Supplement of Long-term NO$_x$ measurements in the remote marine tropical troposphere

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1. O₃ Correction:

NO and NO₂ are in photo-stationary state in the atmosphere, where NO reacts with O₃ to give NO₂ and NO₂ is photolysed to NO:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O} \quad (S1) \]
\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad (S2) \]

When measuring NO and NO₂, NO continues to react with ambient O₃ in the sample line to the instrument, however, no photolysis occurs in the sample line causing an underestimation of NO and an overestimation of NO₂. This can be corrected using the equations described below.

1.1 NO correction

Since NO only reacts with O₃ in the line and is not photolysed back to NO as it would be in the atmosphere during daylight, the decrease in NO can be described by a simple rate equation:

\[ \frac{d[\text{NO}]}{dt} = -k_{\text{NO}+\text{O}_3}[\text{O}_3][\text{NO}] = -k_{\text{O}_3}[\text{NO}] \quad (\text{SI}) \]

where \( k_{\text{NO}+\text{O}_3}[\text{O}_3] = k_{\text{O}_3} \). By integrating between time = 0 and the time it takes to reach the reaction cell (\( t = t_{E1} \)) the following is obtained:

\[ \ln \left( \frac{[\text{NO}]_{E1}}{[\text{NO}]_0} \right) = -k_{\text{O}_3} \times t_{E1} \quad (\text{SII}) \]
\[ [\text{NO}]_0 = [\text{NO}]_{E1} \times e^{k_{\text{O}_3} \times t_{E1}} \quad (\text{SIII}) \]

where \([\text{NO}]_0\) and \([\text{NO}]_{E1}\) are the NO mixing ratio at the inlet and that measured by the PMT, respectively.

1.2 NO₂ correction

NO₂ is measured by converting it photolytically into NO and reacting the NO with O₃ to produce excited state NO₂ which emits chemiluminescent light as it drops to the ground state.
The measured mixing ratio of NO\(_2\) is calculated from the NO signals with ([NO]\(_E2\)) and without ([NO]\(_E1\)) the converter on and the conversion efficiency of the converter (S\(_C\)):

\[
[\text{NO}2]_M = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}}{S_C} \tag{SIV}
\]

To correct the measured NO\(_2\) mixing ratio for reactions with O\(_3\), the following needs to be taken into account:

- NO reacts with O\(_3\) in the line before reaching the converter
- NO\(_2\) is photolysed into NO at the same time as NO continues to react with O\(_3\) inside the converter

The photo-stationary state of NO and NO\(_2\) inside the converter can be described by the following equations:

\[
[\text{NO}]_{PSS} = [\text{NO}]_0 + \Delta\text{NO} \tag{SV}
\]

\[
[\text{NO}2]_{PSS} = [\text{NO}2]_0 - \Delta\text{NO}_2 \tag{SVI}
\]

Where [NO]\(_{PSS}\) and [NO\(_2\)]\(_{PSS}\) are the photo-stationary state mixing ratios of NO and NO\(_2\), respectively, [NO]\(_0\) and [NO\(_2\)]\(_0\) are the mixing ratios of NO and NO\(_2\) at the entrance of the inlet, and \(\Delta\text{NO}\) and \(\Delta\text{NO}_2\) are the change in NO and NO\(_2\) inside the converter. The change in NO and NO\(_2\) will be equal since the only reactions occurring are reactions (S1) and (S2). Thus, the photo-stationary state can be written as:

\[
[\text{NO}]_{PSS} = [\text{NO}]_0 + [\text{NO}2]_0 - [\text{NO}2]_{PSS} \tag{SVII}
\]

\[
[\text{NO}2]_{PSS} = [\text{NO}2]_0 - ([\text{NO}]_{PSS} - [\text{NO}]_0) = [\text{NO}2]_0 + [\text{NO}]_0 - [\text{NO}]_{PSS} \tag{SVIII}
\]

In photo-stationary state, reactions (S1) and (S2) react with the same rate, which can be written as:

\[
k_{O3} \times [\text{NO}]_{PSS} = J_C \times [\text{NO}2]_{PSS} \tag{SIX}
\]

where \(J_C\) is the photolysis rate of the converter. Combining equation (SVIII) and (SIX) gives the following equations for the photo-stationary state of NO:

\[
[\text{NO}]_{PSS} = \frac{J_C}{k_{O3}} \times [\text{NO}2]_{PSS} = \frac{J_C}{k_{O3}} \times ([\text{NO}2]_0 + [\text{NO}]_0 - [\text{NO}]_{PSS}) \tag{SX}
\]

\[
[\text{NO}]_{PSS} = \frac{J_C}{k_{O3}} \times ([\text{NO}2]_0 + [\text{NO}]_0) - \frac{J_C}{k_{O3}} \times [\text{NO}]_{PSS} \tag{SXI}
\]
(1 + \frac{Ic}{k_{o3}}) \times [NO]_{PSS} = \left(\frac{k_{o3} + Ic}{k_{o3}}\right) \times [NO]_{PSS} = \frac{Ic}{k_{o3}} \times ([NO_2]_0 + [NO]_0) \quad \text{(SXI)}

[NO]_{PSS} = \left(\frac{k_{o3}}{k_{o3} + Ic}\right) \times \frac{Ic}{k_{o3}} \times ([NO_2]_0 + [NO]_0) = \left(\frac{Ic}{k_{o3} + Ic}\right) \times ([NO_2]_0 + [NO]_0) \quad \text{(SXII)}

By combining equations (SIX) and (SXII), the photo-stationary state of NO\_2 in the converter can be obtained:

\[ [NO_2]_{PSS} = \frac{k_{o3}}{Ic} [NO]_{PSS} = \frac{k_{o3}}{Ic} \times \left(\frac{Ic}{k_{o3} + Ic}\right) \times ([NO_2]_0 + [NO]_0) \quad \text{(SXIV)} \]

\[ [NO_2]_{PSS} = \left(\frac{k_{o3}}{k_{o3} + Ic}\right) \times ([NO_2]_0 + [NO]_0) \quad \text{(SXV)} \]

The photolysis rate inside the converter is given by:

\[ Jc = \frac{-\ln(1 - S_c)}{t_{c2}} \quad \text{(SXVI)} \]

where \(t_{c2}\) is the time the air is in the converter while it is on.

Inside the converter, the NO mixing ratio moves towards photo-stationary state ([NO]_{PSS}) with a rate of \(k_{o3} + Ic\) since some of the NO\_2 being photolysed to NO in the converter will react with O\_3 in the sample to regenerate NO\_2. This can be described by equation (SXVII), where [NO]_L is the NO mixing ratio at the entrance of the converter:

\[ [NO]_{E2} = [NO]_{PSS} - ([NO]_{PSS} - [NO]_L) \times e^{-(k_{o3} + Ic) \times t_{c2}} \quad \text{(SXVII)} \]

\[ [NO]_{E2} = [NO]_{PSS} - [NO]_{PSS} \times e^{-(k_{o3} + Ic) \times t_{c2}} + [NO]_L \times e^{-(k_{o3} + Ic) \times t_{c2}} \quad \text{(SXVIII)} \]

\[ [NO]_{E2} = [NO]_{PSS} \times (1 - e^{-(k_{o3} + Ic) \times t_{c2}}) + [NO]_L \times e^{-(k_{o3} + Ic) \times t_{c2}} \quad \text{(SXIX)} \]

The NO mixing ratio at the entrance of the converter can be estimated from the loss of NO to O\_3 in the line in the same way as the ozone corrected NO mixing ratio could be determined:

\[ [NO]_L = [NO]_0 \times e^{-k_{o3} \times t_L} = [NO]_{E1} \times e^{k_{o3} \times t_{E1}} \times e^{-k_{o3} \times t_L} \quad \text{(SXX)} \]

\[ [NO]_L = [NO]_{E1} \times e^{k_{o3} \times t_{C1}} \quad \text{(SXXI)} \]

Equations (SXIX) and (SXXI) are combined to give equation (SXXII):

\[ [NO]_{E2} = [NO]_{PSS} \times (1 - e^{-(k_{o3} + Ic) \times t_{c2}}) + [NO]_{E1} \times e^{-(k_{o3} + Ic) \times t_{c2} + k_{o3} \times t_{C1}} \quad \text{(SXXII)} \]

[NO]_{PSS} is isolated to give equation (SXXIII):
\[ [\text{NO}]_{\text{PSS}} = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}x_0e^{-(k_{O3}+J_c)x_tC_2+k_{O3}x_tC_1}}{1-e^{-(k_{O3}+J_c)x_tC_2}} \]  
(SXXXIII)

Lastly equations (SXIII) and (SXXIII) are combined to give equation (SXXIV) and rearranged to give the ozone corrected mixing ratio in equation (SXXV):

\[ \frac{J_c}{J_c+k_{O3}} \times ([\text{NO}]_0 + [\text{NO}_2]_0) = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}x_0e^{-(k_{O3}+J_c)x_tC2+k_{O3}x_tC1}}{1-e^{-(k_{O3}+J_c)x_tC2}} \]  
(SXIV)

\[ [\text{NO}_2]_0 = \left( \frac{J_c+k_{O3}}{J_c} \right) \times \left( \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}x_0e^{-(k_{O3}+J_c)x_tC2+k_{O3}x_tC1}}{1-e^{-(k_{O3}+J_c)x_tC2}} \right) - [\text{NO}]_0 \]  
(SXXV)

1.3 Low O₃ concentration

At low O₃ concentrations \( k_{O3} \) tends towards 0 and becomes very small compared to \( J_c \), such that the calculations for NO and NO₂ become:

\[ [\text{NO}]_0 = [\text{NO}]_{E1} \]  
(SXXVI)

\[ [\text{NO}_2]_0 = \left( \frac{J_c}{J_c} \right) \times \left( \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}x_0e^{-(k_{O3}+J_c)x_tC2}}{1-e^{-(k_{O3}+J_c)x_tC2}} \right) - [\text{NO}]_{E1} \]  
(SXXVII)

\[ [\text{NO}_2]_0 = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}x_0e^{-(k_{O3}+J_c)x_tC2}}{1-e^{-(k_{O3}+J_c)x_tC2}} - [\text{NO}]_{E1} \]  
(SXXVIII)

\[ [\text{NO}_2]_0 = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}}{1-e^{-(k_{O3}+J_c)x_tC2}} = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}}{\frac{\text{S}_C}{1-e^{-(k_{O3}+J_c)x_tC2}}} = \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1}}{\text{S}_C} \]  
(SXXIX)

1.4 Example calculation

An example calculation of the O₃ corrections is shown below, assuming a conversion efficiency of 50% (\( \text{S}_C = 50\% \)), a time of 3.3s from the inlet to the converter (\( t_L = 3.3s \)), a residence time of 1s for the sample in the converter whether the converter is on or not (\( t_{C1}=t_{C2}=1s \)), an ozone mixing ratio of 30 ppb, a temperature of at 298K and therefore, \( k(\text{O}_3 + \text{NO}) = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), a \( k_{O3} = 0.013 \text{ s}^{-1} \).

We start with uncorrected mixing ratios (i.e. measured mixing ratios) of \([\text{NO}]_{M} = 10 \text{ ppt} \) and \([\text{NO}_2]_{M} = 30 \text{ ppt} \):

\[ [\text{NO}]_{E1} = 10 \text{ ppt} \]
\[ [\text{NO}]_{E2} = 30 \text{ppt} \times 0.5 + 10 \text{ppt} = 25 \text{ppt} \]

\[ J_C = \frac{-\ln(1 - S_C)}{t_{C2}} = \frac{-\ln(1 - 0.5)}{1s} = 0.69 \text{ s}^{-1} \]

\[ [\text{NO}]_0 = [\text{NO}]_{E1} \times e^{k_{O3} \times t_{E1}} = 10 \text{ ppt} \times e^{0.013 \text{s}^{-1} \times 4.3\text{s}} = 10.6 \text{ ppt} \]

\[ [\text{NO}_2]_0 = \left( \frac{J_C + k_{O3}}{J_C} \right) \times \left( \frac{[\text{NO}]_{E2} - [\text{NO}]_{E1} \times e^{-(k_{O3} + J_C) \times t_{C2} + k_{O3} \times t_{C1}}}{1 - e^{-(k_{O3} + J_C) \times t_{C2}}} \right) - [\text{NO}]_0 \]

\[ = \left( \frac{0.69 \text{s}^{-1} + 0.013}{0.69 \text{s}^{-1}} \right) \times \left( \frac{25 \text{ppt} - 10 \text{ppt} \times e^{-(0.013 \text{s}^{-1} + 0.69 \text{s}^{-1}) \times 1 \text{s} + 0.013 \text{s}^{-1} \times 1 \text{s}}}{1 - e^{-(0.013 \text{s}^{-1} + 0.69 \text{s}^{-1}) \times 1 \text{s}}} \right) - 10.6 \text{ ppt} \]

\[ = 1.02 \times 39.6 - 10.6 = 29.7 \text{ ppt} \]

This gives a small increase in NO mixing ratio (0.6 ppt or 5.7%) and a small decrease (0.3 ppt or 1%) in NO\(_2\) mixing ratio under these conditions.
3. Uncertainty Analysis:

The uncertainty of a measurement is given as an interval at a confidence level, which describes how certain it is that the true value is within the interval. The interval can be determined from the spread of data, which can be described by several probability distributions. The most common are normal and rectangular distributions. A normal distribution is used when most of the measurements are centred around the mean. The signal-to-noise is reduced by approximately $1/\sqrt{\text{number of averaging points}}$ when averaging the measurements. The uncertainty in the mean of the measurements are estimated using equation (SXXX). To get an uncertainty at the 95 percent confidence interval 2 standard deviations ($\sigma$) are used. A rectangular distribution is when the probability of each measurement is equal. The $1\sigma$ uncertainty is estimated from the half-width of the distribution and the $2\sigma$ uncertainty is estimated from the full width of the distribution as shown in equation (SXXXI). The hourly precision and uncertainty of the instrument are estimated to characterize the uncertainties at the 95 percent confidence interval (Bell, 2001).

Normal distribution uncertainty ($u$) = \[
\frac{2\sigma}{\sqrt{\text{number of averaging point}}}
\] (SXXX)

Rectangular distribution uncertainty = \[
\frac{\text{full-width}}{\sqrt{3}}
\] (SXXXI)

The hourly precision is estimated from the zero count variability, which is directly related to the photon-counting precision of the PMT. The hourly mean ($\bar{x}$) of the zero measurements is subtracted from each individual measurement of the respective hour ($x - \bar{x}$) to give hourly frequency distributions. Photon-counting frequency distributions are best described by a Poisson distribution, however, at high photon-counting rates become indistinguishable from a Gaussian distribution (Silvia and Skilling, 2006). With a yearly mean background count rate of ~1400-3000 count s$^{-1}$ between 2014 and 2019, the frequency distributions can be assumed as Gaussian. Examples of hourly frequency distributions can be observed in figure S1. The standard deviation of each hourly frequency distribution is calculated and divided by the interpolated sensitivity to give a $2\sigma$ NO precision for 1 s data of $23.4 \pm 20.3$ ppt for the hours between January 2014 and August 2019. The $2\sigma$ NO precision for hourly averaged data is $1.0 \pm 0.9$ ppt. The hourly precisions reported here are in good agreement with the previously reported $1\sigma$ precision of 0.30 ppt (Reed et al., 2017) and the $2\sigma$ precision of 0.6-1.7 ppt (Lee et al., 2009). The NO$_2$ precisions are determined by taking the conversion efficiency of the respective converters into account. The hourly $2\sigma$ NO$_2$ precision for hourly averaged data
between March 2017 and August 2019 becomes $1.5 \pm 0.8$ ppt and $2.7 \pm 2.2$ ppt for the BLC and PLC, respectively. The determined NO$_2$ precisions are within the interval of previously reported precisions for the same instrument (Lee et al., 2009; Reed et al., 2017).

The uncertainty of the hourly measurements is estimated by combining all the uncertainties associated with the measurements. This includes uncertainties in the calibrations, artefact determinations, and O$_3$ corrections as well as the precision of the instrument. The precision of the NO and NO$_2$ measurements are both included in the total uncertainty of the NO$_2$ measurements as the NO measurements are subtracted from the NO$_2$ measurements. Each term is converted into ppt to be able to combine them. All the uncertainties are combined using uncertainty propagation:

$$\text{Accuracy} = \sqrt{\text{Precision}^2 + \text{Artefact}^2 + \text{Calibration}^2 + \text{O}_3 \text{Correction}^2} \quad (SXXII)$$

Uncertainty in the calibrations is caused by uncertainty in the flow of calibration gas, the concentration of the calibration gas, the sensitivity, and the conversion efficiency as well as the drift in the sensitivity and conversion efficiency between each calibration. The total uncertainty in the calibrations is determined as the propagation of each term. Each term is calculated as a percentage to be able to combine them before converting the total calibration uncertainty to ppt to combine it with the other uncertainty terms. According to the manufacturers the sample and
calibration mass flow controllers have an uncertainty of 1%, which has been confirmed by a
gillibrator bubble flowmeter. The uncertainty of the concentration of the NO standard used for
calibration is known to ±1% (British Oxygen Company (BOC), certified to UK National
Physical Laboratory (NPL) standard) (BOC certifies that NO/N₂ standards are stable for 5
years). To estimate the uncertainty in the sensitivity and conversion efficiency, the
uncertainties in each measurement used to determine them must be estimated. Equation IV and
V describe the calculation of the sensitivity and conversion efficiency of the instrument,
respectively. The spread of each type of measurement used can be described by a normal
distribution. The percentage uncertainty in the sensitivity and the conversion efficiency can
therefore be determined by equation SXXXIII and SXXXIV, respectively.

\[
\text{Sensitivity Uncertainty } = \frac{u_{NO(1)}}{NO_{(1)}} \quad \text{(SXXXIII)}
\]

\[
\text{CE Uncertainty } = \sqrt{\left(\frac{u_{NO.c(1)}}{NO.c_{(1)}}\right)^2 + \left(\frac{u_{NO.c(2)}}{NO.c_{(2)}}\right)^2 + \left(\frac{u_{NO(1)}}{NO_{(1)}}\right)^2 + \left(\frac{u_{NO(2)}}{NO_{(2)}}\right)^2} \quad \text{(SXXXIV)}
\]

The drift between calibrations contains two terms; one for the sensitivity and one for the
conversion efficiency when estimating the uncertainty for NO₂. Both terms are determined as
the absolute difference between two measurements. The distribution is assumed to be
rectangular as only two measurements are known – each calibration. The differences are
therefore divided by √3 to get the uncertainties. To get them as percentages they are divided
by last determined sensitivity and conversion efficiency, respectively. The total uncertainty in
the calibration is estimated to be 2.78 ± 8.05 % for NO, 3.44 ± 9.32 % for NO₂ using the BLC,
and 3.52 ± 8.67 % for NO₂ using the PLC for the calibrations between January 2014 and August
2019. The individual terms and final uncertainties in the calibrations are summarized in table
S1.
Table S1: Calculated uncertainties associated with the calibrations. The values in bold are the combined uncertainties for each type of measurement. Each uncertainty is given as the mean uncertainty ± 2 standard deviation of the calibration data between January 2014 and August 2019 for NO and from March 2017 to August 2019 for both NO\textsubscript{2} measurements.

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>Probability distribution</th>
<th>Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>Normal</td>
<td>1.00</td>
</tr>
<tr>
<td>Calibration gas concentration</td>
<td>Normal</td>
<td>1.00</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Normal</td>
<td>0.16 ± 0.11</td>
</tr>
<tr>
<td>Drift Sensitivity</td>
<td>Rectangular</td>
<td>2.01 ± 8.45</td>
</tr>
<tr>
<td>CE BLC</td>
<td>Normal</td>
<td>0.44 ± 0.45</td>
</tr>
<tr>
<td>Drift CE BLC</td>
<td>Rectangular</td>
<td>1.24 ± 5.61</td>
</tr>
<tr>
<td>CE PLC</td>
<td>Normal</td>
<td>0.45 ± 0.39</td>
</tr>
<tr>
<td>Drift CE PLC</td>
<td>Rectangular</td>
<td>1.43 ± 4.86</td>
</tr>
<tr>
<td>Total Calibration uncertainty NO</td>
<td></td>
<td>2.78 ± 8.05</td>
</tr>
<tr>
<td>Total Calibration uncertainty NO\textsubscript{2} BLC</td>
<td></td>
<td>3.44 ± 9.32</td>
</tr>
<tr>
<td>Total Calibration uncertainty NO\textsubscript{2} PLC</td>
<td></td>
<td>3.52 ± 8.67</td>
</tr>
</tbody>
</table>

The NO artefact is determined every night using the measurements between 21.00-03.00 UTC-1 (local time). The uncertainty can be described by a normal distribution and the uncertainty is, therefore, estimated from the standard deviation and number of the measurements used to determine the artefact. The NO\textsubscript{2} artefact is determined from measurements of PAG Zero air every 61 hours, where only 3 measurements are used for the artefact. The uncertainty is assumed to be rectangular due to the low amount of measurements used. The difference between the highest and lowest of the PAG Zero measurements is used to get the full-width. As the BLC artefact is corrected using the PLC measurement, the uncertainty in the correction is also determined in the same way and used in the propagation of uncertainties. The drift between the artefacts is estimated in the same way as the drift between the calibrations assuming a rectangular probability distribution. The total uncertainty in the NO and NO\textsubscript{2} BLC artefacts are estimated to be 1.1 ± 3.4 ppt and 7.2 ± 7.2 ppt, respectively. The individual terms and final uncertainties in the artefacts are summarized in Table S2.

Table S2: Calculated uncertainties associated with the artefact determinations. The values in bold are the combined uncertainties for each type of measurement. Each uncertainty is given...
as the mean uncertainty ± 2 standard deviation of the artefact data between January 2014 and August 2019 for NO and from March 2017 to August 2019 for both NO$_2$ measurements.

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>Probability distribution</th>
<th>Uncertainty (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO artefact</td>
<td>Normal</td>
<td>0.6 ± 1.1</td>
</tr>
<tr>
<td>Drift NO artefact</td>
<td>Rectangular</td>
<td>0.7 ± 3.4</td>
</tr>
<tr>
<td>Total NO artefact uncertainty</td>
<td></td>
<td><strong>1.1 ± 3.4</strong></td>
</tr>
<tr>
<td>NO$_2$ artefact</td>
<td>Rectangular</td>
<td>4.6 ± 5.6</td>
</tr>
<tr>
<td>NO$_2$ artefact correction</td>
<td>Rectangular</td>
<td>0.1 ± 1.6</td>
</tr>
<tr>
<td>Drift NO$_2$ artefact</td>
<td>Rectangular</td>
<td>3.0 ± 6.7</td>
</tr>
<tr>
<td>Total NO$_2$ artefact uncertainty</td>
<td></td>
<td><strong>7.2 ± 7.2</strong></td>
</tr>
</tbody>
</table>

Lastly, the uncertainty associated with correcting the measurements for O$_3$ reactions in the inlet is estimated from the uncertainties in the rate coefficient and the O$_3$ concentration. The rate coefficient used is $1.8 \times 10^{-14}$ with an uncertainty of 20% at 298K, which has been evaluated based on 6 studies of the reaction (Atkinson et al., 2004). The uncertainty in the O$_3$ concentration is ±0.07 ppb. With measured concentrations in the range 5-60 ppb, the uncertainty becomes 0.1-1.4%. The combined uncertainty using propagation of uncertainties, therefore, becomes 20 ± 0.001%.

The total hourly uncertainty for each of the three measurements are determined by combining all the uncertainties described using propagation of uncertainties as described in equation SXXXII. The precisions are already calculated as hourly precisions in ppt. The calibration uncertainties are interpolated between each calibration and multiplied by the hourly concentrations of NO and NO$_2$ to get hourly uncertainties in ppt. The artefact uncertainties are interpolated between each artefact determination. And the uncertainty due to ozone corrections are determined by multiplying the determined uncertainties in percentage with the hourly concentrations of NO and NO$_2$. The hourly uncertainties are determined to be 1.4 ± 1.5 ppt, 8.4 ± 7.5 ppt, and 4.4 ± 5.8 ppt for NO, NO$_2$ BLC, and NO$_2$ PLC, respectively.
4. FLEXPART

Back-trajectories are produced using FLEXPART, a Lagrangian particle dispersion model (Pisso et al., 2019; Stohl et al., 1998). Although originally designed to simulate dispersion of pollutants from a point source, FLEXPART has been developed into a comprehensive tool for simulating atmospheric transport. FLEXPART is run offline using meteorological reanalyses or forecasts and can be run either forwards or backwards in time, sampling particles on a global longitude-latitude-altitude grid and enabling analysis of the source regions of a plume (Stohl et al., 2003). The planetary boundary layer (PBL) height is calculated using a Richardson number threshold (Vogelezang and Holtslag, 1996), turbulence is parameterised using the standard gaussian model (Pisso et al., 2019) and the convection parameterisation is based on Emanuel and Živković-Rothman (1999). FLEXPART has been extensively evaluated and shown to be a useful and reliable resource (Forster et al., 2007; Forster et al., 2001; Stohl et al., 1998; Stohl and Trickl, 1999), particularly for investigating transport and sources of pollution (Gressent et al., 2014; Sauvage et al., 2017).

Here, FLEXPART version 10.4 is used in backwards mode, driven by pressure level data from Global Forecast System (GFS) reanalyses at 0.5°×0.5° resolution. 10-day back-trajectory simulations are initialised every 6 hours, releasing 1000 particles from the CVAO site.
5. Supplementary Figures:

![Diagram of the PLC (not to scale). The quartz tube (length = 20 cm, diameter = 1.0 cm, volume = 16 cm³) is held in place by a clamp and clamp stand. Two Hamamatsu Lightningcure V3 diodes (λ = 385 nm) are positioned with the light source facing towards the tube, leaving approximately 2 mm distance between the diode and the glass window of the tube. Diodes are held in place with a clamp and clamp stand.](image-url)
Figure S3: Percentage of NO\textsubscript{x} in the calibration cylinder measured as NO\textsubscript{2} between January 2014 and August 2019. The black circles symbolise the measurements made by the BLC and the red circles symbolise the measurements made by the PLC.
Figure S4: Calculated sensitivities between January 2014 and August 2019.
Figure S5: Calculated conversion efficiencies for the BLC (black) and PLC (red) from January 2014 to August 2019.
Figure S6: The efficiency of the zero volume plotted over time from January 2014 to August 2019.
Figure S7: NO artefact from January 2014 to August 2019, where the black is the average night time measurements and the red are the measurements from the pure air generator (PAG). The PAG measurements can be observed to be significantly higher than the nocturnal measurements in 2019, which can be explained by issues with the compressor supplying the PAG. In 2016 it can be observed to be significantly lower than the nocturnal measurements, which could be due to contaminations, however, the NO\textsubscript{2} measurements from the PAG (figure S8) are not significantly different from other measurements, suggesting an interference in the background measurement during that period.
Figure S8: NO$_2$ PAG artefact measurements from January 2014 to August 2019, where the black is the PLC measurements and the red is the BLC measurements before correcting for NO$_2$ in the PAG air.
Figure S9: NO diurnals for August 2017-July 2018. The coloured area is ±2 standard errors. If there are less than 15 measurements available for the hour, it is not included.
Figure S10: NO$_2$ diurnals for August 2017-July 2018 for the BLC (black) and PLC (red). The coloured area is ±2 standard errors. If there are less than 15 measurements available for the hour, it is not included.
Figure S1: Wind speed diurnals for August 2017-July 2018. The coloured area is ±2 standard errors. If there are less than 15 measurements available for the hour, it is not included.
Figure S12: NOₓ diurnals for August 2017-July 2018. The coloured area is ±2 standard errors. If there are less than 15 measurements available for the hour, it is not included.
6. References


