Potential for Future Threats to Ozone Recovery from 'Short' and 'Very Short-lived' Halocarbons

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1. Introduction

Ozone-depleting substances (ODSs) have both man-made and natural origins (Fig. 1)

Even "natural" ODSs have **human-induced pressures** from cultivation practices and climate change

"Natural" ODSs are invariable either **"short-lived"** (lifetimes of about 1 year) or are **"very short-lived substances"** (VSLS, with lifetimes of <0.5 years)

There are also man-made sources of VSLS, notably various chlorinated solvents

Fig. 1 does NOT include any VSLS and they are **not regulated by the Montreal Protocol on Substances that Deplete the Ozone Layer**

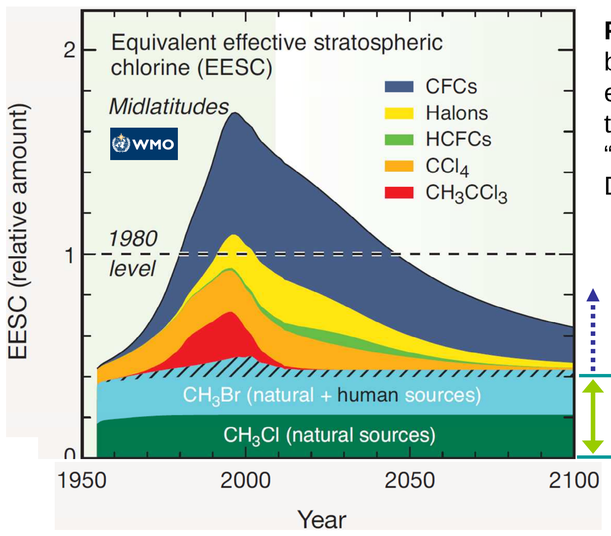
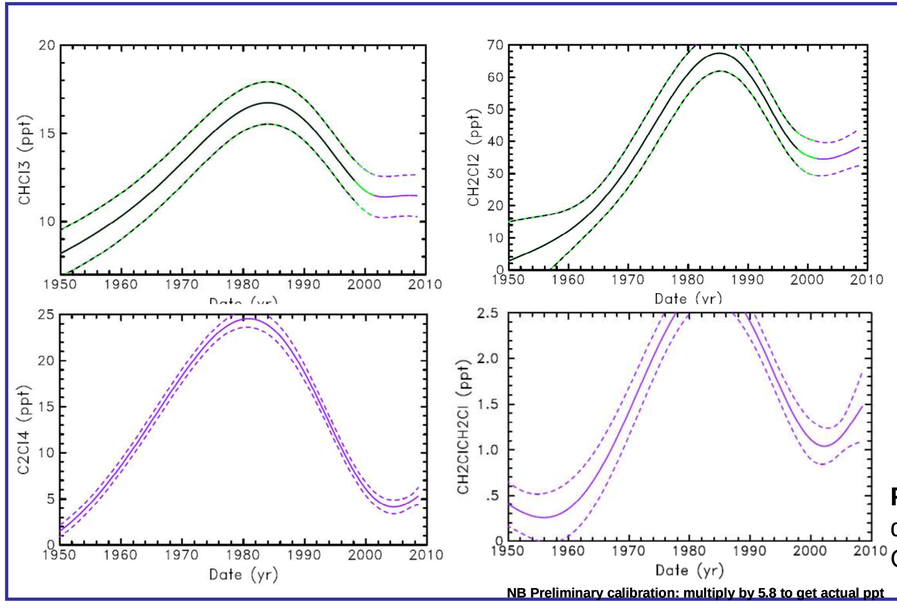


Fig. 1. Amount of chlorine and bromine (expressed as chlorine-equivalent for ozone depletion) in the stratosphere; adapted from "Scientific Assessment of Ozone Depletion: 2010", WMO, 2011

"Substantial uncertainties remain in quantifying the full impact of chlorine- and bromine-containing VSLS on stratospheric ozone."

UNEP "Scientific Assessment of Ozone Depletion: 2010" (WMO, 2011)

2. Time trends of chlorinated gases from firn air



Long term trends of chlorinated VSLS gases have been modelled from measurements in deep snow (firn air) at the NEEM drill site, Greenland (Fig. 2)

Chloroform ($CHCl_3$) declined after the 1980s due to a reduction in chlorine use in the paper industry, but the decline has now stopped

Dichloromethane (CH_2Cl_2), dichloroethane (CH_2ClCH_2Cl) and tetrachloroethene (C_2Cl_4) have started to increase in abundance again in recent years

Fig. 2. Reconstructed time trends of some chlorinated gases derived from modelling depth profiles of their concentrations in Greenland firn

3. VSLS halogen contribution

WMO (2011) states that VSLS gases currently contribute:

~80 (range 40-130) ppt of chlorine; *and*

1 - 8 ppt of bromine, equivalent to 60 - 480 ppt of Equivalent Effective Stratospheric Chlorine (EESC) assuming immediate release of halogens in the lower stratosphere

∴ total = 100 - 610 ppt (a mid-point value of 350 ppt); a substantial fraction of total EESC (Fig. 3)

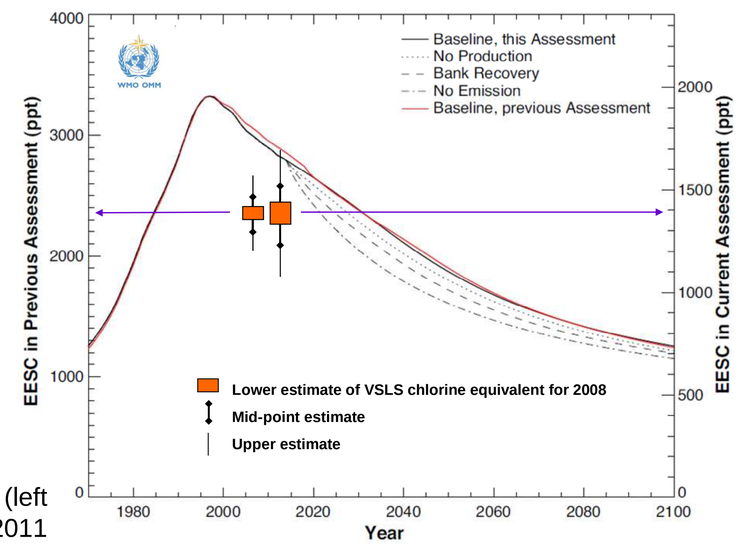


Fig. 3. EESC from VSLS gases in 2008 scaled to WMO 2002 calculated values for EESC at mid-latitudes from all longer-lived gases (left axis) and the updated calculation in WMO 2010 (right axis). Adapted from "Scientific Assessment of Ozone Depletion: 2010", WMO, 2011

Possible cultivation sources:

- Terrestrial crop plants containing the "harmless to ozone layer" gene (HOL) which release methyl halides
- Seaweeds which contain haloperoxidase enzymes and release polyhalogenated hydrocarbons

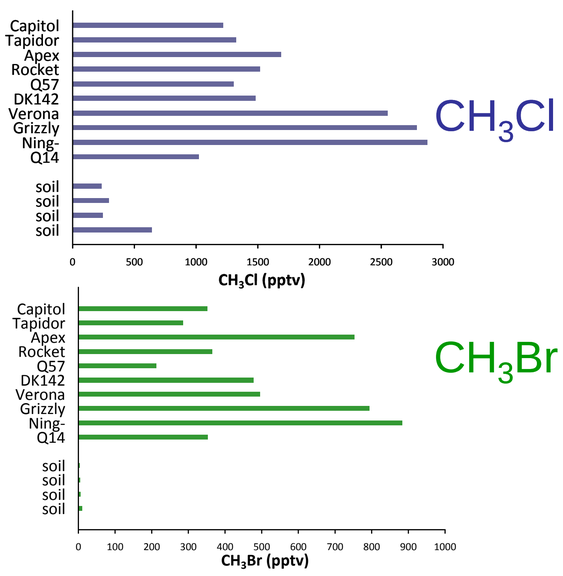


Fig. 4. Methyl halide abundances after enclosing 10 different varieties of winter-flowering oilseed rape (*Brassica napus*) for 4-5 hours

4. Methyl halide emissions by the *Brassica* family

All varieties of oilseed rape (*Brassica napus*) in field trials emitted CH_3Cl, CH_3Br and (not shown) CH_3I (Fig. 4)

It is likely that many plants contain HOL gene orthologues: *Brassica rapa* (turnip) emitted methyl halides and so too did 3 out of 4 varieties of rice (Fig. 5)

There is a linear relationship between soil halogen and production of methyl halides (not shown)

This could be important for rice due to coastal inundation and expansion of crops to less favourable soils

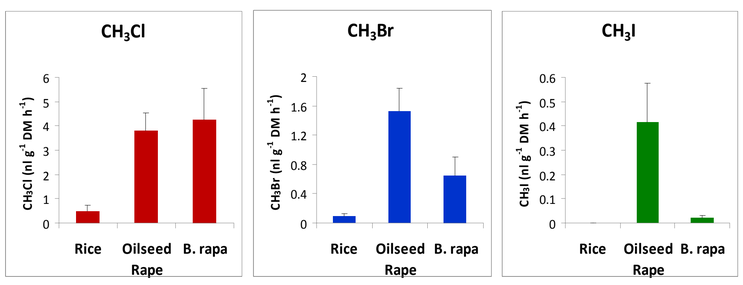


Fig. 5. Methyl halide emissions from *Oryza sativa* (rice), *Brassica napus* (rapeseed) and *Brassica rapa* (turnip)

5. Growth in rapeseed production

Oilseed production is expanding at a phenomenal pace for food and biodiesel (Fig. 6); it almost tripled between 1990 and 2010

The global emission of CH_3Br from oilseed rape is estimated to be 4.0 - 6.1 Gg yr^{-1} for 2008 (WMO, 2011), amounting to 4-5% of **all** emissions, both natural and man-made

This contribution looks set to increase significantly

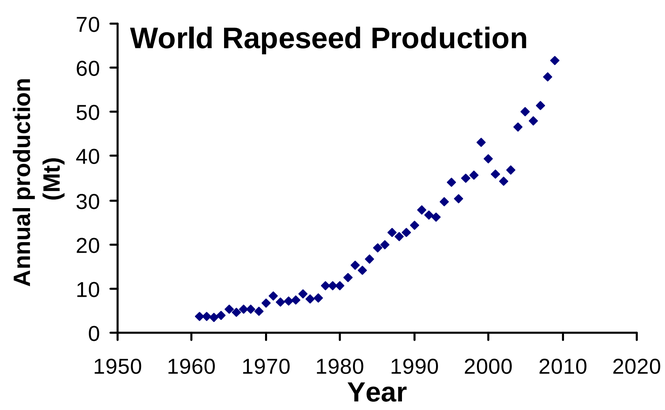


Fig. 6. Global annual production of rapeseed (United Nations Food and Agriculture Organization)

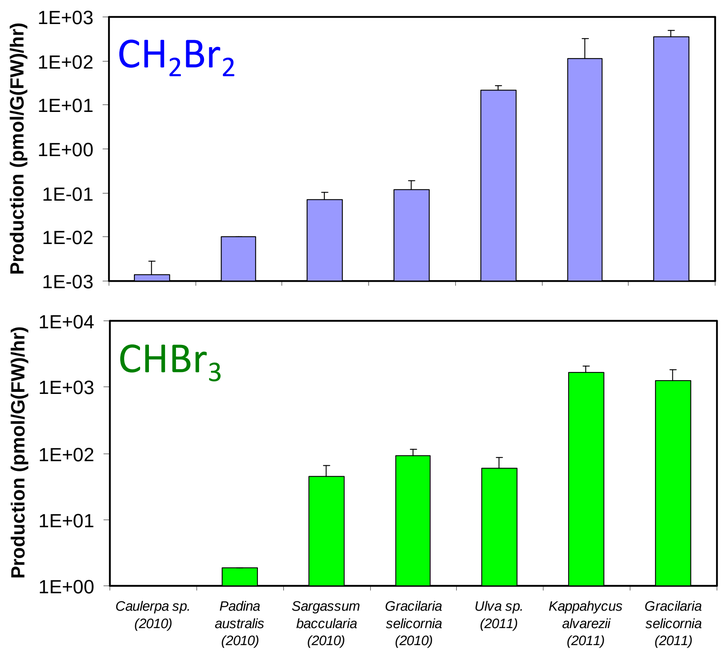


Fig. 7. Emission of two brominated VSLS gases by tropical seaweeds (log scale)

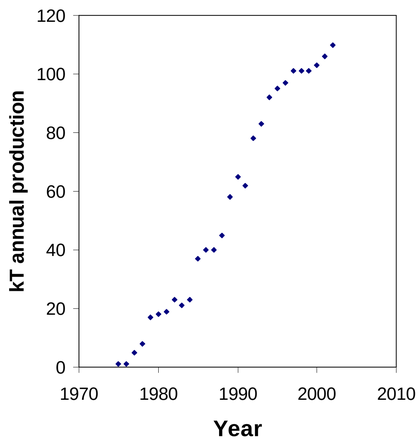


Fig. 8. Combined production of "warm water" *Kappaphycus* spp. by Malaysia, Indonesia and the Philippines (Neish, 2003)

6. Emissions of halogenated VSLS from tropical seaweeds

VSLS emissions from tropical seaweeds have been barely studied, but are pertinent to stratospheric EESC because of the potential for fast convective transport in this region

Emission rates for some typical seaweeds in Malaysia are shown in Fig. 7, including a farmed specimen of *Kappaphycus*; *Caulerpa*, *Sargassum* and *Ulva* are also potential commercial species

About 80% of seaweed cultivation in the tropics is of *Kappaphycus* spp. (Neish, 2003)

Production of tropical seaweeds is growing rapidly (Fig. 8) and total tropical seaweed production reached 200 kT dry weight (approx. 2,000 kT fresh weight) by 2007 (Phang *et al.*, 2011)

We estimate seaweed biomass between 20^0N and 20^0S to be about 20,000 kT fresh weight (after Baker *et al.*, 2001), so present-day levels of seaweed cultivation are already significant

However, the contribution of VSLS from tropical seaweeds relative to mangroves, sediments, marine phytoplankton, etc., is presently unknown

7. Conclusions

The Montreal Protocol does not account for the potential impacts of man-made and natural VSLS, nor short-lived halocarbons from cultivation practices

There is evidence for increasing abundances of chlorinated VSLS

Future increases in halogenated short-lived gases and VSLS are possible due to economic and climate-related pressures

References: Baker *et al.*, *Chemosphere - Global Change Science*, 3, 93-106, 2000; Neish, I.C., *ABC of Eucheuma Seaplant Production*, Monograph 1-0703, SuriaLink InfoMedia, 2003; Phang *et al.*, *Malaysian J. Sci.* 29, 214 - 224, 2010; WMO, *Scientific Assessment of Ozone Depletion: 2006*, WMO, 2007; WMO, *Scientific Assessment of Ozone Depletion: 2010*, WMO, 2011

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