

Interactive comment on “A broadband cavity ringdown spectrometer for in-situ measurements of atmospheric trace gases” by M. Bitter et al.

M. Bitter et al.

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Our ACPD paper “A broadband cavity ringdown spectrometer for in situ measurements of atmospheric trace gases” by M. Bitter et al. received comments from two referees during the open discussion period. We thank the referees for their constructive comments which are addressed below:

Referee 1

Long-duration averages:

The measurement protocol was intermediate between the two extremes identified by the referee, namely either fitting a set of wavelength-resolved ringdown times to each ringdown event (which would be a formidable computational task) or co-adding a large

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number of decay traces and subsequently fitting a single set of ringdown times. We agree that the latter can lead to multi-exponential decays if the instrument experiences mechanical instabilities or the atmospheric absorption/scattering changes during the acquisition period. Therefore we have sought to measure ringdown times over the shortest acquisition period practicable, and we monitor their variation to ensure optimum performance of the instrument.

Each CCD image is the summation of multiple ringdown events integrated on the clocked CCD detector (section 2.4). During Namblex, the number of ringdown events integrated on-chip was usually between 20 and 100, which corresponds to an acquisition time of between 1 and 5 seconds per CCD image for the 20 Hz repetition rate of the laser. The analysis procedure fitted each CCD image separately to generate a unique set of wavelength-resolved ringdown times. Only then was computational averaging performed on ringdown times from sequential CCD images. So for example the data in Figure 12 come from a batch of 10 CCD images, each the on-chip average of 100 ringdown events. These 10 CCD images generated 10 sets of wavelength-resolved ringdown times, which were then averaged to yield a set of mean ringdown times from which the BBCRDS spectrum was calculated. A similar averaging protocol applied to the background data obtained when flushing the cavity with dry filtered nitrogen.

Regardless of the number of CCD images used to calculate the BBCRDS spectrum, all of the fitted ringdown times were retained in the analysis software and used to verify the instrument's performance. Those few CCD images that produced ringdown times substantially different from the mean value of neighbouring images were rejected by the analysis software. Perhaps the best test of the instrument's stability comes from CCD images acquired when flushing the cavity with dry nitrogen because these exclude the effects of atmospheric changes. There was no evidence of multi-exponential behaviour in the flush CCD images of the data reported here, illustrating the instrument's stability against vibration on the timescale needed to acquire a CCD image (a few seconds). The stability over periods of tens of minutes also seems good because typically there

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was no statistically significant difference between flush ringdown times acquired before and after a batch of sample observations. Rather, the flush ringdown times sometimes increased slightly during a sequence of measurements, possibly as a result of water vapour out-gassing from the optical surfaces whilst the mirrors were being purged with dry nitrogen.

Changes in the atmospheric absorption certainly do lead to changes in the ringdown times. However these changes tended to be slow and smoothly varying within a sequence of CCD images because the main contributors to the atmospheric absorption come from the relatively slowly varying aerosol loading and water vapour concentrations. Thus the data used to generate the long-duration average BBCRDS spectra in the upper panel of Figure 7 were selected because their 190 constituent CCD images were acquired over periods when the measured aerosol optical depth and water amount remained fairly constant. Undoubtedly, the amounts of NO_3 varied over the spectra's 42 minute averaging periods and so and the fitted value of $[\text{NO}_3] = 2.7$ pptv represents a time-averaged difference in the NO_3 amounts.

Open path cavity:

The choice of an open cavity was a deliberate one taken, as the referee identified, to avoid losses of the radicals to inlet filters or internal surfaces of the instrument. Inlet/wall losses have been determined for NO_3 and N_2O_5 for this and other instruments [Brown et al., Rev. Sci. Instrum., 73, 3291–3301, 2002] and appropriate corrections to the data can be made. The inlet/wall losses are likely to be substantially larger for a highly condensable species such as OIO, and obtaining a stable source of OIO to quantifying these losses in the laboratory experiments is challenging. We sought to obviate these problems through the use of an open cavity.

During Namblex, aerosol extinction was often the largest attenuation of light circulating inside the ringdown cavity. Clearly aerosol extinction has implications for the longest ringdown times achievable with the instrument. But a longer ringdown time gained by

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filtering ambient aerosol does not necessarily lead to a proportionate increase in sensitivity if the transmission of target species through the filter is inefficient or introduces additional uncertainties. Besides, the aerosol optical depth measured by BBCRDS is an important atmospheric measurement itself, see our forthcoming companion paper.

Broad versus narrowband CRDS and the treatment of water's absorption features:

Ambient water vapour is the largest contributor to the differential structure in atmospheric absorption spectra at the visible wavelengths used in this study. As noted by both referees, a careful subtraction of this structure is necessary in order to fit the weaker underlying differential structure due to NO_3 or I_2 and OIO. This and previous work [Ball & Jones, Chem. Rev., 103, 5239–5262, 2003] provide a quantitative method for doing so in the analysis of BBCRDS spectra. The literature additionally contains many papers addressing the treatment of narrowband features in atmospheric absorption spectra obtained using long- or multi-pass DOAS techniques, including the complications that arise when the detected radiation has passed through an inhomogeneous sample (e.g. the atmospheric transmission at different altitudes).

In contrast, narrowband lasers can be used to target broad absorption features at wavelengths in between water's narrow absorption lines, thereby avoiding instrumental resolution issues. This methodology has been applied by other groups in their highly successful measurements of NO_3 and N_2O_5 [Brown et al., Rev. Sci. Instrum., 73, 3291–3301, 2002; Simpson, Rev. Sci. Instrum., 74, 3442–3452, 2003]. In a variable atmosphere, the ringdown time is determined by other absorbers and aerosol extinction in addition to the target molecule's absorption and, in the studies referenced above, these interferences were identified and carefully excluded so that changes in the ring-down time at a single wavelength at the peak of the NO_3 absorption band yielded quantitative measurements of the absorber. However this requires prior knowledge of the interferences, whereas greater flexibility is afforded by making cavity measurements over a broad range of wavelengths and filtering other contributions to the atmospheric absorption spectrum using DOAS fitting methods. The post-campaign reanalysis of

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BBCRDS spectra to confirm detection of ambient I_2 by the University of East Anglia's long-path DOAS instrument is an additional illustration of the broadband method's flexibility, since neither instruments' operators were expecting to detect I_2 at the time the data were acquired.

There is no fundamental reason why BBCRDS is limited to visible wavelengths. The technique could be applied at other wavelengths if suitable pulsed broadband radiation is available.

DOAS treatment of the aerosol extinction:

It is important to choose the “correct” function to account for the aerosol extinction during the DOAS filtering of BBCRDS data. The aerosol extinction is assumed here to vary smoothly over the range of wavelengths accessed by the BBCRDS instrument: a quadratic or linear function was applied for the 18 nm or 8 nm bandwidths, respectively. Higher order polynomials and a Fourier filtering method were tested with the present analysis procedure but produced less certain retrievals, principally because these higher order functions yield better “fits” to NO_3 , I_2 or OIO absorption cross sections and thereby reduce the amount of differential structure remaining in the filtered absorption spectrum. Unfortunately, the cross sections of OIO around 568 nm vary smoothly over the limited bandwidth of the laser deployed during Namblex, which has a detrimental impact on the detection limit for this species. This is why recent development work on the system has focused on increasing the bandwidth at short wavelengths (see the Conclusions section of the paper).

Interference effects within the mirror substrates and coatings:

We have no experience of these effects.

Coupling light into the ringdown cavity:

The dye laser contained various beam-shaping optics that were used to collimate the light before injection into the cavity. The laser beam was carefully aligned along the axis

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of the cavity using a pair of irises; the input iris remained in place during measurements (Figure 1). Mode beating was not observed for a properly aligned cavity.

Atmospheric path lengths:

The caption to Table 1 has been clarified. The path lengths given in Table 1 are those calculated from typical ringdown times measured in ambient samples at wavelengths away from water vapour's absorption bands. They are those achieved in the field and therefore include ambient aerosol and Rayleigh scattering. Much longer path lengths were accessed when the cavity was flushed with dry filtered nitrogen (e.g. $\tau = 250 \mu\text{s}$ and an equivalent path = 75 km for mirror pair #2, Table 1 and Figure 3b). Aerosol extinction and Rayleigh scattering are excluded from the reflectivities given in Table 1 and Figure 3.

Detection limits:

The uncertainties given with Figures 12 & 13 are the combined result of the (1σ) statistical uncertainty in the concentrations retrieved by the DOAS fitting routine and the systematic errors due to, for example, uncertainties in the absorption cross sections and the water spectral databases, correction of the N_2O_5 amount for the factors addressed in the comment to Referee 2 below etc. . . . Laboratory experiments on increasingly dilute samples of NO_3 have shown that the uncertainty of the retrieved concentration (approx 0.5 pptv [Ball & Jones, Chem. Rev., 103, 5239–5262, 2003]) varies little with the concentration's absolute value between several hundred and 2 pptv. It seems likely therefore that the fitted uncertainty (especially for highly dilute samples) also represents the detection limit achievable with the instrument. The signal-to-noise at any one wavelength in a BCRDS spectrum is quite modest, and would not be sufficient to achieve the detection limits quoted here were it not for the simultaneous measurements and DOAS fitting performed over a range of wavelengths.

We accept the technical corrections and have amended the manuscript accordingly.

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Referee 2

Several of the second referee's comments have been address in our responses to the first referee.

Acquisition of zeroes and flushing the cavity with nitrogen:

The cavity was flushed with dry nitrogen in order measure the ringdown times (or, equivalently, the effective path length) in the absence of losses due to atmospheric absorption/scattering. Nitrogen was used rather than synthetic air simply because the gas could be obtained in high purity at a reasonable cost. Nitrogen and air do have different Rayleigh scattering cross sections and presumably this difference is large enough to be detectable by BCCRDS. Regarding the present work, differences in Rayleigh scattering between the flush and ambient samples due to the identity of bulk gas or changes in ambient pressure would become folded into the baseline by the DOAS fitting procedure. Thus Rayleigh scattering differences contribute to a smaller error in the retrieved aerosol extinction, which ranged between $\alpha(\text{aerosol}) = 1.4 \times 10^{-6}$ and $1 \times 10^{-7} \text{ cm}^{-1}$ at 660 nm for the ambient aerosol encountered during Namblex.

We agree that it is cumbersome to interrupt the open path BCCRDS measurements to insert a glass tube between the mirrors in order to flush the cavity with nitrogen. This procedure was performed at roughly hourly intervals to check the alignment of the cavity and the integrity of the mirrors. The gas fittings on the mirror mounts are mechanically isolated from the mirrors themselves so this procedure does not normally disturb alignment. Eventually, it may be possible to eliminate flushing the cavity because BCCRDS spectra of ambient samples contain absorption features due to water vapour whose concentration can be measured independently by other methods. Thus the differential spectral structure due to known amounts of water vapour could be used to deduce the effective path length of the measurements and hence the absolute concentration of other absorbers.

Measurement of the sum of NO_3 and N_2O_5 :

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The referee is correct in stating that the retrieved $[\text{NO}_3 + \text{N}_2\text{O}_5]$ concentrations are multiplied by a factor of 1.97 to correct for the combined effects of dilution (1.36), incomplete thermolysis of N_2O_5 (1.05) and wall losses (1.38). The uncertainty in the sample's dilution within the heated cavity is small (the accuracy of the flow controllers is a few percent). Chemical modelling of the thermal decomposition of N_2O_5 inside the cavity indicates that this process goes almost (95%) to completion at 60°C . Suppose the sample were 10°C cooler than measured by the thermocouple: our modelling shows decomposition is still 88% at 60°C (only a 7% underestimation of the 1.05 correction factor). Thus the major uncertainty with the net correction factor lies with uncertainty in the wall losses of NO_3 (the first order rate coefficient was measured to within only $\pm 30\%$; line 20 on page 3499). Accordingly we estimate the uncertainty on the net correction factor to be $\pm 35\%$.

The use of a larger flow rate would probably reduce the wall losses, provided that the residence time in the heated tube ensured efficient thermal decomposition of N_2O_5 . Increasing the temperature may be counter-productive since Brown et al [Rev. Sci. Instrum., 73, 3291–3301, 2002] observed increased NO_3 wall losses above 70°C .

Time resolution & the variability of ambient $[\text{NO}_3]$:

We accept that the temporal resolution of the present data (100s), whilst sufficient to capture changes in air masses, is not sufficient to follow rapid variations in NO_3 concentrations. We show in our companion paper that $[\text{NO}_3]$ measured locally at the Mace Head Atmospheric Research Station is heavily influence by NO emissions from the surrounding wetland soil. Nighttime concentrations of $[\text{NO}] = 50$ pptv were common, giving an NO_3 lifetime of 30 seconds. Although the acquisition time of an individual CCD images was approx 10 seconds including read out and storage times, due to the low $[\text{NO}_3]$ on the shoreline it was unfortunately necessary to average data from a number of CCD images. Hence temporal resolution was lost. The instrument could certainly perform more rapid measurements on larger NO_3 concentrations (albeit with a concomitantly poorer detection limit) such as those observed in urban outflow (up to

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50 pptv; Brown et al., J. Geophys. Res., 108, 4299, doi:10.1029/2002JD002917, 2003) and polluted marine environments (up to 25 pptv; Brown et al., Geophys. Res. Lett., 31, L07108, doi:10.1029/2004GL019412, 2004].

S. M. Ball, 26 August 2005

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