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Supplement of

Photochemical production of ozone and emissions of NO_x and CH_4 in the San Joaquin Valley

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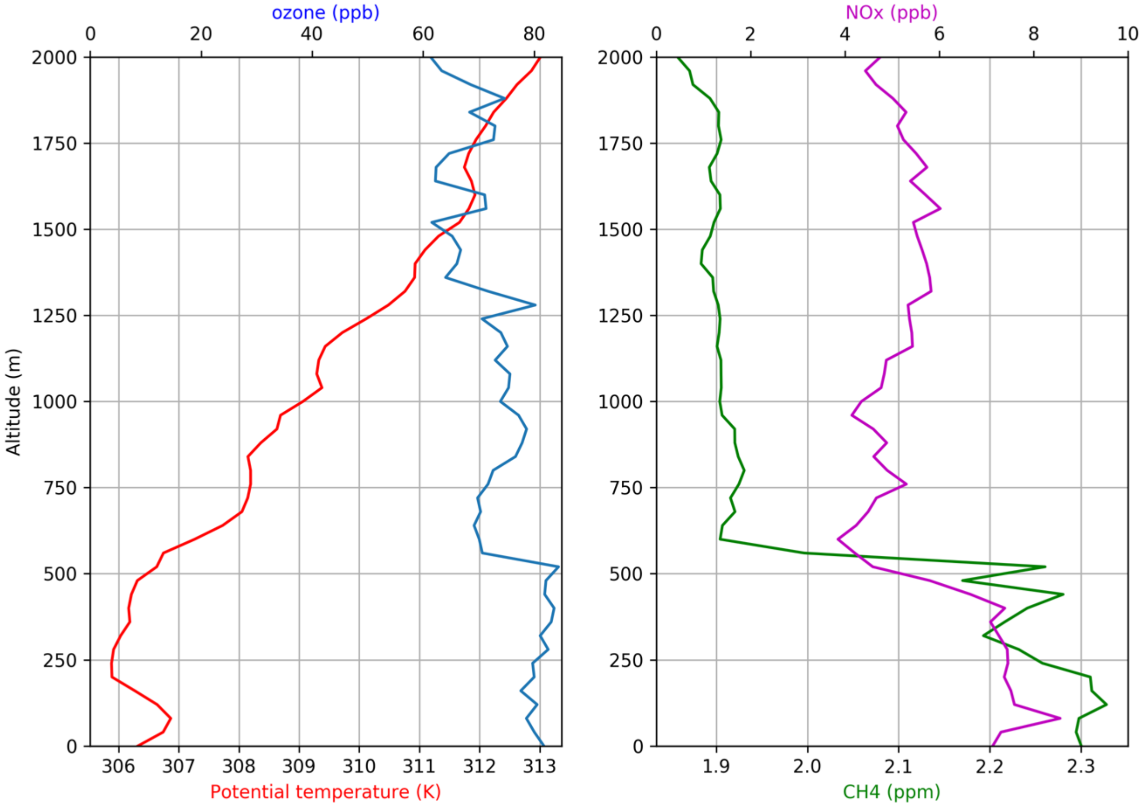

Figure S1. Vertical distribution of scalars (potential temperature – red; ozone – blue; methane – green; NO$_x$ – magenta) observed during an ascending profile over Visalia on August 4, 2016 at 12:30 PST showing an ABL depth of just above 500 m agl.

Section S1. Entrainment Velocity Estimates

The boundary layer entrainment velocities were estimated using a budget analysis of the boundary layer height, z_i,

$$\frac{\partial z_i}{\partial t} = -U\frac{\partial z_i}{\partial x} + w_e + W(z_i)$$

with the observed terms: ABL growth rate, advection, entrainment, and subsidence along with their error estimates reported in Table S1.

Flight Date	WRF W(z_i) (cm/s)	Error Estimate	ABL Growth dzi/dt (cm/s)	Error Estimate	z_i Advection (cm/s)	Error Estimate	Entrainment w_e (cm/s)	Error Estimate	ABL Depth z_i (m)	ABL $\langle\Theta\rangle$ (K)
EPA Flights										
7/27/16	-1.81	0.50	2.81	0.72	0.62	0.54	5.22	1.03	541	311
7/28/16	-1.22	0.50	3.62	1.12	0.21	0.19	4.94	1.24	512	311
7/29/16	-0.83	0.50	0.81	0.59	0.21	0.16	1.51	0.79	492	311
8/4/16	-1.54	0.50	1.13	0.46	0.91	0.20	3.55	0.71	645	307
8/5/16	-1.09	0.50	0.51	0.43	0.23	0.12	1.46	0.67	511	303
8/6/16	-2.00	0.50	-1.01	0.61	0.47	0.13	1.43	0.80	547	305
Averages	**-1.4**		**1.3**	**0.7**	**0.4**	**0.2**	**3.0**	**0.9**	**541**	**309**
Std. Dev.	**0.4**		**1.7**	**0.2**	**0.3**	**0.2**	**1.8**	**0.2**	**55**	**3.7**

Table S1. Observed ABL growth parameters and error estimates that go into estimating the entrainment velocity. From left: the WRF model mean subsidence at boundary layer height (z_i), the measured growth rate of ABL height, the horizontal advection of the inversion base, and the resultant entrainment velocity. The average ABL depth and potential temperature, Θ, over the course of the flights is also reported.

Section S2. NO_x Data Processing

The EcoPhysics chemiluminescence instrument was delivered after a Swiss factory calibration/certification on 5/28/2015. Later that summer, after integration onto the aircraft, California Air Resources Board's (CARB) Mobile Quality Assurance Lab conducted an audit on 7/21/2015 of the aircraft measurements of O_3, NO, NO_2, and temperature. Because we did not set up the lamp cycling software, lamp efficiency correction, and because there was an unexpected offset coming from the lamp, the NO_2 measurement failed the audit. After several more days of "burn-off" and testing the NO_x measurements were improved and a return audit of by CARB's Mobile Lab on 8/6/2015 was successful (ARB Audit #: 57997). In between deployments we performed our own calibrations of the NO_x system via ozone titration of a NIST-certified NO cylinder (typically ~ 100 ppbv) and zero-air dilution. The average slope of all the calibrations was found to be 1.005 (±0.026) and the average offset was 1.1 ppb (±0.4 ppb)(see Figure S2 for an example calibration). Each deployment data set was corrected for the average coefficients of the calibrations performed before and after the deployment.

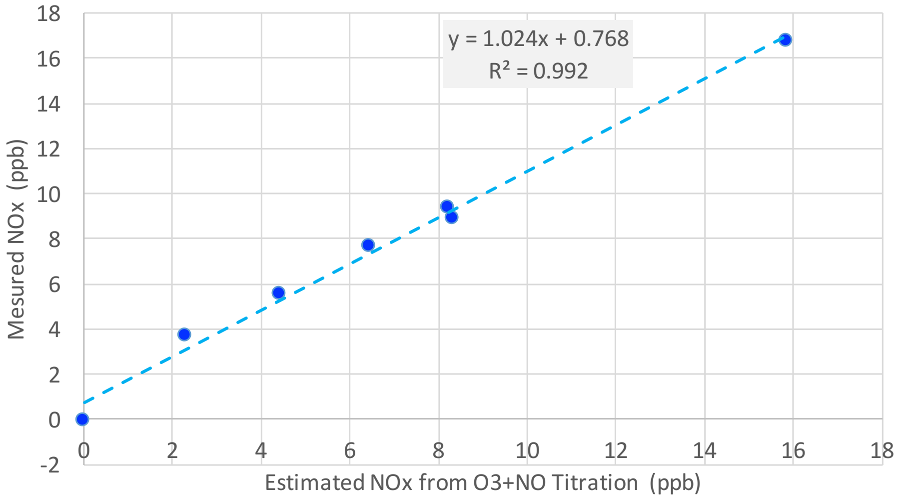

Figure S2. Calibration of EcoPhysics NOx measurements from July 26, 2016.

Section S2.1 Exponential Correction

Analysis of NO_x data from this field campaign revealed a trend of systematic decay in the NO_2 signal for most flights. This trend was corrected in the final dataset. The following describes the laboratory testing that was done to characterize the decay and remove it.

Data was logged for several hours with the lamp on, occasionally switching the lamp off for approximately 1 minute at a time to check the NO signal on multiple separate occasions. The decay signal observed in the airplane was replicated in the lab for all experiments. Since ambient air was being measured, it was assumed that laboratory values of NO and NO_2 will remain fairly constant throughout the duration of each experiment. An exponential correction was then applied using the following procedure:

(1) A time series is created for the species C, where C is either NO or NO_2.

(2) A median value, X, is obtained for C where $t > 3600$ seconds.

(3) With t on the x-axis and ln(C-X) on the y-axis, the linear regression (mx+b) of the scatter plot is taken for all points where $C-X > 0$.

(4) An exponential decay function of time is generated: $f(t) = e^{b}e^{mt}$

(5) The new time-series of C, now corrected for the exponential decay, is generated as follows:

$$C'_t = C_t - [f_t - f_{tmax}]$$

Where t_{max} is the last time series point of the flight. An example corrected time series can be seen in Figure S3.

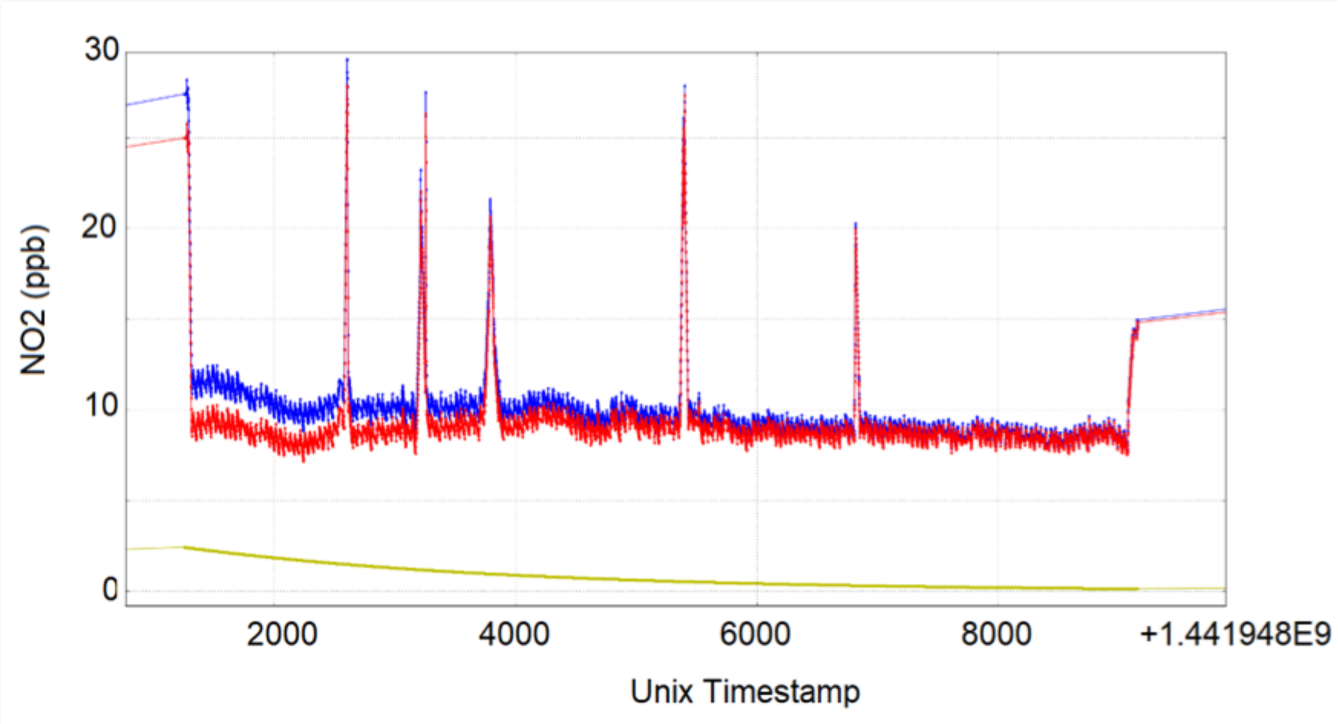

Figure S3. Corrected NO_x signal using an exponentially decaying curve. The blue signal is the raw data, the red is the corrected data and the yellow is the exponential correction factor.

Section S2.2 Altitude Correction

Another artefact of the EcoPhysics chemiluminescence detector is that the sensitivity decreases slightly as a function of altitude, most likely due to reduced oxygen supply to the ozonator. In order to correct for this, we performed a calibration where 107 ppbv of NO is delivered to the instrument. The results of this calibration leads to the following correction:

$$NO_x(corrected) = \frac{107}{106.64 - (0.0027 * z_{m\ MSL})} NO_x(measured)$$

Where $Z_{m\ MSL}$ is the altitude in meters above mean sea level.