Artworks D-NO_X Paint Trial

Report

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1. Summary

This study aimed to assess the efficacy of photocatalytic paint as a means to reduce the concentration of nitrogen oxides, particularly NO_2 in the area of the Artworks Elephant (Figure 1). The Artworks is a creative work hub with businesses in repurposed shipping containers near Elephant and Castle in central London.

Figure 1: The Artworks Elephant (image: Landlease)

In order to evaluate the efficacy of the D-NOx paint on the concentration of Nitrogen Oxides, a monitoring station was installed between September 2014 and November 2015 to measure the NO, NO_2 and NO_X concentrations before and after photocatalytic paint was applied to the courtyard and adjacent walls in the Artworks in May 2015. Changes in concentration were evaluated by comparing daytime and night-time pollution trends using the analysis plan summarised in Figure 2.

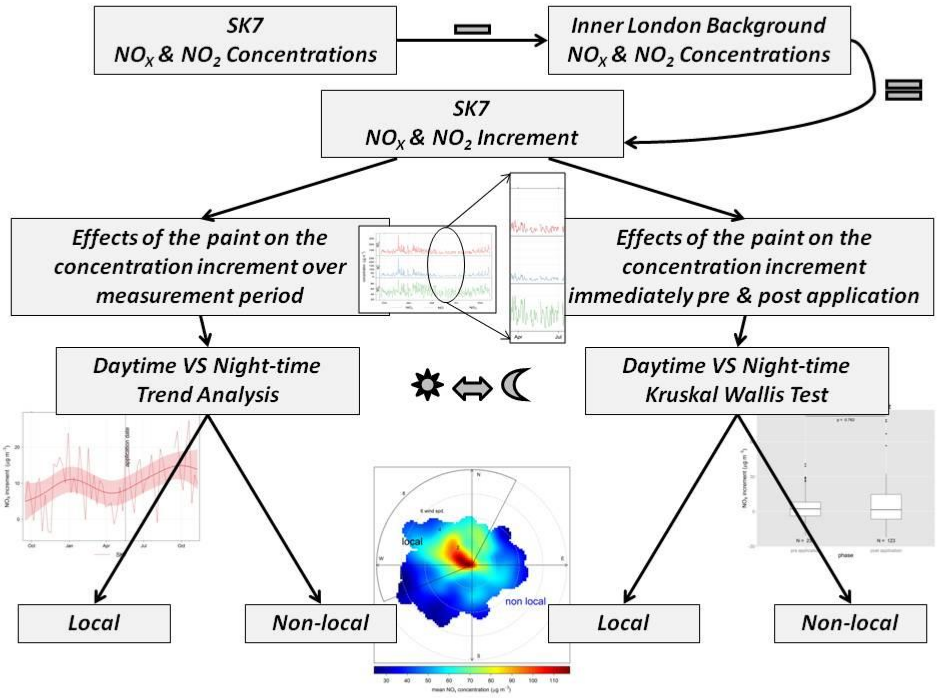

Figure 2: Analysis Overview

Detecting relatively small changes in atmospheric concentrations independent of large scale meteorological variations and the influence of changing local emissions is extremely challenging.

After accounting for these large scale variations by removing the background concentrations, the local increment of NO_X and NO_2 was found to increase through the study; probably due to changes in the traffic patterns. Against this increase in local emissions, no statistically significant difference in NO_X and NO_2 increment concentrations pre and post paint application could be detected.

2. Introduction

Nitrogen oxides are gases, which are comprised of nitrogen dioxide and nitrogen oxide and released into the atmosphere during the combustion of fossil fuels. Nitrogen dioxide can affect our health, including reduced life expectancy. It can also effect vegetation and is a precursor gas to ozone, which in turn is harmful to health, vegetation and materials (COMEAP, 2015; AQEG, 2004).

To protect our health, the European Union and the UK Government have set air quality objectives for air pollutants, such as nitrogen dioxides in their Air Quality Strategy. These objectives are still regularly exceeded and despite many years of investment in exhaust emission abatement technology, moving from Euro 4 to 5 etc. (EC Regulation 715/2007/EC), and policy interventions such as the London Low Emission Zone, the concentrations of pollutants, especially nitrogen dioxide, remain high in many locations, such as the Elephant and Castle Area (Figure 3).

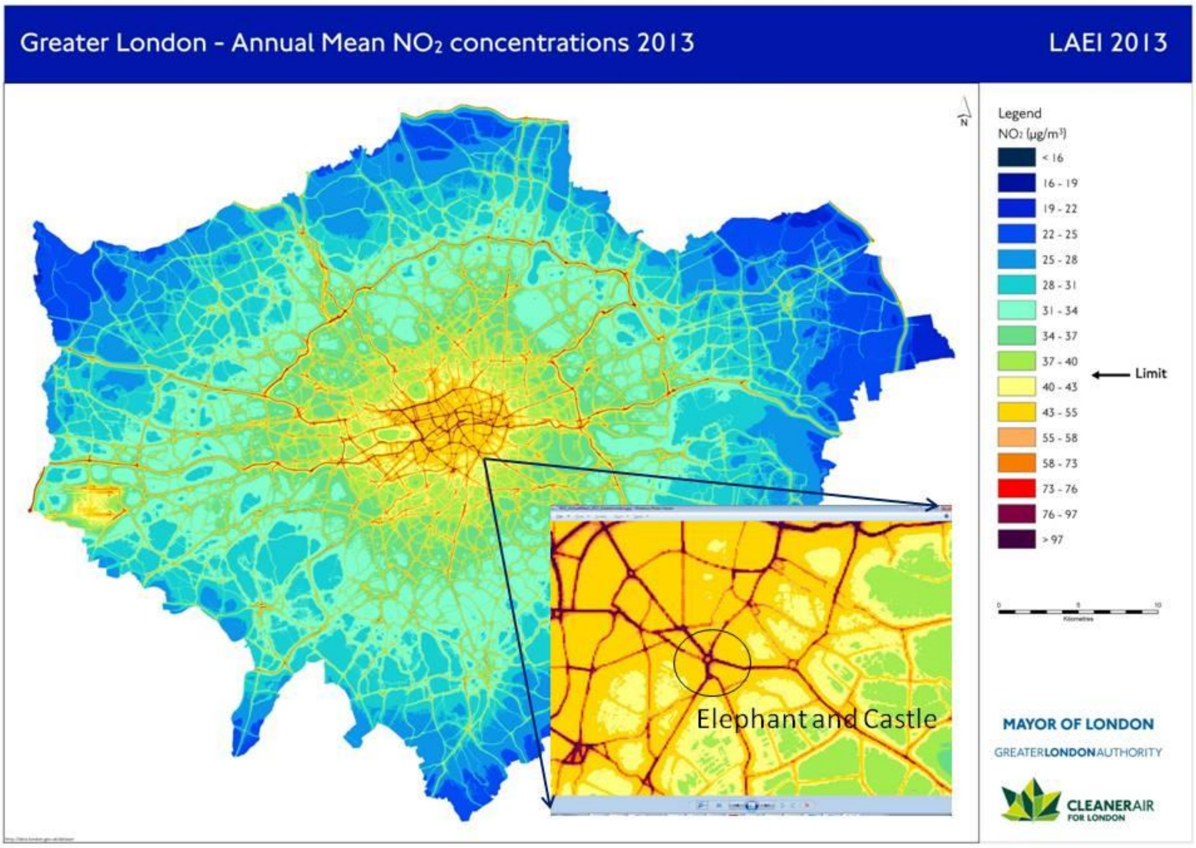

Figure 3: Annual Mean NO_2 concentration (GLA, 2016)

Photocatalytic paint contains titanium dioxide; a compound that acts as a catalyst when exposed to ultraviolet light. Through this photocatalytic reaction the paint can oxidise atmospheric nitrogen oxides to surface absorbed nitrate, which is subsequently washed off. This potentially leads to the removal of nitrogen oxides in the air and has therefore been trialled as an abatement technology (AQEG, 2016).

It is worth noting that it is generally harder to reduce the emissions once they are released into the atmosphere, which the paint is aiming to do, then it is to reduce the emissions at the source. This is because the volume of the ambient atmosphere is large compared to the surface area that can be covered and concentrations in the atmosphere depend on many additional factors.

Under laboratory conditions these paints and other photocatalytic products have been shown to reduce NO_X and NO_2 concentrations, which led to an increased interest in them as a way to reduce ambient NO_2 concentrations in order to meet EU limit values (AQEG, 2016).

However, measuring the efficacy of the paint to reduce ambient NO_2 concentrations is challenging and field trials have had mixed results. PICADA, an EU-funded project, showed reductions of NO_X concentrations (Maggos et al., 2008) but the design was criticised for being unrealistic (high surface to volume ratio) and not applicable to real life situations (AQEG, 2016). Another EU-funded project, Photopac, and a field trial in London did not show strong, compelling evidence that the paint is efficient in reducing ambient concentration of NO_X and NO_2 (Gallus et al., 2015, Barratt et al., 2012).

This study site addresses some of the limitations of the previous London trial site in Camden (Barratt et al., 2012) as it is closer to the road and therefore has higher NO_X concentrations, and a larger area of surrounding surface was painting with photo-catalytic paint.

3. Methods

3.1. *Study area*

The study area was the Artworks Elephant, which is south east of the Elephant and Castle roundabout and station and is part of the Elephant and Castle regeneration work. The Artworks boxpark is a creative work hub with over 30 start-up businesses in repurposed shipping containers. The covered courtyard has a seated area for the adjacent food outlets and is also used as events space.

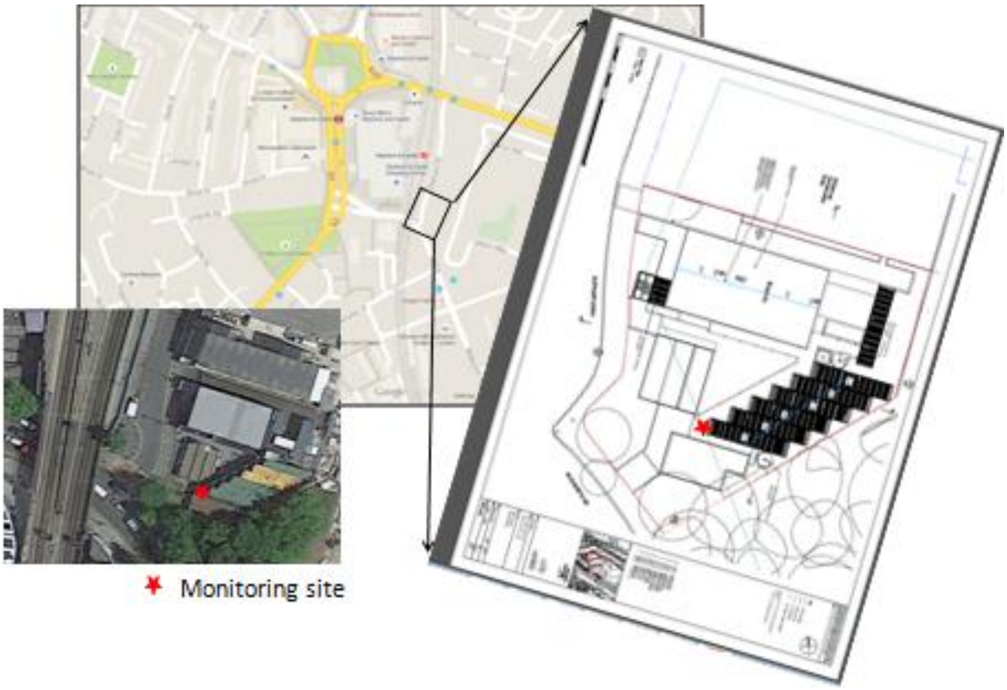

Figure 4: Location, layout and aerial view of the Artworks Elephant and the monitoring site

The Air Quality Monitoring Site (SK7) was located on the ground level in a corridor between the Artworks office/sales unit and unit 3 shipping container (see Figure 4 and Figure 5), adjacent to the courtyard. The inlet was positioned on the corner of the courtyard/in front of unit 3. The monitoring site can be classified as an urban background site as it is representative of the surrounding area but not close to any specific emission source (Clark et al., 2012). It will be representative of similar locations nearby, such as residential areas.

In order to provide a comparison (or control) dataset, data from other London background monitoring sites within the inner ring road were used as reference sites (Figure 5):

- BL0: Bloomsbury urban background, situated on the north-east corner of Russell Square
- CT3: City of London urban background, situated in Sir John Cass school at Duke's Place, Aldgate
- WM0: Westminster urban background, situated on the corner of Horseferry Road and Regency Street
- SK6: Southwark urban background, situated on the north side of St Mary's churchyard, Elephant and Castle

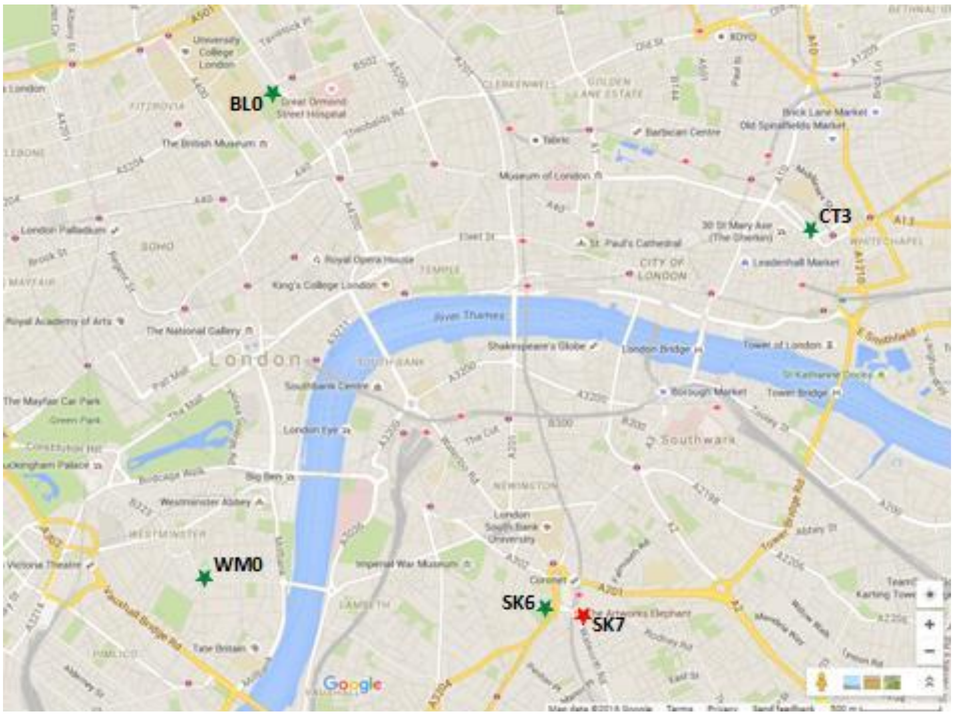

Figure 5: Locations of monitoring sites used in this study (Google maps)

3.2. Measurements

3.2.1. Nitrogen Oxides Monitoring

A standard chemiluminescence NO_X analyser was used to continuously monitor nitrogen oxides concentrations throughout the sampling period. The analyser logged 15 minute mean concentrations.

The instrument was attended monthly to carry out regular calibration and maintenance. The data were ratified to LAQN and AURN QA/QC standards; including the use of independent audits and calibrations traceable to national standards.

3.2.2. Supporting Measurements

"London Mean" meteorological data was used in the analysis; this is a "typical" meteorological data set representing London, which is a composite of data from several instruments co-located with air pollution monitoring sites (Carslaw, 2013). Although these data do not represent the very local meteorological conditions at the monitoring site, they offer a good quality data set representative of the synoptic weather conditions in London.

Solar Radiation measurements were taken from a monitoring station in the Royal Borough of Kensington and Chelsea.

3.2.3. Measurement Uncertainty

Interpreting measurements, in relation to one another or when attempting to detect a change in concentration, requires an understanding of the associated uncertainty. The chemiluminescent analyser used in this study is expected to have an uncertainty less than 15% (CEN, 2002). Previous work undertaken in London (Green et al., 2008) found that over longer periods the between sampler uncertainty reduced to 6% for NO_2 and 8% for NO_X when comparing two analysers. Any change brought about by the photocatalytic paint would need to be greater than this to be significant.

3.3. Study period

The study period comprised just over 13 months, from 19th September 2014 to 11th November 2015. Two phases were defined:

1) Phase-1: from 19th September 2014 to 17th May 2015 – pre paint application

2) Phase-2: from 19th May 2015 – 11th November 2015 – post paint application

3.4. Application of photocatalytic paint

The photocatalytic paint used is a photoactive milky coloured TiO_2 colloid for applying onto surfaces for de-pollution and self clean purposes and dries to a clear film. The paint was applied with a pressure spray gun using the recommended spray application rate of 120-150 grams per m^2 on the 18th of May 2015.

3.5. Data analysis

All data analysis was undertaken on hourly mean concentrations containing at least 3 valid fifteen-minute means. Analyses utilised R statistical software and the Openair function package within it (Carslaw, 2015).

3.5.1. Definition of increment

As the concentrations of pollutants are affected by meteorological conditions, which may make it difficult to assign concentration changes to an intervention, a mean background concentration was calculated using inner London background sites and this mean subtracted from the concentration at the measurement site to provide an increment. In this way, concentration changes due to meteorological conditions should be accounted for and the resulting increment should show a clear signal in case of concentration changes due to the application of the paint.

3.5.2. Local versus non-local increment

Pollution concentrations and calculated increments can be heavily influenced by local sources, which may mask any concentration changes due to an intervention. Therefore some of the analysis was carried out on local versus non-local concentration increments. The split of the local and non-local pollution was done by means of bivariate polar plots calculated by the Openair software (Carslaw and Ropkins, 2012). These plots relate pollution concentrations with wind speed (radial axis) and direction (polar axis). Local pollution sources lead to an increased concentration increment and are clearly visible in the polar plot shown in Figure 8.

3.5.3. Statistical analysis

The Kruskal-Wallis one-way test was applied to test if pollution increments before and after the application of the paint were significantly different, i.e. from a different population. This test is a non-parametric test that can be applied to independent samples of different sizes and variables, which do not have a Gaussian distribution. The null hypothesis (H_0) assumes that samples are from identical populations and was accepted whenever $p>0.05$. If $p<0.05$ the alternative hypothesis (samples come from different populations) was accepted.

4. Results and Discussion

4.1. *Overview of monitoring data*

4.1.1. *Pollution profile*

An overview of the of nitrogen oxides concentrations of all sites is given in Table 1. At the Artworks monitoring site, SK7 (shaded), data capture was 94% and the mean NO_X and NO_2 concentrations were 76 μgm^{-3} and 49.9 μgm^{-3} respectively. Median concentrations were 65 μgm^{-3} and 48 μgm^{-3} for NO_X and NO_2, respectively. Means provide the information necessary to assess regulatory targets but can be heavily influenced by a small number of high concentrations. However, medians provide a better descriptor of the data populations that are log normally distributed; like air pollution concentrations.

Assuming that the analysis period is representative of a calendar year, the annual mean air quality objective (i.e. the 40 μgm^{-3} annual mean limit value) would not have been met for NO_2.

Compared to the other inner London background sites, SK7 shows the highest mean and median concentrations for NO_X and NO_2. The NO_2 concentrations are similar for SK7 and BL0 for both the mean and median but still higher than the other background sites in inner London.

Table 1: Data Summary

NO_2 (μgm^{-3})	SK7	SK6	CT3	WM0	BL0
Min.	2.71	2.78	-0.58	2.54	7.42
1st Qu.	35.42	24.82	29.56	26.65	34.53
Median	48.43	35.20	42.43	41.43	48.60
Mean	49.9	39.48	44.21	43.38	49.87
3rd Qu.	62.53	51.13	56.98	57.38	62.65
Max.	146.50	151.59	126.96	174.72	142.23
NO_X (μgm^{-3})					
Min.	2.57	0.98	1.75	3.22	7.61
1st Qu.	42.70	29.57	34.91	31.56	39.11
Median	64.92	46.62	54.77	52.66	60.20
Mean	76.05	56.07	65.82	63.44	68.38
3rd Qu.	95.46	72.02	84.54	80.98	86.63
Max.	728.55	426.91	467.94	676.17	457.51
NO (μgm^{-3})					
Min.	-0.14	-2.78	-0.75	0.00	0.09
1st Qu.	6.35	2.49	3.87	3.70	3.37
Median	14.84	9.19	10.50	9.85	9.79
Mean	26.15	16.59	21.61	20.06	18.51
3rd Qu.	31.96	19.76	27.23	23.47	24.19
Max.	591.35	330.00	350.77	501.45	325.12
Data Capture	**94%**	77%	**92%**	**97%**	77%

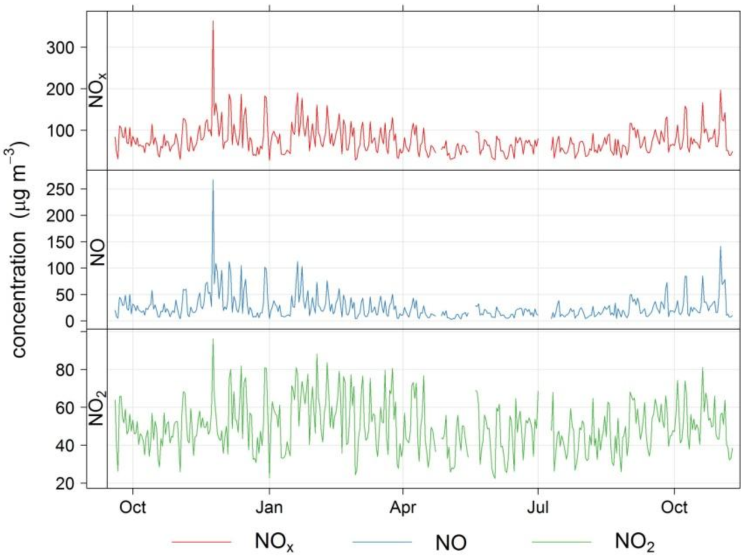

Figure 6: Daily concentrations of NO_X, NO and NO_2 in µgm^{-3} at SK7 monitoring station

Figure 6 shows the daily nitrogen oxides concentrations at the SK7 monitoring station throughout the monitoring period. The highest concentrations were recorded during the winter months (November/December) and lowest concentrations during the summer periods (May/June). These seasonal variations are mainly driven by meteorological conditions with winter months having lower dispersion, which increases the concentration as the source rate stays the approximately same.

The NO_X and NO_2 pollution concentrations at the monitoring location exhibited a clear weekly and diurnal cycle related to traffic from nearby roads (Figure 7). There was a clear morning rush-hour peak after which the concentrations stayed elevated throughout the day. Then, there was another, less pronounced rush hour peak in the evening. Concentrations were lower at the week-ends than during the week, with Sunday having the lowest concentrations overall.

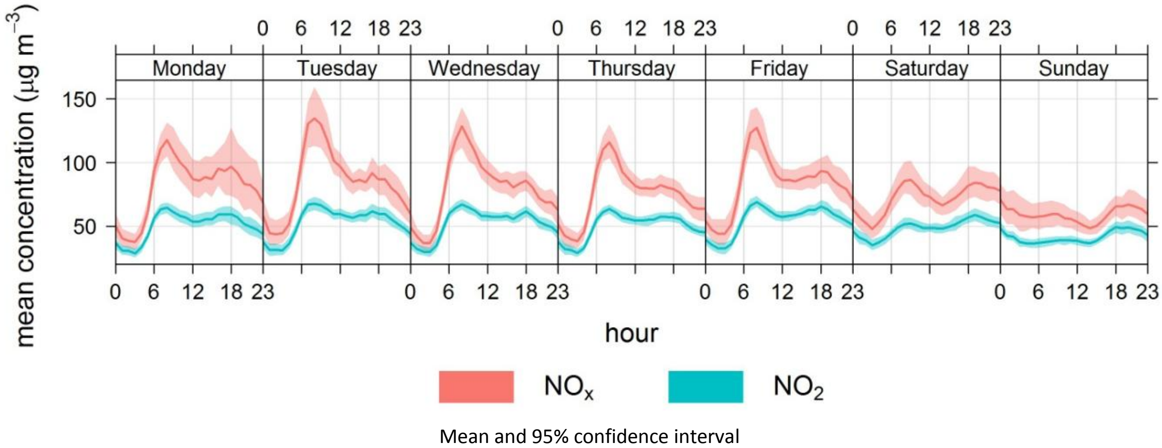

Figure 7: Weekly variation in NO_X and NO_2 concentrations at SK7

4.1.2. *Influence of wind speed and wind direction*

Bivariate polar plots were produced using the openair analysis package in R (http://www.openair-project.org). They show a smoothed concentration surface in relation to wind speed (radial axis) and wind direction (polar axis) and were used to highlight the relative influence of local sources to pollution. Their use in characterising ambient air pollution sources is described in Carslaw et al. (2006).

Polar plots were produced for NO_2 and NO_X for SK7 (Figure 8) and the other inner London background sites (Figure 9). When interpreting such plots it is important to consider that the predominant wind direction for London is south-westerly (Barratt et al., 2012), thus sources from this direction will have a much greater impact than other sources.

1) NO_X 2) NO_2

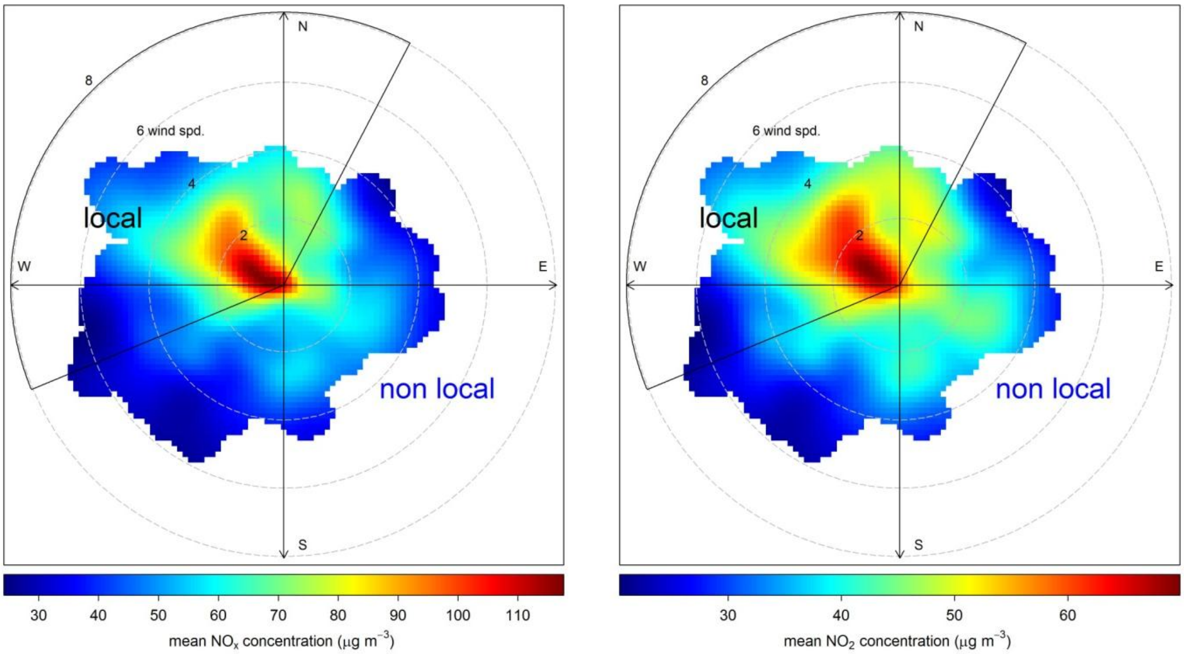

Figure 8: Bivariate polar plots for NO_X and NO_2 at SK7 monitoring station

Figure 8 shows that NO_X and NO_2 concentrations at SK7 were highest during north-westerly winds. This clearly shows that the SK7 site is strongly influenced by the busy Elephant and Castle road system, which is situated to the north/north-west of the station. A secondary source can be observed in north/north-easterly wind direction. This is most probably driven by pollution being blown along Elephant Road from the A201 at this wind direction.

For some of the subsequent analysis we separated the data set into wind directions where the concentrations were mainly driven by local sources (wind direction 247.5-22.5 degree, termed: local) and where the pollution concentrations was closer to background levels (wind direction 22.5-247.5 degree, termed: non-local). This split is indicted in the polar plots in Figure 8.

4.1.3. *Inner London Background*

Pollution concentrations were highly affected by meteorological conditions; this made it difficult to assign concentration changes to an intervention. Therefore concentration changes were evaluated using an increment, which was calculated by subtracting the inner London background concentration from the pollution concentration at the monitoring station. The inner London background concentration is the mean concentration of suitable inner London background sites. When choosing these sites, the data capture should be high and the sites should not be influenced by local sources and therefore represent the background concentrations.

From the four inner London background sites (SK6, CT3, WM0 and BL0) only two sites fulfilled the criteria. SK6 and Bl0 only had a 77% data capture for the sampling period (Table 1), which was below the aim of 90% data capture and, and from the biviariate polar plots (Figure 9) it can be seen that both sites were also strongly influenced by local sources; these local sources are the Elephant and Castle road system in the case of SK6 and for BL0, the busy Southampton Row along Russell Square where the site is situated.

Thus the inner London background was calculated using CT3 and WM0 data when both were available. This background concentration was subtracted from SK7 concentrations to form a concentration increment and to account for the influence of the meteorological conditions. All further data analysis was carried out on this increment.

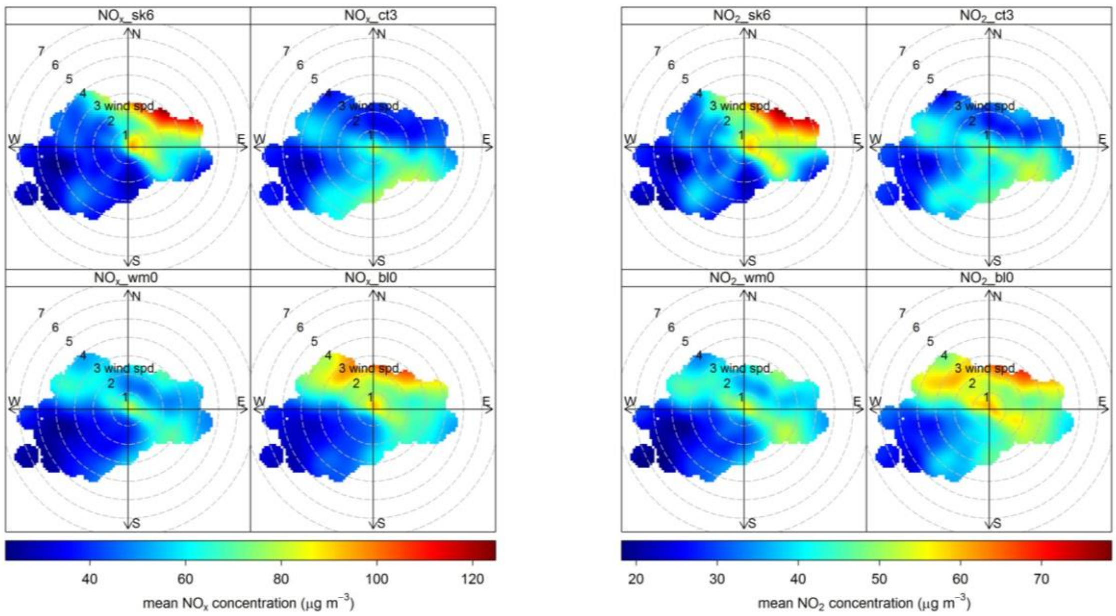

Figure 9: Bivariate polar plots for NO_X (left) and NO_2 (right) for inner London background sites

4.2. *Effects of the paint on the concentration increment over measurement period*

4.2.1. Overall daytime versus night-time increment

Figure 10 shows the time plot of the weekly NO_X and NO_2 concentration increments, split in daytime and night-time concentrations. As the photocatalytic paint only works when exposed to light, the hypothesis was that a decrease in the pollution concentration increment would be observed as a step change in the daytime pollution increment after the paint was applied on the 18th May 2015, but a similar change was not expected to be detectable in the night-time. A smooth line was applied to the time series with a shaded area giving the 95% confidence interval of the data.

This approach was chosen over a direct before and after paint application comparison, as the data set was too short and thus influenced too much by seasonal variation. Ideally the pre and the post dataset would span the same range of seasons to account for this variation but this was not the case for the current dataset.

Even though the night-time and daytime trends differed slightly for the sampling period, there was no obvious pollution reduction after the application of the paint in the daytime time series. On the contrary, there was an overall upwards trend in concentration increment for both NO_X and NO_2.

Night-time concentrations (μgm^{-3})	Daytime concentration (μgm^{-3})

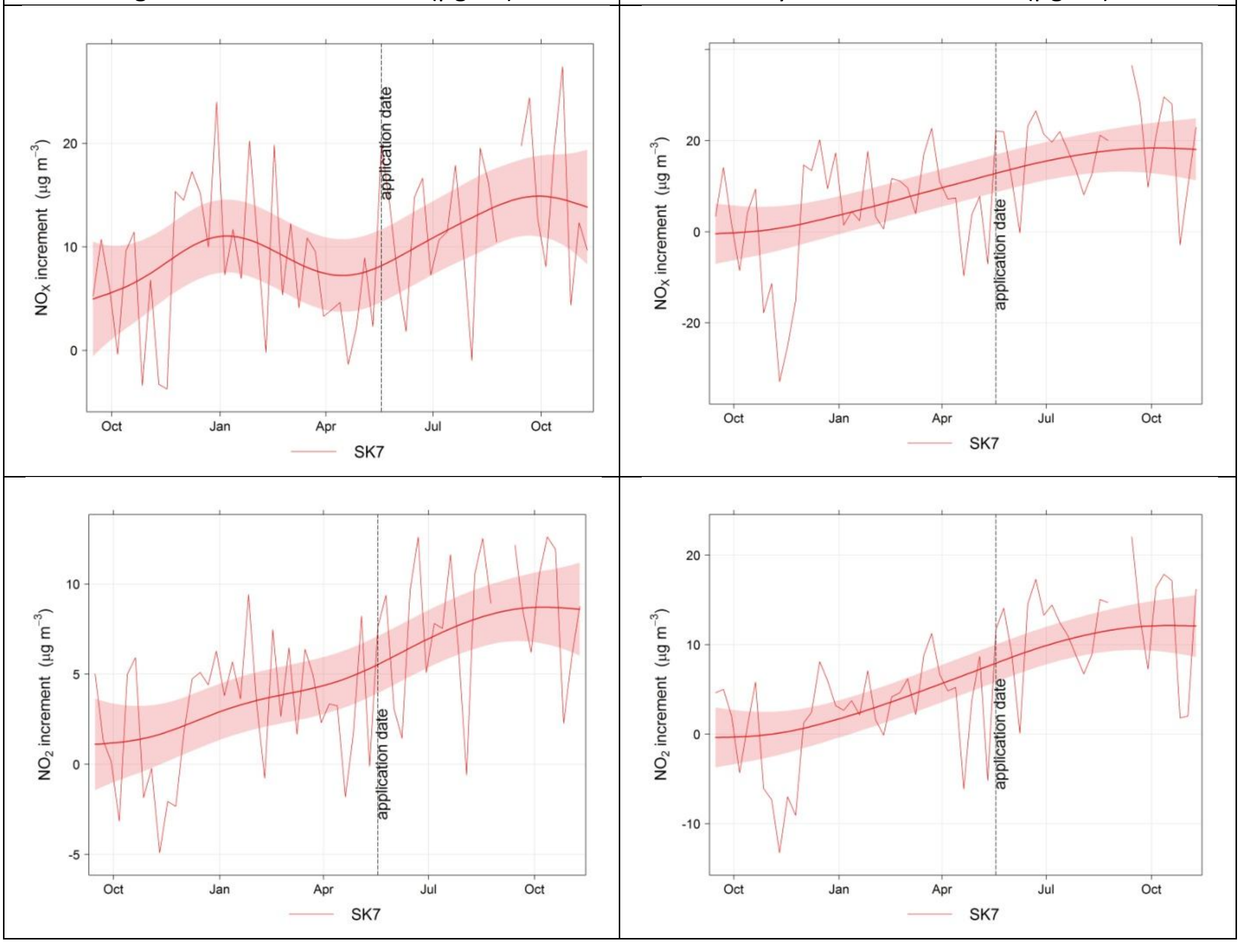

Figure 10: Weekly night-time and daytime timeplots of NO_X (top) and NO_2 (bottom) concentration increment (in ugm-3)

4.2.2. *Daytime versus night-time increment - filtered by wind direction*

As the polar plots have shown, however, SK7 was strongly influenced by the Elephant and Castle road network, which may have masked the influence of the paint. The data were therefore filtered by wind direction as described in section 3.5.2 and 4.1.2: wind directions bringing predominantly local pollution were termed local and the remaining wind directions were regarded as non-local. The dataset was also split into day and night time as in the previous time series. It was expected that any change of pollution concentration would be detected as a step change in the daytime non-local data set as it would not be influenced by local sources that might have changed during the redevelopment of the Elephant and Castle road network.

Figure 11 show the time series of filtered pollution increment data for NO_X and NO_2, respectively. Despite removing the local pollution influence there was still no obvious detectable reduction in the daytime concentration increment. And as with the overall trend, both NO_X and NO_2 daytime concentrations showed an upward trend for both wind sectors.

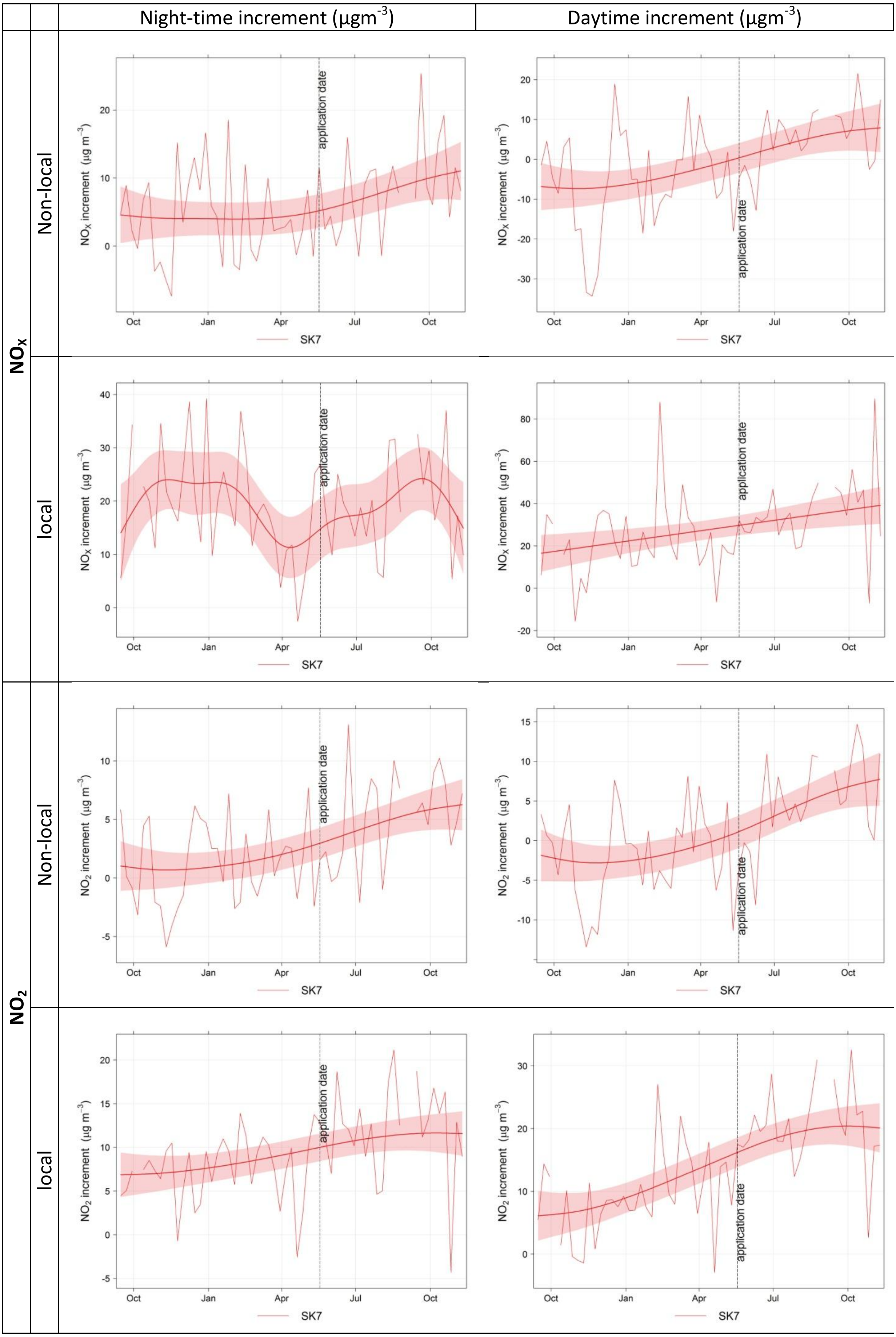

Figure 11: Weekly night time and daytime NO_X and NO_2 concentration increment split by wind direction

4.3. Influence of the D-NOX paint on the concentration increment immediately pre and post application

In order to reduce the impact of long term, local traffic changes a short time period was chosen immediately before and after application of the paint (pre application: 01/04/2015-18/05/2015, post application: 18/05/2015-01/07/2015). The periods chosen had similar solar radiation measurements; this ensured no bias due to photocatalytic activity. However, this analysis is subject to differences in dispersion characteristics either side of the paint application.

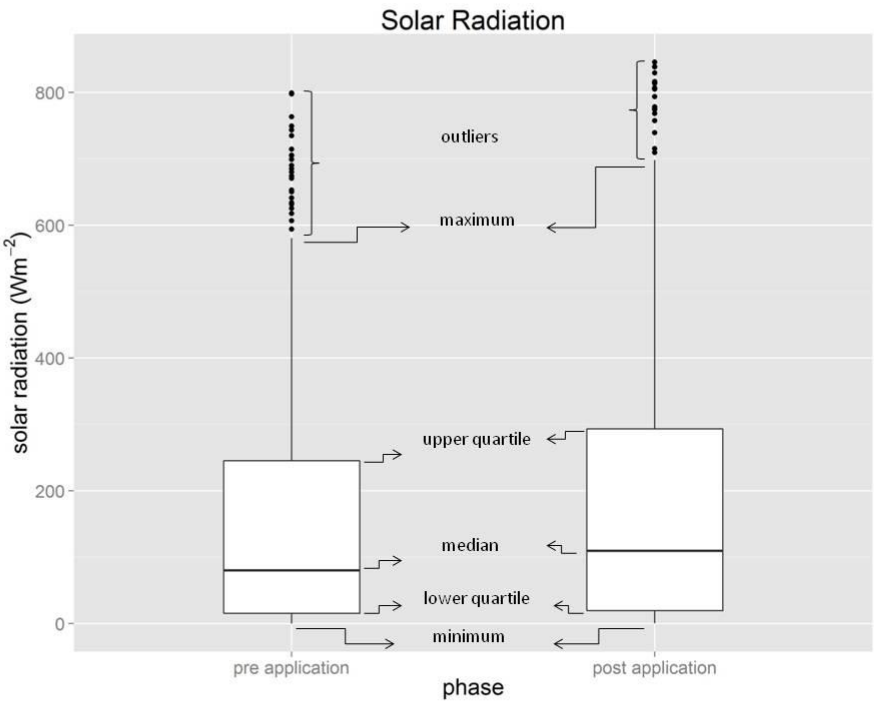

Figure 12: Daytime Solar radiation in the period immediately before and after the paint application

Figure 12 shows the labelled box and whisker plot of the hourly solar radiation in the pre and post paint application period. These time periods were chosen as the solar radiation levels were similar, ranging between 0.0052 (the lowest measurable value) and 836.25 Wm^{-2} in the period before the application and between 0.0052 and 845.75 Wm^{-2} post application. The mean and median were lower in the pre application period (186.56 and 101.27 Wm^{-2}) than in the post application period (218.65 and 139.07 Wm^{-2}), which should have further enhanced the efficacy of the paint and thus a detectable change in concentration increment.

The hourly pollutions increments pre and post paint application were compared for this time period using a non-parametric test (Kruskal-Wallis, see section 3.5.3). As for previous analyses, this analysis was carried out on data filtered for night-time/daytime and separated by wind direction.

Figure 13 and Figure 14 represent the distributions (in a form of a box and whisker plots) of the hourly concentration increments pre and post paint application. The top line marks the *p*-value from the Kruskal-Wallis test. The numerical results are summarized in **Error! Reference source not found.**.

Table 2: Median (1st quartile, 3rd quartile) of the non-local hourly increments of NO_X and NO_2

			Pre-application		Post-application	
			n	(μgm^{-3})	n	(μgm^{-3})
Non-local	**incNO$_X$**	night-time	235	2.31 (-3.82, 8.02)	123	1.51 (-6.68, 14.69)
		daytime	424	-2.02 (-13.01, 8.93)	282	-6.41 (-16.57, 8.73)
	incNO$_2$	night-time	235	1.65 (-3.82, 8.02)	123	1.47 (-5.46, 11.01)
		daytime	424	-0.15 (-7.57, 6.75)	282	-2.77 (-9.91, 6.53)
Local	**incNO$_X$**	night-time	53	7.05 (0.56, 14.15)	118	16.23* (10.47, 22.36)
		daytime	193	14.62 (5.86, 28.07)	418	29.39* (18.87, 40.72)
	incNO$_2$	night-time	53	6.71 (1.21, 10.58)	118	10.79* (7.37, 14.47)
		daytime	193	11.95 (5.60, 18.48)	418	18.51* (13.05, 25.16)

*** $p<0.05$ distribution of post application statistically different from pre application data at a 95% confidence interval**

It can be seen in Figure 13 that the post application increment was higher than the pre application increment for both NO_X and NO_2 for the local pollution wind sector. The night time concentrations, which will not have been influenced by the application of the paint and can thus act as a control, also showed this increase in concentration increment. The p-values of less than 0.05 each indicate that all increases in the post application period are significant to the 95% confidence interval. Having the same change in the daytime as well as the night-time indicates that the change was probably due to a general increase in pollution increment. This could point to changes in the traffic management, which might have led to an increase in traffic and congestion in the Elephant and Castle Road system, as part of the area redevelopment, during which the D-NO_X project was carried out.

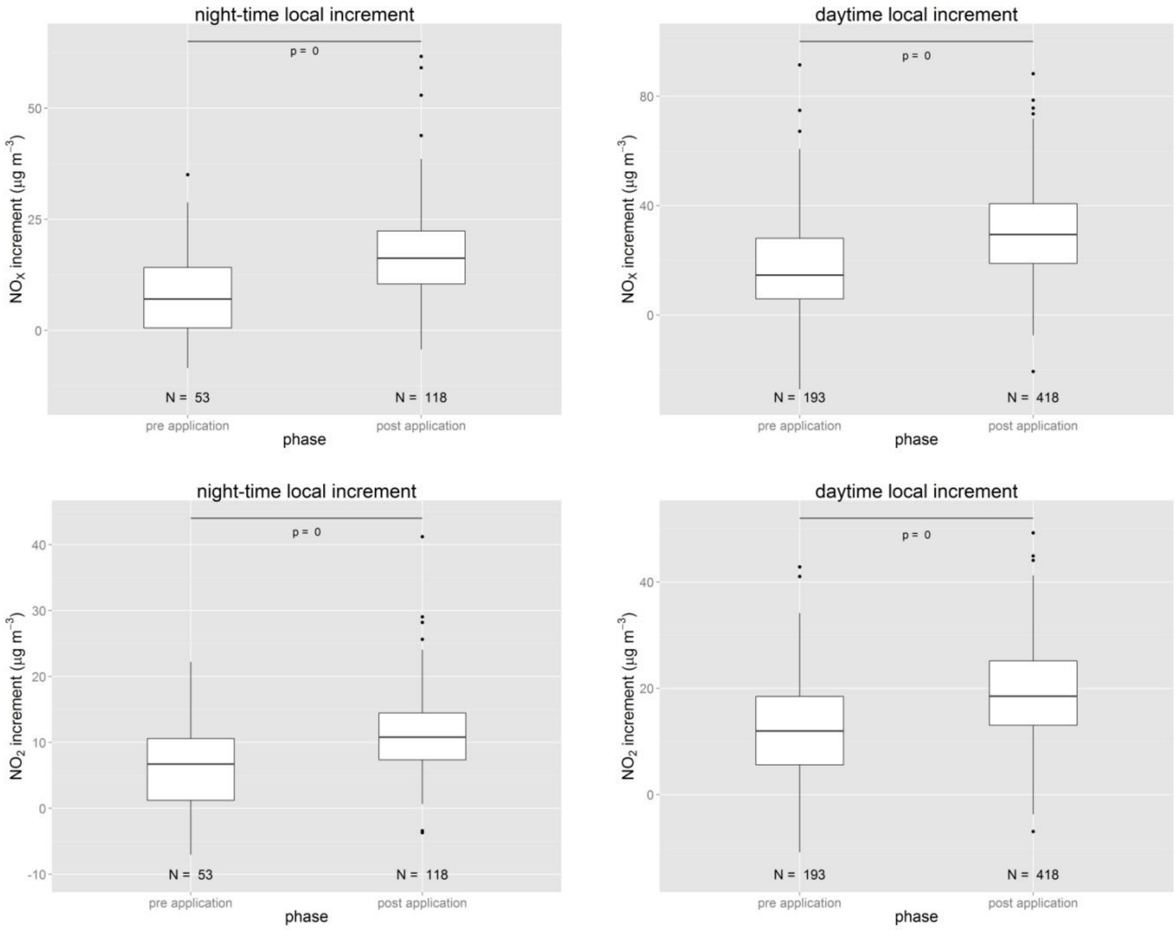

Figure 13: Box and whisker plot of the hourly local NO_X and NO_2 increment during the night/day before and after the application of the paint; p-values of the Kruskal-Wallis test of the difference between the pre and post application periods are also shown; "*N*" indicates the number of available observations

Figure 14 shows the results of the pre and post application comparison for the non-local wind sector. This sector was less influenced by local sources and source changes. In this scenario the post application pollution increment was lower for NO_X and NO_2 in all cases. The night time concentrations showed the same change in concentration increment as the daytime but to a lesser degree. The differences, however, were all above p=0.05 and thus not statistically significant at the 95% confidence interval as tested using Kurskal-Wallis. Furthermore, given that the concentration changes were also all lower than the instrument uncertainty of 6% for NO_2 and 8% for NO_X , the change in concentration increment is insignificant.

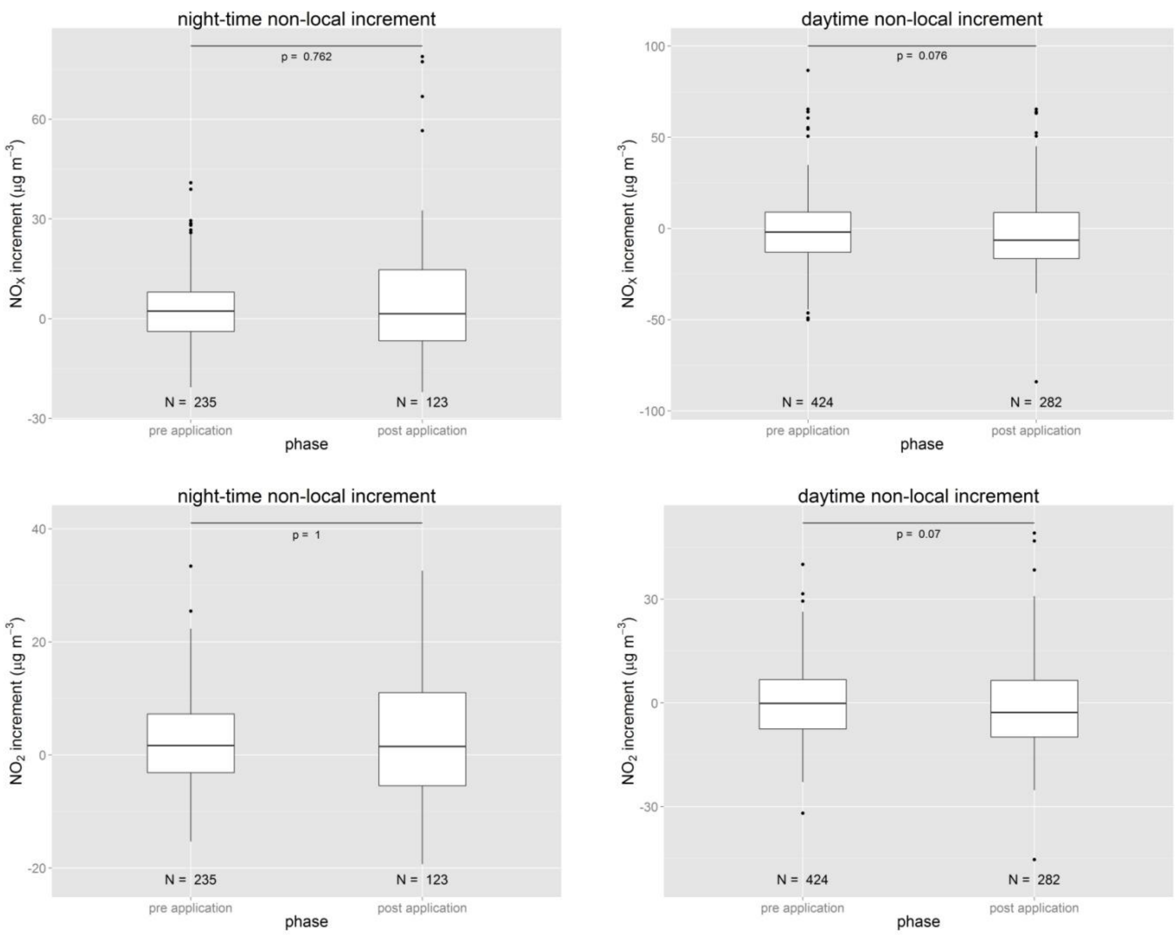

Figure 14: Box and whisker plot of the hourly non-local NO_X and NO_2 increment during the night/day before and after the application of the paint; p-values of the Kruskal-Wallis test of the difference between the pre and post application periods are also shown; "*N*" indicates the number of available observations

5. Conclusions

This study measured nitrogen oxides at the Artworks Elephant from September 2014 until November 2015 to assess the efficacy of D-NO_X paint, which was applied on the 18th May 2015. Highest NO_2 concentration could be observed during the autumn and winter months and overall the annual mean air quality objective would not have been met for NO_2 assuming that the analysis period is representative of the entire year.

This study provided approximately 9 months of data pre-application and 6 months post-application to detect any impact of the D-NO_X paint. Although this afforded a valuable data set for this assessment a simple comparison of before and after paint application was not adequate to account for seasonal variations brought about by meteorological changes. Furthermore, significant changes in traffic activity in the Elephant and Castle area led to changes in local emissions characteristics that potentially masked any effect of the paint. Thus the data were treated and analysed in an attempt to account for these effects:

- To account for changes in NO_X and NO_2 concentrations brought about due to meteorology over the study period, measurements from similar background sites in inner London were subtracted from the Artworks NO_X and NO_2 measurements to provide an increment concentration.
- To minimise the influence of local traffic variations over the study period this increment was further differentiated into local and non-local increments by isolating local sources of NO_X and NO_2. This was achieved by identifying the peak NO_X and NO_2 source directions; these were found to align with the busy road network suggesting that pollution levels were generally highest when emissions were either carried from Newington Butts/the Elephant and Castle road system are or blow along Elephant Road .
- To highlight periods of photocatalytic activity of the paint, NO_X and NO_2 pollution increment were filtered by solar radiation and daytime concentration increments were compared to night-time increments, which acted as a control.

The long term daytime and night-time increments were compared over the study period to see if there was a marked step change in the day-time trend after application of the paint, using the night-time trend as a control. This was not the case and even after separating local from non-local sources, no clear step change could be detected in the day-time time series in either dataset.

As accounting for long term changes was challenging, an alternative approach was attempted to identify any immediate effect which was not masked by these long-term variations: a six week period pre and post the application of the paint was compared using a non-parametric statistical test (Kruskal-Wallis). There was a significant increase in the pollution increment of NO_X and NO_2 in the local wind sector after the application of the paint. This increase was also apparent in the night-time and can probably be attributed to changes in the traffic pattern. However, no statistically significant difference in pre and post application increment could be detected in either NO_X or NO_2 in the non-local pollution sector.

Detecting relatively small changes in atmospheric concentrations independent of large scale meteorological variations and the influence of changing local emissions is extremely challenging.

With the dataset available for this study, it was not possible to detect a change in NO_X or NO_2 concentration due to the application of D-NOx paint.

6. References

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