Quiescent Diffusive and Fumarolic Volcanic Bromocarbon Emissions

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Future scenarios of declining atmospheric burdens of Ozone Depleting Substances (ODS) such as halocarbons after phase-out following international regulation (Montreal Protocol) vary strongly depending on what contribution from natural sources is taken into account. In addition, current and pre-industrial global atmospheric budgets of ODS are poorly balanced by known natural and anthropogenic sources of halocarbons (Butler, 2000). Brominated halocarbons have a high Ozone Depletion Potential, Br is at least 40x as efficient as Cl in polar stratospheric ozone destruction (Solomon et al., 1992). CH3Br is the dominant Br carrier to the stratosphere with sources being ca.: 32% anthropogenic , 39% natural, but ca. 29% unaccounted for (WMO, 1998). Natural sources have been reviewed recently (Gribble, 2000, Butler, 2000), including magmatic inorganic (Bureau, 2000) and volcanic organic sources (Rassmussen et al., 1980; Schwandner et al., 2002).

CH3Br and other bromocarbons have been reported in non-eruptive volcanic gases previously (Jordan et al., 2000; Schwandner et al., 2000). Due to its capability to extremely rapidly hydrolyse (Gan et al., 1995), CH3Br should not be sampled by the caustic soda bottle technique as used by Jordan et al. (2000) whose samples also show signs of air contamination, but by cryogenic separation of steam with subsequent sorbent trapping, as used by Isidorov (1990), Wahrenberger (1996) and Schwandner et al. (2000, 2001). To contribute significantly to the natural Br budget, volcanic gases would have to at least contain 2 ppmv (dry gas) CH3Br, scaled to a global CO2 emission of 66 Tgy-1 (Stoiber, 1995) based on CO2 flux to halocarbon concentration correlations (e.g. CFC-11: R2=0.91, Schwandner et al., 2002). However, CH3Br is not the only volcanogenic bromocarbon. Analysis of diffusive flank and crater degassing on Vulcano island (Italy) showed a strong diffusive component of CH3Br and C2H5Br emissions in 60-100°C hot pristine unvegetated volcanic "soil" close to high-temperature fumaroles. Other ODS found significantly above air, field and analytical system blanks include CH3Cl, CH3I, chlorophenols and chlorobenzenes. Abundances range from upper pptv to ppmv (e.g. CFC-11: max. 1200 pptv diffusive, 3700 pptv fumarolic/dry gas, dry air: 268 pptv).

References

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