GEOPHYSICAL RESEARCH LETTERS, VOL. 38, L13801, doi:10.1029/2011GL047571, 2011

Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using observed depletions in non-methane hydrocarbons

Angela K. Baker,[1] Armin Rauthe-Schöch,[1] Tanja J. Schuck,[1] Carl A. M. Brenninkmeijer,[1]
Peter F. J. van Velthoven,[2] Adam Wisher,[3] and David E. Oram[3]

Received 28 March 2011; revised 12 May 2011; accepted 16 May 2011; published 2 July 2011.

[1] As part of the effort to understand volcanic plume composition and chemistry during the eruption of the Icelandic volcano Eyjafjallajökull, the CARIBIC atmospheric observatory was deployed for three special science flights aboard a Lufthansa passenger aircraft. Measurements made during these flights included the collection of whole air samples, which were analyzed for non-methane hydrocarbons (NMHCs). Hydrocarbon concentrations in plume samples were found to be reduced to levels below background, with relative depletions characteristic of reaction with chlorine radicals (Cl). Recent observations of halogen oxides in volcanic plumes provide evidence for halogen radical chemistry, but quantitative data for free halogen radical concentrations in volcanic plumes were absent. Here we present the first observation-based calculations of Cl radical concentrations in volcanic plumes, estimated from observed NMHC depletions. Inferred Cl concentrations were between 1.3×10^4 and 6.6×10^4 Cl cm^{-3}. The relationship between NMHC variability and local lifetimes was used to investigate the ratio between OH and Cl within the plume, with [OH]/[Cl] estimated to be ~37. **Citation:** Baker, A. K., A. Rauthe-Schöch, T. J. Schuck, C. A. M. Brenninkmeijer, P. F. J. van Velthoven, A. Wisher, and D. E. Oram (2011), Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using observed depletions in non-methane hydrocarbons, *Geophys. Res. Lett.*, *38*, L13801, doi:10.1029/2011GL047571.

1. Introduction

[2] Under special conditions chlorine radicals (Cl) can significantly influence tropospheric chemistry and compete with hydroxyl radicals (OH) that normally dominate the oxidative cycles of the atmosphere [*Platt and Hönninger*, 2003]. Recent observations of halogen oxides (BrO, ClO, OClO) in volcanic plumes provide evidence that volcanic emissions are potential sources of reactive halogen species [*Bobrowski et al.*, 2003; *Bobrowski et al.*, 2007; *Lee et al.*, 2005]. Rather than being directly emitted, reactive halogen species are thought to form when hydrogen halides (i.e., HCl, HBr) emitted by the volcano mix with ambient air, where they can participate in both heterogeneous and homogeneous reactions [*Aiuppa et al.*, 2007; *Bobrowski et al.*, 2007; *Gerlach*, 2004; *Roberts et al.*, 2009; *von Glasow et al.*, 2009]. Although the exact mechanisms are uncertain, it has been suggested that HBr and HCl in volcanic emissions dissolve into the liquid layer of emitted particles, and that subsequent mixing with ambient air and reaction with OH results in the release of reactive halogen species through mechanisms similar to those describing release of halogens from sea salt and in polar regions [*Aiuppa et al.*, 2007; *Bobrowski et al.*, 2007; *Martin et al.*, 2006]. Detection of chlorine containing salts on the surface of particles emitted by Eyjafjallajökull indicates that the initial conditions for Cl release were present [*Gislason et al.*, 2011]. The presence of halogenated species in volcanic plumes indicates a potential influence on tropospheric chemistry through changes in oxidant budgets and subsequent perturbations in the lifetimes of important compounds, such as ozone and methane [*Bobrowski et al.*, 2007; *von Glasow et al.*, 2009].

[3] The eruption of the Eyjafjallajökull volcano in Iceland between 14 April and 24 May 2010 brought volcanic activity to public attention as airspace closures wreaked havoc on European aviation. The response from the scientific community was considerable and a number of measurement activities to study the volcano were brought into action, with a focus on the concentration and dispersion of volcanic ash [*Flentje et al.*, 2010; *Gasteiger et al.*, 2011; *Schumann et al.*, 2011; *Stohl et al.*, 2011]. Accordingly, Lufthansa Airlines provided for three special research flights of the CARIBIC observatory (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container; www.caribic-atmospheric.com) to examine the plume. These volcanic missions were conducted on flights operating without passengers and in a scientific capacity, with flight routes designed to encounter the Eyjafjallajökull plume. Flights were conducted on 20 April, 16 May and 19 May 2010; the plume was probed most extensively during the May flights, and results from these are discussed here. The CARIBIC observatory is unique from other platforms engaged in Eyjafjallajökull observations as analysis included the collection of air samples, allowing for the measurement of non-methane hydrocarbons (NMHCs), which can be useful diagnostics of halogen chemistry.

[4] Depletions of NMHCs in samples collected within the volcanic plume show evidence of reaction with Cl, which is presumed to be a product of volcanic emissions. Here we used the relationship between NMHC depletions and Cl reaction rate constants to identify Cl as the primary NMHC loss mechanism in the volcanic plume and also to estimate the average Cl concentrations encountered during transit.

---

[1] Atmospheric Chemistry Division, Max Planck Institute for Chemistry, Mainz, Germany.

[2] Royal Netherlands Meteorological Institute, De Bilt, Netherlands.

[3] National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich, UK.

0094-8276/11/2011GL047571

Table 1. Compounds Used for the Analysis and Rates of Reaction With OH (k_{OH}) and Cl (k_{Cl}) at 243K[a]

Compound	Chemical Formula	$k_{OH} \times 10^{12}$cm^3 molec^{-1} s^{-1}	$k_{Cl} \times 10^{12}$cm^3 molec^{-1} s^{-1}
ethane	C_2H_6	0.11	55
propane	C_3H_8	0.68	140
i-butane	i-C_4H_{10}	1.66	151[b]
n-butane	n-C_4H_{10}	1.71	205
i-pentane	i-C_5H_{12}	2.08	220[b]
n-pentane	n-C_5H_{12}	2.85	280[b]
acetylene	C_2H_2	0.49	85
perchloroethylene (PCE)	C_2Cl_4	0.07	32
benzene	C_6H_6	1.05	0.00013[b]

[a] *Atkinson* [1997], *Atkinson et al.* [2006], and *Sokolov et al.* [1998].

[b] Room temperature (296–298K).

We also examined the lifetime-variability relationship of NMHCs in the plume encountered on 19 May to estimate the ratio between Cl and OH.

2. Methods

[5] The CARIBIC container houses 16 instruments to measure atmospheric species, which include real-time observations of ozone (O_3), aerosols, sulfur dioxide (SO_2) and bromine oxide (BrO) [*Brenninkmeijer et al.*, 2007]. Additionally, during each flight 28 air samples were collected and analyzed for a suite of 20 NMHCs using gas chromatography coupled with flame ionization detection (GC-FID) [*Baker et al.*, 2010; *Schuck et al.*, 2009]. In plume samples 8 of the 20 compounds were above their detection limits (1–3 ppt), and these were considered in the analysis presented here (Table 1).

[6] Flight paths and sampling locations for 16 and 19 May are shown in Figure 1. Plume samples were identified by coincident measurement of elevated SO_2 (16 May) [*Heue et al.*, 2011] and aerosols (16 and 19 May) (A. Rauthe-Schöch et al., CARIBIC aircraft measurements of Eyjafjallajökull volcanic plumes in April/May 2010, submitted to *Atmospheric Chemistry and Physics*, 2011), and also backward trajectory analysis and comparison with modeled ash dispersion [*Stohl et al.*, 2011; *van Velthoven*, 2010]. On 16 May, 7 samples captured sections of the volcanic plume over Great Britain and Ireland between 3 and 5 km altitude (Figure 1a). On 19 May, 9 samples were collected within the plume over the Norwegian Sea between 4 and 6 km altitude (Figure 1b). Samples collected at comparable altitudes having backward trajectories originating in the same region which did not encounter the ash plume were used to establish background mixing ratios (n = 3 on 16 May, n = 2 on 19 May).

3. Results and Discussion

[7] For those flight sections intersecting the volcanic plume, NMHCs were depleted relative to background mixing ratios, with the exception of benzene, which exhibited little or no depletion (Figure 2). Normally, reaction with OH is the primary removal process for atmospheric NMHCs, with rates of reaction that typically increase with carbon number. Reaction rates with Cl are not only much faster but also show hydrocarbon specific deviations (Table 1). Unlike the alkanes and acetylene, which react ~100 to 550 times faster with Cl than with OH, the reaction of benzene with Cl is much slower [*Atkinson*, 1997; *Atkinson et al.*, 2006; *Sokolov et al.*, 1998].

Table 2. Reduction in Total Measured NMHCs (ΔNMHC), Estimated Transport Times (Δt), Fit Parameters and Cl Estimates for Samples Collected Within the Eyjafjallajökull Volcanic Plume

Sample	ΔNMHC(%)	Δt(h)	r^2 (k_{OH})	r^2 (k_{Cl})	-Slope([Cl]Δt)	$\langle$[Cl]$\rangle$(Cl cm^{-3})
			16 May Flight			
S1[a]	−1	47.0	NC	NC	-	-
S2	−70	33.9	0.37	0.82	4.3×10^9	3.5×10^4
S3	−19	50.1	0.43	0.52	1.1×10^9	6.2×10^4
S4	−1	52.6	0.71	0.79	1.3×10^9	6.6×10^4
S5	−6	45.7	0.80	0.82	2.2×10^9	1.3×10^4
S6	−15	41.5	0.84	0.88	2.0×10^9	1.3×10^4
S7	−25	36.7	0.77	0.98	3.2×10^9	2.4×10^4
mean(stdev)	20(±24)	44(±7)			$2.3(\pm1.2) \times 10^9$	$3.6(\pm2.4) \times 10^4$
			19 May Flight			
S1	−7	23.3	0.55	0.80	1.3×10^9	1.5×10^4
S2	−8	21.6	0.73	0.88	1.7×10^9	2.2×10^4
S3	−1	20.3	0.64	0.72	1.7×10^9	2.3×10^4
S4	−4	18.5	0.62	0.71	1.5×10^9	2.3×10^4
S5	−6	18.4	0.66	0.78	1.3×10^9	2.0×10^4
S6	−26	18.9	0.70	0.93	4.1×10^9	6.0×10^4
S7	−7	23.4	0.63	0.69	1.7×10^9	2.0×10^4
S8	−19	23.4	0.73	0.98	3.6×10^9	4.3×10^4
S9	−18	21.7	0.81	0.97	2.1×10^9	2.7×10^4
mean(stdev)	11(±8)	21(±2)			$2.1(\pm1.0) \times 10^9$	$2.8(\pm1.4) \times 10^4$

[a] Excluded from calculation of mean slope and $\langle$[Cl]$\rangle$ for the flight. NC indicates no correlation.

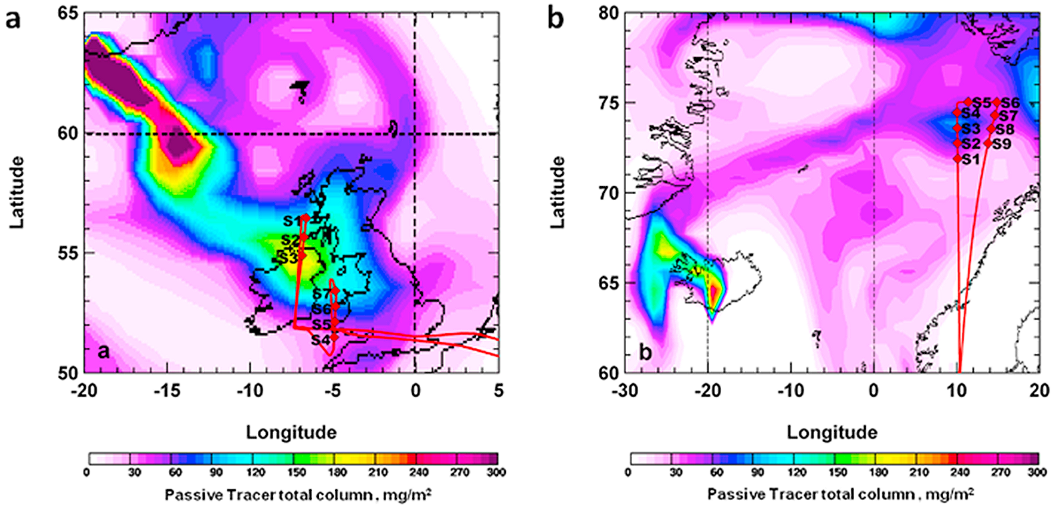

Figure 1. Flight paths (red lines) and sampling locations (diamonds) within the Eyjafjallajökull plume on (a) 16 May and (b) 19 May 2010, superimposed on a FLEXPART model prediction of dispersion of a passive volcanic tracer (total column mass) [*Stohl et al.*, 2011].

The absence of concomitant benzene depletions indicates a non-OH loss process. Although bromine (Br) is also predicted to be present in volcanic plumes, the rates of reaction between Br and the NMHCs considered here are much slower than with either Cl or OH, making it difficult to identify Br chemistry. An exception is acetylene for which reaction with Br comparable to reaction with OH, however, depletions of acetylene were in agreement with those of other NMHCs, and as such provided no evidence of Br contributing to observed NMHC losses.

[8] Depletions of NMHCs attributed to Cl can be related to reaction kinetics by

$$\ln\left([\mathrm{HC}]_{\mathrm{plume}}/[\mathrm{HC}]_{\mathrm{bkgd}}\right) = -\mathrm{k}_{\mathrm{Cl}}\langle[\mathrm{Cl}]\rangle\Delta \mathrm{t} \qquad (1)$$

where $[\mathrm{HC}]_{\mathrm{plume}}$ and $[\mathrm{HC}]_{\mathrm{bkgd}}$ are NMHC plume and background mixing ratios, k_{Cl} is the rate constant for reaction with Cl, and $\langle[\mathrm{Cl}]\rangle$ is the average chlorine concentration encountered over the transport time, Δt [*Jobson et al.*, 1994]. For all but one of the plume samples NMHC depletions (logarithm of the ratios) are closely correlated with the respective reaction rate constants (k_{Cl}), confirming loss through reaction with Cl (Figure 3). In addition to NMHC analysis, samples were also independently analyzed for a number of halocarbons, which included perchloroethylene (C_2Cl_4, PCE). Halocarbons were analyzed using negative ion chemical ionization GC-MS and calibrated on the NOAA 2003 scale [*Worton et al.*, 2008]. Like most of the NMHCs, PCE reacts much faster with Cl than with OH (Table 1), and in the volcanic plume it was indeed depleted in line with Cl kinetics (Figure 3). These depletions cannot be explained without invoking Cl kinetics; the alternative assumption that reaction with OH was the dominant loss process leads to less significant correlations with reaction

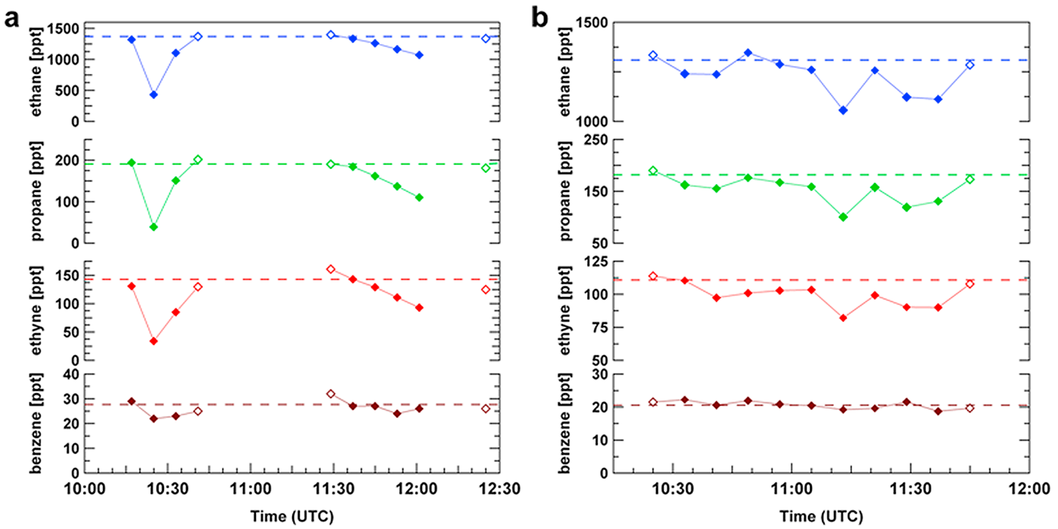

Figure 2. Mixing ratios of selected NMHCs from plume samples (closed symbols) and background samples (open symbols) collected during the flights on (a) 16 May and (b) 19 May. Dashed horizontal lines represent the average background mixing ratio.

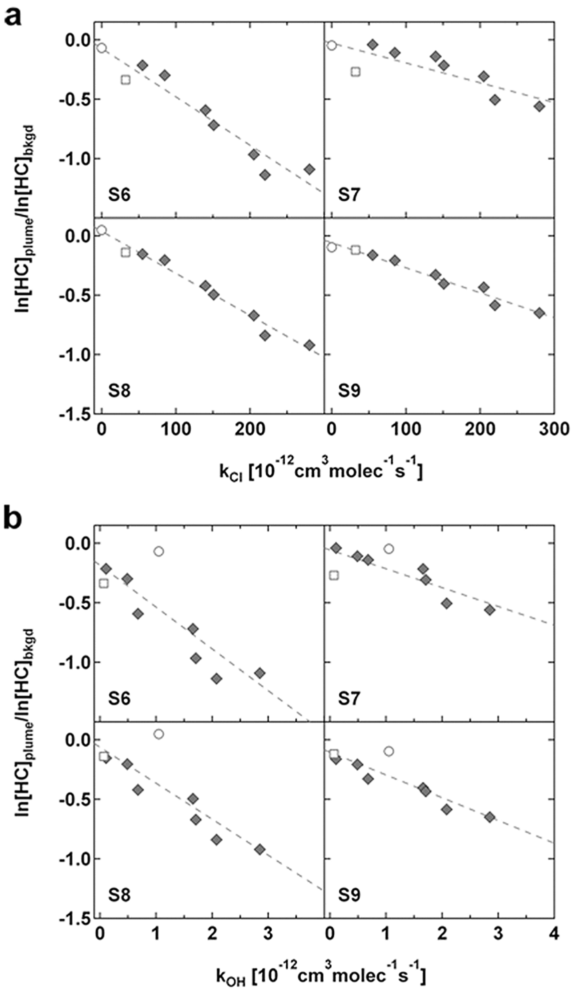

Figure 3. Relationship between NMHC depletions ($\ln([\mathrm{HC}]_{\mathrm{plume}}/[\mathrm{HC}]_{\mathrm{bkgd}})$ and rate of reaction with (a) k_{Cl} and (b) k_{OH} for 4 samples (S6–S9) collected within the volcanic plume on 19 May between 11:25 and 11:45 UTC. Open circles denote benzene, open squares denote PCE. Fit parameters are given in Table 2.

rate constants (k_{OH}) and does not explain the case of benzene, whose depletion does not follow the behavior of the other NMHCs. Moreover, to account for the observed depletions with OH alone, OH concentrations a factor of 10 higher than typical would need to be assumed, which would have caused benzene depletions of at least a factor of 2. Altogether it can be concluded that reaction with Cl was the dominant loss process for NMHCs (and PCE) in the volcanic plume.

[9] As the slopes of the linear fits in Figure 3 represent the product of $\langle[\mathrm{Cl}]\rangle$ and transport time, $\langle[\mathrm{Cl}]\rangle$ can be inferred using Δt. For May 16 (Δt ~34–53h) the range of slopes gives $\langle[\mathrm{Cl}]\rangle$ values of $1.3\text{–}6.6 \times 10^4$ Cl cm^{-3} (mean = $3.6(\pm 2.4) \times 10^4$ Cl cm^{-3}); for 19 May (Δt ~18–24h) inferred $\langle[\mathrm{Cl}]\rangle$ is $1.5\text{–}6.0 \times 10^4$ Cl cm^{-3} (mean = $2.8(\pm 1.4) \times 10^4$ Cl cm^{-3}). While useful for understanding chemical kinetic trends and identifying the primary species contributing to NMHC losses, this method does not provide a complete description of NMHC behavior in the plume, in particular the influence of mixing with background air. However, attributing the slopes to the product of $\langle[\mathrm{Cl}]\rangle$ and Δt allows for comparison between samples and a first-order estimate of $\langle[\mathrm{Cl}]\rangle$.

[10] Of chief concern in understanding tropospheric Cl is the influence on local ozone cycling. In the present case of Eyjafjallajökull, there were no statistically significant depletions or enhancements of ozone during flight sections in the volcanic plume. This is not surprising since, at the inferred Cl concentrations, ozone losses would only be about 2% over a 24h period. In view of the observed high spatial variability of ozone in this region and the potential for in situ production of ozone in the plume from reactions of NMHCs, such minor ozone depletion would not have been detectable.

[11] Another aspect of volcanic plume chemistry of interest is its influence on OH radical production and chemistry. Model predictions vary with differing plume conditions; *Gerlach* [2004] predicts levels of OH "many orders of magnitude above ambient levels" formed in the high temperature initial phase, and work by *von Glasow* [2010] predicts extremely low levels of OH resulting primarily from reaction with SO_2. In situ measurements of volcanic plume OH are rare, however elevated levels of OH and HO_2 were observed ~34h downwind of the Hekla volcano [*Rose et al.*, 2006]. Qualitatively it is already possible using CARIBIC data to rule out extremely high values of OH in the Eyjafjallajökull plume. However, given that oxidation of alkanes by Cl would be a source of OH given sufficient NO_x, it is possible that OH was produced in the plume, although high levels of SO_2 would have countered this production.

[12] To estimate the relationship between Cl and OH in the plume we investigated the relationship between NMHC variability and lifetime. This approach is similar to that of *Jobson et al.* [1999] during polar ozone depletion events and *Pszenny et al.* [2007] in the marine boundary layer. Measurement and modeling studies [*Ehhalt et al.*, 1998; *Jobson et al.*, 1998, 1999] have found that the behavior of a group of relatively short-lived compounds (τ < 2 years) having similar source-sink distributions can be described by

$$S_{\ln X} = A\tau^{b} \qquad (2)$$

In (2), $S_{\ln X}$ is the standard deviation of the natural logarithms of the measured mixing ratios of a given compound, τ is the compound's lifetime, and A and b are fit parameters, which can be qualitatively interpreted as being related to transport time and distance from the source [*Jobson et al.*, 1999]. In the volcanic plume, NMHC lifetimes are presumed to be controlled by reaction with both Cl and OH and can be calculated as

$$\tau = [(k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{Cl}}[\mathrm{Cl}])]^{-1} \qquad (3)$$

Variation of [OH] relative to [Cl] when calculating local lifetime so as to minimize the residuals (maximize the correlation) of the fit to (2) gives an estimate of [OH]/[Cl] in the plume. Typically this approach has been applied to larger data sets to describe the relationship of atmospheric variability with atmospheric lifetime. Here, however, we use the relationship to describe plume variability and its relationship to local lifetime, assuming that the majority of the variability can be attributed to losses occurring within the volcanic plume.

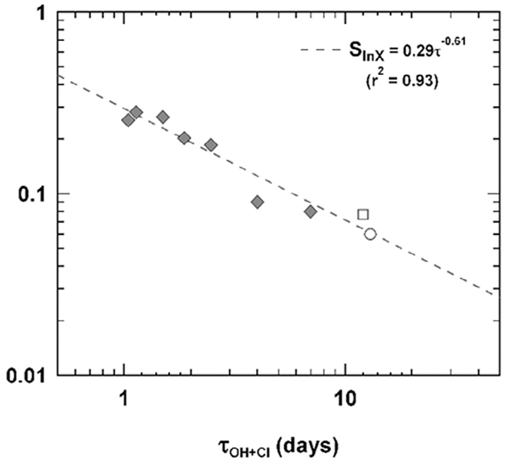

Figure 4. Relationship of plume variability (S_{lnX}) and local lifetime ($\tau_{OH\,+\,Cl}$) for NMHCs measured in samples collected in the volcanic plume during the flight on 19 May, assuming [Cl] of 2.8×10^4 Cl cm^{-3} and an optimized [OH]/[Cl] of 37 (see text). Open circles denote benzene, open squares denote PCE.

[13] As plume samples collected on 19 May present the largest set of samples from within a single plume from Eyjafjallajökull, we chose to examine the lifetime-variability relationships during this flight. We held [Cl] constant at the mean estimated concentration and varied [OH] to obtain the best fit for the data (Figure 4). We note that regardless of concentrations used in the estimate, the same ratio between Cl and OH will give the strongest correlation. Despite the limited number of samples, variability within the plume is found to follow (2) when considering a local lifetime controlled by both Cl and OH, with an optimal ratio of ~37 for [OH]/[Cl]. The relationship is less significant between variability and τ_{Cl} alone, and the relationship breaks down entirely when only considering τ_{OH}.

[14] At the mean [Cl] of 2.8(±1.4) × 10^4 Cl cm^{-3} predicted [OH] is 1.0(±0.5) × 10^6 OH cm^{-3}, which is in reasonable agreement with predictions of ambient OH for the region [*Spivakovsky et al.*, 2000]. This method assumes that all losses (and hence variability) can be accounted for by processes occurring within the volcanic plume, however, some fraction of the variability must have arisen from reaction with OH prior to encountering volcanic emissions and mixing with background air during transport. This is supported by the value obtained for the lifetime dependence exponent b in (2) which can be qualitatively interpreted as describing the influence of sink terms on variability and ranges between 0 and 1, with 0 indicating no chemistry and 1 indicating only chemistry controlling variability [*Ehhalt et al.*, 1998; *Jobson et al.*, 1999]. The value of 0.61 obtained for the volcanic plume data indicates that plume variability was influenced by both chemistry and mixing [*Jobson et al.*, 1998, 1999]. This approach is necessarily a rather general one, but provides a further indication that there was no significant enhancement of OH within the volcanic plume.

4. Conclusions

[15] During flights on 16 and 19 May, 2010 the CARIBIC observatory conducted measurements of atmospheric composition within the Eyjafjallajökull volcanic plume where NMHCs were found to be depleted relative to background in air parcels influenced by volcanic emissions. Behavior of NMHCs in the plume indicated losses dominated by reaction with Cl, and the relative depletions of different NMHCs were used to estimate Cl concentrations of 1.3–6.6 × 10^4 Cl cm^{-3}. Despite being encountered on two different days and having very different transport/processing times results for both flights are in good agreement, with similar Cl estimates. Investigation of NMHC variability within the plume on May 19 showed evidence for local lifetimes controlled by Cl and OH, with [OH]/[Cl] estimated to be ~37. The OH concentration of 1.0(±0.5) × 10^6 OH cm^{-3} inferred from this ratio is a further indication that OH was not enhanced.

[16] In the case of the eruption of Eyjafjallajökull scientific focus was primarily on the volcanic ash and its potential impacts on civil aviation. Unexpectedly, the Eyjafjallajökull eruption provided experimental evidence for chlorine chemistry in the free troposphere, and allowed for the first estimate of chlorine radical concentrations within a volcanic plume.

[17] **Acknowledgments.** We would like to acknowledge Lufthansa for providing for these special research flights, in particular Captain Martin Hoell, Andreas Waibel and Thomas Dauer. A grant from Fraport AG is kindly acknowledged. We would also like to thank Roland von Glasow, Bill Sturges and Jos Lelieveld for useful discussions of the results, and Paul Crutzen for his continuous encouragement of the CARIBIC team.

[18] The Editor thanks an anonymous reviewer for their assistance in evaluating this paper.

References

Aiuppa, A., A. Franco, R. von Glasow, A. G. Allen, W. D'Alessandro, T. A. Mather, D. M. Pyle, and M. Valenza (2007), The tropospheric processing of acidic gases and hydrogen sulphide in volcanic gas plumes as inferred from field and model investigations, *Atmos. Chem. Phys.*, *7*(5), 1441–1450, doi:10.5194/acp-7-1441-2007.

Atkinson, R. (1997), Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, *J. Phys. Chem. Ref. Data*, *26*, 215–290, doi:10.1063/1.556012.

Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, and I. Subcommittee (2006), Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – Gas phase reactions of organic species, *Atmos. Chem. Phys.*, *6*(11), 3625–4055, doi:10.5194/acp-6-3625-2006.

Baker, A. K., F. Slemr, and C. A. M. Brenninkmeijer (2010), Analysis of non-methane hydrocarbons in air samples collected aboard the CARIBIC passenger aircraft, *Atmos. Meas. Tech.*, *3*(1), 311–321, doi:10.5194/amt-3-311-2010.

Bobrowski, N., G. Honninger, B. Galle, and U. Platt (2003), Detection of bromine monoxide in a volcanic plume, *Nature*, *423*(6937), 273–276, doi:10.1038/nature01625.

Bobrowski, N., R. von Glasow, A. Aiuppa, S. Inguaggiato, I. Louban, O. W. Ibrahim, and U. Platt (2007), Reactive halogen chemistry in volcanic plumes, *J. Geophys. Res.*, *112*, D06311, doi:10.1029/2006JD007206.

Brenninkmeijer, C. A. M., et al. (2007), Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system, *Atmos. Chem. Phys.*, *7*(18), 4953–4976, doi:10.5194/acp-7-4953-2007.

Ehhalt, D. H., F. Rohrer, A. Wahner, M. J. Prather, and D. R. Blake (1998), On the use of hydrocarbons for the determination of tropospheric OH concentrations, *J. Geophys. Res.*, *103*(D15), 18,981–18,997, doi:10.1029/98JD01106.

Flentje, H., H. Claude, T. Elste, S. Gilge, U. Köhler, C. Plass-Dülmer, W. Steinbrecht, W. Thomas, A. Werner, and W. Fricke (2010), The Eyjafjallajökull eruption in April 2010—Detection of volcanic plume using in-situ measurements, ozone sondes and lidar-ceilometer profiles, *Atmos. Chem. Phys.*, *10*(20), 10,085–10,092, doi:10.5194/acp-10-10085-2010.

Gasteiger, J., S. Groß, V. Freudenthaler, and M. Wiegner (2011), Volcanic ash from Iceland over Munich: Mass concentration retrieved from ground-based remote sensing measurements, *Atmos. Chem. Phys.*, *11*(5), 2209–2223, doi:10.5194/acp-11-2209-2011.

Gerlach, T. M. (2004), Volcanic sources of tropospheric ozone-depleting trace gases, *Geochem. Geophys. Geosyst.*, *5*, Q09007, doi:10.1029/2004GC000747.

Gislason, S. R., et al. (2011), Characterization of Eyjafjallajökull volcanic ash particles and a protocol for rapid risk assessment, *Proc. Natl. Acad. Sci. U. S. A.*, *108*(18), 7307–7312, doi:10.1073/pnas.1015053108.

Heue, K. P., et al. (2011), SO2 and BrO observation in the plume of the Eyjafjallajökull volcano 2010: CARIBIC and GOME-2 retrievals, *Atmos. Chem. Phys.*, *11*(6), 2973–2989, doi:10.5194/acp-11-2973-2011.

Jobson, B. T., H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper, and R. Leaitch (1994), Measurements of C2-C6 hydrocarbons during the Polar Sunrise1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res.*, *99*(D12), 25,355–25,368, doi:10.1029/94JD01243.

Jobson, B. T., D. D. Parrish, P. Goldan, W. Kuster, F. C. Fehsenfeld, D. R. Blake, N. J. Blake, and H. Niki (1998), Spatial and temporal variability of nonmethane hydrocarbon mixing ratios and their relation to photochemical lifetime, *J. Geophys. Res.*, *103*(D11), 13,557–13,567, doi:10.1029/97JD01715.

Jobson, B. T., S. A. McKeen, D. D. Parrish, F. C. Fehsenfeld, D. R. Blake, A. H. Goldstein, S. M. Schauffler, and J. W. Elkins (1999), Trace gas mixing ratio variability versus lifetime in the troposphere and stratosphere: Observations, *J. Geophys. Res.*, *104*(D13), 16,091–16,113, doi:10.1029/1999JD900126.

Lee, C., Y. J. Kim, H. Tanimoto, N. Bobrowski, U. Platt, T. Mori, K. Yamamoto, and C. S. Hong (2005), High ClO and ozone depletion observed in the plume of Sakurajima volcano, Japan, *Geophys. Res. Lett.*, *32*, L21809, doi:10.1029/2005GL023785.

Platt, U., and G. Hönninger (2003), The role of halogen species in the troposphere, *I*, *52*(2), 325–338, doi:10.1016/S0045-6535(03)00216-9.

Pszenny, A. A. P., E. V. Fischer, R. S. Russo, B. C. Sive, and R. K. Varner (2007), Estimates of Cl atom concentrations and hydrocarbon kinetic reactivity in surface air at Appledore Island, Maine (USA), during International Consortium for Atmospheric Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals, *J. Geophys. Res.*, *112*, D10S13, doi:10.1029/2006JD007725.

Roberts, T. J., C. F. Braban, R. S. Martin, C. Oppenheimer, J. W. Adams, R. A. Cox, R. L. Jones, and P. T. Griffiths (2009), Modelling reactive halogen formation and ozone depletion in volcanic plumes, *Chem. Geol.*, *263*(1–4), 151–163, doi:10.1016/j.chemgeo.2008.11.012.

Rose, W. I., et al. (2006), Atmospheric chemistry of a 33–34 hour old volcanic cloud from Hekla Volcano (Iceland): Insights from direct sampling and the application of chemical box modeling, *J. Geophys. Res.*, *111*, D20206, doi:10.1029/2005JD006872.

Schuck, T. J., C. A. M. Brenninkmeijer, F. Slemr, I. Xueref-Remy, and A. Zahn (2009), Greenhouse gas analysis of air samples collected onboard the CARIBIC passenger aircraft, *Atmos. Meas. Tech.*, *2*(2), 449–464, doi:10.5194/amt-2-449-2009.

Schumann, U., et al. (2011), Airborne observations of the Eyjafjalla volcano ash cloud over Europe during air space closure in April and May 2010, *Atmos. Chem. Phys.*, *11*(5), 2245–2279, doi:10.5194/acp-11-2245-2011.

Sokolov, O., M. D. Hurley, T. J. Wallington, E. W. Kaiser, J. Platz, O. J. Nielsen, F. Berho, M. T. Rayez, and R. Lesclaux (1998), Kinetics and mechanism of the gas-phase reaction of Cl atoms with benzene, *J. Phys. Chem. A*, *102*(52), 10,671–10,681, doi:10.1021/jp9828080.

Spivakovsky, C. M., et al. (2000), Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, *105*(D7), 8931–8980, doi:10.1029/1999JD901006.

Stohl, A., et al. (2011), Determination of time- and height-resolved volcanic ash emissions for quantitative ash dispersion modeling: the 2010 Eyjafjallajökull eruption, *Atmos. Chem. Phys. Discuss.*, *11*(2), 5541–5588, doi:10.5194/acpd-11-5541-2011.

van Velthoven, P. (2010), Meteorological analysis of CARIBIC, R. Neth. Meteorol. Inst., De Bilt. [Available at http://www.knmi.nl/samenw/campaign_support/CARIBIC/.]

von Glasow, R. (2010), Atmospheric chemistry in volcanic plumes, *Proc. Natl. Acad. Sci. U. S. A.*, *107*(15), 6594–6599, doi:10.1073/pnas.0913164107.

von Glasow, R., N. Bobrowski, and C. Kern (2009), The effects of volcanic eruptions on atmospheric chemistry, *Chem. Geol.*, *263*(1–4), 131–142, doi:10.1016/j.chemgeo.2008.08.020.

Worton, D. R., G. P. Mills, D. E. Oram, and W. T. Sturges (2008), Gas chromatography negative ion chemical ionization mass spectrometry: Application to the detection of alkyl nitrates and halocarbons in the atmosphere, *J. Chromatogr. A*, *1201*(1), 112–119, doi:10.1016/j.chroma.2008.06.019.

A. K. Baker, C. A. M. Brenninkmeijer, A. Rauthe-Schöch, and T. J. Schuck, Atmospheric Chemistry Division, Max Planck Institute for Chemistry, Postfach 3060, D-55020 Mainz, Germany. (angela.baker@mpic.de)

D. E. Oram and A. Wisher, National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK.

P. F. J. van Velthoven, Royal Netherlands Meteorological Institute, PO Box 201, NL-3730 AE De Bilt, Netherlands.