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Master's Thesis in the Master's Program Environmental Science

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ABSTRACT

In this study Substance Flow Analysis was used in order to estimate the amount of Polycyclic Aromatic Hydrocarbons (PAHs) that are emitted in the road and traffic area of Gårda, Gothenburg, and reach the stormwater sewer system. Literature search was the main tool used to collect data for the calculation of the emission factors of five traffic related sources: tyres, road material, brake linings, exhaust gases and motor lubricant oil. Based on the emission factors of each source, the number of vehicles and the kilometers of road in the area, the total amount of PAHs was calculated in grams per year. Based on literature information, it was assumed that for PAHs with 2 – 3 rings, 20% of the total vehicle exhaust emissions will end up in stormwater, for the 4-ring PAHs these percentages were 50, and for the 5 – 6 ring PAHs the percentages were 80% distributed to stormwater. Based on the runoff coefficient for precipitation, it was estimated that 80% of the emissions of the other sources will end up in the stormwater at Gårda, and the remaining 20% in other sinks.

All the results were calculated and presented in the form of a minimum and a maximum value in an attempt to bring the amounts emitted as close to an accurate estimation as possible. The final calculations showed that vehicle exhaust, followed by tyres and road material, are the main contributors of the PAHs to stormwater in Gårda. Four-ring PAHs were calculated to occur in the highest amounts in the stormwater system, and some of them belong to the group of probably carcinogenic, while the 5- and 6-ring PAH groups that mainly consist of probably carcinogenic PAHs, were calculated to occur in lowest amounts but still high enough to be alarming. The calculated amounts emitted were confirmed by measurement on PAHs in accumulated sediment in the Gårda stormwater treatment facility.

Key words: Substance Flow Analysis (SFA), Polycyclic Aromatic Hydrocarbons (PAH), roads, traffic, stormwater

Substansflödesanalys (SFA) av polycykliska aromatiska kolväten (PAH) i vägdagvatten

Examensarbete inom masterprogrammet i Miljövetenskap

Anna Siopi
Institutionen för bygg- och miljöteknik
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SAMMANFATTNING

I denna studie har en substansflödesanalys utförts för att uppskatta mängden polycykliska aromatiska kolväten (PAH) som släpps ut i väg- och trafikområdet Gårda i Göteborg och som når dagvattensystemet. Litteratursökning var det viktigaste verktyget som användes för att samla in data för uppskattning av emissionsfaktorer från fem trafikrelaterade källor: däck, vägmaterial, bromsbelägg, avgaser och motorsmörjolja. Baserat på emissionsfaktorer för varje källa, antalet fordon och kilometer väg i området, beräknades den totala mängden PAH som avges i Gårda i gram per år. För PAH med 2 – 3 ringar uppskattades baserat på information från litteraturen att 20% av trafikens avgasemissioner dagvatten, för PAH med 4 ringar motsvarande 50% och för PAH med 5 – 6 ringar transporteras 80% till dagvatten. Baserat på avrinningskoefficienten för nederbörd i området uppskattades att 80% PAH från övriga källor kommer att transporteras till dagvattnet i Gårda och resterande 20% i andra sänkor.

Samtliga resultat beräknades och presenteras med ett lägsta och ett högsta värde i ett försök att få värden som ligger nära en så noggrann uppskattning som möjligt. De slutliga resultaten visade att fordonsavgaser, följt av gummidäck, vägmaterial, är de största källorna till PAH i dagvatten i Gårda. Av PAH:erna är de med 4 ringar, varav några är klassade som möjligt cancerframkallande, de som når dagvattensystemet i allra största mängder. PAH med 5 – 6 ringar, klassade som huvudsakligen cancerframkallande, förekom enligt beräkningarna i mycket lägre mängder, men tillräckligt höga för att vara alarmerande. De beräknade mängderna av PAH i dagvatten bekräftades genom kemiska analyser i ackumulerat sediment i Gårda sedimenteringsanläggning för behandling av dagvatten.

Nyckelord: Substansflödesanalys (SFA), polycykliska aromatiska kolväten (PAH), vägar, trafik, dagvatten

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Abbreviations

CCME: Canadian Council of Ministers of the Environment

CSTEE: Scientific Committee on Toxicity, Ecotoxicity and the Environment

ETRMA: European Tyre and Rubber Manufacturer's Association

HA oils: Highly Aromatic oil

HDV: Heavy Duty Vehicles

POPs: Persistent Organic Pollutants

PCDD/Fs: Polychlorinated dibenzo-p-dioxins and-furans

PBDEs: Polybrominated diphenyl ethers

PAH: Polycyclic Aromatic Hydrocarbons

US EPA: United States Environmental Protection Agency

SFA: Substance Flow Analysis

VTI: Swedish National Road and Transport Research Institute

1. Introduction

In Europe of 2014, 73% of the population lived in urban areas (United Nations, 2014), a number that shows how important urban environment has become for European citizens. Since the traffic system is one of the most important elements of a city, it has also become the center of attention for research regarding the environmental pollution caused by it. This project will more specifically focus on studying pollution of water from the road environment.

Rainfall or melting snow comes in contact with the pollution sources of the traffic system and becomes infused with various pollutants that derive from these sources, carrying them further along the water chain and into surface or groundwater resources. Since road runoff is a pathway for pollutants, both the pollutants and their main sources need to be studied. The sources that will be studied are vehicles, fuels, road construction materials, tyres, and car exhaust while when it comes to the pollutants, attention will be paid to persistent organic pollutants (POPs) and more specifically polycyclic aromatic hydrocarbons (PAHs).

POPs, such as polychlorinated *dibenzo-p-dioxins and-furans* (PCDD/Fs), *polybrominated diphenyl ethers* (PBDEs) and different *organochlorine pesticides*, are hydrophobic, lipophilic chemical substances that attach to organic matter and are often stored in fatty tissue of organisms (Jones and Voogt, 1999). This storage causes their accumulation in the food chain because of the slow metabolism in biota, intensifying that way their negative effects. In addition, many POPs are volatile in environmental temperatures, which make their mobility higher and give them the opportunity to accumulate far from where they were produced. Moreover, they are suspected carcinogenic, such as Polycyclic Aromatic Hydrocarbons (PAHs) and PCDD/Fs, and cause endocrine disruption and damage of the immune system (Jones and Voogt, 1999). These characteristics in combination with their accumulative nature, makes them a dangerous element of stormwater that needs to be studied in order to suggest a prevention action plan for pollution by POPs in urban areas.

An interesting group of POPs is the PAHs which are chemicals that consist of carbon and hydrogen atoms grouped into aromatic rings. They can be naturally or artificially created and they are carcinogenic, mutagenic and teratogenic. In fact, they are the first atmospheric chemical that was suspected to be carcinogenic (Kim et al., 2013). They are considered to have low molecule weight when they have less than four rings and high molecular weight when they have more (Kim et.al., 2013). Higher molecular weight PAHs are mainly in particulate phase and due to their lower vapor pressure they are attached to finer particles in areas with higher emission sources (Mahanraj et al., 2012). The largest part of the total amount of PAH in the environment comes from the incomplete combustion of oil, coal, biomass and coke during energy production or other industrial processes. For example, in 2004 biomass burning made up for 56.7% of the global emission sources of PAHs (Zhang, Tao, 2008)

The aim of this study is to identify and quantify the PAHs and study the sources of emissions and flows. More specifically PAHs in road run-off from vehicles, fuels, road construction materials, tyres, car-care products and car exhaust will be studied and used in order to perform a Substance Flow Analysis (SFAs). The objectives of the study are to:

1) Identify the most important sources of selected PAHs by searching in literature and data bases.
2) Using the generated data for quantifying of PAHs from the mentioned sources.
3) Perform a SFA for PAHs within the Gårda catchment area in Gothenburg.

4) Take samples of sediments for chemical analysis of PAHs at Gårda to confirm the calculated emissions derived from the SFA.

The master project is performed at the department of Civil and Environmental Engineering, division of Water Environment Technology at Chalmers University under the supervision of Associate Professor Ann-Margret Strömvall and PhD candidate Anna Markiewicz.

2. Polycyclic Aromatic Hydrocarbons (PAHs)

2.1. Sources of PAHs

PAHs derive from natural sources through three different processes: 1) pyrolysis of organic material in high-temperature, 2) creation of fossil fuel from organic material in low to medium temperature and 3) biosynthesis by microbes and plants (Neff, 1979). However, the environmental concern is on the anthropogenic sources of PAHs which can be domestic, agricultural, industrial or mobile (Figure 1).

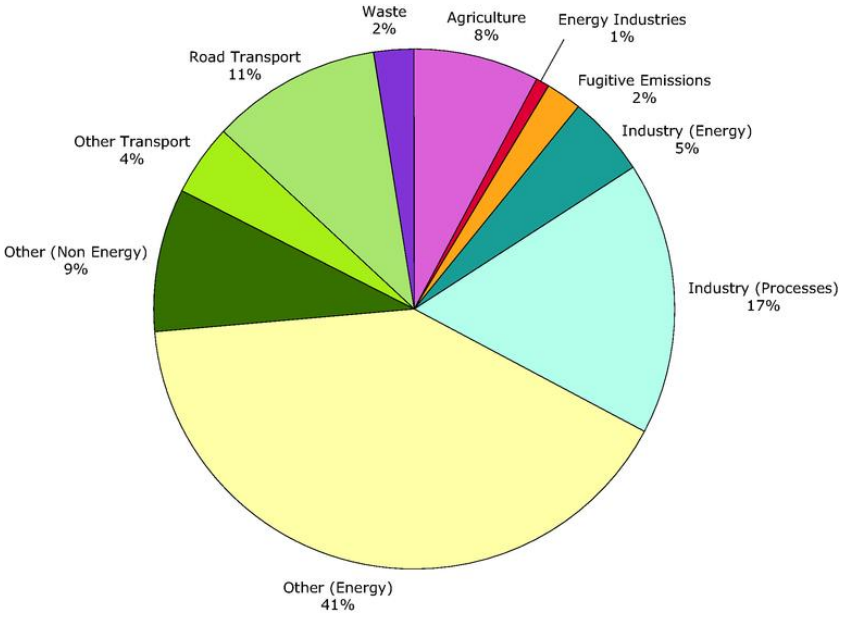


Figure 1: Sector share of PAH emissions, EEA member countries (EEA, 2012)

PAH emissions in the domestic sector come from heating and cooking. The use of coal, oil, gas, waste, wood and other organic material as fuel is the core of the emissions while smoking contributes to the PAH pollution of the indoor air. Domestic heating makes up for 16% of PAH in outdoor air in the US while this percentage reaches 29% in Sweden (WHO, 2010). The PAH emission rate is dependent on the type of fuel and the conditions when it is burnt, such as temperature, moisture and oxygen levels. Combustion of organic fuel at the low temperatures of domestic heating can possibly lead to higher emissions than the combustion at the high temperatures in the industrial sector. Furthermore, since the needs for heating and cooking are different in various places and different season, there is a great geographical variation in the emission patterns (Ravindra et al, 2008).

In agriculture PAHs are produced in open fires for disposal of excess organic materials or land preparation and usually the conditions of the combustion are not optimal. When biomass is

burned, the majority of the PAH emitted are Low Molecular Weight PAHs, like naphthalene, acenaphthylene, phenanthrene, flouranthene and pyrene (Lee, 2010). In some occasions it has been found that PAH emissions of sugarcane combustion can even be compared to the level of emissions in urban centers (Godoi et al, 2004).

Industrial and mobile sources are responsible for the largest part of the total emissions of PAHs. In the industrial sector, aluminum production, coke production, creosote and wood preservation, waste incineration, cement manufacture, petrochemical and related industries, bitumen and asphalt industries, rubber tire manufacturing and commercial heat/power production are the sources of PAHs. In the mobile sector road vehicles, airplanes, trains and other machinery are the major polluters of urban areas. Exhaust emissions are important in this sector and they can be formed either by the creation from smaller molecules in the fuel or storage in engine deposits or by pyrolysis of lubricants (Lee, 2010).

It has been estimated that 36% of the PAH emissions in the environment comes from urban runoff and a big contributor to that statistic are PAHs in road dust (Murakami et al, 2004). Brown et al (2005) suggest that in road dust, pyrogenic sources, and more specifically vehicle emissions, are the ones with the highest concentrations. Road debris in that study showed concentrations of 1.20–11.6 μg/g for 16PAH, while stormwater from two catchment areas had mean concentrations of 5.69 μg/g dw and 105 μg/g dw. Moreover, in the stormwater from the two sites, PAHs with four rings in their molecular structure were the ones with the highest values (Brown et al, 2006). Suggestively, in Krein's et al (2000) study, road runoff samples showed concentrations of 20 – 80 μg kg^{-1} for fluorene, 20 - 140 mg kg^{-1} for phenanthrene, 20 – 150 μg kg^{-1} for anthracene, 300 - 2000 μg kg^{-1} for fluoranthene, 70 – 750 μg kg^{-1} for dibenz[a,h]anthracene, 150 – 700 μg kg^{-1} for benzo[g,h,i]perylene and 80 – 400 μg kg^{-1} for indeno[1,2,3-cd]pyrene.

Associated with vehicles are also some additional components that are sources of PAH such as rubber tires, construction materials of roads and brake linings. The amount of emission is dependent on the type of engine, the type of fuel and products used and also, especially for road vehicles, the way they are driven. Vehicles that use diesel have higher particulate emissions than those using gasoline. Additional emissions derive from the content of the fuel itself. In gasoline vehicles the production of PAH depends on the air/fuel ratio and the use of catalytic converters has contributed to a decrease in PAH emissions. In trains, diesel and diesel/electric locomotives are the main source of pollution while for airplanes emissions depend on the fuel used and the power settings of the engine (Ravindra et al, 2008).

Table 1: Main emission sources of 16 priority PAHs

Chemical, CAS nr. (number of rings)	***Main source of emission / Routs of exposure***
Naphthalene, 91-20-3 (two rings)	Manufacture/use of coal-tar production, wood preserving, tanning, or ink and dye production (EPA, 2000)
Acenaphthylene, 208-96-8 (three rings)	Fumes from vehicle exhaust, coal, coal tar, asphalt, wildfires, agricultural burning and hazardous waste sites (EPA, 2015)
Acenaphthalene, 83-32-9 (three rings)	No Data
Fluorene, 86-73-7 (three rings)	Coal tar pitch volatiles, exhaust from gasoline engines, smoking of tobacco, inhalation of polluted air, ingestion of food and water contaminated by combustion effluents (TOXNET, 2015)
Phenanthrene, 85-01-8 (three rings)	Second most important coal tar constituent in terms of quantity after naphthalene, (Pubchem, 2004)

Anthracene ,120-12-7 (three rings)	Obtained from coal tar (Pubchem, 2005)
Fluoranthene, 206-44-0 (four rings)	Obtained from coal tar (Pubchem, 2004)
Pyrene, 129-00-0 (four rings)	Domestic heating sources, particularly wood burning; gasoline fuel exhaust; coal tar and asphalt; and cigarette smoke (CDC, 2015)
Benzo[a]anthracene, 56-55-3 (four rings)	Gasoline and diesel exhaust, cigarette smoke and smoke condensate, amino acid, fatty acid, and carbohydrate pyrolysis products, coal tar and coal tar pitch, asphalt, soot and smoke, wood smoke, coal combustion emissions, commercial solvents, waxes, mineral oil, and creosote (Iephd, 2015)
Chrysene, 218-01-9 (four rings)	Gasoline, diesel, and aircraft turbine exhausts; coal combustion and gasification; emissions from coke ovens, wood burning stoves, and waste incineration; and various industrial applications such as iron, aluminium, and steel production (RAIS, 2015)
Benzo[b]fluoranthene, 205-99-2 (five rings)	Gasoline exhaust, tobacco leaves, cigarette smoke, carbohydrates, amino acid and fatty acid pyrolysis products, coal tar, and soot (Iephd, 2015)
Benzo[k]fluoranthene, 207-08-9 (five rings)	Cigarette smoke, polluted air; food and water contaminated with products of combustion (Environmental contaminats encyclopedia, 1997)
Benzo[a]pyrene, 50-32-8 (five rings)	By-product of incomplete combustion or burning of organic (carbon-containing) items (EPA, 2006)
Dibenz[a,h]anthracene, 53-70-3 (five rings)	Has been isolated from coal tar pitch and is found in coke oven effluents (Pubchem, 2008)
Benzo[g,h,i]perylene, 191-24-2 (six rings)	Extracted from coal tar to be used in dyes. Also found (as part of a complex mixture of PAHs) in creosote, tar paints, waterproof membranes and other products, is released from vehicle exhausts and domestic wood and coal fires. (SEPA, 2015)
Indeno[1,2,3-cd]pyrene, 193-39-5 (six rings)	Occurs together with other aromatics (Environmental contaminants encyclopaedia, 1997)

2.2.Health effects on humans and animals

The specification of the health effects PAH cause is rather difficult because they are often found in mixtures of chemicals and the isolation of their influence can become complicated. Furthermore, the effects also depend on the concentration, toxicity, routes of exposure and the general health of the individual that is being exposed. None the less, some of the effects of short term exposure to PAH include lung impairments, thrombosis, skin and eye irritation, nausea, while long term exposure can possibly be damaging to the immune and hormonal system of humans. There have been many experiments on animals that show that exposure to PAH causes skin irritation, DNA damage, reproduction defects, tumors and embryotoxic effects (Kim et al, 2013).

Although all these effects are significant, the main concern about PAHs is their possible carcinogenicity. The research started in relation to the exposure within the working environment in 1775 in Britain from Percival Pott who observed cases of scrotal cancer in chimney sweeping workers while Volkman observed skin cancer in workers of the coal industry. Since then, there have been many studies correlating cancer incidents and employment in the soot, car tar and pitch industries (Boström et at, 2002). In Table 1 of the Appendix there are some more details about the carcinogenicity and health effects on humans and animals of the 16 USEPA priority PAHs. In Table 29 of the Appendix there is information about the USEPA and IARC carcinogenic categories.

When it comes to aquatic environments, fish have the highest metabolic capacity of PAH followed by crustaceans and then molluscs. This fact has two very important consequences: firstly, biomagnification through the food chain is not easy and secondly, fish are more vulnerable to carcinogenic metabolites than other aquatic organisms like mussels (Knutzen, 1995). In fish, PAH metabolites cause DNA adduct formation and chromosome damages, while PAH can alter the permeability of the cell membrane in organism which can affect for example the growth of mussels or the fat content of oysters (Knutzen, 1995). In addition to these negative effects, PAHs can cause liver, skin and thyroid tumors, neoplasms, blindness and difficulties on hatching in fish, lower heart rate and respiration in mussels, difficulties to photosynthesize in algae and blood abnormalities in oysters (NOAA, 2009; Eisle, 1987; Knutzen, 1995).

The Canadian Council of Ministers of the Environment (CCME) in its often sited paper "*Canadian Soil Quality Guidelines: Carcinogenic and Other Polycyclic Aromatic Hydrocarbons* (PAHs)", provides interesting information about guideline values of certain PAH for freshwater life and sediment. This information is presented in Table 2.

Table 2: Existing CCME environmental quality guidelines for PAHs as of 2003 (CCME, 2010)

PAHs	*Freshwater life*		*Sediment*			
	Freshwater	Marine	Freshwater		Marine	
	µg/L	µg/L	ISQG[1] µg/kg dw	PEL[2] µg/kg dw	ISQG µg/kg dw	PEL µg/kg dw
naphthalene	1.1	1.4	34.6	391	34.6	391
acenaphthylene	Nd[3]	Nd	5.87	128	5.87	128
acenaphthalene	Nd	Nd	Nd	Nd	Nd	Nd
fluorene	3	Id[4]	21.2	144	21.2	144
phenanthrene	0.4	Id	41.9	515	86.7	544
anthracene	0.012	Id	46.9	245	46.9	245
fluoranthene	0.04	Id	111	2355	113	1494
pyrene	0.025	Id	53	875	153	1398
benzo[a]anthracene	0.018	Id	31.7	385	74.8	693
chrysene	Id	Id	57.1	862	108	846
benzo[b]fluoranthene	Nd	Nd	Nd	Nd	Nd	Nd
benzo[k]fluoranthene	Nd	Nd	Nd	Nd	Nd	Nd
benzo[a]pyrene	0.015	Id	31.9	782	88.8	763
dibenz[a,h]anthracene	Nd	Nd	31.9	782	88.8	763
benzo[g,h,i]perylene	Nd	Nd	Nd	Nd	Nd	Nd
indeno[1,2,3-cd]pyrene	Nd	Nd	Nd	Nd	Nd	Nd

[1] ISQG: Interim Sediment Quality Guidelines, the more conservative value
[2] PEL: Probable Effect Level, the lower value that is associated with adverse biological effect
[3] Nd: No data
[4] Id: Insufficient data

3. Methodology

3.1. Substance Flow Analysis

The basic method used in this study is Substance Flow Analysis (SFA). In SFA, a system is defined in space and time and the existing processes, flows and stocks are accounted for within its boundaries (Stanisavljevic and Brunner, 2014). It is based on the principle of material balance that portraits the total flows (Input + Formation = Output + Degradation + Accumulation) (Hansen and Lassen, 2003). It is a method that can be used to inform about the production, trade and consumption of a substance, provide regulation and policy support, trace flows and understand the fate of substances and possibly, trace the human effects a substance can have (EEA, 2007).

The first step when performing an SFA is the definition of the system and that includes making decisions about the spatial boundaries, functional boundaries, time limits and materials that will be studied. The second step is the quantification of the network through the collection of relevant data from the literature, involved organizations, the collection and analysis of samples etc. The modeling of the data can have the form of accounting, static or dynamic modeling. The final step is the interpretation of the results (Ayres, 2001).

3.1.1. System Definition

The study area of this project is the Gårda catchment area in Gothenburg, Sweden (Figure 2). It has an area of 5.1 ha out of which 2.1 are impervious and the majority of the surface is occupied by the motorway E6 and therefore it is not heavily populated. It has about 78,590 vehicles passing through every day[5] and an air quality monitoring station at street level. Furthermore, the road runoff from this area is collected to a sedimentation facility before its release into the local water stream Mölndalsån (Pettersson et al., 2005; Björklund, 2010).

The analysis will be for the current year, 2015, and it will include the 16 USEPA priority PAHs which are: naphthalene (NAP), acenaphthylene (ACY), acenaphthalene (ACE), fluorene (FL), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLR), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBA), benzo[g,h,i]perylene (BPY) and indeno[1,2,3-cd]pyrene (INP).

Figure 2: The catchment area of Gårda

[5] information about AADT has been acquired from road traffic flow map available at: http://vtf.trafikverket.se/SeTrafikinformation

3.2.Emission factors

In order to calculate the inflow of substances in the study area there is a need to determine the emission factor of each source of PAH. According to the US EPA: "*An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant*". A usual expression of the pollutants is their weight divided by a unit of weight, volume, distance or duration of the activity that is the source of that pollutant (EPA, 2014).

The appropriate way of calculating the emission factors is dependent on the kind of activity that is being studied and the environment of the study area. For example, Johansson et.al (2009), in order to calculate the traffic emission rate, used the amount of the metals emitted in grams, divided by the number of vehicles and kilometers (g/vehicle kilometers; g veh^{-1} km^{-1}). RTI International (2011) in order to calculate the emission factors for organic compound leaks in different equipment types of petroleum refineries used the amount of leaked compound in kilograms per hour per emission source (kg/hr/source). Some more examples of emission factors are given in Table 3.

Table 3: Examples of estimated PAHs emission rates from various sources (Ravindra et al, 2008)

PAHs sources	*Emission rate*	*PAHs sources*	*Emission rate*
Mobile		Industrial	
- Gasoline engine	350 or 26 μg km^{-1}	- Industrial stacks	77 – 3970 μg kg^{-1}
- Gasoline engine	72.5 μg km^{-1}	- Industrial boiler	13,300 μg kg^{-1}
- Gasoline engine	8.1 or 0.7 μg km^{-1}	- Heavy oil	2900 μg kg^{-1}
- Light-duty gasoline	21 μg km^{-1}	- Water tube burner	85 - 320 μg kg^{-1}
- Heavy-duty diesel	1000 μg km^{-1}	- Waste-tyre pyrolysis	4000 μg kg^{-1}
- Diesel engine	240 or 60.2 μg km^{-1}	Domestic	
- Diesel engine	14.3 μg km^{-1}	- Coal	0.95 mg kg^{-1}
- Aircrafts	1.24 mg	- Oak	5 mg kg^{-1}
- Helicopter	63.4 mgl^{-1} Fuel	- Natural gas home appliances	1 – 2000 pg kg^{-1}
- Ships	500 μg km^{-1}	- Wood fuel	24 – 114 mg kg^{-1}
- Ships	410 – 2300 μg kWh^{-1}	- Domestic burning	100 mg km^{-1}

In this study the basis for calculating the emission factors is shown in Table 4. Through research in literature, other studies, data bases and scientific journals, the appropriate information is found in order to carry out the calculations which will be presented in detail in the result section.

Table 4: Calculation of the emission factors in this study

Source	*Emission factor calculation*
Tyres	PAH content * tyre wear per vehicle kilometre
Road surface wear	PAH content * road wear per vehicle kilometre
Brakes	PAH content * brake lining wear per vehicle kilometre
Exhaust gas	Calculated (Ntziachristos and Samaras, 2013)
Motor lubricant oil	PAH content * oil leakage per vehicle kilometre

3.3. Total amount of PAH emissions

The emission factor of a source shows the quantity of a pollutant that is emitted in relation to the activity associated with that source. It is a value that does not on its own show the total amount of that pollutant that is released to the environment. In order to calculate the total amount of PAHs released in the study area of Gårda, the emission factor of a source was multiplied by the amount of cars that pass daily, and by the amount of kilometers of road in the catchment area. This corresponds to the amount of PAHs that are released daily; it was multiplied by 365 to give the amount released yearly.

Emission factor mg/vkm * vehicles/day * km of road = x mg/day = x * 365 * 10-3 g/year (1)

3.4.Sampling

At the end of April, four sediment samples were taken from chambers 1, 3, 5 and 7 in the Gårda underground highway runoff sedimentation construction that is located under a parking facility. With the help of a grab sediment sampler, see Figure 3, and in the presence of an employee by the Swedish Transport Administration hired consultancy, the chambers were opened and sufficient amount of the sediment at the bottom of the champers was collected. The samples were sent to ALS Scandinavia AB to be analysed for, amongst other contaminants, their 16PAHs and oxygenated-PAH (oxy-PAH) content.

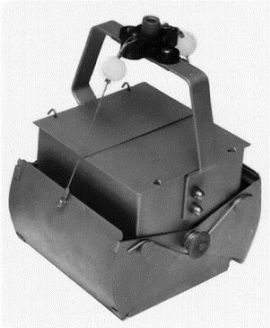


Figure 3: Ekman sediment grab sampler (Dynamic Aqua-Supply Ltd., 2015)

3.5.Total amount of oxy- PAH in the samples

The results from the chemical analysis of PAHs and oxy-PAHs were in mg/kg of dry weight sediment. In order to calculate how these concentrations are translated in g/year of PAHs that enter the water system, there was a need for more information like the accumulation time of the sediment in the chambers and the dry weigh sediment of every chamber. This information was

provided by an older unpublished study of Chalmers University of technology (Strömvall et al., unpublished data). It was measured that the accumulation time of the sediment is 28 months and the dry weight of sediment in every chamber expressed in kilograms as well as the concentrations of the sediment samples of this study expressed in mg/kg of dry weight (dw), are presented in Table 24 is chapter 5.8. Sediment samples were taken for chamber 1,3,5,7, while for the rest a mean value was taken.

To calculate the total amount of PAH released in g/year in the Gårda catchment area, the following calculations were made:

Concentrationsediment * DWsediment / 28 months = x mg/month * 12 months/year * 10-3 = x gsediment/year / 0.36 = x gtotal/year (2)

4. Calculation of emission factors for PAHs

4.1. Emission factor of tyre wear

The PAHs emissions from tyre wear is difficult to calculate because of the complexity of the emission sources. PAHs in tyres are found in the highly aromatic oils (HA oils) that are used during the manufacturing phase in order to make the rubber easier to work with and also make the tread soft. The addition of HA oils improves the grip of the tyres making it easier to brake on a wet road. Sweden is an importer of tyres since 2002 when the facilities of Continental Däck AB stopped their production in the country. That means that the quality of the tyres is dependent mainly on the regulations of the EU (KEMI, 2003).

According to the opinion of the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) on "the scientific evidence of risk to health and the environment from polycyclic aromatic hydrocarbons in extender oils and tyres" published in 2003, the reduction of PAH in tyres will not have a large effect on the total amount of PAHs in the environment because tyre-related PAHs only represent 1% of the total PAH concentrations in sediments (CSTEE, 2003).

Before 2010 there was no mandatory legislation regarding the use of HA oils in tyres, but, since they are still considered carcinogenic and within a precautionary mindset, from the first of January 2010 that has changed. The original Directive 2005/69/EC was turned into the European Regulation 1907/2006/EC (REACH), Annex XVII, entry 50 which came into force in 2010. This regulation affects not only all the tyres produced in the EU but also all the tyres imported, and it mandates the following:

"From 1 January 2010, extender oils shall not be placed on the market for use in tyre production if they contain:

- *More than 1 mg/kg (0,0001 % by weight) BaP, or,*
- *More than 10 mg/kg (0,001 % by weight) of the sum of all listed PAHs:*
  - ✓ *Benzo[a]pyrene (BaP) CAS# 50-32-8*
  - ✓ *Benzo[e]pyrene (BeP) CAS# 192-97-2*
  - ✓ *Benzo[a]anthracene (BaA) CAS# 56-55-3*
  - ✓ *Chrysen (CHR) CAS# 218-01-9*
  - ✓ *Benzo[b]fluoranthene (BbFA) CAS# 205-99-2*
  - ✓ *Benzo[j]fluoranthene (BjFA) CAS# 205-82-3*
  - ✓ *Benzo[k]fluoranthene (BkFA) CAS# 207-08-9*
  - ✓ *Dibenzo[a,h]anthracene (DBAhA) CAS# 53-70-3"* (ETRMA, 2010)

[6] The grams of sediment are divided by 0.3 because only 30% of the total amount ends up in the sediment.

Although now the legislative framework exists, there is one problem that affects the determination of how much tyre-related PAHs are emitted into the environment. The problem is that this Directive covered only new tyres that were being produced or imported after 2010, but not the tyre stocks that already existed in the distribution network (ETRMA, 2010). Consequently, for a period of time tyres with HA were still sold and used. A summer tyre's life span is around 4-5 years and a winter tyre's is 6-7 years (KEMI, 2003) which means that tyres with HA are still in use today. However, it is very difficult to determine the exact percentage of the market.

Even before the EU's ban, 75% of the winter tyres in Sweden had no HA oils in their treads while the majority of the summer tyres did contain HA oils. Trucks and busses that weigh less than 3,500 kg use the same tyres as passenger cars. All the retreated tyres in Sweden were free of HA oils and they make up 20% of the tyre market and the tread of the tyres for heavy goods vehicles is also free of HA oils (KEMI, 2003).

According to The Scandinavian Tire & Rim Organization, a typical passenger car tyre contains 200 to 600g of HA oil which has 0.1g - 0.3g of PAH content per tyre (STRO, 2004), while the tyre wear per kilometre driven is from 0.024 to 1.0g (Björklund, 2010). The European Tyre and Rubber Manufacturer's Association (ETRMA) (2011) performed a compliance test to see if the Reach regulation was being followed, and found that 10% of the tyres tested did not comply. In the study area of this paper, Gårda, 78,590 vehicles pass daily or 28,685,350 vehicles annually. If it is accepted that each vehicle has 4 tyres, that means that 114,741,400 tyres pass annually and accepting that 10% of those contain HA oils, there are 11,474,140 tyres with HA oils that still pass Gårda annually. The motorway and the other main roads that pass through the area cover approximately 5.5 kilometers[7].

Every tyre weights approximately 9 kg (Continental, 2008) and in order to be easier to calculate the emission factor of tyre per vehicle, the PAH content per tyre was calculated as 0.011-0.033 g/kg*tyre (as it was mentioned before there is a 0.1 – 0.3g of PAH per tyre and every tyre weighs 9 kg) or, since every vehicle has 4 tyres, as 0.044 – 0.132 g/kg*vehicle. The emission factor of tyre wear per vehicle was calculated as the minimum PAH content multiplied by the minimum wear and the maximum PAH content multiplied by the maximum wear (Table 5).

Table 5: Emission factor of PAHs from tyres

Emission factor of PAHs from tyres	
PAH content in tyres	0.044 – 0.132 g/kg*vehicle
Tyre wear/km	0.024 – 1.0 g/km (mean 0.20 g/km) (Björklund , 2010)
Emission Factor of PAHs from tyres	$0.001056 * 10^{-3}$ – $0.132 * 10^{-3}$ g/km*vehicle

On the other hand, the Netherlands National Water Board (2008) presents a table with a compilation of measured PAH content from different literature sources. Table 6 shows the minimum and maximum values of the US EPA16 PAH referenced in that paper. These data were the ones that were used for the calculation of the emission factor that was later used for the calculation of the total amount of 16PAH in the study area, due to the fact that the data in the table are more detailed for each specific PAH.

[7] Roughly estimated through google maps

Table 6: Measured US EPA 16 PAH content in tyres (Netherlands National Water Board, 2008)

PAH	*Content (mg/kg/tyre)*	
	Passenger cars	**Lorries**
naphthalene	0.4 – 2.7	4.5
acenaphthylene	-	-
acenaphthalene	0.4 – 5.6	0.3
fluorene	0.1 – 0.4	4.4
phenanthrene	4.2 – 5.5	2.3
anthracene	0.7 – 2.0	0.1
fluoranthene	1.4 – 9.4	3.8 – 15.4
pyrene	3.3 – 24.2	3.5 – 33.2
benzo[a]anthracene	0.8 – 8.5	0.7 – 0.9
chrysene	2.2 – 51.3	2.3 – 5.3
benzo[b]fluoranthene	2.4 – 6.4	6.4
benzo[k]fluoranthene	-	-
benzo[a]pyrene	1.3 – 3.0	0.4 – 2.6
dibenz[a,h]anthracene	0.1 – 1.2	0.2 – 0.8
benzo[g,h,i]perylene	0.5 – 12.9	2.4 – 7.3
indeno[1,2,3-cd]pyrene	0.1 – 2.3	0.4 – 1.0

Using the same assumptions as before, each vehicle has 4 tyre and the tyre wear per driven kilometre is between 0.024 and 1.0g, Table 7 shows the emission factor of tyres for the USE EPA 16 PAHs. Again, the emission factor of tyre wear per vehicle was calculated as the minimum PAH content multiplied by the minimum wear and the maximum PAH content multiplied by the maximum wear.

Table 7: The emission factor of tyres for the 16PAHs

Emission factor of tyres for the 16PAHs	*mg/vkm*	
	Passenger cars	**Lorries**
naphthalene	$38.4*10^{-6}$ – $10.8*10^{-3}$	$432*10^{-6}$ - $18*10^{-3}$
Acenaphthylene	-	-
acenaphthalene	$38.4*10^{-6}$ – $22.4*10^{-3}$	$28.8*10^{-6}$ - $1.2*10^{-3}$
fluorene	$9.6*10^{-6}$ – $1.6*10^{-3}$	$422.4*10^{-6}$ - $17.6*10^{-3}$
phenanthrene	$403.2*10^{-6}$ – $22*10^{-3}$	$220.8*10^{-6}$ - $9.2*10^{-3}$

anthracene	$67.2*10^{-6}$ – $8.0*10^{-3}$	$9.6*10^{-6}$ - $0.4*10^{-3}$
fluoranthene	$134.4*10^{-6}$ – $37.6*10^{-3}$	$364.8*10^{-6}$ – $61.6*10^{-3}$
pyrene	$316.8*10^{-6}$ – $96.8*10^{-3}$	$336*10^{-6}$ – $132.8*10^{-3}$
benzo[a]anthracene	$76.8*10^{-6}$ – $34*10^{-3}$	$67.2*10^{-6}$ – $3.6*10^{-3}$
chrysene	$211.2*10^{-6}$ – $205.2*10^{-3}$	$220.8*10^{-6}$ – $21.2*10^{-3}$
benzo[b]fluoranthene	$230.4*10^{-6}$ – $25.6*10^{-3}$	$614.4*10^{-6}$ - $25.6*10^{-3}$
benzo[k]fluoranthene	-	-
benzo[a]pyrene	$124.8*10^{-6}$ – $12.0*10^{-3}$	$38.4*10^{-6}$ – $10.4*10^{-3}$
dibenz[a,h]anthracene	$9.6*10^{-6}$ – $4.8*10^{-3}$	$19.2*10^{-6}$ – $3.2*10^{-3}$
benzo[g,h,i]perylene	$48*10^{-6}$ – $51.6*10^{-3}$	$230.4*10^{-6}$ – $29.2*10^{-3}$
indeno[1,2,3-cd]pyrene	$9.6*10^{-6}$ – $9.2*10^{-3}$	$38.4*10^{-6}$ – $4.0*10^{-3}$

4.2. Emission factor of road surface wear

Lindgren (1998) describes how PAH concentrations in asphalts are found in the bituminous binders. In this study asphalt mixes were created with three different bituminous binders in the laboratory, and the PAH concentrations were measured in the leachate from those mixtures. Table 8 shows the minimum and maximum values presented (Appendix Table 30).

This data were used to calculate a minimum and maximum PAH emission factor for the road wear. The road wear can vary between 3mg/vkm (vehicles kilometres) and 8mg/vkm (Netherlands National water Board – Water Unit, 2008).

Table 8: PAH concentrations in leachate from different mixtures of asphalt material (Lindgren, 1998)

PAH concentrations in in leachate from asphalt	***mg/kg***
naphthalene	1.2 – 10
acenaphthylene	0.3 – 0.3
acenaphthalene	0.18 – 0.43
fluorene	0.44 – 0.7
phenanthrene	2.9 – 3.8
anthracene	0.82 – 1.9
fluoranthene	4 – 11
pyrene	2.9 – 7.2
benzo[a]anthracene	7 – 22
chrysene	7.7 – 12
benzo[b]fluoranthene	3 – 7.8
benzo[k]fluoranthene	0.76 – 1.2
benzo[a]pyrene	5 – 8
dibenz[a,h]anthracene	3 – 9
benzo[g,h,i]perylene	7.6 – 12
indeno[1,2,3-cd]pyrene	0.94 – 1.1

The emission factor was calculated by multiplying the minimum and maximum road surface wear by the minimum and the maximum PAH content of the samples in Table 9.

Table 9: Emission factors of PAHs from asphalt road material

Emission factor of road material	*mg/vkm*
naphthalene	$3.6*10^{-6}$ - $80*10^{-6}$
acenaphthylene	$0.9*10^{-6}$ - $2.4*10^{-6}$
acenaphthalene	$0.54*10^{-6}$ - $3.44*10^{-6}$
fluorene	$1.32*10^{-6}$ - $5.6*10^{-6}$
phenanthrene	$8.7*10^{-6}$ - $30.4*10^{-6}$
anthracene	$2.46*10^{-6}$ - $15.2*10^{-6}$
fluoranthene	$12.0*10^{-6}$ - $88.0*10^{-6}$
pyrene	$8.7*10^{-6}$ - $57.6*10^{-6}$
benzo[a]anthracene	$21.0*10^{-6}$ - $176.0*10^{-6}$
chrysene	$23.1*10^{-6}$ - $96.0*10^{-6}$
benzo[b]fluoranthene	$9.0*10^{-6}$ - $62.4*10^{-6}$
benzo[k]fluoranthene	$2.28*10^{-6}$ - $9.6*10^{-6}$
benzo[a]pyrene	$15.0*10^{-6}$ - $64.0*10^{-6}$
dibenz[a,h]anthracene	$9.0*10^{-6}$ - $72.0*10^{-6}$
benzo[g,h,i]perylene	$22.8*10^{-6}$ - $96.0*10^{-6}$
indeno[1,2,3-cd]pyrene	$2.82*10^{-6}$ - $8.8*10^{-6}$

4.3. Emission factor of brake linings

Brake wear is caused when the brake linings of a vehicle are subjected to high friction heat during forced deceleration. The brake wear is particles that are released in the environment and contain various chemicals some of which are PAHs (Warner et al, 2001). The brake pad composition, the vehicle type and the driving behavior play an important role in the amount of brake wear while under normal use the front disc brakes last for shorter period of time due to the fact that braking force is higher in the front axle of the vehicle than the back (Warner et al, 2001).

In the literature there are many references to the brake lining wear factors and they vary from paper to paper. Westerlund (2001) have determined for the total brake lining a brake wear factor of 17 to 84 mg/vkm while in the EMEP/EEA emission inventory guidebook 2009, two more authors are sited that report the wear factor from 11 to 29 mg/vkm and from 20 to 47 mg/vkm respectively (Ntziachristos, 2009). Luhana et al. (2002) calculated the average wear factor in cars to be 8.8 mg/vkm. For the calculations in this paper, a gap of 8.8 – 84 mg/vkm was used.

While there are many literature references regarding the wear of brake lining, it is quite difficult to find data about the PAH content. The most referenced document regarding the PAH is Rogge's et al (1996) which provides the following data (Table 10).

Based on these data the emission factor of the brake linings was calculated by multiplying the minimum and maximum brake wear by the available existing PAH content. The results for the brake linings are presented in Table 11.

Table 10: PAH content in brake linings

Polycyclic Aromatic Hydrocarbons	*mg/kg*
naphthalene	nd
acenaphthylene	nd
acenaphthalene	nd
fluorene	nd
phenanthrene	0.97
anthracene	nd
fluoranthene	0.69
pyrene	1.1
benzo[a]anthracene	1.5
chrysene	1.7
benzo[b]fluoranthene	0.42
benzo[k]fluoranthene	0.62
benzo[a]pyrene	0.74
dibenz[a,h]anthracene	nd
benzo[g,h,i]perylene	2.6
indeno[1,2,3-cd]pyrene	nd

Table 11: Emission factors of brake linings

Emission factor of brake linings	*mg/vkm*
naphthalene	nd
acenaphthylene	nd
acenaphthalene	nd
fluorene	nd
phenanthrene	$8.536*10^{-6}$ – $81.48*10^{-6}$
anthracene	nd
fluoranthene	$6.072*10^{-6}$ – $57.96*10^{-6}$
pyrene	$9.68*10^{-6}$ – $92.4*10^{-6}$
benzo[a]anthracene	$13.2*10^{-6}$ – $126*10^{-6}$
chrysene	$14.96*10^{-6}$ – $142.8*10^{-6}$
benzo[b]fluoranthene	$3.7*10^{-6}$ – $35.28*10^{-6}$
benzo[k]fluoranthene	$5.456*10^{-6}$ – $52.08*10^{-6}$
benzo[a]pyrene	$6.512*10^{-6}$ – $62.16*10^{-6}$
dibenz[a,h]anthracene	nd
benzo[g,h,i]perylene	$22.88*10^{-6}$ – $218.4*10^{-6}$
indeno[1,2,3-cd]pyrene	nd

4.4. Emission factors of exhaust gases

The European Environment Agency in its emission inventory guidebook 2013 has published a detailed section about the exhaust emissions from road transport. Three methodologies are used (Tier 1 – 3) and the difference between them is basically the level of detail and information available (Figure 4) (Ntziachristos et al, 2013).

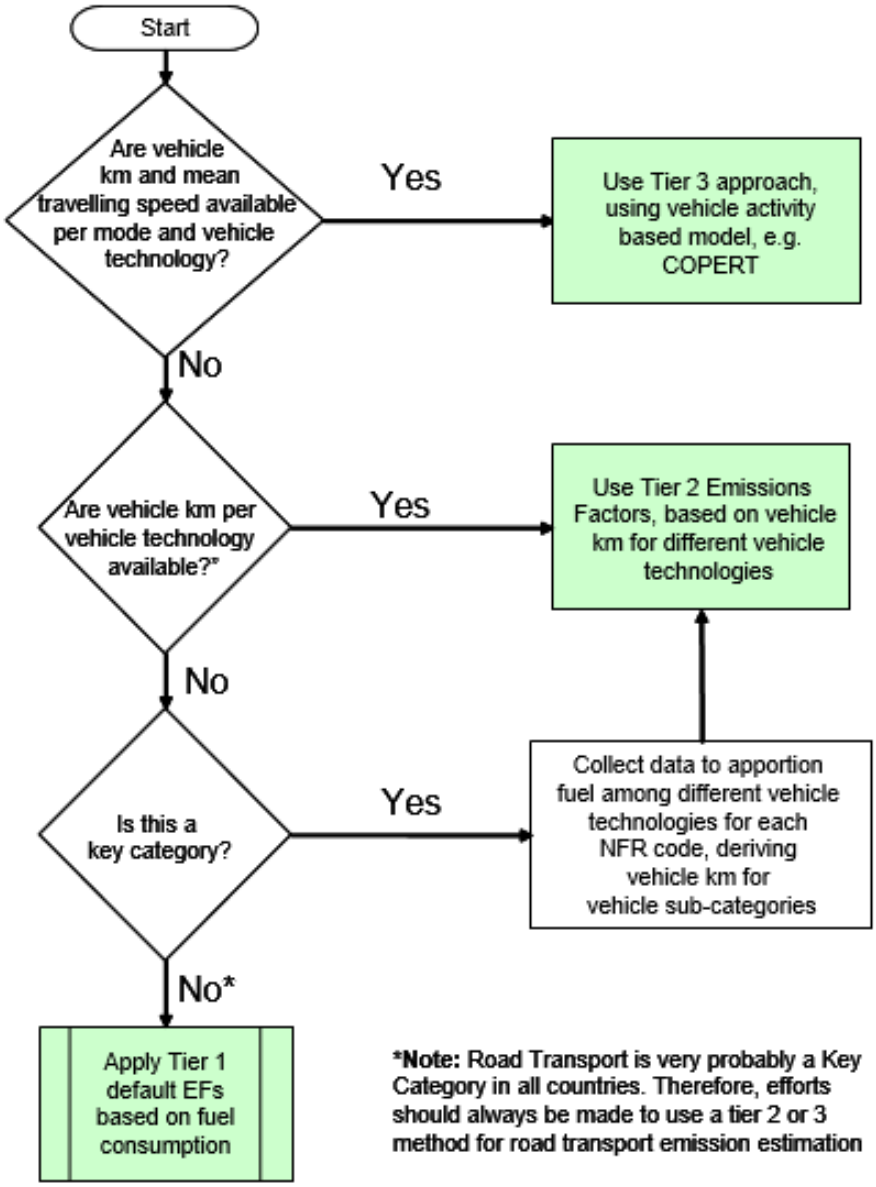


Figure 4: Decision tree for exhaust emissions from road transport (Ntziachristos et al, 2013)

The most detailed data about the PAH content exist in the Tier 3 section, where different types of vehicles are studied with a rough distinction between vehicles using conventional or closed-loop catalysts and direct (DI) or indirect injection (IDI). However, it makes no distinction between hot and cold-start emissions, as it does for other chemicals, and that is the reason why they are named "bulk emissions" (Ntziachristos L. et.al, 2013).

Table 31 in the Appendix provides the emission factors of the 16 PAHs as it was presented in the guidebook 2013. However, within the limits of this paper it is difficult to separate the vehicles in many categories due to the fact that it is difficult to obtain data about the exact number of vehicles in each category that pass the Gårda area daily or annually. This is the reason why an even more generalised table needs to be created with minimums and maximums for each category. Table 12 was created by grouping together the data of the guidebook in order to create a minimum and maximum that made further calculations easier.

Table 12: PAH emission factors for vehicle exhaust (μg/vkm)

PAH	*Gasoline, E85, CNG PC & LCV*	*Diesel PC & LCV*	*HDV*
naphthalene	11.2 – 610	650.5 – 2100	56.6
acenaphthylene	-	25.9	-
acenaphthalene	-	-	-
fluorene	-	-	39.9
phenanthrene	4.68 – 61.7	27.6 – 85.50	23.0
anthracene	0.80 – 7.66	1.37 – 3.40	8.6
fluoranthene	2.80 – 18.2	18.0 – 38.3	21.4
pyrene	1.80 – 5.78	12.3 – 38.9	31.6
benzo[a]anthracene	0.43 – 0.84	2.71 – 3.30	2.4
chrysene	0.43 – 0.53	2.40 – 7.53	16.2
benzo[b]fluoranthene	0.36 – 0.88	0.60 – 3.30	5.45
benzo[k]fluoranthene	0.26 – 0.30	0.19 – 2.87	6.09
benzo[a]pyrene	0.32 – 0.48	0.63 – 2.85	0.90
dibenz[a,h]anthracene	0.01 – 0.03	0.24 – 0.56	0.34
benzo[g,h,i]perylene	0.56 – 2.90	0.95 – 6.00	0.77
indeno[1,2,3-cd]pyrene	0.39 – 1.03	0.70 – 2.54	1.40

4.5. Emission factors of motor oils and lubricants

The use of lubricant oil in vehicle engine serves the purpose of protecting it from corrosion, friction between the different components, while it also carries a variety of protective chemicals (Denton, 2007).

The content of PAHs in lubricating motor oil is not constant. New motor oil contains only a few PAHs and in very low amounts, while the more the oil is used the higher the content becomes. The concentration is not dependent on the age of the vehicle but rather on the age of the lubricant oil itself (Wong, 2000). This is mainly due to the pyrolysis and pyrosynthesis of the oil at the high temperatures in the engine and because of the contamination of the lubricant by fuel combustion products. In a study performed on gasoline vehicle it was found that the PAH content reached its peak at approximately 4,000 miles and then it stabilized, while the five ring PAHs that are more toxic, were detected at 5,800 miles. The results of the same study showed that the total PAH concentration was 10,300 μg/g (Denton, 2007). Moreover, the Dutch Pollutant Release and Transfer Register calculated the loss of lubricant oil by leakage to be 10 mg/vkm (PBL Netherlands Environmental Assessment Agency, 2013).

There is low health hazard from unused oils which have low acute oral and dermal toxicity. Used oil on the other hand, due to all the chemicals, is enriched during the operation of the engine, has

much higher content of toxic chemicals (Denton, 2007). In addition, it has been found that not all engines have the same effect on the lubricant oil. In petrol engines there are more mutagenic chemicals in comparison to diesel engines, possible due to higher combustion temperature in a diesel engine. There is also a difference between leaded and unleaded petrol, with the first having higher mutagenic activity (Clonfero et al., 1996).

It is quite difficult to find data that are divided according to the fuel of the engine and the 16 priority PAHs at the same time. In 1996, Clonfero et al. published results of a sampling in the used oil of thirteen vehicles: three leaded petrol cars, three unleaded petrol cars, three diesel cars and four diesel trucks. Their results are summarized in the Table 13.

Table 13: PAH concentration in different types of used engine oils

Type of engine and vehicle	*PAH concentration (mg/kg)*[8]
Leaded petrol car	1929 - 3891
Unleaded petrol car	2516 - 4605
Diesel car	27 - 197
Diesel truck	27 - 291

On the other hand, Wong and Wang (2000) published data on the PAH content in used engine oil based on sampling from a new and an old gasoline car. The data presented were the US EPA 16 PAH content according to different extraction temperatures, different fluid density of carbon dioxide, different modifiers and different distances driven after oil change.

Focusing on the changes of PAH with the distance driven, the authors took a new and an old car and analysed the PAH content from the change of lubricant oil up to around 3700 km driven. Not all PAHs reached a maximum level at the maximum distance; some reached their highest concentration at half the distance and then the production of these PAHs declined. However, the majority of the PAHs as well as their total amount kept increasing the more the car was driven.

Table 14: US EPA 16 PAHs concentration in lubricant oil use for 3700 km

PAH	*Content (mg/kg oil)*
Naphthalene	0 – 83.3
Acenaphthylene	0 – 4.8
Acenaphthene	0 – 18.9
Fluorene	0 – 84.2
Phenanthrene	0 – 344.3
Anthracene	0 – 96.0
Fluoranthene	0 – 80.4
Pyrene	0 – 95.8
Benzo(a)anthracene	0 – 64.2
Chrysene	0.6 – 26.8
Benzo(b)fluoranthene	0.9 – 47.6
Benzo(k)fluoranthene	1.1 – 26.8
Benzo(a)pyrene	0 – 144.1
Dibezno(a,h)anthracene	0 – 9.0
Indeno(1,2,3-cd)pyrene	0 – 98.3
Benzo (g,h,i)perylene	0 – 101.7

The values between the old and the new car did not have big differences, and the minimum and maximum values of each PAH in the lubricant oil of the old car (Table 14), as well as the data from the concentrations in different type of engines (Table 13), were used for the calculation of

[8] The data are presented in ppm, 1 ppm = 1 mg/kg

the emission factor. The emission factor was calculated by multiplying the minimum and the maximum content, with the loss of lubricant oil by leakage which, as mentioned before, is 10 mg/vkm. Table 15 shows the results for the emission factor for the 16PAH that were used later on for the calculation of the total amount of PAH, while Table 16 show the emission factor of total PAHs in different types of engines for informative purposes.

Table 15: Emission factor of lubricant oil based on km driven

Emission factor of lubricant oil based on km driven	*mg/vkm*
Naphthalene	$0 – 833*10^{-6}$
Acenaphthylene	$0 – 48*10^{-6}$
Acenaphthene	$0 – 189*10^{-6}$
Fluorene	$0 – 842*10^{-6}$
Phenanthrene	$0 – 3443*10^{-6}$
Anthracene	$0 – 960*10^{-6}$
Fluoranthene	$0 – 804*10^{-6}$
Pyrene	$0 – 958*10^{-6}$
Benzo(a)anthracene	$0 – 642*10^{-6}$
Chrysene	$6*10^{-6} – 268*10^{-6}$
Benzo(b)fluoranthene	$9*10^{-6} – 476*10^{-6}$
Benzo(k)fluoranthene	$11*10^{-6} – 268*10^{-6}$
Benzo(a)pyrene	$0 – 1441*10^{-6}$
Dibezno(a,h)anthracene	$0 – 90*10^{-6}$
Benzo (g,h,i)perylene	$0 – 1017*10^{-6}$
Indeno(1,2,3-cd)pyrene	$0 – 983*10^{-6}$

Table 16: Emission factor of lubricant oil based on engine type.

Emission factor of lubricant oil based on engine type	*Mg/vkm*
Leaded petrol car	$19290*10^{-6} – 38910*10^{-6}$
Unleaded petrol car	$25160*10^{-6} – 46050*10^{-6}$
Diesel car	$270*10^{-6} – 1970*10^{-6}$
Diesel truck	$270*10^{-6} – 2910*10^{-6}$

5. Results and discussion

5.1. Tyres

For the calculation of PAHs released from tyres it was not possible to use the total amount of vehicles, 78590, because passenger cars and HDV have different emission factors. According to a report from the Swedish Transport Administration (Trafikverket, 2013), the percentage of heavy vehicles is around 10 – 15%, while the information about AADT that has been acquired from a road traffic flow map show that percentage to be around 9%. As a result the assumption was made that 90% of the total amount of vehicles in Gårda is passenger cars and 10% is HDV. In addition, only 10% of the 78590 vehicles that pass through Gårda are assumed to have tyres with HA oil. Therefore, the calculations involve only 7859 vehicles: 7073 passenger cars and 786 HDV.

Table 17 shows the total amount of 16PAHs emitted from the tyres of passenger cars and HDV. The PAH with the highest maximum values in passenger cars are fluoranthene, pyrene, benzo[g,h,i]perylene, benzo[a]anthracene, chrysene, with the two latter being in the category of possibly carcinogenic, while in lorries the most elevated maximum values originate from fluoranthene, pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene with the last two being in the category of probably carcinogenic (Appendix Table 28 – 29).

Table 17: Total amount of 16PAHs emitted from tyres (g/year)

	Total amount of 16PAHs emitted from tyres (g/year)	
	Passenger cars	**Lorries**
naphthalene	0.5 – 153.3	0.7 – 28.4
acenaphthylene	-	-
acenaphthalene	0.5 – 318.1	0.05 – 1.9
fluorene	0.1 – 22.7	0.7 – 27.8
phenanthrene	5.7 – 312.4	0.3 – 14.5
anthracene	1.0 – 113.6	0.02 – 0.6
fluoranthene	1.9 – 533.9	0.6 – 97.2
pyrene	4.5 – 1374.5	0.5 – 209.5
benzo[a]anthracene	1.1 – 482.8	0.1 – 5.7
chrysene	3.0 – 2913.6	0.3 – 33.5
benzo[b]fluoranthene	3.3 – 363.5	1.0 – 40.4
benzo[k]fluoranthene	-	-
benzo[a]pyrene	1.8 – 170.4	0.1 – 16.4
dibenz[a,h]anthracene	0.1 – 68.2	0.03 – 5.0
benzo[g,h,i]perylene	0.7 – 732.7	0.4 – 46.1
indeno[1,2,3-cd]pyrene	0.1 – 130.6	0.1 – 6.3

There is a significant difference between the minimum and the maximum values of each contaminant that may be a result of different driving styles or conditions. The wear in the tyres can significantly vary according to the speed of the vehicle, whether the road is dry or wet, how loaded the vehicle is and whether or not it brakes often and from high speeds. Since the total amount of PAHs is dependent on the emission factor, and the emission factor on the percentage of tyre wear, the final total amount can have significant variations. Lorries have lower values possibly because they are driven at a lower, steadier speed that does not involve hard acceleration or braking.

5.2. Road surface material

For calculation of the total amount of PAH emitted from the road material presented in Table 18, Formula (1) (page 9) and the emission factor data in Table 9 were used. For example the calculation of the total minimum amount of naphthalene was as follows:

Emission factor mg/vkm * vehicles/day * km of road = x mg/day = x * 365 * 10^{-3} g/year → $3.6*10^{-6}$ mg/vkm * 78590 vehicles/day * 5.5 km = 1.6 mg/day = 1.6 mg/day * 365 days/year * 10^{-3} = 0.6 g/year

In this table the highest values for the maximum emissions are those of naphthalene, fluoranthene, benzo[g,h,i]perylene, benzo[a]anthracene and chrysene. The values present much less variation than the ones in tyre emissions.

Table 18: Total amount of PAH emitted from road asphalt material (g/year)

	Total amount of PAH emitted from road asphalt material (g/year)
naphthalene	0.6 – 12.6
acenaphthylene	0.1 – 0.4
acenaphthalene	0.1 – 0.5
fluorene	0.2 – 0.9
phenanthrene	1.4 – 4.8
anthracene	0.4 – 2.4
fluoranthene	1.9 – 13.9
pyrene	1.4 – 9.1
benzo[a]anthracene	3.3 – 27.8
chrysene	3.6 – 15.1
benzo[b]fluoranthene	1.4 – 9.8
benzo[k]fluoranthene	0.4 – 1.5
benzo[a]pyrene	2.4 – 10.1
dibenz[a,h]anthracene	1.4 – 11.4
benzo[g,h,i]perylene	3.6 – 15.1
indeno[1,2,3-cd]pyrene	0.4 – 1.4

5.3. Brake linings

For calculation of the total amounts of PAHs released from brake linings in Table 19, Formula (1) (page 9) and the emission factor data from Table 11 were. For example the calculation of the total minimum amount of phenanthrene was as follows:

Emission factor mg/vkm * vehicles/day * km of road = x mg/day = x * 365 * 10-3 g/year → 8.536*10-6 mg/vkm * 78590 vehicles/day * 5.5 km = 3.7 mg/day = 3.7 mg/day * 365 days/year * 10-3 = 1.3 g/year

Table 19: Total amount of PAHs emitted from brake linings (g/year)

	Total amount of PAHs emitted from brake linings (g/year)
naphthalene	nd
acenaphthylene	nd
acenaphthalene	nd
fluorene	nd
phenanthrene	1.3 – 12.9
anthracene	nd
fluoranthene	1.0 – 9.1
pyrene	1.5 – 14.6
benzo[a]anthracene	2.1 – 19.9
chrysene	2.4 – 22.5
benzo[b]fluoranthene	0.6 – 5.6
benzo[k]fluoranthene	0.9 – 8.2
benzo[a]pyrene	1.0 – 9.8
dibenz[a,h]anthracene	nd
benzo[g,h,i]perylene	3.6 – 34.5
indeno[1,2,3-cd]pyrene	nd

Some of the specific PAHs were nd (non-detectable) in the chemical analysis (Table 19), but for the specific PAHa analysed the ones with the most elevated maximum values are benzo[g,h,i]perylene, followed by benzo[a]anthracene and chrysene which are classified as probably carcinogenic

5.4. Exhaust gases

For calculation of emissions of PAHs from vehicle exhaust it was not possible to use the total amount of vehicles passing Gårda, because different amounts and different PAHs are emitted from cars driven on gasoline, diesel and there are also differences between passenger cars and HDV vehicles. Based on a publication of Traffic analysis (2014) with data from Gothenburg, it was calculated that of the passenger cars 66% were gasoline and 25% were diesel. There is also a small amount of vehicles that use other type of fuel such as ethanol or electricity. Therefore, and based on these percentages, to calculate the total emissions pf PAHs from vehicle exhaust given in Table 20, 46682 vehicles were calculated as gasoline cars, 17681 vehicles as diesel and 7859 vehicles as HDV.

Table 20: Total amount of PAHs emitted from vehicle exhaust in the Gårda catchment area (g/year)

	Total amount of PAHs emitted from exhaust in the Gårda catchment area (g/year)		
	Gasoline, E85, CNG PC & LCV	**Diesel PC & LCV**	**HDV**
naphthalene	1049.6 – 57165.6	23071.5 – 74538.7	893.9
acenaphthylene	0	920	0
acenaphthalene	0	0	0
fluorene	0	0	630.9
phenanthrene	438.6 – 5782.2	980.7 – 3034.8	362.9
anthracene	75.0 – 749.7	48.6 – 120.7	136.5
fluoranthene	262.4 – 1686.9	638.9 – 1360.2	337.5
pyrene	168.7 – 562.3	436.6 – 1382.9	498.4
benzo[a]anthracene	40.3 – 78.7	96.2 – 117.1	37.7
chrysene	40.3 – 49.7	85.2 – 267.3	256.2
benzo[b]fluoranthene	33.7 – 82.5	21.3 – 117.1	86.0
benzo[k]fluoranthene	24.4 – 28.1	6.7 – 101.9	96.1
benzo[a]pyrene	30.0 – 45.0	22.4 – 101.2	14.2
dibenz[a,h]anthracene	0.9 – 2.8	8.5 – 19.9	5.4
benzo[g,h,i]perylene	52.5 – 271.8	33.7 – 213.0	12.1
indeno[1,2,3-cd]pyrene	36.5 – 96.5	24.8 – 90.2	22.1

For calculation of the data in Table 20, Formula (1) (page 9) and the emission factor data from Table 12 were used. For example the calculation of the total minimum amount of naphthalene in gasoline vehicles was as follows:

Emission factor mg/vkm * vehicles/day * km of road = x mg/day = x * 365 * 10^{-3} g/year → 11.20μg/vkm= 11.20*10^{-3} mg/vkm * 46682 vehicles/day * 5.5 km = 2875.6 mg/day = 2875.6 mg/day * 365 days/year * 10^{-3} = 1049.6 g/year

In general the emissions of this source are significantly higher than the ones form the other sources. Naphthalene, phenanthrene, fluoranthene, anthracene and pyrene are the contaminants with the higher values.

5.5. Motor lubricant oil

For calculation of the data in Table 21, Formula (1) (page 9) and the emission factor data from Table 15 were used. For example the calculation of the total maximum amount of naphthalene in gasoline vehicles was as follows:

Emission factor mg/vkm * vehicles/day * km of road = x mg/day = x * 365 * 10^{-3} g/year → 833*10^{-6} mg/vkm * 78590 vehicles/day * 5.5 km = 360.1 mg/day = 360.1 mg/day * 365 days/year * 10^{-3} = 131.4 g/year

Benzo(a)pyrene and indeno(1,2,3-cd)pyrene that are possibly carcinogenic have high values, as well as benzo (g,h,i)perylene, phenanthrene, anthracene and pyrene.

Table 21: Total amount of PAHs emitted from lubricant oil based on km driven (g/year)

	Total amount of PAHs emitted from lubricant oil based on km driven (g/year)
naphthalene	0 – 131.4
acenaphthylene	0 – 7.6
acenaphthene	0 – 29.8
fluorene	0 – 132.8
phenanthrene	0 – 543.2
anthracene	0 – 151.5
fluoranthene	0 – 126.8
pyrene	0 – 151.1
benzo(a)anthracene	0 – 101.3
chrysene	0.9 – 42.3
benzo(b)fluoranthene	1.4 – 75.1
benzo(k)fluoranthene	1.7 – 42.3
benzo(a)pyrene	0 – 227.3
dibezno(a,h)anthracene	0 – 14.2
indeno(1,2,3-cd)pyrene	0 – 160.5
benzo (g,h,i)perylene	0 – 155.1

5.6. Total amount of PAHs emitted in Gårda

In order to present the emissions of the 16PAHs that are emitted from all the sources in Gårda, Table 22 was created. In this table, the 16PAH were divided into groups according to the number of rings they have in their molecular structure, and they are a result of the addition of the total emissions from each source. In Tables 32 - 34 in the Appendix the analytical collective data are presented.

Table 22: Total amount of PAH based on the number of rings in the molecule (g/year)

	Total amount of PAH based on the number of rings	
	min	max
2rings: Naphthalene	25017	132924
3rings: Acenaphthylene, Acenaphthalene, Fluorine, Phenanthrene, Anthracene ,	3605	13436
4rings: Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene ,	2928	12839
5rings: Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene	367	1779
6rings: Benzo[g,h,i]perylene, Indeno[1,2,3-cd]pyrene,	191	1988

5.7. Different sinks

The above presented emissions of PAHs are mostly particle-bounded emission, and for the vehicle exhaust the PAHs are emitted directly into air and not the entire amount will thus end up in the stormwater in the nearby catchment area. Certain amount of the emissions from Gårda will travel to other catchments while external emission from other areas will enter the study area. A part of the emissions will enter the road runoff either by deposition on the surface of the road and wash-off (dry deposition) or it will be captured in the rain (wet deposition) (Petrucci et al., 2014). Deposition depends on two factors: meteorological conditions such as humidity, wind velocity and air temperature, and surface characteristics such as friction velocity, roughness and surface temperature (Amodio, 2014).

Low molecular weight PAHs (two – three aromatic rings) are gaseous and more soluble in water, while the heavier ones are less volatile or totally adsorbed by dust particles and are also less soluble (OSPAR Commission, 2009). The transportation and deposition of PAHs from the vehicle exhausts depends on their gas/particle partition which is influenced by their molecular weight as well as the two factors mentions above. Since the low molecular weight PAHs are gaseous they are easily dispersed and they can travel very far from their source. The high molecular weight ones (five or more rings) have a high temperature of condensation and as mentioned above they are absorbed by other airborne particles making them more immobile and fast deposited near the source of their emission (Ravindra, 2008).

The PAHs emitted from vehicle exhaust way of traveling and deposition is also supported by a simulation study on the long-range transport potential and overall persistence of PAHs performed by Ding et al (2012). In this study the results showed that benzo[g,h,i]perylene (six rings) had the shortest characteristic travel distance by air while pyrene (4 rings) had significantly higher. In water naphthalene (2 rings) was relatively easily dissolved while benzo[g,h,i]perylene travelled further away.

The above literature review combined with specialists judgment within the atmospheric science, environmental science and stormwater management field was used to make assumption about the amount of PAHs from vehicle exhaust that will end up in the stormwater system at Gårda and the

amount that will end up in other sinks such as the atmosphere. The Gårda area is assumed not to be that highly affected by surrounding catchments because they do not have a heavy traffic load. In addition to that, background concentrations coming from other countries are not going to be taken under consideration due to the fact that they are very low in comparison to the emissions in traffic near areas in Sweden (Björklund, 2011). It was assumed that: for the two and three ring PAHs 20% will end up in the stormwater of Gårda while the rest will go to other sinks, for the four ring PAHs 50% will go to the stormwater and for the five and six ring PAHs 80% will go to the stormwater of the study area and the rest to other sinks. Table 23 shows the resulted amounts of vehicle exhaust in g/year grouped according to number of rings in their molecule.

Table 23: Vehicle exhaust emissions, emissions to stormwater and emissions to other sink (g/year)

	Vehicle exhaust total emissions		***Emissions to stormwater***		*Emissions to Other sinks*	
2rings: Naphthalene	25015	132598	**5003**	**26520**	20012	106078
3rings: Acenaphthylene, Acenaphthalene, Fluorine, Phenanthrene, Anthracene	3593	11738	**719**	**2348**	2874	9390
4rings: Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene	2898	6635	**1449**	**3318**	1449	3317
5rings: Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene	350	700	**280**	**560**	70	140
6rings: Benzo[g,h,i]perylene, Indeno[1,2,3-cd]pyrene	182	706	**146**	**565**	36	141

For the estimation of the amount of the emissions from the other sources that will go to stormwater and to other sinks, the runoff coefficient was used. Runoff coefficient is defined as the amount of precipitation that directly becomes runoff (Norbiato, 2009). In Sweden the runoff coefficient for roads is 0.8 (Svenskt Vatten Utveckling, 2013). In this paper, the assumption was made that the same runoff coefficient that applies to water, will also apply to the pollutants. Thus, it was assumed that 80% of the pollutants will end up in the stormwater while the other 20% will go to other sinks. Table 24 shows the emission to stormwater and other sinks from the rest of the sources.

Table 24: Tyre, road asphalt material, brake linings and motor lubricant oil emissions, emissions to stormwater and emissions to other sink (g/year)

	Tyre, road material, brake linings and motor oil total emissions		***Emissions to stormwater***		*Emissions to other sinks*	
2rings: Naphthalene	2	326	**1.6**	**261**	0.2	65
3rings: Acenaphthylene, Acenaphthalene, Fluorine, Phenanthrene, Anthracene	12	1698	**9.6**	**1358**	2.3	340
4rings: Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene	30	6204	**24**	**4963**	6.2	1241
5rings: Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene	17	1079	**13.6**	**863**	3.8	216
6rings: Benzo[g,h,i]perylene, Indeno[1,2,3-cd]pyrene	9	1282	**7.2**	**1026**	1.7	256

Table 25 shows the total emissions to stormwater and other sinks from all the sources.

Table 25: Total amount of PAHs emitted at Gårda distributed to different sinks according to the number of rings

	Emissions to stormwater		*Emissions to other sinks*	
2rings: Naphthalene	5005	26781	20012.3	106143
3rings: Acenaphthylene, Acenaphthalene, Fluorine, Phenanthrene, Anthracene	729	3706	2876.5	9730
4rings: Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene	1473	8281	1455.5	4558
5rings: Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene	294	1423	73.4	356
6rings: Benzo[g,h,i]perylene, Indeno[1,2,3-cd]pyrene	153	1591	37.5	397

Figure 5 shows the amounts of PAHs calculated to occur in the stormwater at Gårda based on their mean value and grouped according to the number or rings. Figure 6 also shows the mean values of PAHs that will end up in stormwater at Gårda, but apart from their number of rings they are also divided by source of emission. The results show that the most dominant PAHs, excluding naphthalene which is very volatile as it will also be discussed later on, are the ones with four rings in their molecular structure and the main source of emissions is the vehicle exhaust.

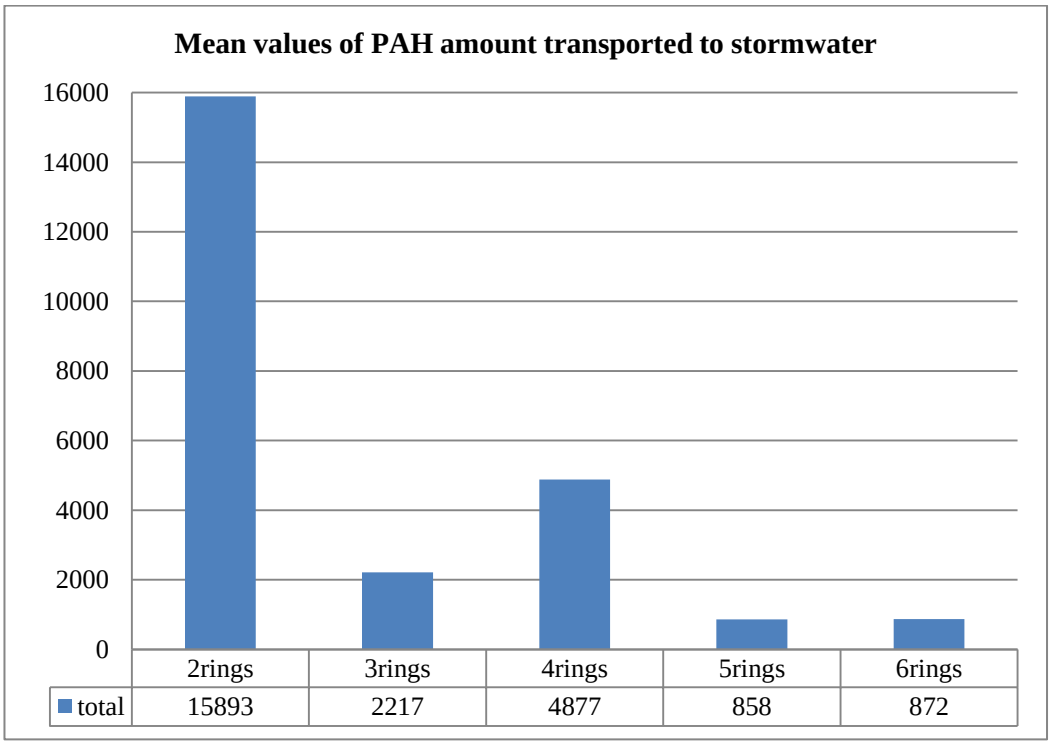
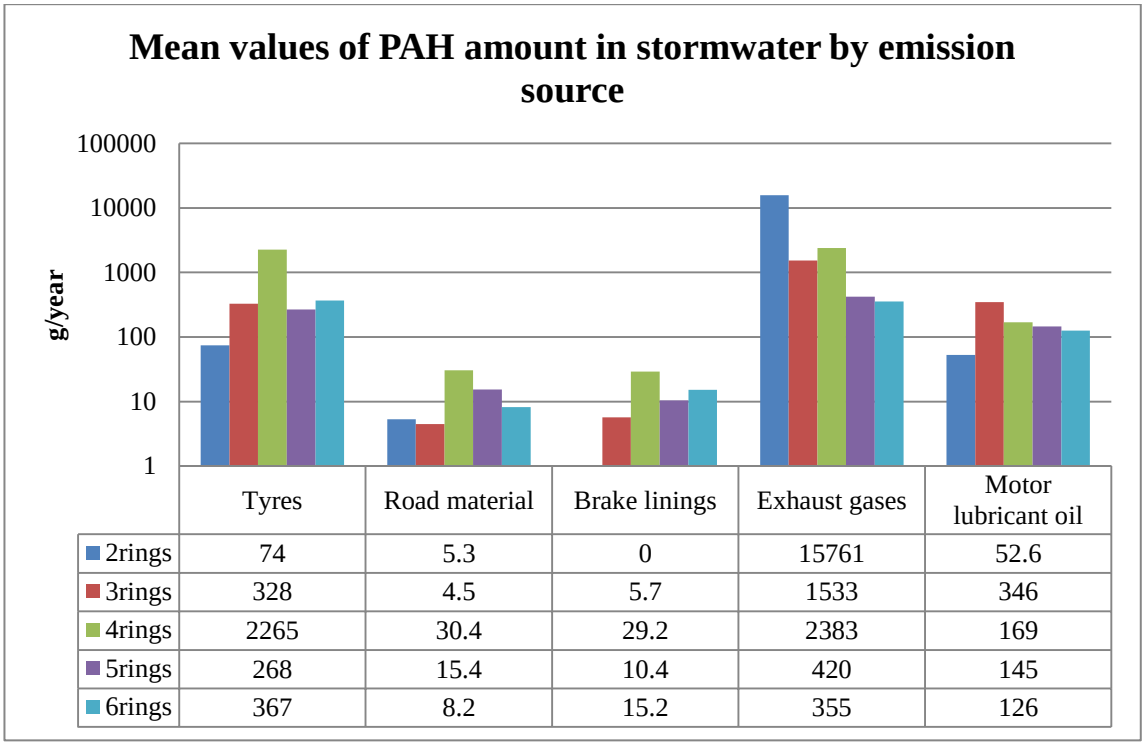


Figure 5: Mean values of PAH amount that ends up in stormwater at Gårda according to the number or rings in the molecule



	Tyres	Road material	Brake linings	Exhaust gases	Motor lubricant oil
2rings	74	5.3	0	15761	52.6
3rings	328	4.5	5.7	1533	346
4rings	2265	30.4	29.2	2383	169
5rings	268	15.4	10.4	420	145
6rings	367	8.2	15.2	355	126

Figure 6: Mean values of PAH amounts in stormwater at Gårda by emission sources and number of rings in the molecule

Figures 7 - 11 present analytically the amount of the PAHs (g/year) of all groups that is transported to stormwater and to other sinks. The results of the amount distributed to water and other sinks are presented with a minimum and a maximum value since that is the way they have been calculated in this study. Figure 7 shows that a very high amount of naphthalene is emitted to water but there is likely that the amount is an overestimation due to the fact that naphthalene is highly volatile and under real conditions a higher amount will escape to the atmosphere instead of being distributed to the stormwater.

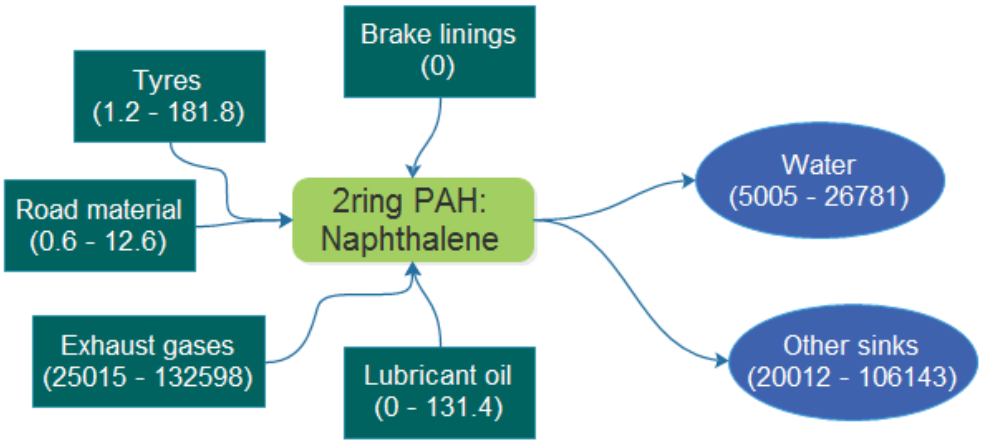


Figure 7: Concentration of 2-ring PAHs that end up in different sinks

PAHs with 3 rings in Figure 8 have a significant maximum value and although they do not belong in the probably carcinogenic group, such a high value is problematic because they do cause alarming issues such as gene mutations (Appendix Table 28).

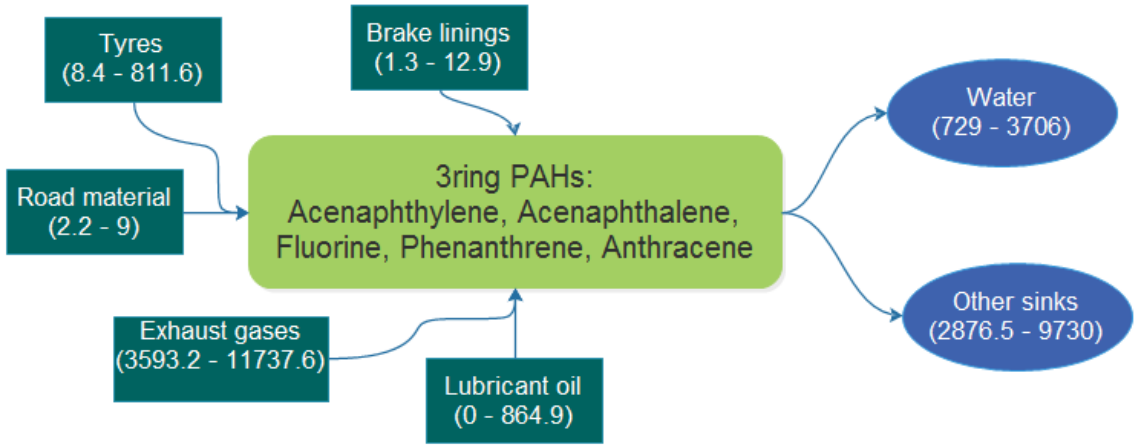


Figure 8: Concentration of 3-ring PAHs that end up in different sinks

Figure 9 is the one with the highest quantities of PAHs transported to stormwater. Fluoranthene and pyrene are marked as non-carcinogenic but benzo[a]anthracene and chrysene are probably carcinogenic which makes the calculated amount alarming.

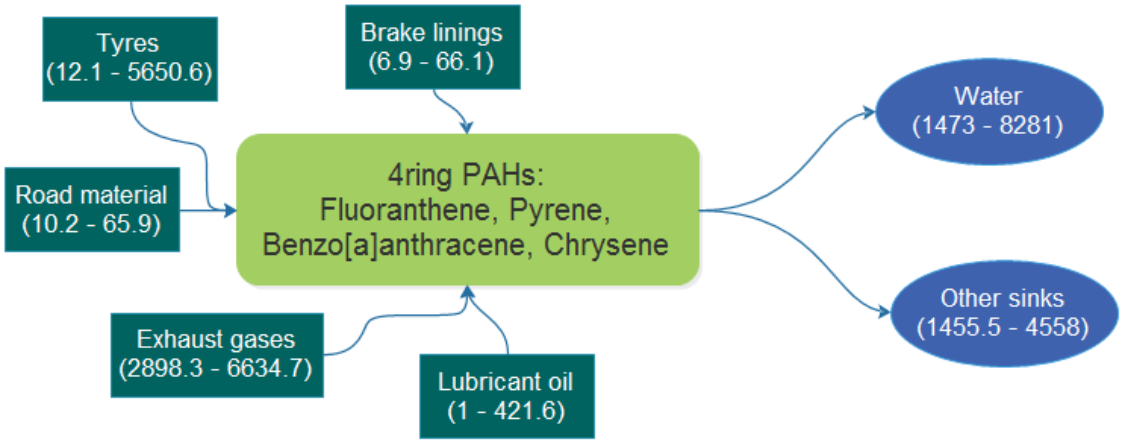


Figure 9: Concentration of 4-ring PAHs that end up in different sinks

The two last figures, Figure 10 and Figure 11, have probably carcinogenic PAHs and their maximum values are quite high, not so much in comparison to the other PAHs but more in relation to the negative health effects they cause to humans and animals.

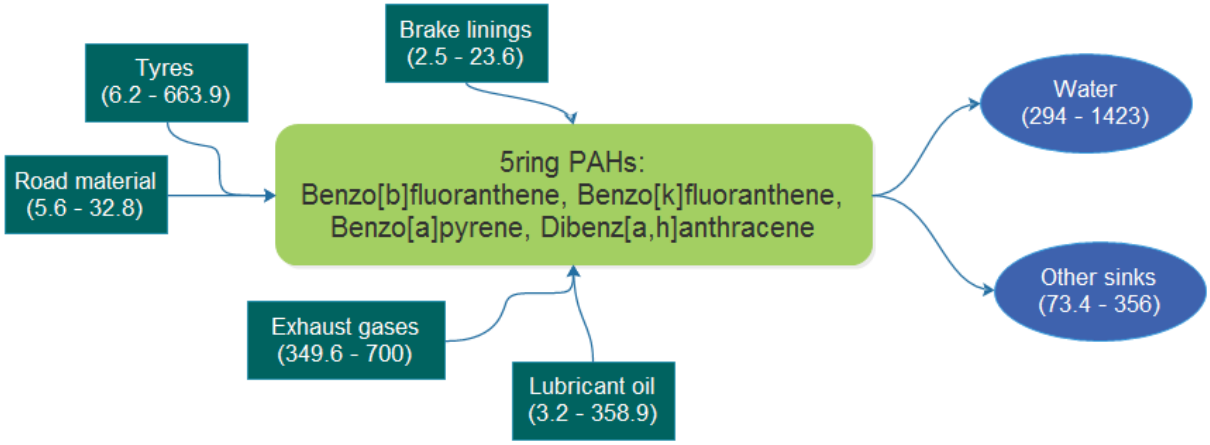


Figure 10: Concentration of 5-ring PAHs that end up in different sinks

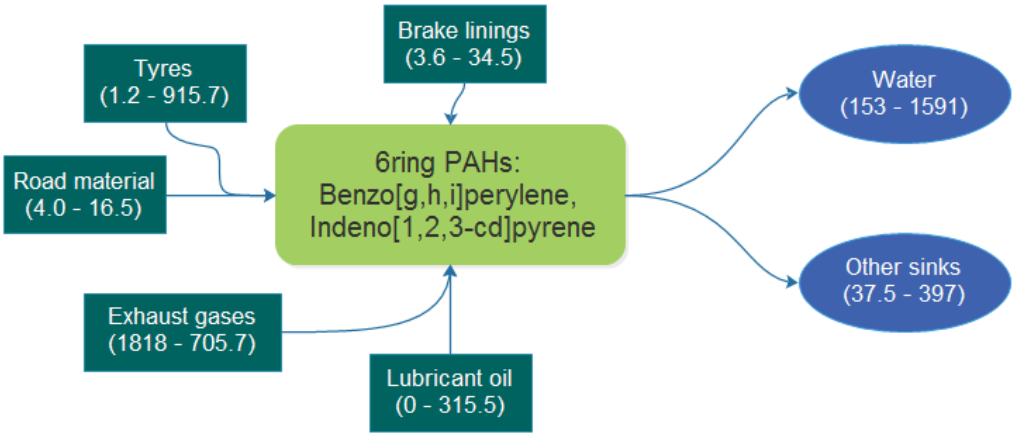


Figure 11: Concentration of 6-ring PAHs that end up in different sinks

5.8. Sampling data

The calculations of this section were based on Formula (2) (page 10). Table 26 presents the dry weight of sediment in every chamber expressed in kilograms as well as the concentrations of the sediment samples of this study expressed in mg/kg of dry weight (dw). The total calculated amount is expressed in g/year.

Table 26: Dry weight sediment (kg) and PAH concentration (mg/kg dw)

Chamber	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*Total amount (g/year)*
Dry weight (kg)	2717	3095	1414	1239	1101	756	1095	5.3
Naphthalene	0.15	0.26	0.37	0.32	0.27	0.24	0.21	3.0
Acenaphthylene	0.1	0.15	0.2	0.17	0.14	0.14	0.14	2.1
Acenaphthene	0.1	0.1	0.1	0.1	0.1	0.1	0.1	2.8
Fluorene	0.1	0.135	0.17	0.16	0.15	0.125	0.1	15.0
Phenanthrene	0.33	0.65	0.97	0.92	0.87	0.805	0.74	3.6
Anthracene	0.1	0.175	0.25	0.21	0.17	0.17	0.17	22.4
Fluoranthene	0.44	0.97	1.5	1.4	1.3	1.2	1.1	34.8
Pyrene	0.69	1.495	2.3	2.15	2	1.9	1.8	6.8
Benzo(a)anthracene	0.11	0.29	0.47	0.425	0.38	0.38	0.38	9.1
Chrysene	0.2	0.4	0.6	0.555	0.51	0.48	0.45	12.5
Benzo(b)fluoranthene	0.26	0.57	0.88	0.75	0.62	0.66	0.7	3.4
Benzo(k)fluoranthene	0.08	0.165	0.25	0.21	0.17	0.16	0.15	7.0
Benzo(a)pyrene	0.14	0.31	0.48	0.42	0.36	0.375	0.39	2.0
Dibezno(a,h)anthracene	0.08	0.08	0.08	0.1	0.12	0.115	0.11	13.3
Benzo (g,h,i)perylene	0.31	0.565	0.82	0.785	0.75	0.735	0.72	5.3
Indeno(1,2,3-cd)pyrene	0.08	0.24	0.4	0.34	0.28	0.28	0.28	5.3

The results were grouped according to the amount of rings each PAH has and are presented in Figure 12.

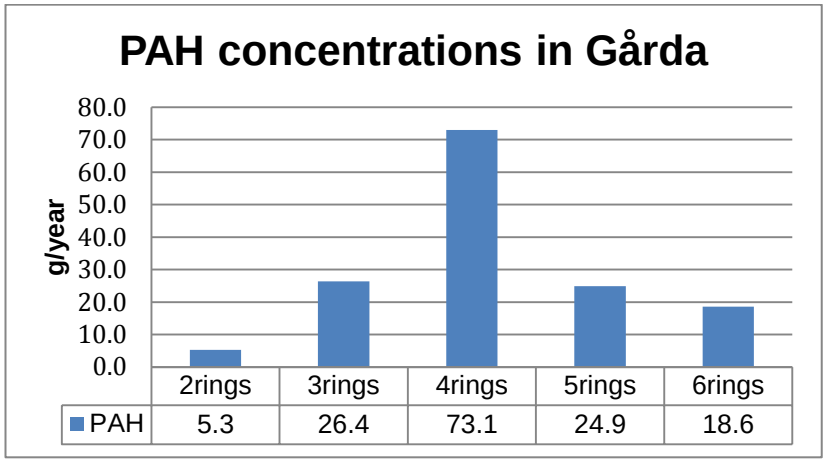


Figure 12: PAH amounts released in the Gårda catchment area based on calculations from measurements of concentration in sediment samples

The results of the chemical analysis also showed that the concentrations of oxygenated Polycyclic Aromatic Hydrocarbons (oxy-PAH) were very high (Appendix Table 35). Oxy-PAHs are degradation products of PAHs that have at least one carbonylic oxygen attached to the aromatic rings. They can be emitted by the same sources but they are also created by the oxidation of PAH after their emission and they are more persistent than other transformation products and more toxic (Lundstedt et al, 2007). This means that the amount of PAH that entered the stormwater was higher than calculated above because some of the PAH were transformed into oxy-PAHs. To calculate the total amount of oxy-PAH in g/year the same calculation method was used as for the PAHs. Their concentrations and final amount is shown in Table 27, while Figure 13 shows the collective PAH and oxy-PAH concentration in the study area, grouped according to the number of rings they have in their molecular structure.

Table 27: Dry weight sediment (kg) and oxy-PAH concentration (mg/kg dw)

Chamber	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*Total amount (g/year)*
Dry weight (kg)	2717	3095	1414	1239	1101	756	1095	2.0
9-fluorenon	0.1	0.12	0.13	0.14	0.14	0.14	0.14	2.4
9,10-antrakinon	0.1	0.15	0.19	0.16	0.12	0.18	0.24	2.1
2-metylantracen-9,10-dion	0.1	0.12	0.13	0.14	0.14	0.17	0.19	1.8
7H-bens(de)antracen-7-on	0.1	0.11	0.12	0.12	0.12	0.12	0.12	2.9
Bens(a)antracen-7,12-dion	0.1	0.11	0.11	0.23	0.34	0.33	0.32	1.7
6H-bens(cd)pyren-6-on	0.1	0.10	0.1	0.10	0.1	0.11	0.11	1.8
Bens(a)fluorenon	0.1	0.11	0.12	0.12	0.12	0.11	0.1	1.6
4H-cyklopenta(def)fenantrenon	0.1	0.10	0.1	0.10	0.1	0.10	0.1	1.8
Naftacen-5,12-dion	0.1	0.12	0.13	0.12	0.1	0.10	0.1	2.0

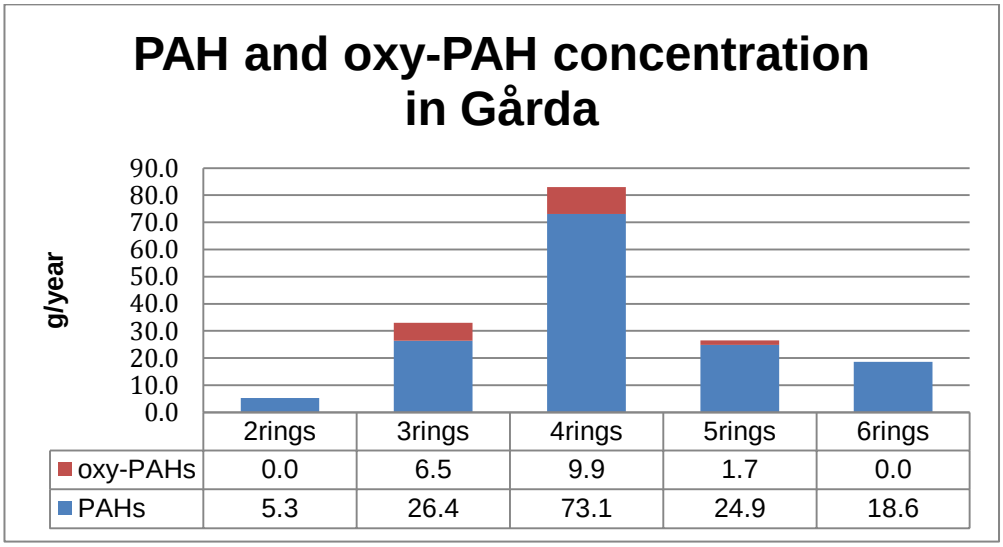


Figure 13: PAH and oxy-PAH amounts emitted at Gårda based on measurements of concentrations in sediment samples

5.9. Comparison of measured and calculated emissions

Comparing the results from the literature data (Figure 10) and the sampling analysis (Figure 13) there are certain similarities and certain differences. The biggest difference is that the values from the sampling and the chemical analysis are lower than the literature values and that might have been a result from the assumptions that had to be made, and indicate that the PAHs sinks in the road environment, as volatilization and sorption to urban surfaces and soils, are important to study further in depth. The second important difference is that the values of naphthalene are much higher in the literature data. This can be explained based on the fact that naphthalene is highly volatile and in reality the majority of the amount emitted would not end up in stormwater but in the atmosphere. The difference may also be explained by uncertainties in the sampling procedure, extraction and chemical analysis of the sediment and measurements, and calculations of the amounts of sediment accumulated yearly in the Gårda catchment area.

The calculations based on the sampling and chemical analysis data show the same trend as the literature data. Four-ring PAH are the dominant ones and that shows that exhaust gases are the largestsource of PAH, while the concentrations of three-ring PAH are an indicator of emissions from tyres which agrees with the outcome of the literature data (Pettersson et al., 2005).

The unpublished study of Chalmers University mentioned before, showed lower values of PAH in the sediment which means that since that study at 2003 there has been even higher accumulation of PAHs in the sediment in the Gårda sedimentation facility indicating a much higher release of PAHs in the area. It is strange that the PAHs concentrations in the sediment is much higher today than 10 years ago, because the road taxes have caused a decrease of the traffic in the Gårda area, and the ban of PAHs in tyres should have caused much lower emission in Gårda. This indicates that more research is needed in the main source of emissions which is the exhaust gases.

6. Conclusions

This study attempted to identify the main PAH emission sources in the catchment area of Gårda, quantify those emissions based on literature data, perform a SFA and compare the results with the results from sample analysis of sediment from the same area. The results of the SFA showed high concentrations of PAHs that end up in the stormwater of the area, mainly coming from vehicle exhaust and secondary from road asphalt material and tyres. PAHs with four rings in their

molecular structure were the dominant ones while PAH with five and six rings had significantly lower values but still high for being probably carcinogenic. The results from the sampling analysis showed lower concentrations in general, but they confirmed the SFA as far as the dominance of the four ring PAHs and the vehicle exhaust as the main source of emission.

The most important limitation when writing this paper was the lack of detailed and uniform data. There is a gap in literature about the amount of the 16PAHs contained in the emission sources of this study. That existing data can give an idea about the released PAH in the road runoff but it is more of an estimation rather than exact measurement.

A second limitation, which is also connected to difficulties in obtaining data, is that it is difficult to find information about the type and number of different vehicles that pass through the study area of Gårda. This difficulty leads to the generalisation of existing data. For example, the specific number of passenger cars and trucks that pass through the area is not known, which lead to the assumption that all vehicles have four wheels with the logic that some trucks have six but there are also motorbikes that have two. A second example is the calculation of exhaust emissions. There are more detailed data about different types of passenger cars but if the number of each type is unknown, these data cannot be used for Gårda.

A third limitation is the date some of the data where published. Some of the data used go as far back as 1996 and there is a possibility that they do not completely reflect reality but rather an approximation of the present situation.

PAHs are mostly studied for their carcinogenicity but apart from that they have many other adverse health effects on various organisms in the terrestrial and aquatic environment. As a result their concentration cannot be allowed to rise without pin pointing the exact reasons for their accumulation as a first step and adapt regulations concerning their emissions as a second.

The high values of the amounts release found from data in the literature and the high concentrations analysed in the sediment are an indication that more sampling and chemical analysis might be necessary in the area in order to identify the reason why the concentrations are in such a high level. A more detailed field study and measurement of the wet and dry deposition in the area might be needed to identify more accurately the sources of PAH and the reasons behind accumulation.

7. References

Amodio M., Catino S., Dambruoso P.R., et.al. (2014), *"Atmospheric Deposition: Sampling Procedures, Analytical Methods, and Main Recent Findings from the Scientific Literature"*, Advances in Meteorology Volume 2014, Article ID 161730, 27 pages, Hindawi Publishing Corporation

Ayres R.; Ayres L. (2001), "*A Handbook of Industrial Ecology",* Edward Elgar Publishing Ltd, Uk

Björklund K. (2010), "*Substance Flow Analysis of phthalates and nonylphenols in storm water",* IWA Publishing, Sweden

Boström C.; Gerde P.; Hanberg A.; Jernström B.; Johansson C.; Kyrklund T.; Rannung A.; Törnqvist M.; Victorin K.; Westerholm R. (2002), "*Cancer Risk Assessment, Indicators, and Guidelines for Polycyclic Aromatic Hydrocarbons in the Ambient Air*", Environ Health Perspect 110(suppl 3):451–489

Brown J.N., Peake B., (2006), *"Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff"*, Science of the Total Environment 359 (2006) 145– 155

Canadian Council of Ministers of the Environment (2010), "*Canadian Soil Quality Guidelines for Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (Environmental and Human Health Effects)", Scientific* Criteria Document (revised). 216 pp.

Clonfero E., Nardini B., Marchioro M., Bordin A., Gabbani G. (1996), *"Mutagenicity and contents of polycyclic aromatic hydrocarbons in used and recycled motor oils"*, Mutation Research 368 (1996) 283-291, Elsevier

Continental (2008), *"Tyre Basics, Passenger Car Tyres"*, Continental AG, Accessed at: https://www.conti-online.com/generator/www/au/en/continental/tyres/general/downloads/download/reifengrundlagen_en.pdf (07/06/2015)

CSTEE (2003), *"Questions to the CSTEE relating to scientific evidence of risk to health and the environment from polycyclic aromatic hydrocarbons in extender oils and tyres"*, European commission, Brussels

Denton J.E. (2007), *"A review of the potential human and environmental health impacts of synthetic motor oils"*, California Environmental Protection Agency Office of Environmental Health Hazard Assessment Integrated Risk Assessment Branch

Ding Z.; Fang L.; Wu Y.; Ma Z.; Liu M.; Wu J.; Gao H. (2012), *"Simulation study on the long-range transport potential and overall persistence of 16 PAHs in Lanzhou"*, College of Earth and Environmental Sciences; Lanzhou University; Lanzhou 730000

Dynamic Aqua-Supply Ltd (2015), *"Water sampling equipment"*, Accessed at: http://dynamicaqua.com/samplingequipment.html (20/06/2015)

Eisler R. (1987) *"Polycyclic Aromatic Hydrocarbon Hazards To Fish, Wildlife, And Invertebrates: A Synoptic Review"*, Biological Report 85(1.11), U.S. Fish and Wildlife Service Patuxent Wildlife Research Center Laurel

EPA (2014), "*Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors"*, Accessed at: http://www.epa.gov/ttn/chief/ap42/index.html, (27/02/2015)

ETRma (2010), *"FAQ and Definitions: Replacement of Highly Aromatic oils in Tyres"*, ETRMA Aisbl, Brussels

ETRma (2011), *"Second testing program confirms: REACH compliance tests continue to give failing grades to tyre import",* press release, Accessed at: http://www.etrma.org/uploads/Modules/Newsroom/pah-2nd-round_press-release_2011-10-17.pdf (19/04/2015)

European Environment Agency (2007), "*Feasibility assessment of using the substance flow analysis methodology for chemicals information at macro level"*, EEA Technical report No1/2007, Copenhagen

European Environment Agency (2012), *"Sector share of PAH emissions (EEA member countries)"*, Accessed at: http://www.eea.europa.eu/data-and-maps/figures/sector-share-of-pah-emissions-eea-member-countries (29/02/2015)

Godoi, A.F.L.; Ravindra, K.; Godoi, R.H.M.; Andrade, S.J.; Santiago-Silva, M.; Van Vaeck, L.; Van Grieken, R., (2004), "*Fast Chromatographic determination of polycyclic aromatic hydrocarbons in aerosol samples from sugar cane burning*", Journal of Chromatography A 1027, 49–53.

Göteborgs Stad (2014), *" Luftkvaliteten i Göteborgsområdet med och utan trängselskatt"*, Västsvenska paketet rapport, Accessed at : http://www.trafikverket.se/contentassets/79c3a9c3cb2c447594dc0dac33bb048c/luftkvalitet_2013_goteborg_sep_2014.pdf (20/02/2015)

Hansen E.; Lassen C. (2003), "*Experience with the Use of Substance Flow Analysis in Denmark"*, Journal of Industrial Ecology, Vol. 6, p.n 3-4

Johansson C., Norman M., Burman L. (2009), "*Road traffic emission factors for heavy metals"*, Atmospheric Environment 43 (2009) 4681–4688, Elsevier

Jones K.C., Voogt P. (1999), ''*Persistent organic pollutants (POPs): state of the science'',* Environmental Pollution 100 (1999) 209-221, Elsevier

KEMI (2003), *"HA oils in automotive tyres"*, Report No 5/03, Swedish National Chemicals Inspectorate, Sweden

Kim K.; Jahan S.; Kabir E.; Brown R. (2013), "*A rewiew of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects"*, Environment International 60(2013) 71-80, Elsevier

Knutzen J. (1995), *"Effects on marine organisms from polycyclic aromatic hydrocarbons (PAH) and other constituents of waste water from aluminium smelters with examples from Norway"*, The Science of the Total Environment 163 (1995) 107-122, Elsevier

Krein A., Schorer M., (2000), *"Road Runoff Pollution By Polycyclic Aromatic Hydrocarbons And Its Contribution To River Sediments"*, Wat. Res. Vol. 34, No. 16, pp. 4110±4115, 200

Lee Byeong-Kyu (2010), "*Sources, Distribution and Toxicity of Polyaromatic Hydrocarbons (PAHs) in Particulate Matter*", Air Pollution, Vanda Villanyi (Ed.), ISBN: 978-953-307-143-5, InTech, DOI: 10.5772/10045.

Lindgren Å. (1998), *"Road Construction Materials as a Source of Pollutants"*, Doctoral Thesis 1998:05, ISSN: 1402-1544, Luleå University of Technology

Luhana, L., Sokhi, R., Warner, L., Mao, H., Boulter, P., McCrae, I., Wright, J., Reeves, N., Osborn, D. 2002, *"Non-exhaust particulate measurements: results"*. Deliverable 8 of the EuropeanCommission DG TREN 5th Framework Particulates project.

Lundstedt S., White P.A., Lemieux C.L., Lynes K.D., Lambert I.B., Öberg L., Haglund P., Tysklind M. (2007), *"Sources, Fate, and Toxic Hazards of Oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) at PAH-contaminated soil"*, AMBIO: A Journal of the Human Environment 36(6):475-485. 2007

Mojanraj R.; Dhanakumar S.; Solaraj G. (2012), "*Polycyclic Aromatic Hydrocarbons Bound to PM2.5 in Urban Coimbatore, India with Emphasis on source Apportionment"*, The Scientific World Journal Volume 2012, Article ID 980843

Murakami M., Nakajima F., Furumai H., (2004), *"Modelling of runoff behaviour of particle-bound polycyclic aromatic hydrocarbons (PAHs) from roads and roofs"*, Water Research 38 (2004) 4475–4483

Neff, J.M. (1979), *"Polycyclic aromatic hydrocarbons in the aquatic environment, sources, fates and biological effects"*, Applied Science Publishers Ltd., Essex, England

Netherlands National Water Board – Water Unit (2008), "Road surface wear", Accessed at: http://www.emissieregistratie.nl/ERPUBLIEK/documenten/Water/Factsheets/English/Road%20surface%20wear.pdf (25/03/2015)

NOAA (2009), *"Polycyclic Aromatic Hydrocarbons and Fish Health Indicatorsin the Marine Ecosystem in Kitimat, British Columbia"*, U.S. Dept. Commer., NOAA Tech. Memo. NMFS-NWFSC-98, 123 p.

Norbiato D., Borga M., Merz R., Blöschl G., Carton A. (2009), *"Controls on event runoff coefficients in the eastern Italian Alps"*, Journal of Hydrology 375 (2009) 312–325, Elsevier

Nordic Larger Cities Co-peration (2003), *"Nordic Larger Cities Environment Indicators"*, Accessed at: http://eldri.reykjavik.is/Portaldata/1/Resources/umhverfissvid/gr_na_borgin/1._kafli/1gogn/Nordic_Larger_Cities_Environment_Indicators,_Nordic_Larger_Cities_Co-operation,_2003.pdf, (20/02/2015)

Ntziachristos L., Boulter Paul (2009), *"EMEP/EEA emission inventory guidebook 2009, Road vehicle tyre and brake wear"*, European Environment Agency, Technical report No 9/2009

Ntziachristos L., Samaras Zissis (2013), *"EMEP/EEA emission inventory guidebook 2013, Exhaust emissions from road transport"*, European Environment Agency

OSPAR Commission (2009), *"Background Document on Polycyclic Aromatic Hydrocarbons (PAHs)"*, Hazardous Substances Series, Norway

PBL Netherlands Environmental Assessment Agency (2013), *"Methods for calculating the emissions of transport in the Netherlands"*, Accessed at:

http://www.pbl.nl/en/publications/methods-for-calculating-transport-emissions-in-the-netherlands (25/05/2015)

Pettersson T.J.R., Stömvall A-M, Ahlman S. (2005), *"Underground Sedimentation System for Treatment of Highway Runoff in Dense City Areas"*, 10th International Conference on Urban drainage, Copenhagen/Denmark

Petrucci G., Gromaire M., Shorshani M.F., Chebbo G. (2014), *"Nonpoint source pollution of urban stormwater runoff:a methodology for source analysis"*, Environ Sci Pollut Res (2014) 21:10225–10242, Springer

Ravindra K.; Sokhi R.; Van Grieken R. (2008), "A*tmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation",* Atmospheric Environment 42 (2008) 2895–2921, Elsevier

Rogge W. F., Hlldemann L. M., Monica A. Marurek,S and Glen R. Cass (1993), *"Sources of Fine Organic Aerosol. 3. Road Dust, Tire Debris, and Organometallic Brake Lining Dust: Roads as Sources and Sinks"*, Environ. Sci. Techno/. 1993, 27, 1892-1904

RTI International (2011), "*Emission Estimation Protocol for Petroleum Refineries"*, Version 2.1: Final ICR Version

Stanisavljevic N.; Brunner P. (2014), "*Combination of material flow analysis and substance flow analysis: A powerful approach for decision support in waste management"*, Waste Management & Research Vol. 32(8) 733-744, Sage

STRO (2004), *"Replacement of highly aromatic oils in tyres: frequently asked questions"*, Accessed at: http://stro.se/wp-content/uploads/2014/05/HA_oils-in-tyres.pdf, (02/04/2015)

Stömvall A-M., Pettersson T.J.R., Björklund K. (unpublished data), *"Metals and Polycyclic Aromatic Hydrocarbons (PAHs) in Road Runoff: Catchment Area Emission Factors (CAEFs), Sediment Particle Distribution"*, Chalmers University, Sweden

Svenskt Vatten Utveckling (2013), *"Utvärdering av Svenskt Vatten rekommenderade sammanvägda avrinningskoefficienter"*, nr 2013-05, Svenskt Vatten AB

Trafikverket (2013), *"Bulleruppföljning av Västsvenska paketet, Del 2: Efter införandet av trängsel-skatten och ändringar i kollektivtrafiken"*, Accessed at: http://www.trafikverket.se/contentassets/79c3a9c3cb2c447594dc0dac33bb048c/rapport-bulleruppfoljning-av-vastsvenska-paketet-del-2_2013.pdf (11/06/2015)

Trafik analys (2014), *"Fordon i län och kommuner - Vehicles in counties and municipalities"*, Accessed at: http://trafa.se/PageDocuments/Fordon_i_laen_och_kommuner_2013.pdf, (22/05/2015)

United Nations (2014), ''*World Urbanization Prospects, the 2014 Revision'',* Department of Economic and Social Affairs, New York

Zhang Y.; Tao S. (2008), "*Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004"*, Atmospheric Environment 43 (2008) 812-819, Elsevier

Warner L. R., Sokhi R. s., Luhana L., Boulter P. G., (2001), *"Non-exhaust particle emissions from road transport: a literature review"*, TRL Limited

Westerlund (2001), *"Metal emissions from Stockholm traffic – wear of brake linings"*, The Stockholm Environment and Health Protection Administration, Stockholm

WHO (2010), "*WHO guidelines for indoor air quality: selected pollutants"*, WHO Regional Office for Europe, Denmark

Wong P.K., Wang J. (2000), *"The accumulation of polycyclic aromatic hydrocarbons in lubricating oil over time - a comparison of supercritical fluid and liquid-liquid extraction methods"*, Environmental Pollution 112 (2001) 407-415, Elsevier

8. Appendix

Table 28: Health effects, carcinogenicity classification and biodegradation of the 16 priority PAHs

Chemical (CAS nr.)	Human health effects	Oral RfD / Inhalation RfC	Cancerogenity categorisation	Animal health effects	Source
Naphthalene (91-20-3)	Hemolytic anemia, cataracts	2E-2 mg/kg-day / 3E-3 mg/m3	Classification – C;	Hemolytic anemia, cataracts, Decreased body weight, nervous system depression, fatal developmental toxicity	http://www.epa.gov/iris/toxreviews/0436tr.pdf
Acenaphthylene (208-96-8)		No data/no data	Classification — D;	Gene mutations	http://www.epa.gov/iris/subst/0443.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Acenaphthene (83-32-9)		0.6 mg/kg/day / no data			http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls_december_2014.pdf
Fluorine (86-73-7)		0.4 mg/kg/day / no data			http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls_december_2014.pdf
Phenanthrene (85-01-8)		No data / no data	Classification — D	Chromosome aberrations, gene mutations	http://www.epa.gov/iris/subst/0459.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Anthracene (120-12-7)		0.3 mg/kg/day / No data	Classification — D	Chromosome aberrations, Sperm abnormalities, Gene mutation	http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls_december_2014.pdf http://www.epa.gov/iris/subst/0434.htm
Fluaranthene (206-44-0)		0.4 mg/kg/day / no data	Classification — D;	Nephropathy, increased liver weights, hema-tological alterations, and clinical effects	http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls_december_2014.pdf http://www.epa.gov/iris/subst/0444.htm
Pyrene (129-00-0)		3E-2 mg/kg/day / No data	Classification — D,	Kidney effects (renal tubular pathology, decreased kidney weights), gene mutation, soerm abnormalities	http://www.epa.gov/iris/subst/0445.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Benz[a]anthracene (56-55-3)	Component of mixtures that have been associated with human cancer.	No data / no data	Classification — B2;	tumours, gene mutation	http://www.epa.gov/iris/subst/0454.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Chrysene (218-01-9)		No data /no data	Classification — B2;	Carcinomas, malignant lymphoma, mutations, chromosome aberrations	http://www.epa.gov/iris/subst/0455.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Benzo[b]fluoranthene (205-99-2)		No data /no data	Classification — B2;	tumours, DNA binding	http://www.epa.gov/iris/subst/0453.htm

					http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Benzo[k]fluoranthene (207-08-9)		No data /no data	Classification — B2;	tumours, DNA binding	http://www.epa.gov/iris/subst/0452.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Benzo[a]pyrene (50-32-8)	Lung cancer has been shown to be induced in humans by various mixtures of PAHs	No data /no data	Classification — B2;	DNA damage, gene mutation, chromosome aberrations, sperm abnormalities	http://www.epa.gov/iris/subst/0136.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Dibenz[a,h]anthracene (53-70-3)		No data / no data	Classification — B2;	Chromosome aberrations	http://www.epa.gov/iris/subst/0456.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf
Benzo[ghi]perylene (191-24-2)		No data / no data	Classification — D;		http://www.epa.gov/iris/subst/0461.htm
Indeno[1,2,3-cd]pyrene (193-39-5)		No data / no data	Classification — B2;	DNA binding	http://www.epa.gov/iris/subst/0457.htm http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf

Table 29: Carcenogenicity classification

USEPA		***IARC***	
A	Human carcinogen	**Group 1**	Carcinogenic to humans
B1	Probable human carcinogen agents for which there is limited human data from epidemiologic studies	**Group 2A**	Probably carcinogenic to humans
B2	Probable human carcinogen agents for whom there is sufficient evidence from animal studies and for which there is inadequate or no evidence from human epidemiologic studies.	**Group 2B**	Possibly carcinogenic to humans
C	Possible human carcinogen	**Group 3**	Not classifiable as to its carcinogenicity to humans
D	Not classifiable as to human carcinogenicity	**Group 4**	Probably not carcinogenic to humans
E	Evidence of non-carcinogenicity for humans		

Sources: IARC, 2015; RAIS, 2013

Table 30: Concentrations of 16 PAHs in bituminous binders and a tyre rubber (Lindgren Å., 1998)

Table 4.1 Content of PAH (µg/g) in bituminous binders and a tyre rubber.

PAH	Bituminous binder			Tyre rubber		
	B 85	B 180	MB 10 000	1	2	3
Naphthalene*	1.2	10	1.9	<0.5	<0.4	<2
Acenaphthylene*	<0.3	<0.3	< 0.3	<0.6	<0.2	<3
Acenaphthene*	0.18	0.43	0.19	<0.1	<0.5	<2
Fluorene*	0.44	0.70	0.53	<0.9	<0.4	<0.2
Phenanthrene	2.9	3.8	3.8	11	2.9	<9
Anthracene	0.82	1.5	1.9	2.3	0.24	<0.7
Fluoranthene	<4	<5	< 11	16	8.3	4.7
Pyrene	2.9	4.9	7.2	54	31	27
Benzo(a)anthracene	<7	<9	22	<6	<0.6	<0.9
Chrysene	7.7	10	< 12	<7	<0.3	<0.2
Benzo(b)fluoranthene	3.0	4.8	7.8	3.5	1.5	0.73
Benzo(k)fluoranthene	0.76	0.94	1.2	0.86	0.43	0.32
Benzo(a)pyrene	5.0	6.0	8.0	4.0	<0.5	<0.4
Dibenzo(ah)anthracene	<6	<3	<9	<6	<0.5	<0.3
Benzo(ghi)perylene	<8	7.6	<12	< 16	<3	<2
Indeno(123cd) pyrene	1.1	0.94	1.1	1.6	<3	<1
Sum (16 PAH) µg/g	26	52	56	93	44	33

* Substances consisting of less than 3 benzene rings.

Table 31: PAHs and POPs bulk emission factors (Ntziachristos, Samaras, 2013)[9]

Species	Bulk emission factors (µg/km)					
	Gasoline, E85, CNG PC & LCV		Diesel PC &LCV		HDV	LPG
	Convent.	Euro I & on	DI	IDI	DI	
indeno(1,2,3-cd)pyrene	1.03	0.39	0.70	2.54	1.40	0.01
benzo(k)fluoranthene	0.30	0.26	0.19	2.87	6.09	0.01
benzo(b)fluoranthene	0.88	0.36	0.60	3.30	5.45	
benzo(ghi)perylene	2.90	0.56	0.95	6.00	0.77	0.02
fluoranthene	18.22	2.80	18.00	38.32	21.39	1.36
benzo(a)pyrene	0.48	0.32	0.63	2.85	0.90	0.01
pyrene	5.78	1.80	12.30	38.96	31.59	1.06
perylene	0.11	0.11	0.47	0.41	0.20	
anthanthrene	0.07	0.01	0.07	0.17		
benzo(b)fluorene	4.08	0.42	24.00	5.21	10.58	0.71
benzo(e)pyrene	0.12	0.27	4.75	8.65	2.04	
triphenylene	7.18	0.36	11.80	5.25	0.96	0.48
benzo(j)fluoranthene	2.85	0.06	0.32	0.16	13.07	
dibenzo(a,j)anthacene	0.28	0.05	0.11	0.12		
dibenzo(a,l)pyrene	0.23	0.01		0.12		
3,6-dimethyl-phenanthrene	4.37	0.09	4.85	1.25		0.18
benzo(a)anthracene	0.84	0.43	3.30	2.71	2.39	0.05
acenaphthylene			25.92	25.92		
acenapthene			34.65	34.65		
fluorene					39.99	
chrysene	0.43	0.53	2.40	7.53	16.24	
phenanthrene	61.72	4.68	85.50	27.63	23.00	4.91
napthalene	11.20	610.19	2100	650.5	56.66	40.28
anthracene	7.66	0.80	3.40	1.37	8.65	0.38
coronene	0.90	0.05	0.06	0.05	0.15	
dibenzo(ah)anthracene	0.01	0.03	0.24	0.56	0.34	

[9] PC: passenger cars LCV: light commercial vehicles (< 3.5 t) HDV: heavy-duty vehicles (> 3.5 t)
LPG: liquefied petroleum gas CNG: compressed natural gas
E85: An ethanol fuel blend of up to 85 % denatured ethanol fuel and gasoline by volume

Table 32: Total amount of 16PAHs from tyres, road material and brake linings (g/year)

	Tyres				Road material		Brake linings	
	Passenger cars (mg/vkm)		HDV (mg/vkm)					
	Min	Max	Min	Max	min	max	min	max
naphthalene	0.55	153.35	0.68	28.40	0.6	12.6	0	0
acenaphthylene	0	0	0	0	0.1	0.4	0	0
acenaphthalene	0.5	318.1	0.0	1.9	0.1	0.5	0	0
fluorene	0.1	22.7	0.7	27.8	0.2	0.9	0	0
phenanthrene	5.7	312.4	0.3	14.5	1.4	4.8	1.3	12.9
anthracene	1.0	113.6	0.0	0.6	0.4	2.4	0	0
fluoranthene	1.9	533.9	0.6	97.2	1.9	13.9	1.0	9.1
pyrene	4.5	1374.5	0.5	209.5	1.4	9.1	1.5	14.6
benzo[a]anthracene	1.1	482.8	0.1	5.7	3.3	27.8	2.1	19.9
chrysene	3.0	2913.6	0.3	33.5	3.6	15.1	2.4	22.5
benzo[b]fluoranthene	3.3	363.5	1.0	40.4	1.4	9.8	0.6	5.6
benzo[k]fluoranthene	0	0	0	0	0.4	1.5	0.9	8.2
benzo[a]pyrene	1.8	170.4	0.1	16.4	2.4	10.1	1.0	9.8
dibenz[a,h]anthracene	0.1	68.2	0.0	5.0	1.4	11.4	0	0
benzo[g,h,i]perylene	0.7	732.7	0.4	46.1	3.6	15.1	3.6	34.5
indeno[1,2,3-cd]pyrene	0.1	130.6	0.1	6.3	0.4	1.4	0	0

Table 33: Total amount of 16PAHs from exhaust gases and motor lubricant oil (g/year)

	Exhaust gases						
	Gasoline		Diesel		HDV	Lubricant oil	
	min	max	min	max		min	max
naphthalene	1049.6	57165.6	23071.5	74538.7	893.9	0	131.4
acenaphthylene	0.0	0.0	920.0	920.0	0.0	0	7.6
acenaphthalene	0.0	0.0	0.0	0.0	0.0	0	29.8
fluorene	0.0	0.0	0.0	0.0	630.9	0	132.8
phenanthrene	438.6	5782.2	980.7	3034.8	362.9	0	543.2
anthracene	75.0	749.7	48.6	120.7	136.5	0	151.5
fluoranthene	262.4	1686.9	638.9	1360.2	337.5	0	126.8
pyrene	168.7	562.3	436.6	1382.9	498.4	0	151.1
benzo[a]anthracene	40.3	78.7	96.2	117.1	37.7	0	101.3
chrysene	40.3	49.7	85.2	267.3	256.2	0.9	42.3
benzo[b]fluoranthene	33.7	82.5	21.3	117.1	86.0	1.4	75.1
benzo[k]fluoranthene	24.4	28.1	6.7	101.9	96.1	1.7	42.3
benzo[a]pyrene	30.0	45.0	22.4	101.2	14.2	0	227.3
dibenz[a,h]anthracene	0.9	2.8	8.5	19.9	5.4	0	14.2
benzo[g,h,i]perylene	52.5	271.8	33.7	213.0	12.1	0	160.5
indeno[1,2,3-cd]pyrene	36.5	96.5	24.8	90.2	22.1	0	155.1

Table 34: Total amount of 16PAHs all sources (g/year)

	Total	
	min	max
naphthalene	25016.8	132924.0
acenaphthylene	920.2	928.0
acenaphthalene	0.7	350.3
fluorene	631.9	815.1
phenanthrene	1791.0	10067.6
anthracene	261.4	1274.9
fluoranthene	1244.1	4165.4
pyrene	1111.6	4202.4
benzo[a]anthracene	180.8	870.9
chrysene	392.0	3600.2
benzo[b]fluoranthene	148.7	780.0
benzo[k]fluoranthene	130.1	278.1
benzo[a]pyrene	71.8	594.4
dibenz[a,h]anthracene	16.4	126.8
benzo[g,h,i]perylene	106.6	1485.7
indeno[1,2,3-cd]pyrene	84.1	502.2

Table 35: PAH and oxy-PAH sediment samples lab results

PAHs		Chamber 7	Chamber 1	Chamber 3	Chamber 5
naftalen	mg/kg TS	0.21	0.15	0.37	0.27
acenaftylen	mg/kg TS	0.14	<0.1	0.2	0.14
acenaften	mg/kg TS	<0.1	<0.1	<0.1	<0.1
fluoren	mg/kg TS	<0.1	<0.1	0.17	0.15
fenantren	mg/kg TS	0.74	0.33	0.97	0.87
antracen	mg/kg TS	0.17	<0.1	0.25	0.17
fluoranten	mg/kg TS	1.1	0.44	1.5	1.3
pyren	mg/kg TS	1.8	0.69	2.3	2
bens(a)antracen	mg/kg TS	0.38	0.11	0.47	0.38
krysen	mg/kg TS	0.45	0.2	0.6	0.51
bens(b)fluoranten	mg/kg TS	0.7	0.26	0.88	0.62
bens(k)fluoranten	mg/kg TS	0.15	<0.08	0.25	0.17
bens(a)pyren	mg/kg TS	0.39	0.14	0.48	0.36
dibens(ah)antracen	mg/kg TS	0.11	<0.08	<0.08	0.12
benso(ghi)perylen	mg/kg TS	0.72	0.31	0.82	0.75
indeno(123cd)pyren	mg/kg TS	0.28	<0.08	0.4	0.28
Oxy-PAH					
9-fluorenon	mg/kg TS	0.14	<0.1	0.13	0.14
9,10-antrakinon	mg/kg TS	0.24	<0.1	0.19	0.12
2-metylantracen-9,10-dion	mg/kg TS	0.19	<0.1	0.13	0.14
7H-bens(de)antracen-7-on	mg/kg TS	0.12	<0.1	0.12	0.12
bens(a)antracen-7,12-dion	mg/kg TS	0.32	<0.1	0.11	0.34
6H-bens(cd)pyren-6-on	mg/kg TS	0.11	<0.1	0.1	<0.1
bens(a)fluorenon	mg/kg TS	<0.1	<0.1	0.12	0.12
4H-cyklopenta(def)fenantrenon	mg/kg TS	<0.1	<0.1	<0.1	<0.1
naftacen-5,12-dion	mg/kg TS	<0.1	<0.1	0.13	<0.1