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Evidence of an increasing NO_2/NO_X emissions ratio from road traffic emissions

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Abstract

A statistical analysis of roadside concentrations of nitrogen oxides (NO_X) and nitrogen dioxide (NO_2) in London shows that from 1997 to 2003 there has been a statistically significant downward trend (at the $p = 0.004$ level) in NO_X averaged across a network of 36 sites. Conversely, there has been no statistically significant trend in the concentrations of NO_2 over the same period. Hourly modelling using a simple constrained chemical model shows that the NO_2/NO_X emissions ratio from road traffic has increased markedly from a mean of about 5–6 vol% in 1997 to about 17 vol% in 2003. Calculations show that if the NO_2/NO_X emissions ratio had remained the same as that towards the beginning of each time series, 14 out of the 36 sites would have shown a statistically significant downward trend in NO_2 at the $p = 0.10$ level compared with only five that did. The increase in the NO_2/NO_X emissions ratio from road traffic in recent years has therefore had a significant effect on recent trends in roadside NO_2 concentrations. It is shown that the increased use of certain types of diesel particulate filters fitted to buses is likely to have made an important contribution to the increasing trends in the NO_2/NO_X emissions ratio. However, it is unlikely that these filters account for all of the observed increase and other effects could be important, such as the increased penetration of diesel cars in the passenger car fleet and new light- and heavy-duty engine technologies and management approaches.

Keywords: Primary NO_2; Nitrogen dioxide; Diesel particulate filter; Trend analysis; Mann–Kendall; London; Urban air quality

1. Introduction

1.1. Background

Nitrogen dioxide (NO_2) represents an important urban pollutant in most European cities. Concerns over the health impacts of NO_2 have prompted legislation at a national and international level. In Europe, the EU First Daughter Directive (99/30/EC) sets an annual mean limit of $40\,\mu g\,m^{-3}$, and an hourly limit of $200\,\mu g\,m^{-3}$ not to be exceeded on more than 18 occasions each year. The Directive requires compliance by 1 January 2010. In the UK, recent projections show that many urban areas will not meet the annual mean limit by 2010 (AQEG, 2004). In the UK, there is also a system of Local Air Quality Management (LAQM) which recognises that national or international measures will not always be the best way to deal with localised air quality problems. The LAQM process has led to 132 (out of 407) local authorities declaring air quality management areas, for which further effort will be required to meet air quality limits (AQEG, 2004). Of the 132 authorities, 92% were for NO_2, 45% for PM_{10} and 4% for sulphur dioxide. The declarations for NO_2 were all related to road traffic sources; although in some cases

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industrial sources were considered important. LAQM in the UK shows NO_2 to be an important pollutant and road traffic to be the most important source affecting concentrations.

1.2. Recent trends in roadside NO_X and NO_2 concentrations in London

Trends in the concentration of NO_X and NO_2 have been calculated for 36 air pollution monitoring sites in London. Thirty-two of these sites are classified as kerbside (<1 m from the kerb) or roadside (<5 m from the kerb); four are defined as urban background sites, but are strongly influenced by local road sources. Trends have been considered from January 1997 to December 2003. Fig. 1 shows the monthly mean trend in NO_X and NO_2 for all sites. Fig. 1 shows that concentrations of NO_X show a strong seasonal component, with concentrations being consistently higher during the winter months. There is no clear seasonal component to monthly mean NO_2 concentrations. Also apparent from Fig. 1 is that concentrations of NO_X have declined from 1997 to 2003. For NO_2 there is no clear trend in concentration. In order to quantify whether the trends in NO_X and NO_2 are statistically significant, a seasonal Mann–Kendall test has been applied (Hirsch et al., 1982). The test, which has proved popular for water quality studies, is a non-parametric test that can be applied to data that are not normally distributed and where there are missing data. Applying the test to the data in Fig. 1 shows that there is a statistically significant downward trend in NO_X at the $p = 0.004$ level. For NO_2, no statistically significant trend was detected ($p = 0.63$). The Mann–Kendall technique only detects the presence of a trend and does not quantify it. An approach often used in conjunction with the Mann–Kendall technique is the calculation of a slope using the method of Sen (Gilbert, 1987). Calculating the Sen slope for NO_X, showed that the concentration decreased on average by 6.1 ppb yr^{-1}. Individual site trends are considered later in Table 2.

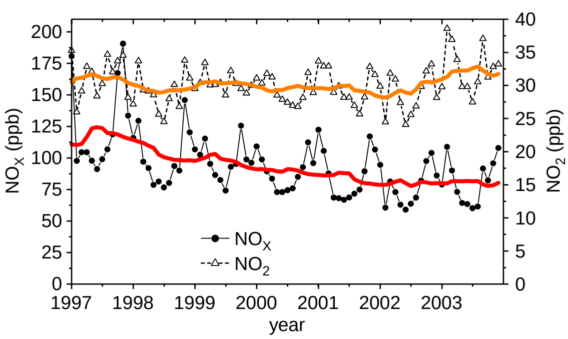

Fig. 1. Trends in monthly mean concentrations of NO_X and NO_2 averaged across 36 air pollution monitoring sites in London (1997–2003). A 12 month moving average trend has been fitted to both datasets.

Despite a comparatively large reduction in concentrations of NO_X at roadside locations, concentrations of NO_2 have remained relatively constant. It is important to consider why there has been no statistically significant downward trend in roadside NO_2 concentrations. It was known that exceptional meteorological conditions during 2003 led to elevated concentrations of many pollutants (Fuller, 2004), but it has not been established how these conditions affected NO_2 concentrations. This paper addresses the following issues. First, a simple chemical modelling technique is applied to the data from air pollution measurement sites to quantify the trend in the road transport NO_2/NO_X emissions ratio (assumed to relate to primary NO_2 emissions, i.e., directly emitted NO_2) on a monthly basis. Second, the results from this technique are checked against other data to ensure their validity. Finally, trends in NO_2/NO_X ratios are considered in relation to factors affecting this ratio, such as road transport emissions control technologies.

2. Method

2.1. Estimating the NO_2/NO_X emissions ratio from ambient measurements

Carslaw and Beevers (2005b) describe a technique for estimating the NO_2/NO_X ratio from road transport emissions based on an analysis of ambient measurements. In London, there is a large number (>30) of roadside monitoring sites that measure hourly concentrations of NO_X and NO_2 using the chemiluminescence technique. London is therefore an excellent location in which to consider the road transport contribution to NO_X and NO_2 concentrations. The increment in NO_X and NO_2 concentrations above nearby background values is dominated by contributions from road traffic sources adjacent to the roadside monitoring sites.

Briefly, the increment in NO_X and NO_2 concentration at a roadside monitoring site above a nearby background site is partitioned into NO_2 that is chemically derived through the reaction between NO and ozone (O_3) and that which is emitted directly by road vehicles. The technique is constrained by assuming that the difference between roadside and background NO_X concentrations each hour is due to NO_X emissions from road vehicles adjacent to the roadside monitoring site. A simple set of chemical equations is used to describe the time-dependent change in NO, NO_2 and O_3 concentrations as vehicle plumes are mixed with background air. By considering different values of the assumed NO_2/NO_X emissions ratio from road traffic and the time available for the NO–O_3 reaction to take place, the best agreement between hourly NO_2 concentrations between