POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONTAMINATION IN SNOW DUMP SITE SEDIMENTS

A pilot study to assess and characterize PAH species retained in snow dump site sediments

Lahti University of Applied Sciences
Master's Degree Programme in Environmental Technology

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous class of
environmental micropollutants produced by combustion processes. They
are commonly produced in urban areas by vehicles and from road dust.
The United States Environmental Protection Agency (EPA) has included
16 PAHs (PAH16) on their list of Priority Pollutants. During the winter in
northern climates PAHs may be entrained with urban snow and removed
to snow disposal sites or snow dumps. The fate of PAHs in snow dumps is
not well understood. This study attempts to determine if PAH16 species
are retained within snow dump site soils. Four snow dump sites and four
control sites were selected in the Lahti region of South Central Finland.
Soil samples were collected from each site and tested by GC-MS to
determine which PAH16 species were present and their concentrations. All
16 PAHs were detected in the dump sites. Statistically significant
differences were found between the dump and control sites in the
observed concentrations of 13 of PAH16 species.

Keywords: PAHs, urban, snow, snow dumps, pollution, polycyclic aromatic
hydrocarbons

Contents

1 INTRODUCTION

Modern cities rely on an open and safe network of roadways, pedestrian and cycle paths to transport goods, provide services and conduct daily business. The winter season in temperate and higher latitudes may bring weather conditions that hamper the use of urban transportation networks. Below freezing temperatures and precipitation in the forms of freezing rain, sleet and snow may cause significant disruptions to traffic, especially in areas which do not historically experience or are ill equipped to handle such conditions. A quick internet search for phrases such as "snow causes chaos" , "snow causes pile up" or "snow causes problems" will yield thousands of results, mostly news stories about traffic accidents, many sadly, involving multiple fatalities.

Snow falling in urban areas presents problems for residents and city managers. How cities have dealt with snow is an interesting subject and has even been included in a video game, Cities:Skylines Snowfall (Paradox Interactive, 2016), a simulation game in which players must manage the wintertime needs of their city, such as providing heating to residents and keeping roadways clear of snow. The history of snow handling in the US is the subject of the book *Snow in the Cities: A History of America's Urban Response* by Blake McKelvey (1995) in which he writes:

> *The snowstorm experiences and responses of American cities Supply fruitful material for environmental as well as urban historians. As with most historical subjects the topic is multi-dimensional. Not only was the natural environment pulsating and unpredictable, buffeting selected cities at different times and with varied frequency and intensity, but the impact of similar storms also changed radically as the cities grew in size and technological complexity. And as the man-made urban environment developed, it's response expanded to include, in addition to private and cooperative adjustments, concerted efforts by agencies of commerce and communication to*

maintain their services; in time it also inspired municipal regulations that led finally to active civic programs for snow plowing and snow removal.

Automotive traffic became the primary mode of transport in cities beginning the early 20th century, and also marks the beginning of modern snow removal practices, which center on plowing snow and accumulated ice from roads and pedestrian paths, and spreading sand and salt to improve traction and melt the remaining ice.

As occasionally happens, this solution has led to a set of new problems. Firstly, snow plowing and removal is expensive. New York City has spent an average of $55.3 million annually from 2003 to 2014 to clear their streets. In Finland, Helsinki has budgeted 21 - 22 million euros for snow clearing work in 2016 (Särkkä, 2016). Helsinki removed 320 000 dump trucks of snow in 2012 (approximately 3.2 to 4.5 million cubic meters of snow) (Keskinen, 2012). The city of Lahti, in South Central Finland removed over 500 000 m^3 of snow from their streets during the 2012-2013 snow season (Figure 1), while the city of Heinola, a smaller city within the Lahti area, removed about 10 000 m^3. The Lahti region is the focus of this study.

Snow removal and deicing programs also present environmental problems, which began to be widely recognized in the mid 20th century. Initially, scientists and environmental experts and the public began to notice that salt used in deicing operations on roadways was causing automotive body corrosion, damaging roadside plant life, polluting fresh surface and ground waters, and causing fish kills (Cheshire, 2016). Additionally, the sand or grit applied to roadways may cause significant problems in stormwater collection systems and receiving waters by filling sediment traps, blocking drainage pipes and smothering benthic plants and animals.
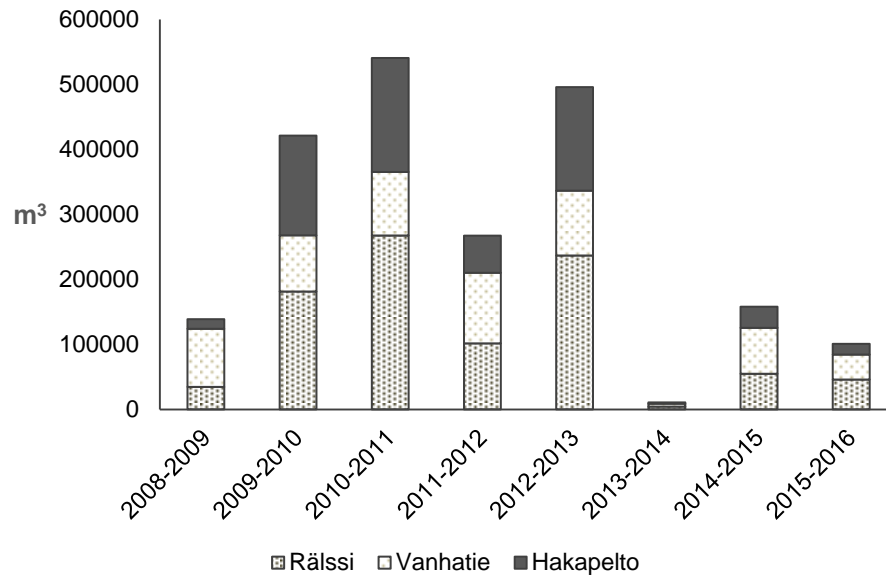
Figure 1: Volume of snow removed to Lahti area snow dumps

Figure 2: Plowed snow stored in a park in Hyvinkää, Finland.

Additionally, research has shown that snow is a very effective trap for air pollutants (Nazarenko et al., 2016). Even snow which falls as far away from urban areas as Antarctica (Na et al., 2011) may contain detectable quantities of anthropogenic pollutants. Snows which accumulate in urban areas may then, unsurprisingly, contain high concentrations of pollutants other than salt, sediment and litter. Recent studies from Canada, Finland, Sweden and other countries with significant annual snowfall have shown that urban snow may contain high concentrations of pollutants such as heavy metals, oils, nutrients, nanosized soot particles, as well as

polycyclic aromatic hydrocarbons (PAHs), which are the focus of this study. More information about PAHs will be given in the next section.

Figure 3: Plowed snow stored on the roadside, Hyvinkää, Finland.

Plowed snow and ice accumulates in piles and ridges along roadways, in on-street parking spaces and in parks and other urban green spaces over the course of the winter (Figures 2 and 3). Eventually the accumulation becomes too great, and the material must be removed from the city. This is typically done by using frontend loaders to fill dump trucks which then deliver the snow, ice and entrained litter, pollutants and debris to a disposal site. The final disposal of the snow maybe accomplished in one of several different ways: By dumping into a nearby water body, such as a river, lake, harbor or sea; By melting using large snow melting devices; Or by stockpiling in snow dumps or other wasteland sites where it is allowed to passively melt over the course of the following spring and summer months. Melt water from the sites is typically allowed to infiltrate into the ground, or collects in shallow basins where it may stage up and discharge to surface waters. Snow dumps are the focus of this work

While, as previously mentioned, many studies have examined the contaminates present in urban snows, and many have looked at PAHs, relatively little, if any, work has been done to determine if PAH species are retained in the soil at snow dump sites after the accumulated snow has melted away. This study aims to address this lack of information

This research is important because it looks at snow dumping sites that have been in use for many decades in areas that have historically received significant annual snow fall. Current climate models predict that as climate change progresses, and weather patterns shift, areas which do not currently received significant amounts of snow could begin to experience heavy annual snowfalls. By studying the quality of soils in current snow dump sites I hope to provide valuable information about the long term impacts of this handling option.

The original idea for this research project came from my interest in urban stormwater and pollution prevention, and was originally going to examine bacterial loadings from urban snow melt. However, due to impracticalities of analysing bacterial samples and through discussions with my thesis advisors at LAMK and with professors and researchers at the University of Helsinki's Department of Environmental Ecology, my focus shifted to looking at chemical contamination in snow dump sites. At the suggestion of Dr. Anna-Lea Rantalainen and examination of PAHs was selected as the subject of my project since some work had recently been done at the University of Helsinki on these compounds, and so knowledge, equipment and supplies were available for my use.

2 FRAMEWORK OF THE STUDY

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic chemical compounds formed from the fusion of two or more benzene rings. PAHs containing up to four benzene rings are known as light PAHs, while those containing more than four rings are called heavy PAHs (Wenzl et al., 2006). In solid form they are typically colorless, white or yellowish, with their individual characteristics determined by the arrangement of the benzene rings, with hundreds of different known combinations. PAHs range in molecular weight from 128.16 g (Naphthalene) to 300.36 g (Coronene), with lighter compounds being more volitile than heavier compounds. It has been shown that some PAHs can be carcinogenic and mutagenic (Kim et al., 2013, Nisbet & LaGoy, 1992) and are also potent immune-suppressants. The Environmental Protection Agency (EPA) of the United States has included 16 individual PAHs (Figure 4) in its list of 126 Priority Pollutants, and it is this group of PAHs that are examined in this study.

Some PAHs occur naturally as the result of forest and brush fires, but they are typically of anthropogenic origin, being created and released to the atmosphere during the incomplete combustion of garbage, wood, biomass, and hydrocarbon fuels (gasoline, diesel and other fuel oils, and coal) (EPA, 2008). Due to their structure, PAHs commonly bind to organic matter in the environment, maybe highly hydrophobic, and resistant to biological degradation. Lighter compounds may unbind more easily from organic matter and re-volatilize to the atmosphere while heavier compounds tend to remain attached and accumulate in sediments and soils. PAHs are common urban pollutants and many studies have shown that PAHs may occur in urban surface and storm waters and sediments (Honkonen & Rantalainen, 2013 & 2016; Ngabe et al., 2000, Paul & Meyer, 2001; etc..), in the urban atmosphere (Halsall, et al., 1994; Menichini, 1992; Tang, N. et al., 2005; etc..) and in the soils of urban and industrial areas (Gan et al., 2009; Tang, L. et al., 2005; Trapido, 1999; Teaf et al., 2008, etc..).
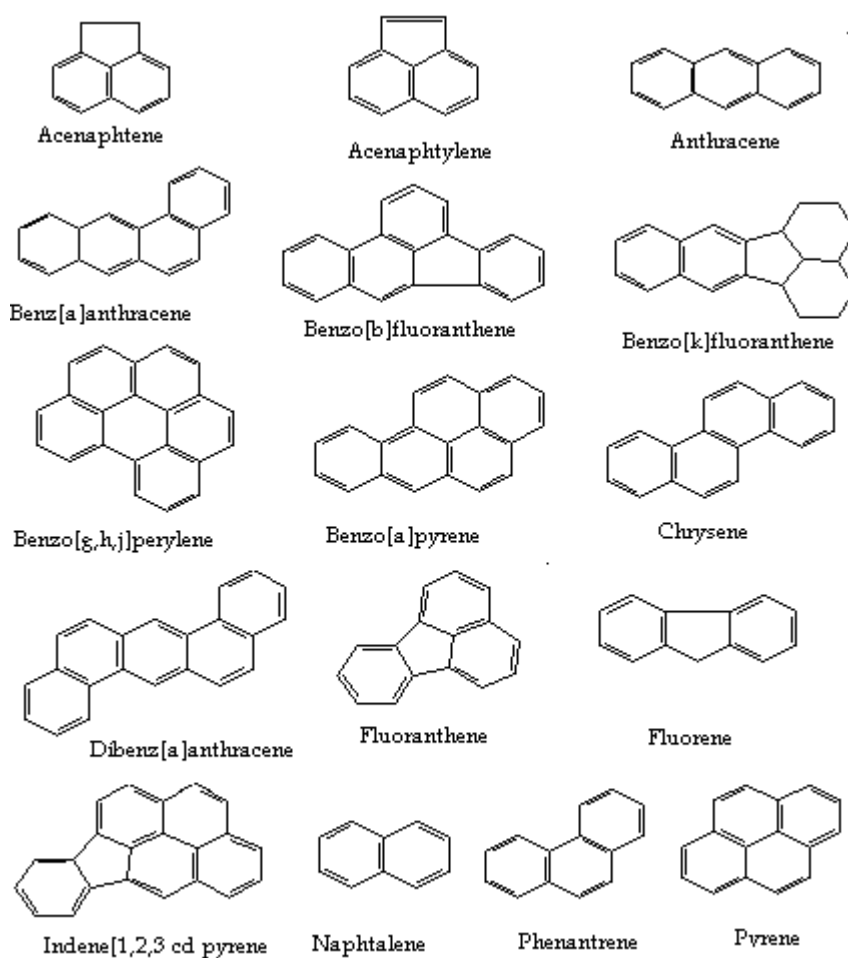
Figure 4: PAHs included in the EPA's list of Priority Pollutants and their molecular structures (Mugica, et al. 2010)

If released during cold weather, these compounds are less volatile, and may be entrained and deposited during snow showers. Recent work by Nazarenko et al. (2016) has demonstrated that snow acts as an efficient scavenger of pollutants, including PAHs, from vehicle exhaust. Studies have also shown that PAHs of anthropogenic origin occur in areas far removed from urban and industrial centers (Aamot et al., 1996; Garban et al., 2002; Mazzera et al., 1999; etc..), indicating that these compounds are easily transported in the atmosphere, deposited with snow fall, and that they have a long life in the environment. Indeed, PAHs are ubiquitous in the modern environment (Abdel-Shafy & Mansour, 2016).

It is not surprising, then, that snow and ice removed directly from city roadways and transported to dump sites may carry with it pollutants from those environments, including PAHs. Research has shown that snow may act as a transport medium for many types of urban and traffic derived contaminates, such as metals, salts, litter and nutrients (Oberts, 1994; Reinosdotter & Viklander, 2005; Reinosdotter, 2007; etc..). Pollution in roadside snows was recently studied in Lahti, Finland by Kouppämaki, et al. (2014), where they found a strong correlation between traffic volume and concentrations of PAHs, total suspended solids, phosphorus and heavy metals. Viklander (1996) as well as Droste & Johnson (1993) have conducted research on the deposition from urban snow of a host of parameters, including BOD, total and fecal coliforms, chlorides, sulfates, specific conductance, suspended solids, and metals. However, a literature review shows that little if any work has been done to determine what, if PAH species are retained in the soil at snow disposal sites. This study aims to address this lack of information.

Some general hypotheses regarding the retention of PAHs in the disposal site soils may be made based on the known behaviors of these compounds. It is expected that heavy fraction PAHs will be primarily particle bound and are expected to remain in dump site sediments, whereas it is expected that lighter fraction and less hydrophobic PAHs species may be released with melt water from the site to surface or subsurface waters, or to volatilize into the atmosphere during the melt season, and so may not be found in the soils, or maybe found in lower concentrations relative to the snow deposit.

This research could provide municipalities with valuable information regarding the effectiveness or necessity of melt water and soil treatments to remove PAH pollutants prior to release to the environment or off-site uses. Additionally, this research assesses sites that have historically dealt with significant annual snow falls. As climate change progresses over the coming decades and weather patterns continue to alter, areas where

significant snow handling is not currently necessary may experience heavier annual snow volumes, requiring the implementation of snow handling programs. By assessing the condition of currently used sites, this research can provide municipal decision makers and leaders in these areas with data regarding the potential future condition of snow disposal sites, and assist them with the development of snow handling programs and regional master plans.

3   MATERIALS AND METHODS

3.1   Characteristics and climate of the study locality

Four (4) snow dump sites and four (4) corresponding control sites were selected in south-central Finland, near the cities of Lahti and Heinola (Figure 5).

Figure 5

Finland has a population of just over 5.5 million as of September 2016 (Tilastokeskuksen, 2016) and a population density of 16.25/km^2. Lahti (60°59′ N 025°39′ E) was charted in 1904 and is as of September 2016 is the 8th largest city in Finland, with a population of approximately 119,263, an area of 135 km^2, and a population density of 883/km^2 (Maanmittauslaitos, 2016; Tilastokeskuksen, 2016). Heinola (61°12′ N

026°02′ E), located 35 km to the NNE of Lahti, was chartered in 1776 and is the 55th largest municipality in Finland, with a population of 19,393, a total area of 676 km^2, and a population density of 28.83/km^2 (Maanmittauslaito, 2016; Tilastokeskuksen, 2016). The official area of Heinola includes a large surrounding rural area as well as lakes, while the built core of Heinola city as an approximate area of 40 km^2, with a population density of about 300/km^2.

Finland is located in far northern Europe between the 60th and 70th parallels, and has a boreal climate described by the Köppen climate classification system as class Dfc, defined by having a cold continental type climate with cold summers, no dry season and with cold, wet winters (Finnish Meteorological Institute, 2016a). Snowfall and snow season length vary considerably over Finland. Typically the higher elevation areas in Lapland have the longest snow season and the greatest amount of snow, while the southern coastal areas and islands in the Finnish Archipelago have the shortest snow seasons and the least accumulation (Finnish Meteorological Institute, 2016b). Maps depicting various attributes of snowfall in Finland are given in Figure 6. Annual snowfall volume may also vary significantly from year to year, as can be seen in Figure 1. During the 2012-2013 snow season Lahti removed over 500 000 m^3 of snow from their streets (Figure 1) (per. com., Mika Lastikka, Supervisor, Lahti Department of Street Maintenance), while Heinola removed about 10,000 m^3 (per. com., Jari Hämäläinen, Supervisor, Heinola Department of Street Maintenance).

Figure 6: (a) Average date of first snow cover, (b) Average starting date of permanent snow cover, (c) Average ending date of permanent snow cover, (d) Average snow depth (cm) on March 15th, (e) Average snow depth (cm) on March 31st, (f) Average number of days with snow cover (1981-2010 normal period) (Finnish Meteorological Institute, 2016)
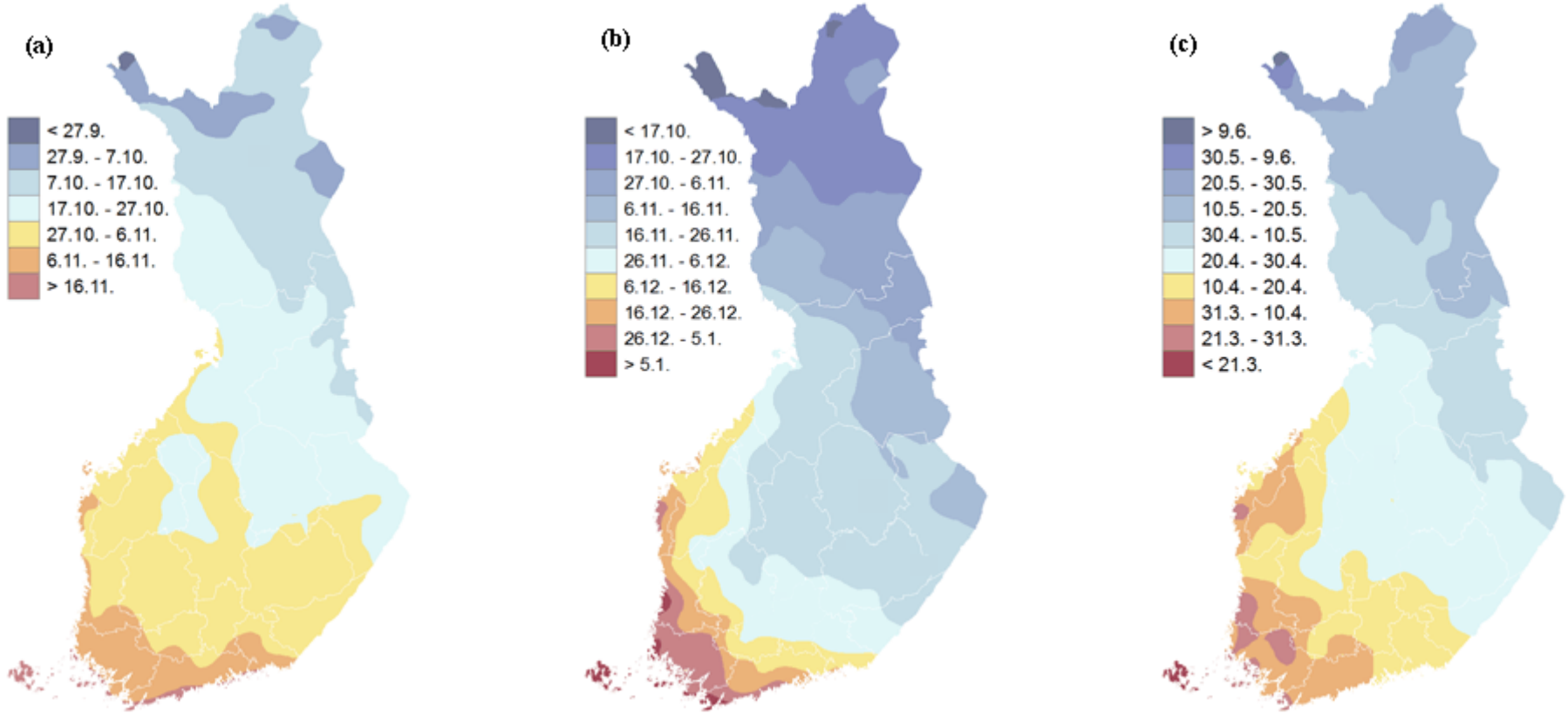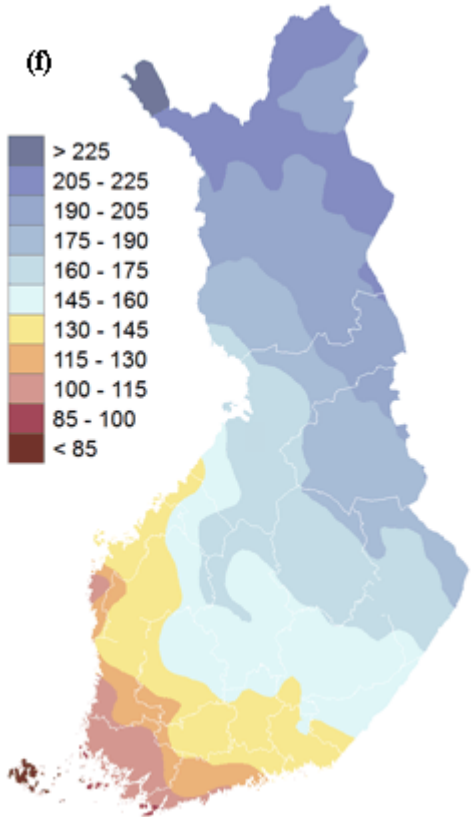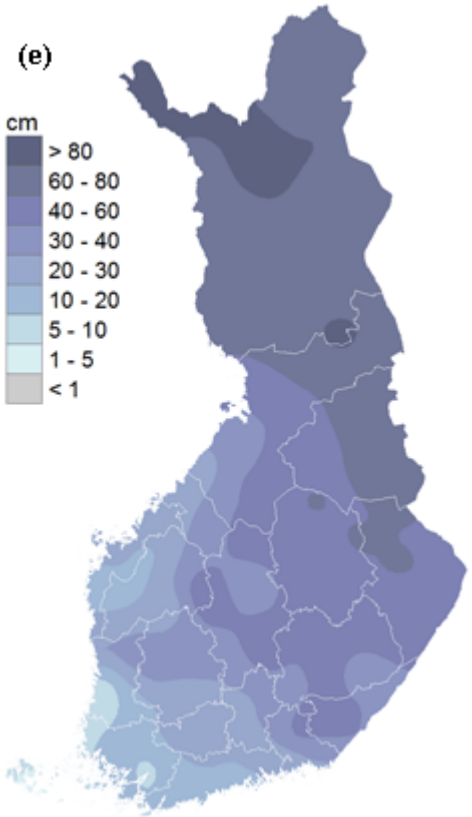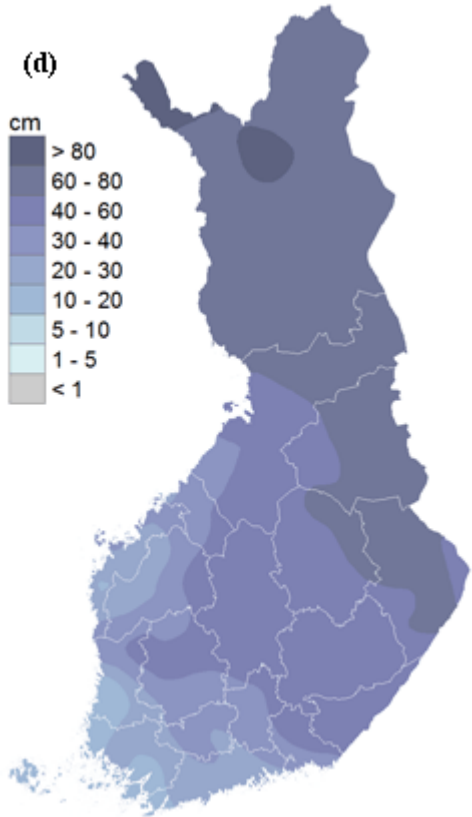
Figure 6: (continued)

3.1.1 Snow dump sites

Maps for each sampling site, including site layout and sampling locations may be found in the Appendix 1.

The Hakapelto site (60°58'33.0"N 25°43'09.6"E) is located approximately 3 km east of Lahti city center, 430 m west of Highway (Valtatie) 4. The site is largely surrounded by a remnant mixed forest. A large medical equipment manufacturing facility lies approximately 250 m to the southwest of the site, while the nearest residential property lies 200 m to the west. The Hakapelto site covers a total area of about 2.1 ha, is used solely as a snow dump, and hosts no other waste disposal services or facilities. The snow storage area covers approximately 0.75 ha of the site. A small ponding area covering about 316 m^2 has been constructed at the north end of the site to provide some retention of melt water before it is allowed to discharge offsite to surface waters.

The Vanhatie site (61°00'23.8"N 25°40'28.6"E) has a surface area of approximately 1 hectare and is located at Vanhatie 18, approximately 2.75 km NNE of Lahti city center, 500 m west of the intersection of Vääksyntie (Route 24) and Savontie (Route 140). A concrete mixing plant as well as a heavy construction materials staging yard are situated adjacent to the site but were not included in the calculation of the study site area. The site is bordered to the west by remnant spruce forest and to the south by the river Joutjoki, but is otherwise surrounded by industrial and commercial properties. A small ponding area has been constructed at the south end of the site to provide some retention of melt water before it is allowed to discharge offsite to Joutjoki.

The Rälssi site (60°56'40.5"N 25°35'37.0"E) is located approximately 5,65 km SSW of Lahti city center, 650 m southwest of the intersection of Ala-Okeroistentie (Route 296) and Helsingintie (Route 140). The site has a total surface area of nearly 40 hectares, of which approximately 1.4 ha are used solely as a snow dump. The majority of the site receives and stores a variety of waste products from construction and earthmoving operations. A

retention basin with a surface area of 3,300 m2 has been constructed at the south end of the site to provide some retention of storm water and snow melt before it is allowed to discharge offsite to surface waters.

The Lakeasuontie site (61°13'22.7"N 26°04'11.8"E) is located at Lakeasuontie 145, approximately 2.5 km NE of Heinola city center. The surrounding area is primarily forested land, though low density suburban developments lie within 300 m of the site. The site has a total surface area of approximately 2.18 ha, of which 1.07 ha serves as a snow disposal area. The other half of the site is used for fill soil and rubble storage. Drainage from the site discharges to surface waters from a 2,270 m^2 ponding area at the northern end of the site.

3.1.2 Sampling

Sampling was conducted during the fall 2014 to summer 2015. Sampling locations were chosen to be near the foot of the tipping wall in the case of the dump sites, and to 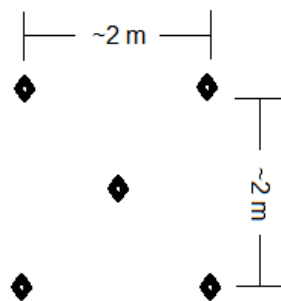be more than 50 meters away from the dump site for the control sites, and situated so that runoff contamination from the dump site could not occur.

Figure 7

Five (5) subsamples of approximately 5 grams each were taken from each site, with individual subsamples being taken at four (4) points located ~2 m from the central point, in a cross shape (Figure 7), following the sampling procedure of the LUCAS soil survey (Carre, et al., 2013). Samples were collected from the mineral soil layer. Sediments at snow dump sites were observed to be composed primarily of small gravel, with an insignificant humic surface layer, and so samples were taken from the top 10 centimetres of the soil after first scraping away the uppermost 1 to 2 cm. Control sites were located in forested land which in some cases presented an organic layer 15 to 25 cm thick. This layer was removed as much as possible, and subsamples were taken from the top 10 cm of the

mineral soil layer beneath. Subsamples were combined in clean, food-grade glass jars and stored at -20 ºC until they could be analysed.

3.1.3 Reagents and equipment

Samples were processed using acetone, hexane, sodium sulfate and silica gel 60 (70-230 mesh ASTM) from Merck KGaA (Darmstadt, Germany). Dichloromethane, 150 mm disposable glass Pasteur pipettes, 1.5ml clear glass vials and 0.05ml clear glass micro-inserts were purchased from VWR International S.A.S. (Fontenay-sous-Bois, France). Extraction of the samples was accomplished using a Thermo Scientific Dionex™ ASE™ 350 Accelerated Solvent Extractor, Dionex™ ASE™ stainless steel extraction cells, Dionex™ ASE™ cellulose filters and Dionex™ ASE™ pelletized diatomaceous earth drying agent which were purchased from Thermo Fisher Scientific, Waltham, Massachusetts, USA. The extracts were evaporated using a nitrogen multichannel evaporator from Lebisch (Bielefeld, Germany). An internal standard mixture of deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and a recovery standard (anthracene-d10) were provided by Dr Ehrenstorfer GmbH (Augsburg, Germany).

3.1.4 Sample preparation and analysis

Samples were removed from the freezer and spread onto clean paper, covered with additional clean paper, and allowed to thaw and dry for no more than two (2) days at room temperature. The samples were then sieved through a Retsch 300 µm stainless steel sieve, and the <300 µm fraction collected. The sieve was washed between uses with hot tap water and dish soap, rinsed with hot tap water, rinsed 3 times with distilled water and dried with clean paper towels.

Percent dry weight (%DW) was determined by placing ±2.5 mg of the sample material into pre-weighed ceramic crucibles (Figure 8), which were then reweighed and placed in an oven at 105°C overnight before being

removed and reweighed. %DW was then calculated by dividing the dried weight by the original weight and multiplying by 100.
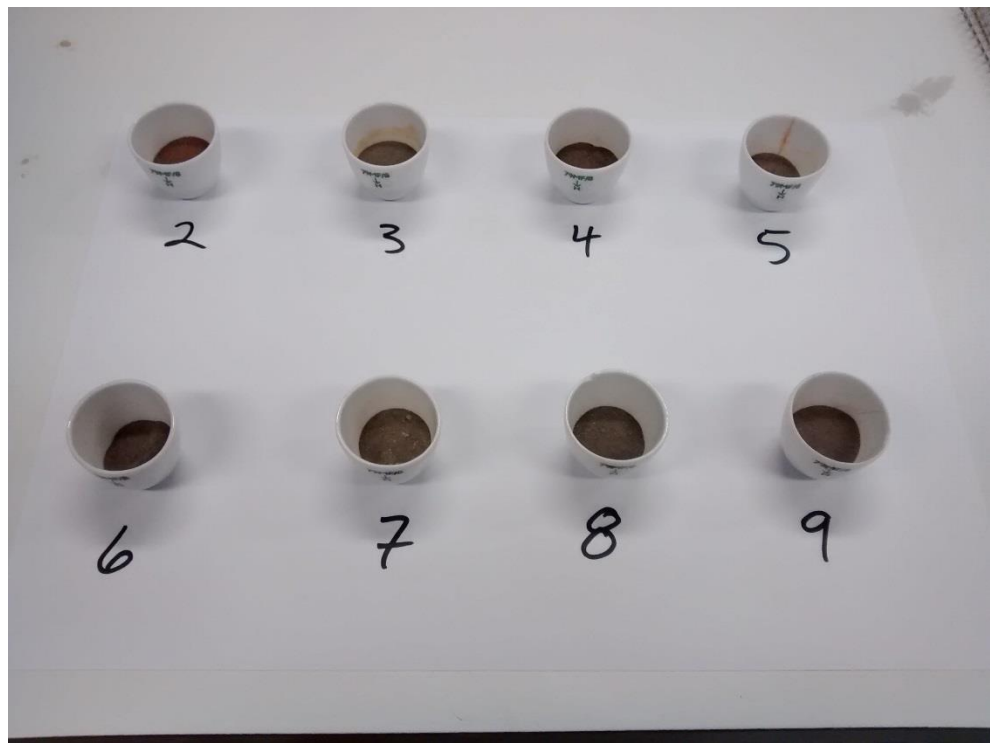

Figure 8: Sieved sediment samples in crucibles prior to ignition in muffle furnace

Percent organic matter (%OM) was obtained using the same sample according to the standardized loss-on-ignition method (SFS 3008 1990). The dried samples were combusted in a muffle furnace at 550°C for 4 hours, allowed to cool to approximately 100 °C, then placed in a silica gel desiccator for at least 1 hour prior to being reweighed. %OM was determined by subtracting the combusted weight from the DW to obtain the mass of organic matter, then dividing this mass by the DW of the sample and multiplying by 100.

Samples for PAH analysis by GC-MS were also taken from the <300 µm fraction. Approximately 1 gram of the sample material was weighed out and placed into Thermo Scientific Dionex™ ASE™ 150/350 stainless steel extraction cells with cellulose filters. 200ng (50 µl of 4 ng/µl solution) of deuterated PAH mixture was added to each sample as an internal standard. Sufficient Dionex™ ASE™ Prep DE pelletized diatomaceous

earth drying agent was added to fill each extraction cell. A blank extraction cell was also created which contained only the internal standard and drying agent. These cells were then loaded onto the Thermo Scientific Dionex™ ASE™ 350 device, which extracted the soluble organic material from the samples by first heating the samples to 100. °C for 5 mins, then flushing them with 1:1 hexane - acetone solution

Approximately 20 ml of 1:1 (v/v) hexane - acetone solution and extracted organics was collected from each sample (Figure 9). These extracts were then concentrated to 0.5 - 1 ml under a gentle flow of nitrogen while being heated at 37 ºC in a multichannel evaporator (Figure 10). ±5 ml of hexane was then added to the concentrates, and the solutions were again evaporated to 0.5 - 1 ml to remove any residual acetone from the extraction process. ±2ml of hexane and ±180mg of sodium sulfate were then added to the concentrated extract to remove any remaining water.

Figure 9: Thermo Scientific Dionex 350 extractor and collected sample extracts

Figure 10: Extracts undergoing evaporation

Cleanup columns were constructed using 150mm disposable glass Pasteur pipettes packed with approximately 1 gram of silica gel which had been activated in an oven at 160°C overnight. Each column was flushed and conditioned using sufficient hexane to saturate the silica gel and to allow ±5ml of hexane to pass through the column, which was then collected to waste.

The extracted samples were then added to the clean-up columns. The sample tubes were rinsed with ±5ml dichloromethane, which was added to the clean-up column. The extracts were then eluted through the columns using ±10ml of DCM each, and collected to clean Kimax test tubes (Figure 11).

Figure 11: Extracted samples being eluted through silica gel cleanup columns

±10ml of cleaned extract was collected from each column. These were again evaporated under a gentle nitrogen flow to ±0.5ml. 200ng (20 µl of 10ng/µl) of anthracene-D10 recovery standard was then

added to each sample. The sample tubes were rotated so that the sidewalls of the tube were rinsed with the sample to ensure that the full volume of the recovery standard was incorporated and well mixed. ±10μl from each sample was then transferred to 0.05ml glass inserts within 1.5ml glass vials using disposable Pasteur pipettes. The vials were then capped and loaded onto the sampling tray of a Shimadzu GC–MS-QP5000 system equipped with an AOC-20i+s auto injector (Figure 13). The GC-MS was fitted with a Zebron 26.5m (30m original length) ZB-5MS capillary GC column (Phenomenex, Inc., Torrance, California, USA) with an internal diameter of 0.25 mm and a film thickness of 0.25 μm. Both the inlet temperature and the mass spectrometer interface temperature were set to 280 °C. The oven temperature program for PAHs was as follows: 80 °C for 1 min, 10 °C/min to 250 °C, 7 °C/min to 280 °C and 20 °C/min to 320 °C, where it was held for 5 min.

Figure 12: Cleaned and concentrated PAH extracts prior to GCMS analysis

4   RESULTS

Results from organic matter (OM) analyses are presented in Table 1, and show that dump sites contain substantially less organic matter than the control sites. The raw data values from the GC-MS analyses are presented in Appendix 2, and show that dumpsite sediments do contain PAHs in higher concentrations than those found in control site soils. Limit of quantification (LOQ) values were determined for each compound by Dr. Anna-Lea Rantalainen using a 10:1 signal to noise ratio, meaning that a peak would only be recognized if it was at least 10 times greater than the magnitude of the background noise. Example chromatograms from the GC-MS analyses are provided in Figures 13 and 14:

Table 1

Sample ID	Sample Type	%DW	Total OM (g)	%OM
Hakapelto Ctrl	control	99.50%	0.142	6.49%
Hakapelto	dump	99.79%	0.122	5.75%
Lakeasuontie Ctrl	control	98.92%	0.25	10.79%
Lakeasuontie	dump	99.82%	0.072	3.26%
Rälssi Ctrl	control	99.21%	0.215	10.62%
Rälssi	dump	99.72%	0.116	5.02%
Vanhatie Ctrl	control	99.30%	0.306	14.13%
Vanhatie Ctrl 2	control	98.15%	0.463	16.56%
Vanhatie Ctrl 3	control	98.40%	0.878	33.90%
Vanhatie Ctrl 4	control	99.13%	0.48	19.43%
Vanhatie Ctrl 5	control	98.36%	0.921	33.01%
Vanhatie	dump	99.91%	0.078	3.42%
Vanhatie 2	dump	98.15%	0.18	5.39%
Control site average OM			0.457	18.90%
Dump site average OM			0.114	4.63%

Data obtained from the first Vanhatie Control site was found to contain significant levels of PAH contamination and so could not be used as a control for the Vanhatie Dump site. An additional four (4) control samples (Vanhatie Ctrl 2, 3, 4 & 5) were collected from this area in June and August 2015. These samples were taken from the locations shown on the Vanhatie site map in Appendix 1. Of these additional samples only Vanhatie Cntrl 3 was found suitable to serve as a control sample. Possible

reasons for this contamination are presented in the Discussion section. An additional sample was also taken from the Vanhatie Dump site in June 2015. This sample was found to be similar to the original Vanhatie Dump site sample in PAH concentrations. The results of these two samples were averaged together to obtain a single value for the Vanhatie Dump site.

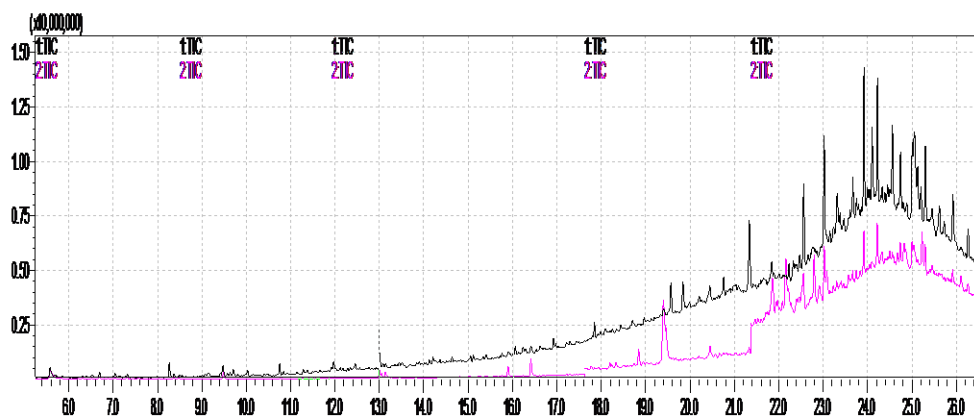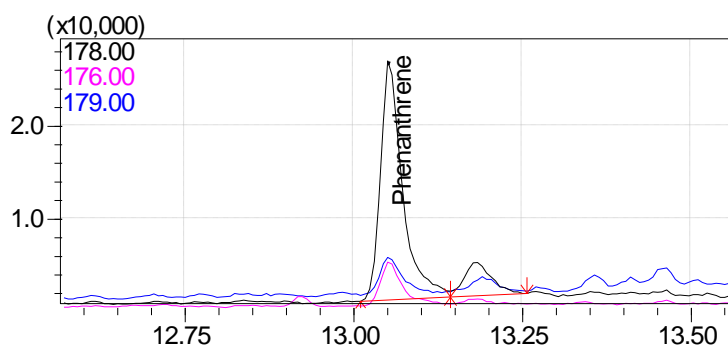**Figure 13:** Example total chromatogram from GC-MS analysis of snow dump site sample

Figure 14: Chromatogram showing phenanthrene peak from GC-MS analysis of snow dump site sample

Percent recovery values for each of the internal standards are given at the bottom of the raw data table in Appendix 2. VA Ctrl 3, 4 & 5 show extremely high recoveries. This is believed to have been caused by an incorrect dosing of recovery standard, and so was not considered as grounds to discard these results.

Raw GC-MS data was corrected for lab contamination by subtracting the appropriate Blank values from the analyte results. Results found to be below LOQ (< LOQ) were assigned a value of ½ LOQ (0.5 x LOQ). Where

Blank values were detected, but were < LOQ, the sample data was not corrected by subtracting ½ LOQ. Blank corrected values are given in Appendix 2B.

Concentrations of PAH compounds were calculated as nanograms PAH per gram dry weight (ng/g DW) using the Blank corrected values. This was accomplished by dividing the detected mass of the PAH by the sample weight multiplied by the percent dry weight of the sample (ng PAH / sample weight (g) x % dry weight). Dry weight concentrations of PAHs are given in Appendix 2C.

Concentrations of PAH compounds were then calculated as nanograms PAH per gram dry weight organic matter (ng/g OM). This was undertaken because PAHs preferentially bond with organic matter and so samples which contain higher levels of organic matter may be expected to also contain higher levels of PAH contamination. Therefore, expressing PAH content as a function of OM allows for samples with extremely different %OM values to be compared. PAH concentrations per gram dry weight OM are given in Appendix 2D.

5   DISCUSSION

5.1   Results from GC-MS analyses

All sixteen PAHs that were analyzed for were detected in the snow dump
site sediments. The individual DW concentrations of the 16 PAHs found in
this study ranged from below the limit of quantification (<LOQ) to 216.21
ng/g DW in the dump site sediments (Figure 15), and from <LOQ to 44.74
ng/g DW in the control sites (Figure 16). In the dump sites, the occurrence
of the most abundant individual PAH by mass was found to be pyrene at
the Vanhatie site, with an observed DW concentration of 216.21 ng/g
(Figure 15). In the control sites, the most abundant occurrence of an
individual PAH by mass was found to be benzo [b] fluoranthene at the
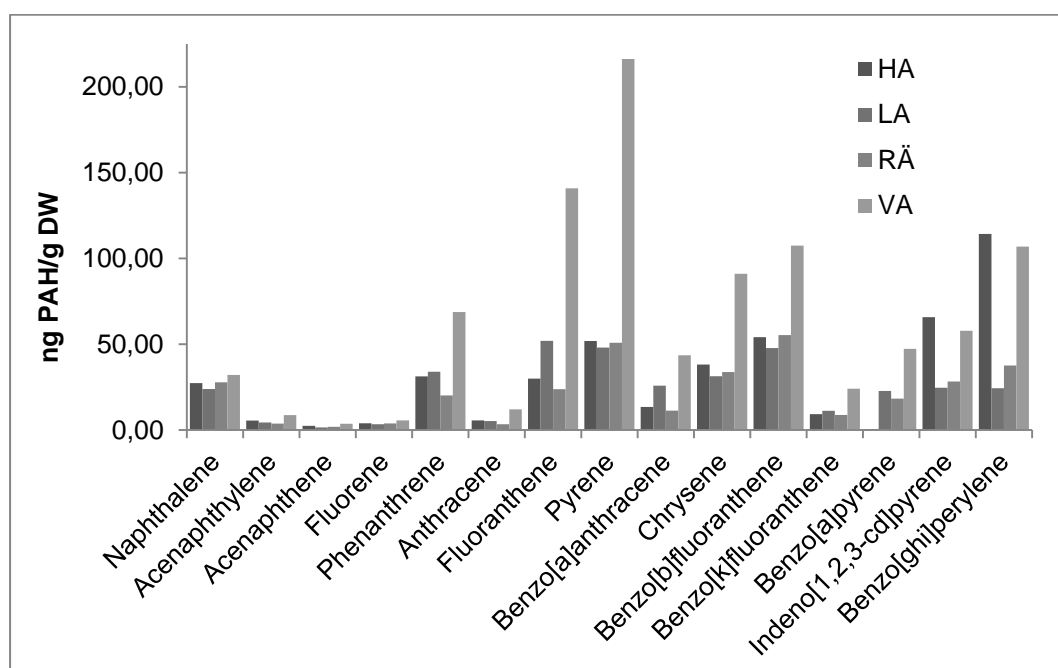Rälssi control site, with observed DW concentrations of 44.74 ng/g.

Figure 15: Dry weight PAH concentrations observed at snow dump sites

The total DW mass of all 16 PAHs (PAH16) found in the snow dump sites
ranged from 334.64 ng/g DW at Rälssi site to 970.98 ng/g DW at the
Vanhatie site, while the PAH16 DW mass found in the control sites ranged
from 13.88 ng/g DW at the Vanhatie site to 181.46 ng/g DW at the Rälssi
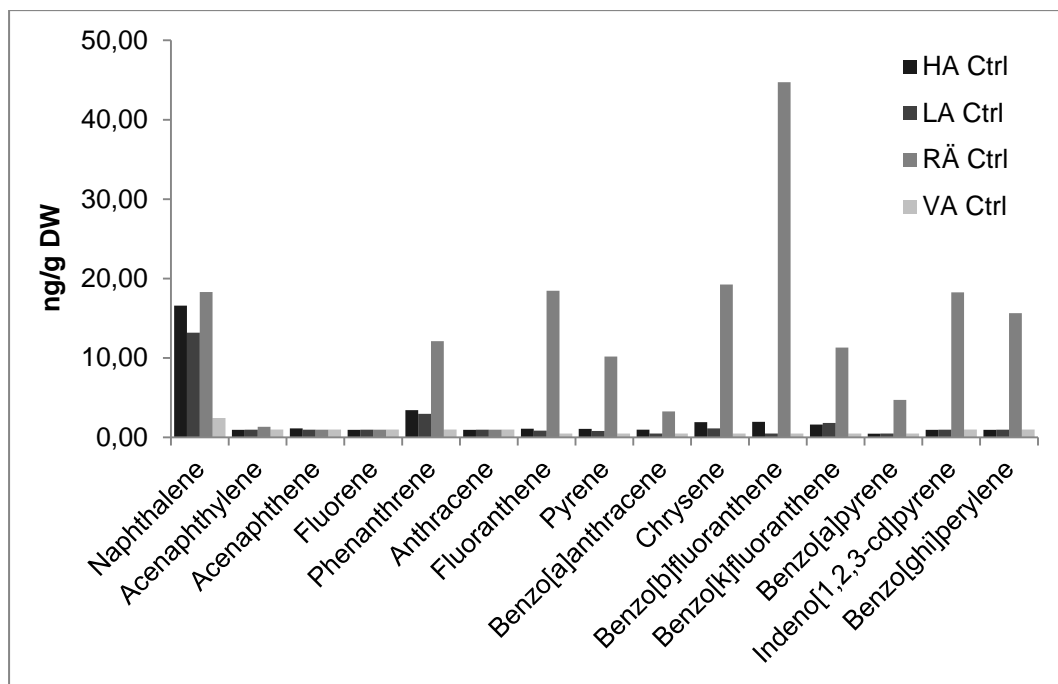site (Figure 17).

Figure 16: Dry weight PAH concentrations observed at control sites

Sum total DW concentrations for individual PAH species found in dump and control sites are given in Figure 18. The most abundant single PAH by DW mass in dump sites was found to be pyrene, with a total DW concentration of 367.08 ng/g, while the least abundant PAH species was acenaphthlene, with a total DW concentration of 9.65 ng/g.
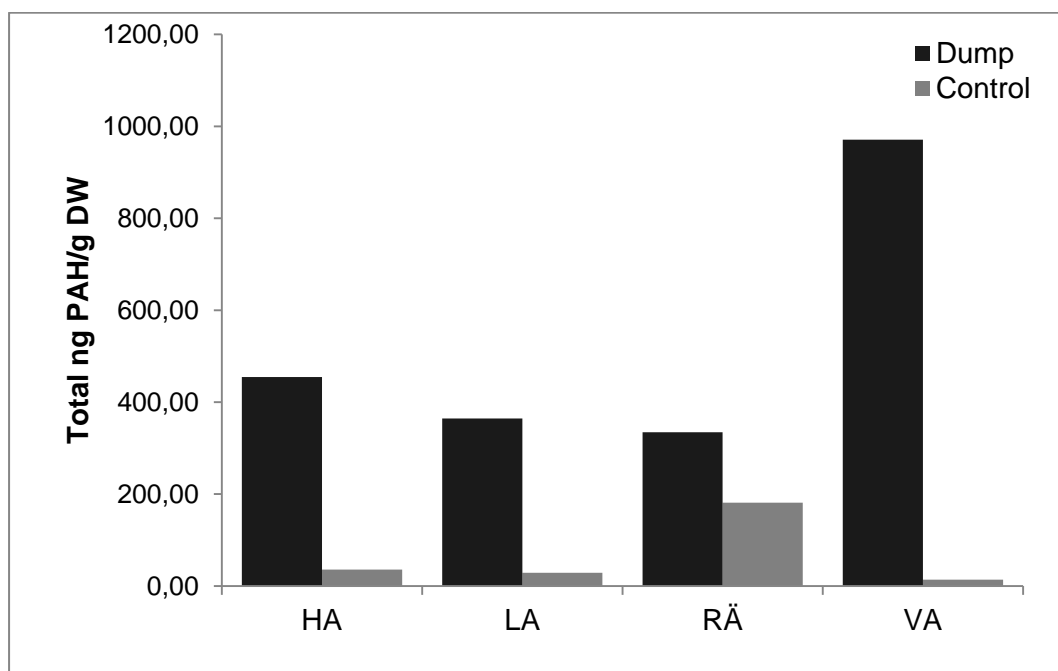

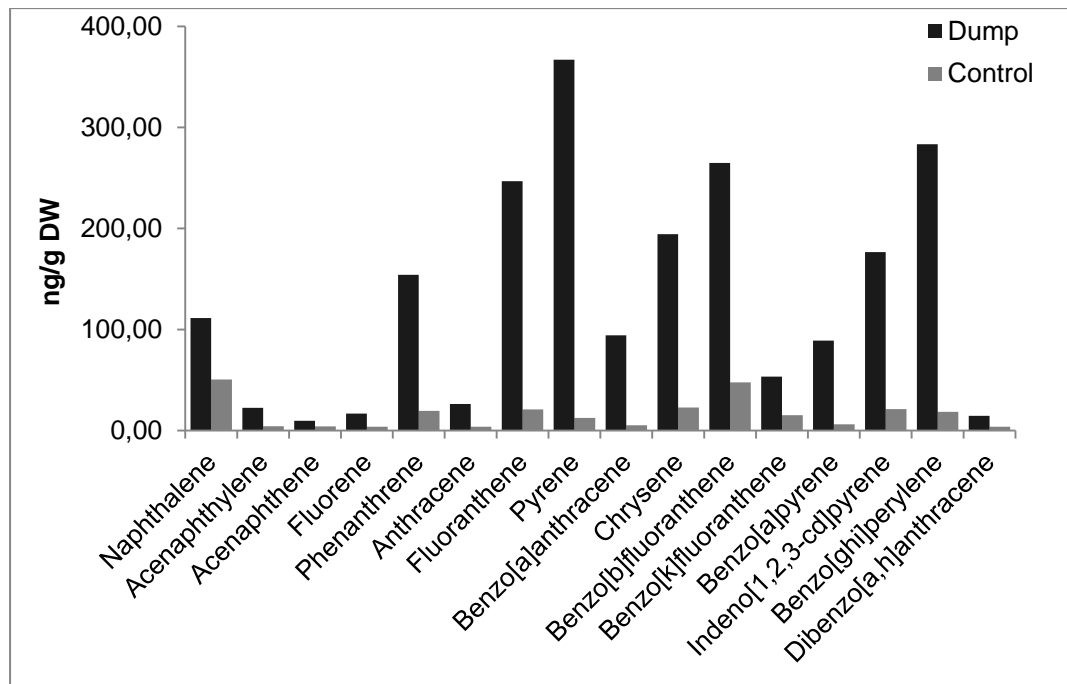**Figure 17:** Total DW mass of PAHs found in deposit and control sites

Figure 18: DW concentrations of individual PAHs observed in dump and control sites

The individual concentrations of the 16 PAHs per gram OM ranged from 3.89 to 1757.66 ng/g OM in the dump sites (Figure 19), and from <LOQ to 208.20 ng/g OM in the control sites (Figure 20). In the dump sites, the most abundant individual PAH by concentration was found to be pyrene at the Vanhatie site, with an observed DW concentration of 1622.63 ng/g OM. In the control sites, the most abundant individual PAH by mass was found to be benzo [b] fluoranthene at the Rälssi control site, with observed DW concentrations of 208.20 ng/g OM.

The total mass per gram OM of all 16 PAHs found in the snow dump sites ranged from 2884.87 ng/g OM at the Rälssi site to 8027.07 ng/g OM at the Vanhatie site, while the total concentration found in the control sites ranged from 13.88 ng/g OM at the Vanhatie site to 181.46 ng/g OM at the Rälssi site (Figure 21). The sum total DW masses per gram OM for individual PAH species found in dump and control sites are given in Figure 22.
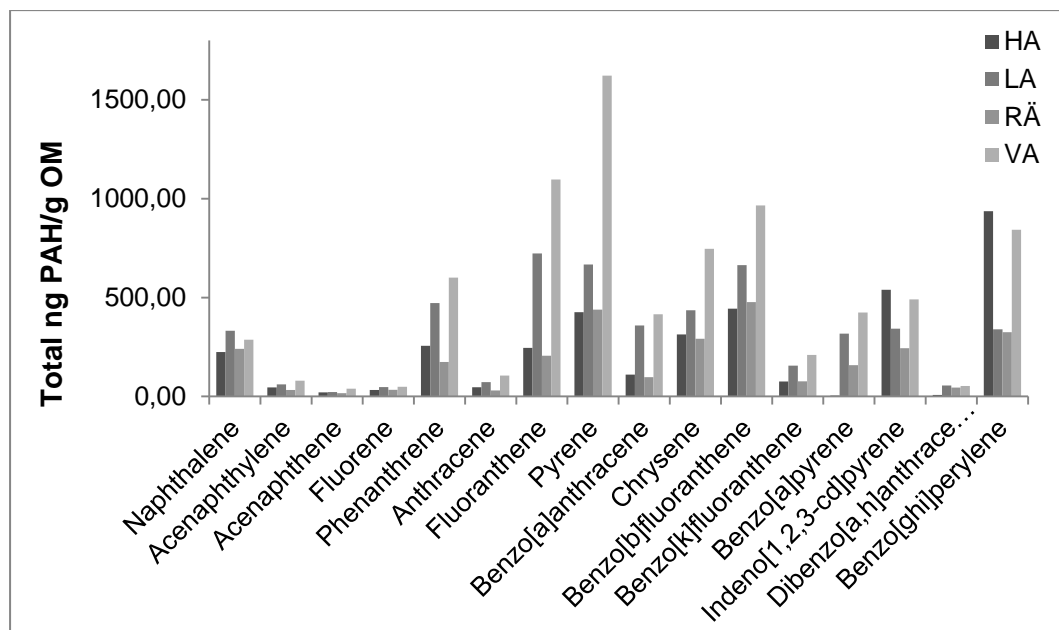
Figure 19: Dry weight PAH concentrations per g OM observed at snow dump sites

The total mass per gram OM of all 16 PAHs found in the snow dump sites ranged from 2884.87 ng/g OM at the Rälssi site to 8027.07 ng/g OM at the Vanhatie site, while the total mass found in the control sites ranged from 13.88 ng/g OM at the Vanhatie site to 181.46 ng/g OM at the Rälssi site (Figure 21). The sum total DW masses of individual PAH species found in dump and control sites are given in Figure 22.
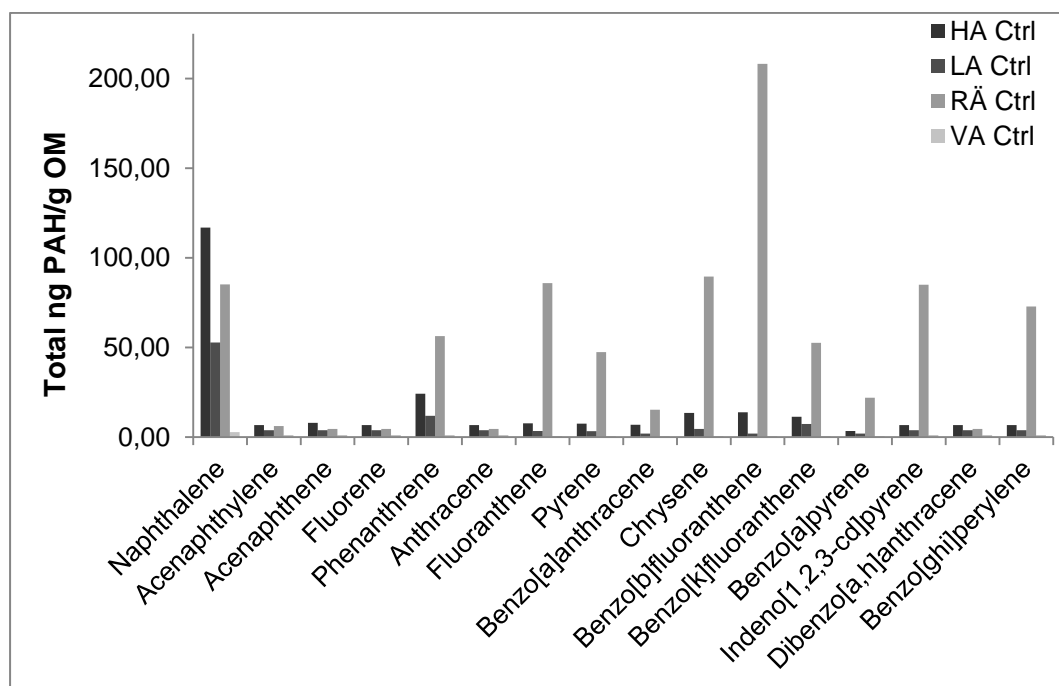

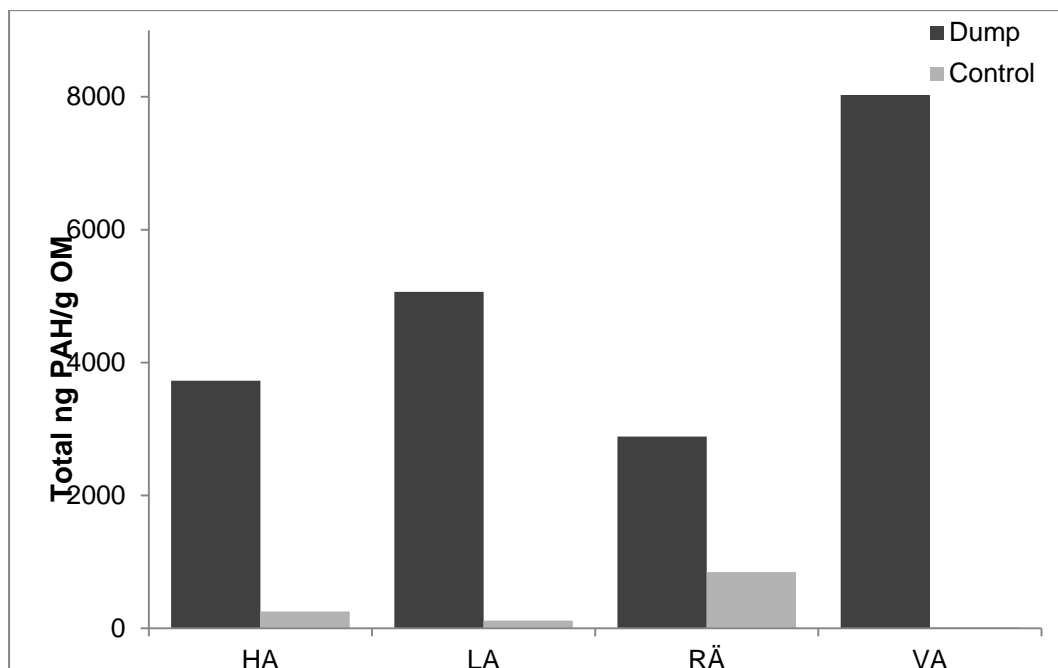**Figure 20:** Dry weight PAH concentrations per g OM observed at control sites

Figure 21: Total DW concentrations of PAHs per g OM found in deposit and control sites

The most abundant single PAH by DW mass per gram OM in dump sites was again found to be pyrene, with a total DW concentration of 3154.38ng/g OM, while the least abundant PAH species was acenaphthlene, with a total DW concentration of 97.43 ng/g OM.
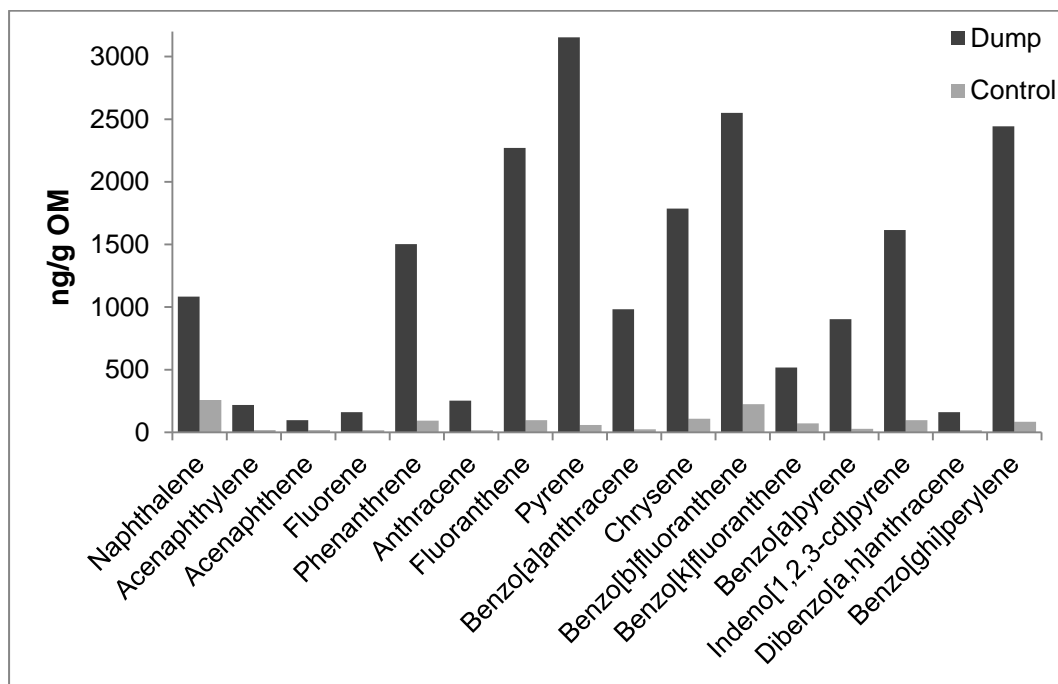

Figure 22: Total DW concentrations of individual PAHs per g OM observed in dump and control sites

Though some differences do exist between the DW and per gram OM concentrations of individual PAH species, the two datasets are largely comparable, and so for brevity only the DW data will be further examined in detail in this thesis. Exceptions will be made for chrysene and dibenzo[a,h]anthracene, which show significant differences in the DW and per gram OM concentrations.

The most abundant individual PAH species by DW concentration found in the dump site samples were pyrene, benzo[ghi]perylene, benzo[b]fluoranthene, fluoranthene, chrysene and indeno[1,2,3-cd]pyrene, which made up over 72% of the PAH16 DW concentration. The most abundant individual PAH species by DW concentration in the control sites were found to be naphthalene, benzo[b]fluoranthene, chrysene, indeno[1,2,3-cd]pyrene, fluoranthene, and phenanthrene, which made up approximately 70% of the PAH16 DW concentration. A comparison of the relative abundances of individual PAHs between the dump and control sites is shown in Figure 23. The average molecular masses of the 6 most abundant PAHs from the dump sites was found to be 239 while the average for the 6 most abundant PAHs from the control sites was found to be 211, indicating that heavier, less volatile PAHs are more abundant in the snow dump sites than in the control sites. This data is presented in Table 2.
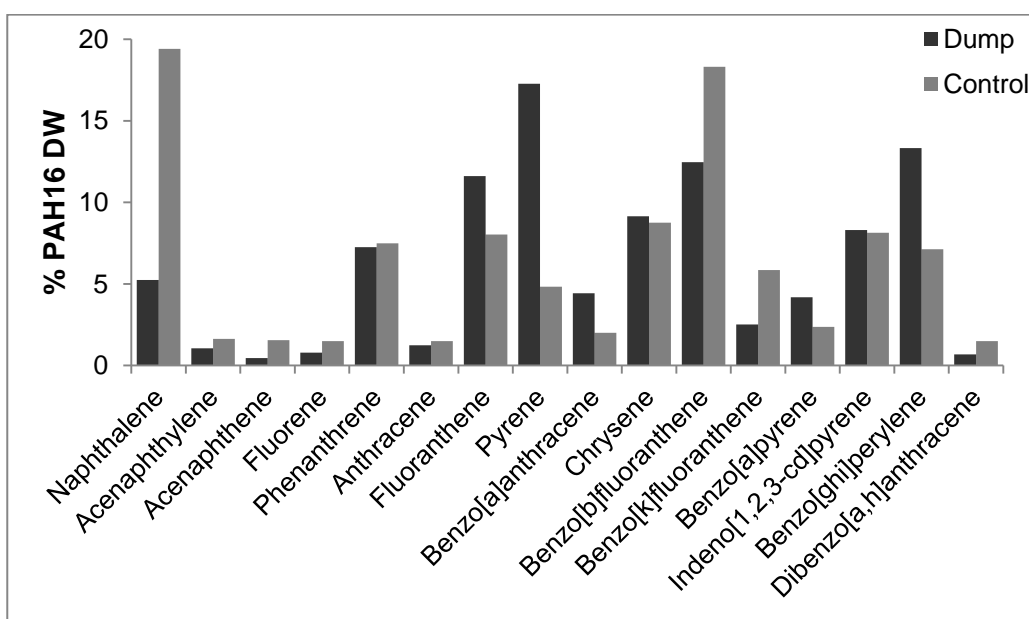

Figure 23: PAH species by relative abundance

Parameter	mol. mass	Dump	%PAH16 Dump	Control	%PAH16 Control
Naphthalene	128	111.36	5.24	50.53	**19.41**
Acenaphthylene	152	22.45	1.06	4.24	1.63
Acenaphthene	154	9.65	0.45	4.05	1.56
Fluorene	166	16.83	0.79	3.88	1.49
Phenanthrene	178	154.18	7.26	19.50	**7.49**
Anthracene	178	26.34	1.24	3.88	1.49
Fluoranthene	202	246.73	**11.61**	20.90	**8.03**
Pyrene	202	367.08	**17.28**	12.58	4.83
Benzo[a]anthracene	228	94.22	4.43	5.23	2.01
Chrysene	228	194.42	**9.15**	22.79	**8.76**
Benzo[b]fluoranthene	252	264.82	**12.46**	47.68	**18.32**
Benzo[k]fluoranthene	252	53.41	2.51	15.24	5.85
Benzo[a]pyrene	252	89.00	4.19	6.17	2.37
Indeno[1,2,3-cd]pyrene	276	176.57	**8.31**	21.17	**8.13**
Benzo[ghi]perylene	276	283.33	**13.33**	18.56	7.13
Dibenzo[a,h]anthracene	278	14.54	0.68	3.88	1.49

Table 2: Molecular mass, DW concentration & percent abundance for individual PAH species. % values in bold are the 6 most abundant PAHs from the dump and control sites.

5.2   Statistical analyses and results

Tests were then applied to the data presented above to determine if the variance between the observed concentrations of PAH contaminates in the dump and the control sites is likely the result of chance, or if a statistically significant difference exists.

R: A Language and Environment for Statistical Computing (R Core Team, 2015) was used for all statistical analyses. Due to the small size and the paired nature of the data set, the two sample t-test for means was selected as the primary method of analysis. However, the t-test is a parametric test, and so assumes that the data are normally distributed. The Shapiro-Wilk Test was first used to determine if the sample data met the normality requirement. If the data was found to be non-normal, then mathematical transformations were applied in an effort to adjust the distribution of the data towards normality. If these transformations failed the data was assumed to be non-normal, and the non-parametric Wilcoxon-Mann-Whitney test was performed. Alpha was equal to 0.05 for all tests. Table 3 presents the observed p-values from all t and U tests performed.

Parameter	DW	per g OM
Naphthalene	0.016	0.002
Acenaphthylene	0.026	0.027
Acenaphthene	0.035	0.036
Fluorene	0.029	0.007
Phenanthrene	0.046	**0.052**
Anthracene	0.022	0.014
Fluoranthene	0.029	0.028
Pyrene	0.024	0.021
Benzo[a]anthracene	0.012	0.020
Chrysene	**0.051**	0.005
Benzo[b]fluoranthene	0.023	0.026
Benzo[k]fluoranthene	**0.079**	**0.056**
Benzo[a]pyrene	**0.343**	**0.065**
Indeno[1,2,3-cd]pyrene	0.026	0.012
Dibenzo[a,h]anthracene	**0.343**	0.000
Benzo[ghi]perylene	0.015	0.006

Table 3: Observed p-values (α =0.05) from t and U tests for dry weight PAH content and as a function of organic matter content (ng PAH/g OM). All tests showed significant difference between dump and control sites, with the exception of those shown in bold.

As shown in the above table, the majority of the PAHs analyzed show a significant difference in observed concentrations between snow dump and control sites. The results for each PAH, transformations, tests used and insignificant p-values are discussed in the following subsection. Plots of individual PAH DW concentrations are presented in Appendix 3A.

5.2.1 Occurance of individual PAHs

Naphthalene

The DW concentration of naphthalene observed in the dump site samples ranged from 23.89 to 32.17 ng/g, and in the control sites from 2.44 to 18.31 ng/g. The total DW mass found from all dump sites was 111.36 ng, making it the 8th most common PAH observed, while it was the most abundant PAH found in the control sites with a total observed mass of 50.53 ng.

The Shapiro-Wilk test showed the DW concentration of naphthalene to be normally distributed (p = 0.722) and so transformation of the data was not needed. The t-test results confirm a significant difference (p = 0.016) between the mean DW PAH concentrations of naphthalene in the dump

and control sites. This indicates that mean naphthalene concentrations are elevated in the snow dump sites relative to controls.

Acenaphthylene

The DW concentration of acenaphthylene observed in the dump site samples ranged from 3.76 to 8.76 ng/g, and in the control sites from 0.95 to 1.33 ng/g. It ranked 13th in terms of abundance in dump sites and 12th in control sites, with observed DW masses of 22.45 ng and 1.63 ng respectively.

The Shapiro-Wilk test showed the DW concentration of acenaphthylene to be normally distributed (p = 0.084) and so transformation of the data was not needed. The t-test results confirm a significant difference (p = 0.026) between the mean DW PAH concentrations of acenaphthylene in the dump and control sites. This indicates that mean acenaphthylene concentrations are elevated in the snow dump sites relative to controls.

Acenaphthene

The DW concentration of acenaphthene observed in the dump site samples ranged from 1.57 to 3.69 ng/g, and in the control sites from 0.96 to 1.13 ng/g. It was the least abundant PAH observed in dump sites and the 13th most abundant in control sites, with observed DW masses of 9.65 ng and 1.56 ng respectively.

The Shapiro-Wilk test showed the DW concentration of acenaphthene to be slightly non-normal (p = 0.046) and so a square root transformation was applied, which successfully normalized the data (p = 0.109).The t-test of transformed data confirmed a significant difference (p = 0.035) between the mean DW PAH concentrations of acenaphthene in the dump and control sites. This indicates that mean acenaphthene concentrations are elevated in the snow dump sites relative to controls.

Fluorene

The DW concentration of fluorene observed in the dump site samples ranged from 3.37 to 5.61 ng/g, and in the control sites from 0.95 to 0.99 ng/g. It ranked 14th in abundance in dump sites and was one of the three least abundant PAHs in control sites, with observed DW mass of 16.83 ng and 3.88 ng respectively.

The Shapiro-Wilk test showed the DW concentration of acenaphthene to be slightly non-normal (p = 0.044). All attempts to normalize the distribution via transformations failed and so the data were assumed to be non-normal. The non-parametric Wilcoxon rank sum test was used and confirmed a significant difference (p = 0.029) between the mean DW PAH concentrations of fluorene in the dump and control sites. This indicates that mean fluorene concentrations are elevated in the snow dump sites relative to controls.

Phenanthrene

The DW concentration of phenathrene observed in the dump site samples ranged from 20.18 to 68.78 ng/g, and in the control sites from 0.99 to 12.11 ng/g. It ranked 7th in terms of abundance in dump sites and 6th in control sites, with observed DW masses of 154.18 ng and 19.50 ng respectively.

The Shapiro-Wilk test showed the DW concentration of phenathrene to be normally distributed (p = 0.120) and so transformation of the data was not needed. The t-test results confirm a significant difference (p = 0.046) between the mean DW PAH concentrations of phenathrene in the dump and control sites. This indicates that mean phenathrene concentrations are elevated in the snow dump sites relative to controls.

Anthracene

The DW concentration of anthracene observed in the dump site samples ranged from 3.45 to 12.05 ng/g, and in the control sites from 0.95 to 0.99 ng/g. It ranked 12th in terms of abundance in dump sites and was one of

the three least abundant in control sites, with observed DW masses of 26.34 ng and 3.88 ng respectively.

The Shapiro-Wilk test showed the DW concentration of anthracene to be non-normal (p = 0.017) and so a square root transformation was applied, which successfully normalized the data (p = 0.055).The t-test of transformed data confirmed a significant difference (p = 0.022) between the mean DW PAH concentrations of anthracene in the dump and control sites. This indicates that mean anthracene concentrations are elevated in the snow dump sites relative to controls.

Fluoranthene

The DW concentration of fluoranthene observed in the dump site samples ranged from 23.87 to 140.88 ng/g, and in the control sites from 0.50 to 18.46 ng/g. It ranked 4th in terms of abundance in dump sites and 5th in control sites, with observed DW masses of 246.73 ng and 20.90 ng respectively.

The Shapiro-Wilk test showed the DW concentration of fluoranthene to be non-normal (p = 0.006) and so a square root transformation was applied, which successfully normalized the data (p = 0.263).The t-test of transformed data confirmed a significant difference (p = 0.029) between the mean DW PAH concentrations of fluoranthene in the dump and control sites. This indicates that mean fluoranthene concentrations are elevated in the snow dump sites relative to controls.

Pyrene

The DW concentration of pyrene observed in the dump site samples ranged from 48.05 to 216.21 ng/g, and in the control sites from 0.50 to 10.19 ng/g. It was the most abundant PAH found in dump sites and the 5th most abundant in control sites, with observed DW masses of 246.73 ng and 20.90 ng respectively.

The Shapiro-Wilk test showed the DW concentration of pyrene to be non-normal (p = 0.001) and so a square root transformation was applied, which

successfully normalized the data (p = 0.109).The t-test of transformed data confirmed a significant difference (p = 0.024) between the mean DW PAH concentrations of pyrene in the dump and control sites. This indicates that mean pyrene concentrations are elevated in the snow dump sites relative to controls.

Benzo[a]anthracene

The DW concentration of benzo[a]anthracene observed in the dump site samples ranged from 11.30 to 43.64 ng/g, and in the control sites from 0.48 to 3.27 ng/g. It ranked 9[th] in abundance in dump sites and was the 11[th] most abundant PAH in control sites, with observed DW masses of 94.22 ng and 5.23 ng respectively.

The Shapiro-Wilk test showed the DW concentration of benzo[a]anthracene to be non-normal (p = 0.042) and so a square root transformation was applied, which successfully normalized the data (p = 0.292).The t-test of transformed data confirmed a significant difference (p = 0.012) between the mean DW PAH concentrations of benzo[a]anthracene in the dump and control sites. This indicates that mean benzo[a]anthracene concentrations are elevated in the snow dump sites relative to controls.

Chrysene

The DW concentration of chrysene observed in the dump site samples ranged from 31.35 to 91.05 ng/g, and in the control sites from 0.50 to 19.25 ng/g. It ranked 5[th] in terms of abundance in dump sites and 3rd in control sites, with observed DW masses of 194.42 ng and 22.79 ng respectively.

The Shapiro-Wilk test showed the DW concentration of chrysene to be normally distributed (p = 0.065) and so transformation of the data was not needed. The t-test resulted in a weakly insignificant difference (p = 0.051) between the mean DW PAH concentrations of chrysene in the dump and control sites. However an analysis of the concentration per gram OM

showed a strongly significant difference (p = 0.005). This indicates that mean chrysene concentrations are elevated in the snow dump sites relative to controls.

Benzo[b]fluoranthene

The DW concentration of benzo[b]fluoranthene observed in the dump site samples ranged from 47.83 to 107.49 ng/g, and in the control sites from 0.48 to 44.74 ng/g. It ranked 3rd in terms of abundance in dump sites and 2nd in control sites, with observed DW masses of 264.82 ng and 47.68 ng respectively.

The Shapiro-Wilk test showed the DW concentration of benzo[b]fluoranthene to be normally distributed (p = 0.141) and so transformation of the data was not needed. The t-test results confirm a significant difference (p = 0.023) between the mean DW PAH concentrations of benzo[b]fluoranthene in the dump and control sites. This indicates that mean benzo[b]fluoranthene concentrations are elevated in the snow dump sites relative to controls.

Benzo[k]fluoranthene

The DW concentration of benzo[k]fluoranthene observed in the dump site samples ranged from 8.84 to 24.10 ng/g, and in the control sites from 0.50 to 11.30 ng/g. It ranked 11th in terms of abundance in dump sites and 8th in control sites, with observed DW masses of 53.41 ng and 15.24 ng respectively.

The Shapiro-Wilk test showed the DW concentration of benzo[b]fluoranthene to be normally distributed (p = 0.153) and so transformation of the data was not needed. The t-test resulted in a weakly insignificant difference (p = 0.079) between the mean DW PAH concentrations of chrysene in the dump and control sites. An analysis of the concentration per gram OM showed a slightly stronger, yet still insignificant difference (p = 0.056). This indicates that mean

benzo[k]fluoranthene concentrations may not be elevated in the snow dump sites relative to controls.

Benzo[a]pyrene

The DW concentration of benzo[a]pyrene observed in the dump site samples ranged from 0.47 to 47.32 ng/g, and in the control sites from 0.48 to 4.72 ng/g. It ranked 10th in abundance in both dump and control sites, with observed DW masses of 89.00 ng and 6.17 ng respectively.

The Shapiro-Wilk test showed the DW concentration of benzo[a]pyrene to be non-normal (p = 0.01). All attempts to normalize the distribution via transformations failed and so the data were assumed to be non-normal. The non-parametric Wilcoxon rank sum test was used and showed an insignificant difference (p = 0.343) between the mean DW PAH concentrations of fluorene in the dump and control sites. An analysis of the concentration per gram OM showed a stronger, yet still insignificant difference (p = 0.065). This indicates that mean benzo[a]pyrene concentrations may not be elevated in the snow dump sites relative to controls.

Indeno[1,2,3-cd]pyrene

The DW concentration of indeno[1,2,3-cd]pyrene observed in the dump site samples ranged from 24.64 to 65.79 ng/g, and in the control sites from 0.95 to 18.26 ng/g. It ranked 6th in terms of abundance in dump sites and 4th in control sites, with observed DW masses of 176.57 ng and 21.17 ng respectively.

The Shapiro-Wilk test showed the DW concentration of indeno[1,2,3-cd]pyrene to be normally distributed (p = 0.115) and so transformation of the data was not needed. The t-test results confirm a significant difference (p = 0.026) between the mean DW PAH concentrations of indeno[1,2,3-cd]pyrene in the dump and control sites. This indicates that mean indeno[1,2,3-cd]pyrene concentrations are elevated in the snow dump sites relative to controls.

Dibenzo[a,h]anthracene

The DW concentration of dibenzo[a,h]anthracene observed in the dump site samples ranged from 0.95 to 5.23 ng/g, and in the control sites from 0.95 to 0.99 ng/g. It ranked 15th in terms of abundance in dump sites and was one of the three least abundant PAHs found in control sites, with observed DW masses of 14.54 ng and 3.88 ng respectively.

The Shapiro-Wilk test showed the DW concentration of dibenzo[a,h]anthracene to be to be non-normally distributed (p = 0.004). All attempts to normalize the distribution via transformations failed and so the data were assumed to be non-normal. The non-parametric Wilcoxon rank sum test was used and showed and insignificant difference (p = 0.343) between the mean DW PAH concentrations of dibenzo[a,h]anthracene in the dump versus control sites. Analysis of the concentration per gram OM showed a strongly significant difference (p = 0.0004), indicating that mean concentrations are elevated in the dump sites relative to controls. However, this is not a strong result, and additional samples are needed to confirm if a true difference exists.

Benzo[ghi]perylene

The DW concentration of benzo[ghi]perylene observed in the dump site samples ranged from 24.43 to 114.29 ng/g, and in the control sites from 0.95 to 15.64 ng/g. It ranked 2nd in terms of abundance in dump sites and 7th in control sites, with observed DW masses of 283.33 ng and 18.56 ng respectively.

The Shapiro-Wilk test showed the DW concentration of benzo[ghi]perylene to be non-normal (p = 0.015) and so a square root transformation was applied, which successfully normalized the data (p = 0.12).The t-test of transformed data confirmed a significant difference (p = 0.015) between the mean DW PAH concentrations of benzo[ghi]perylene in the dump and control sites. This indicates that mean benzo[ghi]perylene concentrations are elevated in the snow dump sites relative to controls

6 CONCLUSIONS

GC-MS Analyses of soil samples from four urban snow dump sites and four adjacent control sites in southern Finland show that 13 of EPA's 16 PAH priority pollutants are found in significantly elevated concentrations in the soils of snow dump sites compared to control sites.

Also, the molecular mass distribution of these PAHs indicates that the contamination observed in the dump sites is skewed towards heavier PAHs, while lighter, more volatile PAHs dominate the distribution in the forested control sites. This observation is consistent with particle bound PAHs being delivered along with snow removed from urban streets. After the winter, as the snow deposit melts over the course of several months the light PAHs are expected to volatilize to the atmosphere, while heavy PAHs remain attached to particles in the residual sediments left in the dump site. The greater relative abundance of light PAHs in the forested control sites is also consistent with this reasoning, as volatile PAHs sorb onto the waxy coverings of tree foliage, and are then deposited on the forest floor with leaf litter. The dump sites do not receive this input of light PAHs, since they are largely barren of vegetation

This work shows that urban snow removal programs provide a pathway for PAHs to leave the urban environment and to accumulate in disposal sites.

Future work is needed to determine if and how PAHs migrate from the dump sites and how deep into the subsurface different PAH species penetrate. Also, it is reasonable to suspect that concentrations of volatile, low mass PAHs may peak during or immediately after the melt period, and will then decrease through the summer and into the autumn, and so another possible study should examine how PAH concentrations change over the course of the year.

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APPENDICES

Appendix 1. Site layout maps

A: Hakapelto snow dump site

● Control sample	Tipping wall		
● Dump site sample	Dump area	**Hakapelto**	
Ponding area	Site area		1:2 037
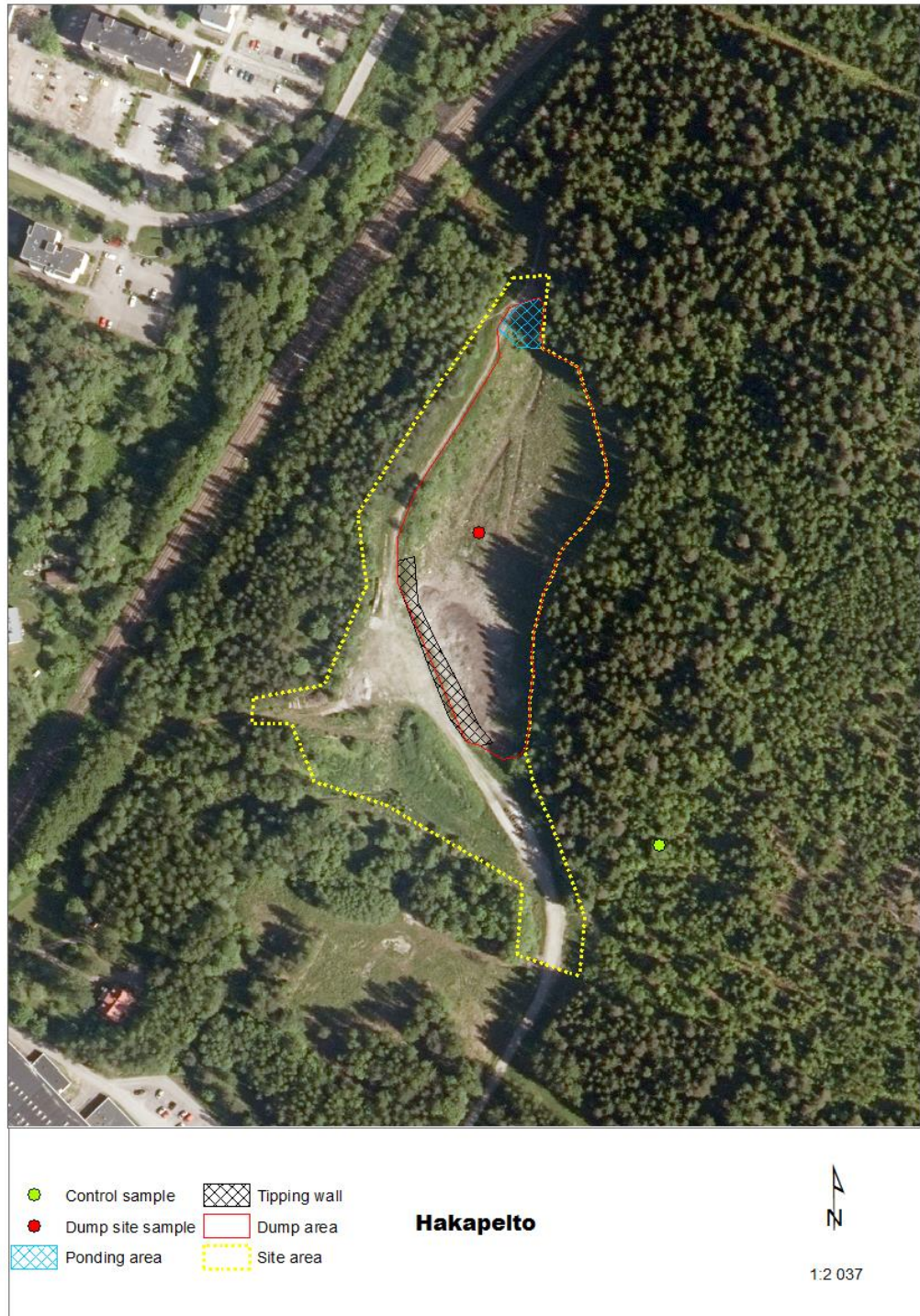
B: Rälssi waste disposal and snow dump site
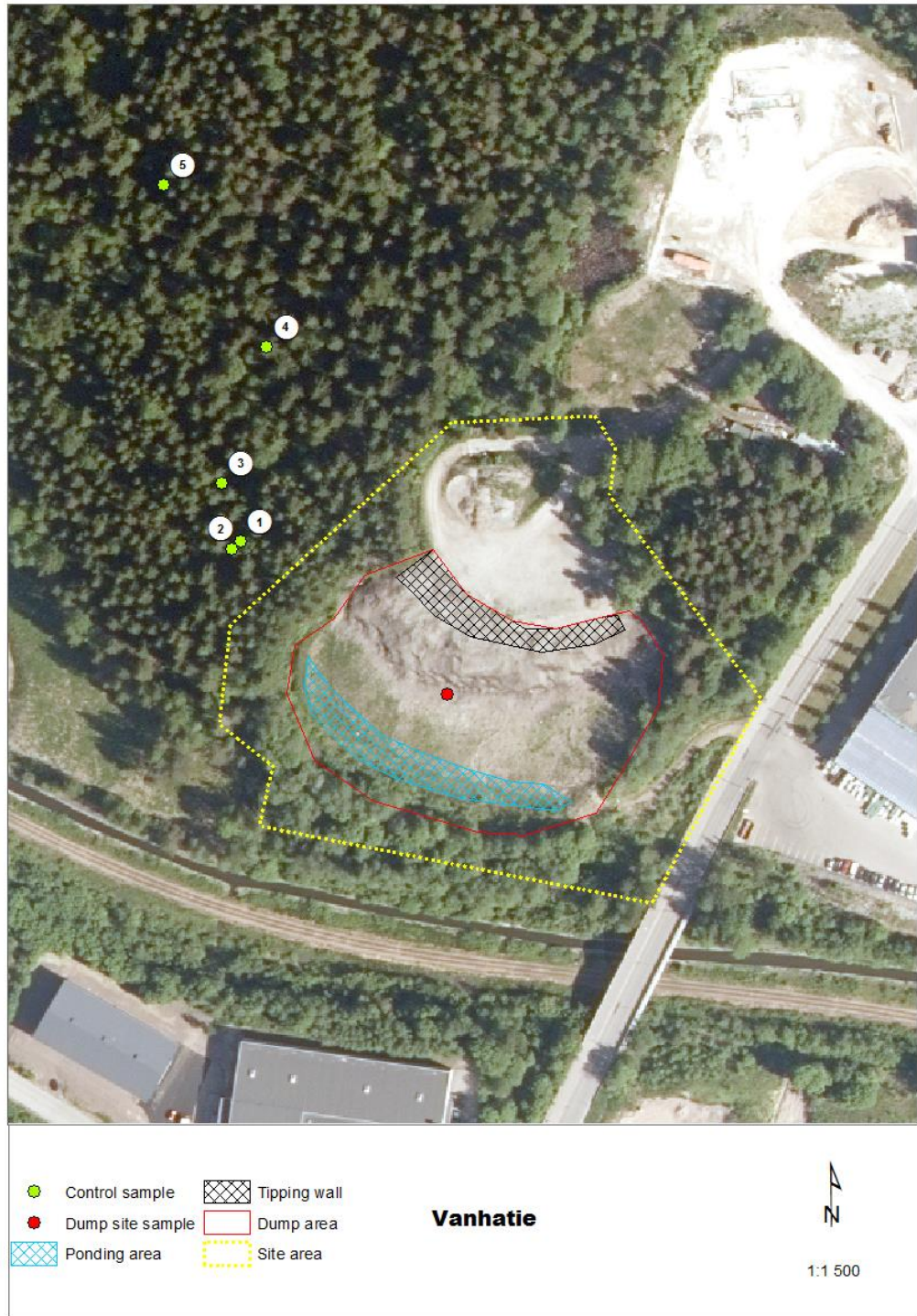

Control sample | Tipping wall
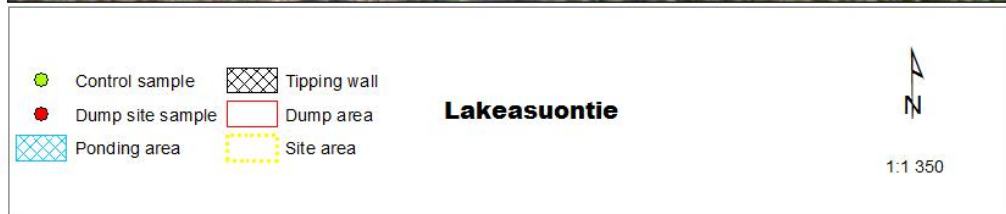Dump site sample | Dump area
Ponding area | Site area

Rälssi

1:5 350

C: Vanhatie snow dump site

Vanhatie

1:1 500

D: Lakeasuontie snow dump site

Legend:
- Control sample (green dot)
- Dump site sample (red dot)
- Ponding area
- Tipping wall
- Dump area
- Site area

Lakeasuontie

1:1 350

Appendix 2. Data tables

A: Raw PAH mass data (ng), LOQ values (ng/g) and percent recoveries from GC-MS analysis of snow dump and control site samples

Parameter	HA	HA Ctrl	LA	LA Ctrl	RÄ	RÄ Ctrl	VA	VA 2	VA Ctrl 1	VA Ctrl 2	VA Ctrl 3	VA Ctrl 4	VA Ctrl 5	Blank1	Blank2	Blank3	LOQ
Naphthalene	45.19	33.69	41.31	29.99	45.57	35.21	47.45	62.64	156.11	281.94	23.58	126.72	313.89	16.31	25.13	21.13	2
Acenaphthylene	5.83	< LOQ**	4.59	< LOQ*	3.95	1.37	8.92	9.76	32.49	48.76	< LOQ*	12.12	50.49	< LOQ*	< LOQ**	< LOQ*	2
Acenaphthene	2.59	1.18	1.64	< LOQ*	2.03	< LOQ*	5.27	2.54	< LOQ*	< LOQ*	0.02 (< LOQ)	< LOQ**	5.57	< LOQ*	< LOQ*	< LOQ*	2
Fluorene	4.18	1.88 (< LOQ)	3.53	1.74 (< LOQ)	4.07	1.58 (< LOQ)	5.06	6.92	4.47	8.57	< LOQ**	4.03	< LOQ**	0.01 (< LOQ)	1.36 (< LOQ)	< LOQ*	2
Phenanthrene	38.78	9.46	41.41	8.93	27.04	18.36	68.66	89.72	184.49	431.22	3.7	185.66	407.02	5.86	5.6	11.37	2
Anthracene	5.91	0.45 (< LOQ)	5.47	< LOQ*	3.62	1.36 (< LOQ)	10.99	14.75	11.33	22.74	0.18 (< LOQ)	7.65	0 (< LOQ)	< LOQ**	1.02 (< LOQ)	< LOQ*	2
Fluoranthene	33.31	2.91	56.23	2.65	26.82	20.83	92.11	214.9	189.92	432.56	0.39 (< LOQ)	196.5	378.27	1.77	2.75	2.46	1
Pyrene	58.55	4.95	54.11	4.68	57.23	14.35	125.01	349.8	153.09	323.61	1.54	90.64	276	3.83	6.05	5.87	1
Benzo[a]anthracene	14.16	1.02	27.04	0.85 (< LOQ)	11.86	3.38	49.8	44.16	24.36	46.03	0.51 (< LOQ)	15.06	< LOQ**	0.51 (< LOQ)	1.14	0.22 (< LOQ)	1
Chrysene	40.27	2.01	32.81	1.17	35.46	19.87	69.07	127	51.92	139.28	0.37 (< LOQ)	76.53	< LOQ**	0.19 (< LOQ)	1	0.16 (< LOQ)	1
Benzo[b]fluoranthene	57.04	2.06	50.05	0.02 (< LOQ)	58.1	46.18	105.96	123.34	78.76	166.6	< LOQ**	174.66	185.22	< LOQ**	< LOQ**	< LOQ**	1
Benzo[k]fluoranthene	9.73	1.69	11.75	1.89	9.28	11.67	21.73	29.76	21.56	43.7	< LOQ**	28.87	23.65	< LOQ**	< LOQ**	< LOQ*	1
Benzo[a]pyrene	0.01 (< LOQ)	< LOQ**	23.9	< LOQ*	19.27	4.87	46.32	54.64	32.29	54.43	< LOQ**	32.94	< LOQ**	< LOQ*	0.8 (< LOQ)	< LOQ*	1
Indeno[1,2,3-cd]pyrene	69.3	1.16 (< LOQ)	25.78	1.5 (< LOQ)	29.67	18.85	48.53	75.29	58.8	94.82	< LOQ*	59.36	63.47	0.09 (< LOQ)	0.95 (< LOQ)	< LOQ**	2
Dibenzo[a,h]anthracene	0.51 (< LOQ)	< LOQ*	4.13	< LOQ*	5.49	< LOQ*	8.25	0.3 (< LOQ]	4.1	11.25	< LOQ**	4.98	57.3	< LOQ*	< LOQ*	0.12 (< LOQ)	2
Benzo[ghi]perylene	120.39	< LOQ**	25.56	< LOQ**	39.54	16.15	71.57	157.93	68.31	125.1	< LOQ**	92.06	148.26	0.12 (< LOQ)	1.32 (< LOQ)	< LOQ*	2

% Recovery																
Naphthalene-D8	63.18	51.98	49.69	62.53	54.09	54.56	65.88	72.18	69.46	53.29	206.85	115.50	1430.62	63.96	89.24	182.90
Acenaphthene-d10	77.16	67.58	79.31	72.47	71.08	73.42	84.13	98.44	83.56	71.14	245.34	180.31	1059.32	79.78	98.79	225.58
Phenanthrene-D10	92.19	88.52	104.10	94.96	86.54	93.48	97.86	104.13	99.91	93.42	240.24	218.29	485.44	101.04	105.04	78.52
Chrysene-D12	81.64	86.30	91.15	86.15	76.73	86.45	79.52	103.49	86.75	95.90	236.55	229.10	244.35	100.68	97.46	275.18
Perylene-D12	82.02	63.07	88.13	80.16	66.17	41.22	60.73	91.74	75.22	100.33	225.40	129.33	439.37	99.15	89.51	266.10

HA = Hakapelto
LA = Lakeasuontie
RÄ = Rälssi
VA= Vanhatie

* No peak is found in Window/Band range.
** Ratio of reference ion does not match.

B: Blank corrected PAH masses (ng)

| Parameter	HA	HA Ctrl	LA	LA Ctrl	RÄ	RÄ Ctrl	VA	VA 2	VA Ctrl	LOQ
Naphthalene	28.88	17.38	25.00	13.68	29.26	18.90	31.14	37.51	2.45	2
Acenaphthylene	5.83	< LOQ**	4.59	< LOQ*	3.95	1.37	8.92	9.76	< LOQ*	2
Acenaphthene	2.59	1.18	1.64	< LOQ*	2.03	< LOQ*	5.27	2.54	< LOQ	2
Fluorene	4.18	< LOQ	3.53	< LOQ	4.07	< LOQ	5.06	6.92	< LOQ**	2
Phenanthrene	32.92	3.60	35.55	3.07	21.18	12.50	62.80	84.12	< LOQ	2
Anthracene	5.91	< LOQ	5.47	< LOQ*	3.62	< LOQ	10.99	14.75	< LOQ	2
Fluoranthene	31.54	1.14	54.46	0.88	25.05	19.06	90.34	212.15	< LOQ	1
Pyrene	54.72	1.12	50.28	0.85	53.40	10.52	121.18	343.75	< LOQ	1
Benzo[a]anthracene	14.16	1.02	27.04	< LOQ	11.86	3.38	49.8	43.02	< LOQ	1
Chrysene	40.27	2.01	32.81	1.17	35.46	19.87	69.07	126.00	< LOQ	1
Benzo[b]fluoranthene	57.04	2.06	50.05	< LOQ	58.1	46.18	105.96	123.34	< LOQ**	1
Benzo[k]fluoranthene	9.73	1.69	11.75	1.89	9.28	11.67	21.73	29.76	< LOQ**	1
Benzo[a]pyrene	< LOQ	< LOQ**	23.9	< LOQ*	19.27	4.87	46.32	54.64	< LOQ**	1
Indeno[1,2,3-cd]pyrene	69.3	< LOQ	25.78	< LOQ	29.67	18.85	48.53	75.29	< LOQ*	2
Dibenzo[a,h]anthracene	< LOQ	< LOQ*	4.13	< LOQ*	5.49	< LOQ*	8.25	< LOQ	< LOQ**	2
Benzo[ghi]perylene	120.39	< LOQ**	25.56	< LOQ**	39.54	16.15	71.57	157.93	< LOQ**	2

C: Blank corrected dry weight PAH concentrations (ng/g) and standard deviations for dump and control site samples.

Parameter	HA	HA Ctrl	LA	LA Ctrl	RÄ	RÄ Ctrl	VAAve	VA Ctrl 3	LOQ	SD Controls	SD Snowdumps	SD All
Naphthalene	27.42	16.59	23.89	13.19	27.88	18.31	32.17	2.44	2	11.84	9.93	11.74
Acenaphthylene	5.53	**0.95**	4.39	**0.96**	3.76	**1.33**	8.76	**0.99**	2	3.34	3.39	3.86
Acenaphthene	2.46	**1.13**	**1.57**	**0.96**	**1.93**	**0.97**	3.69	**0.99**	2	1.18	1.35	1.57
Fluorene	3.97	**0.95**	3.37	**0.96**	3.88	**0.97**	5.61	**0.99**	2	2.15	2.10	2.37
Phenanthrene	31.25	3.44	33.97	2.96	20.18	12.11	68.78	**0.99**	2	27.79	28.60	32.91
Anthracene	5.61	**0.95**	5.23	**0.96**	3.45	**0.97**	12.05	**0.99**	2	4.80	4.94	5.72
Fluoranthene	29.94	1.09	52.04	**0.85**	23.87	18.46	140.88	**0.50**	1	59.05	66.49	76.71
Pyrene	51.95	1.07	48.05	**0.82**	50.88	10.19	216.21	**0.50**	1	92.08	106.49	123.00
Benzo[a]anthracene	13.44	**0.97**	25.84	**0.48**	11.30	3.27	43.64	**0.50**	1	18.32	19.00	21.68
Chrysene	38.23	1.92	31.35	1.13	33.79	19.25	91.05	**0.50**	1	37.27	39.62	45.23
Benzo[b]fluoranthene	54.15	1.97	47.83	**0.48**	55.36	44.74	107.49	**0.50**	1	44.50	43.72	48.60
Benzo[k]fluoranthene	9.24	1.61	11.23	1.82	8.84	11.30	24.10	**0.50**	1	9.44	9.56	10.73
Benzo[a]pyrene	**0.47**	**0.48**	22.84	**0.48**	18.36	4.72	47.32	**0.50**	1	19.88	21.12	22.94
Indeno[1,2,3-cd]pyrene	65.79	**0.95**	24.64	**0.96**	28.27	18.26	57.88	**0.99**	2	23.57	26.98	27.07
Dibenzo[a,h]anthracene	**0.95**	**0.95**	3.95	**0.96**	5.23	**0.97**	4.41	**0.99**	2	2.13	2.50	2.82
Benzo[ghi]perylene	114.29	**0.95**	24.43	**0.96**	37.67	15.64	106.94	**0.99**	2	44.27	53.73	55.86
Total ng PAH/g DW	**454.68**	**36.00**	**364.61**	**28.95**	**334.64**	**181.46**	**970.98**	**13.88**				

SD = Standard deviation

D: Blank corrected dry weight PAH concentrations per gram of organic matter (ng/g OM) and standard deviations for dump and control site samples

Parameter	HA	HA Ctrl	LA	LA Ctrl	RÄ	RÄ Ctrl	VAAve	VA Ctrl 3	SD Controls	SD Snowdumps	SD All
Naphthalene	224.72	116.86	331.82	52.74	240.33	85.21	287.03	2.78	48.71	48.44	156.36
Acenaphthylene	45.36	6.72	60.92	3.86	32.44	6.18	79.70	1.13	2.55	20.38	39.27
Acenaphthene	20.15	7.93	21.77	3.86	16.67	4.51	38.84	1.13	2.80	9.89	17.85
Fluorene	32.53	6.72	46.85	3.86	33.43	4.51	48.75	1.13	2.30	8.60	20.29
Phenanthrene	256.16	24.21	471.85	11.84	173.96	56.35	600.53	1.13	23.92	195.60	293.77
Anthracene	45.99	6.72	72.60	3.86	29.73	4.51	105.17	1.13	2.30	32.99	42.12
Fluoranthene	245.42	7.67	722.83	3.39	205.75	85.93	1096.89	0.57	41.13	423.86	429.99
Pyrene	425.78	7.53	667.35	3.28	438.61	47.43	1622.63	0.57	22.01	566.99	613.85
Benzo[a]anthracene	110.18	6.86	358.89	1.93	97.41	15.24	415.66	0.57	6.64	165.38	188.77
Chrysene	313.35	13.51	435.48	4.51	291.25	89.58	746.08	0.57	42.04	209.52	286.16
Benzo[b]fluoranthene	443.84	13.85	664.30	1.93	477.21	208.20	965.71	0.57	101.55	239.19	374.61
Benzo[k]fluoranthene	75.71	11.36	155.95	7.29	76.22	52.61	209.46	0.57	23.53	65.38	79.45
Benzo[a]pyrene	3.89	3.36	317.22	1.93	158.28	21.96	424.00	0.57	10.07	183.89	182.01
Indeno[1,2,3-cd]pyrene	539.23	6.72	342.17	3.86	243.70	84.98	490.36	1.13	40.60	135.73	205.29
Dibenzo[a,h]anthracene	7.78	6.72	54.82	3.86	45.09	4.51	53.19	1.13	2.30	22.04	30.32
Benzo[ghi]perylene	936.77	6.72	339.25	3.86	324.77	72.81	843.06	1.13	34.53	324.43	350.33
Total ng PAH/g OM	**3726.86**	**253.49**	**5064.07**	**115.81**	**2884.87**	**844.50**	**8027.07**	**15.81**			

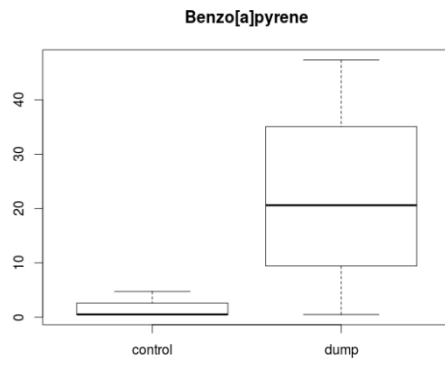**SD = Standard deviation**

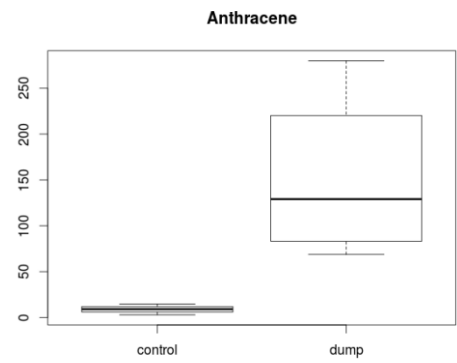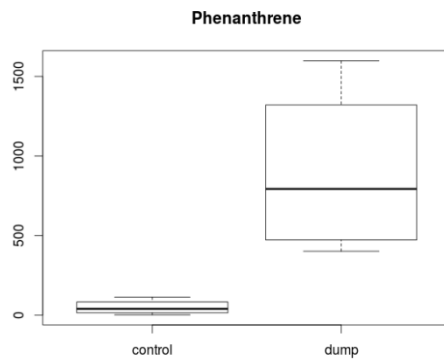**Appendix 3.** Mean concentrations of individual PAH species

A: DW mean concentrations of individual PAHs
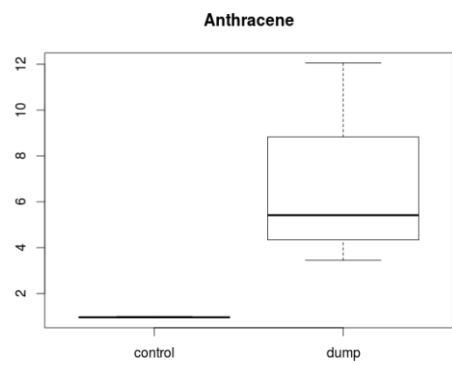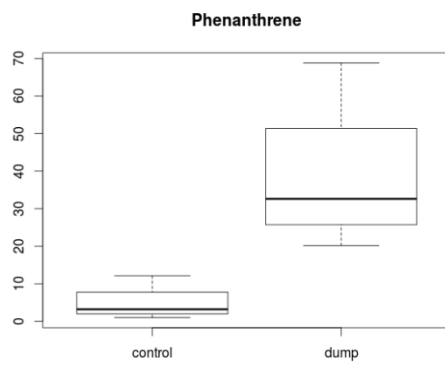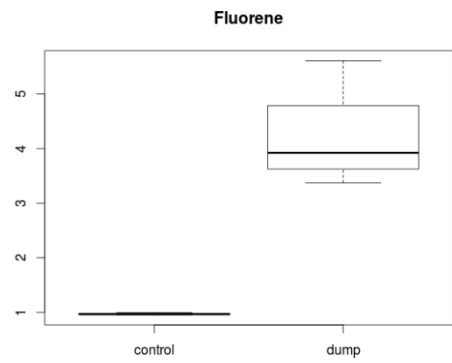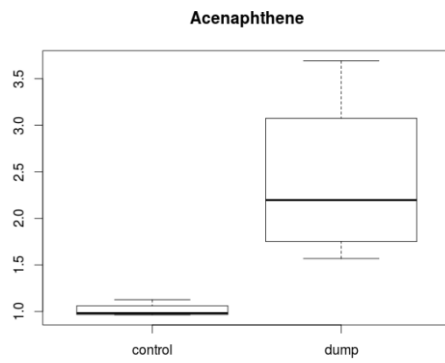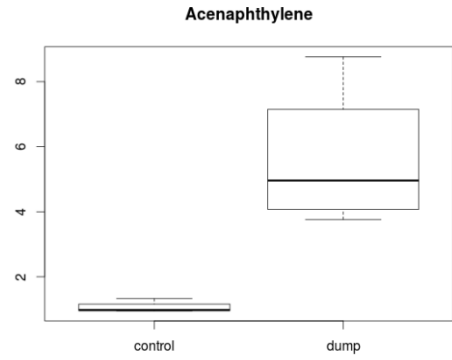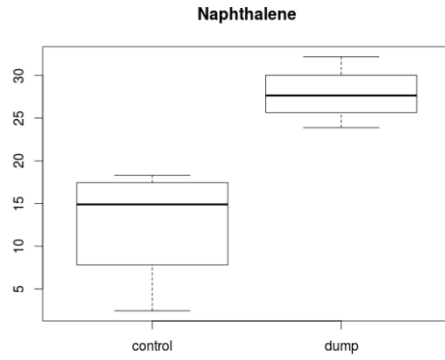
A: DW mean concentrations of individual PAHs (continued)
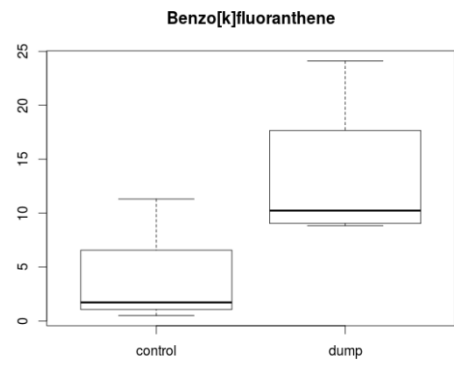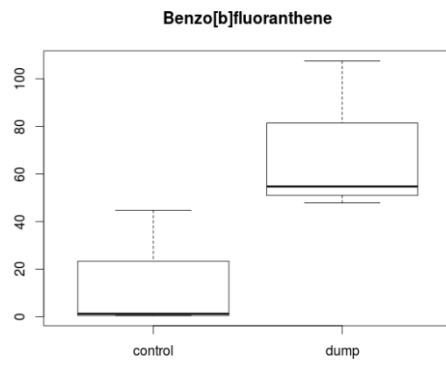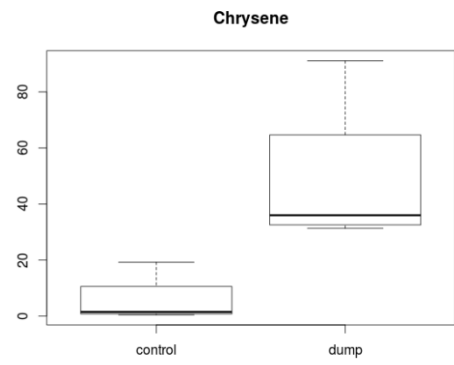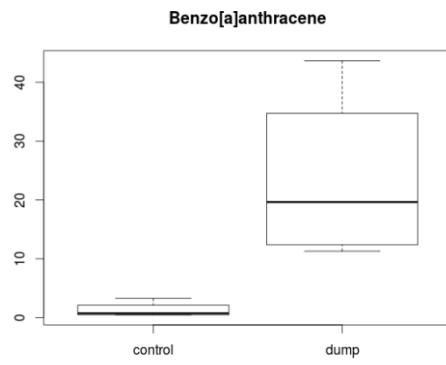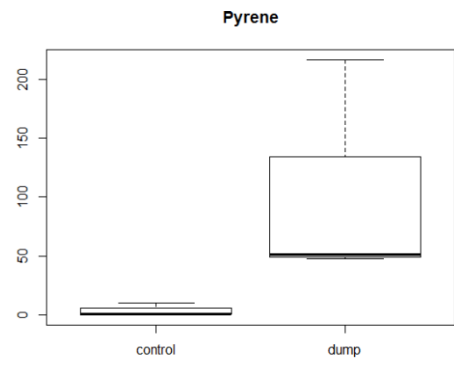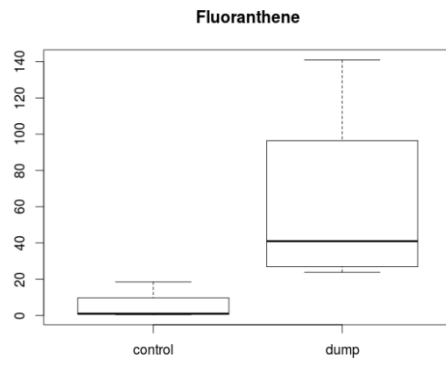
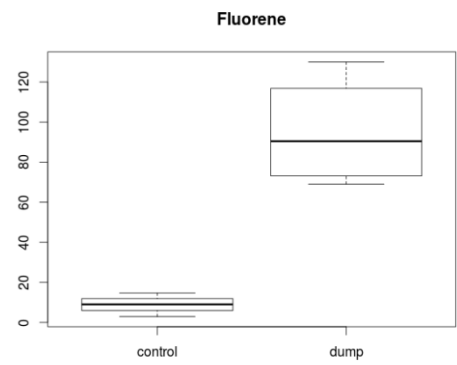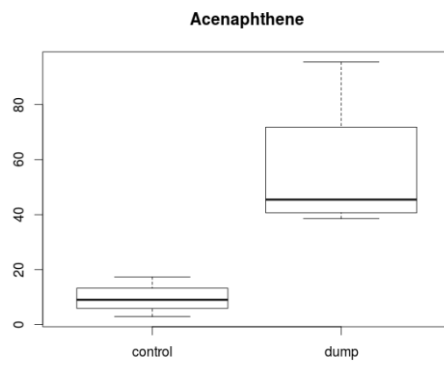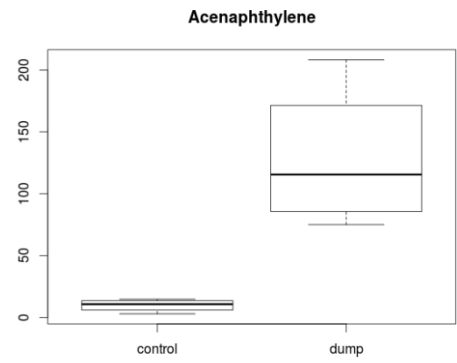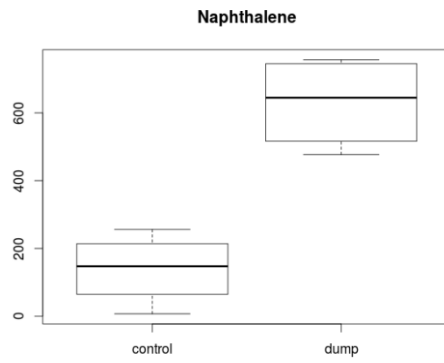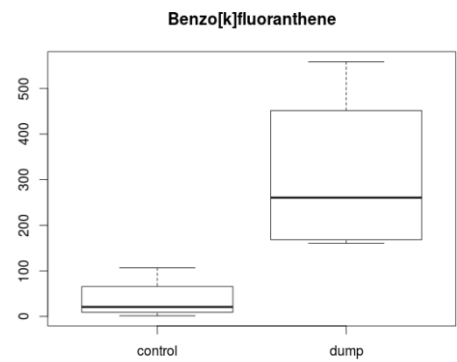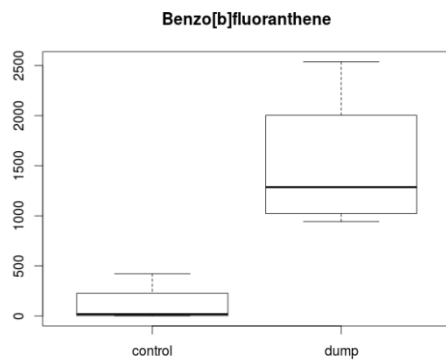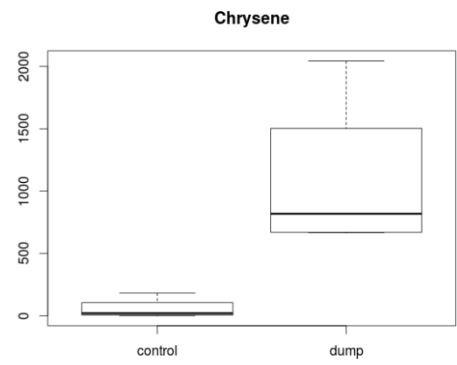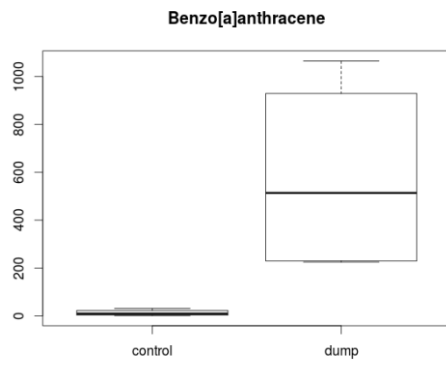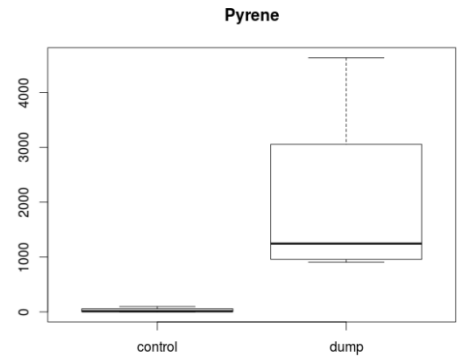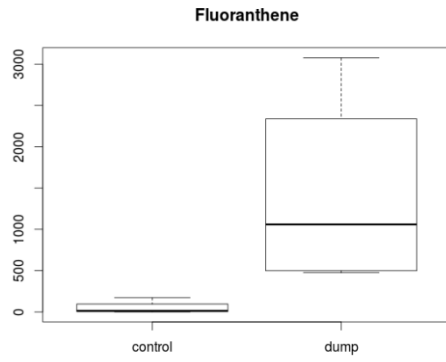**A:** DW mean concentrations of individual PAHs (continued)
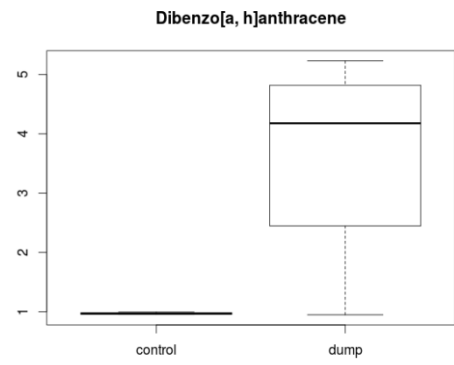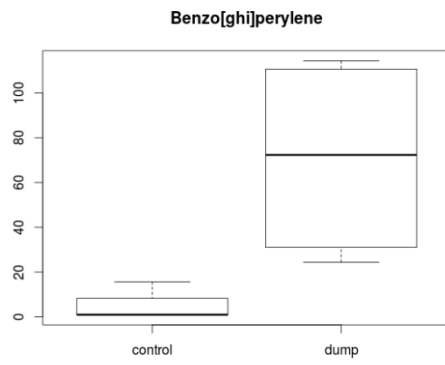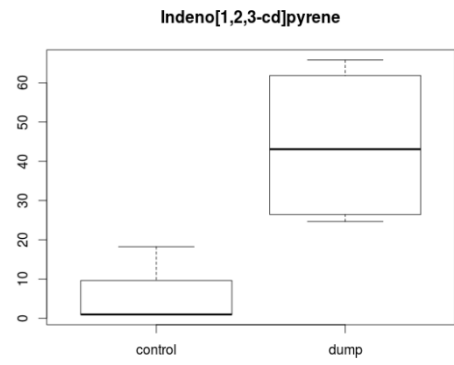
B: DW mean concentrations of individual PAHs per gram OM

B: DW mean concentrations of individual PAHs per gram OM (continued)