Supplementary Material

1 Weighted emission factors

We weighted emission factors, shown in Figure S5, was calculated as a weighted mean with vehicles in circulation in 2011 and emission factors for 2011, both obtained from CETESB (2015).

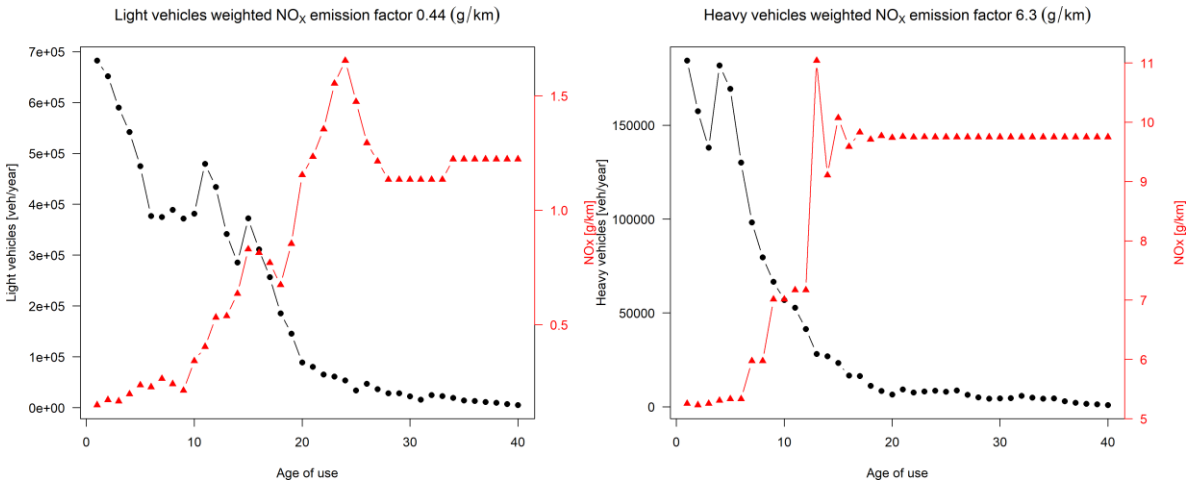

Figure S1. NO_X weighted emission factors for light and heavy vehicles.

2 WRF simulation quality analysis

To assess the quality of WRF simulation we calculate the statistical indicator in Table A1. The results are shown in Table S2. We then compare them with the recommended benchmark of Emery et al. (2001).

To calculate wind direction MB and MAGE we use the following equation based on Reboredo et al. (2015):

$$MB = \sum_{i=1}^{N} \frac{D}{N}$$

$$MAGE = \sum_{i=1}^{N} \frac{|D|}{N}$$

If Mi < Oi:

$$D = (M_i - O_i) \text{ if } |M_i - O_i| < |360 + (M_i - O_i)|$$
$$D = 360 + (M_i - O_i) \text{ if } |M_i - O_i| < |360 + (M_i - O_i)|$$

If Mi > Oi:

$$D = (M_i - O_i) \text{ if } |M_i - O_i| < |(M_i - O_i) - 360|$$
$$D = (M_i - O_i) - 360 \text{ if } |M_i - O_i| < |(M_i - O_i) - 360|$$

$$D = (M_i - O_i)\, if\, |M_i - O_i| < |(M_i - O_i) - 360|$$
$$D = (M_i - O_i) - 360\, if\, |M_i - O_i| > |(M_i - O_i) - 360|$$

Further, according to Keyser and Anthes (1977) and Pielke (2013), model skill is estimated if It satisfies these criteria (Table S3):

1. $\sigma_M \cong \sigma_O$
2. $RMSE < \sigma_O$
3. $RMSE_{UB} < \sigma_O$

Where:

$$RMSE_{UB} = \sqrt{\sum_{i=1}^{N} \frac{[(M_i - \bar{M}) - (O_i - \bar{O})]^2}{N}}$$

$$\sigma_O = \sum_{i=1}^{N} \frac{(O_i - \bar{O})^2}{N}$$

$$\sigma_M = \sum_{i=1}^{N} \frac{(M_i - \bar{M})^2}{N}$$

Table S1. Statistical indicator for WRF simulation of T2, RH2, WS10 and WD10.

	T2 (ºC)	RH2 (%)	WS10 (m/s)	WD10 (º)
N	1842	1843	1885	1864
FAC2	1.00	0.99	0.67	-
MB	0.28	-5.03	0.79	-16.24
MAGE	1.60	9.73	1.17	55.08
NMB	0.01	-0.08	0.43	-
NMGE	0.07	0.16	0.63	-
RMSE	1.98	12.79	1.52	-
R	0.94	0.85	0.45	-
IOA	0.83	0.74	0.18	-

Table S2. Skill analysis for T2, RH2 and W10

	T2 (ºC)	RH2 (%)	WS10 (m/s)
$\bar{O}$	22.14	61.25	1.86
$\bar{M}$	22.41	56.22	2.65
σ_O	5.74	22.09	0.91
σ_M	4.98	19.71	1.41
RMSE	1.98	12.79	1.52
$RMSE_{UB}$	1.96	11.76	1.40
σ_M/σ_O	0.87	0.89	1.55
$RMSE_{UB}/RMSE$	0.99	0.92	0.92
$RMSE_{UB}/\sigma_O$	0.34	0.53	1.54

3 Test with another background concentration

We perform a test by using measurements from a different AQS as MUNICH background information. We select Santos AQS (light blue diamond in Figure 4). This AQS recorded lower O_3 concentration and higher NO concentrations than Ibirapuera AQS. Figure S1 shows a comparison of MUNICH results against background and observation concentrations for O_3, NO_x, NO, and NO_2 and Figure S2 shows the diurnal profile. Table S4 shows the statistical indicator of the tests.

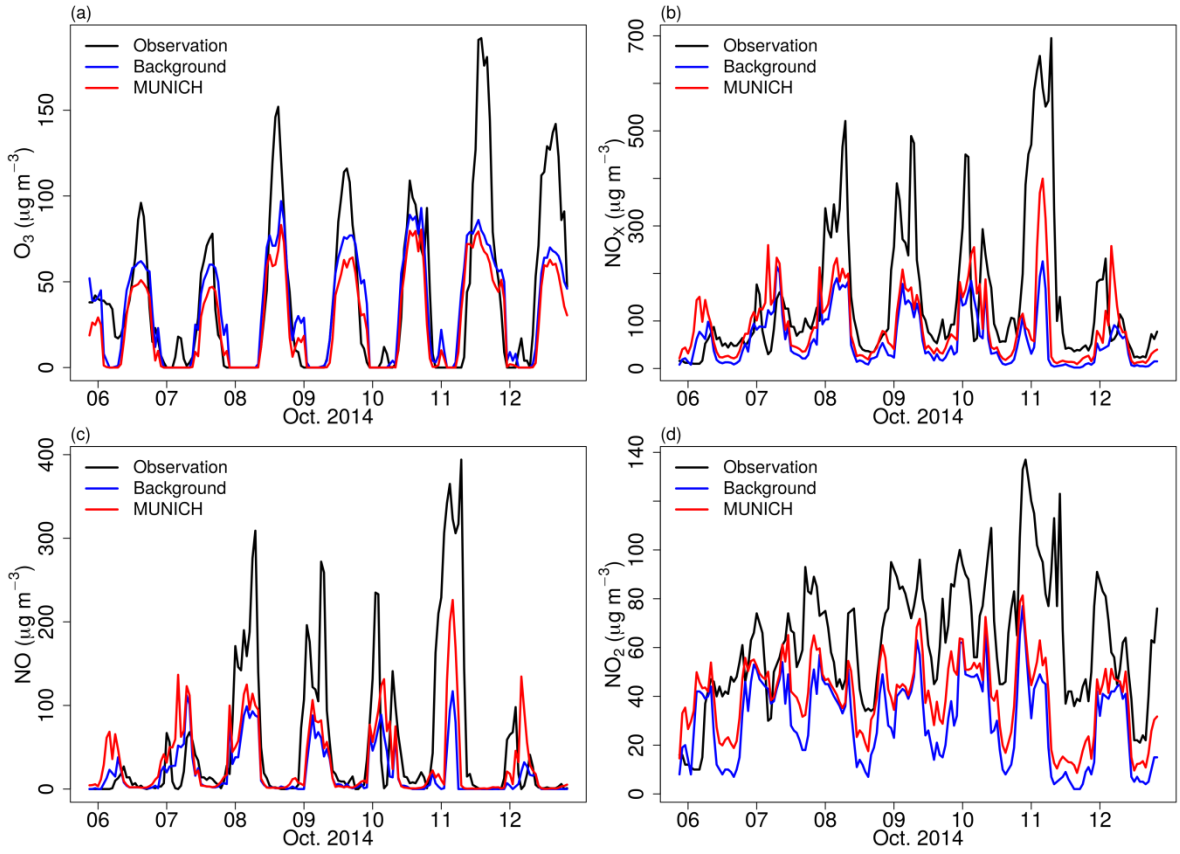

Figure S2. Comparison of MUNICH results against background and observation concentrations for (a) O_3, (b) NO_x, (c) NO, and (d) NO_2 for Pinheiros urban canyon using Santos AQS measurements as background concentrations.

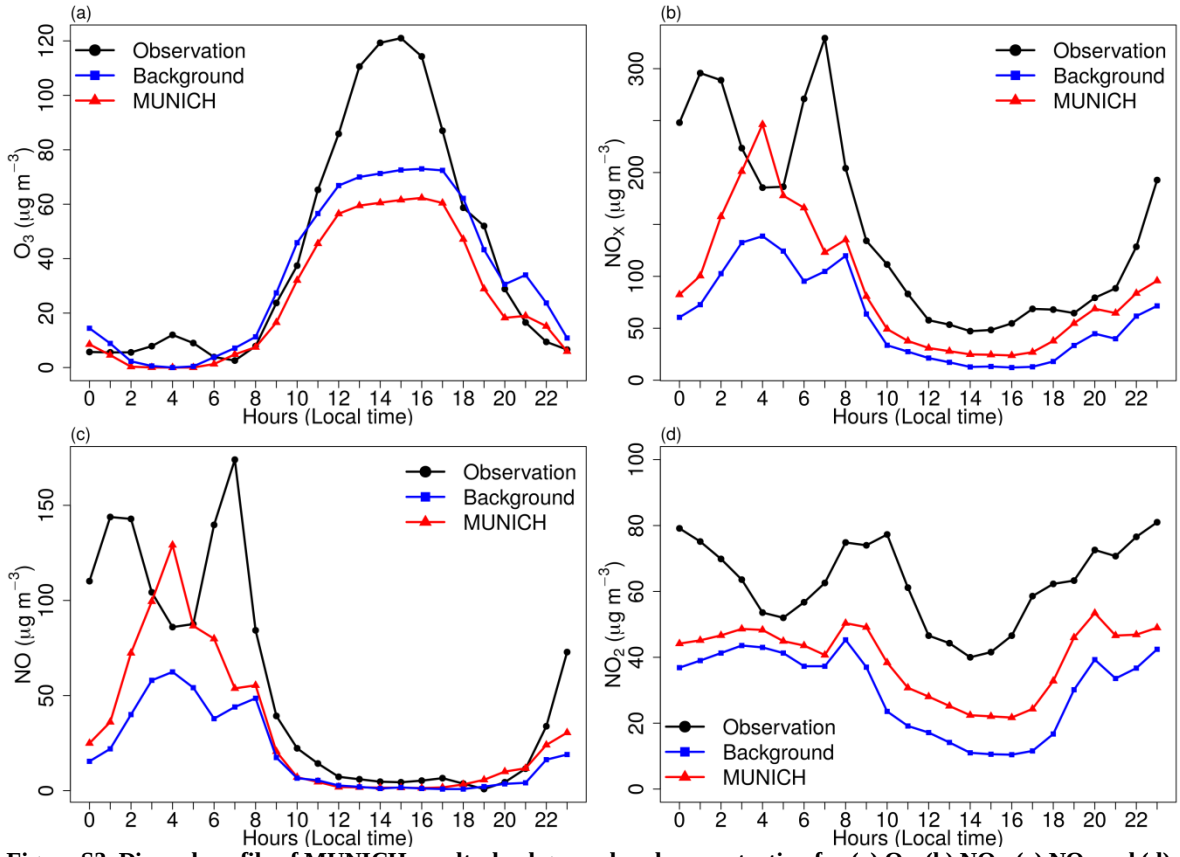

Figure S3. Diurnal profile of MUNICH results, background and concentration for (a) O_3, (b) NO_x, (c) NO, and (d) NO_2 for Pinheiros urban canyon using Santos AQS measurements as background concentration.

Table S3. Statistical indicators for O_3, NO_x, NO, and NO_2 for comparison of MUNICH using Ibirapuera AQS as background and MUNICH using Santos AQS as background against observations from Pinheiros AQS.

		$\bar{M}$[a]	$\bar{O}$	σ_M	σ_O	MB	NMB	NMGE	RMSE	R	|FB|	NMSE	FAC2	NAD
O_3	MUNICH Ibi.	54.5	41.5	62.1	47.5	13.0	0.3	0.3	22.2	1.0	**0.3**	**0.2**	**0.6**	**0.1**
	MUNICH San.	25.7	41.5	26.9	47.5	-15.8	-0.4	0.5	32.5	0.8	**0.5**	**1.0**	**0.4**	**0.2**
NO_X	MUNICH Ibi.	88.9	146.4	57.4	150.3	-57.4	-0.4	0.5	128.5	0.7	**0.5**	**1.3**	**0.7**	**0.2**
	MUNICH San.	88.4	146.4	75.4	150.3	-57.9	-0.4	0.6	137.3	0.6	**0.5**	**1.5**	**0.5**	**0.2**
NO	MUNICH Ibi.	18.7	54.6	28.7	88.9	-35.9	-0.7	0.8	80.7	0.7	1.0	6.4	0.1	0.5
	MUNICH San.	31.9	54.6	43.6	88.9	-22.7	-0.4	0.8	76.1	0.6	**0.5**	**3.3**	**0.3**	**0.3**
NO_2	MUNICH Ibi.	45.8	62.7	23.4	25.9	-16.8	-0.3	0.3	21.2	0.9	**0.3**	**0.2**	**0.9**	**0.2**
	MUNICH San.	39.5	62.7	15.9	25.9	-23.1	-0.37	0.4	32.1	0.5	**0.5**	**0.4**	**0.7**	**0.2**

[a] $\bar{M}$- Model value mean, $\bar{O}$ - Observation mean, σ_M - model standard deviation, σ_O - observation standard deviation, MB - mean bias, NMB - normalized mean bias, NMGE - normalized mean gross error, RMSE - root mean square error, R - correlation coefficient, FB - fractional mean bias, NMSE - normalized mean-square error, FAC2 - fraction of predictions within a factor of two , and NAD - normalized absolute difference. Values in bold satisfied Hanna and Chang (2012) acceptance criteria.

4 NO_X emission increase

We conduct a sensitivity simulation in which NO_x emissions are increased by four relative to the calibrated emission case, and maintaining VOCs emission as the original case scenario. Figure S3 shows a comparison of MUNICH results against background and observation concentrations for O_3, NO_x, NO, and NO_2. Figure S4 shows the diurnal profile. Though there was an improvement in O_3 simulation, improbable NO_x concentrations are simulated, too. Table S5 shows the statistical performance indicator of this test.

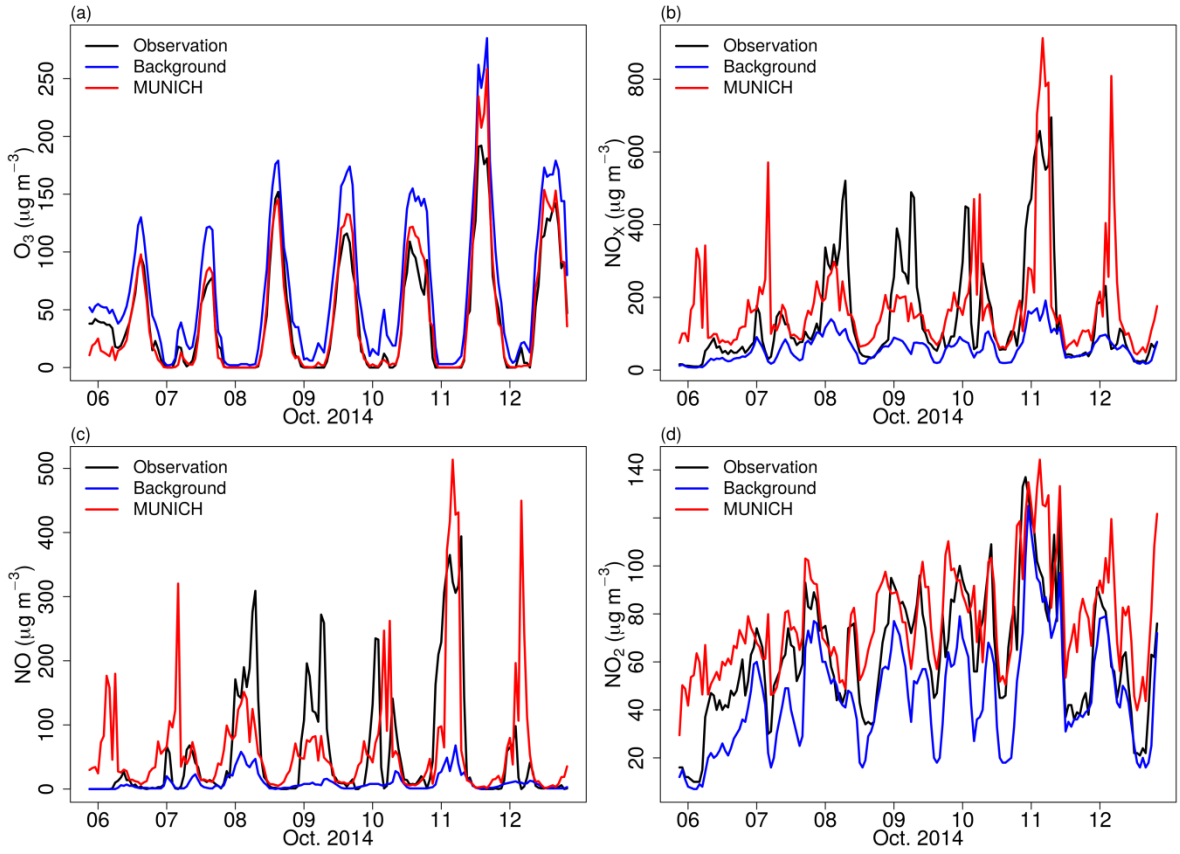

Figure S4. Comparison of MUNICH results against background and observation concentrations for (a) O_3, (b) NO_x, (c) NO, and (d) NO_2 for Pinheiros urban canyon using increased NO_x emissions by four.

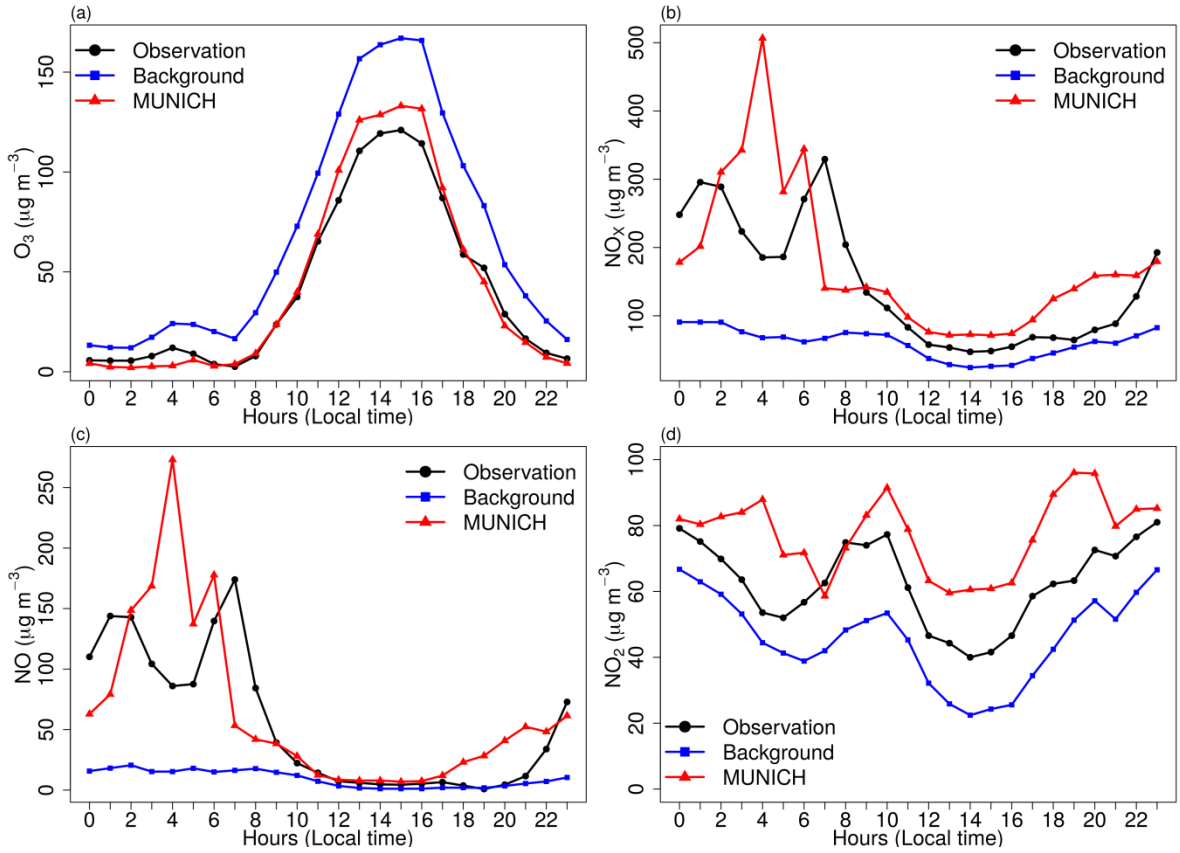

Figure S5. Diurnal profile of MUNICH results, background and concentration for (a) O_3, (b) NO_x, (c) NO, and (d) NO_2 for Pinheiros urban canyon using increased NO_x emissions by four.

Table S4. Statistical indicators for O_3, NO_x, NO, and NO_2 for comparison of MUNICH using increased NO_X emission by four.

	$\bar{M}$[b]	$\bar{O}$	σ_M	σ_O	MB	NMB	NMGE	RMSE	R	|FB|	NMSE	FAC2	NAD
O_3	43.2	41.5	54.8	47.5	1.7	0.0	0.2	13.6	1.0	**0.0**	**0.1**	**0.6**	**0.0**
NO_X	175.0	146.4	147.4	150.3	28.6	0.2	0.6	146.5	0.5	**0.2**	**0.8**	**0.6**	**0.1**
NO	63.6	54.6	89.1	88.9	9.0	0.2	0.9	87.1	0.5	**0.2**	**2.2**	**0.4**	**0.1**
NO_2	77.4	62.7	22.2	25.9	14.8	0.2	0.3	22.7	0.8	**0.2**	**0.1**	**0.9**	**0.1**

[b] $\bar{M}$- Model value mean, $\bar{O}$ - Observation mean, σ_M - model standard deviation, σ_O - observation standard deviation, MB - mean bias, NMB - normalized mean bias, NMGE - normalized mean gross error, RMSE - root mean square error, R - correlation coefficient, FB - fractional mean bias, NMSE - normalized mean-square error, FAC2 - fraction of predictions within a factor of two , and NAD - normalized absolute difference. Values in bold satisfied Hanna and Chang (2012) acceptance criteria.