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Abstract

In January 2016 the United Kingdom's southern European Monitoring and Evaluation Programme (EMEP) level-2 air pollution monitoring "supersite" was relocated from Harwell, Oxfordshire to Chilbolton Observatory, Hampshire. As no co-location study was undertaken, this work retrospectively investigates whether the supersite relocation has led to discontinuities in the time series of concentrations of commonly studied gaseous pollutants (NO_x, NH_3, SO_2 and O_3) and particulate matter (PM2.5 and PM_{10}). Two years of measurements pre- and post- relocation (2014-15 and 2016-17 respectively) were analysed in conjunction with meteorological variables and local emission data. The *deweather* package was applied to the concatenated time series to minimise the influence of meteorology. Similar average concentrations of $PM_{2.5}$, PM_{10}, SO_2 and O_3 were observed, but there were substantial differences in that of NO_x and NH_3 (increase by factors of ~1.6 and ~3, respectively). The considerably higher NH_3 concentrations at Chilbolton are attributed to the close proximity of mixed farmland, in particular to a strong south-westerly source contributing to ~50% of the annual average. NO_x and PM concentrations in easterly winds arriving at Chilbolton are ~2.7 and ~1.5 times larger than at Harwell, from sources including the M3 motorway and Greater London. Westerly concentrations of NO_x remain similar, therefore despite a higher frequency of westerly wind, annual mean concentrations are larger. Lower concentrations of PM arriving from the west result in similar annual averages. The

secondary inorganic and black carbon components of PM were broadly similar between the sites. The differences in average NO_x and NH_3 at Chilbolton must be taken into account when considering long-term regional trends based on the southern UK supersite data.

1. Introduction

Atmospheric pollution has a significant influence on human and ecosystem health. Inhalation of ozone (O_3) and particulate matter has been linked to cardiovascular and respiratory diseases (WHO, 2006, 2013). Deposition of acidic gases causes acidification of terrestrial and aquatic ecosystems, and nitrogen deposition (e.g. from nitrogen oxides, NO_x, or ammonia, NH_3) leads to eutrophication (Sutton *et al.*, 2011; RoTAP, 2012).

Monitoring of air pollutant concentrations is important for quantifying these effects and their spatio-temporal trends (Fagerli *et al.*, 2008; Malley *et al.*, 2014). In Europe, the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, www.emep.int) has the aim of providing member states with this quantitative information (Tørseth *et al.*, 2012). Measurements within EMEP are made at rural sites representative of the surrounding area (Spangl *et al.*, 2007; Joly *et al.*, 2012) and adhere to prescribed sampling methods and siting criteria detailed by the Chemical Coordinating Centre (EMEP-CCC) to ensure comparability (Kuhlbusch *et al.*, 2014). Spatially distributed sites provide data for evaluation of regional models (Fagerli *et al.*, 2008; Cape, 2009; Malley *et al.*, 2014), whilst hourly measurements for 40+ years allow characterisation of emission patterns and separation of long-term trends from interannual variability (Tørseth *et al.*, 2012). Such data help establish achievable mitigation strategies (Pope *et al.*, 2014) and track impacts of implemented measures.

The UK has been a member of EMEP since its inception in 1979, and currently operates two level-2 "supersites" (UNECE, 2004a, 2004b) at Auchencorth Moss in southern Scotland, and Chilbolton Observatory in southern England (Defra, 2018a, 2018b; figure 1) measuring a wide range of pollutants. The southern supersite, Chilbolton, opened in January 2016 following the closure of the previous site (Harwell, figure 1) in December 2015, which had been active for several decades. The aim of this study is to investigate whether the move from Harwell to

Chilbolton led to a temporal change in the chemical climate recorded by the southern rural UK supersite. Given the extensive instrumentation, duplicate measurements could not be run for any overlap period. An analysis is presented of measurements in the years directly pre- and post- relocation (2014-15 and 2016-17 respectively), focussing on nitrogen oxides (NO_x), ammonia (NH_3), sulphur dioxide (SO_2), particulate matter <10 and 2.5 μm in diameter (PM_{10} and $PM_{2.5}$, respectively) and ozone (O_3).

2. Method

2.1 Site details

The Harwell supersite is predominantly surrounded by agricultural land near Didcot, Oxfordshire (lat: 51.571°, lon: −1.325°, altitude: 126 m), 70 km west of London and 20 km south of Oxford (figure 1). The closest minor road is ~400 m to the west and a dual-carriageway (A34) ran ~2 km to the east. The town of Didcot is ~6.4 km to the north-east. Approximately 8 km in the same direction was a coal and oil fired power station ("Didcot A"), formerly a nearby major point source of NO_x and SO_2 (Abdalmogith *et al.*, 2006; Vieno *et al.*, 2010), that closed on 22nd March 2013 and was demolished in 2016. "Didcot B", a natural gas power plant on the same site, remains operational. Measurement of atmospheric pollutants at Harwell started in 1976 (UKEAP, 2015) prior to its incorporation as an EMEP level-2 supersite (UNECE, 2004b). Operations ceased on 31st December 2015.

The Chilbolton Observatory site is located ~50 km south of Harwell in an agricultural (mainly arable) landscape, ~200 m south-east of the edge of Chilbolton village, Hampshire (lat: 51.150°, lon: −1.438°, altitude: 78 m) and 100 km south-west of London (Defra, 2018b). Two single-carriageway main roads run ~1 km to the west (A3057), and ~3 km to the south (A30) (figure 1). The site began monitoring as an EMEP level-2 supersite on 11th January 2016, after instrument relocation from Harwell.

Figure 1: (a) Locations of the UK EMEP "supersites" at Auchencorth Moss (pink), Harwell (blue), Chilbolton Observatory (orange) and the meteorological station at Benson (red). (b) Maps of the ~50 km × 50 km area surrounding Harwell (top, blue diamond) and Chilbolton (bottom, orange diamond) from OpenStreetMap (https://openstreetmap.org). The boxes surrounding each site show the 15 km × 15 km area used for comparisons with the UK National Atmospheric Emissions Inventory (NAEI) based upon the 5 km × 5 km resolution of the agricultural NH_3 emissions.

2.2 Measurement data

The full suite of measurements at the two sites is summarised in UK Eutrophying and Acidifying Pollutants (UKEAP) network reports (UK-AIR Library, 2018), a subset of which are investigated in this work (table 1, and Supplementary Information figure S1). Concentration data were downloaded from the UK Department for Environment, Food and Rural Affairs (Defra) online data repository (UK-AIR Data Selector, 2018).

Data are evaluated here for the two years either side of site relocation (Harwell 2014-15 and Chilbolton 2016-17, respectively). Data capture statistics are given in table 1. O_3, NO_x, SO_2, PM_{10} and $PM_{2.5}$ measurements derive from the UK Automatic Urban and Rural Network (AURN). Instrumentation selection, calibration and data ratification follow EU Air Quality Directives (2008/50/EC), and data are archived as hourly averages (UK-AIR Library, 2018). Hourly measurements of NH_3 and other trace gases, together with water-soluble ions within $PM_{2.5}$ and PM_{10}, are provided by the Monitor for AeRosols and Gases in Air (MARGA) instrument (EMEP, 2007; Stieger *et al.*, 2017) with data quality assurance processes as described in Twigg *et al.* (2015).

Hourly meteorological data comprise on-site measurements at Harwell and Chilbolton (CFARR, 2003). Data were also downloaded for the meteorological station at Benson, Oxfordshire (lat: 51.616°, lon: −1.096°, altitude: 57 m), marked on figure 1(a), from the NOAA Integrated Surface Database using the *worldmet* package (Carslaw, 2017; NOAA, 2018) for the full time period being considered. These data were used to validate use of concatenated meteorological time series from the two supersites (see supplementary information).

2.3 Meteorological detrending

To examine for evidence of a step-change in concentration coincident with site relocation, the *deweather* function (Carslaw, 2015) was applied to concatenated Harwell and Chilbolton datasets (2014-17) in a technique known as "meteorological normalisation" (Grange *et al.*, 2018). This accounts for non-linear and complex relationships between predictors, such as meteorological or temporal variables (Carslaw *et al.*, 2009), allowing changes in time series not directly caused by these predictors to be identified. Models are built using a stochastic process that results in reduced variance of the final model (Friedman, 2002), but consequently a slightly different model is produced with each run (Elith *et al.*, 2008). A set of 10 identically-

built *deweather* models were performed for each pollutant time series, using meteorological predictor variables measured at the same site as the pollutants. Further details of the model, including comparisons using different meteorological data, are given in the supplementary information (section S2 and figure S3).

2.4 Emission Inventories

Annual emission estimates for NH_3, NO_x, SO_2, $PM_{2.5}$ and PM_{10} were obtained from the UK National Atmospheric Emission Inventory (NAEI, http://naei.beis.gov.uk/) for both locations. Individual species emissions were taken from the 2015 inventory and were aggregated over the 15 km × 15 km area surrounding each site shown in figure 1. The areas were defined according to the gridded agricultural sector NH_3 emissions which have a spatial resolution of 5 km × 5 km, but for all other pollutants the underlying resolution was 1 km × 1 km.

3. Results and discussion

3.1 Overview

Table 1 summarises the annual mean concentration and corresponding 95% confidence interval for each pollutant for each year. Chilbolton MARGA measurements have the lowest data capture (54-58%) since these measurements did not commence until 11th February 2016, and instrument issues led to missing data between 9th July and 1st September 2016. Between August 2014 and September 2015 a plume from the volcanic eruption at Holuhraun, Iceland, passed over the UK and is observed in the SO_2 time series (figure S1). Similarly in spring 2014, elevated PM concentrations were caused by a combination of Saharan dust and ammonium nitrate formed from European emissions (Vieno *et al.*, 2016) (figure S1). Other PM episodes are also apparent between 2014 and 2017 (figure S1), typically accumulating in low wind speeds and lasting no more than a few days (Defra, 2015, 2016, 2017).

Table 1: Annual mean concentrations (with 95% confidence intervals) and annual percentage data capture of measurements for the investigated species at Harwell (2014-15), and Chilbolton (2016-17).

Species	Instrument	Annual mean concentration ± 95% confidence intervals / $\mu g\ m^{-3}$ (Data capture / %)			
		Harwell 2014	Harwell 2015	Chilbolton 2016	Chilbolton 2017
SO_2	Monitor for AeRosols and Gases in Air (MARGA)	0.245 ± 0.028 (94%)	0.150 ± 0.0027 (70%)	0.157 ± 0.0044 (58%)	0.131 ± 0.0032 (79%)
HONO		0.464 ± 0.0068 (94%)	0.340 ± 0.0049 (70%)	0.494 ± 0.011 (58%)	0.454 ± 0.008 (79%)
HNO_3		0.159 ± 0.0029 (94%)	0.138 ± 0.0032 (68%)	0.159 ± 0.0050 (57%)	0.162 ± 0.0037 (80%)
NH_3		1.96 ± 0.049 (95%)	2.05 ± 0.044 (70%)	5.88 ± 0.22 (54%)	6.23 ± 0.18 (82%)
		Automatic Urban and Rural Network (AURN)			
O_3	UV absorption	56.0 ± 0.45 (99%)	57.1 ± 0.42 (98%)	48.9 ± 0.53 (97%)	51.5 ± 0.48 (98%)
NO_x	Chemiluminesence	10.5 ± 0.30 (97%)	9.20 ± 0.22 (97%)	18.5 ± 0.49 (91%)	13.8 ± 0.35 (97%)
NO_2		7.99 ± 0.20 (97%)	7.68 ± 0.16 (97%)	14.3 ± 0.25 (91%)	11.2 ± 0.19 (97%)
PM_{10}	TEOM-FDMS	14.3 ± 0.27 (74%)	15.1 ± 0.21 (89%)	14.9 ± 0.25 (85%)	13.3 ± 0.19 (98%)
$PM_{2.5}$		9.06 ± 0.19 (96%)	8.55 ± 0.17 (96%)	9.45 ± 0.19 (93%)	7.38 ± 0.17 (98%)
SO_2	UV fluorescence	1.01 ± 0.054 (98%)	0.939 ± 0.013 (93%)	0.876 ± 0.017 (64%)	0.763 ± 0.013 (89%)

3.2 NO_x

The average 2016 and 2017 concentration of NO_x at Chilbolton was approximately 1.6 times greater than the average 2014 and 2015 concentration at Harwell (annual means of 18.5 and 13.8 $\mu g\ m^{-3}$ *c.f.* 10.5 and 9.20 $\mu g\ m^{-3}$ respectively, table 1). The NO_x *deweather* time series also shows an abrupt increase coincident in timing with the relocation of the measurement site (figure 2(a)).

In contrast to the greater average NO_x concentrations at Chilbolton, the total local NO_x emissions integrated over the 15 km × 15 km area around Harwell are more than 5 times greater than from the same-size area around Chilbolton (figure 3). The NO_x emissions close to Harwell are dominated by specific sources including Didcot town, Didcot B power station in the north-

east, and a high traffic flow on the dual-carriageway (A34) running north-south 2 km to the east. Across the 225 individual 1 km × 1 km grid squares within the area surrounding Harwell, 47% of total local emissions are contributed by the grid square with the highest emissions, whilst the 25 highest emission grid squares contribute 84%. Similar analysis at Chilbolton show less dominance of local emissions from the single highest (6%) and 25 highest (61%, including part of the A303, ~8 km north) grid squares.

Figure 2: Modelled pollutant concentrations of (a) NO_x, (b) NH_3, (c) $PM_{2.5}$, (d) PM_{10} and (e) O_3 predicted using the *deweather* function for R (Carslaw, 2015) applied to concatenated time series of hourly measurements at Harwell until 31st December 2015 and at Chilbolton from 11th January 2016. Modelled data have been smoothed by plotting the daily mean predicted concentration.
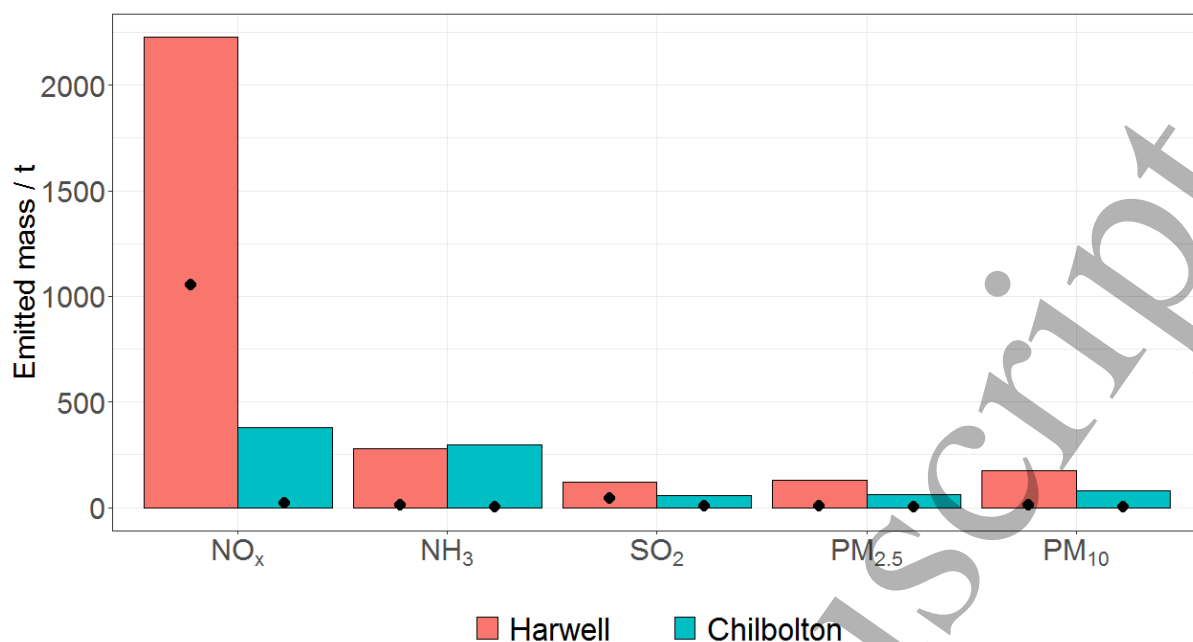
Figure 3: Annual emissions of NO_x, NH_3, SO_2, $PM_{2.5}$ and PM_{10} from the National Atmospheric Emissions Inventory database (NAEI, http://naei.beis.gov.uk/) for the 15 km × 15 km areas centred on the Harwell and Chilbolton sites. Underlying data are at 5 km × 5 km grid resolution for agricultural NH_3, and 1 km × 1 km for all other pollutant maps. The bar shows the total emissions, whilst the black point indicates the emission from the component grid square with the maximum emission across the contributing grid squares.

These differences in NO_x source configurations are illustrated by pollution wind roses (figure 4). The aforementioned sources north of Harwell generate the most polluted air transported to the site, but do not contribute significantly more to the annual average than other directions. Considering NO_x to have an atmospheric lifetime of ~4-6 h in the mid-latitudes (Beirle *et al.*, 2011) and an average wind speed of ~15 km h^{-1} for southern England (figure S2; CFARR, 2003; NOAA, 2018), the London pollution plume could plausibly be observed at both sites. It appears Harwell is less influenced by London (~100° bearing) than Chilbolton (~70°), for which this wind direction provides a dominant contribution to the annual average. However the M3 motorway also contributes NO_x to this wind direction, stretching for ~56 km between Chilbolton and London. Traffic along the length of the M3 (~95 km) and other major roads are the probable reason why a larger average concentration of NO_x (>2.2 times higher) is observed in easterly (0-180°) than in westerly winds (181-360°, table 2). More frequent westerly winds during 2017 led to a reduced annual average compared with 2016 (13.8 *c.f.* 18.5 μg m^{-3}).
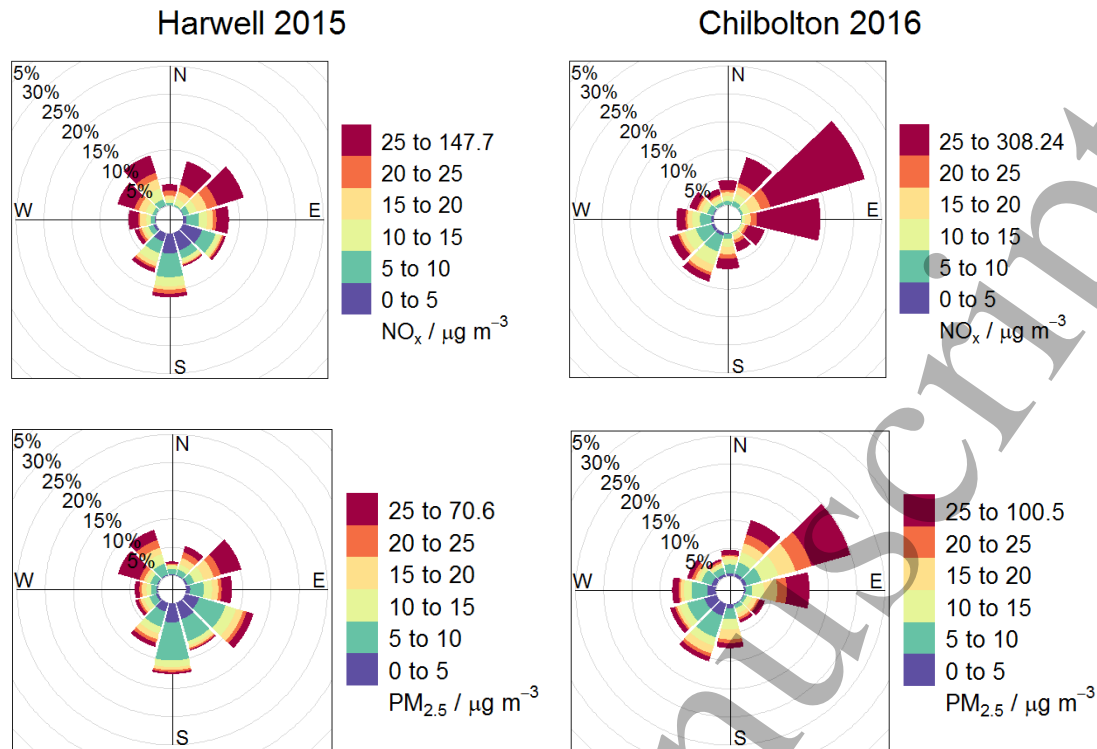
Figure 4: Pollution wind roses for NO_x and $PM_{2.5}$ concentrations at Harwell in 2015 and at Chilbolton in 2016, depicting the contribution of 5 µg m^{-3} concentration bins in each wind sector to the annual mean concentration. Wind and pollutant concentration measurements were co-located and the underlying time resolution was hourly for both. The maximum hourly concentration in each year is the upper-limit value of the red segment in each legend.

Table 2: Annual mean concentrations of hourly NO_x measurements for easterly (0-180°) and westerly (181-360°) wind directions. The remaining percentage of data (% NA) includes hours where NO_x concentration or wind direction were not recorded.

Site and year	Mean NO_x concentration / µg m^{-3}		Percentage of total annual wind / %		
	Westerly	Easterly	Westerly	Easterly	NA
Harwell 2014	11.1	10.0	39	59	2
Harwell 2015	10.5	8.60	34	55	11
Chilbolton 2016	12.0	28.6	54	35	11
Chilbolton 2017	10.2	22.6	69	28	3

The importance of wind direction to NO_x concentrations at both sites is reflected in the relative importance of variables used in the *deweather* models (table S2). Wind direction had the largest mean relative importance of 19.1%, closely followed by ambient temperature (18.7%) and (long-term) trend (18.4%). Unsurprisingly, predicted concentrations of NO_x are elevated at

lower ambient temperatures (≤10 °C) and during colder months (October-February), as these conditions limit the dispersion of emissions (AQEG, 2004), and there is a higher demand for domestic heating. The importance of the trend variable is a consequence of the abrupt increase in NO_x at the time of site relocation in the concatenated *deweather* time series (figure 2(a)). This supports the interpretation of a real difference in annual mean NO_x concentration between Harwell and Chilbolton.

3.3 NH_3

The annual mean NH_3 concentrations at Chilbolton in 2016 and 2017 (5.88 and 6.23 μg m^{-3}, respectively, table 1) are about 3 times higher than at Harwell in 2014 and 2015 (1.96 and 2.05 μg m^{-3}, respectively), the greatest difference of all pollutants investigated. Although data capture at Chilbolton in 2016 was rather low (58%), and most missing data occurred during the summer (figure S1) when NH_3 concentrations are typically larger (Tang *et al.*, 2018), therefore the annual average in 2016 is likely biased low by the missing data.

Application of the *deweather* model to the concatenated time series of NH_3 concentrations (figure 2(b)) confirms a distinct increase in mid-February 2016, coincident with commissioning of the MARGA at Chilbolton. Trend is the dominant variable in the *deweather* model (45.5 ± 0.6%, figure S4 and table S2). The raw time series shows elevated springtime concentrations at Harwell (figure S1), consistent with typical livestock manure and synthetic fertiliser applications observed in NW European springtime (Vieno *et al.*, 2016). These springtime peaks are mirrored in the predicted concentrations of NH_3 during 2014 and 2015, and reflected by the partial dependency of the week-of-year variable predicting increased concentrations during Julian weeks 5-20 (figure S4). Following site relocation the *deweather* time series showed NH_3 concentrations remaining high, with large and infrequent peaks that demonstrate little seasonality. Despite this, maximum hourly NH_3 at Chilbolton in 2016 and 2017 were during spring (126 μg m^{-3} on 22nd March 2016 and 94.4 μg m^{-3} on 24th May 2017).

Ammonia has a short atmospheric lifetime and high spatial heterogeneity in its sources (Vogt *et al.*, 2013; Dammers *et al.*, 2017), so receptor concentrations are significantly influenced by local emissions. The contrasting concentrations at Harwell and Chilbolton are not reflected in the total NAEI estimates of local NH_3 emissions, which show similar averages over the 15 km × 15 km area surrounding each site (figure 3). However, the total at Harwell includes

contribution from a disproportionately large 1 km × 1 km grid square over the site of Didcot B power station, over 3.4 times greater than any other grid square surrounding either site. When emissions from only the agricultural sector are considered, the greatest emissions are associated with the 5 km × 5 km grid square also containing the site, suggesting the presence of a nearby agricultural source or sources.
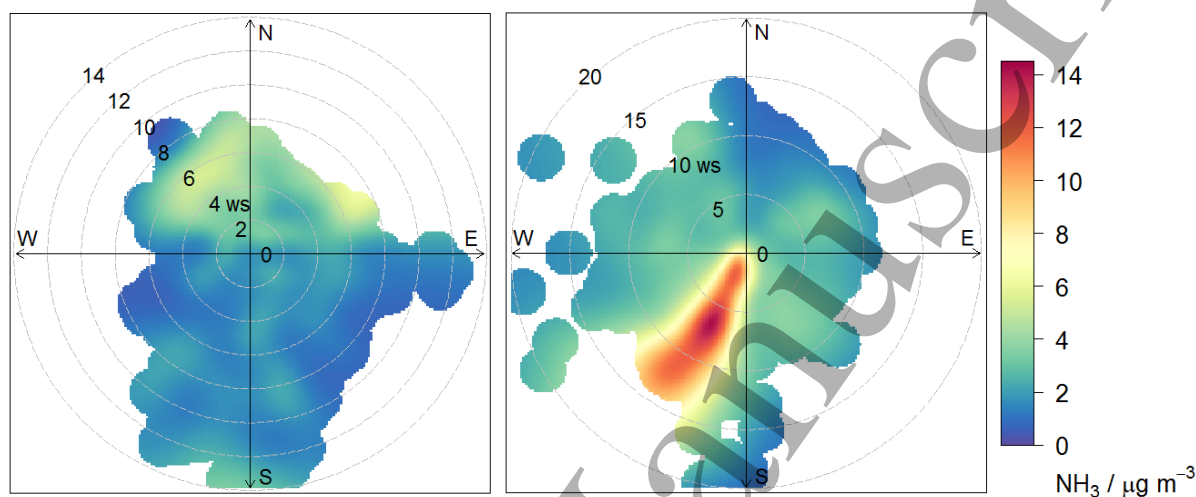

Figure 5: Polar plots of hourly NH_3 concentration (MARGA) as a function of hourly wind speed and direction at Harwell 2015 (left) and Chilbolton 2016 (right). Wind and NH_3 concentration measurements were co-located.

Polar plots of NH_3 concentration as a function of wind speed and direction for both sites (figure 5) reveal an obvious dominant local source to the south-west of Chilbolton. Figure 6 demonstrates the difference in concentration between this source and background NH_3 at Chilbolton in 2016, by dividing prevailing wind into four direction sectors: east (E, 30-180°), south-west (SW, 180-250°), north-west (NW, 250-350°) and north (N, 350-30°). The N sector appears to reflect background NH_3 levels, with a mean concentration of 2.2 μg m^{-3}, comparable to average NH_3 concentrations measured at Harwell across all wind directions (figure 5). Mean concentrations in E, NW and SW sectors are higher (3.1, 3.4 and 7.1 μg m^{-3}, respectively) and demonstrate an inverse relationship with wind speed, suggesting nearby sources at Chilbolton. Approximately 1.5 km from the site in the SW sector is the centre of a cattle farm, whilst a further 1.5 km in the same direction is a mushroom farm, likely to release NH_3 at regular intervals coinciding with mushroom growth cycles (Sather *et al.*, 2008). For the remaining E/NW sectors, NH_3 concentrations presumably reflect levels associated with the surrounding

intensively managed arable land, which in general are larger emitters than agricultural activities near Harwell.
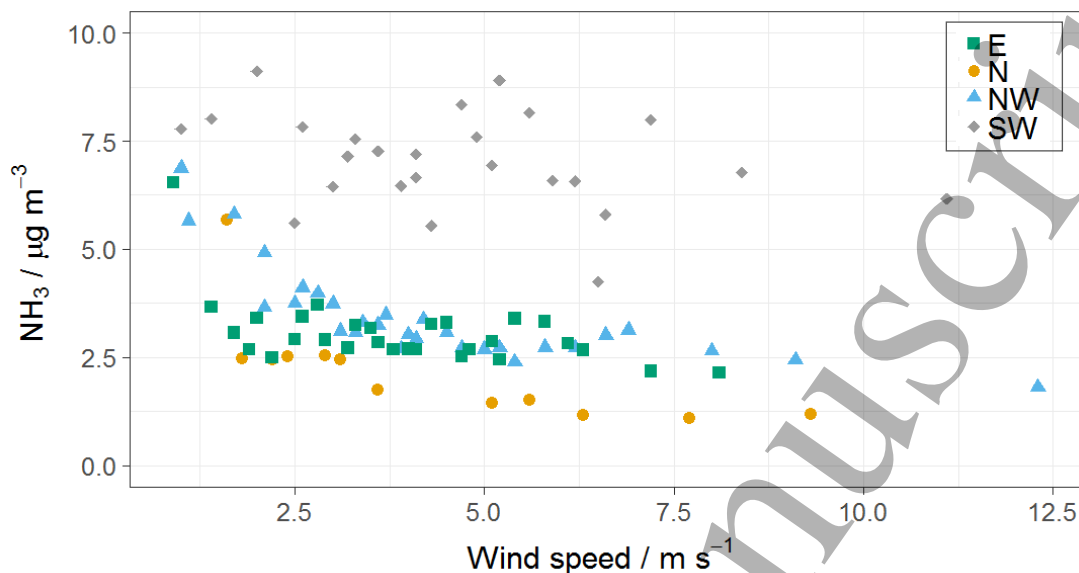

Figure 6: Hourly NH_3 concentrations (MARGA) as a function of wind speed at Chilbolton in 2016, for the four wind direction sectors: north (350-30°), south-west (180-250°), east (30-180°) and north-west (250-350°). Data points are medians of 50 hourly measurements sorted by ascending wind direction, following Flechard *et al.* (1998).

3.4 SO_2

Hourly SO_2 concentrations at both sites are determined by two different measurement methodologies (table 1) but there was poor agreement between them (figure S5). This is anticipated, as the limit of detection (LOD) of the UV fluorescence analyser (1.5 ppb, ~4 μg m^{-3}) is approximately two orders of magnitude greater than that of the MARGA (0.04 μg m^{-3} (Makkonen *et al.*, 2012)). The aim of the AURN SO_2 analysers is to detect pollution events (Twigg *et al.*, 2016) where concentrations could exceed national/EU limit values (hourly and daily means of 350 and 125 μg m^{-3}), whereas the MARGA is designed to monitor changes in background concentrations of SO_2. Extending the time series of SO_2 measurements at Harwell back to 2012 shows that there was a large reduction in concentrations in early 2013 (figure 7), coincident with the closure of Didcot A coal and oil power station, which whilst operational was one of the largest SO_2 emission sources in the UK (Vieno *et al.*, 2010). Following this

event there are no discernible changes in SO_2 concentration, including through the site relocation, apart from a singular peak in August 2014 which can be attributed to an Icelandic volcanic eruption (Twigg *et al.*, 2016). Whilst the emission inventory estimates greater local SO_2 emissions around Harwell than around Chilbolton (figure 3), these are overwhelmingly dominated at Harwell by Didcot B power station. The relative infrequency of north-easterly wind to the site, coupled with the elevated source of these emissions, resulted in little influence of Didcot B on ambient measured concentrations. Consequently, there is effectively no change in measured SO_2 arising from the site relocation.
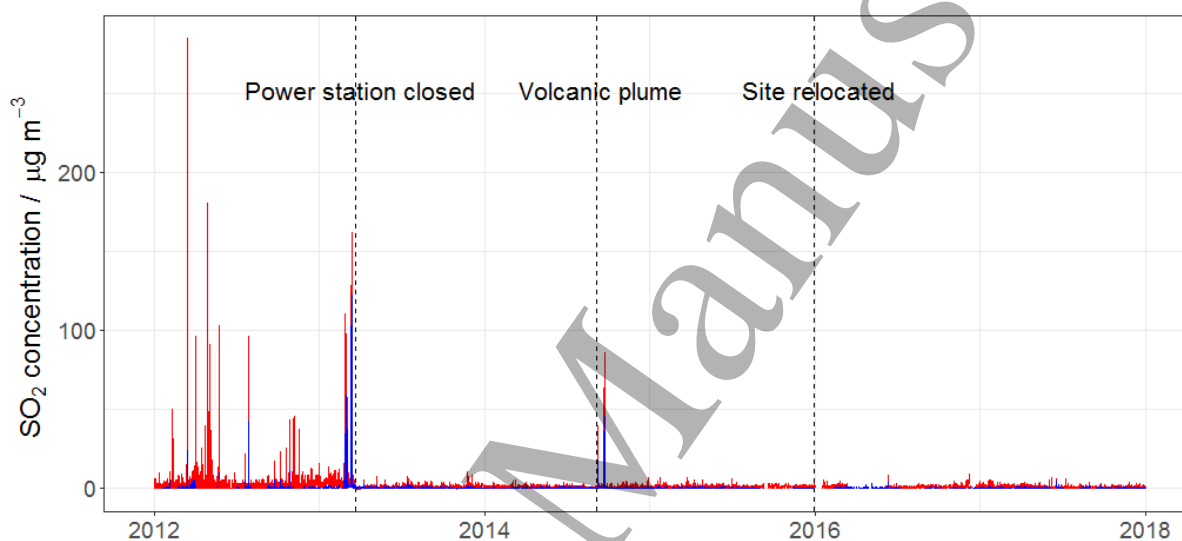

Figure 7: Time series from 1st January 2012 to 30th September 2017 of hourly SO_2 concentrations measured using UV fluorescence in the AURN (red), and by the MARGA (blue). Vertical dotted lines show the closure of Didcot A power station (22nd March 2013), the volcanic eruption plume from Holuhraun, Iceland passing over the UK (September 2014) and the site relocation from Harwell to Chilbolton in early January 2016.

3.5 Particulate Matter

Data capture was high for total PM_{10} and $PM_{2.5}$ (table 1), but poorer for the individual species concentrations. Annual mean concentrations of PM_{10} and $PM_{2.5}$ were similar at Harwell and Chilbolton (2014 & 2015 average PM_{10} = 14.7 µg m^{-3}, 2016 & 2017 average PM_{10} = 14.1 µg m^{-3}; equivalent data for $PM_{2.5}$ = 8.8 and 8.4 µg m^{-3}), indicating no substantive change in long-term mean PM concentration at the time of site relocation. There was also no significant

difference in the number of PM_{10} daily mean exceedances of 50 μg m^{-3} before and after site relocation: twice each year at Harwell, 3 times at Chilbolton in 2016 and once in 2017.

The *deweather* models for both $PM_{2.5}$ and PM_{10} (figures 2(c) and (d)) show temporal variability, but no evidence of a significant step-change in concentration at the time of site relocation. The model predicted lower concentrations of PM_{10} in June 2016 because measured values in this period 12th June – 31st July 2016 (mean of 7.6 μg m^{-3}) were substantially lower than the mean for the rest of the time series (14.4 μg m^{-3}). There is a similar effect in the modelled $PM_{2.5}$ time series. Model disagreement in the latter part of the $PM_{2.5}$ *deweather* time series is presumed to be due to the presence of a large measurement value (186.8 μg m^{-3}, 27th April 2017), almost twice any other hourly $PM_{2.5}$ concentration. The stochastic nature of the *deweather* function resulted in some models being built using this data point, while others were not.

The annual NAEI emissions integrated over the 15 km × 15 km area surrounding each site are substantially greater around Harwell than Chilbolton for both PM_{10} and $PM_{2.5}$ (figure 3). Locations of high $PM_{2.5}$ emissions within the area surrounding Harwell include those with substantial NO_x emissions (Didcot town, Didcot B power station and the A34). The 25 1 km^2 grid squares with highest PM emissions around Harwell contribute 63% to the total, whereas the equivalent at Chilbolton contribute 54%. As with NO_x, an increase in $PM_{2.5}$ concentrations is observed in the prevailing easterly wind at Chilbolton as compared to Harwell (13.2 in 2016 *c.f.* 8.1 μg m^{-3} in 2015, table S3), however westerly winds have lower concentrations (6.8 *c.f.* 9.6 μg m^{-3}), which accounts for the comparable annual averages pre- and post- relocation. The same conclusions apply for PM_{10} (figure S6).
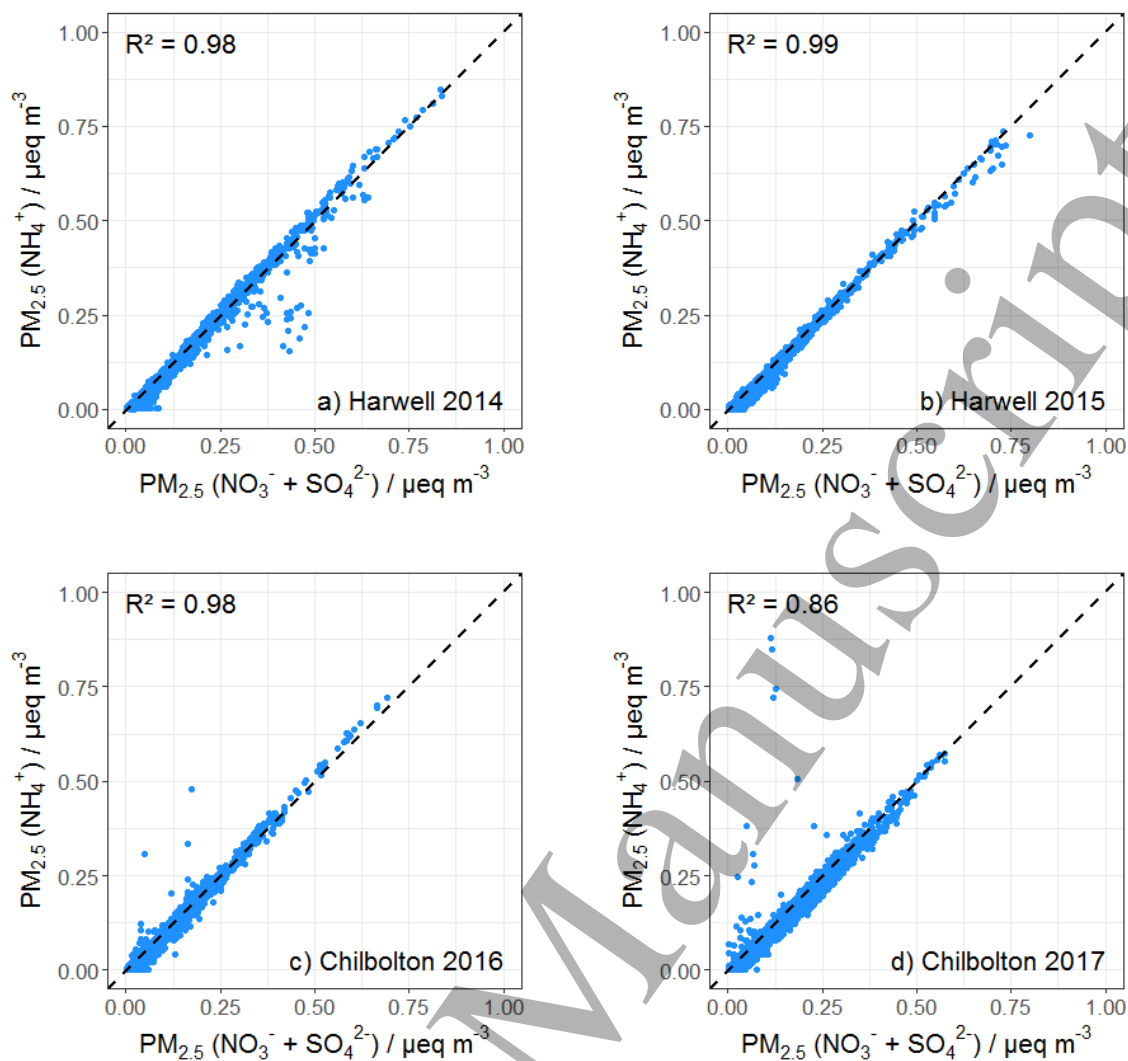
Figure 8: Measured ion balance (in µeq m^{-3}) between NH$_4^+$ and the sum of NO$_3^-$ and SO$_4^{2-}$ in PM$_{2.5}$ during the two years at Harwell (2014 and 2015) and Chilbolton (2016 and 2017). Black dotted line illustrates 1:1 ratio.

Data capture for MARGA measurements were poorer than for TEOM-FDMS measurements (table 1). Nevertheless for all secondary inorganic aerosol (SIA) ions analysed, the data capture rate was sufficient for comparisons of annual measurements (all years >58%). Anthropogenically-derived NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ dominate PM$_{2.5}$ at both sites, contributing an average of 58% to total measured mass at Harwell (2014-15) and 59% at Chilbolton (2016-17). The calculated SIA ion balance for PM$_{2.5}$ (figure 8) shows good correlation for all years, despite a few events of exception. More acidic aerosols are observed in 2014, with the greatest excess in September where concentrations of SO$_4^{2-}$ were significantly elevated from the Holuhraun eruption plume passing over the UK (Twigg *et al.*, 2016). Both years at Chilbolton exhibit a

large excess of basic aerosol on days reaching high NH_4^+ concentrations (8.64 and 22.6 μg m^{-3} on 22nd March 2016 and 11th March 2017 respectively; table 3). In general, all years appear to have a slight bias towards basic aerosol, and are comparable to observations at the northern UK EMEP supersite (Auchencorth Moss; Twigg *et al.* 2015). Similar observations apply to the coarse fraction ($PM_{coarse} = PM_{10} - PM_{2.5}$), where SIA contributes 15% to total aerosol mass at both Harwell (2014-15) and Chilbolton (2016-17). Annual average black carbon measurements (Aethalometer, Black Carbon Network) are comparable at ~0.40 μg m^{-3} between Harwell (2014-15) and Chilbolton (2016-17). Given the comparable total PM at both sites, this indicates that there is also a similar contribution of secondary organic aerosols (SOA) in both fractions.

Table 3: Annual mean particulate NH_4^+, NO_3^- and SO_2^{2-} concentrations measured by MARGA in PM_{10} and $PM_{2.5}$. Key: max = maximum hourly measurement of the year, μ_A = arithmetic annual mean and σ_A = arithmetic standard deviation across the year.

	2014 μg m^{-3}			2015 μg m^{-3}			2016 μg m^{-3}			2017 μg m^{-3}		
$PM_{2.5}$	NH_4^+	NO_3^-	SO_4^{2-}	NH_4^+	NO_3^-	SO_4^{2-}	NH_4^+	NO_3^-	SO_4^{2-}	NH_4^+	NO_3^-	SO_4^{2-}
max	15.2	47.4	29.9	13.2	38.0	13.3	13.0	33.7	9.98	22.6	29.0	13.5
μ_A	1.25	2.62	1.87	0.94	2.33	1.87	1.28	2.98	1.43	1.05	2.78	1.38
σ_A	1.75	4.17	2.20	1.46	3.95	1.04	1.51	3.78	1.04	1.49	3.69	1.23
PM_{10}												
max	16.0	50.9	31.4	13.8	41.2	13.9	12.8	34.0	9.7	21.6	35.9	15.8
μ_A	1.31	2.97	2.02	0.98	2.65	1.48	1.35	3.50	1.55	1.17	3.37	1.61
σ_A	1.82	4.42	2.32	1.51	4.17	1.09	1.53	4.04	1.05	1.61	4.15	1.33

3.6 Ozone

Data capture for hourly O_3 concentrations was high (>98% for each year, table 1). Annual mean concentrations of O_3 were somewhat lower after the site relocation, 48.9 and 51.5 μg m^{-3} for 2016 and 2017 respectively at Chilbolton, compared with 56.0 and 57.1 μg m^{-3} for 2014 and 2015 at Harwell (table 1). However, the *deweather* model time series for O_3 data (figure 2(e)) does not show evidence of a step-change associated with the site relocation (the modelled decrease in mid-2016 is coincident with the similar observation for PM). The slightly lower annual mean background O_3 at Chilbolton than at Harwell may be due to interannual variability

in O_3, but the lower background concentration is also consistent with an inverse concentration relationship with the unambiguously higher background NO_x at Chilbolton.

4. Conclusions

The relocation of the southern UK EMEP supersite from Harwell to Chilbolton in January 2016 has not resulted in discontinuities in average measured concentrations of $PM_{2.5}$, PM_{10}, SO_2 and O_3 (based on two-year pre- and post-relocation time comparisons), but has led to substantial increases in average concentrations of NO_x and NH_3, by a factor of ~1.6 and ~3, respectively.

Concentrations of NO_x and PM in easterly wind arriving at Chilbolton are ~2.7 and ~1.5 times larger than at Harwell, from common sources including the M3 motorway and Greater London. Prevailing winds from the west contribute similar NO_x concentrations at both sites, therefore despite a higher frequency of westerly wind at Chilbolton, the larger easterly concentrations result in larger annual means. Westerly winds carry lower concentrations of PM to Chilbolton than Harwell, thereby resulting in similar annual averages. Measurements show no substantive difference in the contribution of secondary inorganic aerosols (SIA) and black carbon to the total PM mass between the two site locations, although more NH_4^+ events are observed in the SIA at Chilbolton. Background concentrations of NH_3 at both sites reflect the presence of mixed farmland; however the contribution of very strong local sources to the south-west of Chilbolton cause the large increase in annual average between sites.

In conclusion, when considering long-term regional trends based on the southern UK supersite data, the increase in NO_x and NH_3 at Chilbolton must be taken into account and the Harwell and Chilbolton datasets should be treated separately.

Acknowledgements

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