Response to reviews

Modelling carbonaceous aerosol from residential solid fuel burning with different assumptions for emissions

Ots et al. https://www.atmos-chem-phys-discuss.net/acp-2017-568/

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This complete response document is ordered as follows:
Response to Referee #1
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Additional minor edits the authors picked up during responding to the reviews
Marked-up manuscript

Anonymous Referee #1

We thank the reviewer for their very supportive comments. We respond to each comment individually below. The reviewer's comments are in italics and blue font, our responses are in normal text.

This is a very useful contribution to an ongoing and important debate on the impacts on PM concentrations of wood burning.

1. *Abstract: It doesn't mention the Redist analysis. Wouldn't it be worth saying that a simple redistribution of emissions according to population is not correct?*

We have included the following in the Abstract:
"A third experiment, *Redist* - all emissions redistributed linearly to population density - is also presented as an indicator of the maximum concentrations an assumption like this could yield."
And the following in the Conclusions:
"A third experiment, *Redist* - all emissions redistributed linearly to population density – is also presented as an indicator of the maximum concentrations an assumption like this could yield. It is recognised however that this is not realistic as the most densely populated areas (of large apartment buildings) are unlikely to have many individual fireplaces."

2. *Comment on whether the degree day factors actually reflect the use of these wood burners would be useful.*

Yes, people in London do use wood and coal for heating purposes. We have now included the relevant references in "Section 2.2: Model experiments":
"Recent studies in London have shown that local contributions of SFOA coincide with days of low temperature (Fuller et al., 2014; Crilley et al., 2015). Therefore, degree-day factors were included to modulate the daily variation in emissions from the SNAP2 sector according to ambient temperature (i.e. increasing the emissions during colder days)."

3. *Whilst there is an under prediction at K&C and the Waters paper (3x the emissions) - most experiments are using base emissions of NAEI, why is this? I have read the Waters paper and it not only gives the 3x factor but also the wood use in different UK regions. You did not use these data but could you comment on how the different scenarios you did run compare?*

The Waters' paper is certainly very relevant and should be used to inform a re-evaluation of the National Atmospheric Emissions Inventory (NAEI) assumptions about the extent and spatial distribution of wood and coal burning in urban and rural areas over the UK. However, the paper is a summary of survey information on domestic combustion habits not an emissions database. To derive emissions of SFOA would require combining data and assumptions about amount of wood burned, the appliance types and a range of emission factors, which is well beyond the objectives of our paper. Secondly, the data in the Waters paper were presented for 12 regions (e.g. London, East Midlands, Scotland, Wales, etc.) rather than the much finer grid that could be used in a national atmospheric chemical transport model (e.g. we aggregate NAEI's 1kmx1km emissions to our model grid – 5kmx5km). Again, the production of new gridded SFOA emissions is well beyond the objectives of our paper, but we note in conclusion of our work that the Waters paper and our modelling study help inform development of updated national emissions inventories for domestic combustion PM.

4. *P13 line 3-4 - What about European assumptions bearing in mind the results in Belgium. Could you comment on how important the long range transport of these emissions are and could be if the results in Belgium and UK are reflected more widely in Europe?*

We have added the following sentences to the top of "3 Results and Discussion" (as that is where we first mentioned European import):
"In our experiments, we did not modify European emissions – we used exactly what has been reported to the CEIP. While there is reason to believe European emissions of SFOA are also underreported, we do not believe this to have a major influence on the surface concentrations of SFOA over the UK as even our Base4x experiment (Fig. 3b) only indicates very modest regional transport of our SFOA to Europe.

5. *It would be good to provide a quick comparison of the Marylebone and Kensington site results. Looking at the map they are close to each other and I guess they have very similar SFOA concentrations. Is this the case? In addition, whilst I realize that you have used what data is available for the UK, could you say something about the limitations in addressing the wood burning emissions inventories UK wide using a small number of sites close to each other in the SE of England.*

This is a good idea and we have now included the annual average measured concentrations in the captions of Figures 5 and 6: "The annual average measured SFOA concentrations at these sites were 0.9 µg m^{-3} at Marylebone Road, and 1.0 µg m^{-3} at North Kensington." We agree that only using sites from the same area (Southern England) is not ideal but these datasets are really rather unique – especially in its length as well as the fact that for January 2012 we have 4 sites operating simultaneously, two of each type (urban and rural). However, acknowledging the limitations of using a small number of sites close to each other is exactly why we later present comparisons with the Aethalometer data, including sites from a national network.

6. *Page 11 line 9 - where it says for more discussions see Ots 2016a, why not just add a sentence discussing the measurement uncertainty?*

Agreed, we have added the following sentences:
"For example, Ots et al. 2016a presented scatter plots of daily averaged concentrations of the different OA components derived from measurements with the two different AMS instruments at the North Kensington site during the winter IOP (the cToF-AMS versus the HR-ToF-AMS). While these comparisons showed good correlations between the two measurements (0.88 to 0.95 for the primary OA components, 0.77 for secondary OA), on some days the absolute measured concentrations of specific components do differ, sometimes by more than a factor of two."

7. *Page 11 fig 7 - it is clear that the diurnal profile of SFOA is similar at all sites and not reflected in the currently used emissions profile for this source. I have read the work of Fuller in London which showed there to be a strong evening peak in emissions from domestic wood burning, especially at weekends. It would have been good to test an alternative emissions profile, which better reflects the burning of wood and would have been helpful for other model users.*

We agree that the diurnal cycles specified for these emissions need to be modified. We did something very similar in our cooking OA paper (Ots et al. 2016b); cooking oil/meat frying OA is a source that is currently not included in European emissions at all. However, for the work in hand, we felt that including experiments for the spatial distribution and total amount was already quite a lot to present, and that the overall -71% normalised mean bias of modelled vs measured SFOA at London North Kensington should be addressed before the more finer temporal-scale issue of hourly emissions profiles. We acknowledge and call for further work on this in several places in the manuscript, including in the Abstract and the Conclusions.

8. *Fig 8. results - 14th-15th Jan was also a weekend could you comment on the likely weekday to weekend use of wood burners as well as the weekend evening use. What was the evening temperature during these events?*

This is a very good point to make, thank you!
We have included a note about this (plus our subsequent observation that ambient temperatures were somewhat lower during this period) in the Results (italics was already there, **bold font text we have added now**):
"*Nevertheless, southern England did experience a sustained high-pressure weather system during these days,* **including noticeably lower temperatures for 14-18 Jan than average (Crilley et al. 2015: Fig.2).** *Sustained high pressure usually leads to a very stable atmosphere with descending air masses. Therefore, these high concentrations could have been caused by meteorological build-up, and it is possible the model set-up underestimated the strength of this effect.* **Furthermore, 14-15 Jan was a weekend whereby people are more likely to spend time home and therefore potentially use their fireplaces more than on weekdays."**

9. *Fig 11 - Comment on Detling daily data. The daily average measurements around the 17th Jan doesn't seem to be reflected in the plot. Is this because of <75% data capture?*

Yes that is the reason. We have now expanded the information about the threshold where Fig. 11 is first introduced:
"Time-series of daily-average concentrations during the winter IOP are shown in Fig. 11. At Detling, the measurements commenced the morning of 16-Jan (Fig. 8a) but since we used a data capture threshold of 75%, 16-Jan and 17-Jan did not include sufficient hourly data points to present measured daily averages for this site."

10. *Figure 13. I don't really see much point in comparing the results of the model at Marylebone Road, so you should remove this plot.*

The paper provides the following explanation for presenting the data shown in Figure 13. "Although the pollutant levels measured close to the traffic source at the Marylebone Road roadside site and the modelled concentrations are not fairly comparable due to the differences in spatial scale (major road vs 5 km model resolution), they are included to illustrate the range of concentrations in a megacity."

We believe that the above remains a relevant reason for presenting the comparisons at Marylebone Road also.

11. *Figure 14. Could you rescale these plots? You can barely make out the modelled EC in many of them?*

We have now added some vertical space to these plots, as well as given the borders of the boxes (previously grey) the same colour as the insides so the very thin ones become more noticeable. The final ACP paper has more space per page than the ACPD format (55 lines vs 35 lines) so the editorial staff will have more space to stretch the figure as well (our image format is PDF so typesetting it on a larger surface will not lose quality). The description of Figure 14 now says "Each box is the interquartile range - IQR," rather than what is on Figure 13: "*Middle line: median, boxes: 25th and 75th quartiles (i.e. the interquartile range - IQR),*" as you could not make out the median line on most of the very thin modelled boxes anyway.

Anonymous Referee #2

We thank the reviewer for their supportive comments on the interest and suitability of the work for publication in ACP. We respond to each comment individually below. The reviewer's comments are in italics and blue font, our responses are in normal text.

The paper contains interesting information on important sources of emissions in a major urban area. I have one major concern, but after attention to the points below this paper should be suitable for publication on ACP.

1. *My main worry concerns the assumption that the SFOA (and other POA) emissions are inert. In most VBS modelling studies such emissions are allocated to a number of VBS bins, and allowed to evaporate and react with OH. Further, the results presented for London in Xu et al. (2016) do not show any large SFOA contribution to the low- volatility OM mass, suggesting that the high fractions found in Young et al were of semi- volatile OA. Assuming inert emissions will tend to overestimate the PM concentrations associated with this POA. The authors should re-visit and investigate the implications of their inert assumption.*

The reason this study does not present model simulations with the volatile treatment of SFOA is that for the AMS-PMF data, primary (SF)OA and oxygenated (secondary) OA are separated. Therefore, the direct comparisons with SFOA measurements here do not include the semivolatile components as those would only become condensed after atmospheric ageing but then they would be measured as oxygenated OA, not SFOA. The volatile components and secondary OA precursors are not needed to test the main hypothesis of this paper – that the spatial distribution of wood and coal burning emissions should not be assumed to be zero in smoke control areas. Using primary components to demonstrate this is sufficient.

This is not to say, of course, that SFOA emissions do not include precursors for SOA. The inclusion of semivolatile SOA precursors from SFOA is of course necessary to close the gap between total measured OA and total modelled OA. Indeed, the work by Xu et al. (2016) to which the reviewer refers above (and other work) acknowledge that oxygenated OA likely contains secondary and/or aged SFOA.

However, having reviewed our original text towards the end of Section 2.1 ("In all the experiments presented here, SFOA is assumed to be non-volatile and it does not undergo atmospheric ageing") we acknowledge that we were not clear on the point we make above. We have therefore added another sentence so that this description now reads: "In all the experiments presented here, SFOA is assumed to be non-volatile and does not undergo atmospheric ageing. This is not because it is assumed that there is no aging of SFOA emissions but because the model simulations compare against AMS-PMF determinations of primary SFOA concentrations."

2. *Connected to this, what is the likely status of the emission measurements behind the SFOA inventory for the UK? Do the techniques used to produce the emission factors include condensables? With so much focus on one emission category, and the fact that condensables are a 'hot' topic (Denier van der Gon et al, 2015, Ciarelli et al., 2017), the authors should inform the readers more about such properties.*

This issue of volatility and associated uncertainties seems to be ignored throughout the manuscript.

We have indicated in our response to comment 1 that we have not 'ignored' the issue of volatility because it is not important but because it is not needed in this examination of spatial patterns and magnitudes of primary SFOA $PM_{2.5}$ emissions against primary SFOA measurements. We agree that the issue of 'condensables' in measuring and reporting PM levels is indeed a 'hot' topic. This issue applies to both ambient measurements and to the emissions at source that underpin emissions factors and inventories. It also an issue that is not just confined to solid-fuel burning. For example, one of our previous papers examined the influence of IVOC emissions associated with diesel vehicles (determined from ambient measurements but not currently included in emissions inventories) on the generation of additional anthropogenic SOA: Ots et al. (2016) "Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign", Atmos. Chem. Phys., 16, 6453-6473. The measurement and modelling communities have long been aware of a need to attempt harmonisation in measurement conditions and reporting of PM and associated condensable emissions (e.g. dilution tunnel conditions etc.) across source sectors and across countries. The issue is raised in various fora, e.g. CEIP and TFMM, but it is challenging and slow to agree and implement. In this study we included the best-available county-by-country domestic sector $PM_{2.5}$ emissions as reported to CEIP. This includes instances of countries that do report condensables as part of their PM emissions, e.g. Belgium (who report these as part of the total PM emissions, not separately), and countries that don't. Without considerable more coordination of measurement and reporting it not possible to make any evidence-based adjustments to the CEIP emissions. In the revised paper we have added a further sentence towards the end of Section 2.1 (after the new sentence inserted in response to comment 1): "It is likely that domestic $PM_{2.5}$ emissions reported to CEIP vary by country according to whether condensables are included in the $PM_{2.5}$ emissions but the specific information is not known."

Other comments

3. *Page 2, L10. The Bergstrom reference is a PhD Thesis. Give the published papers instead.*

Thank you for pointing this out. We now only include the following relevant published reference from the thesis: Denier van der Gon et al. 2015.

4. *Page 2, L5-15. What about emissions from cooking?*

We believe it extremely unlikely that there are significant primary PM emissions associated with use of solid fuels solely for the purpose of domestic cooking in the UK and the rest of Europe. (We assume that this what the reviewer intended by their question.) We have not encountered any literature to suggest that solid fuel for cooking is a source that needs to be considered. This is not to deny that some domestic solid-fuel heat sources may also be used for cooking. It is certainly the case, however, that there are PM emissions associated with the cooking process, but these have different chemical signature and are categorised separately by AMS-PMF measurements. We have previously undertaken model investigations of this cooking source: Ots et al. (2016) "Model simulations of cooking organic aerosol (COA) over the UK using estimates of emissions based on measurements at two sites in London", Atmos. Chem. Phys., 16, 13773-13789.

5. *Page 2, L16. What is the 'Great London Smog' - give a reference.*

We have now included the following reference:
Bell, M. L., Davis, D. L., and Fletcher, T.: A retrospective assessment of mortality from the London smog episode of 1952: the role of influenza and pollution, Environmental Health Perspectives, 112, 6–8, http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1241789/, 2004.

6. *Page 2, L33. I believe Belgium has also included condensables in their emissions estimates, which brings me back to the point raised above.*

Yes, Belgium does include condensables in their total PM emissions estimates from this source, but not separated out. We have responded in detail to the earlier version of this comment above (comment no. 2).

7. *Page 3, Sect. 2.1: The text should give some details about the SOA framework used here. What assumptions are made about SVOC, IVOC, and aging? What was done for ASOA and BSOA?*

The modelling framework for ASOA and BSOA is as described in the literature cited in the paper, viz:
Ots, R. et al.: Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign, Atmos. Chem. Phys., 16, 6453-6473, 2016.
Simpson, D. et al.: The EMEP MSC-W chemical transport model - technical description, Atmos. Chem. Phys., 12, 7825-7865, 2012.
As we respond above in response to comment no. 1, we do not undertake any 'aging' treatment for SNAP 2 emissions because the AMS-PMF data provide separate data for primary (SF)OA and oxygenated (secondary) OA. Condensable components of SNAP2 emissions are therefore not needed to test the main hypothesis of this paper – that the spatial distribution of wood and coal burning emissions should not be assumed to be zero in smoke control areas. Using primary components to demonstrate this is sufficient. In order to make this point more directly in our revised paper we have added text to Section 2.1, as we have detailed in our responses above.

8. *Page 3. The statistics given for model performance are useful, but they seem only to refer to London. How about elsewhere, since this paper deals with the UK as a whole?*

We agree that only using sites from the same area (Southern England) is not ideal but these datasets are really rather unique – especially in their length, time resolution and chemical speciation, as well as the fact that for January 2012 we have 4 sites operating simultaneously, two of each type (urban and rural). However, acknowledging the limitations of using a small number of sites close to each other is exactly why we later present comparisons with the Aethalometer data, including sites from a national network.

9. *Page 4, Add the ion labels for SO4, NH4 and NO3. (For example NO3 is a gaseous compounds important for night-time chemistry, whereas I think the authors mean the nitrate ion.)*

Thank you for pointing out this error. The ions are now labelled.

10. *Page 5, L4 claims that Ots et al. (2016a) showed that modelled SFOA were substantially underestimated at North Kensington, but according to Table 3 of that paper the SFOA PMF factors were convolved with the OOA2 factors.*

The data reported in Table 3 was from the following paper, where the measurement dataset and the derivation of the different factors is described in detail: Young, D. E., Allan, J. D., Williams, P. I., Green, D. C., Flynn, M. J., Harrison, R. M., Yin, J., Gallagher, M. W., and Coe, H.: Investigating the annual behaviour of submicron secondary inorganic and organic aerosols in London, Atmos. Chem. Phys., 15, 6351–6366, doi:10.5194/acp-15-6351-2015, 2015.

In the study by Young et al. (2015), a year of measurements were performed using the c-ToF-AMS (compact) and it is the PMF factors from that dataset that contain the two convolved PMF factors. Section 4.4 of the paper describes how these two convolved factors were dealt with. In brief, both factors had a strong and similar diurnal cycle, so the effect of being convolved was reduced by using daily averaged concentrations. In the current work presented here, these daily average concentrations are used for the annual comparisons, thus the issue of the convolved factors should not be significantly influencing the overall observations. In contrast, concentration data from the HR-ToF-AMS (high-resolution) instrument are used for the hourly comparisons presented in the current work. The PMF factors resulting from the HR-AMS data were not found to be convolved, which is likely due to a combination of the fact that the measurements were high resolution and the HR-ToF-AMS was deployed only during the intensive observation periods, rather than the full year like the c-ToF-AMS. Consequently, hourly comparisons presented in this work use the HR-ToF-AMS data.

In summary, whilst we acknowledge the general issue of convolved factors, it is not likely influencing the overall results in the current study since datasets of the appropriate time resolution were used for each of the cases and each of these datasets had been treated so as to reduce the issue.

11. *Page 6, Fig. 2. Units of Mg/km2 would be easier for comparison with other studies.*

We have added the following to the caption: “20 Mg per (our) grid square is 0.8 Mg km^{-}.^{2}”

12. *Page 11, Sect 3.2. Measured profiles of SFOA result from a mixture of emissions profiles, atmospheric dispersion, and PMF interpretation. The model should capture the first two, but I wonder how much PMF contributes. For example, if the diurnal emissions profile is responsible for the concentrations profile, why would SFOA emissions peak around midnight for N. Kensington?*

We anticipate that the peak around this time is due to the product of the impacts of greater evening local emissions and reducing boundary layer height and increasing atmospheric stability during night-time.

13. *Page 12, L13 and associated text and Figures. Were these "exceptional" concentrations also seen for other pollutants, for example NO2. Would model performance for other components help the analysis here? (Also, the word exceptional seems a bit excessive here. Are such concentrations really so infrequent?)*

These concentrations (e.g. 12 μg m^{-3} daily average at Harwell) are indeed exceptional as this is just one component. The recommended maximum daily average concentration for total PM$_{2.5}$ is no more than 10 μg m^{-3} and that must accommodate all components: organic and inorganic, not just SFOA. Furthermore, our Figures 5 shows that daily average concentrations throughout the year exceed 4 μg m^{-3} only a few days a year.

Comparisons with other pollutants are presented in Figure 6 in:
Ots, R., et al.: Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign, Atmos. Chem. Phys., 16, 6453–6473, doi:10.5194/acp-16-6453-2016, 2016a.

14. *Page 21. The WRF model is also open source, and details should be included here. I think section 5 and 6 could also be merged, since the code is mentioned in both. Currently it is confusing though, since Sect. 5 says code should be obtained from www.emep.int, but Sect. 6 says code is from the University of Edinburgh.*

The ACP submission instructions request these two separate sections. Where we mention “code” in Section 6, we do not mean the core source code but the scripts used to initialise a model simulation (i.e. linking all our input files to the model executable). We have now changed the word “code” to “scripts” in Section 6.

15. *Appendices: This type of information is typically provided as Supplementary material.*

We will take the advice of the ACP editor (or production team) on this point.

Anonymous Referee #3

We thank the reviewer for their support that our work is sound and deserving of publication in ACP after response to their comments. We respond to each comment individually below. The reviewer's comments are in italics and blue font, our responses are in normal text.

The manuscript by Ots et al. presents a modeling study that explores the uncertainty of the residential and non-industrial combustion emissions sector over the UK and Ireland. The uncertainty estimates, translated into sensitivity experiments in the manuscript, are driven from past studies (Ots et al., 2016) and comparisons with measurements. The model domain covers the whole UK and Ireland, although the analysis is heavily based on comparisons with data in London.
The work presented is a standard modeling approach, where an emissions sector is perturbed and the different model versions are compared against measurements, to evaluate which of the scenarios under study is performing best against some metric, which in this case it is a fraction of organic aerosols (solid fuel OA; SFOA) and black/elemental carbon. The analysis does not have any mistakes, although one can argue that the approach of non-volatility and ageing for SFOA deserves improvement, especially given the temperature-dependent parameterization presented for the emissions during cold days. The results are not surprising either; a low bias in SFOA is improved by increasing its emissions, and rather linearly, as seen in Table 3. For both sites studied, the NMB presented in Table 3 for the combRedist experiment is roughly equal to the arithmetic mean of the Base and Redist simulations, which is what one would expect from the experimental design. In addition, no attempts have been made to link this work with either the study in Belgium mentioned in the manuscript, or with other relevant areas, limiting the scope of the work as presented. The last sentence of the conclusions also supports my concern about the limited scope of the study, again, as presented in the manuscript. Regardless, I believe that the work is sound and de- serves publication in ACP after addressing my comments below.
Specific comments

1. *p. 3, l. 25: The FINN inventory has natural fires only, or all open burning? Some of the open biomass burning is anthropogenic (e.g. deforestation, agricultural fires).*

Yes, thank you. We have now changed "natural fires" to "open burning (including wild fires and agricultural burning)".

2. *Section 2.2: The way I understand the degree-day factors equation is that it does not affect days with temperature higher than 18 C, but it increases emissions for colder days. If this is correct, isn't it going to increase the annual totals? In addition, why not apply the same approach hourly (section 3.2) and get a more natural diurnal variability, instead of the imposed one?*

Yes, the reviewer's understanding is correct, it does not increase the annual total. Regarding the second question (why not apply this on hourly temperatures):
Firstly, the work we present in this manuscript did not create and make methodological changes to how the degree-day factors, we used them as described in Simpson et al. (2012): The EMEP MSC-W chemical transport model - technical description, *Atmos. Chem. Phys.*, 12, 7825–7865, doi:10.5194/acp-12-7825-2012.

Secondly, while we agree that the hourly profiles used in this study (also based on the above reference) need review (in our abstract we write: “The model results also suggest the assumed temporal profiles for residential emissions may require review to place greater emphasis on evening (including ‘discretionary’) solid-fuel burning.”) we do not think hourly variation in temperature has a very direct effect on increased heating. This may be true for thermostat-based central heating systems (gas or electricity `fuelled`), but solid fuel burning means that people need to be home and awake (i.e. even if the temperature drops overnight, people will not wake up and start burning wood and coal). Therefore, the hourly profile of SFOA emissions is unlikely to be driven by changes in temperature on an hourly basis.

3. *p. 5, l. 7: Please start a new paragraph with “The experiments Base, . . .”*

Agreed and done.

4. *Section 3.1: How far apart are the two stations? Are they in adjacent gridboxes, the same one, really far away? How about differences in local influences, if any?*

The two stations are about 4.5 km apart, in separate adjacent model grid cells. Detailed maps of these sites (overlaid with residential and workday population density at 1 km resolution) can be found in Fig. 1 in Ots et al. (2016) “Model simulations of cooking organic aerosol (COA) over the UK using estimates of emissions based on measurements at two sites in London”, Atmos. Chem. Phys., 16, 13773-13789, reproduced below:

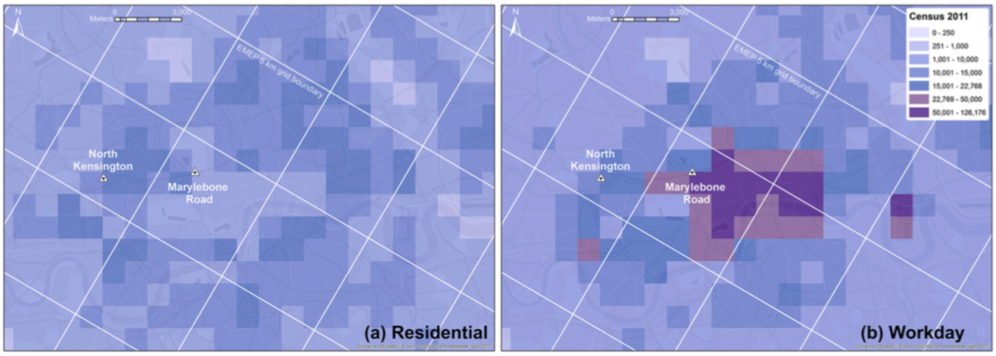

Figure 1. Residential **(a)** and workday **(b)** population density in central London at 1 km × 1 km resolution. The residential population maps are based on Reis et al. (2016). While the same methodology is applied to derive workday population maps, they are not yet published due to delays in the provision of workday population census data for Scotland. Also shown are the measurement sites and the EMEP4UK 5 km × 5 km grid used in this study (white lines). Underlying map contains Ordinance Survey (OS) data © Crown Copyright 2015.

We have now included the following in Section 3.1 (paragraph 2) of this manuscript:
“These two sites are ~4.5 km apart, in adjacent model grid cells, and represent different kinds of urban areas. North Kensington is comparatively residential whereas Marylebone Road is near central London and therefore exhibits very high numbers of people during the workday. More discussion on this, including detailed maps can be found in Ots et al. (2016b).”

5. *p. 11, l. 16-17: Why only correlation and not the other metrics? More generally, this is an important piece of information and should be expanded, even though it is already published.*

Agreed, we have added the following sentences:
"For example, Ots et al. 2016a presented scatter plots of daily averaged concentrations of the different OA components derived from measurements with the two different AMS instruments at the North Kensington site during the winter IOP (the cToF-AMS versus the HR-ToF-AMS). While these comparisons showed good correlations between the two measurements (0.88 to 0.95 for the primary OA components, 0.77 for secondary OA), on some days the absolute measured concentrations of specific components differ, sometimes by more than a factor of two."

6. *Figure 7: Some error bars or other means that present temporal variability can be very informative here.*

Overall, we agree with this comment that it is useful to try to present the variability, and not just the final aggregated (in this case the mean) values. However, since we plot 4 individual lines on each panel here, we think that adding for example the standard deviation around each line would make the information on the panels overlap each other and the plot would become `too busy`. A solution could be to separate pairs of these lines on separate plots (e.g. as we've done in Figs. 5 and 6) but since the focus of this paper is not diurnal profiles we feel that increasing the figure count and the total length of this paper for this is not justified.

7. *The AMS instruments mentioned also measure total PM1 OA. It would have been very informative if the discussion included a comparison with those data as well, either (preferably) alongside the comparisons with SFOA, or (at least) in the same way the BC/EC comparison is presented.*

Comparisons with other components of OA (HOA and ASOA) are presented already in our previous publication: Ots, R., et al.: Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign, Atmos. Chem. Phys., 16, 6453–6473, doi:10.5194/acp-16-6453-2016, 2016a. The AMS instruments also assign concentrations to a COA (cooking OA) component which are not routinely modelled because there are no cooking emissions in the emissions inventory for the model. However, in another paper we used the AMS-measured COA concentrations for a model exploration of potential magnitude and spatial distribution of primary COA emissions: Ots et al. "Model simulations of cooking organic aerosol (COA) over the UK using estimates of emissions based on measurements at two sites in London", Atmos. Chem. Phys., 16, 13773-13789, 2016b.

8. *p. 16, l. 18-19 and Figure 13, last row: This site does not add anything to the discussion, I recommend to remove it.*

The paper provides the following explanation for presenting the data shown in Figure 13. "Although the pollutant levels measured close to the traffic source at the Marylebone Road roadside site and the modelled concentrations are not fairly comparable due to the differences in spatial scale (major road vs 5 km model resolution), they are included to illustrate the range of concentrations in a megacity."

We believe that the above remains a relevant reason for presenting the comparisons at Marylebone Road also.

9. *p. 20, l. 28: I am not entirely convinced that "the combRedist experiments improved the comparisons". Only the negative NMB was really targeted with the experimental design, and it is expected that increased emissions of an inert aerosol tracer will increase aerosol levels at surface, especially close to sources, thus reducing (or even eliminating) the negative bias. Figures 13 and 14, which represent a more regional picture, do not show any significant improvement for that particular simulation either.*

We agree that the Base4x experiment only targets the negative model NMB, for the reason the reviewer states: "*it is expected that increased emissions of an inert aerosol tracer will increase aerosol levels at surface*". Hence the aim of the combRedist experiment: namely, to investigate the effect of redistribution of some of the SFOA emissions on both the negative NMB (caused by the fact that the NAEI does not currently assign emissions to smoke control areas), as well as on the other mod-obs metrics presented in this manuscript (r, NMGE, COE), i.e. the redistribution of SFOA sources affects SFOA concentrations in the different air masses arriving at these sites, not just the emissions assigned to the local grid cell. For example, in Detling and Harwell, combRedist had a much lower NMGE and a much better COE than Base4x (Table 4). Furthermore, Figures 13 and 14 show that these tests do not cause completely unnecessary effects in, for example, Northern Ireland, i.e., that we are not completely removing SFOA from lower populated areas and simply ending up with it in the most densely populated areas of London.

10. *Appendix A1 contains textbook information and it is not necessary, although it consists of a nice collection of references and the discussion is fluid, so I am hesitating to propose to remove it. Appendices A2-A4 should be supplementary material. Appendix A5 should move in section 3.5.*

    We remain of the opinion that the material in this section contains relevant information to the interpretation of our comparisons of modelled EC with measured BC, the latter of which is measured at many more sites geographically spread across the UK, than with measurements of EC which are made only at 3 sites (2 of which are in London). We believe it is important to challenge the model with the greater amount of measured BC data but also wish to remind readers of issues associated with equating BC and EC. We will take the advice of the ACP editor (or production team) on whether this material is most appropriate as an Appendix or as Supplementary Material, but given its relative brevity we would prefer to keep it as an Appendix.

Technical corrections

11. *p. 5, l. 4: Is Hjj correct (so please explain) or it should have been Hdd? p. 9, l. 9: Please take this sentence out of the parentheses.*

    Yes, it should have been Hdd, not Hjj. We have now fixed this, thank you!

Additional minor edits the authors picked up during responding to the reviews:

- We use the term solid fuel in the first sentence of the introduction but we only define it several sentences later. We have replaced the first instance of solid fuel with “wood and coal”, the first sentence now reads: “Globally, wood and coal burning from residential heating…”
- In the abstract we broke this originally one long sentence into two separate ones

  The *Base4x* scenario yielded better daily and hourly correlations with measurements than the *combRedist* scenario for year-long comparisons of the solid fuel organic aerosol (SFOA) component at the two London sites. However, the latter scenario better captured mean measured concentrations across all four sites.

Modelling carbonaceous aerosol from residential solid fuel burning with different assumptions for emissions

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Abstract. Evidence is accumulating that emissions of primary particulate matter (PM) from residential ~~solid fuel~~ wood and coal combustion in the UK may be underestimated and/or spatially misclassified. In this study, different assumptions for the spatial distribution and total emission of PM from solid fuel (wood and coal) burning in the UK were tested using an atmospheric chemical transport model. Modelled concentrations of the PM components were compared with measurements from aerosol mass spectrometers at four sites in central and Greater London (ClearfLo campaign, 2012), as well as with measurements from the UK black carbon network.

The two main alternative emission scenarios modelled were *Base4x* and *combRedist*. For *Base4x*, officially reported $\mathrm{PM}_{2.5}$ from the residential and other non-industrial combustion source sector were increased by a factor of 4. For the *combRedist* experiment, half of the baseline emissions from this same source were redistributed by residential population density to simulate the effect of allocating some emissions to the smoke control areas (that are assumed in the national inventory to have no emissions from this source). The *Base4x* scenario yielded better daily and hourly correlations with measurements than the *combRedist* scenario for year-long comparisons of the solid fuel organic aerosol (SFOA) component at the two London sites~~, whereas~~. However, the latter scenario better captured mean measured concentrations across all four sites. A third experiment, *Redist* - all emissions redistributed linearly to population density, is also presented as an indicator of the maximum concentrations an assumption like this could yield.

The modelled elemental carbon (EC) concentrations derived from the *combRedist* experiments also compared well with seasonal-average concentrations of black carbon observed across the network of UK sites. Together, the two model scenario simulations of SFOA and EC suggest both that residential solid-fuel emissions may be higher than inventory estimates and that the spatial distribution of residential solid-fuel burning emissions, particularly in smoke control areas, needs re-evaluation. The model results also suggest the assumed temporal profiles for residential emissions may require review to place greater emphasis on evening (including 'discretionary') solid-fuel burning.

1 Introduction

Globally, ~~solid fuel~~ wood and coal burning from residential heating and from cooking activities is a major source of both indoor and outdoor $\mathrm{PM}_{2.5}$ (particulate matter with diameter $< 2.5\,\mu\mathrm{m}$) air pollution (WHO, 2015). As developed countries commit to renewable energy targets, the use of wood and biomass in residential heating is likely to increase (replacing some of the natural gas based heating systems~~(WHO, 2015)~~; (WHO, 2015)). Within Europe, residential wood burning is estimated to be the single largest anthropogenic primary source of organic carbon (OC), contributing ~60% of total OC emissions from European countries ~~(Denier van der Gon et al., 2015; Bergström, 2015)~~(Denier van der Gon et al., 2015). In some countries, both wood and coal are burned in residential stoves and other small combustion plants. A number of particle source apportionment studies, particularly those based on positive matrix factorisation of aerosol mass spectrometry measurements (AMS-PMF studies), have thus attributed organic aerosol (OA) from this source as solid fuel OA (SFOA), which is a combination of the commonly known biomass burning OA (BBOA) factor plus coal burning OA (Allan et al., 2010; Young et al., 2015a; Xu et al., 2016). In addition to heating, some residential solid fuel burning in European urban areas can also be attributed to recreation (i.e. fireplaces for ambience; Fuller et al. (2013)).

Since the Great London Smog of 1952 (Bell et al., 2004), several legislative interventions have substantially reduced the use of solid fuels for residential heating in the UK by subsidising infrastructure and availability of oil and natural gas, as well as the implementation of smoke control areas (Fuller et al., 2013). For example, almost all of London is now a smoke control area where solid fuel burning is prohibited unless undertaken in approved wood burners (Fuller et al., 2013). This control is applied only to appliances with a chimney; incidental sources such as bonfires or barbecues are permitted.

There is evidence, however, that the smoke control legislation is no longer actively enforced. Several recent studies have reported substantial local contributions of emissions from solid fuel burning to particle concentrations in London coinciding with days of low temperature (Fuller et al., 2014; Crilley et al., 2015). This is relevant as, currently, the UK's National Atmospheric Emissions Inventory (NAEI) assumes zero residential emissions of non-approved solid fuel burning in smoke control areas (i.e. that there is full legal compliance). Furthermore, the NAEI only includes estimates of emissions from officially-sold solid fuels (NAEI, 2013), but there is reason to believe that much fuel wood is not obtained through commercial outlets and falls outside the economic administration and therefore is not included in official statistics (Denier van der Gon et al., 2015). For example, a recent UK Wood Use Survey concluded that the official national consumption of domestic wood fuel is underestimated by a factor of 3 (Waters, 2016). Furthermore, the survey showed that 31% of wood fuel is sourced from the informal “grey” market of wood (i.e. own garden, other landowners’ gardens, waste wood, etc.).

The results of the UK survey are in line with recent evaluations of wood burning emissions in Belgium, which also concluded that their official inventory has underestimated the amount of wood burned in residential settings by more than a factor of 3 (Lefebvre et al., 2016). Belgium has since included these increased emissions estimates (adding estimates for non-commercial wood sources to officially reported sales) in the amount reported to the Centre on Emission Inventories and Projections (CEIP) of the European Monitoring and Evaluation Programme (EMEP). The authors of the Belgian study urge countries that currently do not make estimates of non-officially traded or sourced wood to follow the same practise and start reporting these.

Model-measurement comparisons of a range of gaseous and particulate pollutants (Ots et al., 2016a) show that modelled concentrations of SFOA at the North Kensington site in London are substantially underestimated (normalised mean bias, NMB, of -71%) compared to an annual dataset of PMF apportionment of AMS measurements collected during the 2012 Clean Air for London campaign (ClearfLo; Bohnenstengel et al. (2014); Young et al. (2015a); Xu et al. (2016)). The aim of this work is to use these measurements of SFOA as the basis for an atmospheric chemical transport model exploration of potential closure of this discrepancy.

2 Methods

2.1 Model description

EMEP4UK is a regional application of the EMEP MSC-W (European Monitoring and Evaluation Programme Meteorological Synthesizing Centre-West) chemical transport model (Vieno et al., 2009, 2010, 2016; Ots et al., 2016a, b). The EMEP MSC-W model is a 3-D Eulerian model that has been used for both scientific studies and to support policy making in Europe. A detailed description of the EMEP MSC-W model, including references to evaluation and application studies is available in Simpson et al. (2012), Schulz et al. (2013), and at www.emep.int. The model configuration used here was based on version v4.5. The model has 21 vertical layers, extending from the surface to 100 hPa. The lowest vertical layer is ~40 m in height, and the horizontal resolution over an inner domain covering the British Isles is $5\,\mathrm{km} \times 5\,\mathrm{km}$. The model uses one-way nesting from an extended European domain (simulated with $50\,\mathrm{km} \times 50\,\mathrm{km}$ horizontal resolution). The model was driven by output from the Weather Research and Forecasting (WRF) Open Source model (www.wrf-model.org, version 3.1.1) including data assimilation of 6-hourly meteorological reanalysis from the US National Center for Environmental Prediction (NCEP)/National Center for Atmospheric Research (NCAR) Global Forecast System (GFS) at 1° (~100 km) resolution (NCEP, 2000).

Gridded anthropogenic emissions were obtained from NAEI (NAEI, 2013) for the UK, and from CEIP (CEIP, 2015) for the rest of Europe. All emissions are apportioned across a standard set of emission source sectors, following the sector structure defined in the Selected Nomenclature for Air Pollutant (SNAP, Table 1; EEA (2013)). Daily emissions from ~~natural fires~~ open burning (including wild fires and agricultural burning) were taken from the Fire INventory from NCAR version 1.0 (FINNv1, Wiedinmyer et al. (2011)). Primary PM emissions reported as $\mathrm{PM}_{2.5}$ and PM_{10} in NAEI and CEIP were speciated into elemental carbon (EC), hydrocarbon-like OA (HOA) from fossil fuel combustion, OA from domestic combustion (SFOA =

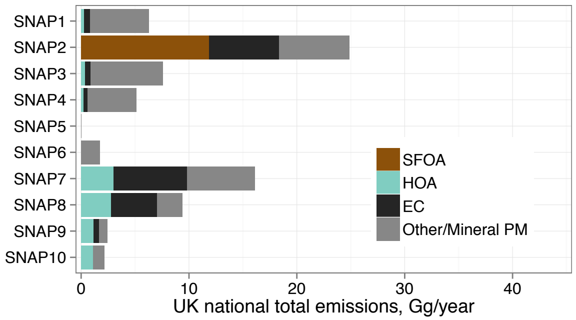

Figure 1. Annual UK $\mathrm{PM}_{2.5}$ emissions by SNAP sector as specified in the NAEI (for year 2012), with each sector split into primary OA (HOA or SFOA), EC, and remaining PM following Kuenen et al. (2014). Source: Ots et al. (2016a).

BBOA + coal OA) and remaining primary PM for each source sector using splits developed by Kuenen et al. (2014), as shown in Fig. 1. In all the experiments presented here, SFOA is assumed to be non-volatile and it does not undergo atmospheric ageing. This is not because it is assumed that there is no aging of SFOA emissions but because the model simulations compare against AMS-PMF determinations of primary SFOA concentrations. It is likely that domestic PM2.5 emissions reported to CEIP vary by country according to whether condensables are included in the PM2.5 emissions but the specific information is not known.5

Table 1. SNAP source sectors as specified in the emissions input to the model (CEIP, 2015).

SNAP1	Combustion in energy and transformation industries
SNAP2	Residential and non-industrial combustion
SNAP3	Combustion in manufacturing industry
SNAP4	Production processes
SNAP5	Extraction and distribution of fossil fuels
SNAP6	Solvent and other product use
SNAP7	Road transport
SNAP8	Other mobile sources and machinery
SNAP9	Waste treatment and disposal
SNAP10	Agriculture

The performance of this version of the EMEP4UK model simulating a standard suite of gas-phase components and secondary inorganic aerosol PM components is reported in Ots et al. (2016a) comparing with a full year of measurements in London in 2012. In brief, Ots et al. (2016a) reported an NMB of -1% and $r = 0.79$ for ozone, an NMB of -32% and $r = 0.78$ for $\mathrm{NO_x}$, an NMB of $+6\%$ and $r = 0.73$ for $\mathrm{SO_4^{2-}}$, an NMB of -12% and $r = 0.65$ for $\mathrm{NH_4^+}$, and an NMB of -23% and $r = 0.57$ for $\mathrm{NO_3^-}$.

2.2 Model experiments

In this study, four different cases were considered. The *Base* case model experiment uses the same emission inventory dataset as Ots et al. (2016a) (i.e. as reported by the NAEI using the splits in Fig. 1), but with a small adjustment in the daily variation in emissions due to temperature, called degree-day factors (Simpson et al., 2012). ~~Degree-day factors~~ Recent studies in London have shown that local contributions of SFOA coincide the days of low temperature (Fuller et al., 2014; Crilley et al., 2015). Therefore, degree-day factors were included to modulate the daily variation in emissions from the SNAP2 sector according to ambient temperature (i.e. increasing the emissions during colder days). SNAP2 includes $\mathrm{PM}_{2.5}$ emissions from both residential and small (non-industrial) commercial combustion, but the residential part dominates with annual emissions for 2012 of 19 Gg from residential, 1 Gg from commercial and 5 Gg from stationary military combustion (NAEI, 2013). The domination of the residential emissions means that no large additional uncertainty is introduced by applying the degree-day factors to the whole of SNAP2.

A degree-day is defined as $H_{dd,j} = max(18°C - T_j^{24h}, 1)$, where j is the day number and T^{24h} is the daily averaged temperature in $°C$. These degree-days are divided by the annual mean ~~$(\overline{H_{jj}})$~~ $(\overline{H_{dd}})$ to obtain degree-day factors (Simpson et al., 2012). For this work, degree-day factors pre-calculated by the EMEP MSC-W Centre based on European Centre for Medium-Range Weather Forecasts (ECMWF) 2012 meteorological simulations for the 50 km × 50 km domain (Schulz et al., 2013) were disaggregated using the simple area-weighting method assuming homogeneity for degree-day factors within the 50 km to 5 km conversion.

In the second model experiment (*Base4x*), emissions from SNAP2 were increased by a factor of 4 (based on the NMB of -71% at the London North Kensington site). SNAP2 is the only sector with SFOA emissions in the set-up used (Fig. 1). The spatial distribution was unchanged.

For the third experiment (*Redist*), the annual reported $\mathrm{PM}_{2.5}$ emissions from SNAP2 were re-gridded linearly by residential population density (census data from Reis et al. (2016)) in order to test the assumption made by the NAEI that only smokeless fuels are used in smoke control areas. The total emission was unchanged.

Finally, the fourth experiment, *combRedist*, was a hybrid of the *Base* and *Redist* experiments, where, for each grid cell, half the emissions of *Base* and half of *Redist* (of the SNAP2 sector) were added together, i.e. $combRedist_{emis} = 0.5\times\ Base_{emis} + 0.5\times\ Redist_{emis}$.

The experiments *Base*, *Redist*, and *combRedist* therefore use the same total emission; the only difference is in the spatial distribution of the emissions. All four experiments use the same temporal variation for SNAP2, including degree-day factors. The emissions used for the four experiments are summarised in Table 2. In all of these experiments, SFOA is assumed to be non-volatile ~~.~~ (see Sect. 2.1 for more information on this). The emission maps of these four experiments are shown in Fig. 2, and the resulting modelled annual average surface concentrations of SFOA are shown in Fig. 3.

Table 2. Summary of the four experiments for $\mathrm{PM}_{2.5}$ emissions from SNAP2. In all experiments, $\mathrm{PM}_{2.5}$ is split into three components as follows: 48% is SFOA, 26% EC, and 26% other/mineral PM (as in Fig. 1).

Experiment	SNAP2 $\mathrm{PM}_{2.5}$ emission	Spatial distribution
Base	25 Gg	NAEI
Base4x	100 Gg	NAEI
Redist	25 Gg	Population density
combRedist	25 Gg	NAEI + Population density

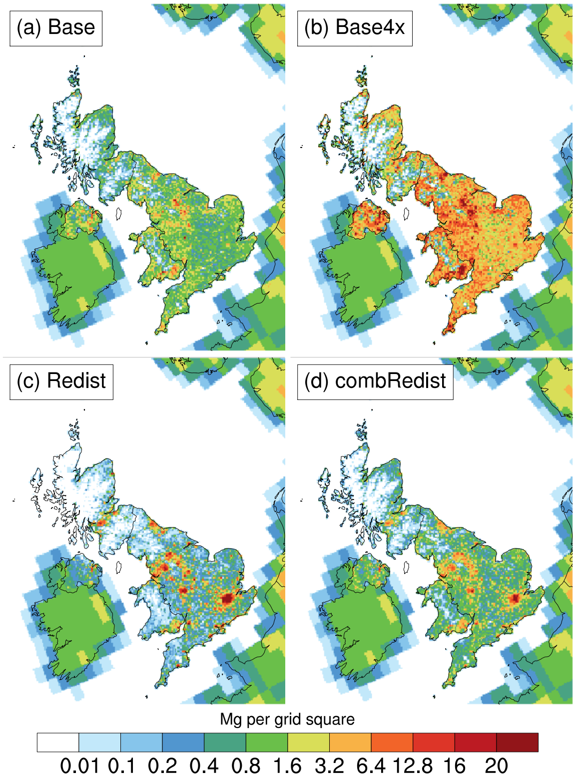

Figure 2. Total SFOA emissions (defined as 48% of $\mathrm{PM}_{2.5}$ from SNAP2) for the year 2012 in the inner nesting domain for the four scenarios of this study: (a) *Base*: as in the NAEI, (b) *Base4x*: Base increased by a factor of 4 over the whole of UK, (c) *Redist*: UK emissions redistributed to residential population density (national total same as Base), (d) *combRedist*: half of the total emission redistributed to residential population density, half as reported by NAEI (a combination of (a) and (c)). The national total is the same for (a), (c), and (d). All UK emissions are aggregated to the 5 km × 5 km grid (20 Mg per grid square is 0.8 $\mathrm{Mg\,km^{-2}}$) from an initial resolution of 1 km × 1 km reported by the NAEI. The emission resolution is 50 km × 50 km for other countries (as in CEIP). Note the non-linear scale.

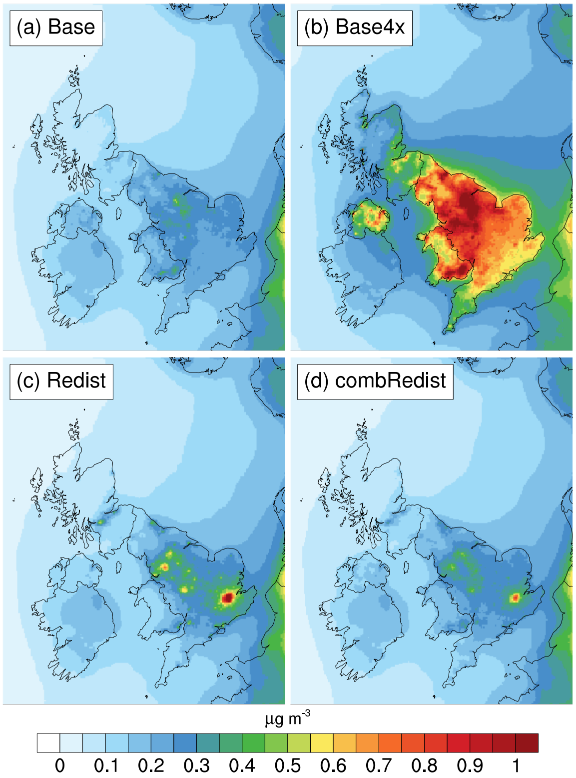

Figure 3. Annual average modelled surface SFOA concentrations for the year 2012 using the emission scenarios shown in Fig. 2: (a) *Base*: as in the NAEI, (b) *Base4x*: *Base* increased by a factor of 4 over the whole of UK, (c) *Redist*: UK emissions redistributed by residential population density (national total same as *Base*), (d) *combRedist*: half of the total emission redistributed by residential population density, half as reported by NAEI (a combination of (a) and (c)). The national total is the same for (a), (c), and (d).

2.3 Comparison with measurements

Modelled $\mathrm{OA}_{2.5}$ (OA with diameter $< 2.5\ \mu\mathrm{m}$) is compared with non-refractory submicron (NR-PM_1) OA measured by Aerodyne AMS instruments at the London North Kensington and London Marylebone Road sites in central London (urban background and roadside, respectively), and at the Harwell and Detling rural sites located to the west and east of London, respectively (Bohnenstengel et al., 2014; Young et al., 2015a, b; Xu et al., 2016). The locations of the AMS measurement sites used in this study are shown in Fig. 4. The discrepancy introduced by the different size fractions of modelled and measured concentrations is small as at an urban background site, ~90% of organic carbon in $\mathrm{PM}_{2.5}$ is in the submicron fraction (Harrison and Yin, 2008).

Different types of AMS instruments were deployed in the ClearfLo campaign. At the London North Kensington site a compact time-of-flight AMS (cToF-AMS) was deployed for a full calendar year (January 2012 – January 2013), and an additional high-resolution time-of-flight AMS (HR-ToF-AMS, DeCarlo et al. (2006)) was deployed for the winter Intensive Observation

Period (IOP). The measurements at Marylebone Road were taken with a Q-AMS (Quadrupole AMS; Jayne et al. (2000)). HR-ToF-AMS instruments were deployed at Detling and Harwell during the winter IOP (not the whole year). PMF analysis was applied to each dataset to apportion measured OA into different components (Ulbrich et al., 2009). A detailed description of the derivation and optimization of the factors retrieved from the AMS data at Detling can be found in Xu et al. (2016), at London North Kensington in Young et al. (2015a) and Young et al. (2015b), at London Marylebone Road in Detournay et al. (2017) (all of these analyses were performed with the PMF2 solver), and at Harwell in Di Marco et al. (2017) (using the ME-2 solver). The limitations and uncertainties of these measurement datasets have been discussed in Ots et al. (2016a, b) .

Figure 4. Locations of the ClearfLo measurement sites used in this work. London North Kensington is an urban background site, London Marylebone Road is a roadside site, Harwell and Detling are rural background sites (Source: Ots et al. (2016a)). Underlying map from © OpenStreetMap contributors.

The following numerical metrics were used for model evaluation: FAC2 (Factor of 2) - the proportion of modelled concentrations that are within a factor of 2 of the measured concentrations; NMB - normalised mean bias; NMGE - normalised mean gross error, which is defined as:

$$NMGE = \frac{\frac{1}{n}\sum_{i=1}^{n}|M_i - O_i|}{\overline{O}}, \tag{1}$$

where M_i is the *i*th modelled value, O_i is the corresponding measured value, $\overline{O}$ is the mean measured value, and *n* is the total number of observations; *r* - correlation coefficient; and COE - coefficient of efficiency, which is defined as:

$$COE = 1.0 - \frac{\sum_{i=1}^{n}|M_i - O_i|}{\sum_{i=1}^{n}|\overline{O} - O_i|}. \tag{2}$$

A COE of 1 indicates perfect agreement between model and measurements. Although the COE does not have a lower bound, a zero or negative COE implies that the model cannot explain any of the variation in the observations (Legates and McCabe, 2013).

3 Results and Discussion

Figure 3 shows the annual mean modelled SFOA surface concentrations for the year 2012. In the model, SFOA is emitted as 48% of $\mathrm{PM}_{2.5}$ from the SNAP2 source sector, and it is advected as a non-volatile and chemically inert species (but it is included in the total OA budget for the absorptive partitioning of secondary organic aerosol species). The gradients of SFOA surface concentrations visible over the North Sea and the English Channel are indicators of European transport. Over the UK, SFOA concentrations follow the pattern of the prescribed local emissions, with the spatial distributions of the experiments with and without redistributed national emissions being substantially different from each other. The *Base* and *Base4x* scenarios (spatially gridded as reported by the NAEI) assigned most emissions to Northern England, Wales and Northern Ireland, leaving major cities such as London, Manchester, Leeds, Birmingham, and Glasgow almost unnoticeable in the concentration fields (these, and many other urban locations, are designated as smoke control areas). In contrast, the *Redist* experiment highlights all of these urban areas, because the SFOA emissions were redistributed linearly by residential population density. The *combRedist* experiment shows these residential hot-spots while also retaining some of the spatial pattern from the officially reported distribution.

In our experiments, we did not modify European emissions, we used exactly what has been reported to the CEIP. While there is reason to believe European emissions of SFOA are also underreported, we do not believe this to have a major influence on the surface concentrations of SFOA over the UK as even our Base4x experiment (Fig. 3b) only indicates very modest regional transport of our SFOA to Europe.

3.1 Daily evaluation - London Marylebone Road and North Kensington annual datasets

Time-series of measured and modelled daily-average SFOA concentrations for the London Marylebone Road and North Kensington sites are shown in Fig. 5 (*Base*, and *Base4x*) and Fig. 6 (*Base*, and *combRedist*). These figures also highlight the date of the annual bonfire celebrations around Guy Fawkes Night (5th of November) to draw attention to an increase in SFOA emissions that can not be simulated with the model, given that the temporal variation is prescribed using a regular approach (i.e. hour-of-day, day-of-week, month-of-year) which does not include information about specific days and events. (The small difference between the *Base* experiment time-series in these figures and a similar comparison in Ots et al. (2016a) is due to the use of degree-day factors.) For convenience, the evaluation statistics presented on these time-series (as well as for the Redist experiment) are given in Table 3.

These two sites are ~ 4.5km apart, in adjacent model grid cells, and represent different kinds of urban areas. North Kensington is comparatively more residential whereas Marylebone Road is near central London and therefore exhibits very high numbers of people during the workday. More discussion on this, including detailed maps can be found in Ots et al. (2016b)

The experiments result in better daily-average SFOA model-measurements agreement than the *Base* case at the two sites. The only exception is the *Redist* simulation at Marylebone Road, where the underestimation of the *Base* case is replaced with an equivalent overestimation (NMB of -59% and $+57\%$, *Base* and *Redist*, respectively, Table 3). There is a small decrease in the *r*-value, and an increase of the NMGE, which is caused by the modelled values of *Redist* being greater than those of the

Table 3. Evaluation statistics for modelled vs measured daily-average concentrations of SFOA for the ClearfLo year-long datasets (year 2012).

Site	Experiment	NMB	NMGE	*r*	COE
Marylebone Road	*Base*	-59%	64%	0.60	-0.23
	*Base*4x	14%	54%	0.67	-0.02
	Redist	57%	79%	0.57	-0.51
	combRedist	-1%	51%	0.59	0.03
North Kensington	*Base*	-69%	70%	0.73	0.03
	Base4x	-18%	42%	0.78	0.42
	Redist	33%	57%	0.71	0.21
	combRedist	-18%	43%	0.73	0.41

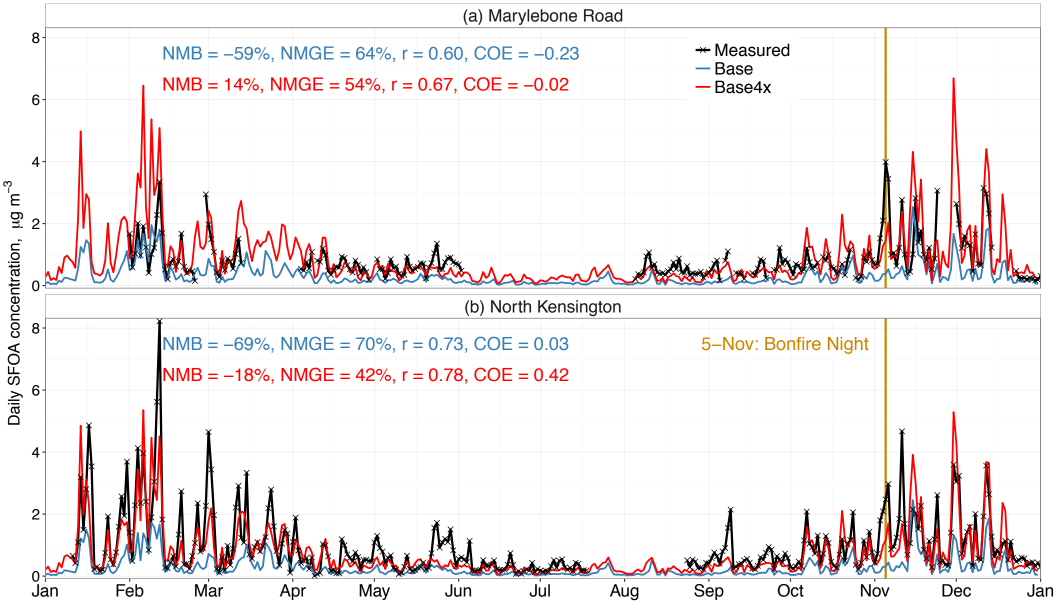

Figure 5. Time-series of measured and modelled (*Base* and *Base4x* experiments) daily-average SFOA concentrations at the (a) Marylebone Road, and (b) North Kensington measurement sites, year 2012. The vertical line marks the date of 'bonfire night', November 5th. The annual average measured SFOA concentrations at these sites were 0.9 µg m^{-3} at Marylebone Road, and 1.0 µg m^{-3} at North Kensington.

Base experiment. For the London North Kensington site, the *Redist* experiment is an improvement compared to the *Base* run, although the concentrations are also overestimated (NMB = +33%, *Redist*). This is expected, as areas with high population densities would include large apartment buildings which are unlikely to have individual fireplaces. Therefore a completely

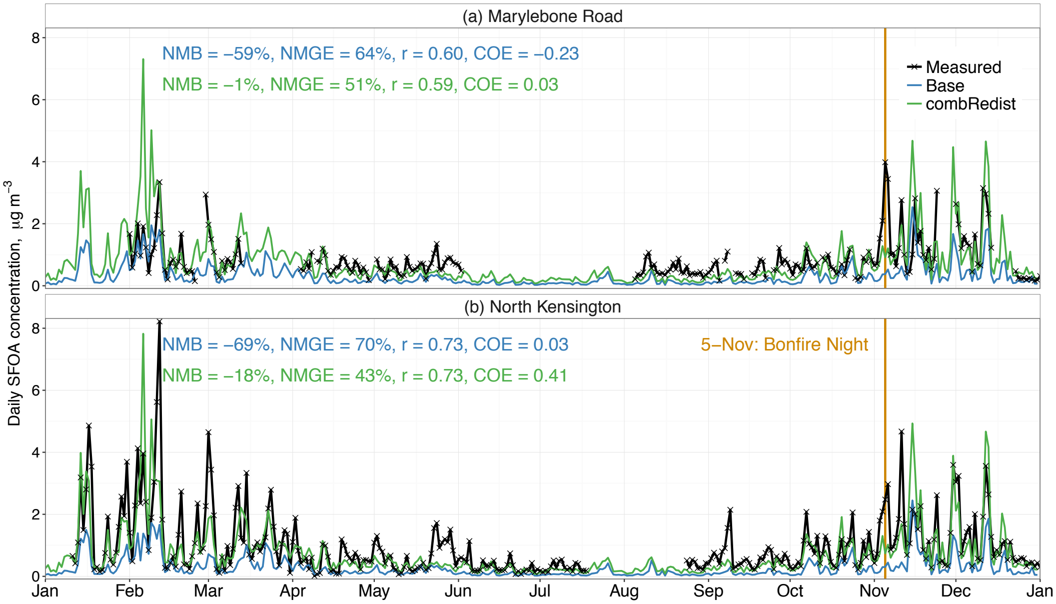

Figure 6. Time-series of measured and modelled (*Base* and *combRedist* experiments) daily-average SFOA concentrations at the (a) Marylebone Road, and (b) North Kensington measurement sites, year 2012. The vertical line marks the date of 'bonfire night', November 5th. The annual average measured SFOA concentrations at these sites were 0.9 $\mu\mathrm{g\,m^{-3}}$ at Marylebone Road, and 1.0 $\mu\mathrm{g\,m^{-3}}$ at North Kensington.

linear redistribution of residential emissions is not correct, but this experiment gives an indication of the maximum effect that population density could have on SFOA concentrations.

Both the *Base4x* and *combRedist* experiments have better predictive abilities for the AMS-PMF measured concentrations of SFOA at the two sites in London than the *Base* case emissions simulation. The NMGE at the Marylebone Road site is reduced to 54% (*Base4x*) or 51% (*combRedist*), compared to 64% for the *Base* case simulation. At the North Kensington site, NMGE is reduced to 42% (*Base4x*) or 43% (*combRedist*), compared to 70% for the *Base* case simulation. The *Base4x* results in improvements in the r-value: 0.67 (*Base*: 0.60) and 0.78 (*Base*: 0.73) at Marylebone and North Kensington, respectively, whereas with the *combRedist* emissions, the r-values of daily-average concentrations remain the same as *Base*: 0.59 (0.60) and 0.73 (0.73), at Marylebone Road and North Kensington, respectively. The improvement in COE values is similar for both experiments (Table 3) at both sites. Both experiments decreased the NMB at North Kensington to -18% (*Base4x* and *combRedist*) from -69% (*Base*), whereas at Marylebone Road, the *Base4x* reaches an overestimation of NMB = $+14\%$ while the *combRedist* matches the measured mean SFOA: NMB = -1% (NMB of *Base* at the Marylebone Road measurement site: -59%). It should be noted, however, that there are several days in November and December where both the *Base4x* and *combRedist* experiments overestimate SFOA concentrations compared to measurements.

In summary, in comparison with daily-average measurements of SFOA concentrations at two sites in London the *Base4x* and the *combRedist* experiments resulted in similar improvements in NMGE and COE, the *Base4x* experiment had better r-

values, and the *combRedist* experiment better matched the annual mean concentrations of SFOA at the two sites. Nevertheless, it should be noted that AMS-PMF apportionment measurements are also subject to uncertainty which limits the expected correlation with the model~~(for~~. For example, Ots et al. 2016a presented scatter plots of daily averaged concentrations of the different OA components derived from measurements with the two different AMS instruments at the North Kensington site during the winter IOP (the cToF-AMS versus the HR-ToF-AMS). While these comparisons showed good correlations between the two measurements (0.88 to 0.95 for the primary OA components, 0.77 for secondary OA), on some days the absolute measured concentrations of specific components do differ, sometimes by more than a factor of two. For further discussion on this see ~~Ots et al. (2016a))~~Ots et al. (2016a, b).

The following sections evaluate these experiments with respect to hourly-average measurements taken with the High Resolution (HR-ToF-AMS) instruments during the ClearfLo winter IOP, which included two rural background sites - Harwell and Detling - as well as the London North Kensington site.

3.2 Hourly averaged diurnal profiles of SFOA concentrations, winter IOP

Hourly averaged diurnal profiles of measured and modelled SFOA concentrations at the ClearfLo winter IOP sites are shown in Fig. 7. The profiles of measured concentrations at the rural background sites (Detling and Harwell), and the urban background site (North Kensington) all show a pronounced maximum in the evening (after 18:00), and a much smaller peak at around 9:00. In the model, the hourly emission factors applied to the SNAP2 sector have similar magnitudes for morning and evening thus underestimating the higher evening concentrations seen in the measurements (in this work, the same diurnal emission profile was used for all countries). This temporal misclassification of emissions for the UK is expected to have a detrimental effect on all of the model hourly evaluation statistics, except NMB.

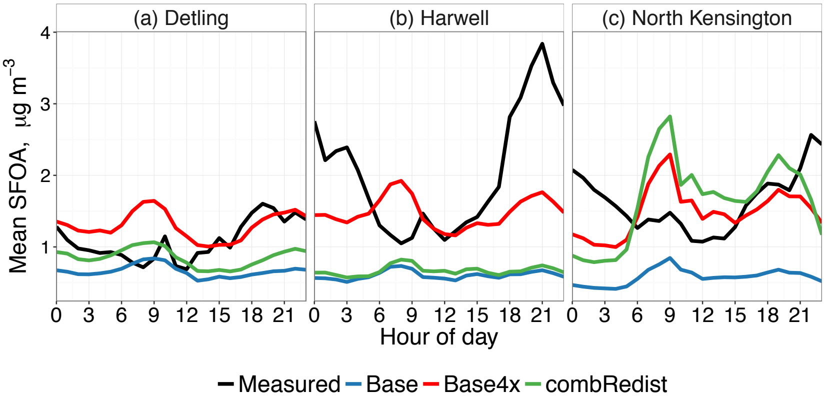

Figure 7. Hourly-averaged diurnal profiles of modelled and measured SFOA concentrations at the (a) Detling, (b) Harwell, and (c) North Kensington measurement sites, winter IOP 2012.

3.3 High SFOA episode: 13-Jan–18-Jan, 2012

Time-series of hourly-average measured and modelled (*Base*, *Base4x*, and *combRedist* experiments) SFOA concentrations at the ClearfLo winter IOP sites are shown in Fig. 8. Note the very high concentrations measured at Harwell from 13 to 18 Jan. North Kensington and Detling also exhibited elevated concentrations (although not as high as Harwell) on these days, especially on 17 Jan. During this episode, both the *Base4x* and *combRedist* experiments simulate similar concentrations for the North Kensington site, whereas for Harwell and Detling, the *Base4x* gives higher concentrations than *combRedist* and is therefore slightly closer to the very high measured concentrations. Note that *Base4x* only increased the UK emissions, not European ones. Hence the increase in *Base4x* concentrations compared with *Base* is not fourfold.

Daily-average maps of modelled SFOA surface concentrations during these days are shown in Fig. 9 (*Base4x*), and Fig. 10 (*combRedist*). Time-series of daily-average concentrations during the winter IOP are shown in Fig. 11~~(using a~~. At Detling,

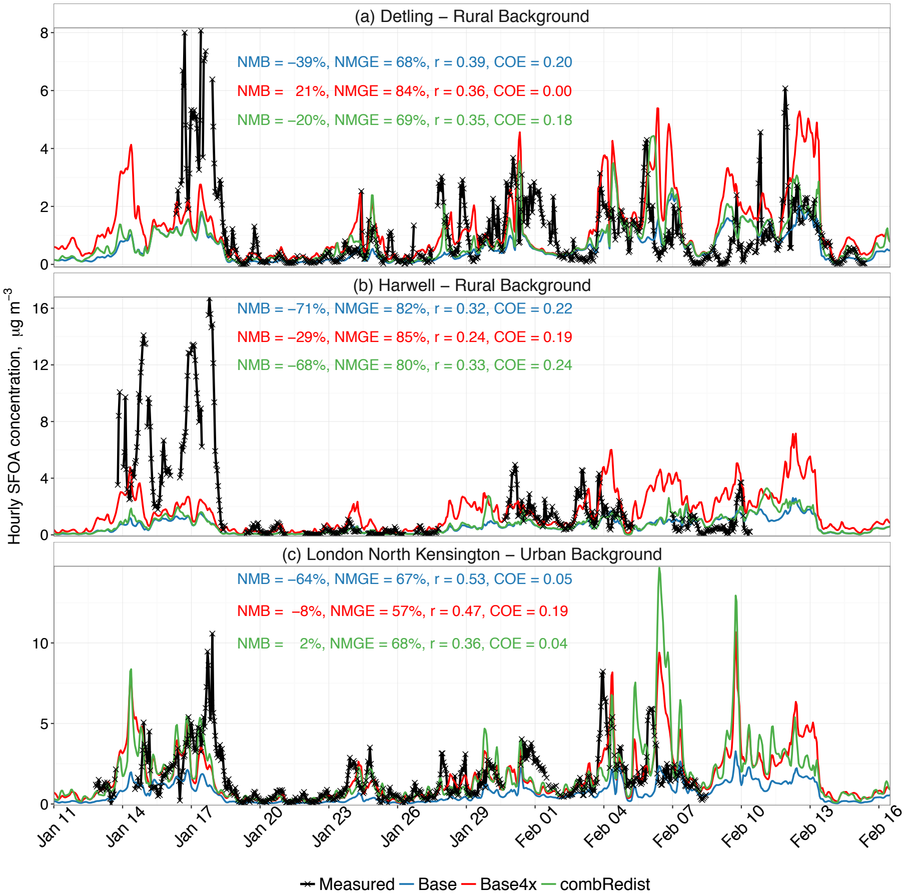

Figure 8. Time-series of measured and modelled hourly average SFOA concentrations at the (a) Detling, (b) Harwell, and (c) London North Kensington measurement sites, winter IOP 2012. Note the different scales on the y-axis.

the measurements commenced the morning of 16-Jan (Fig. 8a) but since we used a data capture threshold of 75%~~of valid hourly values to derive a measured daily average)~~, 16-Jan and 17-Jan did not include sufficient hourly data points to present measured daily averages for this site. Ots et al. (2016a) demonstrated that a rural background site can on occasion exhibit substantially higher concentrations than central London due to atmospheric import of polluted air masses from Europe creating a strong spatial gradient. The daily-average concentration maps, however, do not indicate European gradients over southern England during 13 to 18 Jan. Nevertheless, southern England did experience a sustained high-pressure weather system during these days~~.~~, including noticeably lower temperatures for 14–18 Jan than average (Crilley et al. (2015): Fig. 2). Sustained high pressure usually leads to a very stable atmosphere with descending air masses. Therefore, these high concentrations could have been caused by meteorological build-up, and it is possible the model set-up underestimated the strength of this effect. Furthermore, 14-15 Jan was a weekend whereby people are more likely to spend time home and therefore potentially use their fireplaces more than on weekdays.

The exceptional concentrations measured especially at Harwell (and to a lesser extent at Detling) could have been caused by (i) missing local sources in the area, (ii) over-reporting of the concentrations by AMS measurements or by the PMF analysis applied to apportion measured OA into its components, (iii) meteorological build-up, or (iv) a combination of these. However,

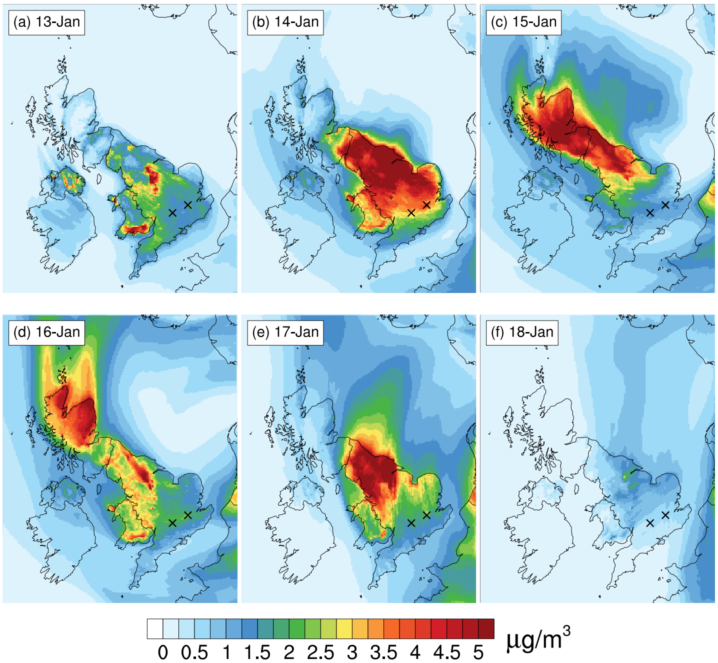

Figure 9. Daily-average modelled (*Base4x* experiment) SFOA surface concentrations during the episode of high SFOA concentrations at the beginning of the winter IOP, year 2012. The black crosses mark the measurement site locations, left: Harwell, right: London North Kensington.

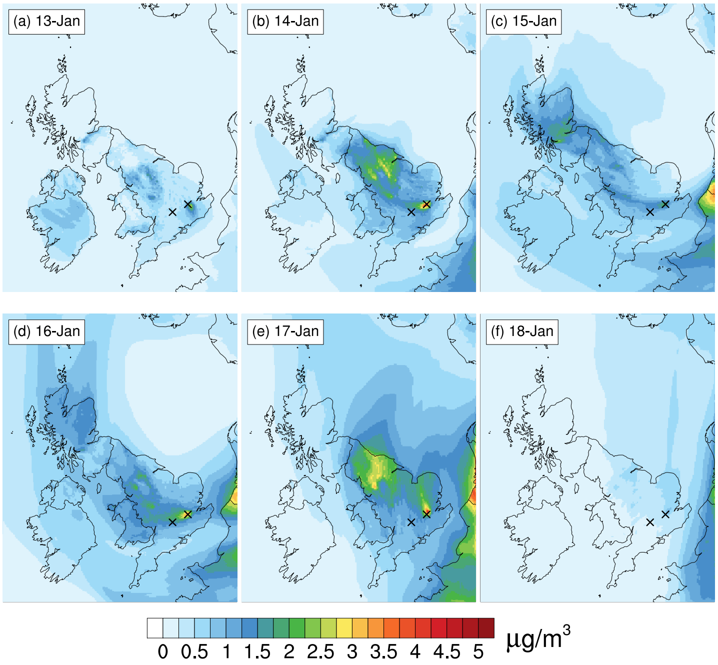

Figure 10. Same as Fig. 9, but for the *combRedist* experiment.

the specific origin of the large discrepancy between model and measurements at the Harwell site during these four days remains unknown.

3.4 Hourly evaluation statistics during the rest of the ClearfLo winter IOP, 2012

Table 4 presents the hourly evaluation statistics at the Detling, Harwell, and London North Kensington sites during the winter IOP (as in Fig. 8) but excluding the period of largely unexplained high SFOA concentrations episode between 13 Jan–18 Jan. These r-values (0.35–0.53; range of hourly r-values for all three sites) are lower than the daily-average r-values in comparison with the annual datasets shown in Figs. 5 and 6 (0.59–0.78). This is expected as the diurnal emissions profile used for all European countries assigns equal amounts of residential combustion emissions to the morning and evening which does not match the measured diurnal SFOA profiles at these three sites (as was shown in Fig. 7).

For Detling, the *Base* case run underestimates the mean measured SFOA concentration by -27% (NMB), the *Base4x* experiment results in an overestimation of $+49\%$, and the *combRedist* yields a close match with -3%. For Harwell, the *Base* scenario has a NMB of -36%, which becomes an overestimation of $+64\%$ with the *Base4x* experiment. The *combRedist* emissions have a minor effect on modelled concentrations at Harwell (NMB of -31%; compared with -36% for the *Base* case; the other evaluation statistics of *combRedist* are also close to those of the *Base* case). At North Kensington, hourly comparison

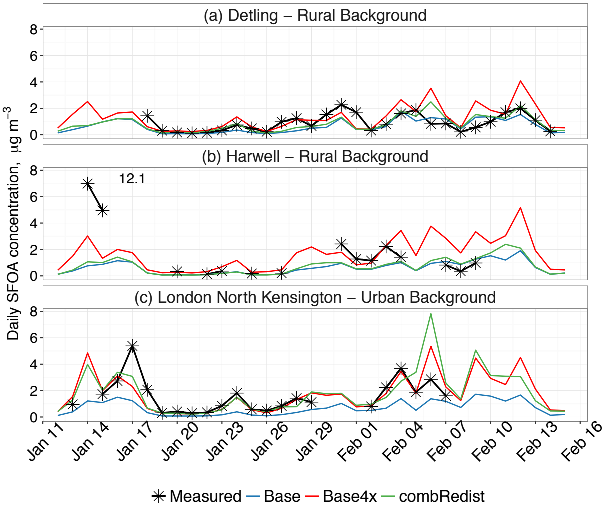

Figure 11. Daily-average measured and modelled SFOA concentrations at the (a) Detling, (b) Harwell, and (c) North Kensington measurement sites, year 2012. On panel (b), the concentration measured at 16-Jan is given as a text label.

shows similar results for the two experiments as was also seen in the daily evaluation. Both emissions cases capture the mean concentration well, but the *Base4x* experiment yields a better *r*-value than *combRedist* experiment .

Table 4. Evaluation statistics for modelled vs measured hourly-average concentrations of SFOA during the ClearfLo winter IOP measurement sites as in Fig. 8, but excluding the period of 13 Jan–18 Jan.

Site	Experiment	NMB	NMGE	*r*	COE
Detling	*Base*	−27%	66%	0.38	0.19
	Base4x	48%	92%	0.45	−0.14
	combRedist	−3%	68%	0.41	0.16
Harwell	*Base*	−36%	69%	0.43	0.18
	Base4x	64%	105%	0.42	−0.24
	combRedist	−31%	68%	0.44	0.19
North Kensington	*Base*	−64%	66%	0.53	0.06
	Base4x	−1%	56%	0.53	0.20
	combRedist	12%	73%	0.35	−0.04

3.5 Comparison of modelled EC with measured EC and BC

Locations for the UK black carbon (BC) measurement network existing in 2012 are shown in Fig. 12. All of the measurement sites use an Aethalometer to measure optically-absorbing aerosol on a filter tape. Optical absorption is converted to an effective black carbon (eBC, referred to as just BC in this work) concentration using a mass-specific absorption cross-section (MAC). Three sites (Harwell, London North Kensington, and London Marylebone Road) also have daily-average filter measurements that are analysed for elemental carbon (EC) with a thermal optical technique in which the split between EC and OC can vary depending on instrumental and analysis parameters. Comparisons of the daily measurements of EC-R (measured EC corrected using reflectance), EC-T (corrected using transmittance), and daily-averaged BC are presented in Appendix A, along with a discussion of the sources of method biases. Substantial discrepancies in reported concentrations exist (at times, more than a factor of 2). Furthermore, the sign and the magnitude of discrepancies differ by season and by measurement site. Consequently, detailed (i.e. hourly or daily) model-measurement evaluation is not justified, and only seasonally-averaged concentrations are presented in this section.

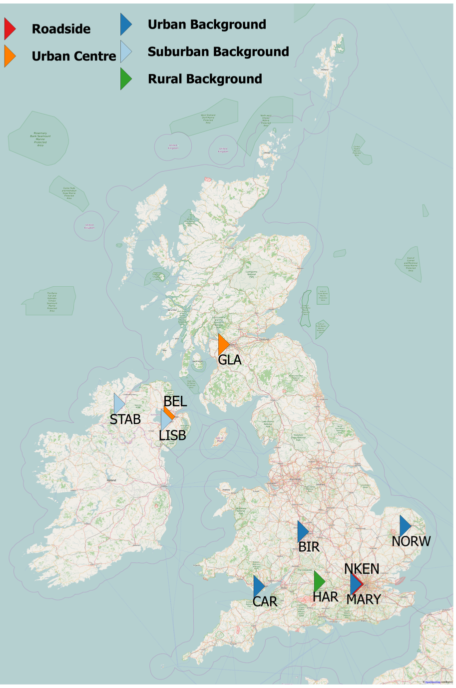

Figure 12. BC-network measurement site locations in 2012. Site names are abbreviated as follows: GLA - Glasgow Centre, STAB - Strabane, BEL - Belfast Centre, LISB - Lisburn Dunmurry, BIR - Birmingham Tyburn, NORW - Norwich Lakenfields, CAR - Cardiff, HAR - Harwell, NKEN - London North Kensington, MARY - London Marylebone Road. Underlying map from © OpenStreetMap contributors.

Seasonal boxplots of daily-average concentrations of measured BC, EC-T, EC-R, and modelled concentrations of EC for Harwell, North Kensington, and Marylebone Road are shown in Fig. 13. In addition to emissions from domestic heating, these concentrations also include all other sources of EC, mainly traffic. Within each panel, the different datasets were made to be of equal size, i.e. days with missing measurements, or with measurements below the limit of detection for EC-R or EC-T values, were also removed from measured BC as well as from the modelled time series. Although the pollutant levels measured close to the traffic source at the Marylebone Road roadside site and the modelled concentrations are not fairly comparable due to the differences in spatial scale (major road vs 5 km model resolution), they are included to illustrate the range of concentrations in a megacity.

For Harwell, modelled EC concentrations from the *Base* and *combRedist* experiments are similar, but concentrations from the *Base4x* experiment are higher. This is consistent with the comparison of modelled and measured SFOA concentrations in the *Base4x* experiment which overestimates wood and coal burning contributions at the two rural sites near London (Harwell and Detling, excluding 13–18-Jan). Fig. 13 shows that the *Base* and *combRedist* modelled EC concentrations are close to measured EC-R during all seasons except autumn for which overestimations of several pollutants for many different days and periods are discussed in Ots et al. (2016a). Generally, measured BC concentrations are higher than measured or modelled EC, but during winter, measured BC, measured EC-R and modelled EC (*Base* or *combRedist* experiments) are a close match, whereas measured EC-T is substantially lower.

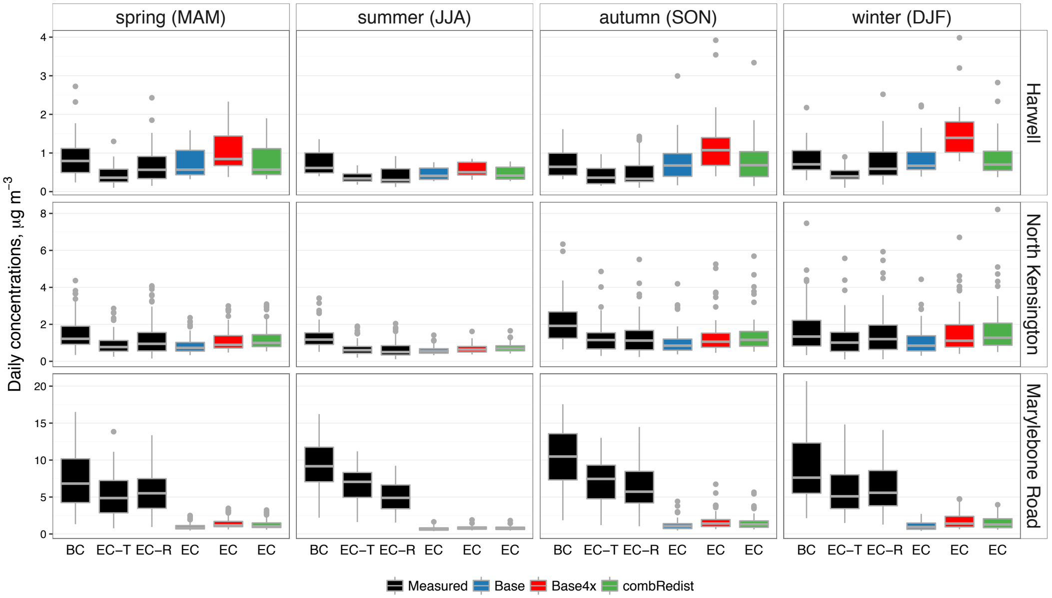

Figure 13. Seasonal boxplots of daily-average concentrations of measured BC, EC-T, EC-R, and modelled EC concentrations at Harwell, London North Kensington, and London Marylebone Road, the three measurement sites that measure both BC and EC, year 2012. Middle line: median, boxes: 25th and 75th quartiles (i.e. the interquartile range - IQR), whiskers extend to 1.5×IQR, and all daily values beyond the whiskers are plotted individually.

At North Kensington, both the *Base4x* and *combRedist* experiments result in similarly higher concentrations than the *Base* run, and these experiments match the measurements of EC-R well. At Marylebone Road, modelled concentrations are substantially lower than are measured. This is expected as Marylebone Road is a roadside site with heavy traffic flows and the concentrations captured at the measurement site are therefore much higher than a 5 km × 5 km × 40 m model grid cell average.

Seasonal boxplots of daily-average concentrations of measured BC and modelled EC at all the other BC network measurement sites are presented in Fig. 14. For these urban sites, both the *combRedist* case and the *Base4x* case yield a higher modelled concentration than the *Base* run and bring the modelled EC into better agreement with measured BC. There are no sites for which the *combRedist* yields a lower modelled concentration than the *Base* run (i.e. for these, urban, sites, the redistribution does not make the comparison worse). Therefore, based on BC measurements at these sites in different parts of the UK (which are on average higher than measurements of EC-T or EC-R), the experiments conducted for the investigation of spatial distribution of residential wood and coal burning do not result in unrealistic EC concentrations. The three sites in Northern Ireland (BEL, LISB, and STAB in Fig. 14) exhibit a stronger seasonal cycle in the measurements than the other sites (i.e. relatively greater increase for autumn and winter), indicating stronger traditions of residential solid fuel burning in this part of the UK.

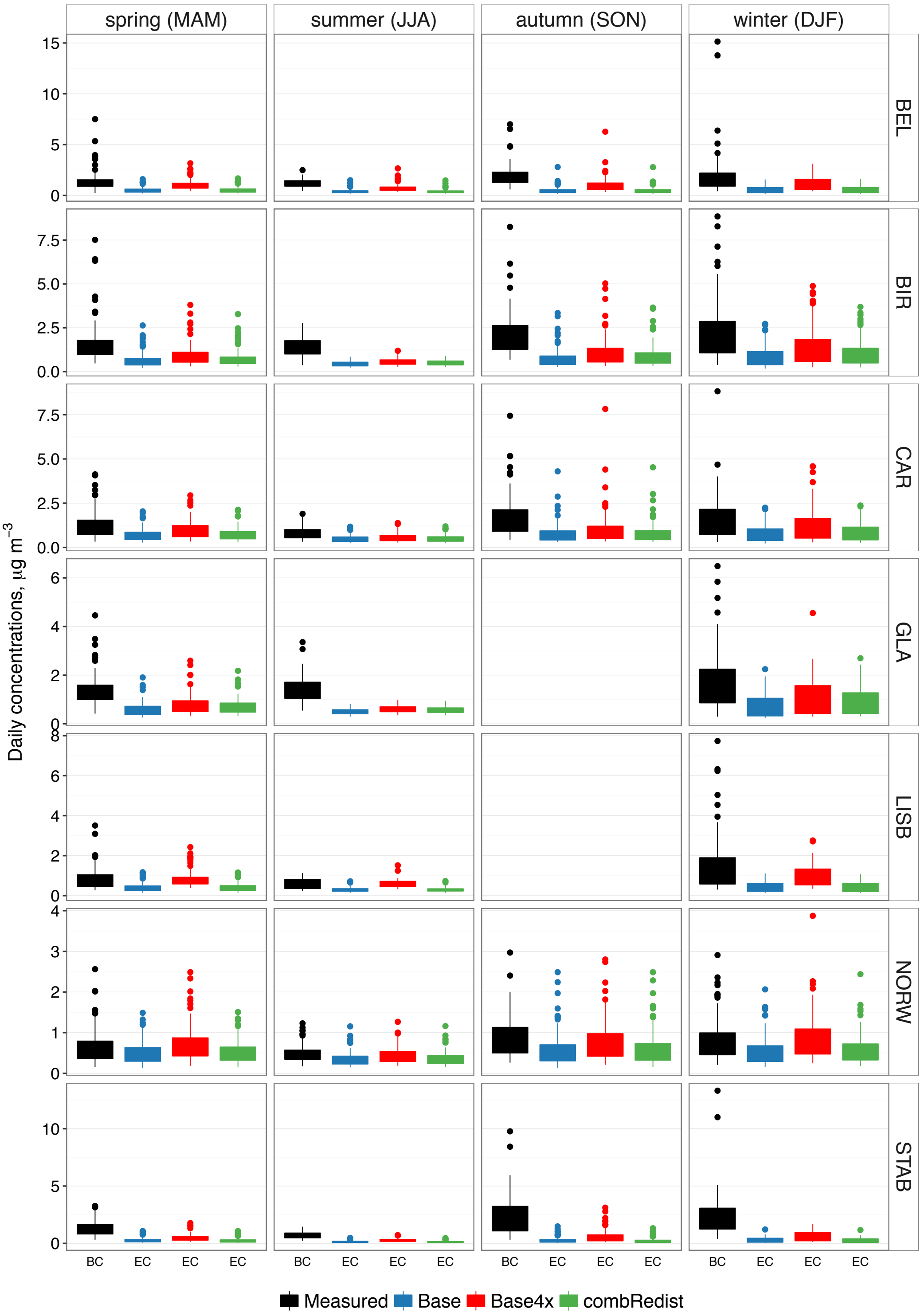

Figure 14. Seasonal boxplots of daily-average concentrations of measured BC and modelled EC concentrations at the BC-network measurement sites, year 2012. Site name abbreviations are given in Fig. 12. ~~Middle line: median, boxes: 25th and 75th quartiles (i.e.~~ Each box is the interquartile range - IQR~~)~~, whiskers extend to 1.5×IQR, and all daily values beyond the whiskers are plotted individually.

4 Conclusions

In this study, different assumptions for the spatial distribution and total emitted amount of PM emissions from solid fuel burning in the UK were tested with the EMEP4UK atmospheric chemical transport model. These model experiments were conducted to investigate the large model underestimations of SFOA concentrations compared with aerosol source apportionment measurements which arise when using the officially-reported PM emissions inventory (a NMB of -71% at the London North Kensington urban background site, for example). The two main scenarios considered were *Base4x*, and *combRedist*. For *Base4x*, officially reported $\mathrm{PM}_{2.5}$ from the SNAP2 emission source sector (residential and other non-industrial combustion) were increased by a factor of 4. For the *combRedist* experiment, half of the emissions from SNAP2 were redistributed linearly by residential population density to extend emissions into smoke control areas. The emission total for the *combRedist* experiment was the same as that officially reported (i.e. equal to the *Base* scenario, and 4 times less than in the *Base4x* scenario). A third experiment, *Redist* - all emissions redistributed linearly to population density, is also presented as an indicator of the maximum concentrations an assumption like this could yield. This is not however completely realistic as the most densely populated areas (of large apartment buildings) are unlikely to have many individual fireplaces.

Comparison of model output with AMS-PMF measurements of SFOA concentrations at an urban background and roadside site in central London (a smoke control area), shows that *Base4x* yielded better daily and hourly correlations than the *combRedist*. Therefore, for certain air masses, the spatial distribution reported by the national emissions inventory appears reasonable. However, the *Base4x* overestimated SFOA concentrations at the rural sites, whereas the *combRedist* better captured mean measured concentrations across the range of site types and locations. The *combRedist* was intentionally simplistic (exactly 50% of the national total was spatially redistributed), so a better agreement might be, for example, *Base2x* + 30% redistributed to population density (or another combination of *Base* emissions and redistribution to include emissions for smoke control areas). The results also suggest that refinement of the prescribed temporal profiles for residential emissions may also be required as the measurements indicated higher levels of SFOA concentrations in the evening than in the morning, whereas the emissions profiles used here emitted relatively more during the morning. It is acknowledged that the experiments undertaken here investigated only potential discrepancies in the national atmospheric emissions inventory, and not other potential sources of model-measurement discrepancy such as shortcomings in model quantification of dry and wet deposition, both of which also depend on accurate model description of the meteorology.

Modelled concentrations of elemental carbon were compared with different measurements: EC-R, EC-T, and black carbon (BC). Substantial discrepancies were noted between the different measurements of this component of PM, so detailed comparison with the model was not presented. However, based on seasonal-average concentrations at the BC network sites over the UK, it was shown that the concentrations derived from the *combRedist* experiments improved the comparisons of modelled vs observed concentrations. Therefore, some redistribution of SNAP2 emissions into smoke control areas, as also suggested by the SFOA comparisons, appears justified. Overall, our results suggest that simulations of SFOA can be improved by adjusting the spatial distribution of the national emissions inventory.

5 Code availability

The EMEP model is OpenSource and can be downloaded from www.emep.int. The WRF model is OpenSource and can be downloaded from https://www.mmm.ucar.edu/weather-research-and-forecasting-model.

6 Data availability

Processed measurement data used in this study are available through the ClearfLo project archive at the British Atmospheric Data Centre (http://badc.nerc.ac.uk/browse/badc/clearflo). The model data (input, ~~code~~scripts, relevant output) are archived at the University of Edinburgh and are available on request.

Appendix A: Measured EC-R, EC-T, BC

A1 Overview

Because of its diverse origins and chemical processing, airborne carbonaceous particulate matter exists in a continuum of different forms – from pure graphitic-like elemental carbon (EC) at one end through to an array of highly chemically-functionalised organic compounds at the other (Gelencsér, 2004). This raises the issue of at what level of chemical oxidation/functionalisation should EC no longer be categorised as EC but as organic carbon (OC). In practice, EC, and an alternative measure for the ‘sooty carbon’ content of particulate matter – black carbon (BC) – are both measurement defined, rather than chemically defined (Petzold et al., 2013; Lack et al., 2014). EC is defined by thermal methods (heating up a PM sample and burning off the more volatile organic components such that what is only burnt off at highest temperatures is called EC; Chow et al. (2007)), and BC is defined by optical methods (measuring how opaque the material is to transmission of visible or near infrared wavelengths to determine effective black carbon, or eBC; Bond and Bergstrom (2006)). So by definition EC and eBC are not measuring the same thing, and both methods require choices in the quantification process. For example, the EC method requires choice on the temperature programme and pyrolysis correction approach used to assign a distinction between EC and OC (Chow et al., 2004; Cavalli et al., 2010), while the eBC method requires a ‘shadowing’ correction (Virkkula et al., 2007) and imposition of a mass-specific absorption coefficient (MAC) to convert optical absorbance to mass concentration (Andreae and Gelencsér, 2006; Quincey et al., 2009). These issues have been the subject of much discussion in the literature, some of which is cited above, with development of standard protocols and terminology. In general, however, measurements of EC and eBC on the same samples are very highly correlated, and to a first approximation EC and eBC data values can both be used in comparison of model output of EC against measurements. For the remainder of this Appendix, eBC is refered to as BC.

A2 Measurements of EC-T and EC-R

The UK Particle Numbers and Concentration Network collects daily samples of PM_{10} onto binder-free pure quartz filters using a Partisol 2025 sampler at three measurement stations: London Marylebone Road (kerbside), London North-Kensington (urban background) and Harwell (rural background). These filters are analysed at the UK National Physics Laboratory (on a Sunset Laboratory Carbon Aerosol Analysis Lab instrument). The protocol used to quantify total carbon (TC) of the sample is a variation of the NIOSH protocol known as Quartz (Quincey et al., 2009). During the heating of the sample, some organic matter will be converted to elemental carbon by pyrolysis. This conversion is monitored by continuously measuring the transmittance (T) and reflectance (R) of the sample. The T or R signal is used to apportion TC into OC and EC by taking account of carbonaceous material that was OC, but become pyrolised into EC during the heating process. However, the quantification of the pyrolysed OC differs whether T or R is used, adding uncertainty to the measurements.

Figure A1 illustrates the uncertainty of the EC split from TC using transmittance (EC-T) and EC split from TC using reflectance (EC-R). For Harwell and North Kensington, EC-R is higher than EC-T (on average over the full dataset) which agrees with the findings of Chow et al. (2004). However, it can be noted that for both Harwell and North Kensington, in the lower range ($<$ ~0.4 $\mu\mathrm{g\,m^{-3}}$ for Harwell, $<$ ~0.6 $\mu\mathrm{g\,m^{-3}}$ for North Kensington), EC-T is higher than EC-R, whereas above these values, EC-R is higher than EC-T.

Figures A2, A3, and A4 split the points in Fig. A1 into seasons for Harwell, North Kensington, and Marylebone Road, respectively. In spring and winter, EC-T is lower than EC-R (NMB from -7% to -35%), whereas during summer EC-T is higher than EC-R (NMB from $+19\%$ to $+31\%$). In autumn, average measured concentrations of EC-R and EC-T are similar (NMB from -2% to $+10\%$), but substantial scatter can be seen for some days as measured concentrations of EC-T and EC-R can differ from each other by more than a factor of 2. These consistent findings at all three sites suggest that the different methods for quantifying of EC with the same instrument are dependent on season.

A3 Measurements of BC

Measurements of BC use an Aethalometer (Magee AE22) and involve the collection of $\mathrm{PM}_{2.5}$ onto a quartz tape, for which the absorption α [$\mathrm{m^{-1}}$] is measured by single-pass attenuation of 880 nm light, corrected for scattering. The absorption is converted to BC concentration using a mass-specific absorption cross section (MAC). The measurements are reported with an hourly timestep. The assumption of a single value for the MAC can lead to uncertainties due to (Heal and Quincey, 2012):

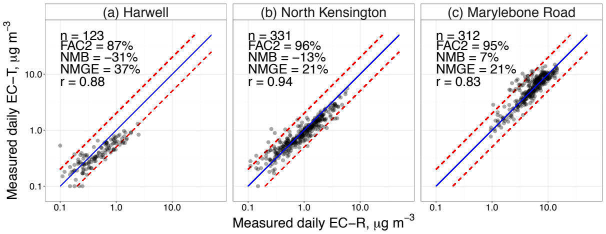

Figure A1. Scatterplot of measured daily-average EC split from TC using transmittance (EC-T) and EC split from TC using reflectance (EC-R), year 2012. Data below the detection limit ($<$ $0.1\ \mu\mathrm{g\,m^{-3}}$) have been removed, leading to the lower number of data points for Harwell.

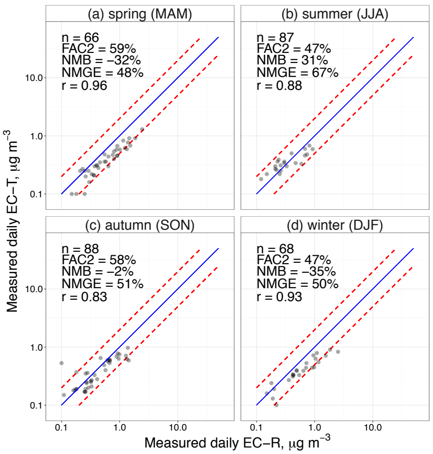

Figure A2. Scatterplot of measured daily-average EC split from TC using transmittance (EC-T) and EC split from TC using reflectance (EC-R) at the Harwell site split by seasons, year 2012.

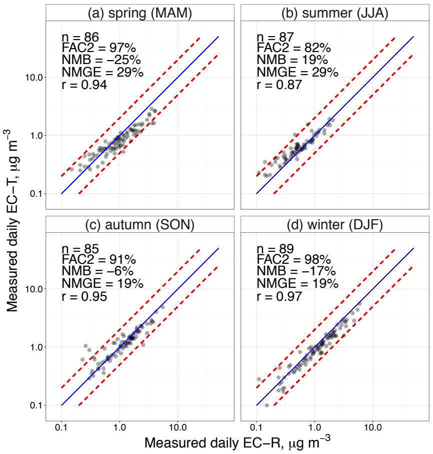

Figure A3. Scatterplot of measured daily-average EC split from TC using reflectance (EC-R) against EC split from TC using transmittance (EC-T) at the North Kensington site split by seasons, year 2012.

- Atmospheric oxidation changing the MAC of the sample (making it appear less dark).
- Variations in the size distribution of the particles leading to variations in the MAC.
- Variations in the external and internal mixing with other particles in the sample leading to variations in the optical properties of the sample.

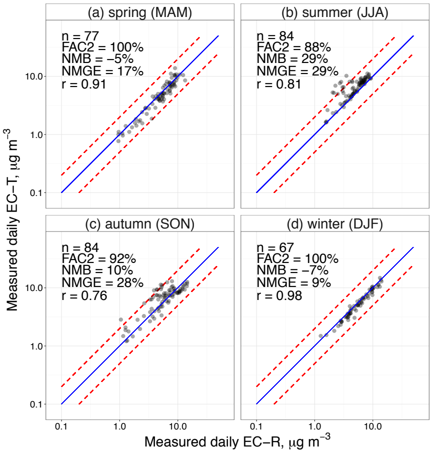

Figure A4. Scatterplot of measured daily-average EC split from TC using reflectance (EC-R) against EC split from TC using transmittance (EC-T) at the Marylebone Road site split by seasons, year 2012.

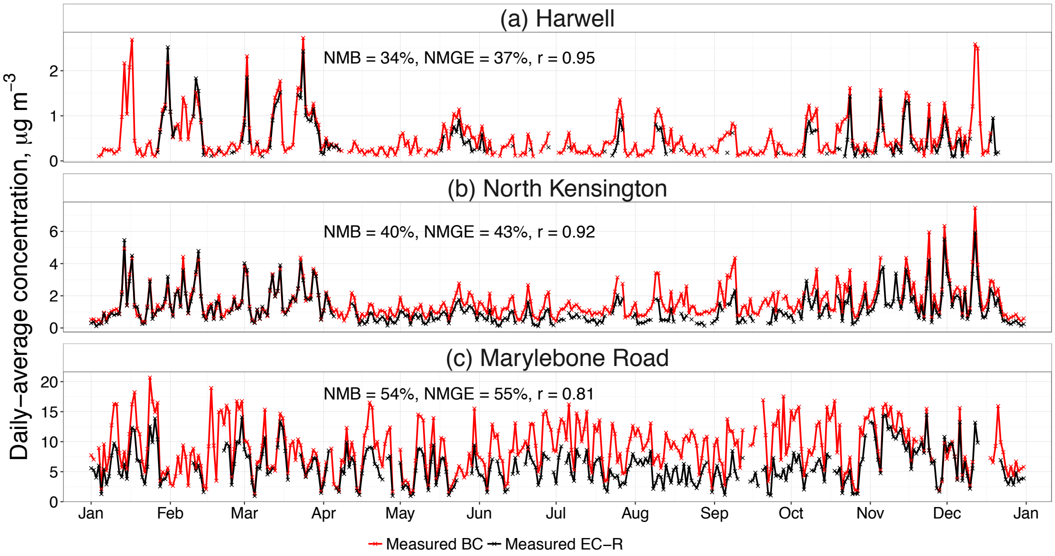

Figure A5. Time-series of daily-average measured EC-R and BC concentrations at the (a) Harwell, (b) North Kensington, and (c) Marylebone Road measurement sites, year 2012.

A4 Measured BC vs measured EC

Figure A5 shows daily-average time-series of measured EC-R and BC for the three measurement sites that have both sets of measurements. For Jan–March and Oct–Dec, measurements of BC and EC-R at the Harwell and North Kensington sites are a close match to each other, whereas from April to September, BC is consistently higher than EC-R. At Marylebone Road, winter and early spring months have better agreement than the summer, but BC is overestimated compared to EC-R throughout the year.

A5 Appendix summary

There are several inherent and methodological uncertainties in quantifying the refractory part of carbonaceous aerosol as EC or BC. Overall, the mean absolute values of the different measurements relate to each other as follows: BC $>$ EC-R $>$ EC-T, but the magnitudes of the differences, and in some cases also the order, vary for seasons and for individual sites.

Author contributions. R.O. designed, executed and analysed the model experiments. R.O. and M.R.H. wrote the manuscript. L.X., L.R.W., S.C.H., and N.L.N. collected and processed the AMS measurements at the Detling Winter IOP site, D.E.Y., J.D.A, H.C, and D.C.G. at the London North Kensington site, and E.M., C.M, and A.D. at the London Marylebone Road site and the Harwell site. M.V manages the EMEP4UK project. S.R. processed the population density data. I.A.M. processed the Base case emissions inventory. All authors contributed to the final version of the manuscript.

Competing interests. The authors declare that they have no conflicts of interest.

Disclaimer. None.

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NCAR command language (NCL) was used to produce the maps (NCAR, 2015), and R, openair and ggplot2 for the analysis and all other plots (R Core Team, 2016; Carslaw and Ropkins, 2012; Wickham, 2009).

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