Final Report Summary - SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere)

Executive Summary:

It is well known that halogens (e.g. chlorine, bromine and iodine) contributed to the past decline of ozone in the global stratosphere. More than 25 years after the first discovery of the Antarctic Ozone Hole and the ratification of the Montreal Protocol in 1987 and its amendments, reductions in ozone destroying halogens are now becoming obvious in the stratosphere. It has been realized however that not only man-made but also naturally emitted, so-called organic Very Short Lived Species (VSLS) are also contributing to the stratospheric halogen load. This is most noticeable for stratospheric bromine and iodine where the contribution by VSLS has been estimated to be 20% and 100%, respectively. The world’s largest sources of VSLS are various types of marine biota (mostly micro- and macro algae) as well as abiotic processes in near surface oceanic waters, though details of their emissions, the atmospheric transport, transformation and delivery to the stratosphere were not well characterized before. The SHIVA project addressed all these issues by experimental and theoretical studies. Further, the relevance of VSLS for past present and future stratospheric ozone was investigated using global chemical transport models (CTM) and prognostic chemistry climate models (CCM). The main outcomes of SHIVA are:

1. Globally the most important emitters of brominated VSLS (primarily CHBr3, and CH2Br2) are phytoplankton of various types (i.e. haptoc-, chryso-, and chlorophytes), but VSLS emissions by natural or cultivated macro-algae are potentially regionally also important. Emissions from the latter are likely to increase in the future given the current projected rise in seaweed cultivation, particularly in tropical regions.

2. Cyanobacteria - besides photochemical production - seem to be potent CH3I emitters, but the largest oceanic source of iodine to the atmosphere are emissions of I2 and HOI, produced by inorganic reactions involving ozone, and in certain oceanic regions other iodinated VSLS such as CH2I2 and CH2ClI.

3. For the major halogenated VSLS (CHBr3, CH2Br2, and CH3I) of stratospheric relevance, best estimates of global sea-air fluxes (source/sink) are +2.96/-0.56 1.09/-0.12 and 1.45/-0.0001 Gmol atoms/year, including oceanic sources and sinks for the first time.

4. Theoretical and as well as experimental studies indicate that less than 0.3ppt of organic and inorganic iodine are transported into the stratosphere.

5. For different longitudes of the tropics, typical upper tropospheric mixing ratios of brominated VSLS range between 3.5 (WMO-2011) and 4.2 ppt, and in particular for the western Pacific VSLS mixing ratios of 4.1±0.6ppt (SHIVA 2011) and 4.2±0.6 ppt (CARBIC) are found.

6. This may correspond to a stratospheric injection of 1.5-2 ppt bromine due to organic source gas (SG), while the inorganic method suggests a total source and product gas (PG) injection of 4 – 5ppt VSLS. Further since modeling suggests that 75% of the injection is due to organic SG and 25% due to inorganic PG injection, together with the combined uncertainties of both methods, progress towards a consistent picture of VSLS bromine in the stratosphere has been made during SHIVA.

7. From its maximum (20-21ppt) reached in the stratosphere around 2000, total stratospheric bromine is presently decreasing
at a rate of (0.8-0.9 ± 0.2)% per year and reached a level 19-20 ppt in 2011.

8. Theoretical studies indicate that VSLS-derived bromine presently reduces O3 by about 15 percent at low-latitudes to several percent at high-latitudes, and up to 20% O3 in polar regions during winter. Radiative forcing due to reduced ozone by VSLS released halogens also leads to modified stratospheric temperatures and transport.

9. Since stratospheric chlorine is likely to decrease in future, the influence of VSLS released bromine on stratospheric ozone will also diminish due to its effect in the combined ClOx/BrOx ozone loss cycles.

10. In a future warmer world, VSLS emissions and their contribution to stratospheric bromine loading may increase by 15-60% from present, assuming only physical forcings.

Finally, all data collected during SHIVA can be found here (ftp server shiva.iup.uni-heidelberg.de) and are available for use by the wider community.

Project Context and Objectives:

The year 2012 marked the 25th anniversary of the Montreal Protocol on ozone depleting substances (ODS). After two and half decades of signing the protocol and its subsequent amendments involving global participation, the future trend in the atmospheric ODS (mostly of halogenated origin) from anthropogenic activities is thought to be understood well (assuming universal compliance with international agreements). Likewise the science behind the Montreal Protocol has matured over three decades, to the point where model agreement on the impact on stratospheric ozone of predicted ODS trends is tight for scenarios where climate and climate gases do not vary. Hence stratospheric levels of ozone destroying halogens (e.g. chlorine, bromine and iodine) have been reported to decline now (e.g. for chlorine, and bromine see WMO, 2011; Dorf et al., 2006; Hendrick et al.,2008) or to be irrelevant (e.g. for iodine see WMO,2011; Bösch et al., 2003; Butz et al., 2009) for the destruction of stratospheric ozone.

Increasing scientific evidence, however, suggested that there are additional contributions to the stratospheric halogens (e.g. mostly bromine and iodine) from mostly biogenically-derived, halogen-containing “Very Short-Lived Substances” (VSLS) and Medium Short-Lived Substances (MSLS) (e.g. for details see chapter 2 in WMO, 2007, or in chapter 1 of WMO, 2011) (Figure 1). One particularly problematic aspect of the uncertain contribution of VSLS, MSLS, and their inorganic product gases (PGs) to stratospheric halogen loading was that it may be very sensitive to changes in climate and therefore cause significant surprises in the future, unless the system is better understood.

Most of the VSLS have sources in the ocean, the terrestrial ecosystem, or are produced by biomass burning (the first two would be a natural contribution, the latter mostly an anthropogenic) (Redeker et al., 2004; Chuck et al., 2005; Yang et al., 2005; WMO, 2007 and WMO, 2011). The relative importance of these sources and the biological contribution to VSLS emissions was largely unknown but the biogenic production was thought to be dominant. Moreover, while it was clear that by enzyme-mediated synthesis (e.g. bromo-peroxidase) marine bacteria, fungi, and especially micro- and macro-algae (seaweeds) are potent producers of halogenated VSLS, their specification according to their relevance for stratospheric ozone was yet largely unclear.

Evidences obtained from prior field observations as well as theoretical studies suggested that for the contributions of VSLS to stratospheric bromine mostly marine emission of CHBr3 and CH2Br2 - but not exclusively - are relevant, while for stratospheric iodine marine emissions of CH3I and CH2I2 are potentially crucial (WM-2011). Further inorganic sources for atmospheric iodine were also suspected to be relevant in this context.

Within the SHIVA project, the stratospheric budget of bromine could be tightened, and its declining stratospheric trend now can firmly be confirmed. For iodine, further evidence was found that its concentrations in the tropical tropopause layer (TTL) and lowermost stratosphere are too low to be significant for stratospheric ozone loss (Butz et al., 2009, and Tegtmeier et al., 2013).
At project beginning the atmospheric transformation and transport through the troposphere to the upper troposphere of these crucial species was far from being well understood, but one major pathway was thought to lead from the western Pacific source region into the upper tropical troposphere, and finally into the stratosphere (e.g. Fueglistaler et al., 2004 and 2009; Ashfold et al., 2012). Alternatively, ODS emitted from surface sources, in particular those located on the continents, e.g. plant emissions or biomass, may also become rapidly transported into the upper troposphere or lower stratosphere by deep convection (e.g. Danielson, 1982).

Figure 1: Schematic showing principal chemical and dynamical pathways for halogenated VSL source gases (SGs) and organic/inorganic product gases (PG) between the boundary layer and the stratosphere (WMO, 2007).

Since direct oceanic and atmospheric measurements of these critical species in the western Pacific were largely lacking at project beginning, their source strengths could be estimated only from inverse modeling using different atmospheric transport models (Warwick et al., 2006; Kerkweg et al., 2008; Liang et al., 2010; Ordonez et al., 2012). Therefore, more field observations from critical regions (e.g. in upwelling and tropical waters) appeared necessary, in order to improve previously existing global emission inventories of halogenated VSLS relevant for stratospheric ozone (e.g. Ziska et al., 2013).

Another uncertainty arose from the divergent estimates of the contribution of VSLS to the stratospheric halogens being in particular large for bromine 1–8ppt, or about 5 to 30% of the total stratospheric bromine content. In part, this uncertainty arose from systematic lower estimates based on the organic method as compared to the inorganic method, and largely diverging estimates among those, most experimental studies addressing the inorganic bromine method. Here a common uncertainty of the inorganic method came into play since photochemical corrections to estimate total bromine from measured BrO were all affected by uncertainties in thermo-chemical and kinetic data, which were in particular large for the formation and destruction of BrONO2 at stratospheric temperature. Within SHIVA, new field data on the formation and destruction of BrONO2 became available which tend to resolve largely the existing gap in VSLS derived bromine among the organic and inorganic method (Kreycy et al., 2013).

More uncertainties arose from the poor understanding of various aspects of radiative and dynamical troposphere/stratosphere coupling that can significantly change the dynamical and chemical structure of the stratosphere. This lack of understanding was partly caused by the fact that global models that are used for climate predictions (atmosphere/ocean general circulation models: AOGCMs) did not resolve stratospheric chemistry, while global models of atmospheric circulation and detailed stratospheric chemistry (chemical climate models: CCMs) typically did not include an interactive ocean. Efforts to close the gap between AOGCMs and CCMs were underway from both sides by including detailed stratospheric chemistry in AOGCMs or by coupling CCMs to ocean models; but these required further development.

In summary, model predictions of future ozone loss due to halogenated VSLS were based on a constant input of natural ODS into the stratosphere, but the entire classification of halogenated VSLS and MSLS, partly of natural origin, have been excluded from most predictions, despite strong evidence that they contribute to the stratospheric halogen budget (WMO, 2007, and WMO, 2011). In all cases the impact of natural ODS will be highly sensitive to climate change in terms of their emissions to the atmosphere, their transport, and their chemical processing.

Since the future changes in the mechanisms that regulate these processes were largely unknown, the VSLS and MSLS have the potential to cause significant surprises in the future evolution of the ozone layer in the changing climate, unless they are better understood. These uncertainties were partly solved within the SHIVA project (e.g. Dessens et al., 2009, Schofield et al., 2011, Ordóñez et al., 2012, Hossaini et al., 2012b, Aschmann et al, 2013, Ziska et al., 2013, and studies under way).

SHIVA aimed at improving our understanding of the role halogenated VSLS and MSLS play for present and future stratospheric ozone, expressed in 4 overall themes:
Main SHIVA objectives

At the beginning of the SHIVA project in 2009, lacking understanding in the role halogenated VSLS may play in past, present and future global ozone came with all relevant processes related to the atmospheric fate of VSLS. These included their marine sources and emissions, their atmospheric transport and transformation, uncertainties in their contribution to the stratospheric halogen budget and finally how they may modify stratospheric ozone and transport in a climate change affected world. Therefore, at the beginning of the project the following major objectives had been identified:

1. The oceanic emission strengths of a suite of halogenated gases in two prominent source regions, i.e. the western Pacific and the tropical Atlantic, needed to be further characterized. These studies aimed at investigations of the source strengths of the targeted substances as a function of season, climate-sensitive factors (such as sea surface temperature (SST), nutrient supply and biological activity) and meteorological parameters in the near surface air (e.g. temperature and wind speed). Intentionally these studies comprised station and ship-based measurements, as well as a literature review and the construction of an ocean–lower atmosphere database of all available halogenated VSLS and MSLS measurements, including those of SHIVA. The collected data would be used for the development of interpretable air–sea gas flux products, for the modelling component of SHIVA and for the investigation of parameterisations and sensitivity studies in order to predict possible climate feedbacks on oceanic emissions of the target gases.

2. The atmospheric transport and transformation of the halogenated SGs and PGs within the tropical troposphere, the tropical tropopause layer (TTL) and the tropical lower stratosphere (LS) would be investigated by systematic field and modelling studies. The field studies performed within SHIVA (e.g. in the western Pacific were suspected to be to key region for VSLS emissions relevant to stratospheric) should combine ship and aircraft measurements, both using sophisticated instrumentation. The data gained during these field studies would further be corroborated by ground-, aircraft- and balloon-borne and satellite observations, which would be undertaken by the partners within nationally funded projects. The transport and transformation modelling should include process-oriented studies to assist interpretation of the field observations and studies that should include air mass trajectory and meso-scale convective modelling. Major emphasis would be put on the fate of brominated and iodinated substances.

3. The past, present and likely future trend of the total halogen burden, and measures of it such as effective equivalent chlorine (EECl) and effective equivalent stratospheric chlorine (EESC), would be established for the global stratosphere. Analysis of past and present trends of the targeted halogens (chlorine, bromine and iodine) would be continued using available and future data from the respective measurements taken by the project partners. Future trends of stratospheric halogens would be established by including surface data of the longer-lived halogenated species (LLS) and their atmospheric lifetimes, as well as the likely contribution of VSLS and MSLS to the individual halogen burdens.

4. The impact of long- and short-lived halogenated trace gases and their inorganic product gases would be investigated for past, present and future ozone within the upper troposphere, TTL and global stratosphere. These studies would include global chemical transport model (CTM) simulations driven by past and present decadal long assimilated meteorological fields and those calculated with general circulation models (GCMs) for the future climate of Intergovernmental Panel of Climate Change (IPCC) standard simulations.

Besides investigating all the relevant processes leading from the mostly marine emissions of halogenated VSLS, their atmospheric transport, transformation into product gases, to the entry of source and product gases into the stratosphere by experimental and theoretical models, central aims of SHIVA would address the role halogenated VSLS played in past, present and future global ozone. Worth noting was that, while the recent influence of VSLS on global ozone and transport could be diagnosed from experimental data and further assessed from theoretical studies, their impact on future ozone has been much harder to be assessed. Here major uncertainties were coming into play when assessing the role of VSLS in the future climate change affected world. These range from uncertainties in predicting the future oceanic fertility, sea surface temperatures, the mostly wind velocity driven efficiencies of water atmosphere boundary layer transport, and vertical transport in the atmosphere in relevant regions, as well as uncertainties related in predicting the future oxidation capacity of the lower
atmosphere, as well as the composition and dynamics of the overlaying stratosphere. Accordingly, any prediction the role halogenated VSLS may play for future stratospheric ozone would remain highly uncertain.

Project Results:

See attachment, including Figures and Tables

Potential Impact:

See attachment, including Figures and Tables

List of Websites:

http://shiva.iup.uni-heidelberg.de/

Related information

<table>
<thead>
<tr>
<th>Result In Brief</th>
<th>Predicting ozone layer depletion</th>
</tr>
</thead>
</table>

Reported by

RUPRECHT-KARLS-UNIVERSITAET HEIDELBERG
Germany
See on map

Subjects

Environmental Protection

Last updated on 2014-07-08
Retrieved on 2019-07-31

© European Union, 2019