Measurements of sulphur dioxide in rural air: data quality issues

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Summary

Discrepancies between long-term average SO_2 concentrations measured by UV-Fluorescence monitors in the AURN and DELTA denuders from AGA-Net are caused by inadequate performance of UV-F monitors at low concentrations. The hourly data are essential for measuring possible exceedances of limit values – for which the AURN was established – and there is no suggestion that they are no longer fit for that purpose. However, as operated at present they should not be used to provide data for assessing long-term average concentrations. The DELTA denuders in AGA-Net were specifically designed for that purpose, and provide the data needed to assess rural (and suburban) concentrations for model evaluation across the UK.

Background

With the large decline in rural sulphur dioxide emissions and concentrations it became clear in the late 1990s that the daily bubbler measurements were no longer fit for purpose, and alternatives were sought. Initially, filter packs were tested, and found to have improved detection limits, but with the advent of the 'nitric acid' network using the DELTA denuder systems in 1998, the possibility of using DELTAs to measure average concentrations of SO_2 in rural air was mooted and tested. The results of the tests were reported to Defra (Rural Sulphur Dioxide Monitoring in the UK: Data Summary 2001-2005.AEAT/ENV/R/2292 Issue 1. December 2006) and showed that the DELTA denuders provided monthly average concentrations that were well correlated with filter-packs, but with a small positive bias. Quoting:

> *"This comparison allows the following statements to be made:*
> - *The three samplers generally show the same qualitative behaviour with time*
> - *The filter-pack and denuder measurements are in good agreement although the denuder measurements are slightly larger.*
> - *Both the filter-pack and denuder measurements are lower than those of the bubbler. This is especially noticeable during the period from Spring 2002 when there was a significant discrepancy between the filter-pack and bubbler measurement."*

It was concluded that the denuder approach was preferable (there being concern over losses of SO_2 in the filter pack) and the method was adopted for use in the 'nitric acid' network (now AGA-Net).

A comparison of monthly data from denuders and filter packs from the report is reproduced below (Figure 1: original report Figure 3.7a). A separate analysis of annual average data from 33 complete years of paired data from up to 12 sites is shown as Figure 2. Also shown in Figure 2 are annual data from a UV-F analyzer operated at Sutton Bonington for CEH – not part of the AURN.

It is clear from Figure 2 that there was good agreement between the two monitoring methods (UV-F and DELTA) at this site, and that the decision to adopt the DELTA system for long-term rural measurement in the UK was well justified.

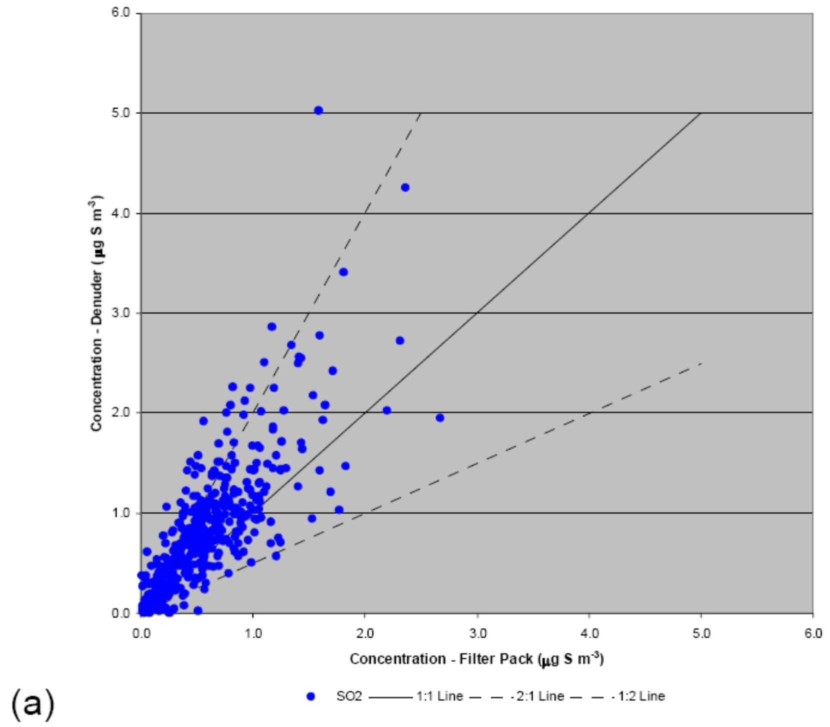

Figure 1: reproduction of Figure 3-7 – *Scatter Plots of the Monthly Concentrations of Denuder Sulphur Dioxide vs Filter-pack Sulphur Dioxide*

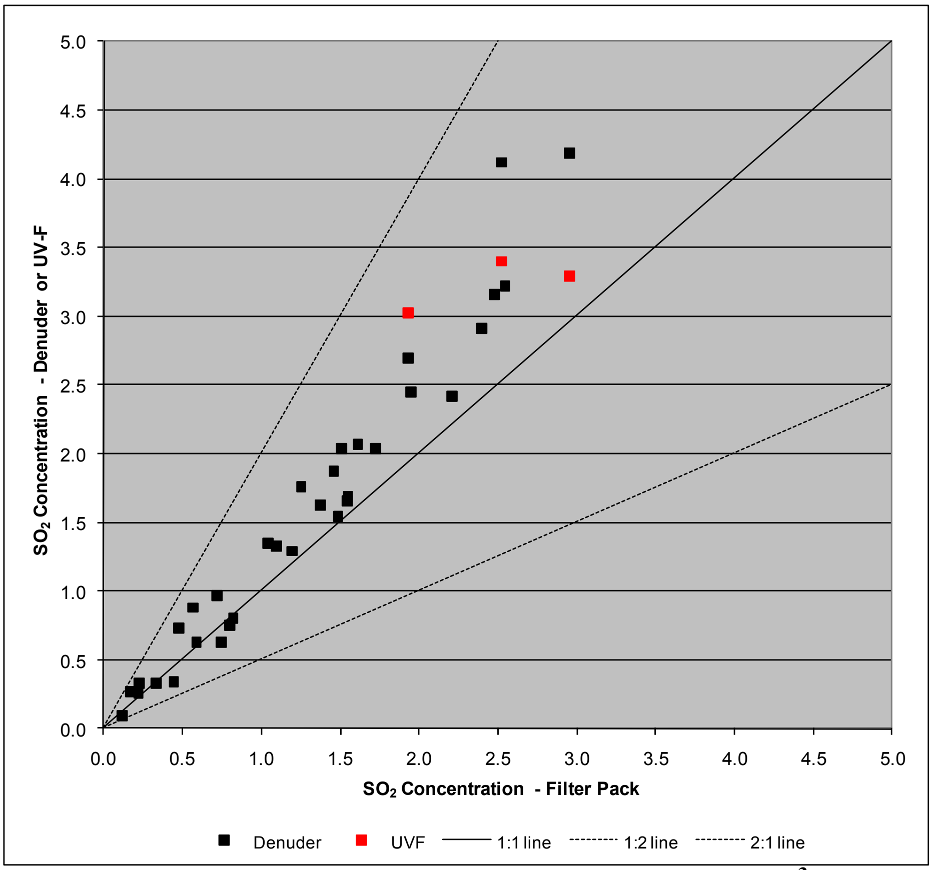

Figure 2: comparison of annual average SO_2 concentrations (µg m^{-3}) from co-located samplers. Horizontal axis – filter packs; vertical axis – DELTA denuders (black) or UV-F (red).

Comparison of DELTA denuders and UV-F analyzers

The AURN uses UV-Fluorescence analyzers to measure SO_2. These are designed to operate continuously and provide hourly average data. The question was raised at the modelling meeting on 28 Jan 2011 as to the accuracy of SO_2 measurements at rural sites in the UK, given the difference between data measured by UV-F instruments operated as part of the AURN, and DELTA denuders operated as part of AGA-Net. Figure 3 demonstrates the issue, using data from sites where SO_2 is measured by both techniques.

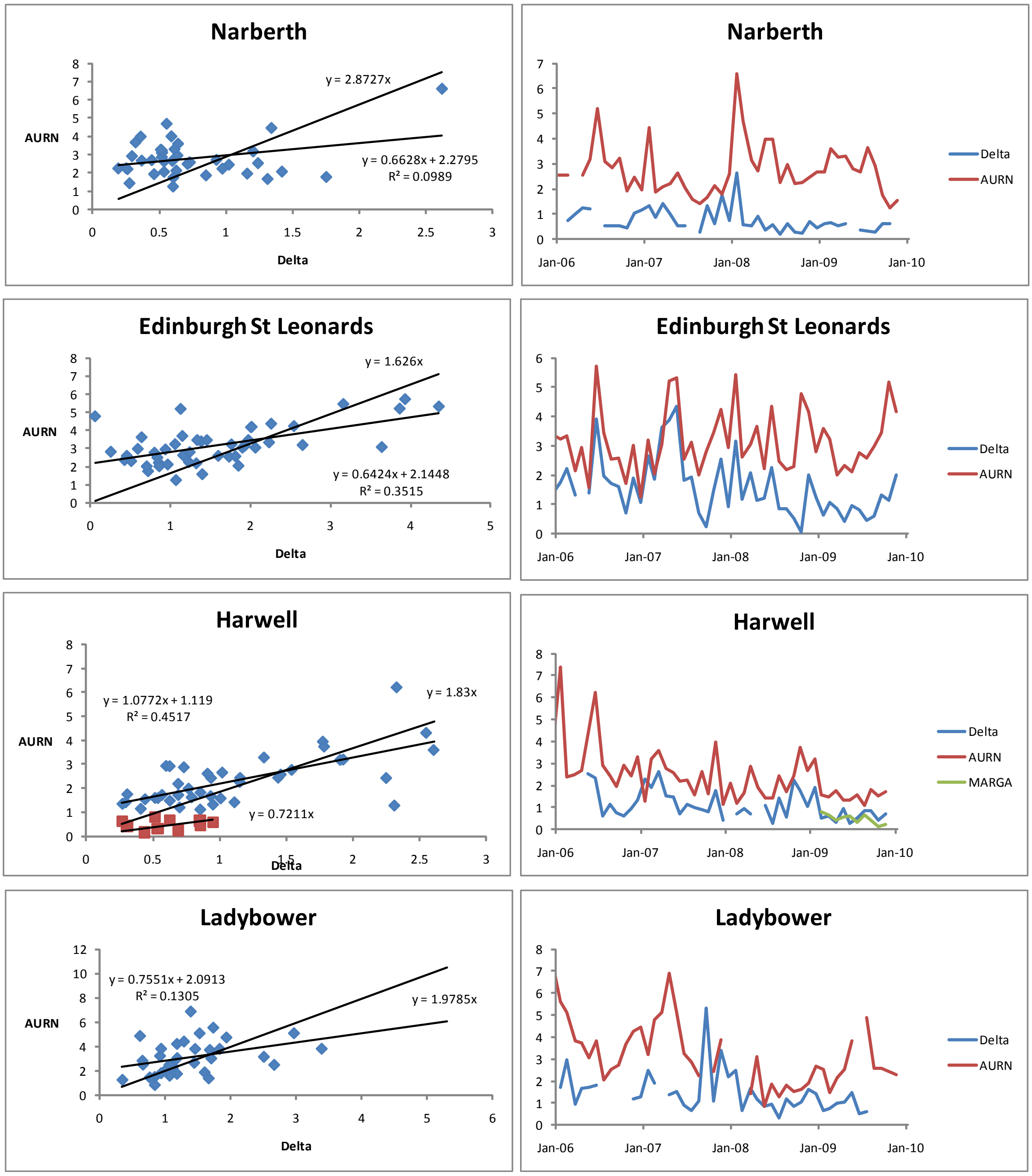

Figure 3: comparison of monthly average SO_2 measurement data (µg SO_2 m^{-3}) between UV-F (AURN) and DELTA denuders (AGA-Net) at 4 sites between 2006 and 2009.

It should be noted from Figure 3 that the UV-F from the AURN and DELTA data follow each other reasonably well (i.e. are correlated in time) even though the absolute values are different. What could be responsible for these differences?

Reasons for the discrepancy

1. Sampling height

There are systematic differences in measurement height between the two methods: the UV-F analyzers sample from a height of 3 – 3.5 m through a pumped sample inlet, whereas the DELTA denuders sample directly from a height of 1.5 m. At some sites this may be partly responsible for the apparent difference in measurements, if there are rapid rates of localised SO_2 deposition that deplete the concentration; this would be most noticeable at sites with low average wind speeds where surface removal is not adequately compensated for by mixing from higher in the atmosphere. Given the locations of the sites (not particularly sheltered from wind) the difference in sampling heights may play only a small role in the observed measurement differences.

2. UV-F vs. DELTA measurements

Comparisons between UV-F analyzers and DELTA measurements are not restricted to AURN sites. CEH has operated UV-F analyzers (usually instruments with a low limit of detection, typically <0.1 ppb) at Sutton Bonington and at Auchencorth, using different data recording and calibration protocols from those used by the AURN. The good agreement between UV-F and DELTA measurements at Sutton Bonington was shown above for annual average data in Figure 2 (red symbols). This relationship can be seen more clearly in a comparison of individual monthly data from the site between 2000 and 2004, in Figure 4. The overall agreement is good, but with a tendency for the UV-F instrument to over-read at lower concentrations, shown by the positive intercept in the fitted regression lines, which in the case of simple linear regression is statistically significantly different from zero.

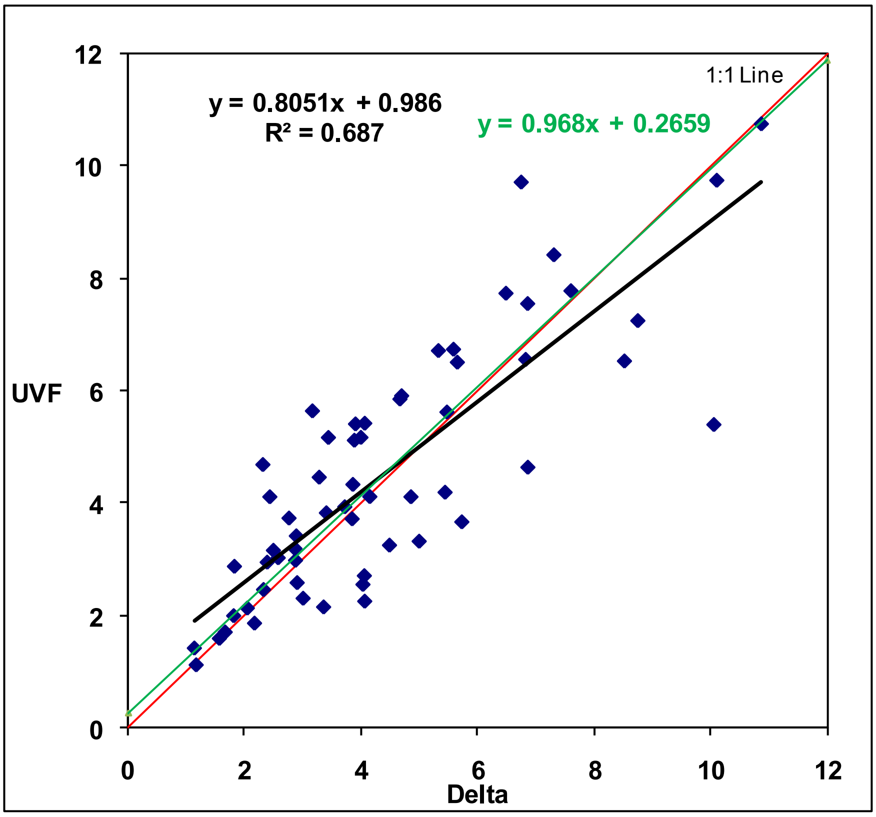

Figure 4: Comparison of UV-F and DELTA monthly SO_2 data from Sutton Bonington, 2000-2004 (orthogonal regression in green, simple linear regression in black).

At Auchencorth Moss, the EMEP Supersite, measurements of SO_2 are made using 3 independent techniques: UV-F (high sensitivity, Thermo Model 43C), DELTA denuders and MARGA (wet denuder). The data averaged monthly (to match deployment of the DELTA system) are shown in Figure 5. It is clear that the DELTA and UV-F data, while not identical, track each other well, and the MARGA systematically underestimates the monthly averages. Part of the reason for this is the relatively poor data capture rate for the MARGA, but probably more important is its slow response to occasional rapid peaks in concentration, which are a characteristic of this remote site.

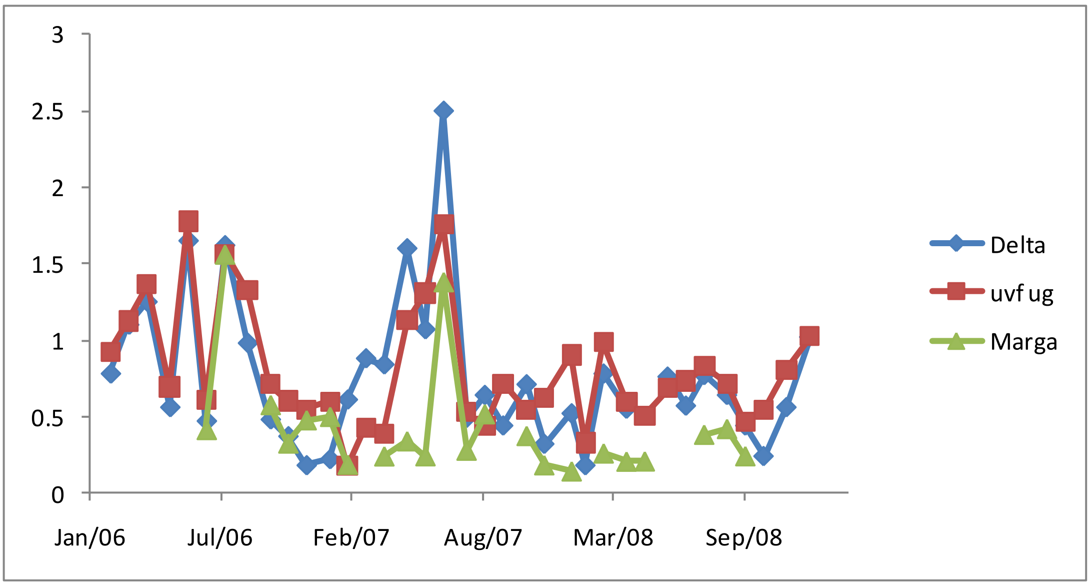

Figure 5: monthly average SO_2 concentrations (µg m^{-3}) at Auchencorth Moss from mid-2006 to 2008, using 3 different measurement techniques.

The relationship between the UV-F data and the DELTA data is shown in Figure 6, and, as at Sutton Bonington, there is a significant non-zero intercept, with the UV-F instrument reading higher at low concentrations.

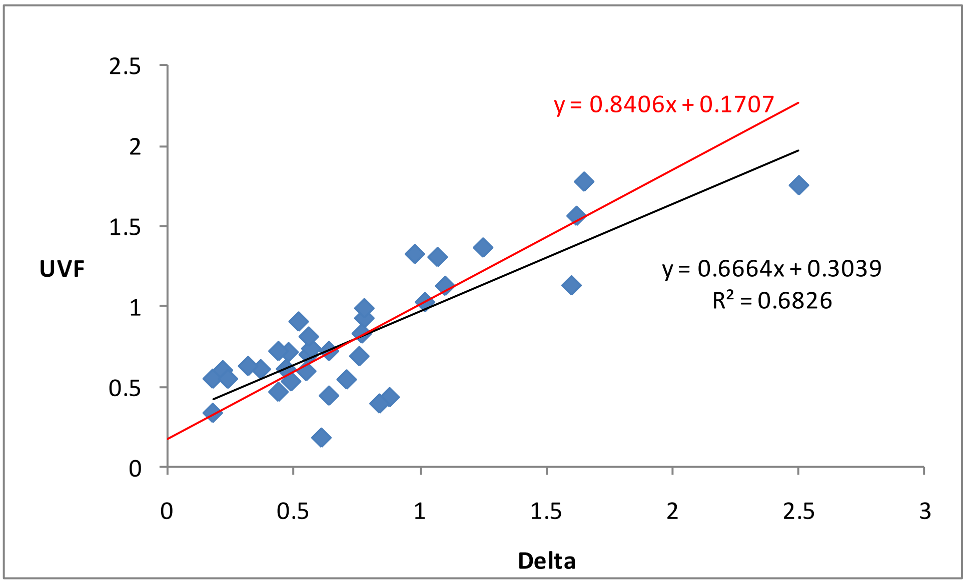

Figure 6: comparison of monthly average SO_2 concentrations (µg m^{-3}) at Auchencorth Moss from mid-2006 to 2008: vertical axis – UV-F, horizontal axis – DELTA. Orthogonal regression in red, simple linear regression in black.

The conclusion to be drawn is that the problem identified in Figure 3 is not related to the measurement principle (UV-F or DELTA). For SO_2 analyzers having a low limit of detection and operated as research instruments, the UV-F and DELTA data agree very well, albeit with a tendency for the UV-F instrument to over-read at the lowest concentrations. So why are there problems at AURN sites?

3. The AURN operating protocol

Closer scrutiny of the site at Harwell identifies important features of the data and point to the source of the observed discrepancies. Since 2009 this site has also operated a MARGA, and as can be seen from Figure 3, the MARGA data are in good agreement with the DELTA data. Both the MARGA and the AURN analyzers provide hourly data, allowing a closer scrutiny of their characteristics. The hourly data for 2009 are shown in Figure 7 (AURN in red, MARGA in blue). Immediately obvious is the 'banding' of the data at 2.7 µg m^{-3} (equivalent to a reading of 1 ppb), and a less obvious band at half that value. This suggests that data are not reported with sufficient precision at low concentrations, leading to the possibility of positive bias, either because of instrumental or data-logging operating protocols. This can be seen more clearly in Figure 8, which expands Figure 7 for the months of October to December.

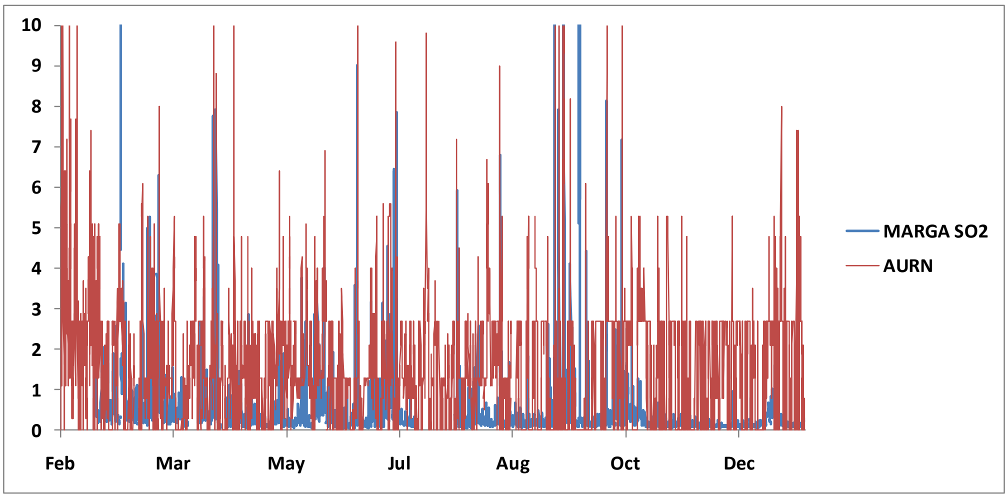

Figure 7: hourly SO_2 data from Harwell in 2009, from AURN (UV-F) and MARGA analysers (µg m^{-3})

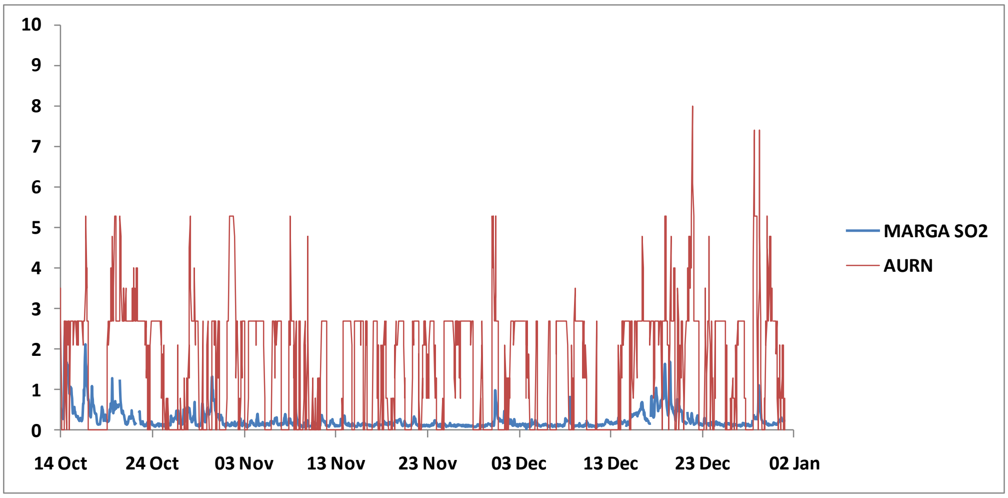

Figure 8: hourly SO_2 data from Harwell, October - December 2009, from AURN (UV-F) and MARGA analysers ($\mu g\ m^{-3}$)

This leads to the relationship between hourly values shown in Figure 9, where the banding is still obvious. Note that there is a lot of scatter, and that the best-fit line intercepts the x-axis at around 1.1 $\mu g\ m^{-3}$ yet the slope is close to unity. There is a very strong positive bias to the UV-F data at low concentrations ($< 2\ \mu g\ m^{-3}$). This behaviour is also illustrated in the frequency distribution of the measurements (Figure 10) where the MARGA data present a typical log-normal distribution with smoothly-varying data and the AURN data is marked by clear spikes at multiples of 0.1 ppb (0.3 $\mu g\ m^{-3}$).

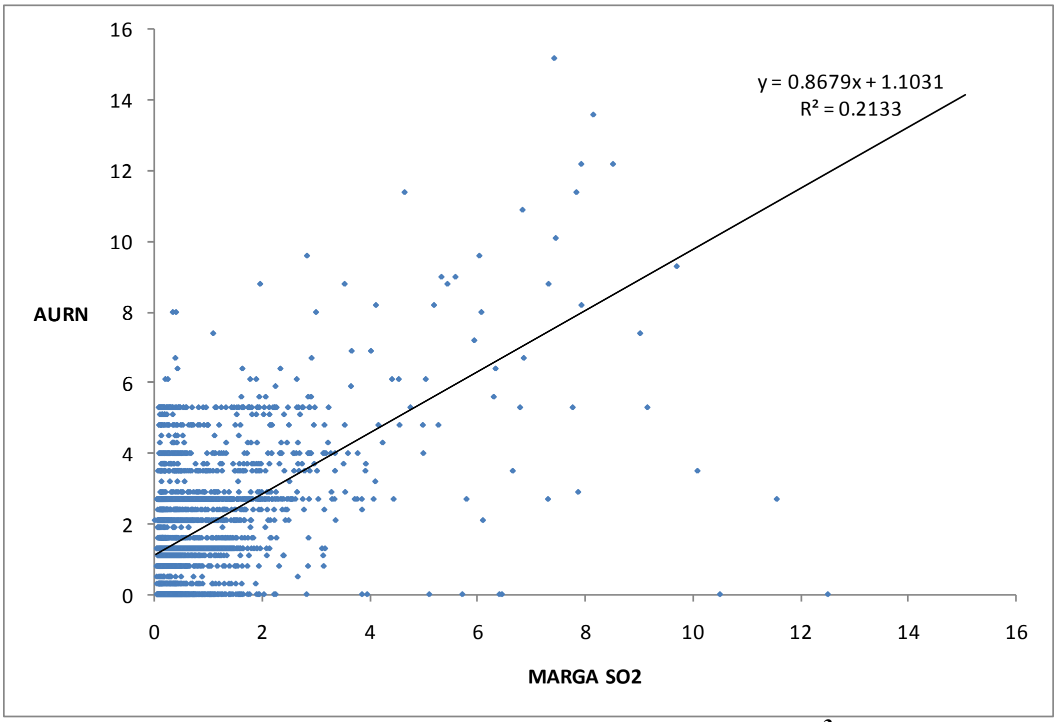

Figure 9: relationship between hourly SO_2 concentrations ($\mu g\ m^{-3}$) at Harwell in 2009, comparing AURN (UV-F) and MARGA data.
Orthogonal regression gives y=0.861x + 1.106

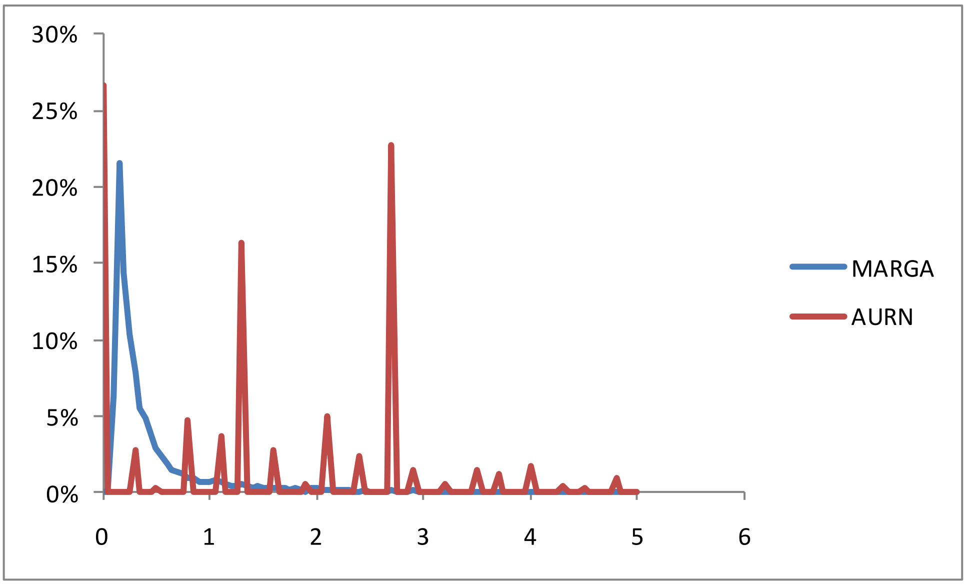

Figure 10: Frequency distribution (% of hourly data) vs SO_2 concentration (µg m^{-3}) at Harwell in 2009, from AURN (UV-F) and MARGA data.

The marked 'discretization' of the reported data suggests that much information is being lost by rounding errors, either in the data-logging system, or in the subsequent data processing. The pattern of SO_2 distribution in Figure 10 suggests a very serious problem which completely disguises the underlying log-normal distribution of the monitoring data, and casts doubt on the validity of any averaged data derived from the data set.

The clear conclusion to be drawn from the data is that measured SO_2 concentrations from the UV-F instruments, as deployed in the AURN network, are incorrect. The method of operation is not fit for the purpose of measuring the low ambient SO_2 concentrations currently observed throughout many of the AURN sites (particularly those classified as 'rural'). There are two issues here: the stability and precision of the instruments themselves, and the protocols under which they are operated.

3.1 UV-F analyzers

UV-fluorescence is an efficient and effective method for measuring SO_2 in ambient air, with few interferences from other molecules. However, some interference (positive) from UV-fluorescing hydrocarbons is possible, and most instruments are fitted with a hydrocarbon 'kicker' to minimise such interference. At most of the rural AURN sites it is unlikely that this would be a problem. Commercial instruments have published limits of detection and zero drift – these vary slightly from manufacturer to manufacturer, but are typically of the order of ±0.2 ppb. For example, the manual for the Thermo Model 43B Pulsed fluorescence SO_2 analyzer quotes a precision of 0.2 ppb and a drift of less than 0.2 ppb per day (which, however, could be as much as 3.8 µg m^{-3} per week). The Model 43C Trace Level analyzer quotes its best lower detection limits as 0.03 ppb RMS with 300 sec averaging time, with a corresponding lower detection limit of twice that, and again, a zero drift of <0.2 ppb per day. It also reports potential interferences from NO and m-xylene < 1 ppb (though this may be a printing error, and >1 ppb is intended).

The instruments (Model 43B) used in the AURN network therefore would appear to have an inherent precision of no better than 0.5 µg m^{-3}, and the possibility of a zero drift of several µg

m^{-3} per week. These numbers should be compared with the annual average concentrations recorded at the AURN sites in Figure 3 of between 2 and 4 µg m^{-3}.

3.2 AURN protocol

The site operators' manual (Site Operators Manual Automatic Urban and Rural Network, Defra and the Devolved Administrations, Report No: AEAT/ENV/R2750, March 2009) lays down criteria for routine checks and calibrations, e.g. that the requirement for an acceptable zero value is that it should not drift by more than 2 ppb (5 µg m^{-3}) over 10 minutes and should be within 4 ppb (10 µg m^{-3}) of the previous calibration. These checks are not adequate for establishing a correct zero value where the measurements mostly fall in the range 0-5 µg m^{-3} (0 – 2 ppb).

3.3 Data-logging and discretization

As noted above, the data from the Air Quality database are constrained to be multiples of 0.1 ppb (~ 0.3 µg m^{-3}), which would be appropriate for an analyzer with a precision of that level. However, the distribution of the actual hourly data values shows much greater levels of discretization than expected, or likely to be 'real'. It could be that the readings are logged as integer values of ppb, and averages over the hour create apparent better precision in the hourly averages. Logging of the analogue outputs (if available) would provide a better integrated value than logging the digital outputs, as appears to be the case. It is possible that the discretization occurs not during data-logging, but during subsequent data processing – either way, this appears to be a remediable shortcoming in the process.

CONCLUSIONS

From consideration of all the above, it is clear that the discrepancies in SO_2 measurements between the AURN UV-F analyzers and the DELTA denuders can be satisfactorily explained as a deficiency in the precision and accuracy of the measurements reported from the current SO_2 UV-F analyzers. It is not clear whether the problem is with the instruments themselves, the data-logging, the operation of the instruments or the subsequent data-processing. It appears that UV-F instruments <u>can</u> provide reliable long-term monitoring data at low ambient concentrations, but not as operated within the AURN. The hourly data are, however, essential for measuring possible exceedances of limit values – for which the AURN was established – and there is no suggestion that they are no longer fit for that purpose. However, as operated at present they should not be used to provide data for assessing long-term average concentrations because of the limitations described above. The DELTA denuders in AGA-Net were specifically designed for that purpose, and provide the data needed to assess rural (and suburban) concentrations for model evaluation across the UK.