Volcanogenic Chlorofluorocarbons and the Recent CFC Anomalies

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Volcanogenic chlorofluorocarbons and the recent CFC anomalies
A white paper prepared at the request of the Scientific Assessment Panel (SAP) of the Montreal Protocol

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Recent reports of enhanced emissions of chlorofluorocarbons indicate the possibility of large-scale noncompliance with the Montreal Protocol, with the apparent source region being in East Asia [Montzka et al., 2018; Adcock et al., 2018; Lin et al., 2019]. In light of these recent observations, it has been proposed that the chlorofluorocarbon anomalies may be the result of natural, volcanic processes. Historically, the prospect of production of chlorofluorocarbons from volcanoes has aroused a large degree of skepticism. Nevertheless, reports of volcanogenic CFCs arise in the literature sporadically.

The first report of CFCs in fumarolic gases was produced by Stoiber and colleagues [1971], who sampled gases at Sapper fumarole in Guatemala using a device similar to the Giggenbach flask [Giggenbach, 1975] and analyzed by GC-MS. Quantification was not performed, but HCFC-22, HFC-21, CFC-11, and CFC-113 were identified. Soviet scientist Isidorov and colleagues also employed GC-MS to evaluate the trace halocarbon flux from volcanic vents and wrote prolifically on the subject [Isidorov et al., 1986, 1990, 1992, 1993]. Isidorov specified that the concentrations of CFCs determined were often 3 – 4 magnitudes higher than the background concentrations and 1 – 3 magnitudes greater than urban air [Isidorov, 1995].

In situ measurements of the Mt. Saint Helens stratospheric plume did not demonstrate CFC-11 or CFC-12 enhancement [Inn et al., 1981]. Rasmussen et al. [1979] used similar techniques to Isidorov and Stoiber at Mauna Loa and Kilauea; though they detected CFC-11 and CFC-12, the concentrations of these gases were in the same ratio as with ambient air. During four field campaigns over 2 years, Frische et al. [2006] collected repeated fumarolic gas samples in the Central America Volcanic Arc and concluded that “the investigated volcanoes do not constitute a significant natural source for CFCs, HFCs, HCFCs, [and] halons”.

Jordan [2003] reviewed a number of trace gas inventories at volcanic vents and found that ambient air concentrations of CFCs typically exceed volcanic gas samples. Schwandner et al. [2004, 2013] reported exceedingly large quantities of CFC-11 at some sampling sites obtained at Vulcano, Italy which they attribute to geochemical sources. Tassi et al. [2012] also evaluated Vulcano but were unable to confirm the CFC results of Schwandner et al. [2004], as the concentrations of these components were below the detection limit of their instrumental methodology.

Povarov and Isidorov [2003] and Symonds et al. [1988] provided thermodynamic models which demonstrate that, if volcano-magmatic processes were to emit a significant quantity of chlorofluorocarbons to the atmosphere, they would have to be non-thermodynamic in character. Povarov and Isidorov [2003] stated, “Consequently, CF₂Cl₂, CFC₁₃, and CCl₄ have no globally significant source associated with direct efflux of volcanic and mantle gases”.

Depth profiles of atmospheric gases trapped in Antarctic firn provide evidence that, if there were a natural source of CFCs, the contribution to the atmospheric burden is minimal relative to current concentrations from anthropogenic sources [Butler et al., 1999; Sturrock et al., 2002; Petrenko et al., 2009; Montzka 2019]. Similarly, analyses of groundwater show that any preindustrial source of CFCs to the atmosphere must be very small [Busenberg and Plummer, 1992; Nielsen et al., 2001].
The weight of the evidence points against volcanogenic production of the quantities of excess CFC-11 recently reported. The current estimate of the CFC-11 anomaly is $\sim$13 Gg/annum [Montzka et al., 2018]. Schwandner et al. [2004] estimate a global volcanic flux of CFC-11 of $(8.56 \pm 4.7) \times 10^3$ Gg/annum on the basis of their measurements of CFC-11 emissions from the CFC-rich Vulcano; this total flux estimate is more than three orders of magnitude smaller than the observed CFC-11 anomaly. Furthermore, the most recent estimates of total chlorine flux from all volcanic vents range between 12 – 170 Tg Cl/annum [Halmer et al., 2002; Aiuppa et al., 2009], which would make the observed CFC-11 anomaly between 0.006 – 0.08% of the total volcanic chlorine emission budget. Such a high halocarbon percentage is quantitatively unrealistic in the absence of yet-to-be-described catalytic processes; the thermodynamic models of Symonds et al. [1988] and Povarov and Isidorov [2003] both calculate component halocarbon mass fractions of ten or more magnitudes smaller than HCl.

If the observed enhancement in CFCs were due to volcanogenic production, relevant questions to ask would be: *Why are these volcanogenic emissions suddenly significant now?* and *Why would these emissions be coming from a region in continental East Asia where there are relatively few active volcanoes?*

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**References**


