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The atmospheric lifetime of black carbon

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Abstract

Black carbon (BC) in the atmosphere contributes to the human health effects of particulate matter and contributes to radiative forcing of climate. The lifetime of BC, particularly the smaller particle sizes ($PM_{2.5}$) which can be transported over long distances, is therefore an important factor in determining the range of such effects, and the spatial footprint of emission controls. Theory and models suggest that the typical lifetime of BC is around one week.

The frequency distributions of measurements of a range of hydrocarbons at a remote rural site in southern Scotland (Auchencorth Moss) between 2007 and 2010 have been used to quantify the relationship between atmospheric lifetime and the geometric standard deviation of observed concentration. The analysis relies on an assumed common major emission source for hydrocarbons and BC, namely diesel-engined vehicles. The logarithm of the standard deviation of the log-transformed concentration data is linearly related to hydrocarbon lifetime, and the same statistic for BC can be used to assess the lifetime of BC relative to the hydrocarbons. Annual average data show BC lifetimes in the range 4 to 12 days, for an assumed OH concentration of 7×10^5 cm^{-3}. At this site there is little difference in BC lifetime between winter and summer, despite a 3-fold difference in relative hydrocarbon lifetimes. This observation confirms the role of wet deposition as an important removal process for BC, as there is no difference in precipitation between winter and summer at this site. BC lifetime was significantly greater in 2010, which had 23% less rainfall than the preceding 3 years.

Highlights

- Hydrocarbon and black carbon concentrations are log-normally distributed
- Standard deviation of log(concentration) of hydrocarbons correlates with lifetime
- Black carbon lifetimes, by analogy, are between 4 and 12 days at this site
- Black carbon lifetime is determined by rainfall, and similar in summer and winter

Keywords

Air quality monitoring, global climate models, aethalometer, hydrocarbon lifetime.

1. Background

Systematic measurements of black particles from combustion, variously referred to as 'soot', 'black smoke' or 'black carbon' started in London towards the end of the 19th century (Harrison, 2006), although the poor air quality in London was recognised several centuries earlier, e.g. John Evelyn's 1661 pamphlet, *Fumifugium* (Jenner, 1995). Measurements of 'smoke' in Kew Gardens a century ago were more than 100 times larger than values observed since 2000. More recent recorded changes in 'black smoke' between 1962 and 2000 reflect changes in emissions and types of source. The primary source of BC emissions in the UK is now diesel engines (Novakov and Hansen, 2004). Measurement methods have changed over time, and attempts have been made to reconcile long-term datasets where different methods overlap (Harrison, 2006). Modern urban measurements often rely on light transmission data from an aethalometer (Hansen et al., 1984). 'Black smoke' measurements in the UK have been cross-referenced to aethalometer data (Quincey et al., 2011), but the current values of 'black carbon' (BC) are still operationally defined in terms of the measurement methods, even if greater attention is paid nowadays to size-selective sampling, and interferences from organic particulate matter. Decreases in 'elemental carbon' (EC) concentrations have been observed elsewhere, e.g. in the USA (Murphy et al., 2011). The relationship between BC and EC has been explored (Ahmed et al., 2009), showing that the terms are not synonymous. A suggestion has been made that BC measured by an aethalometer should be referred to as 'black carbon equivalent' (BCe) (Hyvärinen et al., 2011), but in this paper the term BC will be used.

BC has an obvious impact on the environment in terms of aesthetics and degradation of structures (blackened buildings in cities), but more important is its impact on human health (see e.g. (WHO, 2003)). With recent improvements in air quality in western Europe and North America, such issues are less important than in the developing world, where BC, particularly indoors from cooking and heating, poses a major threat to health (Ramanathan et al., 2011). On a global scale, BC is an important contributor to radiative forcing (Forster et al., 2007; Ramanathan and Carmichael, 2008), being involved in direct climate forcing, and also in aerosol indirect forcing (Chen et al., 2010) and semi-direct effects on cloud cover (Koch and Del Genio, 2010). Recent interest in BC has been stimulated by the possibility of rapid managed decreases in the rate of climate change which could be achieved by controls on the emissions of BC, delivering simultaneous beneficial effects on human health, particularly in source regions (Shindell et al., 2012). Calculation of the short-term response to such controls was achieved by considering global climate models where the roles of BC and tropospheric ozone were simulated under a wide range of different scenarios. The footprint of the effects of BC clearly depends on its lifetime in and removal from the atmosphere.

Early measurements of 'soot' showed similar long-range transport behaviour to sulphate aerosol, with transport distances of 1000 km or more, and implied removal by precipitation scavenging (Rodhe et al., 1972). The following quarter-century saw a large increase in research on 'carbonaceous aerosols' (Penner and Novakov, 1996), and an overview of more recent research is provided by Strawa et al. (Strawa et al., 2010). Despite a general

understanding that BC is primarily removed from the atmosphere by wet deposition, recent measurements show that scavenging ratios for elemental carbon (EC) were much smaller than for sulphate (Cerqueira et al., 2010). However, measurements of air and precipitation composition at individual sites cannot necessarily determine whether the measured aerosol composition reflects the air mass in which the precipitation formed, as was evident from the data from Portugal, which showed very low scavenging ratios for EC. Although EC may be hydrophobic when emitted, it acquires hydrophilic characteristics by incorporation in mixed aerosol and/or surface oxidation (a process referred to as 'BC ageing') and participates in cloud processes. However, direct measurements in cloud water have indicated that only a small fraction of BC is internally mixed, and that cloud scavenging of BC may not be very efficient (Chylek et al., 1996).

The atmospheric lifetime of BC relative to both wet and dry deposition is usually assumed to be around one week (Ramanathan and Carmichael, 2008). This estimate is consistent with global model estimates of around 5d, based on the ECHAM5-HAM model (Stier et al., 2005); an estimate of 8d as a global average is obtained from the ratio of column burden to sources in an earlier version of the ECHAM model (Lohmann et al., 1999). However, the need for more relevant measurements of BC ageing has been noted. Despite the relatively small effect of scavenging ratio for BC on a global scale, the impact of sulphate aerosol on BC ageing, and therefore its role in clouds and removal rate, is regionally very important in determining BC lifetime, and therefore its radiative properties (Stier et al., 2006).

2. Methods

2.1. Black carbon

This study used a single-wavelength (880 nm) Aethalometer^{TM} (Model AE-16, Magee Scientific, Berkeley, CA, USA), with a $PM_{2.5}$ sampling inlet, which measures the light attenuation by particles trapped on a quartz fibre tape which is advanced automatically once the attenuation reaches a pre-set value. Values of BC were recorded every 5 minutes, as reported using the manufacturer's algorithm, and corrections were subsequently made to the data to account for changes in attenuation with the accumulation of material on the quartz fibre tape (Virkkula et al., 2007), but using a 30-minute average before and after tape advance. In this approach, the correction is empirical, and based on the rate of change in attenuation when a new area of quartz tape is exposed, on the assumption that air concentrations are constant before and after. This correction was performed manually to avoid artefacts caused by transient peaks in concentration. The correction is expressed as a factor k in the equation:

$$BC_{corrected} = (1 + k.ATN).BC_{aethalometer} \quad (1)$$

where ATN is the recorded attenuation every 5 minutes, and k is calculated to normalize the measured concentration before and after the tape advances. k is typically around 0.002.

2.2. GC-FID analysis of hydrocarbons – details

Hourly samples of air were taken using a cooled trap (Perkin Elmer TurboMatrix [Perkin Elmer, Cambridge, UK], sorbent trap Carbopack^{TM} B + Carbosieve^{TM} SIII [Sigma-Aldrich, Poole, UK] held at -30 °C, air flow rate 20 ml min^{-1}), followed by thermal desorption into a gas chromatograph (Perkin Elmer Clarus 500) fitted with two columns (50m x 0.22 mm x 1µm methyl silicone [BP1, SGE Europe Ltd., Milton Keynes, UK] and 50m x 0.32 mm alumina/Na_2SO_4 PLOT [Thames Restek UK Ltd, Saunderton,UK]) and dual flame ionization detection, and operated as part of the UK Automatic Hydrocarbons Network (http://uk-air.defra.gov.uk/networks/network-info?view=hc). Routine calibration (twice monthly) was carried out using a NPL 30 component EC mixture [National Physical Laboratory, Teddington, UK]. Chromatograms were analysed using custom software [Matchfinder, AEA Technology, Harwell, UK].

2.3. Site description

Measurements were made, starting in June 2006, at Auchencorth Moss, one of the two 'supersites' in the U.K. that report to EMEP (UNECE European Monitoring and Evaluation Programme, www.emep.int). The site is located on open moorland, approximately 20 km south of Edinburgh in central Scotland (lat. 55°47'30"N, lon. 3°14'35"W) at an elevation of 267 m asl. In the prevailing wind direction, to the south-west, the closest major emission source is 220 km away (Belfast, N.Ireland), while the city of Edinburgh and the small towns in the county of Midlothian to the north and north-east are emission sources from traffic and domestic coal combustion. There is a coal-fired power station (Cockenzie) ca. 25 km to the north-east, and another (Longannet) ca. 40 km to the north-west. The nearest major road runs north:south approximately 1.5 km to the east of the site, with relatively low traffic flow (7000 vehicles d^{-1}; http://www.dft.gov.uk/traffic-counts/cp.php?la=Midlothian).

3. Theory

Interest in the lifetimes of substances transported through the atmosphere, in terms of the statistical distribution of measured values at a point, goes back to the work of Junge (1974). His ideas were further developed (Jobson et al., 1999; Jobson et al., 1998) to the more general form expressed in terms of the standard deviation of the natural logarithm of the mixing ratio ($\sigma_{\ln(\chi)}$) for short-lived gases which are removed from the atmosphere by first-order, or pseudo-first-order, removal rates. The relationship is expressed as:

$$\sigma_{\ln(\chi)} = A\,\tau^{-b} \qquad (2)$$

where τ is the lifetime of the species in question and A is a fitting parameter. The exponent b has a value between 0 and 1, and indicates the relative importance of turbulent mixing and chemical reaction in the air mass upwind of the measurement point. A value for b of 0 represents the situation where the measurement point is close to sources, while a value of b close to 1 is more typical of remote oceanic environments. The relationship has been demonstrated to hold for a wide range of data, with values of b ranging from 0.28 (Boulder, Colorado) to 0.56 (Chebogue Point, Nova Scotia) (Jobson et al., 1998), and up to 0.97 for the

Airborne Southern Hemisphere Ozone Experiment (Jobson et al., 1999). The exponent *b* appears to be characteristic of the site, and does not vary between summer and winter, even though lifetimes (e.g. of alkanes to reaction with hydroxyl (OH) radical) can vary between seasons by an order of magnitude. A similar seasonal constancy was observed in a subsequent application of the approach, in this case to estimate the OH concentration based on the known loss rate of radon (Williams et al., 2001). Even where there are no 'known' lifetimes available (removal of Rn), the approach has been used to estimate OH concentrations in continental (Bartenbach et al., 2007; Karl et al., 2001) and coastal air (Williams et al., 2000), using lifetimes based on removal rates through photolysis, reaction with OH and reaction with ozone (O_3). Necessarily, the interpretation of the relationship assumes common sources of the trace gases used, and sufficiently slow reaction rates that measured concentrations at the measurement site are above the limit of detection of the measurement system. The lifetime provides an estimate of the average loss rate integrated over the path from emission to measurement, and should be directly comparable with the lifetime expressed as τ = (atmospheric burden) / (emission rate) used by modellers.

In this study we use the empirical measurements of $\sigma_{\ln(\chi)}$ for a range of hydrocarbons, where the main loss rate is through reaction with OH (rather than photolysis or reaction with O_3), measured at the Auchencorth Moss site to establish the parameters *A* and *b* in equation (1), and apply these to the $\sigma_{\ln(\chi)}$ for BC to estimate BC lifetime. Although BC is not removed from the atmosphere by reaction with OH, its average removal rate can be considered as effectively first-order, through the stochastic scavenging in cloud and precipitation along the path from emission to measurement. Given that vehicle diesel engine emissions are the major source of BC in western Europe (Novakov and Hansen, 2004) it is not unreasonable to assume that the spatial emission patterns of hydrocarbons and BC are similar, and that both pollutants follow similar atmospheric pathways. In the calculations below we have used an annual average estimated value for (OH) relevant to northern hemisphere mid-latitudes of 7 x 10^5 cm^{-3}, with a factor of 3 difference between winter (3.5 x 10^5 cm^{-3}) and summer (1.05 x 10^6 cm^{-3}), based on two 6-month averages (Goldstein et al., 1995). In practice, the parameter *b* in equation (1) does not depend on the actual (OH) assumed, but the scaling factor *A*, and the absolute estimate of the lifetime, do depend on the value chosen.

The values of $\sigma_{\ln(\chi)}$ are derived from $\ln(\chi)$ vs. normal-probability (*z*) plots, where the effective lower limit of quantitation can be assessed from the measurement data themselves in terms of marked deviation from linearity at low concentrations. In practice, data points at the upper end of the distribution may deviate from a pure log-normal distribution because of the influence of local sources, so the estimate of $\sigma_{\ln(\chi)}$ has been made from the slope of $\ln(\chi)$ vs. *z* for values of *z* excluding the highest 1% of the data. This method allows the use of measurements for hydrocarbons where a significant proportion of the measurement data falls below the limit of detection. An example, for n-butane in 2010, is shown in Figure 1.

4. Results

4.1. BC data

Data from the 4 years 2007 to 2010 have been analyzed as separate datasets and as a combined dataset. Summary statistics for each of the years are given in Table 1 for the corrected data (see section 2.1 above). The correction factor *k* varied systematically throughout the year in each of the 4 years (Figure 2), showing a similar seasonal pattern and magnitude to the values found at Hyytiälä, Finland (Virkkula et al., 2007).

BC data were then aggregated from 5-minute values to hourly averages, to match the sampling frequency of the hydrocarbons. Geometric mean and standard deviation did not vary much from year to year (Table 1). The average wind speed and direction at the site are shown in Figure 3, where the predominant SW flow is clearly seen.

Average BC concentrations showed the highest values in (infrequent) SE flow (Figure 4), possibly from the nearest major road, but also from air masses originating in continental Europe. Sources of BC to the NE (Edinburgh and local small towns) and the NW (power station) can also be identified. Similar spatial patterns were observed for the hydrocarbons (data not shown). In order to minimise the contribution from local sources and ensure a well-mixed boundary layer, the data for both BC and hydrocarbons were filtered to include only data with a SW local wind direction (180-270°), and wind speed above 2 m s^{-1}. This had only a small effect on the overall statistical distribution of the data (Table 1), but with systematically lower (geometric) mean concentrations from the cleaner SW sector. These filtered datasets are used for the lifetime analysis. Average BC concentrations over 2007-2010 were higher in winter than in summer (geometric mean 0.12 μg m^{-3} for April-September and 0.17 μg m^{-3} for October-March); the average diurnal, seasonal and day-of-week patterns are shown in Figure 5, with the seasonal pattern of rainfall.

The diurnal pattern shows little evidence of large traffic-related emissions in morning and evening, as expected for a site remote from emissions, but is dominated by the diurnal cycle in mixing depth. The depletion of a shallower boundary layer during the night is followed by incorporation of BC from higher in the troposphere as overnight temperature inversions are broken up in the morning. The average rate of decrease after midnight can be used to estimate an approximate dry deposition velocity of 0.8 mm s^{-1}, based on a nocturnal boundary layer depth of 50 m. This deposition velocity is consistent with average night-time values measured for particles at the same site of <0.5 mm s^{-1}, given that the size range of BC within the $PM_{2.5}$ sampling cut-off is not known, and that the deposition velocity varies significantly with particle size in the sub-micron range (Nemitz et al., 2002).

There was a relatively small (but measurable) effect of day-of-week, but without the expected clear distinction between weekend and working day that would be observed for a site dominated by local sources. Although the minimum is on Sunday, the data suggest a time lag and smoothing, with average transport times of around 1 day from emission.

The seasonal pattern may reflect different mixing-layer depths, long-range transport patterns, rates of removal between emission and measurement and/or seasonal variations in emissions, although the latter are likely to be small if dominated by vehicle emissions. The seasonal concentration pattern is inversely related to that for rainfall, implying that BC is removed in wet deposition. However, rainfall at the site may not necessarily be a good predictor of rainfall along the air mass trajectory from the emission source, and the occurrence of rain may reflect systematic differences in air mass trajectories, and potentially different source areas. Nevertheless, there was a highly significant effect ($p < 10^{-6}$, t-test with unequal variances) of rainfall at the site on BC concentrations; on days with no rain the ratio of concentrations of BC to ethane (the longest-lived of the hydrocarbons) had a geometric mean of 0.13, while on days with at least 1 mm rainfall the geometric mean ratio was 0.07. Assuming a constant emission ratio, this implies that removal rates by rainfall were approximately double those on dry days.

4.2 Hydrocarbon data

All the hydrocarbons used in this study showed approximately log-normal frequency distributions (Figure 1), with the values of σ_{lnX} and geometric mean as shown in Table 2. A wider range of hydrocarbons was available after 2007 when data processing was improved and lower limits of detection became possible. Where the number of samples above the limit of detection was too small (< 50%) the data were not used in estimating lifetimes (τ). The reaction rates with (OH) at 283K (Atkinson et al., 2006) were combined with the assumed annual average OH concentration of 7×10^5 cm^{-3} to give the lifetimes in Table 2. Only hydrocarbons for which the main loss process is reaction with OH, rather than with O_3 or by photolysis, are used.

An example of the relationship between $\ln(\sigma_{lnX})$ and $\ln(\tau)$ is shown in Figure 6. The exponent of equation 2 (*b*) has the value 0.33, similar to continental remote sites, as noted above. Also shown is the value of σ_{lnX} for BC for the same year, and the estimated lifetime. Values for each of the 4 years are summarised in Table 3. The variation between years is small for 2007 to 2009, but the larger estimate in 2010 is beyond the 95% confidence interval of the predictions for earlier years. The most obvious explanation is related to rainfall in each of the years (Table 3); there was 23% less rain in 2010 than the average of the preceding 3 years.

There is a marked difference in behaviour in summer and winter; in summer (April – September) the OH concentrations are assumed to be 3 times the average for the winter 6 months (see above). This leads to different hydrocarbon lifetimes; 0.5 and 1.5 times those given in Table 2, in summer and winter, respectively. An example of the difference between summer and winter is shown in Figure 7 for 2009. Note that the hydrocarbon lifetimes are longer in winter, but the BC lifetime is shorter (Table 3), emphasising the different seasonal patterns of removal through OH reaction (hydrocarbons) or wet deposition (BC). However, the seasonal rainfall pattern in 2009 does not support the seasonal difference in BC lifetime. This implies that other factors may be important, including the seasonal ratio in (OH). If both summer and winter hydrocarbon data sets are constrained to the same fitted line, the BC

lifetime is similar in winter and summer at 6-8 days. Changing the ratio of summer (OH) to winter (OH) from the value of 3 (assumed here) does not change the slopes of the fitted lines in Figure 7, but moves the datasets parallel to the horizontal axis. Fitting a single regression line to both summer and winter data gives a smaller range in BC lifetimes (8d summer, 6d winter) but with larger associated uncertainties (Table 3). The relatively small effect of the chosen OH concentration ratio (summer:winter) can be assessed by allowing this parameter to vary so that the regression is optimised (maximum value of correlation coefficient), when the BC lifetime becomes 10d summer, 7d winter, and the OH concentration ratio increases from 3 to 6.3, i.e. (OH) = 1.9 x 10^5 cm^{-3} in winter and 1.2 x 10^6 cm^{-3} in summer (Figure 8). The BC lifetimes in Table 3 are inversely proportional to the chosen value for average OH concentrations, i.e. if (OH) were doubled, the estimated BC lifetime would be halved.

5. Discussion

The 'black carbon' measured by an aethalometer is not the same as elemental carbon (EC), and to some extent BC is defined by its means of measurement. However, there is a very close relationship between 'aethalometer BC' and other measures of BC and EC in the atmosphere. Measurements of BC by different methods over a 2-week study in rural air (ten Brink et al., 2004) differed in their absolute concentrations by a factor of 2, despite high correlations; the aethalometer BC concentration data agreed well with the average of all the methods for measuring EC, especially at lower concentrations. A subsequent study on BC and EC in urban air (1-5 μg m^{-3}) compared 8 different techniques using daily data over 25 d (Hitzenberger et al., 2006). The average reported concentrations were similar for all methods, including an aethalometer, but the reason for poor temporal correlations between some of the methods was not further explored. Comparisons of aethalometer and filter data for BC showed excellent correlations at 3 sites in the north-eastern USA and at a rural site in Turkey, although the quantitative comparisons varied across sites (Ahmed et al., 2009).

In a UK context, measurements of 'Black Smoke' provide a historical record going back over 50 years, and studies of the relationship between these data and other measures of BC and EC have been conducted (Quincey et al., 2009). Good qualitative agreement of aethalometer data with EC and 'Black Smoke' measurements was seen at the kerbside site, and a preliminary investigation of daily filter data with the aethalometer at Auchencorth in 2006 suggested that the filter method was under-reading at the low rural concentrations. A more detailed study of the relationship between 'Black Smoke' and aethalometer BC (Quincey et al., 2011) showed good correlations between the two types of measurement.

Routine measurements of BC in $PM_{2.5}$ are made across the UK using aethalometers, at a range of different sites from kerbside to rural, with annual average BC concentrations from 8.8 μg m^{-3} in London, to 0.5 μg m^{-3} at Harwell and 0.8 μg m^{-3} at Folkestone, the latter two sites being designated 'rural' (Butterfield et al., 2011). Analysis of the Harwell data for 2010 using a criterion of hours with mean wind speed exceeding 2 m s^{-1} for direct comparison with Auchencorth, gives a geometric standard deviation of 2.46 and a geometric mean concentration of 0.4 μg m^{-3} (cf. Table 1). The Auchencorth site in this context is best

described as 'remote rural'; the geometric mean concentrations are given in Table 1 and correspond to annual arithmetic means (for comparison with UK network data) of 0.25 to 0.28 μg m^{-3}. The nearest site in the network to Auchencorth is a suburban site in Edinburgh, with an annual mean (2010) of 1.2 μg m^{-3}, showing the large differences that occur over relatively short distances (ca. 20 km) between urban and rural areas.

Rural UK concentrations are similar to those observed elsewhere in Europe, with similar statistical characteristics. The geometric standard deviation for BC measured at a rural coastal site in Lithuania (East Baltic) in 2008/9, derived from the published percentile data (Bycenkiene et al., 2011), was 2.23, with geometric mean of 0.4 μg m^{-3}. This paper also presented a summary of global measurements of BC concentrations. Recent measurements at 5 sites in rural Finland showed concentrations ranging from 0.05-0.07 μg m^{-3} in the remote Arctic to maximum values in winter in south-east Finland (Virolahti) of 0.4 μg m^{-3} (Hyvärinen et al., 2011). Closer to the UK, measurements at Mace Head on the west coast of Ireland between 1989 and 1996 gave annual geometric mean concentrations in the 'clean sector', i.e. for wind direction between 180° and 300°, between 0.01 and 0.02 μg m^{-3}, with geometric standard deviations between 2.14 and 2.86 (Cooke et al., 1997). Subsequent data up to 1998 showed values below 0.1 μg m^{-3} for over half the time with a strong dependence of concentrations on air mass origin. For comparison, at Auchencorth, concentrations were below 0.1 μg m^{-3} for 11% of the time. Lowest average concentrations at Mace Head (0.05 μg m^{-3}) were seen in westerly Atlantic trajectories and the highest (1.0 μg m^{-3}) in south-easterly trajectories. The measurements were used to calculate the European emissions of BC (Derwent et al., 2001). It was suggested that removal rates by dry deposition of long-range transported BC would be around 10% d^{-1}, i.e. a lifetime of around 10 d. The vertical distribution of BC in the boundary layer was investigated in a series of summertime aircraft flights around the UK, and showed that refractory BC aerosol had concentrations between 0.05 and 0.3 μg m^{-3} with higher concentrations close to sources and in the lower part of the atmosphere, and values around 0.005 μg m^{-3} at altitudes over 2000m (McMeeking et al., 2010). Concentrations in the boundary layer were lowest (0.02 – 0.06 μg m^{-3}) over the North Sea in north-easterly air flow, similar to the mean concentrations seen in clean Atlantic air at Mace Head.

The inverse dependence of BC concentrations on precipitation, implying an important role for wet deposition as a removal mechanism for BC, was noted in the Mace Head data (Cooke et al., 1997), where long-range transported BC and weather systems leading to precipitation were likely to be spatially correlated. At Auchencorth, the small difference between summer and winter BC lifetimes (Table 3) reflects the lack of a pronounced summer:winter difference in precipitation amount measured at the site, with 450 ± 60 mm in summer and 470 ± 70 mm in winter (error is standard deviation over 4 years 2007-2010). Although most precipitation at the site occurs in south-westerly (Atlantic) flow, the air mass trajectories of BC and rain-producing clouds are unlikely to be identical, and BC lifetime will be determined by deposition along the trajectory and not simply as measured by the local precipitation amounts. Nevertheless, the increased lifetime estimated for 2010 relative to the preceding years is associated with a large decrease in annual rainfall amount in 2010.

It should be noted that lifetimes calculated using the methods presented here are not directly comparable for different measurement periods, i.e. the separately calculated lifetimes for summer and winter in 2009 (Table 3) cannot be simply averaged to obtain the annual average lifetime. Care must therefore be taken in using such datasets to infer lifetimes for one period from measurements made over a different period.

6. Conclusions

The availability at the same site of meteorological data, BC measurements and concentrations of a range of VOCs has made possible an estimate of BC lifetime, on the assumption that the emission sources of the major VOCs and of BC in the $PM_{2.5}$ size range are similar, which appears to be reasonable for western Europe. There is also a necessary assumption that the loss rates, and therefore lifetimes, of both VOCs and BC are first-order processes, with sufficiently slow removal rates that differences in day-time and night-time removal rates, important for VOC removal by OH radical reaction, can be averaged along the air mass trajectory between source and measurement site. The suite of VOCs chosen for this exercise is limited to those for which the major removal process is oxidation by OH rather than by ozone or NO_3 radicals. Necessarily, the largest uncertainty is in the effective average OH radical concentration to use, and its seasonal variation. Despite an assumed 3-fold variation between winter and summer in the OH concentration, and therefore in the calculated VOC lifetimes, the calculated lifetime for BC is similar between the two half-year periods, reflecting the very different removal mechanisms for BC from the atmosphere (wet and dry deposition). The absolute lifetime depends proportionately on the assumed OH concentration of 7×10^5 cm^{-3} as an annual average. The lifetimes (4–12 d) vary between years, possibly reflecting different weather patterns and rainfall amounts.

The estimated BC lifetime at this site is consistent with previous estimates of 5 to 8 days as global averages, and with average transport distances in excess of 1000 km or more (Bycenkiene et al., 2011; Rodhe et al., 1972). The calculated lifetimes are likely to be site-dependent, but the method is applicable to any site having the appropriate long-term measurements available, and remote from confounding local sources.

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8. References

Ahmed, T., Dutkiewicz, V.A., Shareef, A., Tuncel, G., Tuncel, S., Husain, L., 2009. Measurement of black carbon (BC) by an optical method and a thermal-optical method: Intercomparison for four sites. Atmospheric Environment 43, 6305-6311.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., Troe, J., Subcommittee, I., 2006. Evaluated kinetic and photochemical

data for atmospheric chemistry: Volume II-gas phase reactions of organic species. Atmos. Chem. Phys. 6, 3625-4055.

Bartenbach, S., Williams, J., Plass-Dülmer, C., Berresheim, H., Lelieveld, J., 2007. In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive two-dimensional gas chromatography (GCxGC-FID): use in estimating HO and NO_3. Atmos. Chem. Phys. 7, 1-14.

Butterfield, D., Beccaceci, S., Sweeney, B., Williams, M., Fuller, G., Green, D., Grieve, A., 2011. 2010 Annual Report for the UK Black Carbon Network. National Physical Laboratory, Teddington, Middlesex (http://uk-air.defra.gov.uk/reports/cat05/1108251248_2010_BC_Network_Report.pdf)

Bycenkiene, S., Ulevicius, V., Kecorius, S., 2011. Characteristics of black carbon aerosol mass concentration over the East Baltic region from two-year measurements. Journal of Environmental Monitoring 13, 1027-1038.

Carslaw, D.C., Ropkins, K., 2012. openair — an R package for air quality data analysis. Environmental Modelling & Software. Volume 27-28, 52-61.

Cerqueira, M., Pio, C., Legrand, M., Puxbaum, H., Kasper-Giebl, A., Afonso, J., Preunkert, S., Gelencsér, A., Fialho, P., 2010. Particulate carbon in precipitation at European background sites. Journal of Aerosol Science 41, 51-61.

Chen, W.T., Lee, Y.H., Adams, P.J., Nenes, A., Seinfeld, J.H., 2010. Will black carbon mitigation dampen aerosol indirect forcing? Geophysical Research Letters 37.

Chylek, P., Banic, C.M., Johnson, B., Damiano, P.A., Isaac, G.A., Leaitch, W.R., Liu, P.S.K., Boudala, F.S., Winter, B., Ngo, D., 1996. Black carbon: Atmospheric concentrations and cloud water content measurements over southern Nova Scotia. Journal of Geophysical Research 101, 29105-29110.

Cooke, W.F., Jennings, S.G., Spain, T.G., 1997. Black carbon measurements at Mace Head, 1989-1996. J. Geophys. Res. 102, 25339-25346.

Derwent, R.G., Ryall, D.B., Jennings, S.G., Spain, T.G., Simmonds, P.G., 2001. Black carbon aerosol and carbon monoxide in European regionally polluted air masses at Mace Head, Ireland during 1995-1998. Atmospheric Environment 35, 6371-6378.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. Changes in atmospheric constituents and in radiative forcing, in: Solomon, S., et al. (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.

Goldstein, A.H., Wofsy, S.C., Spivakovsky, C.M., 1995. Seasonal variations of nonmethane hydrocarbons in rural New- England-constraints on OH concentrations in Northern midlatitudes. Journal of Geophysical Research-Atmospheres 100, 21023-21033.

Hansen, A.D.A., Rosen, H., Novakov, T., 1984. The aethalometer — An instrument for the real-time measurement of optical absorption by aerosol particles. Science of the Total Environment 36, 191-196.

Harrison, R.G., 2006. Urban smoke concentrations at Kew, London, 1898-2004. Atmospheric Environment 40, 3327-3332.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L., Puxbaum, H., 2006. Intercomparison of thermal and optical measurement methods for elemental carbon and black carbon at an urban location. Environmental Science & Technology 40, 6377-6383.

Hyvärinen, A.P., Kolmonen, P., Kerminen, V.M., Virkkula, A., Leskinen, A., Komppula, M., Hatakka, J., Burkhart, J., Stohl, A., Aalto, P., Kulmala, M., Lehtinen, K.E.J., Viisanen, Y., Lihavainen, H., 2011. Aerosol black carbon at five background measurement sites over Finland, a gateway to the Arctic. Atmospheric Environment 45, 4042-4050.

Jenner, M., 1995. The politics of London air John Evelyn's *Fumifugium* and the Restoration. The Historical Journal, 38, 535-551.

Jobson, B.T., McKeen, S.A., Parrish, D.D., Fehsenfeld, F.C., Blake, D.R., Goldstein, A.H., Schauffler, S.M., Elkins, J.C., 1999. Trace gas mixing ratio variability versus lifetime in the troposphere and stratosphere: Observations. Journal of Geophysical Research-Atmospheres 104, 16091-16113.

Jobson, B.T., Parrish, D.D., Goldan, P., Kuster, W., Fehsenfeld, F.C., Blake, D.R., Blake, N.J., Niki, H., 1998. Spatial and temporal variability of nonmethane hydrocarbon mixing ratios and their relation to photochemical lifetime. Journal of Geophysical Research-Atmospheres 103, 13557-13567.

Junge, C.E., 1974. Residence time and variability of tropospheric trace gases. Tellus 26, 477-488.

Karl, T., Crutzen, P.J., Mandl, M., Staudinger, M., Guenther, A., Jordan, A., Fall, R., Lindinger, W., 2001. Variability-lifetime relationship of VOCs observed at the Sonnblick Observatory 1999-estimation of HO-densities. Atmospheric Environment 35, 5287-5300.

Koch, D., Del Genio, A.D., 2010. Black carbon semi-direct effects on cloud cover: review and synthesis. Atmospheric Chemistry and Physics 10, 7685-7696.

Lohmann, U., Feichter, J., Chuang, C.C., Penner, J.E., 1999. Prediction of the number of cloud droplets in the ECHAM GCM. J. Geophys. Res. 104, 9169-9198.

McMeeking, G.R., Hamburger, T., Liu, D., Flynn, M., Morgan, W.T., Northway, M., Highwood, E.J., Krejci, R., Allan, J.D., Minikin, A., Coe, H., 2010. Black carbon measurements in the boundary layer over western and northern Europe. Atmos. Chem. Phys. 10, 9393-9414.

Murphy, D.M., Chow, J.C., Leibensperger, E.M., Malm, W.C., Pitchford, M., Schichtel, B.A., Watson, J.G., White, W.H., 2011. Decreases in elemental carbon and fine particle mass in the United States. Atmos. Chem. Phys. 11, 4679-4686.

Nemitz, E., Gallagher, M.W., Duyzer, J.H., Fowler, D., 2002. Micrometeorological measurements of particle deposition velocities to moorland vegetation. Q. J. Roy. Met. Soc. 128, 2281-2300.

Novakov, T., Hansen, J.E., 2004. Black carbon emissions in the United Kingdom during the past four decades: an empirical analysis. Atmospheric Environment 38, 4155-4163.

Penner, J.E., Novakov, T., 1996. Carbonaceous particles in the atmosphere: A historical perspective to the Fifth International Conference on Carbonaceous Particles in the Atmosphere. J. Geophys. Res. 101, 19373-19378.

Quincey, P., Butterfield, D., Green, D., Coyle, M., Cape, J.N., 2009. An evaluation of measurement methods for organic, elemental and black carbon in ambient air monitoring sites. Atmospheric Environment 43, 5085-5091.

Quincey, P., Butterfield, D., Green, D., Fuller, G.W., 2011. Black Smoke and Black Carbon: Further investigation of the relationship between these ambient air metrics. Atmospheric Environment 45, 3528-3534.

Ramanathan, N., Lukac, M., Ahmed, T., Kar, A., Praveen, P.S., Honles, T., Leong, I., Rehman, I.H., Schauer, J.J., Ramanathan, V., 2011. A cellphone based system for large-scale monitoring of black carbon. Atmospheric Environment 45, 4481-4487.

Ramanathan, V., Carmichael, G., 2008. Global and regional climate changes due to black carbon. Nature Geoscience 1, 221-227.

Rodhe, H., Persson, C., Åkesson, O., 1972. An investigation into regional transport of soot and sulfate aerosols. Atmospheric Environment (1967) 6, 675-693.

Shindell, D., Kuylenstierna, J.C.I., Vignati, E., van Dingenen, R., Amann, M., Klimont, Z., Anenberg, S.C., Muller, N., Janssens-Maenhout, G., Raes, F., Schwartz, J., Faluvegi, G., Pozzoli, L., Kupiainen, K., Höglund-Isaksson, L., Emberson, L., Streets, D., Ramanathan, V., Hicks, K., Oanh, N.T.K., Milly, G., Williams, M., Demkine, V., Fowler, D., 2012. Simultaneously Mitigating Near-Term Climate Change and Improving Human Health and Food Security. Science 335, 183-189.

Stier, P., Feichter, J., Kinne, S., Kloster, S., Vignati, E., Wilson, J., Ganzeveld, L., Tegen, I., Werner, M., Balkanski, Y., Schulz, M., Boucher, O., Minikin, A., Petzold, A., 2005. The aerosol-climate model ECHAM5-HAM. Atmos. Chem. Phys. 5, 1125-1156.

Stier, P., Seinfeld, J.H., Kinne, S., Feichter, J., Boucher, O., 2006. Impact of nonabsorbing anthropogenic aerosols on clear-sky atmospheric absorption. J. Geophys. Res. 111, D18201.

Strawa, A.W., Kirchstetter, T.W., Puxbaum, H., 2010. Special Issue for the 9th International Conference on Carbonaceous Particles in the Atmosphere. Journal of Aerosol Science 41, 1-4.

ten Brink, H., Maenhaut, W., Hitzenberger, R., Gnauk, T., Spindler, G., Even, A., Chi, X., Bauer, H., Puxbaum, H., Putaud, J.-P., Tursic, J., Berner, A., 2004. INTERCOMP2000: the comparability of methods in use in Europe for measuring the carbon content of aerosol. Atmospheric Environment 38, 6507-6519.

Virkkula, A., Makela, T., Hillamo, R., Yli-Tuomi, T., Hirsikko, A., Hameri, K., Koponen, I.K., 2007. A simple procedure for correcting loading effects of aethalometer data. Journal of the Air & Waste Management Association 57, 1214-1222.

WHO, 2003. Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide. WHO, Bonn, Germany.

Williams, J., Fischer, H., Harris, G.W., Crutzen, P.J., Hoor, P., Hansel, A., Holzinger, R., Warneke, C., Lindinger, W., Scheeren, B., Lelieveld, J., 2000. Variability-lifetime relationship for organic trace gases: A novel aid to compound identification and estimation of HO concentrations. Journal of Geophysical Research-Atmospheres 105, 20473-20486.

Williams, J., Gros, V., Bonsang, B., Kazan, V., 2001. HO cycle in 1997 and 1998 over the southern Indian Ocean derived from CO, radon, and hydrocarbon measurements made at Amsterdam Island. Journal of Geophysical Research-Atmospheres 106, 12719-12725.

Table 1. Statistical summary of hourly-averaged BC concentration data at Auchencorth. The geometric mean concentration is exp(mean ln(χ)) and geometric standard deviation is exp($\sigma_{\ln(\chi)}$).

year	Whole dataset			SW wind direction, wind speed > 2 m s^{-1}		
	Geometric std deviation	Geometric mean (μg m^{-3})	% data capture	Geometric std deviation	Geometric mean (μg m^{-3})	% data capture
2007	2.53	0.17	64	2.41	0.15	70
2008	2.59	0.17	77	2.36	0.12	72
2009	3.00	0.14	95	2.83	0.10	97
2010	2.64	0.18	92	2.46	0.13	95

Table 2. Hydrocarbons used in lifetime analysis, from hourly data filtered to include only times with mean wind speed > 2 m s^{-1} and with wind directions between S and W. Lifetime (τ_{OH}) refers to lifetime with respect to reaction with an average OH concentration of 7 x 10^5 cm^{-3} at 283K.

Hydrocarbon	τ_{OH} (d)	σ_{lnX}				Geometric mean conc (μg m^{-3})				% data above LOD			
year		**2007**	**2008**	**2009**	**2010**	**2007**	**2008**	**2009**	**2010**	**2007**	**2008**	**2009**	**2010**
Ethane	79	0.39	0.39	0.41	0.56	0.36	1.59	1.70	1.62	100	100	100	100
Ethyne	21	0.69	0.51	0.53	0.68	0.03	0.16	0.18	0.15	64	79	81	78
Propane	17	0.65	0.65	0.72	1.00	0.19	0.90	0.81	0.68	94	99	87	98
n-butane	7.5	0.81	0.84	0.88	1.14	0.08	0.36	0.31	0.26	91	96	74	91
i-butane	8.3	0.76	0.81	0.89	1.09	0.05	0.22	0.18	0.17	92	95	73	90
n-pentane	4.4	0.70	0.83	0.97	1.09	0.03	0.12	0.06	0.06	99	96	76	83
i-pentane	4.5	0.79	0.90	1.01	1.10	0.04	0.15	0.11	0.10	98	93	78	88
n-hexane	3.1		1.06	1.02	1.14		0.02	0.04	0.02		47	68	60
2-Me pentane	3.1		1.16	1.19	1.12		0.02	0.03	0.02		41	63	55
benzene	14		0.94	0.54	0.88		0.06	0.19	0.15		38	53	95
toluene	2.8		1.53	1.24	1.37		0.02	0.07	0.05		28	46	76

Table 3. Estimated lifetime for BC in each year (2007-2010) based on the lifetimes of hydrocarbons and the values of σ_{lnX} for BC (Table 1). Parameters *A* and *b* refer to equation (1). Uncertainties in lifetime estimates are 95% confidence interval of the prediction.

year	***A***	***b***	**BC Lifetime (95% CI) (days)**	**Rainfall (mm)**
2007	1.13	0.21	4.4 (2.0 – 9.5)	986
2008	1.67	0.34	7.4 (5.4 – 10.1)	959
2009	1.61	0.33	4.1 (3.1 – 5.5)	901
2010	1.61	0.23	11.5 (8.4 – 15.8)	731
seasonal				
2009 summer	1.94	0.32	10.8 (8.1 - 14.4)	492
2009 winter	1.63	0.35	4.7 (3.2 – 7.0)	409
2009 all year (OH)summer/(OH)winter = 3	1.99	0.39	8.1 (±1.5) d (summer), 6.3 (±1.3) d (winter)	
2009 all year (OH)summer/(OH)winter = 6.3	1.84	0.34	9.8 (±1.5) d (summer), 7.3 (±1.2)d (winter)	

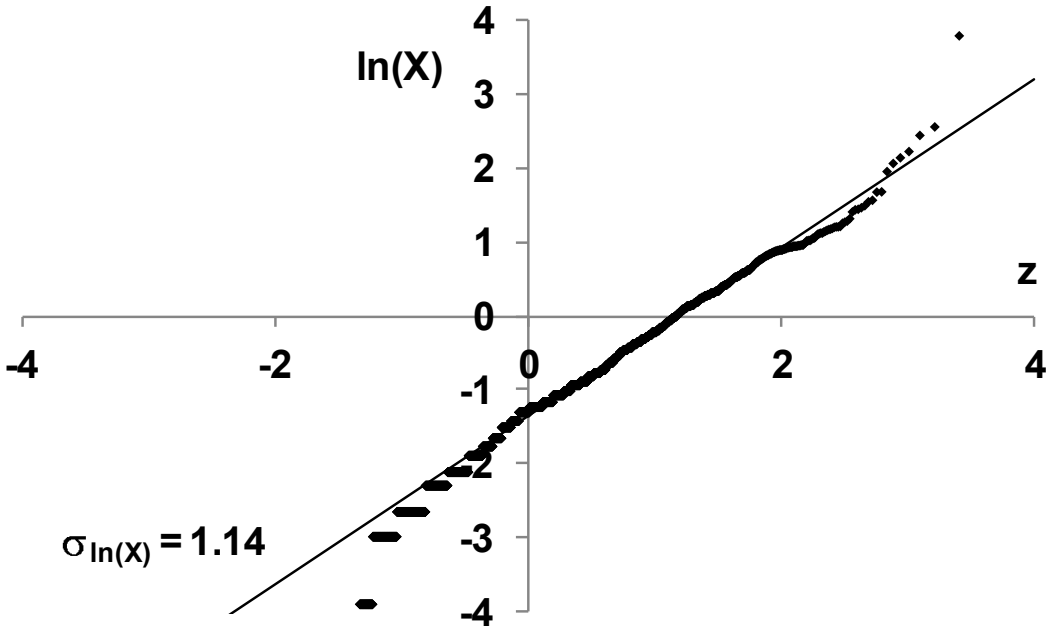

Figure 1. Plot of the natural logarithm of hourly n-butane concentrations (μg m^{-3}) in 2010 vs. the standard normal variate (z), showing the derivation of $\sigma_{\ln(\chi)}$ from the slope of the fitted straight line. 7.5% of the hourly data were recorded as below the limit of detection (0.02 μg m^{-3}).

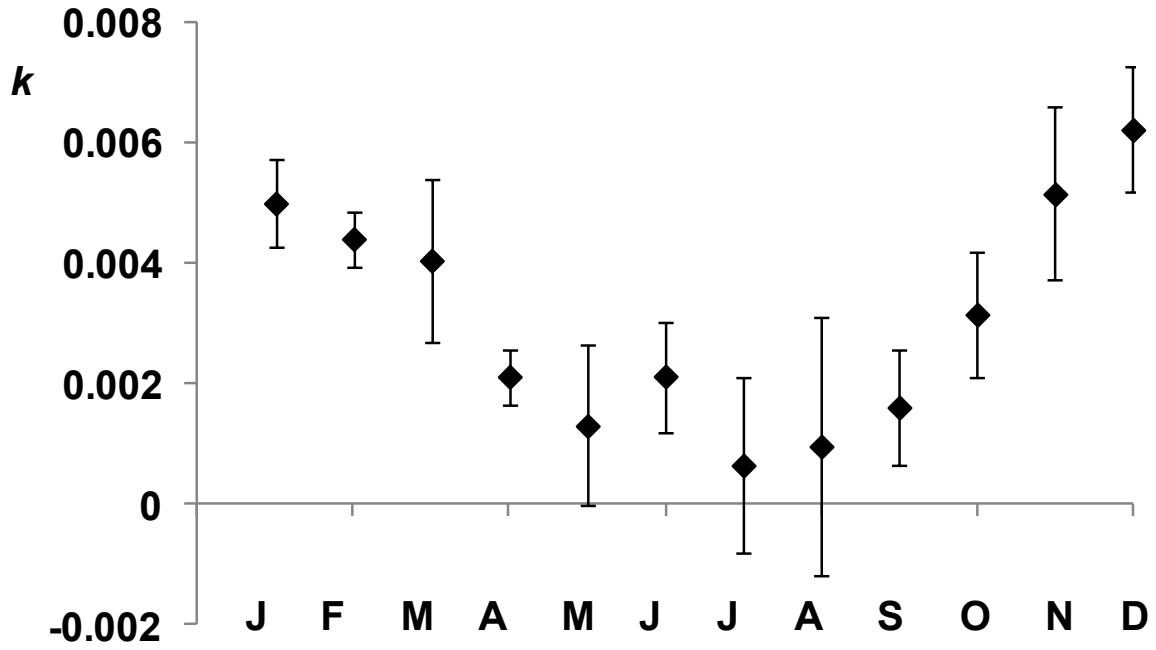

Figure 2. Seasonal variation of the correction factor k from 2007 to 2010. Error bars show the standard deviation over the 4 years of the monthly averages.

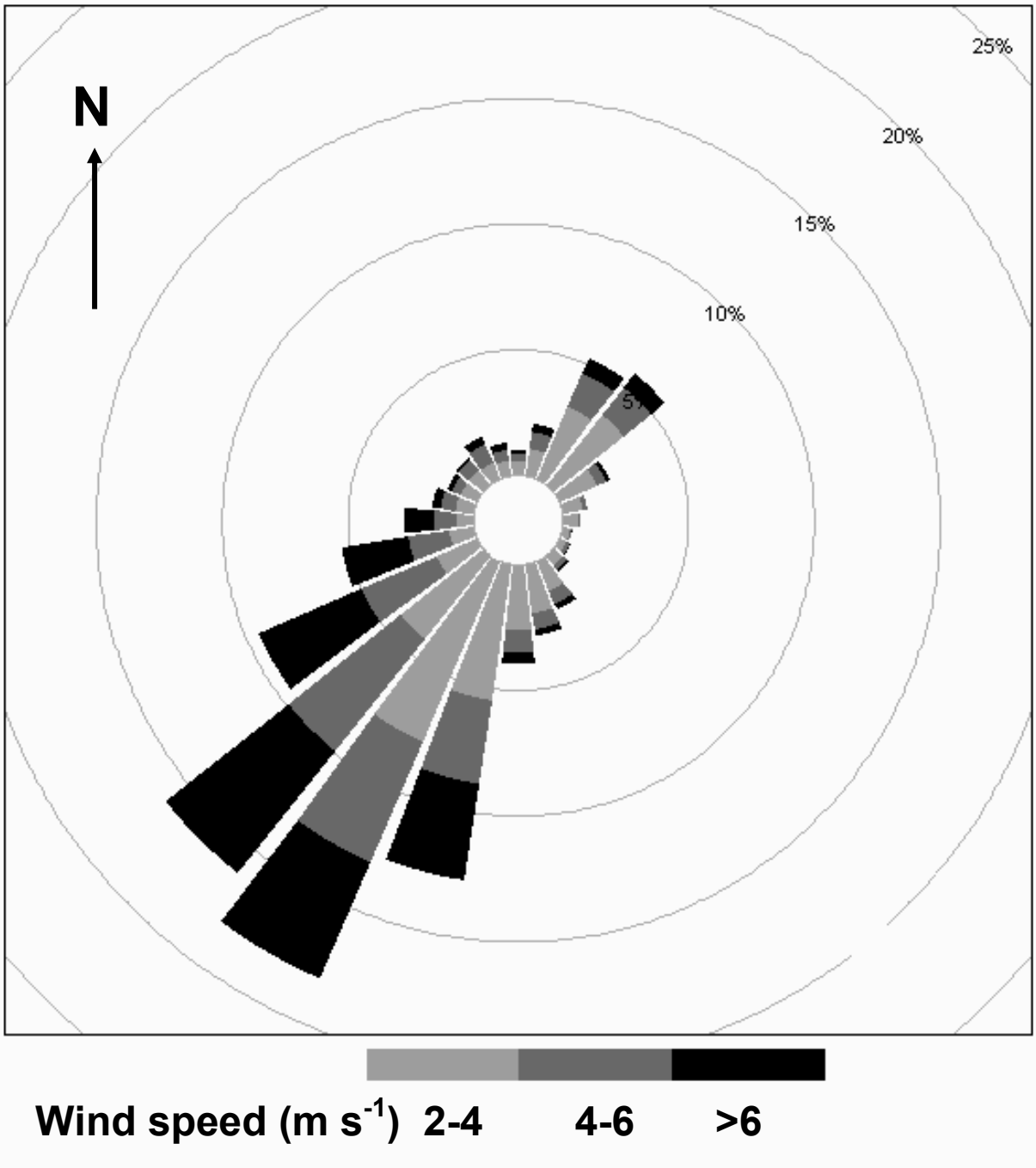

Figure 3. Frequency distribution of hourly averaged wind speed and direction (2007-2010) at Auchencorth for periods with wind speed > 2 m s^{-1} (graphics: open air (Carslaw and Ropkins, 2012)).

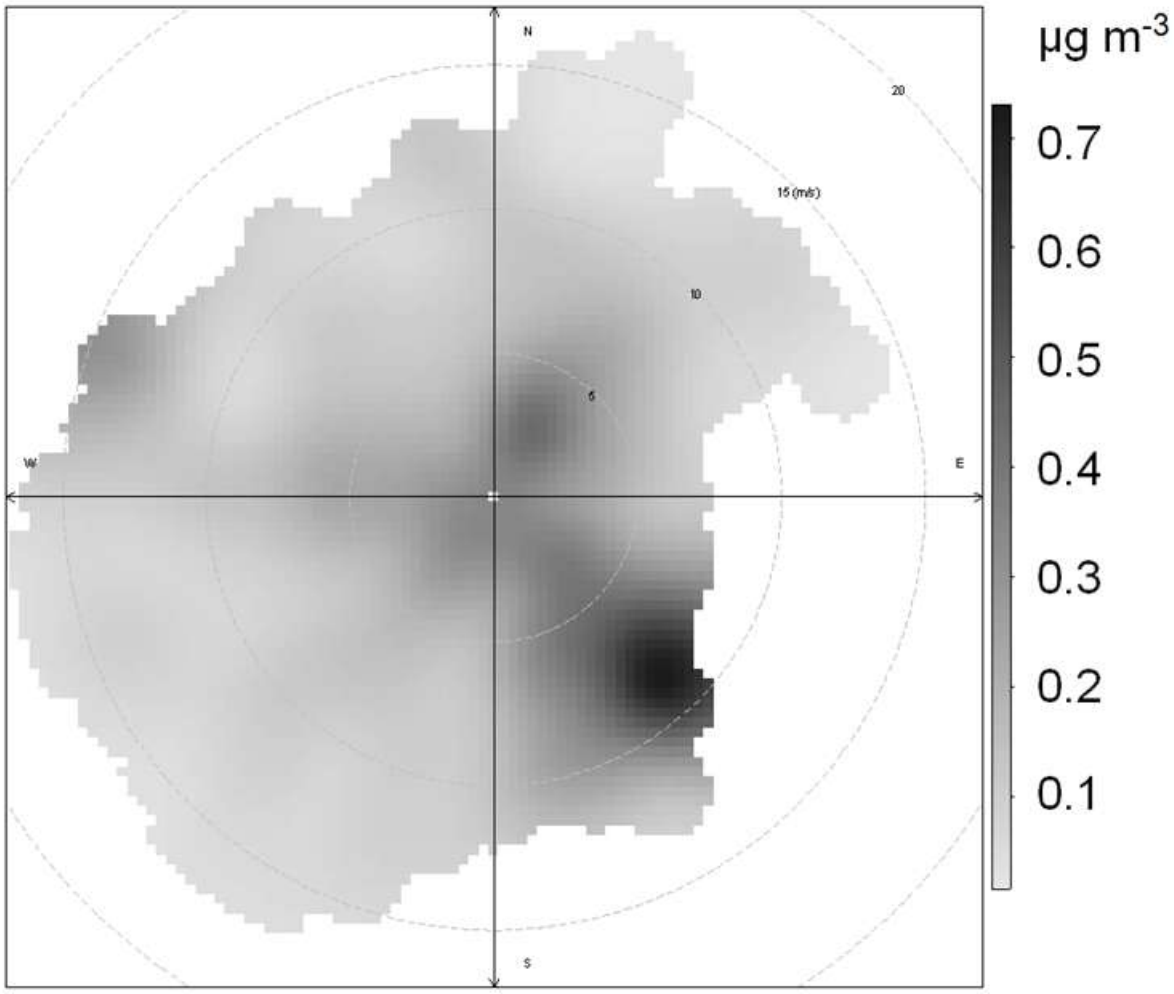

Figure 4. Average BC concentration (µg m^{-3}) as a function of wind direction (north at top) and wind speed (concentric circles at 5 m s^{-1} intervals) for 2007-2010 at Auchencorth Moss, showing sources to SE, NE and NW (graphics: open air (Carslaw and Ropkins, 2012)).

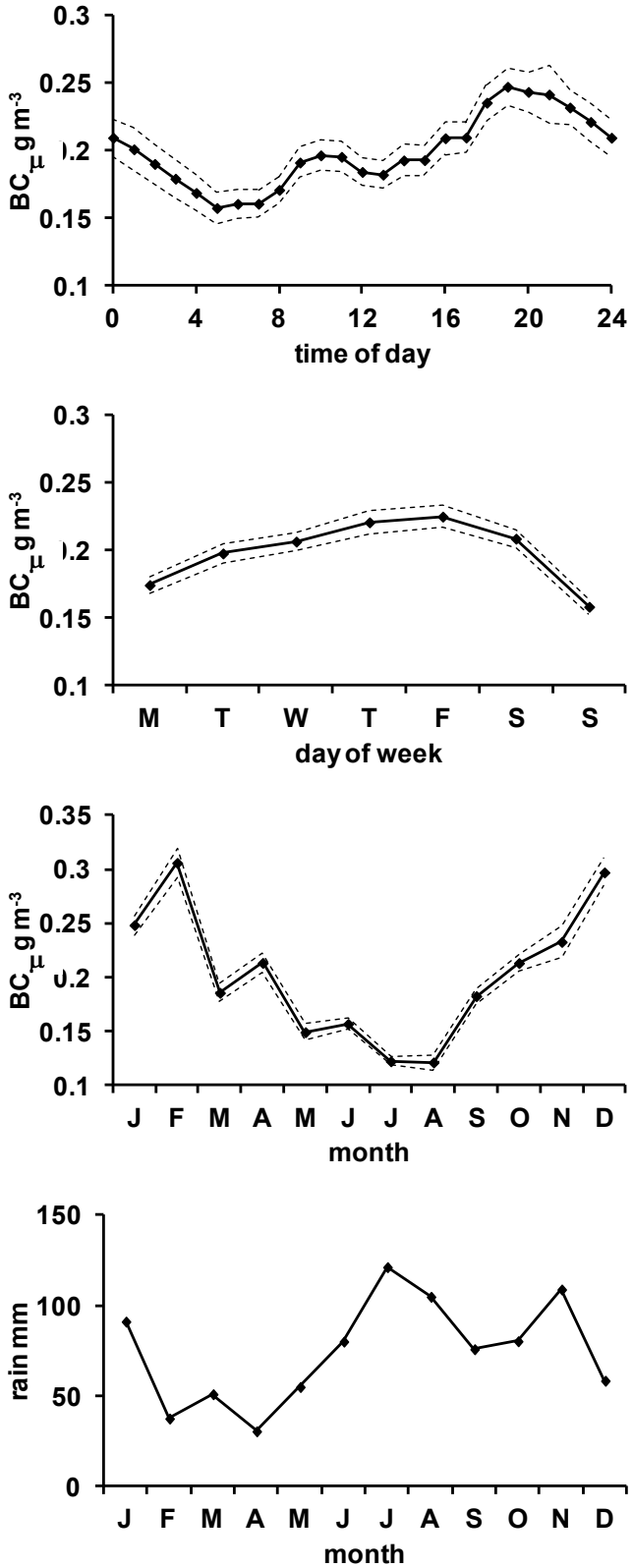

Figure 5. Arithmetic mean diurnal, seasonal and day-of-week patterns of BC concentrations ($\mu g\ m^{-3}$) for 2007-2010 at Auchencorth, for filtered data (wind speed > 2 m s^{-1} and wind direction between S and W). Dashed lines show 95% confidence interval of mean. Seasonal rainfall data (mm $month^{-1}$) as an average over 2007-2010 are also shown.

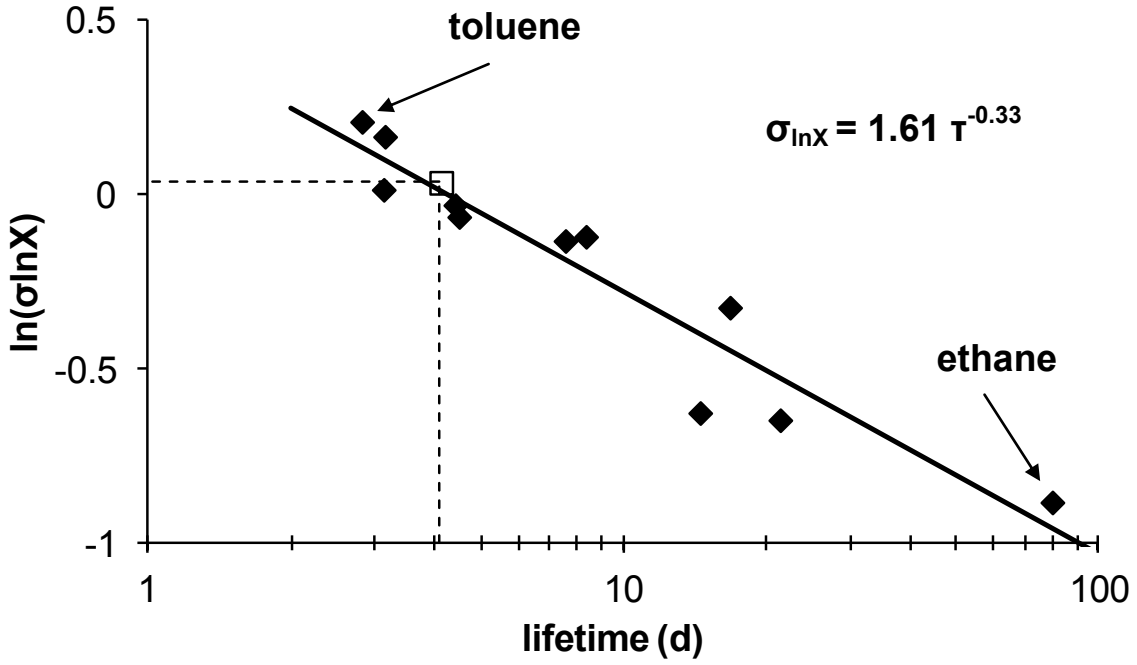

Figure 6. Plot of $\ln(\sigma_{lnX})$ vs. lifetime for the 11 hydrocarbons listed in Table 2 for 2009 data. The value of $\ln(\sigma_{lnX})$ for BC (Table 1, open square symbol) corresponds to a lifetime of 4.1 days (dashed line)

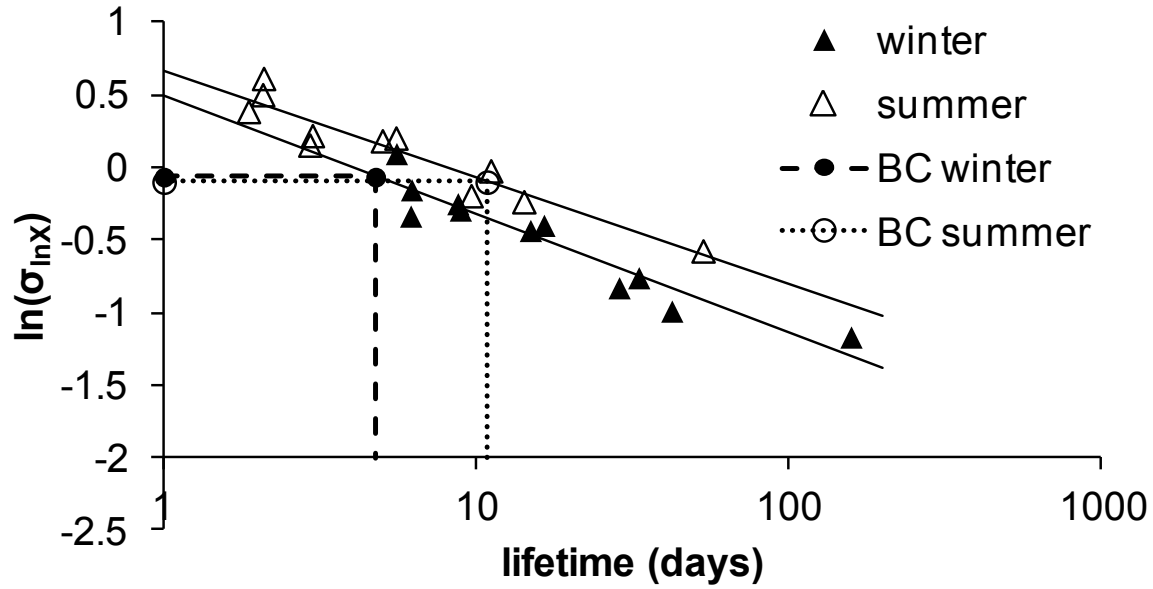

Figure 7. Plot of $\ln(\sigma_{lnX})$ vs. lifetime for the 11 hydrocarbons listed in Table 2 for 2009 data, plotting summer (April - September) and winter (October – March) separately. The values of $\ln(\sigma_{lnX})$ for BC (filled or closed circles) correspond to a lifetimes of 4.7 days (winter) and 10.8 days (summer) (Table 3). If all data are fitted to a common regression line the relevant lifetimes are 6.3 days (winter) and 8.1 days (summer).

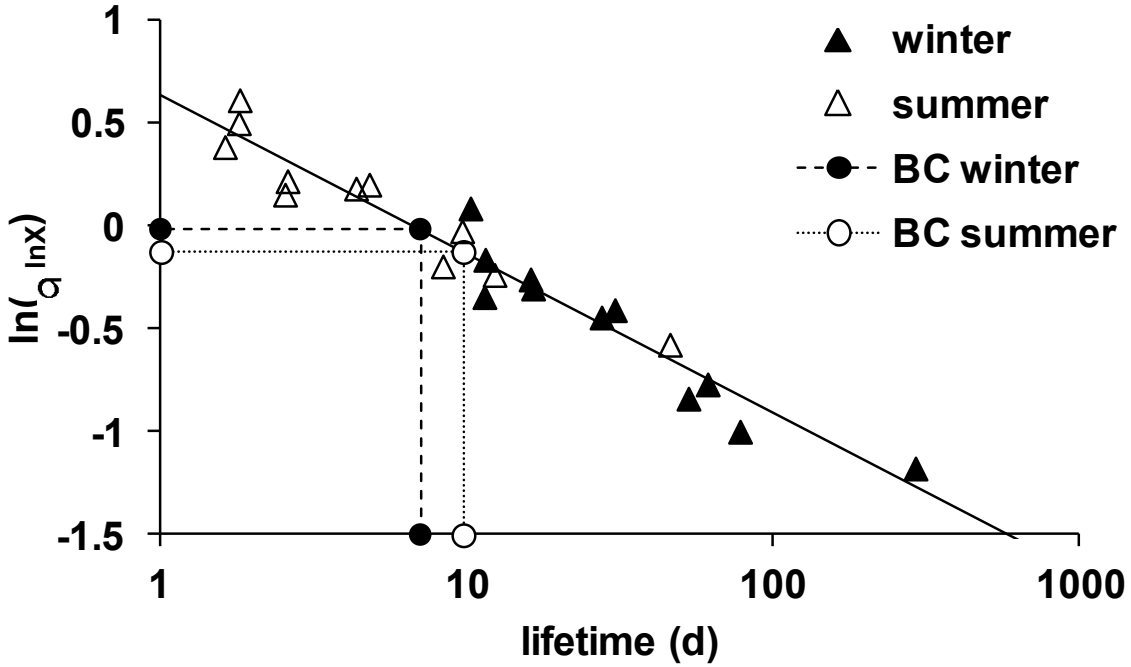

Figure 8. Plot of $\ln(\sigma_{lnX})$ vs. lifetime for the 11 hydrocarbons listed in Table 2 for 2009 data, plotting summer (April - September) and winter (October – March) separately, but fitted to a common regression line, and with the ratio of $(OH)_{summer}$: $(OH)_{winter}$ optimised to give the greatest correlation, equivalent to an $(OH)_{summer}$: $(OH)_{winter}$ ratio of 6.3. The values of $\ln(\sigma_{lnX})$ for BC (filled or closed circles) correspond to a lifetimes of 7.3 days (winter) and 9.8 days (summer) (Table 3). Note the longer hydrocarbon lifetimes in winter.