KAUNAS UNIVERSITY OF TECHNOLOGY

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POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN AIRSHED: FROM EMISSIONS TO LIVING ENVIRONMENT

Doctoral dissertation
Physical sciences, Chemistry (03P)

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

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Daktaro disertacija
Fiziniai mokslai, Chemija (03P)

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LIST OF ABREVIATIONS

BaP – Benzo[*a*]pyrene

CarPAHs – carcinogenic polycyclic aromatic hydrocarbons

CPAHs – Combustion polycyclic aromatic hydrocarbons

EI – Electron ionization

ELPI – Electrical low pressure impactor

GC/MS – Gas chromathography with mass spectroscopy

HMW – High molecule weight

HRGC/LRMS – High/Low resolution gas chromathography

IAQ – Indoor air quality

LDT – Long-distance transport

LMW – Low molecule weight

LOD – Limit of detection

MEQ – Mutagenecity equivalency factor

MLR – Multiple Linear Regressions

MOUDI – Micro orifice uniform deposition impactor

PAH – Polycyclic aromatic hydrocarbons

PM – Particulate matter

PM_1 – Particulate matter with aerodynamic diametre 1 μm

PSD – Particle size distribution

QC – Quality control

SD – Standard Deviation

SIM – Single Ion Monitoring

SPMD – Semipermeable Membrane Device

TEQ – Toxic equivalency factor

TSP – total suspende particles

US EPA – United States, Environmental Protection Agency

λ – Air exces ratios

1. INTRODUCTION

1.1. Background

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 organic compounds that primarily form during the combustion of organic materials at high temperatures and oxygen-deficient environment. These compounds contain two or more fused benzene rings in a linear, angular or cluster molecular structure.

PAHs are broadly found in different environments from water, food, air. The major sources of PAHs in environment include energy production, domestic heating, waste combustion, industrial processes, vehicle emissions, forest fires, oil spils, and others. PAHs are ubiquitous because of their physical-chemical properties. In ambient air, they are partitioned between particulate and vapor phases. This duality causes problems during the evaluation of the human exposure, because of various pathways to environments where humans reside. Although widely researched, many processes for PAH formation during combustion processes and their effects of particle formations, as well as transformation in the enmvironment are still unclear.

Because of their carcinogenic, mutagenic and toxic properties, 16 PAHs have been included in priority pollutant lists by the European Commission and USA EPA (IARC 2010; European Comission 2001). The World Health Organization added 17 more PAHs to theses lists, making in total 33 compounds under regulation. Benzo[*a*]pyrene is the most investigated PAH, characterized as a highly carcinogenic compound, having the annual limit value of 1 ng/m^3 (Directive 2004/107/EC 2005).

The dissertation aim is the characterization of PAHs in urban environment throughout their entire life cycle. Several representative and little-researced processes of emissions and urban environments were investigated. From the emission perspective, selected biomass fuels and street dust deposits were researched. Ambient and indoor air of near-street and suburbian environments as well as schools and kindergartens were researched for the presence of PAHs. The results contribute to the global database on the formation, transformation, oxidation, penetration, decomposition, and exposure of PAHs.

1.2. Objectives of the dissertation

The aim of the dissertation is to research the formation and dispersion of polycyclic aromatic hydrocarbons (PAHs) in urban environment.

Goals of the dissertation:

1. To determine emissions of PAHs from the combustion of agricultural waste derived biomass fuels with respect to the composition and morphologhy of fuels.
2. To quantitatively characterize emissions of PAHs from the aerosolization of street dust.
3. To characterize variations of PAH concentrations in outdoor air of urban near-street public buildings.
4. To determine PAH concentrations in primary schools located in various urban settings.
5. To determine PAH variation in single family homes associated with wintertime solid fuel burning episodes.
6. To compare active and passive sampling techniques of PAHs by in situ measurements in urban single family home sittings.

1.3. Scientific novelty

The dissertation presents an integrated assessment of PAHs in urban environment, tracing the pathway of these pollutants from the sources of emission to human exposure. Such approach is novel and scientifically sound.

The following specific novel aspects were covered:

- Determination of PAH emissions from combustions of not-yet-investigated agriculture waste derived biomass fuels.
- The emissions of PAHs from street dust deposits were investigated for the first time.
- The characterization of PAHs in school environment is novel among very few studies in this area.
- The use of combined active and passive sapling techniques for the investigation of the influence of fuel burning emissions on indoor air quality is novel.
- Integrated research of PAHs in air of public and residential environment fill the gap of knowledge and contribute to the databases of human exposure.

2. LITERATURE REVIEW

2.1. Background

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 chemicals, composed of carbon and hydrogen atoms with a fused ring structure in linear, angular, or cluster arrangements (see **Table 2.1**). Airborne PAHs are mainly formed as a result of an incomplete combustion processes (WHO 1987; Baek et al. 1991; Mastral et al. 2000a). The most common sources of PAHs in an urban environment are the fuel combustion for heating (biomass, coal, natural gas) and the propulsion of vehicles with an internal combustion engine (gasoline, diesel, liquefied petroleum gas), as well as food cooking, candle burning, aerosolized street dust particles and long-distance transport (Callén et al. 2008; Mostert et al. 2010; Cvacka et al. 1998; Wu et al. 2006; Zimmermann et al. 1999). PAHs are broadly distributed in every air-based environment, even in the cleanest one (Vestenius et al. 2011), and were proved to be cancer-causing air pollutants (Ravindra et al. 2008). Because of their carcinogenic, mutagenic and toxic properties 16 PAHs are included in European Commission and USA EPA priority pollutant list (see **Table 2.1**) (IARC 2010; European Comission 2001). The World Health Organization 17 more PAHs to this list, making in total 33 compunds under regulation. Benzo[*a*]pyrene is the most investigated PAH, characterized as highly carcinogenic compound. It should be noted that European annual limit value for benzo[*a*]pyrene in PM_{10} fraction is 1 ng/m^3 (Directive 2004/107/EC 2005). This compound is targeted because of its highest toxicity load in airborne particulate PAH. Some of the most early attemts to assess of cancer risk were performed with fourty nine PAHs (IARC 1984). The human exposure to PAHs mostly occurs via complex mixtures of individual PAHs. The Toxic Equivalency Factor (TEF) is indroduced to estimate carcinogenic effect of complex PAHs mixtures (USEPA 2005; WHO 2000).

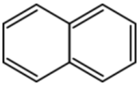
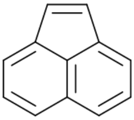
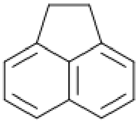
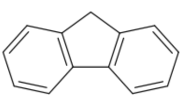
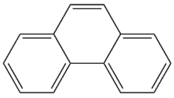
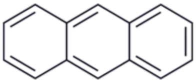
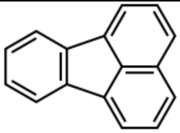
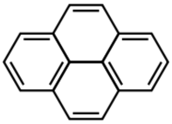
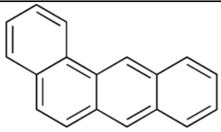
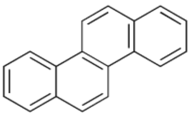
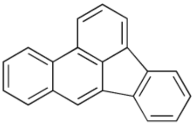
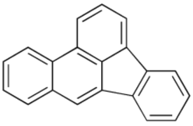
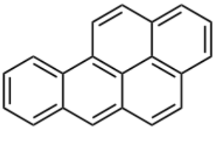
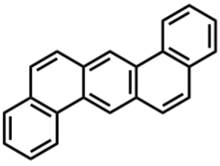
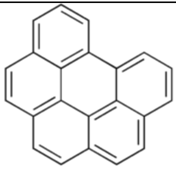
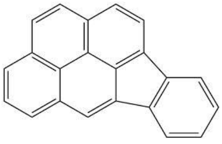
2.2. Properties and chemistry of PAHs

PAHs are thermaly stable compaunds. Because of a high melting temperature, low vapor presure (10^{1}-10^{-10} Pa) PAHs are partited between particulate and vapor phase. This partition depends on many factors such as temperature, pressure, humidity etc.In ambient air, most of the low molecule mass and high vapor pressure (2-3 rings) PAHs are present in the vapor phase. On the contrary, 4-ring PAHs having low vapor pressure commonly are present in the particulate phase. The phase distribution comprehensively depends on environmental conditions. During summertime more PAHs get transferred to the vapor phase. In winter, the reverse processes were observed (Zhu et al. 2009). Volatility of PAHs depens on molecule mass and number of aromatic rings. Naphthalene mostly is present in vapour phase, while benzo[*a*]pyrene exists in particulate phase. Most of the particulate phase PAHs are found in aerosol particles smaller than 1 μm in diametre (Chen et al. 1997). Typical partitioning of vapor and particle PAHS in ambient air is presented in **Figure 2.1** Main properties of most researched PAHs are tabulated in **Table 2.2.**

The association of fine particles with mutagenic and carcinogenic compounds such as polycyclic aromatic hydrocarbons may contribute to acute health effects and potentially result in long-term health risks (Faaij 2006). PAHs are products of incomplete combustion and are often generated through open burning, incineration, industrial power generation, and vehicle emissions. Among other pollution sources surface depositions on roads/highways contain many toxic micropollutants such as heavy metals and PAHs (Loo 2008; Cardellichio et al. 2010). Typical outdoor concentrations of benzo[*a*]pyrene as reported in Duisburg, Amsterdam and Helsinki range 0.1-1 ng/m^3 (Sikanen et al. 2008). However, notably higher benzo[*a*]pyrene outdoor concentration has been reported in Prague and Zagreb (3.0 ng/m^3 and 3.2 ng/m^3, respectively) (Sikanen et al. 2008; Williams et al. 2012).

PAHs with varying properties and origins may be adsorbed on particulate matter, and increasing attention has been paid to the profiles in environmental samples (Faaij 2006; Williams et al. 2012; Szidat et al. 2007; Bari et al. 2010; Liu and Nazaroff 2010; Boman et al. 2003). In fact, it has been well-documented that indoor PAH concentrations are influenced by both indoor and outdoor sources (Launhardt et al. 1998; Chandrasekaran et al. 2013). Moreover, because of chemical reactions in atmosphere that involve PAHs, N_yO_x, and O_3, significant amounts of various nitrated, amino and hydroxylated PAHs are produced.

Table 2.1. Chemical structures of the 16 PAHs indicated as the most harmful to human health

			
Naphthalene	Acenaphthylene	Acenaphthene	Fluorene
			
Phenanthrene	Anthracene	Fluoranthene	Pyrene
			
Benz[*a*]anthracene	Chrysene	Benzo[*b*]fluoranthene	Benzo[*k*]flouranthene
			
Benzo[*a*]pyrene	Dibenz[*a,h*]anthracene	Benzo[*g,h,i*]perylene	Indeno[*1,2,3-c,d*]pyrene

Most of PAHs have hydrophobic properties and low solubility in water. At the same time they have lipophilic properties and tend to accumulate in fats and dissolve in organic solvents.

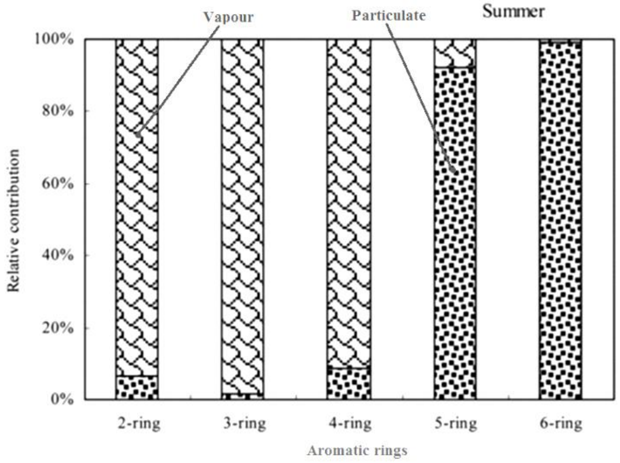


Figure 2.1. Typical PAH vapor and particle partition in ambient air (Zhou et al. 2012)

Table 2.2. Properties of main PAHs

Compound	Number of aromatic rings	MW, g/mol	MP, C	BP, ºC	VP, Pa	S, g/m	*Log* K_{ow}	*Log* K_{oc}
Naphthalene	2	128	81	218	8.64	31	3.37	3.11
Acenaphthene	3	152	96	278	0.161	38	3.92	3.79
Acenaphthylene	3	154	92	265	0.893	16	4	3.83
Fluorene	3	166	116	295	0.0425	1.9	4.18	4.15
Anthracene	3	178	216	340	0.00102	0.045	4.54	4.41
Phenantrene	3	178	101	339	0.881	1.1	4.57	4.22
Fluoranthene	4	202	111	375	0.000707	0.26	5.22	4.74
Pyrene	4	202	156	360	0.000335	0.13	5.18	4.82
Benz[*a*]anthracene	4	228	160	435	2.66E-05	0.011	5.91	5.66
Chrysene	4	228	255	448	0.19		1.65	5.37
Benzo[*b*]fluotanthene	5	252	168	481	6.67E-05	0.0015	5.8	5.89
Benzo[*k*]fluoranthene	5	252	217	481	0.000067	0.0008	6	5.89
Benzo[*a*]pyrene	5	252	175	495	ND	0.0038	6.04	5.71
Benzo[*e*]pyrene	5	252	178		ND	0.004		
Indeno[*1,2,3*-*c,d*]pyrene	6	276	164	536	1.33E-07	0.00019	6.58	6.14
Benzo[g,h,i]perylene	6	276	277		1.33E-08	0.00026	6.5	
Dibenz[a,h]anthracene	5	278	267	524	1.33E-07	0.0006	6.75	5.97
Coronene	7	300	>350	525	2,0*10-10	0.00014	6.75	

MW – molecular Weight; MP – melting point; BP – boiling point; VP – vapour pressure; S – solubility in water; K_{OW} – Octanol-water partitioning coefficient; K_{OC} – soil organic carbon-water partitioning coefficient.

Formation of PAHs. The main process of PAH formation is the combustion process in oxygene deficient conditions which occur in various combustion devices. The formation mechanism during combustion process is not fully clear. Harvey (1991) concluded that PAHs form from free radicals of organic molecules in gaseous phase. At the same time, many researchers suggest that most of airborne particulate PAHs condense from vapor phase. This transformation takes place between formation phase in the source and entering to environment. Skjot-Rasmussen (2004) confirmed this teory by performing an experiment with pure methane combustion under anaerobic conditions. This theory was based on a principle of the lowest energy-free radicals are bound to aromatic structures and form stable organic compaunds. According to Ravindra et al. (2008) pyrolysis and pyrosythesis are two main mechanisms that explain formations of PAHs. When the temperature of environment exceeds 500 °C, carbon-hydrogen and carbon carbon bounds are broken, forming free organic radicals. These free radicals form acetylene, which further condenses and forms aromatic rings (**Figure 2.2**).

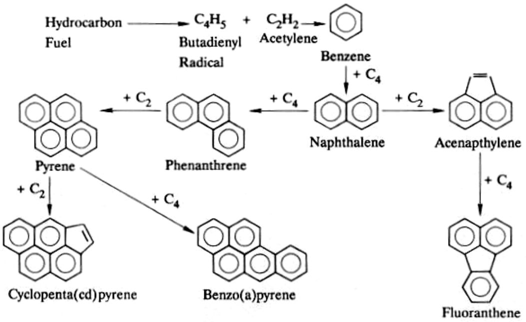


Figure 2.2. Pyrosynthesis, the proposed pathway for PAH formation (Ravindra et al. 2008)

Bartok (1991) proposed three possible mechanisms for formation of PAH during combustion: slow Deils-Alder condensation; fast reaction of free radicals; reaction of ions. The optimal temperature of PAH formation during combustion process is about 800 °C, depending on combustion coditions. The optimal formation temperature was also studied by Mastral et al. (1996).

PAHs play a very important role in the formation of combustions particles. Similarly to molecular PAHs, the formation mechanism of soot or aerosol particles during the combustions is not yet finaly discovered. In general, the involvement of PAHs in the formation of aerosol particles may be broken down to several mechanisms (Bockhorn et al. 2009):

a) Formation of molecular precursors of soot;
b) Nucleation or inception of particles from heavy PAH molecules;
c) Mass growth of particles by addition of gas phase molecules;
d) Coagulation via reactive particle–particle collisions;
e) Carbonization of particulate material;

f) Oxidation of PAHs.

Proposed pathway of the aerosol particle formation, in a fuel rich flame, is presented in **Figure 2.3**.

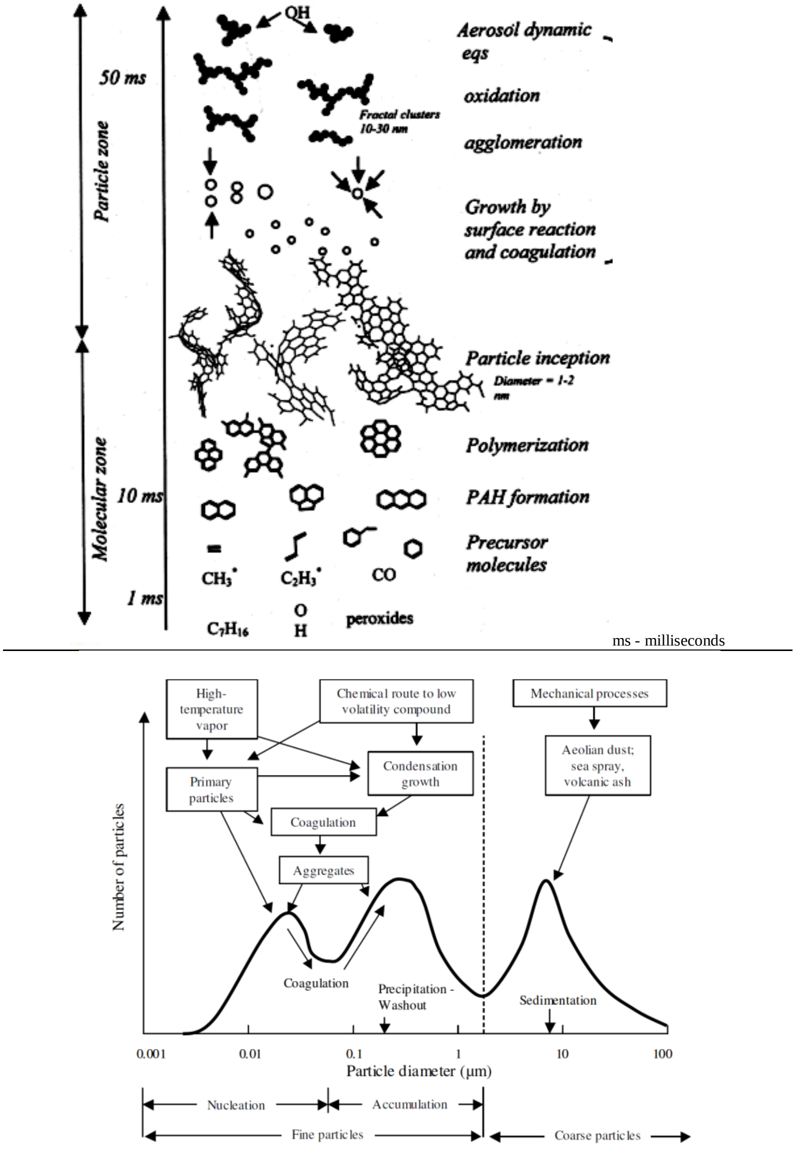
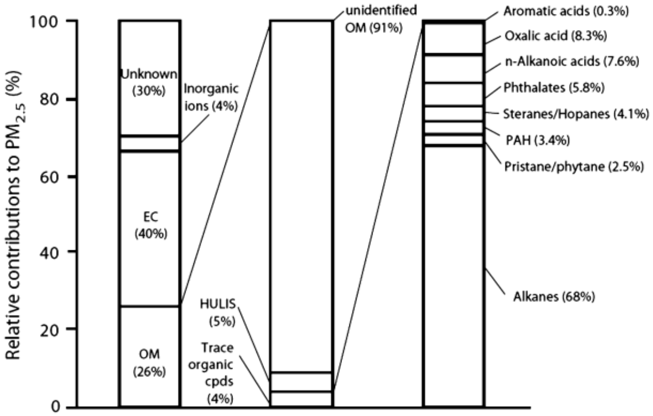


Figure 2.3. Pathway of organic aerosol particle formation (Great Britain 2001; Mansurov 2005)

An example composition of a $PM_{2.5}$ aerosol particle is presented in **Figure 2.4** (Haddad et al. 2009). The total mass of identified PAHs contributes only about 3 % of total mass of $PM_{2.5}$ aerosol particles, yet 91 % of the total organic matter was not identified, implicating an extremely large bouquet of chemical substances present in particles.



EC – elental carbon, OM – organic matter

Figure 2.4. Typical $PM_{2.5}$ composition in urban air

2.3. Sources of PAHs

Main antropogenic sources of PAHs in environment may be classifed into two groups: pyrogenic and petrogenic. Pyrogenic sources can be characterized as combustion and pyrolysis processes, including various combustion, food preparation, thermal industrial processes etc. Petrogenic sources mainly include spills of oil products that contain PAHs and evaporation of PAHs from materials such as petroleum products, tars, and asphalt. Emissions of benzo[*a*]pyrene from various sources are presented in **Table 2.3** (Liu et al. 2007; Liu et al. 2006; Chang et al. 2006).

Table 2.3. Emissions of benzo[*a*]pyrene from various sources

Emission source	Concentrations of benzo[*a*]pyrene			
	In surrounding air, µg/m^3	In emissions, µg/m^3	Particulate concentration in emissions, µg/kg	In ash, µg/kg
Energy production (coal; oil products) 50 MW	0.005-0.150	0.2-8	0.1-0.3	1.4
Energy production (coal; oil products) 5 - 50 MW	0.6-50	4-250	3-50	-
Energy production (coal; oil products) up to 5 MW	1-10000	0.1-6000	1.2-9	3100
Heavy fuel oil	0.1-1	1-6	5-103	-
Pottery kilns	0.05-50	2-80	1-200	1-2
Asphalt production	20-300	80- 1100	2-30	2-3
Oil refinery	0-15	0- 40	-	-
Transport vehicles: Petrol	0.09-0.23	-	-	-
Transport vehicles:Diesel	0.20-0.70	-	4-10	-

Benzo[*a*]pyrene is often reffered to as an indicator of PAH compound group, because of it strong relationship to other PAHs (Khalili et al. 1995). Other PAHs have also been attributed to specific sources (**Table 2.4**) (Ravindra et al. 2008; Chang et al. 2006).

Table 2.4. Source specific airborne PAHs

Source of PAHs	PAHs
Combustion of coal	Fluorantene, fluorene, pyrene
Cooking	Antracene, phenantrene, benzo[*a*]pirene
Waste inceneretion	Pyrene, phenantrene, fluorene
Wood combustion	Retene, benzo[*a*]pirene, fluorantene
Fuel vehicle	Fluorene, benzo[*a*]pirene, benzo[*b*]fluorantene
Diesel vehicle	Fluorene, benzo[*a*]pirene, benzo[*b*]fluorantene, benzo[*k*]fluorantene

Sources and emissions. The half-lives of PAHs are long enough for these pollutants to be transported from the sources to living and working environments (Fromme et al. 2004). The fuel burning in residential heating boilers, emissions from vehicles and weather conditions unfavorable for pollution dispersion cause the increase of PAH concentration several times during cold seasons in Nordic countries (Ravindra et al. 2008; Bari et al. 2009). The penetration of particulate and vapor phase PAHs into buildings through windows, doors, cracks and ventilation system is a significant source of indoor PAHs (Shi and Zhao 2012; Chen et al. 2012). The sources of PAHs may also be indoors (Fromme et al. 2004; Orecchio 2011).

Possible indoor sources of PAHs at schools are food cooking (Shen et al. 2012), domestic heating (fuel burning) (Bari et al. 2009), and burning of candles (Orecchio 2011).

Sabin et al. (2004) investigated exposure of children to PAHs during trips in school buses. Fan et al. (2012) determined PAH concentrations in urine of children from elementary schools. Exposure of children to particulate matter, volatile organic compounds as well as various organic and inorganic substances were studied by Almeida et al. (2011). Despite of the fact that levels of most of the air pollutants at schools are regulated, there is lack of complex studies on indoor and outdoor PAHs in schools, which in turn may lead to reviewing of air quality standards and support recommendations for air quality improvement.

Children are one of the most sensitive groups of the society in respect to the ambient air quality (Fiala et al. 2001). Pupils of primary schools daily spend from 4 to 6 hours in premises of a schoolhouse.

Emissions from energy production. Europe is turning its energy production towards the renewable energy (Faaij 2006). Biomass is considered as one of the most important and promising fuels worldwide, mostly due to its renewability and nearly neutral balance of CO_2 emissions (Cardellichio 2010; Loo 2008). Because of the increased consumption, fuel producers introduce various types of new biomass fuels (Sikanen 2008). At the same time, numerous studies have shown emissions of various gas-phase and particle phase pollutants such as fine and coarse particulate matter, polycyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, xylenes, dioxins, and furans during combustion of biomass fuels (Williams et al. 2012). Up to 80% of total PM emission during winter in Europe is carbonatious and mostly comes from combustion of biomass for heating purposes (Szidat et al. 2007).

Emissions from the biomass combustion and its effect to the human health are comparable to emissions from the combustion of the fossil fuel (Zhang and Smith 2007). These emissions have a critical effect on a quality of the ambient air and at the same time can penetrate indoors (**section 4.2.1**; Liu and Nazaroff 2001) in settlements, using biomass as a primary fuel for energy production (Bari et al. 2010). Presumably, the decreased quality of the ambient air later corresponds to the increased cases of adverse health effects to human beings (Boman et al. 2003). The production of the biomass fuel will continue growing, thus the pollution arising during the combustion process, must be assessed and managed.

The processes of the formation of pollutants during the biomass combustion have been well researched. The type of biomass, characteristics of a burner and combustion conditions have a major effect on the formation of pollutants (Chandrasekaran et al. 2013; Launhardt et al. 1998). Some researchers found that emissions from the combustion of biomass fuels were higher than emissions from the combustion of coal (Ross et al. 2002). Concentrations of PAHs and PCBs may increase several times due to the inefficient combustion (Atkins et al. 2010). Whilst the latter is aimed to be controlled by the constant tuning of combustion devices, new biomass/fuel products constantly appear in the market and their fuel-like properties are not well researched. These fuels have a different morphology (logs/pellets/chips/grains), composition (various wood or other biomass species), elemental composition, moisture, ash content, and calorific value. Achieving optimal conditions of combustion with such unknown/new type of biomass fuel sometimes is a difficult task. Not all burners on the market are capable in efficiently burning of these new types of fuel, because some of them are characterized by high ash, chlorine, sulfur, nitrogen, or moisture content which leads to an inefficient combustion and high emissions.

This issue gained substantial attention by researchers worldwide. For example, Sippula et al. investigated emissions from the combustion of Finnish wood species (birch, spruce, pine, alder, and willow) in a small scale burner, as well as emissions of mixtures of heavy fuel oil and wood. (Sippula et al. 2007) Several reports were published on the emissions from Portuguese wood combustion and residues of agriculture (Alves et al. 2011; Fernandes et al. 2011; Gonçalves et al. 2010; Launhardt et al. 1998).

Secondary PAH sources. Urban motor traffic has been associated with many adverse effects on both human health and the environment. Ambient pollution is generated from direct vehicle exhaust (Maricq 2007), the evaporation of vehicle fuel (Duffy et al. 1999), brake and tire wear, abrasion of the road surface and the re-suspension of dust that has accumulated on streets (Thorpe and Harrison 2008). The resulted pollutants include gas-phase compounds and particulate matter. During the process of dispersion, the pollutants undergo physical and chemical changes and may settle in the immediate vicinity of the street, or be transported long distances. Particulate matter is known as the most complex pollutant generated by motor vehicles. Primary particulates consist mainly of exhaust particles containing multiple organic compounds generated by the incomplete combustion of fuels, including polycyclic aromatic hydrocarbons. These emissions, from engines operated on both conventional fuels (Marr et al. 1999; Zielinska et al. 2004; Lin et al. 2006; Yang et al. 2008) and other fuels, e.g. biodiesel (Chien et al. 2009; Krahl et al. 2009; Kalam et al. 2008), have been extensively investigated. Interest (and concern) has been heightened by recent studies showing that PAHs particularly may be associated with particle-related health disorders (Bekki et al. 2009; Ramgolam et al. 2009). Hence, PAH concentrations have been widely monitored in ambient outdoor air (Simcik et al. 1999; Saarnio et al. 2008) and indoor air (Fischer et al. 2000; Ilgen et al. 2001). In many northern countries, deposits of inert material such as sand and gravel accumulate on the streets at curbsides as a result of winter de-icing activities and use of studded vehicle tires, which increase the rate of abrasion of the road surface, and introduce additional particles into the air (Gustafsson et al. 2008; Norman and Johansson 2006). When the snow has melted and the accumulated particles dry, they may be re-suspended in the ambient air and cause limit values for PM_{10} concentrations to be exceeded.

The mechanisms of particle lift-off in wind erosion events (which are of rather similar mechanism to the processes in street dust deposits) have been well researched (Shao 2008). In general, the lift-off of soil particles is determined by the balance between aerodynamic, gravity and cohesive forces. For small particles (<20 μm), aerodynamic forces play major role at the higher air velocities, causing the dis-integration and lift-off. At lower air velocities, cohesion forces may be a strong limiting factor.

Street dust is directly exposed to vehicle exhaust emissions and thus may adsorb emitted particles and PAHs. It has been observed that street dust-bound PAHs may act as secondary air pollutants (Manoli et al. 2002, 2004; Boonyatumanond et al. 2007; Liu et al. 2007) and as surface water contaminants (Mai et al. 2003). In 1993, Rogge et al. demonstrated that, in the Los Angeles area, road dust was the third most significant source of fine organic carbon particle emissions to the urban atmosphere after direct vehicle emissions and cooking. In order to evaluate the emission of particles from street dust, the cited authors performed a simple resuspension experiment by collecting street dust, placing it in a Teflon bag, agitating it under positive pressure, separating the aerosol using a 2.0 μm cut-off cyclone, collecting on a filter and subsequently determining more than 100 organic compounds, including PAHs. In later research, PAHs have been determined mainly as constituents of street dust rather than as potentially resuspended particles, although dust has been size-fractionated before the determination of PAHs. Agarwal (2009) utilized a coarse screen of 2 mm, while Murakami et al. (2005) and Yang et al. (1999) employed screens of four stages down to 32 μm. In the latter study the smallest fraction was further subdivided using an 8-stage micro-orifice uniform deposit impactor, but the resuspension process was not described. PAHs have also been analyzed without size fractionation of street dust and soil (Pereira et al. 2006; Wang et al. 2009).

Local air pollution. The burning of solid biomass for heat energy production is one of the sources of renewable energy. The usage of biomass in the global primary energy balance is estimated to grow, bringing a commercial perspective to investors. The estimates vary broadly ranging from 4.8 Gtoe to 24 Gtoe (Williams et al. 2012). However, biomass combustion can be a major source of emissions of fine particulate matter ($PM_{2.5}$), black carbon (soot), dioxins, polycyclic aromatic hydrocarbons cause negative short and long-term health effects.

Recent studies indicate a rising concern to reduce emissions from wood-fired heating in residential areas and underline the importance of using good wood combustion technologies to improve the air quality (Piazzalunga et al. 2013; Huttunen et al. 2012; Kaivosoja et al. 2012; Meyer 2012; Goncalves et al. 2012; Bari et al. 2011; Bari et al. 2010).

The Danish Centre for Environment Research has conducted very detail studies on pollution from residential wood burning, and found that it is responsible for about 80 % of Danish PAH emissions, 70 % of $PM_{2.5}$, 60 % of black carbon, 50 % of dioxin and contributes significantly to emissions of VOCs (volatile organic compounds) and CO (ozone precursor). In comparison, all Danish power plants emit about 2 % of the total $PM_{2.5}$ emissions but produce more than 60 % of the energy (Press-Kristensen 2013).

The importance of the wood combustion to the local air quality was estimated by measuring different air pollutants and conducting chemical mass balance modelling (Hellen et al. 2008). PM_{10}, $PM_{2.5}$, PAH and VOC concentrations in the ambient air were measured in a typical Finnish residential area. The effect of wood combustion was more clearly seen for organic compounds than for fine particle mass. PAH-concentrations were often several times higher at the residential area than in the background.

Glasius and co-authors (2008) investigated the influence of the wood combustion on particle levels and composition in a village residential area. The local contribution to $PM_{2.5}$ was about 1.2 ± 0.4 mg/m^3 (95 % confidence interval), corresponding to about 10 % of $PM_{2.5}$ and reaching 2.6 ± 0.4 mg/m^3 for the evening period (16:00–23:00). Levels of particulate PAHs and monosaccharide anhydrides (levoglucosan and mannosan, MA) were higher during most evenings compared to the background site. The average concentration for PAHs was 10.9 ± 7.1 ng/m^3 and 5.9 ± 2.9 ng/m^3 and for MA 313-237 ng/m^3 and 168-89 ng/m^3 in the residential and background areas, respectively.

A study of the domestic wood burning and $PM_{2.5}$ trace elements was conducted by Molnar and co-workers (2005). The personal exposure and indoor levels showed high correlations for all species, while the personal exposure levels were usually higher than or equal to the indoor levels. The associations between personal exposure and outdoor levels were generally weak except for outdoor S and $PM_{2.5}$ levels that were both highly correlated with the personal exposure levels.

The characterisation of PM and carcinogenic PAHs in wintertime wood-fired heating in residential areas revealed that the contribution of carcinogenic PAHs was 44 % of total PAHs (Bari et al. 2011).

The impact of the domestic wood burning on indoor levels of PAHs was studied by Gustafson et al. (2008). Indoor and outdoor concentrations of 27 PAHs were measured during wintertime in homes with (n = 13) or without (n = 10) wood-burning appliances. Twenty-four hour indoor levels of anthracene, benzo[*g,h,i*]fluoranthene, cyclopenta[*c,d*]pyrene, benz[*a*]anthracene, chrysene/triphenylene, benzo[*a*]pyrene, indeno[*1,2,3-c,d*]pyrene, benzo[*g,h,i*]perylene, and coronene were significantly (about 3 to 5-fold) higher in homes with, compared with homes without, wood-burning appliances.

Personal exposure and stationary measurements indoors and at ambient site of the suspected or known carcinogenic compounds was performed in Sweden (Gustafson et al. 2007). Significantly higher indoor levels of benzene were found in the wood-burning homes (3.0 $\mu g/m^3$) compared with the reference homes (1.5 $\mu g/m^3$).

2.4. Review of analytical methods for PAH analysis

Various standardized methods have been developed for sampling and analysis of atmospheric PAH. Most of these methods are based on high volume sampling, sample preparation and analysis. EPA Method TO-13A "Determination of Polycyclic Aromatic Hydrocarbons in Ambient Air Using Gas Chromatography/Mass Spectrometry" is based on the collection of particulate phase PAHs on filters, sequentially vapor phase PAHs are collected by sorbent (XAD-2 or Polyurethane foam – PUF) using a high volume sampler (US EPA 1999). About 300 m^3 of air is necessary to be drawn through the filter and sorbent to obtain a sufficient amount of sample for the detection of PAH compounds. Soxhlet extraction following concentration in Kuderna-Danish evaporator is used. Cleaning and fractioning of sample is performed in columns filled with silica gel and anhydrous Na_2SO_4, followed by that the concentration by the nitrogen stream. Internal and external standardization are used for the quantitative and qualitative analysis. Deuterated PAHs are used as an internal standard, inserting a known amount of the compound into the sample. For external standardization, native target PAHs is used. The speciation of PAH compounds is conducted by gas chromatography with mass spectroscopy detection. An advantage of this technique is that it is capable of detecting low concentrations of PAHs in ambient air. On the other hand, this method has many disadvantages, including high solvent consumption (hexane, dichloromethane, pentane, acetone and other consumables). The method is very complex and time consuming. Other well-established and standardized methods e.g. ASTM D 6209, ISO 12884 have also been critizised for the same issues.

When sampling for PAHs, researchers have to deal with phase ubiquity. Particulate phase PAHs are usually collected on glass, quartz filters, which can be heated to remove residual organic compounds before sampling. Aerodynamic samplers of PM_{10}, $PM_{2.5}$ and PM_1 are usually used for the separation of the required aerosol particle fraction. In case of vapour phase, PAHs are collected on sorbents, such as PUF, XAD-4, XAD-2, polydimethylsiloxane, or the combinations of the above. Sampling flow rate may be in range from 4 l/min to 1.6 m^3/min depending on PAH concentration in environment (Liu et al. 2002). Low concentrations of PAHs require high volume of sampled air in order to reach detection limits.

Once PAHs are traped on a filter or in a sorbent material, they can be affected by environmental factors that may affect the final concentration. Oxidazing compounds such as ozone and NO_2, wich are drawn through the collected PAHs, react and produce oxy-PAHs and nitro-PAHs, respectively. These reactions can reduce PAH concentration up to 50 % (Schauer et al. 2003). This problem can be avoided by using denuders upstream of PAH samplers. The evaporation of particulate PAHs can overestimate vapor fraction and understimate particulate fraction because of subsequential sampling design.

Various initiatives have been conducted by multiple researchers to address sampling-related issues and optimize the analysis of samples (Song et al. 2002; Net et al. 2014; Sanchez et al. 2013; Conde et al. 2004).

Efficient extraction of target compounds from sample material is very important. Many researchers currently use different methods for sample preparation. In the first phase, a sample is treated with solvent such hexane, dichloromethane, acetone, or various mixtures of them in order to extract PAHs. In many cases volume of solvent used for extraction is reduced from 50 ml to 5 ml per sample, depending on sample size and extraction technique. The extraction of PAHs from a samle may be conducted via various methods, including liquid-liquid extraction; Soxhlet extraction; ultrasonic extraction; microwave-assisted extraction; pressured liquid extraction; solid-phase extraction and many other methods (Liu et al. 2007; Poster et al. 2006). Pressure and temperature of extraction also can be varied to accelerate the process (Sucharova et al. 2014).

Cleaning and fractioning of the sample is necessary because of their complexity. Various aliphatic and aromatic hydrocarbons are presented at the same time. Cleaning procedure helps removing unwanted components. Generally, non polar and slightly polar solvents are used. Silica gel is a preferred sorbent for purpose of separating PAHs from the sample matrix. This sorbent can be easily activated at 150 °C. Anhydrous sodium sulphate is used as a drying agent to remove moisture from the sample. Moisture must be removed if GC system is used for the identification. PAHs often elute from the cleaning column with the mixture of hexane and dichloromethane (50/50 % V/V). If necessary, the fractioning of the sample can be performed by eluting separate fractions using various solvents, such as hexane (elutes aliphatic hydrocarbons) or dichloromethane (monoaromatics). The sample cleaning and fractioning is conducted in columns filled with various materials, most popular being silica gel and aliumina.

Because of individual physico-chemical properties recovers differently samples are spiked with external deuterated or isotopically-labeled congener PAHs. Ratios of target and spiked compounds lets determined recovery coefficient and real concentration. External standardization of target native compounds is necessary to achieve a representative qualitative analysis of PAHs.

Modern analytical tools such as high resolution mass spectroscopy, various automated and enhanced sample preparations tools help reducing processing time and minimize the usage of chemicals. Analysis of an environmental PAH sample is a challenge because of complexity of a sample. GC/MS is the most common technique for PAH analysis, followed by HPLC/UV (at 256 nm wavelength) or HPLC/MS systems. The advantage of GC/MS over other techniques lies in a greater selectivity, resolution, and sensitivity. The increased sensitivity of the mass spectroscopy allowed using low volume samplers due to the reduced instrument detection limit. HPLC/MS system has an advantage over GC/MS system because it has ability to analyze less volatile and higher molecule mass compounds.

The separation of PAHs in the GC requires slightly polar stationary phase GC columns. Some of the most widely used sorbents include 5 % phenyl methylpolysiloxane or 100 % methylpolysiloxane. The injection volume of sample usually varies from 1 to 5 µl. The temperature ramp programme must be used for the proper PAH separation in the GC system. Mass scanning range for MS ranges from 35 to 500 m/z (amu).

Since the environmental concentration of PAH compounds is very low (pg/m^3 or ng/m^3 order of magnitude), the determination of the method limit of detection is very important. The LOD depends on many factors, most important of these being sensitivity and selectivity of analytical instrument, and conditions of analysis. GC/MS only detects compounds that elute from a collum and its molecular ion fragments are detected by mass spectrometer. The LOD can be calculated as three standard deviations of a blank sample response. In cases when blank sample response is to low, the determination of the LOD may become complicated.

2.5. Conclusions to the literature review

Very little information on the abundance and distribution of PAHs in Lithuania is available. Previously published studies are limited to investigations of BaP concentrations at a background station located on the Baltic sea coast and levels of 16 PAHs in the air (using passive sampling on PUF type samplers) and soil at five sites in the country (Milukaite et al. 2006). Although many researchers have evaluated interactions between street dust and PAHs, very few have addressed the potential for resuspension of PAHs from street dust. There is therefore a need to understand how resuspended PAHs are distributed between the commonly studied PM fractions (TSP, PM_{10} and $PM_{2.5}$) and how resuspension is influenced by the key variable, air (gust or wind) velocity.

The formationa and emission of pollutants during fuel combustion is of continuous research relevance. With the growing significance of biomass fuels, the characterization of new biomass fuels is criticall because in order to obtain a reliable database of their impact to the environment.

Children are some of the most susceptible groups for air quality, and schools represent environments where children spend significant amount of their daily life. Very little information about PAHs in school environment exists in literature.

Keeping in mind the evidence of the effects of local heating and transport emissions on indoor air quality, the characterization of vapor and particulate phase indoor and outdoor PAHs at schools is of great importance, since it allows estimation of the exposure of children to combustion related pollutants and prevent possible threats to children's health. Although numerous data has been published on the contribution of the combustion sources to ambient air, the data on the penetration of PAHs to indoor environment is still scarse.

3. RESEARCH METHODOLOGY

This chapter covers general analytical procedures that were commonly employed in the subsequent result chapters. Additional information on the design of experiments directly relating to certain stages of the dissertations is presented in appropriate sub-chapters, entitles as “Experimental design”

Table 3.1 summarizes the analytes researched throughout the dissertation. List of individual analytes depending on needs in different studies was diverse.

Table 3.1. List of the analytes in separate studies

The analytes	Studies					
	Study 4.1.1	Study 4.1.2	Study 4.2.1	Study 4.2.2	Study 4.2.3	Study 4.2.4
Mass of aerosol particles	+	+	+	+	+	
Particulate PAHs	+	+	+	+	+	+
Size-segragated PAHs	+				+	
Vapor PAHs	+			+	+	+
Naphthalene		+	+	+		
Acenaphthene	+	+	+	+	+	+
Acenaphthylene	+	+	+	+	+	+
Fluorene	+	+	+	+	+	+
Anthracene	+	+	+	+	+	+
Phenantrene	+	+	+	+	+	+
Fluoranthene	+	+	+	+	+	+
Pyrene	+	+	+	+	+	+
Benz[*a*]anthracene	+	+	+	+	+	+
Chrysene	+	+	+	+	+	+
Retene						
Benzo[*b*]fluotanthene	+	+	+	+	+	+
Benzo[*k*]fluoranthene	+	+	+	+	+	+
Benzo[*a*]pyrene	+	+	+	+	+	+
Benzo[*e*]pyrene	+	+	+	+	+	+
Indeno[*1,2,3-c,d*]pyrene	+	+	+	+	+	+
Benzo[*g,h,i*]perylene	+	+	+	+	+	+
Dibenz[*a,h*]anthracene	+	+	+	+	+	+
Methylated PAHs		+	+			+

3.1. Preparation and handling of substrates

General scheme of steps of analytical method are presented in **Figure 3.1**. The size-segregated particulate matter and PAHs were collected mostly on two types of substrates: aluminum foils and quartz filters. Filters were heated at 400 ^{0}C for 6 hours with the aim to remove residual organic carbon, and left to cool in the thermostat with an adjustable relative humidity (50 %) and temperature, 20 ± 1 ^{0}C for 24 h. Before and after sampling, the substrates were gravimetrically analyzed using a microbalance (MXA-5, Radwag Wagi Elektroniczne, Poland). Accuracy of microbalance was 1 µg. After the gravimetrical analysis, the substrates were stored in a freezer at -20 ^{0}C till the chemical analysis. The samples of gaseous PAHs were stored in a freezer at -20 ^{0}C till sample preparation and chemical analysis.

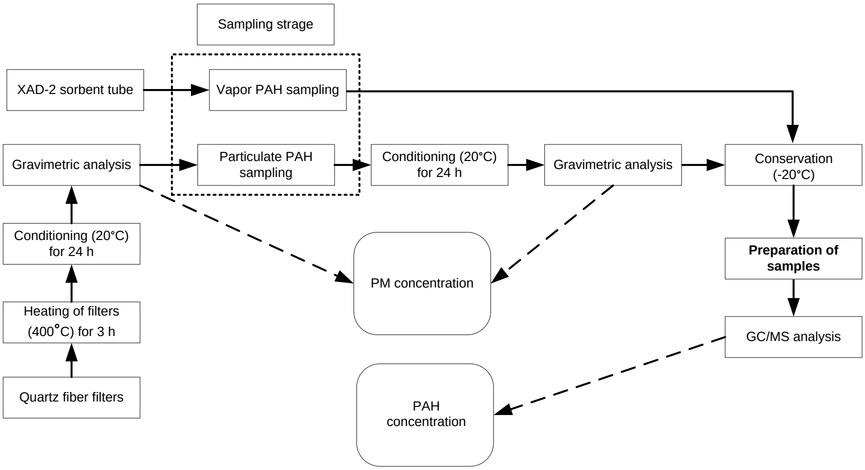


Figure 3.1. General scheme of analytical procedures

3.2. Sample extraction and preparation

Collected particle phase PAHs were extracted from filters by means of an ultrasonic extractor (Emmi-30HC, EMAG GmgH, Germany) in 10 ml of dichloromethane (GC, SigmaAldrich, USA) for 10 minutes. The extraction procedure was repeated 3 times with a final volume of the extract of 30 ml. Before the extraction an internal standard was added to the samples. Prior to the analysis a recovery estimation standard was added, and the volume of a sample was further reduced to 0.5 ml. A silica gel and anhydrous sodium sulfate was employed for the sample cleaning and moisture removal. A mixture of hexane and dichloromethane was used for the elution of samples. After a cleaning procedure, the sample was concentrated to 0.1 ml and the recovery standard was added. The prepared samples were stored in a refrigerator at 4 ^{0}C.

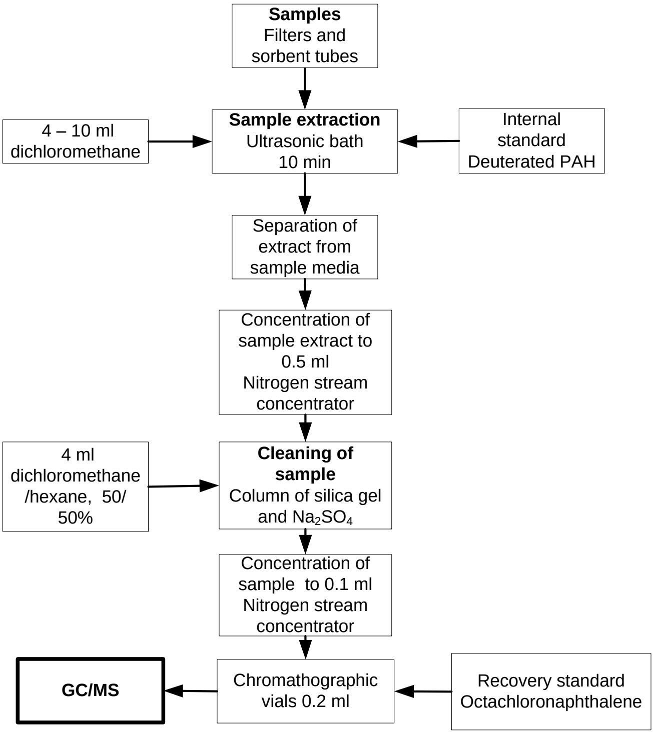


Figure 3.2. Steps of PAH samples preparation procedures

3.3. Qualitative and quantitative analysis

The GC/MS system (GCMS-QP2010 Ultra, Shimadzu, Japan) with capillary column Rxi-5ms (Restek, USA) was used for the quantitative analysis of the extracted PAHs. For studies **4.1.2** and **4.2.1** the MS instrument a 5973 model connected to a 6890N GC, both made by Agilent Technologies Inc., Santa Clara, CA, USA) was used.

The injection volume was 2 µl, splitless mode, temperature of injector 250 ^{0}C, column flow 0.58 ml. The temperature program was set to from 50 ^{0}C (3 min), 10 ^{0}C/min to 300 ^{0}C (10 min). The MS scanning was perfomed from 30 to 450 m/z.

3.4. Calculation of PAH concentration

PAH mass was calculated using the folowing equation

$$M_{ng} = \frac{A_{Samle} \cdot A_{IS,STD} \cdot M_{K,STD}}{A_{K,STD} \cdot A_{IS,Sample} \cdot M_{IS,Sample}} \text{ (ng)} \qquad \textit{Equation 1.}$$

where:

A_{Sample} – peak area of individual PAH in sample chromathogram;
$A_{IS,STD}$ – peak area of internal standard compaund in standard chromathogram;
$M_{K,STD}$ – mass of individual PAH in standard solution (ng);
$A_{K,STD}$ – peak area of individual PAH in standard chromathogram;
$A_{IS,Sample}$ – peak area of internal standard in standard chromathogram;
$M_{IS,Sample}$ – mass of internal standard compaund in standard sample.

Recovery coefficient of internal standard compaunds was calculated as follows:

$$RC = \frac{A_{RS,STD} \cdot A_{RS,Sample}}{A_{IS,STD} \cdot A_{IS,Sample}} \cdot 100\ (\%) \qquad \textit{Equation 2.}$$

where:
$A_{RS,STD}$ – peak area of recovery standard compaund in standard chromathogram;
$A_{IS,Sample}$ – peak area of internal standard compaund in sample chromathogram;
$A_{IS,STD}$ – peak area of internal standard compaund in standard chromathogram;
$A_{RS,Sample}$ – peak area of rocovery standart compaund in sample chromathogram.

PAH concentration in ambient air was calculates as follows:

$$C = \frac{M_{ng}}{FR \cdot T \cdot 0.001}\ (\mathrm{ng/m^3}) \qquad \textit{Equation 3.}$$

were:
M_{ng} – amount of individual PAH in sample;
FR – sampling flow rate (l/min);
T – duration of sampling (min).

An example chromathogram of a PAH sample is presented in **Figure 3.3**.

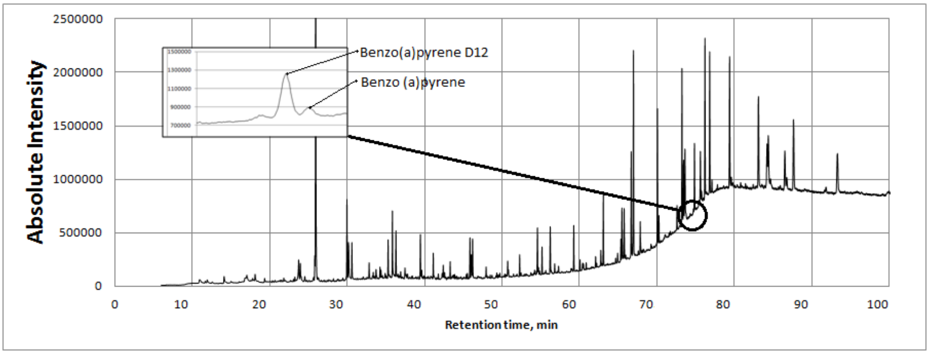


Figure 3.3. Chromatogram of PAH sample

3.5. Quality control and assurance

The sampling, the sample preparation, and the analysis were performed according to the good laboratory management practice (European Parliament Directive 87/18/EEC). The gas flowmeter was calibrated by a manufacturer and checked by the metrological center. One sampling blank sample and one laboratory blank sample were analyzed for every 10 samples. The amount of any given compound in the analyzed blank samples has not exceeded the lowest point of the calibration curve. The target PAH standard stock solution was used for the linear response measurement. The calibration curve of target PAH compounds consisted of 10, 5, 2.5, 1.25, 0.65, 0.31, 0.16 ng/µl standard solutions. Solutions of deuterated PAH compounds were used as the internal standards. A standard solution of octachloronaphtalene was used as a recovery standard for the measurement of recovery coefficients of internal standard solution compounds in real samples. The extraction procedures of PAHs were validated in a series of recovery experiments.

4. RESULTS AND DISCUSSION

4.1. Polycyclic Aromatic Hydrocarbon emissions from main sources in urban environment

4.1.1. Polycyclic Aromatic Hydrocarbons emissions from the combustion of agriculture biomass waste pellets

Detailed aim of the research

The aim of this study was to characterize emissions of size-segragated particulate and vapor phase PAHs at optimal conditions and a stable regime from the combustion of several agriculture residue derived fuels in a small scale, modern pellet burner.

Experimental design

Fuels utilized in the experiments. The following seven fuels were evaluated in the experiments: wood pellets, sunflower shell pellets, straw pellets, buckwheat shells, corn stalk pellets, wheat grain screening residues, and sewage (wastewater) sludge pellets. These agricultural residue derived fuels presented by Lithuanian agricultural/food processing and environmental companies. Due to the similarities they are representative for vast area of Central-Eastern Europe. These fuels have a high potential to be widely utilized for energy production in the small-scale and medium-scale plants.

Table 4.1. The morphology of the tested biomass fuels

			
Wood pellets Shape - Cylinder D – 6 mm; L – 10-15 mm	Sunflower stalk pellets Shape - Cylinder D – 8 mm; L – 10-20 mm	Straw pellets Shape - Cylinder D – 8 mm; L – 10-20 mm	Buckwheat shells Shape - Shell D – 5 mm; L – 4 mm
			
Corn stalk pellets Shape - Cylinder D – 6 mm; L – 10-15 mm	Wheat grain screening residues Shape - Irregular D – 1-2 mm	Sewage (wastewater) sludge pellets Shape – Irregular D – 5 mm; L – 8-10 mm	

D – Diameter; L – Length.

The municipal sewage sludge was investigated as an alternative to biomass fuels, although its application for environmental purposes must be controlled. The morphology of the fuels presented in **Table 4.1**. The characteristics (elemental composition, moisture and ash content, calorific value) of the above listed fuels are presented in **Table 4.2**. The investigation of fuel parameters was performed according to, respectively: moisture – EN 14774-1; ash content – EN 14775; calorific value – EN 14918; carbon and nitrogen content – EN 15104:2011; sulfur content – EN 15104:20; chlorine content – EN 15104:201.

The laboratory set-up for the experimental modeling of emissions from the combustion of biomass fuels is schematically presented in **Figure 4.1**. The combustion experiment was performed in a laboratory. A commercial 13 kW pellet boiler (KSM-175-13-U, UAB Kalvis, Lithuania) was adopted for the experiments. The pelletized fuel was supplied to the combustion chamber from a storage tank by a screw transporter. The removal of ash from the combustion chamber to the storage tank was organized by a mechanized rake followed by a screw transporter. Both the supply rate of fuels and the regime for the removal of ash were regulated for each tested type of fuels. The supply of air to the combustion chamber was organized by a controlled blower. The setup was entirely controlled by a user interface, including the feed of fuels and air, as well as the removal of ashes. The supply of the fuel was continuous during the entire experiment. Exhaust gases were directed to a thermally-insulated exhaust duct (a diameter of 150 mm). The water utilized for controlling the temperature of the combustion chamber was cooled in a heat exchanger. The temperatures in the combustion chamber and exhaust gases were also recorded by temperature probes. The exhaust gas velocity was monitored by an anemometer (Portable Thermal Anemometer Series 2440, Kurz Instruments Inc., USA), and the flow rate was calculated accordingly.

Combustion conditions. Before starting each experiment, the heat transfer medium (water) was preheated to 70 °C by an additional natural gas boiler. After reaching the intended temperature, the supply of fuel and air was initiated. The stable combustion regime was reached by adjusting the supply of fuels and air, and the removal of ash. The optimal combustion conditions were set by measuring the temperature and carbon monoxide (CO) concentration in the exhaust gas. The feed rates of biomass fuels were: wood pellets 1.68 kg/h; sunflower shell pellets 1.38 kg/h; straw pellets 1.58 kg/h; buckwheat shells 1.02 kg/h; corn stalk pellets 1.8 kg/h; wheat grain screening residues 1.2 kg/h; sewage sludge pellets 1.08 kg/h. The conditions of combustion (temperature of water in the boiler, flue gas temperature, and a coefficient of an excess air λ) were kept stable during the measurements. Every measurement cycle was repeated two times with the same combustion conditions. After each measurement cycle the boiler was cleaned in order to remove all residuals and particles. Ash from the combustion zone was removed by an automatic rake every 60 min. During the removal, concentrations of pollutants in the exhaust gas increased several times. This period was not taken into account of sampling and all the data was eliminated. The temperature in the boiler during optimal combustion process for all experiment was 65 ºC. Results include data from

14 measurement cycles using 7 different biomass fuels. Each measurement cycle took about 2 h.

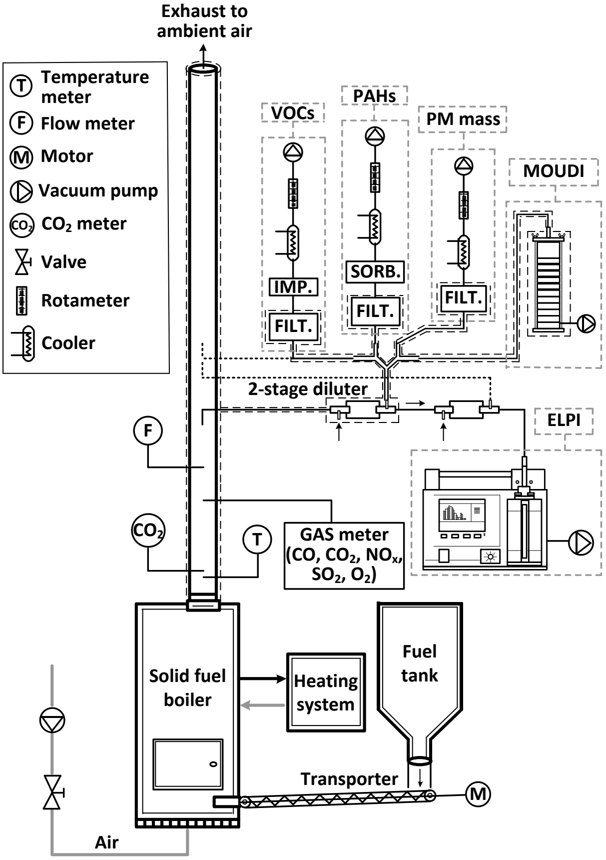


Figure 4.1. The experimental setup for testing the PAH emissions from the burning process

Sampling of pollutants. The gaseous pollutant measurement probe was installed to the exhaust duct 0.3 m above the boiler. The samples of PAHs were taken in the exhaust duct to ensure minimized turbulence. The real time size-segregated particle concentration and samples were taken using the low pressure electric impactor (ELPI+) (Dekati Inc., Finland), at a flow rate of 10 l/min. The combustion aerosol was diluted using the dilution system of two-stage heated ejector diluters (DI-1000, Dekati Inc., Finland). The dilution factor (approx. 50 times) was determined by measuring carbon dioxide (CO_2) concentration before and after the dilution. The dilution air was treated in order to remove particulate matter (PM), nitric oxides (NO_x) and hydrocarbons. Aerosol samples were collected on aluminum foil substrates (25 mm). In addition, micro orifice uniform deposition impactor

(MOUDI) 110 (MSP Corp., USA) at 30 l/min and PM_{10} (Dekati Inc., Finland) at 10 l/min impactors were utilized to collect size-segregated aerosol samples for gravimetrical and chemical analyses. The total suspended particulate matter (TSP) fraction of the aerosol was collected on quartz fiber filters (Pall Corp., USA), by using filter cassettes, at an air flow rate 2 l/min. The gaseous phase PAHs were sampled using a XAD-2 sorbent tubes (SKC Inc., USA), at an air flow rate 2 l/min.

Particulate and vapor phase PAH samples were taken at a steady state for a shorter period of time. All latter devices (except of the ELPI) were sampling from the first stage of the diluter, thus utilizing the dilution factor of 7. It must be noted that most of the particles larger than 10 μm (fly ash), were lost during the process of the ejector dilution thus our results represent only fine fraction of the aerosol.

The gaseous pollutants in the combustion emissions were described by a real time instrument IMR 2000 (IMR Environmental Equipment, Inc., Germany). The following pollutants and parameters were measured: O_2, CO, CO_2, NO_x, SO_2, temperature, and λ. The data were recorded every 5 sec and stored in a computer.

The data analysis. Results of analyses were statistically processed using SPSS 12 (IBM Corp., USA) and Origin 9 (OriginLab Corp., USA) software. Descriptive statistics were used for the representation particulate and vapor phase PAH levels. Considering a small sample of fuels (n = 7), the Spearman ranking correlation coefficient (r) was used for determination of relationship between fuel properties and emissions. Emissions levels were presented as #(particle number)/kg and g(particle mass)/kg for dry basis of fuel and were normalized to 6 % oxygen concentration. The amount of pollutant per kg of fuel was selected as a unit of measurements, because in a small scale energy production, the amount of fuel is a more tangible unit, compared to the amount of energy.

Analytical methods. Concentrations of PAHs in the solid phase were analyzed in PM_{10} samples, and in various fractions of ELPI+ and MOUDI. PM fractions of ELPI+ were grouped to the following groups: Fraction 1 (0.017-0.26 μm); Fraction 2 (0.4-1 μm); Fraction 3 (1.6-10 μm). MOUDI samples were grouped as: Fraction 1 (0.056-0.18 μm); Fraction 2 (0.32-1 μm); Fraction 3 (1.8-18 μm).

Results and discussion

The characterization of fuels. The calorific value of the tested biomass fuels ranged from 14.1 to 17.0 MJ/kg. The sewage sludge pellets had a calorific value lower than other fuels 11.9 MJ/kg, but it was sufficient for a self supported combustion. The content of moisture in the tested fuels ranged from 5.1 to 12.7 %, i.e. within the range where fuels may burn efficiently. The straw and sewage sludge pellets had the lowest calorific values (associated with a relatively high moisture content, low carbon content and relatively high ash content). Characteristics of sewage sludge were similar to these found by Pettersson et al. Sunflower stalk pellets were carrying the highest calorific value, together with wood pellets. The latter appeared to be the “cleanest” fuel with a low ash content (0.42 %), sulfur (0.011 %), and chlorine (0.005 %). Among biomass fuels, wheat grain screening residues contained the highest concentrations of N, S, and Cl. As expected, the sewage sludge was of the lowest quality as a fuel, characterized by a low calorific value (11.9 MJ/kg) and high ash content (35.20 %), almost 10 times higher compared to the biomass fuels. Properties of biomass fuels were similar to these reviewed by Vassilev et al (2010).

Table 4.2. The proximate analysis and the calorific value of the researched fuels

Biomass fuel type	C, %w/w	O, %w/w	H, %w/w	N, %w/w	S, %w/w	Cl, %w/w	Humidity content, %w/w	Ash content, %w/w	Calorific value, MJ/kg
Wood pellets	46.15	40.97	5.30	0.046	0.011	0.005	7.10	0.42	16.9
Sunflower stalk pellets	42.38	38.66	4.94	0.665	0.117	0.041	10.10	3.10	17.0
Straw pellets	39.15	36.40	5.17	0.798	0.053	0.025	12.30	6.10	14.1
Buckwheat shells	49.05	38.10	5.69	0.560	0.025	0.022	5.10	1.45	15.9
Corn stalk pellets	45.26	38.35	5.92	0.194	0.028	0.010	7.54	2.70	15.6
Grain screenings	42.07	36.21	4.37	2.450	0.155	0.056	10.90	3.80	14.8
Sewage sludge pellets	33.21	12.85	3.06	2.575	0.363	0.049	12.70	35.20	11.9

Emission factors and size distribution of PM. The emissions of size-segregated particulate matter (TSP – total suspended particles, PM_{10} – particulate matter, having and aerodynamic diameter smaller than 10 μm, $PM_{2.5}$, and PM_1), as measured during the combustion of tested biomass fuels, are presented in **Table 4.3**.

Table 4.3. The emission factors for TSP, PM_{10}, $PM_{2.5}$ and PM_1 fractions (g/kg)

PM fraction	PM emissions, g/kg						
	Wood pellets	Sunflower stalk pellets	Straw pellets	Buckwheat shells	Corn stalk pellets	Grain screenings	Sewage sludge pellets
TSP*	0.43	4.01	1.15	1.95	0.88	5.16	5.45
$>PM_{10}$ $+PM_{10}$**	0.29	3.42	0.96	1.91	0.80	4.91	5.33
PM_{10}	0.28	3.41	0.96	1.91	0.80	4.90	5.31
$PM_{2.5}$	0.28	3.41	0.95	1.90	0.80	4.87	5.23
PM_1	0.28	3.34	0.93	1.74	0.77	4.39	5.03

* Represents TSP fraction sampled by a cassette
**Represents TSP fraction sampled by the PM_{10} impactor

The PM emission factors were mostly represented by the PM_1 fraction (PM_1/TSP > 0.8 in case of all fuels), since most of particle mass was concentrated in sub-micrometer particles. These ratios are comparable to those obtained by Fernandes et al. (2011) and McDonald et al. (2000). It must be noted, that fly ash particles (> 10 μm) were not adequately included to the TSP fraction, due to losses of larger particles in the ejector diluter. More detailed analysis of the particle size distributions is presented later in this section.

The TSP emissions ranged in the order of magnitude from 0.43 g/kg (wood) to 5.45 (sludge) g/kg, PM_{10} – 0.28-5.31 g/kg, $PM_{2.5}$ – 0.28-5.23 g/kg, and PM_1 – 0.28-5.03 g/kg. The variation in PM emissions was relatively high among the fuels. In general, the tested biomass fuels may be classified into two groups. The first group (sunflower stalk pellets, grain screenings, and sewage sludge pellets) were characterized by relatively high emissions (> 2.00 g/kg) of PM in all fractions. This group of fuels was characterized by a high sulphur, chlorine, and ash content. The correlation analysis supports the relationship between PM_1 concentration and sulphur ($r = 0.89$), chlorine ($r = 0.93$) and ash content ($r = 0.71$). The second group (wood pellets, straw pellets, buckwheat shells and corn stalk pellets) were characterized by a relatively low PM emission (< 2.00 g/kg). The hydrogen and oxygen content in the fuel negatively affected PM emissions ($r = -0.82$; $r = -0.71$). These relationships were obtained during the optimal combustion conditions in our setup. However, the type of the combustion installation, combustion conditions, and the load of fuel have been shown to have a more determining effect to the formation of PM compared to fuel composition (Boman et al. 2011).

The emission factors for wood pellets were lower compared to earlier studies in a wood stove but in general, PM emissions were at comparable levels to earlier studies (Alves et al. 2011; Gnclaves et al. 2012). $PM_{2.5}$ emissions from combustion of traditional Portuguese wood briquettes in a woodstove ranged from 6.7 to 16.3 g/kg. PM_{10} emissions were comparable to those found by Conclaves et al. The sewage sludge again was characterized as the most polluting fuel, having high ash and moisture content. This fuel also contains a substantial amounts of lipids, which has been shown to contribute to the increased PM emissions, e.g., Fernandes et al. (2011) found the highest PM emission from combustion of Olive tree (among other local Portuguese biomass fuels), which also contains a high concentration of lipids. Grain screenings (5.16 g/kg) and sunflower stalk pellets (4.01 g/kg) were also emitting high quantities of TSP.

Particle size distributions (PSDs), based on the number and mass concentrations, are presented in **Figure 4.2**.The PSD based on number concentration was bimodal in case of all fuels, and reflected nucleation (0.017-0.03 μm) and accumulation (0.26-0.64 μm) modes. The latter was more pronounced in all cases. The highest emission of particles (particles number concentration) in the fraction of 0.17 to 0.26 μm occurred in cases of wood pellets ($7.1\cdot10^{15}$ #/kg), straw pellets ($2.3\cdot10^{16}$ #/kg), and wheat grain screening residues ($4.3\cdot10^{16}$ #/kg). The combustion of buckwheat shells ($3.3\cdot10^{16}$ #/kg), corn stalk pellets ($3.4\cdot10^{15}$ #/kg) and sewage sludge pellets ($4.8\cdot10^{16}$ #/kg) produced the highest concentration of slightly larger particles in the range from 0.26 to 0.40 μm. The largest concentration mode was obtained for sunflower stalk pellets ($1.9\cdot10^{16}$ #/kg), at 0.40 to 0.64 μm. The high emission of PM in case of buckwheat shells may be attributed to morphology (size and shape) of shells which led to a comparatively less efficient combustion, confirmed by higher CO emissions ($r = 0.77$). High PM emissions in case of the sewage sludge may be attributed to the high ash content, which also led to an inefficient combustion and formation of the highest CO emissions. Earlier studies on the fuel combustion processes reported various patterns of PSDs. Hays et al. found that PM size distribution was unimodal for all tested American common wood fuels, with the mode in a range from 0.3 to 0.7 µm (Hays et al. 2003). PM emissions in this mode were from 3 to 12 g/kg. The PM number PSD found by by Lamberg et al. (2011) was bimodal with modes in Aitken and accumulation modes. Sippula et al. (2007) found clearly expressed unimodal PM number size distribution. The differences in PSDs generally depend on many factors, including different combustion devices and techniques, combustion conditions, and sample conditioning. The temperature of the combustion, the flue gas residence time in the burner, the load of the fuel, the oxygen access ratio, as well as the type of fuel, composition and geometry of fuel were named as the most influencing factors (Jiang et al. 2014).

The PSD based on the mass concentration from all the fuels was unimodal, but varied in a relatively large interval from 0.18 to 1 µm. In case of wood pellets (0.302 g/kg), sunflower shell pellets (2.343 g/kg), straw pellets (0.731 g/kg), and sewage sludge pellets (4.651 g/kg), the highest concentration was reached in the interval from 0.18 µm to 0.32 µm. Corn stalk pellets (0.803 g/kg) and wheat grain screening residues (3.021 g/kg) produced slightly larger particles (0.52-0.32 µm), while buckwheat shells (2.617 g/kg) emitted largest particles (0.56-1µm). Such PSD is typical for the emission from the biomass fuel combustion. Johansson et al. found similar unimodal PSD with the highest mode in the fraction from 1 to 0.1 µm (Johansson et al. 2004). PM mass PSD found by Lamberg et al. (2011) was unimodal with the highest mode in the range from 0.9 to 0.1 µm. Large variation in PM emissions of different size fractions shows that the combustion conditions and the composition of fuel has a high influence on the formation of PM.

In earlier chapter we emphasized the importance of CO as an indicator of the efficiency of combustion conditions. The CO emissions varied in a range from 0.57 g/kg (wood pellets) to 47.2 g/kg (sewage sludge pellets), which corresponded to the concentrations in the exhaust from 94.1 to 13698.7 mg/Nm^3. Although CO concentration varied broadly, the CO/CO$_2$ stayed below < 0.1 (0.00036 to 0.054) indicating sufficient combustion conditions (Fernandes et al. 2011). The CO emission is not regulated for these small boilers by European directive, but obtained values for sunflower stalk pellets, buckwheat shells and sewage sludge pellets were relatively high. This group of fuels with highest emissions of CO is not recommended for this type of combustion equipment. In addition to operational issues, the impact to the environment is overly negative. Moreover, the emission of CO correlated with other products of incomplete combustion: benzene ($r = 0.76$), PAH ($r = 0.93$) and PM ($r = 0.77$).

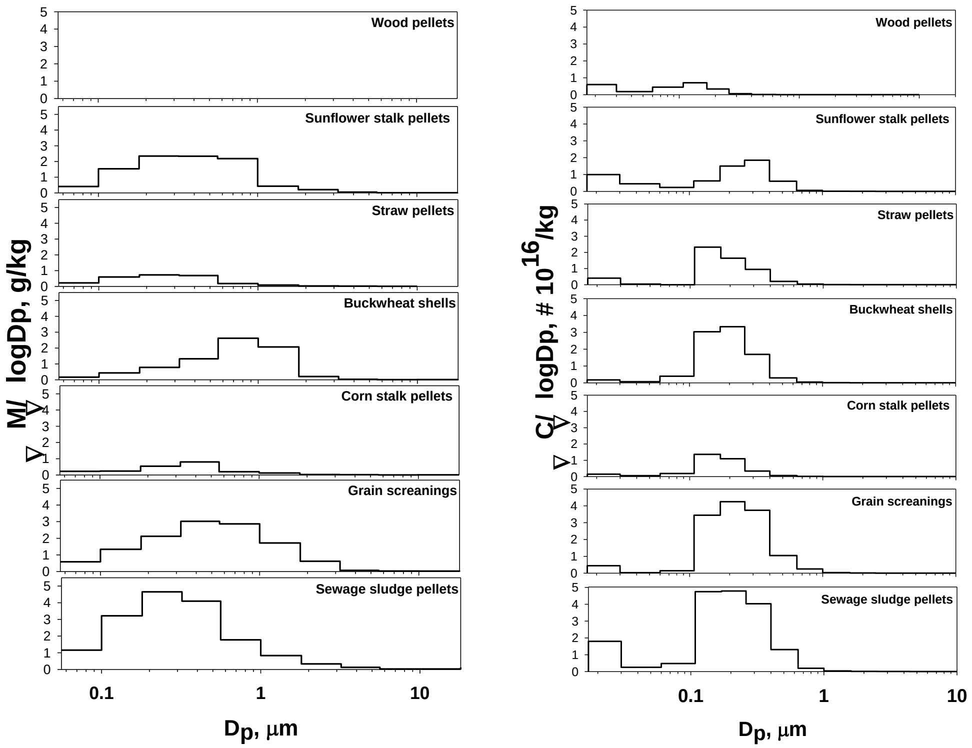


Figure 4.2. Particle size distributions based on number and mass concentrations of the combustion aerosol

Emissions of PAHs. The emissions of PAHs generally followed the PM emission pattern: the most PM emitting fuels also exhibited high PAH emissions. The emissions of size segregated particulate and vapor ∑PAH and benzo[*a*]pyrene are presented in **Table 4.4**. The most of investigated PAH emissions were in vapor phase from 68.9 to 89.1 %. Vapor phase PAHs emissions depended on combustion quality and had a strong relationship with CO (r = 0.71). The relationship between particulate phase PAHs and CO was weaker (r = 0.51), but total PAH (vapor + particulate) emissions had a very strong relationship with CO (r = 0.94). This dependence may be similar to the formation process and oxidation of organic material in the oxygen deficient environment. PM as a partial product of the inefficient combustion also had strong relationship with total emissions of PAHs (r = 0.83). Wood pellets emitted the lowest amount of PAHs (particulate ∑PAHs – 51.1 µg/kg; BaP – 5.1 µg/kg). The amount of emitted PAHs for wood pellets was lower compared to earlier studies. Keshtkar and Ashbaugh reported ∑PAH emissions from the combustion of agricultural residues in a laboratory simulated combustion chamber at a level of 18.6 mg/kg. Lee et al. (2005) determined total PAH emissions from combustion of hardwood at a level of ~ 9 mg/kg, while the combustion of coal yielded up to 25 mg/kg of ∑PAHs. Venkataraman et al. (2002) found ∑PAH emissions from the combustion of wood (*Acacia nilotica*) in a traditional Indian stove at a range from 2 to 5.5 mg/kg. Emissions from combustion of logs of Douglas-firr (*Pseudotsuga* sp.) and white oak (*Quercus* sp.) in a noncatalytic woodstove and a fireplace was in a range from 0.651 to 7.136 mg/kg of dry basis (Hays et al. 2003). It is evident that the above cited studies utilized less efficient combustion devices. In our case, we have obtained relatively high PM emissions but lower PAH emissions, indicating low soot content in the exhaust gas.

Table 4.4. Particulate size-segregated and vapor phases ∑PAH and benzo[*a*]pyrene emissions during combustion of the researched fuels, μg/kg

PM fraction, μm	Wood pellets		Sunflower stalk pellets		Straw pellets		Buckwheat shells		Corn stalk pellets		Grain screenings		Sewage sludge pellets	
	ΣPAH	BaP	ΣPAH	BaP	ΣPAH	BaP	ΣPAH	BaP	ΣPAH	BaP	ΣPAH	BaP	ΣPAH	BaP
0.056-0.18	32.1	4.1	71.4	5.4	253.3	2.6	66.6	9.8	87.7	8.5	147.8	5.8	1024.8	113.1
0.32-1	8.2	0.6	42.9	3.5	59.3	1.4	322.5	32.9	67.2	4.5	194.6	8.9	715.1	71.0
1.8-18	10.8	0.4	14.8	0.6	11.1	0.4	6.2	5.0	10.8	1.5	59.4	1.6	83.1	4.8
ΣParticulate	51.1	5.1	129.1	9.5	323.6	4.3	395.4	47.7	165.7	14.5	401.8	16.3	1823.1	189.0
ΣVapor	418.3	-	535.5	-	242.4	-	1460.0	-	366.4	-	1256.1	-	5389.6	-
Total	469.4	5.1	664.6	9.5	566.0	4.3	1855.4	47.7	532.1	14.5	1657.9	16.3	7212.7	189.0

The highest PAH emissions among tested biomass was of buckwheat shells (total PAH – 1855.4 μg/kg) closely followed by grain screenings (1657.9 μg/kg). The benzo[*a*]pyrene emission was the highest in the case of buckwheat shells (47.7 μg/kg) followed by grain screenings (16.3μg/kg) and corn stalk pellets (14.5 μg/kg). Apparently, the fuel morphology played the major role in the formation of PAHs. Smaller particles of fuel caused increased cases of incomplete combustion thus generating higher emission of the products of partial combustion. The sewage sludge was the most polluting fuel, producing emission of PAHs higher by an order of magnitude compared to the biomass fuels (total PAH – 7212.7 μg/kg; benzo[*a*]pyrene – 189 μg/kg). This is a much higher value compared to the values, found in the earlier studies: the total PAH concentration in the fly ash from the combustion of the sewage sludge in an incinerator emission was found in the range from 11 to 228 μg/kg (Lee et al. 2005). Although particle size of this fuel was closer to pellets, a different type of high molecular mass hydrocarbons (lipids, proteins), a lack of fuel-bound oxygen and high ash content resulted in a less efficient combustion (Calvo et al. 2013; Wang et al. 2002).

The linear relationship between particulate benzo[*a*]pyrene and ∑PAH emissions of the PM mode (0.32-1.8 μm) was strong ($r = 0.94$, $p < 0.05$), while in the other size fractions 0.056-0.32 μm ($r = 0.21$) and 1.8-18 μm ($r = 0.06$) the relationship was not observed. In addition, particulate ∑PAH emissions were related to NO_x ($r = 0.82$). A negative relationship between PAH emissions and oxygen content in the fuel ($r = -0.96$) and calorific value of fuel ($r = -0.78$) was observed. A higher calorific value and oxygen content lead to a higher combustion efficiency, which in turn causes lower emissions of products of incomplete combustion.

Table 4.4 presents the emissions of size segregated ∑PAH and benzo[*a*]pyrene. These size fractions (0.056-0.18 µm; 0.32-1 µm; 1.8-18 µm) were obtained by pooling samples collected by MOUDI. The main mass of the ∑PAH and benzo[*a*]pyrene emissions were located in the fine particle range (0.056-1.8 µm) confirming the origin of PAHs from primary combustion nanoparticles. At the same time, the mode was different among the tested fuels. Wood pellets, sunflower shell pellets, straw pellets, corn stalk pellets and wheat grain screening residues resulted in maximum ∑PAH and benzo[*a*]pyrene emissions at the PM fraction of 0.056 to 0.18 µm. Buckwheat shells and sewage sludge pellets carried the highest PAH concentration in 0.32-1 µm fraction. These fuels were also prominent for the release of overall larger PM, thus the PAHs were attached to those larger particles as well. Earlier studies also found similar size distributions of PAHs. Venkataraman et al. has discovered a unimodal distribution with mode at 0.4-1.01 µm (Venkataraman et al. 2002). Similarly, no clear relationship between PAH and PM emission was discovered. The mode of PAH emissions during combustion of agriculture residues was reported to be located at 0.18 to 0.1 µm (Keshtkar and Ashbaugh 2007). Hays et al. (2003) found that size segregated distributions has unimodal presence, with the highest mode from about 0.3 to 0.1 µm Venkataraman et al. (2002) used traditional metal, fired-clay and mud stoves without any control of combustion parameters. Similar uncontrollable experiments were performed by Hays et al. in a fireplace and woodstoves (Hays et al. 2003). Chandrasekaran et al. found that not only a type of fuel but also a type of combustor can influence the mode of particulate phase PAHs (Chandrasekaran et al. 2013).

The particulate phase PAHs was dominated by fluoranthene, pyrene, chrysene and benzo[*g,h,i*]perylene (**Figure 4.3**). The vapor phase had the highest emissions of acenaphthylene, fluorene and phenanthrene. In general, there was a substantial variation among individual PAH emissions among fuels. This variation was mostly determined by the ratio of fluoranthene and pyrene vs. benzo[*g,h,i*]perylene. The later revealed constantly elevated emissions (from 11.6 µg/kg for wood pellets to 133.3 µg/kg for sewage sludge pellets) compared to other higher mass PAHs, such as indeno[*1,2,3-c,d*]pyrene, and dibenz[*a,h*]anthracene. The emissions of benzo[*g,h,i*]perylene were the highest among PAHs in case of wood pellets, straw pellets, and buckwheat shells. In cases of sunflower pellets, corn stalk pellets, grain screenings, and wastewater sludge pellets, the concentration of pyrene was the greatest, followed by the fluoranthene. The emissions of chrysene also peaked up in case of wood pellets, sunflower stalk pellets, and wastewater sludge. Another marker of biomass combustion retene was not analyzed in our study. Most of wood combusted in Lithuanian stoves is of leafy origin, while retene was associated specifically with coniferous wood (e.g. pine wood) combustion (Fine et al. 2004). Emissions of individual PAHs, discovered in our study, were several times lower compared to other studies. Singh et al., found that predominant PAHs in emissions from combustion of USA traditional wood were fluoranthene (11.4 mg/kg), pyrene (10.7 mg/kg), chrysene (4.7 mg/kg) and benz[*a*]anthracene (8.9 mg/kg). Similar trends were found in a birch combustion emission study, where predominant PAHs were fluorine, anthracene, phenanthrene, fluoranthene and pyrene (Hedberg et al.

2002). Venkataraman et al. (2002) also found that predominant PAHs were fluoranthene, pyrene and benz[*a*]anthracene.

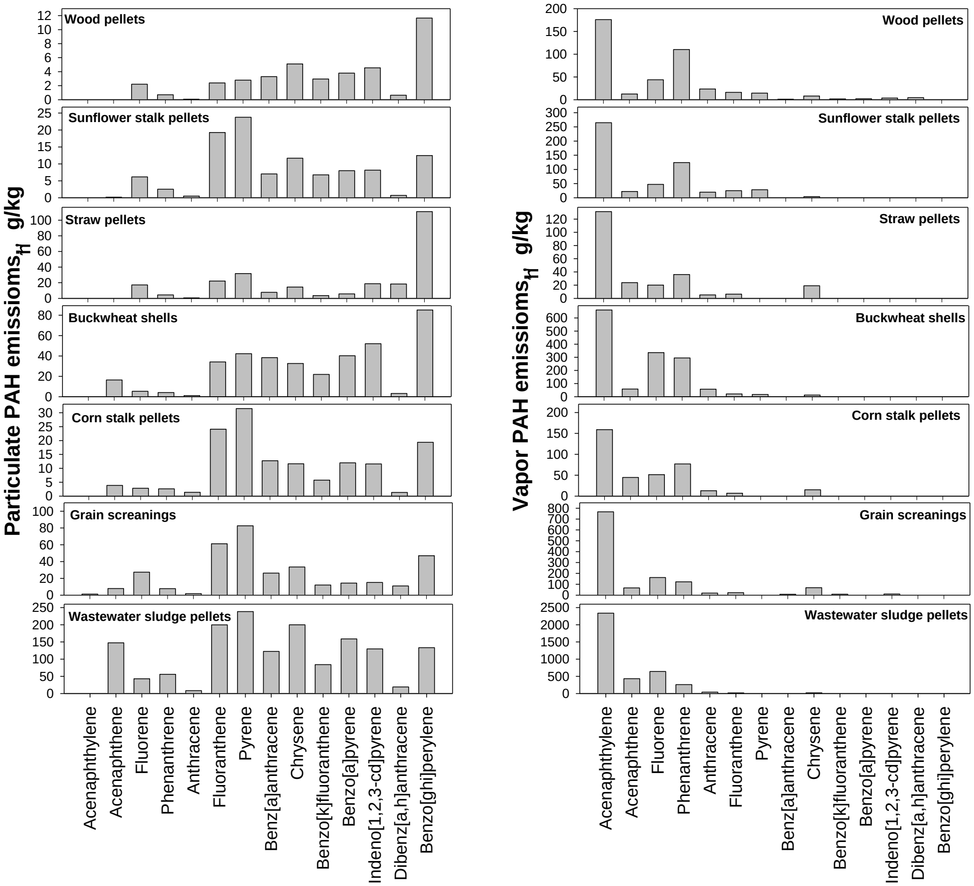


Figure 4.3. The emissions of particulate phase and vapor phase PAHs in emissions from the combustion of the tested fuels (µg/kg)

Summary of findings

Emissions of aerosol particles and PAHs from combustion of wood, agricultural residue derived fuels, and sewage sludge were investigated under optimal burning conditions in a small residential boiler. The composition and characteristics of selected fuels were in sufficient ranges for self-sustained combustion.

PM emissions were mostly represented by the PM_1 fraction (PM_1/TSP >0.8) in case of all fuels. TSP emissions ranged from 0.28 to 5.23 g/kg. The lowest PM number and mass emissions resulted from wood pellets, while the highest from the sewage sludge. The most of the particulate matter by number concentration was in accumulation mode. PM emissions were influenced by sulphur (r = 0.89), chlorine (r

= 0.93) and ash content (r = 0.71). The relationship between PM and other products of incomplete combustions were found.

Total emissions of PAHs were in a range from 469.4 µg/kg (wood pellets) to 7212.2 µg/kg (sewage sludge). The vapor phase PAH emissions were predominant (from 68.9 to 89.1 % of total PAH emission). The vapor phase PAHs were dominated by acenapthylene, fluorene and phenatrene, while the particulate phase was mostly composed by fluoranthene, pyrene, chrysene and benzo[*g,h,i*]perylene, particularly in the accumulation mode (0.32 to 1.8 µm). In general, there was a substantial variation among individual PAH emissions in cases of various fuels. While emissions of PM were comparable to earlier studies, the emissions of PAHs were significantly lower.

4.1.2. Resuspension of Polycyclic Aromatic Hydrocarbons from street dust

Detailed aim of this research

The purpose of this study was to quantitatively assess the resuspension of particulate matter and PAHs from street dust.

Experimental design

Description of sampling locations. Samples of street dust were collected from two locations in the city of Kaunas, Lithuania (Eastern Europe). The first location (Site 1) was in a one-way, three-lane street (Kęstučio g.), which is located in a city center with an average daily traffic flow of approximately 19000 vehicles, including 810 diesel-fuelled public transport buses. Peaks in traffic flow were less pronounced at this location than at Site 2, in a two-lane street (Vyduno al.) with an average daily traffic flow of 12000 vehicles and pronounced peaks during rush hours. The traffic at the latter site included approximately 540 diesel-fuelled buses per day. The street serves as a connection between the city center and suburban zones.

Resuspension chamber. The experimental system is illustrated schematically in **Figure 4.4.** This design may be attributed to the “fluidization” type, according to (Gill et al. 2006). The experimental chamber was built from organic (plexi) glass, measuring 55.3 x 31.3 x 40.3 cm, with an internal volume of 0.061 m^3. The interior of the chamber was covered by grounded aluminum foil to prevent electrostatic charge formation causing particle deposition on the chamber walls. A mass of 300 g of street dust was used in each experiment. A baffle was installed before the outlet orifice to create turbulence in the chamber and prevent the direct exit of coarse particles. The movement of air streams inside of the chamber was modeled using SolidWorks simulation software (version 2010, Dassault Systemes SolidWorks Corp., Concord, MA, USA).

Air flow was generated by a ventilator that was controlled by a frequency converter to achieve the air velocity specified for each experiment. The air was circulated through steel pipes (10 cm internal diameter) and two filtration steps were utilized to remove particulates from the “carrier” air. Most resuspended particles were collected immediately after the sampling probes by a coarse filter before air was returned to the ventilator, then a High Efficiency Particulate Air (HEPA, Class

11) filter was installed before the chamber entrance to reduce the particle content as far as practicable.

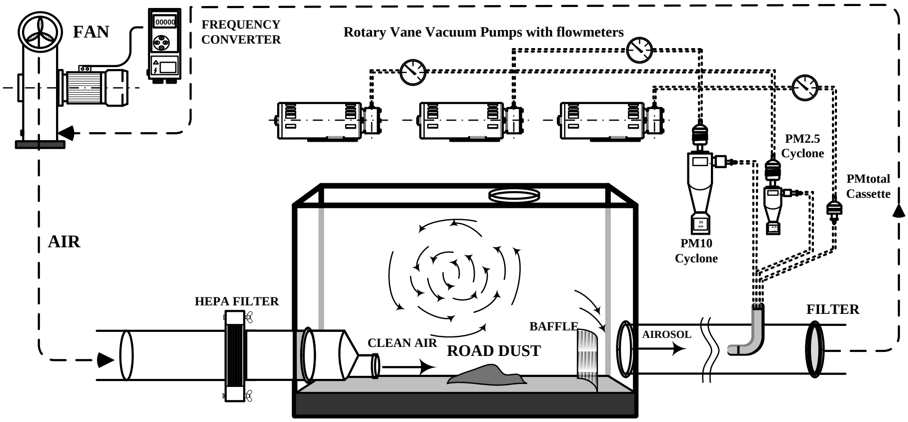


Figure 4.4. Experimental system for simulation the resuspension of road dust

The air velocity was measured using a thermal anemometer (Model 425, testo AG, Lenzkirch, Germany), the tip of which was positioned 10 cm from the air outlet. The flow was held constant throughout each experiment. After initial test runs, three flow velocities were selected for experiments: 8 m/s, 10 m/s and 15 m/s. Lower flow velocities did not aerosolize significant amounts of particles and higher flow velocities caused very intense aerosol production. The air velocity range in our experiment agrees with that published by Shao et al. 1993.

Preparation and properties of sampled street dust. The moisture content of the collected samples was determined gravimetrically by weighing sub-samples before and after drying in an oven at 105 ^{o}C for 24 hours. In order to normalize their water content (at <1 %), and thus avoid variations in results due to variations in their moisture levels, the rest of the samples (from both sites) were stored at ambient temperature in a room environment for seven days. A separate experiment was conducted to determine the fractional composition of dried dust using a sand sieve with seven mesh sizes ranging from >2.5 to <0.16 mm.

PM sampling and concentration measurement. Resuspended dust was collected on glass microfiber filters (GF/A, Whatman plc, Maidstone, UK, diameter 25 mm, pore size 1.6 μm). The microfiber filters were heated in an oven for 4 hours at 500 ^{o}C and conditioned for 24 hours at 20±1°C before and after sampling.

Three particulate samples were taken in parallel: a total particulate (PM_{total}), PM_{10} and $PM_{2.5}$ fractions. Three replicates were also taken of each sample with the intention to minimize the standard error of the experiment. All samples were taken using iso-axial sampling probes (each for particular size fraction, total three probes mounted together) under isokinetic flow conditions. The PM_{10} and $PM_{2.5}$ fractions were separated, at an air sampling flow rate of 16.7 l/m (1 m^3/h), by cyclones (URG Corporation, Chappel Hill, NC, USA) with appropriate cut-off sizes. The PM_{total} fraction was collected by diverting the air flow (at 16.7 l/m) to a 25 mm polypropylene cassette fitted with a filter. Three separate rotary vane vacuum pumps equipped with flow meters were used to maintain the desired sampling flow rates.

A mixed full-factorial experiment was designed using two sites and three air velocities as factors. The responses included three particle size ranges and three replicates of road dust sample from each of two locations. Consequently, 54 particulate samples were taken and analyzed. The design and processing of results was carried out using Multiple Linear Regression (MLR) technique, implemented in Modde 7 software package (Umetrics, Inc.)

A range of data was obtained from the experiments, including the initial calculation of particle mass concentrations (mg/m^3) in exhaust air. However, such data did not support the direct calculation of particulate emissions under normal environmental conditions and were consequently re-calculated as particle and PAH emissions per kg of deposited dust (mg/kg or pg/kg). The presented emission factors may be converted to emission rate (mass/time) by dividing mass/mass factor by a constant of 360 (duration of resuspension experiment). A total of 32 PAHs were determined (**Table 4.5**.).

Table 4.5. List of the analyzed PAH compounds

Name	**Abbreviation**	**Number of rings**	**Name**	**Abbreviation**	**Number of rings**
Naphthalene	Nap	2	Fluoranthene	Fla	4
2-methylnaphthalene	2MeNap	2	1-methylfluoranthene	1MeFla	4
1-methylnaphthalene	1MeNap	2	Pyrene	Pyr	4
Biphenyl	Bph	2	1-methylpyrene	1MePyr	4
2,3-dimethylnaphthalene	dMeNap	2	Retene	Re	4
2,3,5-trimethylnaphthalene	tMeNap	2	Benz[*a*]anthracene	BaA	4
Acenaphthylene	Acy	3	Chrysene[a]	Chry	4
Acenaphthene	Ace	3	2-methylchrysene	2MeChry	4
Fluorene	Fl	3	Benzo[*b*]fluoranthene	BbF	5
1-methylfluorene	1MeFl	3	Benzo[*k*]fluoranthene	BkF	5
Phenanthrene	Phe	3	Benzo[*a*]pyrene	BaP	5
1-methylphenanthrene[a]	1MePhe	3	Perylene[a]	Per	5
2-methylphenanthrene	2MePhe	3	Dibenz[*a,h*]anthracene	dBaAnt	5
3-methylphenanthrene	3MePhe	3	Indeno[*1,2,3-c,d*]pyrene	IndP	6
Anthracene	Ant	3	Benzo[*g,h,i*]perylene	BghiPer	6
1-methylanthracene	1MeAnt	3			
2-phenylnaphthalene	2PheNap	3			

Results and Discussion

Particle re-suspension vs. air velocity. Particle concentrations (presented as mg of resuspended particles per kg of street dust) generated by the different air velocities are presented in **Figure 4.5**. The graph shows the generation of particles during tests of dust samples from two locations – Site 1 (city center) and Site 2 (connecting streets). There was substantial variation in the mass of particles thus generated, both within each PM fraction and between sample locations. In general, an increase in air velocity resulted in an increase in the mass of air-borne particles.

The air velocity has been distinguished by the MLR analysis as a factor significantly influencing variation of PM emissions in all measured size fractions ($p<0.01$). For the $PM_{2.5}$ fraction, increasing the air speed from 8 to 10 m/s resulted in a 2.6-fold increase in concentration of air-borne particles (C_{10}/C_{8}) for dust from Site 1 and a 2.1-fold increase for dust from Site 2. The corresponding increases observed for the PM_{10} fraction were 2.4 and 1.9 fold, and for the PM_{total} fraction the increases were 1.5 and 2.4 fold respectively. A further increase of air speed from 10 m/s to 15 m/s resulted in increased concentrations of air-borne particles by the following factors (C_{15}/C_{10}): $PM_{2.5}$ 1.8 and 2.9, PM_{10} 1.9 and 2.5, PM_{total} 2.2 and 2.4. Thus, the re-suspension of particles increased stepwise with the stepped increases in air velocity.

The PM_{total} fraction contained the greatest amount of particulate mass in each run. The ratio of PM concentrations in the fractions PM_{10}/PM_{total} in re-suspended dust from Site 1 ranged from 0.31 (8 m/s) to 0.48 (10 m/s) and in re-suspended dust from Site 2 from 0.40 (10 m/s) to 0.49 (8 m/s). The ratio of particulate concentrations in the $PM_{2.5}/PM_{10}$ fractions in re-suspended dust from Site 1 ranged from 0.064 (8 m/s) to 0.069 (10 m/s) and in re-suspended dust from Site 2 from 0.024 (8 m/s) to 0.030 (15 m/s). The low $PM_{2.5}/PM_{10}$ ratios confirmed that there were relatively small fractions of fine (< 2.5 μm) particles in the street dust. However, the PM_{10} fraction contributed up to half of the mass of particulates in the PM_{total} fraction. Relatively large variations were observed in the measurements of the PM_{total} concentration between replicates (the CV ranged from 0.21 to 0.82 at different air velocities). Visual examination of the sampled media revealed that a high proportion of very coarse particles (up to 500 μm) were sampled, but that they did not remain on the filter during its removal from the cassette. This was not considered to be a major limitation, since events of this type were anticipated and the data were analyzed accordingly. On the other hand, relatively large variation between runs may also be affected by the fact that the three sampled fractions are affected by different lift-off mechanisms. Although the $PM_{2.5}$ and PM_{10} fractions may be easily lifted by aerodynamic forces and are less affected by gravity forces, the cohesion may be a limiting factor at lower air velocities. The air velocity of ~ 8 m/s represents minimally disturbed system, where the dust reentrainment starts occurring, mostly based on aerodynamic forces, but the break-up of aggregates does not occur. At ~ 15 m/s, particles become fully disturbed both by aerodynamic and mechanical forces. The balance and influence of the gravity, aerodynamic and cohesion forces is relatively complex and cannot be easily assessed (Shao 2008).

The data indicated that street dust collected close to the city center exhibited slightly different behavior in terms of resuspension of the fine PM fraction. For example, at 8 m/s the $PM_{2.5}$ emission factor was 23.6±11.2 mg/kg for dust from Site 1, while for dust from Site 2 the $PM_{2.5}$ emission factor was 8.18±10.7 mg/kg. A similar trend was observed at higher air velocities (60.9±34.2 vs. 17.4±18.9 mg/kg at 10 m/s and 110.8±53.4 vs. 49.6±50.6 mg/kg at 15 m/s). The city center dust $PM_{2.5}$ emission factors were generally more than double those of the dust sampled at the connecting road site. When assessing the emission factors for coarser particles (PM_{10} and PM_{total}) the difference between dust samples from the two locations was not pronounced. The MLR analysis has revealed that site factor was significant for

$PM_{2.5}$ fraction ($p < 0.05$), but not for PM_{10} and PM_{total} fractions ($p = 0.83$ and 0.50, respectively). The absolute differences in $PM_{2.5}$ emissions were substantial despite the high standard deviations between replicate experiments, and may be attributed to differences in the physical properties of the dust at each sample location. Visual examination of the dust samples revealed that deposits from Site 2 contained more humic substances and were darker in color than those from Site 1. Fractionation by multi-step sieving demonstrated that the dust sample from Site 2 contained a higher mass proportion of particles smaller than 160 μm (25.3 % at Site 2 vs. 9.7 % at Site 1). This finding suggests that particle size distribution data obtained by sieving cannot be used alone to predict the resuspension potential of a material. The humic substances present in the dust probably bind the fine particles and thus hinder resuspension by enhancing the cohesive force and preventing of disaggregation of particles. The humic substances also attract water so that, although samples of dust from both sites were dried at room temperature for a week, the Site 2 dust contained more moisture (1.1 %) than the dust from Site 1 (0.8 %). Although the moisture content of the deposits was equilibrated as far as practicable in an attempt to obtain comparable data under laboratory conditions, the moisture content of street dust is not controlled. During dry weather it reaches values from 1 to 6% (data were obtained by measuring freshly sampled deposits). Thus, the experimental results obtained reflect the resuspension potential of street dust under conditions of prolonged dry weather.

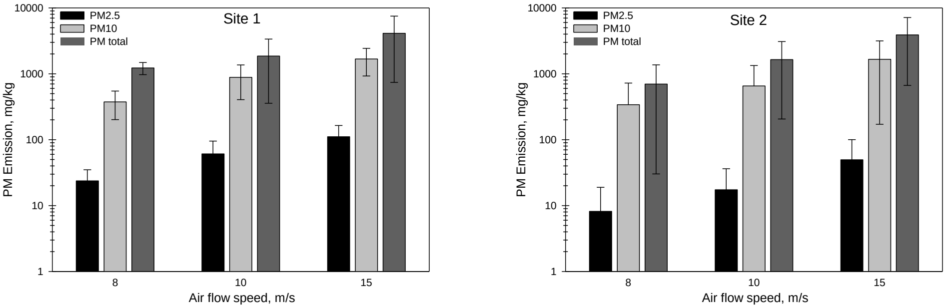


Figure 4.5. Emission of particulate matter from street dust (ng of resuspended PM per kg of street dust) at various air velocities. Site 1 – dust sample from a city center street; Site 2 – dust sample from connecting street

PAHs in resuspended PM. The concentrations of 32 PAHs (**Table 4.4**) were determined in particles deposited on the sample filters during each experiment. Four compounds – acenaphthene, 2,3,5-trimethylnaphthalene, 1-methylfluoranthene, and 2-methylchrysene – were not detected during any experimental runs and hence are not further considered.

The PAH concentration in each particle fraction was analyzed from several perspectives. First, the total PAH concentrations we found in resuspended street dust were compared to those obtained in other studies. Next, the dust samples collected from the two sampling sites were compared in terms of PAH distributions in airborne particles of various sizes. Thirdly, the generation of PAHs in each particle fraction ($PM_{2.5}$, PM_{10}, and PM_{total}) as a function of air velocity was assessed.

It was not possible to compare the data obtained in this study fully with data from corresponding studies because different methods were used to prepare the dust samples. The main objective of the present study was to measure PAHs in resuspended street dust. No other similar data are available in the scientific literature, since even those of (Rogge et al. 1993) were not presented as PAH concentrations. Concentrations of PAHs in soil systems have been reported by other researchers, including 718±209 mg/kg (fraction <1 mm, 16 EPA PAHs, Nintero′I City, Brazil, Netto et al. (2006)); 7458±4794 mg/kg (unprocessed, 25 PAHs, Dalian, China, Wang et al. (2009)); 4694±3028 mg/kg (fraction <2 mm, 16 EPA PAHs, Delhi, India, Agarwal (2009)). The data obtained in the present study were lower by a factor of 10^{-5} than these values – 0.015±0.0069 mg/kg (PM_{total} at 15 m/s), 0.0075± 0.0047 mg/kg (PM_{10} at 15 m/s), 0.0029±0.0018 mg/kg ($PM_{2.5}$ at 15 m/s) – but this was because only the proportion of PAHs that was resuspended was measured. It has been shown that, depending upon location, a significant proportion of the soil PAH burden may be bound to heavy particles in the size range 63 to 250 μm (Yang et al. 1999; Murakami et ak. 2005). Thus, although such “coarse” particles may contribute significantly to surface water pollution, they have a lower impact on air pollution. The levels of PAHs in street dust in Lithuania are expected to be lower than those in China or Brazil, but the difference in PAH concentrations between street dust and the aerosolizable dust fraction is substantial and suggests that the concentration of PAHs in street dust may not be the representative indicator of particle-bound PAHs as air pollutants.

Variation of resuspended PAH concentration between sampling locations. In the dust samples from both locations, the PAH content of the PM fractions (expressed as mg/kg of dust) increased with the particle size. $PM_{2.5}/PM_{10}$ and $PM_{2.5}/PM_{total}$ PAH concentration ratios were calculated for PAHs with similar numbers of benzene rings in order to estimate the distribution of resuspended PAHs between the particle size fractions. Samples from the two locations exhibited different patterns of PAH distribution: the median ratios for almost all PAHs in the sample from Site 1 (city center) fell in the range from 0.1 to 0.9, while the median ratios for most 3-5 ring PAHs in the sample from Site 2 (connecting street) had median ratios less than 0.1. These findings suggest that a substantial proportion of PAHs was resuspended in the $PM_{2.5}$ fraction of the dust collected in the city center, while a higher proportion of PAHs was attached to “coarse” particles (2.5-10 μm) in the dust from the connecting road. The median $PM_{2.5}/PM_{10}$ and $PM_{2.5}/PM_{total}$ ratios were similar, except for those of the lighter PAHs in the sample from Site 2, which suggests that PAHs were mostly resuspended in the PM_{10} fraction. The significance of site factor in the MLR analysis varied among different PAHs. For total PAHs, this factor was significant ($p < 0.05$) for PM_{10} and PM_{total} fraction. $PM_{2.5}$ fraction was significantly affected in case of only 4 PAHs, while for PM_{10} and PM_{total} the site factor significantly influenced the release of 20 and 18 PAH compounds, respectively.

The differences in PM resuspension between street dust samples were compared to variations between particle-bound PAH concentrations. The ratios of PAH concentrations found in Site 1/Site 2 samples were calculated. The PAH content of the fine particulate fraction of the resuspended dust from the sample from the city center (Site 1) was significantly higher than that of the sample from the other site, especially at a low air velocity. The average concentration ratio in the $PM_{2.5}$ fraction generated from Site 1/Site 2 samples, for all measured PAHs, at 8 m/s was 3.6. At higher air velocities this ratio was three-fold higher. For the PM_{10} fraction, the corresponding Site 1/Site 2 concentration ratios ranged from around 0.6 at 8 m/s to approximately 0.2 at 15 m/s. For the PM_{Total} fraction the ratio was about 1.1 at 8 m/s, but declined to around 0.25 at 15 m/s. Thus, the $PM_{2.5}$ fraction of dust from Site 1 provided the highest transfer of PAHs to the aerosol, but the trend did not extend to larger particles, suggesting that compositional differences in street dust may affect the binding of PAHs to different particle size fractions.

Variation of resuspended PAH concentrations with air velocity. The analysis of PAH concentration ratios in particle size fractions did not identify a clear effect of air velocity on the distribution of PAHs between particle size fractions. The MLR analysis has revealed that for PAHs the velocity factor was not statistically significant factor for all size ranges at a confidence level of 95 %.

For each sample location, column plots representing the average measured concentration of total PAHs±SD are shown in **Figure 4.6**, and those of individual PAHs are presented in **Figure 4.7** and **Figure 4.8**. The concentrations of PAHs in resuspended dust did not always increase linearly with the air velocity. The expected pattern of increasing PAH concentration with air velocity was observed for the dust from Site 2 (connecting street) and the concentrations of many PAHs increased with the wind speed for all three particle size ranges. However, a different pattern was observed for PM_{10}, in which the concentrations of 3-5 rings PAHs reached maxima at an air speed of 10 m/s.

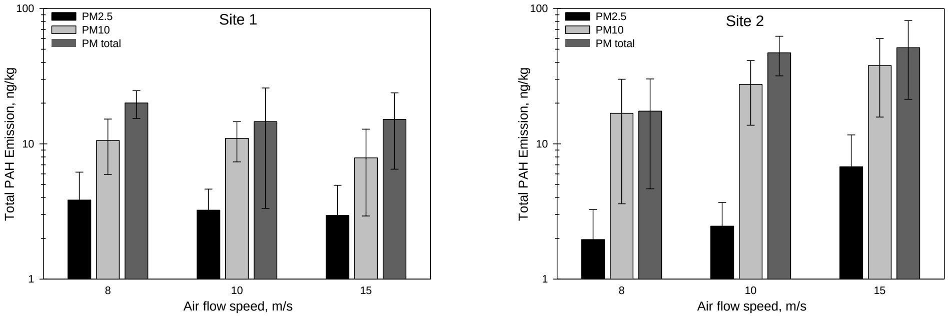


Figure 4.6. Emission of PM-bound total PAHs from street dust (ng of resuspended PAHs per kg of street dust) at different air velocities. Site 1 – dust sample from city center street; Site 2 – dust sample from connecting street

For the dust sample from Site 1 (city center), an increase in air speed seemed to hinder the transfer of PAHs to the aerosol. The PAHs were most effectively resuspended at 8 m/s, and at 10 m/s the concentrations were lower (although they remained within 1 standard deviation of the previous value, thus not statistically significant), most substantially in the PM_{total} fraction for 3-ring PAHs (anthracene - 2-phenylnaphthalene). The concentrations of PAHs containing 4-5 rings were lowest in the PM_{total} and $PM_{2.5}$ fractions at an air velocity of 10 m/s. The dependence of particle mass on wind velocity was evident, but for PAHs other factors, probably including the particle size distribution, composition and carbon content of the dust, must also be considered and their effects should be further researched.

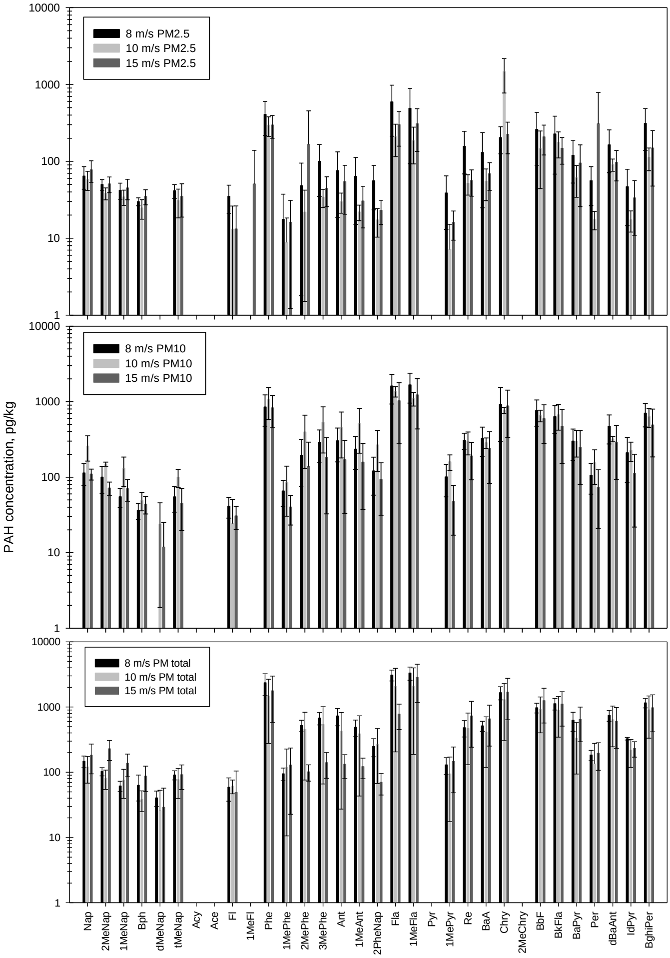


Figure 4.7. Emission of PM-bound individual PAHs from street dust (pg of resuspended PAHs per kg of street dust) at different air velocities (Site 1 – city center)

Characteristic ratios of PAHs in resuspended PM. The data were further analyzed to explore characteristic concentration ratios of specific PAHs. Rajput and Lakhani (2009) have compiled available data on diagnostic ratios of PAH concentrations that identify particular sources of PAHs in ambient air. The approach has been applied by Wang et al. (2009) to PAHs in street dust. Since it is based on ratios rather than absolute values, the method is also suitable for comparing data from soil and airborne particle analysis.

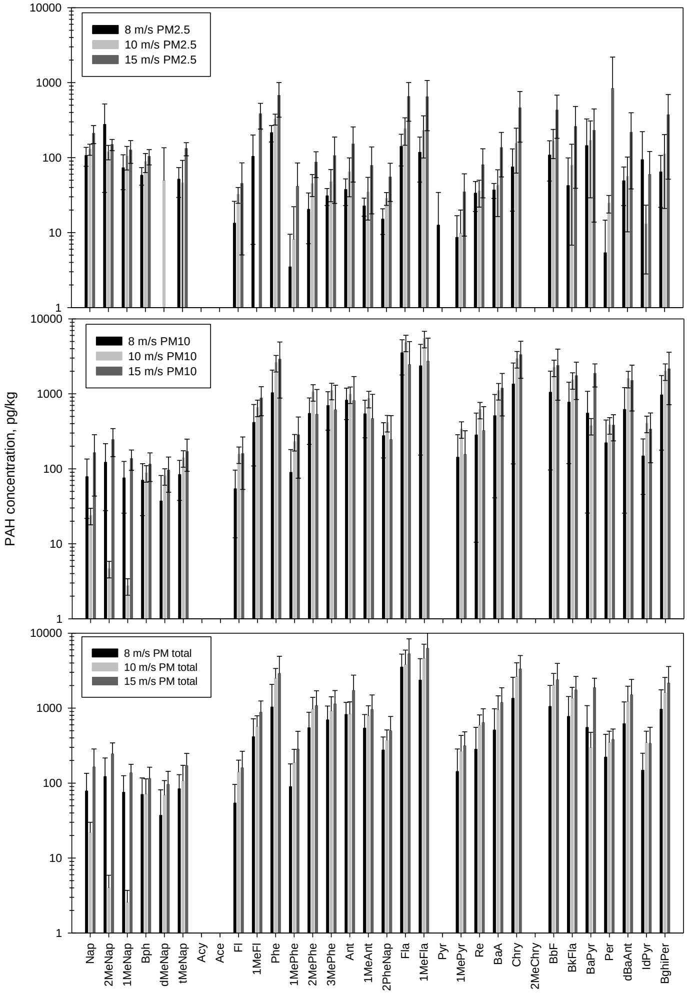


Figure 4.8. Emission of PM-bound individual PAHs from street dust (pg of resuspended PAHs per kg of street dust) at different air velocities (Site 2 – connecting street)

A Fla/(Fla + Pyr) ratio of 0.4-0.6 indicates that PAHs in air-borne particles are probably derived from gasoline (Tsapakis and Stephanou 2003), while a ratio of 0.6-0.7 indicates a diesel-related source of PAHs (Sicre at al. 1987). In the present study, the ratios of PAHs for all size fractions and air velocities varied around 0.5 (**Table 4.6**), thus confirming a traffic-related origin of the PAHs, predominantly from gasoline emissions. A BaA/(BaA + Chry) ratio between 0.22 and 0.55 indicates a gasoline source of PAHs (Simcik et al. 1999), while a ratio of 0.38 to 0.64 indicates a diesel emission source (Sicre et al. 1987). Wang et al. (2009) obtained ratios between 0.35 and 0.50, confirming the petrogenic origin of particles in street dust they examined. In the present study, at 8 m/s air speed, the ratio was 0.33-0.39. At higher air speeds, the ratio declined to 0.20-0.28, again presumably indicating a greater contribution from gasoline. Low values (0.18-0.22) of the ratio of IndP / (IndP + BghiPer) generally indicate a gasoline source (Khalili et al. 1995; Tang et al. 2005), but substantially higher ratios were observed in the present study, ranging from 0.33 to 0.50, indicating a diesel exhaust source. Combustion PAHs (CPAHs, the sum of Fla, Pyr, BaA, Chry, B(b+k)F, BaP, IndP and BghiPer, after Rogge et al (1993) and Rajput and Lakhani (2009) contributed significantly to the total concentrations of resuspended PAHs in all measured fractions of PM, ranging from 0.56 to 0.79 in city center dust and from 0.39 to 0.69 in dust from the connecting street. The higher values for city center dust may indicate either higher concentrations of CPAHs in the dust or a greater potential for resuspension of CPAHs. Although generally slightly higher ratios were found in the present study, the data agree with the value of 0.58 reported by Rajput and Lakhani (2009). The ratio of six carcinogenic PAHs – BaA, BaP, dBaAnt, BbF, BkF, IndP (Netto et al. 2004; Rajput and Lakhani 2009) - to total PAHs (CarPAHs/TPAHs) ranged between 0.14 and 0.28.

Table 4.6. Diagnostic PAH ratios in various resuspended particle fractions at various air velocities (mean±standard deviation; CarPAHs – carcinogenic PAHs, CPAHs – combustion PAHs)

Air velocity:	8 m/s			10 m/s			15 m/s		
Fraction	$PM_{2.5}$	PM_{10}	PM_{total}	$PM_{2.5}$	PM_{10}	PM_{total}	$PM_{2.5}$	PM_{10}	PM_{total}
Site 1 (city center street)									
Fla/(Fla+Pyr)	0.55±0.09	0.49±0.00	0.48±0.02	0.53±0.01	0.55±0.08	0.50±0.01	0.51±0.04	0.46±0.07	0.27±0.21
BaP/(BaP+Chy)	0.36±0.05	0.28±0.11	0.27±0.08	0.04±0.01	0.28±0.09	0.22±0.04	0.28±0.08	0.21±0.04	0.28±0.09
BaA/(BaA+Chy)	0.34±0.13	0.31±0.15	0.24±0.02	0.04±0.01	0.27±0.05	0.24±0.02	0.24±0.01	0.22±0.04	0.27±0.06
IP/(IP+BghiP)	0.34±0.00	0.39±0.05	0.39±0.02	0.45±0.04	0.34±0.04	0.42±0.01	0.44±0.12	0.37±0.05	0.38±0.04
BaP/BghiP	0.39±0.04	0.42±0.05	0.54±0.14	0.55±0.14	0.46±0.05	0.42±0.18	0.76±0.40	0.48±0.20	0.68±0.27
IP/BghiP	0.52±0.01	0.66±0.13	0.64±0.04	0.84±0.15	0.52±0.10	0.72±0.04	0.83±0.40	0.61±0.13	0.63±0.10
CarPAHs/TPAHs	0.24±0.02	0.26±0.01	0.22±0.01	0.17±0.03	0.23±0.03	0.26±0.05	0.24±0.04	0.25±0.00	0.29±0.05
CPAHs/TPAHs	0.64±0.04	0.70±0.02	0.66±0.01	0.77±0.03	0.57±0.09	0.66±0.02	0.56±0.08	0.68±0.04	0.69±0.03
Site 2 (connecting street)									
Fla/(Fla+Pyr)	0.56±0.04	0.61±0.25	0.47±0.01	0.53±0.05	0.46±0.04	0.46±0.02	0.51±0.05	0.46±0.02	0.48±0.00
BaP/(BaP+Chy)	0.50±0.37	0.28±0.03	0.25±0.01	0.47±0.22	0.10±0.01	0.31±0.01	0.31±0.07	0.38±0.18	0.29±0.01
BaA/(BaA+Chy)	0.39±0.21	0.27±0.03	0.25±0.01	0.22±0.02	0.26±0.01	0.30±0.02	0.23±0.04	0.26±0.01	0.45±0.30
IP/(IP+BghiP)	0.45±0.05	0.37±0.04	0.37±0.01	0.33±0.19	0.44±0.03	0.40±0.01	0.37±0.02	0.43±0.08	0.39±0.03
BaP/BghiP	5.87±9.37	0.53±0.09	0.50±0.03	1.69±1.33	0.19±0.00	0.64±0.03	0.65±0.27	1.58±1.77	0.62±0.04
IP/BghiP	0.84±0.19	0.59±0.10	0.58±0.03	0.57±0.46	0.78±0.09	0.66±0.03	0.59±0.05	0.79±0.28	0.65±0.08
CarPAHs/TPAHs	0.25±0.05	0.19±0.09	0.22±0.01	0.20±0.07	0.23±0.01	0.23±0.00	0.19±0.05	0.25±0.05	0.28±0.11
CPAHs/TPAHs	0.39±0.06	0.66±0.04	0.68±0.01	0.48±0.12	0.66±0.04	0.66±0.01	0.50±0.07	0.68±0.03	0.68±0.04

The air velocity did not appear to affect the characteristic PAH ratios. Although there were some air velocity-related trends in particle-bound PAH generation when expressed as absolute concentrations, the ratios within each particle size fraction did not exhibit a clear dependence. To summarize, variations of the same order were observed for different air speeds and particle size fractions. This implies that characteristic ratios should be determined and interpreted carefully for both street dust and air-borne aerosols, especially regarding particle size fractions. Furthermore, data obtained under laboratory conditions may be influenced by the simulated conditions, such as resuspension mechanism and low particle humidity.

Summary of findings

This experimental investigation of resuspension of particulate matter and polycyclic aromatic hydrocarbons from street dust has confirmed that street dust is a potentially significant source of urban air pollution. The results show that street dust may not only emit fugitive dust, but may also be a substantial source of PAHs bound to the particle size fractions ($PM_{2.5}$, PM_{10}, PM_{total}) investigated.

The mass concentrations of $PM_{2.5}$, PM_{10} and PM_{total} in the experimentally created aerosol increased proportionally with increases in air speed from 8 m/s to 15 m/s. Fine particles ($PM_{2.5}$) contributed only slightly (2-7%) to the overall mass of resuspended particles, but the PM_{10} fraction contributed up to 50% of the resuspended particles mass. A substantial difference in particle resuspension was observed between dust from the city center street and dust from the connecting street; the city center dust yielded twice as high levels of fine particles than the connecting street sample (e.g., 23.6±11.2 vs. 8.18±10.7 mg/kg at 8m/s, 110.8±53.4 vs. 49.6±50.6 mg/kg at 15 m/s), whereas the PM_{10} and PM_{total} particle fractions were comparable for both samples. The concentrations of PAHs in the resuspended dust showed similar differences between sample locations, which could be attributed to differences in the granulometric composition of the samples dust. The higher levels of humic substances in the dust from the connecting street may have affected particle cohesion forces and hence lower aerosolization.

Total PAHs concentration in resuspended dust has reached 0.015±0.0069 mg/kg (PM_{total} at 15 m/s), 0.0075±0.0047 mg/kg (PM_{10} at 15 m/s), 0.0029±0.0018 mg/kg ($PM_{2.5}$ at 15 m/s). The concentrations of PAHs associated with resuspended particles were lower by five orders of magnitude than those measured in previous studies of non-resuspended street dust. This suggests that the PAH concentration of non-resuspended total street dust is not the best predictor of air-borne PAHs. The effect of air velocity on the concentration of PAHs in resuspended dust was ambigous, not showing statistically significant dependence. The characteristic ratios of PAHs (as markers of contributory sources) indicated substantial variation between the size fractions and air velocities.

The calculated emission factors may be employed for dispersion modeling of PM and PAHs from street dust.

4.2. Polycyclic Aromatic hydrocarbons in air of various urban environments

4.2.1. Polycyclic Aromatic Hydrocarbons in outdoor air of near street buildings

Detailed aim of this research

The aim of this study was to investigate indoor and outdoor particle-bound PAHs at two urban locations in Kaunas, Lithuania.

Experimental design

Sampling locations and experimental set-up. Two sampling locations in the city of Kaunas (popullation 361000 in 2009; total area 157 km^2), Lithuania, were chosen. Both locations are urban and may be classified as “traffic” sampling sites, since they are located in close proximity to streets with dense traffic. The first location (henceforth referred to as Location 1) was beside a two-lane street (Vyduno al.) with an average daily traffic of over 12000 vehicles, with pronounced peaks during rush hours. This street connects the city centre to outer residential areas and carries a moderate level of bus traffic; approximately 300 diesel-fuelled public busses and 850 diesel-fuelled microbuses (important public transport vehicles in Kaunas) travel along it every day.

The second location (Location 2) was on a one-way three-lane street (Kestucio g.). This street is in the city centre, with an average daily traffic of approx. 19 000 vehicles, including 450 diesel public busses and 1820 microbuses. The traffic peaks were less pronounced in this location.

In Location 1 air was sampled at an indoor site inside a room and an outdoor site on the balcony on the 3rd floor of a 5-story university dormitory, located 12 m away from the street. The room was occupied by two non-smoking students who carried out their routine activities (no thermal aerosol generation was expected). Outdoor air was sampled at Location 2 from a storage facility on the first floor of a university faculty building, 3 m away from the street. The indoor site was an unoccupied room visited only occasionally by sampling crew and other university staff. The sampling locations are depicted in **Figure 4.9**.

In order to estimate seasonal fluctuations in the atmospheric abundance of the two main PM size fractions ($PM_{2.5}$ and PM_{10}), and the particle-bound PAH content of these fractions, daily samples were taken at the outdoor sites over two-week periods in January and April at Location 1, and in February and March at Location 2. In addition, the levels of the PM_4 fraction at both indoor and outdoor sites were monitored in week-long daily sampling campaigns; at Location 1 samples were obtained in January and April, while at Location 2, samples were taken in February and March. In each case samples were collected (as described below) over eight hour periods during weekdays.

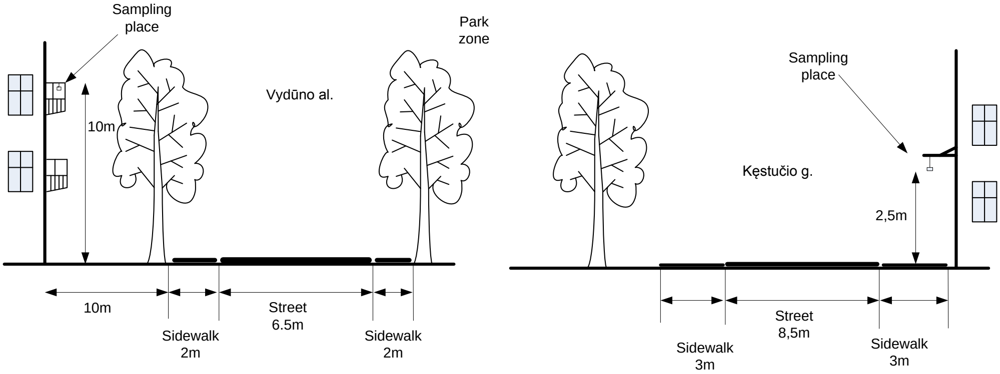


Figure 4.9. Scheme of the sampling locations

Sampling and concentration measurement. Air-borne particulate matter was collected on glass microfiber filters (GF/A, Whatman International Ltd., Maidstone, UK; diameter 25 mm, pore size 1.6 μm) over a sampling period of 8 hours. Before use, the microfiber filters were heated in an oven for 4 hours at 500 ^{o}C and conditioned for 24 hours at 20±1°C before and after sampling. Finally, PM mass concentrations (μg/m^3) were obtained from the gravimetric analysis of samples, using a MXA5 microbalance (Radwag, Poland).

The PM_{10} and $PM_{2.5}$ fractions were separated at an air sampling flow rate of 16.7 l/min (1 m^3/h) by cyclones (URG Corp, Chappel Hill, NC, USA) with appropriate cut-off sizes, and separate rotary vane vacuum pumps equipped with flow-meters. To minimise indoor noise nuisance for residents, the PM4 fraction was sampled using flow rate of 2.2 l/min (0.13 m^3/h) by SKC Conductive Plastic Cyclones for respirable dust sampling with personal sampling pumps.

Quality control. For the PAH analyses a certified reference material (SRM 1649a urban dust) was used as a quality control sample. The measured levels of the 12 PAHs rarely deviated more than 10 % from the certified levels. The QC results were considered acceptable during the whole study. Blanks were processed in parallel with the samples in this study. Some PAH residues were found on blank filters target compounds were found in the blanks, but in no case was the amount of any given compound in any blank greater than 10 % of the amount found in any non-blank sample.

Modelling long-distance transported pollution. Air mass back trajectories were computed using the NOAA ARL HYSPLIT Model to investigate the effect of long-distance transported pollution. For each sampling day, 96-hour air mass back trajectories were computed at start-up time and stop time at three starting heights (100, 200, and 500 m above ground level). The trajectories were divided into four trajectory classes or sectors, representing different source areas - Eastern Europe, Western Europe, the Nordic region (Finland, Norway, Sweden and the Baltic countries) and an eastern sector named Russia (including Russia, Belarus and Ukraine) - or remained undetermined (for trajectories that shifted classes during the sampling day). These sectors are similar to those used in a recent publication from Estonia (Orru et al. 2010). The classification was based on the criterion that all trajectories during a sampling period must share a major path belonging to the same class.

Statistical calculations were performed using Wilcoxon’s rank sum test implemented in SAS System for Windows, version 9.2.23 Statistical significance refers to $p < 0.05$ in two-tailed tests.

Results and discussion

The $PM_{2.5}$ and PM_{10} outdoor concentrations measured in this study are compared with those reported in various other cities around the world in **Table 4.7**. The results from the winter campaign (January-February) revealed very minor differences in $PM_{2.5}$ and PM_{10} concentrations (the average $PM_{2.5}/PM_{10}$ ratio was 0.95 at Location1 and 0.90 at Location 2). This indicates that both fractions were generated by the same source. Most of the PM_{10} mass consisted of fine particles, which probably originated from street dust. The average concentrations of particulate matter in Kaunas were comparable to that in most other European sites. In general there was little difference between the PM concentrations at Locations 1 and 2. $PM_{2.5}$ concentrations were lower during the spring sampling campaign, for PM_{10} no significant seasonal concentration variations were observed. The average measured $PM_{2.5}$ and PM_{10} concentrations were compared to those obtained from the Lithuania Environmental Protection Agency’s automated monitoring station at Kaunas The average measured concentrations were comparable to EPA monitored concentrations (see **Table 4.7**). At Location 1, the winter $PM_{2.5}$ concentration was 34.5±15.2 μg/m^3 while in spring it was 24.7±12.2 μg/m^3; at Location 2 the corresponding values were 36.7±21.7 and 22.4±19.4 μg/m^3, respectively.

Table 4.7. Comparison of $PM_{2.5}$ and PM_{10} concentrations (μg/m^3) in world cities and Locations 1 and 2 (this study), and automated monitoring station, EPA

	Kaunas, Lithuania			Oxford, Ohio	Madrid, Spain	Bern, Switzerland	Athens, Greece	Belgrade, Serbia	Beirut, Liban	Teheran, Iran	Istambul, Turkey	Barcelona, Spain	Berlin, Germany	San Paulo, Brazil
	Location 1	Location 2	Automated monitoring station, EPA											
$PM_{2.5}$[a]	34.5±15.2	36.7±21.7	26.81±12.43	15.7	34	24.6	40.2	61	40	24.3	27.7	27.7	30	20.9
$PM_{2.5}$[b]	24.7±12.2	22.4±19.4	23.19±11.75											
PM_{10}[a]	35.2±14.6	39.7±20.3	33.91±20.03	16.3	48	40.2	75.5	72	76	122.1	40.4	40.6	38	10.7
PM_{10}[b]	41.7±11.8	34.2±20.6	32.55±22.88											
	Current study			Wojas et al. 2007	Artinano et al. 2003	Hueglin et al. 2005	Chaloulakou et .2003	Tasic et al. 2005	Shaka et al. 2004	Kakooei et al.2007	Karaca et al.2005	Querol et al.2001	Lenschow et al.2001	Miranda et al. 2007
a – winter sampling period														
b – spring sampling period														

The outdoor PAH concentrations measured at the two sampling locations in this study are presented in **Figure 4.10**. High molecular weight PAHs with five to six rings, such as benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, benzo[*g,h,i*]perylene predominated, while low molecular weight compounds were present only in smaller quantities. High concentrations of the 4-ring PAHs fluoranthene and pyrene were also observed. These findings are as expected, since 90 % of 5-6 ring PAHs are adsorbed on particles and only 10 % partition into the vapour phase, 4-ring PAHs are found in similar amounts in both phases, while PAHs with 2-3 rings are found predominantly (> 90 %) in the vapour phase (Odabasi et al. 1999). Five PAH components, i.e. acenaphthylene, 2,3,5-trimethylnaphthalene, 1-methylfluoranthene, 1-methylfluorene, and 2-methylchrysene, were not detected in any samples.

The mean sum PAH concentrations at Locations 1 and 2 in the winter campaign were 75.1±32.7 and 32.7±11.8 ng/m^3, respectively. This difference is greater than expected from the difference in traffic intensity at the two sites, suggesting that there is another significant source of PAH emissions at Location 1 in addition to the traffic.

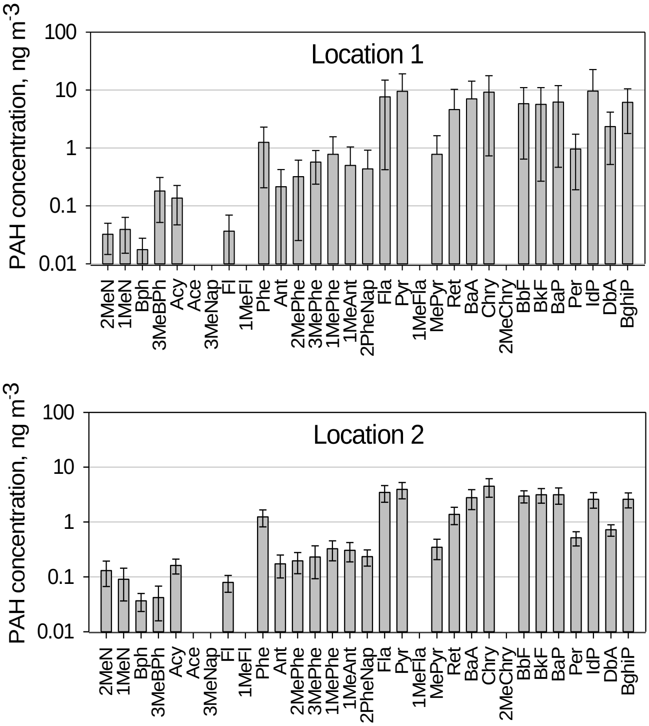


Figure 4.10. Mean concentrations of PAHs measured in the PM$_{2.5}$ fraction

As shown in

Table 4.8 the concentrations of most PAHs observed in this study are higher than those reported by other authors, particularly at Location 1. Comparison of benzo[*a*]pyrene levels in the PM$_{2.5}$ fraction reported by Saarnio et al. (2008) showed that in Western European cities concentrations varied from 0.1 to 1.1 ng/m^3 and in Eastern and Central European cities from 3.0 to 3.2 ng/m^3. Benzo[*a*]pyrene levels at

Location 2 were similar to those reported in Prague and Zagreb. It should be noted that the European limit value for benzo[*a*]pyrene is 1 ng/m^3 in PM_{10}.

Table 4.8. Comparison of average PAH concentrations measured in the $PM_{2.5}$ fraction, ng/m^3, in this study (Locations 1 and 2) and in other cities

Compound	This study Location 1	This study Location 2	Kurkimäki	Bologna	Duisburg	Prague	Amsterdam	Helsinki	Zagreb	Atlanta
			Finland	Italy	Germany	Czech R.	Netherlands	Finland	Croatia	USA
			Hellen et al.	Stracquandanio et al.	Saarnio et al.				Sisovic et al.	Li et al.
			2008	2007	2008				2005	2009
	winter	winter	winter	winter	winter	winter	Winter	spring	winter	winter
Phenanthrene	1.3±0.6	1.2±0.4	2.5	0.9	0.7	4.8	0.8	0.3		0.15
Anthracene	0.2±0.1	0.2±0.1	0.4							0.02
Fluoranthene	7.6±3.4	3.5±1.2	4.4		1.6	6.4	1.3	0.5	3.7	0.14
Pyrene	9.5±4.1	3.9±1.3	4.0	1.4	1.3	5.6	0.9	0.4	4.7	0.17
Retene	4.6±1.3	1.4±0.5								0.14
Benz[*a*]anthracene	7.0±3.0	2.8±1.1	1.3	1.1						0.19
Chrysene	9.2±4.1	4.5±1.7	1.6	2.2						0.23
Benzo[*b*]fluoranthene	5.8±2.0	3.0±0.7		2.5					3.5	0.61
Benzo[*k*]fluoranthene	5.6±1.9	3.1±0.9		0.9					2.1	0.18
Benzo[*a*]pyrene	6.2±3.9	3.2±1.0	1.3	1.7	1.1	3.0	0.3	0.1	3.2	0.42
Indeno[*1,2,3-c,d*]pyrene	9.6±1.8	2.6±0.8	2.2							0.59
Dibenz[*a,h*]anthracene	2.3±1.9	0.7±0.2	0.4							0.02
Benzo[*g,h,i*]perylene	6.1±2.9	2.6±0.8	1.5	2.7					4.1	0.31
Sum PAHs	75.1±32.7	32.7±11.8								3.17

The abundance of compounds such as benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, benzo[*g,h,i*]perylene that are characteristic of vehicular emissions suggests that traffic is probably one of the most important sources of PAH emissions at the investigated sites in Kaunas. However, although the traffic intensity is lower at Location 1 than at Location 2, levels of certain individual PAHs at Location 1 were found to be up to four times greater than at Location 2, possibly because most buildings are heated by the district supply system at Location 2, while at Location 1 most households have independent heating systems. To identify the sources of the various PAH emissions more clearly, the data were subjected to correlation analysis, factor analysis and a comparative analysis of indicative ratios and fractions. The intercorrelation matrix of the measured PAH concentrations are shown in **Table 4.9**.

As can be seen from the table, inter-correlation among PAH concentrations are generally very high for most of PAHs analysed. At Location 2 low molecular weight (LMW) compounds correlate with high molecular weight (HMW) compounds better than at Location 1, but the correlations of chrysene, benzo[*a*]pyrene and dibenz[*a,h*]anthracene with other PAH concentrations is weaker. Diesel fuel reportedly contains high concentrations of LMW compounds, but because of pyrosynthesis during combustion in diesel engines the emission rate of HMW PAHs is greater than that of LMW PAHs (Lim et al. 2005; Marr et al. 2006). Therefore, the high correlations of LMW and HMW PAH concentrations may be due to emissions from diesel engines.

It should be noted that correlations of 1-methylphenanthrene with most of the other PAHs, including high molecular weight compounds, are very high. The high observed concentrations of alkylated PAHs relative to unsubstituted PAHs may indicate the presence of petrogenic sources (Simo et al. 1999; Soderstrom and Bergquist 2003; Gustafson and Dickhut 1997). Although the concentrations of methylated compounds observed in this study were lower than those of the corresponding unsubstituted species, the abovementioned correlations between the concentration of 1-methylphenanthrene and those of most of the other PAH analytes suggests that significant quantities of the observed PAHs were derived from unburned fuel.

Table 4.9. Spearman rank correlation matrix between PAH compounds

Location 1

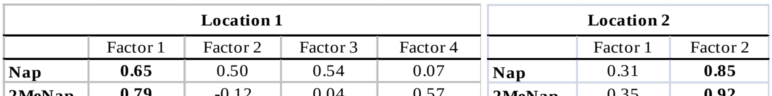
	Nap	2MeNap	1MeNap	Bhp	Acy	Fl	Phe	Ant	2MePhe	1MePhe	1MeAnt	2PhNap	Fla	Pyr	MePyr	Ret	BaAnt	Chry	BbF	BkF	BaP	Per	IdP	DbA	BghiP	
Nap		0.61	0.72	0.68	0.71	0.75	0.84	0.76	0.76	0.72	0.74	0.75	0.66	0.67	0.66	0.64	0.55	0.59	0.63	0.63	0.58	0.40	0.54	-0.05	0.34	Nap
2MeNap	0.82		0.62	0.48	0.73	0.67	0.58	0.45	0.58	0.65	0.58	0.58	0.52	0.52	0.42	0.49	0.30	0.32	0.42	0.37	0.24	0.14	0.25	0.09	-0.02	2MeNap
1MeNap	0.83	0.97		0.79	0.34	0.59	0.46	0.13	0.30	0.25	0.27	0.28	0.14	0.14	0.11	0.12	-0.04	-0.03	0.08	0.06	0.00	-0.22	0.20	-0.41	-0.21	1MeNap
Bhp	0.53	0.77	0.82		0.60	0.78	0.59	0.46	0.49	0.45	0.49	0.51	0.38	0.37	0.35	0.35	0.22	0.27	0.34	0.31	0.22	-0.07	0.26	-0.35	-0.16	Bhp
Acy	0.77	0.90	0.93	0.72		0.92	0.92	0.88	0.85	0.82	0.80	0.77	0.71	0.70	0.66	0.69	0.60	0.64	0.65	0.63	0.57	0.45	0.37	0.21	0.38	Acy
Fl	0.75	0.92	0.97	0.73	0.93		0.87	0.75	0.68	0.59	0.61	0.58	0.49	0.45	0.41	0.39	0.35	0.41	0.35	0.37	0.37	0.21	0.07	0.17	0.13	Fl
Phe	0.75	0.92	0.95	0.73	0.98	0.97		0.95	0.95	0.91	0.93	0.92	0.87	0.85	0.84	0.82	0.79	0.80	0.81	0.82	0.77	0.65	0.65	0.15	0.60	Phe
Ant	0.75	0.92	0.95	0.73	0.98	0.97	1.00		0.98	0.97	0.97	0.96	0.94	0.93	0.92	0.89	0.87	0.90	0.89	0.90	0.81	0.71	0.64	0.20	0.65	Ant
2MePhe	0.75	0.92	0.95	0.73	0.98	0.97	1.00	1.00		0.98	0.99	0.98	0.96	0.95	0.93	0.91	0.91	0.91	0.92	0.93	0.87	0.78	0.70	0.21	0.70	2MePhe
1MePhe	0.72	0.88	0.93	0.68	0.97	0.98	0.98	0.98	0.98		0.99	0.98	0.98	0.97	0.96	0.95	0.91	0.92	0.95	0.95	0.84	0.78	0.74	0.23	0.73	1MePhe
1MeAnt	0.78	0.95	0.98	0.78	0.95	0.98	0.98	0.98	0.98	0.97		0.99	0.97	0.96	0.95	0.93	0.92	0.92	0.94	0.95	0.87	0.79	0.73	0.18	0.71	1MeAnt
2PhNap	0.75	0.92	0.95	0.73	0.98	0.97	1.00	1.00	1.00	0.98	0.98		0.98	0.97	0.96	0.93	0.91	0.92	0.93	0.95	0.86	0.76	0.77	0.13	0.70	2PhNap
Fla	0.75	0.92	0.95	0.73	0.98	0.97	1.00	1.00	1.00	0.98	0.98	1.00		0.99	0.99	0.97	0.95	0.96	0.97	0.98	0.85	0.84	0.83	0.23	0.81	Fla
Pyr	0.72	0.88	0.93	0.68	0.97	0.98	0.98	0.98	0.98	1.00	0.97	0.98	0.98		0.99	0.98	0.96	0.97	0.98	0.99	0.86	0.84	0.84	0.24	0.81	Pyr
MePyr	0.77	0.88	0.93	0.67	0.90	0.98	0.95	0.95	0.95	0.97	0.97	0.95	0.95	0.97		0.98	0.97	0.97	0.99	0.99	0.87	0.86	0.85	0.23	0.83	MePyr
Ret	0.75	0.92	0.95	0.73	0.98	0.97	1.00	1.00	1.00	0.98	0.98	1.00	1.00	0.98	0.95		0.93	0.93	0.97	0.97	0.84	0.82	0.83	0.20	0.78	Ret
BaAnt	0.73	0.85	0.90	0.62	0.93	0.97	0.97	0.97	0.97	0.98	0.95	0.97	0.97	0.98	0.98	0.97		0.99	0.97	0.98	0.93	0.95	0.74	0.38	0.88	BaAnt
Chry	0.73	0.53	0.58	0.33	0.62	0.63	0.63	0.63	0.63	0.65	0.62	0.63	0.63	0.65	0.73	0.63	0.75		0.97	0.98	0.92	0.93	0.75	0.38	0.87	Chry
BbF	0.72	0.83	0.87	0.53	0.90	0.95	0.93	0.93	0.93	0.97	0.92	0.93	0.93	0.97	0.97	0.93	0.98	0.73		0.98	0.88	0.88	0.82	0.24	0.84	BbF
BkF	0.73	0.85	0.90	0.62	0.93	0.97	0.97	0.97	0.97	0.98	0.95	0.97	0.97	0.98	0.98	0.97	1.00	0.75	0.98		0.90	0.89	0.83	0.27	0.85	BkF
BaP	0.73	0.53	0.58	0.33	0.62	0.63	0.63	0.63	0.63	0.65	0.62	0.63	0.63	0.65	0.73	0.63	0.75	1.00	0.73	0.75		0.88	0.57	0.25	0.69	BaP
Per	0.63	0.78	0.85	0.63	0.92	0.93	0.95	0.95	0.95	0.97	0.92	0.95	0.95	0.97	0.95	0.95	0.98	0.73	0.95	0.98	0.73		0.60	0.57	0.93	Per
IdP	0.73	0.85	0.90	0.62	0.93	0.97	0.97	0.97	0.97	0.98	0.95	0.97	0.97	0.98	0.98	0.97	1.00	0.75	0.98	1.00	0.75	0.98		-0.06	0.72	IdP
DbA	0.53	0.45	0.47	0.10	0.63	0.57	0.58	0.58	0.58	0.65	0.50	0.58	0.58	0.65	0.58	0.58	0.67	0.67	0.75	0.67	0.67	0.63	0.67		0.59	DbA
BghiP	0.73	0.85	0.90	0.62	0.93	0.97	0.97	0.97	0.97	0.98	0.95	0.97	0.97	0.98	0.98	0.97	1.00	0.75	0.98	1.00	0.75	0.98	1.00	0.67		BghiP
	Nap	2MeNap	1MeNap	Bhp	Acy	Fl	Phe	Ant	2MePhe	1MePhe	1MeAnt	2PhNap	Fla	Pyr	MePyr	Ret	BaAnt	Chry	BbF	BkF	BaP	Per	IdP	DbA	BghiP	

Location 2

Pyrene and chrysene are known to be emitted during industrial oil burning, fluoranthene and pyrene are typically emitted by both petrol and diesel vehicles, while chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene are characteristic of emissions from diesel vehicles (Rajput et al. 2010). The high correlations between the concentrations of chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, fluoranthene and pyrene corroborate the importance of traffic as a source of PAH emissions at the investigated sites. However, it should be noted that the correlation of retene with HMW PAHs is also very high. Retene has been suggested as an indicator of biomass burning and has a unique formation mechanism or environmental pathway (Li et al. 2009; McDonald et al. 2000). Wood and peat are very commonly-used fuels for heating individual houses in Kaunas.

To obtain further indications of the likely origins of the detected PAHs, sum concentrations of nine major combustion-derived PAHs (CPAHs; fluoranthene, pyrene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[*1,2,3-c,d*]pyrene, benzo[*g,h,i*]perylene and CPAH/Sum PAH ratios were calculated. These ratios are reported to be 0.51, 0.41, and 0.30 for emissions from automobiles with catalytic converters, other automobiles, and heavy duty diesel trucks, respectively (Rogge et al. 1993). The CPAH: Sum PAH ratio at Location 1 was as high as 0.78, suggesting that traffic is not the only important source of CPAHs in Kaunas.

Table 4.10. Results of factor analysis of PAH concentrations



Location 1				
	Factor 1	Factor 2	Factor 3	Factor 4
Nap	**0.65**	0.50	0.54	0.07
2MeNap	**0.79**	-0.12	0.04	0.57
1MeNap	**0.94**	-0.03	0.32	-0.03
Bph	**0.81**	0.18	0.43	0.27
Acy	**0.99**	0.12	0.04	0.03
Fl	**0.99**	0.07	0.04	-0.09
Phe	**0.98**	0.16	0.11	-0.04
Ant	**0.94**	0.30	0.16	0.05
2MePhe	**0.95**	0.26	0.14	0.00
1MePhe	**0.95**	0.28	0.12	0.07
1MeAnt	**0.90**	0.33	0.24	0.11
2PheNap	**0.93**	0.32	0.18	0.07
Fla	**0.82**	0.53	0.13	0.18
Pyr	0.64	**0.73**	0.12	0.21
MePyr	0.44	**0.82**	0.22	0.29
Re	0.17	0.58	0.32	**0.73**
BaA	0.18	**0.97**	0.12	0.07
Chry	0.28	**0.95**	-0.02	0.14
BbF	0.45	**0.83**	0.32	0.07
BkF	0.37	**0.86**	0.33	0.05
BaP	0.04	**0.90**	0.07	0.00
Per	-0.17	**0.96**	-0.18	-0.07
IdP	0.42	0.62	0.56	0.01
DbaA	-0.35	0.04	**-0.91**	-0.09
BghiP	0.05	**0.88**	-0.24	-0.09

Location 2		
	Factor 1	Factor 2
Nap	0.31	**0.85**
2MeNap	0.35	**0.92**
1MeNap	0.62	**0.76**
Bph	0.65	0.63
Acy	**0.86**	0.49
Fl	**0.85**	0.52
Phe	**0.90**	0.41
Ant	**0.90**	0.43
2MePhe	**0.90**	0.42
1MePhe	**0.91**	0.40
1MeAnt	**0.92**	0.39
2PheNap	**0.92**	0.38
Fla	**0.91**	0.41
Pyr	**0.90**	0.43
MePyr	**0.88**	0.47
Re	**0.92**	0.38
BaA	**0.86**	0.50
Chry	**0.90**	0.35
BbF	**0.90**	0.44
BkF	**0.89**	0.46
BaP	**0.89**	0.32
Per	**0.87**	0.48
IdP	**0.87**	0.47
DbaA	**0.92**	0.18
BghiP	**0.85**	0.51

Factor analysis of the measured PAH concentrations provided further insights into the influence of traffic and fuel combustion on the air quality in Kaunas (**Table 4.10**). The analysis revealed two factors influencing PAH concentrations at Location 2 and four factors at Location 1. It is apparent that the retene and dibenz[*a*,*h*]anthracene observed at Location 1 arise from a different source from that of the other combustion PAHs. By contrast, at Location 2, it is likely that traffic is the major source of PAHs, with a small quantity of the most volatile PAHs arising from a different source.

As discussed by Saarnio et al. (2008), neither the levels of individual PAHs nor the ratios of their concentrations can be regarded as highly specific indicators of emission sources for several reasons: PAHs originate from a large variety of combustion sources with only slightly different emission profiles; PAHs have widely differing vapour pressures and reactivities; and particulate PAH concentrations depend on the ambient temperature and solar radiation intensity as well as on the total particulate mass concentration (Saarnio et al. 2008). Furthermore, some compounds, especially those that are semi-volatile (2-4 rings), may be lost during long sampling campaigns. Nevertheless, their concentration ratios can give hints about the relative importance of possible sources (see **Figure 4.11**).

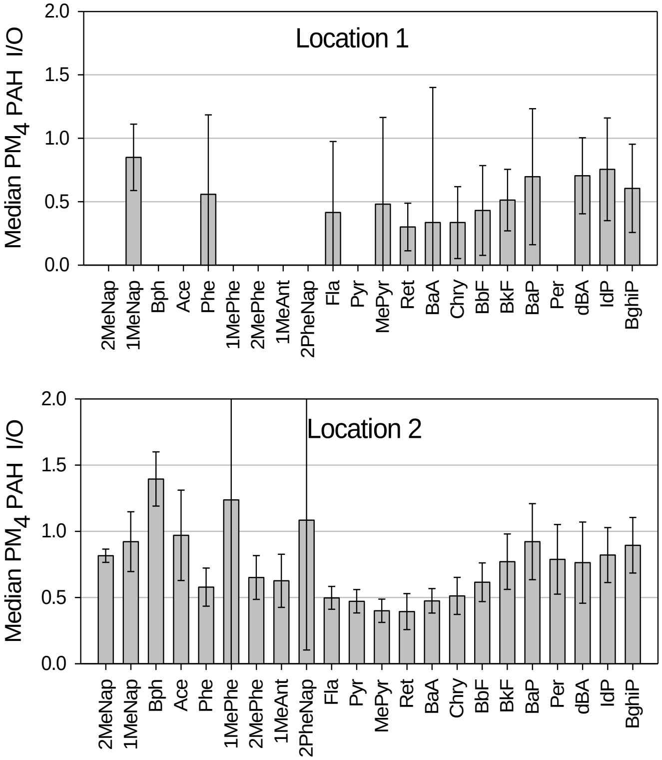


Figure 4.11. Ratios of indoor to outdoor (I/O) PAH concentrations in PM_4 at Locations 1 and 2

In addition, indicative PAH concentration fractions and ratios were calculated, and the results were compared to data from a comprehensive study of PAHs in size-segregated particulate matter from European urban sites performed by Saarnio et al. (2008) and from a similar study by Tang et al. (2005) in China, Japan and Russia (Saarnio et al. 2008; Stracquadaniov et al. 2007). Only data from cold seasons were included.

The observed indeno[*1,2,3-c,d*]pyrene: (indeno[*1,2,3-c,d*]pyrene+ benzo[*g,h,i*]perylene) ratio is comparable to that reported in other studies, confirming that traffic is a significant source of PAH emissions at both locations examined. This conclusion is further supported by the benz[*a*]anthracene: (benz[*a*]anthracene+chrysene) and benzo[*a*]pyrene: (benzo[*a*]pyrene+chrysene) ratios. The influence of fossil fuel combustion on PAH levels in Kaunas is indicated by the benzo[*a*]pyrene: benzo[*g,h,i*]perylene and benzo[*a*]pyrene: chrysene ratios.

The ratio of air-borne PAH concentrations in indoor environments to those in outdoor environments (I/O ratios) can be used to determine whether the major PAH source(s) are located indoors (in which case I/O > 1) or outdoors (in which case I/O < 1). I/O ratios for PAHs bound to the PM_4 fraction are presented in **Figure 4.11**. The low observed I/O ratios may indicate that PAH emissions at the locations studied arise primarily from outdoor sources. It should be noted that the buildings at both locations have old windows with wooden frames that are fairly permissive in terms of air circulation. Thus, residents of older buildings that are close to roads may be significantly exposed to PAHs and PM in general.

Influence of long-distance transported pollution on $PM_{2.5}$ and PAH levels. The trajectory analysis showed that air masses coming from Eastern Europe carried significantly higher levels of pollutants than those from other regions; air masses from other regions in Europe all had similar $PM_{2.5}$ levels (see **Table 4.11**). We would prefer, air masses from the Nordic countries usually carry lower pollutant loads, as the median levels suggest, but high concentrations in masses from the Nordic sector on some days probably explains the lack of significant differences in $PM_{2.5}$ levels (Orru et al. 2010; Johanesson et al. 2010).

Table 4.11. Summary of the trajectory analysis, the four different classes and the number of trajectories belonging to each class (within brackets), mean and median $PM_{2.5}$ concentrations and the p-values for the Wilcoxon's rank sum test between pairs of trajectory classes

Region	$PM_{2.5}$ (μg/m^3)		p-value of the rank sum test		
	Mean	Median	Russia	Western Europe	Nordic
Eastern Europe (9)	45.7	42.0	0.0318	0.0119	0.0464
Russia (10)	27.2	23.7		0.9575	0.4716
Western Europe (6)	23.3	24.9			0.8388
Nordic (13)	25.5	15.4			
Unclassified (5)	25.3	16.8			

For a few of the PAHs (naphthalene, 2-methylnaphthalene, acenaphthylene, fluorene, phenantrene, and anthracene; not presented in the table), significantly higher concentrations were observed on days when the air originated from Eastern Europe rather than from one or more of the other regions, but in most cases no such differences were observed.

The higher concentrations of $PM_{2.5}$ on days when the air originated from Eastern Europe was expected because anthropogenic emissions in Eastern Europe are higher than in the other regions. However, no consistent differences in levels of PAHs in air originating from different regions were observed, suggesting that local sources contribute most of the sampled concentrations of the PAHs.

Summary of findings

The mean outdoor $PM_{2.5}$ concentration at Location 1 in winter was 34.5±15.2 $\mu g/m^3$ while in spring it was 24.7±12.2 $\mu g/m^3$, at Location 2 the corresponding values were 36.7±21.7 $\mu g/m^3$ and 22.4±19.4 $\mu g/m^3$, respectively. The mean PM_{10} concentrations at Location 1 in winter and spring were 35.2±14.6 $\mu g/m^3$ and 41.7±11.8 $\mu g/m^3$, respectively, while at Location 2 the corresponding values were 39.7±20.3 $\mu g/m^3$ and 34.2±20.6 $\mu g/m^3$. $PM_{2.5}$ concentrations were lower during the spring sampling campaign, but no significant seasonal variations in PM_{10} concentrations were observed. This study demonstrates that PM levels in Kaunas are comparable to those observed in many other European locations.

The levels of most PAHs analyzed in this study, especially at Location 1, are notably higher than those reported elsewhere in Europe. The mean sum PAH concentrations at Locations 1 and 2 in the winter campaign were 75.1±32.7 ng/m^3 and 32.7±11.8 ng/m^3, respectively. The experimental results corroborated the hypotheses that 5-6 and 4-ring PAHs originate from automotive emissions, are bound to street dust and dispersed over the area. Thus, street dust may not only emit fugitive dust, but also be a substantial source of particle-bound PAHs. A trajectory analysis showed that long-range transport is also a source of $PM_{2.5}$ in the region, but the PAHs within the $PM_{2.5}$ are of local origin

4.2.2. Particulate and vapor phase polycyclic aromatic hydrocarbons in indoor and outdoor air of primary schools

Detailed aim of this research

The aim of this study was to characterized particulate and vapor phase PAHs in indoor and outdoor of primary schools of Kaunas city, Lithuania.

Experimental design

Sampling locations. The sampling campaign was performed during the winter of 2011/2012. The sampling period at each location was five working days. Daily $PM_{2.5}$ fraction samples at each location were collected for 8 hours (from 8AM to 4PM) representing the active period of school life, TSP and vapor phase samples were collected for 24 h. The sampling campaign included sampling locations at five primary schools in the city of Kaunas (population 311000 in 2012; total area 157 km^2), Lithuania. The primary schools were chosen with the aim to obtain the representative data from various urban environments. Premises in all sampling locations had natural ventilation systems, thus the classrooms were often ventilated by opening windows.

Table 4.12. Characteristics of the investigated five primary schools of Kaunas city, Lithuania

	Site #1	Site #2	Site #3	Site #4	Site #5
Location in city	Center	Suburb	Urban area	Urban area	Suburb
	Kęstučio g. 44	Romainių g. 28	T. Masiulio g. 10	Partizanų g. 46	Kariūnų pl. 5
Number of children	158	87	215	1123	310
Year of construction	1975	1969	1957	1969	1960
Stories	2	1	3	3	2
Ventilation type	Natural	Natural	Natural	Natural	Natural
Heating system	Centralized	Local/ natural gas	Centralized	Centralized	Local/ natural gas
Food coocking inside	Yes	Yes	Yes	Yes	Yes
Ventilating through windous	Often	Very rarely	Rarely	Rarely	Medium
Industy	None	None	A lot	None	None
Recently refurbishement	No	No	Yes	No	No
Vehicle thaffic intensity	High	Medium	High	Very high	Low
Surounding buildings	2-5 storey multifamily/office	1-2 storey single family	4-5 storey multifamily buildings	5-12 storey multifamily buildings	1-2 storey single family
Individual builers for heating in the neighborhood	None	Many	None	None	Many

The characteristics of sampling locations are presented in **Table 4.12**. The first location (site #1) was a kindergarten situated in the central part of the city (river valley area). The building was surrounded by 3-4 storey district heated buildings and streets with high traffic intensity (approx. 19000 vehicles/day). The second location (site #2) was a primary school located in the suburban area surrounded by the pine-tree forest. The third location (site #3) was a 3-storey primary school, representing a living area with an intensive industry and a heavy traffic. The fourth location (site #4) was a 3-storey primary school, representing multi-family apartment building area. The fifth location (site #5) was a primary school in a residential area with single family houses, equipped with the individual heating systems utilizing wood, natural gas and coal as fuel.

Sampling procedures. Three types of PAH samples were collected during the sampling campaign: particulate phase PAHs in $PM_{2.5}$ (particles, smaller than 2.5 μm in the aerodynamic diameter) and TSP (total suspended particles) fractions, as well as vapor phase PAHs. Particulate phase $PM_{2.5}$ samples were collected on quartz filters (Whatman International Ltd., UK; diameter 25 mm, pore size 1.6 μm) using Personal Environmental Monitor (PEM) samplers for respirable dust sampling with personal sampling pumps (MSP Corporation, USA) at the air flow rate of 10 lpm. Particulate phase TSP fraction samples were collected on glass microfiber filters (GF/A, Whatman International Ltd, UK, diameter 25 mm, pore size 1.6 μm) at a flow rate of 2 l/min. The vapor phase PAH samples were taken using XAD-2 sorbent tubes (SKC Inc., USA) at a flow rate of 2 l/min. The sampling air flow rate was adjusted using an automatic flow meter (Defender 510, MesaLabs, USA). Filters were heated at 500 ^{0}C for four hours before sampling in order to remove residual organic compounds. After sampling filters and sorbent tubes were placed in a cooling box, transported to the laboratory, and stored in a freezer at -20 ^{0}C.

The particulate phase ($PM_{2.5}$) samples were collected in parallel at three classrooms of the same school and one location outdoors. The concentrations of particulate phase (TSP fraction) and vapor phase PAHs were measured in one classroom of each school. The samplers in the classrooms were placed at two meter height and one meter distance from the walls. Outdoor samplers were put into special enclosure and attached to the window frame at three meters height. The special enclosures were constructed to protect samplers from rain and snow. Total, 100 daily ($PM_{2.5}$) 8 hour and 20 daily (TSP/XAD-2) 24 hour samples were collected.

Data analysis. Results of analyses were statistically processed using SPSS 12 software (IBM Corp., USA). Descriptive statistics were used for the representation of average PAH levels (median, 25th and 75th percentiles, minimum and maximum values). The factor analysis was used to identify possible sources of PAHs. The varimax raw rotation procedures were applied for normalization of factor axis. Each factor was considered as significant if the loading was higher than 0.6. Median values were determined to characterize Indoor/Outdoor and Diagnostic ratios of data sets. Friedman ANOVA method was used to compare indoor PAH concentrations at different classrooms of the same school. Toxicity (TEQ) and mutagenicity (MEQ) equivalent concentrations based on toxicity of benzo[*a*]pyrene were calculated similarly to Jung et al. (2010) and Castro et al. (2011).

Results and discussion

Variation of PAH concentrations in the indoor and outdoor air of schools. Cumulative concentrations of 15 analyzed PAHs (ΣPAHs) from five primary schools of Kaunas city are presented as boxplots in **Figure 4.12**. ΣPAHs in $PM_{2.5}$ fraction indoors ranged from 20.3 ng/m^3 (minimum) to 131.1 ng/m^3 (maximum), while average one school (median) concentration ranged from 31.9 to 72.8 ng/m^3, respectively. ΣPAHs in $PM_{2.5}$ outdoors ranged from 40.7 to 121.2 ng/m^3, median one school concentration ranged from 58.9 to 85.2 ng/m^3 respectively. In all sampling sites ΣPAHs in $PM_{2.5}$ fraction was significantly higher outdoors than indoors. The highest median value of ΣPAHs in $PM_{2.5}$ in outdoor air was observed at site #4 (85.2 ng/m^3), possibly reflecting cold start vehicle emissions from a nearby parking lot. The lowest median concentration was identified at site #5 (58.9 ng/m^3), which was situated in a relatively clean urban area. The indoor variation of ΣPAHs in $PM_{2.5}$ fraction was not statistically significant ($p > 0.05$) in most of the schools, except site #1, where one classroom has indicated significantly lower PAH levels. The variation of PAH concentration in Site #1 may be attributed to different distances of classroom from the street. One classroom was located the furthest from the street (some 100 m) compared to the other classrooms.

The analysis of PAH distributions between particulate and vapor phases revealed that the particulate phase (TSP) ΣPAHs ranged from 19.9 ng/m^3 (minimum) to 80.3 ng/m^3 (maximum), while vapor phase ΣPAHs ranged from 35.6 to 80.6 ng/m^3. Respectively, the median values of ΣPAH in TSP ranged from 36.1 ng/m^3 (site #3) to 63.2 ng/m^3 (site #4), while the median values of ΣPAH in vapor phase ranged from 67.3 ng/m^3 (site #4) to 372.5 ng/m^3 (site #2). Median values of ΣPAHs in vapor phase were five-fold higher compared to those in particulate phase. The same trends were observed in all sampling sites, except site #4, where median concentrations of vapor and particulate phases were almost equal. Daily variation of PAH concentration is illustrated in **Figure 4.12**. Seasonal variation PAH concentrations was not investigated in this research. The collected date provides outlook for the cold period of year, possibly representing highest pollution. We have not analyzed seasonal variation.

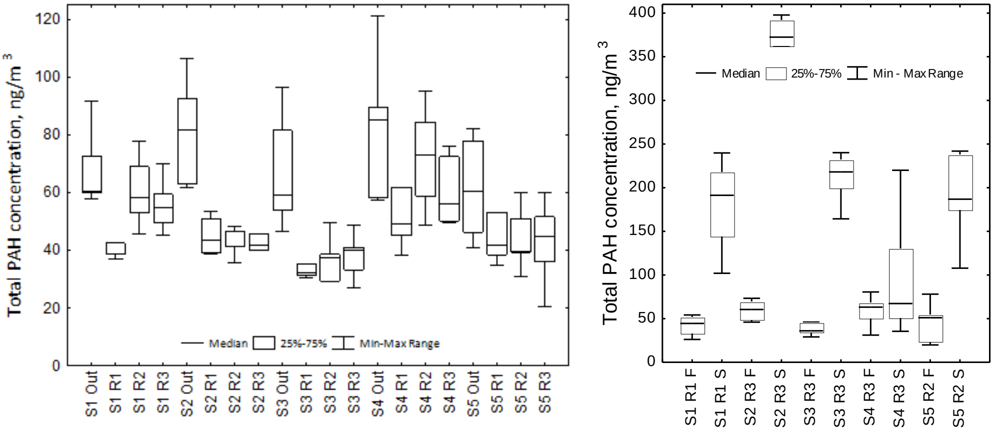


Figure 4.12. Particulate and vapor phase ΣPAH concentrations in various classrooms and schools. Left: concentrations of PAHs particulate phase ($PM_{2.5}$) indoors and outdoors; right: concentrations of total PAHs in vapor phase (S) vs. particulate (TSP) phase (F)

Individual PAHs have their own chemical, physical and toxicological properties, thus it is important to analyze concentration levels of individual compounds. The boxplots of 15 individual particulate phase ($PM_{2.5}$) PAH concentrations are presented in **Figure 4.13**. Concentrations of naphthalene appeared be the highest among 15 PAHs in all sampling sites, ranging from 0.1 to 115.3 ng/m^3, with the highest median concentration of 26.3 ng/m^3 at the site #4. Median concentrations of naphthalene at the sites #1, #2, #3 and #5 were very similar and ranged from 11.9 to 15.3 ng/m^3.

Among three-ring PAHs, phenantrene and fluorene were the most abundant in all sampling sites. For example, the concentration of phenantrene in all sites was remarkably high (up to 115.3 ng/m^3 at site #1). Median concentration values of phenantrene at all sampling sites varied from 2.49 to 6.35 ng/m^3 outdoors, and from 2.56 to 6.74 ng/m^3 indoors.

Four-ring compounds (pyrene to chrysene) reached high concentrations in some cases, for example 20 ng/m^3 at site #1. At the same time, average concentrations were at a level of 1.5 ng/m^3. A maximum concentration among all the sites of benzo[*a*]pyrene (five-ring PAH) ranged from 0.4 to 8.4 ng/m^3, median concentration ranged from 1.0 ng/m^3 in site #3 to 3.2 ng/m^3 in site #1. It must be pointed out that our measurement campaign was carried out in winter period and samples were taken only in day-time. The values registered in our study exceed the annual threshold values. At the same time, the registered values indicated actual exposure of school children, these cannot be directly compared, since our measurements were performed during peak pollution time.

Concentration levels of outdoor particulate phase PAHs were similar to those reported in earlier studies (**section 4.2.1**). The levels registered in Kaunas during both studies were higher compared to those measured in Western European cities (Johannesson et al. 2009) and similar to those in Eastern and Central European cities as well as Hangzhou (Saarnio et al. 2008; Zhu et al. 2009). This may be attributed to the prevailing influence of a rather old traffic fleet (the average age of vehicles in Lithuania is aprox. 12 years) as well as the impact of emissions from detached single family homes. This trend was especially pronounced for the city centre (site #1), where high concentrations of heavy PAHs were registered. For example the peak concentrations of benzo[*g,h,i*]perylene reached 45.1 ng/m^3. In other sites concentrations were at least two times lower, with only pronounced peaks of fluorene (sites #2-4) and anthracene (site #5).

Phase distribution of PAHs. The phase of individual compounds is very important considering transportation, penetration, decomposition processes and health risk assessment of PAHs (Zhou et al. 2013). The pathways of the transportation of particulate or vapor phase pollutants to the human body differ. PAHs in ambient air are divided between vapor and particulate phases depending on the volatility of a compound, ambient air temperature, humidity, and concentration of free radicals in the aerosol (Lohmann and Lammel 2004).

The gas-particle phase partition of 15 PAHs as obtained in this study showing phase distribution expressed as the mean of the relative concentration in both phases. Most of low molecular mass PAHs such as naphthalene, acenaphtylene and acenaphtene were partitioned in the vapor phase (79.6-100 %). Anthracene was found in particles only, except site #4 where the amount of anthracene in particulate phase constitutes of 94 % of total mass. Fluorene, phenanthrene, fluoranthene, and pyrene in all sites were almost equally divided between vapor and particle phases. The majority of high molecule mass PAHs from benz[*a*]anthracene to benzo[*h,g,i*]perylene were in particle phase (62.4-100 %).

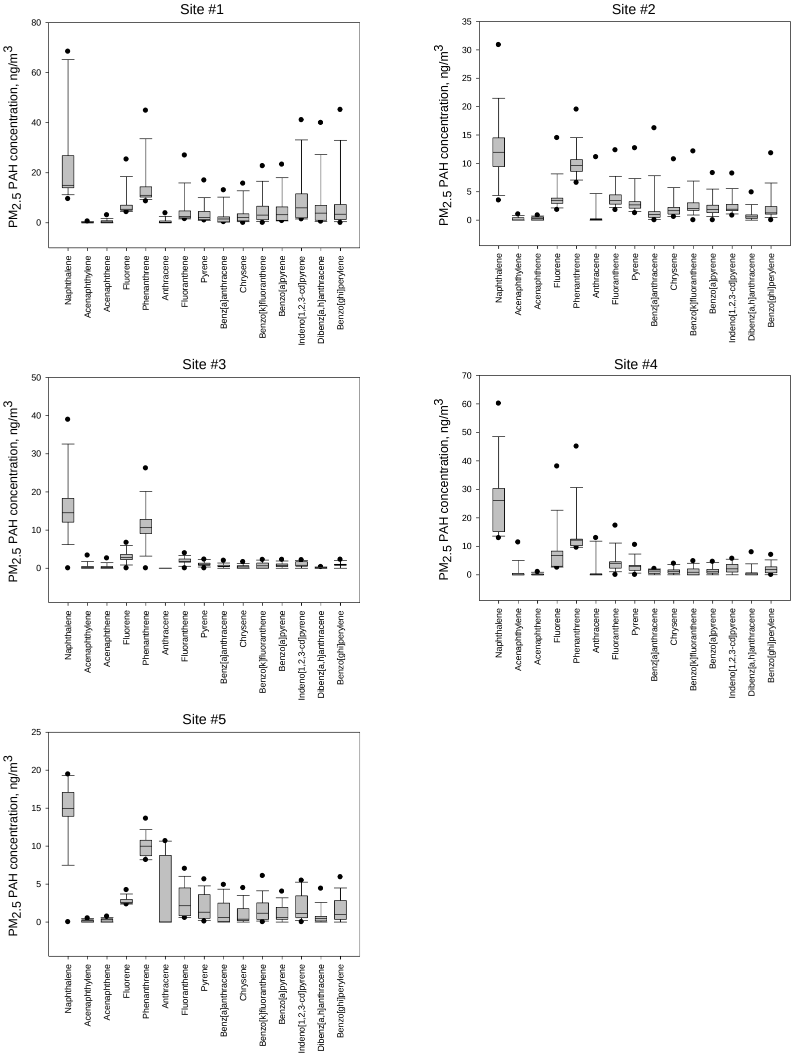


Figure 4.13. Ranges of concentrations of individual PAHs in particulate phase (PM$_{2.5}$) from investigated schools. Midlines represent median, box 25TH and 75TH percentiles, whiskers 5TH and 95TH percentiles, dots minimum and maximum concentrations

The phase distribution of PAHs in sites #1, #2 and #3 was very similar to that obtained during winter time sampling campaign by Zhou et al. (2013). In these sites heavy PAHs existed mostly in particulate phase, while lighter ones were most abundant in vapor phase. In sites #4 and #5, a larger share of heavy PAHs in vapor phase was registered. This may be explained by the evaporation of PAHs at a room temperature, after the penetration to the indoor environment from the outdoor air. Vestenius et al. (2011) pointed out that the concentration of PAHs in the particulate phase is closely related to the ambient temperature. A low ambient temperature resulted in higher amounts of PAHs in the particulate phase.

Sources analysis

Indoor to Outdoor ratios. One of the most important aspects of the air quality management process is the identification of the source of pollutants. Indoor-to-outdoor concentration ratios (I/O) of individual PAHs provide a rough identification of the pollution origin.

Average $PM_{2.5}$ I/O ratios of the 15 PAHs from all investigated sites are presented in **Figure 4.14**. In general, the observed outdoor PAH concentrations were higher than those indoor indicating mostly the contribution of outdoor pollution to the indoor air.

In all sampling sites ratios of naphthalene, fluorene, and phenantrene were close and sometimes exceeded unity, indicating an indoor source of these PAHs. This corresponds to the findings of (Jia and Batterman 2010), showing that higher concentrations of lighter PAHs could originate from the indoor activities, i.e. food cooking or evaporation from building materials. At sites #1 – #4 I/O ratios of acenaphytele and acenaphtene were about 0.3 and in some cases close to zero. Ratios of four-ring PAHs at sites # 3 and #4 were lower than 0.5, showing that outdoor sources of these compounds were prevailing. In all sampling sites, higher molecule mass PAHs showed lower I/O ratios, indicating outdoor origin of the contaminants.

Diagnostic ratios. The method of diagnostic ratios calculates binary ratios of two PAHs that are frequently found in emissions (Ravindra et al. 2008). Certain values of these ratios indicate particular sources of PAHs.

Diagnostic ratios of the total concentration of two and three-ring PAHs (ΣLMW) to four and six-ring PAHs (ΣHMW) indicate whether the origin of PAHs is pyrogenic or petrogenic. In case of $\Sigma LMW/\Sigma HMW > 1$, a possible source of PAHs is petrogenic; otherwise the source may be considered as pyrogenic (Zhang et al. 2008). In all sampling sites diagnostic ratios of $\Sigma LMW/\Sigma HMW$ were > 1 (**Table 4.13**), indicating petrogenic origin of PAHs. This is somewhat questionable, since it may be expected that the origin of most PAHs would be pyrogenic. In section 4.2.1 was indicated that motorized transport and burning of fuel for heating purposes were the two main sources of PAH emissions in Kaunas. This was confirmed that the ratio of benz[*a*]anthracene to chrysene in all sampling sites was > 0.35, indicating combustion of fuel (Yunker et all. 2002) and/or vehicular emissions (Akyüz and Çabuk 2010). In general, such ratios are very crude indicators of possible sources, especially in ambient air (Galarneau, 2008). On the other hand, our results might have been influenced by indoor cooking emissions, which have been shown to have the $\Sigma LMW/\Sigma HMW > \sim 5$ (Li et al. 2003).

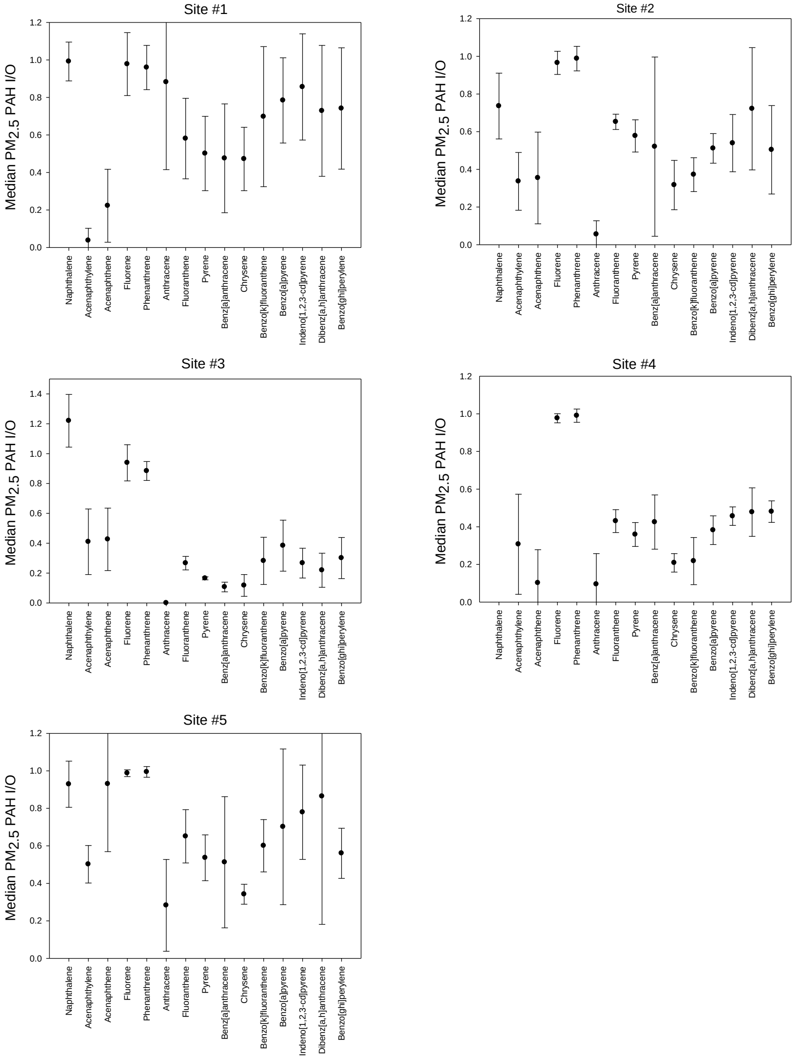


Figure 4.14. Average of particulate phase $PM_{2.5}$ fraction PAHs Indoor to Outdoor ratios from different sampling sites. Midpionts represents average, whiskers are minimum and maximum values

The traffic was the most likely source of PAHs at Sites #1 and #4. These locations were situated in a close vicinity to high-traffic streets and equipped with district heating system. Sites #2 and #5 were located in residential areas with single family houses. Most of which were equipped with autonomous fuel burning systems and utilized heat from wood, coal, peat or natural gas. In these sampling sites possible sources of PAHs were combined emissions from fuel burning and motorized transport. Site # 3 was located in the living area, close to an industrial site (a steel smelting factory and a regional power plant) and heavy traffic streets.

The ratios of the concentrations of combustion PAHs (ΣCPAH - fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-c,d*]pyrene, benzo[*g,h,i*]perylene) and total PAHs (ΣPAHs) in all sampling sites were < 1. According to Ravindra et al. (2008) in case of ratio equal to unity, combustion of fossil fuels is the primary source of PAHs.

The ratio of fluoranthene/(fluoranthene+pyrene) in all sampling sites (indoor and outdoor measurements) exceeded value 0.5. This indicates of the combustion of wood and/or coal as the source of PAHs emissions.

The ratios of indeno[*1,2,3-c,d*]pyrene and benzo[*g,h,i*]perylene in all sampling sites were close to 0.5, again indicating wood and/or coal combustion (Yunker et al. 2002). The ratios of benzo[*a*]pyrene and benzo[*g,h,i*]perylene in sampling sites #1 and #3 were ~ 0.6, and in sites #2, #4 and #5 the ratio was > 0.6 indicating traffic emissions (Katsoyiannis et al. 2007). The ratios of benzo[*a*]pyrene and chrysene benzo[*a*]pyrene /(benzo[*a*]pyrene + chrysene) in all sampling sites ranged from 0.32 to 0.66 and were close to values indicating diesel fuel combustion emissions - from 0.46 to 0.73, (Sienra et al. 2005; Simcik, et al. 1999).

Most of observed PAH diagnostic ratios indicated traffic (with a contribution of diesel) and fossil fuel (with contribution of wood) combustion as main sources of PAHs in schools. In sampling sites #1 and #4 main influencing source was vehicle emissions, in sites #2 and #5 mix of vehicles and wood/coal combustion. In sampling site #5 the main sources were mixture of vehicle and industrial burning processes.

Table 4.13. Diagnostic ratios of PAHs from schools in Kaunas

Diagnostic ratio	Site #1		Site #2		Site #3		Site #4		Site #5	
	Out.	Ind.	Out.	Ind.	Out.	Ind.	Out.	Ind.	Out.	Ind.
Fluorene/(Fluorene + Pyrene)	0.64	0.79	0.37	0.63	0.37	0.75	0.38	0.74	0.54	0.77
Anthracene/(Anthracene + Phenanthrene)	0.02	0.03	0.51	0.02	n.d.	0.03	0.51	0.14	0.50	0.51
Fluoranthene/(Fluoranthene + Pyrene)	0.55	0.58	0.53	0.57	0.53	0.63	0.54	0.60	0.56	0.64
Benz[*a*]anthracene/(Benz[*a*]anthracene + Chrysene)	0.47	0.40	0.37	0.39	0.60	0.51	0.24	0.42	0.56	0.50
Indeno[*1,2,3-c,d*]pyrene/(Indeno[*1,2,3-c,d*]pyrene + Benzo[*h,g,i*]perylene	0.52	0.50	0.49	0.56	0.49	0.50	0.54	0.52	0.54	0.51
Benzo[*a*]pyrene/Benzo[h,g,i]perylene	0.62	0.62	0.91	1.32	0.57	0.73	0.87	0.71	0.64	0.73
Phenanthrene/(Phenanthrene+Anthracene)	0.98	0.97	0.49	0.98	n.d.	0.97	0.49	0.86	0.50	0.49
Pyrene/Benzo[*a*]pyrene	1.51	0.94	1.26	1.56	3.30	1.70	2.30	1.98	3.32	1.66
Fluoranthene/Pyrene	1.22	1.40	1.12	1.34	1.11	1.76	1.15	1.50	1.28	1.81
Indeno[*1,2,3-c,d*]pyrene/Benzo[h,g,i]perylene	1.07	1.03	0.96	1.30	0.97	1.00	1.16	1.10	1.15	1.05
Benzo[*a*]pyrene/(Benzo[*a*]pyrene+Chrysene)	0.46	0.62	0.41	0.56	0.37	0.66	0.32	0.48	0.32	0.54
ΣLMW/ΣHMW	1.26	2.93	0.72	2.13	1.16	4.34	1.78	4.90	6.24	5.44
ΣCPAH/ΣPAHs	0.43	0.30	0.62	0.38	0.57	0.18	0.44	0.23	0.19	0.30

Factor analysis. The factor analysis is another method used to identify and quantify potential sources of PAHs indoors and outdoors based on the correlation and joint variation of PAH concentrations (Ravindra et al. 2008). Results of the factor analysis are presented in

Table 4.14. The analysis suggested two main sources of PAHs combustion of fuel (sites #2 and #5) and vehicle emissions (#1, #3 and #4). A separate factor in site #3 may indicate the influence of industrial activities on PAH concentration. The results from indoors and outdoors of the same sampling site were different, potentially indicating the influence of the volatility and phase-transformation of individual PAHs as well as the presence of indoor sources, such as cooking.

Table 4.14. Results of factor analysis

PAH	Site #1 In			Site #1 Out			Site #2 In		Site #2 Out				Site #3 In			Site #3 Out			Site #4 In				Site #4 Out		Site #5 Int				Site #5 Out		
	F1	F2	F3	F1	F2	F3	F1	F2	F1	F2	F3	F4	F1	F2	F3	F1	F2	F3	F1	F2	F3	F4	F1	F2	F1	F2	F3	F4	F1	F2	F3
Naphthalene	0.00	**0.64**	0.38	0.02	0.38	**-0.83**	0.21	**-0.89**	**-0.91**	-0.37	0.21	0.01	-0.24	0.09	**-0.95**	-0.25	0.33	**-0.90**	**0.98**	0.14	0.06	0.00	-0.40	**-0.80**	0.25	**0.95**	0.05	0.02	-0.21	**-0.97**	-0.14
Acenaphthylene	-0.08	-0.05	**-0.95**	-0.26	-0.32	**-0.91**	-0.07	**-0.74**	-0.09	0.24	-0.01	**0.97**	-0.17	0.18	**-0.95**	**-0.76**	0.55	0.08	0.04	-0.53	0.41	-0.39	0.28	**0.93**	**0.94**	0.04	0.22	-0.14	0.11	**-0.96**	-0.24
Acenaphthene	**0.86**	-0.27	-0.23	-0.20	-0.03	**-0.92**	-0.54	0.18	**-0.75**	-0.52	0.27	-0.30	-0.06	0.10	**-0.98**	-0.18	**-0.98**	0.04	-0.05	-0.01	**-0.93**	-0.12	-0.42	**0.89**	-0.10	0.02	0.07	**0.96**	-0.22	**-0.96**	0.15
Fluorene	0.10	**0.97**	0.11	0.60	**-0.62**	-0.29	0.24	**-0.95**	0.40	0.31	**0.73**	-0.46	-0.14	**0.86**	-0.46	-0.54	-0.15	**-0.82**	**0.99**	0.11	0.03	-0.05	-0.43	**-0.89**	0.48	-0.71	-0.08	0.23	-0.03	**-0.65**	**-0.76**
Phenanthrene	0.10	**0.98**	0.10	**0.94**	0.25	-0.22	-0.07	**-0.97**	-0.19	0.28	**0.94**	0.05	-0.08	**0.94**	-0.26	**-0.72**	0.55	-0.39	**0.97**	0.20	0.03	0.03	0.51	**-0.85**	**0.70**	0.46	0.04	0.27	**0.83**	0.21	0.36
Anthracene	**0.95**	-0.14	0.09	0.11	**0.88**	0.03	**-0.98**	-0.05	0.11	-0.47	**0.87**	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	-0.07	0.14	**0.95**	**-0.95**	-0.29	-0.49	0.30	-0.26	**-0.63**	**-0.97**	-0.22	-0.01
Fluoranthene	0.15	**0.98**	-0.01	**0.98**	-0.13	0.16	**-0.97**	-0.20	-0.13	**0.98**	0.08	0.16	0.17	**0.94**	0.07	**0.90**	0.11	0.35	**0.88**	0.42	0.01	-0.01	**0.99**	0.09	**0.95**	-0.10	0.06	0.09	**1.00**	0.05	-0.02
Pyrene	0.24	**0.96**	-0.05	**0.97**	-0.13	0.21	**-0.99**	-0.11	-0.14	**0.97**	0.09	0.17	0.51	**0.80**	-0.02	**0.92**	0.10	0.37	**0.80**	0.55	0.02	0.00	**0.99**	0.08	**0.96**	-0.08	0.05	0.03	**1.00**	0.04	-0.03
Benz[a]anthracene	**0.90**	0.41	0.01	**0.88**	-0.11	0.46	**-0.98**	-0.01	0.22	**0.97**	-0.01	-0.07	**0.92**	0.17	0.10	**0.94**	0.01	0.34	0.19	**0.84**	0.06	0.03	**1.00**	0.06	**0.96**	0.04	0.23	0.06	**0.98**	0.04	0.17
Chrysene	**0.61**	0.77	-0.04	**0.81**	-0.03	0.58	**-0.99**	0.01	0.42	**0.88**	0.18	0.14	**0.98**	0.00	0.05	**0.93**	0.00	0.34	0.22	**0.83**	-0.13	0.14	**1.00**	0.02	**0.95**	0.10	0.26	0.01	**0.89**	0.09	0.46
Benzo[k]fluoranthene	**0.93**	0.32	0.05	**0.94**	-0.27	0.14	**-0.97**	0.00	0.54	0.44	**0.71**	-0.02	**0.93**	-0.01	0.12	**0.90**	0.00	0.43	0.19	**0.68**	0.55	0.18	**0.95**	-0.31	**0.81**	0.19	0.46	0.10	**0.83**	0.14	0.54
Benzo[a]pyrene	**0.92**	0.38	0.07	0.16	0.53	**0.83**	**-0.94**	0.09	**0.67**	0.60	0.42	-0.16	**0.95**	0.02	0.16	**0.91**	0.03	0.34	0.53	**0.80**	0.14	-0.14	**1.00**	-0.02	**0.77**	0.13	0.58	0.08	**0.84**	0.10	0.54
Indeno[1,2,3-cd]pyrene	**0.90**	0.43	0.08	0.18	**0.74**	0.65	**-0.96**	0.06	**0.95**	0.12	0.09	-0.27	**0.85**	0.22	0.27	**0.88**	-0.02	0.44	0.43	**0.85**	-0.03	-0.24	**1.00**	0.02	**0.70**	0.07	**0.70**	0.11	**0.96**	0.06	0.25
Dibenz[a,h]anthracene	**0.96**	0.01	0.12	-0.49	**0.85**	-0.16	**-0.94**	-0.15	**0.94**	-0.18	0.28	0.03	0.26	**0.58**	0.44	**0.67**	0.34	0.66	**0.95**	0.25	0.06	0.02	**0.96**	0.16	0.00	0.08	**0.98**	0.10	**0.61**	0.00	0.77
Benzo[ghi]perylene	**0.91**	0.28	-0.03	-0.21	**0.95**	0.20	**-0.99**	-0.03	**0.95**	-0.24	0.17	-0.11	**0.88**	0.06	0.25	**0.77**	-0.10	0.63	**0.68**	0.68	0.00	-0.12	**1.00**	0.04	0.51	-0.09	**0.81**	0.00	**0.90**	0.07	0.42
Expl. Var.	7.19	5.56	1.16	5.91	4.04	4.30	9.83	3.32	5.29	5.13	3.15	1.43	5.53	3.61	3.44	8.34	1.85	3.47	6.25	4.59	1.40	1.22	10.53	4.05	7.54	1.81	2.91	1.53	8.98	3.36	2.46
Prp. Totl.	0.48	0.37	0.08	0.39	0.27	0.29	0.66	0.22	0.35	0.34	0.21	0.10	0.40	0.26	0.25	0.60	0.13	0.25	0.42	0.31	0.09	0.08	0.70	0.27	0.50	0.12	0.19	0.10	0.60	0.22	0.16

Health risk assessment. The calculated health risk assessment indicators are presented in **Table 4.15**. Outdoor TEQ(BaP) were higher than indoor one in all sites. In each classroom of the same school the equivalent cancerogenic and mutagenic concentrations were similar. The lowest outdoor and indoor TEQ(BaP) and MEQ(BaP) were observed in site #3. This could be associated with the minimal ventilation through windows in order to prevent heat lost.

Table 4.15. Calculated BaP cancerogenic TEQ(BaP) and mutagenic MEQ(BaP) equivalent concentrations, ng/m^3

	Site #1				Site #2				Site #3				Site #4				Site #5			
	Out.	R1	R2	R3	Out.	R1	R2	R3	Out.	R1	R2	R3	Out.	R1	R2	R3	Out.	R1	R2	R3
TEQ(BaP)	73.96	50.81	30.76	44.09	13.89	7.59	4.55	9.86	6.75	1.88	1.20	1.45	9.55	4.64	11.59	3.47	9.83	4.46	3.44	2.27
MEQ(Bap)	19.25	14.23	8.51	14.56	9.05	3.86	3.48	5.46	5.75	2.00	0.81	1.42	8.13	3.30	4.01	1.91	4.06	3.38	1.78	2.04

The highest carcinogenic equivalent concentration was observed in Site #1. These TEQ(BaP) equivalent concentration were several times higher that found by Halek et al. (2008). The values were 7-10 higher compared to other sites and were mostly influenced by higher concentrations of dibenzo[*a,h*]antracene and other four/five ring PAHs. Moreover, the PAH concentration indoors was the highest among tested sites. This is attributed to the location in the city center and a very intensive traffic around the site. The frequent opening of windows for ventilation, especially during high pollution events, had a significant influence on high indoor TEQ(BaP).

The equivalent concentrations as calculated in our study based on benzo[*a*]pyrene were at higher levels compared to those calculated by Jung et al. (2010). Equivalent toxicity concentration was several times higher than by Zorn et al. (2005) in all sampling sites.

The increased TEQ and MEQ levels in the city center location indicate that management of IAQ in a kindergarten based only on natural ventilation may not be feasible. The issues of pollutant penetration should be addressed by the installation of mechanical ventilation with the treatment of the incoming air. This would allow efficient removal of CO_2 from the indoors but at the same time providing higher quality air to the indoors.

Summary of findings

The concentrations of polycyclic aromatic hydrocarbons measured in primary schools during winter period in Kaunas, Lithuania were elevated, compared to other studies in Europe. This may be attributed to the increased emissions of pollutants from traffic and energy production during cold season. At the same time, the distribution of PAHs between particulate and vapor phases was similar to other studies, with the total concentrations of vapor phase PAHs exceeding particle phase PAH concentrations several times. The most abundant PAH in all sampling sites was naphthalene.

Several source apportionment methods were applied to determine possible sources of indoor and outdoor PAHs. Indoor/Outdoor ratios indicated that in most cases particulate and vapor phase PAHs penetrated from outdoors into the indoor air. Methods of diagnostic ratios and factor analysis determined two main sources PAHs: traffic emissions (school #4) and the combustion of biomass and fossil fuel in private houses for heating (school #2). Health risk assessment based on the carcinogenic equivalent concentrations revealed that the equivalent concentrations in the city center were several times higher compared to other similar studies indicating a potential to causing PAH-related adverse health effects.

4.2.3. Impact of local burning on Polycyclic Aromatic Hydrocarbons in indoor and outdoor air of residential houses

Detailed aim of this research

The target of this study was to characterize the emissions of size-segragated particulate and vapor PAHs in indoor and outdoor air in order to define outdoor-indoor transport of above mentioned pollutants from residential fuel burning.

Experimental design

Sampling locations. The city of Kaunas (pop. 311000; total area 157 km^2), Lithuania, is situated in the confluence of the Nemunas and Neris rivers. The central part of the city has a well-developed network of collective heating system. During recent years, due to the rising costs of fossil fuels, a shift from the collective heating to the in-house energy production became more prominent. These individual energy production units mostly depend on solid fuel (usually wood chips or pellets, sometimes hard coal), although natural gas supply lines are also widely available. A common phenomenon which occurs in the districts of lower income is the incineration of the calorific fraction of municipal waste, potentially contributing to serious emissions of aromatic species of hydrocarbons to the ambient air.

Six sampling locations in the city of Kaunas, Lithuania, were chosen. Four locations may be classified as “urban” and two locations as “suburban” sampling sites (see **Table 4.16**). The first and the second locations (henceforth referred to as L1 and L2) were “urban” sites situated at the city districts with high density of one-family (mostly lower income) houses (1000-1400 houses/km^2) built in the period of 1930-1970. The majority of houses had poor thermal insulation and utilize natural gas or solid fuel stoves and boilers.

Table 4.16. Characterization of locations, examined residential buildings and meteorological conditions

#	Street, district	Type of location	Type of ventilation	Measurement period	House density, house/km^2	Type of heating *	Type of windows **	Outdoor temperature, ^{0}C	Wind speed, m/s	Relative humidity, %
1	Kalpoko st., Zaliakalnis	Urban	Natural	01.20 - 01.25	1000-1400	S-B, NG	P, DP	-13	0.87	87
2	Vytenio st., Vilijampole	Urban	Natural	01.27 - 02.01 08.26 – 08.30	1000-1400	S-B, NG	W, D	-4 16	3.72 1,22	91 72
3	Lazdynu st., Rokai	Sub-urban	Natural	02.03 - 02.08	400-600	S-B, WP	W, T	0	2.18	92
4	Banaicio st., Vijukai	Sub-urban	Natural	02.17 - 02.22	< 400	HP	W, DP	-4	2.18	86
5	Lakunu st., Aleksotas	Urban	Natural	02.24 - 03.01 09.02 – 09.06	600-1000	S-B, W	P, T	1 13	3.24 2.66	76 78
6	Uosio st., Zaliakalnis	Urban	Natural	03.03 - 03.08	> 1400	S-B, NG	P, T	-1	3.17	67

Examined buildings:

* Type of heating: S-B - stove-boiler, HP - heat pump, W- wood, WP – wood pallets, NG - natural gas.

** Type of windows: P - plastic, W - wooden, D - double pane glass, T – triplex pane glass; DP - double pane glass packs.

The third location (L3) was a "suburban" site situated in the southern part of the Kaunas city. One-family houses were built during the period of 1960-1980; the average density of the buildings was 400-600 houses/km^2.The vast majority of buildings have poor thermal insulation and are heated by wood or other solid fuels.

The fourth location (L4) was a "suburban" site in the north-west part of the city. It was a rapidly developing low density one-family house district (< 400 houses/km^2) with newly built houses (2000-2012). The houses were well thermally insulated and equipped with up-to-date stoves and boilers. One third of the houses used natural gas or generate heat by heat pumps, the rest of the houses were heated by wood.

The fifth and the sixth locations (L5 and L6) were "urban" sites situated in the city districts built in the period of 1960-1980. Both locations are in the elevated one-family house areas close to the streets with an intensive motorised traffic. L5 was situated in the area with a fairly high density of one family houses (600-1000 houses/km^2), while L6 represented an area with very high density of one family houses (> 1400 houses/km^2).

PM$_{2.5}$ sampling and gravimetric analysis. Daily samples of PM were collected outdoors and indoors over the six-week period in January, February, and March of 2013. The identical analysis has been conducted in L2 and L5 in September, 2013. In each case, samples were collected over twenty-four hour periods during weekdays.

Size-resolved outdoor ambient aerosol samples were taken using the low pressure electric impactor (ELPI+, Dekati Inc., Finland). ELPI+ divided aerosol particles to 15 fractions (0.017-10.0 μm). Aerosol samples were collected on 25 mm diameter aluminum foil substrates. Real-time concentrations of aerosol samples were registered in one-minute intervals for five days in each location. In addition, substrates were analysed gravimetrically after 3 days of sampling using a microbalance (MX5, Radwag Wagi Elektroniczne, Poland).

The PM$_{2.5}$ fraction of the ambient aerosol was collected on quartz fiber filters (25 mm and 37 mm, respectively) over a sampling period of 24 hours, using URG PM$_{2.5}$ cyclone (URG Inc., USA), at a sampling flow rate of 16.7 l/min. The samples were drawn by a membrane pump, checking the flow rate by an automatic flow meter Defender 530, Mesa Laboratories, Inc., USA).

Indoor aerosol samples were taken using a micro-orifice uniform deposition impactor (MOUDI) (Model 100-NR, MSP Corp., USA), which collected ten fractions of the particles (0.056-18 μm), at an air intake flow rate of 30 l/min. Aerosol samples were collected on 47 mm diameter aluminum foil substrates, which were further processed by the gravimetric analysis. The PM$_{2.5}$ fraction was also sampled indoors by a cyclone sampler, similarly to the outdoors. Real time concentrations of aerosol particles were registered by an optical particle counter (OPC) (Handheld 3016IAQ, Lighthouse Inc., USA), which divided PM into six fractions (0.3-10 μm).

The values of temperature and relative humidity were continuously recorded by air quality meters (7545 IAQ-CALC, TSI Inc., USA). In the outdoor environment, the entire set of the devices was placed in a specially constructed weather-protected chamber with a temperature-controlled environment to prevent the overheating of the devices.

Results and discussion

PM concentration size distribution seasonal variation. The $PM_{2.5}$ outdoor concentrations measured in this study were comparable to the most other European sites (Molnar et al. 2005; Glasius et al. 2008; Reisen et al. 2013). Due to the particular meteorological, relief, house density and other conditions (**Table 4.16**) there was difference between the $PM_{2.5}$ concentrations at different locations. The outdoor median of $PM_{2.5}$ concentration in winter period ranged from 23.6 $\mu g/m^3$ at L6 to 94.6 $\mu g/m^3$ at L1. The same for indoor ranged from 13.4 $\mu g/m^3$ (L6) to 33.7 $\mu g/m^3$ (L1).

The particle size distribution (PSD), expressed by the relative concentration of particles, is presented in the **Figure 4.15**. The major part of the PM mass in winter period consisted of fine particles ($PM_{2.5}$), which shows that burning processes were predominant; respectively, the minor part of the PM was inhalable coarse particles ($PM_{2.5-10}$), which indicates that the contribution from roadways and/or dusty industries was also present (**Figure 4.15**). Summer measurements demonstrated rather equal PM mass distribution between fine particles and inhalable coarse particles.

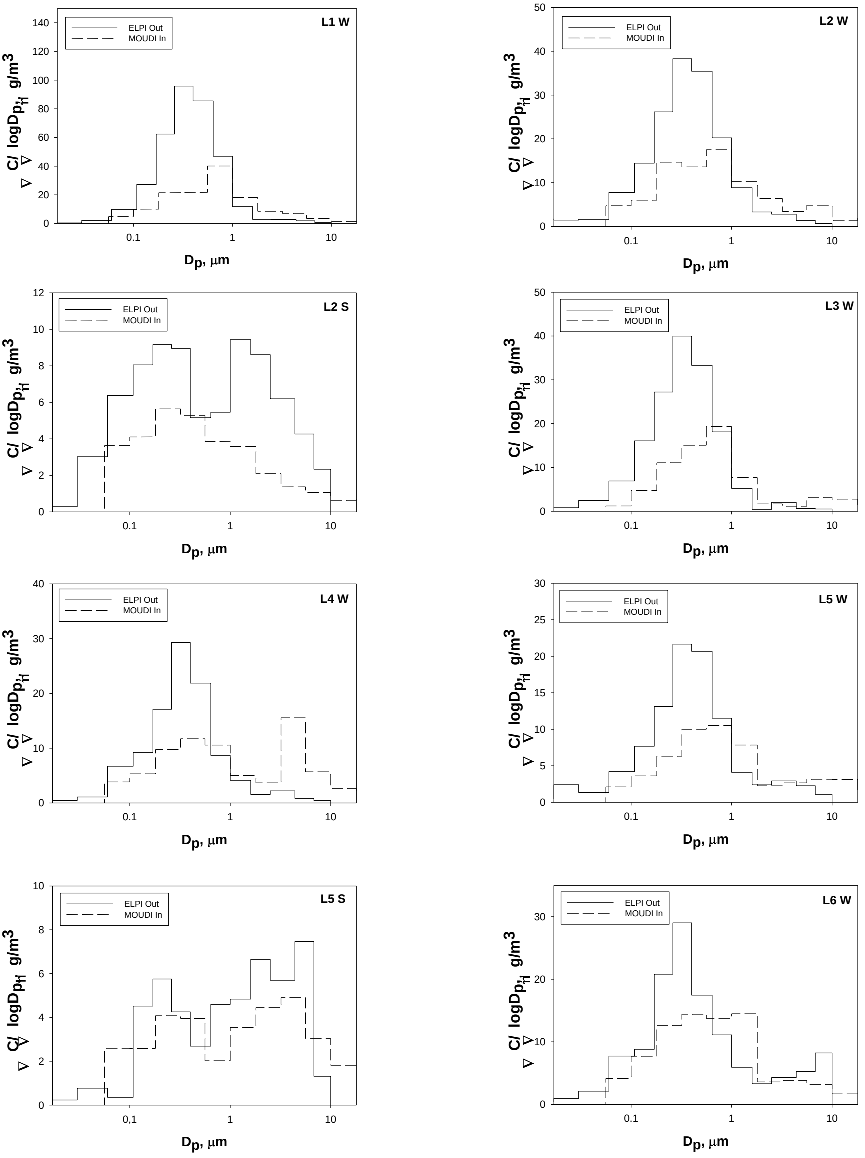


Figure 4.15. Particle size distribution (PSD) of PM at Locations 1-6: W – winter measurement campaign; S – summer measurement campaign

Winter outdoor measurements showed 5-fould median of $PM_{2.5}$ concentrations compared to summer measurements, while winter indoor measurements showed 2.8-time higher median of $PM_{2.5}$ concentrations compared to the summer measurements.

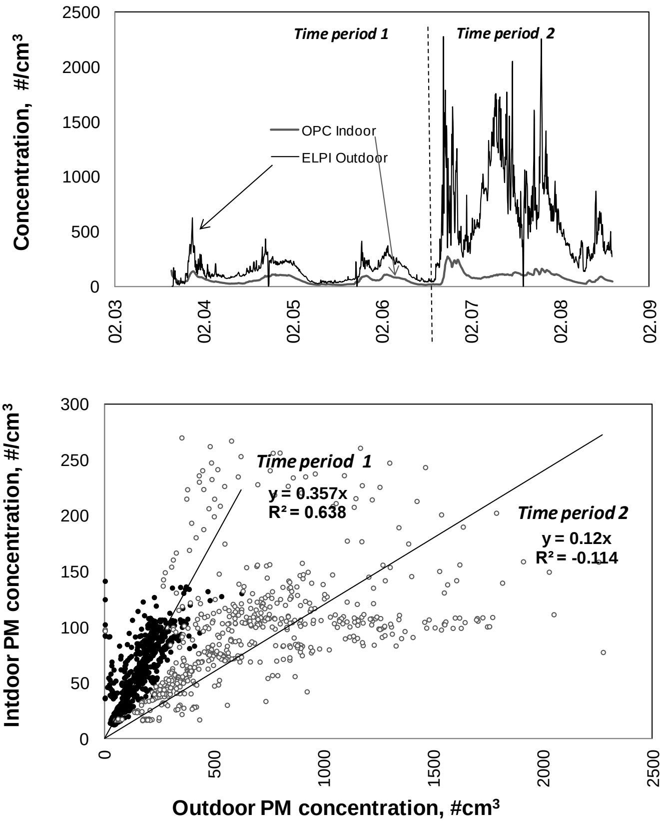


Figure 4.16. Fluctuations of outdoor vs. indoor $PM_{2.5}$ concentrations at Location 3

The indoor median of $PM_{2.5}$ concentration in winter measurement campaign was 22.29 μg/m^3, while summer indoor measurements showed thrice lower concentrations. Comparison of outdoor and indoor winter measurements showed that mean median outdoor $PM_{2.5}$ concentration was 2.2-times than indoor concentration, while median outdoor $PM_{2.5}$ concentration in summer was 1.2-times than indoor concentration. When analysing time series of $PM_{2.5}$ outdoor and indoor concentrations it was observed that some data segments follow the same trends.

PAH concentration and size distribution. We have hypothesized that outdoor PAH concentrations should be significantly influenced by the emissions of individual stoves and boilers during the cold winter period. This has been demonstrated by numerous earlier studies (Piazzalunga et al. 2013; Bari et al. 2009; 2010; 2011) as well as our research in Kaunas, although focussing on traffic emissions (section **4.2.1** and **4.1.2**). A more specific aim was to determine the distributions and ratios of size-segregated PAHs in indoor environments, thus implying the actual exposure of the inhabitants to the pollution from outdoors.

The total outdoor PAH concentration ranged from 20.9 ng/m^3 (L5) to 89.3 ng/m^3 (L4). The registered levels are comparable to our earlier experiments and other studies in Scandinavia. Locations 1 and 4 revealed higher PAH concentrations, mostly due to more intense emissions in the area during cold and stable weather conditions (average night temperature outside -13.3 and -4.2 °C, respectively, with the occurrences of temperature inversion conditions during night time/morning). It must be noted, that these two locations represented contrastingly different areas of the city (city centre vs. suburban area).

Indoors, the total PAH concentrations were mostly lower to the order of magnitude (from 5.1 ng/m^3 at L5 to 60.0 ng/m^3 at L3). The L3 stood out for the indoor PAH concentration, reflecting the indoor emissions from the biomass fuel boiler. Although this was a modern pellet-type automatic boiler installed in the first floor, it released fugitive combustion emissions to the indoor environment, which further dispersed to upper floors (measurements were conducted in the second floor). The influence of in-home biomass boilers to the indoor PAH concentration and health effects were demonstrated earlier (Gustafson et al. 2008; Naeher et al. 2007).

The summertime measurements at L2 and L6 yielded comparable PAH concentrations (26.8 ng/m^3 at L2 and 27.2 ng/m^3 at L6), although these sites were located in urban areas with rather substantial traffic.

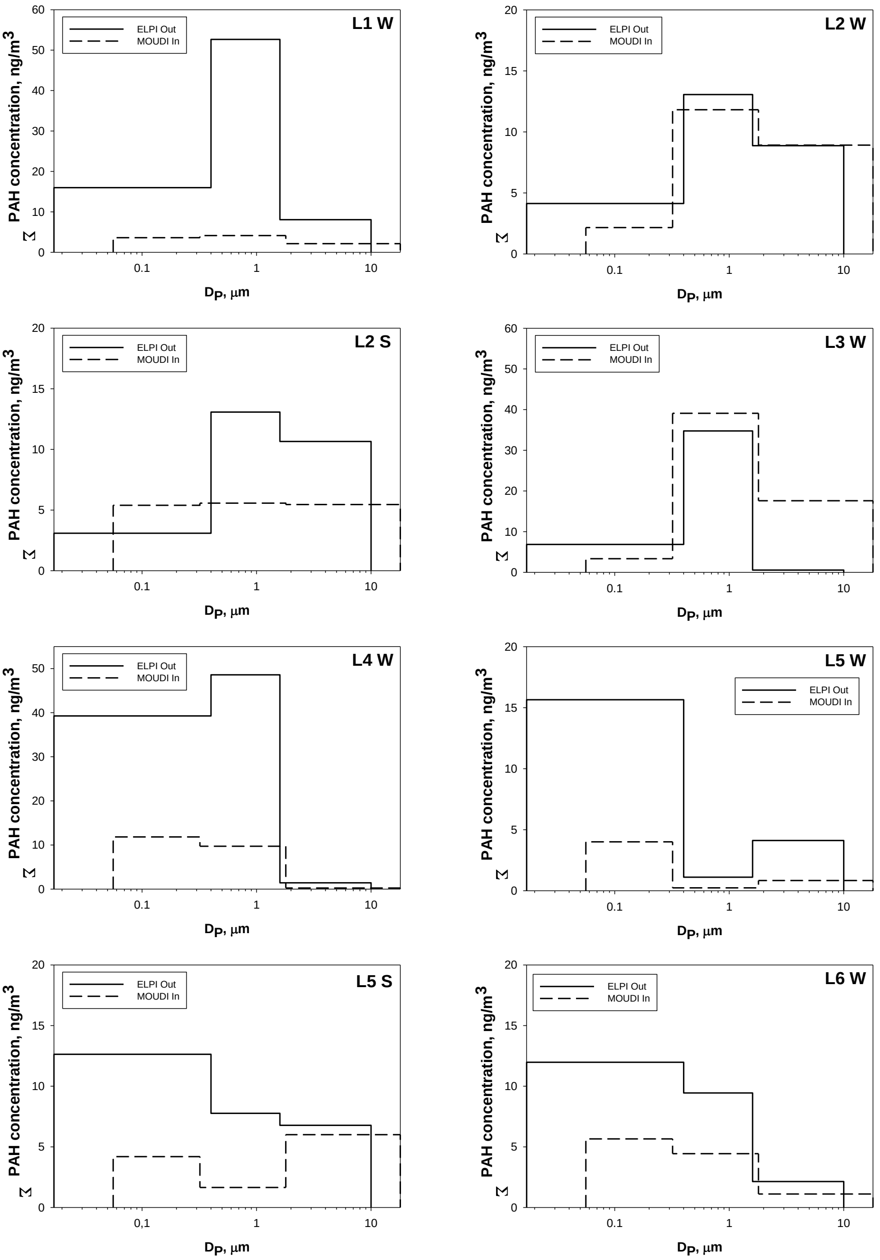


Figure 4.17. Particle size distribution (PSD) of PAHs at Locations 1-6: W – winter measurement campaign; S – summer measurement campaign

The three-stage particle size distribution obtained from pooling the ELPI+ (outdoor) and MOUDI (indoor) analysis has revealed that the total PAH concentration outdoors had a clearly distinguished accumulation mode (0.4-1.1 µm, **Figure 4.17**) in most locations. In several locations, namely 5 and 6, the nucleation mode was more pronounced, possibly indicating fresh emissions from nearby homes. At L3, where the PAH concentrations were affected by the indoor biomass combustion source, the accumulation mode was also evident, followed by a relatively pronounced coarse mode, which was not present outdoors.

Although the levels of indoor PAHs were substantially lower, the PAH size distribution resembled that of outdoors in most locations. The sampling was mostly performed in rooms of dwelling that were not constantly occupied and mostly stayed with closed door. Thus, a significant coarse mode was not present in all measurements, except of L3, where the IAQ was heavily impacted by emissions of pellet stove and had some traffic of inhabitants passing the samplers. In general, the similarities of indoor and outdoor PAHs size distributions suggest that the source of PAHs may be outdoor pollution.

PAH diagnostic ratios. The binary ratio method for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions (Ravindra et al., 2008). PAHs related to combustion sources are emitted at high temperatures as gases; when cooled they condense on particulates (Marr et al., 2006). PAH diagnostic ratios should be used with caution, as their values may change during the environmental fate of these compounds (Tobiszewski and Namiesnik 2012). Numerous studies report PAH diagnostic ratios for identification of pyrogenic vs. petrogenic and petroleum vs. diesel emission sources, while only few studies provide diagnostic ratios for burning of solid fuels (wood, coal) for energy production (Yunker et al. 2002; De La Torre-Roche at al. 2009).

In this sub-chapter we aimed at the application of PAH ratios method for the identification of solid fuel burning emission sources. The outdoor and indoor diagnostic ratios of PAHs are provided in the **Table 4.17**. The samples were collected close to the sources. The highest emissions in winter measurement campaign were registered during the dark period of the day, when atmospheric photoreactions are slow. From the provided list of diagnostic PAHs ratios it was designated that diagnostic ratio of low molecular weight PAHs fluoranthene/(fluoranthene+pyrene) in particulates could serve as identifier of residential solid fuel burning. The fluoranthene/(fluoranthene+pyrene) ratio seems to be more conservative compared to other diagnostic ratios of PAHs. The respective half-lives of fluoranthene and pyrene are 74 and 21 h for silica gel-adsorbed PAHs, 23 and 31 h for alumina, and 44 and 46 h for fly ash (Behymer and Hites, 1985). The diagnostic ratio of fluoranthene/(fluoranthene+pyrene) in all sampling sites (indoor and outdoor measurements), except outdoor measurements at L1 in winter, exceeded value 0.5. This indicates combustion of wood or coal as the source of PAHs emissions (De La Torre-Roche et al. 2009).

Table 4.17. Indoor and outdoor PAHs diagnostic ratios

Diagnostic ratios		**Fluorene/(Fluorene + Pyrene)**	**Anthracene/(Anthracene +Phenanthrene)**	**Fluoranthene/(Fluoranthene + Pyrene)**	**Benz[*a*]anthracene/(Benz[*a*]anthracene + Chrysene)**	**Indeno[*1,2,3-c,d*]pyrene/(Indeno[*1,2,3-c,d*]pyrene+ Benzo[*g,h,i*]perylene)**	**Benzo[*a*]pyrene/Benzo[*g,h,i*]perylene**	**Benzo[*a*]pyrene/(Benzo[*a*]pyrene+Chrysene)**	**ΣLMW/ΣHMW**	**ΣCB/ΣPAHs**
L1 W	Outdoor	0.26	0.09	0.45	0.44	0.61	1.11	0.44	0.49	0.78
	Indoor	0.46	-	0.54	0.65	-	1.4	0.65	0.24	0.87
L2 W	Outdoor	0.68	-	0.59	0.53	0.25	0.79	0.53	0.29	0.84
	Indoor	0.82	0.04	0.75	0.32	0.25	0.79	0.32	0.43	0.78
L2 S	Outdoor	0.91	0.16	0.7	0.62	-	-	0.62	1.72	0.46
	Indoor	1	0.3	-	0.73	0.31	0.64	0.73	1.21	0.48
L3 W	Outdoor	0.57	-	0.77	0.63	0.28	2.11	0.63	0.27	0.88
	Indoor	0.44	0.01	0.54	0.52	0.36	0.4	0.52	0.16	0.92
L4 W	Outdoor	0.61	0.24	0.67	0.65	0.49	1.38	0.65	0.47	0.76
	Indoor	0.92	0.12	0.77	0.75	0.28	1.53	0.75	0.52	0.71
L5 W	Outdoor	0.89	-	0.57	0.29	-	0.79	0.29	0.62	0.66
	Indoor	1	-	-	0.5	0.5	0.48	0.5	0.55	0.74
L6 W	Outdoor	0.77	-	0.6	0.44	0.28	2.19	0.44	0.65	0.71
	Indoor	-	-	-	-	-	-	-	1.87	0.64
L6 S	Outdoor	-	0.14	-	0.73	0.45	1.28	0.73	0.59	0.69
	Indoor	-	0.22	-	0.67	0.29	0.66	0.67	0.45	0.72

At the same time the diagnostic ratio of indeno[*1,2,3-c,d*]pyrene and benzo[*g,h,i*]perylene at sampling locations L2, L3, L4 and L6 ranged from 0.25 to 0.49, indicating petroleum combustion (Yunker et al. 2002). The obtained results support findings of Mostert et al. (2010) that during low temperature processes (e.g. wood burning), low molecular weight PAHs are usually formed, whereas high temperature processes, such as the combustion of fuel in engines, emit higher molecular weight PAH compounds. The exceptional case at L1, when diagnostic ratio of particle bound fluoranthene/(fluoranthene+pyrene) indicated burning of fossil fuel and diagnostic ratio of particle-bound indeno[*1,2,3-c,d*]pyrene and benzo[*g,h,i*]perylene showed burning of wood or coal, could be explained by uncontrolled domestic wastes burning. Mixed solid household wastes such as plastics, rubbers, cartons, paper and cardboard together with yard trimmings could be an issue of localized PAHs emissions (Estrellan and Iino 2010). The assumption that PAHs emissions could also originate from the uncontrolled domestic wastes burning would require further studies.

I/O ratios of PM and PAHs. The I/O ratio of PM concentrations in indoor environments to those in outdoor environments (I/O ratios) can be used to determine whether the major PM source(s) are located indoors (in which case I/O > 1) or outdoors (in which case I/O < 1). I/O ratios for the $PM_{2.5}$ fraction are presented in **Figure 4.18**. The low observed I/O ratios indicate that airborne PM at the locations studied arise primarily from outdoor sources. The exceptions were L2 in winter and L6 in summer sampling campaigns. In the first case the max reported I/O ratio was 5.53, which showed significant discrete indoor PM pollution; the second case registered I/O ratio was 1.84, which indicated permanent source of indoor PM pollution.

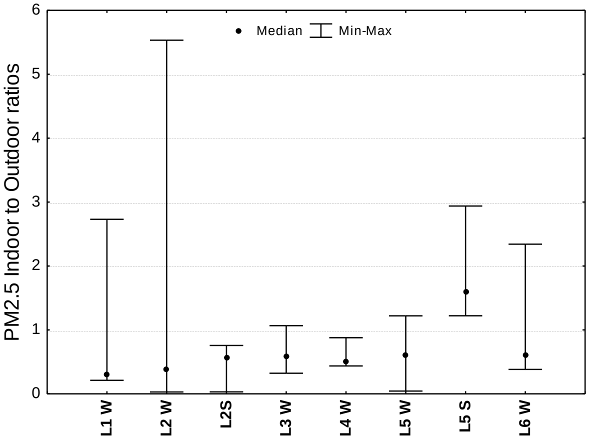


Figure 4.18. Ratios of indoor to outdoor (I/O) PM concentrations in $PM_{2.5}$ at Locations 1-6: W - winter measurement campaign, S – summer measurement campaign

It should be noted that the buildings differed in type of windows: from old windows with wooden frames that are fairly permissive in terms of air circulation to modern ones with double-pane glass packs that are characterised by low air permissibility. Thus, residents of older buildings may be more extensively exposed to outdoor PM compared to residents of newly built houses.

The I/O ratio of PAHs was calculated by pooling PAH concentrations from the three analysed fractions. The PAH concentration was mainly determined by the accumulation mode. In many occasions, the concentration in nucleation and coarse modes was below the detection limit, especially indoors in summer, thus making it impossible to calculate the I/O ratio.

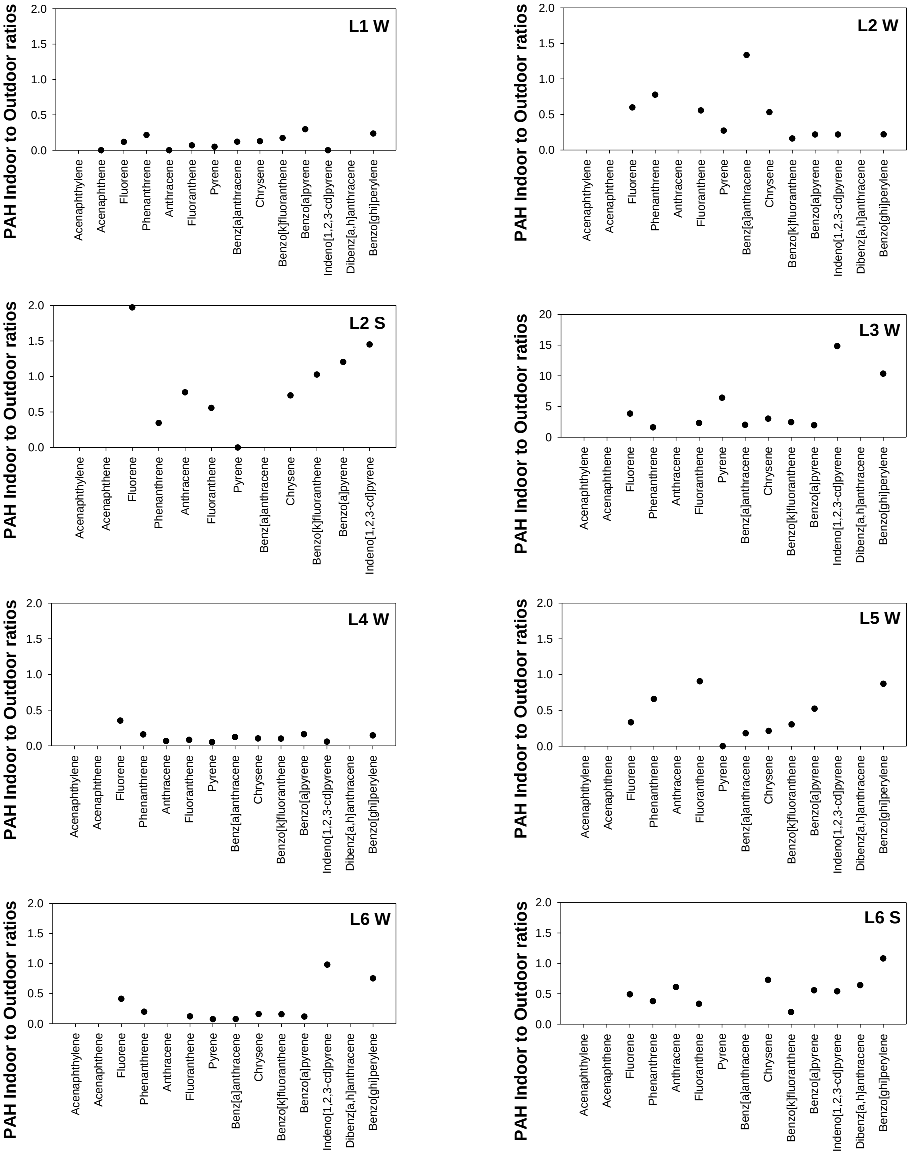


Figure 4.19. Ratios of indoor to outdoor (I/O) PAH concentrations in Locations 1-6: W - winter measurement campaign, S – summer measurement campaign

The analysis of I/O ratios of the individual PAHs has revealed some interesting findings, allowing further considerations of the indoor sources of PAHs. Mainly, two patterns of the I/O ratio could be distinguished: a) uniform distribution of I/O ratios among various PAHs (L1, L2, and L4) at a level <0.5; b) varying I/O ratios of PAHs (L3, L5, L6, including summer measurements) in a broad range from 0.2 to 1 and above (L3) (**Figure 4.19**). These two patterns of I/O distributions appeared to be associated with the presence of indoor PAH sources. L3 and L5 had operating wood-fired heating system inside, although at least one storey away. L6 had a wood fireplace, which was operated once during sampling campaign, thus affected the results. The I/O ratio has revealed the influence of the indoor boilers in L5 and L6, although the concentration of PAHs was lower then outdoors. Moreover, an increase in chrysene and fluoranthene was noticeable in each of the three buildings. These two PAHs were not specifically associated with biomass combustion, but in our study, they seem to indicate to the indoor combustion source. We also suggest that in the buildings where no indoor PAH source was present the I/O ratio may indicate a crude estimate of the amount of outdoor combustion-related pollution that penetrated to the indoor environment. This ratio ranged from 0.11 to 0.36 at L1, 0.08 to 0.33 at L2, 0.05 to 0.23 at L4. This corresponds to the tightness of the building envelope: L4 was newly built house with thermal insulation and efficient windows, while L1 and L2 were older buildings with no thermal insulation and less efficient windows, resulting in ~ 10 % higher penetration of outdoor fine particles carrying PAHs.

Summary of findings

The outdoor median of $PM_{2.5}$ concentrations in winter period ranged from 23.6 $\mu g/m^3$ at Location 6 to 94.6$\mu g/m^3$ at Location 1. Respectively, indoor median of $PM_{2.5}$ concentrations varied from 13.4 $\mu g/m^3$ at Location 6 to 33.7$\mu g/m^3$ at Location 1. It was observed that $PM_{2.5}$ outdoor and indoor fluctuation of concentrations follow the same trends. The particle size distribution analysis revealed that major part of the particulate matter in winter period consisted of fine particles ($PM_{2.5}$), which shows that burning processes were predominant. The low indoor to outdoor (I/O) concentration ratios may indicate that outdoor sources are more intensive with respect to PM emissions.

The total outdoor PAH concentration in winter ranged from 20.9 ng/m^3 at Location 5 to 89.3 ng/m^3 at Location 4. Indoors, the total PAH concentrations were mostly lower, varying from 5.1 ng/m^3 at Location 5 to 60.0 ng/m^3 at Location 3. The obtained particle size distribution revealed that the total PAH concentration outdoors had a clearly distinguished accumulation mode (0.4-1.1 μm) in most locations. In several locations the nucleation mode was more pronounced, possibly indicating fresh emissions from nearby homes. At Location 3, where the PAH concentrations were affected by the indoor biomass combustion source, the accumulation mode was also evident, followed by a relatively pronounced coarse mode, which was not present outdoors. In general, the similarities of indoor and outdoor PAHs size distributions suggest that the source of PAHs may be outdoor pollution. The analysis of I/O ratios revealed two patterns of the I/O ratio: a) uniform distribution of I/O ratios among various PAHs at a level < 0.5; b) varying I/O ratios of PAHs in a broad range from 0.2 to 1 and above. The first pattern suggests that outdoor combustion-related pollution that penetrated into indoor environment predominates, while the second one indicates indoor sources of solid fuel burning. The authors suggest that diagnostic ratio of particle-bound fluoranthene/(fluoranthene+pyrene) > 0.5 could indicate origin of residential solid fuel burning.

In winter measurement campaign concentration levels similarly as concentration levels of $PM_{2.5}$ and PAHs were considerably higher compared to summer measurements.

4.2.4. Comparison of active and passive sampling campaigns of Polycyclic Aromatic Hydrocarbons in indoor and outdoor air

Detailed aim of this research

The aim of this study was to compare active and passive sampling technique for investigation the influence of domestic energy production on outdoor and indoor PAH levels.

Experimental design

Sampling locations are described in previous research (see **Table 4.16**).

Sampling of pollutants. Gaseous PAHs were collected using the passive sampling by the semipermeable membrane devices (SPMD). Semipermeable membrane (Environmental Sampling Technologies Inc., USA) is composed of low density nonporous polyethylene (LDPE) tube containing lipid triolein (ratio of polyethylene and triolein 4:1). Membrane is 91.4 cm length, 2.5 cm width; the thickness of polymer – 75-90 µm. LDPE polymer contains 0.5-1 nm holes through which only dissolved or gaseous low molecular weight organic compounds can be penetrate before and after sampling.

SMPDs were attached to stainless steel holders and further placed into stainless steel sampler. The sampler is designed to ensure sufficient air flow and to protect membranes from UV light. The samplers were deployed at two meter height.

The active sampling was used to detect the particle phase and vapor PAHs. The gaseous phase PAHs were sampled using the XAD-2 sorbent (SKC Inc., USA), at an air flow rate 2 l/min. The TSP fraction of aerosol was collected on quartz fiber filters (25 mm, Tissuquartz), by using filter cassettes, at an air flow rate 2 l/min.

Analytical methods. SPMDs were shipped for analysis to Exposmeter AB, Sweden. The set of 16 USEPA recommended PAHs were analysed as well as methylated species: 1-methylnaphtalene, 2-methylnaphtalene, 1,6-dimethylnaphtalene, 2,3,5-trimethylnaphtalene, 2-methylfenantrene, 2,4-dimethylfenantrene, 1,2,6-trimethylfenantrene, 1,2,8-trimethylfenantrene, dibenzothiophene, 2-methyldibenzothiophene, 2,8-dimethyldibenzotiophene, 2,4,7-trimethyldibenzothiophene, 1-methylfluoranthene, 1-methylchrysene, 6-ethylchrysene.

Quality control. Repeated and blank samples were exposed for the quality assurance of SPMDs results. The analysis of the blank samples were the same as for membranes used in the experiments. The results of the blank samples haven't showed any contamination, all the materials met the quality requirements of the materials sheets.

Data analysis. Results of analyses were statistically processed using SPSS 12 (IBM Corp., USA) and Origin 9 (OriginLab Corp., USA) software. Descriptive statistics were used for the representation of average PM, PAH, gaseous pollutant levels (median, 25th and 75th percentiles, minimum and maximum values). Spearman ranking correlation (SCF) was used for determination relationship between two parameters. Diagnostic ratio analysis was used for determination of ratio values of different fuels.

Results and discussion

PAH levels in SPMDs. As illustrated in **Figure 4.20**. the sum concentration of 16 PAHs investigated in SPMDs ranged from 10 to 138 ng/day outdoors, from 5 to 59 ng/day indoors in sampler and from 4 to 44 ng/day indoors in naked SPMDs during winter sampling campaign. In summer the sum concentration of PAHs varied from 11 to 19 ng/day outdoors, from 19 to 27 ng/day indoors in sampler and from 14 to 19 ng/day in naked SPMDs.

Seasonal differences as well as influence of fuel burning for domestic heating purposes on the concentration of PAHs is well reflected – PAH concentrations in SPMDS deployed outdoors in winter were from 1.7 to 7.6 times higher than the respective concentration in summer, the difference being statistically significant at $p<0.05$. The highest difference in winter was found at L3 where burning of wood and sometimes coal prevails in the surroundings. In winter the ratio of the highest and the lowest concentration of PAHs in SPMDs deployed outdoors were 13.8 while in summer this ratio was only 1.7. Difference in concentrations of PAHs deployed indoors in winter and summer did not appear to be statistically significant. However at all locations investigated in summer concentrations of PAHs were higher indoors than outdoors. This indicates cooking and other activities as a source PAHs indoors.

If compared Kaunas data with the results obtained in Söderström et al. (2005) study in which SPMDs were used to investigate spatial variations between outdoor urban, rural and remote sites in five European countries, we may see that PAH levels outdoors estimated in this study are similar than those found in SPMDs deployed outdoors in Sweden and Poland (in 2000). PAH levels outdoors in Kaunas were also similar to levels at six sites in the Bangkok region, Thailand as reported by Söderström et al. (2003). In Bangkok total sum PAH concentrations in SPMDs 131-134 ng/day were reported at sites with high traffic intensity while at rural area the respective PAH concentrations was 17 ng/day what is close to the lowest PAH concentration in Kaunas – 10 ng/day. PAH data in this study were also similar to those reported by Ravindra et al. (2006) in Belgium and Zhu et al. (2013) from Dalian city in China – the sum concentration of 16 priority PAHs ranged from 81 to 158 ng/day if calculated per standard SPMD.

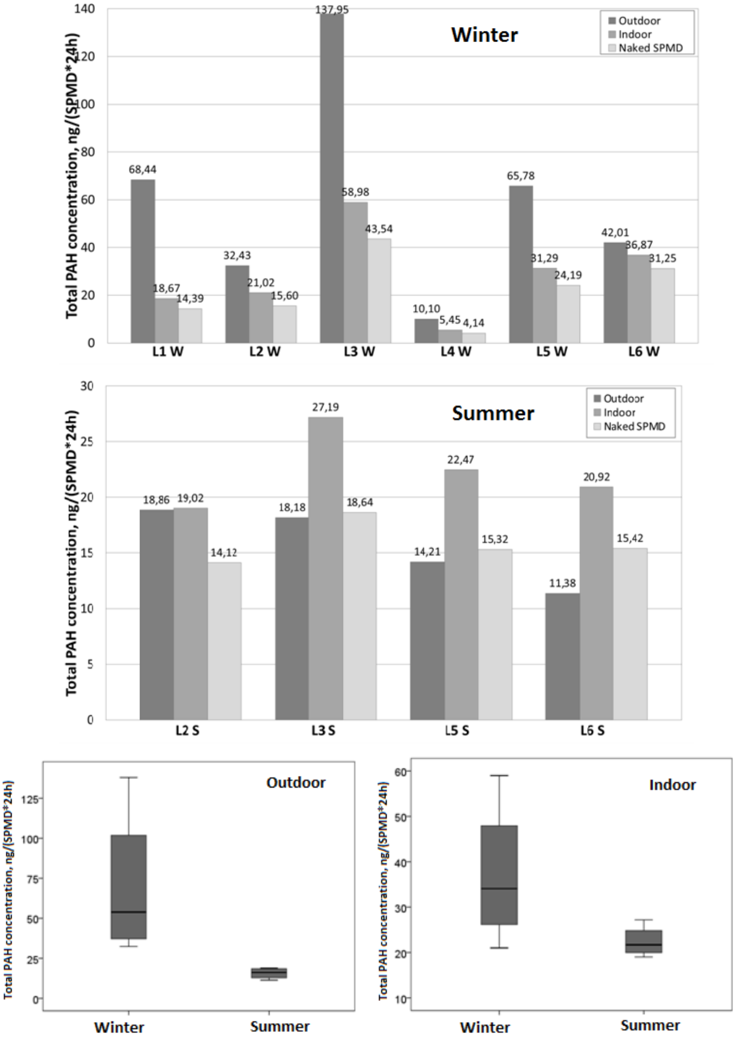


Figure 4.20. Indoor and outdoor winter (left) and summer (right) sampling period total vapor phase PAH concentrations in different locations

Strandberg et al. (2006) reports PAH levels in SPMDs deployed indoors inside of 15 single-family Swedish houses located in an area where domestic wood burning is widespread. They reported PAH concentration in SPMDs 30-350 ng/dayin wood burning houses and 30-60 ng/day in non-wood burning houses. Interesting to note that in our study these levels were lower – 4-44 ng/day. Concentrations of methylated PAHs in this study were also generally lower than in Sweden (Strandberg et al. 2006).

Table 4.18. Average ratios of PAH concentration in SPMDs deployed naked/in sampler

	Winter season						Summer season			
	L1	L2	L3	L4	L5	L6	L2	L3	L5	L6
16 PAHs	0.7	0.74	0.74	0.76	0.77	0.85	0.74	0.69	0.68	0.74
Methylated PAHs	0.84	0.66	0.56	0.50	0.51	0.70	0.60	0.72	0.90	0.82

SPMD sampling techniques. There are several factors to consider when using SPMDs as outdoor and indoor air samplers. Sampling conditions in outdoor air measurements may differ significantly leading to bias in data. A high wind speed reduces the thickness of boundary layer and hence increases the uptake When SPMDs are deployed in outdoors studies it is important to provide enough shelter from the wind, but sufficient air circulation around the sampler should be ensured that uptake rates are not reduced (Söderström et al. 2004). However in indoor air studies slow air movement around the membrane may cause the thickness of boundary layer to increase especially if the SPMD is in a sampler. If SPMDs are exposed without any sampler a concern related to photo-degradation appears. However it might not be a major concern if SPMDs are deployed in places not affected by direct sunlight (Strandberg et al. 2006). The average ratios of PAH concentration in uncovered or “naked” SPMDs and SPMDs deployed in sampler are given in **Table 4.18**. Lower levels of PAHs are found in naked SPMDs most likely due to photodegradation of susceptible species. However statistically significant difference ($p < 0.05$) for unsubstituted PAHs was observed only in summer. More intensive sunlight might have caused lower ratio during summer campaign. For methylated PAHs the difference in winter and summer was not obvious.

Vapour and particle phase PAHs. As demonstrated in **Figure 4.21**, the pattern of total concentrations of vapour and particle phase PAHs at six locations is different from that one of SPMD data (**Figure 4.20**). It should be noted that sampling periods were different. SPMD data represent average for 28 days, while data of active sampling represent weekly data. In winter the highest sum PAH value 286.8 ng/m^3 was measured at L1, there was higher level at L2. During sampling at L1 bad atmospheric mixing conditions were reported with very low wind speed. Also at L1 the lowest weekly temperature was reported and presumably more intensive domestic fuel burning for heating purposes what is reflected on PAH data. However in winter concentration of PAHs at the other four locations did not differ significantly including L4 which is least densely populated with dominating gass boilers in the surroundings.This leads to a conclusion that weekly measurement campaigns give quite episodic air pollution characterisation however longer measurement campaigns in many cases might be too costly. Also doing measurements inside noise generated by pumps should be also taken into consideration.

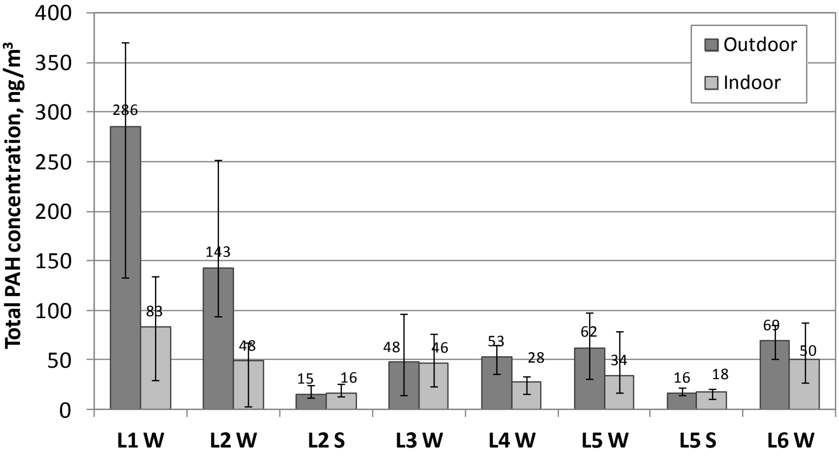


Figure 4.21. Total (SUM) concentrations of vapour and particle phase PAH in indoor and outdoor during the experiment. Bar represents median concentrations, whiskers minimum and maximum concentrations

The samples investigated were dominated by low molecular weight compounds, the highest values were observed of fluorene, phenanthrene. The distribution pattern of individual PAH concentration for L3 is demonstrated in **Figure 4.22** and is very similar to observation by other authors (Ravindra et al. 2006; Ma et al. 2011; Zhu et al. 2014).

Concentrations of PAHs in vapour phase were on the average 3-4 fold higher than in the particulate phase.

Table 4.19 presents comparison of vapour phase as well as particle phase concentrations of PAHs at different places worldwide also gives a comparison of PAH levels in Kaunas measured by active and passive sampling. Concentrations of vapour phase PAHs measured using SPMDs in this study were in a range from 5.4 to 90.0 ng/m^3 in winter and in a range from 6.7 to 11.0 ng/m^3 in summer while concentrations measured by active sampling were from 37.8 to 208.2 ng/m^3 and from 15.2 to 16.4 ng/m^3 respectively. PAH levels in this study measured with SPMD methodology were similar to those found in urban locations in Poland, Belgium and some regions of China. However levels of particle phase PAHs in winter where noticeably higher than in all places in Europe and were lower if compared to locations in China.

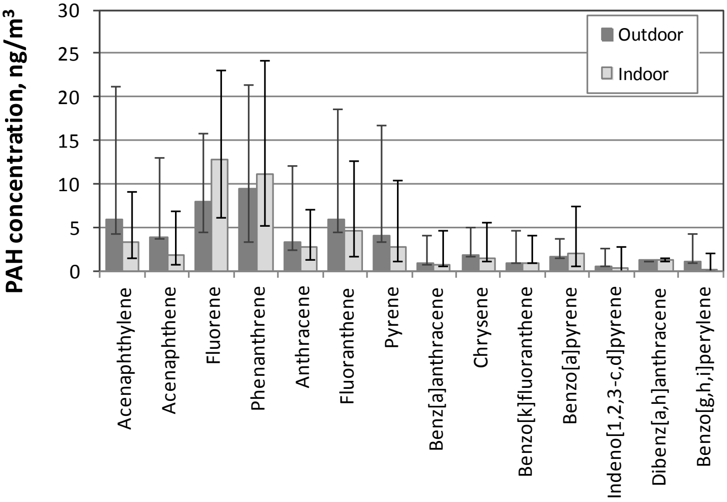


Figure 4.22. Concentration of individual PAHs at L3 during winter campaign. Bar represents median concentrations, whiskers minimum and maximum concentrations

Table 4.19. Comparison of concentration of vapour and particle phase ∑16 PAHs at different locations, ng/m^3

Kaunas	This study	SPMD*	summer	5.4-90.0		
			winter	6.7-11.0		
		XAD	summer	37.8-208.2	PM$_{2.5}$	9.4-59.7
			winter	15.2- 16.4		1.8-3.2
Birmingham, *UK*	Alam et al., 2013	XAD-4	winter	44.4-49.8	PM$_{2.5}$	4.4-9.3
Flanders, *Belgium*	Ravindra et al., 2006	PUF high vol.		15.6-110	PM$_{2.5}$	0.9-8.7
Vicinity of Athens, *Greece*	Vasilakos et al., 2007	PUF high vol.		23.7-26.4	PM$_{total}$	3.08-3.21
Dalian, *China*	Zhu et al., 2014	PUF high vol.		40.8-155.0	PM$_{total}$	3.2-90.6
Xialolongmen (background)	*China* Wang et al., 2011	PUF high vol.		18.5-84.8	PM $_{10}$	104.1
Gubeikou (rural)				88.0-355.8		1.7-251.7
Donghe (rural)				291.0-1267.7		12.9-348.8
Beijing, (urban)				127.8-756.6		3.2-222.7
Beijing, *China*	Ma et al., 2011	PUF high vol.		118.7	PM$_{total}$	104.1
Singapore, *Singapore*	He at al., 2009	PUF high vol.		36.4		

Diagnostic ratios of particulate and vapour phase PAHs. Most commonly used diagnostic ratios, as summarized in **Table 4.20**, show dominance of pyrogenic sources at most locations investigated. Also data demonstrate dominance of low molecular compounds to high molecular compounds both outdoors and indoors. However it should be noted that efficiency of diagnostic ratios as a source identification tool has been questioned by various authors. Katsoyannis et al. (2014) demonstrated that transport of PAHs over a few kilometres can be enough to cause a change in the source identification interpretation, the most robust for air concentrations appeared to be ratio Benz[*a*]anthracene / (Benz[*a*]anthracene + Chrysene). In our study the distance from PAH emission sources was not big, thus use of diagnostic ratios has certain relevance.

Indoor to outdoor ratios (I/O) of individual PAH concentrations in winter obtained with SPMD as well as active sampling are shown in **Figure 4.23**. In most cases the I/O < 1 was observed what indicates that PAH emissions at the locations studied arise primarily from outdoor sources.

Table 4.20. Diagnostic ratios calculated from vapour and particle phase ∑16 PAH concentrations during winter sampling campaign

Diagnostic ratio	L1 W Out	L1 W In	L2 W Out	L2 W In	L3 W Out	L3 W In	L4 W Out	L4 W In	L5 W Out	L5 W In	L6 W Out	L6 W In	Petrogenic	Pyrogenic	Fuel combust.	Grass/coal/wood combust.	Non-traffic	Traffic
													Katsoyannis et al. 2014				Rogge at al. 1993	
Anthracene/(Anthracene +Phenanthrene)	0.30	0.12	0.26	0.07	0.26	0.20	0.58	0.54	0.23	0.14	0.21	0.08	< 0.1	> 0.1				
Fluoranthene/(Fluoranthene + Pyrene)	0.49	0.69	0.62	0.23	0.59	0.64	0.70	0.71	0.47	0.62	0.46	0.31	< 0.4	> 0.4	0.4 – 0.5	> 0.5		
Benz[*a*]anthracene/(Benz[*a*]anthracene + Chrysene)	0.59	0.52	0.54	0.91	0.33	0.35	0.38	0.68	0.64	0.62	0.57	0.78	< 0.2	> 0.35				
Indeno[*1,2,3-c,d*]pyrene/(Indeno[*1,2,3-c,d*]pyrene + Benzo(ghi)perylene)	0.57	0.31	0.37	0.94	0.36	0.69	0.63	0.82	0.18	0.15	0.52	0.52	< 0.2	> 0.2	0.2 – 0.5	> 0.5		
ΣLMW/ΣHMW	1.99	3.30	3.98	3.85	3.04	3.78	2.56	2.81	2.66	2.51	2.60	2.07						
ΣCPAH/ΣPAHs	0.51	0.67	0.69	0.76	0.63	0.69	0.67	0.86	0.63	0.66	0.62	0.61					0.51	0.51

* Calculation into ng/m^3 was done based on methodology by Cranor et al. 2009

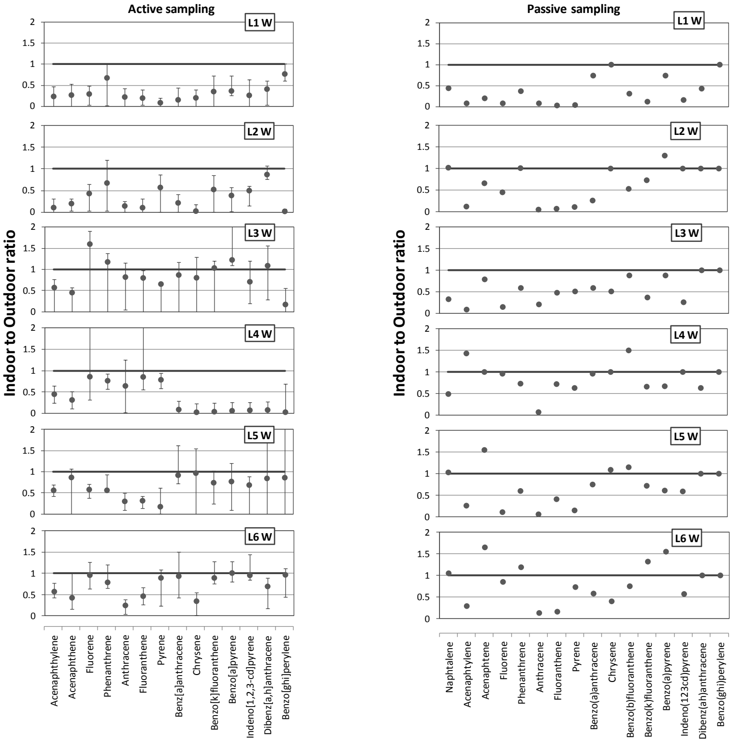


Figure 4.23. Outdoor to indoor ratios of individual PAH concentrations in winter obtained with active sampling (left) as well as SPMDs (right)

Summary of findings

Seasonal differences as well as influence of fuel burning for domestic heating purposes on PAH concentration outdoors were better reflected in data obtained using SPMD methodology than in the data based on active sampling. In winter PAH levels were higher outdoors than indoors while in summer the situation was the opposite. Diagnostic ratio analysis revealed dominance of pyrogenic sources at most locations investigated. PAH levels in this study measured with SPMD methodology were similar to those found in urban locations in Poland, Belgium and some regions of China. However levels of particle phase PAHs in winter where noticeably higher than in all places in Europe and were lower if compared to locations in China.

SPMD methodology proved itself for measurements of PAHs indoors despite of quite low air velocities. In winter concentration of PAH in sampler protected and naked membranes did not differ significantly, for simplicity reasons SPMDs might be used uncovered. Protective sampler is needed for deployment of SPMDs both outdoors and indoors under conditions of more intensive sunlight.

CONCLUSIONS

1. Emissions of polycyclic aromatic hydrocarbons (PAHs) from combustion of wood, agricultural residue derived fuels, and sewage sludge were in a range from 469.4 µg/kg (wood pellets) to 7212.2 µg/kg (sewage sludge). The vapor phase PAH emissions were predominant (from 68.9 to 89.1 % of total PAH emission). The vapor phase PAHs were dominated by acenapthylene, fluorene and phenatrene, while the particulate phase was mostly composed by fluoranthene, pyrene, chrysene and benzo[*g,h,i*]perylene, particularly in the accumulation mode of aerosol (0.32-1.8 µm). A substantial variation among individual PAH emissions in cases of various fuels was found. The emissions of PAHSs in case of sunflower shell pellets, buckwheat shells, and sewage sludge pellets was higher due to their chemical composition (mostly ash content) and morphology (small or irregular particle size). A different morphology should be developed to minimize the formation of PAHs.
2. Street dust was confirmed to be a potentially significant source of urban air pollution by PAHs. Total PAHs concentration in resuspended dust has reached 0.015±0.0069 mg/kg (in total suspended particles – TSP fraction at a resuspension air velocity of 15 m/s). The concentrations of PAHs associated with resuspended particles were lower by five orders of magnitude than those measured in previous studies of non-resuspended street dust. This suggests that the PAH concentration of non-resuspended total street dust is not the best predictor of air-borne PAHs.
3. The levels of PAHs near street buildings in Kaunas city were notably higher than those reported elsewhere in Europe. The mean sum PAH concentrations were among 32.7±11.8 and 75.1±32.7 ng/m^3, revealing significantly higher concentrations during winter period. 5-6 and 4-ring PAHs originated from automotive emissions, are bound to street dust and dispersed over the area.
4. The concentrations of PAHs measured in primary schools of Kaunas city during winter period were elevated, compared to other studies in Europe. This may be attributed to the increased emissions of pollutants from traffic and energy production during cold season. The concentrations of vapor phase PAHs exceeded particle phase PAH concentrations several times. Indoor/Outdoor ratios indicated that in most cases particulate and vapor phase PAHs penetrated from outdoors into the indoor air. Health risk assessment based on the carcinogenic equivalent concentrations revealed that the equivalent concentrations in the city center were several times higher compared to other similar studies indicating a potential to causing PAH-related adverse health effects.
5. The cocentrations of average total outdoor PAHs in six single family homes in winter ranged from 20.9 to 89.3 ng/m^3. Indoors, the total PAH concentrations were mostly lower, varying from 5.1 to 60.0 ng/m^3. Total PAH concentration outdoors had a clearly distinguished accumulation mode (0.4-1.1 µm). The

similarities of indoor and outdoor PAHs size distributions suggest that the source of PAHs may be outdoor pollution. Several patterns of Indoor/Outdoor ratio were distinguished representing outdoor combustion-related pollution that penetrated into indoor environment, and indoor sources of solid fuel burning. The diagnostic ratio of particle-bound fluoranthene / (fluoranthene + pyrene) > 0.5 could indicate origin of residential solid fuel (other than biomass) burning.

6. Seasonal variation as well as the influence of fuel burning for domestic heating purposes on outdoor PAH concentration were better reflected by the semipermeable sembrane device method compared to the active sampling. The semipermeable sembrane device method was able to adequately measure indoor PAH concentrations despite of the passive technique. The concentration of PAHs during winter measurements in sampler protected vs. naked membranes did not differ significantly, suggesting low influence of UV radiation of PAH degradation.

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LIST OF PUBLICATIONS ON THE TOPIC OF THE DISSERTATION

PUBLICATIONS

Publications, included in the Institute for Scientific Information (ISI) Main database

1. Krugly, Edvinas; Martuzevicius, Dainius; Puida, Egidijus; Buinevicius, Kestutis; Stasiulaitiene, Inga; Radziunienė, Inga; Minikauskas, Algirdas; Kliucininkas, Linas. Characterization of gaseous- and particle-phase emissions from the combustion of biomass-residue-derived fuels in a small residential boiler // Energy & fuels. Washington : American Chemical Society. ISSN 0887-0624. 2014, Vol. 28, iss. 8, p. 5057–5066. [Science Citation Index Expanded (Web of Science)]. [0,125]. [IF (E): 2,733 (2013)]
2. Martuzevicius, Dainius; Kliucininkas, Linas; Prasauskas, Tadas; Krugly, Edvinas; Kauneliene, Violeta; Strandberg, Bo. Resuspension of particulate matter and PAHs from street dust // Atmospheric Environment. Oxford : Pergamon-Elsevier Science. ISSN 1352-2310. 2011, Vol. 45, iss. 2, p. 310-317. [ISI Web of Science; Academic Search Premier; BIOSIS; Chemical Abstracts (CAplus); COMPENDEX; Science Direct; 0,236].
3. Krugly, Edvinas; Martuzevicius, Dainius; Sidaraviciute, Ruta; Ciuzas, Darius; Prasauskas, Tadas; Kauneliene, Violeta; Stasiulaitiene, Inga; Kliucininkas, Linas. Characterization of particulate and vapor phase polycyclic aromatic hydrocarbons in indoor and outdoor air of primary schools // Atmospheric Environment. Oxford : Pergamon-Elsevier Science. ISSN 1352-2310. 2014, Vol. 82, iss. 2, p. 298-306. [ISI Web of Science; Academic Search Premier; BIOSIS; Chemical Abstracts (CAplus); COMPENDEX; Science Direct; 0,125].
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6. Kauneliene, Violeta; Krugly, Edvinas; Kliucininkas, Linas; Stasiulaitiene, Inga; Radziuniene, Inga; Auzbikaviciute, Agne; Tomsejb, Tomas; Bergqvistc, Per-

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Other conference proceedings and theses

1. Krugly, Edvinas. Puida, Egidijus. Buinevicius, Kestutis. Stasiulaitiene, Inga. Prasauskas, Tadas. Radziuniene, Inga. and Martuzevicius, Dainius. Size-segragated particulate PAH emissions from combustion of local agriculture residue pellets. Aerosol technology 2014, 16 - 18 June 2014. Karlsruhe, Germany.
2. Krugly, Edvinas. Kauneliene, Violeta. Kliucininkas, Linas. Stasiulaitiene, Inga. Radziuniene, Inga. Prasauskas, Tadas. and Martuzevicius, Dainius. Particle and vapour PAHs in residential areas of Kaunas, Lithuania. NOSA Aerosol Symposium 29 th -30 th January, 2014 Stockholm, Sweden.
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