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Air quality—climate forcing double whammy from domestic firelighters

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Renewable biomass plays a crucial role in transitioning toward climate-friendly heating sources; however, not without its collateral damage in terms of the disproportionately high effects on local air quality. The associated proliferation of residential heating appliances around the world, including developed regions like Europe, where an estimated 70 million are housed, does not appear to be abating. Here, we identify super self-concentrating ambient pollution events whereby solid-fuel residential heating haze is infused with a hitherto unaccounted for firelighter smoke that contributes additional adsorbing black carbon. This black carbon-organic aerosol combination results in a strong positive radiative forcing (up to 149 W m^{-2}) and alters the boundary layer thermodynamics sufficiently so as to further suppress pollutant dilution and dispersion leading to extraordinary high submicron particulate matter (PM_1: 166 µg m^{-3}). Unfortunately, there is no silver lining in this cloud until the promotion of solid biomass fires with firelighters for ignition is replaced by a co-benefit policy.

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INTRODUCTION

Ambient aerosols adversely affect human health, causing millions of premature deaths every year worldwide[1–3]. Carbonaceous aerosols, including organic aerosol (OA) and black carbon (BC), are important components of ambient aerosols, typically accounting for more than 50% of the total aerosol mass in polluted urban areas[4,5]. In addition to the health effects, carbonaceous aerosols also play an important role in the climate system[2,6,7]. In particular, BC, the major light-absorbing part of carbonaceous aerosol, was found to be second only to carbon dioxide in causing global warming[8], and is regarded as a key warming agent. Due to the strong positive (warming) radiative forcing by BC, its reduction has been targeted for near-term climate change mitigation[9].

Biomass burning is a major emission source of the atmospheric OA, partly due to its higher emission factor than conventional pollution sources e.g., traffic and industrial activities[10–12]. The residential burning of wood and peat (an accumulation of partially decayed vegetation) is recently found to cause extreme air pollution events that rivaled the pollution levels in some of the most polluted cities e.g., Beijing, China[13]. Along with OA, BC can also be emitted at a lesser extent as a result of incomplete combustion of biomass with its relative emissions depending on the types of biomass and combustion conditions[14–16], and the typical BC to OA ratio is <0.1[16]. It is, therefore, not surprising that wood or other biomass-based solid-fuel burning is reported to be the dominant OA source in the urban atmosphere e.g., Paris, at the same time fossil fuels i.e., diesel vehicular emissions, are the predominant source of BC due to its higher BC to OA ratio[17].

To inform effective and specifically targeted emission control policies, sophisticated fingerprinting strategies for OA source apportionment have been developed (e.g., the AQ network at www.macehead.org in Ireland[13] and the Aerosols, Clouds, and Trace gases Research InfraStructure (ACTRIS) in Europe). However, due to the poorly investigated links between emission source, energy consumption and ultimately the culprit for air pollution and climate change[18], implications for policymaking from current air quality monitoring studies are usually not clear. Moreover, it remains a challenge to identify new aerosol sources that are atmospherically relevant while they are missing and/or ignored in the current emission inventories[19–21].

In this study, we present air quality and climate effects of previously unrecognized aerosol source, i.e., kerosene-based firelighters that emit more BC than all biomass fuels put together. Kerosene (EC No. 232-366-4), produced by the distillation of crude oil, consists of hydrocarbons with carbon numbers predominately in the range of C9 to C12[22,23], making it highly flammable. Kerosene (or paraffin)[24] based solid firelighters are commercially available in many countries across Europe, as well as in the United States and Canada[25,26], but its aerosol emissions are often ignored compared to typical domestic solid fuels e.g., wood and coal. Our findings of firelighter being the dominant BC sources are based on laboratory experiments and a sequence of ambient air pollution events, monitored at an urban background site in Dublin within the Irish AQ network[13]. Details of the source characterization experiments, and ambient aerosol measurements are presented in the Methods Section. Briefly, for source characterization, an aerosol chemical speciation monitor (ACSM) and an aethalometer (AE-33) were deployed to measure the particulate emissions from peat, wood, and coal burning, as well as the emissions from commercially available firelighters used in Ireland, while the suite of ambient sensors run in parallel is described in a previous study[13].

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RESULTS

Submicron aerosol composition and time trends

The Irish AQ network (www.macehead.org) incorporates four aerosol mass spectrometer nodes that are strategically positioned across Ireland to capture and quantify local sources and long-range transport of air pollution. The chemical composition of PM_1 is being continuously sampled on a near real-time basis since August 2016[13]. Supplementary Fig. 1 shows the time series of the carbonaceous aerosol of OA and BC from 1 September 2016 to 31 August 2017 at one node of the network deployed in a low-density residential area of south Dublin, as well as the collocated particle volume and $PM_{2.5}$ mass concentration (3 km apart). Over the entire year, OA and BC were well correlated with a linear correlation coefficient r of 0.85 and slope of 2.4 (Supplementary Fig. 2a), suggesting OA and BC have similar emission sources, i.e., domestic heating (Supplementary Table 1). However, the OA to BC ratio varied a lot during the pollution events, ranging from 1:1 to 10:1. Variations in OA:BC ratio are usually caused by changes in source contributions (e.g., traffic or residential heating: peat, wood, coal, and heating oil; Supplementary Table 1) or burning conditions as well as the evaporation and/or condensation of OA during the transport from the emission sources to the sampling site.

To investigate contributions from different carbonaceous aerosol (OA + BC) sources, we focus on a sequence of five night-time air pollution episodes with PM_1 that consecutively intensified from background concentrations of <5 μg m^{-3} to a maximum peak of 166.5 μg m^{-3} for the final event in the series (Fig. 1a). These events are typical of the residential site and occur throughout winter every year on a regional scale (including residential and kerbside sites[27]) in Dublin (Supplementary Fig. 3) and other Irish cities (e.g., Galway in Supplementary Fig. 2b)[28], as well as in small towns and rural areas[29]. The time series of the chemical composition of measured PM_1 components (i.e., OA, sulfate, nitrate, ammonium, chloride, and BC) for the five events are presented in Fig. 1a. The five episodes (i.e., Ep 1–5; Fig. 1a) occur from 20:00 to 24:00 local time and represent concentrations over a larger residential area as evident by a high correlation coefficient (r of 0.90) and slope (0.99) between PM_1 at the measurement site and $PM_{2.5}$ at the neighboring (3 km away) EPA monitoring site, Rathmines (Supplementary Fig. 4). In addition to the particulate emissions, meteorological parameters also contributed to high concentrations restricting dispersion during pollution events. The low wind speed (<4 m s^{-1}) and low temperatures (<10 °C) coupled with the high relative humidity (RH > 80%) trapped PM_1 components on a regional scale (Supplementary Fig. 4). Carbonaceous aerosol (OA + BC) was the dominant component of PM_1, accounting for 86–89% (42.7–147.1 μg m^{-3}) of PM_1 (Fig. 1a). In contrast, inorganic aerosol (i.e., the sum of sulfate, nitrate, ammonium, and chloride) accounted for a small fraction (11–14%, or 5.4–19.3 μg m^{-3}) of PM_1.

Carbonaceous aerosol sources—a missing source from firelighter

Using the OA mass spectra of oil, peat, coal, and wood-burning (see Method Section)[30–32] as the anchoring profiles in MultiLinear Engine (ME-2) analysis, their respective contributions to the measured ambient OA were evaluated (Supplementary Fig. 5). The peat-burning OA was responsible for the largest fraction of OA, on average, accounting for 43% of the total OA (Supplementary Fig. 5). During the pollution episodes, the peat burning OA factor increased its share to 44-53% (15.7–49.2 μg m^{-3}; Fig. 1b). Similarly, the contribution of wood-burning OA factor also increased during pollution episodes (up to 15% or 17.6 μg m^{-3}). Combined, the biomass burning OA factor (Peat + Wood) accounted for up to 72% (66.8 μg m^{-3}) of the total OA during pollution episodes (Fig. 1b). In addition to the biomass burning factor, oil-burning was also an important source, accounting for 23–26% (8.2–22.3 μg m^{-3}) of OA during episodes. In contrast, the coal burning OA factor accounted for only a small fraction of OA (<5% or <1.8 μg m^{-3}). The small contribution of coal was consistent with the decline in coal use since the coal-ban was implemented in Dublin in 1990[33]. Additionally, an oxygenated OA (OOA) factor was resolved, likely associated with the aging of precursor gaseous emissions from biomass burning[34]. Although the concentration of OOA increased during episodes (3.7–7.4 μg m^{-3}), its fraction decreased (Fig. 1b).

The large contribution of peat and wood-burning OA is consistent with their high emission factors (Fig. 2 and Supplementary Table 2). Specifically, the emission factors of 108.2 mg/MJ for wood burning, 64.7 mg/MJ for peat burning and 23.3 mg/MJ for coal burning were derived for these fuels (Supplementary Table 2). Submicron aerosol emissions from wood and peat burning were comprised mostly of OA (>90% of PM_1) while coal burning emissions comprised roughly equal amounts of OA (52%) and BC (45%; Fig. 2). As a comparison, BC accounted for less than 5% of the wood and peat burning emissions. The OA to BC ratio derived from the lab experiments was found to be 23.4 for wood-burning, 23.8 for peat burning and 1.2 for coal burning, consistent with the ranges reported in the literature (Supplementary Table 3). Using these ratios, BC from the total of solid-fuel burning factors (i.e., peat, wood, and coal) were calculated to account for only 5% of the ambient BC measured during the five pollution episodes (Supplementary Fig. 6a). In addition to solid-fuel burning, oil burning contributed to 23–26% (8.2–22.3 μg m^{-3}; Fig. 1b) of OA, despite its low emission factor (5 mg/MJ of PM_1; Supplementary Table 2) but owing to its prevailing use (oil burning is a major domestic heating fuel in Ireland[20]; Supplementary Table 1), therefore, the oil burning contributions to BC were evaluated next.

Emissions from oil burning result in OC/BC ratio of 0.8[16] equivalent to a value of 1.1 for the OA to BC ratio (Supplementary Table 3), assuming the hydrocarbon-like OA (HOA) to OC ratio of 1.4 for emissions from oil[35]. Using this ratio, we were able to derive the oil contribution to ambient BC and adding it to the previously accounted solid fuels (i.e., the sum of peat, wood, and coal burning) increased the explained BC fraction to ~49% (Supplementary Fig. 6b). The remaining >50%, however, were unaccounted for by the combined solid-fuel and oil burning emissions. By expanding the same analysis over the period from November 2016 to February 2017 in Dublin (Supplementary Fig. 7) and from February to April 2016 in Galway (Supplementary Fig. 8), we consistently found that solid-fuel burning BC, on average, could only explain a small fraction (<20%) of the measured BC. Adding oil BC increased the explained fraction of BC, with most data points located within the ratio range of 0.5:1 to 2:1 (Supplementary Fig. 7). However, roughly half of the BC could not be explained (Supplementary Fig. 7b) during pollution episodes with BC concentrations over 50 μg m^{-3} in Dublin.

Firelighters were then investigated as the source of this 'unexplained' BC fraction as they are commonly used to ignite solid fuels and were shown to have significantly (an order of magnitude) higher BC emission factor (~150 mg MJ^{-1}; Fig. 2) than solid fuels themselves (~5 mg MJ^{-1}) as confirmed by both offline and online instrumentation[31]. In our combustion experiment, 0.1 kg or one cube of firelighter (3% of the test fuel weight) was used to ignite 3.5 kg of test fuels (See method section). However, firelighter emissions were mainly comprised of BC as confirmed when firelighter was tested separately (Supplementary Fig. 9a), while the biomass-based fuel burning emission (e.g., peat burning in Supplementary Fig. 9b) was mostly organic, consistent with the high OA:BC ratios (Supplementary Table 3). The firelighter contribution to the BC signal normally lasted over 15 min (Supplementary Fig. 9a). Although overall solid-fuel burning lasted over 1 h, most of the emissions occurred within the first 30 min (Supplementary Fig. 9b). Therefore, firelighter and peat burning time scales were on the same order. Moreover, different household light fires on different times and quite often supplement

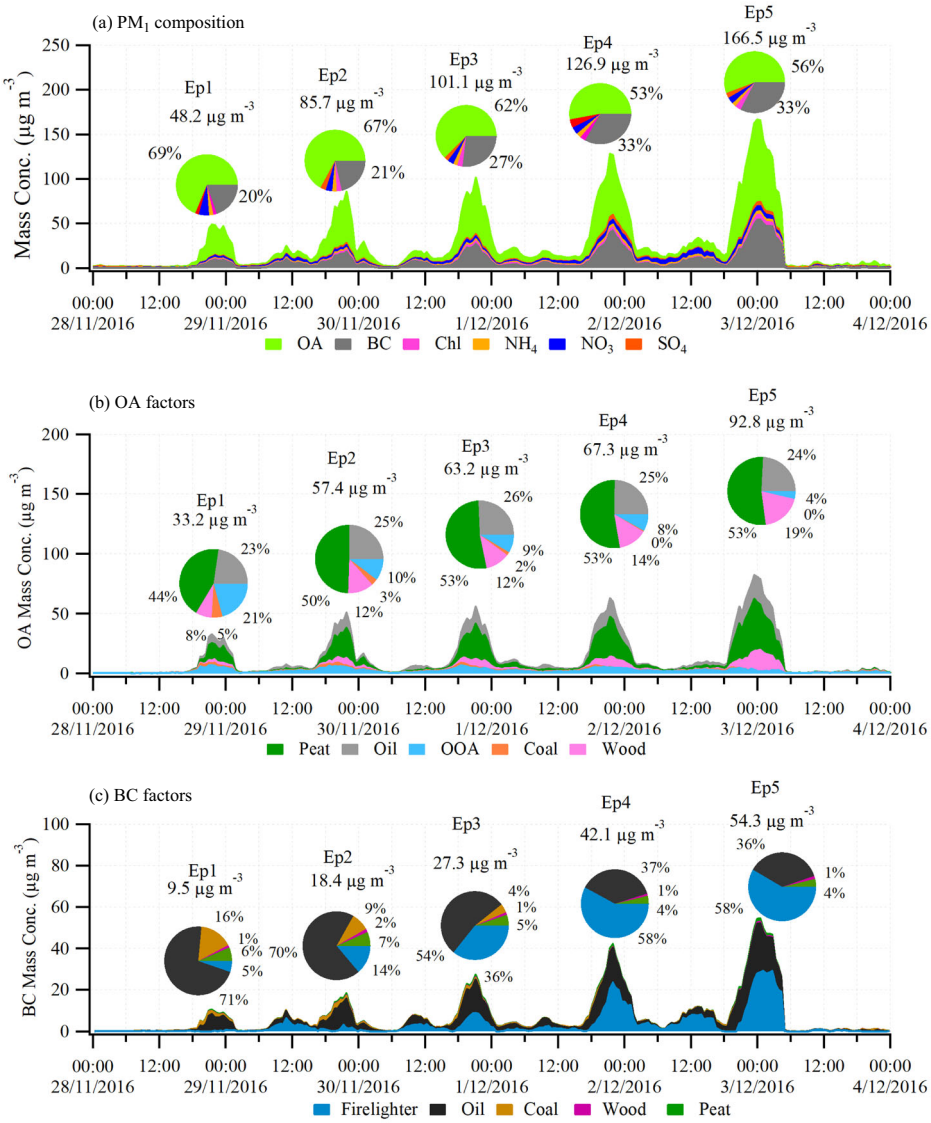


Fig. 1 Trends in concentration, composition, and sources of submicron aerosol in five self-concentrating pollution events in suburban Dublin. Time series of **a** PM_1 components, measured in suburban Dublin from 28 November to 4 December 2016 (full measurements are available in the supplementary). Inset pie charts are the relative fraction of the chemical composition in PM_1 during pollution episodes (i.e., Ep 1, 2, 3, 4, and 5). The values above the pie charts are the PM_1 concentration in each episode; **b** OA factors and the relative fraction of OA factors in episodes; and **c** BC factors and the relative contribution of BC factors in episodes. BC data was averaged to 30 min from the original time resolution of 1 min to match the time stamp of ACSM.

firelighters in the course of fire, therefore, BC and OA time evolutions can be difficult to detangle. Emissions from firelighters were, thus, deemed to be the potential source of this unexplained (51%, on average; Supplementary Fig. 6b) BC fraction, even though their use can be relatively small (3-10% of solid-fuel mass).

Note that the impact of traffic emissions was considered to be minor (<5%) in the evening events as derived from OA source apportionment, diurnal distributions of sources, and our previous study at the kerbside showing traffic emissions contributing mostly during rush hours (before 20:00)[27], while these episodes occurred in the hours of 20:00–24:00.

Figure 1c shows the estimated contribution of BC from the burning of oil, peat, wood, coal, and firelighters to the ambient BC during the five episodes with BC concentrations ranging from 9.5 to 54.3 μg m^{-3}. As discussed above, during episodic pollution events, the burning of biomass (peat and wood) contributed significantly (52-72%) to the OA, but its contribution to BC was <8% (2.8 μg m^{-3}; Fig. 1c). In contrast, oil and firelighter contributed substantially to BC, with oil-burning accounting for 36–72% (6.8–19.8 μg m^{-3}) of the total BC and firelighter accounting for 5–58% (0.5–31.7 μg m^{-3}). During the two most severe episodes (i.e., Ep 4 and Ep 5), firelighter burning contributed to over half (58% or 24.3–31.7 μg m^{-3}) of the BC. At the same time, peat and wood-burning contributions were the highest (67–72%) to the OA fraction. Therefore, the higher use of peat and wood fuels was accompanied by the higher consumption of firelighters, which then contributed substantially to the BC emissions.

The firelighter burning contributions were further evaluated by constraining their OA spectral profiles along with peat, wood, coal, and oil using the ME-2 model (Supplementary Fig. 10). Firelighters are made predominantly of peat or cellulose and kerosene

resulting in OA mass spectra similar to those of peat burning ($r = 0.91$ and slope = 0.92; Supplementary Fig. 10b) and oil-burning ($r = 0.87$ and slope = 0.55; Supplementary Fig. 10c). However, the unique combination of the two, and the difference from the mass spectra of the pure fuels at specific m/z's (range from <5% to >100%; Supplementary Fig. 10d) has enabled a separation of firelighter contribution to ambient OA concentrations. Firelighter contribution to OA was relatively minor but increased progressively with the growth in the solid-fuel usage: from <1% (0.1 μg m^{-3}) in Ep 1 to 12% (or 9.6 μg m^{-3}) in Ep 5 (Supplementary Fig. 10e), which is consistent with the increasing firelighter contribution to BC trends discussed above (from 5% (0.5 μg m^{-3}) in Ep 1 to over 50% (31.7 μg m^{-3}) in Ep 5.

The effect of uncertainties, arising from both the PMF (positive matrix factorization) modeling and the OA/BC ratio method, was evaluated. While the uncertainty from the PMF analysis was <10%, the uncertainties due to variations in OA/BC ratios for different burning and/or ambient conditions could be more significant[16]. Supplementary Table 4 provides the lower/upper limits of firelighter contributions to the total BC during the pollution episodes accounting for these variations in OA/BC ratios. For the most polluted case (i.e., Ep 5), firelighter BC contribution was in the range of 19–74%, strongly suggesting the significant contribution to BC concentrations coming from the firelighter burning albeit with large uncertainties associated with its attribution.

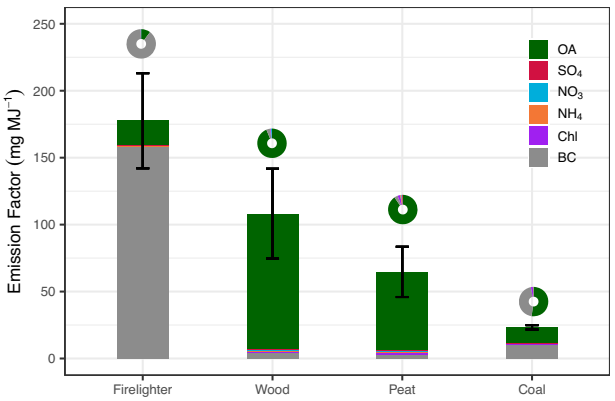


Fig. 2 Chemically speciated PM emission factors for firelighter and solid fuels. Emission factors for residential wood, peat, coal, and firelighter burning based on the direct ACSM and AE-33 measurement. Donut pie charts are the relative fraction of the chemical composition of direct particulate emissions from the tested fuels. Error bar stands for one standard deviation for the total EF.

Top-of-atmosphere radiative forcing due to firelighter BC

The extraordinarily high concentrations of BC are likely to perturb the radiative budget through both the increased scattering associated with the increase in non-absorbing pollution particles and the increased absorption associated with the increased BC. The net radiative forcing impact manifests itself in the top-of-atmosphere radiative forcing (ΔF) which is calculated for the air pollution episodes (referred to as the 'Firelighter' case here; Fig. 3), corresponding to the highest levels of BC, or absorbing aerosol encountered from solid-fuel burning. This is compared to a reference summer case (called 'reference' here, Fig. 3), with only minimal contribution from solid-fuel burning. As shown in Fig. 3a, the reference summer case aerosols exhibited cooling properties (ΔF of −16 W m^{-2}, mean value), whereas particles originating from the solid-fuel burning had a strong warming potential with a maximum positive ΔF of +149 W m^{-2} (mean value of +56 W m^{-2}). The warming was induced by absorbing aerosols, mainly BC, despite its less dominant contribution to the total aerosol load (~30%). The enhancement of BC absorption by internally mixed non-absorbing/absorbing compounds is a known phenomenon[6], where black carbon particles from biomass burning emissions exhibit a strong optical lensing effect leading to an absorption enhancement of up to 140%; i.e., coating of BC particles by other material causes enhanced refraction and reflection of the light, resulting in further absorption by the BC[36]. The warming effect of biomass burning aerosol emissions was also evident in the derived Absorption Aerosol Index (AAI), which showed higher median values (−0.16) during the heating season and firelighter events (−0.061) when compared to the summer values (~−0.69) (Supplementary Fig. 11).

A potential effect of the aforementioned warming is the alteration of the evolution of planetary boundary layer height (PBL), or specifically, the mixing layer (ML) which is shown in Fig. 3b. The relaxation of the ML height was stronger for the summer case throughout the night, presumably due to more cooling during the early morning hours/night and after 08:00, the ML height is seen to increase rapidly from 300 m to 800 m. In contrast, for the firelighter case, a modest rise from 500 m to 600 m is seen. Effectively, the profile of the mixing height is flattened and lowered in altitude by the altered dispersion of the BC and its impact on PBL dynamics.

ML heating at night is promoted by freshly emitted BC within the ML and is suppressed during the day by the BC aloft, contributing to the heating of the layers above the mixed PBL. This is the so-called dome effect[37], where particles remain in the residual layer above the mixing PBL from previous day emissions or transported from neighboring regions. These effects combined, leading to reduced vertical mixing in an increasingly more stabilized mixing layer, can produce this effect of enriching the fraction of BC in the ML leading to extraordinarily high concentrations and warming rates encountered.

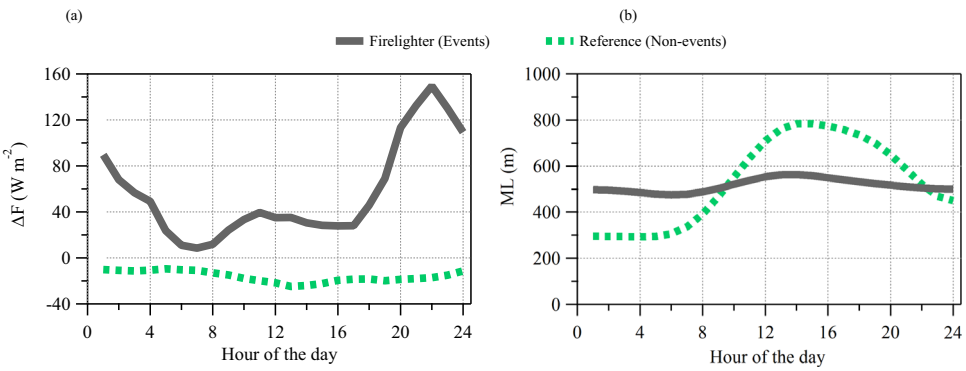


Fig. 3 Firelighter BC causes positive radiative forcing and impacts the evolution of planetary boundary layer. a Averaged diurnal variation of Top-of-Atmosphere radiative forcing (ΔF in W m^{-2}) over the entire firelighters case (Firelighter) and the reference summer case (Reference) with no pollution events observed; **b** diurnal variation of mixing layer (ML in m) during the firelighter and reference summer case.

DISCUSSION

Here we have shown another aspect of the use of biomass for space heating, where they not only contribute to the air quality deterioration directly, but the means of lighting them with solid firelighters adds disproportionally to this negative impact and even dominates the black carbon emissions with its own climate implications. The average BC concentrations (>7 μg m^{-3}) in a moderate and relatively clean European city, Dublin, are disconcerting and comparable to the heavily polluted cities in the world (e.g., 15.9 μg m^{-3} of BC in Dehli, India[38] and 5.5 μg m^{-3} in Beijing, China[39]; Supplementary Table 5). However, firelighter BC emissions have not been documented in any database including EDGAR, EMEP, TNO, NEI or RETRO[40].

In this study, BC emission from firelighter burning alone was estimated to be 0.025 ± 0.12 Gg yr^{-1} in the campaign year of 2016, approximately five times higher than that from the already documented source of fossil solid-fuel (Supplementary Fig. 12). Therefore, firelighter BC should not be overlooked or ignored in ambient air quality and climate studies where residential biomass burning OA (BBOA) is identified using conventional source apportionment methods[41]. For example, the reported OA to BC ratio for biomass burning was 3.6 in winter Paris[17], which is much lower than the values measured for wood burning or other biomass-based material (Supplementary Table 3), suggesting strong co-emitting BC sources other than biomass burning. Across Europe, biomass burning OA has been found in 19 out of 22 sites including both urban and non-urban sites[41]. Therefore, the means of lighting biomass, and the corresponding air quality and climate effects can be stronger than solely represented by the biomass burning OA fraction in total OA. In particular, biomass usage as a carbon-neutral energy source[42] is promoted in climate mitigation scenarios[43] resulting in high consumption over Europe and worldwide[19,44,45]. A rising trend in biomass consumption as a climate 'friendly' alternative to fossil fuels is observed and poses a real threat to our environment and health (Supplementary Fig. 12). Solid biomass fuels might potentially reduce greenhouse gas emissions; however, this reduction comes at the expense of clean air[46]. This has important implications for the energy budget, where, despite the potential reduction of net CO_2 emissions from biomass burning, it still contributes to the overall warming or positive radiative forcing due to BC released from firelighters that are required to ignite the biomass. Likewise, the net warming appears to also induce a positive feedback effect with ML[37], where ML evolution is flattened due to BC absorption within the residual BL and above it, at different times of the day, resulting in lower ML heights during pollution events that further reduces aerosol dispersion and mixing volume, enhancing the aerosol concentration, including that of BC. Any increase in the current 70 million households[47] using solid fuels over Europe would be followed by an increase in PM emissions, including both OA coming from fuels directly and BC from the firelighters.

While one can hardly regulate the use of firelighters directly, the promotion and direction towards solid biomass usage should discontinue now, which would also result in the reduction of the use of firelighters. Inexplicably, however, the recent trends show an opposite effect where biomass consumption is only increasing (Supplementary Fig. 12). The problem may lie in the fact that greenhouse gases are the subject of global agreements and air pollution control is attributed to local legislation authorities, therefore, these two issues (tackling climate change and mitigating air quality) are rarely addressed simultaneously[48,49]. More importantly, neither air pollution mitigation nor tackling climate change can be effective without sophisticated source apportionment of OA and BC or understanding their atmospheric interactions[13]. For example, despite increasing scientific evidence on biomass burning contribution to the air quality[50] and its effect on climate, with the smoke from biomass burning containing a mixture of both absorbing and scattering particles[6], it is still not in a focus of regulatory bodies. Likewise, present-day air quality and climate models do not have a comprehensive treatment of OA and, due to missing key sources of primary particles (firelighters and biomass burning as only one example; Supplementary Table 6) and secondary aerosol precursors/formation processes, result in an under-prediction of carbonaceous aerosol concentrations and their effects[51–53]. Next-generation Air Quality monitoring networks feeding into Air quality and Climate models that, in turn, inform both local and global policy are required to take place and confront the problem.

METHODS

Source measurement of direct emissions from solid-fuel burning

The details about the set-up of our lab burning experiments are available in Trubetskaya et al.[31]. Briefly, test fuels including sod peat (from Ireland), wood logs (softwood grown in Ireland), and coal (imported from Poland) were purchased from local outlets[31]. Solid firelighters were also purchased from a local outlet (TESCO Ireland) and were used to ignite these fuels. Solid firelighters are kerosene (EC No. 232-366-4)-based, containing high levels of hydrocarbons (C9-C12 alkanes). Such types of firelighters are commercially available in local outlets across Ireland (e.g., Tesco, DUNNES, and SuperValu)[23,26,54]. However, the use of kerosene-based firelighters is not just locally relevant because such types of firelighters are also commercially in many other countries in Europe[55–58], as well as in the United States and Canada[26]. Therefore, the use of kerosene-based firelighter represents one of the common ways for ignition in addition to the use of e.g., paper and sticks.

During the combustion experiments, test fuels were combusted in an Irish stove with no emission controls. The aerosol samples generated from the combustion of test fuels were collected using a sampling line connected to the chimney flue. The sampling line was made of ordinary ½ inch copper pipe which extended ~5 cm inside the chimney flue, parallel to air flow. $PM_{2.5}$ cyclone was deployed to remove coarse particles and a water trap was fitted downstream of the sampling line. This was followed by a Dekati diluter (Dekati Ltd.) that allowed a dilution rate in the range of 70-250:1. An ACSM (Aerodyne Research Inc.) and an Aethalometer (AE-33; Magee Scientific) were used to measure the chemical composition of submicron aerosol samples. A Nafion dryer was used to dry the aerosol particles before they entered the ACSM and AE-33. The time resolution of ACSM was set to 2 min while it was 1 min for AE-33. Firelighter (used for ignition) emissions were subtracted from the total emission during the burning of test fuels (typically 3.5 kg used) or not collected (after it burned out) when doing emission factor (EF) calculation (Supplementary Table 2). Firelighter burning (even only 0.1 kg was used; Supplementary Fig. 9a) emitted a large amount of BC. The emission factor calculated from online sampling showed consistency with offline filter measurements that collected all particles from start to end, and subtracted firelighter particles for EF calculation[31].

Ambient measurements in suburban Dublin

The ambient aerosol measurements were conducted at a suburban site in South Dublin using an ACSM and AE-33 with a time resolution of 30 min and 1 min, respectively. The sampling site is located in the Center for Science building in the University College Dublin (UCD) and is ~500 m away from the nearby road[13] (see the map in Supplementary Fig. 3). Ambient air was sampled at a height of around 30 m above the ground. Ambient aerosols were dried with a nafion dryer before they entered the ACSM. In the ACSM, non-refractory submicron aerosols (NR- PM_1; i.e., organic aerosol (OA), sulfate, nitrate, ammonium, and chloride) were vaporized on the heated surface (600 °C). Electron impact (70 eV) was used to ionize the NR- PM_1 vapor while a quadrupole

mass spectrometer was deployed to measure the resulting ions. AE-33 was deployed to measure black carbon (BC) sharing the same inlet as ACSM. AE-33 measured the light absorption of the collected aerosol samples on filter tapes at seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm)[59]. BC mass concentration was calculated from the change in optical attenuation at 880 nm using the mass absorption cross-section 7.77 $m^2\ g^{-1}$.

$PM_{2.5}$ data was obtained from the Irish EPA stations with a time resolution of 1 h or 24 h (See Supplementary Fig. 3). Meteorological parameters including temperature, relative humidity, wind speed, and wind direction were recorded at the meteorological stations (Irish meteorological service) of Dublin airport with a time resolution of 1 h. ML information was retrieved from the HYSPLIT model[60] using NOAA reanalysis data as input.

Source apportionment

Source apportionment of OA was performed with positive matrix factorization (PMF) using the multilinear-engine algorithm (ME-2). Details of the ME-2 modeling set-up was available from Lin et al.[30]. Briefly, the mass spectral profiles of wood, peat, and coal obtained from the source measurement were used as anchoring factor profile, along with hydrocarbon-like organic aerosol (HOA) from the literature. ME-2 modeling was performed with the toolkit of SoFi[61] using the a value approach (version 6.A1). The bootstrap resampling strategy with 100 runs was applied to evaluate the statistic uncertainties of the ME-2 solutions. Criteria including (1) multilinear regression between the BC and the heating-related factors in the evening hours from 8 pm to 11 pm; (2) the fraction of m/z 60 (i.e., f60) in the HOA profile, (3) as well as f60 in peat and wood-burning OA profile; and (4) f44 in OOA profile were applied to select the ME-2 runs which were, subsequently, averaged to get the most optimized solution. In total, five major OA factors of HOA, peat, wood, coal, and OOA were resolved (Supplementary Fig. 5). To further evaluate the OA contribution from firelighter (its major emission was BC), firelighter OA profile was added to the constraining list, forcing its separation from the already identified OA factors (Supplementary Fig. 10). Adding firelighter OA factor did not change the conclusion of biomass burning (wood + peat) being the major OA factor (Supplementary Fig. 10).

Radiative forcing calculations

Top-of-atmosphere radiative forcing (TOA-ΔF) calculations were performed following Haywood and Shine[62]—Eq. 1 below:

$$\triangle F = -DS_0T_{at}^2(1-A_c)\omega_0\beta\delta\left[(1-R_s)^2-\left(\frac{2R_s}{\beta}\right)\left(\frac{1}{\omega_0}-1\right)\right] \quad (1)$$

where S_0 is the solar constant (1370 W m^{-2}), D is the fraction day length (0.5), ω_0 is single scattering albedo, A_c is the fractional cloud cover (0.6), T_{at} is the atmospheric transmission (0.76), β is up-scatter fraction, δ is aerosol optical thickness, and R_s is the surface reflectance. Since the measurement location is inland R_s of 0.13 was taken assuming urban landscape with 10% canopy. ω_0, β, and δ were calculated using the Mie code[63] and with size distribution inputs from the Scanning Mobility Particle Sizer (SMPS), and chemistry (refractive index) inputs from the ACSM and Aethalometer measurements. Because parameters including the solar constant (S_0), the fraction day length (D), the fractional cloud cover (A_c), the atmospheric transmission (T_{at}), and the surface reflectance (R_s) were held constant (i.e., not varying with seasons), the differences in TOA-ΔF from different cases reflected the differences in the chemical composition and size distribution of aerosols from different sources.

Effective density (ρ_{eff}) was calculated using Eq. 2.

$$\rho_{eff} = \sum_{i=1}^{n} \rho_i * mf_i \quad (2)$$

where, ρ_i and mf_i are density and mass fraction of individual chemical compounds.

Effective refractive index (m), was calculated using Eq. 3 with inputs of mass fraction from the AMS and Aethalometer combined, and effective density of the size distribution. Refractive index of BC was taken from Liu et al.[64] and that of organic aerosol from Lu et al.[65].

$$m(\lambda) = \sum_{i=1}^{n} \frac{mf_i}{\rho_i} m_i(\lambda) \quad (3)$$

where mf_i is the mass fraction of the individual chemical species.

β was parameterized from the backscatter fraction (b). For the calculation of δ a well-mixed column of aerosols, with similar physical, optical, and radiative properties, was assumed from sea level up to boundary layer height.

Absorption aerosol index

Certain aerosol types, e.g., biomass-burning aerosols and desert dust, have their absorption spectra peaks in the near ultraviolet wavelength range[66]. This characteristic feature can be used as a fingerprint in identifying such aerosol types. Absorption aerosol index (AAI) quantifies this feature, enhanced absorption at ultraviolet wavelengths, of absorbing aerosols by taking the ratio of absorption at two characteristic wavelengths pairs e.g. 340 nm and 380 nm[67]. AAI for the present study was acquired from OMI onboard AURA satellite, GOME- MetOp-A Level 3 daily average data, using the TEMIS website (https://www.temis.nl/airpollution/absaai/).

DATA AVAILABILITY

The ACSM and AE-33 data are available in the EBAS repository (https://ebas.nilu.no/) and are also available from the corresponding author on request.

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AUTHOR CONTRIBUTIONS

C.L., J.O., and D.C. conceived and designed the experiments; C.L., A.T., J.O., and D.C. performed the experiments; A.V. performed the climate forcing calculation; C.L., J.O., A.V. analyzed the data; C.L., J.O., A.V., and C.O.'D. wrote the manuscript with input from all co-authors.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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