



## Fluxes and origin of halogenated organic trace gases from Momotombo volcano (Nicaragua)

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[1] In order to assess the contribution of quiescent degassing volcanoes to the global halo(hydro)carbon inventory, we have quantified volcanic fluxes of methyl halides ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ ), ethyl halides ( $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$ , and  $\text{C}_2\text{H}_5\text{I}$ ), and higher chlorinated methanes ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ ). About every eight months over a 2-year period (July 2001 to July 2003), gas samples were collected and analyzed from high-temperature fumaroles ( $472^\circ\text{C}$ – $776^\circ\text{C}$ ) at the Nicaraguan subduction zone volcano Momotombo. Using a simultaneous record of trace and main compounds in fumarolic gases as well as  $\text{SO}_2$  fluxes of the plume, we were able to calculate halo(hydro)carbon fluxes for Momotombo and extrapolate our results to estimate halo(hydro)carbon fluxes for the whole Quaternary Nicaraguan volcanic arc and, in addition, for all volcanoes globally. The most abundant halo(hydro)carbon was  $\text{CH}_3\text{Cl}$  with concentrations up to 19 ppmv. Further major halo(hydro)carbons were  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{C}_2\text{H}_5\text{I}$ , and  $\text{C}_2\text{H}_3\text{Cl}$  with an average concentration of 0.20 to 720 ppbv. Estimated mean halo(hydro)carbon fluxes from Momotombo were in the range of 630–5000 g/yr for methyl halides, 49–260 g/yr for ethyl halides, and 2.4–24 g/yr for higher chlorinated methanes. When the results for Momotombo are scaled up to  $\text{SO}_2$  fluxes of the Nicaraguan volcanic transect, fluxes of  $1.7 \times 10^5$  g/yr  $\text{CH}_3\text{Cl}$  and 82 g/yr  $\text{CCl}_4$  are attained for Nicaragua. Scaled up to the estimated global  $\text{SO}_2$  flux, this translates to hypothetical global fluxes of  $5.6 \times 10^6$  g/yr  $\text{CH}_3\text{Cl}$  and  $2.7 \times 10^3$  g/yr  $\text{CCl}_4$ . These volcanic fluxes are negligible compared to global anthropogenic and natural emissions of about  $3 \times 10^{12}$  g/yr  $\text{CH}_3\text{Cl}$  and  $2 \times 10^{10}$  g/yr  $\text{CCl}_4$ .

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## 1. Introduction

[2] More than 300 subaerial volcanoes continuously emit large amounts of organic and inorganic substances into the Earth's atmosphere [Graf *et al.*, 1997; Andres and Kasgnoc, 1998; Halmer *et al.*, 2002]. Numerous data sets exist on the major element composition of volcanic gases [e.g., Carroll and Holloway, 1994; Scarpa and Tilling, 1996] and on the occurrence of minor components (including hydrocarbons) in fumarolic gases [e.g., Capaccioni *et al.*, 1995, 2001; Taran and Giggenbach, 2003], but only a few studies have been carried out on halo(hydro)carbons [e.g., Jordan *et al.*, 2000; Jordan, 2003; Schwandner *et al.*, 2004]. Thus the occurrence, composition, variation and fluxes of halo(hydro)carbons are unknown for most volcanic systems. In fact, some of these substances (e.g.,  $\text{CCl}_4$ ) are involved in the greenhouse effect [Houghton *et al.*, 2001], others (e.g.,  $\text{CH}_3\text{Br}$ ) in the degradation of stratospheric ozone [World Meteorological Organization (WMO), 2003], and most of them have toxic effects on life (see World Health Organization at <http://www.who.int/search/en/>). Since Molina and Rowland [1974] and Stolarski and Cicerone [1974] discovered the degradation effect of chlorine radicals, originating from photolyzed man-made chlorofluoromethanes, on the stratospheric ozone layer, many scientists focused their attention on further possible sources of ozone depleting compounds. Wofsy *et al.* [1975] showed that bromine has the same destructive effects on ozone as chlorine and Solomon *et al.* [1994] confirmed such an effect for iodine. The first measurements of halogenated organic compounds in volcanic gases are from Stoiber *et al.* [1971]. They detected  $\text{CH}_3\text{Cl}$  and  $\text{C}_2\text{HCl}_3$  in fumarole gas samples (95% air content) from Santiaguito volcano in Guatemala. Rasmussen *et al.* [1980] reported elevated levels of  $\text{CH}_3\text{Cl}$  in ambient air samples collected in the vicinity of Kilauea and Mauna Loa volcanoes (Hawaii). Furthermore, Inn *et al.* [1981] measured high concentrations of  $\text{CH}_3\text{Cl}$  in the gaseous constituents of the eruption plume of Mount St. Helens. Considerable amounts of methyl halides ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ ) were also released during thermodesorption experiments of ash emitted during the Mount St. Helens eruption of 18th May 1980 [Rasmussen *et al.*, 1982]. In gas samples from 10 volcanoes of the Kurile Islands, Kamchatka, and Nicaragua, Isidorov *et al.* [1996] detected, e.g., chlorinated methanes. Jordan *et al.* [2000] detected more than 100 halogenated compounds (5 fluorinated, 100 chlorinated, 25 brominated and 4 iodated) in volcanic gases from Kujū and Satsuma Iwojima

volcanoes (Japan) and Etna and Vulcano (Italy), including methyl halides ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ ), ethyl halides ( $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{C}_2\text{H}_5\text{I}$ ) and higher chlorinated methanes ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ ). Schwandner *et al.* [2004] measured the same methyl halides and higher chlorinated methanes as well as ethyl bromide ( $\text{C}_2\text{H}_5\text{Br}$ ) in fumarolic and diffuse gas samples from Vulcano (Italy).

[3] During four field campaigns (17 July to 21 August 2001, 22 February to 21 March 2002, 13 November to 13 December 2002, 9–23 July 2003) we performed a time series sampling of fumarole gases at the Nicaraguan subduction zone volcano Momotombo. In order to calculate halo(hydro)carbon fluxes we measured additionally the  $\text{SO}_2$  flux of the plume with MiniDOAS (Miniaturized Differential Optical Absorption Spectrometer) over two days (18–19 November 2002) [Galle *et al.*, 2003]. Our investigation was focused on halomethanes and ethanes, because such  $\text{C}_1$  and  $\text{C}_2$  compounds exhibit much higher atmospheric lifetimes [WMO, 2003] than longer-chain compounds because of their negligible water solubility [Lide, 1993] that prevents quantitative tropospheric washout. This allows them to reach the stratosphere [Seinfeld and Pandis, 1998], especially through explosive volcanism [Inn *et al.*, 1981; Textor *et al.*, 2003, 2004]. In the stratosphere, degradation releases chlorine, bromine and iodine radicals which act as catalysts for reactions that cause ozone destruction [Seinfeld and Pandis, 1998]. To design ozone protection policies, the relevance of various sources contributing relevant halogenated substances to the atmosphere needs to be clarified. The calculated atmospheric budgets of the methyl halides  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  are largely out of balance, because identified sinks by far overweigh identified sources [Butler, 2000; WMO, 2003; Harper and Hamilton, 2003]. The amounts of missing sources are between 1.05 Tg/yr for  $\text{CH}_3\text{Cl}$  and 0.045 Tg/yr for  $\text{CH}_3\text{Br}$  [WMO, 2003]. These unbalanced atmospheric budgets suggest additional unknown natural sources, and volcanoes could potentially be considered as an important source. Due to the large number of quiescently degassing volcanoes worldwide, they are obvious targets for investigations of their possible contribution of halogenated organic compounds to the atmospheric load.

## 2. Geological and Volcanological Background

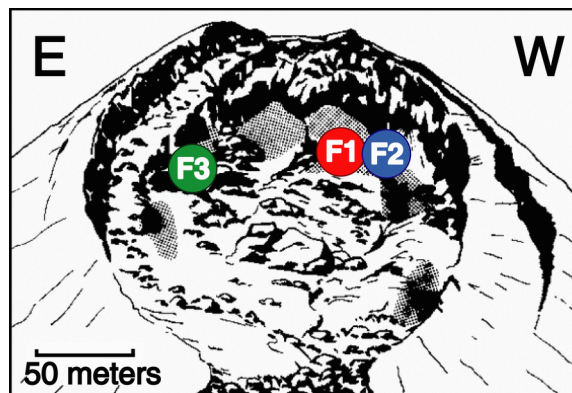
[4] The Quaternary Nicaraguan volcano Momotombo is part of the Central American volcanic

arc, resulting from the subduction of the Cocos Plate underneath the Caribbean Plate along the Middle American trench and extends from Mexico, across Guatemala, El Salvador and Nicaragua to central Costa Rica. The present volcanism in Nicaragua is focused along the volcanic chain known as the Cordillera de los Marrabios, that rises from the Nicaraguan Depression, a large NW-SE trending graben crossing the central part of the country. The Depression is characterized by a mafic igneous basement of oceanic lithosphere [Walther *et al.*, 2000], which is overlain by Cretaceous to Miocene marine sediments (tuffaceous shale, siltstone, greywacke, sandstone and limestone), and buried by the Quaternary ignimbrite deposits of the Malpaisillo and La Sierra Groups [McBirney and Williams, 1965; Elming *et al.*, 2001]. The ocean floor underneath Nicaragua is subducted with convergence rates of  $\sim 8$  cm/yr [DeMets, 2001], and was produced at the East Pacific Rise, is 5.5 km thick and overlain by  $\sim 225$  m of carbonate, which is in turn overlain by  $\sim 200$  m of hemipelagic sediments [Aubouin *et al.*, 1982; Kimura *et al.*, 1997; Walther *et al.*, 2000].

[5] Momotombo volcano (1297 m, 12.25°N, 86.32°W) is situated on the north shore of Lake Managua and represents a stratovolcano near the centre of the volcanic arc that passes through western Nicaragua. The last eruption of basaltic material was in 1905, since that time Momotombo has been in a persistent state of high-temperature fumarolic activity [Menyailov *et al.*, 1986].

[6] Fumaroles are localized at the base of the inner walls of the summit area (Figure 1), and gases were emitted at a wide range of temperatures, from 472°C–478°C at fumarole F3, 600°C–616°C at fumarole F2, and 739°C–776°C at fumarole F1, respectively, at the time of the survey (Table A1).

[7] The magmatic component of volatiles present in fumaroles of the Nicaraguan volcanic arc are derived from subducted marine carbonate and hemipelagic sediments [Patino *et al.*, 2000], altered oceanic crust and the wedge of depleted upper mantle, between the subducting Cocos Plate and the overriding Caribbean Plate [Snyder *et al.*, 2001]. Intensive bend-faulting of the downgoing slab facilitates deep penetration of seawater into the subduction zone [Ranero *et al.*, 2003]. In addition, Momotombo's magmatic plumbing system is associated with thick deep and shallow-water sediment deposits of the Sandino Basin [Snyder and Fehn, 2002; Ranero *et al.*, 2000; Walther *et al.*, 2000]. The potential sources of volatiles presented above are rich in halogens (Table 5), and water is available throughout as a transport medium for fluid



**Figure 1.** Schematic map of the summit crater of Momotombo and sampled fumaroles (courtesy of the Instituto Nicaragüense de Estudios Territoriales (INETER) in Nicaragua). Common “official” fumarole numbers are 9, 7, and 16, respectively, instead of F1, F2, and F3.

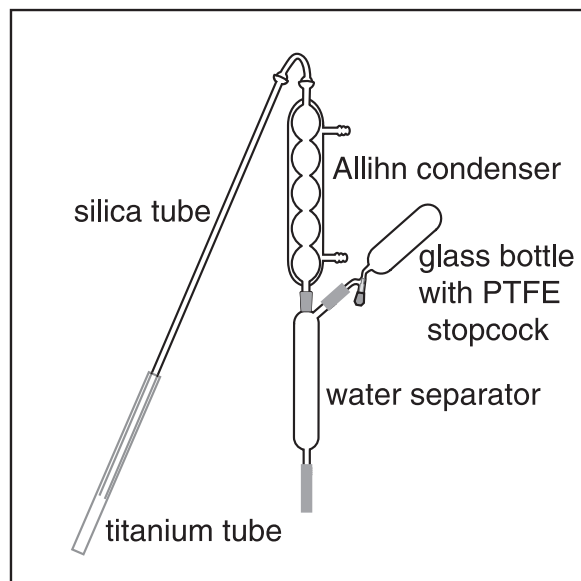
mobile elements. The high fumarole temperatures at Momotombo suggest high proportions of magmatic compounds and comparatively limited interaction with meteoric water or the hydrothermal system. These circumstances make Momotombo a preferred object of investigation.

## 3. Methods

### 3.1. Sampling

[8] For sampling of fumarolic trace gases for halo(hydro)carbon measurements we used 125 mL glass bottles with PTFE-stopcocks. Sample bottles and stopcocks were cleaned prior to usage by washing with aqueous Mucosol<sup>®</sup> solution, rinsing with purified water, drying and degassing in a vacuum oven at 80°C for 8 hours. In blank tests with sampling bottles filled up with purified helium, all relevant compounds were below detection limit. For transport to Nicaragua the bottles were filled up with synthetic air (a purified mixture of 79.5 vol% N<sub>2</sub> and 20.5 vol% O<sub>2</sub>). A few hours before sampling, they were evacuated to 10<sup>-5</sup> mbar. Fumarolic trace gas sampling is performed by pushing a titanium tube into the fumarole and inserting a silica tube with slightly smaller diameter. A water-cooled condenser, a water separator and an evacuated (10<sup>-5</sup> mbar) 125 mL glass bottle which is sealed with a PTFE stopcock is utilized in the sampling train (Figure 2). After flushing the system with fumarolic gas, the sample is sucked into the evacuated glass bottle [Frische *et al.*, 2006]. The application of our sampling method and device for collection of fumarolic gases addressed to halogenated trace compounds is com-





**Figure 2.** Schematic diagram of the setup for trace gas sampling [Frische et al., 2006].

paratively simple (no collection of different aliquots, no use of hazardous chemicals) and fast (reduced time of exposure to fumarolic fumes). Bulk samples for main component and hydrocarbon analysis were taken at the same locations using Giggenbach-type [Giggenbach and Goguel, 1989; Montegrossi et al., 2001] gas sampling. Ambient air samples were taken at the crater rim diametrically opposite of the volcanic plume with the same evacuated glass bottles as used for fumarolic trace gas samples. Outlet temperatures of gas samples were measured on the base of the titanium tube using a K-type thermocouple.

[9] We chose emission points with the highest gas emission rates, and in order to investigate possible variations in the halo(hydro)carbon emissions induced by physical-chemical parameters governing the fumarolic discharges, a wide range of outlet temperatures. High-temperature gas emissions, e.g., of 739°C–776°C at fumarole F1 (Figure 1) and 600°C–616°C at fumarole F2, suggest that a high portion of volatiles came directly from the magma. Lower temperature gases like at fumarole F3 (472°C–478°C) pointed to a more extensive interaction with hydrothermal or meteoric fluids [Fischer et al., 1996].

### 3.2. Analytical Methods

[10] Immediately before proceeding to the analysis of the fumarolic gas samples we injected 2 mL of degassed [Ohsawa et al., 2000] sodium hydroxide

solution (50% in water) into the sample-bottle to absorb the acidic compounds not removed as condensate phase in the field. After measuring the pressure of the remaining headspace gas (the portion of fumarolic gas which is not dissolved in the caustic solution and consisting of N<sub>2</sub>, O<sub>2</sub>, Ar, H<sub>2</sub>, He, CO as well as hydrocarbons and halo(hydro)carbons), the bottle was filled up to 2 bar with blank-tested helium. Fumarolic trace gas and ambient air samples were analyzed with gas chromatography/ion trap mass spectrometry (GC/ion trap-MS) within a mass scan range of 48 to 200 amu [Frische et al., 2006]. Quantification was made using the most abundant fragment ions (see Table 1).

[11] Since some halo(hydro)carbons seem to be unstable under alkaline conditions, we injected the sodium hydroxide solution into the sample shortly before the analysis (less than 10 min) to prevent significant degradation of the analytes. All relevant compounds showed mean degradation rates of 0.4% per hour during tests in an alkaline medium, with a range between 0.0%/h for CCl<sub>4</sub> and 2.2%/h for chloroform.

[12] Calibration of the GC/ion trap-MS was carried out by several injections per day of a working standard gas mixture. The working standard had been calibrated against calibration gases prepared in a three-step static dilution technique (except for C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>5</sub>Br), resulting in an absolute uncertainty of ±10% [Harnisch, 1996; Jordan et al., 2000]. For an approximate quantification of C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>5</sub>Br, the same instrumental response as for C<sub>2</sub>H<sub>3</sub>Cl (vinyl chloride) and CH<sub>3</sub>Br, respectively, was assumed [Jordan et al., 2000]. Detection limits for GC/ion trap-MS are 0.2 pptv for calibration standards (using volumes of

**Table 1.** Investigated Halo(hydro)carbons, Their Formulae, GC/MS Parameters, and Concentrations in Ambient Nicaraguan Air Samples<sup>a</sup>

Name	Formula	Quantifier Ions, m/z	Retention Time, s	Mean Ambient Air, pptv
Methyl chloride	CH <sub>3</sub> Cl	50 + 52	431	610
Methyl bromide	CH <sub>3</sub> Br	94 + 96	613	19
Methyl iodide	CH <sub>3</sub> I	127 + 142	829	4.7
Chloroethane	C <sub>2</sub> H <sub>5</sub> Cl	49 + 64 + 66	673	4.1
Bromoethane	C <sub>2</sub> H <sub>5</sub> Br	108 + 110	842	b.d.l.
Iodoethane	C <sub>2</sub> H <sub>5</sub> I	127 + 156	1041	0.7
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	49 + 84	865	62
Trichloromethane	CHCl <sub>3</sub>	83 + 85	1052	16
Tetrachlorocarbon	CCl <sub>4</sub>	117 + 119	1163	100
Chloroethene	C <sub>2</sub> H <sub>3</sub> Cl	62 + 64	521	1.1

<sup>a</sup>Concentrations in pptv.

**Table 2.** Minimum, Maximum, and Arithmetic Mean Concentrations in Headspace Gas From Fumaroles F1, F2, and F3 of Momotombo<sup>a</sup>

Fumarole	F1			F2			F3		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Temperature, °C	739–776			600–616			472–478		
Number of samples	10			7			5		
Sampling period	2001–2003			2002–2003			2002		
CH <sub>3</sub> Cl	4.2	140	64	9.8	160	60	1000	19,000	9000
CH <sub>3</sub> Br	0.39	67	13	1.7	41	16	120	790	510
CH <sub>3</sub> I	0.33	24	9.5	3.6	32	12	140	1400	720
C <sub>2</sub> H <sub>5</sub> Cl	0.13 <sup>b</sup>	5.4 <sup>b</sup>	1.7 <sup>b</sup>	0.46	12	4.1	49	760	430
C <sub>2</sub> H <sub>5</sub> Br	0.047 <sup>b,c</sup>	0.70 <sup>b,c</sup>	0.35 <sup>b,c</sup>	0.065	2.1	0.59	10 <sup>c</sup>	68 <sup>c</sup>	35 <sup>c</sup>
C <sub>2</sub> H <sub>5</sub> I	0.072 <sup>b,c</sup>	1.2 <sup>b,c</sup>	0.50 <sup>b,c</sup>	0.20	0.99	0.54	6.1	110	48
CH <sub>2</sub> Cl <sub>2</sub>	0.079	1.4	0.50	0.21	1.7	0.86	1.2	52	22
CHCl <sub>3</sub>	0.075 <sup>b</sup>	0.69 <sup>b</sup>	0.24 <sup>b</sup>	0.044	0.72	0.37	0.68	48	20
CCl <sub>4</sub>	0.074	0.34	0.19	0.17	0.62	0.31	0.34 <sup>c</sup>	0.60 <sup>c</sup>	0.45 <sup>c</sup>
C <sub>2</sub> H <sub>3</sub> Cl	0.10	1.1	0.41	0.22 <sup>c</sup>	1.6 <sup>c</sup>	0.82 <sup>c</sup>	2.3	9.9	5.1

<sup>a</sup> Concentrations in ppbv.

<sup>b</sup> One or more samples show concentrations below detection limits (b.d.l.) (see Table A2).

<sup>c</sup> Not quantified (n.q.) in one or more samples (see Table A2).

150 mL), 0.7 pptv for ambient air samples (using volumes of 50 mL), and 20 pptv for fumarolic gas samples from Momotombo (using volumes of 50 mL of the sample/helium mixture). Replicate analysis of individual samples gave values within  $\pm 10\%$ . The analyses were performed around 1.5 months after the collection of the samples. Tests with samples taken one after the other at the same location showed no systematic drift in the concentrations of relevant compounds when analyzed over a one month interval.

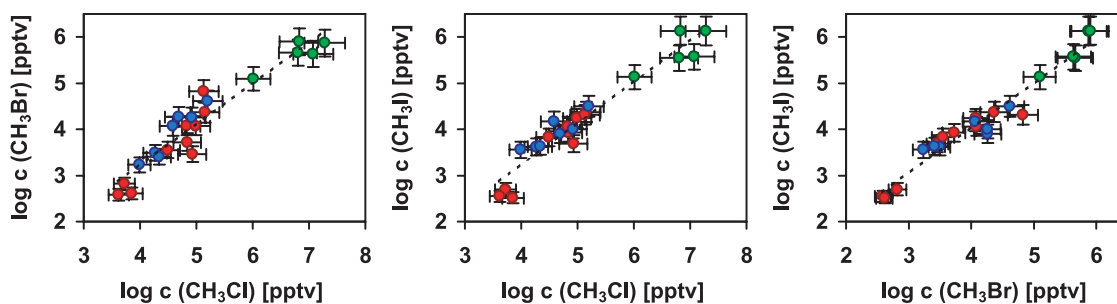
[13] Hydrocarbons (e.g., CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>), SO<sub>2</sub>, as well as the headspace gas fraction of the bulk gas sample (Table A3), were determined with Giggenbach-type methods [Giggenbach and Goguel, 1989; Montegrossi *et al.*, 2001]. Measurements of SO<sub>2</sub> fluxes using the MiniDOAS technique were performed as described by Galle *et al.* [2003].

#### 4. Results

[14] At three locations in the crater of Momotombo we took 22 trace gas samples over a period of two years, from fumaroles discharging in a temperature range of 472°C–776°C. The variety of detected halogenated organic compounds with concentrations up to several orders of magnitude greater than ambient air (Tables 1, 2, and A2) includes short-chain halo(hydro)carbons, halogenated aromatics and heterocycles. Our results are comparable to those of Jordan *et al.* [2000] in gas samples from volcanoes in Italy and Japan. The most abundant halo(hydro)carbon was CH<sub>3</sub>Cl with concentrations

up to 19 ppmv in the headspace gas of fumarole F3. Further major halo(hydro)carbons were (in order of their mean relative abundance) CH<sub>3</sub>I, CH<sub>3</sub>Br, C<sub>2</sub>H<sub>5</sub>Cl, C<sub>2</sub>H<sub>5</sub>I, C<sub>2</sub>H<sub>5</sub>Br, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, C<sub>2</sub>H<sub>3</sub>Cl and CCl<sub>4</sub>. The highest concentrations in halogenated organic trace gases were observed in trace gas samples from fumarole F3. Minimum, maximum and average concentrations of the ten most abundant halo(hydro)carbons are listed for each fumarole in Table 2. A detailed study on the temporal variations of trace gas fluxes at Momotombo will be published elsewhere.

[15] Methyl halides were the predominant species in our samples. Methyl and ethyl halide concentrations correlate well with each other (shown on logarithmic scales in Figures 3–5), the correlation coefficient *R*, obtained from the linear regression of concentrations, range between 0.99 for the positive correlation of C<sub>2</sub>H<sub>5</sub>Br with C<sub>2</sub>H<sub>5</sub>I, and 0.71 for C<sub>2</sub>H<sub>3</sub>Cl with C<sub>2</sub>H<sub>5</sub>I. As depicted in Figure 3, methyl halides show good correlations with each other, giving *R* values of 0.88 for CH<sub>3</sub>Br versus CH<sub>3</sub>Cl, 0.83 for CH<sub>3</sub>I versus CH<sub>3</sub>Cl, and 0.96 for CH<sub>3</sub>I versus CH<sub>3</sub>Br. A good correlation exists between ethyl halides (Figure 4) with *R* values of 0.95 for C<sub>2</sub>H<sub>5</sub>Br versus C<sub>2</sub>H<sub>5</sub>Cl, 0.71 for C<sub>2</sub>H<sub>5</sub>I versus C<sub>2</sub>H<sub>5</sub>Cl, and 0.99 for C<sub>2</sub>H<sub>5</sub>I versus C<sub>2</sub>H<sub>5</sub>Br. As shown in Figure 5, methyl halides and ethyl halides with the same type of halogen in the molecule correlate with *R* values of 0.91 for C<sub>2</sub>H<sub>5</sub>Cl versus CH<sub>3</sub>Cl, 0.95 for C<sub>2</sub>H<sub>5</sub>Br versus CH<sub>3</sub>Br, and 0.99 for C<sub>2</sub>H<sub>5</sub>I versus CH<sub>3</sub>I. Also a correlation between methane and methyl



**Figure 3.** Correlation in concentration between methyl halides ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ ) in headspace gas from fumarole F1 (red), F2 (blue), and F3 (green), respectively, of Momotombo.

halides and between ethane and ethyl halides was observed (Figures 6 and 7). The correlation coefficient of methyl halide versus methane concentrations (Figure 6) range from 0.96 for  $\text{CH}_3\text{I}$  to 0.95 for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ . Ethyl halides versus ethane concentrations show clear positive correlations among each other with R values of 1.00 for  $\text{C}_2\text{H}_5\text{I}$ , 0.98 for  $\text{C}_2\text{H}_5\text{Br}$ , and 0.93 for  $\text{C}_2\text{H}_5\text{Cl}$  (Figure 7). Weak negative correlations (R values from  $-0.72$  to  $-0.57$ ) exist between temperature and methyl and ethyl halides (Figure 8). Such relations have so far not been described from theoretical considerations [e.g., Gerlach, 2004], and remains to be addressed in future studies.

[16] Mobile traverses with the zenith sky mini-DOAS were made at the bottom of Momotombo and  $\text{SO}_2$  fluxes were  $0.53 \pm 0.10$  kg/s on 18 November and  $0.49 \pm 0.12$  kg/s on 19 November.  $\text{SO}_2$  gas plume measurements of the five permanently degassing Nicaraguan volcanoes San Cristóbal, Telica, Cerro Negro, Momotombo and Masaya were repeatedly carried out during 2002 and 2003. The total  $\text{SO}_2$  flux for Nicaragua sums to 17 kg/s (0.54 Tg/yr) (T. H. Hansteen, unpublished data, 2006).

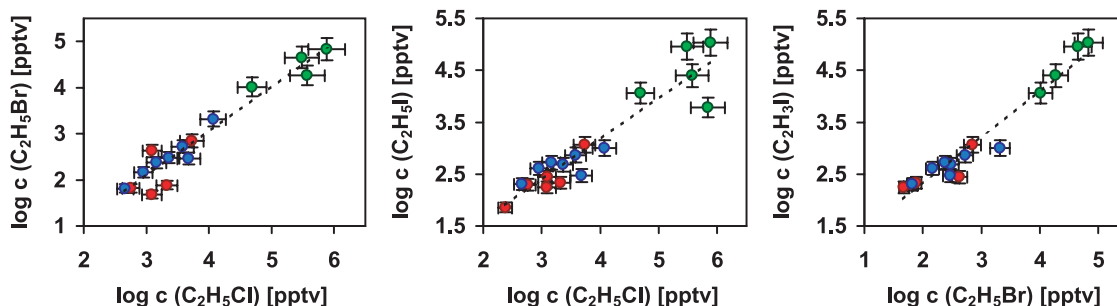
[17] In order to calculate trace gas fluxes  $flux_{(trace\ gas)}$  (1) we scale sulfur data  $c_{(\text{SO}_2)}$  and headspace gas content  $c_{(headspace)}$  from wet chemistry analysis of the bulk sample (Table A3) with the total Momotombo  $\text{SO}_2$  flux estimations of MiniDOAS  $flux_{(\text{SO}_2)}$ .

$$flux_{(trace\ gas)} = \frac{c_{(headspace)} flux_{(\text{SO}_2)}}{c_{(\text{SO}_2)}} \quad (1)$$

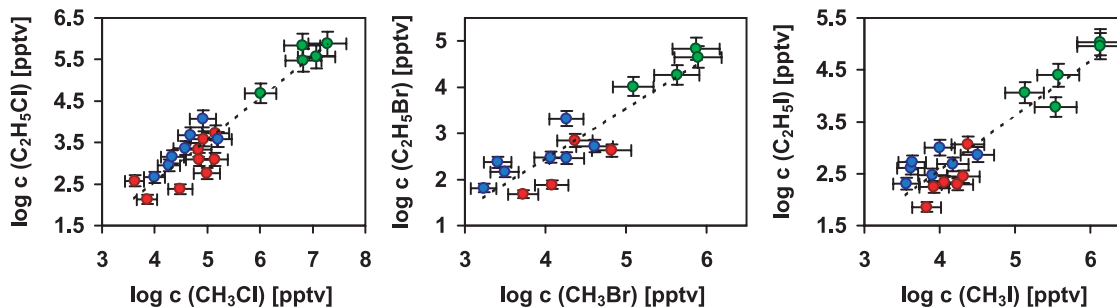
Fluxes of individual compounds  $flux_{(i)}$  are then calculated (2) from their concentration in headspace gas  $c_{(i)}$  in the trace gas sample (Table A2) (Please note that data given in Tables A2 and A3 are molar values, that need to be converted to mass units for their use in mass flux calculations).

$$flux_{(i)} = flux_{(trace\ gas)} c_{(i)} \quad i = \text{compound} \quad (2)$$

Trace gas fluxes from Momotombo were calculated using averaged concentrations obtained from the three observed fumaroles F1, F2 and F3 (Table 3). The arithmetic mean in trace gas composition of fumarole F1, F2 and F3 results in annual fluxes of 5.0 kg  $\text{CH}_3\text{Cl}$ , 630 g  $\text{CH}_3\text{Br}$ , 1.5 kg  $\text{CH}_3\text{I}$ , 49 g  $\text{C}_2\text{H}_5\text{Br}$  and 2.4 g  $\text{CCl}_4$  at Momotombo. On the basis of estimated global volcanic  $\text{SO}_2$  fluxes of 18 Tg/yr [Halmer *et al.*, 2002], our calculations result in



**Figure 4.** Correlation in concentration between ethyl halides ( $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$ , and  $\text{C}_2\text{H}_5\text{I}$ ) in headspace gas from fumarole F1 (red), F2 (blue), and F3 (green), respectively, of Momotombo.



**Figure 5.** Correlation in concentration between methyl halides ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ ) and ethyl halides ( $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$ , and  $\text{C}_2\text{H}_5\text{I}$ ) in headspace gas from fumarole F1 (red), F2 (blue), and F3 (green), respectively, of Momotombo.

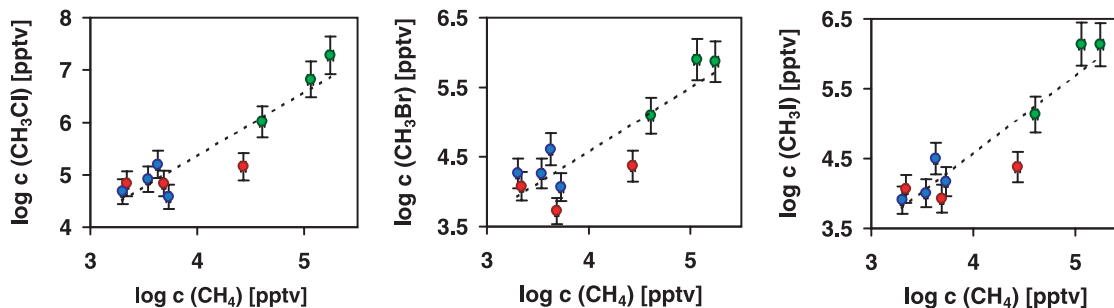
hypothetical annual volcanic halo(hydro)carbon fluxes of 5600 kg for  $\text{CH}_3\text{Cl}$ , 720 kg for  $\text{CH}_3\text{Br}$ , 1700 kg of  $\text{CH}_3\text{I}$ , 55 kg of  $\text{C}_2\text{H}_5\text{Br}$  and 2.7 kg of  $\text{CCl}_4$ .

[18] In order to illustrate the interfumarole variability, however, we additionally scaled the trace gas concentration data from each of the fumaroles to the total Momotombo  $\text{SO}_2$  flux (Table 3). Please note that these calculations are hypothetical and for illustrative purposes only, as solely trace gas concentrations and not fluxes could be measured from each individual fumarole. However, the variability between the fumaroles now becomes evident, showing that flux calculations for trace gases may vary significantly depending on the choice of fumaroles. In the Momotombo case, fluxes calculated using data from only one fumarole would have resulted in deviations from the average values ranging between a factor 0.8 ( $\text{CCl}_4$  at F1) and 43 ( $\text{C}_2\text{H}_5\text{I}$  at F2) (Table 3).

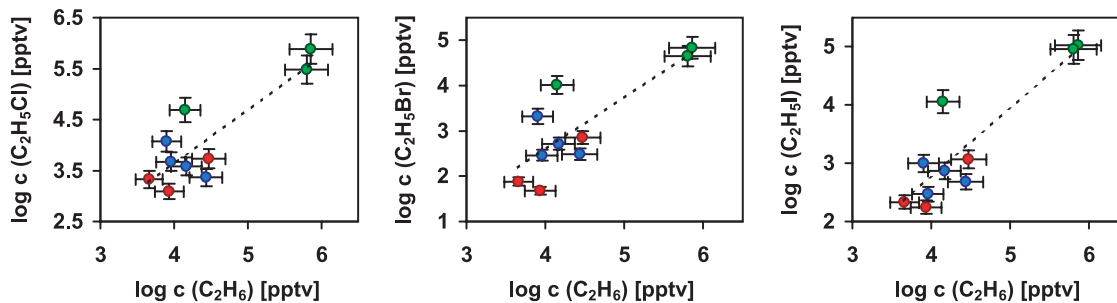
## 5. Discussion

[19] During subduction the slab releases large volumes of water from oceanic sediments, altered

basalts and serpentinite. At the depths of mineral breakdown, fluids are released into the mantle wedge causing melting. When fluid is exsolved from the ascending magma, chlorine, bromine, and iodine, are to a great extent partitioned into the fluid phase [Kravchuk and Keppler, 1994; Bureau et al., 2000], because of their large ionic radii ( $\text{Cl} = 181 \text{ pm}$ ,  $\text{Br} = 196 \text{ pm}$  and  $\text{I} = 220 \text{ pm}$ ) [Mortimer, 1987] that prevent sufficient incorporation into most minerals [Mason and Moore, 1982]. The relative abundance of iodine, chlorine, and bromine in high-temperature magmatic fluids is a function of their concentration in the melt, as well as their fluid/melt partition coefficients ( $D^{f/m}$ ). Experimentally determined  $D^{f/m}$  for albitic melts are 8.1, 17.5 and 104 for chlorine, bromine, and iodine, respectively [Bureau et al., 2000]. This implies that iodine, bromine and chlorine entering the magmatic system should to a large extent be released into the atmosphere during shallow-level magma degassing [Webster et al., 1999]. The strong halogen enrichment in the fluid phase greatly facilitates halo(hydro)carbon formation at shallow depths.



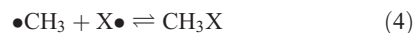
**Figure 6.** Correlation between methane and methyl halide concentrations in headspace gas from fumarole F1 (red), F2 (blue), and F3 (green), respectively, of Momotombo.



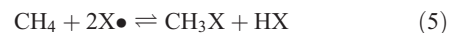
**Figure 7.** Correlation between ethane and ethyl halide concentrations in headspace gas from fumarole F1 (red), F2 (blue), and F3 (green), respectively, of Momotombo.

[20] In our samples the most abundant methyl and ethyl halides were followed in concentration by higher chlorinated methanes. This characteristic distribution sequence suggests that thermally and catalytically activated radical reactions occurring in the gas phase [Jordan *et al.*, 2000] are important for the origin of the halogenated trace gases. In fact, the synthesis of halogenated trace gases is possible as light alkanes like  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  are produced at shallow depth in the volcanic and hydrothermal systems by thermal decomposition of organic matter [Taran and Giggenbach, 2003]. In simple gas-phase catalytic reaction cycles, these hydrocarbons can react with reactive radicals, e.g.,  $\text{Cl}\bullet$  and  $\text{Br}\bullet$  generated in ppb-ppm levels by

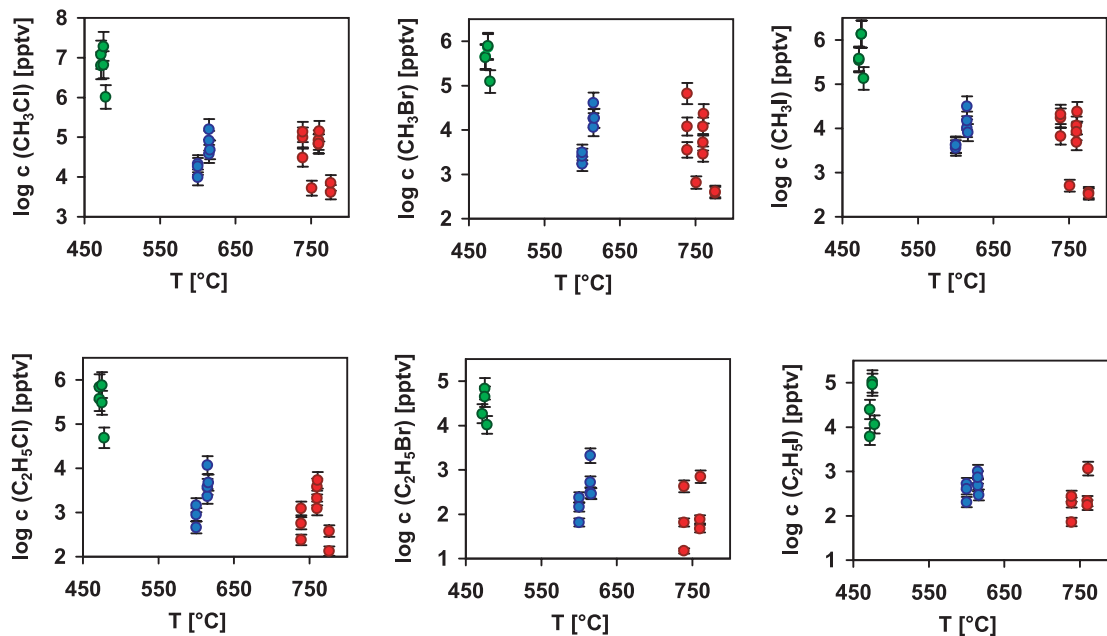
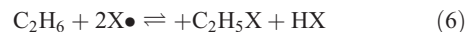
shallow magma degassing [Bobrowski *et al.*, 2003; Gerlach, 2004] (3)–(4).



The total equation of (3)–(4) is (5):



Higher hydrocarbons would react in an analogous way (6).



**Figure 8.** Temperature dependence of methyl halide ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ ) and ethyl halide ( $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$ , and  $\text{C}_2\text{H}_5\text{I}$ ) concentration in headspace gas of fumarole F1 (red), F2 (blue), and F3 (green), respectively, of Momotombo.



**Table 3.** Trace Gas Fluxes of Fumaroles F1, F2, and F3 at Momotombo, Their Arithmetic Mean Values, Flux Estimations for All Nicaraguan Volcanoes, and a Rough Estimation of Resulting Global Fluxes<sup>a</sup>

	Flux Momotombo <sup>b</sup>				Flux	Flux
	Fumarole F1	Fumarole F2	Fumarole F3	Mean F1–F3	Nicaragua <sup>c</sup>	Global <sup>d</sup>
CH <sub>3</sub> Cl	810	150	14,000	5000	170,000	5,600,000
CH <sub>3</sub> Br	210	80	1600	630	22,000	720,000
CH <sub>3</sub> I	350	92	4200	1500	51,000	1,700,000
C <sub>2</sub> H <sub>5</sub> Cl	32	8.3	750	260	9000	300,000
C <sub>2</sub> H <sub>5</sub> Br	6.2	1.4	140	49	1700	55,000
C <sub>2</sub> H <sub>5</sub> I	16	2.8	340	120	4000	134,000
CH <sub>2</sub> Cl <sub>2</sub>	9.1	3.2	61	24	820	27,000
CHCl <sub>3</sub>	8.8	2.0	44	18	600	20,000
CCl <sub>4</sub>	3.1	2.0	2.3	2.4	82	2700
C <sub>2</sub> H <sub>3</sub> Cl	6.6	2.3	11	6.6	220	7400

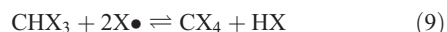
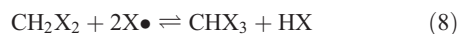
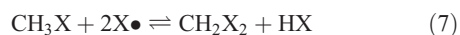
<sup>a</sup> Fluxes in g/yr.

<sup>b</sup> Based on SO<sub>2</sub> fluxes of 0.53 kg/s on 18 November and 0.49 kg/s on 19 November.

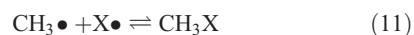
<sup>c</sup> Based on a total volcanic SO<sub>2</sub> flux estimation for Nicaragua of 0.54 Tg/yr (17 kg/s) (T. H. Hansteen, unpublished data, 2006).

<sup>d</sup> Based on a global volcanic SO<sub>2</sub> flux of 18 Tg/yr (570 kg/s) [Halmer *et al.*, 2002].

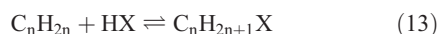
Also higher halogenated hydrocarbons can be synthesized in this way (7)–(9).



Another possible mechanism leading to the generation of these compounds could be the thermal cracking of larger hydrocarbons, which produce smaller hydrocarbons with free radicals (10). Reactions of short chain hydrocarbons with halogen radicals could generate, e.g., methyl and ethyl halides (11)–(12).



Furthermore, electrophilic addition reactions, through catalytic cracking of alkanes on zeolites or silica-alumina (catalysts commonly present in volcanic-hydrothermal environment), could produce unsaturated hydrocarbons (e.g., C<sub>n</sub>H<sub>2n</sub>) and addition of magmatic hydrogen halides could produce haloalkanes (13).



In the specific case of Momotombo the mean molar halogen ratio of the methyl halides CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>I is 10:1.0:1.1 and 11:1.0:1.9 for the ethyl halides C<sub>2</sub>H<sub>5</sub>Cl, C<sub>2</sub>H<sub>5</sub>Br, C<sub>2</sub>H<sub>5</sub>I (Table 4). Fumarole F2 shows the lowest values for chlorinated compounds. Bromine and iodine values from methyl bromide and methyl iodide are comparable at all fumaroles, the ethyl halides show higher values for iodine than for bromine.

[21] The relatively high proportions of bromine and iodine versus chlorine in fumarolic gases from Momotombo point to a driving role of marine sediments in the generation of halogenated trace gases. As can be seen in Table 5, the global iodine distribution is dominated by the marine system. Nearly 70% of iodine in the Earth's crust (including seawater) is calculated to exist in ocean sediments [Muramatsu and Wedepohl, 1998]. Iodine is associated with organic material (e.g., 1020 mg/kg in marine organisms), which results in a relatively low abundance of this element in seawater

**Table 4.** Mean Relative Molar Halogen Ratios of Methyl and Ethyl Halide Concentrations in Headspace Gas From Fumaroles F1, F2, and F3 of Momotombo

	Fumarole F1	Fumarole F2	Fumarole F3	Mean All Fumaroles
CH <sub>3</sub> Cl	9.6 ± 5.7	4.8 ± 0.9	17 ± 8.5	10 ± 5.0
CH <sub>3</sub> Br	1.0 ± 0.5	1.0 ± 0.4	1.0 ± 0.1	1.0 ± 0.0
CH <sub>3</sub> I	1.0 ± 0.3	1.0 ± 0.3	1.2 ± 0.3	1.1 ± 0.1
C <sub>2</sub> H <sub>5</sub> Cl	15 ± 8.4	7.7 ± 3.2	11 ± 5.9	11 ± 2.9
C <sub>2</sub> H <sub>5</sub> Br	1.0 ± 0.2	1.0 ± 0.3	1.0 ± 0.0	1.0 ± 0.0
C <sub>2</sub> H <sub>5</sub> I	2.5 ± 1.3	1.6 ± 0.7	1.5 ± 0.3	1.9 ± 0.5

**Table 5.** Mean Relative Molar Halogen Ratios and Concentrations of Halogens in Different Reservoirs

	Relative Molar Halogen Ratios			Concentrations		
	Chlorine	Bromine	Iodine	Chlorine	Bromine	Iodine
Methyl halides Momotombo F1	5.8–29	1.0–3.2	1.0–1.9	4.2–140 nmol/mol	0.39–67 nmol/mol	0.33–24 nmol/mol
Ethyl halides Momotombo F1	4.5–28	1.0–1.5	1.0–4.9	0.24–5.4 nmol/mol	0.015–0.70 nmol/mol	0.072–1.2 nmol/mol
Condensates Momotombo F1 <sup>a</sup>	1300	1.1	1.0	780 $\mu$ mol/mol	0.64 $\mu$ mol/mol	0.59 $\mu$ mol/mol
Volcanic glasses Fontana <sup>b</sup>	1200	19	1.0	1100 mg/kg	40 mg/kg	3.4 mg/kg
Volc. melt inclusions Fontana <sup>b</sup>	120	1.0	1.0	1300 mg/kg	24 mg/kg	40 mg/kg
Oceanic pelagic clay <sup>c,d</sup>	2700	4.0	1.0	21,000 mg/kg	70 mg/kg	28 mg/kg
Marine organisms <sup>e</sup>	24	1.0	1.5	4700 mg/kg	440 mg/kg	1020 mg/kg
Seawater <sup>c</sup>	1,100,000	1800	1.0	18,800 mg/kg	67 mg/kg	0.06 mg/kg
Meteoric water <sup>c</sup>	4000	4.5	1.0	7.8 mg/kg	0.020 mg/kg	0.007 mg/kg
Primitive mantle <sup>f</sup>	6100	7.9	1.0	17 mg/kg	0.050 mg/kg	0.010 mg/kg
Continental crust <sup>g</sup>	2100	2.0	1.0	472 mg/kg	1 mg/kg	0.8 mg/kg

<sup>a</sup>K. Garofalo (unpublished data, 2006).<sup>b</sup>H. Wehrmann (unpublished data, 2006).<sup>c</sup>Li [1982].<sup>d</sup>Li [1991].<sup>e</sup>Bowen [1979].<sup>f</sup>McDonough and Sun [1995].<sup>g</sup>Wedepohl [1995].

(0.06 mg/kg) and a relative enrichment in marine deep-sea sediments (e.g., 28 mg/kg in oceanic pelagic clay). Bromine, however, exhibits moderate affinity to organic material (e.g., 440 mg/kg in marine organisms) resulting in slightly higher concentrations in marine deep-sea sediments (e.g., 70 mg/kg in oceanic pelagic clay) than in seawater (67 mg/kg). Chlorine is the most conservative of the three halogens, it is enriched in seawater (18,800 mg/kg) and shows no particular affinity for organic material.

[22] Momotombo is underlain by voluminous deep and shallow-water sediment deposits of the Sandino Basin [Snyder and Fehn, 2002; Ranero *et al.*, 2000; Walther *et al.*, 2000], which are supposedly bromine and iodine rich. High Br and I contents in the local upper crust were also indirectly inferred from anomalously high heavy halogen contents in melt inclusions and volcanic glasses from the Fontana Tephra in Nicaragua (Table 5) (H. Wehrmann, unpublished data, 2006). Subduction of large

volumes of bromine and iodine rich marine sediments in combination with shallow level processes such as hydrothermal mobilization of bromine and iodine in the local marine sediment deposits [Snyder *et al.*, 2003] followed by the formation of thermogenic methane [Snyder *et al.*, 2003] would deliver the required reactants (hydrocarbons and halogens) for halo(hydro)carbon synthesis. Investigations of <sup>129</sup>I/I in geothermal gases and fluids from Nicaragua confirm the presence of two different end-members: One magmatic component (~25 Ma old) associated with presently subducting sediments, and a much older crustal component of ~65 Ma [Snyder and Fehn, 2002; Snyder *et al.*, 2003]. These results strongly suggest the involvement of a crustal source in the generation of Nicaraguan volcanic volatiles.

[23] Scaling our data from Momotombo volcano to the estimated global volcanic SO<sub>2</sub> flux of 18 Tg/yr [Halmer *et al.*, 2002] yields an average global

**Table 6.** Comparison of Global Methyl Halide Flux Estimations for Fumarolic Emissions and for All Other Known Emission Sources<sup>a</sup>

	This Work, Value Range	Jordan <i>et al.</i> [2000], Value Range	This Work, Mean Value	Schwandner <i>et al.</i> [2004], Mean Value	All Other Known Emission Sources, <sup>b,c</sup> Value Range
CH <sub>3</sub> Cl	$1.6 \times 10^5$ – $3.4 \times 10^7$	$6.2 \times 10^4$ – $1.2 \times 10^7$	$5.6 \times 10^6$	$7.4 \times 10^7$	$1.9 \times 10^{12}$ – $1.2 \times 10^{13}$
CH <sub>3</sub> Br	$9.0 \times 10^4$ – $2.6 \times 10^6$	$1.9 \times 10^3$ – $8.2 \times 10^5$	$7.2 \times 10^5$	$7.8 \times 10^5$	$7.7 \times 10^9$ – $2.9 \times 10^{11}$
CH <sub>3</sub> I	$1.0 \times 10^5$ – $6.8 \times 10^6$	$5.7 \times 10^3$ – $2.5 \times 10^6$	$1.7 \times 10^6$	$1.3 \times 10^6$	$2.5 \times 10^{11}$ – $1.6 \times 10^{12}$

<sup>a</sup>Flux estimations in g/yr.<sup>b</sup>WMO [2003].<sup>c</sup>Harper and Hamilton [2003].

**Table A1.** Location and Sample Parameter of Trace Gas Samples<sup>a</sup>

Trace Gas Sample ID	Fumarole	Sample Latitude, N	Sample Longitude, W	Elevation, m	Temperature, °C	Date (mm:dd:yyyy)	Local Time <sup>b</sup> (hh:mm)
Mo_2_28	F1	12°25.390'	086°32.321'	1249	751	08:11:2001	1:45 PM
Mo_3_48	F1	12°25.390'	086°32.321'	1249	776	03:08:2002	1:05 PM
Mo_3_49	F1	12°25.390'	086°32.321'	1249	776	03:08:2002	1:15 PM
Mo_4_2	F1	12°25.390'	086°32.321'	1249	760	11:17:2002	11:00 AM
Mo_4_3	F1	12°25.390'	086°32.321'	1249	760	11:17:2002	11:05 AM
<b>Mo_4_15</b>	<b>F1</b>	<b>12°25.390'</b>	<b>086°32.321'</b>	<b>1249</b>	<b>760</b>	<b>11:18:2002</b>	<b>3:00 PM</b>
<b>Mo_4_23</b>	<b>F1</b>	<b>12°25.390'</b>	<b>086°32.321'</b>	<b>1249</b>	<b>761</b>	<b>11:19:2002</b>	<b>7:30 AM</b>
Mo_5_1	F1	12°25.390'	086°32.321'	1249	739	07:12:2003	12:45 PM
Mo_5_2	F1	12°25.390'	086°32.321'	1249	739	07:12:2003	12:50 PM
Mo_5_3	F1	12°25.390'	086°32.321'	1249	739	07:12:2003	12:55 PM
Mo_4_5	F2	12°25.396'	086°32.338'	1240	615	11:17:2002	4:00 PM
<b>Mo_4_12</b>	<b>F2</b>	<b>12°25.396'</b>	<b>086°32.338'</b>	<b>1240</b>	<b>615</b>	<b>11:18:2002</b>	<b>9:45 AM</b>
<b>Mo_4_16</b>	<b>F2</b>	<b>12°25.396'</b>	<b>086°32.338'</b>	<b>1240</b>	<b>615</b>	<b>11:18:2002</b>	<b>3:15 PM</b>
<b>Mo_4_24a</b>	<b>F2</b>	<b>12°25.396'</b>	<b>086°32.338'</b>	<b>1240</b>	<b>616</b>	<b>11:19:2002</b>	<b>7:55 AM</b>
Mo_5_8	F2	12°25.396'	086°32.338'	1240	600	07:12:2003	1:30 PM
Mo_5_9	F2	12°25.396'	086°32.338'	1240	600	07:12:2003	1:35 PM
Mo_5_10	F2	12°25.396'	086°32.338'	1240	600	07:12:2003	1:40 PM
Mo_4_6	F3	12°25.392'	086°32.284'	1231	472	11:17:2002	5:25 PM
Mo_4_7	F3	12°25.392'	086°32.284'	1231	472	11:17:2002	5:30 PM
<b>Mo_4_10</b>	<b>F3</b>	<b>12°25.392'</b>	<b>086°32.284'</b>	<b>1231</b>	<b>475</b>	<b>11:18:2002</b>	<b>8:00 AM</b>
<b>Mo_4_19</b>	<b>F3</b>	<b>12°25.392'</b>	<b>086°32.284'</b>	<b>1231</b>	<b>475</b>	<b>11:18:2002</b>	<b>4:40 PM</b>
<b>Mo_4_22</b>	<b>F3</b>	<b>12°25.392'</b>	<b>086°32.284'</b>	<b>1231</b>	<b>478</b>	<b>11:19:2002</b>	<b>7:00 AM</b>

<sup>a</sup>Samples used for flux estimations are in bold.<sup>b</sup>Local time in Nicaragua is UTC -5h.

volcanic source strength of  $5.6 \times 10^{-6}$  Tg/yr for  $\text{CH}_3\text{Cl}$ ,  $7.2 \times 10^{-7}$  Tg/yr for  $\text{CH}_3\text{Br}$ ,  $1.7 \times 10^{-6}$  Tg/yr for  $\text{CH}_3\text{I}$ ,  $2.7 \times 10^{-8}$  Tg/yr for  $\text{CH}_2\text{Cl}_2$ ,  $2.0 \times 10^{-8}$  Tg/yr for  $\text{CHCl}_3$ , and  $2.7 \times 10^{-9}$  Tg/yr for  $\text{CCl}_4$ . Our estimation of global methyl halide fluxes compare well with data extrapolated from various other subduction zone volcanoes (Kuju, Satsuma Iwojima, Mt. Etna, Vulcano) (Table 6), even though different sampling and calculation methods were used: *Jordan et al.* [2000] took samples with evacuated, empty glass-bottles and utilized literature data for typical fumarolic gas compositions and global  $\text{SO}_2$  fluxes for their flux estimations. *Schwandner et al.* [2004] used adsorption tubes for sampling and estimated fluxes through comparison of their own  $\text{CO}_2$  data with literature data for global  $\text{CO}_2$  fluxes. We believe that our scaling of the results is more realistic, as it is based on a longer-term data record of trace gas and bulk fluid composition in combination with contemporaneously measured  $\text{SO}_2$  fluxes.

[24] The estimated mean global fluxes of the total known nonvolcanic sources for the investigated compounds sum up to 3.0 Tg/yr  $\text{CH}_3\text{Cl}$  [*WMO*, 2003], 0.16 Tg/yr  $\text{CH}_3\text{Br}$  [*WMO*, 2003], 0.30 Tg/yr  $\text{CH}_3\text{I}$  [*Bell et al.*, 2002], 0.84 Tg/yr  $\text{CH}_2\text{Cl}_2$  [*Keene et al.*, 1999], 0.65 Tg/yr  $\text{CHCl}_3$  [*Keene et al.*, 1999], and 0.022 Tg/yr  $\text{CCl}_4$  [*Khalil*, 1999].

Despite the speculative nature of our extrapolation to global volcanic fluxes, the difference of several orders of magnitude between our data and those for anthropogenic fluxes renders our conclusions robust. This further indicates that subduction zone degassing has no significant impact on the global atmospheric budgets of halo(hydro)carbons.

## 6. Conclusions

[25] The similar abundances of halogenated trace gas compounds in fumarolic gas samples from different subduction zone volcanoes [e.g., *Jordan et al.*, 2000; *Schwandner et al.*, 2004] suggest common processes responsible for their formation. Mono-halogenated  $\text{C}_1$  and  $\text{C}_2$  compounds predominate in the fumarolic gas samples from Momotombo while higher chlorinated  $\text{C}_1$  compounds are found at somewhat lower concentrations. This pattern is the likely result of thermally and catalytically activated radical reactions occurring in the gas phase and involving magmatic hydrogen halides and hydrocarbons deriving from thermal decomposition of organic material. Sediment recycling in the Nicaraguan sector of the subduction zone, in combination with the interaction between the magmatic system and marine deposits present at depth in the Nicaraguan Depression, are likely to be responsible for the relatively high

**Table A2.** Halo(hydro)carbon Concentrations and Air Content of Trace Gas Samples<sup>a</sup>

Trace Gas Sample ID	CH <sub>3</sub> Cl, ppbv	CH <sub>3</sub> Br, ppbv	CH <sub>3</sub> I, ppbv	C <sub>2</sub> H <sub>5</sub> Cl, ppbv	C <sub>2</sub> H <sub>5</sub> Br, ppbv	C <sub>2</sub> H <sub>5</sub> I, ppbv	CH <sub>2</sub> Cl <sub>2</sub> , ppbv	CHCl <sub>3</sub> , ppbv	CCl <sub>4</sub> , ppbv	C <sub>2</sub> H <sub>3</sub> Cl, ppbv	Air, <sup>b</sup> mol%
Mo_2_28	5.3	0.66	0.50	b.d.l.	n.q.	b.d.l.	0.31	0.11	0.079	0.19	n.q.
Mo_3_48	4.2	0.39	0.35	0.38	n.q.	b.d.l.	0.28	b.d.l.	0.33	0.13	n.q.
Mo_3_49	7.1	0.41	0.33	0.13	n.q.	n.q.	0.36	0.077	0.34	0.15	n.q.
Mo_4_2	84	2.9	4.9	3.9	n.q.	b.d.l.	1.4	0.35	0.22	0.77	0.0060
Mo_4_3	68	12	12	2.1	0.077	0.21	0.84	0.38	0.22	0.31	0.0068
<b>Mo_4_15</b>	<b>68</b>	<b>5.3</b>	<b>8.4</b>	<b>1.2</b>	<b>0.047</b>	<b>0.18</b>	<b>0.68</b>	<b>0.28</b>	<b>0.078</b>	<b>0.29</b>	<b>0.0045</b>
<b>Mo_4_23</b>	<b>140</b>	<b>23</b>	<b>24</b>	<b>5.4</b>	<b>0.70</b>	<b>1.2</b>	<b>0.73</b>	<b>0.69</b>	<b>0.19</b>	<b>1.1</b>	<b>0.0095</b>
Mo_5_1	98	12	17	0.57	0.066	0.20	0.079	0.075	0.074	0.23	0.026
Mo_5_2	140	67	21	1.2	0.43	0.28	0.14	0.14	0.17	0.78	0.045
Mo_5_3	31	3.6	6.7	0.2	b.d.l.	0.072	0.15	0.079	0.23	0.10	0.033
Mo_4_5	82	18	10	12	2.1	0.99	1.5	0.57	0.33	1.6	0.011
<b>Mo_4_12</b>	<b>38</b>	<b>12</b>	<b>15</b>	<b>2.3</b>	<b>0.30</b>	<b>0.48</b>	<b>0.78</b>	<b>0.43</b>	<b>0.19</b>	<b>n.q.</b>	<b>0.0094</b>
<b>Mo_4_16</b>	<b>160</b>	<b>41</b>	<b>32</b>	<b>3.8</b>	<b>0.52</b>	<b>0.74</b>	<b>0.68</b>	<b>0.24</b>	<b>0.26</b>	<b>0.50</b>	<b>0.013</b>
<b>Mo_4_24a</b>	<b>48</b>	<b>18</b>	<b>8.0</b>	<b>4.7</b>	<b>0.29</b>	<b>0.29</b>	<b>1.7</b>	<b>0.72</b>	<b>0.62</b>	<b>1.5</b>	<b>0.019</b>
Mo_5_8	10	1.7	3.6	0.46	0.065	0.20	0.25	0.20	0.28	0.26	0.035
Mo_5_9	21	2.6	4.3	1.5	0.24	0.52	0.21	0.044	0.17	0.22	0.020
Mo_5_10	18	3.1	4.1	0.89	0.15	0.41	0.11	0.087	0.22	0.16	0.054
Mo_4_6	6300	450	350	690	n.q.	6.1	30	17	n.q.	2.8	0.0094
Mo_4_7	12000	430	380	370	19	25	14	48	0.42	5.9	0.027
<b>Mo_4_10</b>	<b>19000</b>	<b>740</b>	<b>1400</b>	<b>760</b>	<b>68</b>	<b>110</b>	<b>52</b>	<b>25</b>	<b>0.60</b>	<b>9.9</b>	<b>0.012</b>
<b>Mo_4_19</b>	<b>6600</b>	<b>790</b>	<b>1400</b>	<b>300</b>	<b>45</b>	<b>90</b>	<b>15</b>	<b>9.5</b>	<b>n.q.</b>	<b>4.5</b>	<b>0.027</b>
<b>Mo_4_22</b>	<b>1000</b>	<b>120</b>	<b>140</b>	<b>49</b>	<b>10</b>	<b>11</b>	<b>1.2</b>	<b>0.68</b>	<b>0.34</b>	<b>2.3</b>	<b>0.022</b>

<sup>a</sup>Halo(hydro)carbon concentrations are in ppbv; air content is in mol% of bulk sample. Samples used for flux estimations are in bold. Abbreviations: b.d.l., below detection limits; n.q., not quantified.

<sup>b</sup>Based on CFC-12, CFC-113, and CFC-114 measurements in trace gas samples and the headspace gas content of bulk samples [Frische *et al.*, 2006].

bromine and iodine versus chlorine ratios of the halogenated trace gases.

[26] Scaling our halo(hydro)carbon flux estimates for Momotombo volcano to represent hypothetical global emissions suggests that volcanoes are insignificant natural sources of such compounds compared to other natural and anthropogenic sources. We emphasize, however, that volcanoes play a

significant role for atmospheric chemistry through their emission of other chemical compounds (e.g., SO<sub>2</sub>).

## Appendix A

[27] Fumarolic trace gas (Tables A1 and A2) and bulk sample (Table A3) data from Momotombo volcano (Nicaragua).

**Table A3.** Bulk Sample Data Used for Flux Calculations (Table 3) and in Figures 6 and 7<sup>a</sup>

Bulk Sample ID	Fumarole	Sample Latitude, N	Sample Longitude, W	Elevation, m	Temp., °C	Date (mm:dd:yyyy)	Time (hh:mm)	CH <sub>4</sub> , ppbv	C <sub>2</sub> H <sub>6</sub> , ppbv	SO <sub>2</sub> , mmol/mol	Headspace Gas, mmol/mol
Mo_4_10_b	F1	12°25.390'	086°32.321'	1249	760	11:18:2002	9:30 AM	22	61	62	17
Mo_4_50_b	F1	12°25.390'	086°32.321'	1249	760	11:18:2002	3:15 PM	4.9	8.6	23	5.4
Mo_4_43_b	F1	12°25.390'	086°32.321'	1249	760	11:18:2002	3:20 PM	17	25	4.5	7.1
Mo_4_37_b	F1	12°25.390'	086°32.321'	1249	761	11:19:2002	10:30 AM	27	30	30	8.2
Mo_4_49_b	F2	12°25.396'	086°32.338'	1240	615	11:18:2002	10:00 AM	5.4	27	25	2.2
Mo_4_22_b	F2	12°25.396'	086°32.338'	1240	615	11:18:2002	4:10 PM	4.3	15	26	2.8
Mo_4_18_b	F2	12°25.396'	086°32.338'	1240	615	11:18:2002	4:40 PM	0.6	0.7	9.2	1.6
Mo_4_17_b	F2	12°25.396'	086°32.338'	1240	616	11:19:2002	11:30 AM	2.0	9.0	15	2.9
Mo_4_40_b	F3	12°25.392'	086°32.284'	1231	475	11:18:2002	8:20 AM	180	720	27	1.0
Mo_4_52_b	F3	12°25.392'	086°32.284'	1231	475	11:18:2002	5:00 PM	120	630	18	1.0
Mo_4_61_b	F3	12°25.392'	086°32.284'	1231	478	11:19:2002	7:30 AM	41	14	1.7	0.6
Mo_4_41_b	F3	12°25.392'	086°32.284'	1231	478	11:19:2002	8:00 AM	29	7.6	16	0.9

<sup>a</sup>K. Garofalo (unpublished data, 2006).



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