Dear editor, 1.2.2017

We have carefully considered all the referee comments and improved our manuscript according to them. Please, find below referee comments and our answers to them (marked in color red) and manuscript version, where all the changes have been highlighted.

Yours sincerely,

Heidi Hellén

Answers to the Anonymous Referee #1 comments:

Thank you for the very good comments. We have carefully considered all the comments and improved our manuscript accordingly. Please, find below our answers to the general and specific comments marked in red font.

General Comments. In a pre-review of the manuscript it was already mentioned that many variables, such as emission strength of sources, meteorology and chemical properties of analyzed compound are not well addressed and could cause uncertainties and discrepancies among predicted and measured data.

-We have substantially improved the discussion of sources, meteorology and chemical properties in the revised manuscript, as detailed below.

However, the strength of the study is situated in the relationship between the "wood-burning" marker; levoglucosan, and benzo(a)pyrene, and the selection of urban sites and sub-urban sites. Although the authors show the strong correlation between the compounds, it can not appropriately quantify the apportion to BaP form other sources.

-We totally agree with the reviewer. The BaP vs. levoglucosan comparison was not done to apportion quantitatively the source contributions to BaP (and trying to do that would not be justified). This comparison only gives an indication (qualitatively) that the sources of these substances may be partly the same. We have revised the interpretation of these results to be more accurate and more cautious (section 3.1.2, two first paragraphs).

An important part of the manuscript and results is based on a questionnaire and data from studies that have been published by the "Helsinki Region Environmental Services Authority" in Finnish and can not be consulted without knowledge of this language.

-We would just like to comment that some of the authors are from this Authority, and have actually conducted this inventory themselves. This manuscript actually tries to report the key results of this inventory (and the referenced report) in English.

It is not clear what the uncertainties are of the data, and this is also not included in the presented manuscript. Especially, when comparing the results of measured versus calculated values, it is important to mention these uncertainties in order to get an insight on the quality of the outcome. Nevertheless, the around 800 household that were asked on their use of wood combustion gave a clear idea about the importance of this activity.

-Unfortunately, the original emission inventory of Kaski et al. (2016a) does not include a quantitative evaluation of the uncertainties. However, we have added a discussion on these uncertainties based on previous relevant national

studies on this topic. We have, e.g., added standard deviation values to the average amounts of wood burned (section 2.3, p.7).

Moreover, there seems to be no doubt that wood burning is an important source for benzo(a)pyrene in the HMA, which on its term could be useful in the discussion of the influence of semi-urban / semi-rural areas on regional air quality, since biomass burning is promoted as an energy source in the European Union.The applied model is suitable for the studied region, but could be given more discrepancies in areas which are exposed to multiple sources and where wood burning will not be so dominant.

-Yes, we agree: In some other areas, it could certainty prove to be necessary to allow for the influence of e.g. industrial sources or vehicular sources in much more detail.

It would have been interesting to show more monthly data of all D-sites as well as U-sites to get a clearer overview on the results and the relationship between benzo(a)pyrene and levoglucosan, especially in relationship with co-variables, such as meteorological data.

-Monthly data for all U and D sites and all years can be found as supplement Fig. S1 and S2.

-However, we did not perform any co-variable analyses. Unfortunately, the dataset is too small for drawing any statistically valid conclusions in that respect.

Besides these general comments, the following doubts should be clarified:

Specific comments.

Introduction: Pg2.ln8. A reference is missing on the trends in PAH in others parts in EU. In fact Southern Sweden and Northern Finland are not the only regions/sites were PAH (or specific BaP) is not decreasing, and many of these areas face similar situations as in the present study; i.e. combustion of wood or / and coal. Comment this here.

-We corrected this sentence to cover whole EU area and added a reference.

Ln.28. The outcome of the predicted BaP concentrations for the studied area should be mentioned and discussed here. What did the model predict for the studied areas, and was this related to wood combustion?

-it is now mentioned in the manuscript highest values (>0.4 ng/m3) were predicted for central and eastern Europe and that highest concentrations are mostly due to wood combustion.

Pg3. ln2. The studies mentioned here are based on BaP and levoglucosan (and other compounds) measurements, and indicate that there are areas in EU which have high apportion of wood combustion for PAH.

-this comment was added to the text

Ln.8 to 11. This part could be left out from the manuscript, since it deals with PM2.5

and not BaP.

-This part was removed

Ln.11 to Ln15 “In the Helsinki. . .sauna stoves”. This sentence should be removed since it deals with PM2.5.

-This part was removed

Ln23. “The very few studies” dealing with the “quantitative effect of residential wood combustion on the ambient air concentrations of PAHs” should be mentioned here.

-this was added to the text

Ln24. What do the authors consider “reliable estimations of the spatial distribution and temporal variations”? How are these items addressed in the present study? In my view, the authors present many sampling sites, and many sampling years, but few sites are sampled every year. This result is a mix of data that may not improve the reliability of the outcome. Discuss this in the manuscript.

-The first mentioned sentence was somewhat unclear. We have revised it, to refer specifically to modelling.

-We also revised our reference to the present study to be more cautious (only to say what we attempt to do): “In the present study, we attempt to combine several years of measurement data from different stations with dispersion modelling to overcome this issue.”

-We have presented data for eight years for several sites, which is a substantially extensive data set if we consider specifically the measurements of BaP. Due to laborious and expensive measurements of BaP, there are no extensive data sets (i.e. longer term that in this study) available for BaP.

-It is correct (as the reviewer states) that the dataset is not perfect in terms of homogeneity. This is difficult to achieve in practice in a rapidly evolving urban area, and also due to the resource limitations. However, the fact that not all sites measured each year, has been taken into account in the analysis of the results, of course.

Ln27. The authors could rewrite the sentence to: “Wood combustion is a major source of PAH (Shen et al. 2013), although the emission rates depend heavily on a large variety of factors, such as . . .”

-the sentence was rewritten

Pg4.Ln2. The “new inventory” should be discussed and compared to “old” ones.

-We have revised this sentence to clarify the importance of the new inventory. The word ‘new’ was changed to ‘novel’.

Ln3. There is a reference missing for the levoglucosan analysis in ambient air PM. Moreover it is not clear to me why the data of black carbon was not used in the present study, since this measured in the emissions (Gröndahl et al. 2011) in considerable amount (Savolhathi, et al. 2016). The used model should be introduced here.

-A reference on levoglucosan was added.

-The used model was introduced.

-Black carbon data for ambient air was not available for most of the sites. For instance, there are only two annual BC data sets available for detached house areas in the Helsinki metropolitan area; Vartiokylä in year 2009 and Ruskeasanta in year 2014. An analysis based on this dataset would have therefore not yielded reliable conclusions.

Methods: Ln17. There should be a reference or measurements that demonstrate the "minor impact on air quality".

-A suitable reference for source contributions was added (i.e. Soares et al., 2014)

Measurements methods: Pg5.ln14. What is the uncertainty of the analysis at 0.200 ng/m3, and what do the authors mean with "estimated" measurement uncertainty? Please, clarify.

-uncertainty calculation was clarified and reference to standard EN15549 (2008), which was followed, was added. Uncertainty at the concentration level 0.2 ng/m3 was added.

Ln10. Why do you want to pool samples? This will reduce the information of the sample day. Why was this done?

-Samples were pooled to save resources. Sample preparation and analysis of these samples is laborious and expensive. If the main aim is to get annual mean concentrations, pooling to monthly samples is feasible.

Ln20. It is not clear from the text if the samples of PAH and levoglucosan were the same filter, or different filter samples. It is also not clear if the samples for levoglucosan and PAH were collected on the same day and site. This should be clarified here and the sampling strategy should be discussed.

-We added that samples were collected on same days and at same sites as BaP samples

Ln25. It is not clear to me why the authors do not want to evaluate the emission from traffic. They use arguments, but here they have the tools to quantify the contribution. Please, clarify, why you do not want to quantify this contribution.

-We have actually modelled the BaP concentrations from traffic in this area (within the EU funded TRANSPHORM study). However, the concentrations were negligible both compared with the contributions from residential combustion and regional background. The emission coefficients for vehicular traffic are also substantially uncertain. However, we revised this point by adding a reference to these computations.

Ln31 (but also other issues mentioned from on pg.6 to pg7 referring to Kaski 2016). The report should be explained here in more detail, since this inventory is the fundament of your results. The mentioned report for more details is in Finnish, and many people do not control this language. It is also mentioned here that the black carbon emissions were estimated. It would have of major interest to show the results of BC measurements in relation to BaP and other tracers for the apportion of wood combustion (and other sources) on the ambient air.

-We added more detailed information and discussion on the inventory to section 2.3.

-As it was already mentioned before, black carbon data for ambient air was not available for most of the sites. Therefore, it was not included in this study. However, we are currently studying the concentrations and sources of BC at two different sites in the Helsinki metropolitan area. We are planning to publish these new results within 1-2 years.

Pg6. Ln1. What is the influence of these factors on the results in this study? Explain in more detail.

-Discussion on effects of these factors and how we took them into account in this study, was added.

Ln31. What are the uncertainties of these factors in the present study? Is it possible to introduce them in the final result, so the reader understands the error of the calculations and will be able to validate the model better?

-We added discussion on the uncertainties. Unfortunately, only a few studies provide BaP emission factors for typical fireplace types used in Finland, and these do not report sufficiently the inaccuracies of the measured values. Therefore, we considered that it was unfortunately not possible to present quantitative uncertainty estimates for the BaP emissions.

-As we already mention in the paper, it would be very important to perform new combustion experiment studies to achieve more robust knowledge on BaP emission factors and their inaccuracies, especially for sauna stoves and various other fireplace types, as well as for different burning conditions.

Pg7.ln12. What do you mean you did not get enough information form the questionnaire to estimate the influences of meteorological variables on the emissions? These variables have influence on emissions (also see pag.10.ln30 and pg11.ln27). Clarify the reliability the questionnaire.

-We have revised this paragraph. There was not sufficient quantitative information in the inventory regarding how peoples' heating habits change in terms of e.g. ambient temperature. It is clear that they heat more in cold weather, but how exactly this could be quantified for modelling is less clear.

Atmospheric dispersion modelling: Pg7.ln21. It is not clear why the model was run on an hourly base while BaP levels are monthly concentrations. Please, clarify.

-It is better to execute the model for each hour separately, to obtain a predicted time series of concentrations on a higher temporal resolution. The modelled results are not used only for a comparison with the monthly concentrations, but also for other purposes. The predicted averaged monthly concentration values are also more accurate, when these are based on the use of hourly meteorological data, instead of some more coarsely averaged meteorology.

Pg8.ln6. Why was particle bounded BaP treated as an inert gas?...why not as an inert particle, or a reactive particle? Discuss the differences between these possibilities and the influence on the outcome of the model.

-The text has been revised to be more clear, as suggested. The term 'inert gas' is confusing, and it has been replaced with 'inert substance' in the revised text. In the dispersion modelling context, 'inert substance' means simply that the substance (which can be a particle or a gas molecule) transports and diffuses according to

atmospheric turbulence, and no transformation processes are taken into account. On an urban scale, this is a reasonable assumption for BaP – but not necessarily on regional or large scales.

Correlations of the concentrations of BaP and levoglucosan Pg9.ln23. Here it is mentioned that levoglucosan may not be a quantitative tracer due to its reactivity and dependence of combustion conditions, but this could be compared to BaP, which exhibit similar properties. Are they comparable?

-Levoglucosan has been used as a tracer in many studies. However, the main problem in using it quantitatively in this study was much higher contribution of BaP in the sauna stove emissions than in other fireplaces. Saunas are commonly used in Finland, but we were lacking the information of levoglucosan emissions from sauna stoves. Discussion on this was added to the manuscript to section 3.1.2, last paragraph.

Pg.10.ln1. The observed ratio in the present study should be compared to more than one study (Belis et al, 2011). In fact, the Belis study is also based on measurements, like the present study. The observed difference of a factor 10 should therefore be discussed in other terms. It is important here. For your interest; Fine et al. 2004. ENVIRONMENTAL ENGINEERING SCIENCE 21. observed BaP to levoglucosan ratios closer to 0.001 then 0.01. Why was the relationship between BaP and levoglucosan not used to "estimate" the contribution of wood combustion throughout the year and daily, as was done elsewhere (see Belis et al, 2011, or van Drooge & Perez Ballesta. 2009. ENVIRONMENTAL SCIENCE AND TECHNOLOGY.43.7310)?

-In Belis et al. (2011) ratio, which we mention in our manuscript, was average calculated from 10 different biomass burning studies ((Schauer et al., 2001; Fine et al., 2001, 2002, 2004; Hays et al., 2002, 2005; Dhammapala et al., 2007; Schmidl et al., 2008; Bari et al., 2009). It is not a ratio in ambient air, but average in the wood combustion emissions. This is now clarified in the manuscript (section 3.1.2, last para). We also added discussion on emissions of sauna stoves, where abundance of BaP have been found to be much higher than in many other appliance (Tissari et al. 2007).

- In our opinion, it is not possible to estimate the contribution of wood quantitatively using the relationship between BaP and levoglucosan, due to the dependence of the ratio on combustion conditions. As now also mentioned in the manuscript, the abundance of BaP in sauna stove emissions is much higher than in many other appliances, but since there are no ratio of levoglucosan and BaP in sauna emissions available, we cannot use this method for quantitative estimations. Saunas are commonly used in Finland and therefore they are expected to have substantial impact.

Bari, Md. A., Baumbach, G., Kuch, B., Scheffknecht, G., 2009.Wood smoke as a source of particle-phase organic compounds in residential areas. Atmospheric Environment, 43, 4722e4732.

Dhammapala, R., Claiborn, C., Jimenez, J., Corkill, J., Gullett, N., Simpson, C., Paulsen, M., 2007. Emission factors of PAHs, methoxyphenols, levoglucosan, elemental carbon and organic carbon from simulated wheat and Kentucky bluegrass stubble burns. Atmospheric Environment 41, 2660e2669

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the north eastern United States. Environmental Science and Technology 35, 2665e2675.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. Environmental Science and Technology 36, 1442e1451.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of fine particle emissions from the wood stove combustion of prevalent United States tree species. Environmental Engineering Science 21, 705e721

Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., Schauer, J.J., 2002. Speciation of gas phase and fine particle emissions from burning of foliar fuels. Environmental Science and Technology 36, 2281e2295.

Hays, M.D., Fine, P.B., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmospheric Environment 39, 6747e6764.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources. 3. C-1eC-29 organic compounds from fireplace combustion of wood. Environmental Science and Technology 35, 1716e1728.
Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenboeck, G., Marr, I.L., Puxbaum, H., 2008. Chemical characterisation of particle emissions from burning leaves. Atmospheric Environment 42, 9070e9079

Predicted spatial concentration distributions: Pg10.ln24 (and second paragraph). Is not clear how the "differences in meteorological conditions" influence the high and low BaP levels. What are these conditions and how are they different. Please, clarify.

-We used the actual (hourly) met conditions during each year in the dispersion computations. These affect the results, e.g., during colder winters, there are commonly more stable and extremely stable conditions, and the concentrations are therefore relatively higher.

Pg11.ln6 to 12. The comparison to the Czech study is almost irrelevant, since this is another situation, other sampling method and traffic included-model. The comparison could be removed from the manuscript. Are there no other studied to compare, and what would happen with the model outcome if traffic emissions were included?

-The Czech study is not directly comparable to the present study, and we therefore removed this para. We could not find any directly comparable studies.

Comparison of the observed and predicted average annual concentrations. It is not clear why only annual results are compared? Why not monthly results, or at higher temporal resolution. It is interesting to see how the BaP concentrations fluctuate along the year in the different months (or weeks, or days, such as weekend versus weekdays, in the HMA)

-We did not compare monthly averages, because we did not have monthly regional background estimates for the whole period starting from 2008. The measurements in Hyytiälä started in 2009, and therefore we used the median of measurements in 2009-2014 to estimate the annual average background. However, we did not consider this method possible for monthly averages, which may vary considerably from year to year.

It is unclear why 0.135 ng/m3 was add to the "computed concentration".
If this is background, where does it come from? It is a considerable level. Why the regional background from Hyytiaäla was used and not a regional urban background from a urban background station, or urban site with low levels (as observed in this study)?

-This value is regional background. It needs to represent a value outside the urban area. Using a value inside the urban area would results in double-counting of the effect of urban emissions.

Ln.27 and whole paragraph. It is not clear why the temporal variation of the emissions were not addressed better. If this emissions are based on daily to monthly variations (not really clear how), it is not clear why this was not possible to investigate the influence of the meteorological conditions on the emissions.

-The influence of the meteorological conditions on the emissions depends on human behavior, which is unfortunately not known with sufficient accuracy.

The authors declare that many factors, such as meteorological influences on emissions, reactivity of BaP, particle-bounded properties of BaP, and the use of a regional background in the vicinity of the studied area were not taken in to consideration when they started the modelling, but these factors are well known beforehand.

-We have included a comment on the reactivity of BaP in section 2.4, last para. On an urban scale, this has a negligible effect on the concentrations. The particulate properties: if we assume that BaP is within fine PM (PM2.5), which is a reasonable assumption, the dry deposition can be neglected on an urban scale. Regional background was taken into account, using the best available measured data.

Can the authors improve their model?

-Yes. The influence of meteorological factors on the emissions (not only in the atmospheric dispersion as here) could be modelled in more detail (not only using fixed temporal profiles) in the next stage. However, this is not an easy task, and will require substantial research.

Really, mentioning these limitations in the last part of the discussion is not appropriate. These questions are clear from the beginning and should have been introduced right from the start, or the fact that they were not introduced (as was the case here) they should have been mentioned and discussed beforehand.

-These uncertainties have been mentioned and discussed in the methods section in the revised manuscript, such as section 2.4. The methods section is in our view the right place to mention the modelling uncertainties for the first time.

The model is probably not that bad, but misses a clear uncertainty calculation which makes the discussion too speculative.

-We agree that it would be useful to present a detailed uncertainty analysis of the modelling. However, some of the required input information is unfortunately not available. In particular, the uncertainties of the emission factors are not known sufficiently. This is caused by the difficulty of controlling the numerous factors that affect the emissions of small-scale combustion. This study only used the results of the emission studies, but it was not possible here to re-do emission uncertainty investigations.

I recommend to authors to focus on the real results, the chemical analysis that show that the sub-urban (detached house) zone is an area of seriously high BaP concentrations which is link directly to wood burning based on levoglucosan levels.

-The use of the levoglucosan (LG) measurements also have serious limitations. First, the ratio of BaP and LG depends on the sources, and the ratio is not even known for all source groups. This ratio also depends on the actual fuel used and the procedures of combustion. It is therefore not possible to solve the source apportionment issue by using the levoglucosan measurements. In brief, the LG measurements and useful, but can only be used as a supplementary method to understand the contributions from small scale combustion.

This wood burning is confirmed by the habitants of the area which declare in the questionnaire that they use wood for (secondary heating) and saunas. These saunas are probably typical in Nordic countries, while in other areas domestic heating is more important.
-Saunas are actually clearly more important in Finland, compared to the other Nordic countries.

It does not matter. The results from the questionnaire are used in a simple model to see if this wood burning coincides with the measured BaP concentrations. They do, but it is not clear to what extend..since there is an error calculation missing.

-We have studied the available national and international data and publications on this issue, and included the available information on the uncertainties (please see our responses above). However, the state of the art does not make it possible to make a complete uncertainty analysis. This is a new research area, e.g., compared with the study of vehicular or industrial pollution.

The authors could mention that the applications of questionnaires in the case of wood burning are very powerful, since a national/regional inventory on wood burning is not existing or underestimating the real wood consumption, since the wood is often noninvoiced and self-supplying wood. In the context of the present study a comparison with other questionnaires could be made, such as the one by Pastorello et al. 2011. ATMOSPHERIC ENVIRONMENT. 45.2869–2876.

-as suggested by the reviewer comment on usefulness of questionnaires was added in the conclusions of the manuscript.
-reference to Pastorello et al. 2011 was added into section 2.3.

Answers to the Anonymous Referee #2 comments:

Thank you for the very good comments. We have carefully considered all the comments and improved our manuscript according to them. Please, find below our answers to the general and specific comments marked as color red.

The largest problem with the manuscript is the inadequate treatment of uncertainty/variation in the presentation. Averages should be presented together with the uncertainty/variation related to the data, in both text and figures. Typically the standard deviation should be given.

-We have added standard deviations and uncertainties whenever possible (please see also our answers to referee no 1 and for the specific comments below).

Furthermore the text should be checked by a native English-speaking person to correct grammatical errors. I have noted a few here, but not all.

-Native English-speaking person did now the language editing for the manuscript

Specific comments:
Abstract: Explain all abbreviations the first time they occur.

-we did this

Page 2 line 8-9: "This could be related to the ongoing and not decreasing sources."

This is an unspecific and unclear statement. Please clarify.

-this unclear sentence was deleted

P2 line 15: Change to: If we consider the reference level...

- We changed this

P2 line 20: Add relevant references to the first sentence. The first sentence of this paragraph is on PAH, while the rest of the paragraph presents the study of Butt et al. on PM, not PAHs. I suggest to gather the discussion of previous studies according to the components. It would also be useful to present information on emission inventories, especially for Finland.

-this paragraph was changed. The first sentence was combined with discussion on previous studies and part on PM was removed. There are no emission inventories for BaP and wood combustion available for Finland.

P3 L9: Please consider the effect of improved stoves leading to lower emissions per kg wood combusted.

-based on the recommendations other referee and our reconsideration, this paragraph was removed since it was discussing PM and not BaP.

P3 L11: Unclear sentence which needs revision.

-based on the recommendations other referee and our reconsideration, this paragraph was removed since it was discussing PM and not BaP.

P3 L24-25: Please indicate here how this is overcome in the present work.

-we added a sentence 'In this study we combined all ambient air data from 8 years of measurements with a recent emission inventory and dispersion modelling to better characterize wood combustion as a BaP source.'

P4 site descriptions: It would be useful to provide more information on the distance between measurement sites in non-urban areas and nearby houses with wood stoves.
-distance between measurement sites is shown in Fig. 1.
-better description of suburban measurement sites was added. In these 8 areas, the measurement sites were surrounded by detached houses. Wood combustion appliances are used in 90% of the detached houses in the HMA. Fig. 1 shows the number of houses per hectare. The nearest detached houses were located about 10-25 m distance from the measurement sites.

P5 Section 2.2: Please provide more information on the measurement methods, especially the analysis methods for both PAH and levoglucosan (columns, temperature program, standards and so on).

-better descriptions on measurement methods were added

Line18: Did you really use deionized water and not MilliQ water?

- word ‘deionized’ water was changed to ‘MilliQ’ water.

P6 L5: the amount of the wood combusted -> the amount of wood combusted...

-corrected

P6 L19-22: Please provide the standard deviations for these averages.

-we added standard deviations

P8 L19: have been -> are

-corrected

P9 L5-6: Is this data shown?

-This is shown by the box whisker plots in Fig. 2. Reference to this figure was added into the text

P10 L1-4: Please clarify this paragraph.

-more discussion on ratio between BaP and levoglucosan was added

P11 L19: Please discuss the uncertainty associated with this approach.

-Discussion on possible variation of background value has been added into text

P11 L30: Is there previous studies that show this effect?

-we were not able to find any previous studies showing this effect.

P11L31: In general -> Furthermore. Since this is a different problem you discuss.

-this was corrected

P11 L34. Please cite relevant literature here.

-references were added

P12 : Please discuss your results compared to other previous studies.

-discussion on concentration levels were added in the section 3.1.1.

P13 L7-8: Please improve this sentence.

-this sentence was changed

Table 1 and figures: Please provide standard deviations when possible. The points in Figures 2 and 3 are annual values and the variation should be clearly stated (even though it might not be feasible to make box and whisker plots). Bars in Fig. 5 also lacks

indication of the associated variation.

-we added standard deviations between the years into the table 1 and error bars showing the measurement uncertainty into figure 5.

-Seasonal variation is much higher than inter-annual variation. Therefore we think that showing the standard deviation calculated from the monthly variations for single points in figure 2 and 3 would make them unclear. In these figures annual values are compared with each other and with reference values and therefore we wish to keep box and whisker plots describing the inter-annual variation. Seasonal variations are shown in figure 5 and in supplement figures S1 and S2.

Evaluation of the impact of wood combustion on benzo(a)pyrene (BaP) concentrations~~, ; using ambient air~~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 ~~is~~ 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 ~~was~~ is evaluated, using ambient air measurements, emission estimates and dispersion modelling. ~~Measurements~~ The measurements were conducted at 12 different locations during ~~a~~ the period from 2007 to 2015. The spatial distributions of annual average ~~benzo(a)pyrene~~BaP concentrations ~~originated~~ 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 ~~in part~~certain ~~of the~~ suburban detached house areas. However, ~~over~~ in most of the other urban areas, including the centre of Helsinki, the concentrations were below the target value. The measured BaP concentrations ~~were~~ highly correlated with the measured levoglucosan concentrations ~~at~~ 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, ~~being~~ clearly lower than those in suburban detached house

areas. The predicted annual average concentrations ~~agreed fairly well~~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 w~~W~~ood is still widely used as a fuel for residential heating ~~in many countries~~. 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 ~~of~~ for both the total and carcinogenic PAHs (EC, 2004). Generally PAH concentrations ~~in~~ in the European Union ~~area~~ have ~~been~~ slightly decrease~~ding~~ for the period~~during~~~~in~~ 2007-2014; however, ~~, but~~ there are several~~many~~ areas, ~~where~~where~~in which~~ no such significant trend has been observed, or ~~there is~~ even an increasing trend has been noted ~~have been observed~~ (European Environment Agency, 2015; Anttila et al. 2016)~~Even though concentrations of many pollutants have decreased in European Union area during last 20 years, any significant trend for most PAHs was not found in background air of Southern Sweden and Northern Finland (Anttila et al. 2016). This could, be related to the ongoing and not decreasing sources.~~

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 ~~been of~~a concern in Europe, since the concentration levels have been relatively high ~~with respect~~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 ~~that were~~ above the above mentioned target value ~~of BaP~~. If we ~~will~~ 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~~were~~ exposed to BaP values ~~that were~~ 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. ~~Butt et al. (2016) modelled the impact of residential combustion emissions on atmospheric aerosol in 2000, using a global aerosol~~

Formatted: Not Highlight

microphysics model. The largest contributions of residential emissions to annual surface mean $PM_{2.5}$ concentrations were found to occur in East Asia, South Asia, and Eastern Europe. Mortality due to residential emissions was found to be greatest in Asia, with China and India accounting for 50% of simulated global excess mortality.

Guerreiro et al. (2015) evaluated on a European level the main emission sources of BaP, on a European level for the 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 especially (>0.4 ng m^{-3}) 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.

Formatted: Superscript

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 using 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 representing 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 had played an important role on in the PAH concentrations in urban air, even though traffic and coal combustion were found to be the main sources (Jang et al., 2013).

Wood burning for domestic heating is a major emission source of primary $PM_{2.5}$ in many Nordic cities and its role may become even more pronounced in the future, if wood consumption continues to increase (Savolahti et al., 2016). Denby et al. (2010) evaluated the source contribution of wood burning at measurement sites in the Norwegian cities of Oslo and Lycksele to be around 25% for the $PM_{2.5}$ concentrations. In the Helsinki metropolitan area, the $PM_{2.5}$ emissions originated from residential wood burning were found to be 39% of the total annual emissions of all combustion sources (Kaski et al., 2016a,b). Residential wood burning in the Helsinki metropolitan area is spatially concentrated on suburban detached house areas, in which substantial amounts of PM can be emitted from various wood combustion devices, such as, e.g., heat storing masonry heaters and sauna stoves.

Formatted: Highlight

For PAHs wood combustion may be even more significant source than for $PM_{2.5}$. 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 includeding 164 detached houses, wherein which wood was used as a secondary energy source (Hellén et al., 2008).

These~~se~~ above-mentioned studies indicate that there are several areas in the EU, ~~for~~where ~~have high apportion of~~ wood combustion ~~for~~is responsible for a substantial share of the ambient air PAHs.

Formatted: English (United Kingdom)

However, ~~the scientific information is scarce regarding the quantitative effects of residential wood combustion on the ambient air concentrations of PAHs.~~ there are very few studies to date that have addressed~~dealing with~~ the quantitative effects of residential wood combustion on the ambient air concentrations of PAHS. There are also very few studies ~~regarding~~ on the spatio-temporal variation of ~~such~~ these concentrations in urban air. This kind of modelling ~~research~~ has previously been seriously hampered by problems in reliably estimating the spatial distributions and temporal variation of the emissions ~~originated~~ that originate from wood combustion. ~~Here~~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)~~;~~. T~~although t~~he emission~~s~~ rates depend heavily on may different factors. ~~Even though emission inventories indicate that wood combustion is a major source of PAHs (e.g., Shen et al., 2013), estimating wood combustion emissions is challenging, as these depend on numerous 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 ~~based on~~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 ~~all~~ ambient air concentration data from eight~~8~~ years of measurements with a recent emission inventory and dispersion modelling, to better characterize wood combustion as an emission source of BaP ~~source~~.

The main aim of this study is to evaluate quantitatively ~~evaluate~~ the impacts of wood burning on the concentrations of BaP in the Helsinki metropolitan area. We ~~have~~ conducted ambient air measurements ~~during~~ over several years, compiled a ~~new~~ novel emission inventory (which is substantially more detailed compared ~~with~~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 ~~with the~~to concurrently measured concentrations of BaP.

2 Methods

2.1 Site descriptions and sampling periods

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

39% ~~for~~ from small-scale wood combustion, 31% ~~for~~ 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 ~~of the~~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 ~~for this~~ is that ~~the~~ 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~~in~~ this study (see Table 1 and Fig. 1) in the HMA were ~~situated~~ as follows: ~~eight~~ 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 ~~of Kallio~~ 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, N~~n~~umbers 1-8 (Vartiokylä, Itä-Hakkila, Päiväkumpu, Kattilalaakso, Kauniainen, Tapanila, Ruskeasanta and Lintuvaara) were situated in suburban areas with relatively lower traffic volumes. In these ~~8~~eight areas, the measurement sites were surrounded by detached houses. Wood combustion appliances ~~are~~were beign used in 90% of the detached houses in the HMA (see Section 2.3). The s~~S~~treet 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~~ 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 ~~was~~ were compared with data from the rural and remote stations. Rural ~~station~~ 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~~ Station 2 ~~that~~ is situated ~~at~~ 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~~ Southern Finland (Hari and Kulmala, 2005). The r~~R~~emote station of Pallas is situated in Matorova, Northern Finland (68°00'N, 24°14'E, 306 m .a.s.l.), ~~at the~~ a 900 km distance ~~of 900 km~~ from Helsinki. Pallas is located in the subarctic region ~~at~~ in the northernmost limit of the northern boreal forest zone (Hatakka et al. 2003).

Formatted: Font: 10 pt

Formatted: Font: 11 pt

2.2 Measurement ~~methods~~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}; ~~and~~ 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. After ~~that~~ wards the concentrations of BaP were analysed ~~by~~ 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 60°C with a 3 minute hold, followed by an increase of 8°C min^{-1} to 290°C and 20°C min^{-1} to 320°C 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 ~~at the target~~ value (1 ng m^{-3}) and lower concentration (0.2 ng m^{-3}); that value was found ~~was estimated~~ to be 11% and 30%, respectively. The method ~~has been~~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 ~~de~~ionized ~~-~~MilliQ water with an internal standard and analyzed ~~with~~ using high performance anion exchange chromatography-mass spectrometry (Dionex ICS-3000) as described by Saarnio et al. (2010~~2~~). 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

E~~The e~~missions of BaP that originated from small-scale wood combustion were evaluated in the HMA, including the spatial and temporal variation in those emissions. ~~We did not evaluate the emissions of BaP originated from local vehicular traffic, or other potential local sources.~~ We ~~have~~ 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

Formatted: Superscript
Formatted: Superscript
Formatted: Superscript
Formatted: Superscript
Formatted: Superscript
Formatted: Superscript
Formatted: Superscript
Formatted: Superscript
Formatted: Highlight
Formatted: Superscript
Formatted: Superscript
Formatted: English (United Kingdom)
Formatted: Adjust space between Latin and Asian text, Adjust space between Asian text and numbers
Formatted: Font: (Default) Times New Roman
Formatted: Font: (Default) Times New Roman
Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow
Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)
Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)
Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)

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. ~~; however, these contributions were negligible both compared with the contributions from the residential combustion and those from the regional background.~~ Vehicular traffic has also been shown to have a minor influence on the total emissions of BaP on European scale (Guerreiro et al. 2015). ~~; also based on our ambient air measurements at traffic sites (see Section 3.1.) emissions of BaP from traffic are low in the HMA.~~ In addition, ~~to this~~ there are no potential industrial or other local sources of BaP in the Helsinki ~~m~~Metropolitan Area (Soares et al. 2014).

A novel wood combustion emission inventory was compiled for the HMA in 2014 for the following pollutants: ~~particles~~ Particles (PM_1, $PM_{2.5}$ and PM_{10}), ~~nitrogen oxides (~~NO_x~~)~~, non-methane volatile organic compounds (NMVOC), carbon monoxide (CO), black carbon (BC), and ~~benzo(a)pyrene (~~BaP~~)~~ (Kaski et al., 2016a)). ~~For a more detailed description of this inventory, the reader is referred to the report by Kaski et al. (2016a).~~ The BaP emissions ~~originating~~ 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 ~~with~~ a sufficient supply of air (e.g., by controlling batch size) and ~~by the~~ useing ~~of~~ clean dry wood (Tissari et al. 2009). However, ~~Often~~the detailed ~~-~~emission inventories of wood combustion are scarce internationally~~lacking;~~ ~~-~~even information on the amount of wood and the kinds of appliances used ~~may~~can be insufficient~~used at the local scale~~ (Pastorello et al. 2009). ~~In this study, a questionnaires on the use of wood and emission factors for different types of fireplaces from existing literature (Tissari et al., 2007; Todorović et al., 2007; Hytönen et al., 2009; Lamberg et al., 2011) were used to characterize the effects of these factors.~~

The amount of wood combusted, and the procedures and habits for that combustion were estimated ~~by~~ using a questionnaire distributed in the HMA (Kaski et al., 2016a). The ~~aim~~ goal of the questionnaire was to gather quantitative information on the amount of ~~the~~ wood combusted and ~~the~~ its combustion characteristics~~, in order~~ to evaluate its impacts on air quality. ~~-~~The questionnaire was sent to 2500 inhabitants ~~of~~ 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~~ Spatial distribution in the HMA, house construction year and primary heating method. In the HMA~~Finland~~, residential wood combustion is not common as a primary heating method, but it is ~~substantially~~ much more frequently used as a method for supplementary heating. According to official statistics by ~~the~~ 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.

Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)

Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)

Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)

Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)

Formatted: Font: (Default) Times New Roman, 10 pt, Font color: Auto, English (United States)

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Commented [JK1]: Poistin tästä lauseen " also based on our ambient air measurements at traffic sites (see Section 3.1.) emissions of BaP from traffic are low in the HMA."
Sillä artikkeleissa ei tule viitata eteenpäin varsinkaan johtopäätöksiin tai tuloksiin joita joskus myöhemmin artikkelissa tullaan esittämään. Vasta kun data on esitetty ja tulkittu etc. Siihen voidaan viitata.

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Formatted: Font: (Default) Times New Roman, English (United States), Text Outline, Shadow

Formatted: Font: (Default) Times New Roman

Formatted: Subscript

The shares of other primary heating methods were ~~as follows~~; 22% oil or gas combustion, 18% district heating, 4% geothermal heating, 2% wood combustion and 3% unknown heating method (Statistics of Finland).

~~According to~~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 ~~in~~ for the sauna stoves ~~of saunas~~. 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) ~~and~~, only a minor amount was burned in boilers (0.09±0.95 solid-m^3/house). In addition, ~~there are also~~ several other fireplace types used~~to use the~~ 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 ~~was~~ 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, ~~quite~~ only a limited number of studies provide BaP emission factors for the typical types of fireplaces ~~types~~ used in Finland. Therefore, it ~~would be~~is very important to ~~perform~~ 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.

~~The original emission inventory of Kaski et al. (2016a) does not include quantitative evaluation of uncertainties.~~ Karvosenoja et al. (2008) presented an uncertainty evaluation for the $PM_{2.5}$ emissions of residential wood combustion in Finland~~:~~. T~~h~~his~~e~~ uncertainty was estimated to be relatively low ~~(95% confidence limits ±25%)~~ for the amounts of wood burned in different fireplace types (±25% at confidence limits of 95%), whereas it was much ~~and quite~~ higher ~~(lower and higher 95% confidence limits –54% and +88%, respectively)~~ 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. ~~WWe therefore~~ Therefore, we estimated that the uncertainties ~~of~~regarding the amounts of wood used ~~y of BaP emission inventory of the HMA (Kaski et al., 2016a) might be~~are ~~quite~~ similar ~~for the amounts of wood burned but higher for the BaP emissions factors~~to those estimated by Karvosenoja (2008). However, the uncertainties ~~of~~regarding the emission factors of BaP from wood combustion may be higher than those evaluated by Karvosenoja (2008)

for $PM_{2.5}$. The reason ~~for this~~ is that estimates of the $PM_{2.5}$ emission factors from wood combustion are available from several studies (~~references in~~e.g., ~~-~~Karvosenoja et al., 2008 and Savolahti et al., 2016), ~~but~~whereas ~~those~~the estimates for BaP ~~emission factors~~ are ~~only presented in few studies (see previous section)~~much more scarce.

The total amounts of wood burned and its allocation to different fireplace types ~~is dependent~~depends on the primary heating method ~~of~~ for a house (Kaski et al., 2016a). The s~~S~~patial 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 ~~contain~~ include the total emissions from ~~the~~ all fireplace types ~~of~~ in a house, including sauna stoves. For the spatial allocation of these emissions, the geographical location and primary heating method information ~~of~~ 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 ~~shown~~ 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~~did~~ not extract~~get~~ ~~enough input~~sufficient information from these questionnaires to model quantitatively ~~estimate~~ the influence meteorological variables, such as temperature, on the emissions ~~on daily or interannual level~~. ~~It is expected that~~Clearly, ~~for example~~ during ~~on~~ cold period~~winter~~s more wood is used as additional heating, but it was not possible to model this amount quantitatively based on the results of the questionnaire. ~~due to limited data set this was not taken into account in the modelling.~~T~~We t~~herefore, we used the ~~Here only~~ average emission patterns for different months, weekdays and ~~the~~ times of day ~~was described~~, instead of modelling the emissions ~~in terms of~~based on the actual variation of ~~the~~ meteorological parameters.

2.4 Atmospheric dispersion modelling

The atmospheric dispersion of BaP emissions was evaluated ~~with~~using the Urban Dispersion Modelling system ~~that has been~~ developed at the Finnish Meteorological Institute (UDM-FMI). ~~The~~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 ~~source~~sourced Gaussian plume equations for various stationary source categories (point, area, and volume sources). ~~-~~For the selected calculation grid, ~~the~~this system was used to compute an hourly time series of concentrations. The modelling system has been evaluated by Karppinen et al. (2000b).

Formatted: Subscript

Formatted: Subscript

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 ~~of~~at Helsinki-Vantaa (15 km north of the city center) and Helsinki-Harmaja (on an island 7 km south of the city center), and ~~the~~ 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 ~~for~~to the whole spatial domain.

In this study, we ~~have~~ 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 ~~is~~was based on the average heights of the detached and semidetached houses with the study domain and their chimneys ~~within the study domain,~~ 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~~gas~~, i.e., it was assumed to follow atmospheric diffusion, and ~~n~~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 ~~ones~~were at the regional background and remote sites. The BaP concentrations at the street canyon sites (SCs) were quite low and ~~at~~ 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 ~~the vicinity of~~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 ~~their~~a modelling study for Europe, Guirreiro et al. (2016) found the highest BaP concentrations (>0.4 ng m^3) occurred in ~~for~~ Eastern and Central Europe. However, ~~as shown in this study~~ 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), ~~also~~the concentrations at the rural background sites (RB1 and 2) wea~~a~~re relatively high in Finland.

The variation ~~of~~in the annual average BaP concentrations ~~can be~~were compared ~~with~~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 ~~the~~ BaP concentrations, compared with the corresponding effect of small-scale combustion. The increase ~~of the~~in BaP concentrations caused by ~~the~~ regional and long-range transport ~~is~~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~~Northern Finland was clearly lower.

The inter-annual variation of the BaP concentrations at the urban background site (UB) ~~has been~~was modest during 2007–2014 (see Fig. 2). The corresponding variation ~~has been~~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 ~~is~~was substantially smaller and different when compared to that of BaP. ~~-~~Prevedouros et al. (2004) ~~showed~~demonstrated that at many European sites, this seasonal trend of ~~the~~ 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 ~~lifetime~~their lifetimes shorter during the summer (Keyte et al. 2013).

Formatted: Superscript

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). ~~Even if~~However, strictly speaking levoglucosan ~~may~~ should not be used as ~~not be~~ 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~~),).~~ ~~its concentrations are still useful in tracking the biomass combustion emissions.~~

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 ~~add more confidence to our finding~~ 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.

~~wood burning is the most important local source for BaP in this area.~~ The above-mentioned daily and monthly correlations were high ~~not only~~both at the detached house areas~~, but also~~ 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 ~~is~~ was removed as an outlier.

The a~~A~~verage 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, ~~calculated~~ based on~~from ten~~ 10~~10 different~~ biomass burning emission studies ~~has been 0.0011 (Belis et al. 2011)~~. This ratio in emissions is much lower ~~ratio~~ than the corresponding ratio in the~~our~~ ambient air measurements ~~of~~in this study~~, which~~ ~~Our measurements were ambient air measurements and therefore differences in reactivity of the compounds in air may explain part of the difference~~. D~~, i~~fferences in the atmospheric lifetimes of these compounds could~~in air may~~ partially~~ly~~ explain ~~part of~~ the difference. ~~, but also~~ The differences in ~~used~~ the fuel and the procedures of combustion~~way of burning~~ are also expected to have a significant effect on ~~the~~ this ratio. Tissari et al. (2007) found that BaP is much more abundant for~~in the~~ emissions from sauna stoves, compared with the ~~emissions than in 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~~4~~ times higher. Therefore, the sauna stoves commonly used in Finland may explain the high ratio of BaP and levoglucosan ~~found~~ measured in this study. However, ~~Tissari et al. (2007) did not measure levoglucosan and therefore~~the ratio of BaP and levoglucosan in sauna stove emissions has not yet been reported in the literature~~is not available~~.

Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Superscript
Formatted: Subscript

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 ~~of~~in the use of sauna stoves in Finland; ~~these~~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 ~~in~~during colder periods. (Gröndahl et al., 2011; Kaski et al. 2016a)

Separate samples were therefore collected on Saturdays at a detached house area ~~around~~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 ~~during~~for all days (Fig. 5). The values on Saturdays were clearly higher, especially during ~~part of~~the winter months~~, in~~ of January and February, and part of the summer, i.e., June and July. However, the values in June were based only on ~~one~~a single sample on Saturday. ~~T~~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 ~~has~~was not ~~been~~ allowed for in the values of these submitted figures. In this way, the influence of ~~the~~ local emission sources can be visualized more clearly. The same emission values were applied for all years; however, the influence of the hourly variation ~~of the~~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 ~~interannual~~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~~, in which~~ 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}.

~~Sanka et al. (2014) evaluated the spatial variation of the BaP concentrations using dispersion modeling and passive sampling in the city of Liberec in northern Czech Republic. However, the structure and spatial distribution of urban emissions in that city was substantially different compared with the one in the Helsinki Metropolitan Area. They also included local traffic and industrial emissions in the modelling. They found the highest predicted concentrations to occur in the city centre, and close to a bitumen mixing plant. They evaluated that the higher concentrations in the city centre were probably caused by both the higher density of local heating and traffic sources. According to their estimates, 95 % of the urban BaP emissions in winter were originated from domestic heating.~~

3.3 Comparison of the observed and predicted annual average concentrations

To compare the predicted ~~and~~to the measured concentrations, a regional background concentration of 0.135 ng m^{-3} was added to the concentrations computed ~~concentrations~~ from local residential combustion. This value ~~is~~was the median of the measured BaP concentrations at the regional background station of Hyytiälä (RB2) in ~~southern~~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, t~~Real~~he actual hourly values of the regional background depend ~~on~~, e.g., on wind direction~~s~~ and other meteorological parameters~~.~~. As shown in Fig.2, the values at RB2 varied between 0.09 and 0.25. A~~s~~ fairly high temporal ~~high~~ variation in the regional background would also be expected ~~also~~ for ~~background in~~ Helsinki.

The predicted and observed annual average concentrations are presented in Fig. 7. Only ~~the~~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), ~~the~~ 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~~intensity~~ of wood ~~burning~~combustion (although it does take into account the influence of meteorology on the dispersion conditions). ~~In general~~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 ~~the~~ 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 ~~which~~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 ~~the~~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 ~~station of~~s Hyytiälä station in ~~southern~~Southern Finland. However, this site ~~represents~~represented more continental conditions compared with the HMA, and thus, it may not ~~be~~have been sufficiently representative of the study domain.

4 Conclusions

~~Effect~~The effect of local small-scale wood combustion on ~~the~~ 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 ~~the~~ small-scale wood combustion in the HMA in 2014 and the spatial distributions of annual average benzo(a)pyrene concentrations ~~originated~~originating from wood combustion were predicted for ~~four~~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 ~~part~~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 ~~fairly~~reasonably well with the actual measured concentrations.

AtFor street canyons, the measured concentrations of BaP were at the same level as for the urban background, beingbut 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 were 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 southernSouthern 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 withto use in other European countries; they are also more common in Finland, compared with their abundance in the otherthan in Nordic countries. and therefore theySaunas, therefore, have a higher impact on local air quality andthe BaP concentrations than they do in other countries. In other areas domestic heating is more important. Saunas are very common in Finland; they therefore probably have a more pronounced impact on the concentrations of BaP than in any other country globally. The substantial influence of the stoves of 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 was is the main local source of ambient air BaP in the HMA. Local wood combustion was found to have play a substantially more important role for in the concentrations of BaP, compared with those for $PM_{2.5}$.

The applications of questionnaires iswas very useful for compiling the emission inventories of in the case of wood combustion. are very powerful,There was a previously compiled national-scale since a national/regional inventory on wood combustion; however, that inventory burning is not existing or underestimateding the real level of wood combustion. The reason for this is that nsumption, since wood for combustion is commonlyoften non-invoiced orand self-supplyingied. However, cCombining 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 also significance in view of the 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 on thestill regarding BaP emissionemissions and dispersion modelling. In the future studies, it would be valuable to quantitatively measure the BaP emission factors for sauna stoves and for various other fireplace types infor 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 ~~the~~ actual meteorological conditions especially ~~that~~the effects of ~~the~~ ambient temperatures on wood combustion activities for different types of houses and fireplaces. That kind of emission model ~~in combination~~, when combined with dispersion modelling, could potentially ~~substantially~~ improve the accuracy of the BaP concentration predictions substantially, especially ~~regarding their~~for any temporal variations.

Acknowledgements

This study ~~has been a~~was part of the research projects APTA (The Influence of Air Pollution, Pollen and Ambient Temperature on Asthma and Allergies in a Changing Climate~~),~~); MMEA (Measurement, Monitoring and Environmental Efficiency Assessment) ; and the NordicWelfAir (Project #75007: Understanding the link between Air ~~pollution~~Pollution and the Distribution of related Health Impacts and Welfare in the Nordic countries) and BATMAN (Environmental impact assessment of airborne particulate matter: ~~the~~The effects of abatement and management strategies). The funding from the European Commission, the Finnish Funding Agency for Innovation, the Academy of Finland, and the Nordforsk Nordic Programme on Health and Welfare is gratefully acknowledged. ~~The~~This research was also supported by the Academy ~~research fellow project~~Research Fellow Project (Academy of Finland, ~~project~~Project 275608). The original wood combustion activity survey in the HMA was prepared in co-operation ~~by~~with the Work Efficiency Institute, the Helsinki Region Environmental Services Authority, and the Finnish Environment Institute. We also acknowledge Ph.D. Jarkko Tissari from the University of Eastern Finland ~~as well as~~and Ph.D. Niko Karvosenoja and Ph.D. Kaarle Kupiainen from the Finnish Environment Institute for their expertise and kind co-operation in ~~determination of~~determining the emission factors.

References

Anttila, P., Brorström-Lundén, E., Hansson, K., Hakola, H. and Vestenius M.: Assessment of the spatial and temporal distribution of persistent organic pollutants (POPs) in the Nordic atmosphere, Atmospheric Environment, 140, 22-33, 2016.

Belis, C.A., Cancelinha, J., Duane, M., Forcina, V., Pedroni, V., Passarella, R., Tanet, G., Douglas, K., Piazzalunga, A., Bolzacchini, E., Sangiorgi, G., Perrone, M.-G., Ferreroer, L., Fermo, P. and Larsen, B.R.: Sources for PM air pollution in the Po Plain Italy: I. Critical comparison of methods for estimating biomass burning contributions to benzo(a)pyrene, Atmospheric Environment, 45, 7266-7275, 2011.

Butt, E. W., Rap, A., Schmidt, A., Scott, C. E., Pringle, K. J., Reddington, C. L., Richards, N. A. D., Woodhouse, M. T., Ramirez-Villegas, J., Yang, H., Vakkari, V., Stone, E. A., Rupakheti, M., S. Praveen, P., G. van Zyl, P., P. Beukes, J., Josipovic, M., Mitchell, E. J. S., Sallu, S. M., Forster, P. M., and Spracklen, D. V.: The impact of residential combustion emissions on atmospheric aerosol, human health, and climate, Atmos. Chem. Phys., 16, 873-905, doi:10.5194/acp-16-873-2016, 2016.

Denby, B., Karl, M., Laupsa, H., Johansson, C., Pohjola, M., Karppinen, A., Kukkonen, J., Ketzel, M. and Wåhlin, P.: Estimating domestic wood burning emissions of particulate matter in two nordic cities by combining ambient air observations with receptor and dispersion models, Chemical Industry & Chemical Engineerin Quarterly, 16, 237-241, 2010.

Douros, J. and Moussiopoulos, N.: Report on the urban scale model development: overview and validation. TRANSPHORM deliverable D2.3.3. http://www.transphorm.eu/Portals/51/Documents/Deliverables/New%20Deliverables/D2.3.3._c.pdf, 2014

EC (European Council): Directive on relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, 2004/107/EC, 2004.

EN 15549: Air quality – Standard method for the measurement of the concentration of benzo(a)pyrene in ambient air, 2008.

European Environmental Agency: Air quality in Europe – 2015 report. . EEA report No 5/2015. Copenhagen, Denmark doi:10.2800/62459, 2015.

European Environmental Agency: Air quality in Europe – 2016 report. . EEA report No 28/2016. Copenhagen, Denmark doi:10.2800/413142, 2016.

Gianelle, V., Colombi, C., Caserini, S., Ozgen, S., Galante, S., Marongiu, A. and Lanzani, G.: Benzo(a)pyrene air concetrations and emission inventory in Lombardy region, Italy, Atmospheric Pollution Research, 4, 257-266, 2013.

Glasius, M., Ketzel, M., Wåhlin, P., Bossi, R., Stubkjaer, J., Hertel, O. and Palmgren, F.: Characterization of particles from reasidential wood combustion and modelling of spatial variation in low-strength emission area, Atmospheric environment, 42, 8686-8697, 2008.

Gröndahl, T., Makkonen, J., Myllynen, M., Niemi, J. and Tuomi, S.: Small-scale wood combustion in the Helsinki metropolitan area. (in Finnish; Tulisijojen käyttö ja päästöt pääkaupunkiseudun pientaloista), HSY report. 39 p, 2011.

Guerreiro, C., Horalek, J., de Leeuw, F. and Couvidat F.: Mapping ambient concentrations of benzo(a)pyrene in Europe – population exposure and health effects for 2012. ETC/ACM Technical Paper 2014/6, 2015.

Guerreiro, C.B.B., Horalek, J., de Leeuw, F. and Couvidat, F.: Benzo(a)pyrene in Europé: Ambient air concentrations, population exposure and health effects, Environmental Pollution, 214, 657-667, 2016.

Hari, P. and Kulmala, M.: Station for measuring ecosystem-atmosphere relations (SMEAR II), Boreal Env. Res., 10, 315-322, 2005.

Hatakka, J., Aalto, T., Aaltonen, V., Aurela, M., Hakola, H., Komppula, M., Laurila, T., Lihavainen, H., Paatero, J., Salminen, K. and Viisanen, Y.: Overview of the atmospheric research activities and results at Pallas GAW station, Boreal Environ. Res., 8, 365-383, 2003.

Hedberg, E., Johansson, C., Johansson, L., Swietlicki, E. and Brorström-Lundén, E.: Is levoglucosan suitable tracer for wood burning? Comparison with receptor modeling on trace elements in Lycksele, Sweden, J. Air Waste Manage. Assoc., 56, 1669-1678, 2006.

Hellén, H., Hakola, H., Pietarila, H., Kauhaniemi, M. and Haaparanta, S.: Influence of residential wood combustion on local air quality, Science of the Total Environment, 393, 283-290, 2008.

Hennigan, C.J., Sullivan, A.P., Collett, J.L.Jr. and Robinson, A.L.: Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, Geophys. Res. Lett., 37, L09806, 2010.

Formatted: Font: (Default) +Body (Times New Roman)

Formatted: Font: (Default) +Body (Times New Roman), 10 pt

Formatted: Font: (Default) +Body (Times New Roman)

Hytönen, K., Yli-Pirilä, P., Tissari, J., Gröhn, A., Riipinen, I., Lehtinen, K. E. J. and Jokiniemi, J.: Gas–particle distribution of PAHs in wood combustion emission determined with annular denuders, filter, and polyurethane foam adsorbent., Aerosol Sci. Technol., 43, 442-454, 2009.

ISO 12884: Ambient air – Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons – Collection on sorbent-backed filters with gas chromatographic / mass spectrometric analysis, 2000.

Jang, E., Alam, M.S. and Harrison, R.: Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution, Atmospheric Environment, 79, 271-285, 2013.

Karppinen, A., Kukkonen, J., Nordlund, G., Rantakrans, E., Valkama, I.: A dispersion modelling system for urban air pollution. Finnish Meteorological Institute, Publications on Air Quality 28. Helsinki, 58 p, 1998.

Karppinen, A., Kukkonen, J., Elolähde, T., Konttinen, M., Koskentalo, T., Rantakrans, E.: A modelling system for predicting urban air pollution: model description and applications in the Helsinki metropolitan area, Atmos. Environ., 34, 3723-3733, 2000a.

Karppinen, A.,Kukkonen, J., Elolähde, T., Konttinen, M., Koskentalo, T.: A modelling system for predicting urban air pollution: comparison of model predictions with the data of an urban measurement network in Helsinki, Atmos. Environ., 34, 3735-3743, 2000b.

Karvosenoja, N., Tainio, M., Kupiainen, K., Tuomisto, J.T., Kukkonen, J., Johansson, M.: Evaluation of the emissions and uncertainties of $PM_{2.5}$ orginated from vehicular traffic and domestic wood combustion in Finland. Boreal Environ. Res., 13, 465-474, 2008.

Karvosenoja, N., Kangas, L., Kupiainen, K., Kukkonen, J., Karppinen, A., Sofiev, M., Tainio, M., Paunu, V-V., Ahtoniemi, P., Tuomisto J. T. and Porvari, P.:Integrated modeling assessments of the population exposure in Finland to primary PM2.5 from traffic and domestic wood combustion on the resolutions of 1 and 10 km, Air Qual. Atmos. Health., 4, 179-188, DOI 10.1007/s11869-010-0100-9, 2010.

Kaski, N., Vuorio, K., Niemi, J., Myllynen, M. and Kousa, A.: Use of fireplaces; emissions in the Helsinki Metropolitan Area in 2014. (in Finnish with an abstract in English) HSY publications 2/2016. ISBN 978-952-7146-08-8, 2016a.

Kaski, N., Aarnio, P., Loukkola, K. and Portin, H.: Air quality in the Helsinki metropolitan area in 2015, (in Finnish with an abstract in English) HSY publications 6/2016. ISBN 978-952-7146-16-3, 2016b.

Keyte, I.J., Harrison, R.M. and Lammel, G.: Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons-review, Chem. Soc. Rev., 42, 9333-9391, 2013.

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K. Hillamo, R., Hirvonen, M.-R. and Jokiniemi, J.: Physicochemical characterization of fine particles from small-scale wood combustion, Atmospheric Environment 45, 7635-7643, 2011.

Mäkelä, K. and Auvinen, H.: LIPASTO – transport emission database. In: Life cycle assessment of products and technologies. VTT Symposium 262. ISBN 978-951-38-7586-2 (URL: http://www.vtt.fi/publications/index.jsp), ISSN 1455–0873 (URL: http://www.vtt.fi/publications/index.jsp), Publisher: VTT, Vuorimiehentie 5, PL 1000, 02044 VTT. pp. 134-142, 2009.

Formatted: Subscript

Niemi, J.V., Saarikoski, S., Aurela, M., Tervahattu, H., Hillamo, R., Westphal,D.L., Aarnio, P., Koskentalo, T., Makkonen, U., Vehkamäki, H. and Kulmala, M.: Long –range transport episodes of fine particles in southern Finland during 1997-2007, Atmos. Environ., 43, 1255-1264, 2009.

Ozgen, S., Caserini ,S., Galante, S., Giugliano, M., Angelino, E., Marongiu, A., Hugony, F., Migliavagga, G. and Morreale, C.: Emission factors from small scale appliances burning wood and pellets, Atmospheric Environment, 94, 144-153, 2014.

Pastorello, C., Caserini, S., Galante, S., Dilara, P. and Galletti, F.: Importance of activity data for improving the residential wood combustion emission inventory at regional scale. Atmos. Environ., 45, 2869-2876, 2011.

Prevedouros, K., Brorström-Lundén, E., Halsall, C.J., Jines, K.C., Lee, R.G.M. and Sweetman, A.J.: Seasonal and long-term trends in atmospheric PAH concentrations: evidence and implications, Environmental Pollution, 128, 17-27, 2004.

Ravindra, K., Sokhi, R and Grieken, R.V.: Atmospheric polycyclic aromatic hydrocarbons: Source Attribution, emission factors and regulation. Atmospheric Environment, 42, 2895-2921, 2008.

Saarikoski, S.K., Sillanpää, M.K., Saarnio, K.M., Hillamo, R.E., Pennanen, A.S. and Salonen, R.O.: Impact of biomass combustion on urban fine particulate matter in central and northern Europe, Water Air Soil Pollut., 191, 265-277, 2008.

Saarnio, K., Teinilä, K., Aurela, M., Timonen, H. and Hillamo, R.: High-performance anion-exchange chromatography-mass spectrometry method for determination of levoglucosan, mannosan, and galactosan in atmospheric fine particulate matter. Anal. Bional. Chem., 398, 2253-2264, 2010.

Saarnio, K., Niemi, J., Saarikoski, S., Aurela, M., Timonen, H., Teinilä, K., Myllynen, M., Frey, A., Lamberg, H., Jokiniemi, J. and Hillamo, R.: Using monosaccharide anhydrides to estimate the impact of wood combustion on fine particles in the Helsinki Metropolitan Area, Boreal Environmental Research, 17, 163-183, 2012.

Sanka, O., Melymuk, L., Cuor, P., Dvorska, A. and Klanova, J.: Dispersion modeling of selected PAHs in urban air: A new approach combining dispersionb model with GIS and passive sampling, Atmospheric Environment, 95, 88-85, 2014.

Savolahti, M., Karvosenoja, N., Tissari, J., Kupiainen, K., Sippula, O. and Jokiniemi, J.: Black carbon and fine particle emissions in Finnish residential wood combustion: Emission projections, reduction measures and the impact of combustion practices. Atmos. Env. 140, 495-505, 2016.

Schnelle-Kreis, J., Shlorz, M., Orasche, J., Stölzel, M., Peters, A. and Zimmermann, R.: Semi volatile organic compounds in ambient PM2.5. Seasonal trends and daily reasolved source contributions, Environmental Science and Technology, 41, 3821-3828, 2007.

Shen, H., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G., Wang, B., Zhang, Y., Chen, Y., Lu, Y., Chen, H., Li, T., Sun, K., Li, B., Liu, W., Liu, J. and Tao, S.: Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environmental Science and Technology, 47, 6415-6424, 2013.

Silibello, C., Calori, G., Costa, M.G., Mircea, M., Radice, P., Vitali, L. and Zanini, G.: Benzo(a)pyrene modelling over Italy: comparison with experimental data and source apportionment, Atmos. Pol. Res., 3, 399-407, 2012.

Simoneit, B.R.T.: Biomass burning – a review of organic tracers for smoke from incomplete combustion, Appl. Geochem., 17, 129-162, 2002.

Formatted: English (United States)

Formatted: English (United States)

Soares, J., Kousa, A., Kukkonen, J., Matilainen, L., Kangas, L., Kauhaniemi, M., Riikonen, K., Jalkanen, J.-P., Rasila, T., Hänninen, O., Koskentalo, T., Aarnio, M., Hendriks, C. and Karppinen, A.; Refinement of a model for evaluation the population exposure in an urban area. Geosci. Model Dev., 7, 1855-1872, 2014.

Tissari, J., Hytönen, K., Lyyränen, J. and Jokiniemi, J.: A novel field measurement method for determining fine particle and gas emissions from residential wood combustion, Atmospheric Environment, 41, 8330-8344, 2007.

Tissari, J., Hytönen, K., Sippula, O. and Jokiniemi ,J.: The effects of operating conditions on emissions from mansory heaters and sauna stoves, Biomass & Bioenergy, 33, 513-520, 2009.

Todorović, J., Broden, H., Padban, N., Lange, S., Gustavsson, L., Johansson, L., Paulrud, S. and Löfgren, B. E.: Syntes och analys av emissionsfaktorer för småskalig biobränsleförbränning. Slutrapport för avtal 503 0506 och 503 0507 på Naturvårdsverket. Nyköping, Borås, Stockholm, 28 p., http://www.sp.se/sv/units/energy/documents/syntes_final.pdf, 2007.

Yttri, K.E., Dye, C., Slordal, K.H. and Braathen, O.-A.: Quantification of monosaccharide anhydrides by liquid chromatography combined with mass spectrometry: application to aerosol samples from an urban and a sub-urban site influences by small-scale wood burning, J. Air Waste manage Assoc., 55, 1169-1177, 2005.

Vestenius, M., Leppänen, S., Anttila, P., Kyllönen, K., Hatakka, J., Hellen, H., Hyvärinen, A-P., Hakola, H.: Background concentrations and source apportionment of polycyclic aromatic hydrocarbons in South-Eastern Finland. Atmos. Environ., 45, 3391-3399, 2011.

Field Code Changed

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)

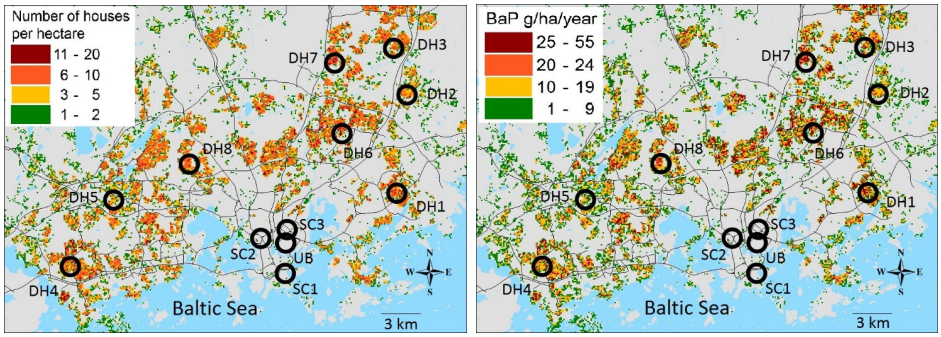


Figure 1: Air quality monitoring sites (diameter of circles 1 km), a) the density of detached and semidetached houses and b) estimated yearly BaP emissions from wood combustion in the Helsinki metropolitan area in 2014. The main road network is shown for clarity.

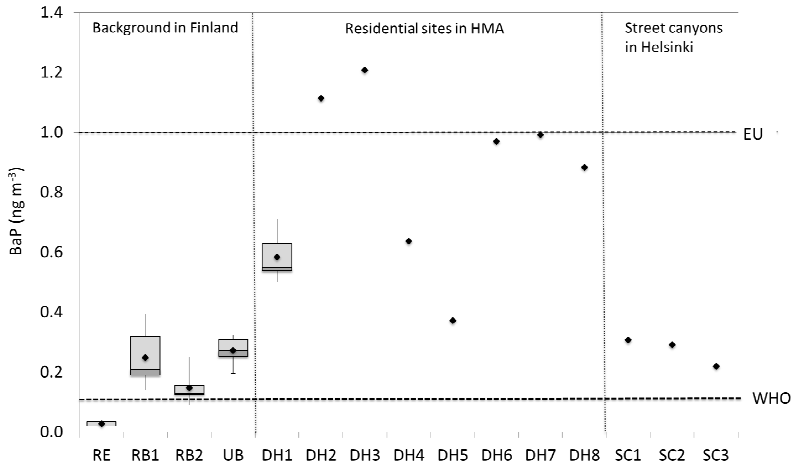


Figure 2: Measured annual means of BaP concentrations (ng m^{-3}) for different stations in Finland, a compilation of results from 2007 to 2015. The box whisker plots represent the smallest value, the 0.25 percentile, the median value, the 0.75 percentile and the largest value for each measuring site. 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)

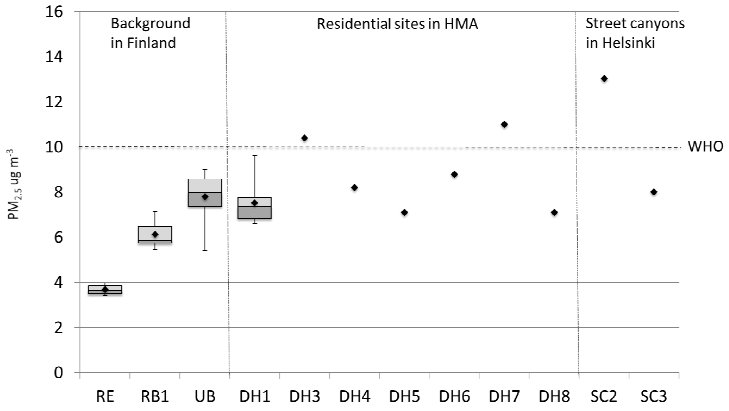


Figure 3: Annual means of $PM_{2.5}$ concentrations (µg m^{-3}) for different BaP measurement stations in Finland. The box whisker plot represents the smallest value, the 0.25 percentile, the median value, the 0.75 percentile and the largest value for each measuring site. The WHO air quality guideline 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)

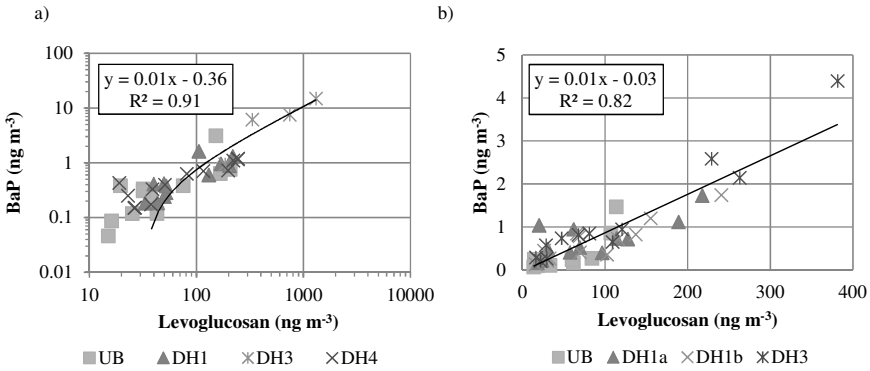


Figure 4: The linear correlation between BaP and levoglucosan concentrations in the urban background (UB) and suburban detached house areas (DH) in Helsinki Metropolitan Area for a) 24 h means in February 2012 and for b) monthly means in 2011. Panels (a) and (b) are presented on logarithmic and linear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

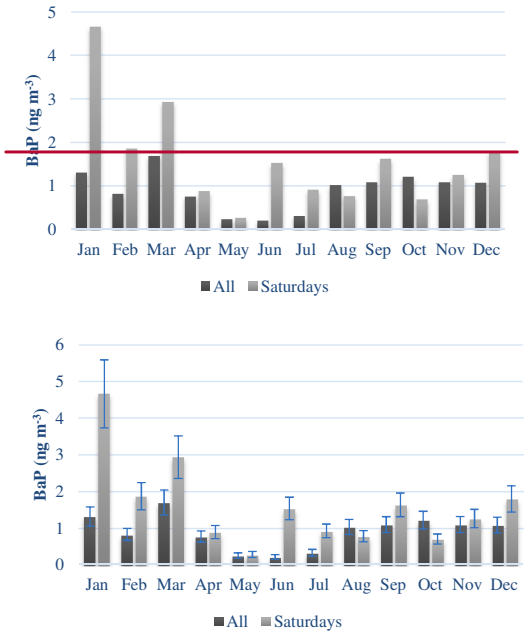
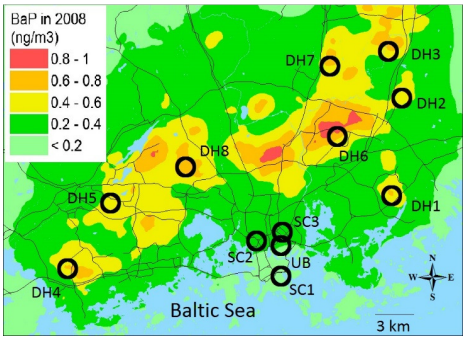


Figure 5: Monthly mean BaP concentrations together with monthly mean concentrations on Saturdays at the detached house area around the measurement site DH6 in Helsinki in 2013. Error bars show the measurement uncertainty.

(a)


BaP in 2008
(ng/m3)
0.8 - 1
0.6 - 0.8
0.4 - 0.6
0.2 - 0.4
< 0.2
DH7
DH3
DH2
DH8
DH6
DH5
DH1
SC3
SC2
UB
SC1
DH4
Baltic Sea
3 km
N
W
E
S

(b)

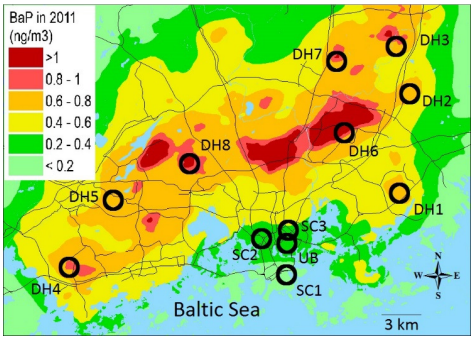

BaP in 2011
(ng/m3)
>1
0.8 - 1
0.6 - 0.8
0.4 - 0.6
0.2 - 0.4
< 0.2
DH7
DH3
DH2
DH8
DH6
DH5
DH1
SC3
SC2
UB
SC1
DH4
Baltic Sea
3 km
N
W
E
S

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.

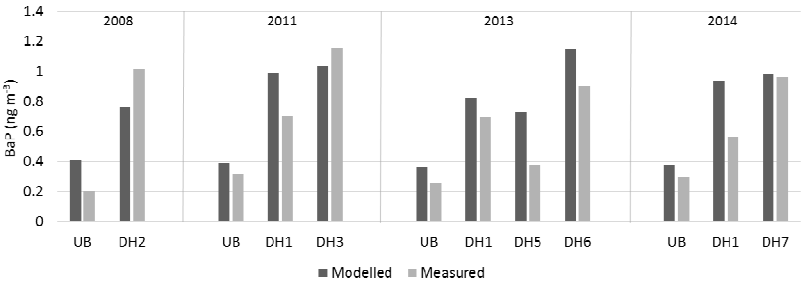


Figure 7: Comparison of predicted and observed annual average BaP concentrations at different sites in the Helsinki Metropolitan Area in 2008, 2011, 2013, and 2014.