First observations of iodine oxide columns from satellite

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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 cloud forming capacity of the atmosphere • new particle formation (via higher oxides \( \text{IO}_x \))

Main sources: marine organohalides (esp. \( \text{CH}_x \text{I}_y \)) and \( \text{I}_2 \) as from seaweed, seasalt e.g.: Mace Head, Ireland: IO correlation with sunshine & low tide

Main experiments: laboratory studies & ground-based research e.g.: Mace Head, Ireland: IO correlation with sunshine & low tide

Halley Bay, Antarctica: IO high values in spring time

Abundances: up to several ppt of IO in the boundary layer

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

The satellite instrument SCIAMACHY

SCIAMACHY (Scanning Imaging Absorption Spectrum 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. \( \text{O}_3, \text{NO}_x, \text{BrO}, \text{HO}_x, \text{SO}_x, \text{HCHO}, \text{and H}_2\text{O} \)
- spectral resolution: 0.4nm in the visible wavelength range (with dark current correction & spectral calibration)
- different branches: • photolysis • reaction with \( \text{HO}_x \) • reaction with \( \text{NO}_x \) • self-reaction of IO also important:
- • sensitive recycling of IO
- • increasing the gas phase halogen reservoir
- high IO values in springtime

Typical fit result: DOAS retrieval, fitting yielding "typical fit result" with the fit setting shown in Figure 1.

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. 418 – 430 nm, 2 absorption bands of \( \text{IO} \))
- Included trace gases: \( \text{NO}_x, \text{BrO} \)
- Other features: Ring effect, straylight correction, quadratic polynomial.

IO absorption cross section:
- strong differential structures in the visible range
- \( \sigma \) suitable for DOAS measurements

Max. absorption cross section: \( \sigma_{\text{max}} = 2 \times 10^{-17} \text{ cm} \cdot \text{molec}^{-1} \)

Detection limit

SCIAMACHY, optical depth: range of magnitude 10^-4

(s/N dependent, as the \( \sigma_{\text{OD}} \) is approximately given by N\( \sigma \) ideal slant column detection limit \( \sigma_{\text{OD},\text{lim}} \))

For IO slant columns: \( \sigma_{\text{OD},\text{lim}} = 5 \times 10^{-17} \text{ molec} \cdot \text{cm}^{-1} \)

This strongly depends on albedo, averaging of spectra, and possible systematic errors! For an albedo of 0.05 instead of 0.9 this limit is 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 \( \text{AMF} \) and the altitude profile are necessary. Calculation with \( \text{AMF} = 4.0 \) (e.g. lower stratosphere, \( \text{AMF} = 1.1 \) (e.g. stratosphere), (e.g. Ireland)

Assuming mixing up to 1km: \( \text{VMR}_{\text{lim}} = 0.5 \times 10^{-15} \text{ ppt} \text{(Antarctica)} \)

\( \text{VMR}_{\text{lim}} = 6 \times 10^{-16} \text{ ppt} \text{(Ireland)} \)

The detection limit lies close to expected IO amounts.

Global distributions from SCIAMACHY

Global distributions 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 observed.
- the largest IO slant column in the monthly mean lies around \( 8 \times 10^{-16} \text{ molec} \cdot \text{cm}^{-2} \), but higher values appear on single days.
- the noise in the IO columns is rather high (several \( 10^{-16} \text{ molec} \cdot \text{cm}^{-2} \)) 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

- • 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.

- • 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.

- • 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.

Seasonal variation in Antarctica

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 BR 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.

For IO slant columns: \( \text{VMR}_{\text{lim}} = 8 \times 10^{-16} \text{ molec} \cdot \text{cm}^{-2} \)

Ratio of ions in sea water: \( \text{Br}^- \times \text{I}^- = 15 \times 1000 \). 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.

Conclusions

- • first global distributions of iodine oxide retrieved from SCIAMACHY data are presented.

- • highest IO values are found at spring time in Antarctica, esp. the Weddell Sea.

- • the importance of IO on a global scale shall be estimated with respect to formation of condensation nuclei and ozone depletion.

Acknowledgements

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Selected references

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See also: wwww.iup.physik.uni-bremen.de/doas