



Temporal changes in field calibration relationships for Aeroqual S500 O₃ and NO₂ sensor-based monitors

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ABSTRACT

Sensor-based monitors are increasingly used to measure air pollutant concentrations, but require calibration under field conditions. We made intermittent comparisons (6 times over a 6-month period) between ozone and nitrogen dioxide concentrations measured by Aeroqual gas-sensitive semiconductor (O₃) and electrochemical (NO₂) sensors (two of each) and reference analysers in the UK Automatic Urban and Rural Network. Each deployment period was split into equal ($n = 48 \times 1$ -hour) training and test datasets, to derive and test calibration equations respectively. We observed significant bivariate linear relationships between *Aeroqual* O₃ and *Reference* O₃ concentrations, and significant multiple linear relationships between *Aeroqual* NO₂ and both *Reference* NO₂ and *Aeroqual* O₃ concentrations. Changes in monitor responses over time (including apparent baseline drift in O₃ sensor output, and discrepancies between the 2 Aeroqual NO₂ sensors) resulted in relatively inaccurate concentrations estimates (*cf.* reference concentrations) from calibration equations derived in the first training period and applied to subsequent *test* deployments (*e.g.* NO₂ RMSE = 47.2 μg m⁻³ ($n = 286$) for a dataset of all *test* periods combined, for one of the two monitor pairs). Substantial improvements in accuracy of estimated concentrations were achieved by combination of repeated intermittent training data into a single calibration dataset (NO₂ RMSE = 8.5 μg m⁻³ for same *test* dataset described above). This latter approach to field calibration is recommended.

1. Introduction

The concentrations of gaseous air pollutants with deleterious health effects, including nitrogen dioxide (NO₂) and ozone (O₃), are monitored to estimate human exposure and to assess compliance with legislation and guidelines. Monitoring is usually conducted at static, automatic monitoring stations that record concentrations at high temporal resolution. However, the cost of these stations, together with practical considerations regarding suitable sites, invariably limits the spatial coverage of automatic networks. Wider geographical networks of passive diffusion samplers (PDS) can mitigate restrictions on spatial coverage [1,2]; however PDS provide limited temporal information, and can be subject to measurement inaccuracies associated with changing meteorological [3] and atmospheric chemistry conditions [4].

Battery-powered real-time hand-held sensor-based monitors for air

pollutants are continually being developed, which have potential to supplement data from existing monitoring networks [5]. Hand-held monitors usually have lower capital costs than automatic analysers, meaning that more could be made available for deployment, potentially increasing the spatial resolution of measurement networks with high temporal resolution concentration measurements [6–9]. The use of such instruments in mobile and personal monitoring has been reported [8,10].

The reference analysers in automatic monitoring stations are usually subject to documented quality control and assurance (QC/QA) procedures that aim to ensure the recorded pollutant concentrations are within specified ranges of accuracy and precision. The control of uncertainty requires resource and effort, so it is not unreasonable to anticipate that outputs from lower-cost, portable monitors are also subject to uncertainties, which may also vary with time. Thus, it is important that portable monitors are subject to

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calibration checks at least as much as reference analysers. An important additional potential limitation of gas sensor-based monitors is their cross-sensitivity to other pollutants and/or to changing environmental conditions [11,12]. For example, the responses of some electrochemical sensors have been shown to be susceptible to variations in temperature or relative humidity [8,13–15]. Sensors for NO₂ have been shown to be cross-sensitive to O₃, meaning that both pollutants must be measured simultaneously to allow correction of the NO₂ sensor response [8–10,16–18]. Consequently, for accurate estimation of ambient concentrations, sensor-based monitors require field calibration under representative ambient conditions.

In this study we evaluated the responses of two pairs of Aeroqual S500 O₃ and NO₂ monitors over time and repeated exposure to outdoor conditions, by deployment adjacent to reference gas analysers. The monitor deployments were designed to be representative of their likely use in practical field measurements: namely repeated cycles of calibration and monitoring (involving switching monitors on and off; removal from a reference site and use in other field measurements at different locations and mobile monitoring; and return to the reference monitoring site). Additionally, we investigated the effects of combination and timing of field calibration of the monitors on the accuracy of calibrated estimates. Our analyses provide insight to the refinement and use of field calibration relationships for these Aeroqual monitors in mobile measurements across geographical areas with widely varying pollution microclimates.

2. Methods

We evaluated two pairs of Aeroqual (www.aeroqual.com) S500 O₃ and NO₂ monitors at the UK Automatic Urban and Rural Network (AURN) Townhead urban background site in Glasgow city centre (55.866°N, 4.244°W; Location map given at: http://www.scottishairquality.co.uk/latest/site-info?site_id=GLKP). Although this site is in an urban background location it is within 1 km of a very busy motorway and intermittently experiences pollution episodes making it well-suited for calibration of sensors. Hourly-average concentration data from the reference analysers (API200A chemiluminescence analyser for NO₂ and Thermo 49i photometric analyser for O₃) at this site were downloaded from <http://www.scottishairquality.co.uk/>. All AURN measurements were subject to documented national QC/QA procedures [19].

The Aeroqual monitors were delivered to our laboratory in June 2014. We deployed the monitors within ventilated waterproof enclosures provided by Aeroqual by attaching to the galvanised steel safety railings surrounding the roof of the AURN monitoring cabin (Fig. A1 in Appendix A: Supplementary Information). The NO₂ monitors contained electrochemical sensors (ENW2, range 0–1 ppm) and are referred to as NO_{2.1} and NO_{2.2}. The O₃ monitors contained gas-sensitive semiconductor sensors (OZU2, range 0–0.15 ppm) and are referred to as O_{3.3} and O_{3.4}. Monitors NO_{2.1} and O_{3.3} were located next to one another on the eastern railing while monitors NO_{2.2} and O_{3.4} were located on the western railing. Mains power was available allowing the monitors to operate continuously. We set the monitors to record gravimetric concentrations (µg/m³) at 1-min intervals, prior to computation of hourly-average concentrations for comparison with the analysers.

Six separate monitor co-location deployment periods were undertaken intermittently over 6 months (November 2015–May 2016) (Table A1 in Supplementary material). We truncated each deployment period to the first 96 h of field deployment to simplify comparison between periods.

3. Results

3.1. Calibration of Aeroqual O₃ monitors

Aeroqual O₃ measurements closely followed temporal trends in the Reference O₃ concentrations, with O_{3.3} generally over-predicting and O_{3.4} generally under-predicting the analyser concentrations (Fig. 1).

We calibrated the response of the O₃ monitors by calculating Ordinary Least Squares (OLS) regression equations between unadjusted Aeroqual O₃ measurements and O₃ concentrations measured by the reference analyser. We compared three methods of calibration - in each method the first 48 h for each deployment period was used as ‘training’ data to generate calibration equations, and the second 48 h was used as ‘test’ data to evaluate the accuracy of the calibrated predictions.

- 1) The first calibration method used the training data [0–48 h] for each deployment period to correct the test data [48–96 h] for the same deployment period *i.e.* a *unique* calibration for each deployment period (referred to as ‘Aq_corr_u’). This method represented calibrations computed at close time intervals to the measurements being corrected.
- 2) The second calibration method used a combination of training data from *all* deployment periods to derive a single global calibration equation for each monitor, which was then applied to the training data for each period (referred to as ‘Aq_corr_a’). This method of calibration, involving interspersed intervals during the extended set of deployments, had a larger number of data points in the calibration, spread over a longer time period, and thus incorporated a larger range of pollution conditions.
- 3) The third calibration method used the calibration equation derived from the training data from the first study period (*November*) to correct the test data from all of the subsequent studies (referred to as ‘Aq_corr_N’). This method represented a ‘one-off pre-measurement campaign’ calibration, and was included to assess how the accuracy and precision of a single calibration might deteriorate over time during extended field measurements.

The calibration equations are summarised in Table 1 and are shown in Fig. A3 in Supplementary material. Similar to the findings observed by Lin et al. [16] we observed limited and inconsistent effects of temperature and relative humidity on the calibration regression equations across the monitors and deployments and therefore these meteorological variables were not included in our analyses.

The calibration equations calculated for each of the three methods were used to adjust the test data. We observed similar overall temporal patterns in the time series of adjusted Aeroqual and Reference O₃ concentrations (adjusted concentration estimates shown for both *training* and *test* data in Fig. A4 in Supplementary material). The Reference O₃ and adjusted Aeroqual O₃ concentrations deviated for a short period at the end of the December deployment, when the reference analyser measured very low O₃ concentrations and the adjusted Aeroqual values were slightly negative. This period corresponded to a winter pollution episode with elevated NO₂ concentrations (Fig. A5 in Supplementary material). None of the three calibration methods accurately adjusted the Aeroqual measurements at these very low O₃ concentrations, presumably as a result of the marked change in pollution concentrations between the training and test data.

All three calibration methods yielded high correlation coefficients ($R^2 > 0.90$) and slopes close to 1 (slope: 0.91–1.07) for the evaluation of adjusted test data against analyser-measured O₃ concentrations (Figs. 2 and S7). However, the scatter plot for the Aq_corr_N calibration (for both Aeroqual units) had a relatively large negative intercept compared to the scatter plots for the other two calibration methods,

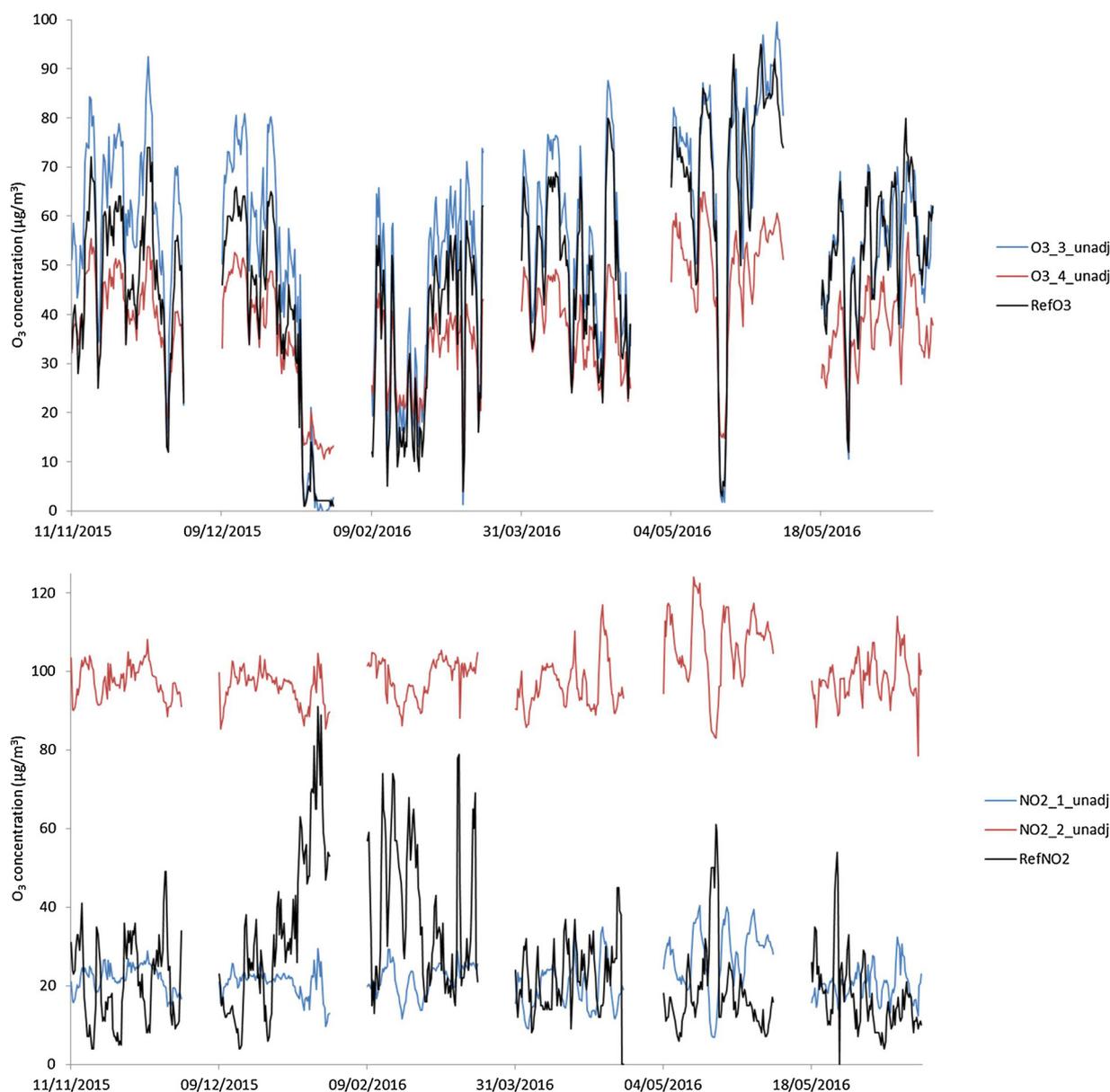


Fig. 1. (a) Time series of unadjusted hourly-averaged O₃ concentrations measured by the two Aeroqual O₃ monitors and by the reference analyser for the full duration of each deployment period. Different deployment periods are separated by gaps in time series. The coefficient of determination (R^2) between the concentrations measured by duplicate Aeroqual O₃ instruments was 0.90. (b) Time series of unadjusted hourly-averaged NO₂ concentrations measured by the two Aeroqual NO₂ monitors and by the reference analyser for the full duration of each deployment period. The coefficient of determination (R^2) between the concentrations measured by duplicate Aeroqual NO₂ instruments was 0.83.

resulting from underestimation of reference analyser O₃. The root mean square error (RMSE), mean bias (MB) and normalised mean bias (NMB) for Aq_corr_N were correspondingly larger than for the other two calibration methods (Table 2, Fig. A7 in Supplementary material).

These evaluation statistics indicated that calibrations derived from training data interspersed regularly throughout the deployment periods provided a more accurate estimate analyser concentrations in the test periods than a single calibration at the start of the deployment periods. For these O₃ monitors there were only small differences in R^2 , RMSE, MB, and NMB statistics between Aq_corr_u and Aq_corr_a methods, with a slightly better fit between adjusted sensor and analyser data for the Aq_corr_u method.

3.2. Calibration of Aeroqual NO₂ monitors

We established in our previous research [16] that the Aeroqual gas-sensitive semiconductor O₃ sensor responds linearly to ambient O₃ concentrations; and that the Aeroqual electrochemical sensor for NO₂ responds to both ambient NO₂ and ambient O₃. For both gases, and both types of sensors, the sensor responses are based on conductivity/current changes (albeit changes of a somewhat different nature for the different sensor types) calibrated for exposure to different concentrations of individual gases by the manufacturer. This provides a physical basis for investigation of responses to both ambient O₃ and NO₂ as potential determinants of conductivity/current change calibrated to monitor outputs. We previously showed that the Aeroqual NO₂ monitor

Table 1

OLS equations for calibration equations for each training period (equivalent to *aq_corr_u*) and a global calibration for a combination of ‘All’ training periods (*aq_corr_a*) for the two pairs of Aeroqual O₃ and NO₂ monitors.

Pollutant	Study period	O _{3,3}	O _{3,4}
O ₃	11–15 Nov 2015	0.94*Ref _{O₃} + 16.11, R ² = 0.85	0.53*Ref _{O₃} + 16.73, R ² = 0.95
	9–13 Dec 2015	1.07*Ref _{O₃} + 9.34, R ² = 0.96	0.59*Ref _{O₃} + 12.19, R ² = 0.90
	9–15 Feb 2016	1.08*Ref _{O₃} + 5.41, R ² = 0.98	0.51*Ref _{O₃} + 15.27, R ² = 0.96
	31 Mar–4 Apr 16	1.06*Ref _{O₃} + 3.61, R ² = 0.99	0.53*Ref _{O₃} + 13.12, R ² = 0.94
	4–8 May 2016	1.05*Ref _{O₃} - 0.07, R ² = 0.99	0.60*Ref _{O₃} + 11.20, R ² = 0.98
	18–22 May 2016	1.00*Ref _{O₃} + 0.83, R ² = 0.99	0.60*Ref _{O₃} + 5.41, R ² = 0.95
	Combined	1.02*Ref _{O₃} + 6.26, R ² = 0.93	0.56*Ref _{O₃} + 12.66, R ² = 0.91
	NO ₂	11–15 Nov 2015	0.10*Ref _{NO₂} + 0.17*O _{3,3} + 8.99, R ² = 0.34
9–13 Dec 2015		0.32*Ref _{NO₂} + 0.28*O _{3,3} - 3.29, R ² = 0.33	0.07*Ref _{NO₂} + 0.19*O _{3,4} + 87.99, R ² = 0.02
9–15 Feb 2016		0.51*Ref _{NO₂} + 0.49*O _{3,3} - 18.95, R ² = 0.92	0.35*Ref _{NO₂} + 1.02*O _{3,4} + 51.98, R ² = 0.63
31 Mar–4 Apr 16		0.50*Ref _{NO₂} + 0.48*O _{3,3} - 20.24, R ² = 0.72	0.15*Ref _{NO₂} + 0.53*O _{3,4} + 70.82, R ² = 0.36
4–8 May 2016		0.54*Ref _{NO₂} + 0.57*O _{3,3} - 23.28, R ² = 0.91	0.38*Ref _{NO₂} + 1.05*O _{3,4} + 47.73, R ² = 0.93
18–22 May 2016		0.17*Ref _{NO₂} + 0.27*O _{3,3} + 2.32, R ² = 0.63	0.15*Ref _{NO₂} + 0.66*O _{3,4} + 71.21, R ² = 0.74
Combined		0.42*Ref _{NO₂} + 0.43*O _{3,3} - 13.19, R ² = 0.67	0.33*Ref _{NO₂} + 0.81*O _{3,4} + 58.00, R ² = 0.62

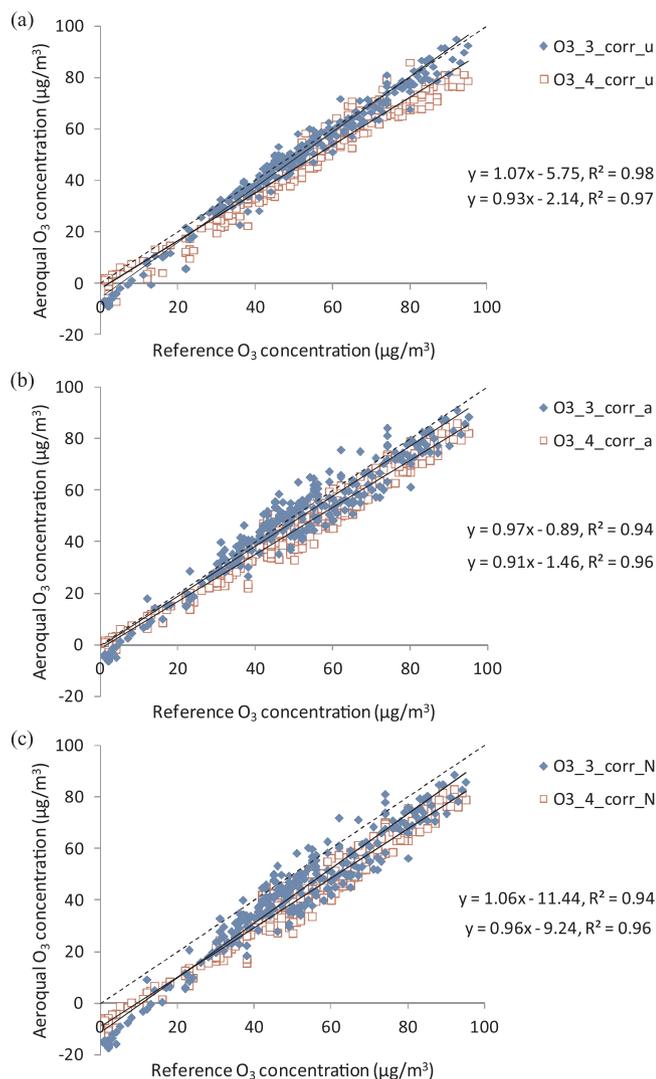


Fig. 2. Scatter plots of adjusted hourly Aeroqual O₃ concentration estimates vs. reference analyser O₃ concentrations for the test data (*i.e.* 2nd half of deployment periods only). (a) O₃*aq* adjusted using calibration derived from training data in each unique deployment period (O₃*aq_corr_u*). (b) O₃*aq* adjusted using calibration derived from training data combined from all deployment periods (O₃*aq_corr_a*). (c) O₃*aq* adjusted using calibration derived from the first deployment period (November) only (O₃*aq_corr_N*).

sensitivity to O₃ concentrations could be characterised by a linear relationship between (*Aeroqual*NO₂ - *Reference*NO₂) vs. *Aeroqual*O₃ which we used to correct the Aeroqual NO₂ concentrations. [16] Preliminary investigations of the Aeroqual NO₂ monitors used in the present work also revealed clear sensitivity of output on O₃ concentration. In our previous method [16], the coefficient for *Reference*NO₂ was effectively constrained to 1, which reflects the expectation that when the Aeroqual sensors are new and recently factory-calibrated their output concentration values should be close to True (*i.e.* reference) NO₂ concentrations:

$$Aeroqual\ NO_2 - True\ NO_2 = a_1 * Aeroqual\ O_3 + b_1 \quad (1)$$

Therefore, we can calibrate Aeroqual NO₂ by rearranging Eq. (1):

$$True\ NO_2 = Aeroqual\ NO_2 - a_1 * Aeroqual\ O_3 - b_1 \quad (2)$$

A potential shortcoming of this approach is that it does not allow for an Aeroqual NO₂ monitor to have a relationship to True NO₂ (*i.e.* to reference analyser NO₂) that is not equal to 1; for example if the response of the sensor in the NO₂ monitor has reduced in time since its factory calibration. A more general model for the Aeroqual NO₂ monitor response is therefore based on the following two underlying relationships:

- 1) Aeroqual O₃ has a linear response to True (reference analyser) O₃, *i.e.*

$$Aeroqual\ O_3 = m_1 * True\ O_3 + c_1 \quad (3)$$

- 1) Aeroqual NO₂ has linear responses to both NO₂ and O₃, and with its response to O₃ being different to the response of the Aeroqual O₃ monitor to O₃, *i.e.*

$$Aeroqual\ NO_2 = m_2 * True\ NO_2 + m_3 * True\ O_3 + c_2 \quad (4)$$

Substituting for True O₃ from Eq. (3) into Eq. (4) yields:

$$Aeroqual\ NO_2 = m_2 * True\ NO_2 + \frac{m_3}{m_1} (Aeroqual\ O_3 - c_1) + c_2 \quad (5)$$

Rearrangement of Eq. (5) into a similar form to Eq. (2) gives:

$$True\ NO_2 = \frac{1}{m_2} * Aeroqual\ NO_2 - \frac{m_3}{m_1 * m_2} * Aeroqual\ O_3 - \left(\frac{c_2}{m_2} - \frac{c_1 * m_3}{m_1 * m_2} \right) \quad (6)$$

where $\frac{m_3}{m_1 * m_2}$ and $\left(\frac{c_2}{m_2} - \frac{c_1 * m_3}{m_1 * m_2} \right)$ are constants.

Eq. (6) is similar to Eq. (2) produced in our previous method [16], except that there is now a coefficient for the Aeroqual NO₂ term that

Table 2

OLS linear regression parameters (and 95% confidence intervals), coefficient of determination and summary statistics for adjusted Aeroqual NO₂ and O₃ concentrations compared to reference analyser concentrations. The calibration adjustments applied were: the second 48 h of each deployment period corrected using the unique calibration derived using the first 48 h of that deployment period (*Aq_corr_u*); the second 48 h of each deployment period corrected using the calibration derived when the first 48 h of data from all studies were combined (*Aq_corr_a*); and the second 48 h of each deployment period corrected using the calibration derived from the first 48 h in the first (November) study only (*Aq_corr_N*).

Monitor	Correction	Slope [95 % C.I.]	Intercept [95 % C.I.] / $\mu\text{g m}^{-3}$	R ²	RMSE / $\mu\text{g m}^{-3}$	MB / $\mu\text{g m}^{-3}$	NMB	n
O _{3_3}	<i>O_{3_corr_u}</i>	1.07 [1.06, 1.09]	−5.75 [−6.77, −4.72]	0.98	4.59	−2.10	−0.04	286
	<i>O_{3_corr_a}</i>	0.97 [0.94, 1.00]	−0.89 [−2.50, 0.72]	0.94	6.25	−2.17	−0.04	286
	<i>O_{3_corr_N}</i>	1.06 [1.03, 1.09]	−11.44 [−13.19, −9.68]	0.94	10.72	−8.54	−0.17	286
O _{3_4}	<i>O_{3_corr_u}</i>	0.93 [0.91, 0.95]	−2.14 [−3.20, −1.07]	0.97	6.94	−5.56	−0.11	286
	<i>O_{3_corr_a}</i>	0.91 [0.89, 0.93]	−1.46 [−2.57, −0.35]	0.96	7.22	−5.68	−0.12	286
	<i>O_{3_corr_N}</i>	0.96 [0.94, 0.99]	−9.24 [−10.41, −8.07]	0.96	11.80	−10.99	−0.23	286
NO _{2_1}	<i>NO_{2_corr_u}</i>	1.09 [0.98, 1.20]	1.25 [−2.06, 4.56]	0.59	15.75	3.65	0.14	286
	<i>NO_{2_corr_a}</i>	1.03 [0.98, 1.08]	3.60 [2.03, 5.17]	0.85	8.50	4.45	0.17	286
	<i>NO_{2_corr_N}</i>	1.33 [1.04, 1.63]	11.79 [2.62, 20.96]	0.22	47.23	20.47	0.78	286
NO _{2_2}	<i>NO_{2_corr_u}</i>	0.80 [0.58, 1.02]	11.02 [4.29, 17.75]	0.16	31.69	5.79	0.22	286
	<i>NO_{2_corr_a}</i>	0.97 [0.89, 1.04]	11.46 [9.24, 13.68]	0.71	14.73	10.59	0.41	286
	<i>NO_{2_corr_N}</i>	0.87 [0.80, 0.93]	16.97 [15.09, 18.88]	0.73	16.21	13.47	0.52	286

may not be equal to 1. To account for this coefficient for Aeroqual NO₂ in practice, a multiple linear regression was fitted to the Aeroqual NO₂ values to derive three fitted parameters:

$$\text{Aeroqual NO}_2 = k_1 * \text{True NO}_2 + k_2 * \text{Aeroqual O}_3 + k_3 \quad (7)$$

The best estimates for k_1 , k_2 and k_3 were then used to calibrate Aeroqual NO₂ concentrations as follows:

$$\text{True NO}_2 = \frac{1}{k_1} (\text{Aeroqual NO}_2 - k_2 * \text{Aeroqual O}_3 - k_3) \quad (8)$$

As for the O₃ monitors, the impact of temperature and relative humidity on NO₂ calibration regression equations was limited and inconsistent and was therefore not considered further.

The Aeroqual monitors were arbitrarily paired in this correction (reflecting the arbitrary pairing when a pair of monitors is used for field measurements), with NO_{2_1} corrected using O_{3_3} and NO_{2_2} corrected using O_{3_4}. The three different calibration methods described in Section 3.1 were used; leading to Aeroqual NO₂ concentrations adjusted using the *Aq_corr_u*, *Aq_corr_a* and *Aq_corr_N* selections of training data (Table 1).

The adjusted Aeroqual NO₂ and Reference NO₂ concentrations were highly correlated over time, with the exception of some concentrations adjusted using the *Aq_corr_u* method (Fig. A5 in Supplementary material). The *Aq_corr_u* (NO_{2_1} only), *Aq_corr_a* and *Aq_corr_N* (NO_{2_2} only) calibration methods resulted in clearly defined linear relationships between adjusted Aeroqual and Reference NO₂ concentrations with R² values ranging from 0.70 to 0.85 (Fig. 3 & Table 2). The regression slope and intercept values were closest to 1 and 0, respectively, R² values highest, and RMSE values lowest for the *Aq_corr_a* selection of training data, for both Aeroqual NO₂ monitors (Figs. 3 & S7 and Table 2). The period of deviation between Aeroqual NO_{2_2_corr_u} and Reference NO₂ is from the December deployment, during which there was a very poor training data regression fit with small coefficients for *Reference_NO2* and O_{3_4} and a large offset (Table 1 & Fig. A6 in Supplementary material). The cause of the poor calibration regression during this particular deployment is not known but may be the result of transient errors in one or other of the Aeroqual monitor measurements in this period.

3.3. Temporal changes in Aeroqual O₃ and NO₂ monitor responses

We calculated the difference between unadjusted Aeroqual O₃ and Reference O₃ concentrations to assess drift in the output of the Aeroqual O₃ sensors during this study (Fig. 4a). The difference generally declined over the 6 months of measurements. This decline may have resulted

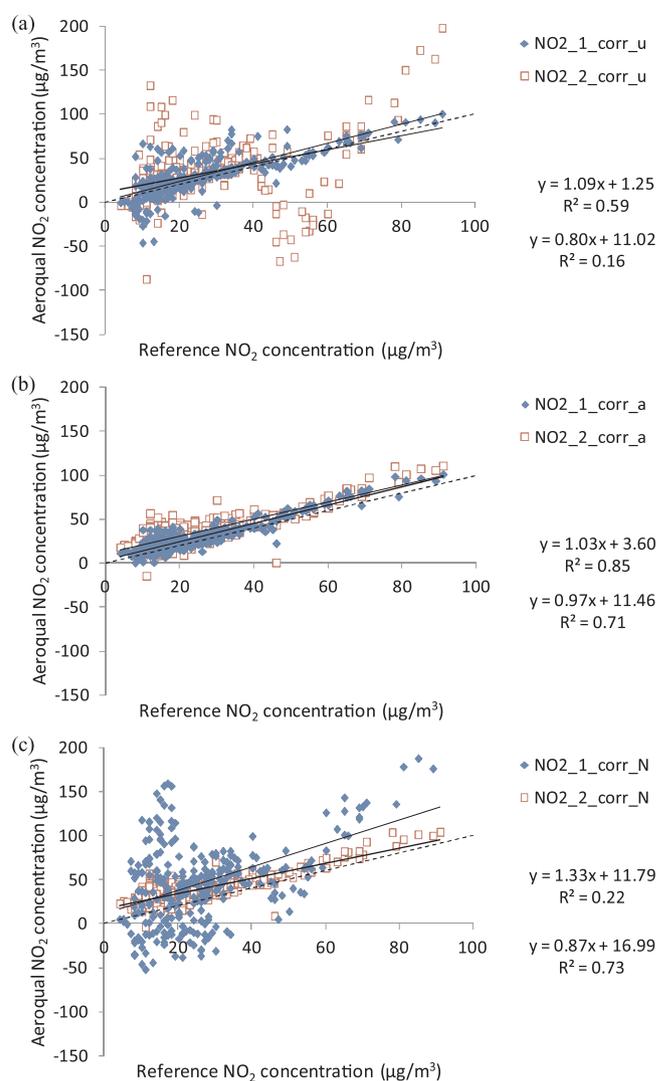


Fig. 3. Scatter plots of adjusted hourly Aeroqual NO₂ concentration estimates vs. reference analyser NO₂ concentrations for the test data (*i.e.* 2nd half of deployment periods only). (a) Aeroqual data adjusted using calibration derived from training data in each unique deployment period (*aq_corr_u*). (b) Aeroqual data adjusted using calibration derived from training data combined from all deployment periods (*aq_corr_a*). (c) Aeroqual data adjusted using calibration derived from the first deployment period (November) only (*aq_corr_N*).

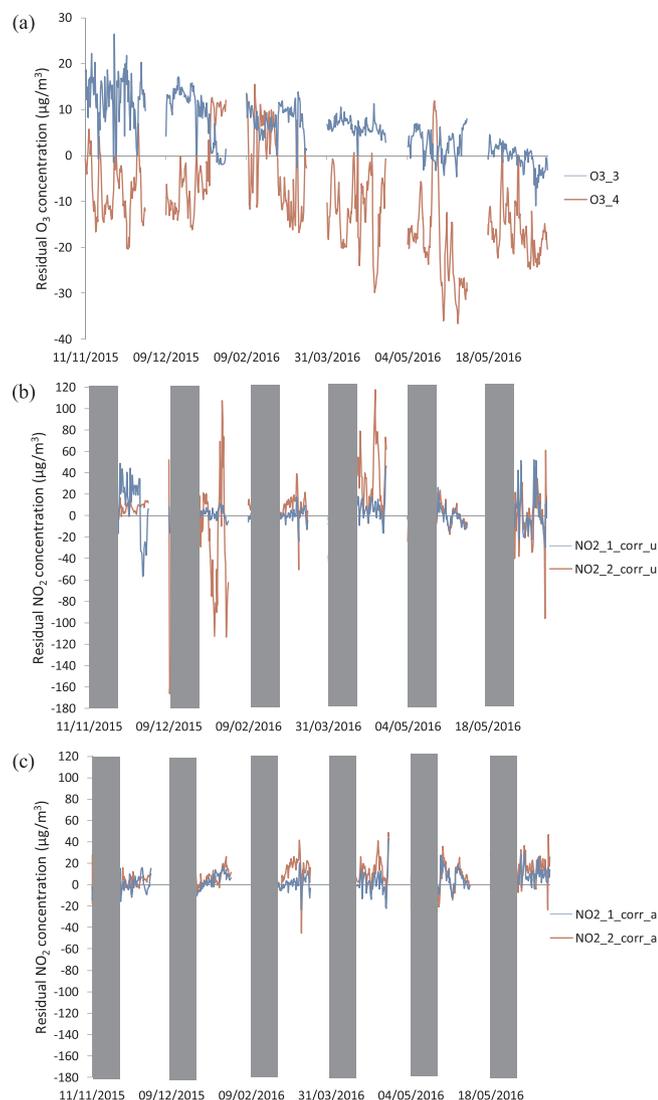


Fig. 4. Residual plots of (a) unadjusted Aeroqual O_3 – reference O_3 ; (b) NO_2 Aq_corr_u – reference NO_2 and (c) NO_2 Aq_corr_a – reference NO_2 over the 96-h deployments. Both training and test data sets are included (training data indicated by grey boxes). Different deployment periods are separated by gaps in time series.

from deterioration in the sensitivity of the O_3 monitors as the sensors aged. However, the calibration procedures overcame these effects to enable reasonably accurate representation of reference analyser concentrations.

We also plotted the difference between Aeroqual and Reference NO_2 concentrations for Aeroqual concentrations adjusted using Aq_corr_u and Aq_corr_a training data selections (Fig. 4b and c). The residual concentrations varied more using the Aq_corr_u calibration method than for the Aq_corr_a method, with periods of large residual values corresponding to deployments with lower correlations between reference and Aeroqual NO_2 concentrations in the data (Table 1). The residual NO_2 concentrations showed no trend across the deployment periods for the Aq_corr_u correction method, as this calibration procedure partly corrected for the temporal drift in the Aeroqual O_3 sensors identified above, while for the Aq_corr_a correction method the residuals generally increased within each individual deployment and across all the deployments.

Daily averages of the hourly residuals for the Aeroqual O_3 and NO_2 measurements adjusted using the first set of training data (Aq_corr_N) were calculated for all of the available study data (including data for

deployments > 96 h in length) (Fig. A8 in Supplementary material). The daily O_3 residuals became more negative during each deployment; however at the start of each deployment the residuals appeared to revert to close to zero, as measured for the first residual values in the Aq_corr_N calibration period in November 2015. This may be indicative of changes in the O_3 sensor response after the monitor has been turned on, with repeated instances of this effect for individual deployments. The Aeroqual NO_2 sensors exhibited a general increase in the daily residuals during each deployment that is likely to have resulted from the use of the Aeroqual O_3 data in the calibration of the Aeroqual NO_2 sensor.

Overall, these observations suggest that it is beneficial to make calibration and field measurements after consistent time periods following monitor start-up (as was done here).

4. Discussion

As a result of technological developments portable monitors are increasingly used to measure ambient pollution concentrations over extended geographical areas, and for mobile and personal monitoring. Field calibration procedures are necessary to improve and quantify the accuracy of estimates of ambient pollution concentrations from portable monitors. In this study we investigated changes in calibration relationships for two pairs of Aeroqual O_3 and NO_2 monitors vs. reference analysers over a period of 6 months as the sensors approached the manufacturer's specified 2-year lifetime. We developed a multiple linear regression calibration method that allowed the Aeroqual NO_2 sensor to have a regression slope with 'true' NO_2 that is not equal to 1 (as was assumed in the method of Lin et al. [16]), due for example to sensor aging, in addition to allowance for a non-unity response to O_3 . The use of multiple linear regression compared to linear regression to correct other portable NO_2 sensors has been observed to produce higher correlation between calibrated sensor estimates and reference NO_2 concentrations [15].

Changes in monitor responses over time (including apparent baseline drift in O_3 sensor output, and discrepancies between the 2 Aeroqual NO_2 sensors) resulted in relatively inaccurate concentrations estimates (cf. reference concentrations) from calibration equations derived in the first training period and applied to subsequent *test* deployments (e.g. NO_2 RMSE = $47.2 \mu\text{g m}^{-3}$ ($n = 286$) for a dataset of all *test* periods combined, for one of the two monitor pairs). Substantial improvements in accuracy of estimated concentrations were achieved by combination of repeated intermittent training data into a single calibration dataset (NO_2 RMSE = $8.5 \mu\text{g m}^{-3}$ for same *test* dataset described above). This latter approach to field calibration is recommended. Our results also highlight the importance, when possible, of calibration of monitors in similar urban pollution environments to where they are to be used, as has been adopted in previous studies [9,10,16]. One recent study [20] used un-calibrated concentrations from the Aeroqual monitors to measure NO_2 and O_3 in indoor office environments with low O_3 concentrations which may have removed the need to adjust the Aeroqual NO_2 monitors for O_3 cross-sensitivity.

Our observations suggest that a single calibration study may not be able accurately to represent the relationship between monitor and reference analyser over an extended period, for example because of unidentified measurement problems during a particular calibration deployment period. In contrast, we have observed that combination of several short calibration deployments over a period of 6 months into a single calibration dataset provided adjusted Aeroqual concentration estimates that agreed more closely with the reference analyser concentrations, provided that for the NO_2 monitors concurrent O_3 monitor measurements were also used as input to the calibration relationship. We observed differences in Aeroqual NO_2 calibrations over shorter time periods (e.g. within 1 month), which may be attributable to differences in the relative pollutant concentration ranges during the calibration periods (it is important to recognise the importance of pollutant

concentration ranges when assessing percentages of explained variation in pollution concentrations with R^2 statistics, and in relation to potential inaccuracies when extrapolating outside of calibration concentration ranges). During a winter pollution episode with elevated NO_2 concentrations none of the calibration methods tested for the O_3 monitor could accurately represent the analyser concentrations, again highlighting the importance of (when possible) calibrating the Aeroqual monitors using pollution concentrations similar to those anticipated during intended field application.

It is important to acknowledge: (a) that sensor drift is likely to exist; (b) it may well not be possible to predict the nature of the sensor drift *i.e.* the rate of sensor drift may not be constant (this is evident in the irregular nature of the drift observed in our measurements (Fig. 4a)); so (c) for practical use in the field these sensors must be (re)calibrated against reference analysers as often as possible. Further refinements to the relatively simple and parsimonious approach we have taken to sensor calibration may be possible, including attempts to characterise the irregular temporal drift in the O_3 sensors, and examination of the effect of reduced frequency calibration on the accuracy of sensor estimates.

In conclusion, our observations indicate that the benefit [in terms of improved accuracy of calibrated NO_2 estimates] of calibration equations averaged by pooling data from a number of calibration periods over a period of a few months (increased size of calibration dataset and potentially increased concentration range) outweighed the disadvantage arising from any monitor drift throughout the overall measurement period. It is possible that the combination of several calibration periods interspersed within the overall measurement period mitigated the risk of only relying on calibration data from short periods when the range of concentrations may have been limited or otherwise unrepresentative. Therefore, out of the 3 calibration methods for NO_2 sensors evaluated in this study, pooling of interspersed calibration data is recommended as a pragmatic approach to calibration of Aeroqual monitors for field deployment. Although the sensors used in this research were approaching the 2-year working lifetime specified by the manufacturer (Aeroqual, 2015 personal communication), our observations suggest that frequent intermittent calibrations as presented above may allow the sensors to remain useable beyond this specified lifetime.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.snb.2018.07.087>.

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