We are grateful to the referees for their insightful comments which helped to improve the manuscript. We provided point-by-point responses to the referee’s comments below where our responses are in blue.

Referee #1

In this study, Lin et al. evaluated the chemical composition and organic aerosol (OA) sources of PM1 monitored simultaneously at a kerbside site and a residential site in Dublin during both non-heating and heating periods. The authors found that vehicle emissions were associated with the significant kerbside increment of black carbon during the non-heating period, but they had a minor impact on air quality at the residential site. Significant contributions of solid fuel burning to OA were observed at both sites during the heating period. The findings in this study provided valuable information for aerosol scientists to better understand the temporal and spatial variations of the concentration, chemical composition, and OA origins of PM1 in Ireland, which could help the formulation of air quality policies and PM1 mitigation strategies in Ireland. Moreover, the paper is well written, and the results are visualized in an appropriate way. Therefore, I recommend it for publication after minor revisions.

Response: We thank the referee for the positive feedback.

Specific comments: 1. Line 14, “*: : :*sources of submicron aerosols (PM1)*: : :*” Actually, the authors performed the source analysis of OA instead of PM1 in this study. Please revise.

Response: Corrected.

2. I think it is more straightforward to use “the non-heating period” and “the heating period” instead of “P1” and “P2” in the manuscript, especially in the figures and tables.

Response: As suggested by the referee, changes have been made to the manuscript, as well as in the figures and tables.

3. Line 149 and 170, the spikes of BC and OA were defined as those with measured concentrations higher than 15 μg/m3 and 5 μg/m3, respectively. What are the criteria to set these two threshold values?

Response: 15 µg m^{-3} and 5 µg m^{-3} are roughly the top 5 percentiles of BC and OA, respectively, during the non-heating period. We have clarified this in the revised manuscript.

4. Line 186. As mentioned by the authors, the dominant wind direction during the non-heating period was southwest while the city center was located to the north of the residential site. Was there any connecting flow between these two sites? If so, how did the BC concentration vary at the two sites under the connecting flows?

Response: Figure R1 shows the wind speed and wind direction frequencies during the entire sampling period. Southwesterly wind dominated over the entire period with over 50% of occurring frequency while north-northwesterly winds had a frequency of ~20% (Figure R1). The sampling site the kerbside is to the north of the residential site. When north-northwesterly wind prevailed, the median BC concentration at the residential site was 1 µg m^{-3} in the morning while it was 5 µg m^{-3} at the kerbside (Figure R2). Thus, the morning rush hour peak of BC was 80% reduced at the residential site when compared with kerbside.

Similarly reduced mixing ratios of NOx were also observed at the residential site (Figure R3). However, for the evening BC peaks occurring at 20:00 – 22:00 (local time), the median BC (3-4 µg m^{-3}) and 75th percentile (6-10 µg m^{-3}) were comparable between the two sites (Figure R2), primarily due to the emissions from residential solid fuel burning. These comments have been added to the revised manuscript/supplementary.

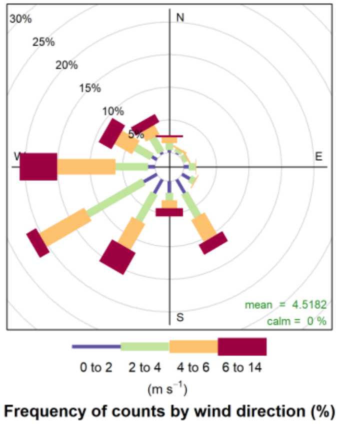


Figure R1. Wind speed and wind direction frequencies during the entire sampling period.

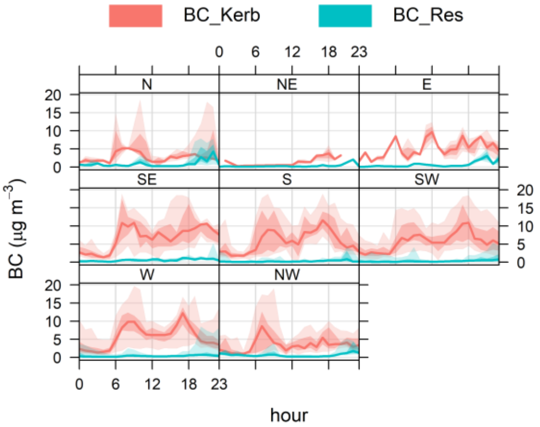


Figure R2. Diurnal patterns of BC measured at the kerbside site (BC_Kerb) and BC at the residential site (BC_Res) under the same wind directions. Solid lines represented median value while shade areas represent 75th and 95th percentiles.

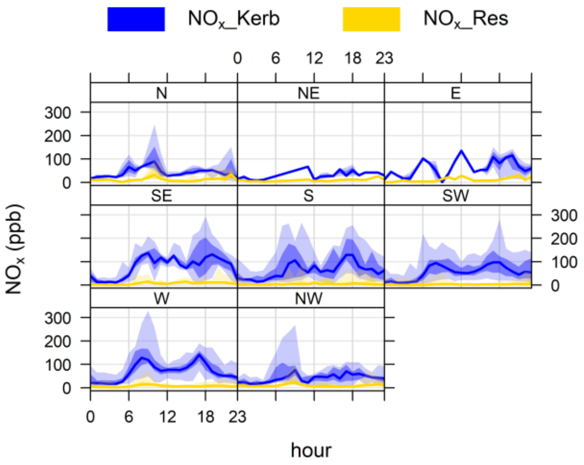


Figure R3. Diurnal patterns of NOx measured at the kerbside site (NO$_x$_Kerb) and NO$_x$ at the residential site (NOx_Res) under different wind directions. Solid lines represented median value while shade areas represent 75th and 95th percentiles.

5. Line 194, Fig. 1c and 1d, another peak concentration was shown in the evening on 29 October, 2018. The authors suggested that these should be due to the residential heating activities. Their impacts on PM1 at residential site are comparable on both dates. However, the burning activity on 31 October showed a greater impact on PM1 than that on the other date at kerbside site. Do the authors have any idea what these burning activities are? Do these kinds of burning activities usually happen during the heating period in Ireland or just special for this sampling period? Are they open-field biomass burning? The reason for me to ask about this is obviously these two burning activities have pulled up the mean values of PM1, OA, BC, NOx etc. at the two sites during the heating period. More information about these burning activities will be helpful for the data interpretation and discussion in line 243-250.

Response: Original data in Fig. 1c was with 5-min resolution while Fig. 1d was 1 h data. As also pointed out by the second referee, we now present hourly averaged data for better comparison. As shown in Fig. R4, at the kerbside, the hourly averaged PM$_1$ peak on 31 October (134.0 μg m^{-3}) was substantially greater than on 28 October (85.0 μg m^{-3}) while the PM1 peaks were comparable at both dates (126.0 vs. 113.1 μg m^{-3}) for the residential site (Figure R4). This is because the pollution level at the kerbside was already elevated due to traffic emissions on 31 October (Figure R4) while the traffic pollution level on 28 October was less significant due to the meteorological conditions (e.g., higher wind speeds as shown in Figure S4). Therefore, heating emissions were added on top of the traffic emissions at the kerbside on 31 October, resulting in higher PM1 concentrations at the kerbside.

These kinds of burning activities from residential heating happen frequently in winter Ireland. In addition to the events reported in this study (winter 2018), our previous studies conducted in winter 2016 at the same residential site have also reported substantial contribution from heating sources (Lin et al., 2018; Lin et al., 2019b). In this study, we extended our measurement to the kerbside and the comparison of simultaneous measurement between the kerbside and residential site improved our understanding of the spatial variation of aerosols and impacts of traffic/heating emissions. These discussions and relevant references have been added to Sect 3.4 in the revised manuscript.

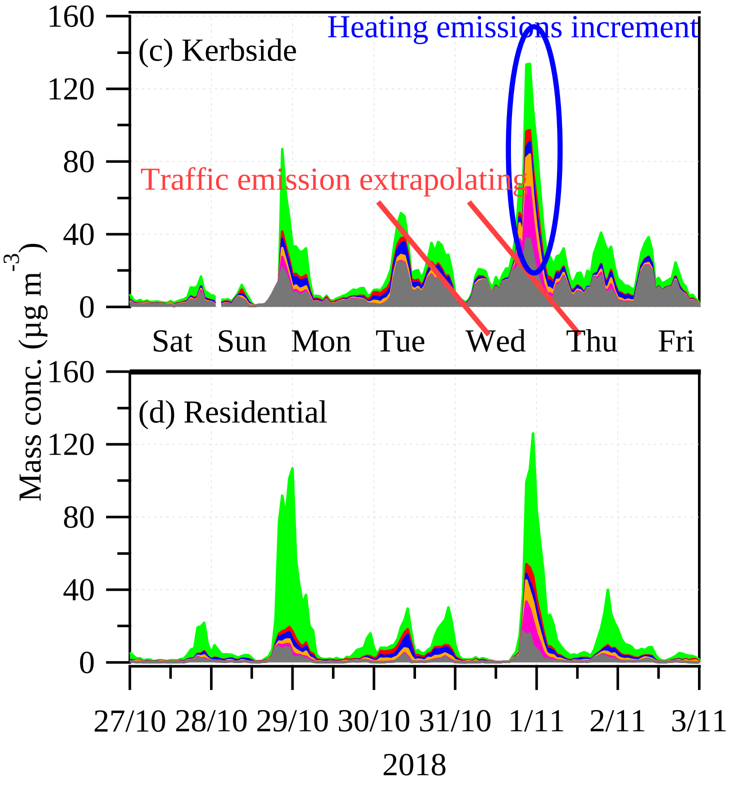


Figure R4. Time series of the species measured by ACSM and AE-33/16 at the kerbside and residential site during the heating period in October 2018. The red line shows the trend of traffic emissions without the influence of heating while the blue cycle highlights the periods with aerosol increment due to heating emissions.

6. Line 234, in addition to the low temperatures in the evening, the PBL during the evening was usually lower than that during the day, and thus PBL could also partly contribute to the higher concentration of COA.

Response: Corrected. It now reads, "…likely due to higher emissions during the evening coupled with relatively low evening temperatures (Fig. S4) and shallower boundary layer."

7. Line 241, could the authors estimate the fraction of OOA that were regionally transported to the kerbside site?

Response: The diurnal trend of OOA (Fig. 4 in the revised manuscript) suggests the background OOA concentration was 0.5 μg m^{-3} while the average OA concentration over the same period was 1.3 μg m^{-3}. Therefore, approximately 38% of the resolved OOA was regionally transported. In the revised text, it now reads, "The diurnal trend of OOA suggests the OOA had a background concentration of 0.5 μg m^{-3} which was higher than HOA (0.1 μg m^{-3}) and COA (0.1 μg m^{-3}), indicating part of

OOA was also associated with regional transport. It is estimated that approximately 38% of the total OOA was regionally transported, i.e., the value of background OOA concentration of 0.5 μg m^{-3} if compared to the total OOA concentration of 1.3 μg m^{-3}."

8. Line 296, it is not clear what are the typical values of HOA/BC for the gasoline vehicles-dominated environment. Please add relevant values and references.

Response: HOA/BC ratios in the range of 0.9-1.7 have been reported in the gasoline vehicles-dominated environment (DeWitt et al., 2015). We have added such values and references in the revised manuscript. It now reads, "Compared to other studies, the HOA/BC ratio in Dublin was lower than the HOA/BC ratios reported for gasoline vehicles-dominated environment (0.9-1.7) but was within the range for the diesel environment (0.03-0.61) (DeWitt et al., 2015), indicating most of the traffic emissions were from diesel vehicles."

9. Was the second ACSM also equipped with a quadrupole mass spectrometer? How were the Q-ACSMs calibrated?

Response: The second ACSM was also a quadrupole ACSM (i.e., Q-ACSM), we have clarified this in the revised Methods Section.

Both ACSMs were calibrated with ammonium nitrate and ammonium sulfate following the procedure described by Ng et al. (2011b). Briefly, monodispersed 300 nm ammonium nitrate/ammonium sulfate particles were generated by an atomizer (Model 9302, TSI) and size-selected by a differential mobility analyzer (DMA; TSI model 3080), and subsequently introduced into the Q-ACSMs to determine the response factor (RF), as well as the relative ionization efficiencies (RIEs) of ammonium and sulfate. We have added the above information in Sect. 2.2 in the revised manuscript.

10. Tables 1 & 2 can be combined into one. Please add PM1 data in the table. Moreover, numbers in the Table should have the same significant figures as those in the main text of the manuscript and figures.

Response: As suggested by the referee we have combined Tables 1 & 2 into one, have added PM1 data, and adjusted the significant figures in the revised table.

11. Several typos: 11. Fig. 4d, the OA concentration should be 8.1 instead of 8.7 μg/m3.

Response: The original Fig. 4d (i.e., pie charts) has now been combined to Fig. 2 in the revised manuscript. We provide the value of OA concentration in Table 1.

12. Line 43, "micron-environment" should be "micro-environment".

Response: corrected.

13. Line 133, should be Crippa et al. (2013).

Response: corrected.

Referee #2

Lin et al. (2020) in this study measured the chemical composition of submicron aerosol (PM1) in two locations in Dublin (kerbside and residential sites) from 4 September to 9 November 2018. Measurements were performed by using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) and an Aethalometer (AE-16 and AE-33). PMF analysis was also implemented on the data. In general, the manuscript is well written though the results presented in the main manuscript do not correspond to the entire period of 4 September to 9 November 2018, but to only two weeks of measurements. The authors chose two periods of the available data, with the first one corresponding to a rather clean period (P1) with low mass concentration of PM1 and another one rather polluted (P2) by local sources (heating purposes). The study presented is very rich in data and analysis. However, these information are not very clear in the main manuscript or not even included (they are left on the supplementary) making the manuscript weak and less readable, especially in the results section. Additionally, the reading might be challenging as OA sources and changes in concentrations are vaguely discussed and not really explained. Moreover, figures need reshaping as labels are not well positioned or data are not clear due to high values of the axis.

Response: We have included more information about the data and their analysis, and have reshaped figures substantially in the main manuscript. In particular, we have added more discussion on OA sources in the result section.

Specific comments: Line 26: "solid fuel burning..." it should be explained for which period is referred to. Solid fuel burning was not present in both periods.

Response: Clarified. Now it reads, "…solid fuel burning (38% or 2.4 μg m^{-3}, resolved only during the heating period)…"

Line 77: the word "monitor" is missing.

Response: Corrected.

Line 107: The 1 hour interval that was set for ACSM in the residential site is really high. This might lead to the lack of data originating from local sources and may affect the corresponding diurnal profiles of OA sources. Authors chose this in order to reduce uncertainty though in Fig. S1b the measured PM1 mass concentration is quite high reaching values greater than the Kerbside site.

Response: We do not expect high variability in local sources at the residential site. In particular, our previous studies (30 min resolution) at the same residential site (Lin et al., 2018) shows the measured PM_1 was in good agreement with the collocated SMPS measurement with 15 min, as well as $PM_{2.5}$ (1 h) at another residential site (i.e., Rathmines station). Moreover, the source apportionment of OA at the residential site suggested the major local sources were domestic solid fuel burning which was consistent with our previous study at the same site (Lin et al., 2018; Lin et al., 2019b). Therefore, we believe the hourly resolution had captured the major local source at the residential site. Future studies using HR-ToF-AMS are to be conducted to study other local emissions at the residential site with higher time resolution (e.g., 5 min).

As the reviewer said, we had high concentrations during the heating period at the residential site. But for most of the time, especially at the beginning of the campaign, the PM_1 concentrations were relatively low (<2 μg m^{-3}). In the revised manuscript, it now reads, "a 1-hour interval was used at the residential site to reduce uncertainty in measurement due to the relatively low concentrations for most of the time"

Line 110: How much the collection efficiency was on average?

Response: The average collection efficiency was 0.5 on average. We have added this information to the revised Method Section.

Line 111: The Rathmines site is mentioned. It was not described before in the manuscript and is referred also afterwards without any information. Please provide some info.

Response: We have provided relevant information regarding the Rathmines site. It now reads, "Chemical compositions of PM_1 were simultaneously measured at a kerbside site in Dublin city centre and a residential site in suburban Dublin, at a distance of ~5 km from the kerbside site (see the map in Fig. S1) while $PM_{2.5}$ was sampled at Rathmines (https://www.epa.ie/air/quality/data/rm/), another residential site at a distance of ~3 from the kerbside and residential sites." Also, reads "… (i.e., Rathmines, Fig. S1) where a tapered element oscillating microbalance (ThermoFisher Scientific) was deployed with 1 h resolution".

Line 118: CO measurements are available for kerbside but they are not presented anywhere in the main manuscript.

Response: We have added a discussion on CO as well as NOx in the main manuscript. It now reads, "Specifically, both NOx and CO showed rush hour peaks during weekdays while such rush hour peaks during weekends were not as prominent as during weekends, consistent with the traffic pattern in Dublin (Fu et al., 2017). The average mixing ratios for NOx and CO were 54.1 ppb (in the range of 5.4-200.0 ppb) and 0.2 ppm (in the range of 0.05-0.8 ppm), respectively."

Line 137: Figure S1 deserves to be in the main manuscript. The overall (2 months period) chemical composition of submicron aerosol (PM1) should also be included for both sites and discussed.

Response: Figure S1 (or Figure R5) has now been moved to the main manuscript with a discussion of the overall chemical compositions of PM_1 for the entire campaign. It now reads, "Figure 1 shows the time series of submicron organic aerosol (OA), sulfate, nitrate, ammonium, chloride, and black carbon (BC) at both the kerbside and the residential site, as well as the time series of $PM_{2.5}$ at Rathmines from 4 September to 9 November 2018. The air quality during the early stage of the sampling period (before 30 September) showed limited influence from residential heating emissions as observed by few pollution spikes in the evening when compared to a later period with prominent evening spikes observed at all three sites (From 1 October to 09 November; Fig. 1). The three sampling sites (i.e., kerbside, residential, and Rathmines) are within a 5 km radius in Dublin city and the time series of PM_1 and $PM_{2.5}$ were well correlated with linear correlation coefficients determination (R^2) in the range of 0.56-0.83 and slopes of 0.72-0.88 (Fig. S1). The good time series correlation between the three sites was mainly driven by the pollution events during the heating period while the slopes of 0.72-0.88 suggested PM_1 explained, on average, 72-88% of $PM_{2.5}$ mass. The poorer correlation (R^2 of 0.56; Fig. S1) between the kerbside PM_1 and Rathmines $PM_{2.5}$ than between the residential PM_1 and Rathmines $PM_{2.5}$ (R^2 of 0.83) was due to traffic emissions which had a greater impact on the kerbside than at both the residential site and Rathmines.

Over the entire period, the mean mass concentration of PM_1 was 11.7 ± 9.7 (one standard deviation) μg m^{-3} at the kerbside with black carbon accounting for 50% of the total PM_1 mass (Fig. 1a), followed by OA (31%), nitrate (6%), sulfate (5%), ammonium (5%), and chloride (2%). At the residential site, the mean PM_1 concentration (6.6 ± 3.1 μg m^{-3}) was roughly half of that at the Kerbside (Fig. 1b). However, the chemical compositions of PM_1 at the residential site was dominated by OA (59% of PM_1), followed by BC (13%). The total inorganic aerosols (sum of sulfate, nitrate, ammonium, and chloride) accounted for 28% of PM_1 at the residential site, slightly higher than at the kerbside (18%), though the concentrations were comparable (1.8 vs. 2.1 μg m^{-3}) between the two sites, suggesting regional sources/formations rather than traffic emissions. In contrast, the greater abundance of BC at the kerbside suggests traffic emissions comprised a high fraction of BC which, however, had a limited impact on the residential site. In particular, BC at the kerbside showed two rush hour peaks, confirming traffic was its major source (Fig. S2). However, the BC was up to 25 times lower at the residential site during the rush hours (Fig. S2), suggesting a minor impact of traffic on the air quality at the residential site due to the effects of the wind direction and the distance from the road. In addition to the rush hour peaks of BC, an additional BC peak in the evening was also observed at both sites due to the emissions from domestic heating activities (discussed later). ”

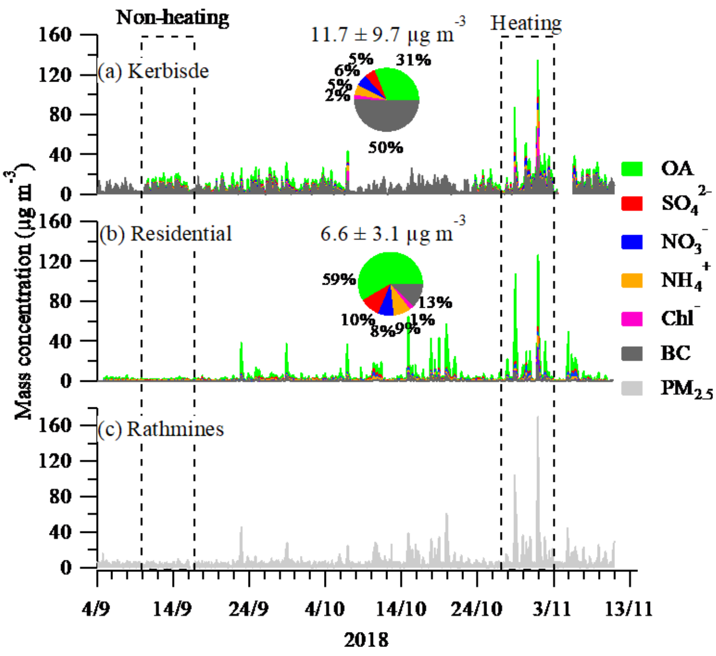


Figure R5 (or Figure 1 in the revised manuscript). Time series of hourly averaged submicron organic aerosol (OA), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Chl^-), and black carbon (BC) at the kerbside (a), residential site (b), and EPA Rathmines station (c) from 4 September to 9 November 2018. Inset pie charts are the chemical composition of PM_1 averaged over the entire period while the numbers (±one SD) above are the average PM_1 concentration. The non-heating period, from 10 September to 17 September, and heating period, from 27 October to 4 November 2018 are marked for further analysis. The data gaps at the kerbside were due to ACSM malfunction.

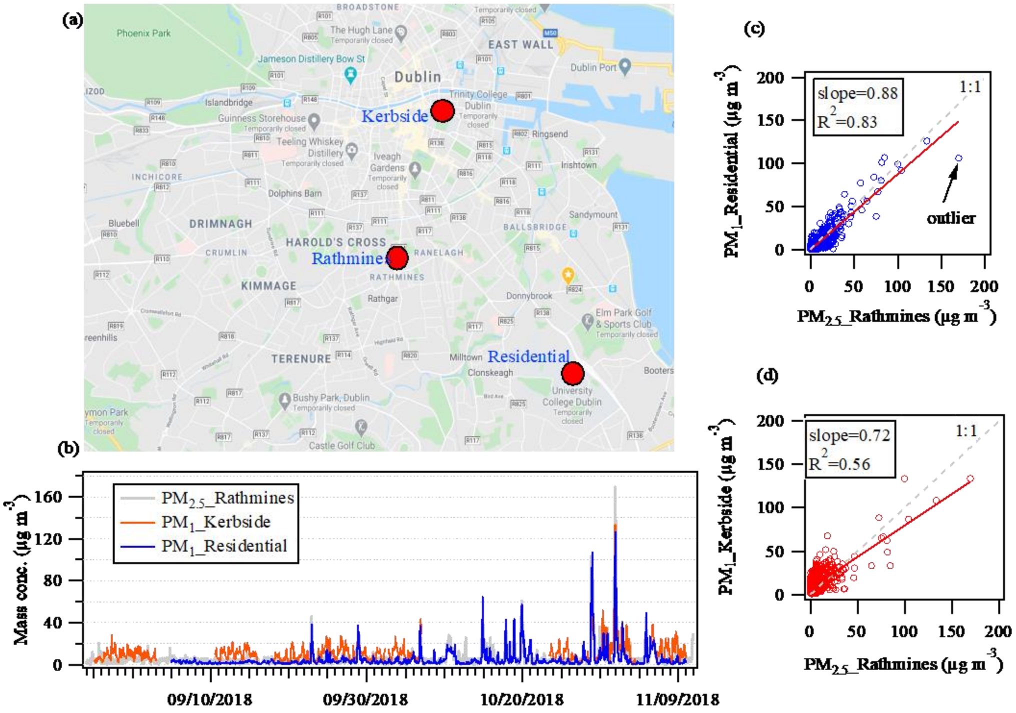


Figure R6 (or Figure S1). (a) Sampling sites for PM_1 measurements in Dublin marked by the red cycles at the kerbside (i.e., Trinity College Dublin) and residential site (i.e., University College Dublin), as well as for $PM_{2.5}$ measurement at Rathmines; (b) time series of PM_1 and $PM_{2.5}$; (c) scatter plot between residential PM_1 and Rathmines $PM_{2.5}$; and (d) scatter plot between Kerbside PM_1 and Rathmines $PM_{2.5}$. Also shown in (c) and (d) are the slopes and correlation coefficients (R^2) from the linear relationship. Note that removing the outlier in (c) resulted in a slope of 0.93 instead of 0.88. The map was adapted from Google Maps.

Line 151: Please specify Fig.1 and Fig.2 with Fig.1a, Fig.2a.

Response: Corrected.

Line 168: Fig.3a is mentioned before Fig. 1b, c,d and Fig. 2b, c, d. Please fix this.

Response: We have now combined the original Fig. 1 and Fig. 2 into one figure (now Fig. 2) in the revised manuscript. For better comparison and visualization of the data, we tend to put the same contents (e.g, time series, diurnal) sampled at the two sites in one Figure (i.e., Fig. 2 and Fig. 3). But in Sect. Results and Discussion, we tend to discuss e.g., time series and diurnal of PM_1 together for the same site.

Line 173: “(Fig. 1)” Please define to which letter of Fig. 1 the text is referring to.

Response: Corrected.

Line 195: “197.3 μg m-3” This value is not consistent for Fig.1 c and Fig. S1a. Please provide the correct figure/ value.

Response: Original Fig. 1c was based on 5-min resolution data while Fig. S1a was based on hourly averaged data. To be consistent and for better comparison, all data are now hourly averaged in the revised manuscript.

Line 207: Nitrate can be also present in higher values due to organonitrates (ON). Have the authors checked the fraction of ON to nitrate?

Response: Organo-nitrates can be well estimated by HR-ToF-AMS based on m/z 30 and 46 (Kiendler-Scharr et al., 2016). However, for UMR Q-ACSM, ambiguity remains due to the insufficient mass resolution to distinguish the interference of CH_2O^+ from NO_2^+ at m/z 30. For such reasons, we have not investigated the fraction of ON to nitrate.

Line 215: “(Fig. S1)” should change to Fig. S1c

Response: Corrected.

Line 226: Fig. 5a is referred before Fig. 4b, c, d.

Response: Corrected.

Line 234: Higher COA mass concentrations could be related to the decrease of boundary layer.

Response: Corrected. Now it reads, “Higher dinner time COA peak (2.7 μg m^{-3}) was observed than lunch time peak (1.6 μg m^{-3}) likely due to higher emissions during the evening coupled with relatively low evening temperatures (Fig. S2) and shallower boundary layer.”

Line 235: Fig. S7 does not correspond to the OOA profile spectrum.

Response: Corrected.

Fig. S6a, b deserves to be in the main manuscript instead of Fig. 5a.

Response: The updated Fig. S6 has been added to the main manuscript.

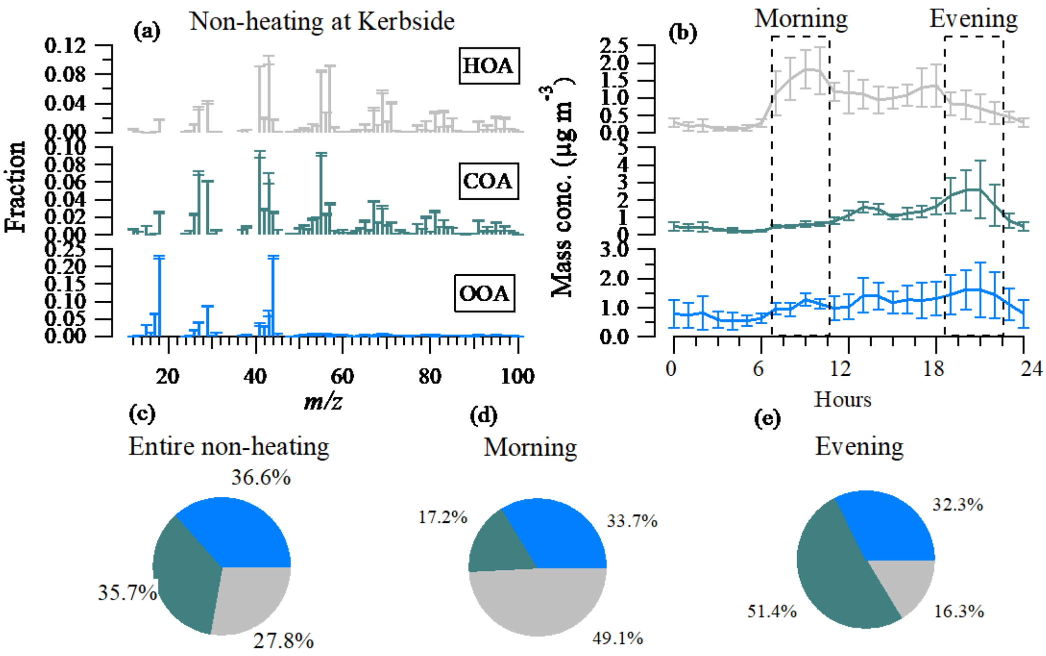


Figure R7 (or Figure 4 in the text) (a) Mass spectral profiles of hydrocarbon-like OA (HOA), cooking OA (COA) and oxygenated OA (OOA) during non-heating at the kerbside; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire non-heating period; (d) over the morning rush hours (7:00-10:00, local time); and (e) over the evening hours from 19:00-22:00. Error bars in (a) and (b) represent one standard deviation.

Line 235: The authors state that OOA resembles of the less volatile OOA (LV-OOA). What criteria lead to this statement?
Response: This was based on the fact that the correlation coefficient (R^2) between the resolved OOA profile and the reference profile of LV-OOA from Ng et al. (2011a) was 0.94 compared to 0.4 between OOA and SV-OOA (Ng et al., 2011a). We have added this point to the revised manuscript.

Line 243: The authors have constrained with ME-2 tool, 4 out of 5 factors with a relative strict α-value. This leads to two factors (wood and coal) contributing fairly low to OA (4% and 8%, respectively), making the results less robust. How confident are the authors about this constraint? It seems that solution was forced to an erroneous solution, comparing the data to the unconstrained ones, where biomass burning factor contributed for approx..20% of OA.
Response: The reason we constrained 4 factors (i.e., HOA (or referred as oil), peat, coal, and wood OA factors) was to evaluate their contribution to ambient OA during the heating period. This was based on priori information that oil, peat, coal, and wood burning were used for heating according to the Central Statistics Office (CSO, 2016) and Sustainable Energy Authority of Ireland (SEAI, 2018). Previous offline (i.e., filter-based) and online (i.e., ACSM/AMS) studies in Ireland winter have identified

ambient OA being associated with the residential burning of oil, peat, coal, and wood burning (Kourtchev et al., 2011; Dall'Osto et al., 2013; Lin et al., 2018). In particular, our previous study has characterized the mass spectral profiles of peat, coal, and wood burning OA factors by simulating their burning in a typical Irish stove with an ACSM (Lin et al., 2017). Peat and wood burning both show biomass features with a prominent contribution at m/z 60 (i.e., f60), a marker fragment for biomass burning (Lin et al., 2017). Therefore, both peat and wood burning have contributed to the BBOA factor as resolved from the free PMF analysis. On the other hand, the increase in the concentration of chloride in the evening suggested coal use for heating, consistent with our previous study (Lin et al., 2017).

However, as pointed out by the referee, large uncertainties might exist with a tight constraint (i.e., a value of 0.1) when constraining 4 out of 5 factors. Therefore, we have conducted a sensitivity test by varying the *a* values of 0-0.5 (or 0-50% variation) for the reference profiles. In addition, a bootstrap-based resampling strategy with a total of 500 runs was applied to examine the statistical uncertainty using SoFi (Version 6.A1; https://datalystica.com/sofi). The following criteria are used for the selection from these ME-2 runs to get the most optimized solution:

1, Correlation between the time series of HOA and NO_x/BC in the morning (7:00-10:00) during weekdays. HOA and NO_x/BC have a common source from traffic emissions in these morning hours.

2, Diurnal cycle of COA. The COA concentrations during mealtime should be higher. In this study, the ratio of COA at 13:00 to the average of COA of 10 and 11 am was monitored.

3, Multi-linear regression between BC and heating-related factors (i.e., HOA (or oil burning), peat, wood, and coal burning) in the evening (19:00-23:00), assuming only the heating-related factors contributed to BC in the evening.

4, Fraction of m/z 60 (i.e., f60) for peat and wood burning OA factors should be higher than 0.006 (Cubison et al., 2011; Lin et al., 2017).

5, Fraction of m/z 44 (i.e., f44) for the unconstrained factor (i.e., OOA). OOA should have higher f44 than primary factors.

Final time series and mass spectra were the averages of the ME-2 runs meeting these criteria. In the revised manuscript, we have clarified these new ME-2 strategies, and have provided the new results.

Line 244: Fig. 4c and Fig. 5a are referred before Fig. 4b and Fig. 5b

Response: Corrected.

Line 245: There is no such high peak in HOA around 23:00, according to Fig. S11b. It seems that on Fig. 5 the 3rd quartile of the data has been used instead of the average values. This is consistent to the average values given in the manuscript. Again, Fig. S11 deserves to be in the main text instead of Fig. 5c.

Response: The original Fig. S11b shows the median and 25th and 75th quartiles while the original Fig. 5c shows the average values of the OA factors stacked on top of each other. To be consistent, we have used the average values in both the main text and supplementary.

As suggested by the referee, we have moved the updated Fig. S11 in the revised manuscript (see the figure below).

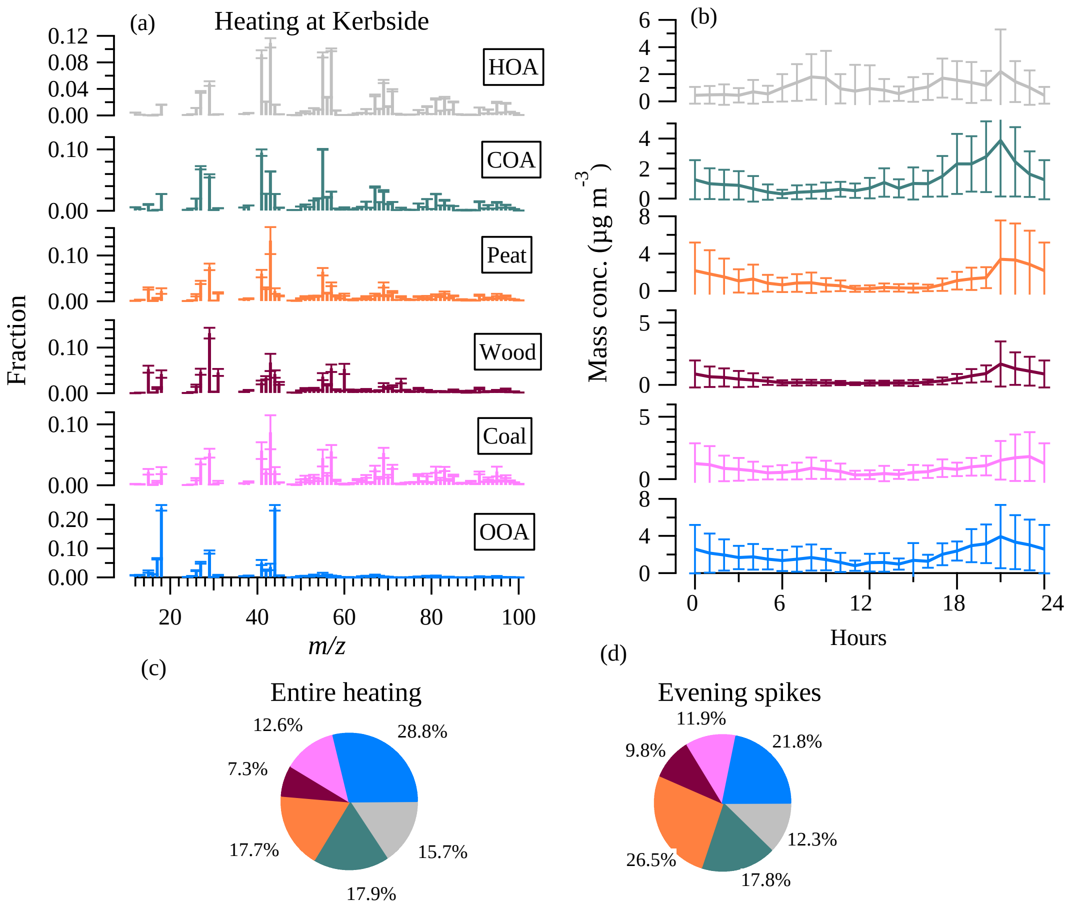


Figure R8 (or Figure 6 in the text). (a) Mass spectral profiles of hydrocarbon-like OA (HOA), cooking OA (COA), peat, wood, coal and oxygenated OA (OOA) factors during heating at the kerbside; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire heating period; and (d) over evening spikes on 28 and 31 October. Error bars in (a) and (b) represent one standard deviation.

Line 253: peat, coal and wood factors contribute one third to the total OA during P2 in kerbside. However, only a line is describing their existence.

Response: We have now added more discussion in the revised manuscript. It now reads, "Peat is an accumulation of partially decayed plant material which is an important domestic fuel source in Ireland (Tuohy et al., 2009). The incomplete decay of vegetation resulted in an increase of *f60* when burned (Lin et al., 2017). However, *f60* in peat profile (0.014) was lower than wood (0.053) probably because wood contained a higher fraction of *m/z* 60-related material e.g., levoglucosan (Fig. 6a). Over the entire heating period, peat burning accounted for 17.7% (1.2 µg m^{-3}) of OA (Fig. 6c). However, during the pollution spikes as seen on 28 and 31 October (Fig. 6d), peat burning increased its fraction to 26.5% (9.2 µg m^{-3}), suggesting peat burning was an important OA emission source. Similarly, wood burning increased its contribution to 9.8% (3.3 µg m^{-3}) during pollution spikes from an average of 7.3% (0.5 μg m^{-3}). The important role of peat and wood burning in driving the pollution events is consistent with our previous study in suburban Dublin (Lin et al., 2018).

The profile of coal burning OA featured very low *f60* (<0.003), consistent with its non-biomass signature as coal is formed from the complete vegetation decay. On average, the coal factor accounted for 12.6% (0.8 μg m^{-3}) of OA. Though the fraction of coal burning decreased during pollution events (11.9%; Fig. 6d), its absolute concentration increased (4.3 μg m^{-3}). Note that chloride also showed a significant increase during the pollution events (Fig. 2c) which was associated with coal burning as our previous coal-combustion experiment showed that chloride emission comprised a high fraction (2-52.8%) of the submicron aerosol from coal burning emissions (Lin et al., 2017). ”

Line 254-255: Could this higher OOA levels be transported by another area and not due to SVOCs?

Response: Compared to the non-heating period, OOA was significantly elevated, coincided with the increase of primary OA factors, in the evening during the heating period. Thus, it is likely that higher OOA levels in the evening during heating were due to the secondary formation/aging of pollution plumes from heating sources. In the revised manuscript, it now reads, “The OOA profile had an *f44* of 0.24 during heating which was similar to that (0.22) during non-heating, indicating similar oxidation levels between the two periods. However, compared to the daytime OOA peak concentrations (1.8 μg m^{-3}), higher OOA concentrations (3.9 μg m^{-3}) were observed in the evening, indicating a more important contribution from the condensation of SVOCs emitted from heating sources and/or their dark aging processes (Tiitta et al., 2016).”

Section 3.3.2: Lacks of discussion.

Response: We have now added more discussion on the OA sources at the residential site during non-heating (Sect. 3.4.2) and heating (Sect. 3.4.3) period.

In Sect. 3.4.2., it now reads, “Free PMF suggested a two-factor solution with one mixed primary OA factor and one OOA (Fig. S8) as a further increase in the number of factors led to the splitting of factors. The diurnal pattern of the primary factor showed a slight increase in the morning but with a larger increase in the evening and night, suggesting potential mixing between HOA and the heating-related factor. Note that the temperature was below 15 ºC in the evening during this period (Fig. S4) and thus sporadic domestic solid fuel burning activities were likely to occur. Our previous study has shown that peat burning occurred in cold summer nights in the west coast city of Galway in Ireland (Lin et al., 2019a). Moreover, the elevated levels of m/z 60 in the evening (at 22:00) suggested emissions from biomass burning (Fig. S8). The correlation between the profile of the unconstrained primary OA factor and the reference profile of peat burning OA (R^2= 0.58) from our previous study (Lin et al., 2017) is better than the profile of biomass burning OA (BBOA; R^2=0.44) from the Ng et al. (2011a). Note that COA was not considered to be a potential OA factor at this location since the sampling site was representative of the residential area with few restaurants around. Moreover, no clear increase in the concentration of POA during lunchtime was observed during this non-heating period and the heating period as discussed later. Therefore, only the reference profile of HOA and peat burning OA factors were constrained during non-heating at the residential site.

The mass spectra and diurnal patterns, as well as the relative contribution of the HOA, peat, and OOA at the residential site during non-heating are shown in Fig. 5. While the profile of HOA is similar between the residential site and the kerbside, its concentration levels at the residential site were significantly lower than at the kerbside. Specifically, in the morning rush hours, the HOA peak concentration was 0.1 μg m^{-3} at the residential site while it was 1.5 μg m^{-3} at the kerbside, with a 15 times difference between the two sites. On average, HOA accounted for 11.8% of OA at the residential site. During the morning rush hours, its fraction increased to 16.0% which was still a minor factor when compared to OOA (58-68% of OA). The low contribution of HOA is consistent with the low mixing ratio of NO_x at the residential site (median: 2.0 ppb) which was 20 times lower than that at the kerbside (Table 1).

The peat profile featured peaks at *m/z* of 27, 29, 41, 43, 55, and 57, which was similar to HOA. However, the differences in *f60* between the peat factor and HOA suggested different sources. *f60* in the peat profile was 0.014 which was higher than that for HOA (<0.003), confirming its biomass nature (Cubison et al., 2011). The diurnal pattern of peat showed increased concentrations at 20:00-22:00, corresponding to their emission time. On average, peat accounted for 23.6% of OA and its fraction increased to 28.1% in the evening. The OOA mass spectral at the residential site featured high contribution at m/z 44 (i.e., *f44*) which was similar to the OOA at the kerbside. However, the diurnal cycle of OOA at the residential site showed no clear pattern, which was different from that at the kerbside. Therefore, most of the OOA at the residential site was likely due to regional transport."

Also, in Sect. 3.4.4, it now reads, "Heating-related OA factors were identified since they all showed elevated concentrations in the evening as indicated by the free PMF solutions (Fig. S10). However, similar to the case at the kerbside, the OA factors were mixed because of the co-emissions from all domestic heating activities. To better evaluate the contribution of potential sources, the reference profiles of HOA (Crippa et al., 2013), peat, wood, and coal were constrained (Lin et al., 2017) using ME-2. Note that COA was not constrained since no lunch meal peaks were identified during this period as discussed above.

In the morning rush hours, HOA showed a peak concentration of 0.4 μg m^{-3} due to traffic emissions, which was, again, largely reduced when compared to the HOA morning peaks (1.8 μg m^{-3}) at the kerbside. However, higher concentrations of HOA (2.0 μg m^{-3}) were observed in the evening due to the emissions of oil burning. Therefore, the majority (estimated at over 80%) of HOA at the residential site was due to oil burning instead of traffic emissions. On average, HOA accounted for 11.8% of the total OA over the entire heating period and its fraction increased slightly to 12.9% during pollution events.

Similar to the kerbside, solid fuel burning, especially peat burning was a very important OA factor, contributing up to 45.5% (34.9% on average) of the OA during the pollution events (Fig. 7c and 7d). Coal (17.8-19.2%) and wood (7.1-7.5%) burning were also contributing substantially over the entire period as well as during pollution events. The importance of solid fuel burning at the residential site echoed our previous studies at the same sites (Lin et al., 2018; Lin et al., 2019b). OOA, on average, accounted for 27.9% (1.4 μg m^{-3}) of OA and the higher OOA concentration during the evening, concurrent to an increase in primary factor concentrations, again suggested its major source was from the condensation of SVOCs emitted from solid fuel burning and/or their dark aging processes (Tiitta et al., 2016)."

Line 258: A peat and a HOA factor were constrained with ME-2. Why the authors chose a peat factor instead of a BBOA one from literature? Does this change the results significantly? Also, a COA factor is not present. Have the authors tried to constrain it? In this case how much was its contribution to the OA? Again Fig. S14a,b should be included in the main text.

Response: The reason we chose to constrain peat factor, instead of BBOA from literature, is that the correlation between the profile of the unconstrained factor and reference peat OA profile (R^2=0.58) is better than BBOA (R^2=0.44). Moreover, the diurnal pattern of the primary factor from the fee PMF solution showed a slight increase in the morning but with a larger increase in the evening and night, suggesting potential mixing between HOA and the heating-related factor. Note that the temperature was below 15 °C in the evening during this period and thus sporadic domestic solid fuel burning activities were likely to occur. Our previous study has shown that peat burning was likely to occur in cold summer nights in the west coast city of Galway in Ireland (Lin et al., 2019a). Moreover, the elevated levels of m/z 60 in the evening (at 22:00) suggested emissions from biomass burning (Fig. S8). The correlation between the profile of the unconstrained primary OA factor and the reference profile of peat burning OA (R^2= 0.58) from our previous study (Lin et al., 2017) is better than the profile of biomass burning OA (BBOA; R^2=0.44) from the Ng et al. (2011a). Note that COA was not considered to be a potential OA factor at this site since the sampling site was representative of the residential area with few restaurants around. Moreover, no clear increase in the concentration of POA during lunchtime was observed during this non-heating period and the heating period. Therefore, only the reference profile of HOA and peat burning OA factors were constrained during non-heating at the residential site. We have added the above comments in the revised manuscript.

The updated Fig. S14a, b has now been moved to the main text (see the figure below).

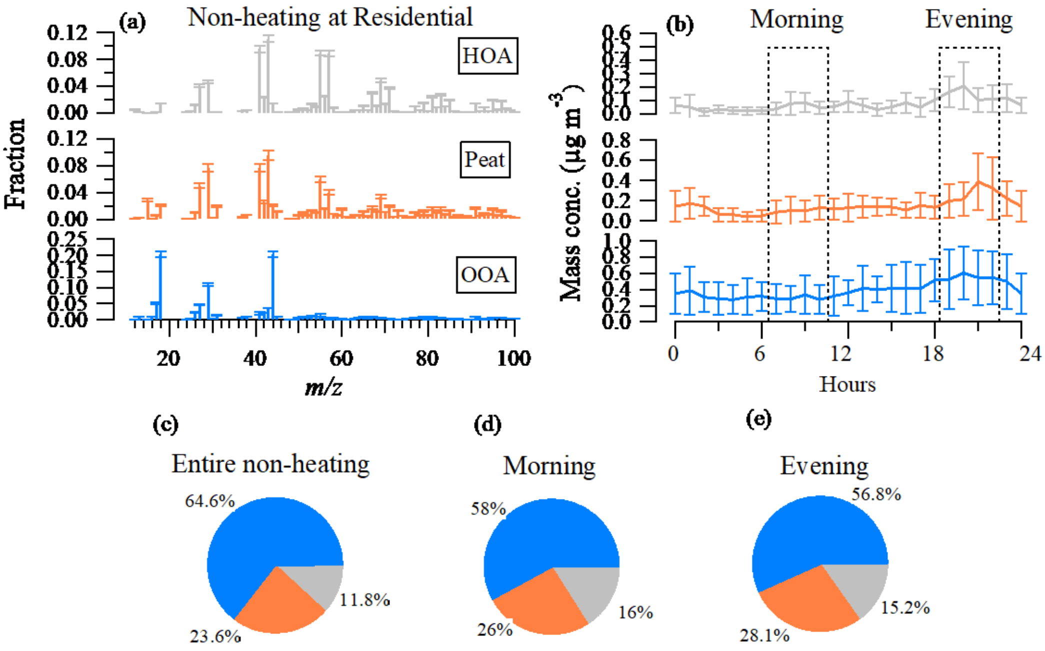


Figure R9 (or Figure 5 in the text). (a) Mass spectral profiles of hydrocarbon-like OA (HOA), peat and oxygenated OA (OOA) during non-heating at the residential site; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire non-heating period; (d) over the morning rush hours (7:00-10:00); and (e) over the evening hours from 19:00-22:00. Error bars in (a) and (b) represent one standard deviation.

Line 265: Again 4 out of 5 factors have been constrained with ME-2 tool. The unconstrained solution of this period (P2) for the residential site is not given in the supplementary so no direct comparisons can be made. How confident are the authors about this solution? Does peat contribute that high (30%of OA) in previous studies? Usually, BBOA accounts for that high percentages.

Response: See the response to the previous comment regarding the constraining strategy.

We have now provided the unconstrained PMF solution for the residential site in the supplementary. In the free PMF solution, heating-related OA factors were identified since they all showed elevated concentrations in the evening. However, similar to the case at the kerbside, the OA factors were mixed because of the co-emissions from all domestic heating activities. To better evaluate the contribution of potential sources, the reference profiles of HOA (Crippa et al., 2013b), peat, wood, and coal were constrained (Lin et al., 2017b) using ME-2.

We have explored the solution space with a large range of a-values (0-0.5) and used the bootstrap resampling strategy to evaluate the statistical uncertainties. We are confident about this solution as the results from this study were consistent with previous studies (Kourtchev et al., 2011; Dall'Osto et al., 2013; Lin et al., 2017).

Peat is a type of biomass since it is an accumulation of partially decayed plant material which is an important domestic fuel source in Ireland (Tuohy et al., 2009). The incomplete decay of vegetation resulted in an increase of *f60* when burned (Lin et al., 2017). However, *f60* in peat profile (0.014) was lower than wood (0.053) probably because wood contained a higher fraction of *m/z* 60-related material e.g., levoglucosan (Fig. 6a). Our previous study has shown that peat burning was contributing substantially in suburban Dublin (Lin et al., 2018; Lin et al., 2019b).

Line 290: Please define R2.

Response: Now defined as linear correlation coefficients determination (R^2)

Line 315: The percentage of OA to PM1 is not consistent to the rest of the text.

Response: Now changed to 46-64%, consistent with the rest of the text.

Section 4. The authors repeat the results as in the abstract and main results with no clear conclusion and “take home message” made by this work.

Response: The content in this Section has been incorporated into Section 3.1 when we discussed the overview of the measurement.

Tables 1 and 2. NOx should be mentioned in ppb.

Response: corrected.

Figure 1. Figure should be replaced by Fig. S1 (without Rathimnes station).

Response: It is now replaced but we tend to keep the $PM_{2.5}$ data from Rathmines station since it provides a good comparison with our measurement. See Figure R5 in the previous reply.

Fig. 1c seems to be wrong in comparison to Fig. S1 that includes all the measured data. Labels of elements seem wrong placed, making them hard to be read.

Response: Corrected. And labels have been re-arranged.

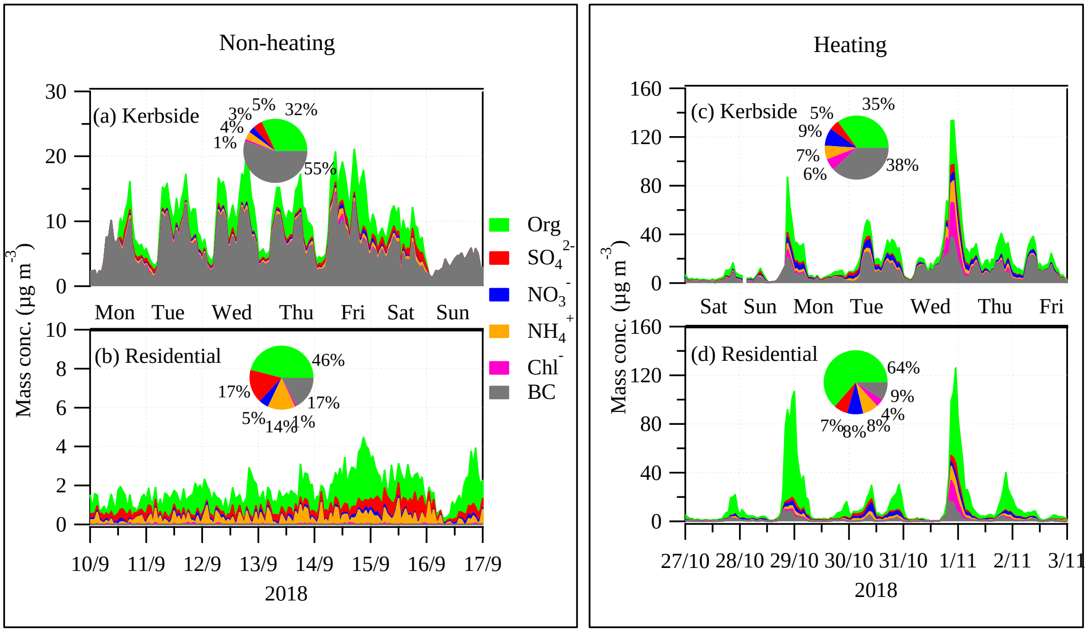


Figure R10 (or Figure 2 in the text). Time series of hourly averaged submicron organic aerosol (OA), sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), chloride (Chl), and black carbon (BC) during non-heating (left panel) and heating (right panel) at the kerbside (a, c) and residential (b, d). Inset pie charts are the relative fraction of the measured PM_1 components. Also shown is the day of the week, including Monday (Mon), Tuesday (Tue), Wednesday (Wed), Thursday (Thu), Friday (Fri), Saturday (Sat), and Sunday (Sun).

Figure 2. All chart pies should have the same size, the (a), (b), (c), (d) labels should be re-arranged accordingly to the main text. SO4 should be written as SO_4^{2-}. The same applies for NH4, and NO3 (for the entire manuscript).

Response: Pie charts now was combined with Fig. 2 with the same size in the revised manuscript (see Figure R10). Labels are re-arranged. And SO4, NH4, NO3, Chl have been changed.

Figure 3. The (a), (b), (c), (d) should be re-arranged. Current Fig. 3b should go up to 5 μg m-3, so that the trend of PM1 components will be visible. SO4, NH4 and NO3 should be changed according to the previous comment for Fig. 2.

Response: Changes made

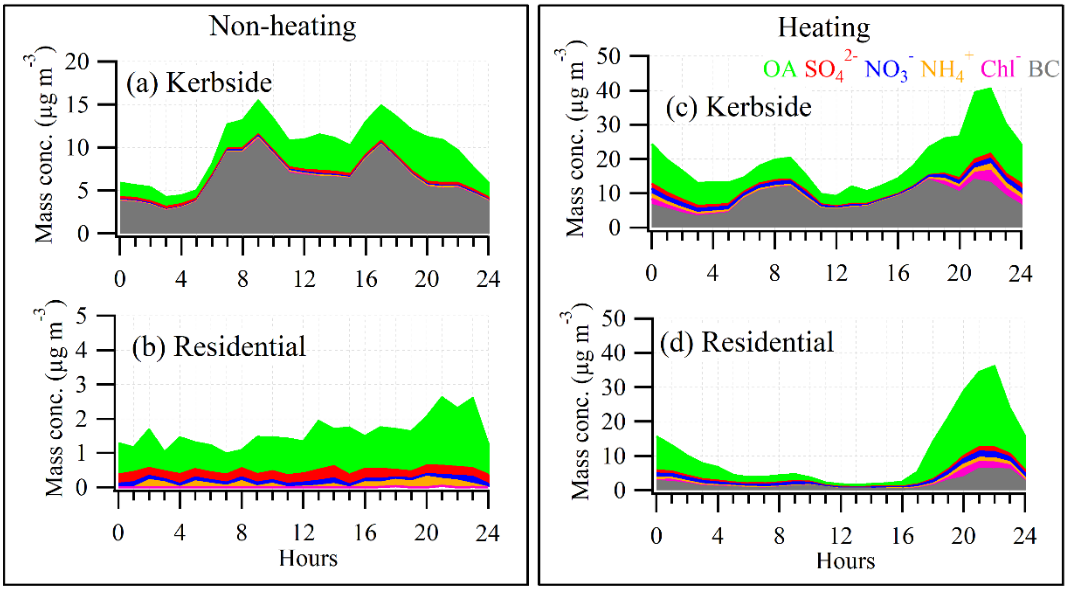


Figure R11 (or Figure 3 in the text). The diurnal cycle of submicron organic aerosol (OA), sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), chloride (Chl$^-$), and black carbon (BC) during non-heating (left panel) and heating (right panel) at the kerbside (a, c) and residential site (b, d).

Figure 4. Pie charts should have all the same size. Labels of factors should have some space between each other. The (a), (b), (c), (d) should be re-arranged accordingly to the main text.

Response: Pie charts with same size are now combined to Figs. 4-7. Also see the response to the previous comment.

Figure 5. The values seem like the 3rd quartile of the data and not the actual average values. Please replace the whole figure according to the above suggestions.

Response: We have replaced the original figure with new figures from our new analysis. See the response to the previous comment.

Figure 7. Define SEAI, CSO. Does this figure correspond to data related to your measurements? Labels of sources should have some space between each other.

Response: SEAI is Sustainable Energy Authority of Ireland (SEAI, 2018) while CSO is Central Statistics Office (CSO, 2016), which is now added to the revised manuscript (Sect. Sources of OA). This figure was presented to show the energy structure regarding traffic and domestic fuels in Ireland and to investigate their possible relationship with the PM pollution. As pointed out by the referee, this figure is not closely related to the measurement we had here. Therefore, we have moved this figure to the supplementary in the revised manuscript.

Major Comments: Having read the paper I am still not sure what the authors want a reader to learn. To my understanding, the authors want to empathize to traffic and vehicular emissions and more precisely to the importance of the diesel ones in the kerbside site. The authors claim that “in residential site, traffic emissions were found to have a minor impact on air quality”. Yet, the HOA contribution to OA is the same (18%) for kerbside and residential sites for P2 period, with its mass average concentration to be 1.2 μg m-3 for kerbside and 1.6 μg m-3 for residential, something in contrast to their final statement.

Response: In this study, we wanted to get insights into the spatial distribution of submicron aerosols in urban Dublin, particularly for traffic emissions. As has been discussed in the Sect. Introduction, our previous study conducted in suburban Dublin has shown that air quality in Dublin was strongly influenced by the emissions from residential solid-fuel burning in winter (Lin et al., 2018). However, the impact of traffic emissions on this residential site was shown to be minor probably due to the distance (~500 m) from the nearest roads, as well as the strict emission standard (Lin et al., 2018). The minor influence of traffic at the residential site was also shown in a west coast city of Galway in Ireland during both summer (Lin et al., 2019a) and winter conditions (Lin et al., 2017). In particular, the diurnal pattern of HOA shows largely enhanced concentration in the evening when compared to that during the morning rush hours, suggesting residential heating is the major source of HOA in suburban Dublin (Lin et al., 2019b). Heating source of HOA is also reported at the urban background site in Paris in addition to traffic (Petit et al., 2014; Zhang et al., 2019). However, the relative importance of traffic and heating to HOA in different urban settings (e.g., kerbside and residential) and different seasons (e.g., heating and non-heating) remain poorly understood.

HOA at the kerbside with rush hour peaks can be regarded as OA emissions from traffic emission as the case at the kerbside during the non-heating period. However, during the heating period, the greater increase in HOA in the evening was associated with oil burning. Specifically, at the residential site, HOA showed a peak concentration of 0.4 μg m^{-3} in the morning rush hours due to traffic emissions, which was largely reduced when compared to the HOA morning peaks (1.8 μg m^{-3}) at the kerbside. However, higher concentrations of HOA (2.0 μg m^{-3}) were observed in the evening due to the emissions of oil burning. Therefore, the majority (estimated at over 80%) of HOA at the residential site was from oil burning instead of traffic emissions. We have added the above comments in the revised manuscript and highlighted it in the Abstract.

The possession of the aethalometer AE-33 at the kerbside site is not taken into advantage by the authors. How much of the measured BC is related to traffic and how much to biomass burning? This could help interpreting better the results of the PMF but also the HOA/BC ratio in section 3.5. Have the authors tried to split BC according to its origins and then conclude to resemblance or not compared to other studies?

Response: A 7-wavelength AE-33 was deployed at the kerbside along with an ACSM. During the non-heating period at the kerbside, BC shows two rush hour peaks, indicating traffic was its major source. Moreover, there was no evidence of biomass burning during non-heating at the kerbside as indicated by the PMF analysis. Therefore, BC during non-heating was exclusively from traffic emissions. The HOA/BC ratio derived from this period can better present the traffic HOA/BC ratio since, during heating period, BC has additional sources from e.g., solid fuel burning. Figure R12 shows the HOA/BC ratio was 0.17 during the non-heating period at the kerbside which indicates a major source of diesel vehicular emissions (DeWitt et al., 2015).

During the heating period, an increase of BC concentration in the evening, with origins from heating (e.g., biomass/coal burning) sources, was also observed in addition to the two rush hour peaks. The Ångström exponent model can separate the BC into traffic BC (BCtr) and wood burning BC (BCwb) (Sandradewi et al., 2008; Zotter et al., 2017). However, in Ireland, coal combustion and oil burning was also contributing the BC in addition to biomass burning and traffic. Thus, the Ångström exponent model could have large uncertainty to attribute the BC into just BCtr and BCwb. For such reasons, we have not included the BC source apportionment in the manuscript. Actually, we are preparing a separate study to address the BC sources.

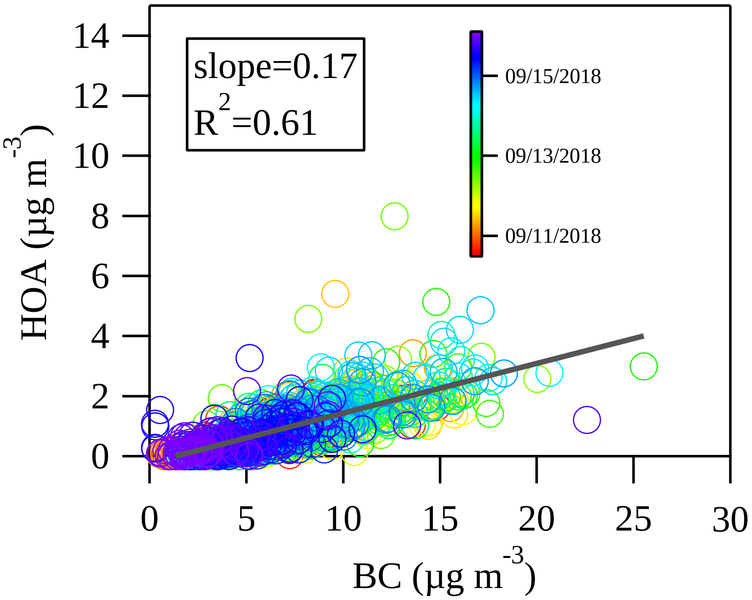


Figure R12. Linear regression between HOA and BC with a slope of 0.17 and R^2 of 0.61 during the non-heating period at the kerbside.

Peat, coal and wood factors play a major role (33-50% of OA) during P2 in both sites, yet the authors do not discuss their significance or any related mechanisms. The authors should pay attention to combustion sources, since they seem to be of greater importance than traffic.

Response: We have now discussed the significance of solid-fuel burning in the revised manuscript. Please find the response to the previous comment.

Also, the PMF solutions for P2 are too constrained. Have the authors tried to constrain less the solution? What are the results?

Response: We have now explored the solution space with less constraint (a value of 0-0.5). Please find the response to the previous comment.

How oxidized the OA factors are? Could the authors calculate the O:C ratio of each factor? This would be really helpful to the scientific community.

Response: Based on *f44*, we can estimate the O:C ratios for OA factors (Aiken et al., 2008; Canagaratna et al., 2015). Depending on the method used, O:C ratio was estimated to be in the range of 0.9-1.1 for OOA and 0.1-0.3 for primary OA factors. For OOA, the O:C ratio suggested OOA was highly processed. Moreover, the OOA profile resembled the less volatile OOA (LV-OOA; R^2 of 0.94) which usually represents well-aged SOA (Ng et al., 2011a). However, the diurnal pattern of OOA in Dublin showed a clear pattern that was strongly influenced by local sources (e.g., solid-fuel burning) and was most likely from fresh SOA instead of well-aged SOA. Note that the unit mass resolution of ACSM makes it hard to separates the contribution between C2H4O+ and CO2+ at m/z 44. Moreover, the "Pieber" effects need to be taken into account when calculating f44 (Pieber et al., 2016). Therefore, we tend not to report O:C ratios for OA factors due the large uncertainties.

References:

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478-4485, 10.1021/es703009q, 2008.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 10.5194/acp-15-253-2015, 2015.

Crippa, M., Decarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J. L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, Atmos. Chem. Phys., 13, 961-981, 2013.

CSO: (Central Statistics Office). Private Households in Permanent Housing Units. https://www.cso.ie/px/pxeirestat/Statire/SelectVarVal/Define.asp?maintable=E4015&PLanguage=0 (accessed on 1 May 2020), 2016.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, Atmos. Chem. Phys., 11, 12049-12064, 10.5194/acp-11-12049-2011, 2011.

Dall'Osto, M., Ovadnevaite, J., Ceburnis, D., Martin, D., Healy, R. M., O'Connor, I. P., Kourtchev, I., Sodeau, J. R., Wenger, J. C., and O'Dowd, C.: Characterization of urban aerosol in Cork city (Ireland) using aerosol mass spectrometry, Atmos. Chem. Phys., 13, 4997-5015, 10.5194/acp-13-4997-2013, 2013.

DeWitt, H. L., Hellebust, S., Temime-Roussel, B., Ravier, S., Polo, L., Jacob, V., Buisson, C., Charron, A., André, M., Pasquier, A., Besombes, J. L., Jaffrezo, J. L., Wortham, H., and Marchand, N.: Near-highway aerosol and gas-phase measurements in a high-diesel environment, Atmos. Chem. Phys., 15, 4373-4387, 2015.

Fu, M., Kelly, J. A., and Clinch, J. P.: Estimating annual average daily traffic and transport emissions for a national road network: A bottom-up methodology for both nationally-aggregated and spatially-disaggregated results, J. Transp. Geogr., 58, 186-195, https://doi.org/10.1016/j.jtrangeo.2016.12.002, 2017.

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Äijälä, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H.-C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophys. Res. Lett., 43, 7735-7744, doi:10.1002/2016GL069239, 2016.

Kourtchev, I., Hellebust, S., Bell, J. M., O'Connor, I. P., Healy, R. M., Allanic, A., Healy, D., Wenger, J. C., and Sodeau, J. R.: The use of polar organic compounds to estimate the contribution of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM2.5 in Cork Harbour, Ireland, Sci. Total Environ., 409, 2143-2155, 10.1016/j.scitotenv.2011.02.027, 2011.

Lin, C., Ceburnis, D., Hellebust, S., Buckley, P., Wenger, J., Canonaco, F., Prévôt, A. S. H., Huang, R.-J., O’Dowd, C., and Ovadnevaite, J.: Characterization of primary organic aerosol from domestic wood, peat, and coal burning in Ireland, Environ. Sci. Technol., 51, 10624-10632, 2017.

Lin, C., Huang, R.-J., Ceburnis, D., Buckley, P., Preissler, J., Wenger, J., Rinaldi, M., Facchini, M. C., O’Dowd, C., and Ovadnevaite, J.: Extreme air pollution from residential solid fuel burning, Nat. Sustain., 1, 512-517, 2018.

Lin, C., Ceburnis, D., Huang, R.-J., Canonaco, F., Prévôt, A. S. H., O’Dowd, C., and Ovadnevaite, J.: Summertime Aerosol over the West of Ireland Dominated by Secondary Aerosol during Long-Range Transport, Atmos., 10, 59-70, https://doi.org/10.3390/atmos10020059, 2019a.

Lin, C., Ceburnis, D., Huang, R. J., Xu, W., Spohn, T., Martin, D., Buckley, P., Wenger, J., Hellebust, S., Rinaldi, M., Facchini, M. C., O'Dowd, C., and Ovadnevaite, J.: Wintertime aerosol dominated by solid-fuel-burning emissions across Ireland: insight into the spatial and chemical variation in submicron aerosol, Atmos. Chem. Phys., 19, 14091-14106, 10.5194/acp-19-14091-2019, 2019b.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.: Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data, Environ. Sci. Technol., 45, 910-916, 2011a.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aerosol Sci. Technol., 45, 780-794, 2011b.

Petit, J. E., Favez, O., Sciare, J., Canonaco, F., Croteau, P., Močnik, G., Jayne, J., Worsnop, D., and Leoz-Garziandia, E.: Submicron aerosol source apportionment of wintertime pollution in Paris, France by double positive matrix factorization (PMF2) using an aerosol chemical speciation monitor (ACSM) and a multi-wavelength Aethalometer, Atmos. Chem. Phys., 14, 13773-13787, 10.5194/acp-14-13773-2014, 2014.

Pieber, S. M., El Haddad, I., Slowik, J. G., Canagaratna, M. R., Jayne, J. T., Platt, S. M., Bozzetti, C., Daellenbach, K. R., Fröhlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jiménez, J. L., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Inorganic Salt Interference on CO2+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies, Environ. Sci. Technol., 50, 10494-10503, 10.1021/acs.est.6b01035, 2016.

Sandradewi, J., Prévôt, A. S. H., Szidat, S., Perron, N., Alfarra, M. R., Lanz, V. A., Weingartner, E., and Baltensperger, U.: Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter, Environ. Sci. Technol., 42, 3316-3323, 2008.

SEAI: (Sustainable Energy Authority of Ireland). Energy Statistics in Ireland. https://www.seai.ie/resources/seai-statistics/key-statistics (accessed on 1 May 2020), 2018.

Tiitta, P., Leskinen, A., Hao, L., Yli-Pirilä, P., Kortelainen, M., Grigonyte, J., Tissari, J., Lamberg, H., Hartikainen, A., Kuuspalo, K., Kortelainen, A. M., Virtanen, A., Lehtinen, K. E. J., Komppula, M., Pieber, S., Prévôt, A. S. H., Onasch, T. B., Worsnop, D. R., Czech, H., Zimmermann, R., Jokiniemi, J., and Sippula, O.: Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging, Atmos. Chem. Phys., 16, 13251-13269, 2016.

Tuohy, A., Bazilian, M., Doherty, R., Gallachóir, B. Ó., and O'Malley, M.: Burning peat in Ireland: An electricity market dispatch perspective, Energy Policy, 37, 3035-3042, 2009.

Zhang, Y., Favez, O., Petit, J. E., Canonaco, F., Truong, F., Bonnaire, N., Crenn, V., Amodeo, T., Prévôt, A. S. H., Sciare, J., Gros, V., and Albinet, A.: Six-year source apportionment of submicron organic aerosols from near-continuous highly time-resolved measurements at SIRTA (Paris area, France), Atmos. Chem. Phys., 19, 14755-14776, 10.5194/acp-19-14755-2019, 2019.

Zotter, P., Herich, H., Gysel, M., El-Haddad, I., Zhang, Y., Močnik, G., Hüglin, C., Baltensperger, U., Szidat, S., and Prévôt, A. S. H.: Evaluation of the absorption Ångström exponents for traffic and wood burning in the Aethalometer-based source apportionment using radiocarbon measurements of ambient aerosol, Atmos. Chem. Phys., 17, 4229-4249, 2017.

The impact of traffic on air quality in Ireland: insights from the simultaneous kerbside and sub-urban monitoring of submicron aerosols

Chunshui Lin[1,2,3], Darius Ceburnis[1], Wei Xu[1,2], Eimear Heffernan[4], Stig Hellebust[4], John Gallagher[5], Ru-Jin Huang[1,2,3*], Colin O'Dowd[1*], and Jurgita Ovadnevaite[1]

[1]School of Physics, Ryan Institute's Centre for Climate and Air Pollution Studies, National University of Ireland Galway. University Road, Galway. H91 CF50, Ireland
[2]State Key Laboratory of Loess and Quaternary Geology and Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, 710061, Xi'an, China
[3]Center for Excellence in Quaternary Science and Global Change, Chinese Academy of Sciences, Xi'an 710061, China
[4]School of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland
[5]Department of Civil, Structural & Environmental Engineering, Trinity College Dublin, the University of Dublin, Ireland.

Correspondence to: Ru-Jin Huang (rujin.huang@ieecas.cn) and Colin O'Dowd (colin.odowd@nuigalway.ie)

Abstract: To evaluate the impact of traffic on urban air quality, the chemical composition of submicron aerosols (PM$_1$) and sources of organic aerosol (OA)~~submicron aerosols (PM$_1$)~~ were simultaneously investigated at a kerbside site in Dublin city centre and a residential site in sub-urban Dublin (~5 km apart) from 4 September to 9 November in 2018. Through the detailed comparison of one-week non-heating period in early September and heating period in late October, black carbon (BC) was found to be the most dominant component (38-55% or 5.6-7.1 μg m^{-3}) of PM$_1$ at the kerbside while ~~organic aerosol (~~OA~~)~~ was the most important (46-~~63~~64% of PM$_1$ or 1.0-8.~~7~~ 1 μg m^{-3}) at the residential site. The daily and weekly cycle of BC at the kerbside during the non-heating period pointed to the major source of vehicular emissions, consistent with that for nitrogen oxides (NO$_x$). However, traffic emissions were found to have a minor impact on air quality at the residential site due to its distance from traffic sources, as well as the effects of wind speed and wind direction. As a result of vehicular emissions and the street canyon effect, the kerbside increment (from urban background) ratio of up to 25:1 was found for BC during the non-heating period~~,~~ but reduced to 10:1 during the heating period due to the additional sources of solid fuel burning impacting the air quality at both sites simultaneously. OA source analysis shows only ~~18~~16-~~27~~28% (0.9-1.0 μg m^{-3}) of OA at the kerbside associated with vehicular emissions, with higher contributions from cooking (18-36% or ~~~~~~1.2 μg m^{-3}), solid fuel burning (~~~33~~38% or ~~~~~~2.~~1~~ 4 μg m^{-3}, resolved only during the heating period), and oxygenated OA (~~31~~29-37% or 1.2-~~2.0~~1.9 μg m^{-3}). At the residential site, solid fuel burning contributed to ~~approximately~~ 6~~5~~0% (4.9~~2.7~~ μg m^{-3}) of OA during the heating period, while oxygenated OA accounted for almost 65% (0.~~5~~ 6 μg m^{-3}) of OA during the non-heating period. Based on simultaneous investigation of PM$_1$ at different urban settings (i.e. residential vs kerbside), this study highlights temporal and spatial variability of sources within Dublin city centre and the need for additional aerosol ~~characterisation~~ characterization studies to improve targeted mitigation solutions for greater impact on urban air quality. Moreover, traffic and residential heating may hold different implications for health and climate as indicated by the significant increment of BC at the kerbside and the large geographic impact of OA from residential heating at both the kerbside and residential sites.

1 Introduction

Aerosol particles adversely affect human health, causing morbidity and premature mortality (Pope III et al., 2002; Cohen et al., 2017; Burnett et al., 2018). In particular, urban areas are usually more polluted than rural areas due to the proximity to pollution sources including traffic, cooking, and various other activities such as residential heating. To make things worse, the street canyon effects in urban areas result in poor dispersion conditions, trapping the pollutants in downtown areas where the streets are flanked by buildings on both sides creating a canyon-like environment (Fuzzi et al., 2015). The term ‘urban increment’ is defined as the increase in air pollution parameters in the urban background above the rural surroundings while ‘kerbside increment’ is defined as the increase in concentrations at a kerbside or street site relative to the urban background (Lenschow et al., 2001; Mues et al., 2013; Fuzzi et al., 2015). Models often underestimate the urban increment let alone kerbside increment, due to the poor grid resolution and not taking into account the urban micro~~n~~-environment such as the urban canyon and urban heat-island effects (Mues et al., 2013). Therefore, field campaigns, especially those simultaneously measuring at different settings (e.g., residential site vs. kerbside) in the urban area, are required to study the spatial variation of aerosols and their sources as well as to provide constraints for the models.

Aerosol can be broadly categorized into two classes: primary and secondary (Fuzzi et al., 2015). Primary aerosols are directly emitted from their emissions sources such as traffic, cooking, and biomass burning while secondary aerosols are formed from their corresponding precursor gases (An et al., 2019). Primary aerosols often show enhanced concentrations when close to their sources (e.g., at the kerbside), while secondary aerosols are more homogeneously distributed (Hallquist et al., 2009; Zhang et al., 2015; Gentner et al., 2017). Mohr et al. (2011) showed a kerbside increment of up to 11 μg m^{-3} for black carbon (BC) and 2.5 μg m^{-3} for hydrocarbon-like organic aerosol (HOA) at a road~~-~~side in Zurich with the mobile measurements using an Aerosol Mass Spectrometer (AMS). While mobile or on-road measurements can provide a detailed characterization of the spatial variation of the chemical components and sources (e.g., traffic) of aerosols, mobile measurements can also be strongly influenced by the emission from a specific source e.g., from an old type truck (or high emitters), not representing the average fleet (Fuzzi et al., 2015). Moreover, mobile measurements are usually conducted at a specific time of the day, failing to capture the temporal variation of aerosols over longer periods (e.g., days to months) (Mohr et al., 2011; Fuzzi et al., 2015). ~~A f~~Fixed installation of instruments at multiple sites simultaneously can, therefore, provide more detailed information about both the temporal and spatial variation of aerosols. Crippa et al. (2013) investigated the temporal evolution of the submicron aerosol at three sites (one urban centre and two urban background sites) in Paris during wintertime. In contrast to the finding by Mohr et al. (2011), Crippa et al. (2013) concluded that the submicron aerosol in Paris was dominated by regional transport and that the emissions from Paris itself had an insignificant impact on the urban backgrounds. The discrepancies between the individual studies may be related to the specific geographic environment and the periods of the measurement (Fuzzi et al., 2015).

Dublin, the capital city of the Republic of Ireland in Western Europe, is home to ~1 million people. Previous study conducted at a suburban site in the residential area in Dublin has shown that air quality was strongly influenced by residential heating sources in winter (Lin et al., 2018). However, the impact of traffic emissions on this residential site was shown to be minor probably due to the distance (~500 m) from the nearest roads, as well as the strict emission standard (Lin et al., 2018). The minor influence of traffic at the residential site was also shown in a west coast city of Galway in Ireland during both summer (Lin et al., 2019a) and winter conditions (Lin et al., 2017). In particular, the diurnal pattern of HOA shows largely enhanced concentration in the evening when compared to that during the morning rush hours, suggesting residential heating is the major source of HOA in suburban Dublin (Lin et al., 2019b). ~~Heating~~ The heating source of HOA is also reported at the urban background site in Paris in addition to traffic (Petit et al., 2014; Zhang et al., 2019). However, the relative importance of traffic and heating to HOA in different urban settings (e.g., kerbside and residential) and different seasons (e.g., heating and non-heating) remain poorly understood.

In this study, the chemical composition of submicron aerosol (PM_1) at both kerbside and residential sites was simultaneously measured from 4 September to 9 November 2018 using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) and an Aethalometer. The chemical composition of PM_1 and sources of OA at these two sites were explicitly characterized and compared during both the non-heating period and the heating period. Finally, the spatial variation and kerbside increment of PM_1, as well as the implications for pollution mitigation strategies in Ireland were discussed.

2 Experimental

2.1 Sampling sites

Chemical compositions of PM_1 ~~Measurements~~ were simultaneously ~~conducted~~ measured at a kerbside site in Dublin city centre and a residential site in sub~~-~~urban Dublin, at a distance of ~5 km from the kerbside site (see the map in Fig. S1) while $PM_{2.5}$ was sampled at Rathmines (https://www.epa.ie/air/quality/data/rm/), another residential site at a distance of ~3 from the kerbside and residential sites. The kerbside site is adjacent to a heavily trafficked street (i.e., Pearse Street) with a traffic flow of ~46,000 vehicles per day, 76% of which consist of private cars, 13% of light goods vehicles, 7% of heavy goods vehicles, 2% of buses, and 2% of motorcycles (Fu et al., 2017). Pearse Street is characterised as an almost symmetrical street canyon i.e. rows of buildings on both sides of the road that are of equal height to the width of the street, and this affects local dispersion of air pollutants (Gallagher et al., 2013; Gallagher, 2016). It is worth noting that a bus stop was positioned ~20 m south from the sampling inlet. Measurements of submicron aerosol at the kerbside took place at ~ 3 m from the busy street. The residential site is located on the campus of University College Dublin (UCD) in south Dublin. The nearest road is ~500 m away from the sampling site at UCD. Measurements at the site were conducted on the roof of the Science building (~30 m above the ground) at UCD from 4 September to 9 November 2018.

2.2 Instrumentation

A quadrupole Aerosol Chemical Speciation Monitor (~~q~~Q-ACSM, Aerodyne Research Inc.) and an aethalometer (AE-33, from Magee Scientific) were deployed at the kerbside site to measure the non-refractory PM$_1$ (NR-PM$_1$) component (i.e. OA, sulfate, nitrate, ammonium, and chloride) and BC, respectively. At the residential site, another Q-ACSM and aethalometer (AE-16) were deployed to measure the PM$_1$ (NR-PM$_1$ and BC) composition simultaneously. At each site, ACSM and AE-33/16 were sampling from the same PM$_{2.5}$ inlet line with isokinetic flow splitting. A detailed description of the ACSM and its operation is given by Ng et al. (2011b) and in our previous study (Lin et al., 2018). Briefly, an ACSM consists of a particle sampling inlet, three vacuum chambers and a quadrupole mass spectrometer. During sampling, the ambient air was drawn into the cyclone with a size cut-off of 2.5 µm at a flow rate of 3 L min^{-1} to remove coarse particles. A Nafion dryer was used to dry the ambient air before reaching the ACSM inlet. In the ACSM particle sampling inlet, the dried aerosol particles were focused into a narrow aerosol beam through the aerodynamic lens system. The beam was directed onto a hot tungsten oven (~600 °C) where the particles were vaporized. The vaporized molecules were ionized by electron impact (70 ~~ev~~eV) and the resulting ions were analyzed by a quadrupole mass spectrometer. Both ACSMs were calibrated with ammonium nitrate and ammonium sulfate following the procedure described by Ng et al. (2011b). Briefly, monodispersed 300 nm ammonium nitrate/ammonium sulfate particles were generated by an atomizer (Model 9302, TSI) and size-selected by a differential mobility analyzer (DMA; TSI model 3080), and subsequently introduced into the Q-ACSMs to determine the response factor (RF), as well as the relative ionization efficiencies (RIEs) of ammonium and sulfate.

The time resolution of ACSM at the kerbside was set at 5 minutes to capture the faster changing variation of PM composition adjacent to the busy road while a 1-hour interval was used at the residential site to reduce uncertainty in measurement due to the relatively low concentrations for most of the time. The ACSM standard data analysis software (v 1.6.1.0) in Igor 6.37 (WaveMetrics Inc.) was used to process the mass concentrations of NR-PM$_1$ components. To account for the aerosol losses during sampling (Middlebrook et al., 2012), a~~n~~ composition dependent collection efficiency (CDCE) was applied. The CDCE (averaged at ~0.5) corrected NR-PM$_1$ shows a good agreement with the PM$_{2.5}$ measurement at another ~~sub-urban~~ residential site in suburban Dublin (i.e., Rathmines, Fig. S1) ~~.~~where a tapered element oscillating microbalance (ThermoFisher Scientific) was deployed with 1 h resolution.

The AE-33 was deployed to measure black carbon (BC) at the kerbside with a time resolution of 1 minute while AE-16 at the residential site had a time resolution of 5 minutes. AE-33 measures light absorption at seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) (Drinovec et al., 2015) while AE-16 measures light absorption solely at 880 nm. BC mass concentration was calculated from the change in optical attenuation at 880 nm in the selected time interval using the mass absorption cross-section 7.77 m^2 g^{-1} (Drinovec et al., 2015).

Carbon monoxide analyzer (Thermo Scientific Model 48i) was employed to measure the CO mixing ratios with a time resolution of 1 minute at the kerbside. NO-NO$_2$-NO$_x$ analyzer (Thermo Scientific Model 42i) was employed to sample NO$_x$ with a time resolution of 1 minute at the kerbside and residential site simultaneously. Meteorological variables (temperature, relative humidity, wind speed, and wind direction) with a time resolution of 1 hour were recorded at the meteorological stations (Irish meteorological service) of Dublin airport (Fig. S2).

2.3 OA Source apportionment

Positive matrix factorization (PMF) ~~with the multilinear engine (ME-2)~~ was utilized for OA source apportionment on the interface of SoFi 6.A1 (Canonaco et al., 2013)~~ by constraining the reference profiles of certain factors~~. Firstly, unconstrained (or free) PMF was applied to examine the OA factors based on their mass spectral profiles, diurnal patterns, and correlations with external measurements (e.g., NOx and BC). However, ~~Because unconstrained PMF or free PMF often suffers from solution ambiguity when some factors have similar temporal variation and/or factor profiles,~~ the free PMF solution could potentially lead to solutions with mixed factors or inaccurate factor attributions when~~-~~ some factors have similar temporal variation and/or factor profiles (e.g., COA and HOA) (Canonaco et al., 2013). This is especially true for the heating-related OA factors during the heating-season in Ireland where oil, peat, wood, and coal were commonly used as domestic heating fuels according to Central Statistics Office (CSO, 2016) and Sustainable Energy Authority of Ireland (SEAI, 2018). Moreover, previous offline (i.e., filter-based) and online (i.e., ACSM/AMS) studies in Ireland winter have identified ambient OA being associated with the residential burning of oil, peat, coal, and wood burning (Kourtchev et al., 2011; Dall'Osto et al., 2013; Lin et al., 2018). In this study, free PMF resulted in highly mixed OA factors (See the supplementary section for the free PMF solutions). ~~-~~Thus, based on this priori information on emission sources, PMF with the multilinear engine (ME-2) was applied to get more environmentally meaningful solutions by constraining the reference profiles with *a* value approach (Canonaco et al., 2013; Lin et al., 2017).

~~In this study, ME-2 was conducted on the interface of SoFi 6.8 (Canonaco et al., 2013).~~

The reference profiles of peat, coal, and wood were taken from a previous study in which the mass spectral signatures of peat, coal, and wood burning OA were characterized by simulating their burning in a typical Irish stove with an ACSM ~~by~~ (Lin et al., 2017). ~~while the~~ HOA and COA were obtained from a study in Paris by Crippa et al. (2013). A sensitivity analysis was undertaken by varying the *a* values (0-0.5 or 0-50% variation) to evaluate the OA factor contribution at different levels of constraint on the reference factor. Moreover, a bootstrap-based resampling strategy with a total of 500 runs was applied to examine the statistical uncertainty (https://datalystica.com/sofi). The following criteria are used for the selection from these ME-2 runs to get the most optimized solution:

1, Correlation between the time series of HOA and NO_x or BC in the morning hours (7:00-10:00) during weekdays. HOA and NO_x/BC have a common source from traffic emissions in these morning hours.

2, Diurnal cycle of COA. The COA concentrations during mealtime should be higher. In this study, the ratio of COA at 13:00 to the average of COA of 10 and 11 am was monitored.

3, Multi-linear regression between BC and heating-related factors (i.e., HOA (or oil burning), peat, wood, and coal burning) in the evening (19:00-23:00), assuming only the heating-related factors contributed to BC in the evening.

4, Fraction of m/z 60 (i.e., f60) for peat and wood burning OA factors should be higher than 0.006 (Cubison et al., 2011; Lin et al., 2017).

5, Fraction of m/z 44 (i.e., f44) for the unconstrained factor (i.e., OOA). OOA should have higher f44 than primary factors.

By inspecting the defined criteria, the ME-2 runs that meet these criteria were selected and averaged as the most optimized solution ~~(See the supplementary section of OA source apportionment for the systematic selection of factors and evaluation of PMF solution ambiguity)~~.

3 Results and discussion

3.1 Overview of aerosol measurement

Figure ~~S~~1 shows the ~~overview of the measurement~~time series of submicron organic aerosol (OA), sulfate, nitrate, ammonium, chloride, and black carbon (BC) at both the kerbside and the residential site, as well as the time series of PM$_{2.5}$ at Rathmines from 4 September to 9 November 2018. The air quality during the early stage of the sampling period (before 30 September) showed limited influence from residential heating emissions as observed by few pollution spikes in the evening when compared to a later period with prominent evening spikes observed at all three sites (From 1 October to 09 November; Fig. ~~S~~1). The three sampling sites (i.e., kerbside, residential, and Rathmines) are within a 5 km radius in Dublin city and the time series of PM$_1$ and PM$_{2.5}$ were well correlated with correlation coefficients (R^2) in the range of 0.56-0.83 and slopes of 0.72-0.88 (Fig. S1). The good time series correlation between the three sites was mainly driven by the pollution events during the heating period while the slopes of 0.72-0.88 suggested PM$_1$ explained, on average, 72-88% of PM$_{2.5}$ mass. The poorer correlation (R^2 of 0.56; Fig. S1) between the kerbside PM$_1$ and Rathmines PM$_{2.5}$ than between the residential PM$_1$ and Rathmines PM$_{2.5}$ (R^2 of 0.83) was due to traffic emissions which had a greater impact on the kerbside than at both the residential site and Rathmines.

Over the entire period, the mean mass concentration of PM$_1$ was 11.7 ± 9.7 (one standard deviation) µg m^{-3} at the kerbside with black carbon accounting for 50% of the total PM$_1$ mass (Fig. 1a), followed by OA (31%), nitrate (6%), sulfate (5%), ammonium (5%), and chloride (2%). At the residential site, the mean PM$_1$ concentration (6.6 ± 3.1 µg m^{-3}) was roughly half of that at the Kerbside (Fig. 1b). However, the chemical compositions of PM$_1$ at the residential site was dominated by OA (59% of PM$_1$), followed by BC (13%). The total inorganic aerosols (sum of sulfate, nitrate, ammonium, and chloride) accounted for 28% of PM$_1$ at the residential site, slightly higher than at the kerbside (18%), though the concentrations were comparable (1.8 vs. 2.1 µg m^{-3}) between the two sites, suggesting regional sources/formations rather than traffic emissions. In contrast, the greater abundance of BC at the kerbside suggests traffic emissions comprised a high fraction of BC which, however, had a limited impact on the residential site. In particular, BC at the kerbside showed two rush hour peaks, confirming traffic was its major source (Fig. S2). However, the BC was up to 25 times lower at the residential site during the rush hour peaks (Fig. S2), suggesting a minor impact of traffic on the air quality at the residential site due to the effects of the wind direction and the distance from the road. In addition to the rush hour peaks of BC, an additional BC peak in the evening was also observed at both sites due to the emissions from domestic heating activities (discussed later).

To better understand the evolution of chemical composition and concentration of PM_1, ~~T~~two periods, with one week of the non-heating period ~~P1~~ from 10 to 17 September and one week of the heating period ~~which represented the non-heating period and P2~~ from 27 October to 4 November, were selected for a more detailed comparison. During non-heating, BC showed the largest kerbside increment, with an increment ratio of 15 (median value) (Fig. S3). During heating, the BC increment ratio was slightly lower (10) primarily due to the additional emission sources of solid fuel burning affecting both sites simultaneously. The kerbside increment of BC was primarily due to vehicular emissions and this was corroborated by the gas pollutant of NO_x which showed an increment ratio of 7-11 (Fig. S3). Note that our measurement represents the average fleet in Dublin and thus the high kerbside increment for BC in Dublin has significant implications for the potentially higher exposure risk at the kerbside. Compared to BC, the kerbside increment of OA was less significant because traffic was not a major source of OA (discussed in Sect. 3.4). However, a higher OA increment ratio (3; median value) was also seen during non-heating than during heating (~2).

~~represented the heating period, were selected as the focus of this study.~~ The meteorological parameters including wind speed, wind direction, relative humidity (RH), and temperature during ~~P1~~ the non-heating and heating period~~P2~~ are shown in Fig. ~~S2~~S4. Specifically, during the non-heating period~~P1~~, south-westerly winds were prevailing, with an average wind speed of 4.5 m s^{-1}, ranging from 1.5 to 9.0 m s^{-1} while, during the heating period~~P2~~, the wind speeds were slightly lower with an average of 3.7 m s^{-1} (range 0.5-8.5 m s^{-1}). The low wind speeds were accompanied by the northerly and easterly winds during ~~P2~~heating period. The temperature during ~~P1~~ non-heating averaged 13.1 ºC, ranging from 8.6 ºC to 18.2 ºC while it was lower during ~~P2~~ heating with an average of 4.5 ºC (range -3.9-11.6 ºC). However, the RH during ~~the P1~~non-heating and heating~~P2~~ were similar, with an average RH of 78.7% (range 57-96%) for ~~P1~~ non-heating and 78.9% (range 44-98%) for heating~~P2~~.

~~3.1~~3.2 Mass concentration and chemical composition of PM_1 during ~~the P1 period~~non-heating

~~3.1.1~~3.2.1 PM_1 at the kerbside during ~~P1~~non-heating

Figure ~~1~~2a ~~and Figure 2~~ shows the time series zoomed in for the non-heating and heating periods and their~~and~~ relative fractions of PM_1 component (i.e., OA, sulfate, nitrate, ammonium, and chloride, and BC) while Fig. 3a shows their diurnal patterns~~, respectively.~~ a~~A~~t the kerbside during non-heating.~~,~~ BC was the most dominant PM_1 component (Table 1), on average accounting for over half (55% or 5.6 µg m^{-3}) of PM_1, followed by OA (32% or 3.3 µg m^{-3}), sulfate (5% or 0.5 µg m^{-3}), ammonium (4% or 0.4 µg m^{-3}), nitrate (3% or 0.3 µg m^{-3}), and chloride (1% or 0.1 µg m^{-3}). In particular, ~~frequent~~ BC spikes (> 15 µg m^{-3}; top 5 percentiles) affected the local air quality substantially during the daytime (6:00 – 21:00, local time, Fig. 3a) and showed higher intensity during rush hours on weekdays. Similar patterns were also observed for NO_x (Fig. ~~S3~~S5) and CO (Fig. ~~S4~~S6) at the kerbside, confirming common traffic sources. Specifically, both NOx and CO showed rush hour peaks during weekdays while such rush hour peaks during weekends were not as prominent as during weekends, consistent with the traffic pattern in Dublin (Fu et al., 2017). The average mixing ratios for NOx and CO were 54.1 ppb (in the range of 5.4-200.0 ppb) and 0.2 ppm (in the range of 0.05-0.8 ppm), respectively.

BC spikes were on the time scale of minutes, indicating certain types of vehicles were the major cause of such pollution plumes. The diesel-powered public buses were firstly suspected as the major emitters of BC because a bus stop was nearby, about ~20 m away from the sampling site. Note the bus services usually start at ~5:30 and end at ~23:00 in downtown Dublin. However, BC spikes were also observed during other times e.g., from 23:00 to 5:30 when public bus services were not available. Moreover, higher intensity and frequency of BC spikes were observed during the morning and evening rush hour peaks. Thus, in addition to the buses, other types of vehicles (e.g., private cars) were also potential contributors to~~ the~~ air pollution. Specifically, ~50 vehicles (manual count) were jammed along the nearby street during rush hours and higher emissions might be associated with the cold starts and idling speeds during such traffic jams. Additionally, the street canyon effect, making the pollutants hard to disperse, were also important factors in driving the high BC concentrations at the kerbside. In particular, the street canyon effect was evidenced by the high background BC concentration (3.0 μg m^{-3}) during the night (from 23:00 to 5:00) when traffic flow was at the lowest (Fig. 3a). As a comparison, the average BC was only 0.4 μg m^{-3} at the residential site during the non-heating period (Table 1).

Similar to BC at the kerbside, OA also shows ~~frequent ~~spikes with concentrations of >5 μg m^{-3} (top 5 percentiles) from 6:00 to 21:00 (Fig. ~~1a~~3a). However, in addition to traffic, cooking and secondary formation were also contributing to the OA mass at the kerbside (discussed in Sect. 3.~~3~~4). In contrast to BC and OA, the time series of the measured inorganic aerosols were relatively smooth (Fig. ~~1~~2b), and did not exhibit any obvious influence from traffic. This is not surprising because vehicles are not direct emitters of these inorganic species, and the introduction of the threshold of 10 ppm (by mass) sulfur for gas/diesel oil led to very low sulphur emissions in Dublin (Regulations, 2008). On average, the sum of inorganic aerosol accounted for a relatively small fraction (13%) of the total PM$_1$ (Fig. 2a).

~~3.1.2~~3.2.2 PM$_1$ at the residential site during ~~P1~~non-heating

The time series of OA, sulfate, nitrate, ammonium, and chloride at the residential site during ~~P1 ~~non-heating are shown in Fig. ~~1b~~2b. Over ~~the entire P1~~this period, the average concentration of PM$_1$ was 2.3 μg m^{-3} at the residential site, around five times lower than that at the kerbside (Table 1). OA was the most dominant species at the residential site, accounting for 46% (1.0 μg m^{-3}) of PM$_1$ (Fig. 2b), followed by BC (17% or 0.4 μg m^{-3}), sulfate (17% or 0.4 μg m^{-3}), ammonium (14% or 0.3 μg m^{-3}), nitrate (5% or 0.1 μg m^{-3}), and chloride (1% or <0.1 μg m^{-3}). ~~Despite the fact that~~Although the measurements at the residential and kerbside were conducted simultaneously, all of the PM$_1$ components showed no obvious trend that could be associated with vehicular emissions at the residential site (Fig. 3b), indicating the impact of traffic emissions from the kerbside had a minor impact on the residential site. Consistently, NO$_x$ concentrations were very low with an average mixing ratio of NO$_x$ of 2.6 ppb (median was 2.0 ppb; Table 1). As discussed above, ~~T~~the low impact of vehicular emissions on air quality at the residential site ~~might be~~was associated with the distance from the emission sources, as well as the effects of wind speed and wind direction. Specifically, the distance between the residential site and the nearest road is ~500 m and ~5 km away from the city centre. ~~South~~The south-westerly wind was dominant during ~~P1~~ the non-heating period with an average wind speed of 4.5 m s^{-1}, ranging from 1.5 to 9.0 m s^{-1} (Fig. ~~S2~~S4).

~~3.2~~3.3 Mass concentration and chemical composition of PM$_1$ during ~~the P2~~ heating~~period~~

~~3.2.1~~3.3.1 PM$_1$ at the kerbside during ~~P2~~heating

During the heating period~~ of P2~~, large pollution spikes were observed in the evening (20:00-23:00) with a simultaneous increase in all NR-PM$_1$ components and BC (Fig. ~~1c~~2c and 3c). Specifically, in the evening on 31 October, the peak PM$_1$ concentration was ~~197.3~~134.0 µg m^{-3} (Fig. ~~1c~~2c) which was more than ~~four times higher than~~double of that the rush hour peak on the same day. Moreover, the evening pollution expanded over the entire evening and went into the night (Fig. 3c), demonstrating the extensive impact ~~from~~ of residential heating activities. On the same day, BC concentration increased up to ~~50~~ 37.5 µg m^{-3} in the evening, ~~more than~~over five ~~ten~~ times higher than the average (7.1 µg m^{-3}). The simultaneous increase in all NR-PM$_1$ components along with BC suggests common heating sources in the evening.

Over the entire heating period~~ of P2~~, the average PM$_1$ concentration was 18.4 µg m^{-3}, ~~around~~ approximately two times higher than that during ~~P1~~ non-heating (~~Fig. 2c~~Table 1). While the average BC concentration increased from 5.6 µg m^{-3} during non-heating~~P1~~ to 7.1 µg m^{-3} during heating~~P2~~, the corresponding BC fraction decreased from 55% to 38%. This is due to the relatively high emissions of other PM$_1$ components (e.g., OA) which were associated with heating sources. Specifically, the average OA concentration was doubled during ~~P2~~ heating (6.5 µg m^{-3}) than during ~~P1~~ non-heating (3.3 µg m^{-3}) with the corresponding fraction increasing from 32% to 35%. Moreover, the average concentration and fraction of sulfate, nitrate, ammonium, and chloride also increased. On average, the fraction of inorganic components increased from 13% (1.3 µg m^{-3}) during ~~P1~~ non-heating to 27% (6.1 µg m^{-3}) during ~~P2~~heating. Among these inorganics, nitrate saw the largest increase from 3% (0.~~28~~ 3 µg m^{-3}) during ~~P1~~ non-heating to 9% (1.6 µg m^{-3}) during ~~P2~~heating, partly due to the cold temperature (Fig. S2) which favoured the gas-to-particle partitioning of semi-volatile NH_4NO_3.

~~3.2.2~~3.3.2 PM$_1$ at the residential site during ~~P2~~heating

The time series of the measured PM$_1$ components at the residential during ~~P2~~ heating is shown in Fig. ~~1d~~2d. During this period, the pollution spikes with a simultaneous increase in the concentrations of NR-PM$_1$ and BC were observed almost every evening. This was in great contrast to that during ~~P1~~ non-heating when no clear pattern in NR-PM$_1$ species was observed (Fig. 3b and 3d). As discussed above, the pollution spikes of NR-PM$_1$ at the residential site showed a simultaneous increase with that at the kerbside (Fig. ~~1c~~2c) and the PM$_{2.5}$ at the Rathmines station (Fig. ~~S~~1c), indicating the three sites were affected by similar residential burning sources and air masses. Over the entire ~~P2~~heating period, the average PM$_1$ concentration was 12.7 µg m^{-3}, which was six times higher than during ~~P1~~non-heating. On average, OA accounted for 63% (8.1 µg m^{-3}) of PM$_1$, making it the most dominant component (Fig. 2d), followed by BC (9% or 2.4 µg m^{-3}), nitrate (8% or 1.1 µg m^{-3}), ammonium (8% or 1.0 µg m^{-3}), sulfate (7% or 0.9 µg m^{-3}), and chloride (4% or 0.6 µg m^{-3}).

3.4 Sources of OA

~~3.2.3~~3.4.1 OA factors at the kerbside during non-heating

~~Figure 4 and Figure 5 show the fractional contributions and diurnal cycles of the resolved OA factors, respectively.~~To resolve the OA sources, free PMF was firstly conducted on the OA matrix. The solution that best represented the data was the three-factor solution because the solutions with more factors provided no meaningful but splitting from the already resolved factors (see Fig. S7 and more details in the supplementary). The three-factor solution identified a hydrocarbon-like OA (HOA) factor from traffic, cooking-like OA (COA) factor from cooking sources, and an oxygenated OA (OOA) factor corresponding to the secondary processes. However, free PMF provided only a sub-optimal solution as the profile of COA contained no m/z 43 which underestimated its contribution or over-estimated the contributions from other factors (Fig. S7). Therefore, ME-2 (Canonaco et al., 2013) was utilized to constrain the reference profiles of HOA and COA (Crippa et al., 2013) with 0-50% constraints (i.e., a value of 0-0.5; see Sect. 2.3) to better evaluate their contributions.

-Figure 4 shows the mass spectra, diurnal pattern, and relative contribution of HOA, COA, and OOA of the optimal ME-2 solution during non-heating at the kerbside. ~~Three OA factors were resolved during P1 at the kerbside, including traffic-related HOA, cooking OA (COA), and oxygenated OA (OOA).~~ The HOA profile was dominated by peaks at *m/z* of 27, 29, 41, 43, 55, and 57, characteristic of the hydrocarbon ion series of [C$_n$H$_{2n+1}$]$^+$ and [C$_n$H$_{2n-1}$]$^+$. The diurnal cycle of HOA featured two rush hour peaks which were consistent with that of BC (Fig. 3a), confirming its traffic source. During the early morning (from 00:00 to 5:00), the HOA concentration was very low (0.1 µg m^{-3}), indicating a low background HOA level. From 6:00, HOA started to increase with a peak HOA value of 1.5 µg m^{-3} at 8:00. After the morning rush hour peak, the HOA concentration was constantly high (1 µg m^{-3}) and reached 1.3 µg m^{-3} at the afternoon rush hour peak (17:00). The HOA returned to the background level at around 23:00, corresponding to the reduced traffic flow during the night (Fu et al., 2017). Despite being adjacent to the busy road in Dublin city centre, on average, HOA accounted for ~~only 27~~27.8 % (0.9 µg m^{-3}) of the total OA (Fig. ~~4a~~4c) with rest attributing to COA (35.7~~6~~% or 1.2 µg m^{-3}) and OOA (36.6~~7~~% or 1.2 µg m^{-3}). During the morning rush hours from 7 am to 10 am, HOA increased its shares to 49.1% of the total OA (Fig. 4d), suggesting a more important role of HOA during rush hours. ~~The diurnal cycle of HOA featured two rush hour peaks which were consistent with that of BC, confirming its traffic source (Fig. 5a). Specifically, the HOA concentration was very low (0.1 µg m^{-3}) from 00:00 to 5:00, indicating a low background HOA concentration. From 6:00, the HOA concentration increased to a peak value of 1.5 µg m^{-3} at 8:00. After the morning rush hour peak, the HOA concentration was constantly high (1 µg m^{-3}) and reached to 1.3 µg m^{-3} at~~

~~the evening rush hour peak (17:00). The HOA returned to the background level at 23:00, corresponding to reduced traffic emissions during the night (Fu et al., 2017).~~

The COA profile is characterized with a *f55* to *f57* ratio of 2.6 (where *f55* and *f57* are the fraction of *m/z* 55 and 57 to the total organic mass, respectively) which was higher than that for HOA (0.9) but was in the range of 2.2-2.8 typical found for COA (Mohr et al., 2012). The identification of COA was associated with the location of the sampling site in Dublin city centre with some restaurants around. The diurnal pattern of COA showed a lunchtime peak at 13:00 and a dinner time peak at 20:00, corresponding to the meal times. Higher dinner time COA peak (2.7 μg m^{-3}) was observed than lunchtime peak (1.6 μg m^{-3}) likely due to higher emissions during the evening coupled with relatively low evening temperatures (Fig. S2) and shallower boundary layer. Similar diurnal patterns for COA were also observed in Barcelona (Mohr et al., 2012), Paris (Crippa et al., 2013), London and Manchester (Allan et al., 2010). ~~The high contribution (36%) of COA was associated with location the sampling site in Dublin city centre with some restaurants around. The diurnal pattern of COA showed a lunch time peak at 13:00 and dinner time peak at 20:00, corresponding to the meal times. Higher dinner time COA peak (2.7 μg m^{-3}) was observed than lunch time peak (1.6 μg m^{-3}) likely due to higher emissions during the evening coupled with relatively low evening temperatures (Fig. S2).~~ On average, COA accounted for 35.7% of OA, but over the evening hours from 19:00 to 22:00, COA increased its fraction to 51.4% of OA.

The OOA profile (Fig. ~~S7)~~4) resembled the less volatile OOA (LV-OOA; R^2 of 0.94) which usually represents well-aged SOA (Ng et al., 2011a). However, the diurnal pattern of OOA in Dublin showed a clear pattern that was strongly influenced by local sources and was most likely from fresh SOA instead of well-aged SOA. Moreover, the morning peak of OOA came about 1 hour later than that for HOA, probably indicating fast SOA formation processes by atmospheric oxidation of SOA precursor gases and/or condensation of semi-volatile VOCs emitted by the nearby traffic. ~~In addition~~Besides, the contribution from cooking sources to OOA was also important as evidenced by the concurrent peaks of OOA with COA. The diurnal trend of OOA suggests ~~The~~ the OOA had a background concentration of 0.5 μg m^{-3} which was higher than HOA (0.1 μg m^{-3}) and COA (0.1 μg m^{-3}), indicating part of OOA was also associated with regional transport. It is estimated that approximately 38% of the total OOA was regionally transported, i.e., the value of background OOA concentration of 0.5 μg m^{-3} if compared to the total OOA concentration of 1.3 μg m^{-3}.

~~3.2.4~~3.4.2 OA factors at the residential site during non-heating

Free PMF suggested a two-factor solution with one mixed primary OA factor and one OOA (Fig. S8) as a further increase in the number of factors led to the splitting of factors. The diurnal pattern of the primary factor showed a slight increase in the morning but with a larger increase in the evening and night, suggesting potential mixing between HOA and the heating-related factor. Note that the temperature was below 15 °C in the evening during this period (Fig. S4) and thus sporadic domestic solid fuel burning activities were likely to occur. Our previous study has shown that peat burning occurred in cold summer nights in the west coast city of Galway in Ireland (Lin et al., 2019a). Moreover, the elevated levels of m/z 60 in the evening (at 22:00) suggested emissions from biomass burning (Fig. S8). The correlation between the profile of the unconstrained primary OA factor and the reference profile of peat burning OA (R^2= 0.58) from our previous study (Lin et al., 2017) is better than the profile of biomass burning OA (BBOA; R^2=0.44) from the Ng et al. (2011a). Note that COA was not considered to be a potential OA factor at this site since the sampling site was representative of the residential area with few restaurants around. Moreover, no clear increase in the concentration of POA during lunchtime was observed during this non-heating period and the heating period as discussed later. Therefore, only the reference profile of HOA and peat burning OA factors were constrained during non-heating at the residential site.

The mass spectra and diurnal patterns, as well as the relative contribution of the HOA, peat, and OOA at the residential site during non-heating are shown in Fig. 5. While the profile of HOA is similar between the residential site and the kerbside, its concentration levels at the residential site were significantly lower than at the kerbside. Specifically, in the morning rush hours, the HOA peak concentration was 0.1 μg m^{-3} at the residential site while it was 1.5 μg m^{-3} at the kerbside, with a 15 times difference between the two sites. On average, HOA accounted for 11.8% of OA at the residential site. During the morning rush hours, its fraction increased to 16.0% which was still a minor factor when compared to OOA (58-68% of OA). The low contribution of HOA is consistent with the low mixing ratio of NO_x at the residential site (median: 2.0 ppb) which was ~20 times lower than that at the kerbside (Table 1).

The peat profile featured peaks at *m/z* of 27, 29, 41, 43, 55, and 57, which was similar to HOA. However, the differences in *f60* between the peat factor and HOA suggested different sources. *f60* in the peat profile was 0.014 which was higher than that for HOA (<0.003), confirming its biomass nature (Cubison et al., 2011). The diurnal pattern of peat showed increased concentrations at 20:00-22:00, corresponding to their emission time. On average, peat accounted for 23.6% of OA and its fraction increased to 28.1% in the evening. The OOA mass spectral at the residential site featured high contribution at m/z 44 (i.e., f44) which was similar to the OOA at the kerbside. However, the diurnal cycle of OOA at the residential site showed no clear pattern, which was different from that at the kerbside. Therefore, most of the OOA at the residential site was likely due to regional transport.

3.4.3 OA factors at the kerbside during heating

Free PMF solutions found the concentration of the heating-related OA factor increased substantially in the evening (Fig. S9). The increase in OA concentration during the evening was likely due to the emissions from the use of oil, peat, coal, and wood in the domestic sector according to Central Statistics Office (CSO, 2016) and Sustainable Energy Authority of Ireland (SEAI, 2018). Previous studies have identified these heating-related aerosols in urban areas in Ireland (Kourtchev et al., 2011; Dall'Osto et al., 2013; Lin et al., 2018). However, due to the temporal covariation of the heating-related OA factors, free PMF led to highly mixed factors which were insufficient to evaluate their respective contributions. ME-2 was, thus, used to constrain the reference profiles of peat, coal, and wood from Lin et al. (2017), along with HOA and COA (Crippa et al., 2013).

Figure 6 shows the mass spectral profiles, diurnal patterns, and relative contributions of the resolved OA factors at the kerbside during heating. ~~During P2, solid fuel burning related OA factors, including wood, peat, and coal, were resolved in addition to HOA, COA, and OOA (Fig. 4c and 5c).~~ Consistent with that ~~for P1~~during non-heating, the HOA factor also showed rush hour peaks in the morning (~~∼~~8:00) and afternoon (~~∼~~17:00) with similar concentrations (~~∼~~1.~~5~~ 8 μg m^{-3}) during ~~P2~~ heating to that during non-heating~~P1~~. However, a third HOA peak (2.2 μg m^{-3}) was also seen at ∼22:00 (Fig. ~~5c~~6b), ~~indicating additional sources from residential heating likely~~ likely from the emission of ~~from~~ oil burning (CSO, 2016; Lin et al., 2017; Lin et al., 2018). Over the entire ~~P2~~heating period, HOA accounted for ~~18~~15.7% (1.2 μg m^{-3}) of OA (Fig. ~~4c~~6c). The relatively small fraction of HOA~~, again,~~ indicates traffic was not the dominant OA source during the heating period~~s~~ despite measurements being adjacent to the busy road in downtown Dublin. Note that HOA during ~~P2~~ heating could only be taken as an upper limit of the primary OA emissions from traffic because of the additional contribution from the oil burning.

COA showed a similar diurnal pattern to that during ~~P1~~ non-heating but with slightly higher concentrations during the heating period~~P2~~, which could be associated with colder temperature and shallower boundary layer. On average, COA accounted for ~~18~~17.9% (1.2 μg m^{-3}) of OA (Fig. 4c).

Peat is an accumulation of partially decayed plant material which is an important domestic fuel source in Ireland (Tuohy et al., 2009). The incomplete decay of vegetation resulted in an increase of *f60* when burned (Lin et al., 2017). However, *f60* in peat profile (0.014) was lower than wood (0.053) probably because wood contained a higher fraction of *m/z* 60-related material e.g., levoglucosan (Fig. 6a). Over the entire heating period, peat burning accounted for 17.7% (1.2 μg m^{-3}) of OA (Fig. 6c). However, during the pollution spikes as seen on 28 and 31 October (Fig. 6d), peat burning increased its fraction to 26.5% (9.2 μg m^{-3}), suggesting peat burning was an important OA emission source. Similarly, wood burning increased its contribution to 9.8% (3.3 μg m^{-3}) during pollution spikes from an average of 7.3% (0.5 μg m^{-3}). The important role of peat and wood burning in driving the pollution events is consistent with our previous study in suburban Dublin (Lin et al., 2018).

The profile of coal burning OA featured very low *f60* (<0.003), consistent with its non-biomass signature as coal is formed from the complete vegetation decay. On average, the coal factor accounted for 12.6% (0.8 μg m^{-3}) of OA. Though the fraction of coal burning decreased during pollution events (11.9%; Fig. 6d), its absolute concentration increased (4.3 μg m^{-3}). Note that chloride also showed a significant increase during the pollution events (Fig. 2c) which was associated with coal burning as our previous coal-combustion experiment showed that chloride emission comprised a high fraction (2-52.8%) of the submicron aerosol from coal burning emissions (Lin et al., 2017).

~~Solid fuel burning accounted for 33% (2.1 μg m^{-3}) of the total OA.~~ The OOA profile had an *f44* of 0.24 during heating which was similar to that (0.22) during non-heating, indicating similar oxidation levels between the two periods. However, compared to the daytime OOA peak concentrations (1.8 μg m^{-3}), higher OOA concentrations (3.9 μg m^{-3}) were observed in the evening, indicating a more important contribution from the condensation of SVOCs emitted from heating sources and/or their dark aging processes ~~Moreover, higher OOA concentrations were observed in the evening and night, indicating an important contribution from the condensation of SVOCs emitted from solid fuel burning.~~ (Tiitta et al., 2016). On average, OOA accounted for a large fraction (29% or 1.9 μg m^{-3}) of OA. During pollution events, OOA still accounted for a significant fraction of OA (22% or 7.8 μg m^{-3}), demonstrating its importance of secondary OA processing.

~~3.2.5~~3.4.4 OA factors at the residential site during heating

~~During P1, OOA, HOA, and peat factors were resolved at the residential site (Fig. 4b and 5b). OOA accounted for the majority (65% or 0.6 μg m^{-3}) of OA. HOA accounted for a low fraction (15% or 0.1 μg m^{-3}) of OA while peat accounted for 20% (0.2 μg m^{-3}) of OA. The absolute concentration of HOA at the residential site was approximately ten times lower (0.1 vs 1.0 μg m^{-3}) than that at the kerbside. The low contribution of HOA at the residential site was expected because HOA, on average, contributed to only 27% of OA even adjacent to the busy road in Dublin city centre (Fig. 4a). The low contribution of HOA is also consistent with the low mixing ratio of NO_x at the residential site (median: 2.0 ppb) which was ~20 times lower than that at the kerbside (Table 1).~~

Heating-related OA factors were identified since they all showed elevated concentrations in the evening as indicated by the free PMF solutions (Fig. S10). However, similar to the case at the kerbside, the OA factors were mixed because of the co-emissions from all domestic heating activities. To better evaluate the contribution of potential sources, the reference profiles of HOA (Crippa et al., 2013), peat, wood, and coal were constrained (Lin et al., 2017) using ME-2. Note that COA was not constrained since no lunch meal peaks were identified during this period as discussed above.

In the morning rush hours, HOA showed a peak concentration of 0.4 μg m^{-3} due to traffic emissions, which was, again, largely reduced when compared to the HOA morning peaks (1.8 μg m^{-3}) at the kerbside. However, higher concentrations of HOA (2.0 μg m^{-3}) were observed in the evening due to the emissions of oil burning. Therefore, the majority (estimated at over 80%) of HOA at the residential site was due to oil burning instead of traffic emissions. On average, HOA accounted for 11.8% of the total OA over the entire heating period and its fraction increased slightly to 12.9% during pollution events.

Similar to the kerbside, solid fuel burning, especially peat burning was a very important OA factor, contributing up to 45.5% (34.9% on average) of the OA during the pollution events (Fig. 7c and 7d). Coal (17.8-19.2%) and wood (7.1-7.5%) burning were also contributing substantially over the entire period as well as during pollution events. The importance of solid fuel burning at the residential site echoed our previous studies at the same sites (Lin et al., 2018; Lin et al., 2019b). ~~During P2, the OA factors, including OOA, wood, peat, coal and HOA, all showed peak concentrations during the night (Fig. 5b). In contrast, during the day, all factors showed very low concentrations (<0.5 μg m^{-3}) despite the high spikes in the evening. HOA at the residential site was attributed to the oil burning because no rush hour peaks of traffic-related HOA were observed at this site. HOA, on average, accounted for 18% (1.6 μg m^{-3}) of OA. Solid fuel burning OA factors showed the largest enhancement with the sum of peat, coal, and wood factors accounting for 50% (4.3 μg m^{-3}) of OA.~~ OOA, on average, accounted for ~~32~~27.9% (~~2.8~~1.4 μg m^{-3}) of OA and the higher OOA concentration during the evening, concurrent to an increase in primary factor concentrations, again suggested its major source was from the condensation of SVOCs emitted from solid fuel burning and/or their dark aging processes (Tiitta et al., 2016).

~~3.3 Kerbside increment of PM_1~~

~~Figure 6 shows the comparison of the measured PM_1 components and NO_x between the kerbside and residential site during P1 and P2. Among the measured PM_1 species, BC showed the largest kerbside increment, with an increment ratio of 16 (median value) during the P1 period (Fig. 6). During the P2 period, BC increment ratio was slightly lower (10) primarily due to the additional emission sources of solid fuel burning affecting both sites simultaneously. BC showed peak concentration during rush hour peaks, corresponding to heavier traffic during these times (Fig. 3). As expected, the kerbside increment of BC was more enhanced during rush hour peaks (Fig. S16), reaching up to 25 for BC. When traffic emissions were at their lowest at night, a small but significant BC increment of 5 was observed, partially due to the street canyon effects, creating a poor dispersion condition in the downtown areas. The kerbside increment of BC was primarily due to vehicular emissions and this was corroborated by the gas pollutant of NO_x which showed an increment ratio of 7-23 (Fig. 6). Note that our measurement represents the average fleet in Dublin and thus the high kerbside increment for BC in Dublin have significant implications for the potentially higher exposure risk at the kerbside. For example, Ljungman et al. (2019) associated higher risk of stroke for exposure to ambient BC from traffic exhaust.~~

~~Compared to BC, the kerbside increment of OA was less significant because traffic was not a major source of OA. However, higher OA increment ratio (3; median value) was also seen during P1 than during P2 (1.5) due to the combined contributions from sources like traffic, cooking, solid fuel burning and secondary formation (see Sect. 3.3). As a comparison, the concentrations of sulfate, nitrate, and ammonium did not show large variations between the two sites again because vehicles are not direct emitters of these secondary aerosols. Instead, the good correlation (R^2=0.53-0.85 and slopes=0.70-0.83; Fig. S17) for the time series of these inorganic aerosols between the two sites, suggesting common sources from e.g., regional transport.~~

~~3.4~~3.5 Implications for emission control

The HOA/BC ratio was ~0.~~16~~ 17 as ~~achieved~~ retrieved from the slope of the linear regression between HOA and BC with a coefficient of determination (R^2) ~~of~~ being 0.61 during the non-heating period (Fig. S11~~8~~), indicating the average traffic in Dublin emitted approximately six times more BC than HOA. Compared to other studies, the HOA/BC ratio in Dublin was lower than the HOA/BC ratios reported for gasoline vehicles-dominated environment (0.9-1.7) but was ~~similar to~~within the range for the diesel environment (0.03-0.61~~26~~) ~~adjacent to the highway in Grenoble~~ (DeWitt et al., 2015), indicating most of the traffic emissions were from diesel vehicles. ~~Actually, d~~Diesel fuel accounted for 73% of the on-road transport energy in Ireland in 2017 (Fig. ~~7a~~S12a). Figure ~~7~~ S12 also shows an increasing trend of diesel fuel usage, indicating worse air quality in the predictable future at the kerbside if diesel vehicular emissions were not controlled.

This study also shows that vehicular emissions appear to impact the air quality adjacent to the roads. In contrast, solid fuel burning has a large geographic impact, affecting overall air quality at the kerbside and residential sites examined in this investigation. Such large geographic impact suggests significant climate effects from residential emissions (Butt et al., 2016) which contain a higher fraction of OA than that for traffic. However, surprisingly, the government~~al~~ census data shows only a few households (<5%) consumed these solid fuels with the majority households (~95%) using~~ed~~ natural gas and electricity as the primary heating sources in 2016 (Fig. ~~7b~~12b). Therefore, if the emissions from this small fraction of households were controlled, good overall air quality and ~~less~~ lower climate forcing can be expected.

4 Conclusion

The chemical composition and sources of submicron aerosol (PM_1) were simultaneously investigated at a kerbside location in downtown Dublin and at a residential site in south Dublin (~5 km apart) using an ACSM and AE33/16 at both sites during both non-heating (i.e., early September) and heating periods (i.e., late October) of 2018. Traffic emissions were found to have a minor impact on air quality at the residential site due to the distance from nearby roadways and other affecting parameters such as wind speed and wind direction. In contrast, the kerbside was found to be highly affected by~~ the~~ diesel vehicular emissions. BC was the most dominant component (38~~44~~-~~59~~55%) of PM_1 at the kerbside location while OA was the most important species (~~43~~46-~~61~~64% of PM_1) at the residential site. During non-heating period, an increment ratio of up to 25 was found for the BC at the kerbside when compared to the level of BC at the residential site primarily due to vehicular emissions. During the heating period, the BC increment ratio was lower (~10) due to the additional sources of solid fuel burning which contributed to the BC concentrations at both sites. Moreover, solid fuel burning was shown to increase PM_1 concentrations substantially with episodic concentrations of >100 $\mu g\ m^{-3}$ being recorded at both sites simultaneously. Source apportionment of OA using ME-2 showed that only ~~18~~16-~~27~~28% of OA could be directly associated with vehicular emissions (i.e., HOA) at the kerbside, with the larger contribution of OA being attributed to cooking, solid fuel burning, and OOA. HOA contributed to ~~15~~11-~~18~~12% of OA at the residential site ~~which was attributed to~~with a large contribution from oil burning instead of traffic because HOA did not show elevated rush hour peaks as found at the ~~residential site~~kerbside. During the heating period, solid fuel burning contributed to ~~approximately~~ over 50% of OA at the residential site, while oxygenated OA accounted for almost 65% of OA during the non-heating period. This study highlights the significant increment of BC due to the traffic emissions at the kerbside and the large geographic impact of OA from residential heating at both the kerbside and residential sites. Therefore, traffic and residential heating might have different health and climate implications as suggested by the temporal and spatial variability of sources within Dublin city centre.

5 Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Also, all data used in the study are available from the corresponding author upon request.

6 Author Contribution

JO, DC, SJ, and CO'D conceived and designed the experiments; CL, JO, DC, and PB performed the experiments; CL, JO, WX, EH, JW, JG, and CO'D analyzed the data; CL prepared the manuscript with input from all co-authors.

7 Competing interests

The authors declare that they have no conflict of interest.

8 Acknowledgments

This work was supported by EPA-Ireland (AEROSOURCE, 2016-CCRP-MS-31), Department of Communications, Climate Action and Environment (DCCAE), the National Natural Science Foundation of China (NSFC) under grant no. 41925015, 91644219 and 41877408. The authors would also like to acknowledge the contribution of the COST Action CA16109 (COLOSSAL) and MaREI, the SFI Research Centre for Energy, Climate and Marine.

9 References:

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478-4485, 10.1021/es703009q, 2008.

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, Atmos. Chem. Phys., 10, 647-668, 2010.

An, Z., Huang, R.-J., Zhang, R., Tie, X., Li, G., Cao, J., Zhou, W., Shi, Z., Han, Y., Gu, Z., and Ji, Y.: Severe haze in northern China: A synergy of anthropogenic emissions and atmospheric processes, Proc. Natl. Acad. Sci., 116, 8657-8666, 10.1073/pnas.1900125116, 2019.

Burnett, R., Chen, H., Szyszkowicz, M., Fann, N., Hubbell, B., Pope, C. A., Apte, J. S., Brauer, M., Cohen, A., Weichenthal, S., Coggins, J., Di, Q., Brunekreef, B., Frostad, J., Lim, S. S., Kan, H., Walker, K. D., Thurston, G. D., Hayes, R. B., Lim, C. C., Turner, M. C., Jerrett, M., Krewski, D., Gapstur, S. M., Diver, W. R., Ostro, B., Goldberg, D., Crouse, D. L., Martin, R. V., Peters, P., Pinault, L., Tjepkema, M., van Donkelaar, A., Villeneuve, P. J., Miller, A. B., Yin, P., Zhou, M., Wang, L., Janssen, N. A. H., Marra, M., Atkinson, R. W., Tsang, H., Quoc Thach, T., Cannon, J. B., Allen, R. T., Hart, J. E., Laden, F., Cesaroni, G., Forastiere, F., Weinmayr, G., Jaensch, A., Nagel, G., Concin, H., and Spadaro, J. V.: Global estimates of mortality associated with long-term exposure to outdoor fine particulate matter, Proc. Natl. Acad. Sci., 115, 9592-9597, 10.1073/pnas.1803222115, 2018.

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

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams,

L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 10.5194/acp-15-253-2015, 2015.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6, 3649-3661, 2013.

Cohen, A. J., Brauer, M., Burnett, R., Anderson, H. R., Frostad, J., Estep, K., Balakrishnan, K., Brunekreef, B., Dandona, L., Dandona, R., Feigin, V., Freedman, G., Hubbell, B., Jobling, A., Kan, H., Knibbs, L., Liu, Y., Martin, R., Morawska, L., Pope, C. A., Shin, H., Straif, K., Shaddick, G., Thomas, M., van Dingenen, R., van Donkelaar, A., Vos, T., Murray, C. J. L., and Forouzanfar, M. H.: Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study 2015, The Lancet, 389, 1907-1918, https://doi.org/10.1016/S0140-6736(17)30505-6, 2017.

Crippa, M., Decarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J. L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, Atmos. Chem. Phys., 13, 961-981, 2013.

CSO: (Central Statistics Office). Private Households in Permanent Housing Units. https://www.cso.ie/px/pxeirestat/Statire/SelectVarVal/Define.asp?maintable=E4015&PLanguage=0 (accessed on 1 May 2020), 2016.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, Atmos. Chem. Phys., 11, 12049-12064, 10.5194/acp-11-12049-2011, 2011.

Dall'Osto, M., Ovadnevaite, J., Ceburnis, D., Martin, D., Healy, R. M., O'Connor, I. P., Kourtchev, I., Sodeau, J. R., Wenger, J. C., and O'Dowd, C.: Characterization of urban aerosol in Cork city (Ireland) using aerosol mass spectrometry, Atmos. Chem. Phys., 13, 4997-5015, 10.5194/acp-13-4997-2013, 2013.

DeWitt, H. L., Hellebust, S., Temime-Roussel, B., Ravier, S., Polo, L., Jacob, V., Buisson, C., Charron, A., André, M., Pasquier, A., Besombes, J. L., Jaffrezo, J. L., Wortham, H., and Marchand, N.: Near-highway aerosol and gas-phase measurements in a high-diesel environment, Atmos. Chem. Phys., 15, 4373-4387, 2015.

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., and Hansen, A. D. A.: The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation, Atmos. Meas. Tech., 8, 1965-1979, 2015.

Fu, M., Kelly, J. A., and Clinch, J. P.: Estimating annual average daily traffic and transport emissions for a national road network: A bottom-up methodology for both nationally-aggregated and spatially-disaggregated results, J. Transp. Geogr., 58, 186-195, https://doi.org/10.1016/j.jtrangeo.2016.12.002, 2017.

Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier Van Der Gon, H., Facchini, M., Fowler, D., Koren, I., Langford, B., and Lohmann, U.: Particulate matter, air quality and climate: lessons learned and future needs, Atmos. Chem. Phys., 15, 8217-8299, 2015.

Gallagher, J., Gill, L. W., and McNabola, A.: The passive control of air pollution exposure in Dublin, Ireland: A combined measurement and modelling case study, Sci. Total Environ., 458-460, 331-343, https://doi.org/10.1016/j.scitotenv.2013.03.079, 2013.

Gallagher, J.: A modelling exercise to examine variations of NOx concentrations on adjacent footpaths in a street canyon: The importance of accounting for wind conditions and fleet composition, Sci. Total Environ., 550, 1065-1074, https://doi.org/10.1016/j.scitotenv.2016.01.096, 2016.

Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prévôt, A. S. H., and Robinson, A. L.: Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions, Environ. Sci. Technol., 51, 1074-1093, 10.1021/acs.est.6b04509, 2017.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155-5236, 2009.

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Äijälä, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H.-C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophys. Res. Lett., 43, 7735-7744, doi:10.1002/2016GL069239, 2016.

Kourtchev, I., Hellebust, S., Bell, J. M., O'Connor, I. P., Healy, R. M., Allanic, A., Healy, D., Wenger, J. C., and Sodeau, J. R.: The use of polar organic compounds to estimate the contribution of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM2.5 in Cork Harbour, Ireland, Sci. Total Environ., 409, 2143-2155, 10.1016/j.scitotenv.2011.02.027, 2011.

Lenschow, P., Abraham, H. J., Kutzner, K., Lutz, M., Preuß, J. D., and Reichenbächer, W.: Some ideas about the sources of PM10, Atmos. Environ., 35, S23-S33, https://doi.org/10.1016/S1352-2310(01)00122-4, 2001.

Lin, C., Ceburnis, D., Hellebust, S., Buckley, P., Wenger, J., Canonaco, F., Prévôt, A. S. H., Huang, R.-J., O’Dowd, C., and Ovadnevaite, J.: Characterization of primary organic aerosol from domestic wood, peat, and coal burning in Ireland, Environ. Sci. Technol., 51, 10624-10632, 2017.

Lin, C., Huang, R.-J., Ceburnis, D., Buckley, P., Preissler, J., Wenger, J., Rinaldi, M., Facchini, M. C., O’Dowd, C., and Ovadnevaite, J.: Extreme air pollution from residential solid fuel burning, Nat. Sustain., 1, 512-517, 2018.

Lin, C., Ceburnis, D., Huang, R.-J., Canonaco, F., Prévôt, A. S. H., O’Dowd, C., and Ovadnevaite, J.: Summertime Aerosol over the West of Ireland Dominated by Secondary Aerosol during Long-Range Transport, Atmos., 10, 59-70, https://doi.org/10.3390/atmos10020059, 2019a.

Lin, C., Ceburnis, D., Huang, R. J., Xu, W., Spohn, T., Martin, D., Buckley, P., Wenger, J., Hellebust, S., Rinaldi, M., Facchini, M. C., O'Dowd, C., and Ovadnevaite, J.: Wintertime aerosol dominated by solid-fuel-burning emissions across Ireland: insight into the spatial and chemical variation in submicron aerosol, Atmos. Chem. Phys., 19, 14091-14106, 10.5194/acp-19-14091-2019, 2019b.

Ljungman, P. L., Andersson, N., Stockfelt, L., Andersson, E. M., Nilsson Sommar, J., Eneroth, K., Gidhagen, L., Johansson, C., Lager, A., and Leander, K.: Long-Term Exposure to Particulate Air Pollution, Black Carbon, and Their Source Components in Relation to Ischemic Heart Disease and Stroke, Environ. Health Persp., 127, 107012, 2019.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci. Tech., 46, 258-271, 10.1080/02786826.2011.620041, 2012.

Mohr, C., Richter, R., DeCarlo, P. F., Prévôt, A. S. H., and Baltensperger, U.: Spatial variation of chemical composition and sources of submicron aerosol in Zurich during wintertime using mobile aerosol mass spectrometer data, Atmos. Chem. Phys., 11, 7465-7482, 10.5194/acp-11-7465-2011, 2011.

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiḿenez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Préṽot, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, Atmos. Chem. Phys., 12, 1649-1665, 2012.

Mues, A., Manders, A., Schaap, M., van Ulft, L. H., van Meijgaard, E., and Builtjes, P.: Differences in particulate matter concentrations between urban and rural regions under current and changing climate conditions, Atmos. Environ., 80, 232-247, https://doi.org/10.1016/j.atmosenv.2013.07.049, 2013.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.: Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data, Environ. Sci. Technol., 45, 910-916, 2011a.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aerosol Sci. Technol., 45, 780-794, 2011b.

Petit, J. E., Favez, O., Sciare, J., Canonaco, F., Croteau, P., Močnik, G., Jayne, J., Worsnop, D., and Leoz-Garziandia, E.:

Submicron aerosol source apportionment of wintertime pollution in Paris, France by double positive matrix factorization (PMF2) using an aerosol chemical speciation monitor (ACSM) and a multi-wavelength Aethalometer, Atmos. Chem. Phys., 14, 13773-13787, 10.5194/acp-14-13773-2014, 2014.

Pieber, S. M., El Haddad, I., Slowik, J. G., Canagaratna, M. R., Jayne, J. T., Platt, S. M., Bozzetti, C., Daellenbach, K. R., Fröhlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jiménez, J. L., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Inorganic Salt Interference on CO2+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies, Environ. Sci. Technol., 50, 10494-10503, 10.1021/acs.est.6b01035, 2016.

Pope III, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., and Thurston, G. D.: Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, Jama, 287, 1132-1141, 2002.

Regulations: Sulphur Content of Heavy Fuel Oil, Gas Oil, and Marine Fuels Regulations, 2008.

Sandradewi, J., Prévôt, A. S. H., Szidat, S., Perron, N., Alfarra, M. R., Lanz, V. A., Weingartner, E., and Baltensperger, U.: Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter, Environ. Sci. Technol., 42, 3316-3323, 2008.

SEAI: (Sustainable Energy Authority of Ireland). Energy Statistics in Ireland. https://www.seai.ie/resources/seai-statistics/key-statistics (accessed on 1 May 2020), 2018.

Tiitta, P., Leskinen, A., Hao, L., Yli-Pirilä, P., Kortelainen, M., Grigonyte, J., Tissari, J., Lamberg, H., Hartikainen, A., Kuuspalo, K., Kortelainen, A. M., Virtanen, A., Lehtinen, K. E. J., Komppula, M., Pieber, S., Prévôt, A. S. H., Onasch, T. B., Worsnop, D. R., Czech, H., Zimmermann, R., Jokiniemi, J., and Sippula, O.: Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging, Atmos. Chem. Phys., 16, 13251-13269, 2016.

Tuohy, A., Bazilian, M., Doherty, R., Gallachóir, B. Ó., and O'Malley, M.: Burning peat in Ireland: An electricity market dispatch perspective, Energy Policy, 37, 3035-3042, 2009.

Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.: Formation of Urban Fine Particulate Matter, Chem. Rev., 115, 3803-3855, 10.1021/acs.chemrev.5b00067, 2015.

Zhang, Y., Favez, O., Petit, J. E., Canonaco, F., Truong, F., Bonnaire, N., Crenn, V., Amodeo, T., Prévôt, A. S. H., Sciare, J., Gros, V., and Albinet, A.: Six-year source apportionment of submicron organic aerosols from near-continuous highly time-resolved measurements at SIRTA (Paris area, France), Atmos. Chem. Phys., 19, 14755-14776, 10.5194/acp-19-14755-2019, 2019.

Zotter, P., Herich, H., Gysel, M., El-Haddad, I., Zhang, Y., Močnik, G., Hüglin, C., Baltensperger, U., Szidat, S., and Prévôt, A. S. H.: Evaluation of the absorption Ångström exponents for traffic and wood burning in the Aethalometer-based source apportionment using radiocarbon measurements of ambient aerosol, Atmos. Chem. Phys., 17, 4229-4249, 2017.

Table 1: Mean, standard deviation (SD), first quartile (Q1), median, third quartile (Q3), and maximum (Max) concentration of the hourly averaged organic aerosol (OA), sulfate (SO$_4$), nitrate (NO$_3$), ammonium (NH$_4$), chloride (Chl), and black carbon (BC) at the kerbside and residential site during the Non-heating period (10/09 – 17/09) and Heating period (27/10 – 03/11 2018)~~period P1 (see Fig. S1 for definition of P1)~~. ~~All~~Aerosol species are in μg m^{-3} and NOx is in ppb.~~.~~

Non-Heating	Kerbside (10/09 - 17/09 2018)						Residential (10/09 – 17/09 2018)					
	mean	SD	Q1	median	Q3	Max	mean	SD	Q1	median	Q3	Max
OA	3.3	2.1	1.8	3.0	4.3	8.7	1.0	0.7	0.5	0.9	1.4	3.3
SO$_4$	0.5	0.4	0.2	0.4	0.7	1.6	0.4	0.2	0.2	0.3	0.5	2.6
NO$_3$	0.3	0.2	0.2	0.2	0.3	0.7	0.1	0.1	0.1	0.1	0.1	0.4
NH$_4$	0.4	0.5	0.1	0.3	0.7	1.4	0.3	0.4	<0.1	0.2	0.5	1.4
Chl	0.1	0.3	<0.1	<0.1	0.2	1.0	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
BC	5.6	4.6	2.6	4.6	7.3	18.2	0.4	0.4	0.2	0.3	0.4	3.0
PM$_1$[a]	10.3	5.1	6.2	9.7	13.5	21.2	2.3	1.3	1.3	2.0	2.8	8.5
NO$_x$	54.1	42.7	17.4	45.1	79.9	200	2.6	2.3	0.8	2.0	4.0	12.2
Heating	Kerbside (27/10 – 03/11 2018)						Residential (27/10 – 03/11 2018)					
OA	6.5	7.9	1.4	3.7	8.3	45.5	8.1	15.5	0.9	2.3	7.0	90.0
SO$_4$	0.9	1.4	0.2	0.5	1.1	8.6	0.9	1.3	0.2	0.4	1.0	8.4
NO$_3$	1.6	1.9	0.2	0.7	2.6	8.3	1.1	1.4	0.1	0.4	1.5	7.8
NH$_4$	1.3	2.5	0.1	0.7	1.5	18.1	1.0	1.7	0.2	0.5	1.3	11.6
Chl	1.0	3.9	<0.1	0.1	0.4	28.5	0.6	2.1	<0.1	0.1	0.2	18.3
BC[b]	7.1	8.3	1.4	3.8	9.6	37.5	1.2	2.4	0.2	0.4	1.0	17.0
PM$_1$	18.4	18.5	5.2	12.3	24.9	134.0	12.7	23.3	2.6	5.7	14.8	126.0
NO$_x$	89.7	85.5	28.5	60.3	123.5	410	16.5	22.6	3.6	8.2	18.0	139.0

[a] PM$_1$ sum of OA, SO$_4$, NO$_3$, NH$_4$, Chl and BC

[b] BC at the residential site was not available during non-heating period and the week after (from 24 September to 30 September) was shown as a reference.

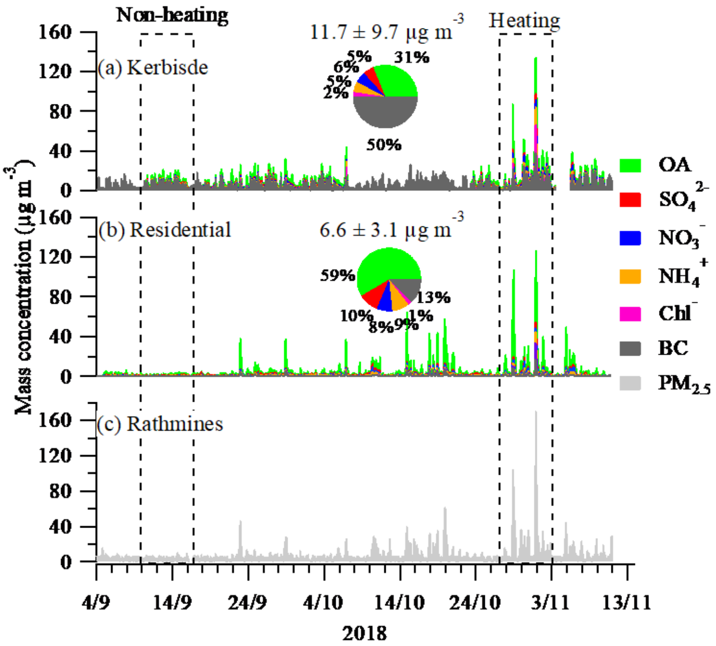


Figure 1. Time series of hourly averaged submicron organic aerosol (OA), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Chl^-), and black carbon (BC) at the kerbside (a), residential site (b), and EPA Rathmines station (c) from 4 September to 9 November 2018. Inset pie charts are the chemical composition of PM_1 averaged over the entire period while the numbers (±one SD) above are the average PM_1 concentration. The non-heating period, from 10 September to 17 September, and heating period, from 27 October to 4 November 2018 are marked for further analysis. The data gaps at the kerbside was due to ACSM malfunction.

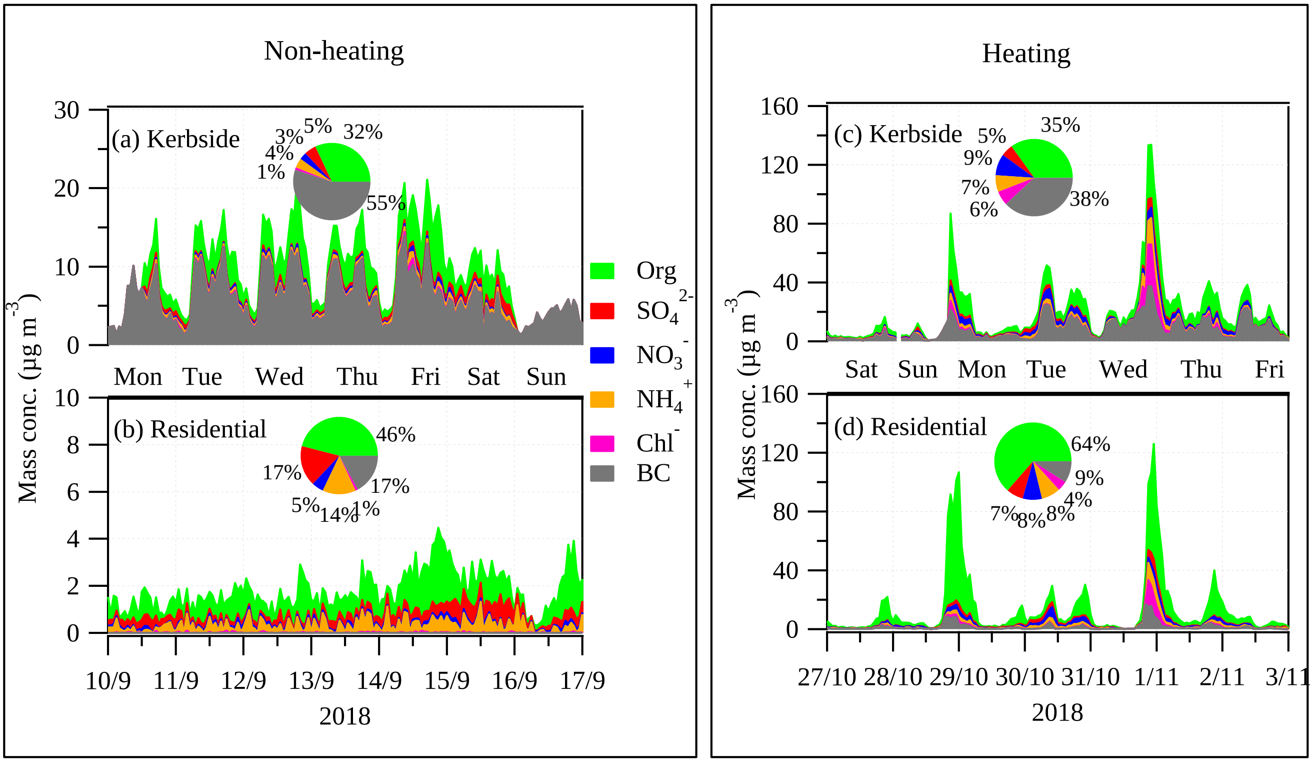
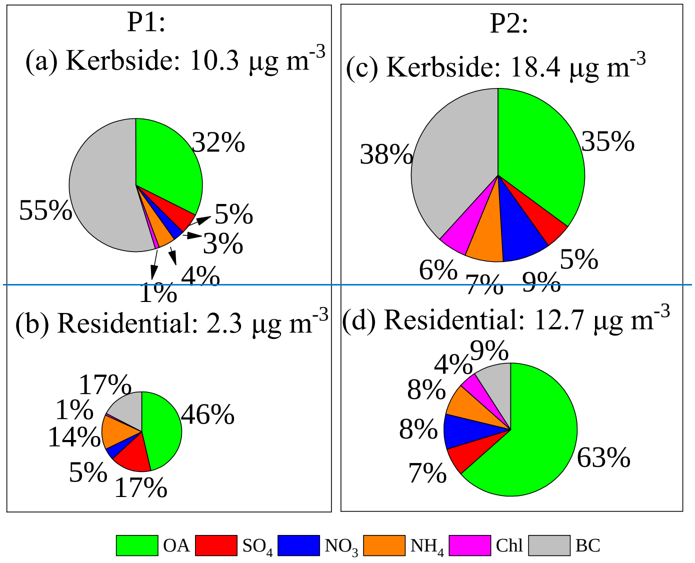


Figure ~~1~~2. Time series of hourly averaged submicron organic aerosol (OA), sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), chloride (Chl), and black carbon (BC) during ~~P1~~ non-heating (left panel) and ~~P2~~ heating (right panel) at the kerbside (a, c) and residential (b, d) ~~(see Fig. S1 for the selection of P1 and P2)~~. Inset pie charts are the relative fraction of the measured PM_1 components. ~~Note that the time resolution for the ACSM at the kerbside was 5 min while it was 1 h at the residential site, and BC data were averaged to match the time step of ACSM.~~ Also shown are the day of the week, including Monday (Mon), Tuesday (Tue), Wednesday (Wed), Thursday (Thu), Friday (Fri), Saturday (Sat), and Sunday (Sun).



~~**Figure 2. Relative contribution of submicron organic aerosol (OA), sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), chloride (Chl) and black carbon (BC) during P1 and P2 at the kerbside (a, c) and residential (b, d). The values above the pie charts are the mean concentration of PM_1 for each site during P1 or P2 and the area of the pie was proportional to the mean concentration.**~~

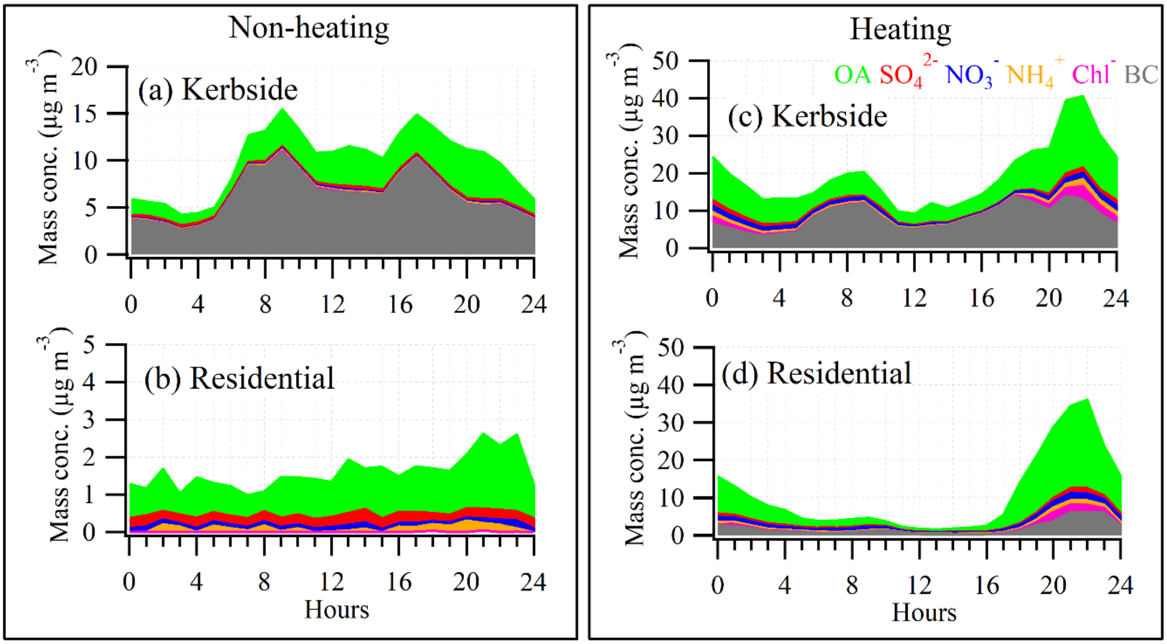


Figure 3. The diurnal cycle of submicron organic aerosol (OA), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Chl$^-$), and black carbon (BC) during non-heating (left panel) and heating (right panel) at the kerbside (a, c) and residential site (b, d).

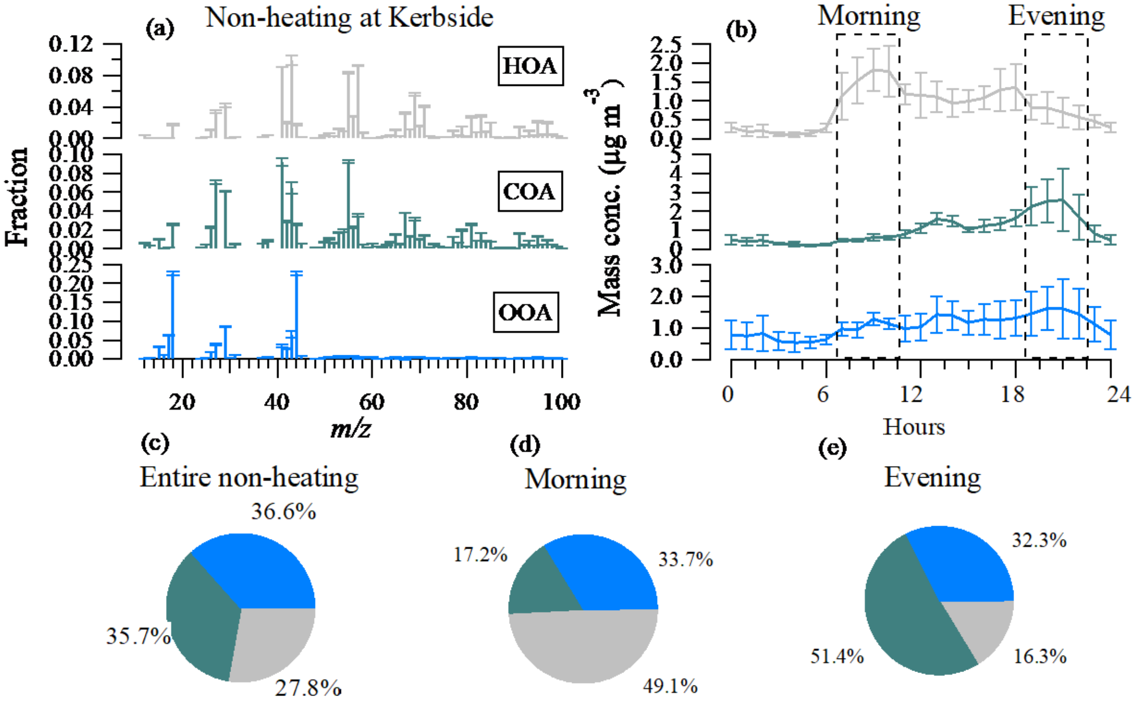


Figure 4. (a) Mass spectral profiles of hydrocarbon-like OA (HOA), cooking OA (COA) and oxygenated OA (OOA) during non-heating at the kerbside; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire non-heating period; (d) over the morning rush hours (7:00-10:00, local time); and (e) over the evening hours from 19:00-22:00. Error bars in (a) and (b) represent one standard deviation.

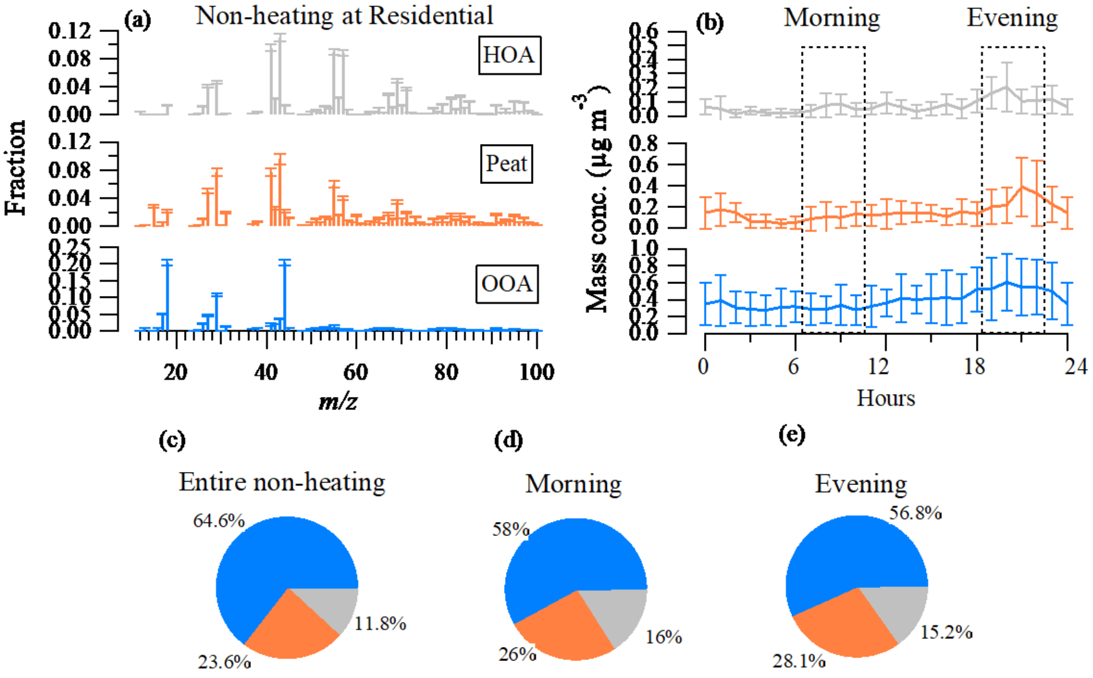
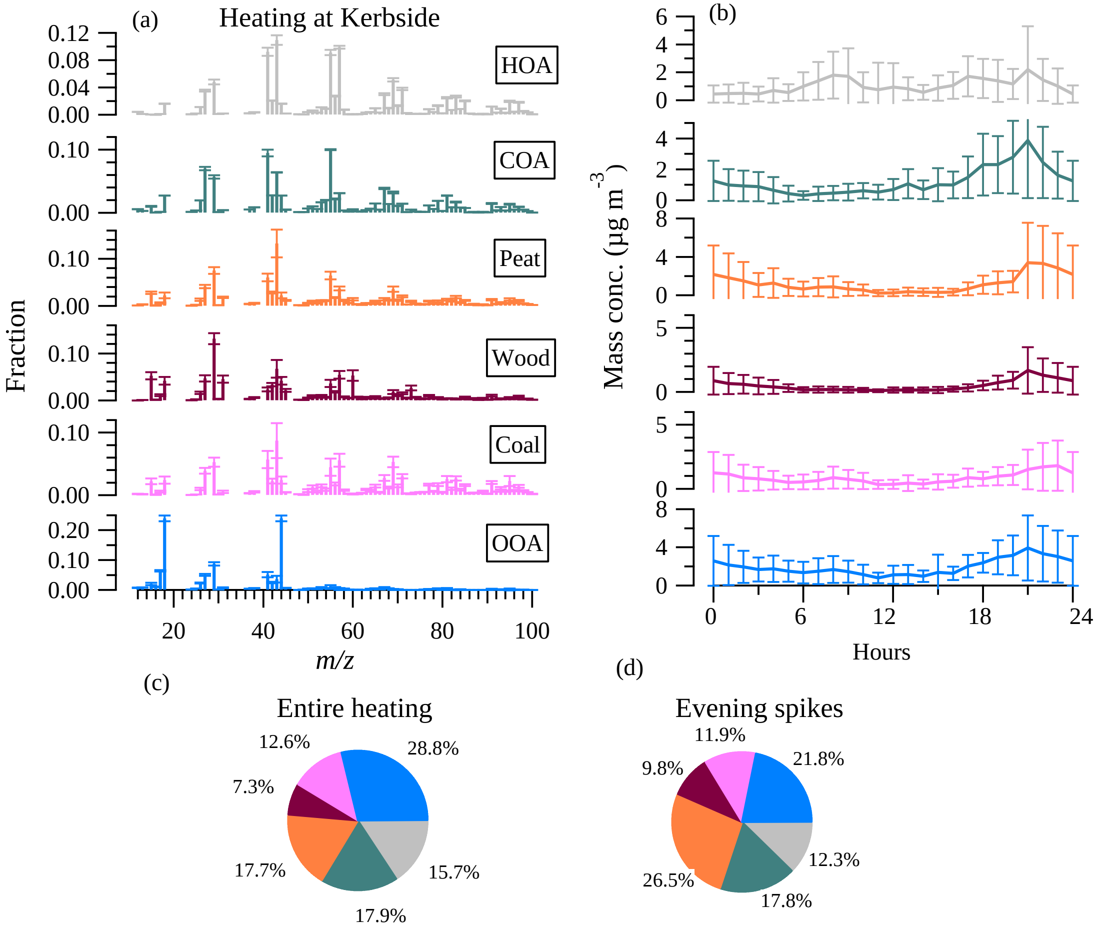


Figure 5. (a) Mass spectral profiles of hydrocarbon-like OA (HOA), peat and oxygenated OA (OOA) during non-heating at the residential site; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire non-heating period; (d) over the morning rush hours (7:00-10:00); and (e) over the evening hours from 19:00-22:00. Error bars in (a) and (b) represent one standard deviation.



1390 **Figure 6. (a) Mass spectral profiles of hydrocarbon-like OA (HOA), cooking OA (COA), peat, wood, coal and oxygenated OA (OOA) factors during heating at the kerbside; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire heating period; and (d) over evening spikes on 28 and 31 October. Error bars in (a) and (b) represent one standard deviation.**

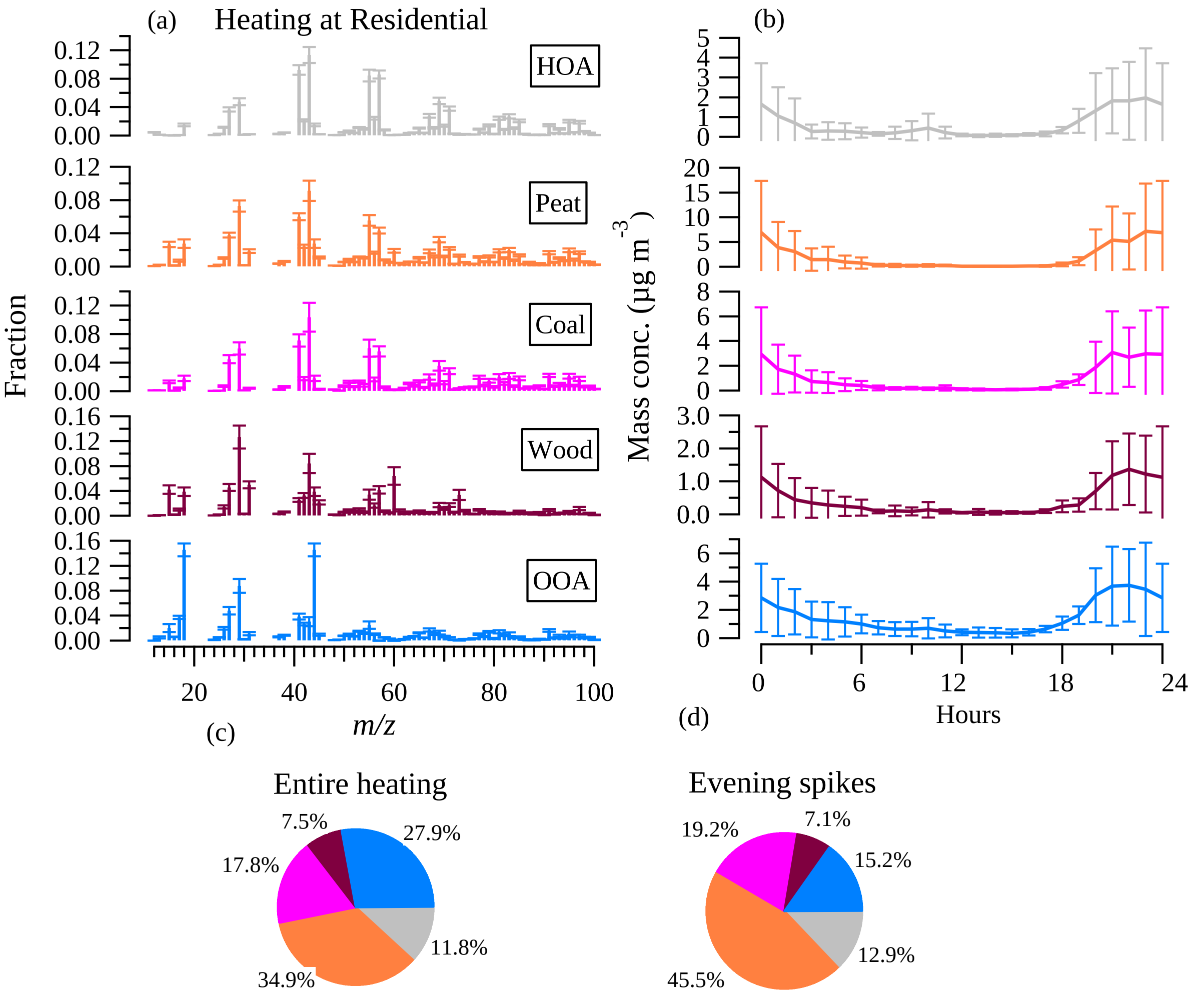
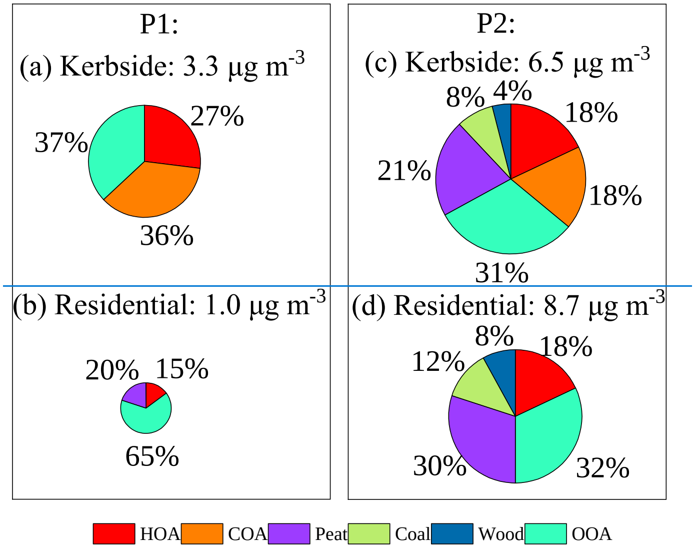
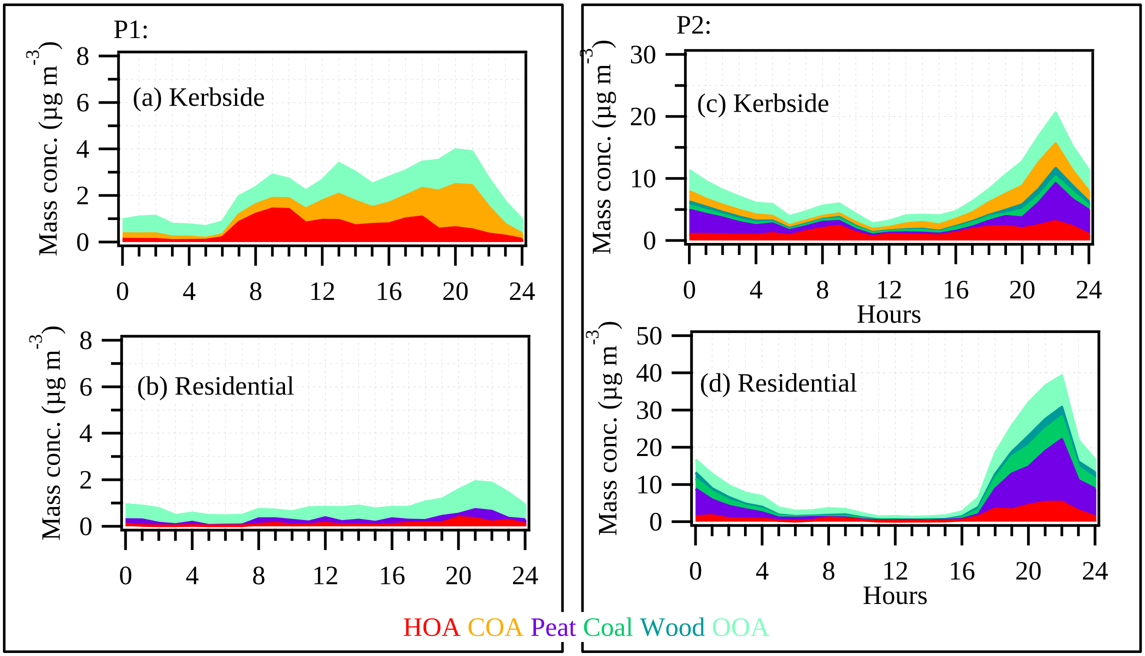


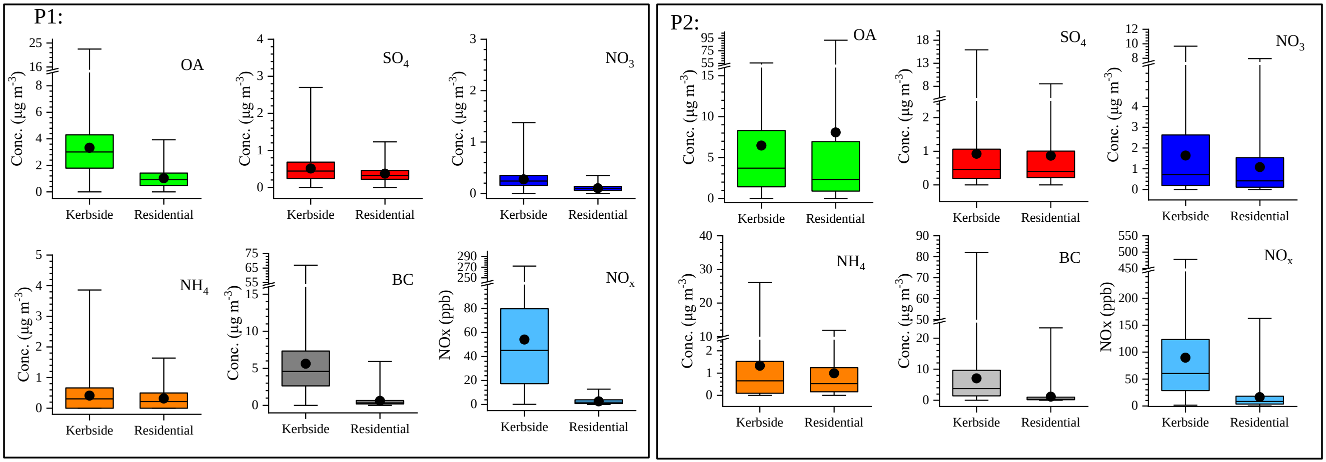
Figure 7 (a) Mass spectral profiles of hydrocarbon-like OA (HOA), peat, wood, coal and oxygenated OA (OOA) factors during heating at the residential site; (b) Diurnal cycle of the OA factors; and (c) relative contribution of OA factors over the entire heating period; and (d) over evening spikes on 28 and 31 October. Error bars in (a) and (b) represent one standard deviation.



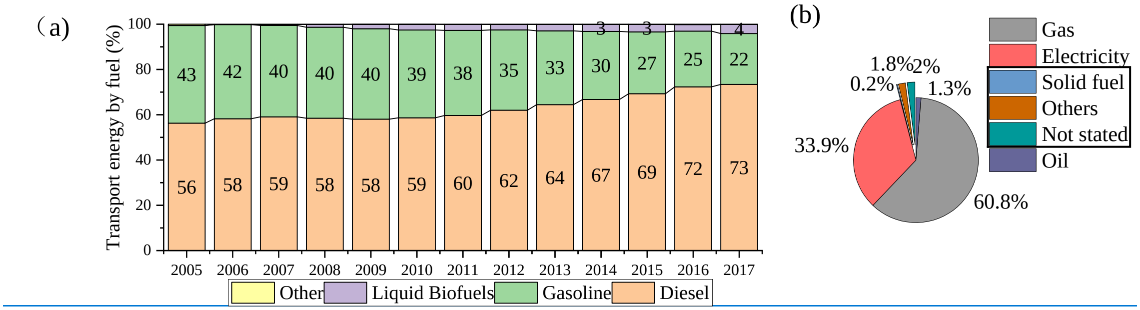
~~**Figure 4.** Relative contribution of organic aerosol (OA) factors, including Hydrocarbon-like OA (HOA), cooking (COA), peat, coal, wood, and oxygenated OA (OOA) during P1 and P2 at the kerbside (a, c) and residential site (b, d). The values above the pie charts are the mean concentration of OA for the site during P1 or P2 and the area of the pie was proportional to the mean concentration.~~



~~**Figure 5.** The diurnal cycle of organic aerosol (OA) factors, including Hydrocarbon-like OA (HOA), cooking (COA), peat, coal, wood, and oxygenated OA (OOA) during P1 and P2 at the kerbside (a, c) and residential site (b, d).~~



~~**Figure 6. Box plots of the of submicron organic aerosol (OA), sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), black carbon (BC), and NO_x during P1 and P2 at the kerbside and residential site. The median, the 25th and 75th percentiles are represented by the middle, lower and upper vertical bars, respectively. The min and the max percentiles are the bottom and top whiskers, respectively. Note that the time resolution for the ACSM at the kerbside was 5 min while it was 1 h at the residential site, and the time resolution was 1 min for the BC measurement at the kerbside while it was 5 min for the residential site.**~~



~~**Figure 7. Contribution of diesel, gasoline, liquid biofuels and other fuels (a) to the total on-road transport energy in Ireland from 2005 and 2017 (SEAI, 2018) and the fraction of the households (b) that claimed to use natural gas, electricity, oil, solid fuels, others, and not stated in Dublin in 2016 (CSO, 2016). Solid fuel, *Others* and *Not stated* are highlighted to show the small fraction of households that are likely to use solid fuels for heating.**~~