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

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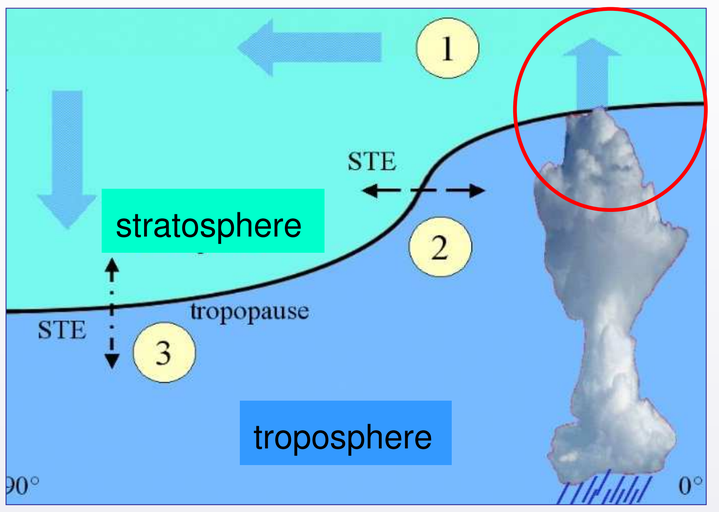
Introduction

- Chlorinated and brominated very short-lived substances (VSLS) are able to reach the stratosphere[1]
- 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

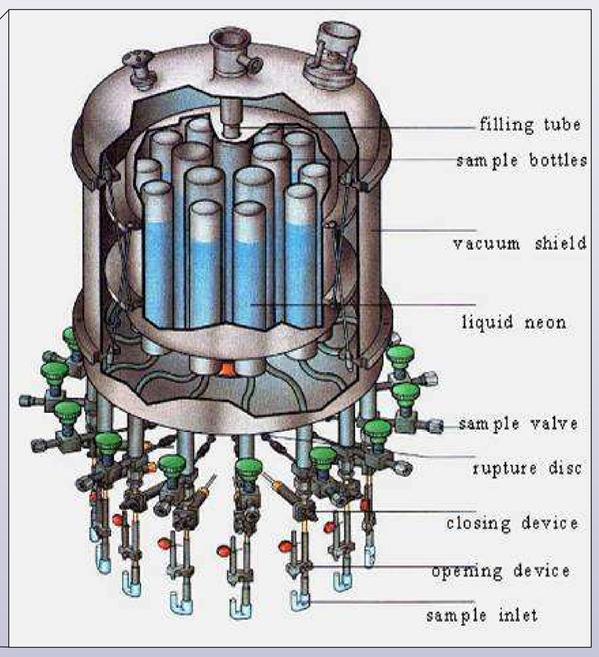


Simplified scheme of air transport into the stratosphere
adapted from www.atmosphere.mpg.de

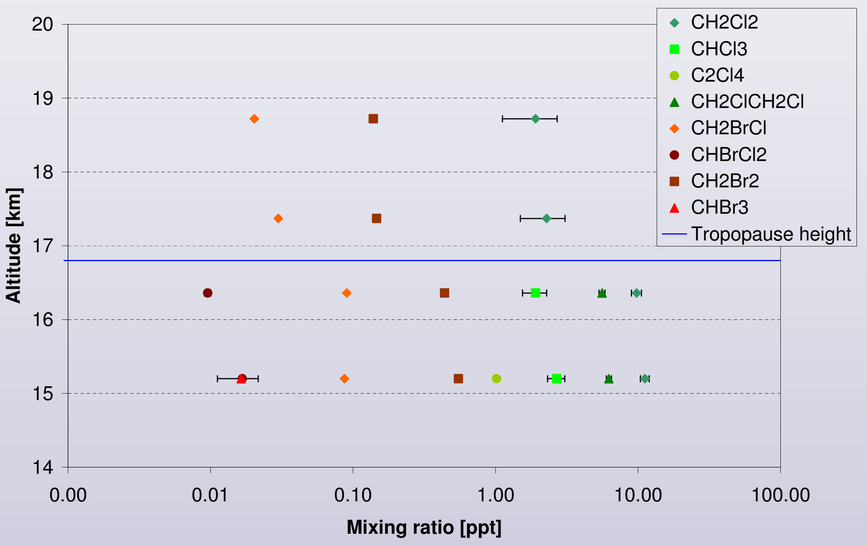
The case study

- 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

Flight BII42: launched in June 2005 near Teresina, Brazil (5°04'S, 42°52'W); samples were collected between 15 and 34 km altitude



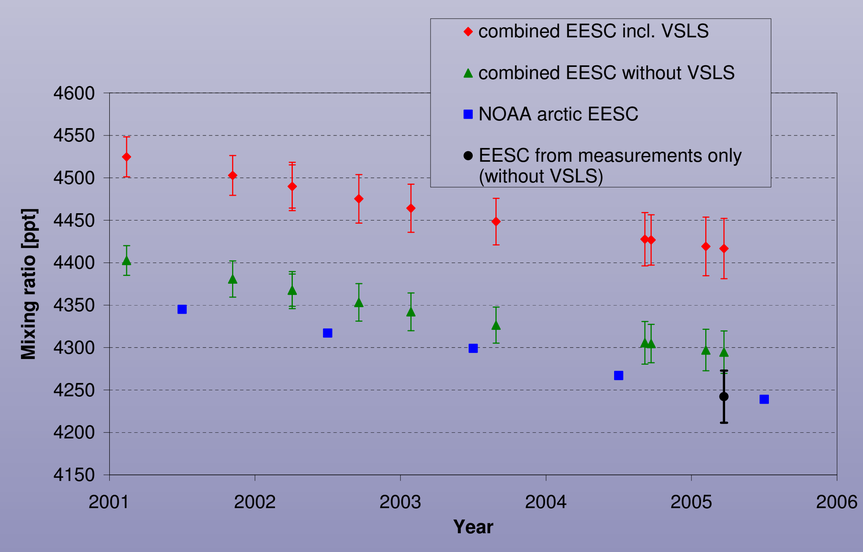
The BONBON whole-air-sampler of the University Frankfurt can collect 15 samples by freezing the air at liquid Neon temperatures



Altitudinal distributions of VSLS. At higher altitudes no signals or low blanks were observed. $CHClBr_2$ and C_2HCl_3 were below detection limits in all samples. C_2Cl_4 (1.0 ppt) and $CHBr_3$ (0.016 ppt) were only detected in the sample taken at 15.2 km

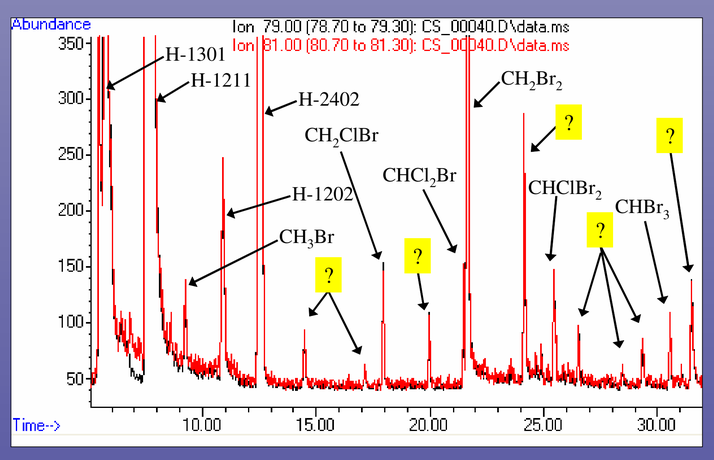
Combined EESC calculation

- The mean age of air was determined for each sample via SF_6 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 Assessment[1] 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 (width parameterisation assuming $\Delta^2/\Gamma = 0.7$)
- 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



Comparison of derived EESCs. The EESCs from measurements in 15.2 km altitude is in good agreement with the NOAA EESC from ground-based measurements. The EESC derived via combination of NOAA and case study data is slightly higher and the VSLS were found to have an additional impact of 122 ppt (see Table for details). The estimated EESC impact range of the 10 VSLS as resulting from upper tropospheric values of WMO, 2007[1] is higher: 237 – 298 ppt

Substance group	Substance (name)	Mean EESC contribution [%]	Mean group contribution [%]
CFCs	CF_2Cl_2 (F12)	24.6	48.3
	$CFCl_3$ (F11)	17.7	
	$CFCl_2CF_2Cl$ (F113)	5.54	
	CF_2ClCF_2Cl (F114)	0.30	
	$CFCl_2CF_3$ (F114a)	0.09	
	CF_2ClCF_3 (F115)	0.04	
Longer-lived CCs and BCs	CH_3Cl	13.7	36.0
	CH_3Br	11.3	
	CCl_4	8.97	
	CH_3CCl_3	2.07	
Halons	CF_2ClBr (H1211)	5.74	11.0
	CF_3Br (H1301)	3.97	
	CF_2BrCF_2Br (H2402)	1.18	
	CF_2Br_2 (H1202)	0.11	
HCFCs	CHF_2Cl (F22)	3.60	4.7
	CH_3CFCl_2 (F141b)	0.72	
	CH_3CF_2Cl (F142b)	0.32	
	$CHFClCF_3$ (F124)	0.04	
Additional VSLS contribution	CH_2Br_2	1.52	2.8
	CH_2Cl_2	0.52	
	CH_2ClCH_2Cl	0.29	
	$CHCl_3$	0.19	
	CH_2BrCl	0.12	
	C_2Cl_4	0.09	
	$CHBr_3$	0.07	
	$CHBrCl_2$	0.02	
	C_2HCl_3	0.0	
	$CHBr_2Cl$	0.0	



The chromatogram of the air sample collected at 15.2 km altitude as analysed with GC-NICI-MS. The displayed 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 C_2H_5Br (bromoethane), $CF_3CHClBr$ (halothane), C_3H_7Br (n-propyl bromide) and CH_2BrCH_2Br (1,2-dibromoethane) but at least four further unidentified brominated compounds remain.[2]

Conclusions

- The mixing ratios of the 18 longer-lived substances observed in the TTL were in good agreement with ground-based measurements
- VSLS were found to elevate the EESC by ~2.8 % and this contribution mostly originated from the two dihalomethanes
- 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

References

(1) WMO 2007: World Meteorological Organization/United Nations Environment Programme, Scientific Assessment of Ozone Depletion: 2006. Global Ozone Research and Monitoring Project–Report No. 50, Geneva, Switzerland, 2007

(2) Laube, J. C., Engel, A., Bönisch, H., Möbius, T., Worton, D. R., Sturges, W. T., Grunow, K. and Schmidt, U., Contribution of very short-lived organic substances to stratospheric chlorine and bromine in the tropics – a case study, Atmos. Chem. Phys. Discuss., 8, 8491–8515, 2008

Acknowledgements

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