

# **MONITORING THE POLLUTION CONCENTRATION GRADIENT AT A LONDON KERBSIDE MONITORING STATION**

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## **ABSTRACT**

Recent predictions of annual mean  $\text{NO}_2$  and  $\text{PM}_{10}$  in London (and elsewhere in the UK) show that by 2005 or 2010 exceedences of the EU Limit Value will be restricted to the near-road environment (AQEG, 2003). It is therefore becoming increasingly important to describe how concentrations decrease as a function of the distance from a road. Almost all monitoring carried out in the UK is conducted at monitoring sites separated by several kilometres, giving no direct indication of the near-road concentration profile. The complexity of the near-road environment also means that is very difficult for dispersion models to produce reliable estimates of the profile.

Simultaneous measurements of  $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were undertaken at distances representative of kerbside and roadside monitoring locations in a single monitoring cabin on the Marylebone Road in London. Measurements made at the two monitoring locations, and the differences between the two, were examined to derive a concentration fall off between the kerbside and roadside. A separate co-location study was carried out where duplicate instruments were installed equidistant from the kerb. Limits of agreement were calculated from the measurements made during this study. These revealed the extent to which individual instruments differed when monitoring at exactly the same location. This study therefore provides information useful for interpreting kerbside measurements from many monitoring sites in the UK and may allow building façade (or back of pavement) concentrations to be estimated, allowing a better assessment of population exposure.

## **INTRODUCTION**

This study provided the first data set of  $\text{NO}_x$ ,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentration fall-off measurements using continuous monitoring in the UK. Previous concentration gradient studies used diffusion tubes that only provide  $\text{NO}_2$  concentrations and had a greater inaccuracy than that expected from continuous instruments. During this study simultaneous  $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  measurements were made at distances relating to kerbside and roadside locations at a single monitoring station. These sampling locations were separated by a distance of 2.42 metres for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  and 4.05 metres for  $\text{NO}_x$ ,  $\text{NO}_2$  and  $\text{O}_3$ . Results are detailed for the two monitoring locations, the relationships between pollutants are considered, and the level of agreement between individual analysers.

## **METHOD**

The monitoring site is situated in Central London on the south side of Marylebone Road. This road is part of the Inner Ring Road and is a major route in and out of London carrying around

90,000 vehicles per day. It is a broad, broken street canyon 60 metres wide at the monitoring point, broken by junctions approximately every 100 metres.

The positions of all the sampling inlets are laid out in Figure 1. The exact distances of the inlets from the kerbside, and in the case of the roadside monitoring equipment their distance from the kerbside monitoring inlet, are shown in Table 1. The sampling points were dictated by the practicalities of monitoring both particulate matter and gaseous pollutants. The maximum separation distance was sought to increase the effect of dilution. For the particulate matter sampling this was limited by the necessity to site the sensor unit directly below the sampling inlet, the sampling inlet; therefore needs to remain within the confines of the cabin footprint. The roadside sampling inlet for NO<sub>x</sub> and O<sub>3</sub> was extended a metre further from the kerbside.

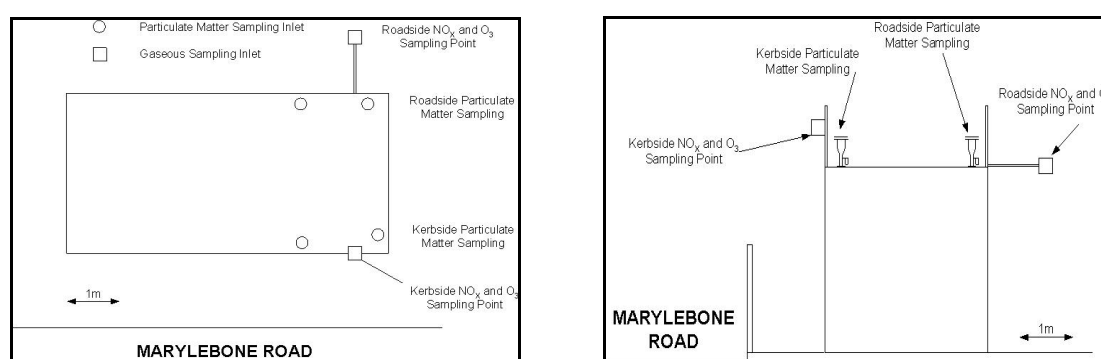


Figure 1: Sampling diagram, plan view of monitoring sites showing sample inlet locations

Instrument	Distance from Kerbside (m)	Distance from Kerbside Instrument (m)
TEOM - Kerbside	1.78	
TEOM - Roadside	4.20	2.42
Gaseous (NO <sub>x</sub> and O <sub>3</sub> ) - Kerbside	1.40	
Gaseous (NO <sub>x</sub> and O <sub>3</sub> ) - Roadside	5.45	4.05

Table 1: Sample inlet distances from the kerbside and the distances between sample inlets

PM<sub>10</sub> and PM<sub>2.5</sub> were measured using the TEOM method. All TEOMs sampled through Rupprecht & Patashnick Co., Inc. PM<sub>10</sub> inlets with a flow of 16.7l min<sup>-1</sup>. The PM<sub>2.5</sub> instruments sampled through an additional PM<sub>2.5</sub> Sharp Cut Cyclone (SCC). Four TEOM were used, two 1400A and two 1400AB. Nitrogen oxides were measured using Environnement AC31M chemiluminescent NO<sub>x</sub> analysers. O<sub>3</sub> was measured using an API 400 (AURN, kerbside) and ML9810 (roadside) ultraviolet photometric ozone analysers.

Between 17th January 2003 and 1st April 2003 sampling was undertaken at these roadside and kerbside locations to investigate the difference between concentrations at kerbside and roadside. Between 3rd April and 30th April the analysers were co-located equidistant from the kerbside to allow an assessment of the agreement between the instruments.

## CO-LOCATION STUDY

It is unrealistic to expect one measurement to agree exactly with another. Measuring agreement between the methods is therefore important to this study, however, many studies use the correlation coefficient ( $r$ ) to quantify the agreement between two measurement methods. This can be misleading as it does not measure the agreement between instruments, only the strength of the relationship between two variables (Bland et al., 1986). Most of the differences between measurements, assuming the distribution is normal, will be within the mean difference ( $\bar{d}$ )  $\pm$  2 standard deviations ( $2\sigma$ ). These limits have been termed the 'limits of agreement' (Bland et al., 1986). As these limits of agreement are based on 2 standard deviations, approximately 95 % of the measurements will fall within these boundaries and it is therefore a good assessment of the comparability of the instruments. The difference between the methods can increase with concentration and therefore the limits of agreement are also calculated as a percentage. These limits are neither precision nor accuracy but contain aspects of both and should therefore be viewed as an independent measurement for assessing the comparability of two pieces of equipment.

As discussed, between 3rd April and 30th April the analysers were co-located equidistant from the kerbside to allow assessment of the agreement between the instruments. The correlation coefficients and the limits of agreement are shown in Table 2. The high correlation coefficients obscure differences highlighted by the limits of agreement analysis, indicating that regression analysis is not appropriate for measuring agreement between instruments.

Short term air quality objectives are defined in terms of either hourly or daily means. It is important to examine the relationship between the instruments as both hourly and daily means. It is clear that the limits of agreement improve when the results are examined as daily means rather than hourly means as shown in Table 2. There was good agreement between the  $\text{NO}_x$  instruments. The co-located  $\text{O}_3$ ,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  instruments were found to differ markedly for both hourly and daily mean measurements. However, this relationship was linear and the data was consequently adjusted using the slopes and intercepts of the regression equations between the co-located instruments. These slopes and intercepts were then applied to the measurements made when the instruments were in separate locations. The larger limits of agreement calculated for these instruments would, in part, have been caused by differences in the instrument model type and, in the case of the  $\text{O}_3$ , logging methodology and calibration source.

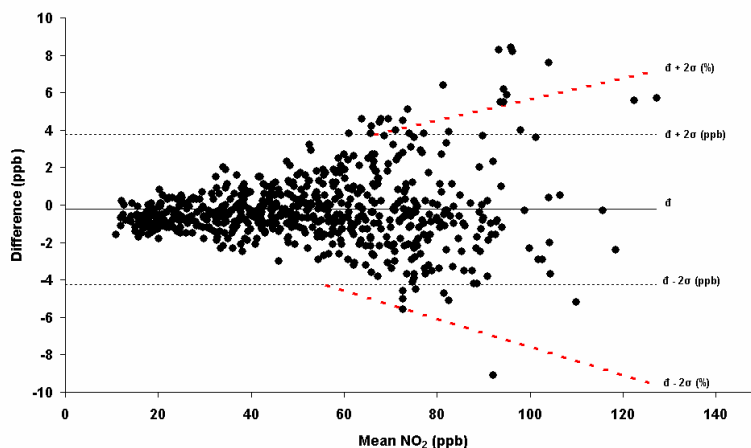
Figure 2 illustrates the relationship between the  $\text{NO}_2$  hourly mean measurements and their limits of agreement in more detail. It demonstrates that the agreement between the  $\text{NO}_x$  analysers is concentration dependent and is therefore better described as a percentage at higher concentrations. The  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  measurements did not demonstrate any concentration dependence; their limits of agreement are therefore expressed solely as an absolute value.

	Correlation coefficient	Hourly mean limits of agreement	Daily mean limits of agreement
$\text{NO}_x$	1.00	$\pm 7$ ppb or $\pm 5.5$ %	$\pm 3.5$ ppb or $\pm 3.5$ %
$\text{NO}_2$	1.00	$\pm 4$ ppb or $\pm 7.5$ %	$\pm 3.4$ ppb or $\pm 6$ %

O <sub>3</sub> *	0.98	±4.5 ppb	±2 ppb
PM <sub>10</sub> *	0.97	±9 µgm <sup>-3</sup>	±4.2 µgm <sup>-3</sup>
PM <sub>2.5</sub> *	0.97	±5 µgm <sup>-3</sup>	±1.4 µgm <sup>-3</sup>

**Table 2: Correlation coefficient and limits of agreement calculated for co-location study**

\*Following adjustment using the slope and intercept of the regression equation



**Figure 2: Hourly mean NO<sub>2</sub> concentrations vs. NO<sub>2</sub> analyser differences in ppb showing limits of agreement**

## KERBSIDE AND ROADSIDE MONITORING

Between 17th January 2003 and 2nd March 2003 sampling was undertaken at roadside and kerbside locations to investigate the near-road concentration gradient. The mean concentrations for the study period, calculated from hourly averages, and the difference between them are shown in Table 3.

	Kerbside mean	Roadside mean	Difference (mean kerbside – mean roadside)	Roadside fall off (see equation 1)
NO <sub>x</sub> (ppb)	183.6	144.6	39.0	29 %
NO <sub>2</sub> (ppb)	52.4	47.7	4.7	19 %
O <sub>3</sub> (ppb)	7.3	7.9	-0.6	-5%
PM <sub>10</sub> (µgm <sup>-3</sup> )	43.0	39.5	3.5	22 %
PM <sub>2.5</sub> (µgm <sup>-3</sup> )	24.4	22.7	1.7	24 %
PM <sub>coarse</sub> (µgm <sup>-3</sup> )	18.6	16.8	1.8	20 %

**Table 3: Kerbside and roadside hourly mean concentrations**

To test whether the differences between the concentrations measured at the kerbside and those measured at the roadside are greater than those attributable to the difference between the instruments they need to be compared to the limits of agreement. The relationship between the kerbside NO<sub>2</sub> hourly measurements and the difference between these and the roadside measurements are shown in Figure 3. The limits of agreement for hourly NO<sub>2</sub> means, calculated from the co-location study period, are also shown in Figure 3. This reveals that the difference between 61% of the hourly NO<sub>2</sub> measurements can be explained by differences between the instruments, despite the higher concentration measured at the kerbside. This is true, to a greater or lesser extent, for all the instruments and indicates that individual hourly mean measurements cannot be compared directly. When the daily mean measurements are

compared in the same way many of the measurements still remain within the limits of agreement, again indicating that individual daily mean measurements cannot be compared directly.

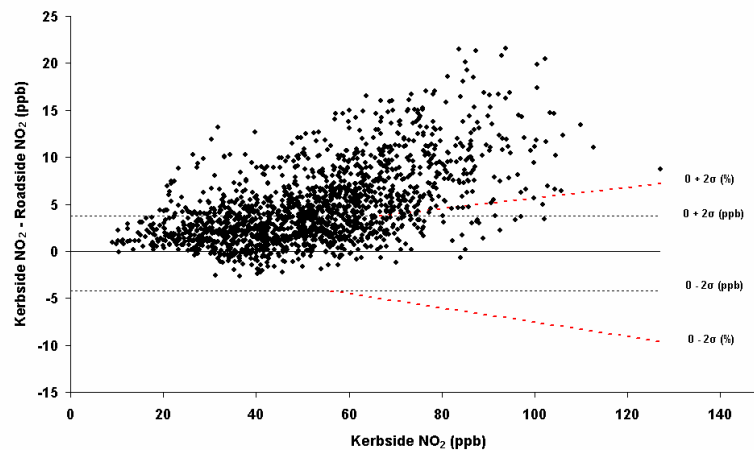


Figure 3: Kerbside NO<sub>2</sub> hourly mean vs. kerbside - roadside hourly mean NO<sub>2</sub> measurements alongside limits of agreement

Measurements from this study have also been compared to background concentrations measured at North Kensington monitoring site, 7.4 km to the west. The background monitoring site at Bloomsbury, 2.9 km to the east, has been used to provide PM<sub>2.5</sub>, as no TEOM PM<sub>2.5</sub> data is available from North Kensington. The kerbside concentration can be viewed as being made up of three components: a background concentration, a roadside increment and a kerbside increment. These components are calculated from the measurements made at the different locations and are shown in Figure 4.

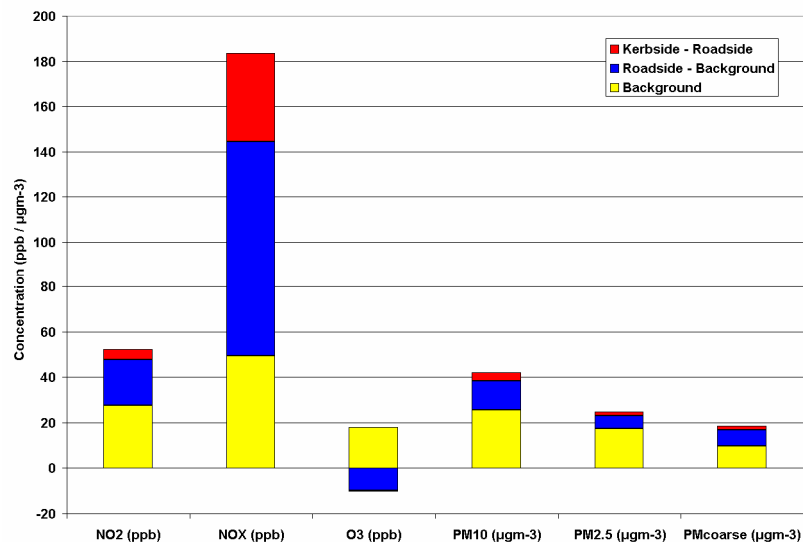


Figure 4: Background, roadside and kerbside components of NO<sub>x</sub>, NO<sub>2</sub>, O<sub>3</sub>, PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>coarse</sub>

The background concentration makes the same contribution to the concentrations at both kerbside and roadside. The difference between the roadside and kerbside locations will therefore be independent of the background concentration. Hence, it is necessary to subtract

the background concentration from the roadside and kerbside concentrations before examining the relationship between them. To calculate the percentage fall in concentration between the kerbside location and the roadside location the following equation has been used:

$$\text{RoadsideFallOff} = \frac{\text{RoadsideConcentration} - \text{BackgroundConcentration}}{\text{KerbsideConcentration} - \text{BackgroundConcentration}} \quad (1)$$

The results of applying this equation are shown in Table 3, alongside the distance between the instruments.

These results demonstrate that there is a substantial fall in concentration between kerbside and roadside. The NO<sub>x</sub> concentration gradient is larger than that for particulate matter. This is probably due to the increased separation of the sampling inlets, allowing for a greater dilution effect. However, the NO<sub>2</sub> gradient is lower than the NO<sub>x</sub> gradient. This suggests that chemistry is contributing to the concentration fall off by converting NO to NO<sub>2</sub> between the kerbside and roadside. The fall off in all particulate matter fractions is of the same order (20-24%). This consistency between kerbside and roadside locations is supported when the relationship between PM<sub>10</sub> and PM<sub>2.5</sub> is examined. Regression analysis of PM<sub>2.5</sub> against PM<sub>10</sub> daily mean measurements for kerbside and roadside yields slopes of 0.61 and 0.62 respectively, and intercepts of  $-4.9 \mu\text{gm}^{-3}$  and  $-5.2 \mu\text{gm}^{-3}$  respectively.

## CONCLUSION

The co-location exercise demonstrated that two similar instruments, operating under the same QA/QC procedures could produce different results. Calculating limits of agreement from the differences between the individual measurements quantified these disparities. Such differences were not immediately obvious when examining the correlation coefficients, indicating that correlation coefficients have limitations when measuring agreement. The limits of agreement of the measurements was seen to increase as a result of variations between the instruments in terms of model type, logging methodology or calibration source as demonstrated by the larger limits of agreement for the TEOM and O<sub>3</sub> measurements.

When the differences between the measurements at the kerbside and roadside were within the limits of agreement. This showed that the differences between individual measurements were small enough to be attributable directly to the variations between the instruments. However, mean concentrations for the whole period of kerbside and roadside monitoring showed that concentrations at the kerbside were elevated above those at the roadside for all the pollutants measured, except O<sub>3</sub> whose concentration varied little. When this concentration gradient was examined, after subtracting the background concentration, the fall off from kerbside to roadside was found to be a relatively constant 20-24% for PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>coarse</sub> (from 1.8 to 4.2 m from the kerb). The concentration gradient was found to be 19% for NO<sub>2</sub> and 29% for NO<sub>x</sub>, from 1.4 to 4.5 m from the kerb.

## **REFERENCES**

**AQEG, 2003. Nitrogen Dioxide in the United Kingdom, DEFRA.**

**Bland, M. J. and Altman, D. G., 1986. Statistical Methods For Assessing Agreement Between Two Methods of Clinical Measurement. The Lancet No.327 (8476), pp.307-310.**

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