



## Statistical analysis of monitoring results from the City of London's NO<sub>x</sub>-reducing paint study



April 2007

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<b>Title</b>	Statistical analysis of monitoring results from the City of London's NO <sub>x</sub> -reducing paint study
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<b>Customer</b>	City of London, Guildhall, PO Box 270, London EC2P 2EJ
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<b>File Reference</b>	ERG\Airquali\London\La\City\Nox_paint_study\CoL_de-nox_paint_statistical report.doc
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<b>Report Number</b>	-
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## Summary

This report uses a range of statistical methods to describe and assess changes in NO<sub>x</sub> and NO<sub>2</sub> pollution concentrations at a study site installed approximately 5m from the centre of a wall painted with NO<sub>x</sub>-reducing paint (2.5m from the closest point of the wall). The wall was painted on 1<sup>st</sup> April 2006. Ratified measurements from the study site were available between 19<sup>th</sup> September 2005 and 1<sup>st</sup> December 2006.

Differences in mean concentrations recorded by the monitoring site prior to and following the intervention (application of the paint onto the wall) may be attributed to changes in emissions profiles from surrounding pollution sources, differences in meteorological conditions or the effects of the NO<sub>x</sub>-reducing paint. Given the short analysis period, changes in emissions profiles are unlikely to be of major importance, however, the effects of meteorology will have a very strong influence, especially given that the pre- and post-intervention periods do not span the same seasons.

Two 'control' methods have been used in the study to try and account for the influence of meteorology. The first uses measurements from nearby background monitoring sites, the second method depends on the assumption that the NO<sub>x</sub>-reduction reaction is driven by UV light, and therefore the paint will have no effect during non-daylight hours.

The rate of change analysis uses percentage change, rather than absolute concentrations to accommodate the higher levels of emissions adjacent to the study site than the background control, and during non-daylight hours. This analysis reports a decrease in daylight NO<sub>x</sub> concentrations of 19% between the pre- and post-intervention periods. However, there is a 6% increase in concentrations relative to the background controls. The decrease in daylight concentrations was comparable to the non-daylight control. The analysis results for NO<sub>2</sub> were similar, with the study site reporting an increase in NO<sub>2</sub> concentrations of 7% relative to the background controls.

Polar plots provide a visual assessment of the direction emissions sources relative to the study site and give equal weighting to all wind speed and directions in the analysis grid. A visual comparison of polar plots pre- and post-intervention reveals evidence of a decrease in overall NO<sub>2</sub> concentrations at the study site, contrary to the results of the previous analysis method. This decrease is also seen in the polar plot of the non-daylight control, so is unlikely to be an effect of the NO<sub>x</sub>-reducing paint.

CUSUM analysis failed to identify any sustained deviation from the reference mean in the NO<sub>x</sub> or NO<sub>2</sub> cumulative sum charts. This means that any a step change in concentrations occurring around the 1<sup>st</sup> April 2006 and indicative of the intervention would have to be minor in comparison with transient changes due to meteorology.

No decrease in NO<sub>x</sub> or NO<sub>2</sub> concentrations attributable to the NO<sub>x</sub>-reducing paint could be identified in measurements from the study site over the analysis period using the methods described. The conclusion of this study is that the paint has no identifiable effect at a distance of approximately 5m. This conclusion would be more robust if the pre- and post-intervention periods were longer and spanned the same seasons, for example, 1 year pre and 1 year post.



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## 1 Introduction

The purpose of this report is to provide statistical analysis of monitoring data from the City of London's NO<sub>x</sub> paint study monitoring site with the aim of identifying a significant affect on ambient NO<sub>2</sub> and NO<sub>x</sub> concentrations attributable to the NO<sub>x</sub>-reducing paint.

Titanium dioxide (TiO<sub>2</sub>) is a strong photocatalyst that breaks down organic compounds on contact when exposed to sunlight in the presence of water vapour. When the TiO<sub>2</sub> coated surface is irradiated by UV light active oxygen is created, which oxidizes NO<sub>x</sub> in the air into nitric acid ions. These ions can then be neutralised and washed away by rainfall.

The rate of reaction depends on the UV intensity of sunlight, the ambient humidity and NO<sub>x</sub> concentrations. Laboratory trials of NO<sub>x</sub> reducing slabs carried out by Mitsubishi Materials<sup>1</sup>, suggest an 80% NO<sub>x</sub> removal rate can be maintained at an intensity of UV light of 1 Wm<sup>-2</sup> and NO concentrations below 1200ppb. Effectiveness was not found to degrade below 80% over an exposure period (i.e., time since application) of 12 months. Each of these conditions would be achieved in typical roadside or background conditions during UK summer or winter; the UV intensity of direct sunlight in summer is 20-30 Wm<sup>-2</sup>, compared to 1 Wm<sup>-2</sup> on a cloudy winter day.

The study site was installed on 16<sup>th</sup> September 2005 at a location approximately 5m from the centre of a south east facing wall of a building on the Sir John Cass School site (2.5m from the nearest point of the wall). This wall was painted with the NO<sub>x</sub>-reducing paint on 1<sup>st</sup> April 2006. Ratified 15 minute mean data from the study site was provided by the City of London up to 1<sup>st</sup> December 2006, allowing a study period of approximately six months pre- and eight months post-intervention. The study site was selected due to its sensitive location close to the school nursery and the proximity to an existing monitoring site within the grounds of the school on the opposite side of the site, thereby providing 'control' data.

Differences in mean concentrations recorded by the monitoring site prior to and following the intervention (application of the paint onto the wall) may be attributed to;

1. changes in emissions profiles from surrounding pollution sources, primarily changes in volume or the nature of vehicle emissions.
2. differences in meteorological conditions.
3. the effects of the NO<sub>x</sub>-reducing paint.

In order to isolate the effects of the NO<sub>x</sub>-reducing paint, the first two factors must be quantified. Given the short analysis period, (1) is unlikely to be of major importance. However, the effects of meteorology will have a very strong influence, especially given that the pre- and post-intervention periods do not span the same seasons.

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<sup>1</sup> Mitsubishi Materials technical sheet available at <http://www.mmc.co.jp/english/event/noxer.pdf>

## 2 Source Data

### 2.1 Continuous monitoring sites used in this study

A continuous NO<sub>x</sub> monitoring site was installed by the City of London specifically to monitor pollution levels close to the wall to be painted with the NO<sub>x</sub> reducing paint (Figure 2-1). In this report, this site is known as the 'study site' and given the name 'CT7 Study Site'. Three other background sites were selected as 'controls' – BL0 Bloomsbury in Westminster 3.5km to the west of the study site, CT1 Senator House 1.3km to the south west and CT3 JCS located on the opposite side of the school site approximately 50m from the study site. These sites were selected for their proximity and high data capture rates during the study period.

Table 2-1 gives the code, location and grid reference of each site along with the approximate linear distance to the wall painted with the NO<sub>x</sub>-reduction paint. For further site details including location maps, see [http://www.londonair.org.uk/london/asp/publicdetails.asp?la\\_id=7](http://www.londonair.org.uk/london/asp/publicdetails.asp?la_id=7).

Site name	Site location	Grid reference	Distance to wall
CT7 Study Site	Study Site - Sir John Cass School eastern perimeter	533529E 181175N	5m (centre)
CT3 JCS	Sir John Cass School western perimeter	533482E 181190N	45m
CT1 Senator House	Roof of Senator House	532242E 180894N	1312m
BL0 Bloomsbury	NE corner of Russel Square, Bloomsbury	530123E 182014N	3503m

Table 2-1: Location details of the monitoring sites used in this study.

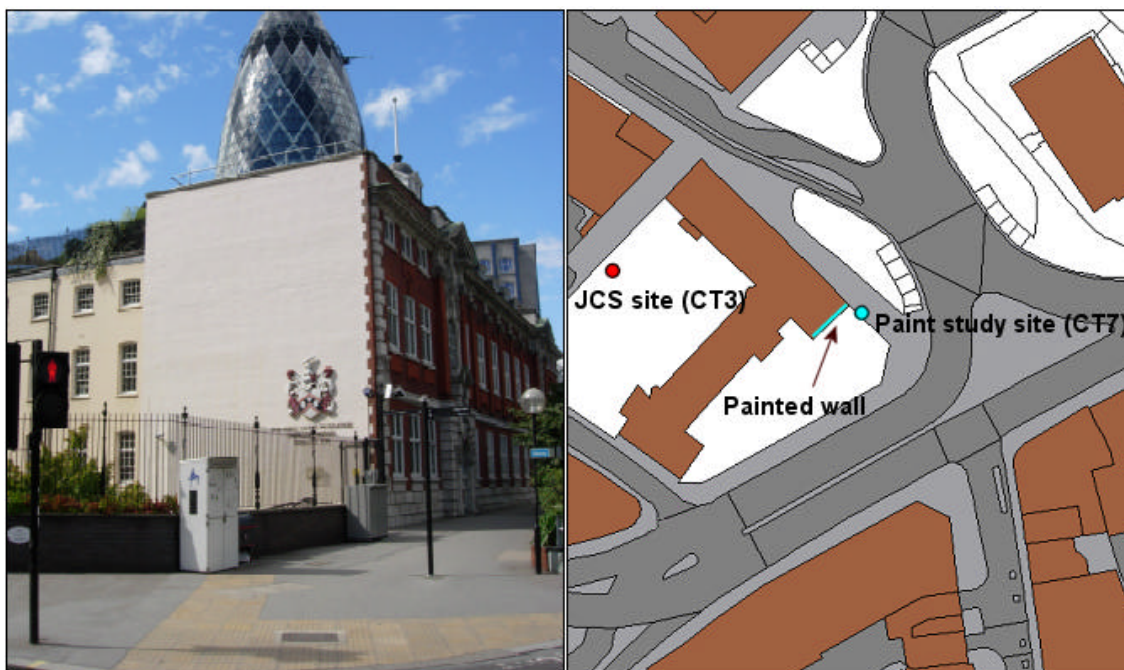


Figure 2-1: Image and plan of the study site. Note the proximity of the road junction to the east of CT7 Study Site.

### 2.2 Data management and QA/QC

All monitoring data used in this study has been fully scaled and ratified. Datasets from CT3 JCS and CT7 Study Site were provided as ratified by City of London, although a portion of the CT7 Study Site dataset required re-ratification by ERG. CT1 Senator House is part of the London Air Quality Network (LAQN) and ratified to LAQN standard. BL0 Bloomsbury is part of Defra's AURN and ratified to AURN standard. These QA/QC standards ensure that measurements are spatially and temporally comparable.



### 3 Descriptive Analysis

#### 3.1 Seasonality

Figure 3-1 shows a timeseries plot of NO<sub>x</sub> concentrations from Bloomsbury over a three year period. It is clear that a seasonal trend exists with higher concentrations recorded during the autumn and winter months, than those recorded during the spring and summer. This is due to the decreased dispersion during cold calm cyclonic conditions, the highest concentrations occurring as a result of temperature inversions. Conversely, during the summer months increased solar heating stimulates vertical dispersion of pollution leading to lower mean concentrations.

This seasonal trend is especially important as the pre- and post-intervention periods fell within different seasons. Pre-intervention monitoring began in September 2005 and ran through until the paint was applied in April 2006. Therefore, the majority of pre-intervention monitoring occurred during the autumn and winter months. At the time of preparing this report, post-intervention measurements were available up to 1<sup>st</sup> December 2006, therefore excluding any of the winter months.

Given this uneven seasonal distribution, one would expect to see a decrease in NO<sub>x</sub> concentrations between the two periods, entirely independent of the effects of the NO<sub>x</sub> reduction paint. This problem is heightened by the fact that the effects of the Titanium Dioxide will also be seasonal, given that the reaction driving the removal of NO<sub>x</sub> compounds is proportional to UV intensity.

Therefore, analyses will have to separate the effects of seasonality, and more specifically meteorology, before any identified effects can be attributed to the paint. Given the short analysis period, long-term trends are unlikely to be of importance.

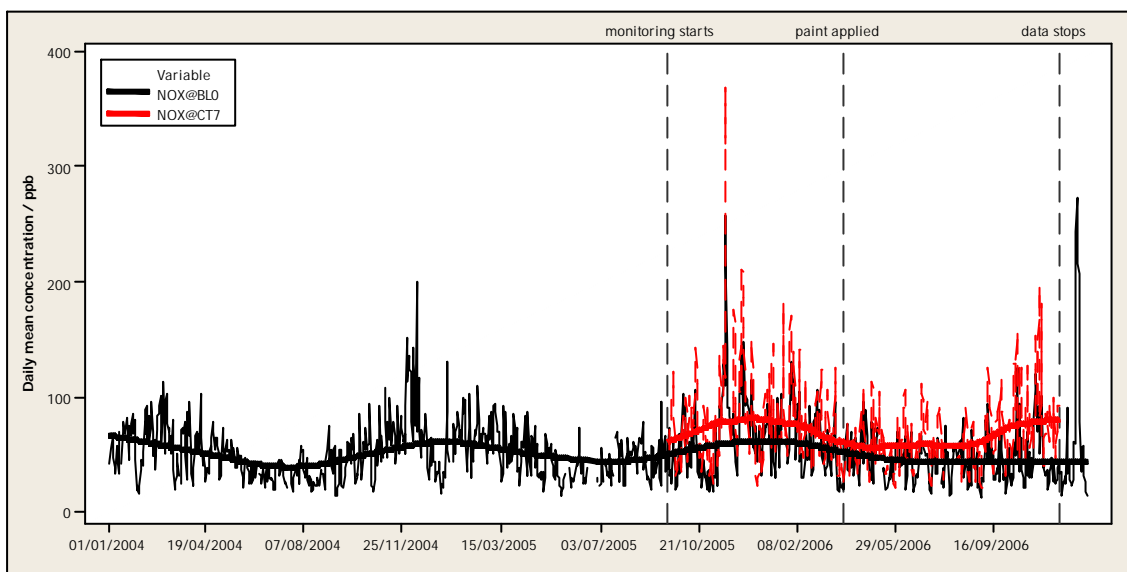


Figure 3-1: Timeseries chart of NO<sub>x</sub> concentrations at BLO Bloomsbury and CT7 Study Site showing seasonal trends represented by smoothed series (Lowess smoothing)

#### 3.2 Descriptive Statistics

Basic descriptive statistics for NO<sub>x</sub>, NO and NO<sub>2</sub> at each of the selected study sites are shown in Table, divided into pre- and post-intervention periods; 17<sup>th</sup> September 2005 to 31<sup>st</sup> March 2006 and 1<sup>st</sup> April 2006 to 1<sup>st</sup> December 2006 respectively. Capture rates for each site are greater than 90% for each period at each site except CT3 JCS post (4382 missing values, 81% capture).

Variable	Period	Values	Missing	Capture	Mean	StDev	75%ile
NO <sub>x</sub> at CT7 Study Site	Pre	18553	263	99%	79.0	58.7	100.1
	Post	21903	1521	94%	64.9	43.6	84.0
NO <sub>x</sub> at CT1 Senator Hse	Pre	17803	1013	95%	50.8	44.8	61.3
	Post	22337	1087	95%	39.6	26.8	48.3
NO <sub>x</sub> at CT3 JCS	Pre	18559	257	99%	55.8	46.8	67.9
	Post	19042	4382	81%	44.5	32.1	54.8
NO <sub>x</sub> at BL0 Bloomsbury	Pre	17937	879	95%	62.4	45.4	84.0
	Post	21960	1464	94%	44.5	31.8	58.0

Variable	Period	Values	Missing	Capture	Mean	StDev	75%ile
NO <sub>2</sub> at CT7 Study Site	Pre	18553	263	99%	35.2	14.3	43.9
	Post	21907	1517	94%	35.2	15.2	44.4
NO <sub>2</sub> at CT1 Senator Hse	Pre	17972	844	96%	27.1	12.1	34.3
	Post	22341	1083	95%	25.1	11.6	31.6
NO <sub>2</sub> at CT3 JCS	Pre	18559	257	99%	29.0	12.6	36.8
	Post	19042	4382	81%	28.8	12.6	35.9
NO <sub>2</sub> at BL0 Bloomsbury	Pre	17937	879	95%	31.9	12.0	40.0
	Post	21960	1464	94%	28.3	12.7	36.0

Table 3-1: NO<sub>x</sub> and NO<sub>2</sub> descriptive statistics for each study site (all units ppb)

Important points to note from these tables are:

- i. At all sites, the means, standard deviations and 3<sup>rd</sup> quartile concentrations are lower in the post-intervention period, except NO<sub>2</sub> at CT7 Study Site where NO<sub>2</sub> concentrations remain the same.
- ii. Mean and 3<sup>rd</sup> quartile concentrations are highest at CT7 Study Site due to the proximity of the road to the southeast, as demonstrated in Section 5. The next highest concentrations are recorded at BL0 Bloomsbury, followed by CT3 JCS. The lowest are recorded at CT1 Senator House.
- iii. The NO<sub>2</sub>:NO<sub>x</sub> ratio is lower at CT7 Study Site than at the other sites, all of which are very similar. This is as expected in locations close to road sources where there is more NO<sub>x</sub> in the form of NO.

## 4 Rate of Change Analysis

### 4.1 Method

This simple screening method compares changes in mean concentrations between the pre- and post-intervention periods. By assessing changes in relation to control sites or periods, some assessment can be made as to whether changes are likely to be caused by the intervention or confounding factors.

As UV light from the sun activates the paint, no effects can be expected during the night. Solarimetry data from LAQN sensors were used to identify hours where incoming solar radiation is zero all year round, providing a 'non-daylight hours' filter. This was set as all measurements taken between 21:00 and 04:00. Conversely, hours where incoming solar radiation was greater than 10Wm<sup>-2</sup> all year round were identified as 09:00 and 16:00. Measurements within these times were classified as 'daylight hours'.

This change analysis compares mean NO<sub>x</sub> and NO<sub>2</sub> concentrations during 'daylight hours' pre- and post-intervention to produce a percentage change in concentration over the period. Two control methods are used. The first uses the background control sites CT1 Senator House, CT3 JCS and BL0 Bloomsbury, as described in Section 2.1. The second uses 'non-daylight hours' data from CT7 Study Site. This allows a comparison of rates of change in each pollutant at the study site with the controls.

### 4.2 Results

Results of the analysis for NO<sub>x</sub> and NO<sub>2</sub> are shown in Table 4-1 and Table 4-2. These show mean concentrations during the pre- and post-intervention periods, then the percentage change over the period. These percentage changes are compared to produce a change relative to the control used, either non-daylight hours or background daylight hours.

Table 4-1 shows that in all cases NO<sub>x</sub> concentrations were lower during the post-intervention period. During daylight hours, NO<sub>x</sub> concentrations at the study site decreased by 18%. During non-daylight hours, the decrease was similar (19%). Therefore there was very little change in concentrations relative to the non-daylight control.

Results from the 'background' control analysis were similar. All of the control sites recorded a decrease of between 20% and 29%. Overall, there was a mean increase in NO<sub>x</sub> concentration of 6% at the study site relative to the controls.

Unlike NO<sub>x</sub>, the mean daylight NO<sub>2</sub> concentration at the study site remained unchanged, while the mean non-daylight concentration increased slightly (0.6ppb or 2%). Therefore, relative to the non-daylight control, the study site reported a slight decrease in mean (Table 4-2). This slight decrease is not reflected in results when the background control is used. The background controls show a decrease in concentrations of between 1% and 11%. Therefore, relative to these controls, daylight NO<sub>2</sub> concentrations at the study site increase by an average of 7%.

Therefore, this analysis finds no evidence of a decrease in mean daylight NO<sub>x</sub> or NO<sub>2</sub> concentrations relative to concentrations recorded during non-daylight hours or concentrations recorded at surrounding background sites.

NO <sub>x</sub>	Pre-mean		Post-mean		Change	Change at study site relative to control
	ppb	mgm <sup>-3</sup>	ppb	mgm <sup>-3</sup>		
<b>Daylight control</b>						
Daylight CT7 Study Site	79.0	151.7	64.9	124.6	-18%	-
Non-daylight CT7 Study Site	61.2	117.5	49.5	95.0	-19%	1%
<b>Background control</b>						
Daylight CT7 Study Site	79.0	151.7	64.9	124.6	-18%	-
Daylight CT1 Senator House	50.8	97.5	39.6	76.0	-22%	4%
Daylight CT3 JCS	55.8	107.1	44.5	85.4	-20%	2%
Daylight BL0 Bloomsbury	62.4	119.8	44.5	85.4	-29%	11%
<i>Overall control mean</i>						6%

Table 4-1: Concentration and percentage change in daylight NO<sub>x</sub> concentrations at the study site, relative to the non-daylight and background controls.

NO <sub>2</sub>	Pre-mean		Post-mean		Change	Change at study site relative to control
	ppb	mgm <sup>-3</sup>	ppb	mgm <sup>-3</sup>		
<b>Daylight control</b>						
Daylight CT7 Study Site	35.2	67.6	35.2	67.6	0%	-
Non-daylight CT7 Study Site	29.8	57.2	30.4	58.4	2%	-2%
<b>Background control</b>						
Daylight CT7 Study Site	35.2	67.6	35.2	67.6	0%	-
Daylight CT1 Senator House	27.1	52.0	25.1	48.2	-7%	7%
Daylight CT3 JCS	29.0	55.7	28.8	55.3	-1%	1%
Daylight BL0 Bloomsbury	31.9	61.2	28.3	54.3	-11%	11%
<i>Overall control mean</i>						7%

Table 4-2: Concentration and percentage change in daylight NO<sub>2</sub> concentrations at the study site, relative to the non-daylight and background controls ( $\mu\text{gm}^{-3}$  concentrations shown as 'NO<sub>2</sub> as NO<sub>x</sub>').

## 5 Bivariate polar plot modelling

### 5.1 Method

Bivariate polar plots can be used to illustrate and identify the relative contributions of surrounding pollution sources upon mean concentrations recorded at a point. Pollutant concentrations, at 15 minute mean resolution, are separated into individual wind direction bins, in this case of 10 degrees. For example, all measurements made during wind directions between 0 and 10 degrees from north are separated, then 10 and 20 degrees etc. These subsets are then subdivided again according to wind speed, in this case 1ms<sup>-1</sup> bins. This produces a polar coordinate grid of mean concentrations for each wind direction and speed that can be applied to a surface contour model to produce surface contour maps. Note that this method has the disadvantage of only providing a visual output, rather than statistical.

As local wind data were not available of any of the study sites, measurements of wind speed and direction were taken from a reliable monitoring site in L.B. Bexley. Measurements from this site are representative of wind conditions above the city canopy, rather than local to the pollutant monitoring sites. This differentiation will introduce some errors in the modelling results.

This analysis first investigates the distribution of concentrations by wind speed and direction at the paint study site in comparison with the 'background control' sites. The analysis is then repeated using the daylight vs. non-daylight hours control.

Results from these analyses will differ to those presented in the change point analysis in Section 4 as they give equal weighting to all wind speeds and directions. Figure 5-1 illustrates how the frequency of wind direction measurements differs between the pre- and post-intervention periods. Approximately 11% of all post-intervention measurements were related to wind directions between 100 and 120 degrees from north, i.e., from the south east, opposed to only 5% during the pre-intervention period. Therefore, if there is a strong pollutant source to the south east of the study site, mean concentrations will have a positive bias. The polar plots remove this bias by showing mean concentrations in each wind speed and direction bin, independent of the frequency of measurements.

Therefore, results from the polar plot analysis can be compared with the rate of change analysis results to investigate the effects of differing meteorology in the pre- and post- intervention periods.

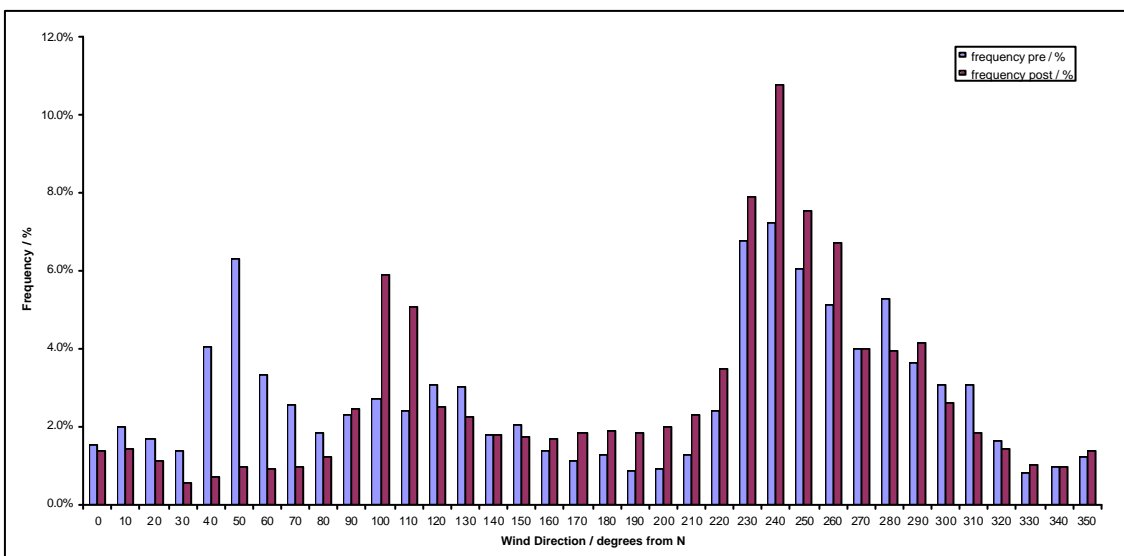


Figure 5-1: Frequency plot of wind direction measurements pre and post intervention.

## 5.2 Results

Figure 5-2 shows Polar plots for the background sites CT1 Senator House and CT3 JCS on the same concentration scale. Contour patterns are very similar at each site with the highest concentrations being recorded during calm conditions ( $< 0.5 \text{ ms}^{-1}$ ) or during south easterly winds of between 3 and 5  $\text{ms}^{-1}$ . Concentrations at CT1 Senator House are lower, a likely function of the site's height above street level.

The corresponding plots for CT7 Study Site and BL0 Bloomsbury are shown in Figure 5-3. As expected from the descriptive statistics, concentrations are generally higher at both sites, with a clear additional source at each. At BL0 Bloomsbury, this is to the north west. At CT7 Study Site the principal additional source is to the south east, although concentrations from all wind directions are higher at this site than the others reflecting the proximity of surrounding roads (Figure 2-1) and suggesting that the surrounding high buildings are affecting local wind patterns.

This basic analysis has revealed that BL0 Bloomsbury has significant local sources of NO<sub>x</sub> pollution and therefore may not appropriate for use as a 'background control' site in some circumstances. CT1 Senator House represents the best 'background control' as it has very little of its own local sources. CT3 JCS appears to be affected by a local source to the southeast of the site, but as this source will also be common to the study site to some degree, it also represents a good 'background control'.

Comparison of pre- and post-intervention periods shows a distinct decrease in NO<sub>x</sub> concentrations at all sites. This result agrees with the rate of change analysis in Section 4. The greatest initial concentrations and change in concentrations is seen at CT7 Study Site. This reflects the increased traffic emission levels surrounding this site, which would be classified as 'roadside'.

The NO<sub>2</sub> analysis is less distinct than the NO<sub>x</sub> analysis. This is to be expected given that much of the NO<sub>2</sub> recorded by the sites will be of secondary, rather than primary source. CT1 Senator House and CT3 JCS, the background controls, appear to show an overall decrease in daylight NO<sub>2</sub> concentrations between pre- and post-intervention periods, CT1 Senator House more so than CT3 JCS (Figure 5-4). This agrees with the rate of change analysis. However, the polar plot of daylight NO<sub>2</sub> at CT7 Study Site, which reported no change in overall mean, appears to show a decrease during most wind speeds and directions (Figure 5-5). There is an increase evident during winds from the south east, i.e., from the nearby road source. This pattern is repeated, although at lower concentrations, in the non-daylight control polar plots, also shown in Figure 5-5.

Therefore, the results of this analysis support those of the rate of change analysis with the exception of the relative change in NO<sub>2</sub> concentrations at CT7 Study Site. The increase in daytime NO<sub>2</sub> relative to the background controls (no change in absolute concentrations) may have been a function of changes in the distribution of wind speed and direction and the local sources of pollution from the south east of the study site.

As Figure 2-1 shows, the wall covered with the NO<sub>x</sub>-reducing paint is located to the west of CT7 Study Site. Concentrations of both NO<sub>x</sub> and NO<sub>2</sub> recorded during westerly winds dropped following the intervention. However, this analysis is not sensitive enough to allow the conclusion that this decrease was over and above that expected due to seasonal and meteorological changes, particularly as air flow at street level around the Study Site would be complicated by the surrounding high buildings.

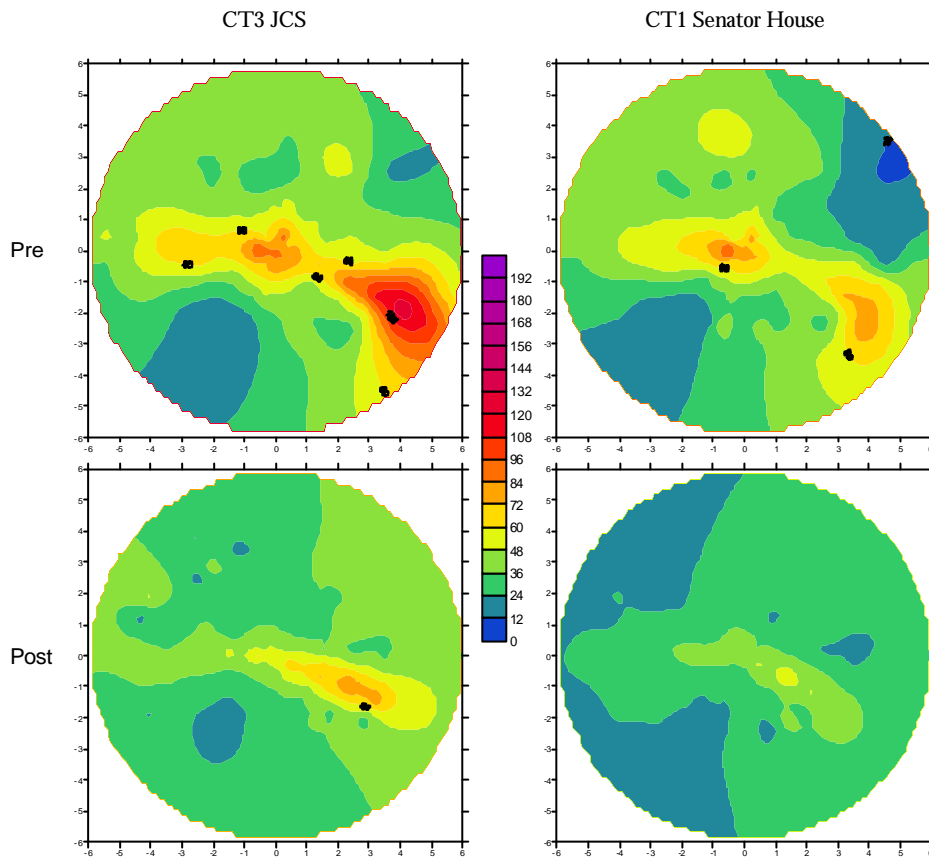


Figure 5-2: Polar plots of NO<sub>x</sub> concentrations in ppb at CT3 JCS and CT1 Senator House pre- and post-intervention.

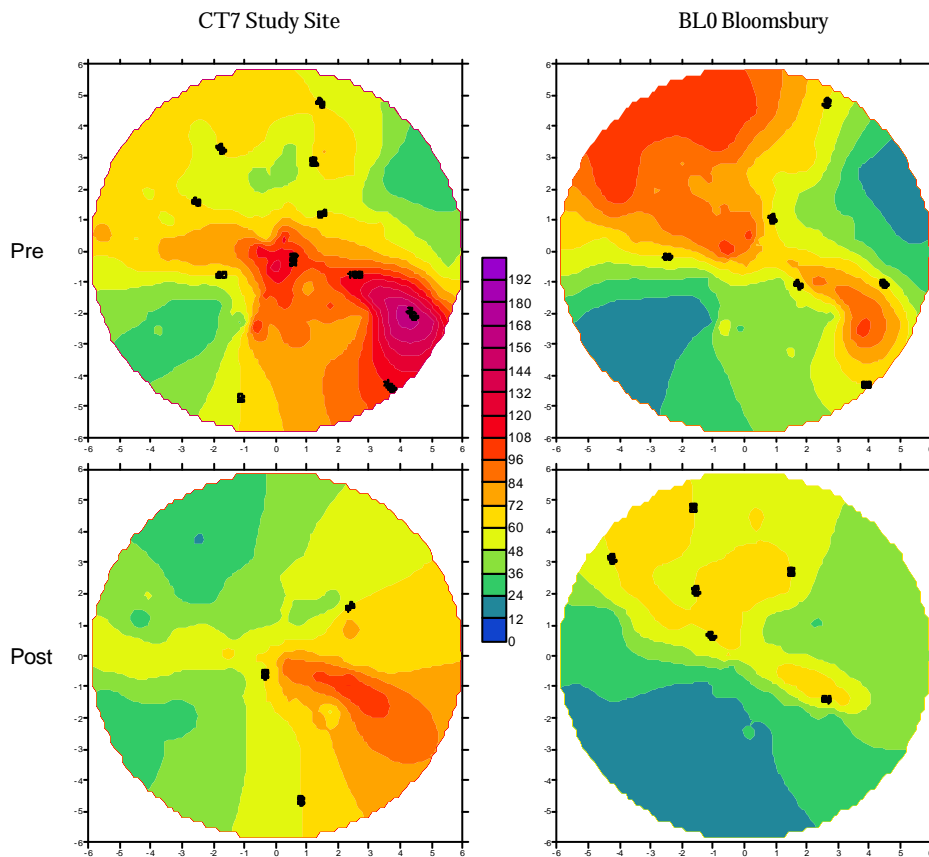


Figure 5-3: Polar plots of NO<sub>x</sub> concentrations in ppb at CT7 Study Site and BL0 Bloomsbury pre- and post-intervention.

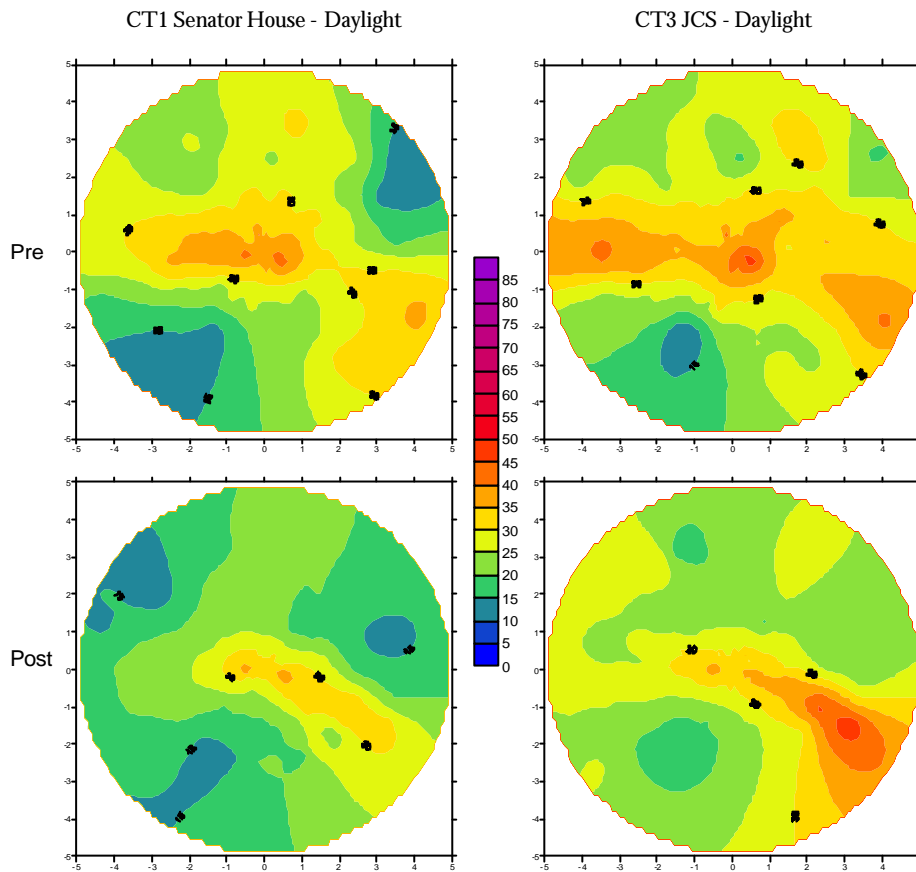


Figure 5-4: Polar plots of daylight NO<sub>2</sub> concentrations in ppb at CT1 Senator House and CT3 JCS pre- and post-intervention.

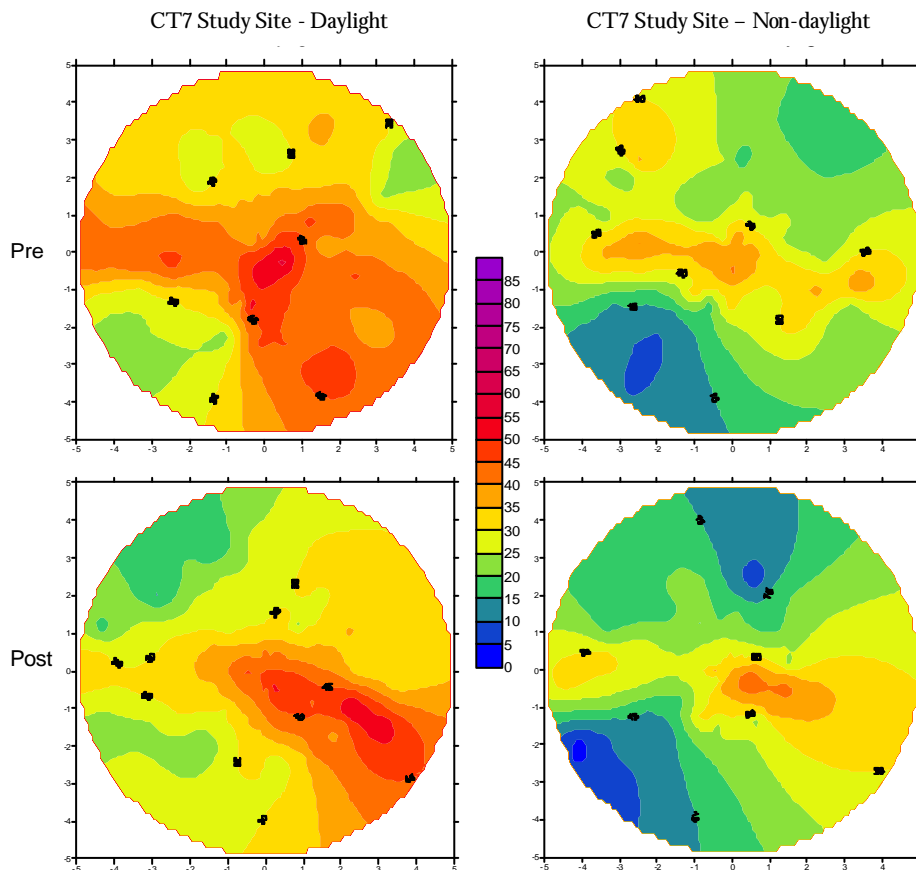


Figure 5-5: Polar plots of daylight and non-daylight NO<sub>2</sub> concentrations in ppb at CT7 Study Site pre- and post-intervention.



## 6 CUSUM change point analysis

### 6.1 Method

Previous analyses have compared aggregated concentrations over the pre- and post-intervention periods and are therefore unable to make an assessment as to the timing of any change due to the intervention. The aim of the CUSUM change point analysis is to establish whether any change in concentrations occurred suddenly, as would be expected if it were due to the application of the NO<sub>x</sub> reducing paint, or over a period of time, which would be more indicative of meteorological influence.

CUSUM (Cumulative Sum) is a statistical method often used in process control environments to detect small and sustained shifts in a process. The CUSUM is the sum, over time  $t$ , of deviations in the observed value of a variable ( $x_t$ ) from a reference value:

$$\text{Cumulative sum } S_t = S_{t-1} + z_t \quad \text{where } z_t = x_t - \mu_0$$

This running total is represented in a time series control chart. While the input data are normally distributed, CUSUM follows a distribution centred on the horizontal axis. If the input data undergoes a sustained change, the CUSUM develops a linear drift centred on a line whose slope is approximately equal to the shift in the mean. The cumulative sum may be split into positive deviations from the mean (SHi) and negative deviations from the mean (SLi). Upper and lower control limits may be set at multiples of the standard deviation to identify when a process goes 'out of control' and whether this shift is sustained over time. There is a time lag dependent on the magnitude of the change and size of control limits before a process is identified as out of control.

In this analysis, the reference value is the mean concentration of NO<sub>x</sub> or NO<sub>2</sub> for the pre-intervention period. This reference value is subtracted from each daylight mean concentration up to 1<sup>st</sup> December 2006. As with previous analyses, 'daylight' is defined as being between the hours of 09:00 and 16:00. The resulting (daily) differences or 'deviations' from this reference value are then added together sequentially to form a series; the first difference forms the first CUSUM of the series, the sum of the first two deviations are added together to form the second CUSUM, the sum of the first three deviations are added together to form the third CUSUM and so on.

The sensitivity of the CUSUM procedure can be adjusted by the setting of  $k$ , a measure of the allowable 'slack' in the system. In the following analyses,  $k$  is set at 0.5, which means that any change in mean less than 0.5 of the standard deviation of the time series is treated as zero change.

There are a number of limitations to the straightforward application of the CUSUM technique as applied in this study, which limit the sensitivity of results. Firstly, the identification of an out of control process depends on readings being statistically independent and following a normal distribution. Pollutant measurements can be expected to have some serial correlation, seasonality and underlying long-term trends. This has the effect that upper and lower control limits can be breached due to seasonal or short-term trends effects. Consequently, only strong signals can be clearly identified as being due to sustained step changes in long-term mean.

### 6.2 Results

The CUSUM chart for daylight NO<sub>x</sub> concentrations at CT7 Study Site reveals a steady downward gradient in the lower CUSUM parameter, SLi, from the end of March 2006 onward (Figure 6-1). However, this decrease is not sustained and the line returns back to zero before the end of the series. This suggests that there was a decrease in concentrations at CT7 Study Site around the time of the intervention, but this decrease was not sustained. The CUSUM chart for daylight NO<sub>x</sub> concentrations at the background control (CT3 JCS) shows a similar trend, although with a shallower and more variable gradient (Figure 6-2). This suggests that the decrease at the study site was, at least in part, connected to transient changes in meteorological conditions.

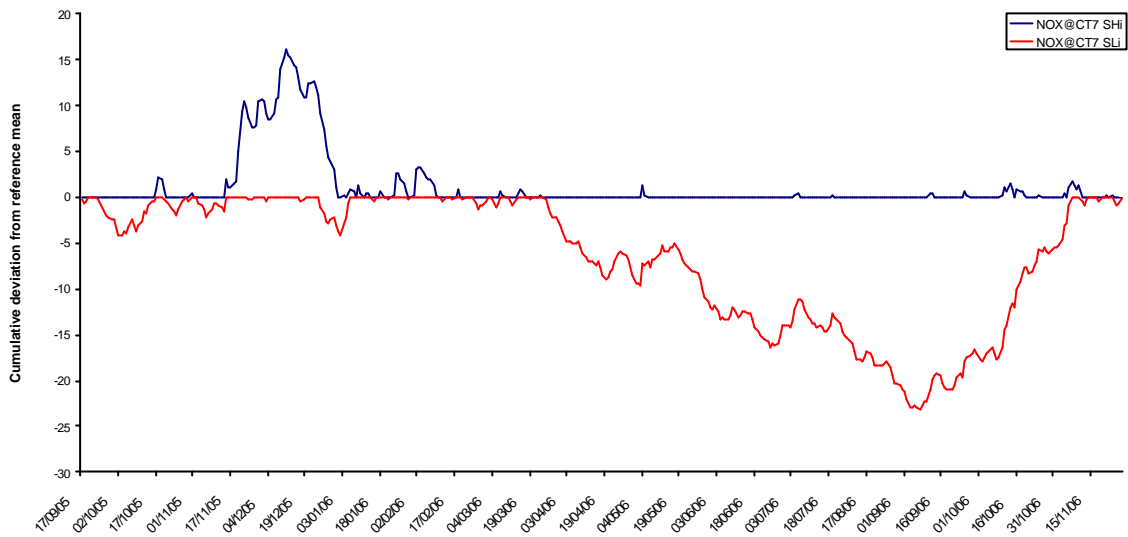


Figure 6-1: CUSUM chart applied to daily mean daylight NO<sub>x</sub> concentrations at CT7 Study Site

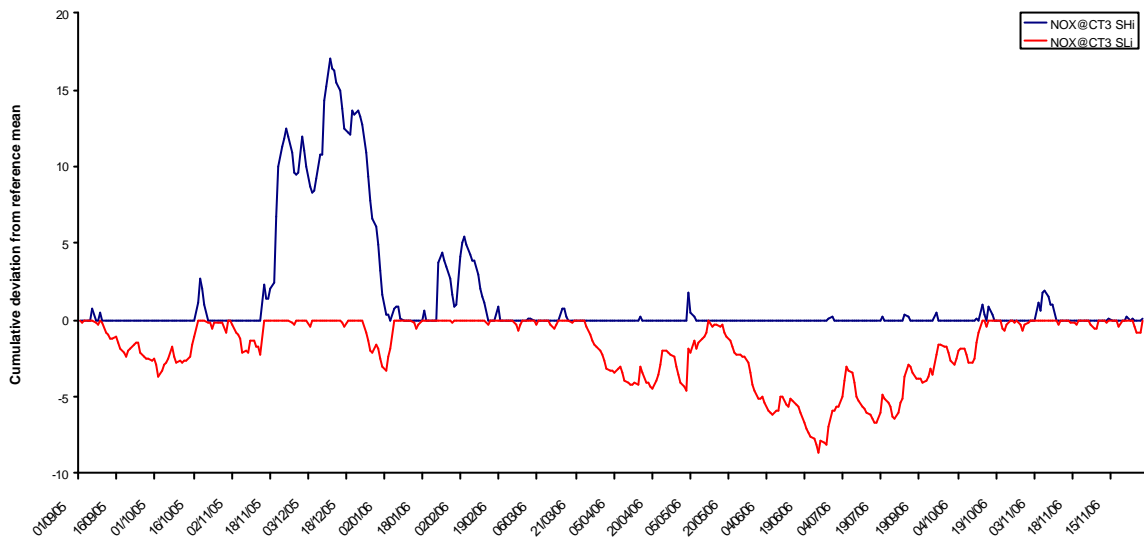


Figure 6-2: CUSUM chart applied to daily mean daylight NO<sub>x</sub> concentrations at CT3 JCS

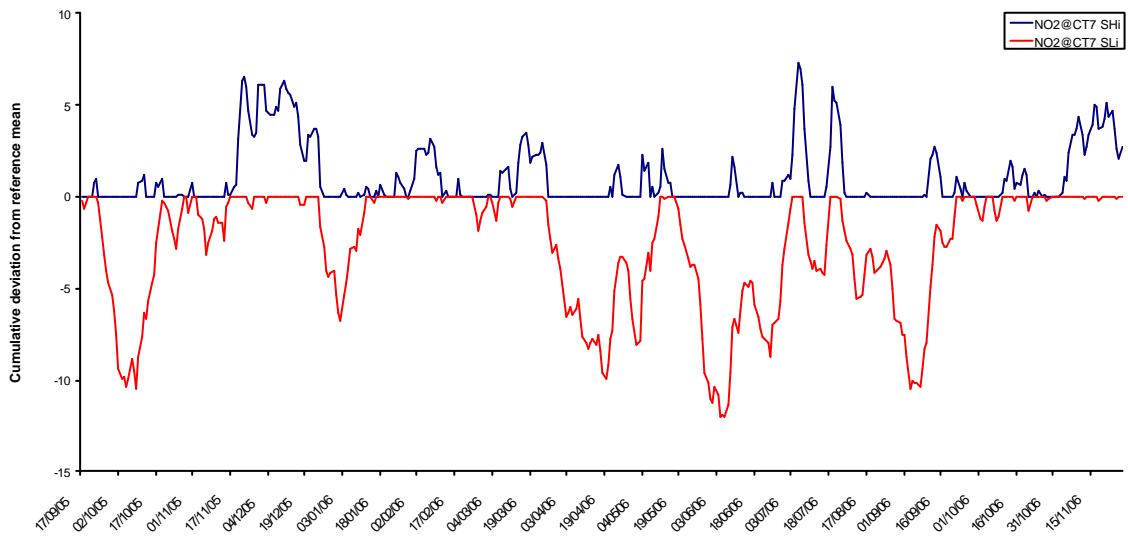


Figure 6-3: CUSUM chart applied to daily mean daylight NO<sub>2</sub> concentrations at CT7 Study Site

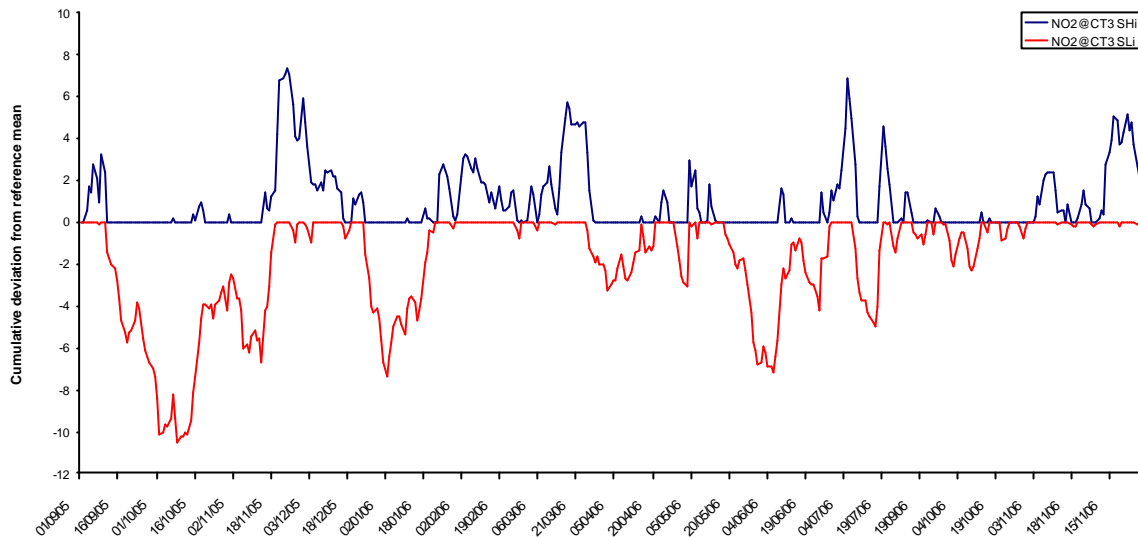


Figure 6-4: CUSUM chart applied to daily mean daylight NO<sub>2</sub> concentrations at CT3 JCS

The corresponding CUSUM chart for daylight NO<sub>2</sub> concentrations at CT7 Study Site shows no steady increase or decrease in concentrations at the intervention point, indicating the absence of a step change in concentrations (Figure 6-3). The pattern at CT3 JCS (Figure 6-4) is similar illustrating the influence of meteorology on both sites.

## 7 Conclusions

This report has used a range of statistical methods to describe and assess changes in NO<sub>x</sub> and NO<sub>2</sub> pollution concentrations at a study site installed approximately 5m from a wall painted with NO<sub>x</sub>-reducing paint. The wall was painted on 1<sup>st</sup> April 2006. Ratified measurements from the study site were available between 19<sup>th</sup> September 2005 and 1<sup>st</sup> December 2006.

The study site is located approximately 5m from a road junction to the south east and would not be classified as a background site. The rate of change analysis in Section 4 used percentage change, rather than absolute concentrations to accommodate the higher levels of emissions adjacent to the study site than the background control, and during non-daylight hours. This analysis reported a decrease in daylight NO<sub>x</sub> concentrations of 19% between the pre- and post-intervention periods. However, this represents a 6% increase in concentrations relative to the background controls. The results for NO<sub>2</sub> were similar, with the study site reporting an increase in NO<sub>2</sub> concentrations of 7% relative to the background controls.

Further information about the nature of this change was identified by the use of polar plots. This method provides a visual assessment of the direction emissions sources relative to the site and gives equal weighting to all wind speed and directions in the analysis grid. A visual comparison of polar plots pre- and post-intervention agreed with the results of the rate of change analysis for NO<sub>x</sub>. However, there was evidence of a decrease in NO<sub>2</sub> concentrations at the study site during winds other than from the south east. This decrease was also seen in the polar plot of the non-daylight control, so is unlikely to be an effect of the NO<sub>x</sub>-reducing paint.

While the previous analysis methods depend on mean concentrations over the analysis period, the CUSUM method attempted to identify a step change in concentrations, indicative of the intervention. CUSUM charts are influenced by transient changes in concentrations driven by meteorological conditions, but step changes are illustrated by a sustained increase or decrease in the cumulative deviations from the reference mean. No such sustained gradient was evident in the NO<sub>x</sub> or NO<sub>2</sub> charts.

Therefore, no decrease in NO<sub>x</sub> or NO<sub>2</sub> concentrations attributable to the NO<sub>x</sub>-reducing paint could be identified in measurements from the study site over the analysis period using the methods described. The conclusion of this study is that the paint has no detectable effect in NO<sub>x</sub> or NO<sub>2</sub> concentrations at a distance of approximately 5m.

There are a number of limitations to this study and its ability to detect change. Ideally, pre- and post-intervention periods should have been one full year each to limit the effects of seasonal differences. A longer analysis period, two years pre- and post-, for example, would also decrease the influence of meteorology but increase the confounding influence of long-term trends in pollution emissions. The study site's position within 5m of a road weakened the effectiveness of comparisons with the background 'control' sites. However, the non-daylight control provided a useful crosscheck. Finally, the study site was placed at a distance of 5m from the centre of the painted wall. Due to the nature of the reduction reaction requiring ambient air to come into contact with the painted surface, a detectable signal would be more likely if the study site's sample inlet were much closer to the wall. However, public exposure is unlikely very close to the painted surface.

It is beyond the remit of this report to consider the reasons for the lack of a signal from the NO<sub>x</sub>-reducing paint.

## 8 References

Barratt B. (2005a). Assessment of recent trends in NO<sub>2</sub> using CUSUM analysis methods. Client: Defra and the Devolved Administrations, March 2005.

Barratt, B., Atkinson, R., Anderson, H.R., Beevers, S., Kelly, F., Mudway, I., Wilkinson, P. (2007). Investigation into the use of the CUSUM technique in identifying changes in mean air pollution levels following introduction of a traffic management scheme. *Atmospheric Environment* (41) 1784-1791.

Carshaw, D.C., Beevers, S.D, Ropkins, K and M.C. Bell (2006). Detecting and quantifying aircraft and other on-airport contributions to ambient nitrogen oxides in the vicinity of a large international airport. *Atmospheric Environment*. 40/28 pp 5424-5434.

Global Engineering photocatalytic products technical document. Available at [www.globalengineering.info](http://www.globalengineering.info)

Mitsubishi Materials. NO<sub>x</sub> Removing Paving Block "NOXER". Technical sheet available at <http://www.mmc.co.jp/english/event/noxer.pdf>