

# Measurements of Iodine monoxide (IO) above Spitsbergen

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**Abstract.** Zenith sky measurements of scattered light have been made at Ny-Ålesund, Spitsbergen (79°N, 12°E) since the beginning of 1995. A differential optical absorption spectroscopy (DOAS) algorithm has been used to retrieve differential slant column densities (DSCD) of IO for the observations from 1995-1998. IO was detected every year for several days within each month. Model simulations result in an estimated stratospheric IO mixing ratio in the range from 0.65 to 0.80 ( $\pm 0.2$ ) pptv in polar spring 1997. In addition, indications for the presence of tropospheric IO have been found in late spring and summer of each year.

## Introduction

In the last 25 years, the chemical removal of stratospheric ozone has generated much research, which has resulted in a dramatic improvement in our knowledge of the physical and chemical processes determining the behaviour of the stratosphere. Nevertheless neither the absolute magnitude nor the seasonal variation of the trend in  $O_3$  is well understood.

Solomon *et al.* [1994] suggested, that iodine chemistry may also contribute to stratospheric  $O_3$  removal. The presence of IO in the atmosphere was first reported from ground based zenith sky DOAS measurements at Ny-Ålesund [Wittrock *et al.*, 1996]. In contrast, an upper limit for IO of 0.2 pptv in the stratosphere was determined from balloon borne solar occultation observations at high latitudes (around 70°N) and mid-latitudes (44°N) [Pundt *et al.*, 1998]. Similarly, ground based FTS solar occultation measurements at Kitt Peak (40°N) derived a limit of 0.2 (+0.3 -0.2) pptv for the mixing ratio of total inorganic iodine ( $I_y$ ) in the stratosphere [Wennberg *et al.*, 1997]. However, observations up to 6 pptv IO in the boundary layer have now been reported for mid-latitudes [Carpenter *et al.*, 1999].

In order to reach the stratosphere in significant amounts, emitted iodine compounds such as alkyl iodides (e.g. [Carpenter *et al.*, 1999] and refs. therein) must have sufficiently long chemical and photochemical lifetimes in the troposphere. In general, the tropospheric photolytic lifetime of organoiodine species is short, but dependent on temperature and solar zenith angle (SZA) it is estimated to extend to a couple of days [Roehl *et al.*, 1997]. Rapid stratosphere-troposphere exchange mechanisms, or exchange during nighttime (e.g. in polar winter) may provide a mechanism by which iodine enters the stratosphere. The study from Davis *et al.* [1996] reports observations of up to 1 ppt  $CH_3I$  in the upper troposphere, supporting such stratospheric iodine sources.

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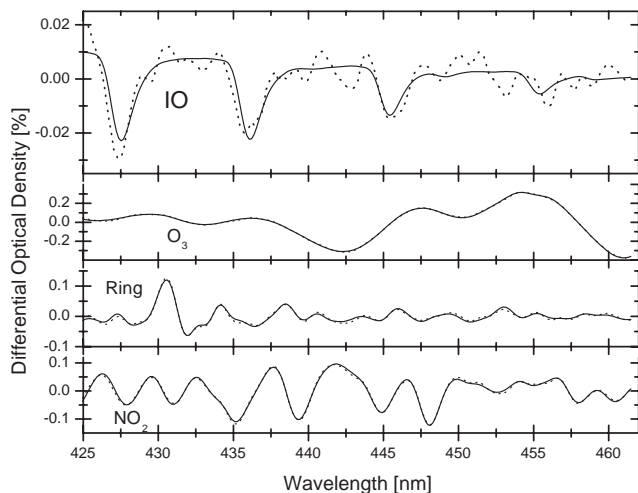
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In this study four years of zenith sky DOAS measurements, made at Ny-Ålesund, Spitsbergen, have been analysed to ascertain the stratospheric IO amount.

## Experiment and data analysis

The details of the spectrograph and telescope arrangement used to make zenith sky scattered sunlight measurements at Ny-Ålesund have been described in detail elsewhere [Wittrock *et al.*, 1996]. Briefly light is collected by a telescope and focused onto a depolarising quartz fibre bundle, which transmits the light onto the entrance aperture of a spectrograph. The resultant spectrum is recorded by a Reticon diode array having 1024 detector elements. During this study the instrument observed in the near-UV and visible in the range from 327 to 491 nm: the spectral resolution being defined by a FWHM of 0.9 nm. The system was accepted as a part of the NDSC network in 1999.

IO has seven strong electronic vibrational bands in the visible and is therefore a suitable candidate for DOAS retrieval from atmospheric spectra. The spectral fitting window of 425 - 461.5 nm, containing the vibrational bands (1-0) to (4-0), was selected for the determination of the slant column amount of IO in this study. The other bands have been excluded, as they may correlate with the OCIO absorption features. For DOAS retrieval, the reference spectra for  $O_4$ ,  $NO_2$  [Burrows *et al.*, 1998] and  $O_3$  have been used together with a synthetic Ring spectrum, which accounts for



**Figure 1.** Example of an IO fit for a spectrum taken on March 1, 1997 (SZA=91.5°). The solid lines are the scaled laboratory spectra for absorbers included in the fit, the dotted lines are the fit results. This fit yields an IO DSCD of  $1.4(\pm 0.4) \cdot 10^{13}$  molec/cm<sup>2</sup>. As background for this fit a spectrum from the same day (SZA = 89°) has been taken.

**Table 1.** Number of days in each month with positive identification of IO (definition see text; in brackets those days, where the diurnal variation of DSCD indicates stratospheric amounts).

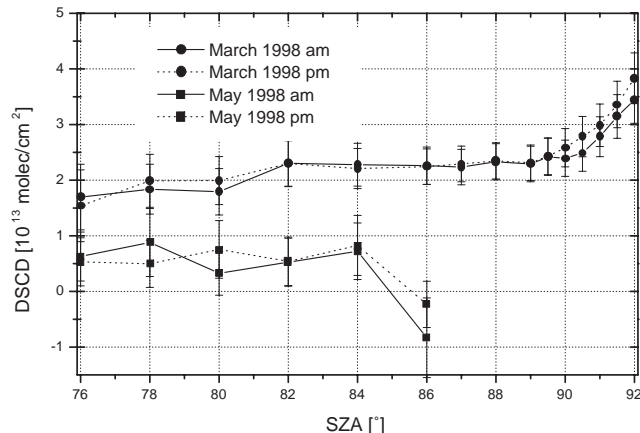
	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct
1995	3 (1)	9 (6)	8 (1)	10 (0)	4 (0)	8 (0)	9 (0)	10 (1)	8 (3)
1996	6 (3)	15 (1)	13 (1)	10 (0)	8 (0)	5 (0)	6 (0)	15 (1)	12 (0)
1997	10 (10)	15 (14)	18 (7)	16 (0)	13 (0)	11 (0)	15 (2)	10 (4)	4 (2)
1998	8 (8)	13 (10)	17 (8)	13 (0)	15 (0)	14 (0)	10 (1)	8 (1)	5 (2)

the effect of Raman scattering in the atmosphere. The IO spectrum used in this analysis is that of *Himmelmann et al.* [1996], normalised to the recommended value of the absorption cross section of the (4,0)-Band around 427.2 nm [*Lazlo et al.*, 1995]. An example of a resultant IO fit is shown in Figure 1.

As the IO signals are relatively small, a variety of tests were made, investigating different sources of interference which might lead to an incorrect identification of IO in the zenith sky observations. No significant correlation could be found with the O<sub>3</sub>, NO<sub>2</sub>, O<sub>4</sub> and Ring spectra. The possible influence of the temperature dependence of the NO<sub>2</sub> cross section has been tested, using two different cross sections (221 and 293 K). No significant changes in the retrieved DSCD of IO occurred. The detection limit depends on the SZA, meteorological conditions and instrumental stability and can be estimated to be in the range of  $2.0(-0.5 + 3) \cdot 10^{-4}$  in optical density, determining the detectable DSCD of IO to be  $6.5 \cdot 10^{12}$  molec/cm<sup>2</sup> in minimum for a single spectrum. For the systematic analysis of the years 1995-1998 a criterion was defined to identify days with the presence of atmospheric IO: all days for which analyses for at least 5 different SZA yield IO DSCD having fitting errors of less than 20% were defined as days, where IO is positively identified.

## Measurement results

Observations have been made each year during the time between sun rises on February 18 and sun sets on October 21. It is important to note, that at 79°N the range of observable SZA is small and varies through the year (Feb.:  $SZA > 86^\circ$ , May:  $57^\circ < SZA < 86^\circ$ ).

**Figure 2.** Mean diurnal variations of IO DSCD for the months March and May 1998 derived from days, when IO was positively identified. As background a spectrum from May 12, 1998 has been taken ( $SZA = 60^\circ$ ).

In Table 1, the number of days from each month on which IO was positively identified is listed. The bracketed value is the number of days, where the diurnal variation of DSCD indicates stratospheric amounts of IO. These are defined as those which exhibit significantly increasing DSCD of IO with increasing SZA larger than  $80^\circ$  [*Perliski et al.*, 1993].

Stratospheric IO is observed in spring and autumn. In autumn the column is smaller than in spring and the frequency of observation is lower. IO did not appear to be enhanced or correlated with the observation of low ozone events, which are characterised by low tropospheric O<sub>3</sub> and high tropospheric BrO.

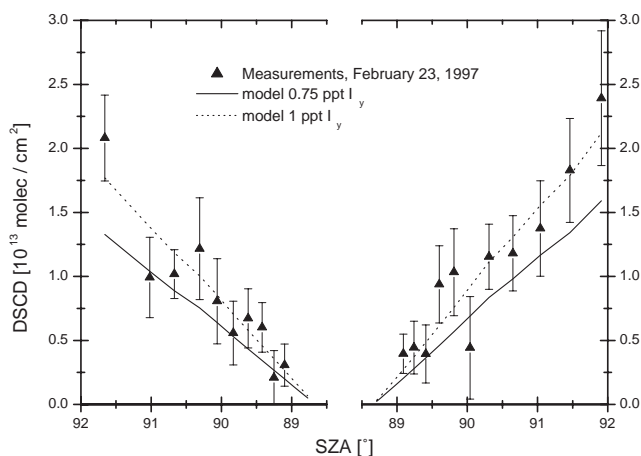
In Figure 2 the average diurnal variation of IO (for days with positively identified IO) in the months March and May 1998 are plotted versus SZA. In order to have a plot combining the different SZA observed, a spectrum taken on the 12th of May was used as the reference measurement in the DOAS analysis also for the March data. As can be seen, the diurnal behaviour of IO in March, which is similar to that in February, shows a fairly symmetric behaviour around noon with a sharp increase of the IO DSCD at large SZA, which is typical for a stratospheric absorber. In May, as shown in Figure 2, decreasing DSCD at higher SZA are found. As will be discussed below, this indicates that later in the season detectable amounts of tropospheric IO are present.

## The Model

The model SLACO has been developed explicitly for the interpretation of DSCD measurements of short lived species such as IO. SLACO combines the atmospheric photochemical model BRAPHO with a ray tracing model. BRAPHO is an atmospheric photochemical box-trajectory model. Detailed information about BRAPHO has been given elsewhere ([*Sinnhuber et al.*, 1999] and refs. therein).

A ray tracing model calculates the atmospheric path of solar rays in full spherical geometry, based on the assumption of single scattering. It takes into account the effects of Rayleigh and aerosol scattering, trace gas and aerosol absorption, refraction and surface reflection. As a function of the scattering height, the local SZA, and the diurnal variation of the species determined by BRAPHO, SLACO computes the slant column amount of every species  $x$  for a given ray. The total slant column amount is calculated by integrating the intensity weighted slant columns of the different rays. The final slant column includes a multiple scattering correction term determined by GOMETRAN [*Rozanov et al.*, 1997].

The used iodine reaction scheme in the stratospheric model calculations is similar to that described in *Solomon et al.* [1994]. However, the kinetic and photochemical parameters are taken from JPL 1997 [*DeMore et al.*, 1997]. Exceptions are IONO<sub>2</sub> and HOI absorption cross sections,



**Figure 3.** DSCD: simulation and measurements Feb 23, 1997, am and pm, noon spectrum as background.

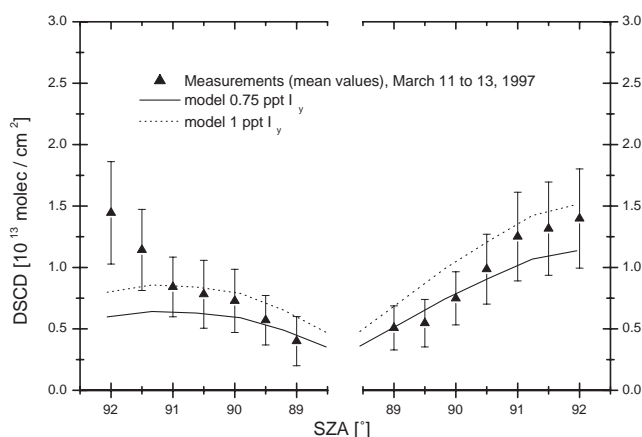
which are taken from IUPAC 1997 [Atkinson *et al.*, 1997].  $I_y$ , defined as the sum of all iodine compounds, has been initialised with either 1 or 0.75 pptv throughout the model stratosphere. The other trace gases were initialised using the output of the SLIMCAT 3d chemical transport model [Chipperfield *et al.*, 1993].

### Interpretation of the measurements

The IO DSCD measurements were interpreted by using the model package SLACO. Figures 3 and 4 show comparisons of the observed and simulated behaviour from days in February and March 1997. As can be seen the selected initial values of stratospheric  $I_y$ , yield simulated IO DSCD in good agreement with those measured.

The influence of tropospheric IO on the observed IO DSCD was investigated explicitly by calculating the DSCD using different tropospheric IO amounts without stratospheric IO contribution and neglecting the diurnal variation of the tropospheric IO. The magnitude and vertical distribution of the tropospheric IO amount was assumed to be similar to that expected at lower latitudes as described by Davis *et al.*. In addition, a constant mixing ratio profile based on amounts of IO measured in the boundary layer [Carpenter *et al.*, 1999] has been used. Figure 5 shows the observed DSCD for February 1998 and the tropospheric DSCD determined as described above. The tropospheric IO leads to negative DSCD at large SZA, regardless the used profile. This demonstrates that the measured IO DSCD in February and March are dominated by stratospheric IO.

An estimate of stratospheric IO can be determined from comparison of the measured IO DSCD with the stratospheric model calculations for different  $I_y$  scenarios. In this manner the IO mixing ratios were calculated to be 0.80 ( $\pm 0.20$ ) pptv in February and 0.65 ( $\pm 0.20$ ) pptv in March 1997 in the lower stratosphere. The stratospheric March IO values are typically smaller than those in February. This may well be because the  $\text{NO}_x$  increases in spring, resulting in a change of  $I_y$  partitioning. For this estimate the tropospheric column of IO is neglected. As the presence of tropospheric IO will lead to negative DSCD (see fig. 5), the neglect of tropospheric IO consequently results in a small underestimation of the stratospheric IO mixing ratio.



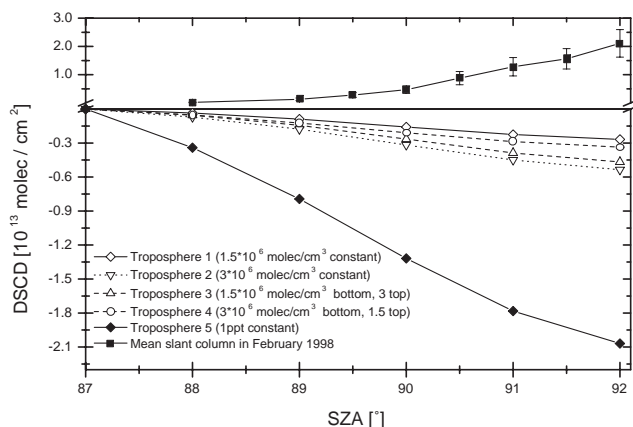
**Figure 4.** DSCD: simulation and measurements from March 11 to 13, 1997 (mean values), am and pm, noon spectra as background.

In contrast the IO behaviour in May 1998 indicates the presence of tropospheric IO. A more detailed and quantitative analysis of the tropospheric IO amount requires detailed modelling of the tropospheric IO chemistry, which is out of the scope of this paper.

### Comparison with other IO studies

The difference between the estimated stratospheric IO amounts at high latitudes found in this study and the upper limits reported by Pundt *et al.* for solar occultation measurements in 1995 is probably a result of different atmospheric conditions. For example the  $\text{NO}_2$  amount above Kiruna at March 21, 1995 was a factor of about 1.5 higher compared to March 13, 1997 above Ny-Ålesund. Simulations indicate that this leads to a decrease in the DSCD for the occultation geometry by a factor of 2. The remaining discrepancy is small and might be due to temporal variations of  $I_y$ .

The evidence for IO reported by Wennberg *et al.* is derived from the sunrise observations by the FTS instrument at Kitt Peak. As a result of both the probable latitudinal gradient in the distribution of stratospheric  $I_y$  and the large



**Figure 5.** Simulated DSCD for different IO background concentrations in the troposphere and the average diurnal variation of the IO DSCD from February 1998.

latitudinal gradient in  $\text{NO}_x$ , large latitudinal gradients in IO are to be expected. Considering this, the range of IO given by Wennberg *et al.* is not directly comparable with our high latitude observations.

## Summary

This study describes the IO-DSCD retrieved from zenith sky DOAS measurements above Spitsbergen from 1995 to 1998. The resultant IO DSCD data set from spring 1997 has been analysed in detail using the SLACO atmospheric model. It has been shown that a significant amount of IO in a range from 0.65 to 0.80 ( $\pm 0.2$ ) pptv is present in the stratosphere above Spitsbergen. Furthermore some indication for tropospheric amounts of IO have been found. A more detailed description of the IO-DSCD time series and its significance for our understanding of atmospheric chemistry will be provided in a forthcoming study, which will also include off-axis observations performed in Ny-Ålesund since summer 1999.

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