



Supplement of

Long-term NO_x measurements in the remote marine tropical troposphere

Simone T. Andersen et al.

Correspondence to: Simone T. Andersen (sta516@york.ac.uk)

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15 1. O₃ Correction:

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



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

24

25 1.1 NO correction

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

$$29 \quad \frac{d[\text{NO}]}{dt} = -k_{\text{NO}+\text{O}_3}[\text{O}_3][\text{NO}] = -k_{\text{O}_3}[\text{NO}] \quad (\text{SI})$$

30 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
31 reaction cell ($t = t_{\text{E1}}$) the following is obtained:

$$32 \quad \ln\left(\frac{[\text{NO}]_{\text{E1}}}{[\text{NO}]_0}\right) = -k_{\text{O}_3} \times t_{\text{E1}} \quad (\text{SII})$$

$$33 \quad [\text{NO}]_0 = [\text{NO}]_{\text{E1}} \times e^{k_{\text{O}_3} \times t_{\text{E1}}} \quad (\text{SIII})$$

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

36

37 1.2 NO₂ correction

38 NO₂ is measured by converting it photolytically into NO and reacting the NO with O₃ to
39 produce excited state NO₂ which emits chemiluminescent light as it drops to the ground state.

40 The measured mixing ratio of NO₂ is calculated from the NO signals with ([NO]_{E2}) and without
 41 ([NO]_{E1}) the converter on and the conversion efficiency of the converter (S_C):

$$42 \quad [\text{NO}_2]_{\text{M}} = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}}}{S_{\text{C}}} \quad (\text{SIV})$$

43 To correct the measured NO₂ mixing ratio for reactions with O₃, the following needs to be
 44 taken into account:

- 45 - NO reacts with O₃ in the line before reaching the converter
- 46 - NO₂ is photolysed into NO at the same time as NO continues to react with O₃ inside
 47 the converter

48 The photo-stationary state of NO and NO₂ inside the converter can be described by the
 49 following equations:

$$50 \quad [\text{NO}]_{\text{PSS}} = [\text{NO}]_0 + \Delta\text{NO} \quad (\text{SV})$$

$$51 \quad [\text{NO}_2]_{\text{PSS}} = [\text{NO}_2]_0 - \Delta\text{NO}_2 \quad (\text{SVI})$$

52 Where [NO]_{PSS} and [NO₂]_{PSS} are the photo-stationary state mixing ratios of NO and NO₂,
 53 respectively, [NO]₀ and [NO₂]₀ are the mixing ratios of NO and NO₂ at the entrance of the
 54 inlet, and ΔNO and ΔNO₂ are the change in NO and NO₂ inside the converter. The change in
 55 NO and NO₂ will be equal since the only reactions occurring are reactions (S1) and (S2). Thus,
 56 the photo-stationary state can be written as:

$$57 \quad [\text{NO}]_{\text{PSS}} = [\text{NO}]_0 + [\text{NO}_2]_0 - [\text{NO}_2]_{\text{PSS}} \quad (\text{SVII})$$

$$58 \quad [\text{NO}_2]_{\text{PSS}} = [\text{NO}_2]_0 - ([\text{NO}]_{\text{PSS}} - [\text{NO}]_0) = [\text{NO}_2]_0 + [\text{NO}]_0 - [\text{NO}]_{\text{PSS}} \quad (\text{SVIII})$$

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

$$61 \quad k_{\text{O}_3} \times [\text{NO}]_{\text{PSS}} = J_{\text{C}} \times [\text{NO}_2]_{\text{PSS}} \quad (\text{SIX})$$

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

$$64 \quad [\text{NO}]_{\text{PSS}} = \frac{J_{\text{C}}}{k_{\text{O}_3}} \times [\text{NO}_2]_{\text{PSS}} = \frac{J_{\text{C}}}{k_{\text{O}_3}} \times ([\text{NO}_2]_0 + [\text{NO}]_0 - [\text{NO}]_{\text{PSS}}) \quad (\text{SX})$$

$$65 \quad [\text{NO}]_{\text{PSS}} = \frac{J_{\text{C}}}{k_{\text{O}_3}} \times ([\text{NO}_2]_0 + [\text{NO}]_0) - \frac{J_{\text{C}}}{k_{\text{O}_3}} \times [\text{NO}]_{\text{PSS}} \quad (\text{SXI})$$

$$66 \quad \left(1 + \frac{J_C}{k_{O_3}}\right) \times [NO]_{PSS} = \left(\frac{k_{O_3} + J_C}{k_{O_3}}\right) \times [NO]_{PSS} = \frac{J_C}{k_{O_3}} \times ([NO_2]_0 + [NO]_0) \quad (SXII)$$

$$67 \quad [NO]_{PSS} = \left(\frac{k_{O_3}}{k_{O_3} + J_C}\right) \times \frac{J_C}{k_{O_3}} \times ([NO_2]_0 + [NO]_0) = \left(\frac{J_C}{k_{O_3} + J_C}\right) \times ([NO_2]_0 + [NO]_0) \quad (SXIII)$$

68 By combining equations (SIX) and (SXIII), the photo-stationary state of NO₂ in the
69 converter can be obtained:

$$70 \quad [NO_2]_{PSS} = \frac{k_{O_3}}{J_C} [NO]_{PSS} = \frac{k_{O_3}}{J_C} \times \left(\frac{J_C}{k_{O_3} + J_C}\right) \times ([NO_2]_0 + [NO]_0) \quad (SXIV)$$

$$71 \quad [NO_2]_{PSS} = \left(\frac{k_{O_3}}{k_{O_3} + J_C}\right) \times ([NO_2]_0 + [NO]_0) \quad (SXV)$$

72 The photolysis rate inside the converter is given by:

$$73 \quad J_C = \frac{-\ln(1 - S_C)}{t_{C2}} \quad (SXVI)$$

74 where t_{C2} is the time the air is in the converter while it is on.

75 Inside the converter, the NO mixing ratio moves towards photo-stationary state ([NO]_{PSS})
76 with a rate of k_{O3} + J_C since some of the NO₂ being photolysed to NO in the converter will react
77 with O₃ in the sample to regenerate NO₂. This can be described by equation (SXVII), where
78 [NO]_L is the NO mixing ratio at the entrance of the converter:

$$79 \quad [NO]_{E2} = [NO]_{PSS} - ([NO]_{PSS} - [NO]_L) \times e^{\{-(k_{O_3} + J_C) \times t_{C2}\}} \quad (SXVII)$$

$$80 \quad [NO]_{E2} = [NO]_{PSS} - [NO]_{PSS} \times e^{\{-(k_{O_3} + J_C) \times t_{C2}\}} + [NO]_L \times e^{\{-(k_{O_3} + J_C) \times t_{C2}\}} \quad (SXVIII)$$

$$81 \quad [NO]_{E2} = [NO]_{PSS} \times (1 - e^{\{-(k_{O_3} + J_C) \times t_{C2}\}}) + [NO]_L \times e^{\{-(k_{O_3} + J_C) \times t_{C2}\}} \quad (SXIX)$$

82 The NO mixing ratio at the entrance of the converter can be estimated from the loss of NO
83 to O₃ in the line in the same way as the ozone corrected NO mixing ratio could be determined:

$$84 \quad [NO]_L = [NO]_0 \times e^{(-k_{O_3} \times t_L)} = [NO]_{E1} \times e^{(k_{O_3} \times t_{E1})} \times e^{(-k_{O_3} \times t_L)} \quad (SXX)$$

$$85 \quad [NO]_L = [NO]_{E1} \times e^{(k_{O_3} \times t_{C1})} \quad (SXXI)$$

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

$$87 \quad [NO]_{E2} = [NO]_{PSS} \times (1 - e^{\{-(k_{O_3} + J_C) \times t_{C2}\}}) + [NO]_{E1} \times e^{\{-(k_{O_3} + J_C) \times t_{C2} + k_{O_3} \times t_{C1}\}} \quad (SXXII)$$

88 [NO]_{PSS} is isolated to give equation (SXXIII):

$$89 \quad [\text{NO}]_{\text{PSS}} = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}} \times e^{-(k_{\text{O}_3} + J_{\text{C}}) \times t_{\text{C2}} + k_{\text{O}_3} \times t_{\text{C1}}}}{1 - e^{-(k_{\text{O}_3} + J_{\text{C}}) \times t_{\text{C2}}}} \quad (\text{SXXIII})$$

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

$$92 \quad \frac{J_{\text{C}}}{J_{\text{C}} + k_{\text{O}_3}} \times ([\text{NO}]_0 + [\text{NO}_2]_0) = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}} \times e^{-(k_{\text{O}_3} + J_{\text{C}}) \times t_{\text{C2}} + k_{\text{O}_3} \times t_{\text{C1}}}}{1 - e^{-(k_{\text{O}_3} + J_{\text{C}}) \times t_{\text{C2}}}} \quad (\text{SXXIV})$$

$$93 \quad [\text{NO}_2]_0 = \left(\frac{J_{\text{C}} + k_{\text{O}_3}}{J_{\text{C}}} \right) \times \left(\frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}} \times e^{-(k_{\text{O}_3} + J_{\text{C}}) \times t_{\text{C2}} + k_{\text{O}_3} \times t_{\text{C1}}}}{1 - e^{-(k_{\text{O}_3} + J_{\text{C}}) \times t_{\text{C2}}}} \right) - [\text{NO}]_0 \quad (\text{SXXV})$$

94

95 1.3 Low O₃ concentration

96 At low O₃ concentrations k_{O_3} tends towards 0 and becomes very small compared to J_{C} ,
97 such that the calculations for NO and NO₂ become:

$$98 \quad [\text{NO}]_0 = [\text{NO}]_{\text{E1}} \quad (\text{SXXVI})$$

$$99 \quad [\text{NO}_2]_0 = \left(\frac{J_{\text{C}}}{J_{\text{C}}} \right) \times \left(\frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}} \times e^{-J_{\text{C}} \times t_{\text{C2}}}}{1 - e^{-J_{\text{C}} \times t_{\text{C2}}}} \right) - [\text{NO}]_{\text{E1}} \quad (\text{SXXVII})$$

$$100 \quad [\text{NO}_2]_0 = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}} \times e^{-J_{\text{C}} \times t_{\text{C2}}} - [\text{NO}]_{\text{E1}} + [\text{NO}]_{\text{E1}} \times e^{-J_{\text{C}} \times t_{\text{C2}}}}{1 - e^{-J_{\text{C}} \times t_{\text{C2}}}} \quad (\text{SXXVIII})$$

$$101 \quad [\text{NO}_2]_0 = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}}}{1 - e^{-J_{\text{C}} \times t_{\text{C2}}}} = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}}}{1 - e^{\left\{ -\left(\frac{-\ln(1 - S_{\text{C}})}{t_{\text{C2}}} \right) \times t_{\text{C2}}} \right\}}} = \frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}}}{S_{\text{C}}} \quad (\text{SXXIX})$$

102

103 1.4 Example calculation

104 An example calculation of the O₃ corrections is shown below, assuming a conversion efficiency
105 of 50% ($S_{\text{C}} = 50\%$), a time of 3.3s from the inlet to the converter ($t_{\text{L}} = 3.3\text{s}$), a residence time
106 of 1s for the sample in the converter whether the converter is on or not ($t_{\text{C1}} = t_{\text{C2}} = 1\text{s}$), an ozone
107 mixing ratio of 30 ppb, a temperature of at 298K and therefore, using $k(\text{O}_3 + \text{NO}) = 1.8 \times 10^{-14}$
108 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a $k_{\text{O}_3} = 0.013 \text{ s}^{-1}$.

109 We start with uncorrected mixing ratios (i.e. measured mixing ratios) of $[\text{NO}]_{\text{M}} = 10 \text{ ppt}$ and
110 $[\text{NO}_2]_{\text{M}} = 30 \text{ ppt}$:

$$111 \quad [\text{NO}]_{\text{E1}} = 10 \text{ ppt}$$

112 $[\text{NO}]_{\text{E2}} = 30\text{ppt} \times 0.5 + 10\text{ppt} = 25\text{ppt}$

113 $J_{\text{C}} = \frac{-\ln(1 - S_{\text{C}})}{t_{\text{C2}}} = \frac{-\ln(1 - 0.5)}{1\text{s}} = 0.69 \text{ s}^{-1}$

114 $[\text{NO}]_0 = [\text{NO}]_{\text{E1}} \times e^{k_{\text{O3}} \times t_{\text{E1}}} = 10 \text{ ppt} \times e^{0.013\text{s}^{-1} \times 4.3\text{s}} = 10.6 \text{ ppt}$

115
$$[\text{NO}_2]_0 = \left(\frac{J_{\text{C}} + k_{\text{O3}}}{J_{\text{C}}} \right) \times \left(\frac{[\text{NO}]_{\text{E2}} - [\text{NO}]_{\text{E1}} \times e^{\{-(k_{\text{O3}}+J_{\text{C}}) \times t_{\text{C2}} + k_{\text{O3}} \times t_{\text{C1}}\}}}{1 - e^{\{-(k_{\text{O3}}+J_{\text{C}}) \times t_{\text{C2}}\}}} \right) - [\text{NO}]_0$$

116
$$= \left(\frac{0.69\text{s}^{-1} + 0.013}{0.69\text{s}^{-1}} \right)$$

117
$$\times \left(\frac{25\text{ppt} - 10\text{ppt} \times e^{\{-(0.013\text{s}^{-1} + 0.69\text{s}^{-1}) \times 1\text{s} + 0.013\text{s}^{-1} \times 1\text{s}\}}}{1 - e^{\{-(0.013\text{s}^{-1} + 0.69\text{s}^{-1}) \times 1\text{s}\}}} \right) - 10.6 \text{ ppt}$$

118
$$= 1.02 \times 39.6 - 10.6 = 29.7 \text{ ppt}$$

119 This gives a small increase in NO mixing ratio (0.6 ppt or 5.7%) and a small decrease (0.3
 120 ppt or 1%) in NO₂ mixing ratio under these conditions.

121

122 3. Uncertainty Analysis:

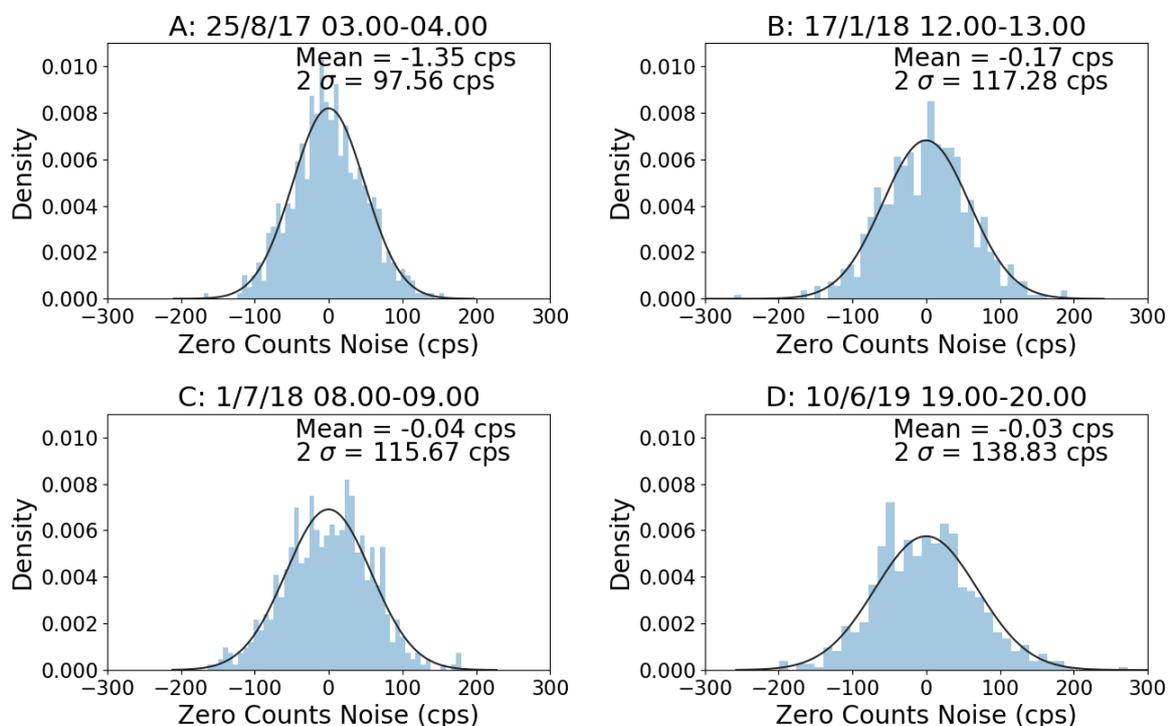
123 The uncertainty of a measurement is given as an interval at a confidence level, which
124 describes how certain it is that the true value is within the interval. The interval can be
125 determined from the spread of data, which can be described by several probability distributions.
126 The most common are normal and rectangular distributions. A normal distribution is used when
127 most of the measurements are centred around the mean. The signal-to-noise is reduced by
128 approximately $1/\sqrt{\text{(number of averaging points)}}$ when averaging the measurements. The
129 uncertainty in the mean of the measurements are estimated using equation (SXXX). To get an
130 uncertainty at the 95 percent confidence interval 2 standard deviations (σ) are used. A
131 rectangular distribution is when the probability of each measurement is equal. The 1σ
132 uncertainty is estimated from the half-width of the distribution and the 2σ uncertainty is
133 estimated from the full width of the distribution as shown in equation (SXXXI). The hourly
134 precision and uncertainty of the instrument are estimated to characterize the uncertainties at the
135 95 percent confidence interval (Bell, 2001).

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

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

138 The hourly precision is estimated from the zero count variability, which is directly related
139 to the photon-counting precision of the PMT. The hourly mean (\bar{x}) of the zero measurements
140 is subtracted from each individual measurement of the respective hour ($x - \bar{x}$) to give hourly
141 frequency distributions. Photon-counting frequency distributions are best described by a
142 Poisson distribution, however, at high photon-counting rates become indistinguishable from a
143 Gaussian distribution (Silvia and Skilling, 2006). With a yearly mean background count rate
144 of $\sim 1400\text{-}3000$ count s^{-1} between 2014 and 2019, the frequency distributions can be assumed
145 as Gaussian. Examples of hourly frequency distributions can be observed in figure S1. The
146 standard deviation of each hourly frequency distribution is calculated and divided by the
147 interpolated sensitivity to give a 2σ NO precision for 1 s data of 23.4 ± 20.3 ppt for the hours
148 between January 2014 and August 2019. The 2σ NO precision for hourly averaged data is 1.0
149 ± 0.9 ppt. The hourly precisions reported here are in good agreement with the previously
150 reported 1σ precision of 0.30 ppt (Reed et al., 2017) and the 2σ precision of 0.6-1.7 ppt (Lee et
151 al., 2009). The NO_2 precisions are determined by taking the conversion efficiency of the
152 respective converters into account. The hourly 2σ NO_2 precision for hourly averaged data

153 between March 2017 and August 2019 becomes 1.5 ± 0.8 ppt and 2.7 ± 2.2 ppt for the BLC
 154 and PLC, respectively. The determined NO₂ precisions are within the interval of previously
 155 reported precisions for the same instrument (Lee et al., 2009; Reed et al., 2017).



156
 157 Figure S1: Examples of hourly frequency distributions of the calculated zero variability.

158 The uncertainty of the hourly measurements is estimated by combining all the uncertainties
 159 associated with the measurements. This includes uncertainties in the calibrations, artefact
 160 determinations, and O₃ corrections as well as the precision of the instrument. The precision of
 161 the NO and NO₂ measurements are both included in the total uncertainty of the NO₂
 162 measurements as the NO measurements are subtracted from the NO₂ measurements. Each term
 163 is converted into ppt to be able to combine them. All the uncertainties are combined using
 164 uncertainty propagation:

165
$$\text{Accuracy} = \sqrt{\text{Precision}^2 + \text{Artefact}^2 + \text{Calibration}^2 + \text{O}_3 \text{ Correction}^2} \quad (\text{SXXXII})$$

166 Uncertainty in the calibrations is caused by uncertainty in the flow of calibration gas, the
 167 concentration of the calibration gas, the sensitivity, and the conversion efficiency as well as the
 168 drift in the sensitivity and conversion efficiency between each calibration. The total uncertainty
 169 in the calibrations is determined as the propagation of each term. Each term is calculated as a
 170 percentage to be able to combine them before converting the total calibration uncertainty to ppt
 171 to combine it with the other uncertainty terms. According to the manufacturers the sample and

172 calibration mass flow controllers have an uncertainty of 1%, which has been confirmed by a
 173 gillibrator bubble flowmeter. The uncertainty of the concentration of the NO standard used for
 174 calibration is known to $\pm 1\%$ (British Oxygen Company (BOC), certified to UK National
 175 Physical Laboratory (NPL) standard) (BOC certifies that NO/N₂ standards are stable for 5
 176 years). To estimate the uncertainty in the sensitivity and conversion efficiency, the
 177 uncertainties in each measurement used to determine them must be estimated. Equation IV and
 178 V describe the calculation of the sensitivity and conversion efficiency of the instrument,
 179 respectively. The spread of each type of measurement used can be described by a normal
 180 distribution. The percentage uncertainty in the sensitivity and the conversion efficiency can
 181 therefore be determined by equation SXXXIII and SXXXIV, respectively.

$$182 \quad \text{Sensitivity Uncertainty} = \frac{u_{\text{NO}(1)}}{\text{NO}(1)} \quad (\text{SXXXIII})$$

$$183 \quad \text{CE Uncertainty} = \sqrt{\left(\frac{u_{\text{NO.c}(1)}}{\text{NO.c}(1)}\right)^2 + \left(\frac{u_{\text{NO.c}(2)}}{\text{NO.c}(2)}\right)^2 + \left(\frac{u_{\text{NO}(1)}}{\text{NO}(1)}\right)^2 + \left(\frac{u_{\text{NO}(2)}}{\text{NO}(2)}\right)^2} \quad (\text{SXXXIV})$$

184 The drift between calibrations contains two terms; one for the sensitivity and one for the
 185 conversion efficiency when estimating the uncertainty for NO₂. Both terms are determined as
 186 the absolute difference between two measurements. The distribution is assumed to be
 187 rectangular as only two measurements are known – each calibration. The differences are
 188 therefore divided by $\sqrt{3}$ to get the uncertainties. To get them as percentages they are divided
 189 by last determined sensitivity and conversion efficiency, respectively. The total uncertainty in
 190 the calibration is estimated to be $2.78 \pm 8.05\%$ for NO, $3.44 \pm 9.32\%$ for NO₂ using the BLC,
 191 and $3.52 \pm 8.67\%$ for NO₂ using the PLC for the calibrations between January 2014 and August
 192 2019. The individual terms and final uncertainties in the calibrations are summarized in table
 193 S1.

194

195 Table S1: Calculated uncertainties associated with the calibrations. The values in bold are the
 196 combined uncertainties for each type of measurement. Each uncertainty is given as the mean
 197 uncertainty \pm 2 standard deviation of the calibration data between January 2014 and August
 198 2019 for NO and from March 2017 to August 2019 for both NO₂ measurements.

Source of uncertainty	Probability distribution	Uncertainty (%)
Flow	Normal	1.00
Calibration gas concentration	Normal	1.00
Sensitivity	Normal	0.16 \pm 0.11
Drift Sensitivity	Rectangular	2.01 \pm 8.45
CE BLC	Normal	0.44 \pm 0.45
Drift CE BLC	Rectangular	1.24 \pm 5.61
CE PLC	Normal	0.45 \pm 0.39
Drift CE PLC	Rectangular	1.43 \pm 4.86
Total Calibration uncertainty NO		2.78 \pm 8.05
Total Calibration uncertainty NO ₂ BLC		3.44 \pm 9.32
Total Calibration uncertainty NO ₂ PLC		3.52 \pm 8.67

199

200 The NO artefact is determined every night using the measurements between 21.00-03.00
 201 UTC-1 (local time). The uncertainty can be described by a normal distribution and the
 202 uncertainty is, therefore, estimated from the standard deviation and number of the
 203 measurements used to determine the artefact. The NO₂ artefact is determined from
 204 measurements of PAG Zero air every 61 hours, where only 3 measurements are used for the
 205 artefact. The uncertainty is assumed to be rectangular due to the low amount of measurements
 206 used. The difference between the highest and lowest of the PAG Zero measurements is used to
 207 get the full-width. As the BLC artefact is corrected using the PLC measurement, the uncertainty
 208 in the correction is also determined in the same way and used in the propagation of
 209 uncertainties. The drift between the artefacts is estimated in the same way as the drift between
 210 the calibrations assuming a rectangular probability distribution. The total uncertainty in the NO
 211 and NO₂ BLC artefacts are estimated to be 1.1 ± 3.4 ppt and 7.2 ± 7.2 ppt, respectively. The
 212 individual terms and final uncertainties in the artefacts are summarized in table S2.

213 Table S2: Calculated uncertainties associated with the artefact determinations. The values in
 214 bold are the combined uncertainties for each type of measurement. Each uncertainty is given

215 as the mean uncertainty ± 2 standard deviation of the artefact data between January 2014 and
216 August 2019 for NO and from March 2017 to August 2019 for both NO₂ measurements.

Source of uncertainty	Probability distribution	Uncertainty (ppt)
NO artefact	Normal	0.6 \pm 1.1
Drift NO artefact	Rectangular	0.7 \pm 3.4
Total NO artefact uncertainty		1.1 \pm 3.4
NO ₂ artefact	Rectangular	4.6 \pm 5.6
NO ₂ artefact correction	Rectangular	0.1 \pm 1.6
Drift NO ₂ artefact	Rectangular	3.0 \pm 6.7
Total NO ₂ artefact uncertainty		7.2 \pm 7.2

217

218 Lastly, the uncertainty associated with correcting the measurements for O₃ reactions in the
219 inlet is estimated from the uncertainties in the rate coefficient and the O₃ concentration. The
220 rate coefficient used is 1.8×10^{-14} with an uncertainty of 20% at 298K, which has been
221 evaluated based on 6 studies of the reaction (Atkinson et al., 2004). The uncertainty in the O₃
222 concentration is ± 0.07 ppb. With measured concentrations in the range 5-60 ppb, the
223 uncertainty becomes 0.1-1.4%. The combined uncertainty using propagation of uncertainties,
224 therefore, becomes $20 \pm 0.001\%$.

225 The total hourly uncertainty for each of the three measurements are determined by
226 combining all the uncertainties described using propagation of uncertainties as described in
227 equation SXXXII. The precisions are already calculated as hourly precisions in ppt. The
228 calibration uncertainties are interpolated between each calibration and multiplied by the hourly
229 concentrations of NO and NO₂ to get hourly uncertainties in ppt. The artefact uncertainties are
230 interpolated between each artefact determination. And the uncertainty due to ozone corrections
231 are determined by multiplying the determined uncertainties in percentage with the hourly
232 concentrations of NO and NO₂. The hourly uncertainties are determined to be 1.4 ± 1.5 ppt, 8.4
233 ± 7.5 ppt, and 4.4 ± 5.8 ppt for NO, NO₂ BLC, and NO₂ PLC, respectively.

234

235 4. FLEXPART

236 Back-trajectories are produced using FLEXPART, a Lagrangian particle dispersion model
237 (Pisso et al., 2019; Stohl et al., 1998). Although originally designed to simulate dispersion of
238 pollutants from a point source, FLEXPART has been developed into a comprehensive tool for
239 simulating atmospheric transport. FLEXPART is run offline using meteorological reanalyses
240 or forecasts and can be run either forwards or backwards in time, sampling particles on a global
241 longitude-latitude-altitude grid and enabling analysis of the source regions of a plume (Stohl
242 et al., 2003). The planetary boundary layer (PBL) height is calculated using a Richardson
243 number threshold (Vogelezang and Holtslag, 1996), turbulence is parameterised using the
244 standard gaussian model (Pisso et al., 2019) and the convection parameterisation is based on
245 Emanuel and Živković-Rothman (1999). FLEXPART has been extensively evaluated and
246 shown to be a useful and reliable resource (Forster et al., 2007; Forster et al., 2001; Stohl et al.,
247 1998; Stohl and Trickl, 1999), particularly for investigating transport and sources of pollution
248 (Gressent et al., 2014; Sauvage et al., 2017).

249 Here, FLEXPART version 10.4 is used in backwards mode, driven by pressure level data
250 from Global Forecast System (GFS) reanalyses at $0.5^\circ \times 0.5^\circ$ resolution. 10-day back-trajectory
251 simulations are initialised every 6 hours, releasing 1000 particles from the CVAO site.

5. Supplementary Figures:

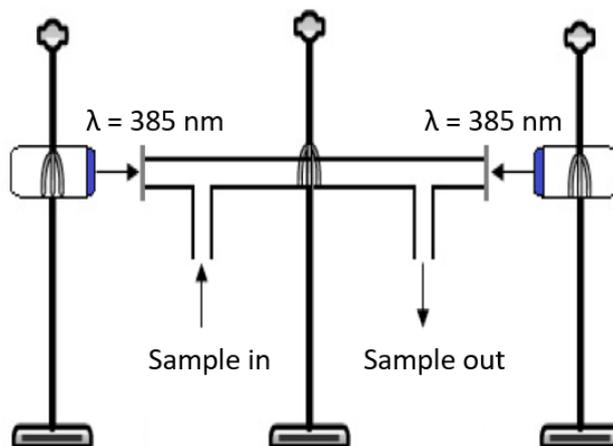


Figure S2: Diagram of the PLC (not to scale). The quartz tube (length = 20 cm, diameter = 1.0 cm, volume = 16 cm^3) is held in place by a clamp and clamp stand. Two Hamamatsu Lightningcure V3 diodes ($\lambda = 385 \text{ nm}$) are positioned with the light source facing towards the tube, leaving approximately 2 mm distance between the diode and the glass window of the tube. Diodes are held in place with a clamp and clamp stand.

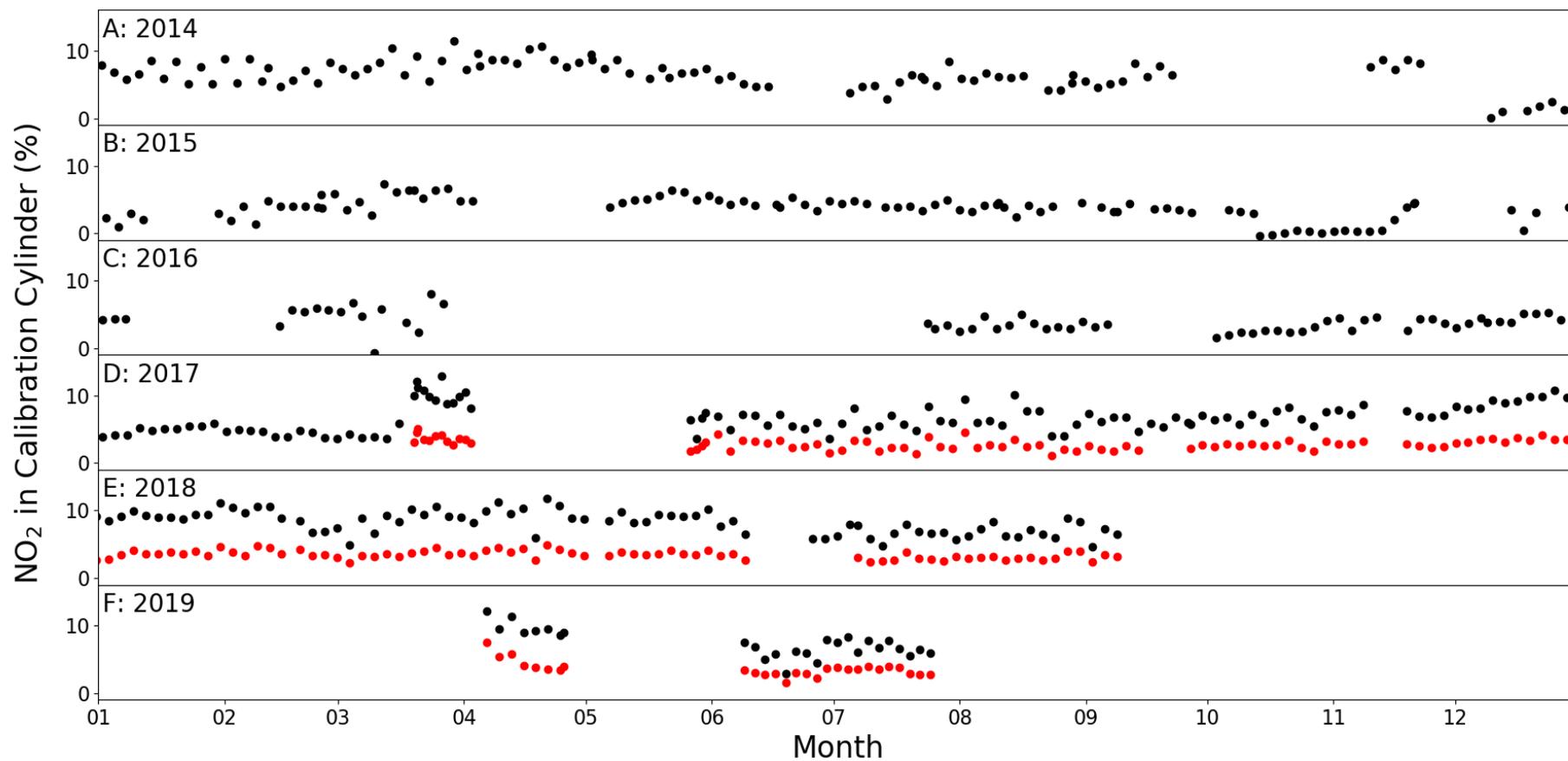


Figure S3: Percentage of NO_x in the calibration cylinder measured as NO₂ between January 2014 and August 2019. The black circles symbolise the measurements made by the BLC and the red circles symbolise the measurements made by the PLC.

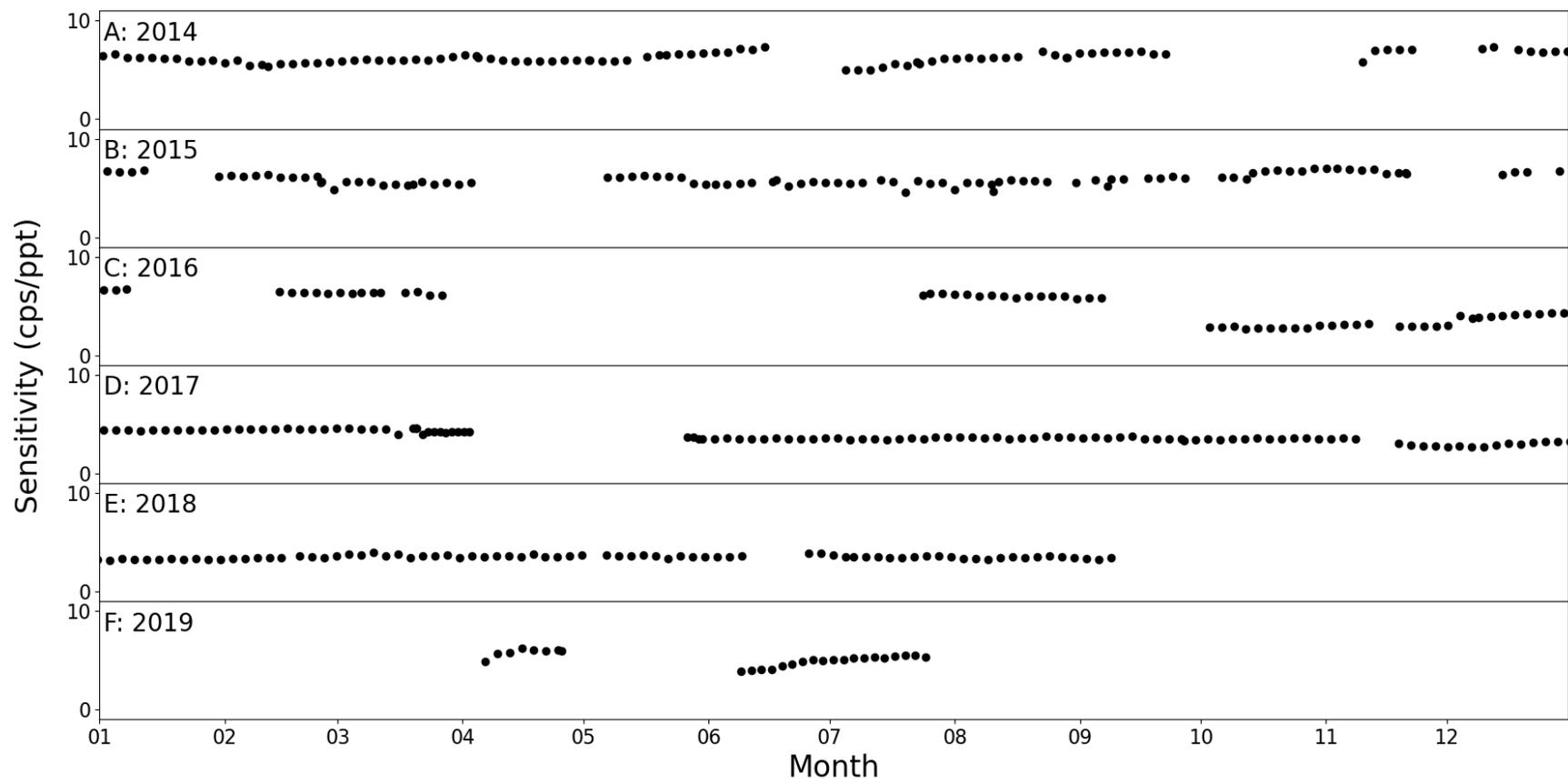


Figure S4: Calculated sensitivities between January 2014 and August 2019.

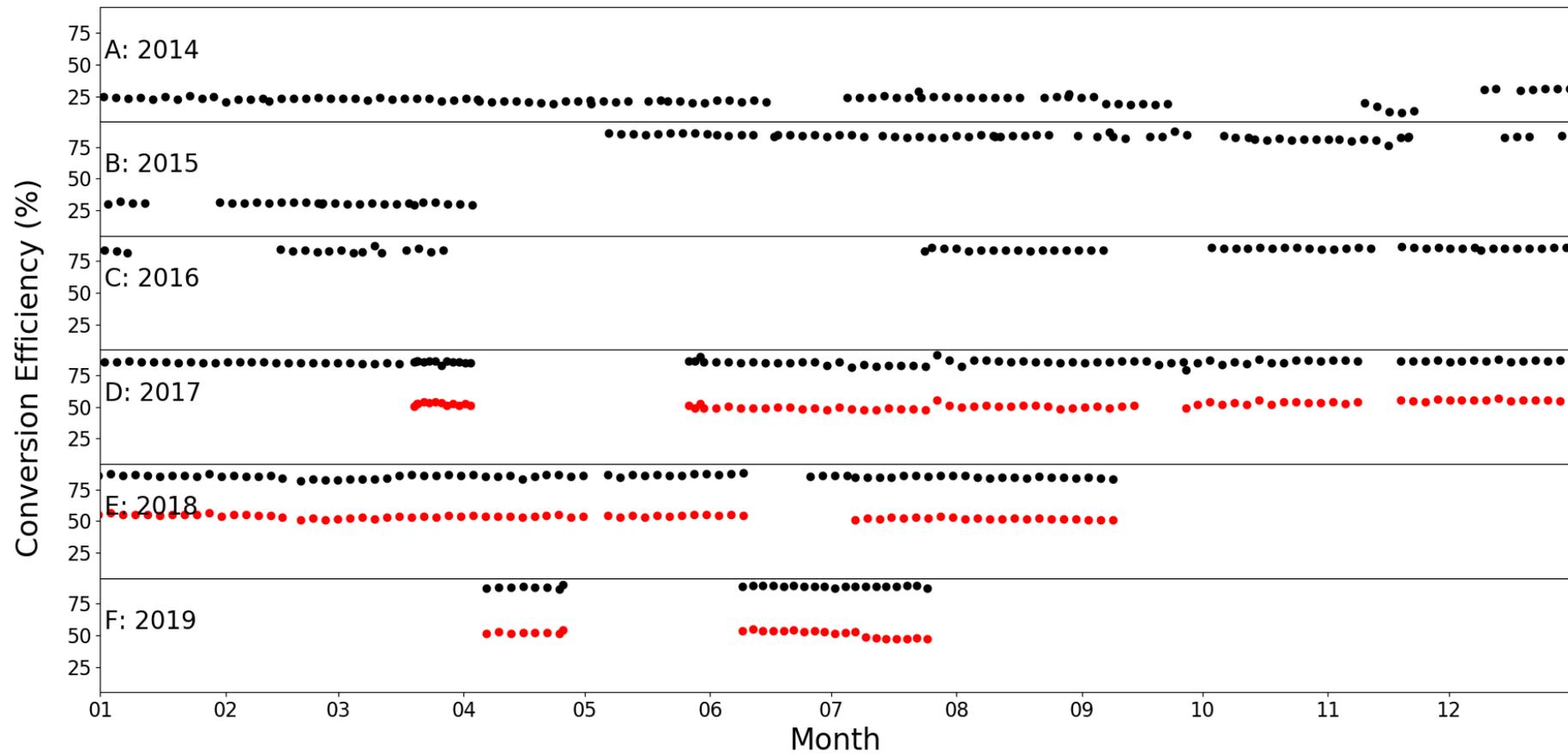


Figure S5: Calculated conversion efficiencies for the BLC (black) and PLC (red) from January 2014 to August 2019.

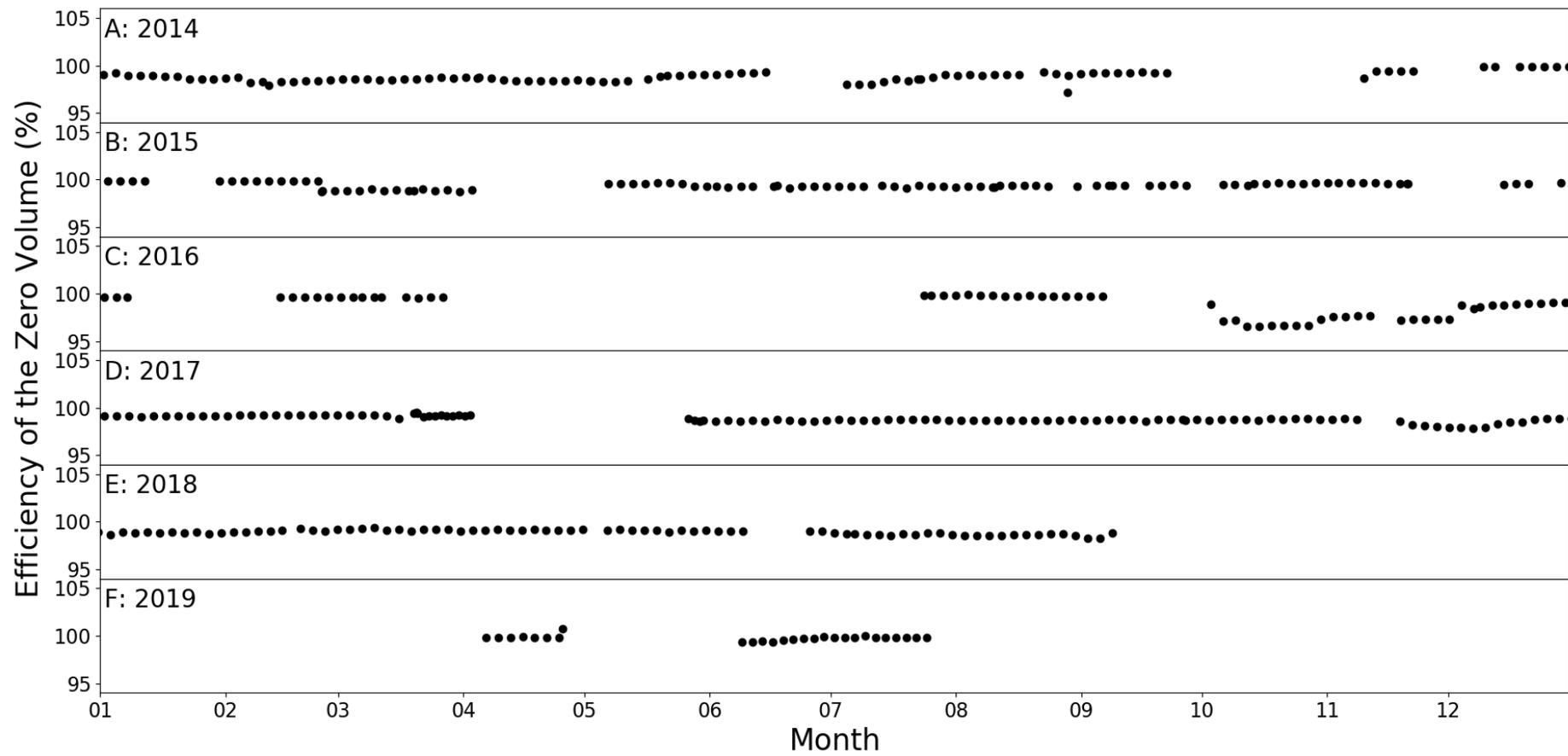


Figure S6: The efficiency of the zero volume plotted over time from January 2014 to August 2019.

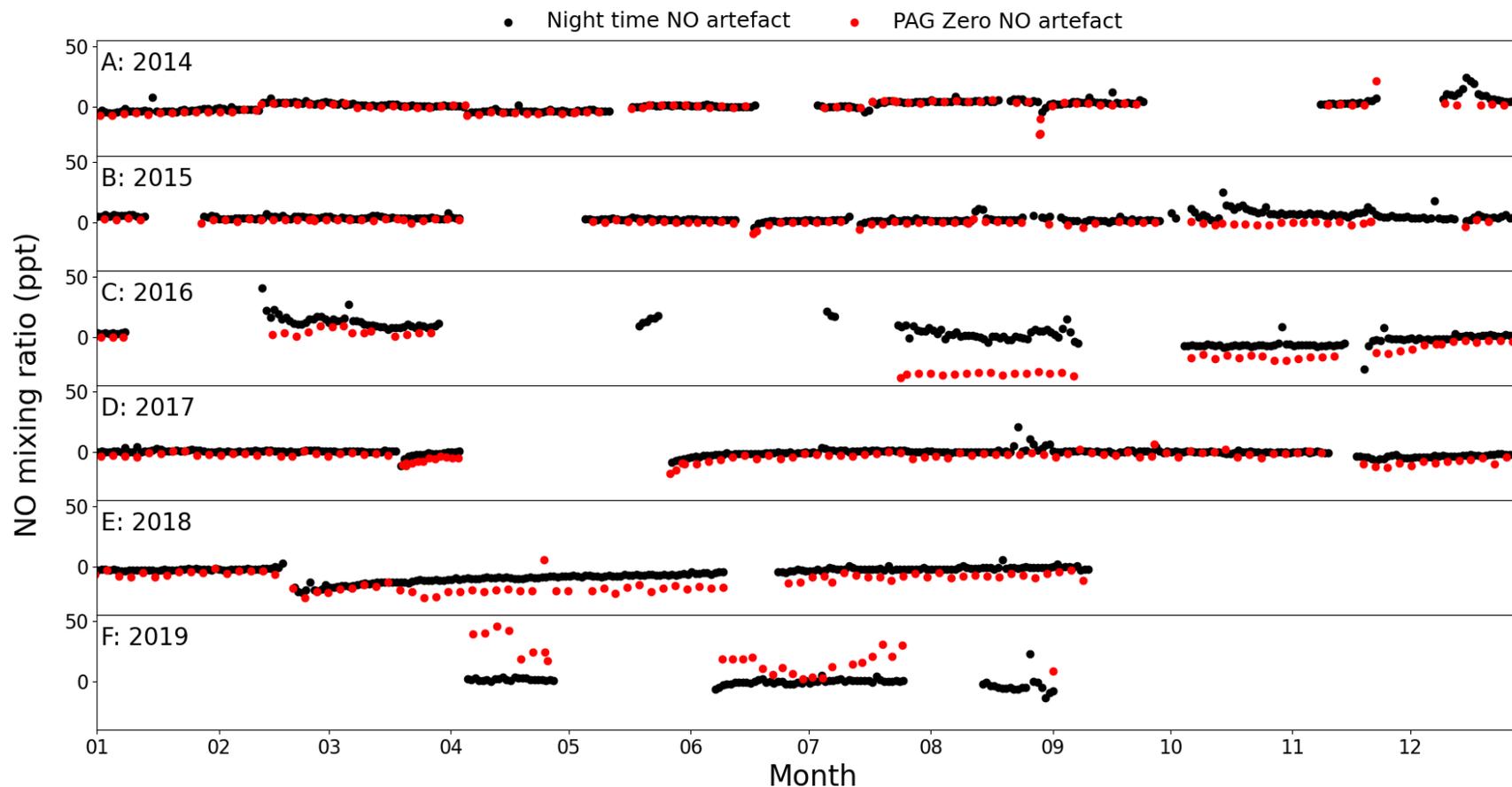


Figure S7: NO artefact from January 2014 to August 2019, where the black is the average night time measurements and the red are the measurements from the pure air generator (PAG). The PAG measurements can be observed to be significantly higher than the nocturnal measurements in 2019, which can be explained 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_2 measurements from the PAG (figure S8) are not significantly different from other measurements, suggesting an interference in the background measurement during that period.

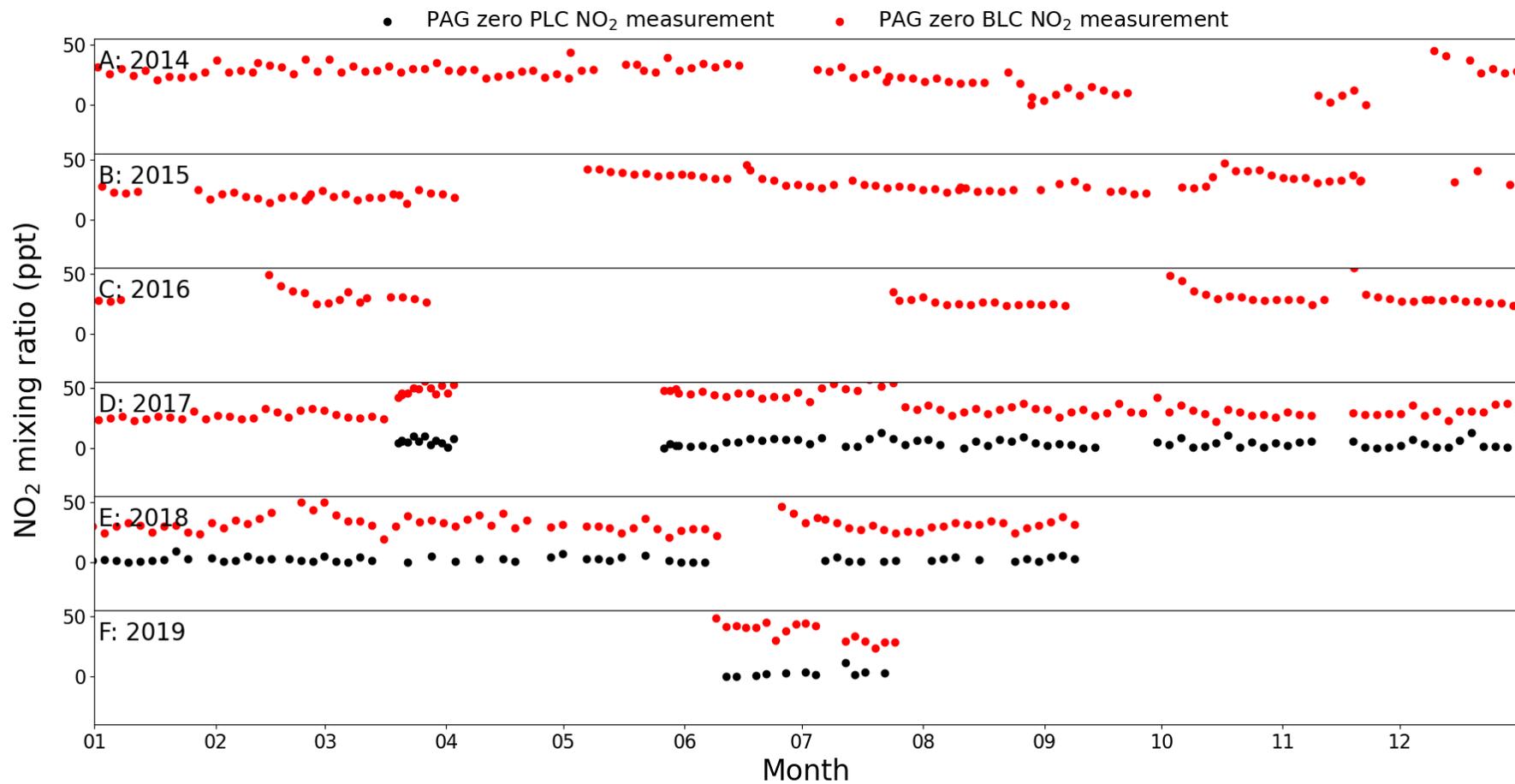


Figure S8: NO₂ PAG artefact measurements from January 2014 to August 2019, where the black is the PLC measurements and the red is the BLC measurements before correcting for NO₂ in the PAG air.

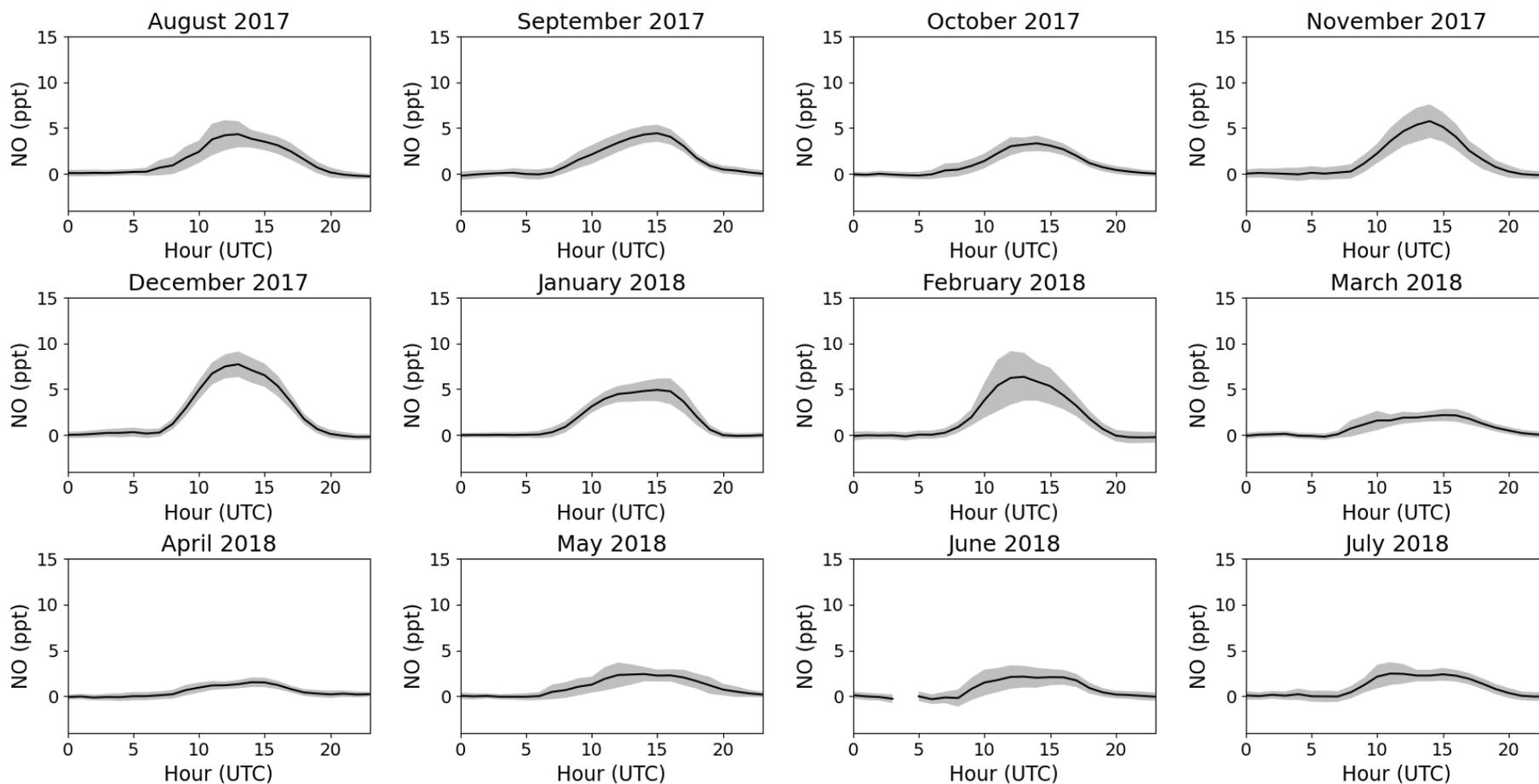


Figure S9: NO diurnals for August 2017-July 2018. The coloured area is ± 2 standard errors. If there are less than 15 measurements available for the hour, it is not included.

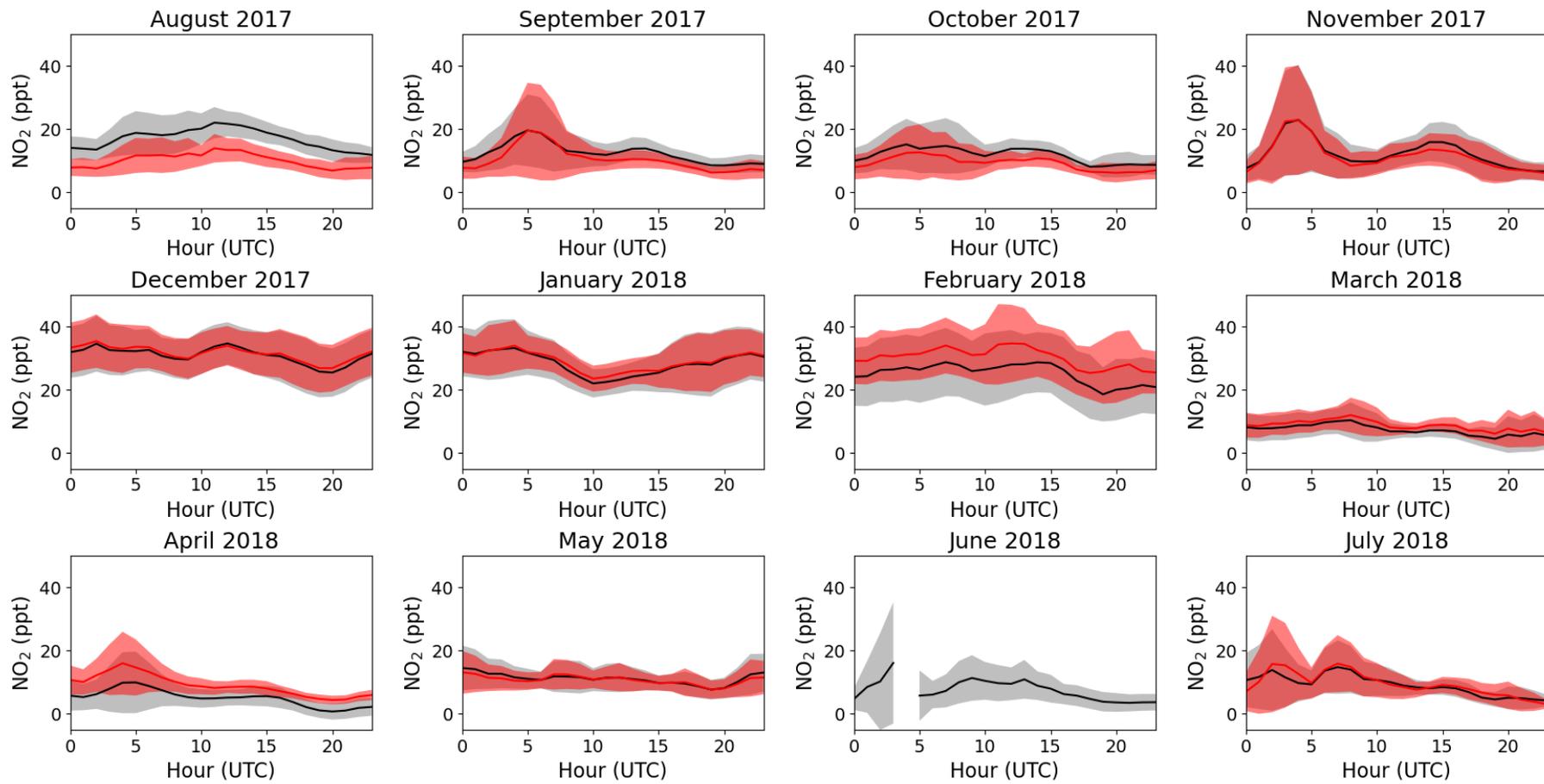


Figure S10: NO₂ diurnals for August 2017-July 2018 for the BLC (black) and PLC (red). The coloured area is ± 2 standard errors. If there are less than 15 measurements available for the hour, it is not included.

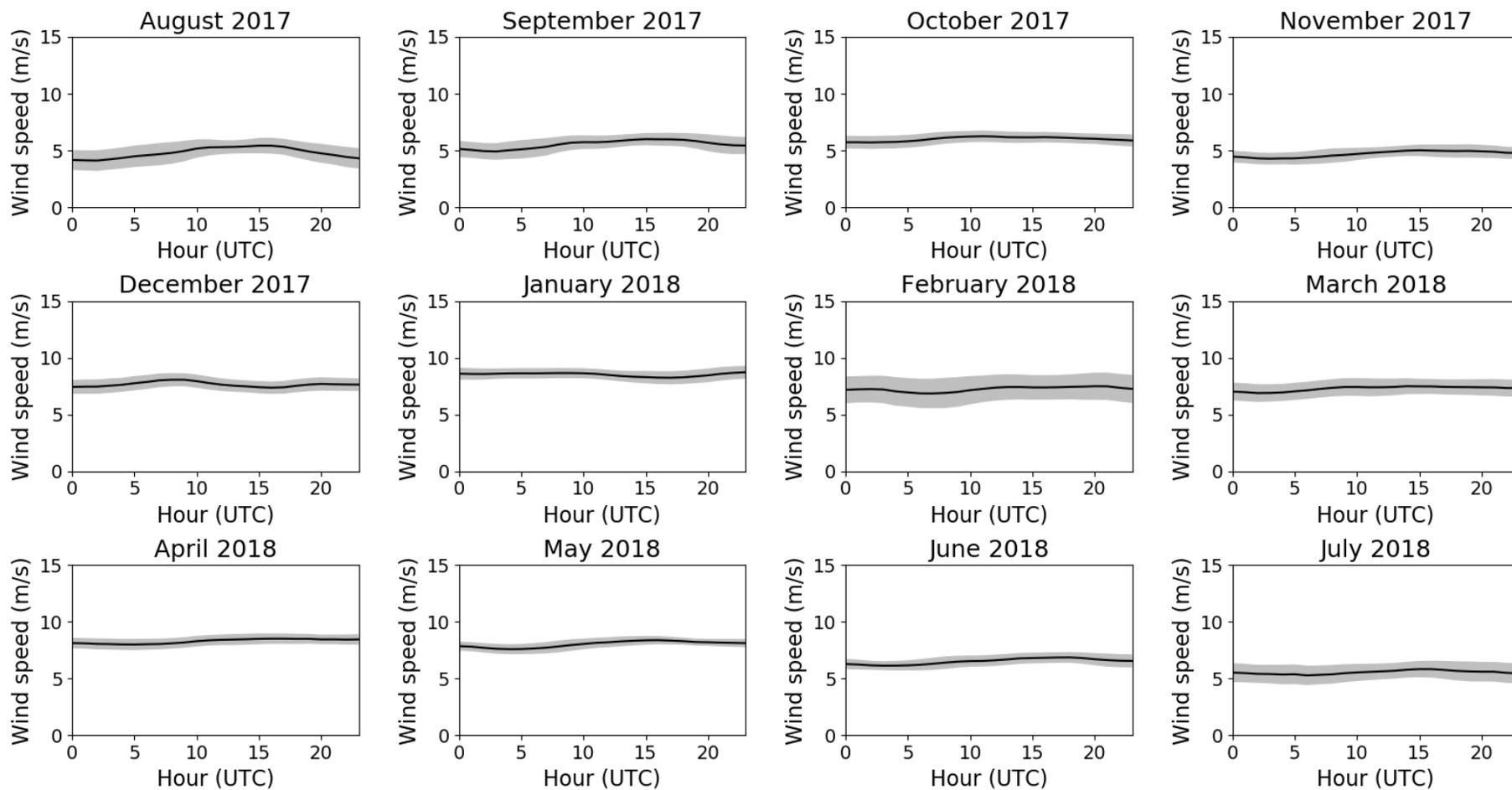


Figure S11: Wind speed diurnals for August 2017-July 2018. The coloured area is ± 2 standard errors. If there are less than 15 measurements available for the hour, it is not included.

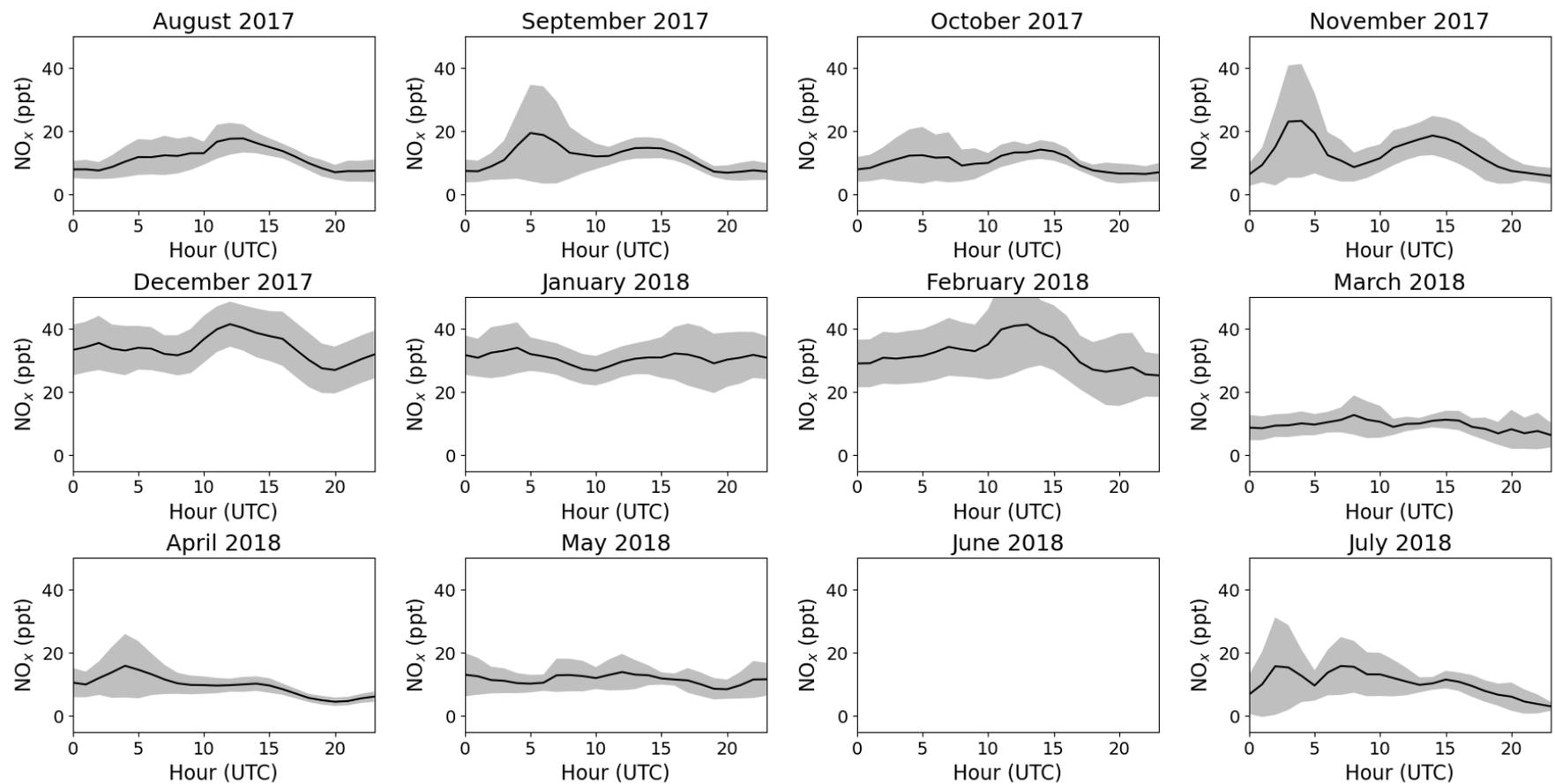


Figure S12: NO_x diurnals for August 2017-July 2018. The coloured area is ± 2 standard errors. If there are less than 15 measurements available for the hour, it is not included.

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