The impact of very short-lived organic substances on stratospheric ozone depletion – A case study

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Introduction

- Chlorinated and brominated very short-lived substances (VSLS) are able to reach the stratosphere1
- The abundances of these substances are highly variable in the troposphere
- Very few measurements of VSLS in the main stratospheric entrance region, the tropical tropopause layer (TTL, see scheme on the right) have been reported
- The impact of VSLS on the abundance of the summed-up bromine and chlorine in the stratosphere is uncertain

The case study

- 11 air samples were collected with a balloon-borne cryogenic whole-air-sampler at altitudes between 15 and 34 kilometres above Brazil in 2005
- 28 chlorinated and brominated substances including 10 VSLS were quantified via cryogenic pre-concentration techniques followed by Gas Chromatography with Mass Spectrometric detection (Frankfurt: GC-EI-MS, UEA: GC-NICI-MS)2
- By combining tropospheric reference data from the ground stations network of NOAA-ESRL and age of air observations the abundances of effective equivalent stratospheric chlorine (EESC) were derived

Combined EESC calculation

- The mean age of air was determined for each sample via SF6 mixing ratios and its tropospheric time trend
- Global tropospheric trend functions were derived for all longer-lived species by using data from the NOAA-ESRL global ground stations network (http://www.esrl.noaa.gov/gmd/) and from the latest WMO’s Ozone Assessment1 in combination with the balloon-borne measurements
- These trends were propagated into the stratosphere by assuming no chemical degradation; the effects of an age-of-air spectrum were included (with parameterisation assuming ΔT = 0.7)
- From the resulting stratospheric entry mixing ratios the EESC was then calculated assuming almost complete chemical degradation when reaching the high-latitude stratosphere (estimate of 40 ppt of organic chlorine left)
- A factor of 60 was used to account for the higher ozone destruction efficiency of bromine
- For the VSLS impact calculation it was assumed, that the concentrations observed in the 15 km sample represent the mean stratospheric entrance mixing ratio

The chromatogram of the air sample collected at 15.2 km altitude as analysed with GC-NICI-MS. The detected ions with a mass/charge ratio of 79 and 81 in a ratio of 1:1 are specific for bromine containing species which indicates that at least eight additional brominated substances are present in the TTL. The peaks at about 14.5, 17, 20 and 26.5 minutes retention time are suggested to belong to C2HBr3 (bromoethane), CFCl3CHBr (halothane), C3H7Br (n-propyl bromide) and CH2BrCH2Br (1,2-dibromoethane) but at least four further unidentified brominated compounds remain.3

Altitudinal distributions of VSLS. At higher altitudes no signals or low blanks were observed. CHClBr and C2HCl were below detection limits in all samples. C2HCl3 (1.0 ppt) and CHBr2 (0.016 ppt) were only detected in the sample taken at 15.2 km

Conclusions

- The mixing ratios of the 18 longer-lived substances observed in the TTL were in good agreement with the estimated EESC from measurements only
- As the VSLS concentrations are highly variable in the troposphere it remains uncertain how representative this impact is. Further investigations in the tropical upper troposphere are needed to quantify e.g. the influences of season, longitude and deep convection
- There are indications for additional organic brominated substances to be present in the tropical upper troposphere and stratosphere. Identification of these substances and quantification of their impact on stratospheric ozone depletion is crucial for future research

The BONBON whole-air-sampler of the University Frankfurt can collect 15 samples by freezing the air at liquid Neon temperatures

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References