An Investigation into the Effects of Off-Shore Shipping Emissions on Coastal Black Carbon Concentrations

David M. Butterfield*, Paul Quincey

Environment Division, National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom

ABSTRACT

Shipping emissions are recognised as a significant but poorly understood contributor to air pollution in the UK. Away from port, lower grade fuels are permitted to be used, to the extent that sulphur emissions from shipping were forecasted to exceed those from all land-based sources in the EU by 2020. To examine the impact of black carbon emissions from shipping, an Aethalometer was installed at Goonhilly Downs on the Lizard peninsula in Cornwall UK, which is typically downwind of busy shipping lanes, with very low background pollution levels, for a full year starting in November 2012. Black carbon and UV component concentrations were combined with local wind speed and direction data to differentiate between shipping emissions, local sources and long-range transport. Black carbon concentrations were compared with PM2.5 mass concentrations from Plymouth Centre to allow for the influence of changes in regional background particulate concentrations. Black carbon concentrations showed no substantial increment above other rural UK locations, although some time periods show small elevated concentrations which could be attributed to emissions from the nearby shipping lanes. The long-term (annual) average contribution to black carbon concentrations from off-shore shipping is estimated to be less than 0.1 µg m⁻³, with the hourly peak values being in the range 1–2 µg m⁻³.

Keywords: Black carbon; Shipping emissions; Aethalometer; Goonhilly.

INTRODUCTION

Shipping emissions are recognised as a significant but poorly understood contributor to air pollution in the UK. A recent European Environment Agency report on the ‘Impact of international shipping on European air quality and climate forcing’ has summarized estimates for the contributions to global NOₓ, SO₂ and PM2.5 emissions from shipping globally as: 10–20% (NOₓ), 10–25% (SO₂) and 15–25% (PM2.5) (EEA, 2013). Black carbon forms a significant fraction of PM2.5 emissions (as described below), and of ambient PM2.5 concentrations. In the UK, data from the Black Carbon Network (2014) shows black carbon makes up approximately 26% of roadside, 11% of urban background and 4% of rural background PM2.5 mass concentrations. Away from port, lower grade fuels are permitted to be used, to the extent that sulphur emissions from shipping were forecasted by the European Union (2005) to exceed those from all land-based sources by 2020. Emissions of soot-like carbon from shipping have so far not been included in the regulations for air pollution, which primarily cover NOₓ, SO₂ and CO₂, but are likely to be significant.

The regulations are set out within MARPOL (2008), an international convention adopted by the IMO in 1973, specifically in Annex VI: Prevention of Air Pollution from Ships. In 2005 this set limits on NOₓ and SO₂ emissions from ship exhausts, and prohibited deliberate emissions of ozone-depleting substances. In 2011, IMO adopted energy efficiency measures which will significantly reduce the amount of greenhouse gas emissions from ships; these measures were included in Annex VI and entered into force on 1 January 2013.

Emissions can be monitored either close to shipping lanes or in ports. The port option has the disadvantages that it will be difficult to isolate the shipping emissions from local traffic and industrial sources, and that ships usually switch to cleaner fuels when in port, so that the monitoring would not be properly representative. The best location to monitor off-shore shipping emissions is therefore a coastal site close to shipping lanes, but away from ports and other local sources.

Previous studies (Petzold et al., 2008; Mueller et al., 2011; Moldanová et al., 2013; Mueller et al., 2015) have examined particulate emissions from shipping, including airborne measurements of black carbon in shipping plumes, rather than their effects on ambient concentrations; Moldanová et al. (2013) found that Elemental Carbon (which should be closely correlated with black carbon) formed 10–38% of...
the PM mass. González et al. (2011), looked at pollutants including black carbon in the port of Santa Cruz de Tenerife, where the black carbon was dominated by vehicle emissions. Black carbon, as a primary pollutant (unlike PM$_{2.5}$ or particle number concentration, for example), and with sensitive monitoring instruments available, should provide an excellent parameter for determining the contribution of shipping emissions at ground-level sites, by choosing locations with low emission contributions from other sources. An investigation of this kind does not appear to have been tried before, and this was the aim of this focussed study.

To examine the impact of black carbon emissions from shipping, an Aethalometer was installed at Goonhilly Downs on the Lizard peninsula at the end of November 2012. The site is approximately 8 km from the coast and the western approaches to the English Channel. There are little to no local sources of black carbon or PM$_{2.5}$ (< 3 kg m$^{-2}$ per year) in the surrounding 1 km × 1 km emission squares in the 2013 dataset from the UK’s National Atmospheric Emission Inventory. There are some domestic dwellings, mainly farm houses, within a radius of 3 km of the monitoring site. These domestic sources may burn wood or solid fuel for heating as they are unlikely to be connected to the natural gas grid. Domestic sources can be a significant emission source for black carbon and UV adsorbing particulates and should have seasonal emission profile. There are no significant industrial or domestic sources between the coast and the site in the arc subscribed from Penzance (26 km) to the NW through south to Falmouth (15 km) to the NE. The French coast is approximately 170 km to the SE. The closest major shipping lane (English Channel) is 60 km to the south, but closer are the coastal freight routes (10 km–20 km) plus local fishing fleets. There is also the marine fuel bunkering facility at Falmouth. The site is also on the edge of the sulphur Emission Control Area (ECA), defined in MARPOL Annex VI (2005), encompassing the English Channel to the Norwegian coast, including the Baltic Sea. The ECA sets limits on the sulphur content of fuel that ships are allowed to use within its area. The area of sea affected is shown in Fig. 1 along with the monitoring stations and local towns of interest referenced in the paper.

Corbett et al. (2007) have estimated the increase in PM$_{2.5}$ mass concentration due to global shipping in the Goonhilly area (and also for the great majority of the United Kingdom) to be of the order 0.2 µg m$^{-3}$ to 0.5 µg m$^{-3}$. Using the range for the proportion of black carbon in PM$_{2.5}$ given in Moldanová et al. (2013) above to provide a crude estimate, black carbon concentrations in Goonhilly due to shipping would be expected to be within the approximate range 0.02–0.2 µg m$^{-3}$, similar to the Aethalometer detection limit of 0.1 µg m$^{-3}$. Measurements took place at Goonhilly for a full year between November 2012 and November 2013, allowing fully representative shipping and weather conditions to be observed.

**AETHALOMETER MEASUREMENT METHOD**

Aethalometers quantify black carbon on filter samples based on the transmission of light through a sample. The sample is collected onto a quartz tape, and the change in absorption coefficient of the sample is measured by a single pass transmission of light through the sample, measured relative to a clean piece of filter. The system evaluates changes in two optical sensors (sample and reference), with the light source both on and off, such that independent measurements of the change in attenuation of the sample are produced for averaging periods of typically five minutes. The absorption coefficient for material added during the period, $\sigma$ (m$^{-1}$), is calculated from the attenuation change, the filter area, and volume of the sample. This is converted to a black carbon concentration for the period, as a first approximation, using a mass extinction coefficient (16.6 m$^{-2}$ g$^{-1}$) chosen by the manufacturer (Magee Scientific Company, 2005) to give a good match to Elemental Carbon. In practice this mass extinction coefficient will vary with factors such as particle size, sample composition and quantity of material already on the filter, as discussed below.

The Goonhilly Aethalometer operated at 2 wavelengths, 880 nm and 370 nm. The 880 nm wavelength is used to measure the black carbon (BC) concentration of the aerosol, while the 370 nm wavelength gives a measure of the “UV component” of the aerosol. At wavelengths shorter than about 400 nm, certain classes of organic compounds (such as polycyclic aromatic hydrocarbons (PAHs), and also certain compounds present in tobacco smoke and smoke from wood burning) start to show strong UV absorbance (Brown et al., 2016). The UV component can therefore in principle be used as an indicator of PAH-type emissions.

The UV component concentration presented in this paper is obtained by subtracting the measured BC concentration from the concentration measured by the 370 nm source. The UV component is not a real physical or chemical material, but a parameter based on UV absorption due to the mix of organic compounds measured at this wavelength. This metric termed ‘UVPM’ is expressed in units of ‘BC Equivalent’.

It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to nonlinearity in the Aethalometer response. Effect of this nonlinearity means that the Aethalometer has reduced sensitivity to black carbon at high filter tape loadings. To correct for this nonlinearity, the Virkkula model (Virkkula et al., 2007) has been used to correct for increased attenuation due to spot darkening during sampling. This uses the simple equation:

$$BC_{corrected} = (1 + k \cdot ATN) \cdot BC_{uncorrected}$$  \hspace{1cm} (1)$$

where $ATN$ is the light attenuation by the filter spot, and $k$ is a parameter determined for each filter spot such that continuity between adjacent filter spots is greatly improved. All of the black carbon and UV component results in this paper have been corrected by this method.

During the measurement period the Aethalometer was serviced 3 times and audited once. Flow measurements from these services and audit were used to correct the concentrations for the difference between true flow and the indicated instrument flow. Instrument performance data
from the audit was also used to verify the correct operation of the Aethalometer. Using data collected from the services and audits the overall measurement uncertainty (95% confidence) for an hourly average black carbon concentration is 13%.

RESULTS

Time Series

Time series graphs of hourly black carbon and UV component concentrations are shown in Figs. 2 and 3. The peaks in black carbon and UV component concentrations above the regular y-axis are generally coincident in time. However, the annual pattern is quite different in the two cases, with the UV component notably higher in Winter than Summer, whereas the black carbon concentrations are not obviously seasonal. This may indicate that the UV component is driven by domestic heating using wood and solid fuel. The above time series are typical of rural network sites, with spikes in concentration interspersed with prolonged periods of low concentrations. It is difficult to tell from the time series alone if any of the raised concentrations are due to ship emissions or long range transport of pollutants from other non-shipping sources.

The high black carbon and UV component concentrations (11.6 µg m⁻³ and 7.0 µg m⁻³ respectively) measured on 1st April were traced to gorse fire upwind of the monitoring site and have been removed from the dataset for all subsequent analysis.

The annual average black carbon concentration, 0.22 µg m⁻³, is similar to that for the most remote rural site in the black carbon network (Auchencorth Moss in Midlothian, 0.2 µg m⁻³), and significantly lower than that at the rural site at Harwell in Oxfordshire (~0.5 µg m⁻³). If no shipping
effects were involved, a low average value would be expected, because the prevailing wind is from the South-West. It is immediately apparent that the long-term average contribution from off-shore shipping is very low. Given that the shipping contribution cannot be higher than the total concentration of 0.22 µg m⁻³, and this is a similar concentration to that found at a very remote site, which can be taken as a guide to the minimum background concentration from regional sources, we conservatively estimate a maximum long-term average from shipping sources at this site of 0.1 µg m⁻³. To help show the similarities to the Auchencorth Moss and Harwell concentrations, Fig. 4 shows the distribution of hourly concentration measurements in the form of a histogram.

Black carbon is a major constituent of PM₂.₅. The closest non-roadside Automatic, Urban and Rural Network (AURN) station to Goonhilly is at Plymouth Centre, situated 80 km to the east, where PM₂.₅ concentrations are measured using a Tapered Element Oscillating Microbalance fitted with a Filter Dynamic Measuring System (TEOM-FDMS). Fig. 5 shows a time series plot of both black carbon and the publicly-available ratified PM₂.₅ concentrations. PM₂.₅
concentrations from July onwards are considerably lower and are often negative, which may indicate that these data are less reliable.

It can be seen that the Goonhilly black carbon concentrations show a similar time profile to the PM$_{2.5}$ concentrations at Plymouth Centre.

In order to highlight any concentrations of black carbon that were anomalously high with respect to the Plymouth PM$_{2.5}$ concentrations, the following procedure was followed. The Plymouth PM$_{2.5}$ concentrations were scaled to those of the Goonhilly BC according to Eq. (2). Due to the changes in behaviour of the Plymouth FDMS data set in July 2013, separate averages were used before and after this date.

\[
Plymouth \text{ scaled } PM_{2.5} = \frac{Plymouth \text{ PM}_{2.5} \times Goonhilly \text{ BC}}{Plymouth \text{ PM}_{2.5}}
\]

The “bar” notation denotes the mean concentration for the measurement metric over each of the two periods. These scaled Plymouth PM$_{2.5}$ concentrations provide an estimate of the local, time-dependent background black carbon concentrations at Goonhilly, based on the assumption that the PM$_{2.5}$ material in Plymouth contains a constant fraction of black carbon. This assumption is acknowledged to be a crude approximation, as can be seen from observing the hour-by-hour ratio of black carbon to PM$_{2.5}$ concentrations at sites where the relevant instruments are collocated. Nevertheless, for the purposes of this study it is not necessary that this local background estimate is robust; the approach is simply a method that will highlight when BC concentrations at Goonhilly appear elevated independently of PM concentrations in Plymouth. This approach should capture occasions when shipping emissions cause elevated concentrations at Goonhilly, although similar effects caused by a drop in local emissions in Plymouth cannot be excluded.
The differences between the Goonhilly black carbon concentrations and the scaled Plymouth PM$_{2.5}$ concentrations were then calculated according to Eq. (3):

$$\text{Difference} = \text{Goonhilly BC} - \text{Plymouth scaled PM}_{2.5} \quad (3)$$

This method should remove any regional background component in the black carbon concentration, i.e., long range transport from Europe. A histogram of these differences is shown in Fig. 6.

The asymmetry of the histogram indicates that several hundred hours of black carbon data over the year may have been anomalously elevated, but generally only by concentrations up to around 1 µg m$^{-3}$. Some specific cases of such anomalies are examined in more detail below.

**Wind Analysis**

Wind data recorded from Culdrose Fleet Air Arm Base, located 6.5 km to the NW of the site, was used to try and discriminate between different pollutant sources. Both Culdrose and Goonhilly are open field sites at similar altitudes so should experience similar wind speeds and directions. Fig. 7 gives the wind rose for Culdrose over the monitoring period. Concentration data has been combined with the wind data to produce polar plots as seen in Fig. 8. The colour represents the measured mean concentration at a specific wind direction and speed, the distance from the centre of the plot corresponds to wind speed, i.e., colours close to the origin are concentrations measured at very low wind speeds whilst colours further from the origin represent concentrations measured at higher wind speeds. The angular position represents the wind direction. The white areas represent wind directions and speeds that did not occur during the measurement period.

If the dataset is broken down into seasons then additional information on emission sources may be extracted i.e., there should be little to no emissions of black carbon from heating sources in the summer period. Seasonal pollution roses are plotted in Fig. 9.

It can be seen from the seasonal plots that there are different pollution sources for black carbon and for the UV component, with none of these sources being obviously local or from shipping. There is a source of black carbon to the East of the site across all seasons with maximum concentrations being recorded in spring and autumn. In the winter there are raised concentrations of black carbon and UV component associated with easterly wind directions, which may indicate emissions from domestic heating and/or long range transport. A similar pollution rose can be plotted showing the difference between the black carbon and the scaled Plymouth PM$_{2.5}$ concentrations, this is shown in Fig. 10.

It can be seen that for most wind directions the Goonhilly black carbon concentrations are very similar to the local background, as estimated by the scaled Plymouth PM$_{2.5}$ concentrations, with concentrations significantly higher than the regional background only when the wind is coming from the NE to SE sector.

**Back Trajectories**

Back trajectories of air masses reaching the Goonhilly site have been calculated using the Draxler and Rolph (2013) Air Resources Laboratory’s HYSPLIT Trajectory Model when Goonhilly black carbon concentrations are larger than the scaled Plymouth Centre PM$_{2.5}$ concentrations. Table 1 gives the details of the back trajectories, while the trajectories are shown graphically in Figs 11–15, where the concentrations are the recorded hourly average concentrations.

Fig. 11 shows elevated black carbon possibly due to emissions from ships using the Falmouth offshore oil terminal and fuel bunkering facility, while Figs. 12, 13 and 14 indicate more clearly elevated black carbon concentrations that may have come from shipping emissions.

In contrast, Fig. 15 shows back trajectories for Goonhilly and Plymouth Centre on 3rd March 2013 when both sites showed elevated concentrations due to long range transport from Europe (and possibly the English Channel) and poor dispersion of local sources.

![Fig. 6. Difference between BC concentrations at Goonhilly and scaled Plymouth TEOM-FDMS PM$_{2.5}$ concentrations.](image-url)
CONCLUSIONS

The black carbon and UV component concentrations measured at the Goonhilly site over a twelve month period show somewhat lower concentrations and similar behaviour to those measured at other UK rural background sites, indicating no substantial increment due to regional shipping emissions (from either local shipping lanes or the English Channel). Using nearby PM$_{2.5}$ data to estimate the local background black carbon concentration, there is no definite signature of significantly elevated concentrations due to local shipping emissions.
Fig. 9. Seasonal black carbon and UV component pollution roses.
Fig. 10. Pollution rose of difference between scaled black carbon and Plymouth Centre PM$_{2.5}$ concentrations. Note: Positive results indicate that Goonhilly black carbon concentrations are above the regional background.

Table 1. Back trajectory details.

| End Date          | Length, hours | Corresponding Figure |
|-------------------|---------------|----------------------|
| 17/05/2013 21:00  | 12            | 11                   |
| 26/05/2013 07:00  | 24            | 12                   |
| 29/09/2013 03:00  | 12            | 13                   |
| 22/08/2013 22:00  | 60            | 14                   |
| 04/03/2013 06:00  | 96            | 15                   |

Fig. 11. 17$^{th}$ May 21:00 hrs 12 hour back trajectory, BC = 1.6 µg m$^{-3}$, Regional background = 0.2 µg m$^{-3}$. 
Fig. 12. 26th May 07:00 hrs 24 hour back trajectory, BC = 1.4 µg m\(^{-3}\), Regional background = 0.2 µg m\(^{-3}\).

Fig. 13. 29th September 03:00 hrs, 12 hour back trajectory, BC = 1.0 µg m\(^{-3}\), Regional background = 0.4 µg m\(^{-3}\).

The long-term (annual) average contribution to black carbon concentrations from off-shore shipping at this site is conservatively estimated to be less than 0.1 µg m\(^{-3}\), with the hourly peak elevations being in the range 1-2 µg m\(^{-3}\), which could be attributed to emissions from the nearby shipping lanes.

Examination of back trajectories shows that some of the periods of black carbon concentrations elevated by 1–2 µg m\(^{-3}\) can be attributed to shipping emissions. Although these conclusions are specific to this site and monitoring period, the twelve month period should minimize the influence of meteorological variations, and the low concentrations measured are a clear indication that the influence of shipping is small in absolute terms.

ACKNOWLEDGEMENTS AND DATA AVAILABILITY

The authors gratefully acknowledge Defra for their help in funding the work and providing the Aethalometer.
instrument from their UK black carbon monitoring network. The Goonhilly concentrations along with the black carbon and UV component concentrations measured by the UK black carbon Network can be accessed from Defra’s UK-AIR website (http://uk-air.defra.gov.uk/data).

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

REFERENCES

2013 Annual Report for the UK Black Carbon Network (2014). NPL Report AS92.
Brown, R.J.C., Butterfield, D.M., Goddard, S.L., Hussain, D., Quincey, P.G. and Fuller, G.W. (2016). Wavelength dependent light absorption as a cost effective, real-time surrogate for ambient concentrations of polycyclic aromatic hydrocarbons. *Atmos. Environ.* 127: 125–132.
Commission of the European Communities (2005). Thematic Strategy on air pollution, COM(2005) 446. Corbett, J.J., Winebrake, J.J., Green, E.H., Kasibhatla, P., Eyring, V. and Lauer, A. (2007). Mortality from ship emissions: A global assessment. Environ. Sci. Technol. 41: 8512–8518. Draxler, R.R. and Rolph, G.D. (2013). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD. EEA (2013). EEA Technical report No 4/2013 “The Impact of International Shipping on European Air Quality and Climate Forcing” ISSN 1725-2237. González, Y., Rodriguez, S., Guerra García, J.C., Trujillo, J.L. and García, R. (2011). Ultrafine particles pollution in urban coastal air due to ship emissions. Atmos. Environ. 45: 4907–4914. Magee Scientific Company (2005). The Aethalometer™. MARPOL (2005). Regulations for the Prevention of Air Pollution from Ships Annex VI, International Maritime Organisation. Moldanová, J., Fridell, E., Winnes, H., Holmin-Fridell, S., Boman, J., Jedynska, A., Tishkova, V., Demirdjian, B., Joulie, S., Bladt, H., Ivleva, N.P. and Niesner, R. (2013). Physical and chemical characterisation of PM emissions from two ships operating in European Emission Control Areas. Atmos. Meas. Tech. 6: 3577–3596. Mueller, D., Uibel, S., Takemura, M., Klingelhoefer, D. and Groneberg, D.A. (2011). Ships, ports and particulate air pollution - An analysis of recent studies. J. Occup. Med. Toxicol. 6: 31. Mueller, L., Jakobi, G., Czech, H., Stengel, B., Orasche, J., Arteaga-Salas, J.M., Karg, E., Elsasser, M., Sippula, O., Streibel, T., Slowik, J.G., Prevot, A.S.H., Jokiniemi, J., Rabe, R., Harndorf, H., Michalke, B., Schnelle-Kreis, J. and Zimmermann, R. (2015). Characteristics and temporal evolution of particulate emissions from a ship diesel engine. Appl. Energy 155: 204–217. Petzold, A., Hasselbach, J., Lauer, P., Baumann, R., Franke, K., Gurk, C., Schlager, H. and Weingartner, E. (2008). Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. Atmos. Chem. Phys. 8: 2387–2403. Rolph, G.D. (2013). Real-time Environmental Applications and DisplaysYstem (READY) Website (http://www.ready.noaa.gov). NOAA Air Resources Laboratory, College Park, MD. Virkkula, A., Mäkelä, T., Hillamo, R., Yli-Tuomi, T., Hirsiikko, A., Hämeri, K. and Koponen, I.K. (2007). A simple procedure for correcting loading effects of aethalometer data. J. Air Waste Manage. Assoc. 57: 1214-1222.

Received for review, December 28, 2015
Revised, July 25, 2016
Accepted, August 8, 2016