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 two 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 ([NO₂]Aeroq – [NO₂]ref) were highly significantly correlated with concurrent Aeroqual O₃ sensor observations [O₃]Aeroq. This permitted effective linear calibration of the [NO₂]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.

**Keywords:** semiconductor gas sensor; electrochemical gas sensor; NO₂; O₃; air pollution exposure.

**Introduction**

Ozone (O₃) and nitrogen dioxide (NO₂) are very important air pollutants subject to mandatory air quality limits in many jurisdictions. Road traffic and static combustion are major sources of the NOₓ gases (NO and NO₂) leading to pronounced spatiotemporal gradients in NO₂ in urban areas (Cyrys et al., 2012). As a consequence of the fast photochemical cycling between NOₓ 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 to 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 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.

**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 NO$_2$ and O$_3$ continuously between 7th 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-info?view=aurn). All data from the reference analysers were subject to the network data review and ratification process. Hourly-averaged NO\textsubscript{2} and O\textsubscript{3} derived from these instruments were downloaded from www.scottishairquality.co.uk, and are denoted as [NO\textsubscript{2}]\textsubscript{ref} and [O\textsubscript{3}]\textsubscript{ref}.

**Results and Discussion**

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

Figure 1 shows the time series and scatter plot of hourly averaged O\textsubscript{3} data. The Aeroqual and UV-absorbance reference analyser O\textsubscript{3} data were highly correlated ($R^2 = 0.91$, $n = 1274$), albeit with a trend for this Aeroqual O\textsubscript{3} sensor to overestimate on average compared with the reference instrument when O\textsubscript{3} concentrations from the latter exceeded ~43 µg m\textsuperscript{-3} (e.g. an Aeroqual value of 86 µg m\textsuperscript{-3} for a reference instrument value of 80 µg m\textsuperscript{-3}), and to underestimate on average for concentrations below a reference instrument O\textsubscript{3} concentration of ~43 µg m\textsuperscript{-3} (e.g. 16 µg m\textsuperscript{-3} Aeroqual value for a reference instrument value of 20 µg m\textsuperscript{-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 Figure 2 show very limited agreement between the Aeroqual NO\textsubscript{2} sensor and the reference NO\textsubscript{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) NO₂ sensor and reference analyser observations was reported in a similar comparison by Delgado Saborit (2012) ([NO₂]Aeroq(GSS) = 0.76[NO₂]ref + 7.05; R² = 0.89).

Some sensitivity of gas sensors to ambient water vapour has previously been noted (Bart et al., 2014). Figure 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 (R² = 0.02 and 0.01, for NO₂ and O₃, respectively), and over a range in ambient RH from ~30% to almost 100%. The negative relationship with RH for the O₃ 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 NO₂ 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 NO₂ sensor observations with RH that might account for the limited agreement between NO₂ sensor and NO₂ reference analyser observations. There were similar lack of associations between ‘Aeroqual – reference analyser’ O₃ and NO₂ deviations and ambient T (data not shown).

Instead, we examined whether the substantial deviation of Aeroqual electrochemical sensor NO₂ measurement from the reference measurement may have been driven by interference from ambient O₃. We used the first two-thirds of the measured data (between 7 June and 24
July) as a ‘test’ dataset to investigate this. Figure 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 \(\mu g\) m\(^{-3}\) in this dataset. The OLS linear regression relationship from the data in Figure 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 Figure 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 (confidence interval: 0.99, 1.07) and an intercept very close to zero (95% CI: \(-1.8, -0.4\)) (Figure 5). Only 13 negative values of \([\text{NO}_2]_{\text{Aeroq-C}}\) out of 425 (~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 Figure 4, nor the differences between the \([\text{NO}_2]_{\text{Aeroq-C}}\) and \([\text{NO}_2]_{\text{ref}}\) values plotted in Figure 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 \([\text{NO}_2]_{\text{Aeroq-C}}\)
against \([\text{NO}_2]_{\text{ref}}\) 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 \([\text{NO}_2]_{\text{Aeroq}}\) observations by reference monitors was feasible. The small amount of scatter remaining in the relationship between \([\text{NO}_2]_{\text{Aeroq-C}}\) and \([\text{NO}_2]_{\text{ref}}\) is assumed to reflect the measurement uncertainties in both the Aeroqual and reference analyser data. The very close agreement between the O\(_3\) sensor readings and the reference O\(_3\) instrument in this study suggests that any cross-interference of the O\(_3\) sensor to other ambient species is negligible for this sensor. The consistent functional relationship observed for adjustment of the NO\(_2\) sensor values by O\(_3\) sensor values likewise suggests that any other cross-interference on the NO\(_2\) sensor is much smaller than that of O\(_3\). Finally, it is noted that a potential operational disadvantage of these portable low-power instruments is the minimum ambient operating temperature of \(–5^\circ\text{C}\) currently specified.

**Conclusions**

An Aeroqual Series 500 ENV O\(_3\) semiconductor oxide gas sensor yielded close agreement with hourly-averaged observations from a reference UV-absorbance O\(_3\) analyser in temperate ambient conditions. Although an Aeroqual NO\(_2\) electrochemical sensor appeared to suffer considerable co-sensitivity to O\(_3\) (to the point of the NO\(_2\) sensor evaluated in this study being inadequate as a measure of NO\(_2\) on its own), it was demonstrated that the O\(_3\) interference can be corrected for by co-deployment with an Aeroqual O\(_3\) 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.

Acknowledgements
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References


Table 1: Statistics for the linear relationships in the ‘test’ evaluation of calibrated Aeroqual NO₂ values ([NO₂]_{Aeroq-C}) against measured [NO₂]_{ref} values resulting from the 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 Figure 5.

<table>
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<tr>
<th>Portion of the full dataset used for the regression to derive [NO₂]_{Aeroq-C}</th>
<th>$R^2$</th>
<th>Slope [95% C.I.]</th>
<th>Intercept [95% C.I.] / µg m⁻³</th>
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<tr>
<td>1st 1/3</td>
<td>0.85</td>
<td><strong>1.00 [0.97, 1.03]</strong></td>
<td><strong>-0.25 [-0.76, 0.25]</strong></td>
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<td>0.88</td>
<td>1.10 [1.07, 1.13]</td>
<td>-2.00 [-2.50, -1.51]</td>
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<tr>
<td>3rd 1/3</td>
<td>0.86</td>
<td>1.07 [1.05, 1.10]</td>
<td><strong>-0.83 [-1.32, -0.34]</strong></td>
</tr>
<tr>
<td>1st 2/3</td>
<td>0.88</td>
<td><strong>1.03 [0.99, 1.07]</strong></td>
<td>-1.10 [-1.82, -0.40]</td>
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<tr>
<td>1st 1/3 &amp; 3rd 1/3</td>
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<td><strong>1.03 [0.99, 1.07]</strong></td>
<td><strong>-0.22 [-0.94, 0.47]</strong></td>
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<tr>
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<td>1.11 [1.08, 1.15]</td>
<td>-1.91 [-2.48, -1.36]</td>
</tr>
</tbody>
</table>
Figure captions

Figure 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 (1,274 pairs of hourly averages).

Figure 2: (a) Time series, and (b) scatter plot, of hourly-averaged [NO₂] from measurements made by the Aeroqual NO₂ monitor and the NO₂ chemiluminescence analyser between 7 June and 15 August 2013 (1,274 pairs of hourly averages).

Figure 3: Scatter plot of the deviations of hourly-average O₃ and NO₂ Aeroqual measurements from their respective reference measurements versus RH.

Figure 4: Relationship between ([NO₂]ₐereoq – [NO₂]ₐeref) and [O₃]ₐereoq measurements between 7 June and 24 July 2013 (849 pairs of hourly averages).

Figure 5. Comparison of the calibrated Aeroqual NO₂ values and measured [NO₂]ₐURN between 25 July and 15 August 2013. The [NO₂]ₐereoq-C values were derived according to the OLS regression established using [NO₂]ₐereoq, [NO₂]ₐeref and [O₃]ₐereoq measured at the same site between 7 June and 24 July 2013.
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(a)

(b)
Figure 2: (a) Time series, and (b) scatter plot, of hourly-averaged [NO₂] from measurements made by the Aeroqual NO₂ monitor and the NO₂ chemiluminescence analyser between 7 June and 15 August 2013 (1,274 pairs of hourly averages).

(a)

(b)
Figure 3: Scatter plot of the deviations of hourly-average $O_3$ and $NO_2$ Aeroqual measurements from their respective reference measurements versus RH.

\begin{align*}
\text{Ref} - \text{Aeroq} & = 0.13x - 30.81 \quad R^2 = 0.02 \\
\text{Ref} - \text{Aeroq} & = -0.03x + 2.45 \quad R^2 = 0.01
\end{align*}
Figure 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).

\[
y = 0.79x - 20.72
\]

\(R^2 = 0.92\)
Figure 5. Comparison of the calibrated Aeroqual NO$_2$ values and measured [NO$_2$]$_{AURN}$ between 25 July and 15 August 2013. The [NO$_2$]$_{Aeroq-C}$ values were derived according to the OLS regression established using [NO$_2$]$_{Aeroq}$, [NO$_2$]$_{ref}$ and [O$_3$]$_{Aeroq}$ measured at the same site between 7 June and 24 July 2013.

(a)

(b)