

The Increasing Importance of primary NO₂ emissions

Summary of Presentation Slides – David Carslaw

Slide #	Comment
1	Front slide
2	Highlight attention to a recent report, soon to be published (http://www.defra.gov.uk/environment/airquality/panels/aeqg/index.htm)
3	What is primary NO ₂ ? Self-evident from slide. Is an issue that has been largely ignored until recently. Most commonly assumed to be 5 % of total NO _x emissions for a range of source types; not just road transport.
4	Types of trends seen – example plot from a London roadside site. Factor of 2 decrease in total NO _x , little change if any in NO ₂ .
5	Summary of the general picture across the UK
6	Several approaches available to estimate fraction of NO ₂ (f-NO ₂) from monitoring data. Focus on two approaches: total oxidant and a simple, constrained chemistry model. Latter has advantage of providing hourly O ₃ predictions at roadside locations where O ₃ is not routinely measured.
7	Trend in f-NO ₂ at busy roadside site in London, also showing changes in bus flows. Buses look important – but do they account for everything. This site is useful to study because of the comprehensive air pollution and traffic measurements.
8	Certain sites have shown relatively abrupt changes in NO ₂ concentrations – can these be characterised to help identify the causes? Describe one method used based on the CUSUM technique. This technique accumulates deviations from a mean and acts as a sensitive way of detecting small changes.
9	Overview of how the technique used. Plot shows a series with some random noise added. There is an enforced step change half way through. Red CUSUM line provides an indication of when change occurred. Histogram shows probability distribution of the change; derived using bootstrap/randomization methods. Paper has further info.
10	CUSUM applied to roadside site in Oxford. For NO _x some indication of changes but not statistically important (see histograms). For NO ₂ , two changes detected that look to be more important. One in 1999 coincides with change to road allowing more buses/fewer cars. The 2002 change occurs at a time when buses were being fitted with particle filters that produce NO ₂ .
11	Trend in f-NO ₂ estimated at Oxford, confirms that changes most likely dominated by increases in f-NO ₂ and not other factors.
12	Similar trends at Marylebone Road. However, changes are more abrupt and uncertainty ranges narrower. Most significant change in February 2003 when congestion charging started. At this time bus numbers increased and buses fitted with CRTs (producing NO ₂). Will return to this later.
13	Now look at hourly concentrations. Plot attempts to speciate the origins of

- NO₂ at Marylebone Rd. Key point is that high NO_x concentrations associated with an increasing proportion of the NO₂ due to primary emissions. This plot based on f-NO₂ of 10 %; primary contribution will double for f-NO₂ = 20 %. Therefore, peak hourly concentrations of NO₂ can be dominated by primary emissions and not other factors in these locations.
- 14 Plot shows scenarios and highlights sensitivity of exceeding the 18 hours 200 µg m⁻³ limit value. Current f-NO₂ ~ 22-24%. Modelling suggests that if f-NO₂ had remained at historical level of 10 %, the hourly limit value would have been met in 2004. Estimate that meeting limit will be delayed by ~ 10 years at this location.
- 15 One site in London (not a big road) has extremely high NO₂ concentrations. Fourth highest flow of buses in the UK. Over 4000 hours > 200 µg m⁻³. This raises the question of what driver exposure might be – ppm NO₂? Need more research on this.
- 16 Nest talk about emissions. Most significant changes in recent years are two technology types: “strong” oxidation cats fitted to diesel cars/vans from Euro III, and continuously regenerating particle filters that deliberately produce NO₂ to help oxidize particles (by effectively lowering the temperature for combustion). Former is no prevalent throughout Europe, latter important in cities with captive bus fleets and the like. Therefore, might expect distribution of changes in NO₂ throughout Europe to be patchy.
- 17 Plot is effective in showing changes in emissions (courtesy of Dr Raymond Gense). Clear for cars at least that it is a diesel problem; important for Euro III, maybe more important for Euro IV. Need to also account for changes in total NO_x emissions.
- 18 So have emissions reduced. Recent data from ITS Leeds using remote sensing. Can only measure NO and not NO₂. However, this work suggests that diesel NO emissions have not decreased by much from pre-Euro I to Euro IV. Indeed if you accept that there is more NO₂ in Euro III/IV diesels then these results may suggest that total NO_x emissions have increased recently. Location was a typical urban one.
- 19 Estimated changes in NO_x and NO₂ in London (courtesy of Sean Beevers, ERG). NO_x emissions decrease substantially, NO₂ almost constant. In central London (more diesel vehicles), even less change in total NO₂ emissions over 10 years.
- 20 This slide makes the point that it is difficult to apportion NO₂ changes from measurements alone. In London (and elsewhere to some extent) lots of changes have occurred at pretty much the same time: increased diesel cars, increased Euro III/IV (oxy cats), increased bus flows, increased uses of particle filters on buses. Care is needed when trying to identify the causes. However, a general view would be an underlying increase due to cars/vans onto which in certain locations, HGV/bus particle filters add.
- 21 Change point analysis of 20 sites in London. Graph shows the distribution of changes i.e. most around 2003 – but remember points in previous slide.
- 22 What of changes in f-NO₂ had not occurred? Set f-NO₂ to that estimated in first year of each time series and use model to project forward and compare

with measured values. At these three different sites, annual mean NO₂ concentrations are substantially higher than would otherwise be expected (19-33 %).

- 23 This slide tries to estimate f-NO₂ from ambient measurements and traffic data. Acts s one way of checking consistency with emissions. The mean f-NO₂ calculated by vehicle type is consistent with what is known about the emissions. Even explains the site with the highest NO₂ in Europe mentioned earlier.
- 24 Using info in previous slide, can estimate that recent changes in f-NO₂ at air pollution monitoring sites in London, a little more than half is due to buss and the rest diesel cars and LGVs. More emissions measurements would help confirm this.
- 25 Highlights that other effects could be important: increased ratio of NO₂/NO_x leads to increased O₃. Also, combination of water vapour, surfaces and NO₂ likely to lead to formation HONO, which is another route through atmospheric chemistry to NO₂ and O₃ (recent paper in press from Mike Jenkin et al. On this – Atmospheric Environment). HONO is detected as NO₂ in chemiluminescent analysers; so some of the NO₂ increases identified likely include HONO. More research needed on this.


Finally thanks all for “listening” and apologies I could not make this interesting conference!

Institute for Transport Studies
FACULTY OF ENVIRONMENT UNIVERSITY OF LEEDS

The increasing importance of primary nitrogen dioxide emissions

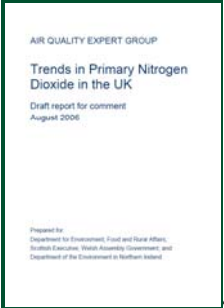
David Carslaw

25-26th September 2007, Prague




Recent report UNIVERSITY OF LEEDS

- UK Air Quality Expert Group (AQEG)
 - Emissions
 - Measurements analysis
 - Modelling
 - Review of potential causes




Report available at: www.defra.gov.uk/environment/airquality/aqeg/index.htm



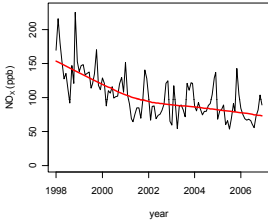
What is primary NO₂? UNIVERSITY OF LEEDS

- Combustion processes result in emissions of NO and NO₂ (= NO_x)
 - NO₂ emitted directly is **primary NO₂** (also referred to as **direct NO₂**)
 - Most NO₂ in atmosphere is formed via ozone (secondary NO₂)
- Commonly assumed that the proportion of NO₂ is small (about 5.0 % by volume) of total NO_x
 - Issue largely ignored until recently
 - First evidence from analysis of ambient measurements in London
 - Volume ratio of NO₂/NO_x referred to as **f-NO₂**

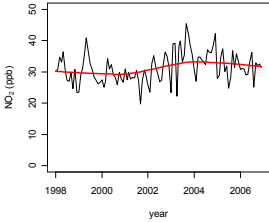


Example trends in NO_x and NO₂ UNIVERSITY OF LEEDS


oxides of nitrogen



nitrogen dioxide




- Monthly data for busy roadside site in outer London
- NO_x has decreased by a factor of two, but no change in NO₂



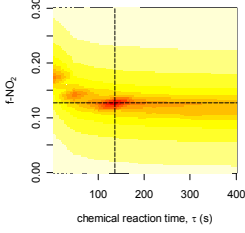

UK monitoring - summary UNIVERSITY OF LEEDS

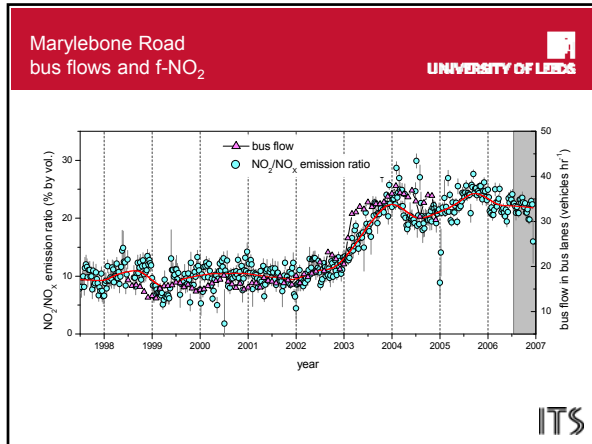
- NO_x has broadly decreased in line with expectations at all site types
- NO₂ has not decreased with expectations at many sites (or has increased)
 - Background sites have generally decreased as expected
 - Roadside/kerbside sites show a mixed picture: increases most apparent in England and in particular London
 - Availability of sites is important (relatively few roadside sites outside London)



Estimating f-NO₂ emissions ratio UNIVERSITY OF LEEDS

- Described in detail in the AQEG report
 - "Total oxidant" approach (Clapp and Jenkin, 2001)
 - Needs hourly NO, NO₂ and O₃
 - Constrained simple chemical modelling (Carslaw and Bevers, 2005)
 - Useful at roadside sites where O₃ is not measured

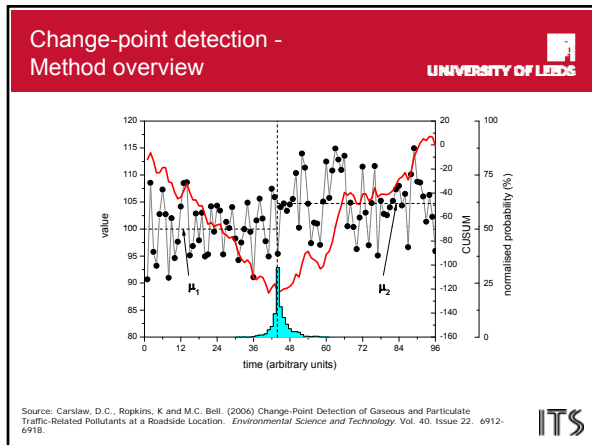


Change-point detection

- Certain sites around the UK have shown reasonably abrupt changes in NO₂
 - Can this be detected and what might the reasons be?
 - Cumulative sum (CUSUM) technique applied
 - Uncertainty level and intervals in timing of change-point quantified using randomization/bootstrap methods
 - Two example sites considered: Oxford Centre and Marylebone Road

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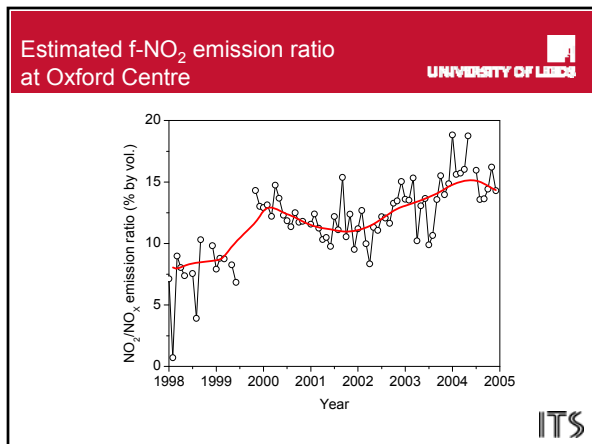


Change-point detection applied to Oxford Centre

- Two NO₂ change-points detected (July 1999 and August 2002)
- July 1999 – Oxford “bus gate”
- August 2002 – particle filters on buses?

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Change-point detection applied to Marylebone Road

- Clear NO₂ change-point detected in February 2003
- Coincides with introduction of congestion charging
- More buses + more buses with continuously regenerating diesel particulate filters

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Origins of NO₂ as a function of NO_x concentration

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- Increasing share of NO₂ due to primary emissions as NO_x increases
- Implications for high percentile hourly mean NO₂ concentrations
- EU limit value of 18 hours > 200 µg m⁻³ per year

Based on 10 % primary NO₂ at Marylebone Road

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Effect of NO₂/NO_x emission ratio on hourly NO₂ limit

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Marylebone Road would probably have met limit value in 2004 if NO₂/NO_x had remained at historically typical values: 10 ± 4 hours (2 σ)

[2004 = 529; 2005 = 853; 2006 = 676 hours]

Meeting 18 hour limit value may be delayed by ~ 10 years due to recent increases in primary NO₂

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Highest concentrations in Europe?

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- Site in inner London
- 5th highest flow of buses in UK
- 2006: annual mean NO₂ **220 µg m⁻³** and **4105 hours > 200 µg m⁻³**
- Driver/passenger exposure?

Source: www.londonair.org.uk

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Vehicle technologies – diesel vehicles

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- “Strong” oxidation catalysts used on light duty vehicles to meet Euro III limits
- To control CO, hydrocarbons, PM
- Consequence is NO → NO₂
- Continuously regenerating particle filters for heavy duty vehicles
- Deliberate production of NO₂ to help oxidise particles, CO and hydrocarbons – lowers temperature at which PM is oxidised

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Recent vehicle emissions testing results – light vehicles

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Source: Raymond Gense (TNO) in Air Quality Expert Group report: Trends in Primary Nitrogen Dioxide in the UK (2007)

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In-use emissions from cars

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- Results from a recent campaign in York using vehicle emissions remote sensing
- Over 6,000 individual vehicle plumes sampled
- Shows how in-use emissions have changed
- pre-Euro = pre 1992
- Euro I = 1992-1996
- Euro II = 1996-2000
- Euro III = 2000-2005
- Euro IV = post 2005
- Little change in diesel NO emissions – has NO_x increased?

Thanks to Dr James Tate (ITS) for these data; plots show 95 % confidence intervals in the mean

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Primary NO₂ emissions inventory - London

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- First inventory developed was for London
- Strong reduction in NO_x and slow decrease in NO₂ to 2010
- Central London shows almost no change from 2000-2010 for NO₂
- Diesel vehicles (taxis and buses)

Source: Sean Beever, Environmental Research Group, King's College London

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Recent vehicle and technology changes

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- In the UK, lots of changes have occurred at similar times
- Increased use of diesel as a fuel in cars
- (In London) increased flows of buses
- Increased use emissions after-treatment

Characterising recent changes in NO₂ in London

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- Change-point methods applied to 20 roadside sites
- Most deviations from "expected" NO₂ concentrations were relatively abrupt
- However – difficult to identify attribution from this alone

Source: Carslaw, D.C. and N Carslaw (2007). Detecting and characterising small changes in urban nitrogen dioxide concentrations. *Atmospheric Environment*, Vol. 41, 4723-4733.

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What if increases in f-NO₂ had not occurred?

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Central London, high traffic flow, typical urban speed (Marylebone Road)

Outer London, high traffic flow, high speed, similar to a motorway (A3)

Inner London, average traffic flow (Tower Hamlets)

Note: 12-month smooth applied.

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Derivation of vehicle f-NO₂ ratio from measurements

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- Estimate primary NO₂ at 37 London sites
- Multiple regression with traffic NO_x emissions:

Buses = 39 (± 2) %
HGVs = 12 (± 5) %
Cars/vans = 18 (± 5) %

- In good agreement with known emissions estimates – even explains the "outlier" site

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Share of f-NO₂ in London (2004)

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- Use derived f-NO₂ ratios for HGVs, buses and car + LGVs
- Apply to 41 sites in London

For NO_x: HGVs = 31 %;
 buses = 26 %;
 car + LGV = 43 %

For NO₂: HGVs = 18 %;
 buses = 46 %;
 car + LGV = 36 %

- Estimated increase in share of primary NO₂ since pre oxy-cat/CRT: buses ~ 60 %; diesel car/LGV ~ 40 %

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NO₂ health effects and related issues



- Recent studies support view that NO₂ as a pollutant is of health concern
 - ATHEA¹
 - US EPA²
- Increased ratios of NO₂/NO_x increase ozone concentrations
- Nitrous acid (HONO) emissions could be important but are currently unquantified
 - Surface formation in presence of NO₂ and water
- Full impacts have not been established

¹ Samoli et al., (2006). Short-term effects of nitrogen dioxide on mortality: an analysis within the APHEA project. *Eur. Respir. J.* 27: 1129–1137.

² US EPA (2007). Integrated Science Assessment for Oxides of Nitrogen – Health Criteria. First External Review draft.



Concluding remarks



- Evidence that the ratio of NO₂/NO_x is increasing across the UK
 - Mostly at roadside sites, most apparent in London
 - By no means uniform
- More analysis is required to understand effects at specific sites
 - Delineate between diesel car/van oxy. cat and bus/HGV catalytically regenerating DPF
- Other effects that should be considered
 - Effect on ozone
 - Quantification of emissions and impacts of HONO

