

# Questions

- Are there differences between  $O_3$  concentrations for the years 1990-1996?

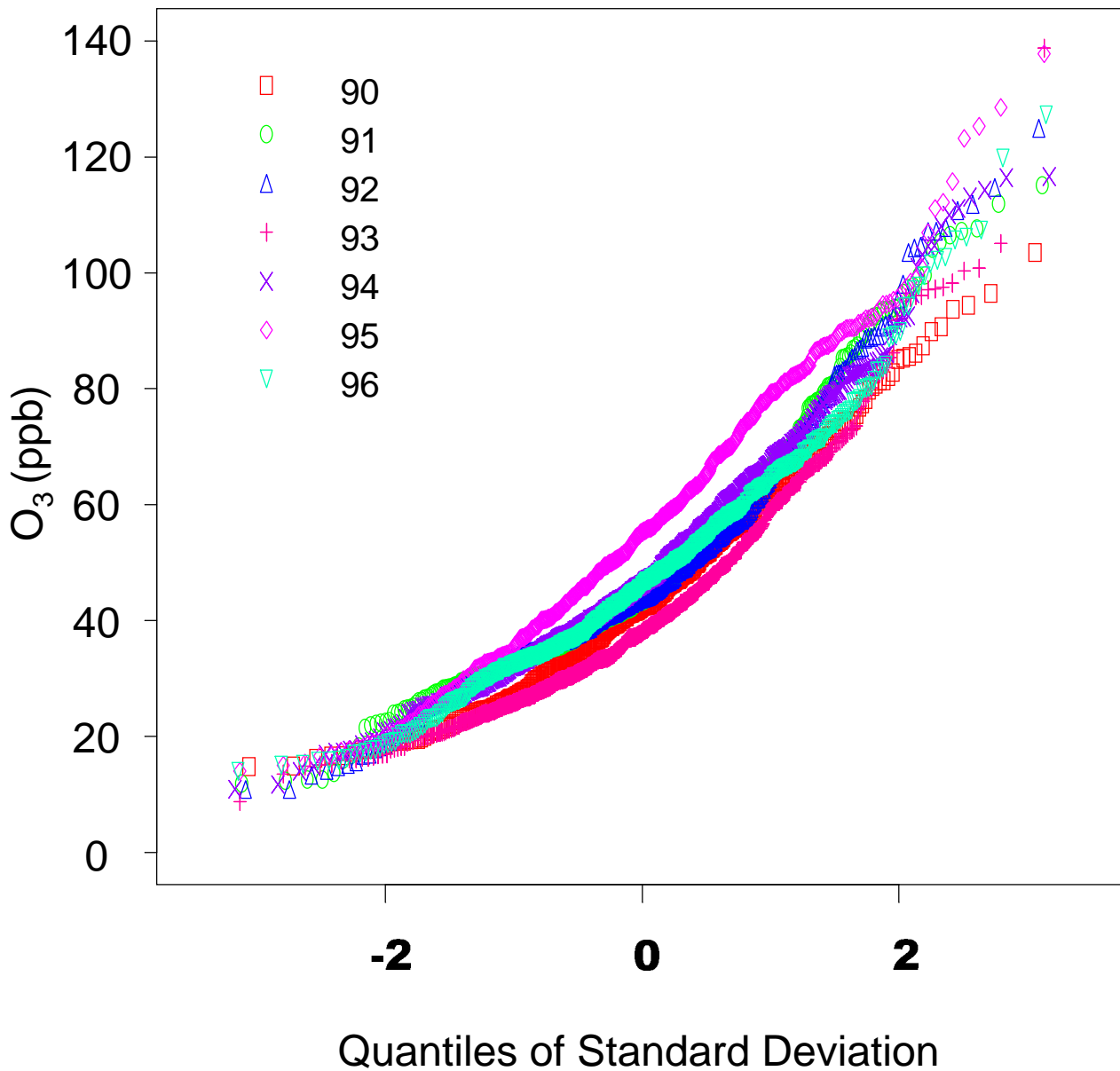
**Yes**

- Which factors best account for variance in the observed  $O_3$ ?

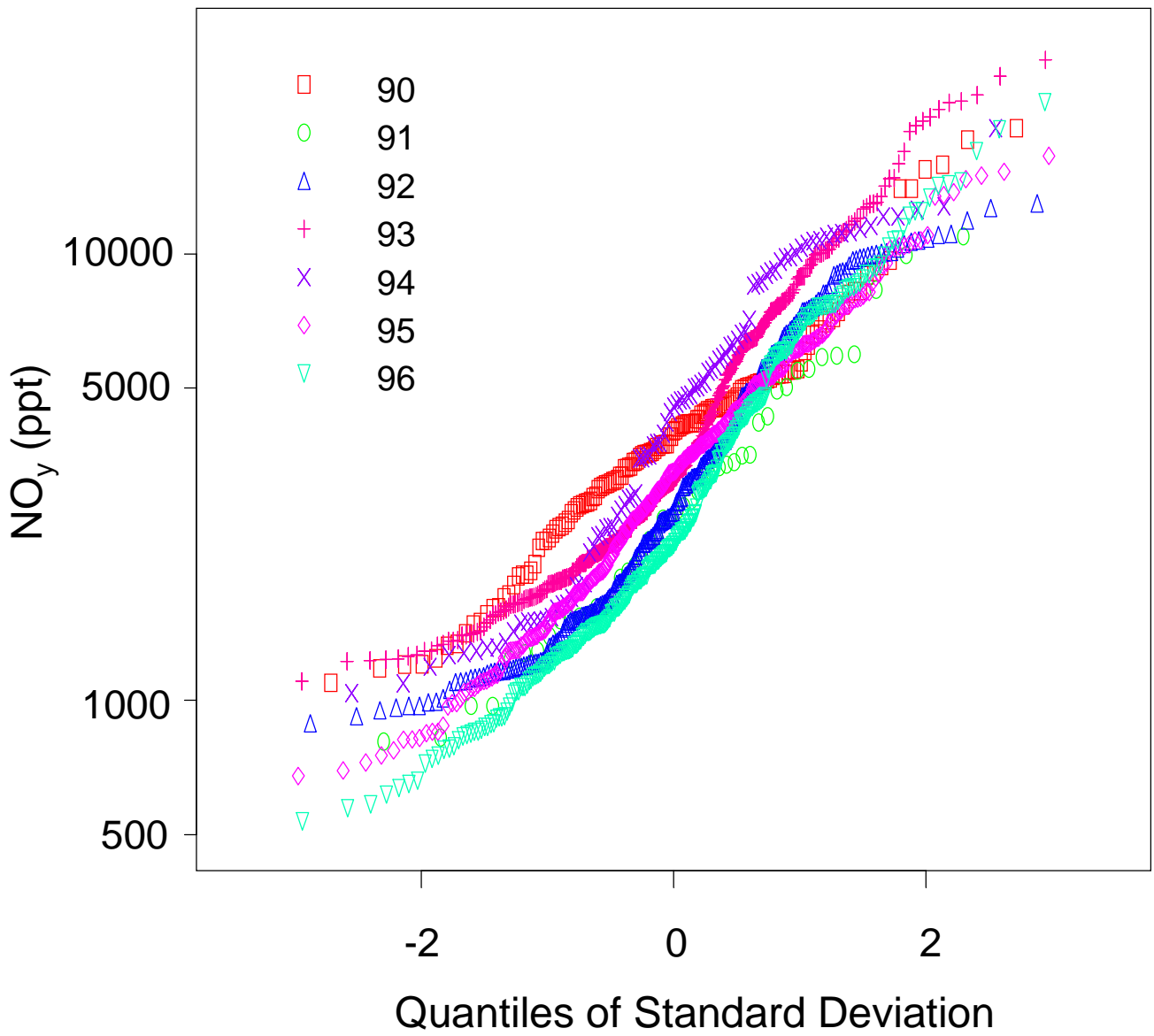
**$NO_y$ - $NO_x$**

- This is remarkable considering that  $NO_x$  oxidation products are have shorter lifetime for deposition than  $O_3$  does.
- Are there differences in chemical processing from year to year?

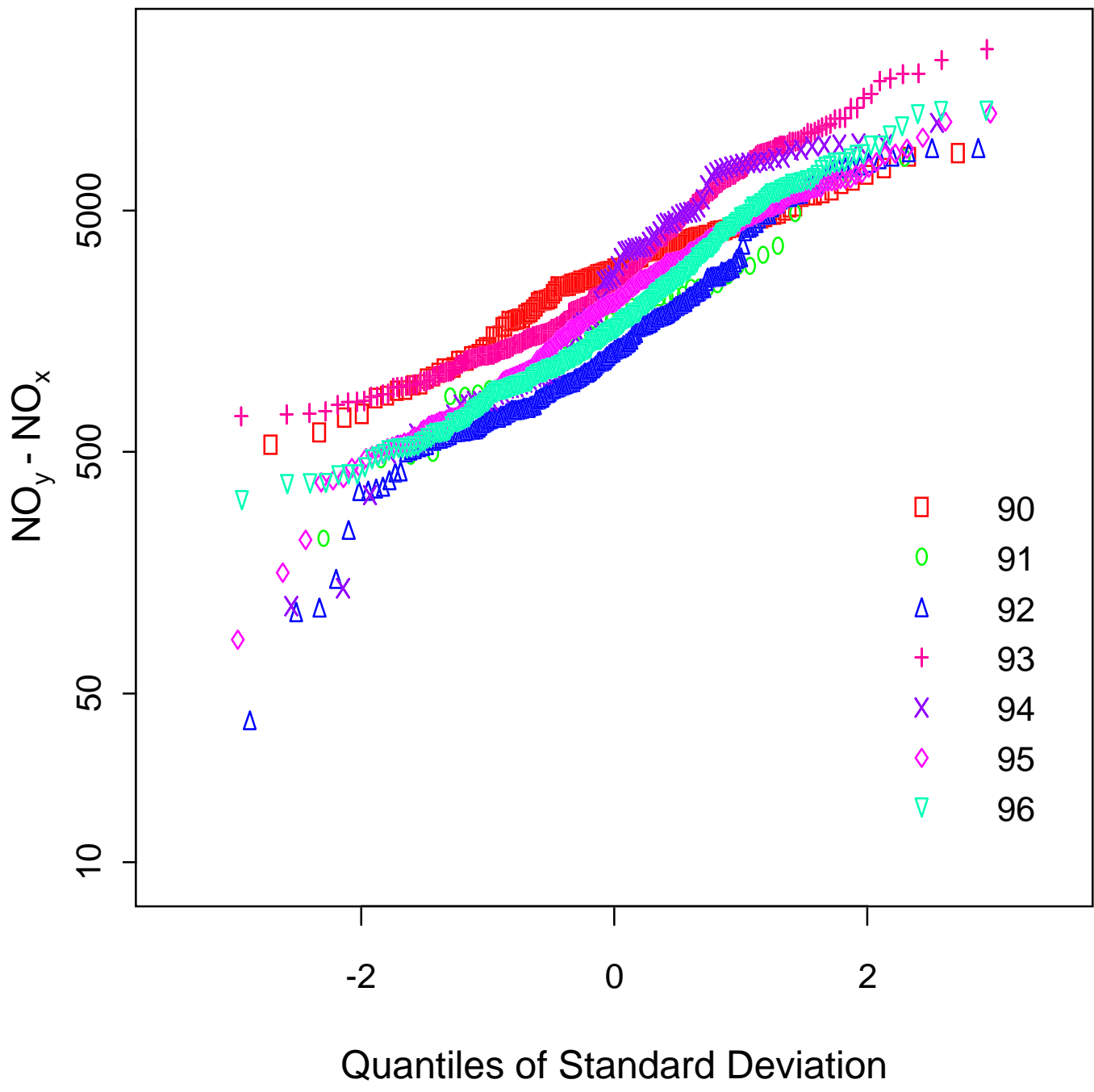
**Yes, the apparent  $O_3$  production efficiency varies by about a factor of 2**

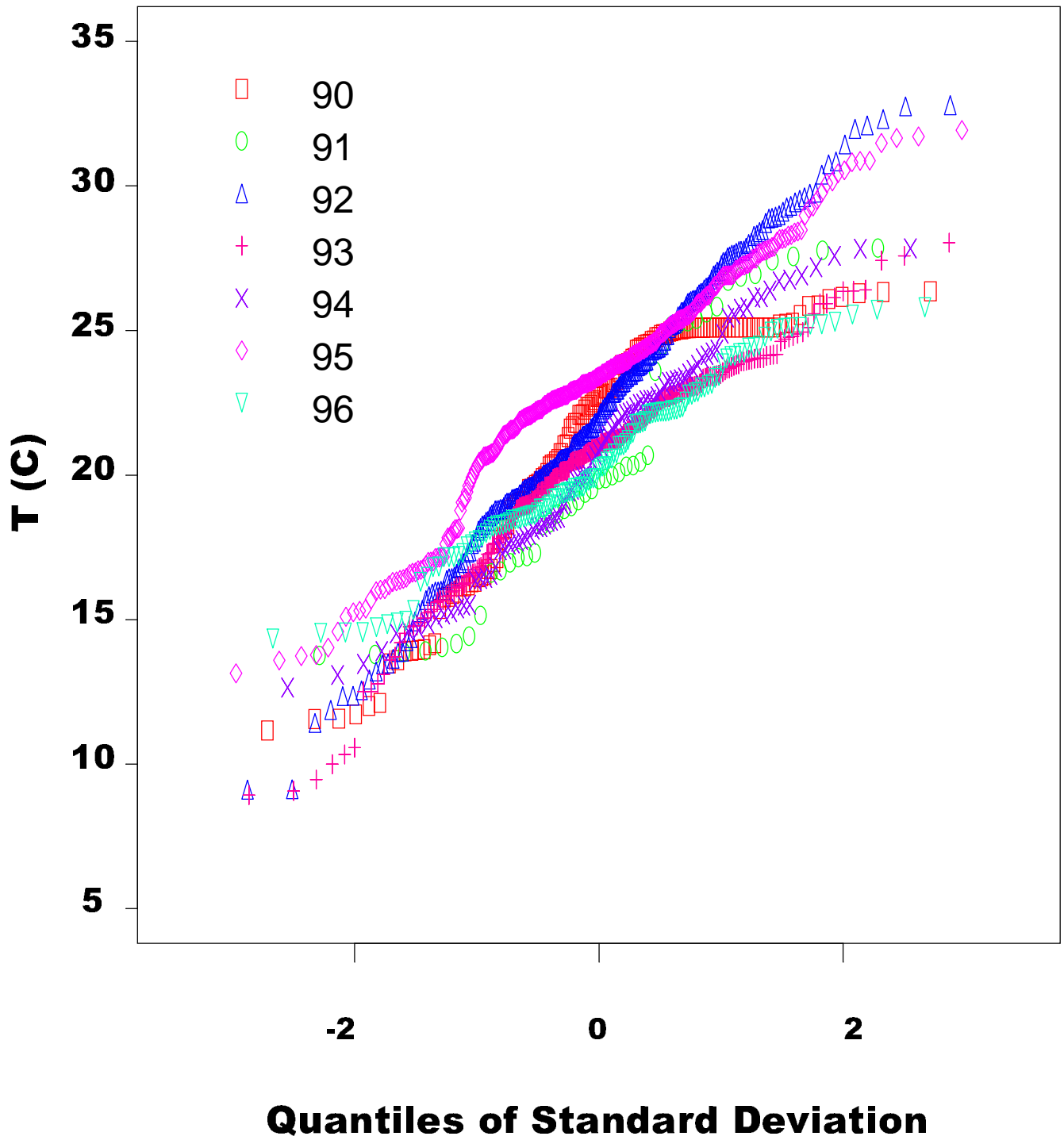


Compare the distribution mid-day O<sub>3</sub> concentrations during the summers of 1990 - 1996. Both the concentration during extreme events and the values around the median differ. Background (or clean) conditions are similar across the years



Likewise, the distribution of  $\text{NO}_y$  (and  $\text{NO}_y - \text{NO}_x$ , next panel) concentrations shows some difference from year to year. The same years are not higher in both  $\text{NO}_y$  and  $\text{O}_3$

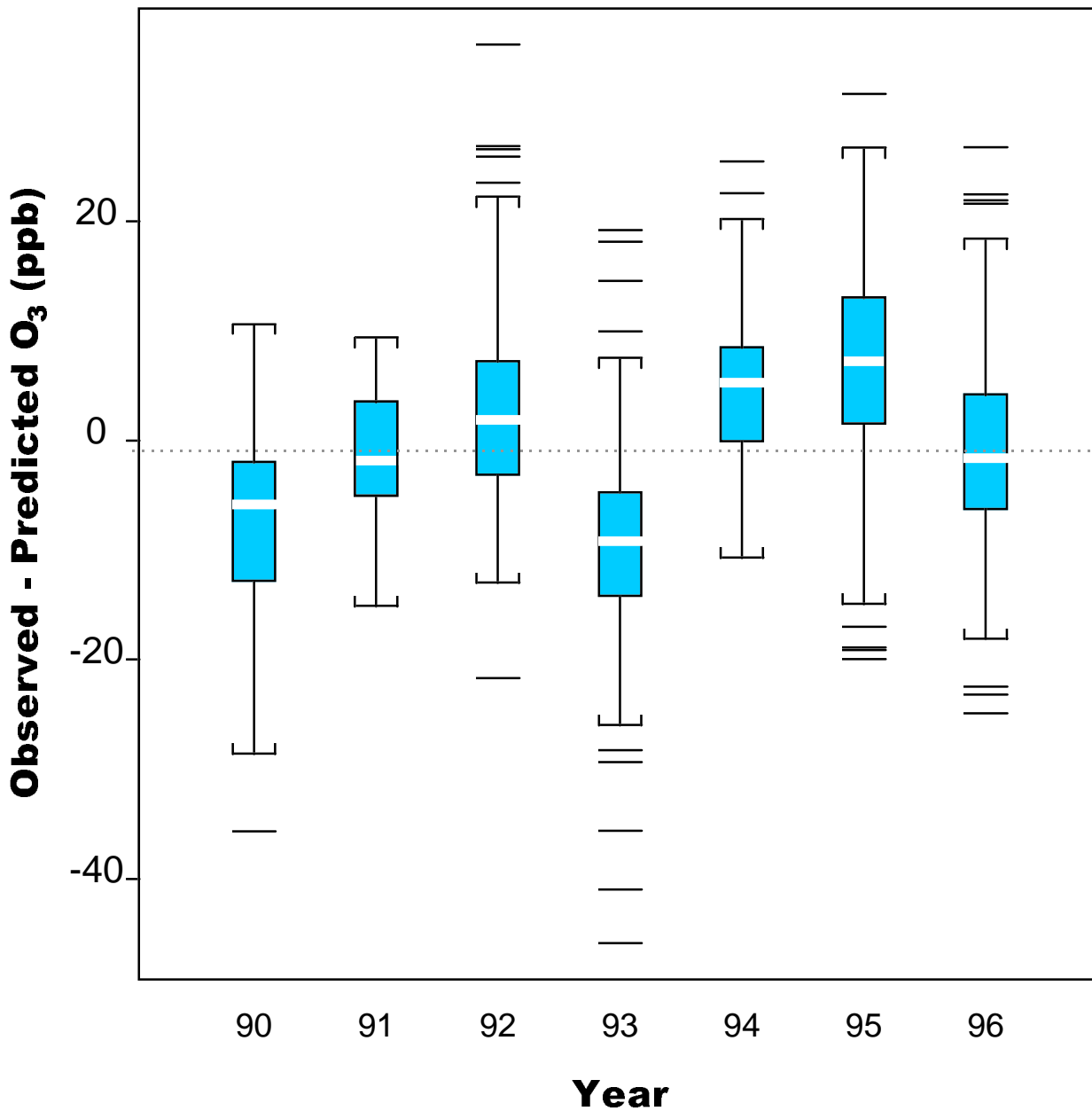




Examine distribution of air temperature to see year-to-year variation

$$O_3 = a_0 + a_1 NO_y - NO_x + a_2 T + a_3 PAR + a_4 f_{hour} + a_6 f_{month} + a_7 f_{wdir}$$

$R^2: 0.70$



The residuals from a model with no annual terms show the existence of significant interannual variation in Ozone concentration that is not explained by interannual variations in the meteorology and precursor concentrations.

Table 1 Coefficients of a Linear model to explain surface Ozone concentrations at Harvard Forest as a function of meteorology, precursor concentrations, and temporal background variation. Different intercepts and NO<sub>y</sub>-NO<sub>x</sub> slopes are allowed for each year.

$$O_3 = a_0 + \sum_{j=10}^{16} a_1^j f_h + a_2^j(\text{NO}_y\text{-NO}_x) + \sum_{j=90}^{96} a_3^j f_y + a_4 T_{\text{air}} + \sum a_5^j f_m$$

a <sub>0</sub> (intercept) =	33 (ppb)
a <sub>1</sub> (hour) =	-2.2,-1.3, -0.7, 0.4, 0.9, 1.1, 1.9 (ppb)
<u>a<sub>2</sub><sup>j</sup>(NO<sub>y</sub>NO<sub>x</sub>):year ppb ppt<sup>-1</sup></u> (apparent ozone production efficiency)	
1990	0.0035
1991	0.0048
1992	0.0064
1993	0.0033
1994	0.0053
1995	0.0072
1996	0.0057
a <sub>3</sub> (year) =	(-2.3, -1.2, 2.2, -5.7, 5.7, 2.4, -1.04) ppb
a <sub>4</sub> (T <sub>air</sub> ) =	1.83 ppb C <sup>-1</sup>
a <sub>5</sub> (month) =	6.29 -1.34 -4.9 ppb

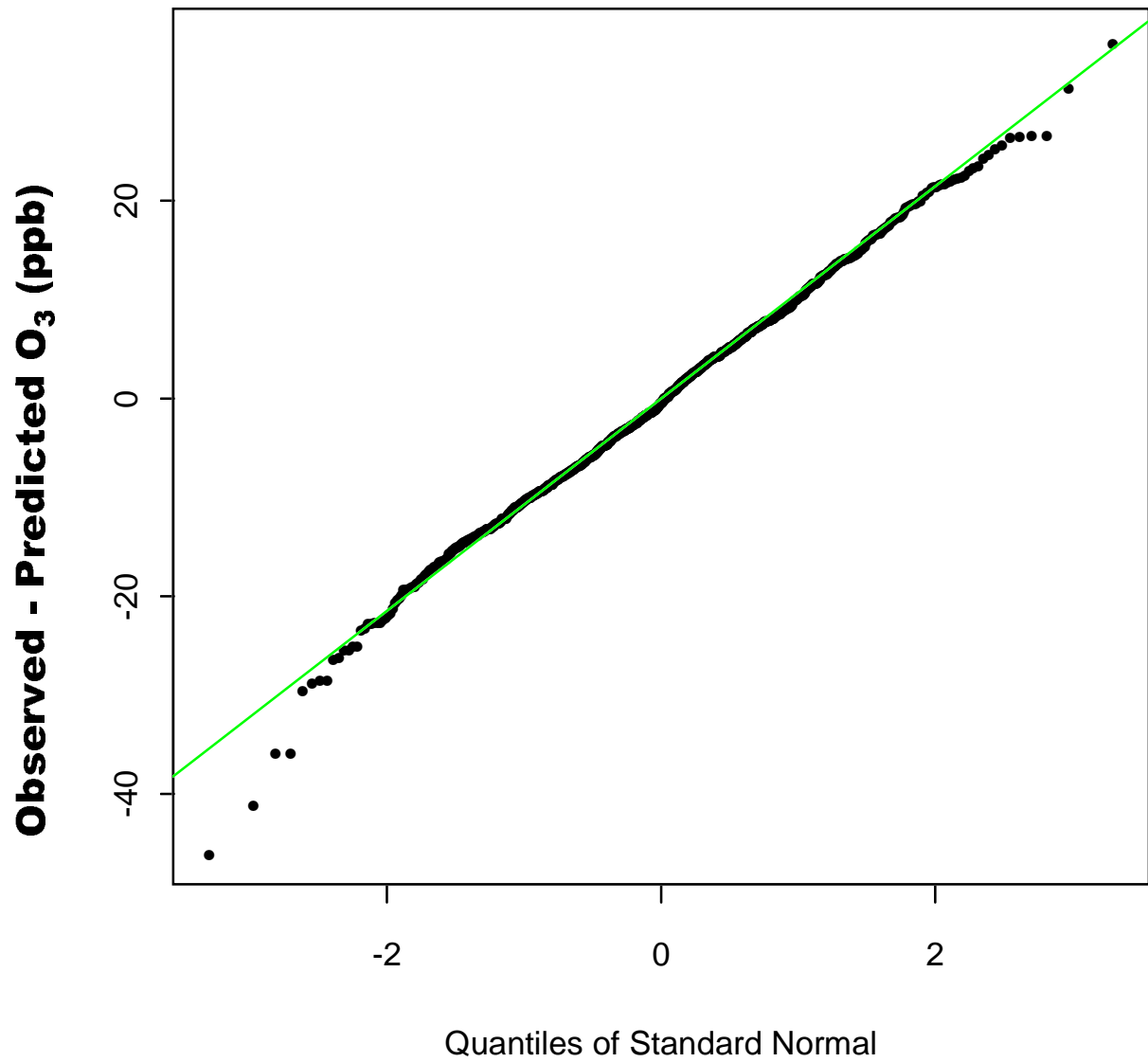
Table 2 Analysis of Variance for a linear model of daytime summer O<sub>3</sub> concentration at Harvard Forest

	Sum of Sq	Mean Sq	F Value	Pr(F)	fraction of variance
hour	10363.3	1727.2	21.5	0	0.027
NO <sub>y</sub> NO <sub>x</sub>	174631.3	174631.3	2175.1	0	0.450
year	68260.3	11376.7	141.7	0	0.176
Tair	34407.4	34407.4	428.5	0	0.089
month	20277.7	10138.9	126.3	0	0.052
NO <sub>z</sub> :year	11442.4	1907.1	27.5	0	0.03
Residuals	68363.3	69.2	--	--	0.18

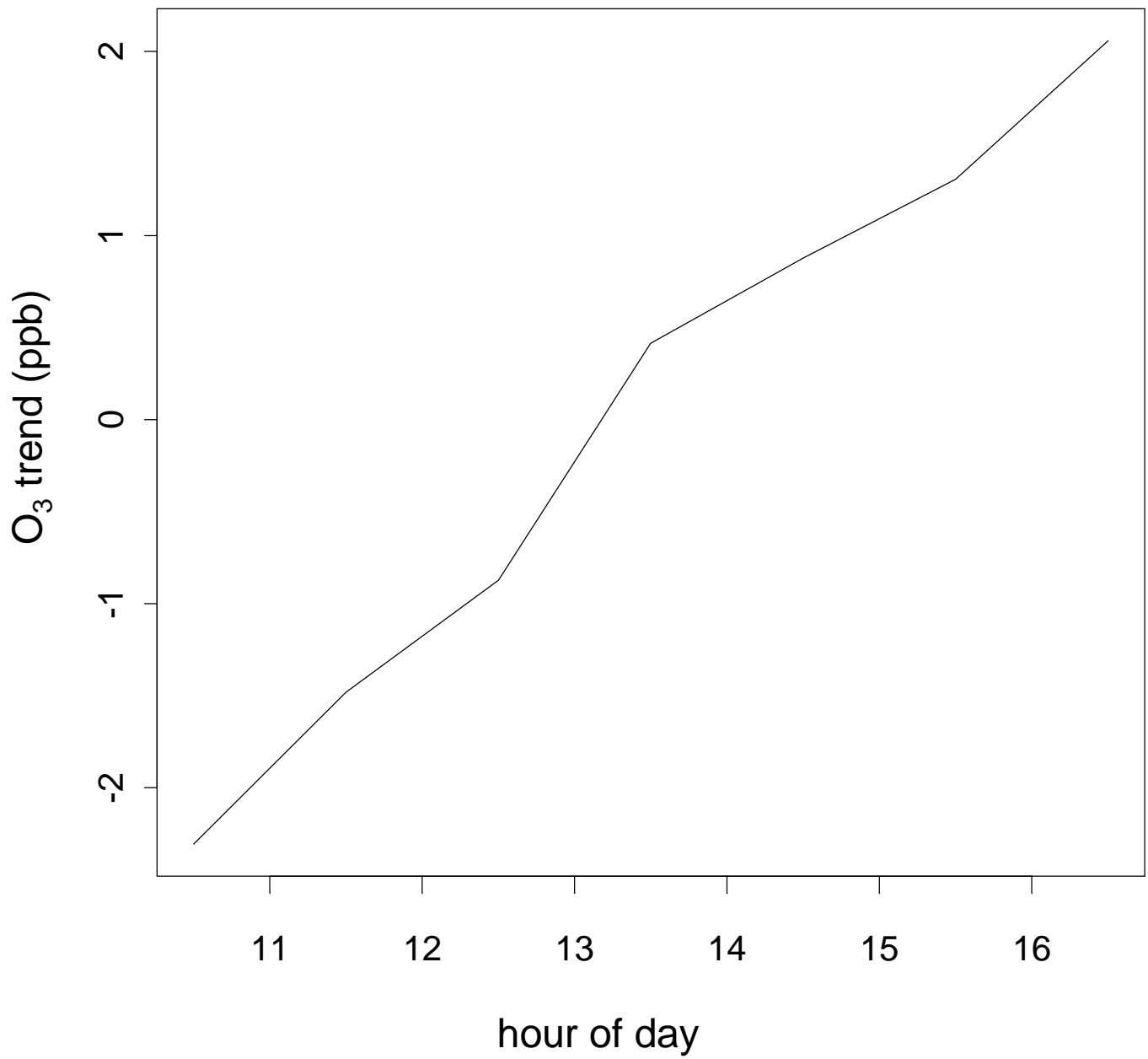
Residual standard error: 8.318 on 988 degrees of freedom

Multiple R-Squared: 0.8237

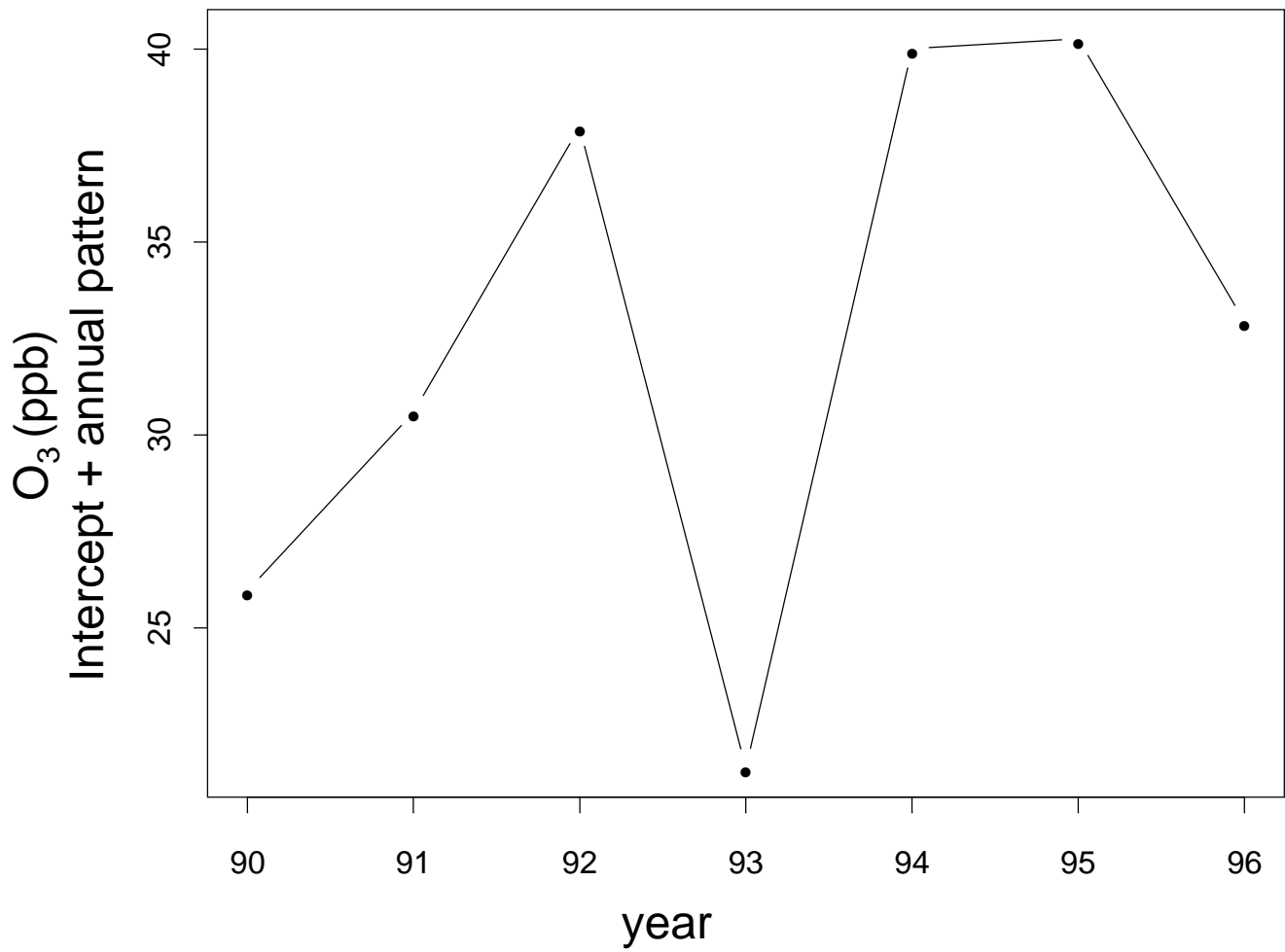
F-statistic: 209.8 on 22 and 988 degrees of freedom, the p-value is 0



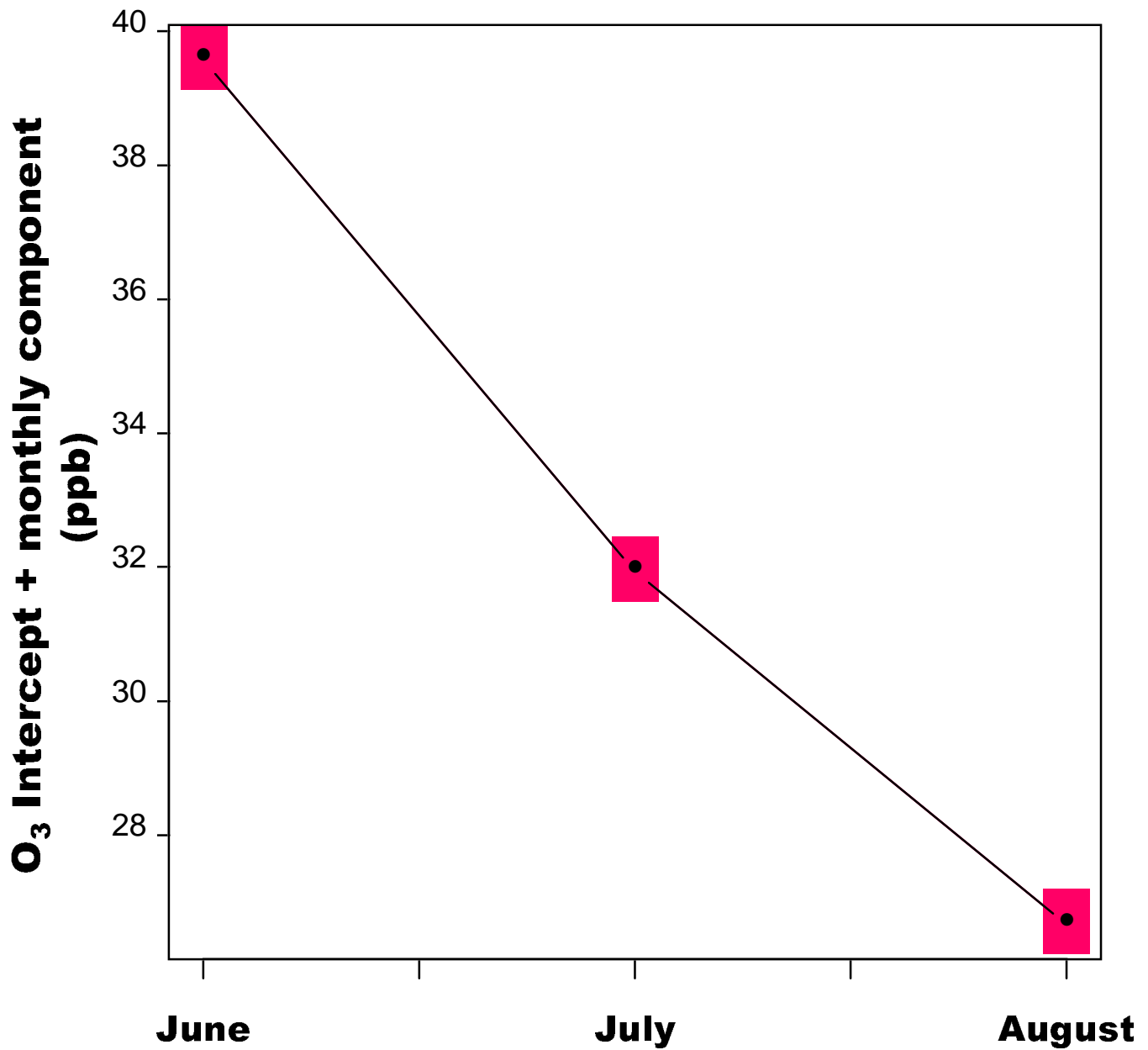
Residuals from the linear model are normally distributed over most of their range



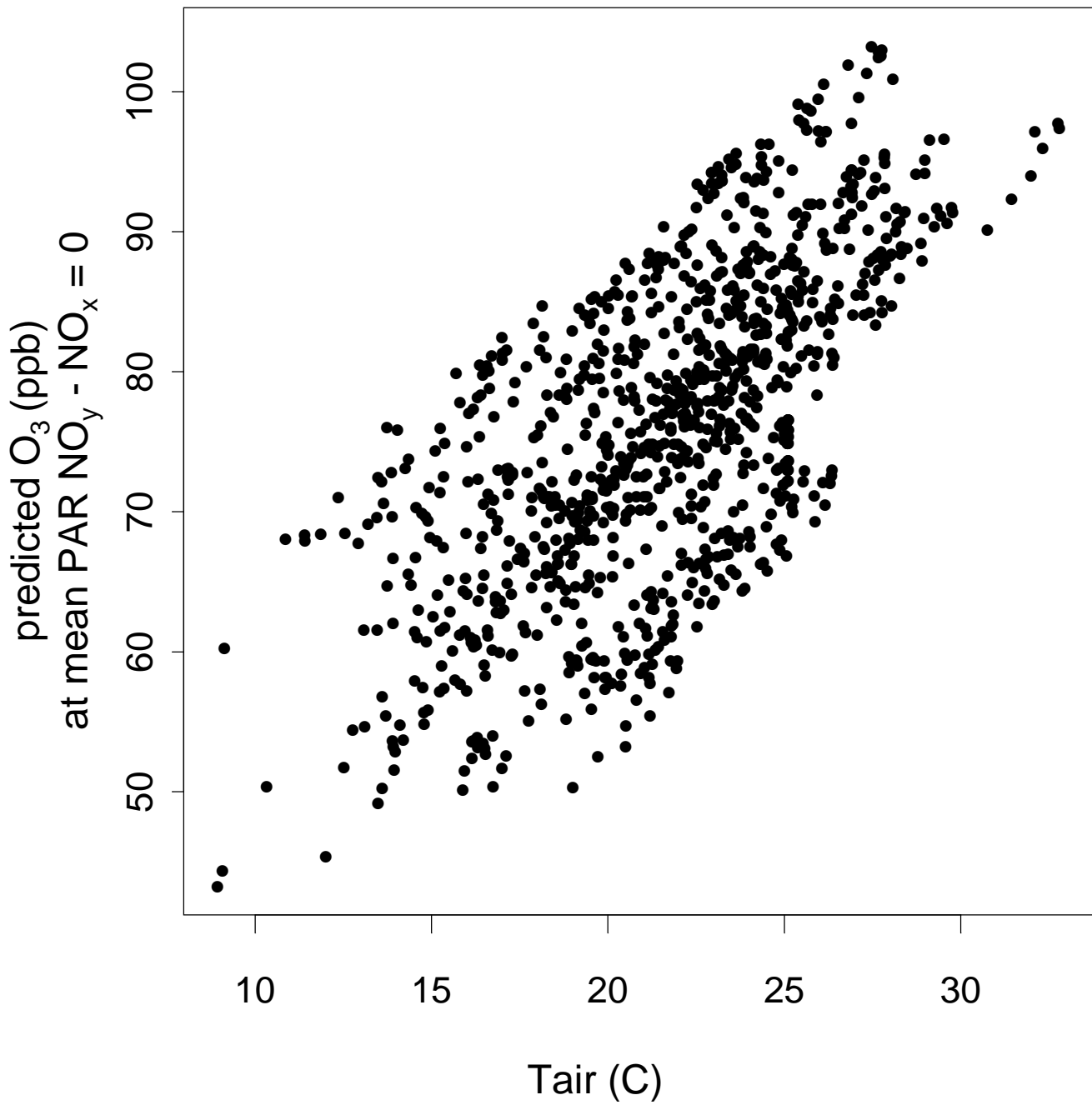
The average diel trend is a 4 ppb increase from 1000 to 1600



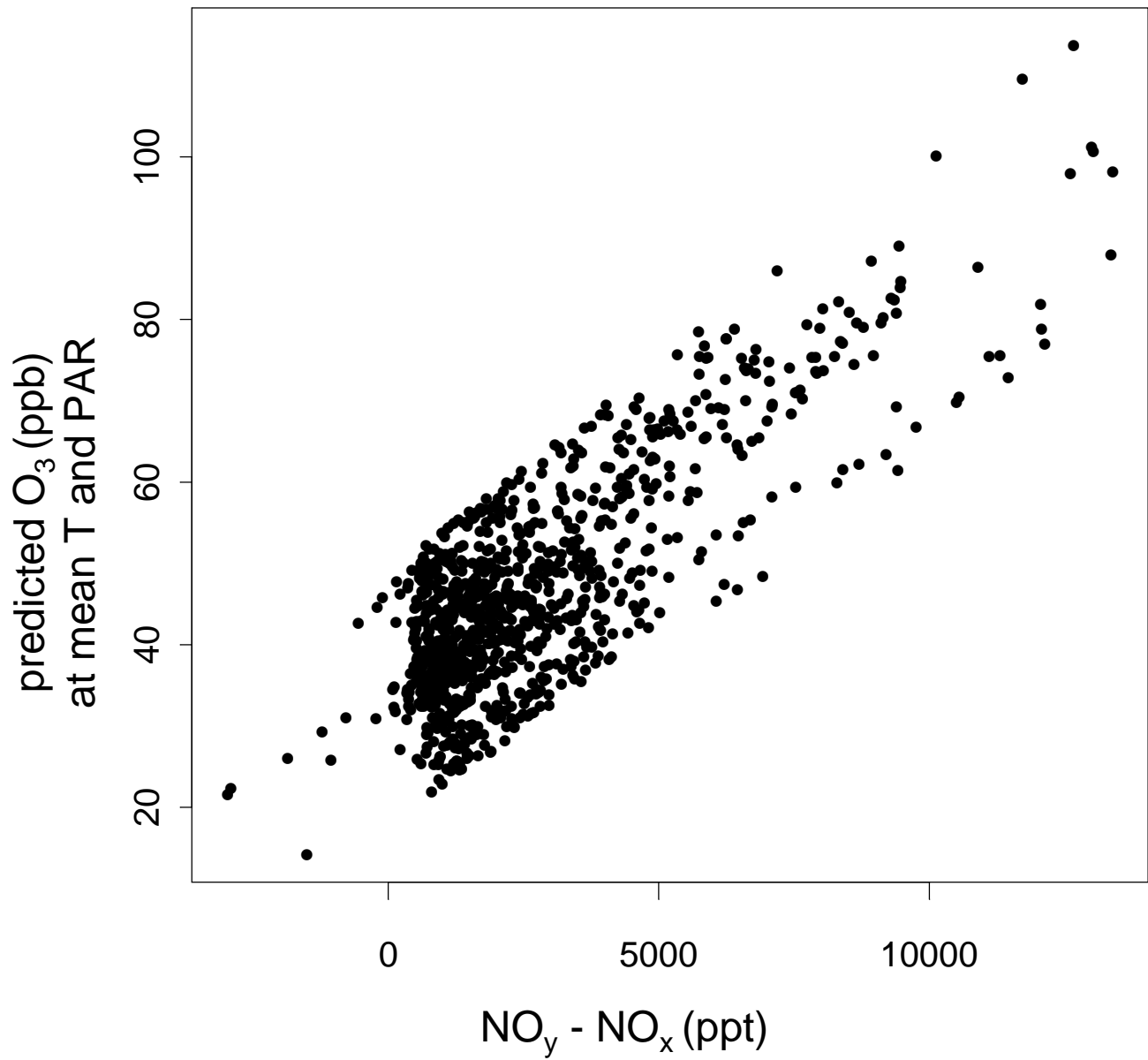
The intercept (background) concentration varies over nearly 20 ppb



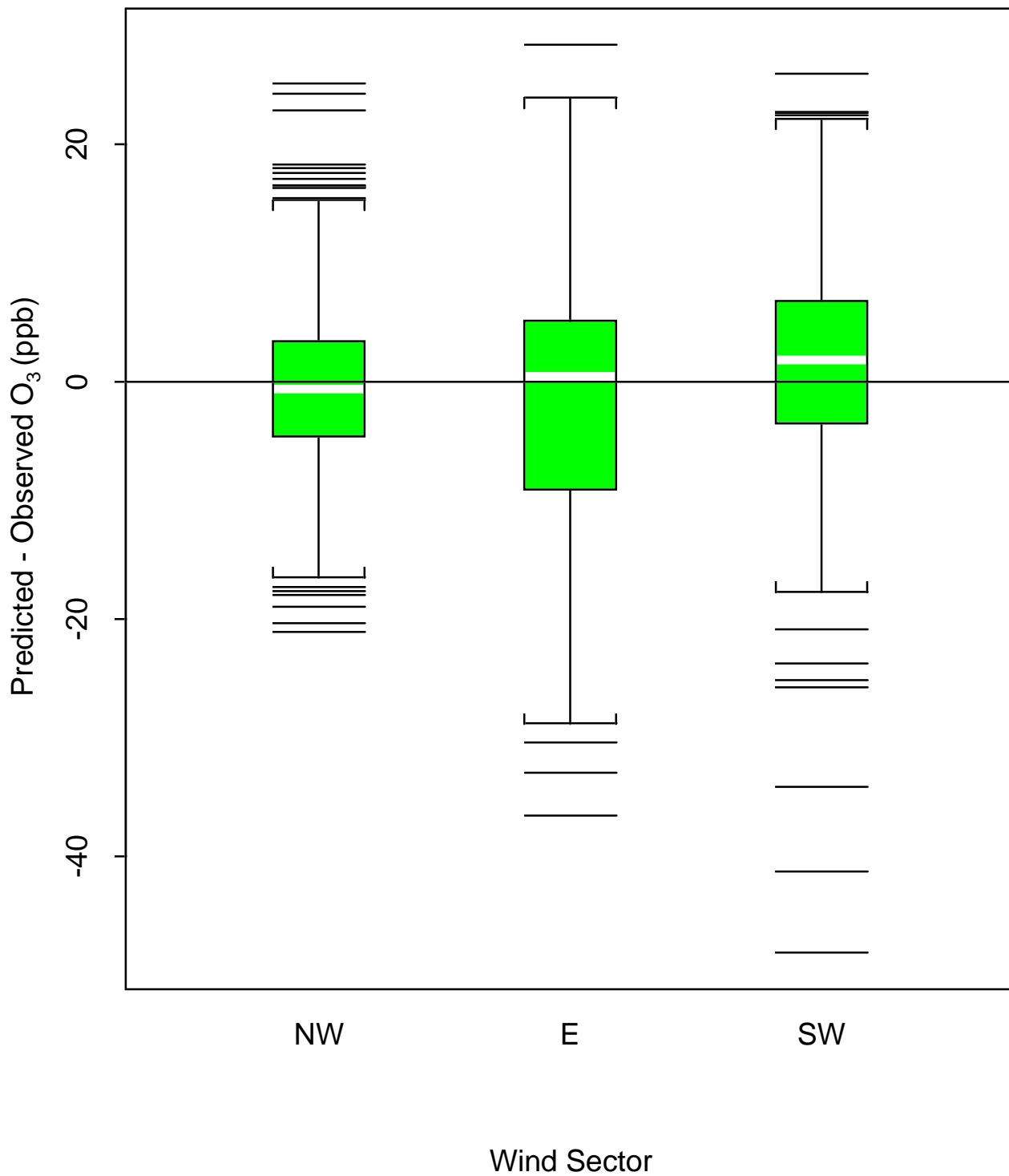
The mean seasonal trend in Ozone background gives an almost 14 ppb decrease from June to August



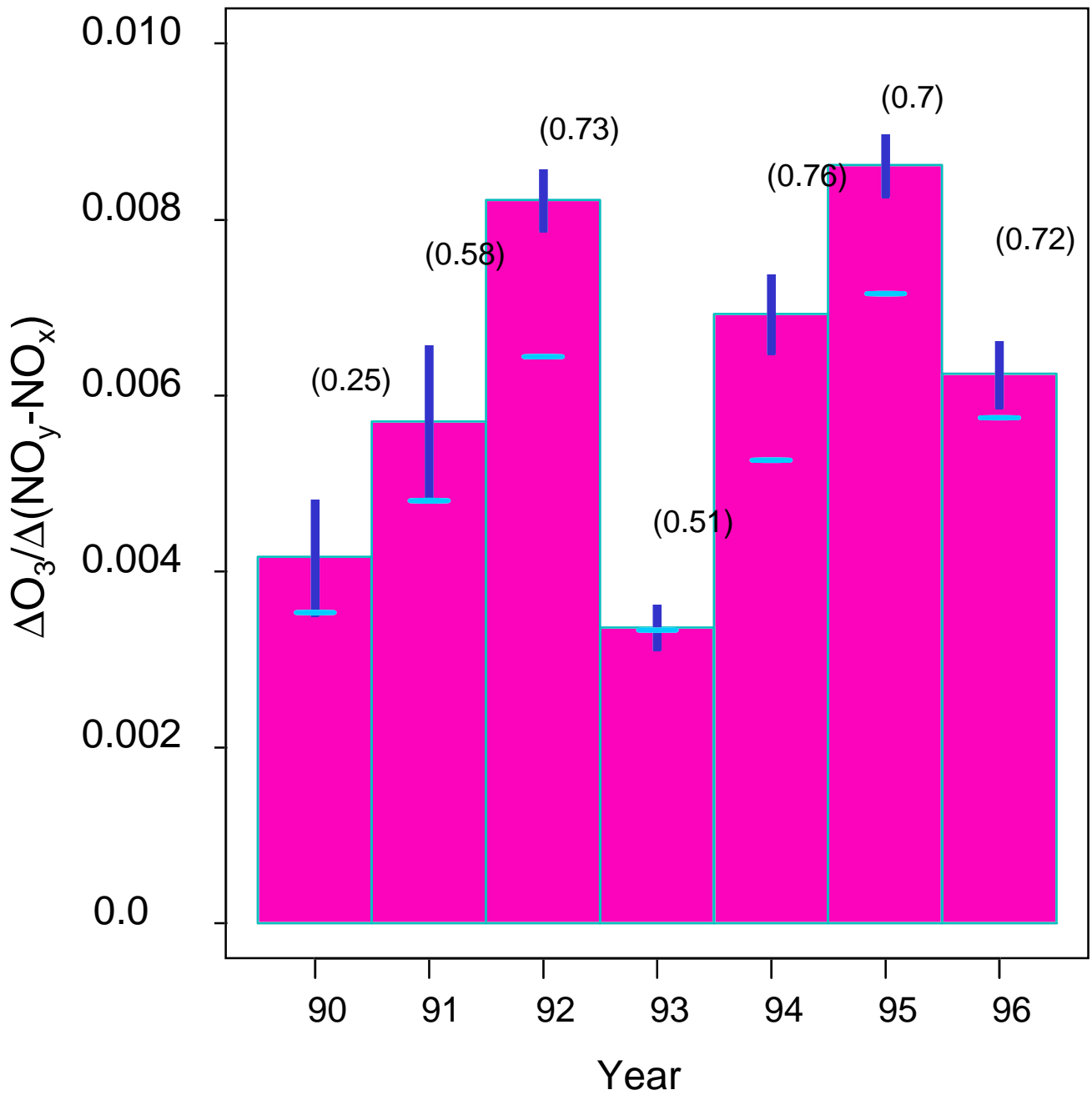
For constant light and NO<sub>y</sub> -NO<sub>x</sub> concentration ozone concentrations vary linearly with temperature. Seasonal and diel trends have not been removed from this plot.



For constant light and temperature ozone concentrations vary linearly with NO<sub>y</sub> - NO<sub>x</sub>.



- The variations in O<sub>3</sub> concentration associated with wind sector are largely removed by the fit to NO<sub>y</sub>-NO<sub>x</sub>. Including wind direction in the predictive model does not improve it any further.



The  $NO_y - NO_x$  coefficient varies from year to year.

$R^2$  for the least squares fit for data from each year is given in ( )

