

Chemistry, sources and partitioning of oxidant in the urban environment

[Atmospheric Environment, 38, 5117-5129, 2004;
Atmospheric Environment, 38, 5131-5138, 2004]

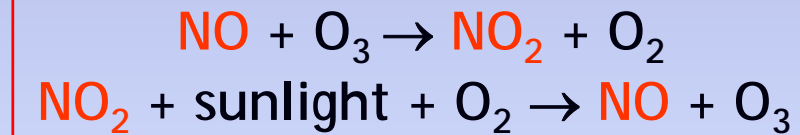
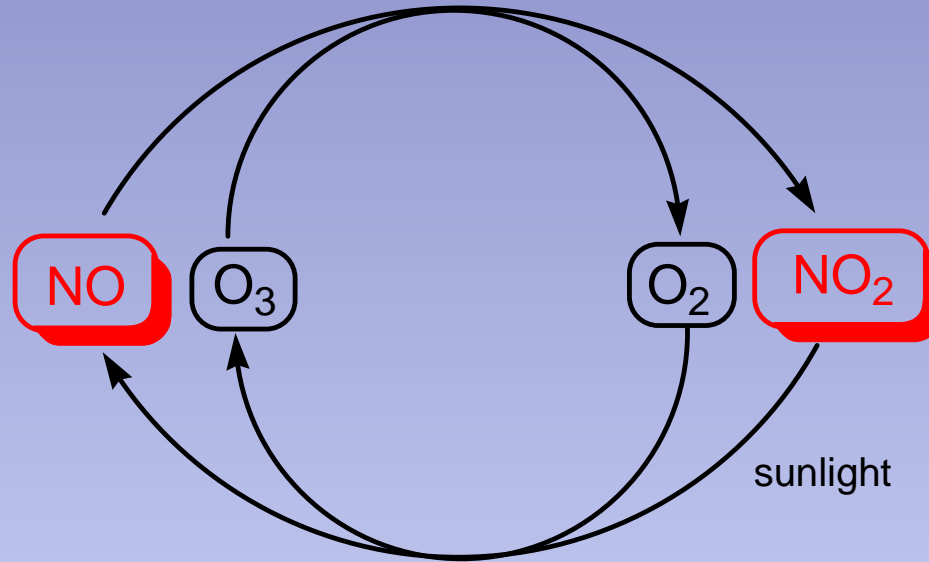
**Imperial College
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Mike Jenkin

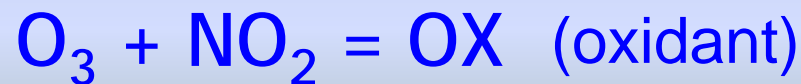
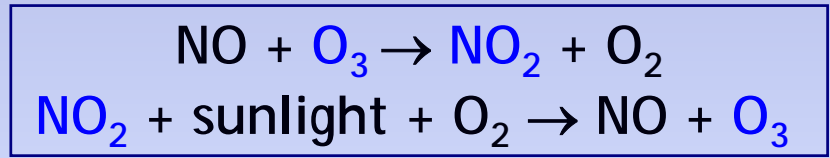
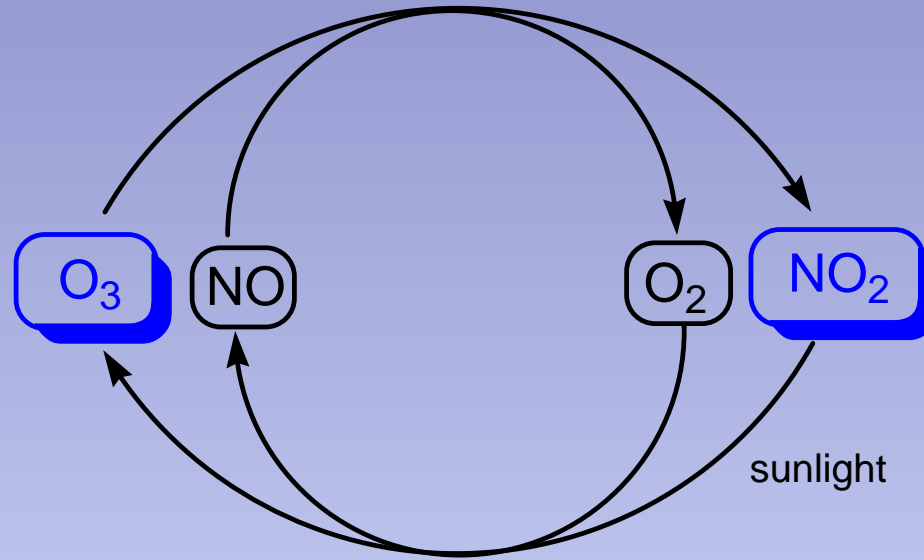
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The chemical coupling of O₃, NO and NO₂



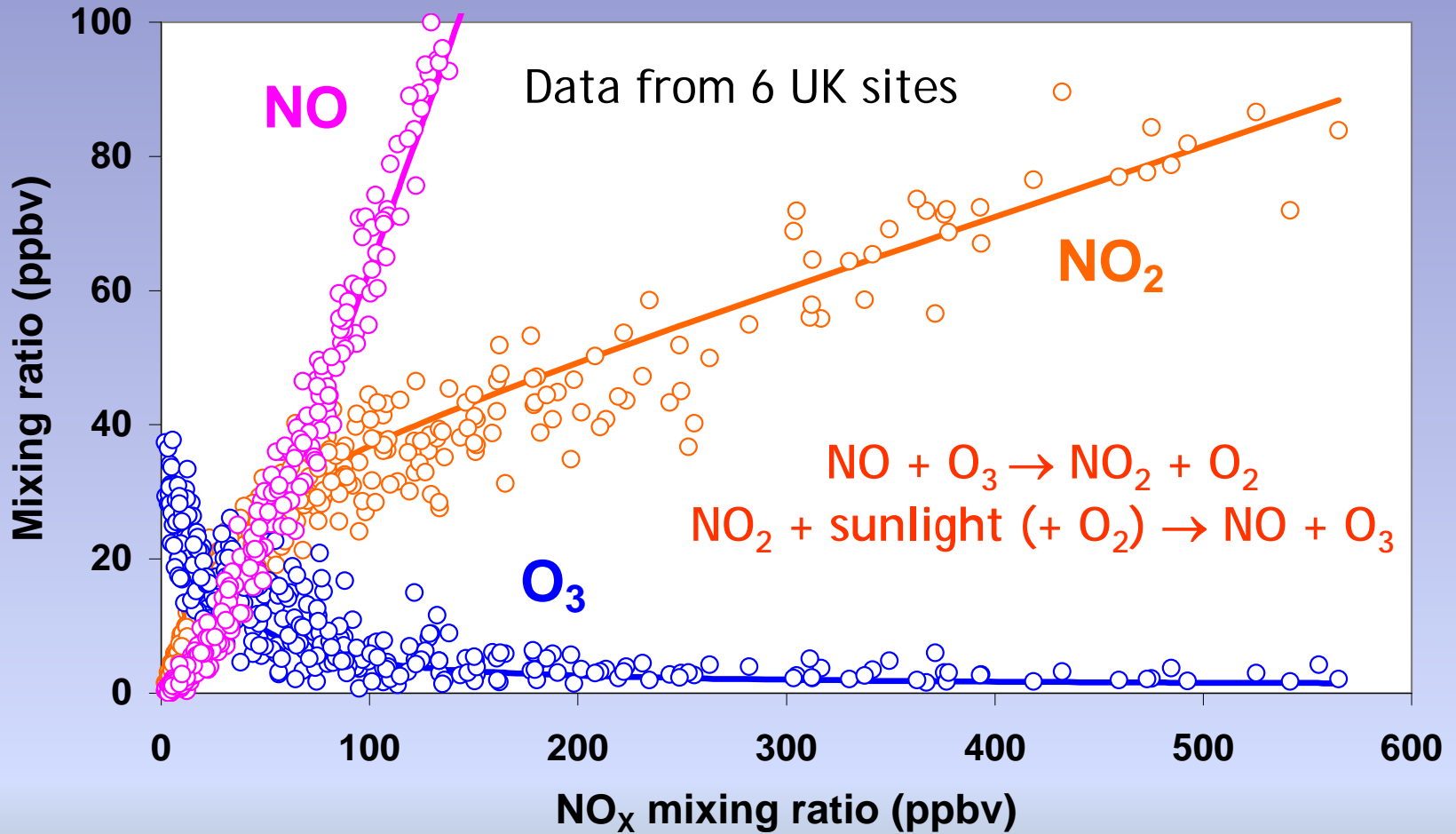
The chemical coupling of O₃, NO and NO₂



(e.g., Kley et al., Atmos. Env., 28, 149, 1994)

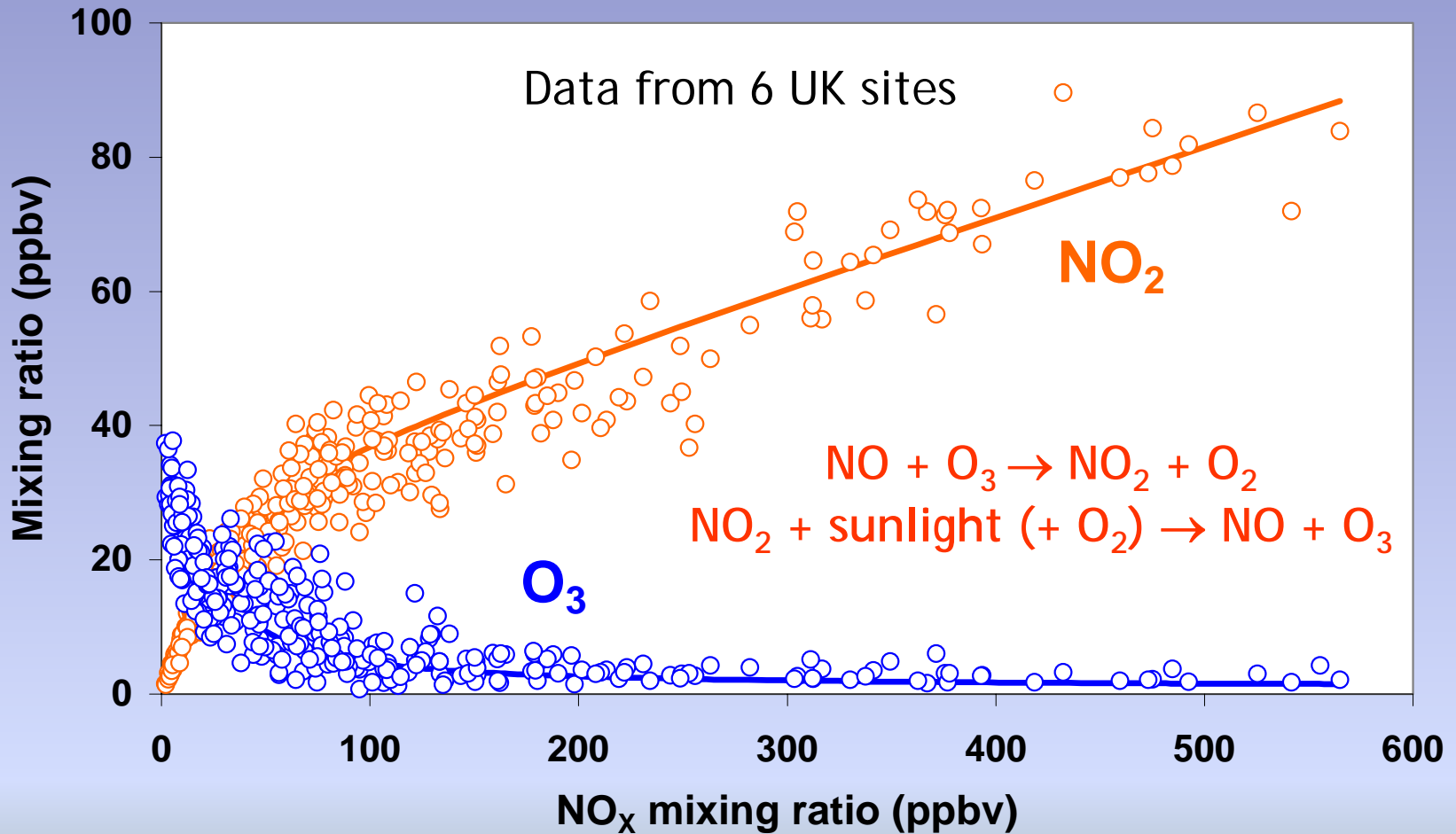
Variation of O₃, NO and NO₂ with NO_x

November 1998 and 1999: Daily average data



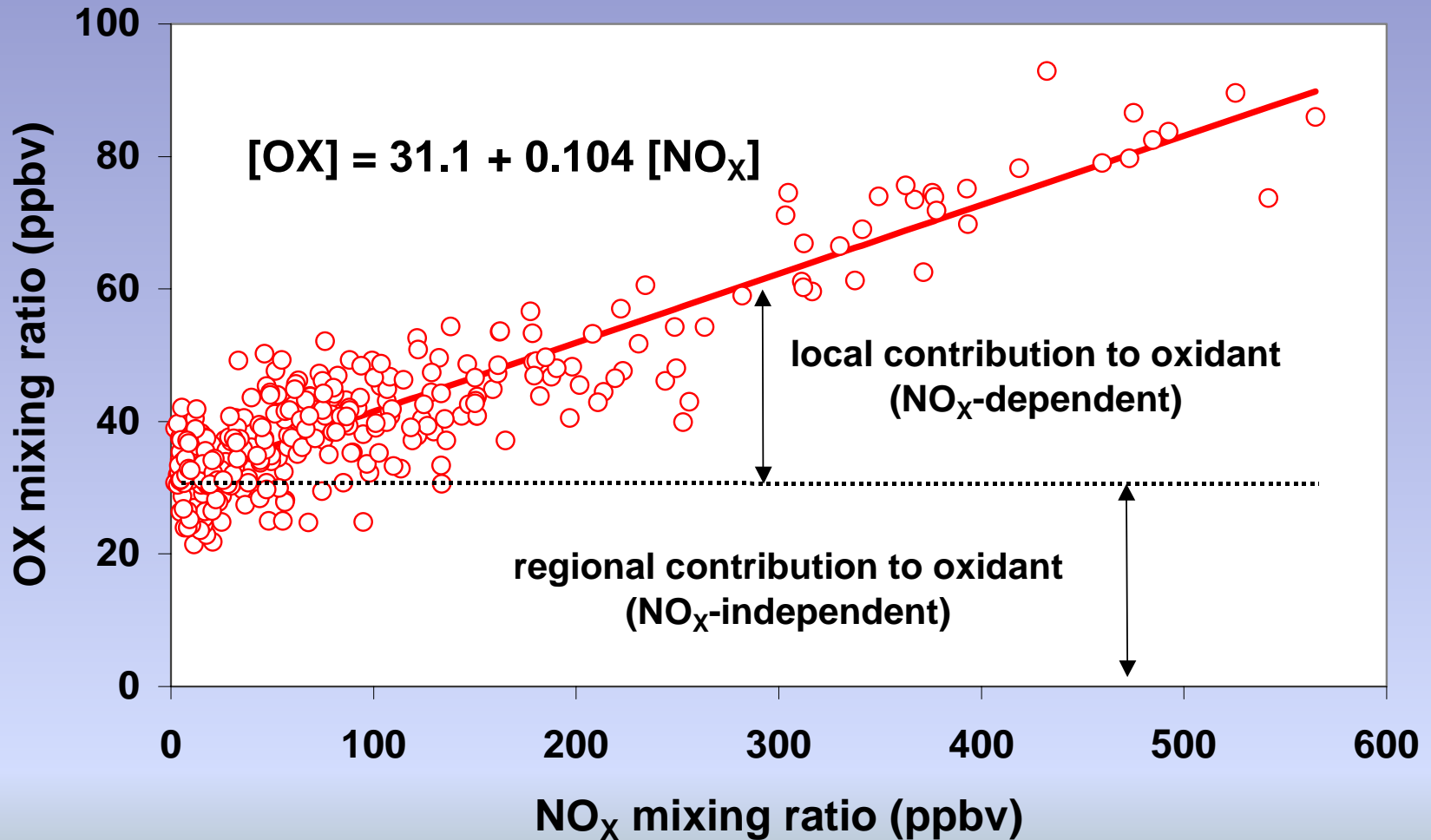
Variation of O₃ and NO₂ with NO_x

November 1998 and 1999: Daily average data



Variation of oxidant ($\text{OX} = \text{O}_3 + \text{NO}_2$) with NO_x

November 1998 and 1999: Daily average data



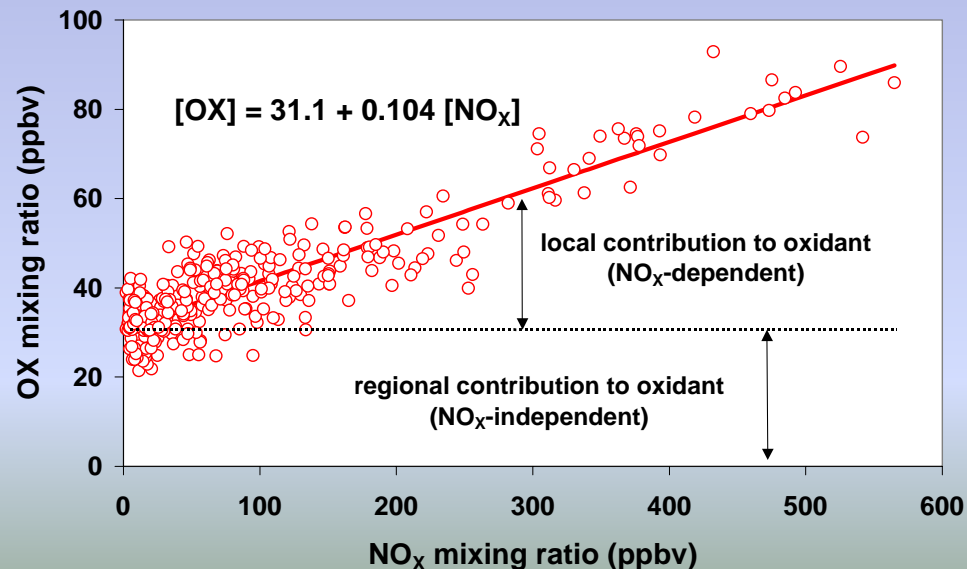
'Regional' and 'local' contributions to oxidant (OX) ?

- Regional contribution

Background O₃ advected from outside the urban area, or mixed down from aloft.

- Local contribution

Important contribution from primary emissions of NO₂



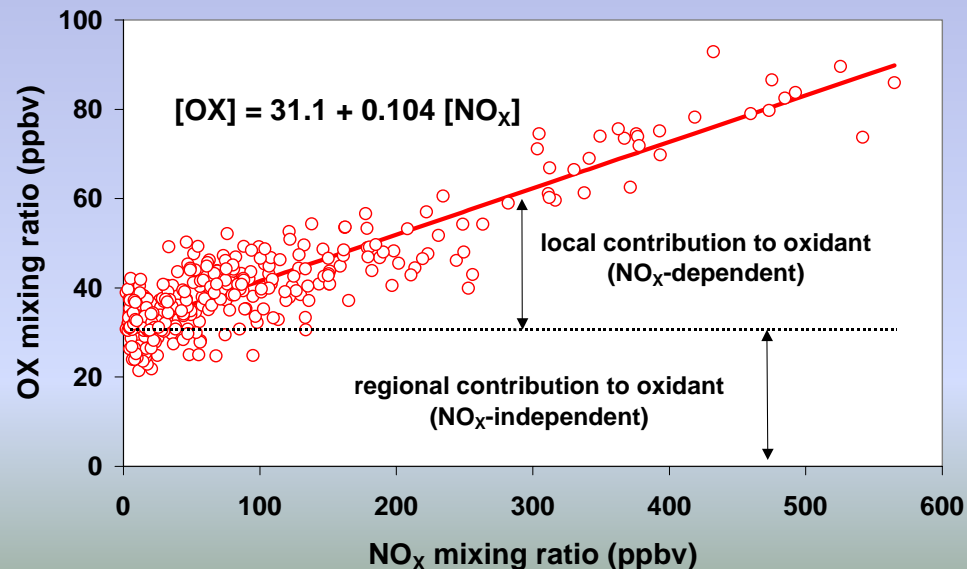
'Regional' and 'local' contributions to oxidant (OX) ?

- Regional contribution = **Background Ozone**

Background O₃ advected from outside the urban area, or mixed down from aloft.

- Local contribution = **Emitted NO₂**

Important contribution from primary emissions of NO₂



Marylebone Road London

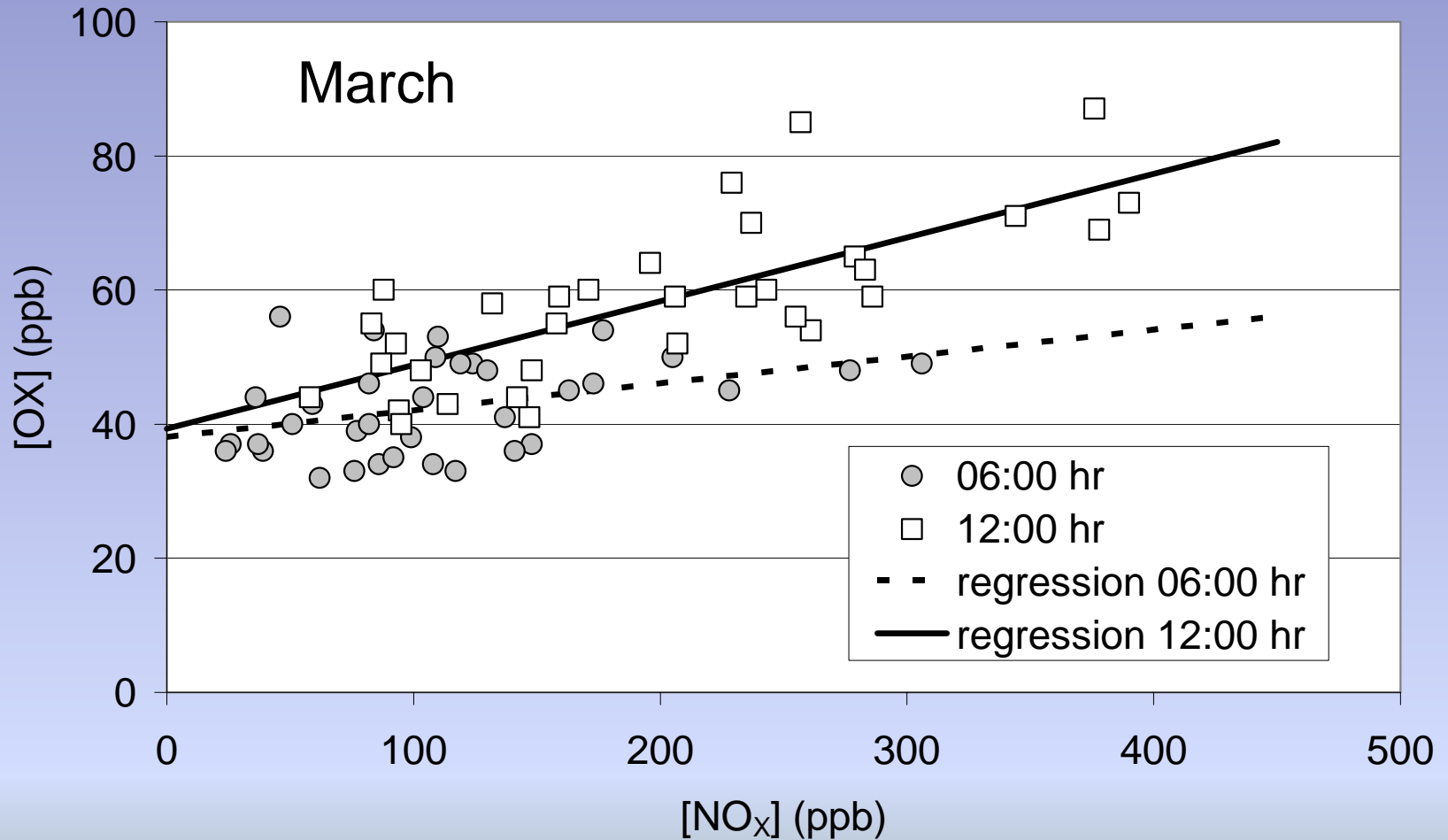
Hourly resolution

- Ozone - UV photometry
- NO_x - chemiluminescence

- Inner London kerbside site (part of AURN)
- 6 lane street canyon
- 80,000 vehicles per day

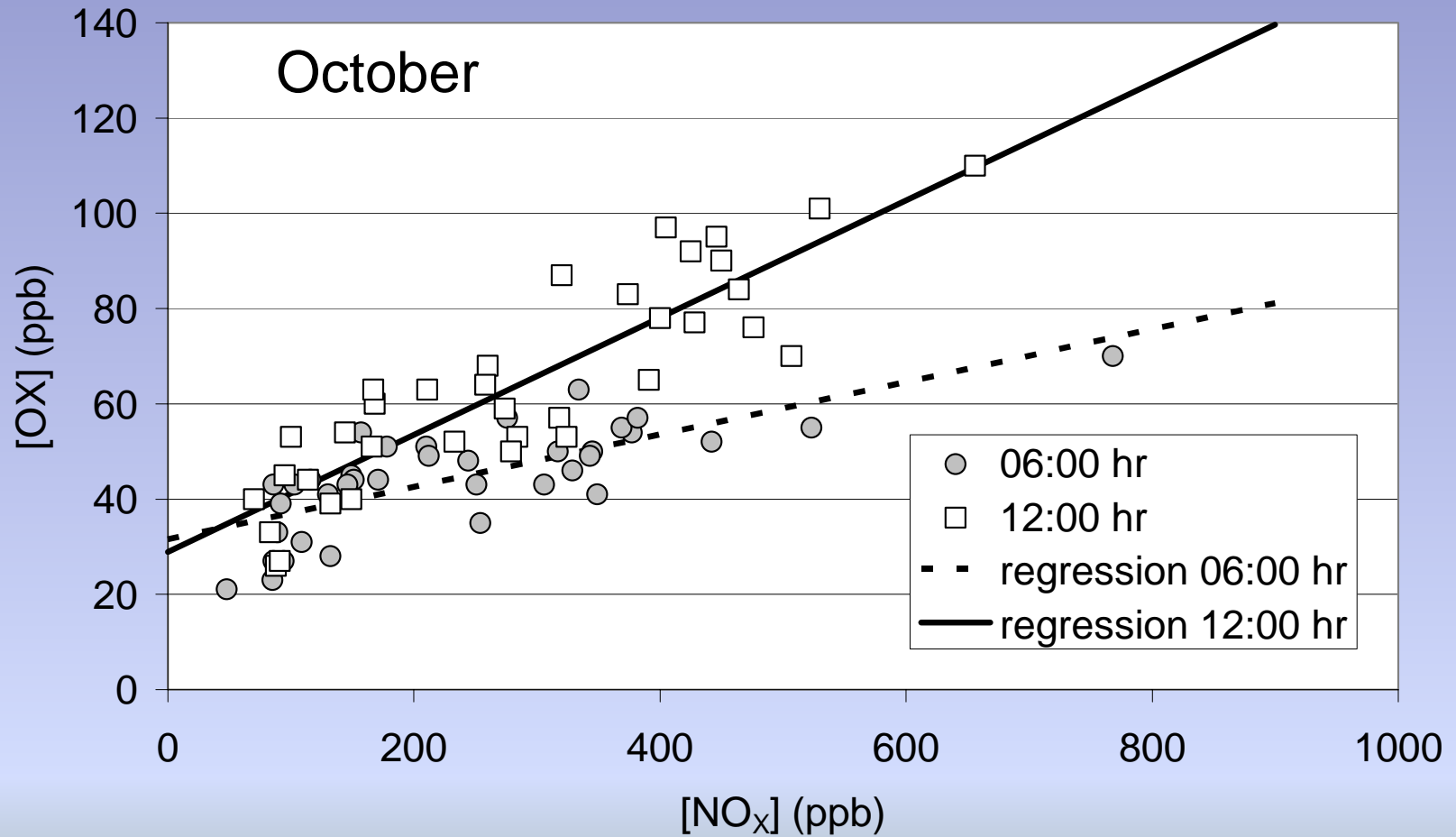
Part 1: Hourly mean data at Marylebone Rd

Weekday data from 1998 and 1999



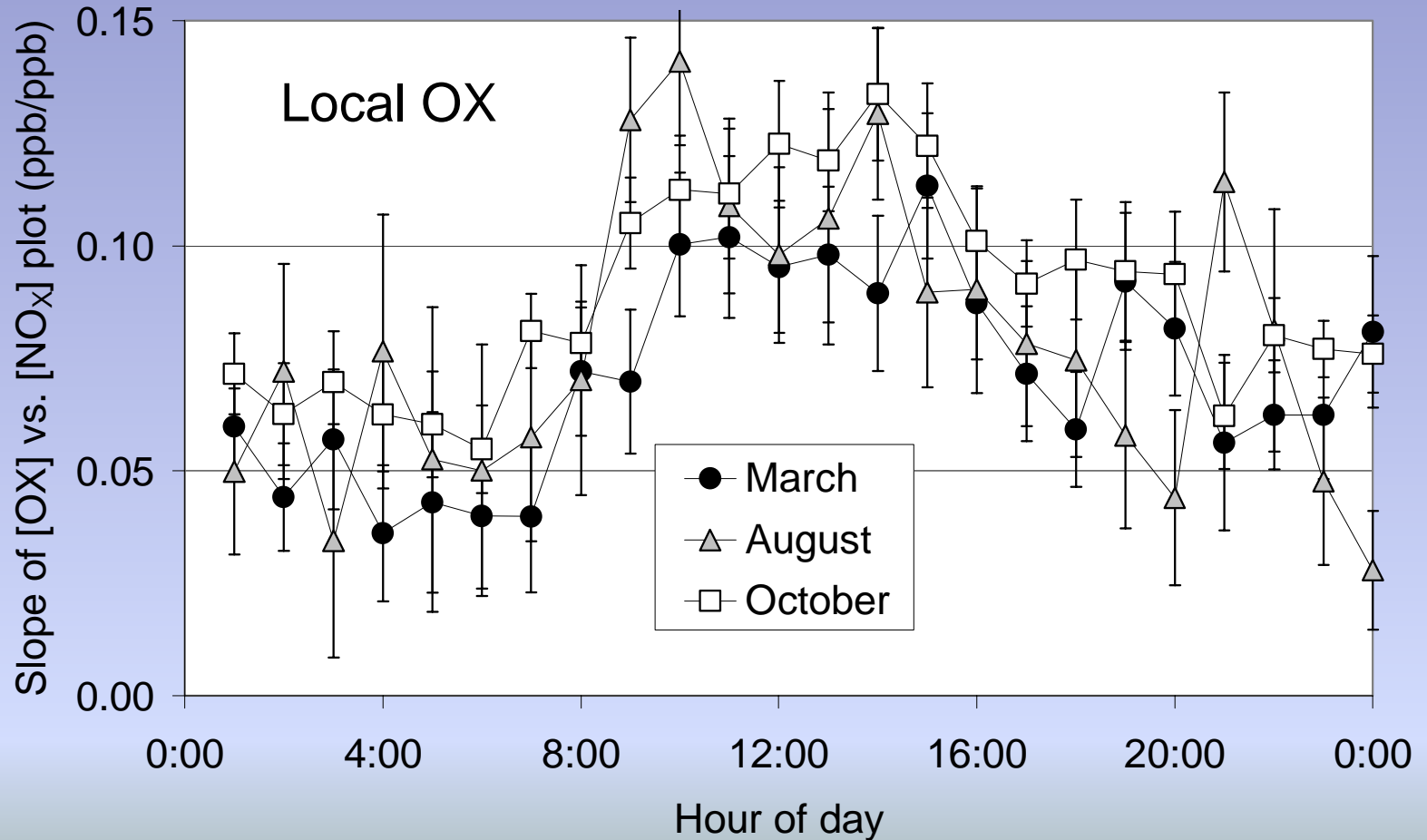
Part 1: Hourly mean data at Marylebone Rd

Weekday data from 1998 and 1999



Diurnal variation of local OX in selected months

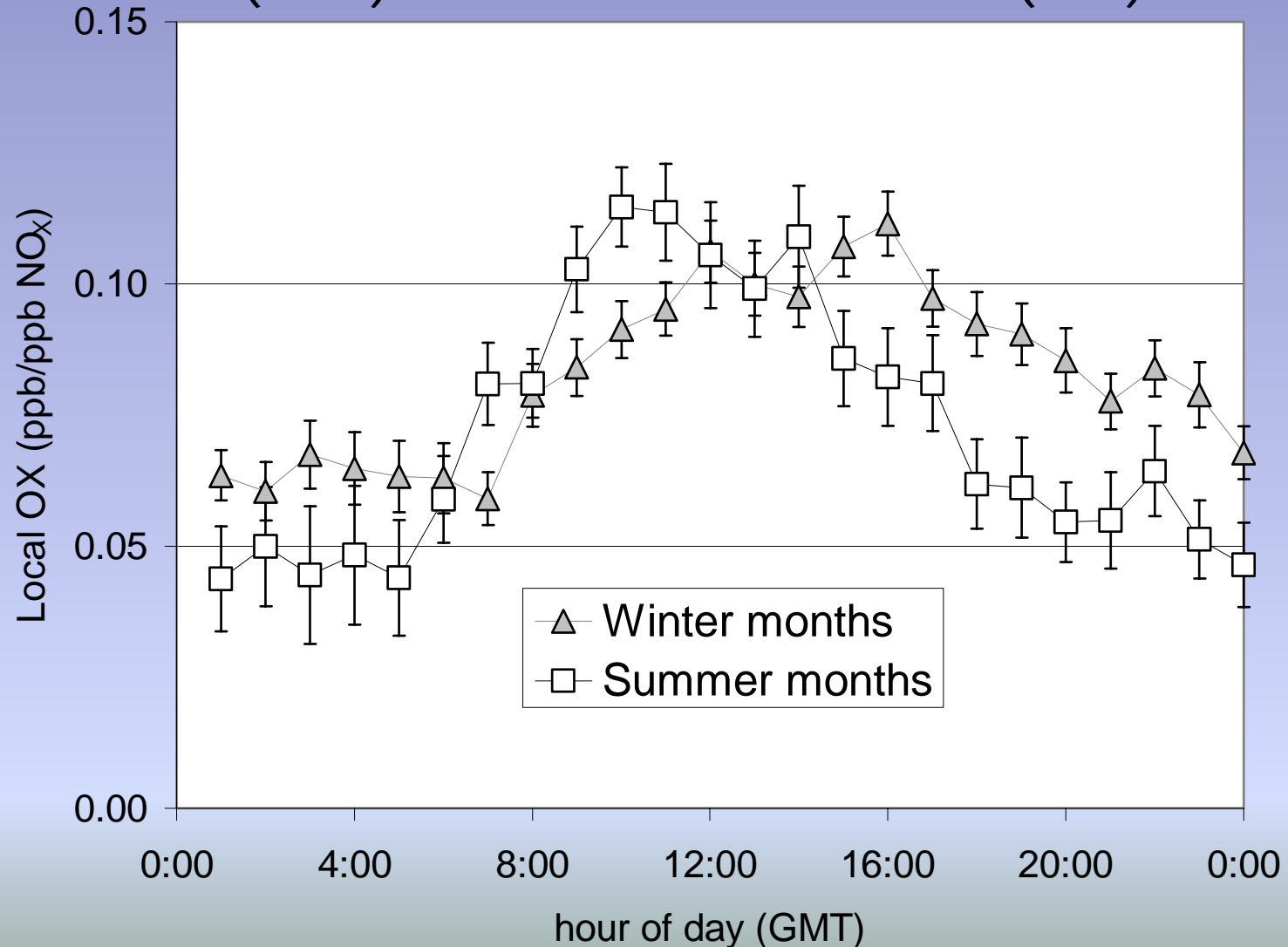
Weekday data from 1998 and 1999



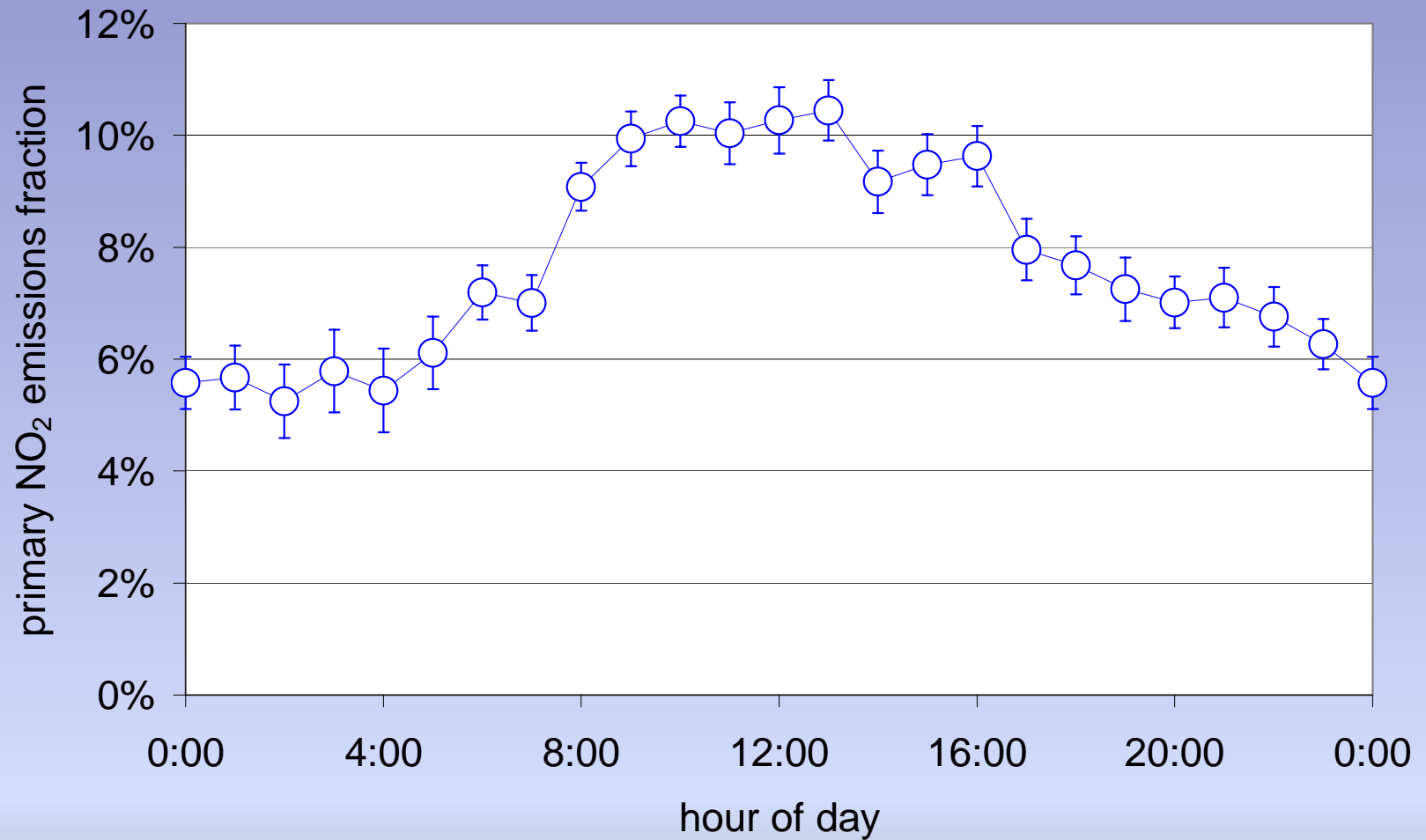
Diurnal variation of local OX: GMT and BST

Winter months: Nov-Mar
(GMT)

Summer months: Apr-Oct
(BST)

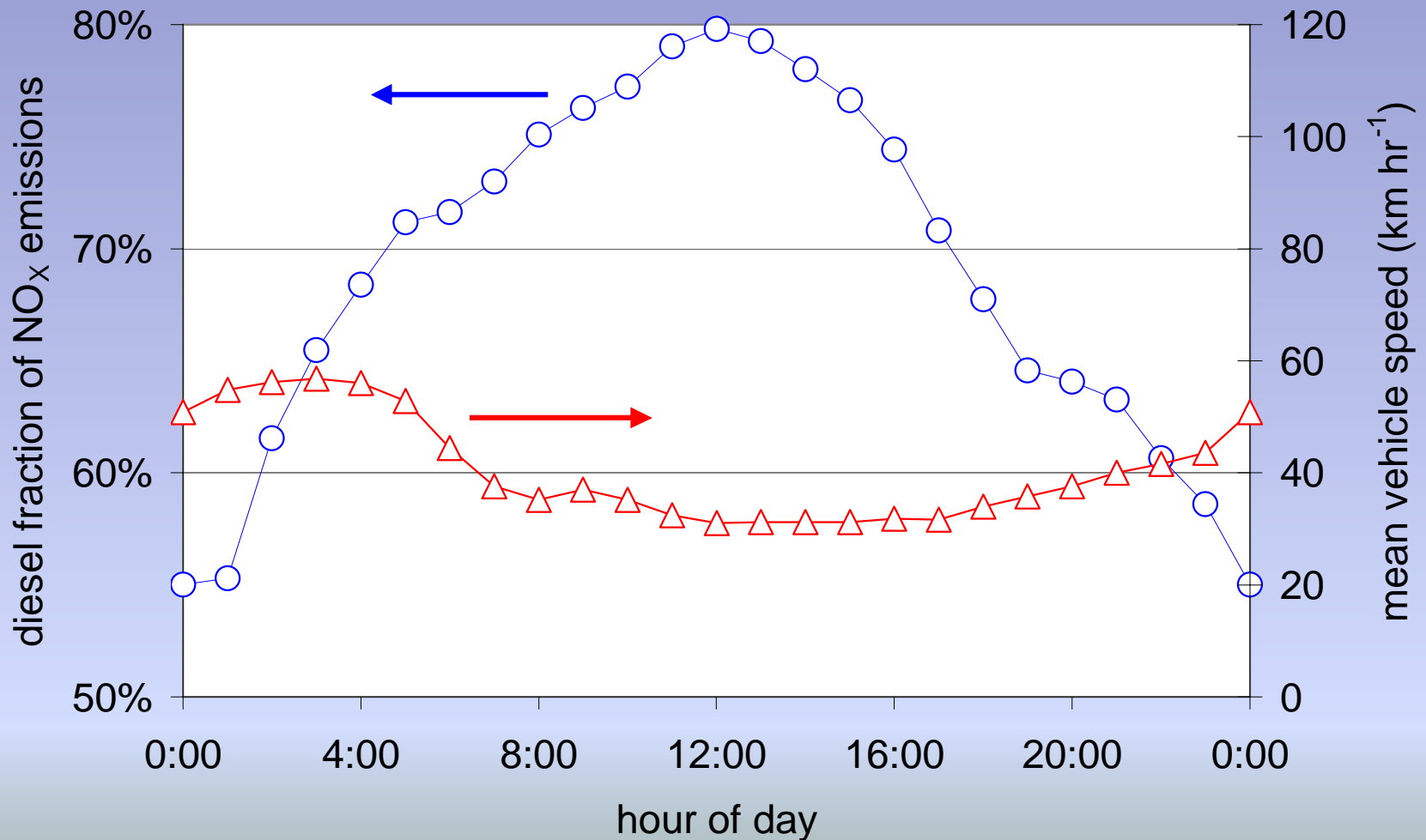


Inferred primary NO₂ fraction: average diurnal cycle

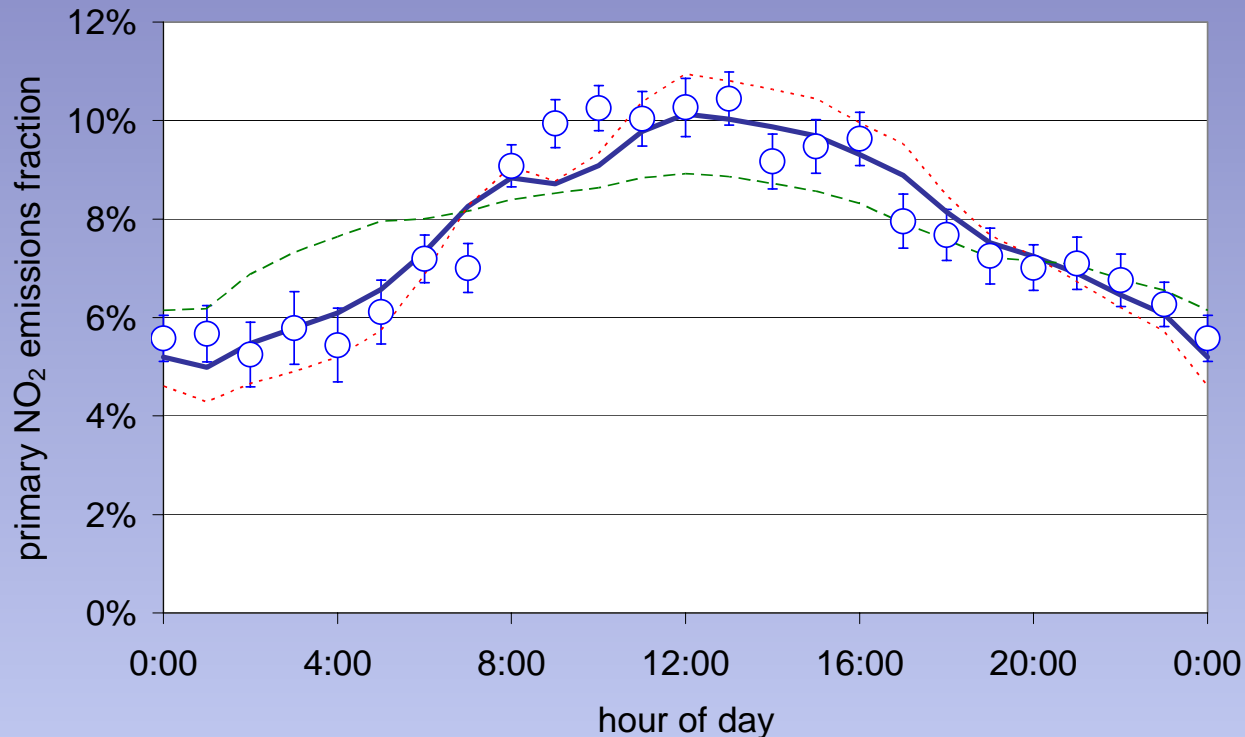


Traffic-related statistics: average diurnal cycle

Diesel NO_x emissions fraction and mean vehicle speed
(David Carslaw, Kings College ERG, personal communication)



Inferred primary NO₂ fraction: average diurnal cycle



- Diesel NO₂/NO_x emission ratio = $0.996 v^{-0.6}$
($\Rightarrow 0.085 @ 60 \text{ km hr}^{-1}, 0.129 @ 30 \text{ km hr}^{-1}$)
- Petrol NO₂/NO_x emission ratio < 0.03

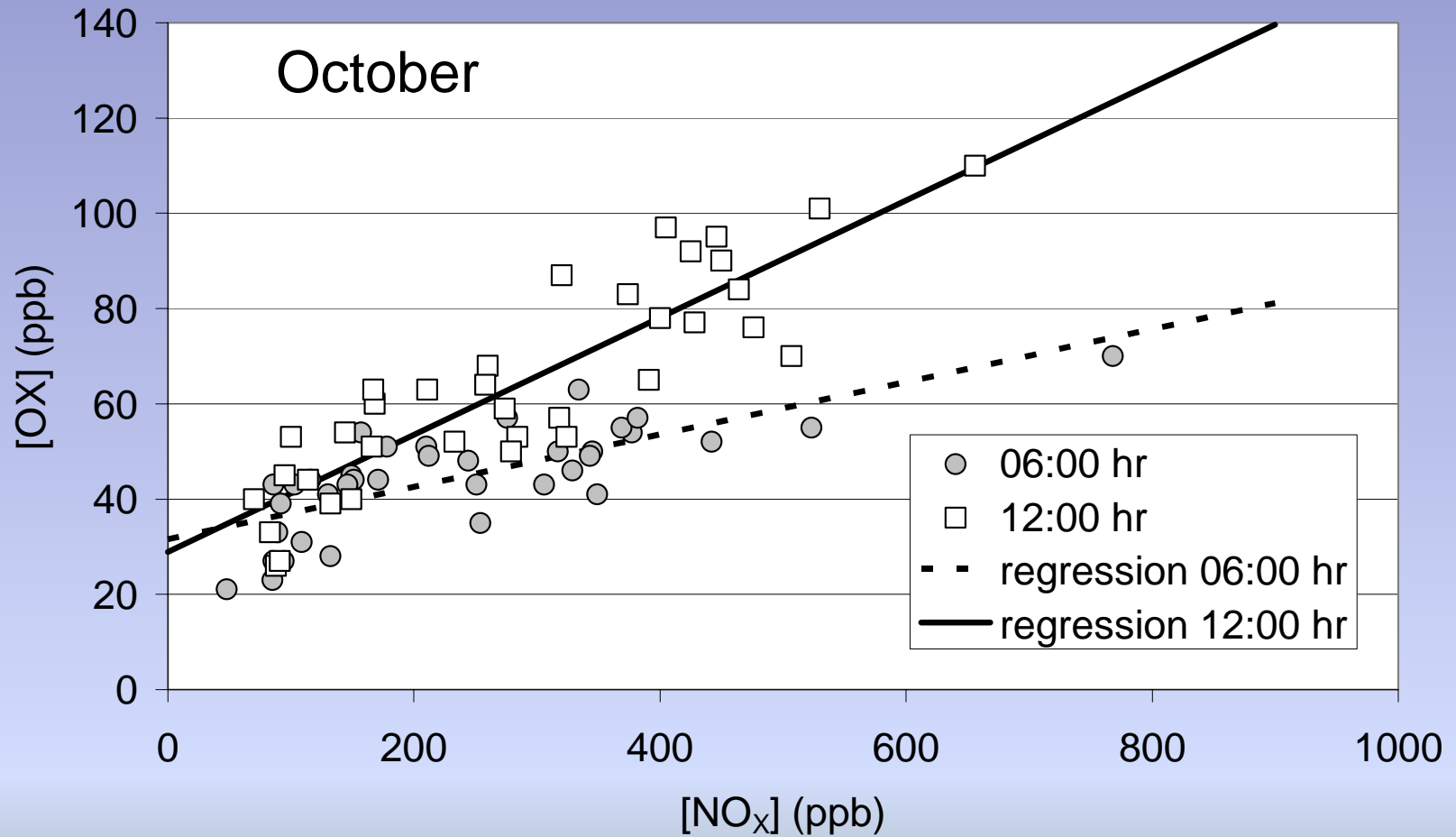
Primary NO₂: comparison with literature

Study	NO _x emission source	NO ₂ /NO _x (volume %)	comment
Jimenez et al., 2000	Diesel truck	5.6 – 10.9	a
Kurtenbach et al., 2001	Vehicle mix	5.0	b,c
	MAN diesel truck	11.0	b,d
	Petrol car	< 0.2	b,d
	Diesel car	5.9	b,d
Carslaw and Beevers, 2004	Diesel vehicles	(12.7 ± 0.1)	e
	Petrol vehicles	(0.6 ± 0.2)	e
This work	Diesel vehicles	99.6 v ^{-0.6}	f,g
		(11.8 ± 1.2)	f,h
	Petrol vehicles	< 3	f

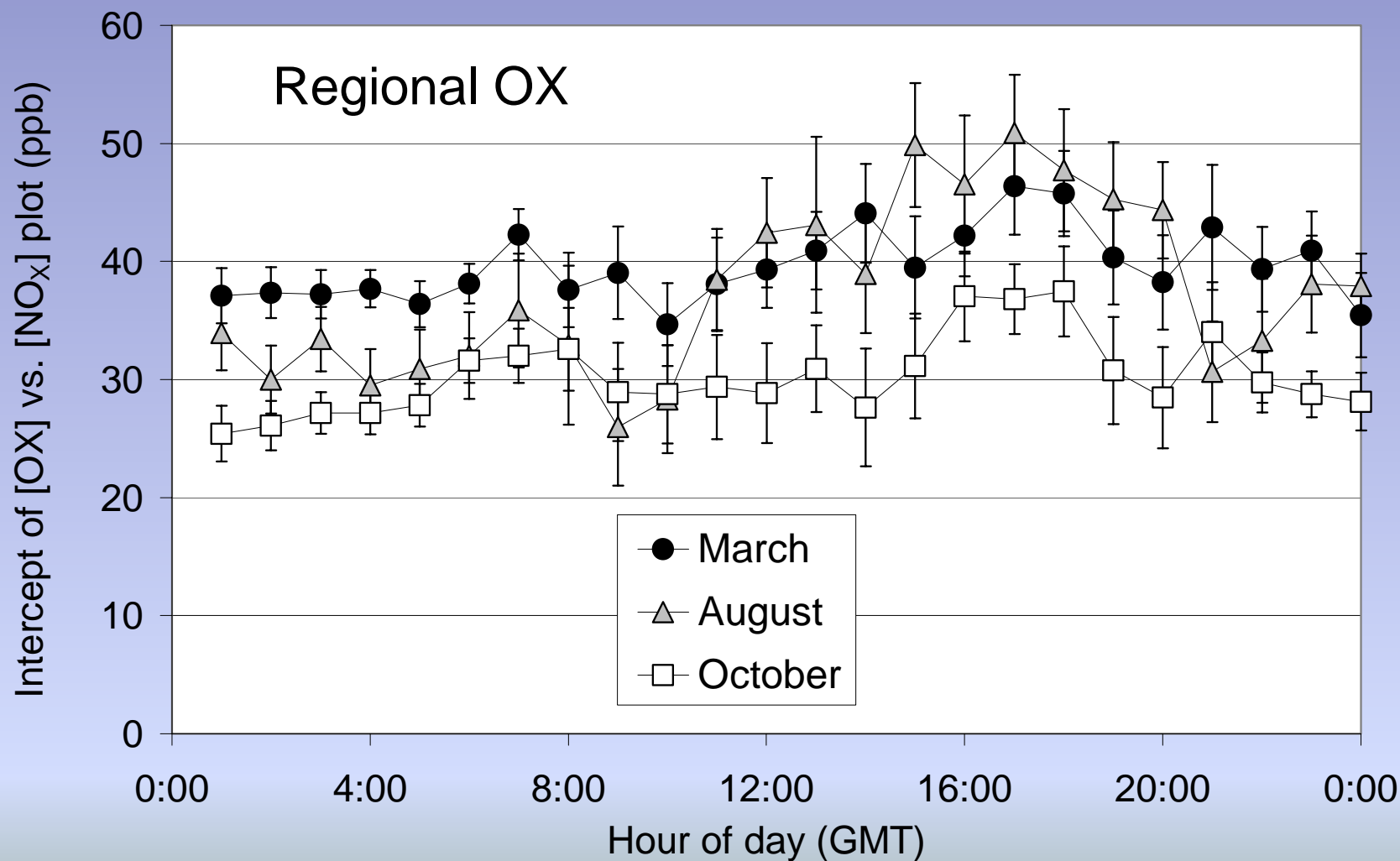
a: Operating at ca. 30 km hr⁻¹ during mild acceleration. Measurements by TILDAS; **b:** Kiesbergtunnel, Wuppertal, Germany. Measurements by DOAS; **c:** traffic mix with ≤ 6% heavy duty trucks, 6% commercial vans, 12.3% diesel cars, 74.7% petrol cars; **d:** single vehicle experiment, 0-40 km hr⁻¹; **e:** Marylebone Rd, London, UK. Derived from differential measurements of [OX] compared to local background site and detailed traffic statistics over period 1998-2002; **f:** Marylebone Rd., London, UK. Derived from [OX] vs [NO_x] dependence using 1998-1999 weekday data, and detailed traffic statistics for 1999; **g:** for 30 < v/km hr⁻¹ < 60; **h:** integrated diurnal contribution.

Hourly mean data at Marylebone Rd

Weekday data from 1998 and 1999

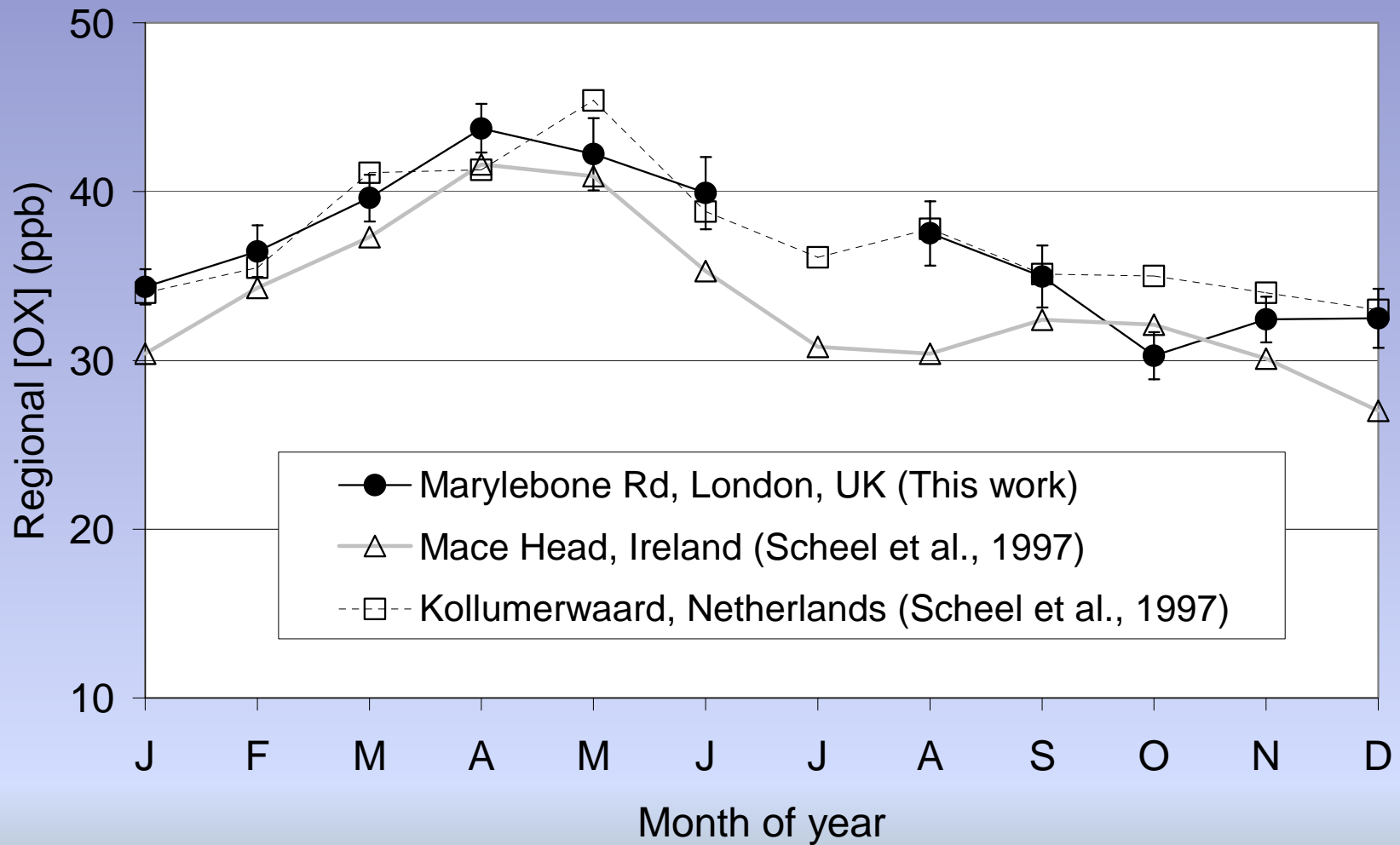


Diurnal variation of regional OX in selected months



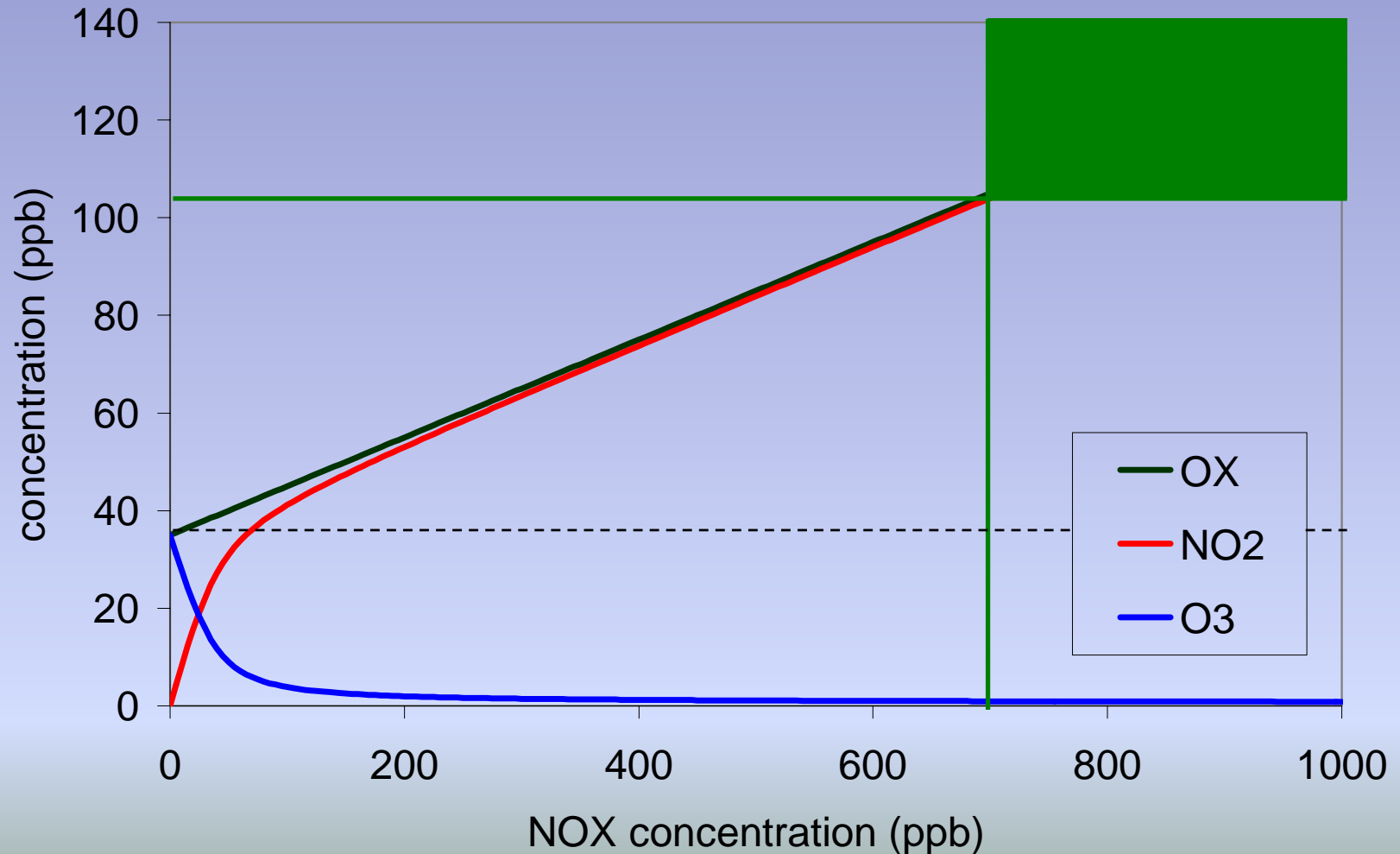
Seasonal variation of regional background OX

Photochemical episode days excluded

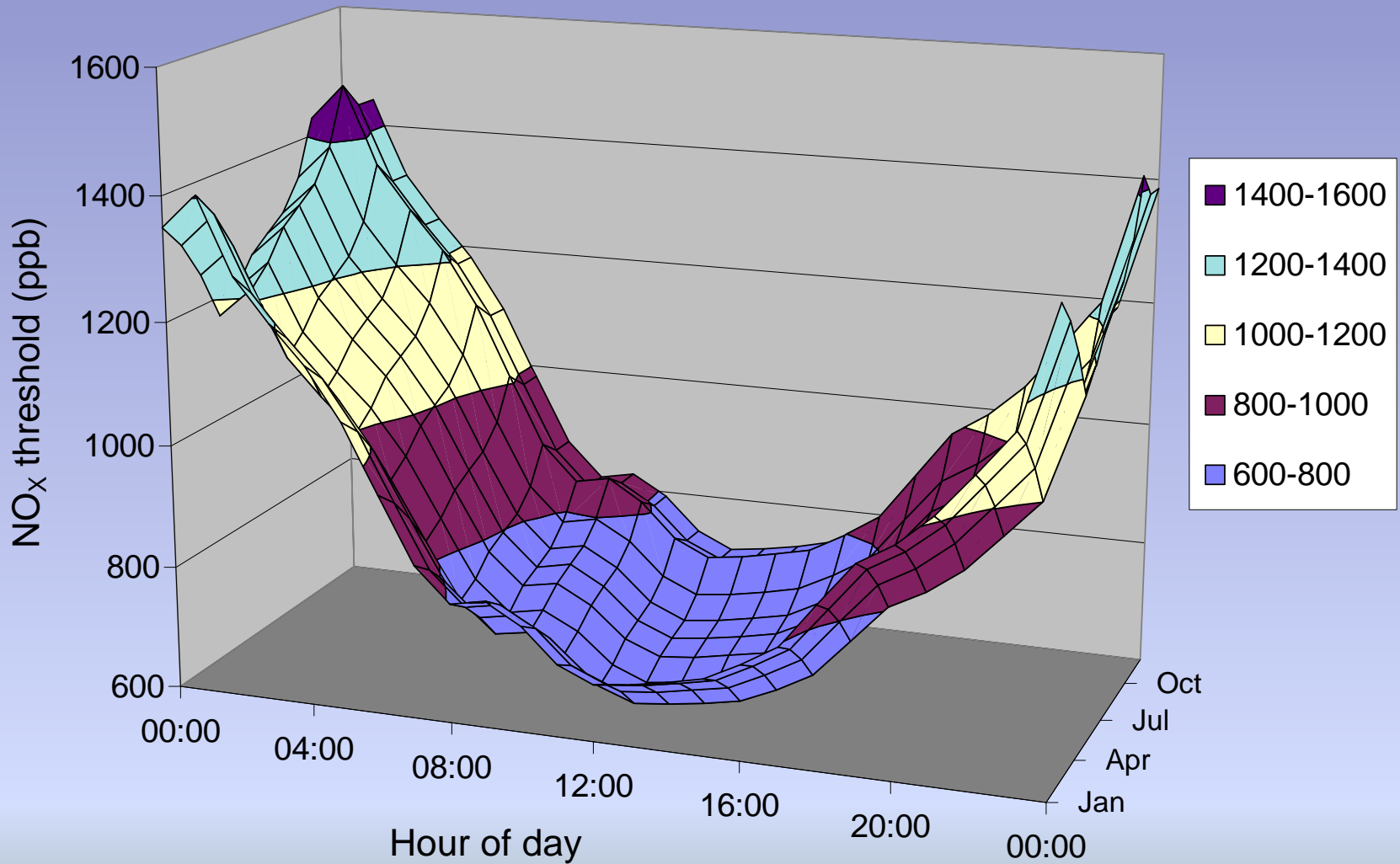


Exceedences of hourly mean limit value

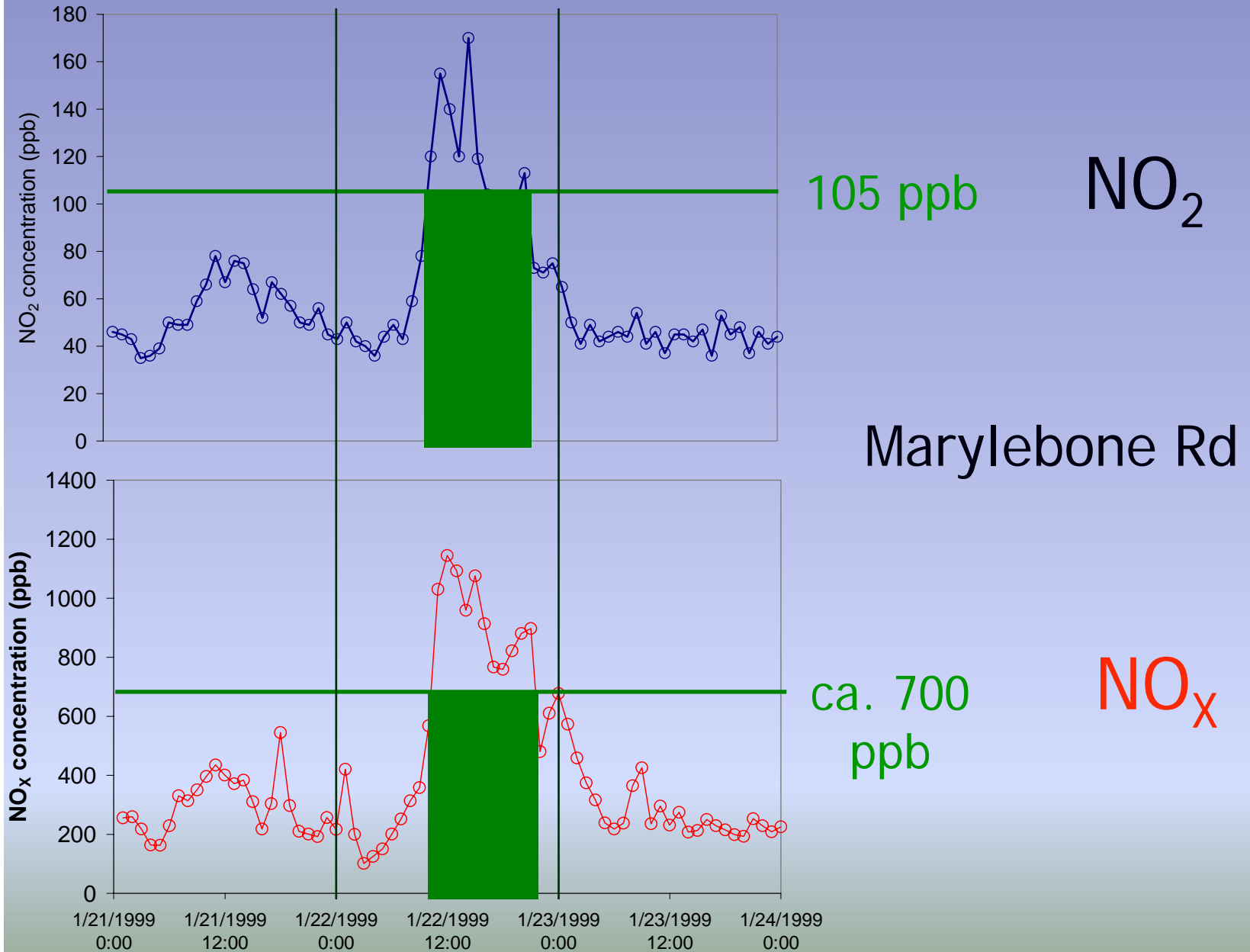
NO₂ hourly mean limit value = 105 ppb (200 μg m⁻³)



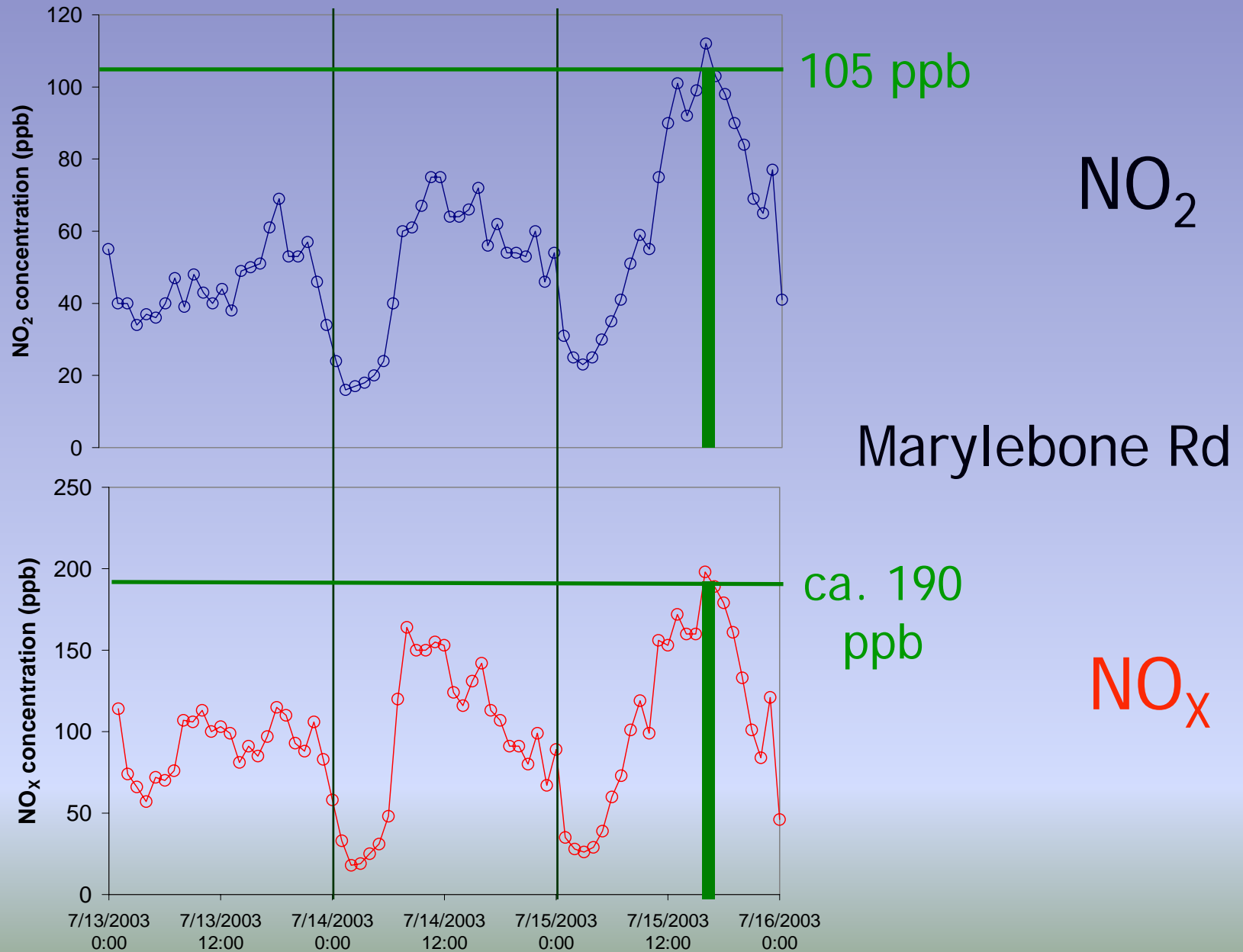
Hourly mean NO_x thresholds corresponding to 105 ppb (200 μg m⁻³) NO₂



Example wintertime NO₂ pollution episode: 22 Jan 1999

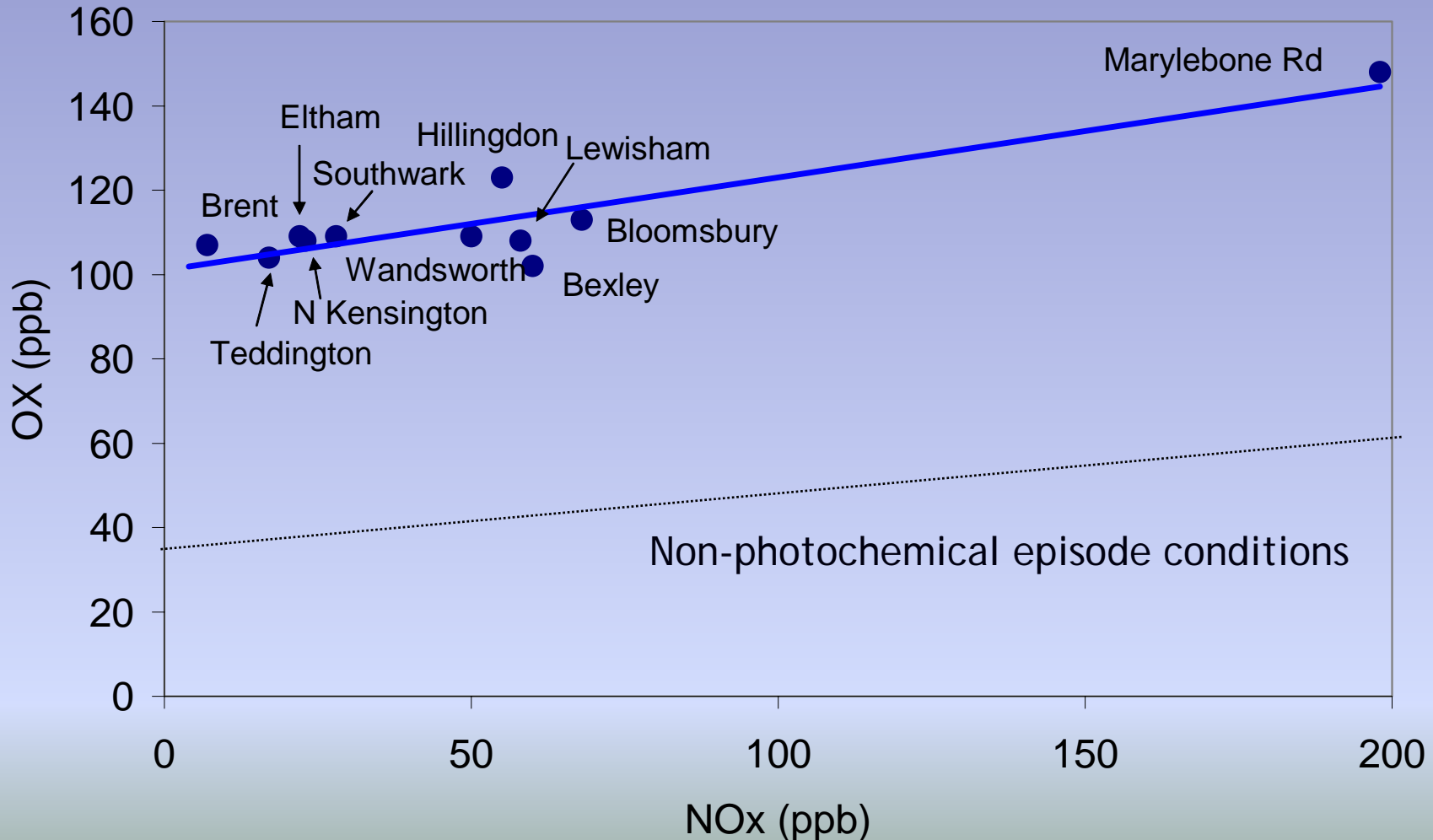


Example summertime NO₂ pollution episode: 15 Jul 2003



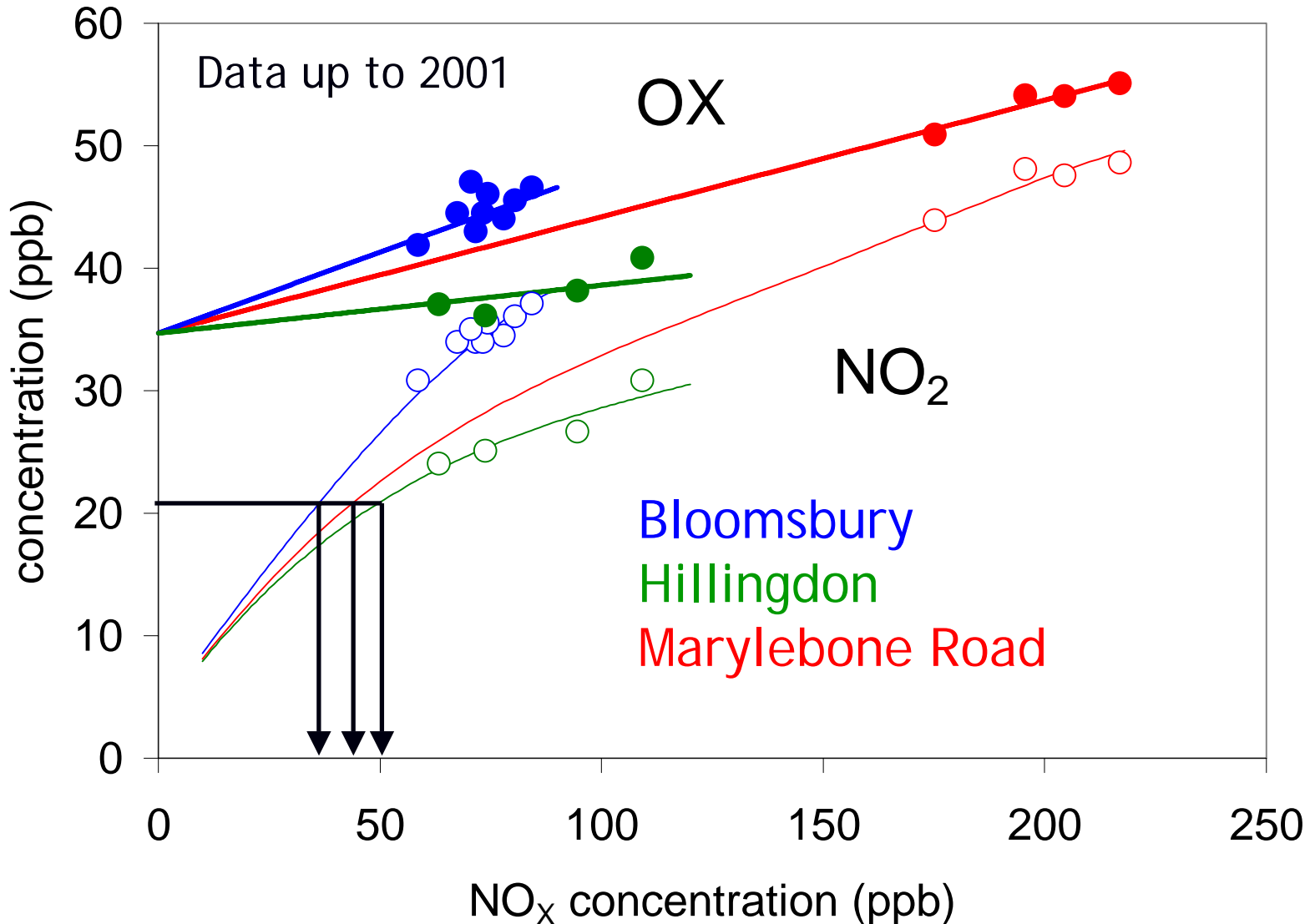
Summertime photochemical pollution episode - 15 July 2003

Peak oxidant (OX) at London sites



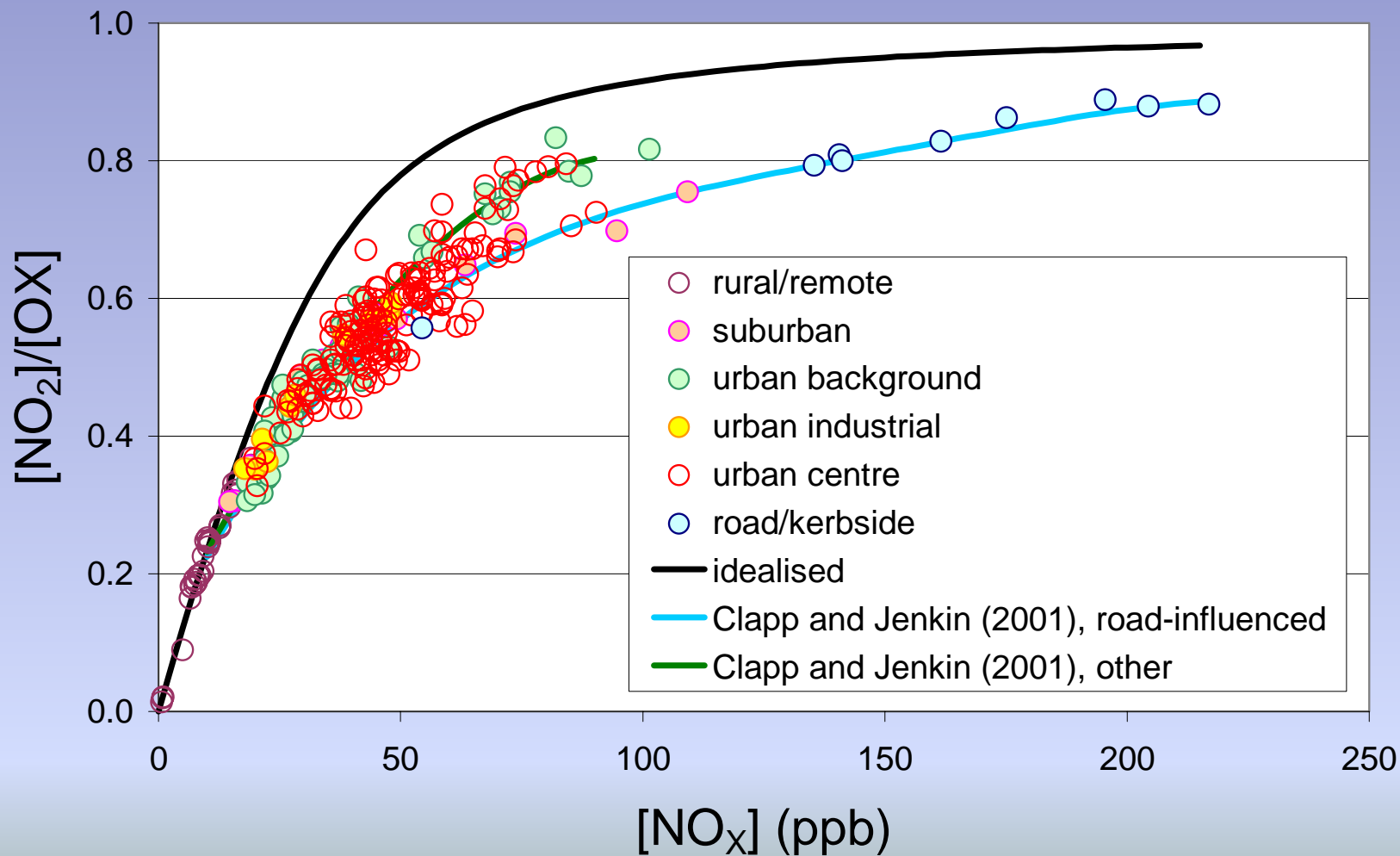
Part 2: Application to annual mean data

NO₂ annual mean limit value = 21 ppb (40 μg m⁻³)



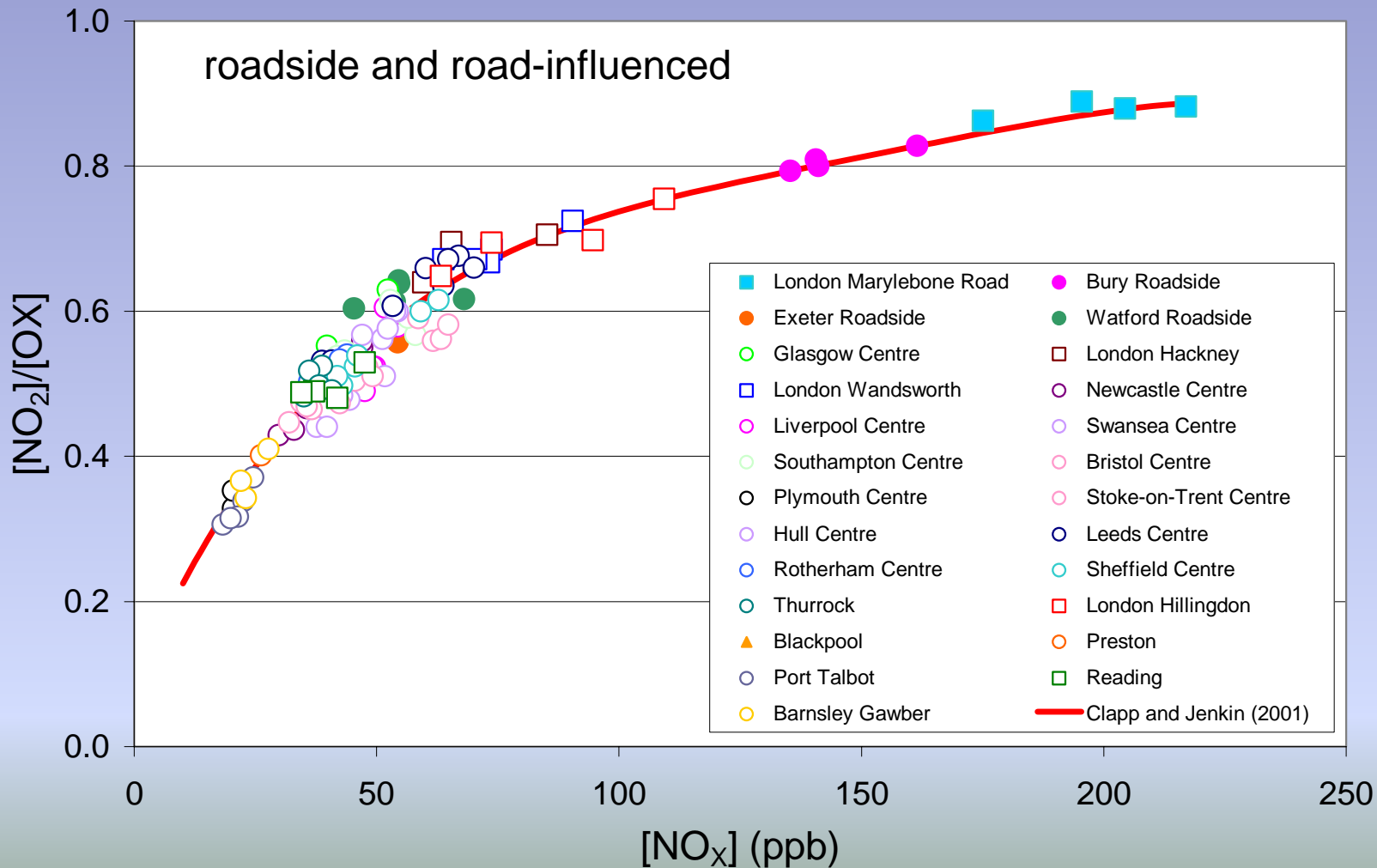
Oxidant partitioning

$[\text{NO}_x]$ -dependence of annual mean $[\text{NO}_2]/[\text{OX}]$



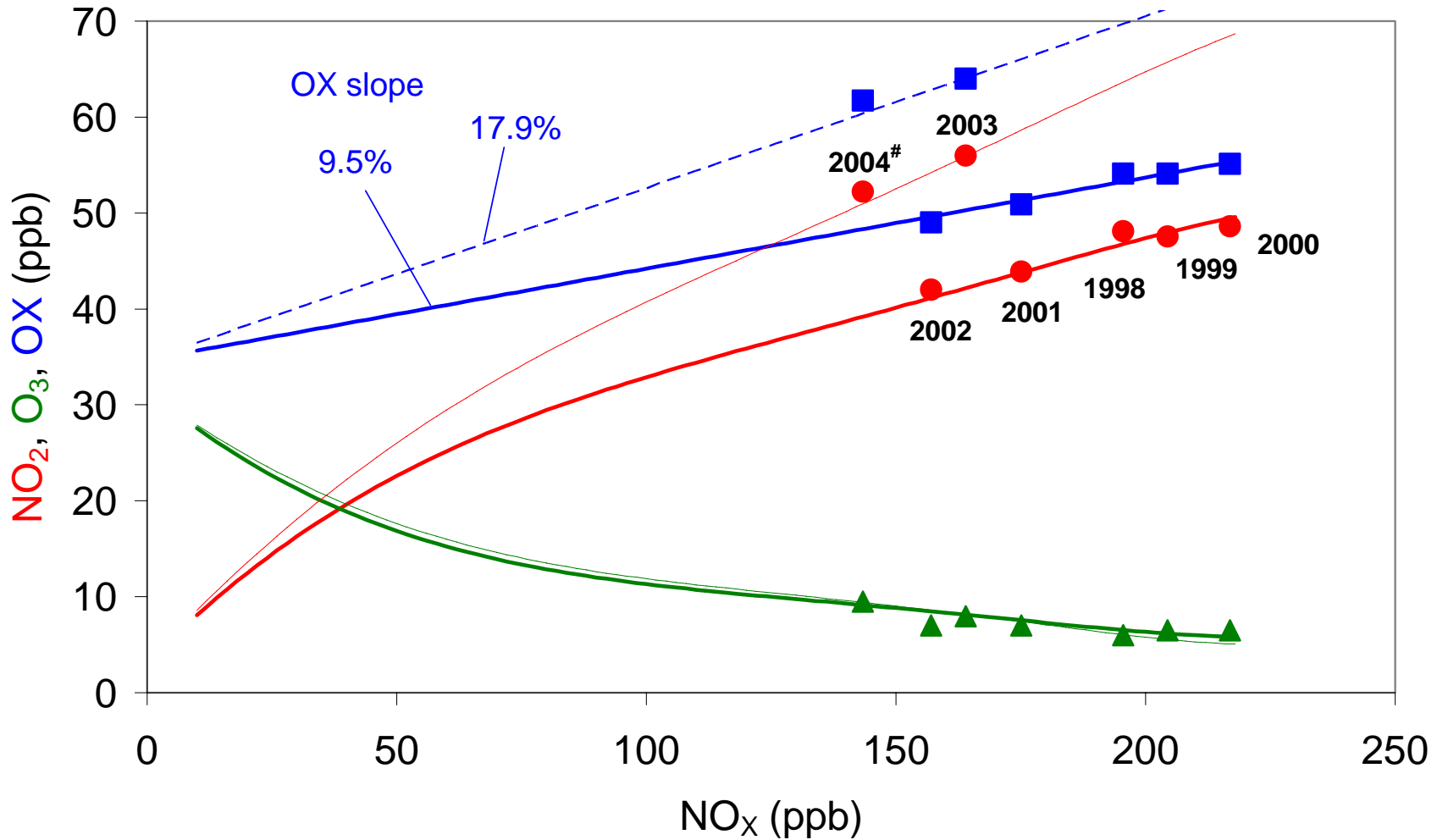
[NO₂]/[OX] vs [NO_x]: Roadside (and road-influenced) sites

$$\begin{aligned}
 [\text{NO}_2]/[\text{OX}] = & (8.962 \times 10^{-2}) + (1.474 \times 10^{-2} [\text{NO}_x]) - (1.290 \times 10^{-4} [\text{NO}_x]^2) \\
 & + (5.527 \times 10^{-7} [\text{NO}_x]^3) - (8.906 \times 10^{-10} [\text{NO}_x]^4)
 \end{aligned}$$



Marylebone Rd - annual mean [NO₂] vs [NO_x] and [O₃] vs [NO_x]

Projected lines are based on analysis of data up to 2001



Possible factors influencing local OX at Marylebone Road in 2003 and 2004

1. Central London congestion charging began in February 2003:
 - Accompanied by increased number of buses (i.e. diesel)
 - Increased traffic around perimeter of charging zone (which includes Marylebone Road)
2. Buses are increasingly being fitted with continuously regenerating traps (CRTs) to reduce particulate emissions:
 - Operation relies on oxidising environment
 - Increased primary NO₂

Concluding remarks

1. Ambient concentrations of oxidant ($OX = NO_2 + O_3$) at urban locations can be interpreted in terms of *regional* and *local* contributions.
2. The local OX source appears to be dominated by primary NO_2 emissions from diesel vehicles:
 - displays distinct diurnal variations at a given site
 - displays large site-to-site variations
3. Variation of $[NO_2]$ with $[NO_x]$ is therefore site dependent and influenced a number of by factors, including:
 - vehicle fleet composition (i.e., diesel vs. petrol)
 - driving conditions (e.g., level of congestion)
 - implementation of exhaust control technologies (e.g., CRTs)

Acknowledgements

- David Carslaw (now Univ. Leeds) - diesel and petrol vehicle NO_x emissions estimates and helpful discussions
- UK Air Quality Expert Group (AQEG) for helping to put work into context

Funding

- UK Natural Environment Research Council (NERC)
- UK Dept for Environment, Food and Rural Affairs (DEFRA), AEQ Division

Variation of O₃ and NO₂ with NO_x

November 1998 and 1999: Daily average data

