INNER-CITY SOURCE APPORTIONMENT USING SPATIAL MODELLING OF BLACK CARBON (BC) TO NITROGEN DIOXIDE (NO_2) RATIOS: A CASE STUDY IN GLASGOW, SCOTLAND.

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1. INTRODUCTION.

The UK Government considers air pollution to be a grave threat to human health and has installed a countrywide series of monitoring stations to measure air pollutants, including Nitrogen Dioxide (NO_2) and Black Carbon (BC).

Two of the most researched monitoring stations in the UK are located at Glasgow High Street (which measures roadside air quality) and Townhead (which measures urban ambient air). While these monitoring stations are well researched, the supply of air pollution within these complex inner-city locations are poorly understood due to the overwhelming impact of nearby road emissions. This work, however, uses the ratio between NO_2 vs BC to focus on more distant pollution sources (for brevity this paper focusses on NO_2, but these principles apply equally to other nitrogen oxides). This ratio assumes that in normal ambient environments, the ratio of BC to NO_2 is low. Sources of BC mainly stem from industrial processes, uncontrolled fires, vehicles, or re-suspension of BC from these sources (Li *et al.* 2019). At the source, NO_2 is generally released in far greater concentrations than BC; indeed, a BC to NO_2 ratio of 10.57% ±1.86% was present along Hope Street (another street within the city), and contrastingly industrial diesel engines from UNG activity in Poland had a NO_2/BC ratio of around 10:1 (~10%), (Grainger 2017, 2018; Ezani *et al.* 2018). Whilst NO_2 is much greater at source, it can quickly mix with ambient air and degrade, whilst BC can become resuspended or even be brought in from air settling regionally (Wang *et al.* 2011; Defra 2019). It is therefore argued that when the ratio between BC and NO_2 is high, sources of nitrogen are taken to be present, such as vehicular and industrial emissions.

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When this understanding is combined with advanced statistical analysis, in this case, the RStudio's OpenAir package (as developed by Carslaw) along with simple back-trajectory analysis, it is possible to show spatial patterns which are conjectured to be undiscovered sources of air pollution.

Using these methods, novel sources of air pollution were found at the High Street monitoring station, which included a local brewery, multi-story car park, and several major road junctions. The Townhead monitoring station appears to be affected by a major bus station, car parking, and a major highway intersection. These techniques could readily be adopted at other monitoring stations to support source apportionment studies.

2. METHODOLOGY.

2.1. Programming.

This chapter uses 'RStudio' which is an open-ware statistical computing platform, with the 'OpenAir' toolset. This platform was used to produce graphs of the temporal and the spatial contribution of air pollution (Carslaw and Ropkins 2012). The 'OpenAir' toolset works similarly to functions in spreadsheets in that calculations are performed on the user's data without having to code "from scratch". Further information, including a toolset manual, can be found on the project's website at; 'davidcarslaw.github.io/openair/'.

The three main individual tools used for this work from the 'openair' toolset include:

- Normalized Temporal Distribution Graphs; show the temporal variation in days, weeks, months, etc.
- Bivariate Polar Plots, which subdivides the air pollution data into a series of hexagonal coordinates based on the prominent meteorological conditions (wind speed and direction). The average data in each bin is plotted, and a color gradient is used to illustrate the concentration of air pollution (or ratios).
- Conditional Probability Function (CPF) Polar Plots. CPF analysis tests the probability of an event occurring if other conditions are met. These CPF values are plotted using the bivariate method.

2.2. Data Source.

The monitoring stations at Glasgow Townhead and High Street were selected for analysis. The hourly data from 7th October 2012 through to the 1st March 2019 (the first day of analysis) were downloaded from the UK Air Data Selector: *uk-air.Defra.gov.uk/data/data_selector*.

These Monitoring Stations relies on a Magee Aethalometer to measure by BC, (Defra 2017). Whilst, an API200A chemiluminescence analyzer was used to monitor the concentration of NO_2 (Defra, 2017). The results for this data were averaged over an hour and uploaded onto the data repository on a governmental open access license. A more advanced explanation of the site locations and instrument details is found at: *uk-air.Defra.gov.uk*.

2.3. Data Screening.

Both datasets were filtered according to two main criteria; these were:

1. Each entry must contain a complete record of meteorological information, NO_2 and BC. Where a data entry does not have a full a set of recordings, the entry was screened out of the analysis.

2. Only 'verified' data was permitted, i.e. partial, provisional, and unverified data entries were screened out of the analysis.

Screening of the data led to almost 20,232 rows of data being screened out from High Street, whereas only 4,684 rows of data were screened at Townhead. High Street was installed 477 days later than Townhead, which accounted for 11,448 hours of blank data. High Street was also more prone to mechanical breakdown since installation as the site was recycled from an older monitoring station within the city. Still, 20,000 lines of good quality data were more than enough for this analysis.

3. RESULTS.

3.1. High Street.

A single element bivariate polar plot of NO_2 is presented in Figure 1.A, this plot shows that the highest concentrations of air pollutants were recorded when wind speeds were low (below ~2 m/sec) and blew from the north (feature I). Though a large elliptical increase in NO_2 and BC concentrations was present when winds blew from the north-east, at wind speeds up to about 6-8 m/sec (feature II). All pollutants had lower concentrations at high wind speeds. There are a series of minor hotspots within the high concentration areas (features III and IV).

Further analysis was necessary to expose faint sources of air pollution. This analysis plotted a ratio of NO_2 to BC using the bivariate polar plot method. Additionally, the Conditional Probability Function (CPF) of the NO_2 to BC ratio were also plotted was used to decide the robustness of the source. However, the certainty of an event occurring was kept low (75th percentile) to discover more diffuse, faint or variable sources of air pollution.
These graphs are presented in Figures 1.B and C.

There were four major features of note on the Ratio Polar Plots, which were significant on the CPF plots; these were:

1. Northerly winds (especially from the North-East) that brought high ratios of Nitrogen to BC, with a probability approaching 100%. These winds led to ratios of 70:1 NO_2 to BC.

2. A more moderate source of NO_2 (0.70% probability), which came from South-South-Easterly winds at high wind speeds (above 4 m/sec). These winds led to concentrations of 50:1 NO_2 to BC.

Besides 'hotspots,' there are also two 'coldspots', where concentrations of BC were high compared to Nitrogen Species. These areas had a probability of high ratios (75th percentile) approaching 0%.

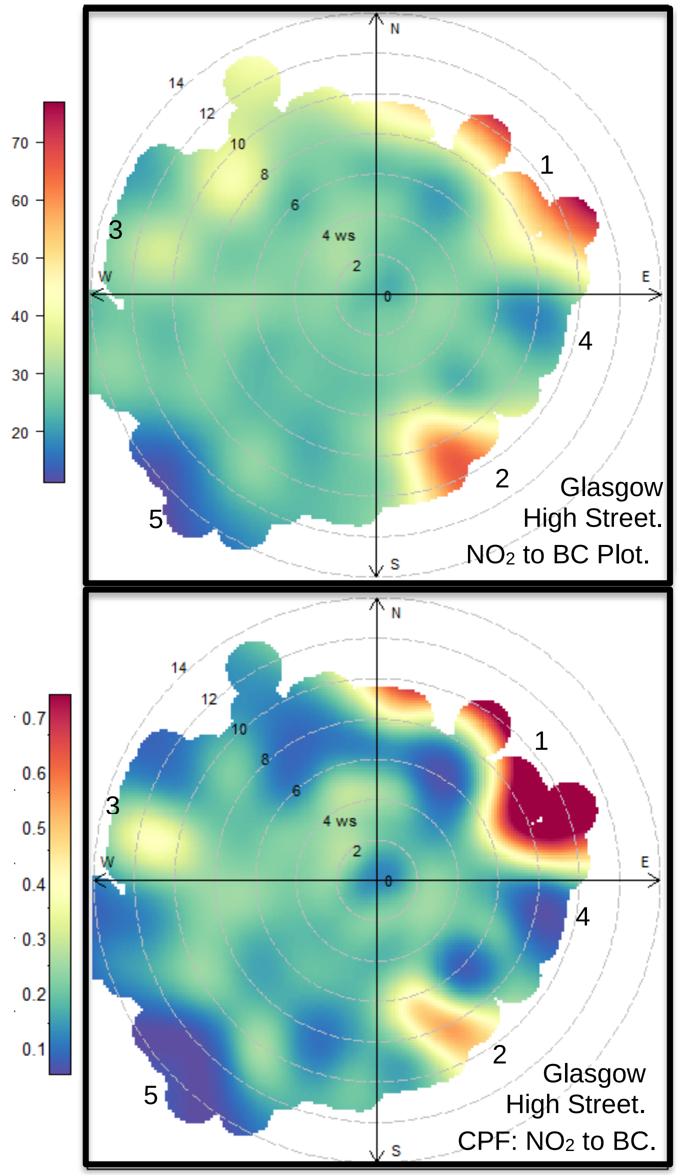
3. High wind speeds from the East-South-East which led to concentrations of 20 μg/m^3 for NO_2 per microgram of BC.

4. High wind speeds from the South West, which led to concentrations of 10 μg/m^3 NO_2: BC.

3.2. Townhead.

Similar to at High Street, the single pollutant polar plots show that the highest concentration of BC and NO_2 at Townhead was found at very low wind speeds (below ~2 m/sec). The NO_2 and BC bivariate polar plots had a 'bull's eye' distribution with moderate to high concentrations (up to 35 μg/m^3 for NO_2) in most wind directions below 2 m/sec. Although NO_2 concentrations over 10 μg/m^3 were present over 5 m/sec. Outside of the central hotspot, the concentrations were about 5 μg/m^3 with minor increases (<1 μg/m^3) echoing NO_2 trend. South-westerly air led to low concentrations of NO_2, compared to other wind directions, as did high wind speeds from the west and south-east.

The distribution of BC was similar to NO_2, in that the highest concentrations (2 μg/m^3) were found below 3 m/sec, echoing the bulls-eye pattern of the NO_2 plot. High wind speeds



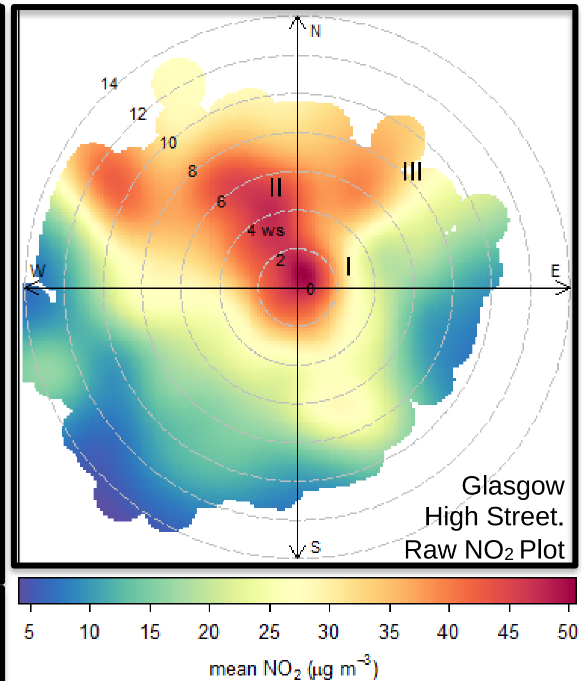


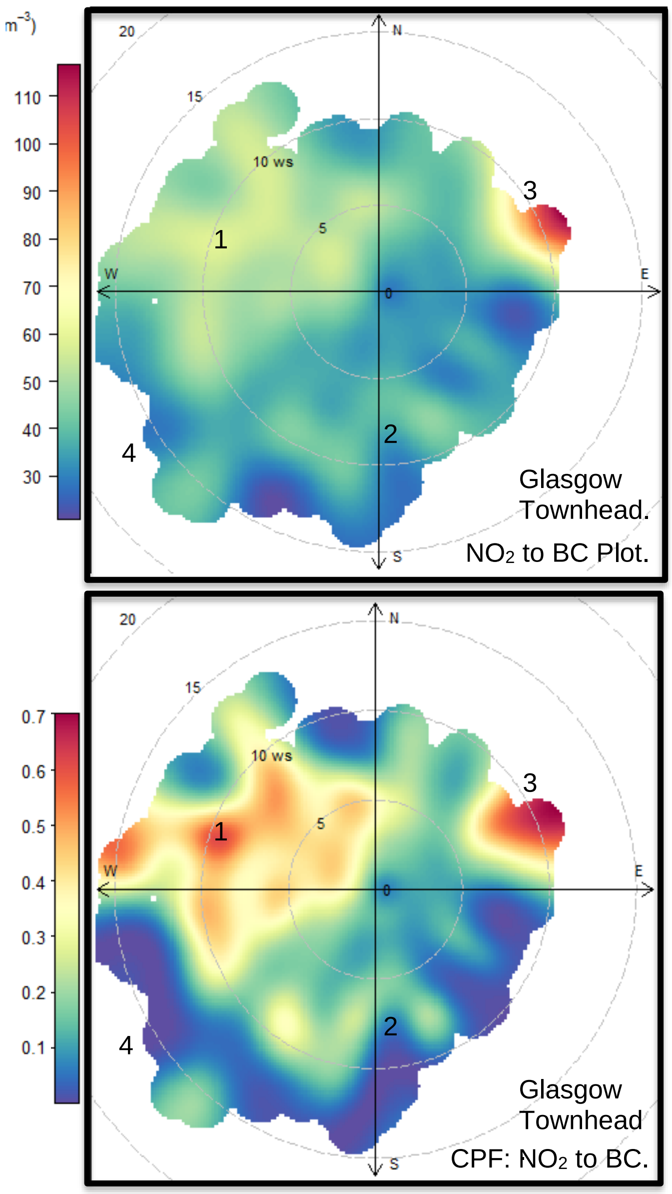
Figure 1. Shows a series of Bivariate Polar Plots produced by the openair toolset on RStudio at the Glasgow High Street Monitoring station. Sub-Figure 1.A. shows the single pollutant polar plot of Nitrogen Dioxide in micrograms per cubic meters. Sub-Figure 1.B. shows the ratio between NO_2 to BC expressed as 'X' Micrograms of NO_2 to 1 µg/m^3 of BC. Sub-Figure 1.C. Finally shows the CPF or conditional probability formula result of high ratios of NO_2 to BC co-existing with certain meteorological information i.e. wind speed and direction. The CPF is expressed as a decimal percentage i.e. 0.7 = 70%.

(>10 m/sec) led to a more drastic decline in BC concentrations, than per NO_2 leading to a BC concentration less than 0.5 µg/m^3.

Again, it was felt that a series of BC to NO_2 ratio plots with CPF analysis would be helpful to gain a better understanding of the proximity of these features. The resulting plots are displayed in Figure 2 B-C.

The ratio and polar probability projections are plotted in Figure 2 (B-C). The similarities between the air pollutants are clearer than with the single-pollutant plot alone, and new potential sources of air pollution could be identified. There were five major features of note on the CPF and Ratio Polar Plots:

1. Hotspot 1: comes from westerly to north-westerly winds rich in NO_2 at most wind speeds, with a CPF probability of >60%. The pattern is enhanced with CPF and shows a 'triskelion' shape. The BC to NO_2, concentration was 1:63 with a 60-70% probability.
2. Hotspot 2: A 'Z shaped' feature appeared on BC: NO_2 plots, but the resolution improved with CPF. The Z shaped feature extends into an F shape with winds from the south-east to south-west. In terms of ratios, BC comprises about 2% (1:50) of the NO_2 concentration. There are a series of coldspots associated with this hotspot, with ratios as low as 30-40:1 BC.



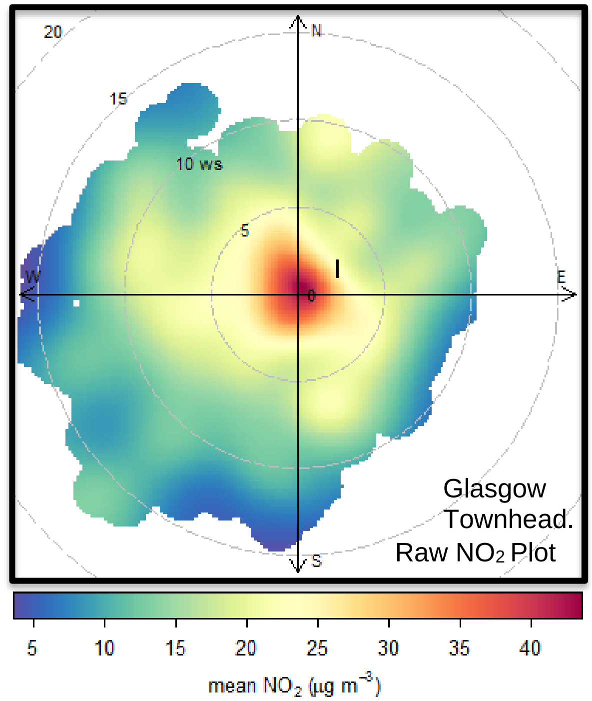


Figure 1. Shows a series of Bivariate Polar Plots produced by the openair toolset on RStudio at the Glasgow Townhead Monitoring station. Sub-Figure 1.A. shows the single pollutant polar plot of Nitrogen Dioxide in micrograms per cubic meters. Sub-Figure 2.B. shows the ratio between NO_2 to BC expressed as 'X' Micrograms of NO_2 to 1 µg/m^3 of BC. Sub-Figure 2.C. Finally shows the CPF or conditional probability formula result of high ratios of NO_2 to BC co-existing with certain meteorological information i.e. wind speed and direction. The CPF is expressed as a decimal percentage i.e. 0.7 = 70%.

3. Hotspot 3: There is a NO_2 rich anomaly to the east-north-east at high wind speeds above 5 m/sec. The anomaly was especially rich in NO_2: BC accounting for a ratio of 110:1 (0.91%); the feature also had a high (70%) CPF probability.

4 Hotspot 4: An independent coldspot from the south-west at high wind speeds with a CPF probability below 10% (showing a consistent source of nitrogen-poor and BC rich air).

Elsewhere within the polar and CPF plots (other than the cold spots and hotspots), there were low concentrations of either BC rich or NO_2 species-rich air. These trends had a ratio of 40:1 NO_2: BC.

3. DISCUSSION.

The single pollutant bivariate polar plots were of limited use in source identification; however, the ratio of BC to NO_2 revealed interesting spatial patterns. The ratio plots between BC and NO_2 helped to indicate key sources of air pollution mainly from vehicular emissions and major road junctions but also from industrial sources. The sources were identified (albeit provisionally) using map based back-trajectory analysis which sought to identify plausible similarly shaped and directionally matching sources, which could be targeted in follow-up mobile air pollution investigations.

3.1. High Street.

Five features were noted on the ratio of polar plots, three of these had a high relative concentration of BC to NO_2, while the other two had low concentrations of BC to Nitrogen. By using back-trajectory analysis, several sources were identified. These features included:

1. Hotspot 1, was likely due to the impact of local air pollution from the A8 High Street combined with heavy traffic located at the intersection between the A8 and Cathedral Street. The reason for the low relative BC ratio may have been due to the mitigative role of vegetation reducing PM emissions, whilst NO_2 seems to have been less impacted by turbulent mixing or degradation.

2. Hotspot 2, may have been sourced from the busy Duke Street multi-storey car park (1170 cars), as the building had large portal openings with an indirect line of sight to the Monitoring Station via an alleyway or landscaping.

3. Hotspot 3, was a coldspot with a high Relative BC concentration to NO_2 this was likely because of a BC rich source. The conjectured source of this BC rich air was the Well Park Brewery, which may emit as much as 1,242 tons of BC annually (Glaser *et al.* 2005; SEPA 2018). Odorous pollution is also an anecdotal brewery-related pollutant in the area (Raresdn 2018).

4. Hotspot 4, was conjectured to be due to a local street canyon effect within the Glasgow High Street enclosed area just to the south of the monitoring station, where the ratio of BC to NO_2, i.e. 10 to 1, and was similar to the Ratios at Hope Street another well-known street canyon.

3.2. Townhead.

Five features were noted on the ratio of polar plots; four of these had a high relative concentration of BC to NO_2. These features included:

1. Hotspot 1 which was likely sourced from several major roads including North Hanover Street, Cowcaddens Road, and the A804 (i.e. Baird, and Kyle Streets) and their intersections. Potentially with a minor contribution from an industrial estate, and the motorway to the north of the Monitoring Station.

2. Hotspot 2 was probably associated with car parking along with St Mungo's Avenue and its busy 60 space cul-de-sac car parks. With lower concentration areas likely corresponding to buildings whereby the BC could resuspend around corners, where-as NO_2 had a much more difficult journey.

3. Hotspot 3 likely came from the 197,000 vehicles which used the Townhead Interchange daily (DoT 2020). Despite the high traffic count, it was good to see that this source only impacted the monitoring station at very high wind speeds.

4. Hotspot 4 was a BC rich feature from the west of the lower part of Hotspot 1; the feature was probably because of Buchanan Bus Station. The BC rich character was likely a result of high wind speeds resuspending legacy BC deposits overshadowing contemporary NO_2 emissions.

3. CONCLUSION

This paper suggests that the ratio pollutant concentrations between BC and Oxides of Nitrogen (in this case, NO_2) are highly useful for source identification studies. Conditional Probability Functions (CPF) also help to create a clearer understanding of the meteorological impact and underlying variability of the source. While Carslaw, in papers from 2006 to 2019, focuses on the ratio of PM to Oxides of Nitrogen, the BC plot is perhaps even more useful, as high BC environments are likely to show combustion-related emissions, both historically (resuspended hotspots) and from soot-rich contemporary sources. In contrast, nitrogen-rich areas may show relatively recent combustion sources such as vehicular emissions.

New, and previously undiscovered, sources of air pollution were identified at the well-studied Glasgow High Street and Townhead Monitoring Stations. The sources of nitrogen supply at the High Street Monitoring Station involve the A8 High Street, road junctions, car parking facilities, and Wellpark Brewery (a previously unknown source of BC). The Townhead Monitoring Station had similar sources of nitrogen-rich air from nearby roads, including the A804, North Hanover Street, St Mungo Avenue, Buchanan Bus Station and importantly, the Townhead Interchange (J15 M8). Before this work, it was conjectured both the Townhead Interchange and Buchanan Bus Station contributed air pollution to the Townhead monitoring station, but little evidence was ever presented any definite linkages between these features.

The methods used in this chapter could enhance source identification at air quality Monitoring Stations where BC and Nitrogen are monitored in real-time. Such methods are likely to benefit air pollution analysis as characteristic shape profiles are produced, which can represent real-world features.

However, these shape, direction and ratio information are only indicative of an anomaly, and field-based air quality monitoring campaigns should be used to characterize the air pollution anomalies fully.

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