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## Introduction

**Iodine** compounds receive growing attention due to their relevance for the atmospheric composition, such as:

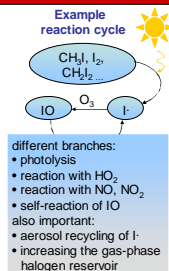
- catalytic ozone destruction
- change of the oxidising capacity of the atmosphere
- new particle formation (via higher oxides OIO, I<sub>2</sub>O<sub>5</sub>)

**Main sources:** marine organoiodines (esp. CH<sub>3</sub>I, CH<sub>2</sub>I<sub>2</sub>) and I<sub>2</sub> as from seaweed, seasalt

**Main experiments:** laboratory studies & ground-based research e.g.: Mace Head, Ireland: IO correlation with sunshine & low tide<sup>[1]</sup> Halley Bay, Antarctica: IO high values in spring time<sup>[5]</sup>

**Abundances:** up to several ppt of IO in the boundary layer<sup>[1,4]</sup>

**Current question:** Is it possible to detect IO from satellite?



## The satellite instrument SCIAMACHY

**SCIAMACHY** (SCanning Imaging Absorption Spectrometer for Atmospheric Chartography):

- eight channel UV-Vis-NIR spectrometer (240 – 2400 nm) onboard the ENVISAT satellite (launched 2002)
- sun-synchronous, near-polar orbit at 800 km altitude
- several atmospheric trace gases can be retrieved e.g. O<sub>3</sub>, NO<sub>2</sub>, BrO, OClO, SO<sub>2</sub>, HCHO, and H<sub>2</sub>O
- spectral resolution: 0.4nm in the visible wavelength range
- viewing geometry: nadir, limb and occultation (sun & moon) here, only nadir data are considered
- typical ground pixel size: 30 x 60 km<sup>2</sup> here, measurements are averaged to 60 x 120 km<sup>2</sup>
- data version used: Level-1 (with dark current correction & spectral calibration)

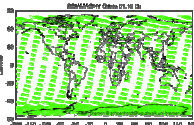


Figure: One day global nadir measurements

## Retrieval Settings and SCIAMACHY detection limit

### DOAS retrieval settings:

For the retrieval of IO, the Differential Optical Absorption Spectroscopy method was used. Fitting window: visible spectral range (e.g. 416 – 430 nm, 2 absorption bands of IO) Included trace gases: NO<sub>2</sub> (223K, 293-223K), O<sub>4</sub> (296K). Other features: Ring effect, straightline correction, quadratic polynomial.

### IO absorption cross section:

strong differential structures in the visible range  
→ IO suitable for DOAS measurements  
Max. absorption cross section: X<sub>max</sub> = 2·10<sup>-17</sup> cm<sup>2</sup>/molec

### Detection limit

SCIAMACHY min. optical depth: order of magnitude 10<sup>-4</sup>. (S/N dependent, as the OD<sub>min</sub> is approximately given by N/S) Ideal slant column detection limit: SC<sub>lim</sub> = OD<sub>min</sub> / X<sub>max</sub> For IO slant columns: SC<sub>lim</sub> = 5·10<sup>12</sup> molec/cm<sup>2</sup>. This strongly depends on albedo, averaging of spectra, and on possible systematic errors! For an albedo of 0.05 instead of 0.9 this limit lies up to 3 times higher.

To convert the slant column detection limit to a mixing ratio detection limit, assumptions on the appropriate air mass factor (AMF) and the altitude profile are necessary. Calculations with sciatran<sup>[6]</sup> yield (at 425 nm):

- AMF = 4.0 (a=0.90, SZA=70°, e.g. Antarctic)
- AMF = 1.1 (a=0.05, SZA=55°, e.g. Ireland)

Assuming mixing up to 1km: VMR<sub>lim</sub> = 0.5 ppt (Antarctic), VMR<sub>lim</sub> = 6 ppt (Ireland) 100m: VMR<sub>lim</sub> = 5.0 ppt (Antarctic), VMR<sub>lim</sub> = 60 ppt (Ireland). → the detection limit lies close to expected IO amounts.

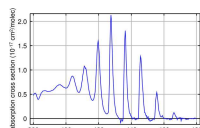


Figure: Absorption Cross Section of IO at room temperature and pressure, FWHM = 1.3 nm. (measured by Peter Spitz, IUP Bremen)

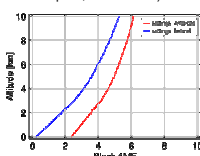


Figure: Block AMF calculated with sciatran version 2.0.

## IO global maps, fit results and discussion

**Global distributions** of IO from SCIAMACHY yield the following observations:

- pronounced IO values are found in springtime Antarctica, esp. the Weddell Sea.
- a pronounced IO maximum in the Arctic region is not surely observed.
- the largest IO slant column in the monthly mean lies around 8·10<sup>12</sup> molec/cm<sup>2</sup>, but higher values appear on single days.
- the noise in the IO columns is rather high (several 10<sup>12</sup> molec/cm<sup>2</sup>) but is reduced strongly by averaging over months.
- some ocean regions show negative values, i.e. smaller IO amounts than the reference spectrum (tropical Pacific, white box), probably indicating some open issue.

### Discussion

- 1 The current standard fitting window includes 2 intensive IO absorption lines. Some problems are thus avoided, but the window is small making fits rather sensitive.
- 2 The desired fitting window including the 3 most intensive absorption lines is currently not feasible due to problems with a Ring feature at 431nm. This will be analysed further.
- 3 Extending the fitting window to smaller wavelengths includes a smaller IO band giving more robust results but emphasising problems in certain regions.

**Important:** The high values in the Antarctic spring do not crucially depend on the fitting window and settings and neither does the seasonal variation discussed in the next part.

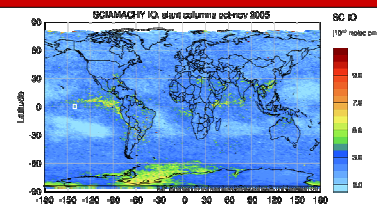
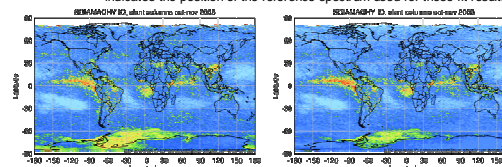


Figure: Global map of IO for Oct-Nov 2005 from SCIAMACHY data. The maximum in the Antarctic is standing out. Other regions with elevated levels also appear but are not as prominent and stable. The white box indicates the position of the reference spectrum used for these fit results.



Global maps of IO for Oct-Nov 2005 from SCIAMACHY for different fit settings, mainly enlarged fitting windows towards smaller wavelengths (left: 412-430 nm, right: 410-430 nm). The values in the Weddell Sea hardly change, while other regions are stronger influenced.

**Typical fit result:** DOAS retrieval, fitting window 416-430 nm, on 1<sup>st</sup> Oct 2005.

Lat = 69.3° S, Long = 29.6° W.

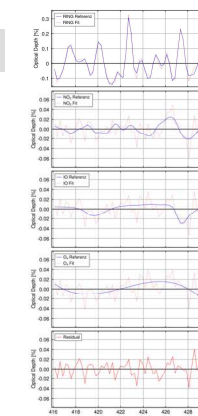
Ring effect

NO<sub>2</sub>

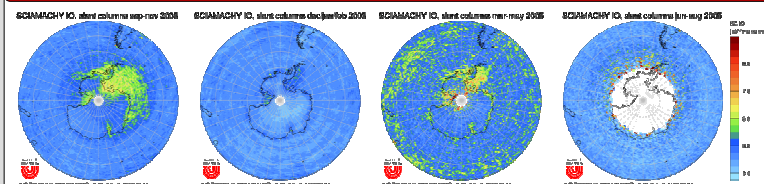
IO

O<sub>4</sub>

Residual



## Seasonal variation in Antarctica



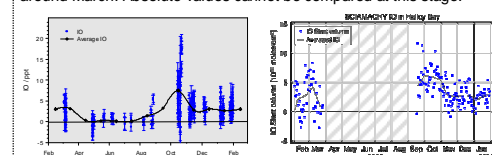
Figures: IO in the Southern Hemisphere for different periods in 2005 from polar spring (left) to polar winter (right).

### Seasonal Variation

Close to the Antarctic continent, IO slant columns start to rise in September reaching the maximum in October. During polar summer, smaller positive values are found, and values increase again slightly in autumn. In winter, hardly any light is available, regions still receiving light show no elevated levels. This shows parallels to the BrO cycle in the Antarctic with its maximum in the same time. For the release of Br atoms, mainly heterogeneous reactions on sea-ice (frost flowers) are discussed<sup>[7]</sup>. Ratio of ions in sea water: [Br<sup>-</sup>]/[I<sup>-</sup>] = 15 000. Therefore, either the release mechanism for I-atoms is a lot more efficient than for Br, or additional factors are relevant. The role of biology in this cycle is probably of importance.

**Comparisons** between IO retrieved from satellite data with ground-based, active Long-Path DOAS measurements were made. Location: Halley-Bay, Antarctica (75.5°S, 26.5°W).

LP-DOAS results from the year 2004 by A. Saiz-Lopez<sup>[5]</sup> suggest a seasonal cycle of IO. Therefore, comparison with satellite data from 2005 is reasonable. In principle agreement with the LP-DOAS results, highest IO values appear around October and a smaller maximum around March. Absolute values cannot be compared at this stage.



Figures: Seasonal variation of IO, (left): measured with active LP-DOAS by Alfonso Saiz-Lopez, Jet Propulsion Laboratory, NASA, CalTech, California, USA. (right): SCIAMACHY IO slant columns within 500km of Halley Bay.

Halley Bay, Antarctica



Courtesy NASA/JPL-CalTech

No data in polar winter due to darkness

## Conclusions

- first global distributions of iodine monoxide retrieved from SCIAMACHY data are presented.
- highest IO values are found at spring time in Antarctica, and reach slant columns of 8·10<sup>12</sup> molec/cm<sup>2</sup> in the monthly mean.
- despite some sensitivities to the fit settings, the maximum in the Antarctic remains stable.
- the IO detection limit lies around 5·10<sup>12</sup> molec/cm<sup>2</sup>, but strongly depends on albedo and systematic effects.
- for low values of IO and in case of local effects, the detection limit of IO from SCIAMACHY is yet too high to allow for ensured detection, especially when iodine species are located only close to the ground.
- more validation with ground-based measurements will be performed, esp. with ship-borne measurements in the Antarctic.
- in the future, the fit quality shall be further improved (esp. the Ring structure problem at 430-431nm will be further investigated).
- the importance of IO on a global scale shall be estimated with respect to formation of condensation nuclei and ozone depletion.

## Acknowledgements

- We thank Peter Spitz for providing the absorption spectrum of IO and Alfonso Saiz-Lopez for the figure of the IO LP-DOAS measurements in Halley Bay.
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