Evaluation of the impact of wood combustion on benzo(a)pyrene (BaP) concentrations; ambient measurements and dispersion modelling in Helsinki, Finland

Heidi Hellén[1], Leena Kangas[1], Anu Kousa[2], Mika Vestenius[1], Kimmo Teinilä[1], Ari Karppinen[1], Jaakko Kukkonen[1] and Jarkko V. Niemi[2,3]

[1] Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland
[2] Helsinki Region Environmental Services Authority, P.O. Box 100, FI-00066 HSY, Helsinki, Finland
[3] Department Environmental Sciences, University of Helsinki, P.O. Box 65, FI-00014 University of Helsinki, Finland

Correspondence to: Heidi Hellén (heidi.hellen@fmi.fi)

Abstract. Even though emission inventories indicate that wood combustion is a major source of polycyclic aromatic hydrocarbons (PAHs), estimating its impacts on PAH concentration in ambient air remains challenging. In this study the effect of local small-scale wood combustion on the benzo(a)pyrene (BaP) concentrations in ambient air in the Helsinki metropolitan area in Finland is evaluated, using ambient air measurements, emission estimates and dispersion modelling. The measurements were conducted at 12 different locations during the period from 2007 to 2015. The spatial distributions of annual average BaP concentrations originating from wood combustion were predicted for four of those years: 2008, 2011, 2013 and 2014. According to both the measurements and the dispersion modelling, the European Union target value for the annual average BaP concentrations (1 ng m^{-3}) was clearly exceeded certain suburban detached house areas. However, in most of the other urban areas, including the centre of Helsinki, the concentrations were below the target value. The measured BaP concentrations highly correlated with the measured levoglucosan concentrations in the suburban detached house areas. In street canyons, the measured concentrations of BaP were at the same level as those in the urban background, clearly lower than those in suburban detached house areas. The predicted annual average concentrations matched with the measured concentrations fairly well. Both the measurements and the modelling clearly indicated that wood combustion was the main local source of ambient air BaP in the Helsinki metropolitan area.

Keywords: PAHs, $PM_{2.5}$, air pollution, air quality, levoglucosan

1 Introduction

In many countries wood is still widely used as a fuel for residential heating. However, residential wood combustion can have a significant effect on air quality by emitting substantial quantities of fine particles ($PM_{2.5}$) and other pollutants (Simoneit et al., 2002). Polycyclic aromatic hydrocarbons (PAHs) are known to be carcinogenic constituents of such fine particles (Ravindra et al., 2008). They are produced due to the incomplete combustion of biomass, coal, oil, and gasoline and diesel fuels. Benzo(a)pyrene (BaP) has been regarded as a marker for both the total and carcinogenic PAHs (EC, 2004). Generally PAH concentrations in the European Union have slightly decreased for the period 2007-2014; however, there are several areas, where no such significant trend has been observed, or even an increasing trend has been noted (European Environment Agency, 2015; Anttila et al. 2016).

The European Commission has set a target value of 1 ng m^{-3} for the annual average concentration of BaP in ambient air (e.g., European Environment Agency, 2015). The ambient air concentrations of PAHs and BaP have a concern in Europe, since the concentration levels have been relatively high compared to the target values (European Environment Agency, 2013, Guerreiro et al., 2015). During 2011-2013, 25-29% of the urban population in the EU was found to be exposed to BaP concentrations above the above mentioned target value. If we consider the reference level of the World Health Organization (WHO), i.e., at 0.12 ng m^{-3}, 85-91% of the urban populations in the EU are beign exposed to BaP values higher than the reference level (European Environment Agency, 2015). This reference level was estimated by assuming the WHO unit risk for lung cancer for PAH mixtures and an acceptable risk of additional lifetime risk of approximately 1 x 10^{-6}.

There is evidence that residential wood combustion is a significant source of airborne PAHs at many locations. Guerreiro et al. (2015) evaluated the main emission sources of BaP, on a European level for concentration levels, population exposure, and potential health impacts. They used a mapping methodology, which combines monitoring data with modelling data and comparing to other supplementary data. They found the ambient air concentrations of BaP to be substantially high in central and central Eastern Europe, but also in some other European regions. The highest concentrations were interpreted to be mostly due to emissions from the domestic combustion of coal and wood.

Silibello et al. (2012) modelled the BaP concentrations in Italy. Their analysis revealed a significant influence of certain national sources on BaP concentrations; the most important emission sector was non–industrial combustion in wood burning devices. In Northern Italy, the ambient air measurements and cluster analysis indicated that wood combustion was the main source of BaP at all other sites, except for the city of Milan (Gianelle et al., 2013; Belis et al., 2011). In Augsburg, Germany, at a site that represenred a typical inner city residential location, the contribution of wood combustion to measured PAH levels was estimated to be as high as 80–95% (Schnelle-Kreis et al., 2007). In the UK, positive matrix factorization results indicated that wood combustion played an important role in the PAH concentrations in urban air, even though traffic and coal combustion

were found to be the main sources (Jang et al., 2013). In Denmark, residential wood combustion has been estimated to account for about 90% of the Danish emissions of BaP (Glasius et al., 2008). In Central Finland, the measured PAH concentrations have been found to be several times lower in regional background air than in a small residential area included 164 detached houses, where wood was used as a secondary energy source (Hellén et al., 2008). These above-mentioned studies indicate that there are several areas in the EU, where wood combustion is responsible for a substantial share of the ambient air PAHs.

However, there are very few studies to date that have addressed the quantitative effects of residential wood combustion on the ambient air concentrations of PAHS. There are also very few studies on the spatio-temporal variation of these concentrations in urban air. This kind of modelling has previously been seriously hampered by problems in reliably estimating the spatial distributions and temporal variation of the emissions that originate from wood combustion. In the present study, we attempt to combine several years of measurement data from different stations with dispersion modelling as a methodology to overcome this problem.

Wood combustion is a major source of PAHs (e.g., Shen et al., 2013). The emission rates depend heavily on may different factors, such as the type and construction of a fireplace, its operating procedures, and the quality of the wood used (e.g., Ozgen et al., 2014; Tissari et al., 2007 and 2009; Savolahti et al., 2016). The information that can be obtained using simultaneous ambient air concentration measurements and dispersion modelling is therefore crucial for accurately estimating the effects of wood combustion emissions on ambient concentration levels and the exposure of populations to these emissions. In this current study, we combined ambient air concentration data from eight years of measurements with a recent emission inventory and dispersion modelling, to better characterize wood combustion as an emission source of BaP.

The main aim of this study is to evaluate quantitatively the impacts of wood burning on the concentrations of BaP in the Helsinki metropolitan area. We conducted ambient air measurements over several years, compiled a novel emission inventory (which is substantially more detailed compared to the previous corresponding inventories) and modelled atmospheric dispersion for four target years utilizing the Urban Dispersion Modelling system (Karppinen et al. 2000b). The concentrations of levoglucosan, a source-specific tracer for biomass burning particles (Simoneit, 2002), were also measured and compared to concurrently measured concentrations of BaP.

2 Methods

2.1 Site descriptions and sampling periods

The Helsinki metropolitan area (HMA) includes four cities-- Helsinki, Espoo, Vantaa and Kauniainen. The total population of the HMA is approximately 1.1 million, while the population of Helsinki is about 0.63 million. The contributions of the different emission source categories to the total combustion emissions of $PM_{2.5}$ in HMA in 2015 were 39% from small-scale wood

combustion, 31% from energy production and other stationary sources, 28% for vehicular traffic and 2% for harbors, according to Kaski et al. (2016a,b).

The centre of Helsinki is located on a peninsula that is surrounded by the Baltic Sea; the main detached house areas are situated to the west, east and north from the city centre (Fig. 1). The annual mean temperature in Helsinki is 5.9 ºC. However, the seasonal variation in temperatures is substantial; the monthly mean minimum and maximum is -4.7 ºC in February and 17.8 ºC in July, respectively. Heating in the HMA is mainly based on an extensive district heating system that has only a minor impact on air quality. The reason is that this heat is mainly obtained from energy plants burning fossil fuels; most of these plants also have very high stacks. However, fireplaces and sauna stoves are commonly used in suburban detached houses.

The measurement sites used for this study (see Table 1 and Fig. 1) in the HMA were as follows: Eight sites were in detached house areas (2008–2015), one was in a urban background (2007–2015), and three were situated within street canyons (2007, 2010 and 2015). The monitoring height at all these stations was approximately 4 m. The Kallio urban background station is situated in a sports field in the city centre; its distance from the closest street with a traffic volume of 6300 vehicles day^{-1} is approximately 80 m. The stations in the detached house areas, Numbers 1-8 (Vartiokylä, Itä-Hakkila, Päiväkumpu, Kattilalaakso, Kauniainen, Tapanila, Ruskeasanta and Lintuvaara) were situated in suburban areas with relatively lower traffic volumes. In these eight areas, the measurement sites were surrounded by detached houses. Wood combustion appliances were beign used in 90% of the detached houses in the HMA (see Section 2.3). The street canyon stations (Unioninkatu, Töölöntulli and Mäkelänkatu) were on busy streets with high traffic volumes and nitrogen oxides (NO_x)concentrations (Table 1). Average traffic density at Unioninkatu was 12 800 vehicles on a $weekday^{-1}$ (7% heavy traffic), at Töölöntulli it was 44 000 vehicles $weekday^{-1}$ (10% heavy traffic) and at Mäkelänkatu 28 000 vehicles $weekday^{-1}$ (9% heavy traffic).

Data from the stations in the HMA were compared with data from the rural and remote stations. Rural Station 1 of Virolahti (60º31’N, 27º40’E, 5 m a.s.l) in Eastern Finland is located at a distance of 160 km from Helsinki in a rural district on the coast of the Gulf of Finland (Vestenius et al. 2011). Rural Station 2 is situated a distance of 210 km north from Helsinki in Hyytiälä (61º51’N, 24º17’E, 181 m a.s.l) and is a boreal forest site that is part of the SMEAR network, SMEAR II (Station for Measuring Ecosystem-Atmosphere Relationships) in Southern Finland (Hari and Kulmala, 2005). The remote station of Pallas is situated in Matorova, Northern Finland (68°00'N, 24°14'E, 306 m .a.s.l.), a 900 km distance from Helsinki. Pallas is located in the subarctic region in the northernmost limit of the northern boreal forest zone (Hatakka et al. 2003).

2.2 Measurement methods

The daily PM_{10} samples were collected on polytetrafluoroethylene (PTFE) filters (FluoroporeMembraneFilters, 3.0 μm, Ø 47mm, Merck Millipore Company, Germany) every 2-4th day by MicroPNS –low volume samplers. The flow rate used was

38 l min^{-1}; the average total collected volume for the 24-hour samples was 55 m^3. For the analysis samples were usually pooled together as monthly samples, soxhlet extracted with dichloromethane, dried with sodium sulfate, concentrated to 1 ml and cleaned using Florisil solid phase extraction (SPE) cartridges. Afterwards the concentrations of BaP were analysed using gas chromatograph-mass spectrometers (GC-MSs, Agilent 6890N and 5973). For chromatographic separation, the J&W DB-5ms– column (50m x 0,25mm i.d., film thickness 0,25 µm) and 5-meter pre-column (Agilent FS) were used. Helium (99.9996%) was used as a carrier gas with a flow of 1 ml min^{-1}. The temperature program started at 60ºC with a 3 minute hold, followed by an increase of 8ºC min^{-1} to 290ºC and 20ºC min^{-1} to 320ºC with a hold of 5 minutes. Deuterated PAH-compounds (phenantrene-d12, chrysene-d12, perylene-d12 and dibenzo(a,h)anthracene-d14, Dr. Ehrenstorfer) were used as internal standards and added to an extraction solvent before extraction. External standards (EPA 610 Polynuclear aromatic hydrocarbons Mix, Supelco) with five different concentration levels were used. In the analysis of BaP, the ISO 12884 (2000) and EN 15549 (2008) standards were followed. Measurement uncertainty was calculated from the partial uncertainties by following the standard EN15549 (2008) for the target value (1 ng m^{-3}) and lower concentration (0.2 ng m^{-3}); that value was found to be 11% and 30%, respectively. The method was previously described in detail by Vestenius et al. (2011).

The levoglucosan concentrations were determined from daily PM_{10} samples taken from the urban background and detached house areas in 2012 and from monthly means in 2011. Samples were collected on PTFE filters on the same days and at same sites as the BaP samples, extracted with 5 ml of MilliQ water with an internal standard and analyzed using high performance anion exchange chromatography-mass spectrometry (Dionex ICS-3000) as described by Saarnio et al. (2010). The used column system consisted of a Carbopac™ PA10 guard (2 mm i.d. x 250 mm length) and analytical (2 mm i.d. x 250 mm length) columns. The eluent was produced by a potassium hydroxide eluent generator (EGC II KOH). The standard solutions were prepared by dissolving a weighed amount of solid levoglucosan (purity 99+%, Acros Organics, NJ, USA) into MilliQ water. Carbon-13-labeled levoglucosan in dimethyl sulfoxide (100 µg ml^{-1}, purity 98%, Cambridge Isotope Laboratories) was used as the internal standard.

2.3 Evaluation of BaP emissions from wood combustion

Emissions of BaP that originated from small-scale wood combustion were evaluated in the HMA, including the spatial and temporal variation in those emissions. We previously modelled the BaP concentrations that originated from local vehicular traffic in this area (Douros & Moussiopoulos, 2014). In this study, the traffic emissions of BaP were calculated from $PM_{2.5}$ exhaust emissions by a scaling factor 0.000031, which was based on traffic emissions used in LOTOS-EUROS model. According to national emission inventory for traffic exhaust emissions, the $PM_{2.5}$ exhaust emission for HMA was 138 tonnes in 2014 and 258 tonnes in 2008 (vtt.lipasto.fi, Mäkelä & Auvinen, 2009). The BaP emission from vehicular traffic is thus less than 5% of the emission from wood combustion. Vehicular traffic has also been shown to have a minor influence on the total

emissions of BaP on European scale (Guerreiro et al. 2015). In addition, there are no potential industrial or other local sources of BaP in the Helsinki Metropolitan Area (Soares et al. 2014).

A novel wood combustion emission inventory was compiled for the HMA in 2014 for the following pollutants: Particles (PM_1, $PM_{2.5}$ and PM_{10}), NO_x, non-methane volatile organic compounds (NMVOC), carbon monoxide (CO), black carbon (BC), and BaP (Kaski et al., 2016a). The BaP emissions that originate from wood combustion depend on numerous factors, such as the type and construction of a fireplace, the operating procedures and habits, and the quality, processing and storage of the wood beign used. For example, in modern fireplaces the BaP emission factors are much lower than in conventional heaters or in sauna stoves (Tissari et al. 2007). Emissions can also be lowered by using a sufficient supply of air (e.g., by controlling batch size) and using clean dry wood (Tissari et al. 2009). However, the detailed emission inventories of wood combustion are scarce internationally; even information on the amount of wood and the kinds of appliances used can be insufficient (Pastorello et al. 2009).

The amount of wood combusted, and the procedures and habits for that combustion were estimated using a questionnaire distributed in the HMA (Kaski et al., 2016a). The goal of the questionnaire was to gather quantitative information on the amount of wood combusted and its combustion characteristics to evaluate its impacts on air quality. The questionnaire was sent to 2500 inhabitants in detached house areas. The response rate was 35%. A stratified sampling procedure was used to ensure the representativity of the replies. The stratification procedure included the following three parameters of these houses; Spatial distribution in the HMA, house construction year and primary heating method. In the HMA, residential wood combustion is not common as a primary heating method, but it is much more frequently used as a method for supplementary heating. According to official statistics by Statistics of Finland and the Helsinki Region Environmental Services Authority (HSY), the total number of detached and semi-detached houses in the HMA in 2014 was about 69 000. Most (52%) of the detached and semidetached houses were primarily heated with electricity. The shares of other primary heating methods were; 22% oil or gas combustion, 18% district heating, 4% geothermal heating, 2% wood combustion and 3% unknown heating method (Statistics of Finland).

Based on the questionnaire (Kaski et al., 2016a), wood combustion was used in approximately 90% of the detached and semidetached houses in the HMA. However, wood combustion was seldom used as a primary heating method in these detached and semidetached houses (only in approximately 2% of the houses); however, it was much more commonly used as a supplementary heating method, and as fuel for the sauna stoves. The annual average amount of wood burned per house was 1.52 (±1.91 standard deviation, SD) solid cubic meters. Most of the wood was used in heat-storing masonry heaters (0.72±1.19 solid-m^3/house) and sauna stoves (0.31±0.77 solid-m^3/house); only a minor amount was burned in boilers (0.09±0.95 solid-m^3/house). In addition, several other fireplace types used wood as a fuel (0.40±1.08 solid-m^3/house; e.g. open fireplaces, ovens and stoves).

In this current study, the emission factors for different types of fireplaces were adopted from the literature (Tissari et al., 2007; Todorović et al., 2007; Hytönen et al., 2009; Lamberg et al., 2011). The BaP emissions from wood combustions were calculated using the following emission factors: 809, 68 and 102 µg MJ^{-1}, for sauna stoves, boilers and other fireplace types (e.g. heat-storing masonry heaters, open fireplaces, ovens, stoves), respectively (Tissari et al., 2007; Todorović et al., 2007; Hytönen et al., 2009; Lamberg et al., 2011). The total BaP emissions from wood combustion were estimated to be 196 kg in the HMA in 2014. The shares of BaP emissions were 2% for primary heating boilers, 67% for sauna stoves and 31% for other fireplace types. The pollutant emissions from sauna stoves are very high since their combustion conditions are usually very poor compared to other fireplace types (e.g. Savolahti et al., 2016 and references therein). Unfortunately, only a limited number of studies provide BaP emission factors for the typical types of fireplaces used in Finland. Therefore, it is very important to undertake new combustion experiment studies to achieve more robust knowledge on the BaP emission factors for sauna stoves and various other fireplace types as well as additional for different burning conditions.

Karvosenoja et al. (2008) presented an uncertainty evaluation for the $PM_{2.5}$ emissions of residential wood combustion in Finland. This uncertainty was estimated to be relatively low for the amounts of wood burned in different fireplace types (±25% at confidence limits of 95%), whereas it was much higher for the emission factors (–54% lower and +88% higher at confidence limits of 95%, respectively). The background information and the methods of evaluation were similar to those found in Karvosenoja et al. (2008) for the emission inventory of this study. Therefore, we estimated that the uncertainties regarding the amounts of wood used are similar to those estimated by Karvosenoja (2008). However, the uncertainties regarding the emission factors of BaP from wood combustion may be higher than those evaluated by Karvosenoja (2008) for $PM_{2.5}$. The reason is that estimates of the $PM_{2.5}$ emission factors from wood combustion are available from several studies (e.g., Karvosenoja et al., 2008 and Savolahti et al., 2016), whereas the estimates for BaP are much more scarce.

The total amounts of wood burned and its allocation to different fireplace types depends on the primary heating method for a house (Kaski et al., 2016a). The spatial distribution of emissions for dispersion modelling was calculated using the following annual BaP emissions estimates for houses that were using different primary heating methods: 2.5, 3.7, 2.0, 4.1, 3.9 and 3.1 g/house for electricity, thermal, district, oil, wood and unknown heating methods, respectively (Kaski et al., 2016a). The previously mentioned values include the total emissions from all fireplace types in a house, including sauna stoves. For the spatial allocation of these emissions, the geographical location and primary heating method information on all 69 000 detached and semidetached houses of the HMA was available from the regional basic register (SePe and SeutuCD) provided by the HSY. The spatial distribution of houses and the BaP emissions are presented in Fig. 1.

The temporal patterns (month, week day, time of day) of the emissions for three different fireplace categories (sauna stoves, boilers and other fireplaces) were estimated based on the information gathered from the questionnaires (Kaski et al., 2016a;

Gröndahl et al., 2011). Unfortunately, we could not extract sufficient information from these questionnaires to model quantitatively the influence meteorological variables, such as temperature, on the emissions. Clearly, during cold periods more wood is used as additional heating, but it was not possible to model this amount quantitatively based on the results of the questionnaire. Therefore, we used the average emission patterns for different months, weekdays and times of day, instead of modelling the emissions based on the actual variation of meteorological parameters.

2.4 Atmospheric dispersion modelling

The atmospheric dispersion of BaP emissions was evaluated using the Urban Dispersion Modelling system developed at the Finnish Meteorological Institute (UDM-FMI). This system includes various local scale dispersion models and a meteorological pre-processor (MPP-FMI, Karppinen et al., 1998 and 2000a). The dispersion modelling of UDM-FMI is based on multiple sourced Gaussian plume equations for various stationary source categories (point, area, and volume sources). For the selected calculation grid, this system was used to compute an hourly time series of concentrations. The modelling system has been evaluated by Karppinen et al. (2000b).

Meteorological input data needed by the dispersion model was evaluated using the meteorological pre-processing model MPP-FMI, based on the energy budget method. The model utilises meteorological synoptic and sounding observations, and its output consists of an hourly time series of relevant atmospheric turbulence parameters and the atmospheric boundary layer height. We used a combination of synoptic observations from the stations at Helsinki-Vantaa (15 km north of the city center) and Helsinki-Harmaja (on an island 7 km south of the city center), and sounding observations from Jokioinen (90 km northwest of Helsinki). The predicted meteorological parameters will vary for each hour of the year, but for each hour, the same value is applied to the whole spatial domain.

In this study, we evaluated the dispersion of BaP that originated from domestic wood combustion. Emissions were uniformly distributed in squares of the size 100m x 100m, and the model was applied to calculate the dispersion that originated from these area sources. The altitude of the releases for domestic wood combustion was assumed to be equal to 7.5 m, including the initial plume rise. This altitude value was based on the average heights of the detached and semidetached houses with the study domain and their chimneys and an estimated average plume rise (Karvosenoja et al., 2010).

The dispersion was separately computed for three different emission source categories: Sauna stoves, boilers, and other fireplaces. The diurnal, weekly, and monthly variations within the emission inventory were applied to each source category. In the dispersion modelling, BaP was treated as an inert substance, i.e., it was assumed to follow atmospheric diffusion, and no chemical or physical transformation was assumed to take place within the urban time scales. We also did not allow for the dry or wet deposition of BaP. The concentrations were computed for the years 2008, 2011, 2013, and 2014 for a receptor grid

with a horizontal grid spacing of 100m x 100m. The influence of terrain on the atmospheric dispersion is parameterised simply as surface roughness.

3 Results and discussion

3.1 Measured concentrations

3.1.1 Annual and seasonal variation of BaP concentrations at different stations

The measured annual means of BaP concentrations at different stations in Finland are presented in Fig. 2 and Table 1. The highest concentrations were measured in suburban residential areas, and the lowest were at the regional background and remote sites. The BaP concentrations at the street canyon sites (SCs) were quite low and the same level as those at the urban background site (UB). The EU target value for BaP (1 ng m^{-3}) was exceeded at two of the residential sites, and the measured concentrations were in near the target value at a few other residential sites. However, at all the other sites, the concentrations were well below the target value. The WHO reference level for BaP (0.12 ng m^{-3}) was exceeded at all the urban and suburban sites every year and at the rural background sites during some years. In a modelling study for Europe, Guirreiro et al. (2016) found the highest BaP concentrations (>0.4 ng m^3) occurred in Eastern and Central Europe. However, BaP concentrations can be high also in other areas of Europe. Compared to measurements compiled at the other background sites in Europe (Vestenius et al. 2011), the concentrations at the rural background sites (RB1 and 2) were relatively high in Finland.

The variation in the annual average BaP concentrations were compared to the corresponding variation for the $PM_{2.5}$ concentrations (Fig. 3). In the case of $PM_{2.5}$, the highest concentration was observed at the busiest street canyon site (SC2). The WHO guideline value for $PM_{2.5}$ (10 µg m^{-3}) was exceeded both at the street canyon site (SC2) and at two of the suburban residential sites (DH3 and DH7). However, the $PM_{2.5}$ concentrations were below the WHO guideline value at most of the residential sites and at every background site.

These results indicate that local traffic has only a minor effect on BaP concentrations, compared with the corresponding effect of small-scale combustion. The increase in BaP concentrations caused by regional and long-range transport was noticeable. The BaP concentrations at one of the regional background sites (RB1) were approximately at the same level as those at the urban background and street canyon sites (Fig. 2). However, the mean BaP concentration at the remote site of Pallas in Northern Finland was clearly lower.

The inter-annual variation of the BaP concentrations at the urban background site (UB) was modest during 2007–2014 (see Fig. 2). The corresponding variation was higher at the residential site 1 (DH1) and at the rural background site 1 (RB1).

The BaP concentrations at all stations in Helsinki have a clear seasonal cycle with the highest values in winter and the lowest ones in summer. At the suburban residential areas (DH1-8), the highest monthly mean values in winter were 1-4 ng m^{-3}, depending on site and year. In summer, the highest monthly values were usually below 1 ng m^{-3}. The monthly variation of BaP concentrations is illustrated in the next sections (see Figs. 4b and 5) and as supplementary information (Fig. S1). In the case of $PM_{2.5}$, the seasonal variation was substantially smaller and different when compared to that of BaP. Prevedouros et al. (2004) demonstrated that at many European sites, this seasonal trend of BaP concentrations is mainly explained by the relatively lower emissions in summer; however, occasionally meteorology and air mass transport can change these patterns. Also, the reactions of BaP are faster and their lifetimes shorter during the summer (Keyte et al. 2013).

3.1.2 Correlation of the BaP and levoglucosan concentrations

Levoglucosan has been shown to be a specific tracer compound for biomass burning, such as residential wood combustion and wild-land fires (Simoneit, 2002; Yttri et al., 2005; Saarikoski et al., 2008; Niemi et al., 2009; Saarnio et al., 2012). However, strictly speaking levoglucosan should not be used as a quantitative tracer for biomass burning from specific sources, due to its reactivity (Hennigan et al., 2010) and a dependency on combustion conditions (Hedberg et al., 2006).

The correlation between the 24-h mean concentrations of BaP and levoglucosan in February 2012 in Helsinki was very high (correlation coefficient R^2=0.91, Fig. 4a). Also monthly mean concentrations in 2011 had a high correlation (R^2=0.82, Fig. 4b). If only the winter months (Jan, Feb, Dec) are considered, then the correlation is even higher (R^2=0.88, N=12). Measured monthly means of BaP and levoglucosan are presented as supplements in Fig. S2. These high temporal correlations indicate that the sources of these two substances are probably mostly the same within the considered domain. However, the results can not be used for a quantitative source apportionment of the BaP concentrations.

The above-mentioned daily and monthly correlations were high both at the detached house areas and in the urban background outside the detached house areas, indicating that the variations of regional and long-range transport were responsible for part of those temporal correlations. Correlation coefficient squared (R^2) for 24-h means for the urban background was 0.82, if one of the 13 parallel samples was removed as an outlier.

The average ratio of BaP and levoglucosan was 0.01 in this study. In biomass burning emissions, Belis et al. (2011) found that the average ratio was 0.0011, based on 10 biomass burning emission studies. This ratio in emissions is much lower than the corresponding ratio in the ambient air measurements in this study. Differences in the atmospheric lifetimes of these compounds could partially explain the difference. The differences in the fuel and the procedures of combustion are also expected to have

a significant effect on this ratio. Tissari et al. (2007) found that BaP is much more abundant for emissions from sauna stoves, compared with the emissions from many other appliances. The specific BaP emissions from sauna stoves were, for example, 38-99 times higher (kg^{-1} of wood burned) when compared to those from conventional masonry heaters, whereas the PM_1 emissions were only four times higher. Therefore, the sauna stoves commonly used in Finland may explain the high ratio of BaP and levoglucosan measured in this study. However, the ratio of BaP and levoglucosan in sauna stove emissions has not yet been reported in the literature.

3.1.3 The effect of sauna stoves and other fireplaces on temporal variation

Sauna stoves that are heated with wood are known to be efficient emitters of PAHs and fine particle mass (Tissari et al. 2007 and 2009). There is a distinct weekly variation in the use of sauna stoves in Finland; they are most frequently used on Saturday afternoons and evenings. Also other fireplaces, except for boilers, are most frequently used during weekends. Clearly, more heating is needed during the colder period of the year, especially in winter; the rate of wood combustion is, therefore, much higher during colder periods. (Gröndahl et al., 2011; Kaski et al. 2016a)

Separate samples were therefore collected on Saturdays at a detached house area near the measurement site DH6 in 2013. On the average, the monthly averaged BaP concentrations were substantially higher on Saturdays, compared to the corresponding mean value for all days (Fig. 5). The values on Saturdays were clearly higher, especially during the winter months of January and February, and part of the summer, i.e., June and July. However, the values in June were based only on a single sample on Saturday. These results indicate that the impacts of wood combustion are indeed highly variable in time.

3.2 Predicted spatial concentration distributions

The spatial distributions of annual average BaP concentrations in the HMA that originated from wood combustion were predicted for four years: 2008, 2011, 2013 and 2014. The results for two years of these years, 2008 and 2011, are presented in Figs. 6a-b. The results for these two years were selected as they represent both the lowest and highest annual average concentrations, due to the differences in meteorological conditions.

The influence of the regional and long-range transported background was not allowed for in the values of these submitted figures. In this way, the influence of local emission sources can be visualized more clearly. The same emission values were applied for all years; however, the influence of the hourly variation in meteorological factors on atmospheric dispersion was taken into account for only all the target years. The predicted differences between the BaP concentrations were, therefore, due solely to the inter-annual variability in the meteorological conditions.

As expected, the spatial variation of the pollution distribution (Fig. 6) was closely associated with the corresponding variation of the emissions (Fig.1b), which in turn was closely associated with the density of the detached and semidetached houses (Fig. 1a). The highest concentrations occurred in the detached house areas where the highest annual average concentrations (in the selected calculation grid with horizontal spacing of100 m x 100 m) were 1.0 and 1.3 ng m^{-3} for 2008 and 2011, respectively. In 2011, the concentrations were clearly higher than they were in 2008. In the center of Helsinki, however, the annual average concentration from local wood combustion was below 0.2 ng m^{-3}.

3.3 Comparison of the observed and predicted annual average concentrations

To compare the predicted to the measured concentrations, a regional background concentration of 0.135 ng m^{-3} was added to the concentrations computed from local residential combustion. This value was the median of the measured BaP concentrations at the regional background station of Hyytiälä (RB2) in Southern Finland in 2009-2014. This regional background value was assumed to be a constant both in time and throughout the entire urban area. Clearly, the actual hourly values of the regional background depend, e.g., on wind direction and other meteorological parameters. As shown in Fig.2, the values at RB2 varied between 0.09 and 0.25. A fairly high temporal variation in the regional background would also be expected for Helsinki.

The predicted and observed annual average concentrations are presented in Fig. 7. Only those days with measurements were taken into account. The predicted concentrations agreed fairly well with the measured concentrations for four detached house areas (DH2, DH3, DH6, and DH7). For two detached house areas (DH1 and DH5), agreement was relatively worse. In case of the urban background site (UB), the agreement varied from year to year. For most stations and years (except for DH2 in 2008 and DH3 in 2011), the computed concentration was higher than the observed value.

One probable reason for the disagreements between modelled and observed concentrations was the inaccurate description of the temporal variation of emissions. The treatment of the temporal variation of emissions in the model is based on temporal variation coefficients (monthly, weekly and daily). However, the model did not take into account the influence of the daily or inter-annual variation of meteorological conditions (especially that of the ambient temperature) on the amount of wood combustion (although it does take into account the influence of meteorology on the dispersion conditions). Furthermore, the uncertainty of emission factors can be substantial. Such uncertainties are partly caused by a scarcity of experimental studies regarding the emissions of various fireplace types, especially for the stoves of saunas (Section 2.3). Such uncertainties are also partially caused by the wide variation of emission factors in terms of the quality and processing of fuels, the quality and structure of heaters, and combustion techniques and procedures (e.g., Ozgen et al., 2014; Tissari et al., 2007 and 2009; Savolahti et al., 2016).

The model also does not take into account the reactivity of BaP in the air. Heterogeneous reactions of BaP on particle surfaces may have an effect on concentrations especially in the summer (Keyte et al. 2013). However, the detailed chemical transformation equations of these reactions are still insufficiently known; it is also expected that most of the BaP molecules are located inside the bulk particles and may, therefore, not be accessible for these reactions. Therefore, BaP is expected to be removed mainly by the dry and wet deposition of particles; the degradation of BaP through chemical reactions, however, is expected to have a relatively smaller effect on the measured BaP concentrations.

Another factor that causes differences between the modelled and the observed concentrations is the spatial resolution of the modelling; the emission sources were assumed to be located in grid squares with a size of 100m x 100m. However, measurements represent specific spatial points; especially in the case of small-scale combustion, so the measured values may be influenced by very local distributions of sources and other features.

The regional background concentration was based on the measured values at the s Hyytiälä station in Southern Finland. However, this site represented more continental conditions compared with the HMA, and thus, it may not have been sufficiently representative of the study domain.

4 Conclusions

The effect of local small-scale wood combustion on BaP concentrations was studied, using ambient air measurements, emission estimates, and dispersion modelling. Measurements were conducted at 12 different locations during the period from 2007 to 2015. A novel emission inventory was compiled for small-scale wood combustion in the HMA in 2014 and the spatial distributions of annual average benzo (a) pyrene concentrations originating from wood combustion were predicted for 4 meteorologically different years: 2008, 2011, 2013 and 2014.

Both the measurements and the dispersion modelling showed that the European Union target value for the annual average BaP concentrations (1 ng m^{-3}) was clearly exceeded in some of the detached house areas. The WHO reference level for BaP (0.12 ng m^{-3}) was exceeded at all urban and suburban sites every year and at rural background sites during most of these years. The predicted annual average concentrations agreed reasonably well with the actual measured concentrations.

For street canyons, the measured concentrations of BaP were at the same level as for the urban background, but clearly lower than those in suburban detached house areas. This result indicates that the influence of local vehicular traffic on the BaP concentrations is very small, or almost negligible, in the street environments of the HMA. The measured BaP concentrations

also highly correlated with the measured levoglucosan concentrations, thus supporting the finding that wood combustion is the dominant source of BaP. Regionally and long-range transported pollutants also were shown to have a notable impact on BaP concentrations in the HMA and Southern Finland.

The concentrations of BaP were clearly higher on Saturdays, when the stoves of saunas and other combustion devices are frequently used. Saunas are very commonly used in Finland, compared to use in other European countries; they are also more common in Finland, than in Nordic countries. Saunas, therefore, have a higher impact on local air quality and BaP concentrations than they do in other countries. The substantial influence of the stoves used for saunas was one of the main reasons, why wood combustion emissions were found to be highly variable in time and space in this study.

Based on both measurements and modeling, it can be concluded that wood combustion is the main local source of ambient air BaP in the HMA. Local wood combustion was found to play a substantially more important role in the concentrations of BaP, compared with those for $PM_{2.5}$.

The application of questionnaires was very useful for compiling the emission inventories of wood combustion. There was a previously compiled national-scale inventory on wood combustion; however, that inventory underestimated the real level of wood combustion. The reason is that wood for combustion is commonly non-invoiced or self-supplied. However, combining the information obtained from ambient air measurements, wood combustion emission estimates (based on questionnaires) and atmospheric dispersion modeling enabled a quantitative characterization of the influence of residential wood combustion to be created. These results can be used in urban and environmental planning, regarding the impacts of small-scale combustion; these results also have significance for ongoing and future environmental and climate change mitigation policies.

Although the predicted and measured annual concentrations in this instance agreed fairly well, there are several research needs still regarding BaP emissions and dispersion modelling. In future studies, it would be valuable to quantitatively measure the BaP emission factors for sauna stoves and various other fireplace types for various operating conditions so as to reduce the uncertainly of these emission estimates. It would also be useful to construct an emission model that would take into account the impact of actual meteorological conditions especially the effects of ambient temperatures on wood combustion activities for different types of houses and fireplaces. That kind of emission model, when combined with dispersion modelling, could potentially improve the accuracy of the BaP concentration predictions substantially, especially for any temporal variations.

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Table 1: Information on the measurement sites, and mean BaP, $PM_{2.5}$ and NOx concentrations and standard deviations between the years in parentheses.

Classification of site	Code	Name of site	Sampling year(s)	BaP (ng m^{-3})	$PM_{2.5}$ (µg m^{-3})	NOx (µg m^{-3})
Detached house area 1	DH1	Vartiokylä	2009-2015	0.6 (0.08)	7.5	21
Detached house area 2	DH2	Itä-Hakkila	2008	1.1	-	-
Detached house area 3	DH3	Päiväkumpu	2011	1.2	10.4	21
Detached house area 4	DH4	Kattilalaakso	2012	0.6	8.2	18
Detached house area 5	DH5	Kauniainen	2013	0.4	7.1	13
Detached house area 6	DH6	Tapanila	2013	1.0	8.8	22
Detached house area 7	DH7	Ruskeasanta	2014	1.0	10.8	19
Detached house area 8	DH8	Lintuvaara	2015	0.9	7.1	14
Street canyon 1	SC1	Unioninkatu	2007	0.3	-	76
Street canyon 2	SC2	Töölöntulli	2010	0.3	13.0	166
Street Canyon 3	SC3	Mäkelänkatu	2015	0.2	8.0	108
Urban background	UB	Kallio	2007-2015	0.3 (0.04)	7.8	28
Rural background 1	RB1	Virolahti	2007-2015	0.2 (0.1)	6.1	5.1
Rural background 2	RB2	Hyytiälä	2009-2015	0.1 (0.05)	-	2.2
Remote background	RE	Pallas	2009-2015	0.03 (0.01)	3.7*	1.0

*only for years 2011, 2012, 2014 and 2015

a) b)

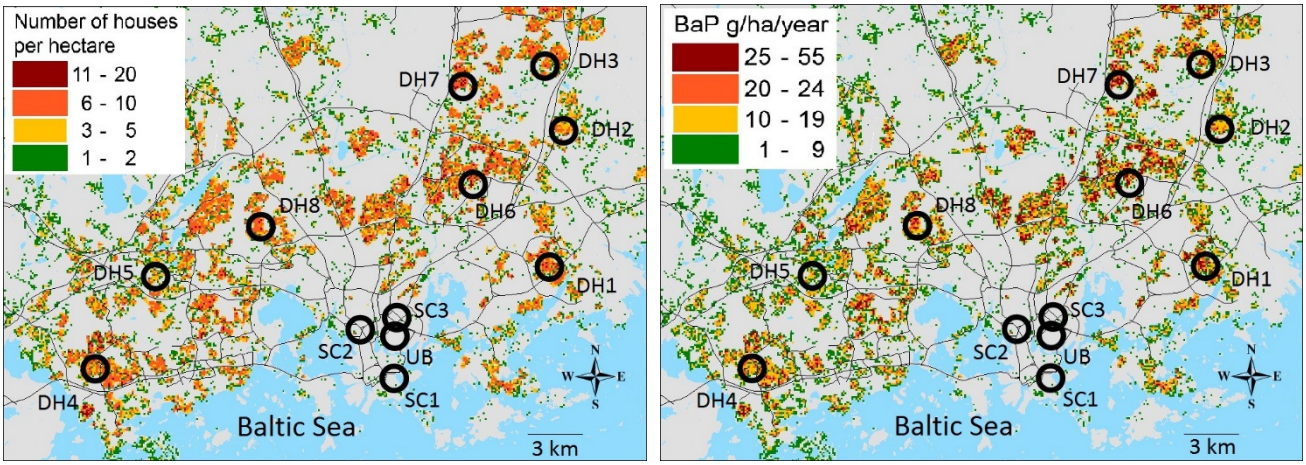


Figure 1: Air quality monitoring sites (diameter of circles 1 km), a) the density of detached and semidetached houses and b) estimated yearly BaP emissions from wood combustion in the Helsinki metropolitan area in 2014. The main road network is shown for clarity.

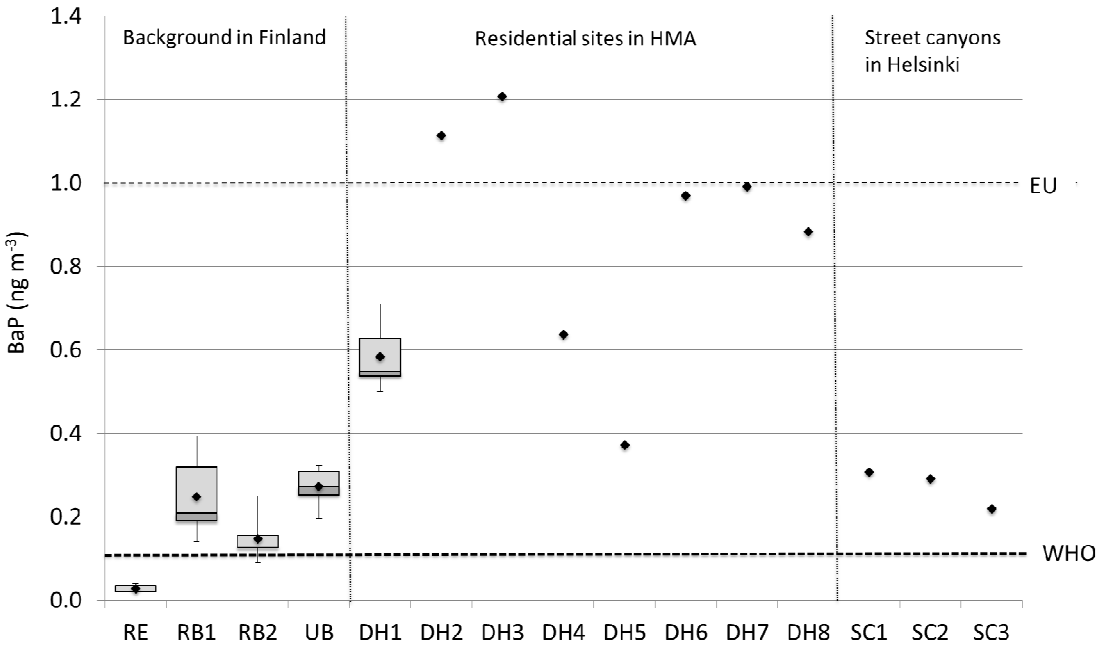


Figure 2: Measured annual means of BaP concentrations (ng m^{-3}) for different stations in Finland, a compilation of results from 2007 to 2015. The box whisker plots represent the smallest value, the 0.25 percentile, the median value, the 0.75 percentile and the largest value for each measuring site. There was only one measured annual mean value at the sites, for which whisker plots have not been presented. The EU target value of 1 ng m^{-3} and the WHO reference level 0.12 ng m^{-3} are marked as dashed lines. (HMA=Helsinki metropolitan area)

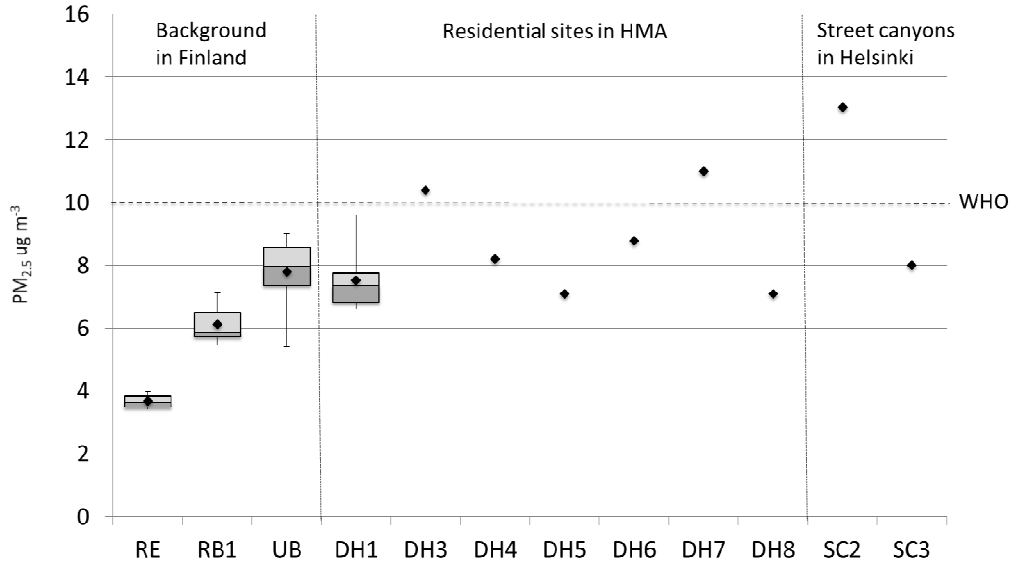


Figure 3: Annual means of $PM_{2.5}$ concentrations (µg m^{-3}) for different BaP measurement stations in Finland. The box whisker plot represents the smallest value, the 0.25 percentile, the median value, the 0.75 percentile and the largest value for each measuring site. The WHO air quality guideline is marked as a dashed line. The presented $PM_{2.5}$ data is for the same years as for BaP in Fig. 2 and Table 1, except for the value at station RE, which is only for the years 2011, 2012, 2014 and 2015. (HMA=Helsinki Metropolitan Area)

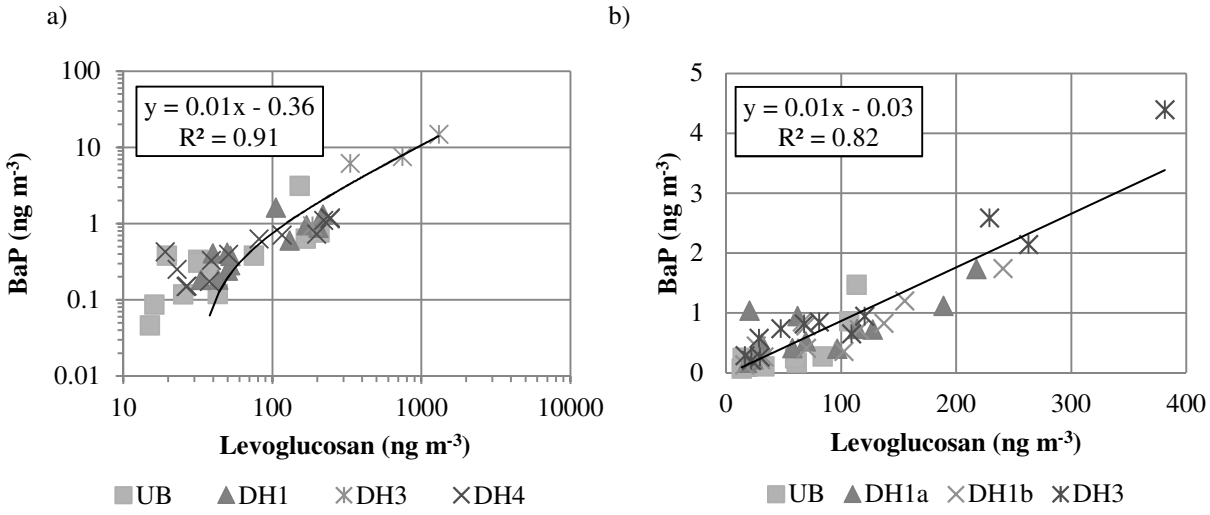


Figure 4: The linear correlation between BaP and levoglucosan concentrations in the urban background (UB) and suburban detached house areas (DH) in Helsinki Metropolitan Area for a) 24 h means in February 2012 and for b) monthly means in 2011. Panels (a) and (b) are presented on logarithmic and linear scales, respectively. The number of data points is 41 (panel a) and 48 (panel b).

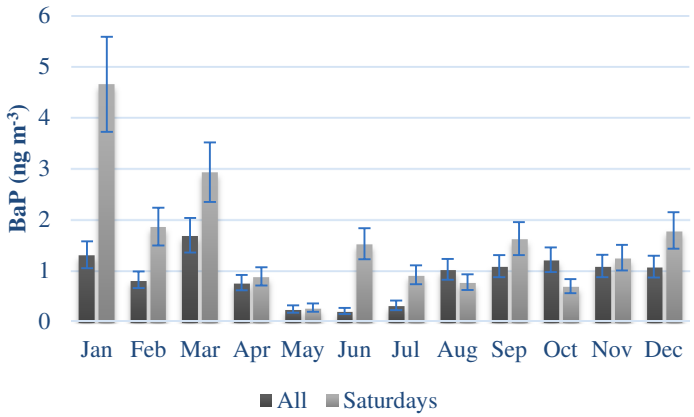
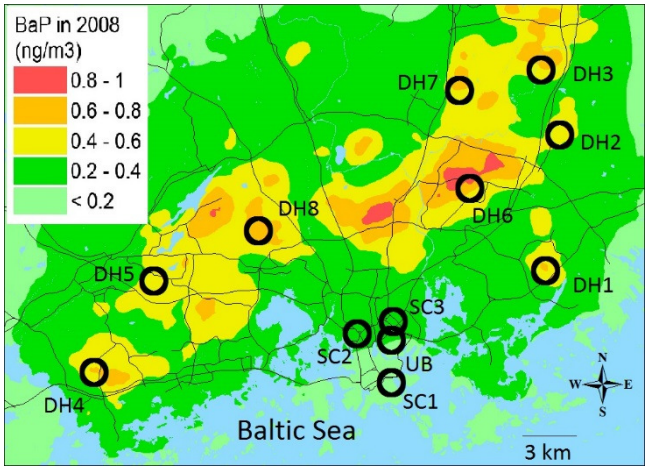


Figure 5: Monthly mean BaP concentrations together with monthly mean concentrations on Saturdays at the detached house area around the measurement site DH6 in Helsinki in 2013. Error bars show the measurement uncertainty.

(a)



(b)

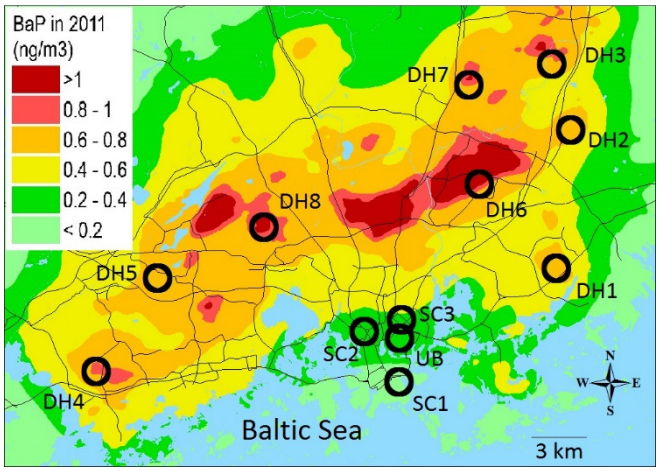


Figure 6: The predicted spatial distributions of the annual average concentrations of BaP originating from wood combustion in the Helsinki Metropolitan Area in 2008 (a) and 2011 (b). Influence of the regional and long-range transported background is not included in the values of these figures. The main road network is shown for best clarity.

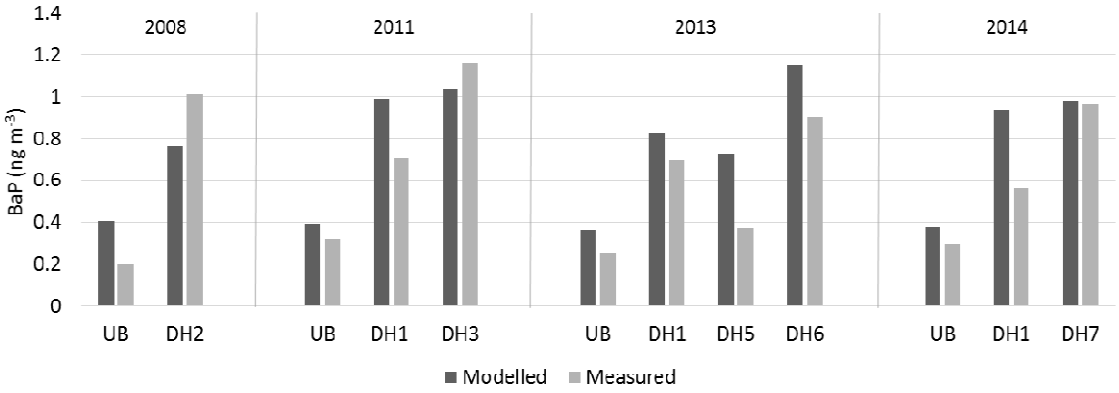


Figure 7: Comparison of predicted and observed annual average BaP concentrations at different sites in the Helsinki Metropolitan Area in 2008, 2011, 2013, and 2014.

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