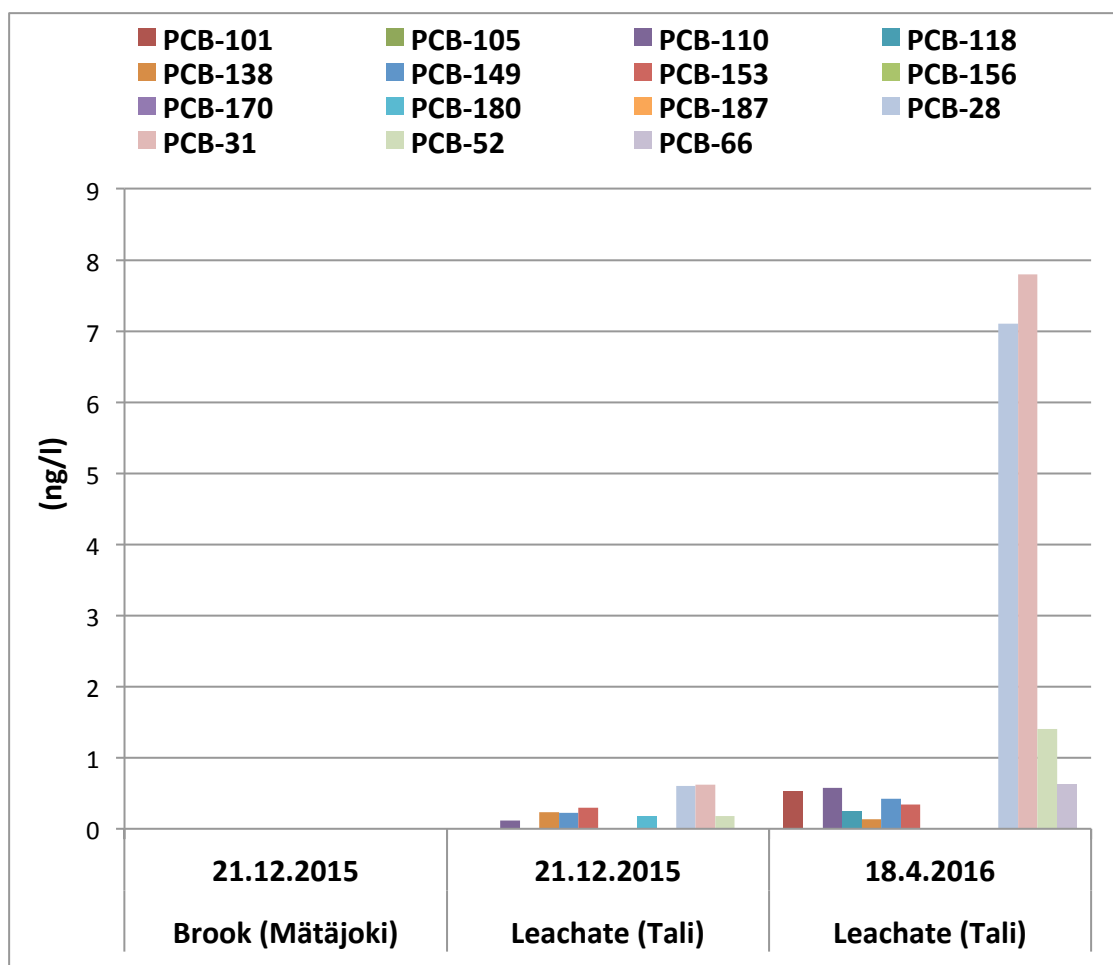


FIGURE 20. Concentrations of analyzed PCB congeners by samples

In the both leachate samples, altogether 11 PCB congeners were detected from 15 analyzed congeners. There were no PCBs detected in the brook sample. The total PCB concentrations were 2.45 ng/L in the sample taken in December 2015 and 19.17 ng/L in the sample taken in April 2016. PCB-31 (7.8 ng/L) and PCB-28 (7.1 ng/L) showed the highest concentrations within all the analyzed compounds and they occurred prevalently in the leachate sample taken in December 2015. The high concentrations of these less chlorinated PCB congeners in the leachate may be due to higher volume of more concentrated leachate from the landfill as PCBs of lower rate of chlorination tends to be more water soluble. The concentrations of more chlorinated congeners, as PCB-153, PCB-149 and

PCB-138, were rather constant considering both samples which contributes to this. The concentrations are tabulated in Appendix 4.

It is known that PCBs have been produced in Helsinki during the time the landfill was in use (Aluehallintovirasto 2015). PCBs have been shown to discharge from the landfill along leachates in the earlier studies as well (FCG 2014). In October 2015 there has been detected higher concentrations of PCBs on the same site the highest concentration being 58 ng/L in the case of PCB-28 (FCG 2016). Regardless the difference in the concentrations in comparison to the samples analyzed in this study, the same trend in the concentrations depending on the rate of chlorination seems to occur. There are no limit values or environmental quality standards set for PCBs.

7.4 Phthalates

The concentrations of 11 phthalate compounds were determined from the water samples. The results are shown in Figure 21.

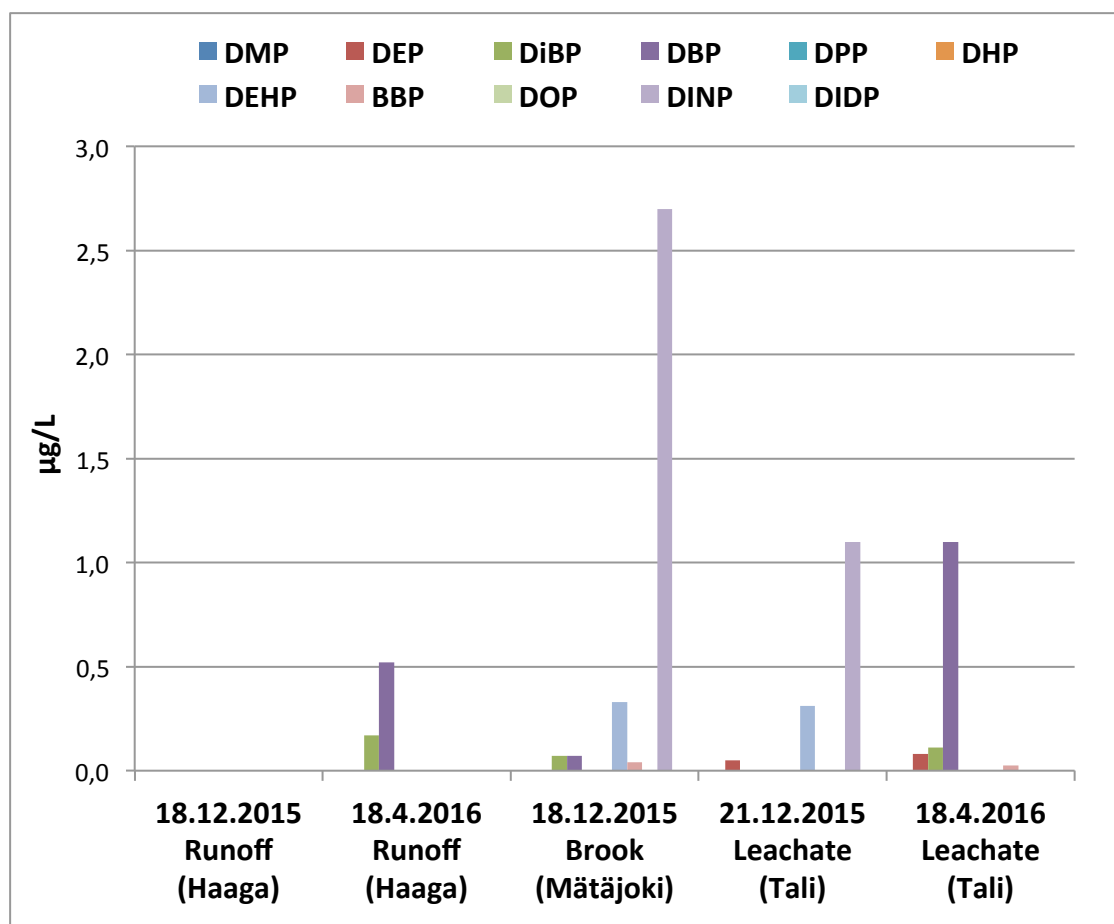


FIGURE 21. Determined phthalate concentrations

Phthalates were detected in all the samples excluding runoff sample taken in December 2015. Altogether six phthalate compounds were found. Dibutyl phthalate (DBP), di-2-ethylhexyl phthalate (DEHP) and diisononyl phthalate (DINP) occurred in prevalent concentrations considering all the phthalate compounds included. Other compounds detected were diethyl phthalate (DEP), diisobutyl phthalate (DiBP) and benzyl butyl phthalate (BBP), in rather low concentrations. The total phthalate concentration of the brook sample was 3.21 µg/L. DINP was found with the highest concentration of 2.70 µg/L in that sample. Also DEHP occurred with the concentration of 0.33 µg/L. The total concentrations of the leachate samples were 1.46 µg/L in the sample taken in December 2015 and 1.314 µg/L in the sample taken in April 2016. DINP was found prevalently also in the leachate sample taken in December 2015 with the concentration of

1.10 µg/L. In the samples taken in April 2016, the prevalent phthalate compound was DBP which concentrations were 1.10 µg/L in the leachate sample and 0.52 µg/L in the runoff sample. The phthalate concentrations are tabulated in Appendix 5.

Distinction in the concentrations between the samples taken in December 2015 and April 2016 might be explicable by variation in the amount of organic and solid material in the samples as well as water solubilities within phthalate compounds. Water solubility of DBP is reported to be 10 mg/L whereas in the case of DINP it is 0.20 mg/L (U.S. Consumer Product Safety Commission Directorate for Health Sciences, 2001; California Environmental Protection Agency, 2010). Therefore, as water insoluble DINP consequently tends to get adsorbed to solid material, larger amount of organic and other solid material contributes to higher DINP concentration in the samples taken in December 2015. This applies to the high DINP concentration in the sample taken from brook as well, while DINP was not present in either of the runoff samples. DBP occurred mainly in the samples taken in April 2016, in leachate to larger extent. DEHP was present in the brook and leachate samples only taken in December 2015 with relatively low concentrations.

The Water Framework Directive classifies DEHP as harmful and hazardous substance for aquatic environment. EQS values are not set for DEHP. (Valtioneuvoston asetus vesiympäristölle vaarallisista ja haitallisista aineista annetun valtioneuvoston asetuksen muuttamisesta 868/2010, 12 §; 1308/2015, 10 §.)

As the effects of phthalates to marine species have been found to start in the concentrations of ng/L, especially the high concentrations in the brook raises concerns regarding the biota of the Mätäjoki brook and Iso-Huopalahti where the brook discharges to.

7.5 Polybrominated diphenyl ethers

The concentrations of 10 PBDE compounds were determined from the water samples. The results are shown in Figure 22.

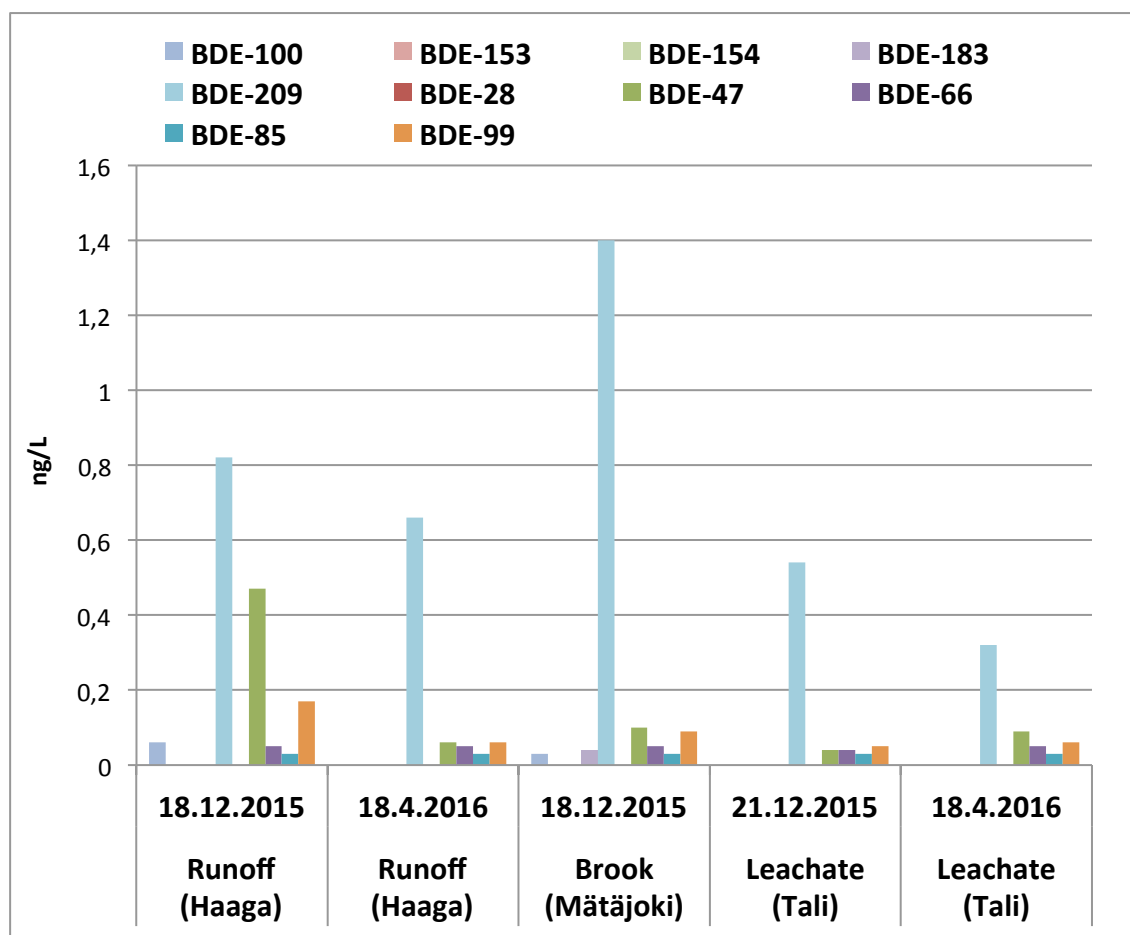


FIGURE 22. Concentrations of analyzed PBDE congeners

Among 10 PBDE congeners, seven were detected. The highest total PBDE concentrations were in the brook sample (1.74 ng/L) and in the runoff sample taken in December 2015 (1.60 ng/L). BDE-209 occurred prevalently in all the samples, in the brook sample (1.40 ng/L) and in the runoff samples with the highest concentrations. Also BDE-47 (0.47 ng/L) and BDE-99 (0.17 ng/l) were found with relatively high concentrations especially in the runoff sample taken in December 2015. The high

concentrations of BDE-209 may be a result of its still ongoing use as decaBDE in certain applications even though it is regulated in the EU. The PBDE concentrations are tabulated in Appendix 6.

The Water Framework Directive (2013/39/EU) defines MAC-EQS value for the sum of the concentrations of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 congeners for sea and other surface waters (Valtioneuvoston asetus vesiympäristölle vaarallisista ja haitallisista aineista annetun valtioneuvoston asetuksen muuttamisesta 868/2010, 12 §;1308/2015, 10 §). The sum of these congeners in the Mätäjoki brook was 0.00022 µg/L, and, therefore the given MAC-EQS value of 0.014 µg/L was not exceeded. The sums of the congeners in the runoff samples were 0.0007 µg/L in December 2015 and 0.00012 µg/L in April 2016 which were not exceeded either. The Water Framework Directive classifies tetra-, penta-, hexa- and heptaBDEs as harmful and hazardous substances to aquatic environment. However, decaBDE group, which mainly consists of BDE-209 congener, is not prioritized under the Water Framework Directive.

7.6 Perfluorinated alkylated substances

The concentrations of 18 PFASs were determined from the water samples. The results are shown in Figure 23.

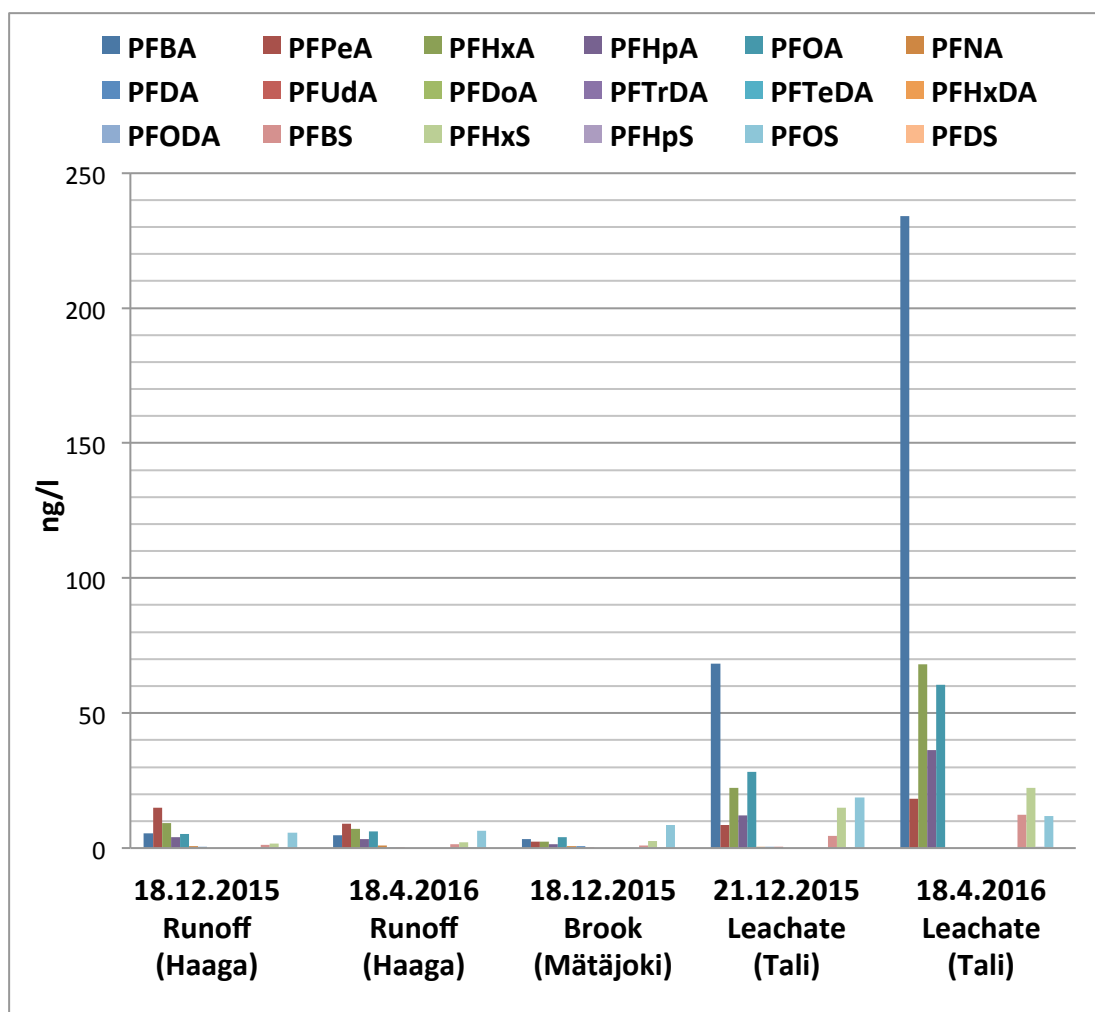


FIGURE 23. Determined PFAS concentrations by samples

Altogether 12 out of 18 PFASs were detected occurring prevalently in the leachate samples. The total PFAS concentrations in the leachate samples were 463.90 ng/L in the sample taken in April 2016 and 179.43 ng/L in the sample taken in December 2015. Perfluorobutanoic acid (PFBA, 234 ng/L), perfluorooctanoic acid (PFOA, 60.40 ng/L), perfluorohexanoic acid (PFHxA, 68.10 ng/L) and perfluoroheptanoic acid (PFHpA, 36.40 ng/L) showed the highest concentrations in the leachate sample taken in April 2016. The same compounds occurred prevalently in the leachate sample taken in December 2015 as well. The PFAS concentrations are tabulated in Appendix 7.

As the water solubility of PFAS increases when the carbon chain length shortens it might explain the high concentrations of short chain PFASs such as PFBA and PFHxA in the leachate. Products containing PFOA may contain shorter chain PFASs as well because they may be produced unintentionally during the production process of PFOA. (Perkola 2016c.)

MAC-EQS value of sea and other surface waters is defined for PFOS (7.2 µg/L) but it was not exceeded as the concentration in the Mätäjoki brook was 0.00858 µg/L and in the urban runoffs 0.00567 µg/L in the sample taken in December 2015 and 0.00648 µg/L in the sample taken in April 2016. PFOS is classified as harmful and hazardous substance for aquatic environment. (Valtioneuvoston asetus vesiympäristölle vaarallisista ja haitallisista aineista annetun valtioneuvoston asetuksen muuttamisesta 868/2010, 12 §;1308/2015, 10 §.)

8 CONCLUSIONS

All the studied hazardous substances and microplastics were detected in the samples to certain extent. The former landfill was found to be a source of some of these pollutants to the environment. The highest concentrations of PAHs, PFASs and PCBs were found in the leachate samples. However, the prevalent occurrence of compounds with high water solubility in the sample taken in April 2016 indicates larger volume of more concentrated leachate infiltrated through the landfill. Therefore, pollutants were released from the landfill increasingly in the spring in comparison to autumn, most likely due to a heavy rain event after a longer dry period and before the actual sampling in the spring.

A few individual compounds of phthalates (DINP) and PBDEs (BDE-209) were found in the highest concentrations in the Mätäjoki brook. Phthalates were present mainly in the leachate compared to the runoffs and therefore the landfill seems to be a relevant source of these compounds to the Mätäjoki brook as well. In addition to the leachate and the Mätäjoki brook, PBDEs were found also in the runoffs in relatively high concentrations. This indicates a wide range of potential emission sources for PBDEs along with the drainage basin areas of both the urban runoff of Haaga and the Mätäjoki brook.

In the water samples taken in December 2015, implications of higher amount of organic and other solid material were seen in comparison to the samples taken in April 2016. As low water soluble compounds tend to get adsorbed in solid material, a higher concentration of certain compounds in the samples of larger amount of organic material may contribute to the occurrence of these compounds. PAHs of higher molecular mass as well as DINP and DEHP of phthalates, which are known to be low on water solubility, were increasingly found in the samples taken in December 2015.

In general, microplastic fibres were found more in the runoff samples compared to the brook samples. On the contrary, larger amount of

particles were found in the brook samples. As it was not possible to take the microplastic samples directly from the leachate, a clear correlation between the concentrations of pollutants and microplastics in the leachate can not be made. However, PAHs, PFASs, PBDEs and microplastics were all found in lower concentrations in the runoff samples taken in April 2016 in comparison to December 2015. This shows the significance of the sampling time as the concentrations of both, microplastics and the harmful substances, can vary depending on the season and weather conditions.

Certain PAH compounds exceeded the given MAC-EQS limit values for sea and other surface waters in the Mätäjoki brook and the runoff of Haaga. Other MAC-EQS values given for PFOS and the sum of certain PBDE congeners were not exceeded. Even though the concentrations of the certain POP compounds were rather low, it does not mean that they are totally harmless. These compounds have impacts on the environment and organisms even with very low concentrations, which is why all the emissions and loads should be prevented. Also the high concentrations of phthalates, especially DINP, in the Mätäjoki brook were close to the concentrations that has been shown in earlier studies to cause harmful effects on biota (Oehlmann et al. 2009).

As microplastics were found in both the runoff and the Mätäjoki brook it shows their capability to act as a source and a pathway of microplastics to the marine environment. Leachates can be an emission source of harmful substances, especially in the case of an old closed landfill without proper surface structures and systems to collect and treat the leachates.

A renovation of Tali's old landfill will be carried out within the next few years. The renovation covers the construction of solid surface structures and the systems for collecting the leachate waters running from the landfill to the sewer system. The leachates will be directed to the municipal waste water treatment plant to be purified. The renovation is planned to be conducted between the years of 2016 and 2018. (Aluehallintovirasto 2015.) The improvement is very welcome since it is important to prevent

all the possible emissions and loads of POP compounds to the environment.

However, the landfill has been discharging leachate into the brook for over 30 years, and the concentrations of the pollutants in the leachate and therefore in the brook have been presumably higher before. Therefore, it would be interesting to have more comprehensive study on certain chemical emissions in order to estimate the actual loads.

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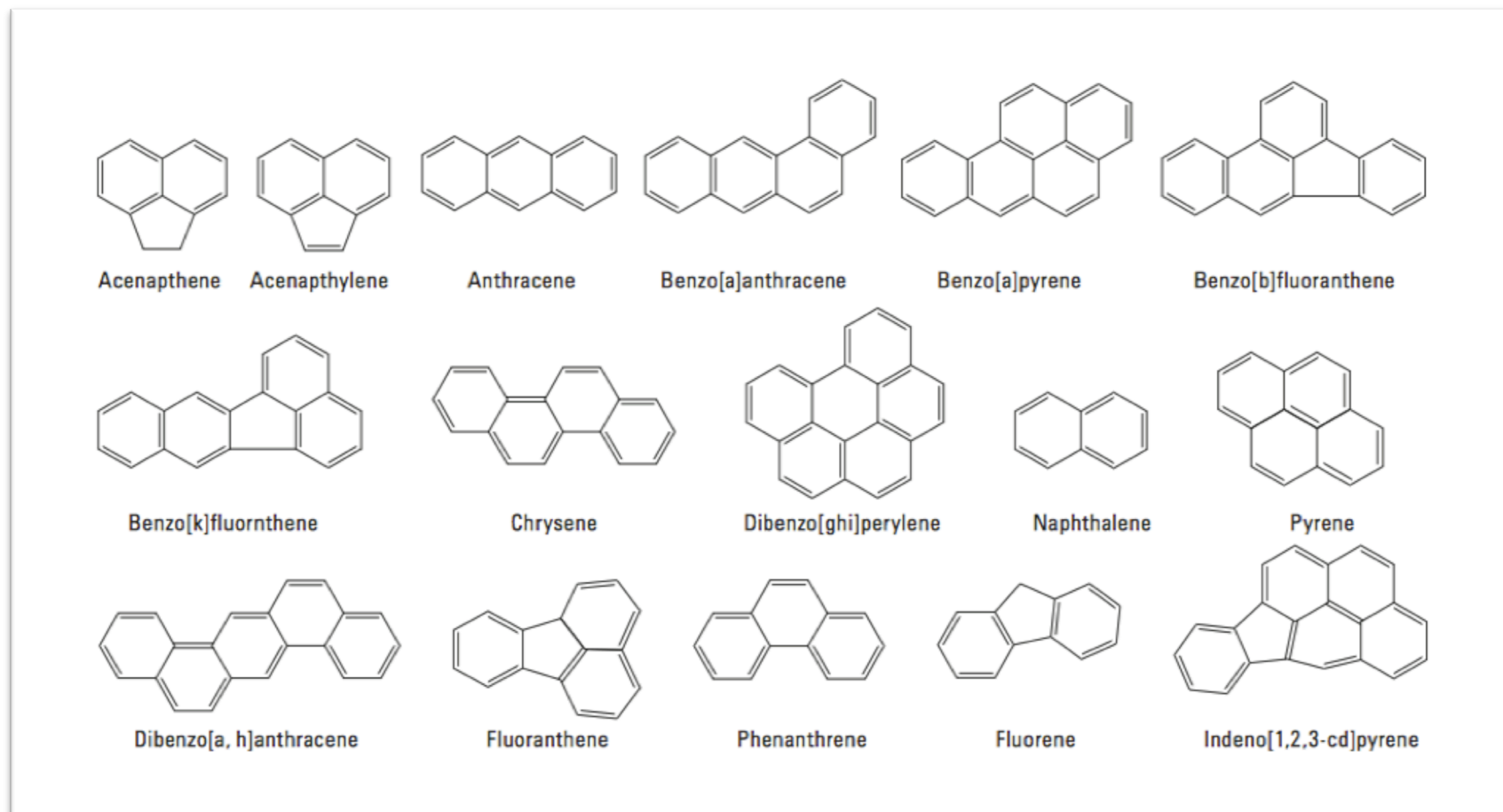
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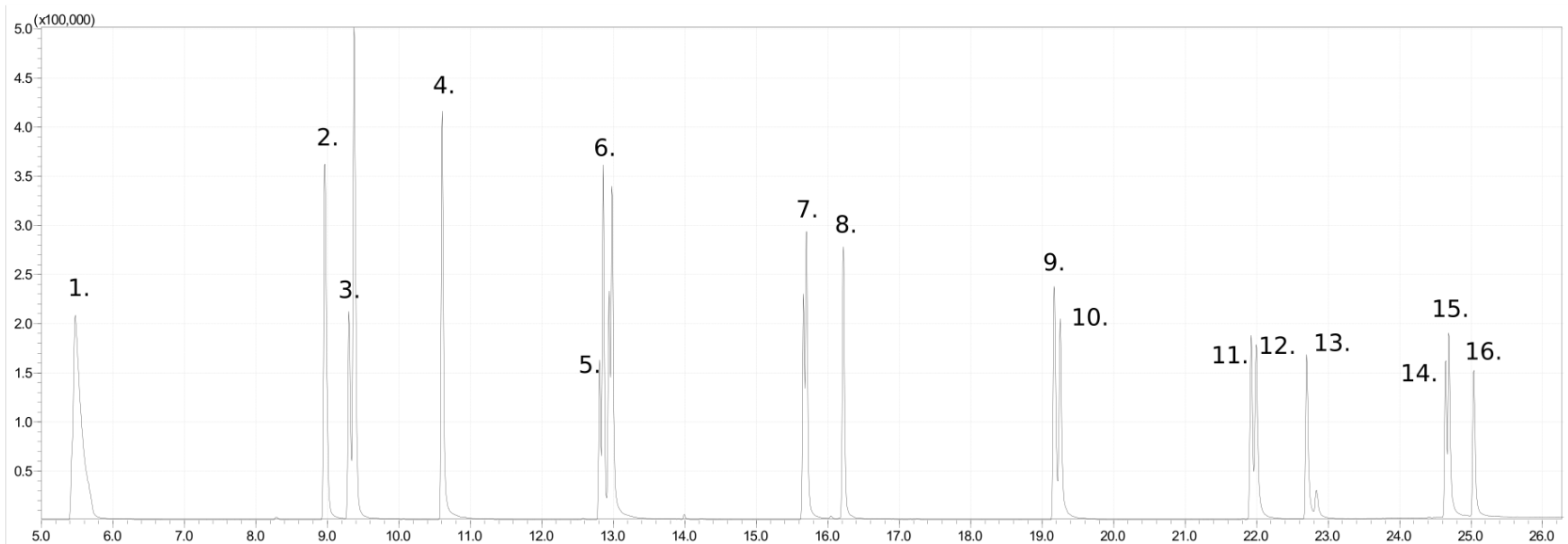
APPENDICES

APPENDIX 1	The chemical structures of 16 PAH-compounds analyzed in the study (Pule et al. 2012)
APPENDIX 2	GC chromatogram of analyzed PAH compounds
APPENDIX 3	PAH result table
APPENDIX 4	PCB result table
APPENDIX 5	Phthalates result table
APPENDIX 6	PBDE result table
APPENDIX 7	PFAS result table
APPENDIX 8	Map of the sampling points

APPENDIX 1



APPENDIX 2



1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene

5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene

9. Benzo[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene

13. Benzo[a]pyrene
14. Indeno[1,2,3-cd]pyrene
15. Dibenzo[a,h]anthracene
16. Benzo[ghi]perylene

APPENDIX 3

PAH	Abbreviation	Concentration µg/L					LOQ
		18.12.2015 Runoff (Haaga)	18.4.2016 Runoff (Haaga)	18.12.2015 Brook (Mätäjoki)	21.12.2015 Leachate (Tali)	18.4.2016 Leachate (Tali)	
Naphthalene	NAP	<0.005	<0.005	<0.005	<0.005	8.472	0.005
Acenaphthylene	ACY	<0.005	<0.005	<0.005	<0.005	<0.005	0.005
Acenaphthene	ACP	<0.005	<0.005	<0.005	<0.005	1.591	0.005
Fluorene	FLR	<0.005	0.007	<0.005	0.009	4.889	0.005
Phenanthrene	PHE	<0.005	0.008	<0.005	0.006	4.392	0.005
Anthracene	ANT	<0.005	<0.005	<0.005	<0.005	0.34	0.005
Fluoranthene	FLT	0.097	0.016	0.012	0.036	0.371	0.005
Pyrene	PYR	0.105	0.014	0.063	0.062	0.186	0.005
Benzo[a]anthracene	BaA	<0.016	<0.016	<0.016	0.019	<0.016	0.016
Chrysene	CHR	0.161	<0.016	0.03	0.036	<0.016	0.016
Benzo[b]fluoranthene	BbF	<0.021	<0.021	0.177	0.09	<0.021	0.021
Benzo[k]fluoranthene	BkF	<0.021	<0.021	0.035	0.062	<0.021	0.021
Benzo[a]pyrene	BaP	0.489	<0.021	0.107	0.043	<0.021	0.021
Indeno[1,2,3-cd]pyrene	IcP	0.286	<0.021	0.103	0.052	<0.021	0.021
Dibenzo[a,h]anthracene	DhA	<0.021	<0.021	<0.021	<0.021	<0.021	0.021
Benzo[ghi]perylene	BgP	0.678	<0.021	0.129	0.062	<0.021	0.021
	Σ16PAH	1.816	0.045	0.656	0.477	20.241	
	Σ7PAH	1.55	0.016	0.563	0.345	8.843	
Abbreviations: Σ16PAH, total PAH. Σ7PAH, sum of naphthalene, fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene.							

APPENDIX 4

PCB	Abbreviation	Concentration ng/L		
		21.12.2015 Leachate (Tali)	18.4.2016 Leachate (Tali)	LOQ
2,2',4,5,5'-Pentachlorobiphenyl	PCB-101	<0.08	0.53	0.08
2,3,3',4,4'-Pentachlorobiphenyl	PCB-105	<0.13	<0.13	0.13
2,3,3',4',6-Pentachlorobiphenyl	PCB-110	0.12	0.58	0.08
2,3',4,4',5-Pentachlorobiphenyl	PCB-118	<0.13	0.24	0.13
2,2',3,4,4',5'-Hexachlorobiphenyl	PCB-138	0.23	0.13	0.11
2,2',3,4',5',6-Hexachlorobiphenyl	PCB-149	0.22	0.42	0.11
2,2',4,4',5,5'-Hexachlorobiphenyl	PCB-153	0.30	0.34	0.11
2,3,3',4,4',5-Hexachlorobiphenyl	PCB-156	<0.13	<0.13	0.13
2,2',3,3',4,4',5-Heptachlorobiphenyl	PCB-170	<0.08	<0.08	0.08
2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB-180	0.18	<0.11	0.11
2,2',3,4',5,5',6-Heptachlorobiphenyl	PCB-187	<0.11	<0.11	0.11
2,4,4'-Trichlorobiphenyl	PCB-28	0.60	7.10	0.08
2,4',5-Trichlorobiphenyl	PCB-31	0.62	7.80	0.11
2,2',5,5'-Tetrachlorobiphenyl	PCB-52	0.18	1.40	0.08
2,3',4,4'-Tetrachlorobiphenyl	PCB-66	<0.11	0.63	0.11
	Σ15PCB	2.45	19.17	
	Σ7PCB	1.49	9.74	
	Abbreviations: Σ15PCB, total PCB. Σ7PCB, sum of PCB congeners 28, 52, 101, 118, 138, 153 and 180.			

APPENDIX 5

Phthalate	Abbreviation	Concentration µg/L						
		18.12.2015 Brook (Mätäjoki)	21.12.2015 Leachate (Tali)	LOQ		18.4.2016 Leachate (Tali)	18.4.2016 Runoff (Haaga)	LOQ
Dimethyl phthalate	DMP	<0.02	<0.02	0.02		<0.10	<0.10	0.10
Diethyl phthalate	DEP	<0.05	0.05	0.05		0.08	<0.05	0.05
Diisobutyl phthalate	DiBP	0.07	<0.05	0.05		0.11	0.17	0.05
Dibutyl phthalate	DBP	0.07	<0.05	0.05		1.10	0.52	0.05
Dipentyl phthalate	DPP	<0.01	<0.01	0.01		<0.01	<0.01	0.01
Dihexyl phthalate	DHP	<0.01	<0.01	0.01		<0.01	<0.01	0.01
DI-2-ethylhexyl phthalate	DEHP	0.33	0.31	0.30		<0.30	<0.30	0.02
Benzyl butyl phthalate	BBP	0.04	<0.02	0.02		0.02	<0.02	0.30
Dioctyl phthalate	DOP	<0.01	<0.01	0.01		<0.01	<0.01	0.01
Diisononyl phthalate	DINP	2.70	1.10	1.0		<1.0	<1.0	1.0
Diisodecyl phthalate	DIDP	<1.0	<1.0	1.0		<1.0	<1.0	1.0

APPENDIX 6

PBDE	Abbreviation	Concentration ng/L					LOQ
		18.12.2015 Runoff (Haaga)	18.4.2016 Runoff (Haaga)	18.12.2015 Brook (Mätäjoki)	21.12.2015 Leachate (Tali)	18.4.2016 Leachate (Tali)	
2,2',4,4',6-Pentabromodiphenylether	BDE-100	0.06	<0.03	0.03	<0.03	<0.03	0.03
2,2',4,4',5,5'-Hexabromodiphenylether	BDE-153	<0.03	<0.03	<0.03	<0.03	<0.03	0.03
2,2',4,4',5,6'-Hexabromodiphenylether	BDE-154	<0.03	<0.03	<0.03	<0.03	<0.03	0.03
2,2',3,4,4',5',6-Heptabromodiphenylether	BDE-183	<0.03	<0.03	0.04	<0.03	<0.03	0.03
2,2',3,3',4,4',5,5',6,6'-Decabromodiphenylether	BDE-209	0.82	0.66	1.40	0.54	0.32	0.03
2,4,4'-Tribromodiphenylether	BDE-28	<0.03	<0.03	<0.03	<0.03	<0.03	0.03
2,2',4,4'-Tetrabromodiphenylether	BDE-47	0.47	0.06	0.10	0.04	0.09	0.03
2,3',4,4'-Tetrabromodiphenylether	BDE-66	0.05	0.05	0.05	0.04	0.05	0.03
2,2',3,4,4'-Pentabromodiphenylether	BDE-85	0.03	0.03	0.03	0.03	0.03	0.03
2,2',4,4',5-Pentabromodiphenylether	BDE-99	0.17	0.06	0.09	0.05	0.06	0.03

APPENDIX 8

