



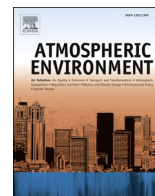
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Technical note

Evaluation and calibration of Aeroqual series 500 portable gas sensors for accurate measurement of ambient ozone and nitrogen dioxide



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ABSTRACT

Low-power, and relatively low-cost, gas sensors have potential to improve understanding of intra-urban air pollution variation by enabling data capture over wider networks than is possible with 'traditional' reference analysers. We evaluated an Aeroqual Ltd. Series 500 semiconducting metal oxide O₃ and an electrochemical NO₂ sensor against UK national network reference analysers for more than 2 months at an urban background site in central Edinburgh. Hourly-average Aeroqual O₃ sensor observations were highly correlated ($R^2 = 0.91$) and of similar magnitude to observations from the UV-absorption reference O₃ analyser. The Aeroqual NO₂ sensor observations correlated poorly with the reference chemiluminescence NO₂ analyser ($R^2 = 0.02$), but the deviations between Aeroqual and reference analyser values ($[\text{NO}_2]_{\text{Aeroq}} - [\text{NO}_2]_{\text{ref}}$) were highly significantly correlated with concurrent Aeroqual O₃ sensor observations $[\text{O}_3]_{\text{Aeroq}}$. This permitted effective linear calibration of the $[\text{NO}_2]_{\text{Aeroq}}$ data, evaluated using 'hold out' subsets of the data ($R^2 \geq 0.85$). These field observations under temperate environmental conditions suggest that the Aeroqual Series 500 NO₂ and O₃ monitors have good potential to be useful ambient air monitoring instruments in urban environments provided that the O₃ and NO₂ gas sensors are calibrated against reference analysers and deployed in parallel.

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1. Introduction

Ozone (O₃) and nitrogen dioxide (NO₂) are important air pollutants subject to mandatory air quality limits in many jurisdictions. Road traffic and static combustion are major sources of the NO_x gases (NO and NO₂) leading to pronounced spatiotemporal gradients in NO₂ in urban areas (Cyrus et al., 2012). As a consequence of the fast photochemical cycling between NO_x and O₃, concentrations of O₃ also exhibit strong spatiotemporal variability in urban areas (McConnell et al., 2006; Malmqvist et al., 2014). At present, NO₂ and O₃ are measured using expensive, but traceably-calibrated, fixed-site monitors in sparse networks, or via passive diffusion samplers (Martin et al., 2010; Matte et al., 2013). The former lack spatial resolution, whilst the latter lack temporal resolution.

The development of low-power gas-sensitive semiconductor and electrochemical technology has potential to improve

understanding of intra-urban air pollution variation by enabling simultaneous data capture, at lower net cost, over wide urban networks (Mead et al., 2013; Williams et al., 2013; Bart et al., 2014), and via peripatetic and mobile sampling designs (Abernethy et al., 2013; Saraswat et al., 2013). However, the quality of the data generated by these monitors compared with established techniques remains a concern (Snyder et al., 2013), in particular interference in the sensing of NO₂ by O₃ (Williams et al., 2009; Mead et al., 2013). One such type of monitor is the Aeroqual Ltd. Series 500 ENV portable gas monitors (www.aeroqual.com/category/products/handheld-monitors). These are relatively compact and lightweight (460 g), and can be operated from an inbuilt battery (for ~8 h) or from mains power. Interchangeable metal oxide semiconductor and electrochemical sensors permit continuous monitoring of a range of gases at low mixing ratios (Williams et al., 2009). The Aeroqual monitors are a factor of approximately 5–10 times lower cost than standard air quality monitoring instrumentation for these gases.

In this study, we evaluated the capabilities of two Aeroqual Series 500 portable gas monitors, one with a semiconductor oxide O₃ sensor (OZU 0–0.15 ppm) and one with an electrochemical NO₂

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sensor (GSE 0–1 ppm), to measure ambient concentrations of these gases in Edinburgh, UK. We demonstrate the applicability of a linear calibration for the NO₂ sensor using parallel measurements of the O₃ sensor and deployment of both against reference instruments.

2. Methods

The two Aeroqual monitors were placed under a weatherproof plastic shelter at ~1.5 m elevation above the ground on a post adjacent to the cabin housing the O₃ and NO₂ reference gas analysers of the Edinburgh St. Leonard's air quality monitoring station (55.946 °N, 3.182 °W). The site is near the centre of the city of Edinburgh, UK, and is classified as urban background in the UK national network (<http://uk-air.defra.gov.uk/data>). The air inlet for the reference analysers was approximately 1.8 m horizontal

distance from and 1.2 m higher than the Aeroqual monitors. The Aeroqual sensor inlets were positioned so that the sensor heads were level with the lower edge of the waterproof shelter and sampled freely flowing ambient air in close vicinity to the reference analysers. The monitoring location was approximately 30 m from the nearest road (with no other primary pollutant sources nearby) hence any differences in pollution concentrations resulting from the small separation distance between the reference analyser and Aeroqual monitor inlets were anticipated to be minor in the comparison of observed concentrations. The Aeroqual units were used as received, with mains power; the waterproof enclosure available from Aeroqual was not used. An Onset HOBO U23 Pro v2 External Data Logger (with solar radiation shield) was also attached to the shelter to record ambient *T* and RH at 1 min resolution.

The Aeroqual monitors were programmed to record 5-min average concentrations of NO₂ and O₃ continuously between 7th

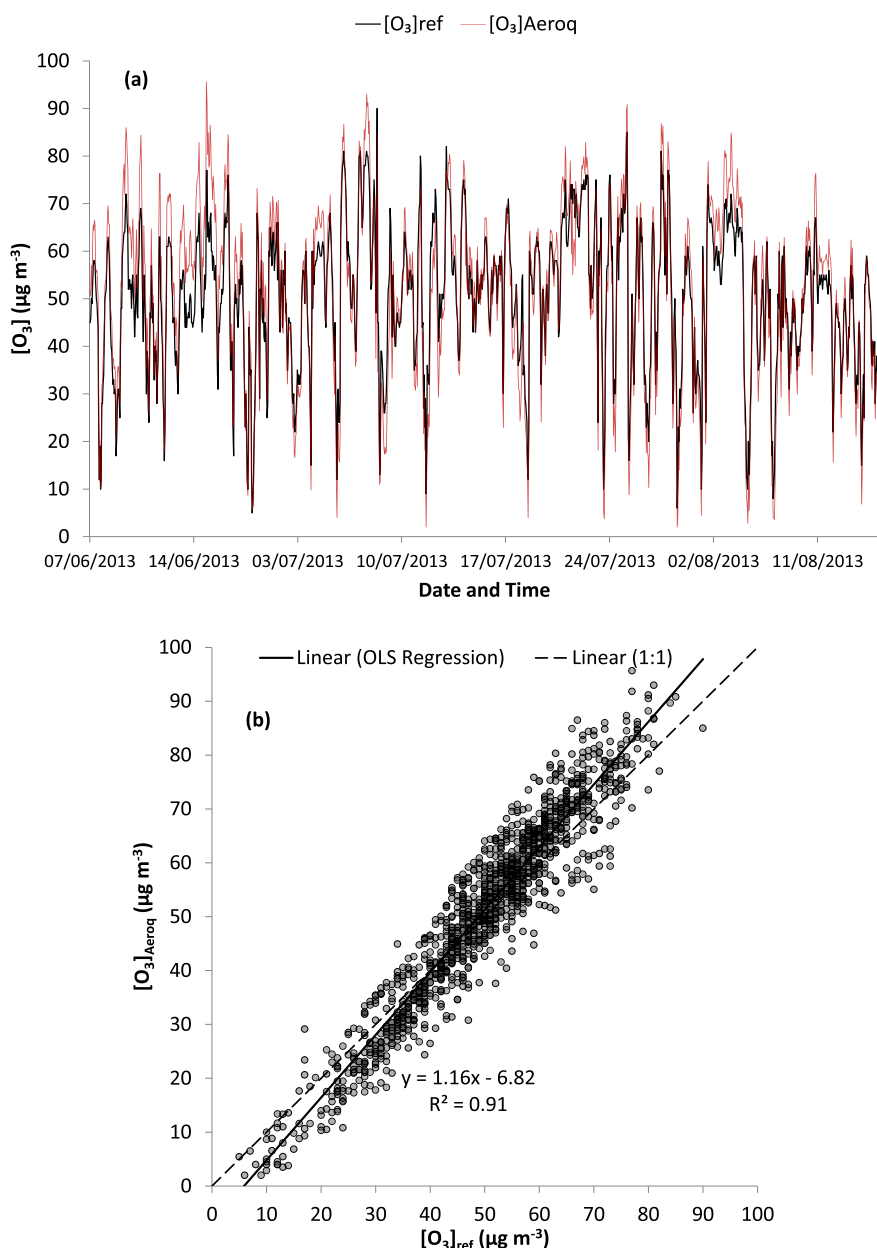


Fig. 1. (a) Time series, and (b) scatter plot, of hourly-averaged [O₃] from measurements made by the Aeroqual O₃ monitor and the O₃ UV absorption analyser between 7 June and 15 August 2013 (1274 pairs of hourly averages).

June and 15th August 2013. Data were downloaded to a laptop every two weeks, at which time the internal clocks of both monitors were synchronised via the Aeroqual software with the laptop, which was in turn regularly synchronised with Internet Time Servers.

Time stamps for the 5-min averages downloaded from the Aeroqual monitors were adjusted from BST to GMT. The 5-min averages were aggregated to hourly means, denoted as $[\text{NO}_2]_{\text{Aeroq}}$ and $[\text{O}_3]_{\text{Aeroq}}$. No data capture threshold was set for the averaging.

The NO_2 reference instrument was an EnviroTechnology Model 200E chemiluminescence analyser (range 0–20 ppm, precision 0.5%) and the O_3 reference instrument was an EnviroTechnology Model 400E photometric analyser (range 0–10 ppm, precision <0.5%). Both instruments were maintained and calibrated in accordance with the QA/QC protocol for the UK ambient air quality monitoring network ([http://uk-air.defra.gov.uk/networks/network-](http://uk-air.defra.gov.uk/networks/network-info?view=aur)

[info?view=aur](http://uk-air.defra.gov.uk/networks/network-info?view=aur)). All data from the reference analysers were subject to the network data review and ratification process. Hourly-averaged NO_2 and O_3 derived from these instruments were downloaded from www.scottishairquality.co.uk, and are denoted as $[\text{NO}_2]_{\text{ref}}$ and $[\text{O}_3]_{\text{ref}}$.

3. Results and discussion

The ambient hourly T (range: 10–33 °C; mean \pm sd: 19 ± 4 °C) in this study was within the operating range of the Aeroqual sensors (–5–45 °C). The vast majority of the hourly RH measurements (29–97%; $69 \pm 17\%$) were also in the sensor operating range of 0–95% (<3% of hourly RH measurements were in the range 95–97%).

Fig. 1 shows the time series and scatter plot of hourly averaged O_3 data. The Aeroqual and UV-absorbance reference analyser O_3

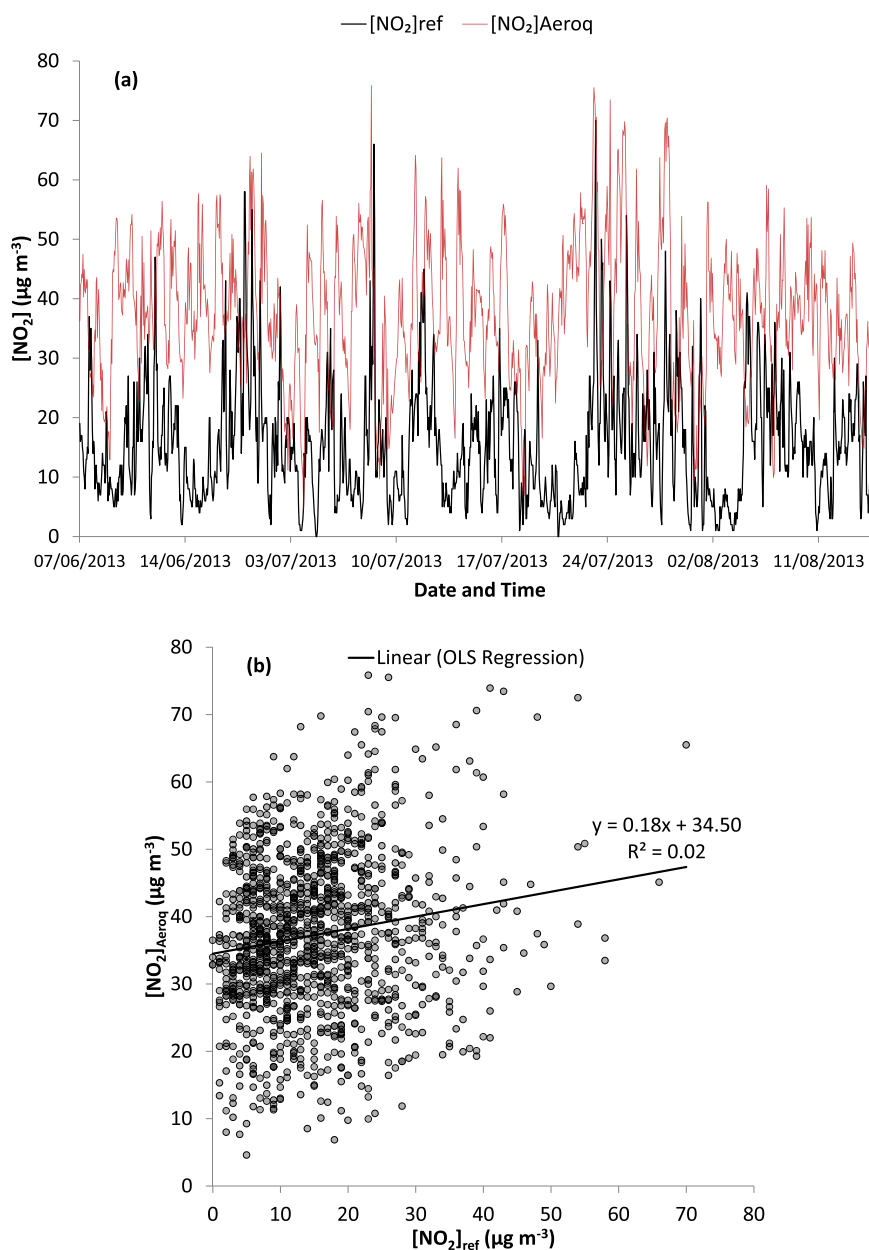


Fig. 2. (a) Time series, and (b) scatter plot, of hourly-averaged $[\text{NO}_2]$ from measurements made by the Aeroqual NO_2 monitor and the NO_2 chemiluminescence analyser between 7 June and 15 August 2013 (1274 pairs of hourly averages).

data were highly correlated ($R^2 = 0.91$, $n = 1274$), albeit with a trend for this Aeroqual O_3 sensor to overestimate on average compared with the reference instrument when O_3 concentrations from the latter exceeded $\sim 43 \mu\text{g m}^{-3}$ (e.g. an Aeroqual value of $86 \mu\text{g m}^{-3}$ for a reference instrument value of $80 \mu\text{g m}^{-3}$), and to underestimate on average for concentrations below a reference instrument O_3 concentration of $\sim 43 \mu\text{g m}^{-3}$ (e.g. $16 \mu\text{g m}^{-3}$ Aeroqual value for a reference instrument value of $20 \mu\text{g m}^{-3}$). These small systematic differences are readily corrected for by application of the linear relationship shown in the figure.

In contrast, the time series and scatter plot in Fig. 2 show very limited agreement between the Aeroqual NO_2 sensor and the reference NO_2 chemiluminescence analyser ($R^2 = 0.02$, and sensor overestimation compared with the reference analyser by approximately 3-fold on average). In contrast, a closer correspondence of an Aeroqual gas-sensitive semiconductor (GSS) NO_2 sensor and reference analyser observations was reported in a similar comparison by Delgado-Saborit (2012) ($[\text{NO}_2]_{\text{Aeroq(GSS)}} = 0.76 [\text{NO}_2]_{\text{ref}} + 7.05$; $R^2 = 0.89$).

Some sensitivity of gas sensors to ambient water vapour has previously been noted (Bart et al., 2014). Fig. 3 shows the relationships between the deviations in the observations of both Aeroqual sensors from their respective reference analyser values and the ambient RH recorded by the HOBO logger. Although the deviations of both sets of Aeroqual values appear to show some trends with RH, these are very weak and the correlations correspondingly poor ($R^2 = 0.02$ and 0.01 , for NO_2 and O_3 , respectively), and over a range in ambient RH from $\sim 30\%$ to almost 100% . The negative relationship with RH for the O_3 sensor is consistent with the observations of Bart et al. (2014), although the latter present a slightly greater negative trend, albeit with considerable scatter as is the case with our data. We observe a small, but again non-significant, positive trend between Aeroqual NO_2 deviations and RH. Overall, we conclude that any systematic impact of RH on our sensor bias and imprecision is limited. In particular, there is no obvious systematic relationship of Aeroqual electrochemical NO_2 sensor observations with RH that might account for the limited

agreement between NO_2 sensor and NO_2 reference analyser observations. There were similar lack of associations between 'Aeroqual – reference analyser' O_3 and NO_2 deviations and ambient T (data not shown).

Instead, we examined whether the substantial deviation of Aeroqual electrochemical sensor NO_2 measurement from the reference measurement may have been driven by interference from ambient O_3 . We used the first two-thirds of the measured data (between 7 June and 24 July) as a 'test' dataset to investigate this. Fig. 4 shows the plot of $([\text{NO}_2]_{\text{Aeroq}} - [\text{NO}_2]_{\text{ref}})$ against $[\text{O}_3]_{\text{Aeroq}}$ for these data, indicating a highly significant linear correlation ($R^2 = 0.92$, $n = 849$) up to the maximum $[\text{O}_3]_{\text{Aeroq}}$ observation of almost $100 \mu\text{g m}^{-3}$ in this dataset. The OLS linear regression relationship from the data in Fig. 4 was used to derive calibrated hourly $[\text{NO}_2]_{\text{Aeroq-C}}$ data from the original $[\text{NO}_2]_{\text{Aeroq}}$ and $[\text{O}_3]_{\text{Aeroq}}$ data for the remaining one-third of the study period (25 July to 15 August). The time series and scatter plot of the $[\text{NO}_2]_{\text{Aeroq-C}}$ values with the reference data are shown in Fig. 5. The major axis linear regression (which allows for uncertainty in both sets of data) shows close agreement between calibrated Aeroqual NO_2 data and reference instrument observations for this test dataset with a correlation coefficient, $r = 0.94$ ($R^2 = 0.88$), a slope not significantly different from unity (95% confidence interval: 0.99, 1.07) and an intercept very close to zero (95% CI: -1.8 , -0.4) (Fig. 5). Only 13 negative values of $[\text{NO}_2]_{\text{Aeroq-C}}$ out of 425 ($\sim 3\%$ of the 'test' dataset) were generated in this calibration.

Neither the differences $([\text{NO}_2]_{\text{Aeroq}} - [\text{NO}_2]_{\text{ref}})$ plotted in Fig. 4, nor the differences between the $[\text{NO}_2]_{\text{Aeroq-C}}$ and $[\text{NO}_2]_{\text{ref}}$ values plotted in Fig. 5, showed any trend with time. This indicates that the measurements used to derive both the calibration relationship and its subsequent application were not subject to long-term drifts on the timescales of the data collection in this study.

The proportion of the full dataset assigned to derivation of calibrated Aeroqual NO_2 values above was arbitrary. Table 1 presents statistics for the linear relationships in 'test' evaluations of $[\text{NO}_2]_{\text{Aeroq-C}}$ against measured $[\text{NO}_2]_{\text{ref}}$ values derived from the use of different portions of the time series of measurements as the 'training' dataset for generation of the linear calibration for $[\text{NO}_2]_{\text{Aeroq-C}}$ values. The R^2 values for the 'test' evaluations of

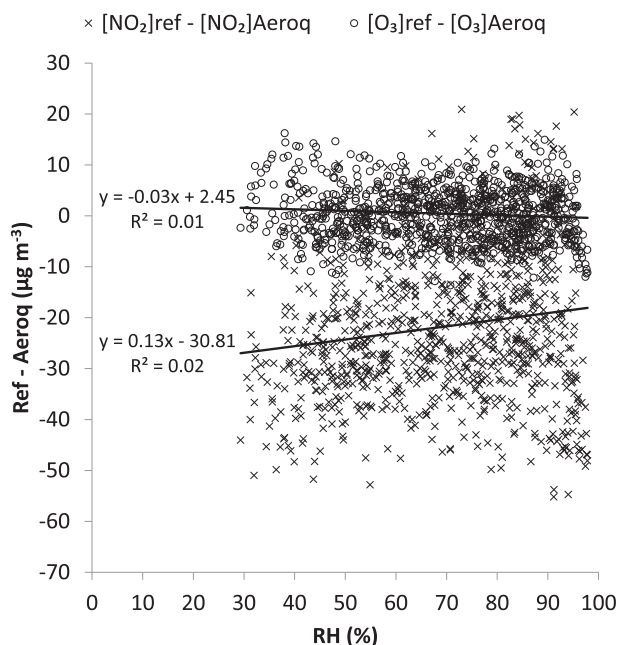


Fig. 3. Scatter plot of the deviations of hourly-average O_3 and NO_2 Aeroqual measurements from their respective reference measurements versus RH.

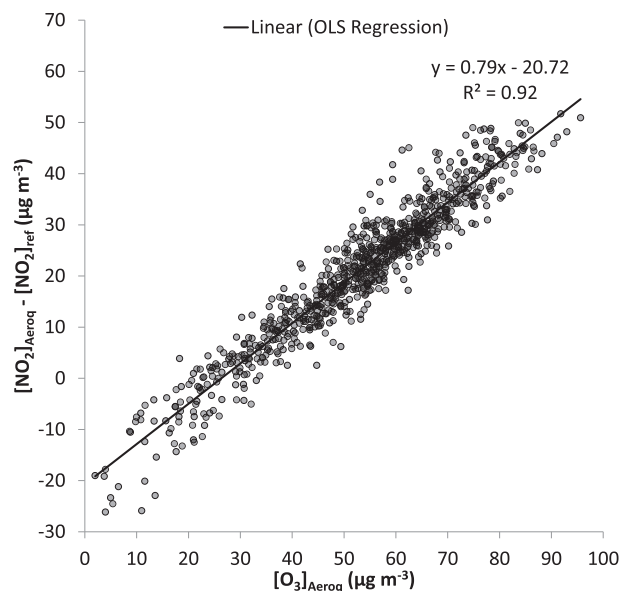


Fig. 4. Relationship between $([\text{NO}_2]_{\text{Aeroq}} - [\text{NO}_2]_{\text{ref}})$ and $[\text{O}_3]_{\text{Aeroq}}$ measurements between 7 June and 24 July 2013 (849 pairs of hourly averages).

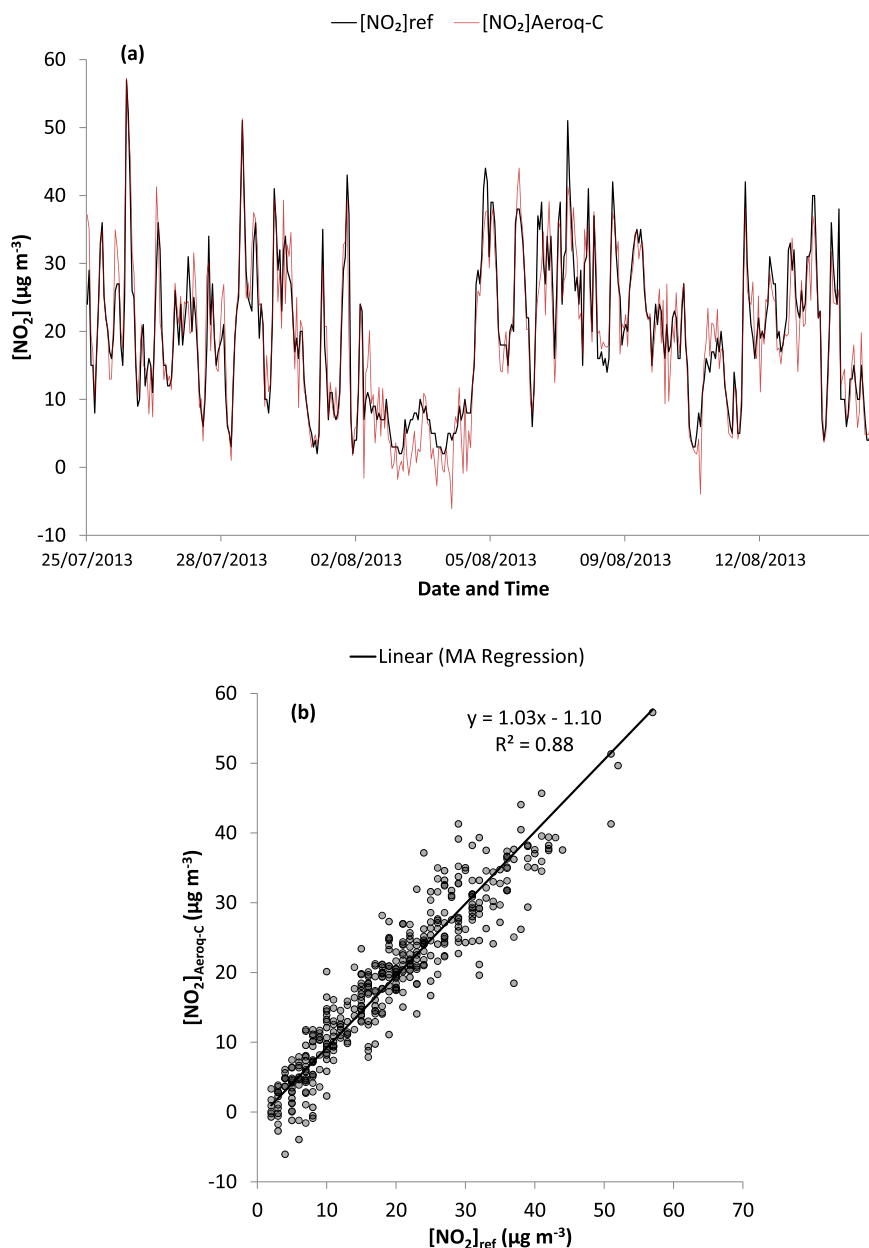


Fig. 5. Comparison of the calibrated Aeroqual NO₂ values and measured [NO₂]_{AURN} between 25 July and 15 August 2013. The [NO₂]_{Aeroq-C} values were derived according to the OLS regression established using [NO₂]_{Aeroq}, [NO₂]_{ref} and [O₃]_{Aeroq} measured at the same site between 7 June and 24 July 2013.

[NO₂]_{Aeroq-C} against [NO₂]_{ref} values exceed 0.85 in all the examples in Table 1. The parameters of the regressions have some variation, but the slopes are all within 12% of each other and the intercept never exceeds 2 µg m⁻³. As before, there were no long-term trends in the calibration performance (within the duration of this study) with splits between 'training' and 'test' data given in Table 1.

These results demonstrate that accurate linear calibrations of our [NO₂]_{Aeroq} observations by reference monitors was feasible. The small amount of scatter remaining in the relationship between [NO₂]_{Aeroq-C} and [NO₂]_{ref} is assumed to reflect the measurement uncertainties in both the Aeroqual and reference analyser data. The very close agreement between the O₃ sensor readings and the reference O₃ instrument in this study suggests that any cross-interference of the O₃ sensor to other ambient species is negligible for this sensor. The consistent functional relationship observed for adjustment of the NO₂ sensor values by O₃ sensor

values likewise suggests that any other cross-interference on the NO₂ sensor is much smaller than that of O₃. Finally, it is noted that a potential operational disadvantage of these portable low-power instruments is the minimum ambient operating temperature of -5 °C currently specified.

4. Conclusions

An Aeroqual Series 500 ENV O₃ semiconductor oxide gas sensor yielded close agreement with hourly-averaged observations from a reference UV-absorbance O₃ analyser in temperate ambient conditions. Although an Aeroqual NO₂ electrochemical sensor appeared to suffer considerable co-sensitivity to O₃ (to the point of the NO₂ sensor evaluated in this study being inadequate as a measure of NO₂ on its own), it was demonstrated that the O₃ interference can be corrected for by co-deployment with an

Table 1

Statistics for the linear relationships in the 'test' evaluation of calibrated Aeroqual NO₂ values ([NO₂]_{Aeroq-C}) against measured [NO₂]_{ref} values from use of different splits of the full time series of measurements between 'training' and test datasets. Slope and intercept parameters in bold do not differ significantly (at the 95% level) from unity and zero, respectively. The shaded line in the table corresponds to the example shown in Fig. 5.

Portion of the full dataset used for the regression to derive [NO ₂] _{Aeroq-C}	R ²	Slope [95% C.I.]	Intercept [95% C.I.]/ μg m ⁻³
1st 1/3	0.85	1.00 [0.97, 1.03]	-0.25 [-0.76, 0.25]
2nd 1/3	0.88	1.10 [1.07, 1.13]	-2.00 [-2.50, -1.51]
3rd 1/3	0.86	1.07 [1.05, 1.10]	-0.83 [-1.32, -0.34]
1st 2/3	0.88	1.03 [0.99, 1.07]	-1.10 [-1.82, -0.40]
1st 1/3 & 3rd 1/3	0.85	1.03 [0.99, 1.07]	-0.22 [-0.94, 0.47]
2nd 2/3	0.87	1.12 [1.08, 1.17]	-1.88 [-2.59, -1.20]
1st 1/2	0.85	1.01 [0.97, 1.04]	-0.22 [-0.83, 0.36]
2nd 1/2	0.87	1.11 [1.08, 1.15]	-1.91 [-2.48, -1.36]

Aeroqual O₃ sensor plus prior calibration alongside an NO₂ reference instrument. Individual sensor heads may vary in performance so further tests with different instruments at different locations are clearly required to confirm the findings. Overall, however, this study suggests that the Aeroqual Series 500 NO₂ and O₃ monitors could be potentially useful ambient air monitoring instruments.

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