Atmos. Chem. Phys. Discuss., 12, C5346–C5349, 2012
www.atmos-chem-phys-discuss.net/12/C5346/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Iodine emissions from the sea ice of the Weddell Sea" *by* H. M. Atkinson et al.

H. M. Atkinson et al.

hkro@bas.ac.uk

Received and published: 3 August 2012

We thank the authors of the two short contributions for the thoughtfulness they have brought to their questions, which are serious and important.

.

Responses to Interactive comment by U. Friess.

The manuscript of Atkinson et al. presents a very comprehensive set of measurements from a ship cruise in the Weddell Sea. The suite of iodine compounds measured during this campaign represents a unprecedented dataset which offers the opportunity to study the mechanisms of iodine release in detail. However, in my opinion some questions regarding the measurement technique and the influence of I2 on ozone chemistry

in the marine boundary layer remain.

The first question is related to the IO dataset measured by the MiniDoas instrument. From our experience, scattered light measurements by an Ocean Optics 2000 spectrometer in a MiniDOAS setup results in residual structures with an RMS of at least 5 x 10-4. The peak cross section of IO amounts to about 3 x 1017 cm2, resulting in a detection limit for the IO slant column of approximately 2 x 1013 molec cm-2. With an AMF of about 10 for elevation angles of 4° and 50° for measurement and reference, respectively, the detection limit is only slightly below the observed VCD values of 3 x 1012 molec cm-2. Therefore it would be useful for the reader to provide a more detailed discussion of random and systematic error sources in addition to the uncertainty in mixing layer height which is the only error source mentioned in the manuscript.

Response: The MAX-DOAS measurements of IO are but a small part of the data set and are supplemented by satellite measurements of IO, so it is not appropriate to show more figures in the main part of the paper. However, Dr Friess raises an important point. We do not see such large residual features in our data, possibly because of the better thermal control of the spectrometer and detector from having the system indoors, so the errors on each slant column are usually less than 1 x 1013 molec cm-2. Also, by taking daily values we average over many spectra. We have now included the following: “Errors on slant columns given by the spectral fitting program mostly varied between 3 and 8 x 1012 molec cm-2, though a few values are as large as 12 x 1012 molec cm-2. The standard deviation of IO slant columns at each elevation on each day mostly varied between 3 and 6 x 1012 molec cm-2, though a few values are as large as 30 x 1012 molec cm-2. Hence there is some consistency between the spectral fit and scatter of the points, except there are some occasional outliers on some days, hence our decision to use daily medians rather than daily means. Dividing by the mean AMF results in an error on the individual vertical columns of 0.5 to 1 x 1012 molec cm-2. The number of elevation scans on each day ranged from 4 to 48, with a mean value of 19. It is unclear if the error in vertical column would reduce by the averaging, but if so

ACPD

12, C5346–C5349, 2012

it would then be mostly less than 0.2 x 1012 molec cm-2."

A plot showing the fitted cross sections and the residual of a spectral analysis and another plot showing the diurnal variation of the IO dSCDs for different elevation angles would help to estimate the trustworthiness of these measurements, which are very close to (if not below) the detection limit achievable by an USB2000 spectrometer. A very large wavelength range (409 – 474 nm) has been chosen for the IO spectral retrieval. This wavelength range contains a relatively strong water vapour absorption band centred around 443 nm. It is well known that, both owing to saturation effects and uncertainties in the water vapour absorption cross section, including this absorption band leads to unreasonably high residuals. To our experience, the residual including this absorption band is significantly higher than if the upper limit of the fitting window is below 440 nm, making the IO retrieval very difficult even in the dry Antarctic atmosphere. Again, to give the reader an impression of the fit quality, it would be useful to include an example plot of the spectral retrieval.

Response: Showing the fit to a single spectrum is not useful as with our elevation angles and exposure times one cannot discern an IO signature by eye. However, the residuals are mostly small as exemplified by the small errors from the spectral fit quoted above. Also, it is hard to discern the diurnal variation as we have restricted ourselves to SZA < 80°. But the values we deduce are broadly similar to those deduced from satellite measurements in Figure 5, so we and the reader should have faith in their trustworthiness.

The second question relates to the very high I2 mixing ratios of up to 12 ppt observed during the campaign. Given a photochemical lifetime of 1.2 s and a complete oxidation of the resulting I atoms to IO by ozone would result in a ozone loss rate of 20 ppt/s (not including the additional ozone loss by the catalytic IO/IO and IO/HO2 cycles). This means that not only exorbitantly high IO concentrations should be expected, as you discuss based on the THAMO model results, but also that the background ozone of typically 20 ppb in the lowermost 20 m of the atmosphere would be destroyed within 15

ACPD

12, C5346–C5349, 2012

min, or within the whole boundary layer within approximately three hours. Apparently, a significant ozone destruction has not been detected. How do your ozone observations fit into this picture?

Response: This is the whole quandary thrown up by the set of measurements in our paper. It would not be the first time that measurements have conflicted with preconceived theory. Dr Friess has a recent example of his own concerning measurements of IO within the snowpack – a fine piece of work but in complete contrast to theoretical expectations.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 11595, 2012.