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## Volcanically influenced iron and aluminum cloud water deposition to Hawaii

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### Abstract

Fog or cloud water (CW) deposition plays an important role in particle scavenging and the delivery of trace constituents to the Earth's surface. In this study, CW concentrations of total dissolvable iron (Fe) and aluminum (Al) were measured in 60 samples spanning 26 individual CW events throughout 1999 in Hawaii Volcanoes National Park on the island of Hawaii. Al concentrations ranged from 8 to 10,489 nM, with a median of 344 nM while Fe concentrations ranged from < 1 to 6419 nM with a median of 32 nM. CW deposition fluxes for Fe and Al ranged from 0.15–0.52 mmol Fe m<sup>-2</sup> yr<sup>-1</sup> and 0.62–1.35 mmol Al m<sup>-2</sup> yr<sup>-1</sup>, depending on the estimation method used. The large range in concentrations is higher than expected for a relatively pristine ecosystem. It appears that this inconsistency is due to emissions from the currently active nearby volcano, Kilauea. Categorizing CW events into volcanically versus less or non-volcanically impacted events suggests that although volcanically impacted events only accounted for 12% of fog water deposition, Kilauea Volcano was responsible at least 42% of the measured CW Al deposition and 61% of the CW Fe deposition measured for 1999.

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### 1. Introduction

Atmospheric deposition is an important source of nutrients to tropical ecosystems (e.g. Chadwick et al., 1999). Until recently, most deposition studies focused solely on determining the magnitude of precipitation and dry deposition. Research over the past decade

indicates that in some locations a third important deposition pathway operates via the impaction of wind driven clouds on surrounding vegetation (Lovett et al., 1982; Weathers and Likens, 1997; Miller and Friedland, 1999). Often referred to as occult or fog deposition, cloud water (CW) deposition may be an important source of water to many coastal and montane ecosystems (Vogelmann, 1973; Azvedo and Morgan, 1974; Lovett, 1984; Dawson, 1998; Miller and Friedland, 1999; Pounds et al., 1999; Foster, 2001; Larrain et al., 2002; Nadkarni and Solano, 2002; Carrillo (néé Heath) and Huebert, 2002). Several studies have also indicated that trace element and nutrient concentrations are generally much higher in CW than in rain for a given site and that CW fluxes may provide a significant deposition pathway (Waldman et al., 1982; Dollard et al., 1983; Weathers et al., 1986, 1988, 2000; Collett et al., 1993, 1999; Khwaja et al., 1995; Heath and

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Huebert, 1999; Ghauri et al., 2001). Thus, CW may play a direct role in supplying nutrients and trace elements to potentially limited ecosystems.

The trace metal and nutrient chemistry of CW, particularly in relatively pristine regions, remains poorly characterized (Lovett et al., 1982; Weathers et al., 1988, 2000; Lovett and Kinsman, 1990; Bergin et al., 1994; Khwaja et al., 1995; Heath and Huebert, 1999; Plessow et al., 2001; Watanabe et al., 2001). Most studies have focused on industrialized areas, where anthropogenic inputs of trace elements are high (Waldman et al., 1982; Dollard et al., 1983; Munger et al., 1983; Jacob et al., 1985; Weathers et al., 1986; Collett et al., 1999; Bridges et al., 2002; Fisak et al., 2002; Herckes et al., 2002a,b; and many others). As a result, it has been difficult to assess the role of cloud water deposition in the biogeochemical cycling of nutrients and trace metals, particularly iron (Fe) and aluminum (Al), in terrestrial ecosystems.

The Hawaiian Island Chain is an almost ideal site for studying natural cloud water deposition due to its remote location in the middle of the North Pacific Ocean. Furthermore, these islands provide a unique ecosystem for studying the role of specific nutrient supply processes and their potential impact on forest ecology over timescales ranging from 300 to 4.1 million years (Chadwick et al., 1999). Recent studies by Heath and Huebert (1999) and Carrillo et al. (2002b) suggest that volcanic activity contributes substantially to nutrient deposition on the island of Hawaii. It now appears that volcanic activity may also play a role in trace metal CW deposition in this area. Sansone et al. (2002) examined the composition of the aerosol plume created by the interaction of hot lava from Kilauea Volcano (the currently active Volcano on the island of Hawaii) with seawater at the point where the lava enters the ocean. In that study, they found extremely high concentrations of Fe and Al in the aerosol plume which corresponded to local deposition rates that may be as much as 16,000 times the natural background deposition rates. During 1999, we collected 60 individual samples over the course of 26 cloud events in Hawaii Volcanoes National Park on the island of Hawaii in order to determine the impact that volcanic activity may have on the composition of CW Fe and Al concentrations and fluxes.

## 2. Methods

### 2.1. Sample collection

Throughout 1999, CW samples were collected near Thurston Lava Tube in Hawaii Volcanoes National Park on the island of Hawaii (19°15'N, 155°15'W). The sample site is approximately 1190 m above sea level and is well removed from vehicular traffic. Because the site is

on the windward side of the island, it frequently receives orographic rain (2–3 m yr<sup>-1</sup>) and fog (Giambelluca and Schroeder, 1998). Several chemical and meteorological measurements (e.g. rainfall, dry deposition, wind direction, etc.) have been made semi-continuously at this site since 1993 (Heath and Huebert, 1999, Carrillo et al., 2002a,b). CW samples were collected in the middle of a 50 m × 30 m clearing (approximately 15 m from the nearest canopy edge) on top of a 14 m high tower using an active string (0.05 cm diameter FEP Teflon) CASC CW collector (Daube et al., 1987). The tower stands 1 m above the nearby forest canopy that is comprised of *Meterosideros polymorpha* (Ohia) and *Cibotium glaucum* (Tree fern) and *Hedychium gardnerianum* (Ginger). The collector opening was downward facing to minimize contamination by precipitation and remained sealed between CW events.

The CW collector uses a fan to pull cloudy air through an opening where the droplets impact on teflon strings. The water was collected in soap and distilled water cleaned Teflon or HDPE bottles, then transferred to clean room bags for storage. We sampled CW only when liquid water content (LWC) determined by a Gerber Scientific Particle Volume Monitor exceeded 0.02 g m<sup>-3</sup>. Foggy days were further classified into separate events if more than 2 h had elapsed with no measurable rain or throughfall during the sample collection period. When CW events were of sufficient duration, sequential samples were collected at approximately 4 hr intervals. Prior to sample collection, greater than 1 l of deionized water was sprayed through the CW collector and the last 30 ml of deionized water rinse was saved as the field blank. Immediately after collection, chloroform was added to all samples and blanks (0.5% v/v final solution) and the samples were refrigerated.

### 2.2. Sample analyses

Immediately prior to the Fe and Al analyses, CW samples were acidified with 1 ml 6 N sub-boiled HCl<sup>-1</sup> and, when necessary, diluted with 18 MΩ water. Total dissolvable Fe and Al concentrations were determined using direct flow injection techniques based on the methods of Measures et al. (1995) and Resing and Measures (1994). Pre-concentration flow injection methods were modified for direct injection by replacing the pre-concentration column with a 185 μl sample loop and using an acidified (1 ml 6 N sub-boiled HCl<sup>-1</sup>) 18 MΩ water carrier rather than the acidified seawater carrier used in the above methods.

Total dissolvable Fe concentrations were determined by spectrophotometric detection of dimethyl-*p*-phenylenediamine dihydrochloride (DPD)-oxidized by Fe (III). The direct injection methodology had a typical precision of 2.0% at 0.7 nM Fe and a detection limit of 0.049 nM Fe. Total dissolvable Al was determined by

spectrofluorometric detection of the fluorescent Al-lumogallion chelate with a precision of 8% at 1.7 nM and detection limit of 0.93 nM. Each sample was determined at least in duplicate and the standard deviation of these determinations is reported. Standards were made by addition of known amounts of a commercial Fe and Al standard (Fisher Chemical) to acidified 18 M $\Omega$  water. Standard curves were run approximately every 3 h or approximately every 20 samples.

All CW samples were also analyzed for the inorganic ions NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> using a Dionex 300 series ion chromatograph. Anions were analyzed on an OmniPac, Pax-500 column with a 25 mM H<sub>2</sub>SO<sub>4</sub> autoregenerant and a 1–35 mM NaOH/5% methanol eluant solution. Cations were analyzed on an IonPac CS-12 column with a 20 mM HCl/2 mM MSA eluant and a self-regenerating cation suppressor. Non-sea-salt (NSS) ions were determined assuming that all of the measured Na<sup>+</sup> is of marine origin. Much of this data is presented in a related paper by Carrillo et al. (2002a).

### 2.3. Cloud water deposition

CW deposition rates were determined using the mass balance method described by Carrillo and Huebert (2002) in which the water inputs, rain (R) and CW, are balanced by removal via throughfall (TF), stemflow (SF), canopy storage (CS), and evaporation (E). R, TF and SF were measured directly, CS was determined using the method described by Juvik and Nullet (1993) and E was calculated using the Penman–Monteith equation for a wet canopy (Monteith, 1965). CW input was then calculated by difference (Juvik and Nullet, 1993). R was measured on top of the tower using a Texas Instruments TE-525 tipping bucket rain gauge (0.254 mm per tip). TF measurements were made at a forest site located approximately 1.5 km away (but at the same elevation) using four, 6.4 m sections of 2.54 cm aluminum angle. Collection troughs were created by arranging the angle sections into an X shape approximately 1–2 m high. All TF collected in the trough was drained into one of two TE-525 rain gauges. Each gauge measured the TF from two troughs and tipped with a water input of 0.0120 mm. The troughs and tipping bucket gauges were cleared of debris weekly. SF measurements were also made at the forest site. Collectors were made of sheet metal (steel or aluminum) that was wrapped around individual tree trunks in order to create tree collection collars. Each collar continuously drained into a collection container. Seams were sealed to prevent leaks and checked weekly. SF was measured on four Ohia trees, two large tree ferns, and two small tree ferns as these are the dominant species at this site

(Vitousek et al., 1995). Once a week, the volume of water collected was recorded.

We determined a CS value based on the maximum CS amount (CS<sub>max</sub> is the largest amount of water that the dry forest can hold) for each event. CS<sub>max</sub> was estimated by analyzing events with rain but no fog, or very thin fog, following the methodology described in detail by Juvik and Nullet (1993). We calculated aerodynamic resistance using the methodology described by Hicks et al. (1985), where aerodynamic resistance is related to the wind speed and the standard deviation of the wind direction. E was then estimated for every hour of a fog event for which sufficient data was available and a mean hourly value calculated. For all events with insufficient data, the hourly mean E rate was applied.

### 3. Results

During 1999, fog was present for approximately 20% of the year. There were 592 CW events (LWC > 0.02 g m<sup>-3</sup>) that lasted an average of 5.7 h over the 338 d monitored. Of those events, only 250 (lasting an average of 17 h) were sufficiently foggy that water could be collected. In 1999, fog input was determined to be 204 cm and precipitation 357 cm. Both amounts are higher than the mean fog input of 165 cm (std. dev. = 40 cm) and a precipitation input of 248 cm (std. dev. = 86 cm) determined from 1995 to 2000 (Carrillo and Huebert, 2002). While it may be desirable to measure the elemental concentration of every CW event throughout the year, it was not possible given the labor intensive sampling procedures necessary for CW collection and the high fog frequency at this site. Of the 47 CW events, for which samples were collected for fog chemistry, only 26 events (60 samples) were measured for Fe and Al due to sample volume constraints. Thus, these measurements reflect CW events that had higher LWC and/or were longer in duration.

For almost every event sampled, we obtained a field blank. Field blank concentrations ranged from 5–169 nM Al and 2–86 nM Fe with median concentrations of 49 nM Al and 11 nM Fe (Table 1). There was no correlation between acidity and blank concentration or between sample and blank concentration. Field blank collections were not originally optimized for Fe and Al analysis. Thus, it was unclear whether blank concentrations for each event should be subtracted only from the first sample collected during that event (as done with the base cation and anion measurements, Heath and Huebert, 1999; Carrillo et al., 2002a,b) or from all the samples measured within that event. Therefore, field blanks were not subtracted from the sample concentrations presented here. This does not change any conclusions drawn from these results although, as discussed

Table 1  
Al and Fe CW concentrations (nM) and fluxes ( $\text{mmol m}^{-2}\text{yr}^{-1}$ )

	Al	Fe
All sample blanks		
Range	5–168	2–86
Median $\pm$ std. dev.	49 $\pm$ 50	11 $\pm$ 18
All samples		
Median $\pm$ std. dev.	344 $\pm$ 1708	32 $\pm$ 885
Flux		
Estimated by volume	1.35	0.52
Estimated by median conc.	0.62	0.15
Volcanic samples		
Median $\pm$ std. dev.	913 $\pm$ 3324	209 $\pm$ 1791
Flux		
Estimated by volume	N/A	N/A
Estimated by median conc.	1.86	0.42
Non-volcanic samples		
Median $\pm$ std. dev.	211 $\pm$ 790	24 $\pm$ 275
Flux		
Estimated by volume	1.23	0.32
Estimated by median conc.	0.43	0.05

below, the calculated CW depositions will represent slight overestimates for this area.

Sample concentrations ranged from 8 to 10,489 nM Al and from < 1 to 6419 nM Fe (Table 2). Median concentrations were 344 nM Al and 32 nM Fe (Table 1). The total annual CW flux of Fe and Al was estimated using two different methods. The first method simply multiplies the median concentration obtained for all events by the total CW deposition for the year. In the second method, the CW flux was determined by summing the volume weighted average concentration for each measured event by that event water flux and then scaling this value to the total annual CW deposition measured. These two different estimates result in fluxes that differ by more than 50% (Table 1). We believe that the estimate based on median concentrations is an underestimate as a small number of high concentration events may result in substantial deposition. The mean flux of Fe and Al via CW deposition was  $0.33 \pm 0.27 \text{ mmol Fe m}^{-2}\text{yr}^{-1}$  and  $0.98 \pm 0.51 \text{ mmol Al m}^{-2}\text{yr}^{-1}$  (Table 1).

#### 4. Discussion

The CW deposition fluxes ranged from 0.62 to  $1.35 \text{ mmol Al m}^{-2}\text{yr}^{-1}$  and  $0.15\text{--}0.52 \text{ mmol Fe m}^{-2}\text{yr}^{-1}$ , depending on the estimation method used. This large difference is due in part to the fact that CW concentrations varied by several orders of magnitude both within and between CW events. There are few measurements of

Al and Fe concentrations in CW and even less that document the CW fluxes of these constituents. Nonetheless, our measurements of Hawaii CW Fe and Al fluxes are similar to those measured at other high elevation sites in England ( $0.07 \text{ mmol Fe m}^{-2}\text{yr}^{-1}$ , Dollard et al., 1983), France ( $0.233 \text{ mmol Al m}^{-2}\text{yr}^{-1}$  and  $0.1 \text{ mmol Fe m}^{-2}\text{yr}^{-1}$ , Herckes et al., 2002a), and Germany ( $0.99\text{--}3.42 \text{ mmol Al m}^{-2}\text{yr}^{-1}$ , Wrzesinsky and Klemm, 2000). What is surprising about this comparison, however, is that the Hawaii CW deposition numbers fall towards the higher deposition values of the comparison sites (e.g. Germany), which are significantly impacted by anthropogenic sources.

Median CW concentrations were 344 nM Al and 32 nM Fe. These median concentrations are among the lowest concentrations ever measured in CW (e.g. Munger et al., 1983; Behra and Sigg, 1990; Jickells et al., 1992; Erel et al., 1993; Khwaja et al., 1995; Sedlak et al., 1997; Collett et al., 1999; Plessow et al., 2001; Watanabe et al., 2001; Cini et al., 2002; Herckes et al., 2002b). In fact, Hawaii Al and Fe CW concentrations are similar to the total Al and Fe concentrations found in rain in the North Pacific (Enwetok Atoll, Al  $\sim 80 \text{ nM}$  and Fe  $\sim 20 \text{ nM}$ , Arimoto et al., 1985). While median Al and Fe CW concentrations are low, the range in concentrations measured within and between events is substantial: 8–10,489 nM Al and <1–6,419 nM Fe. These higher CW concentration events have concentrations similar in magnitude to those that have been measured in heavily anthropogenically impacted sites (Munger et al., 1983; Wrzesinsky and Klemm, 2000; Plessow et al., 2001; Cini et al., 2002; Herckes et al., 2002b). In addition, these studies found clear correlations between acidic CW and elevated trace metal concentrations, similar to the relationship found in this study (Fig. 1). However, the Hawaiian Islands, and this site in particular, are far removed from significant industrial influences. Therefore, we suggest an alternate source of high CW Fe and Al concentrations in our sampling area, the currently active Kilauea Volcano.

The latest eruption period of Kilauea volcano has been ongoing since 1983 at Pu'u 'O'o vent, approximately 15 km east of Kilauea Caldera and 10 km east of our sampling site. In addition to the gases vented at Pu'u 'O'o, lava tubes and surface lava flows link this crater to the ocean, where lava has been intermittently pouring into the sea, forming a large aerosol cloud. This aerosol plume was recently analyzed by Sansone et al. (2002) and was found to have Fe and Al concentrations of  $\sim 250 \mu\text{M}$ , 100–1000 times higher than the CW concentrations determined in this study. Direct measurements of volcanic gases, particles, and sublimates from Kilauea Volcano have also found substantial enrichments of Fe and Al (Naughton et al., 1974; Crowe et al., 1987).

We can make a link between elevated Fe and Al concentrations in CW and volcanic activity using back

Table 2

Average Al and Fe concentrations measured in individual CW events during 1999 at Volcanoes National Park, where no standard deviation is reported, only a single determination was possible

Sample (Year Day)	pH	NSS SO <sub>4</sub> <sup>2-</sup> (μM)	F <sup>-</sup> (μM)	Al (nM)	±Std. dev.	Fe (nM)	±Std. dev.
24C	4.49	8	1.34	415	7.5	43	0.9
24D	4.5	13	1.02	226	1.1	18	0.3
24E	4.3	27	0.95	22	0.2	18	0.2
25B	4.96	4	0.74	164	21.3	28	0.9
25C	4.82	5	0.37	326	0.3	11	0.4
25E	4.54	8	0.35	66	3.6	38	0.7
32B		6	0.29	117	9.8	46	1.2
32C		39	0.48	427	17.1	181	4.3
32D		47	0.61	399	0.8	112	0.2
42A		242	11.66	1557	9.3	606	2.4
42B		173	11.86	693	3.5	168	0.3
44A		112	4.87	1744	8.7	918	3.7
44B	4.13	32	3.08	482	16.4	126	1.3
44C	3.9	46	3.16	709	34.7	134	0.1
46A	3.42	122	14.78	847	22.0	246	1.5
46B		169	8.70	926	5.6	128	0.1
46C		138	10.84	486	5.3	121	0.7
87B		93	0.61	1339	1.3	63	3.3
87C		38	0.50	519	8.3	21	
87D		18	0.46	236	2.4	21	1.1
87E		15	0.39	174	38.3	14	0.4
87F		41	0.54	878	42.1	247	4.0
87G		35	0.55	485	35.4	102	0.1
87H		55	0.41	4959	5.0	1491	1.5
121A	2.66	1459	191.94	10489	115.4	6419	32.1
121B	2.79	1017	59.41	8931	35.7		
122A		1	7.86	913	2.7	100	2.5
122C	3.8	27	12.01	787	3.9	26	0.1
122E	3.52	47	6.20	602	22.9	267	3.2
123B	3.46	176	4.85			38	0.7
124A		1883	38.69	6499	78.0	3257	6.5
124B	2.72	1160	31.45	2875	2.9	1282	3.8
124C	2.87	542	19.89	988		362	26.1
216A	3.75	24	2.00	7	0.01	0.3	0.1
224A		15	1.51	277	8.9	32	0.03
224B	4.01	29	1.16	185	2.6	64	2.0
224D	4.19	11	1.51	105	5.6	4	0.1
224E		19	1.26	81	4.1	23	2.5
228B	4.82	1	0.76	49		2	
228C	4.4	8	0.57	8	0.4	3	0.1
228D		39	0.61	160	0.2	13	
238C	4.06	18	0.42	75	0.7	5	0.01
243B	3.59	34	0.45	19		32	1.8
279A	4.48			432	3.9	58	0.3
279C	4.26	20	0.92	181	2.0	13	0.2
281A	3.47	79	1.12	442	24.3	72	1.5
294C	3.91	15	3.71	197	10.0	6	
294D	3.95	8	2.33	168		12	
294E	3.5	34	2.03	224	6.0	13	2.2
298C	4.58	17	1.09	157	0.2	7	0.02
298D	4	98	0.70	575	74.8	18	0.5
308C	3.74	21	2.90	132	4.5	7	0.6
309B	3.84	40	2.34	496	15.4	146	1.9
309D		50	2.25	1030	7.2	332	2.0

Table 2 (continued)

Sample (Year Day)	pH	NSS $\text{SO}_4^{2-}$ ( $\mu\text{M}$ )	$\text{F}^-$ ( $\mu\text{M}$ )	Al (nM)	$\pm$ Std. dev.	Fe (nM)	$\pm$ Std. dev.
318B		12	1.49	1732	15.6	860	42.1
345B	3.21	126	17.18	504	29.2	173	0.2
345C	3.43	39	3.39	184	7.2	27	2.7
345D	2.91	99	11.27	201	20.1	66	0.7
348A	3.37	128	5.14	597	18.5	150	0.2
351A	4.46	6	3.90	73	0.4	4	0.3
351B	4.58	5	4.13	139	1.4	7	0.2

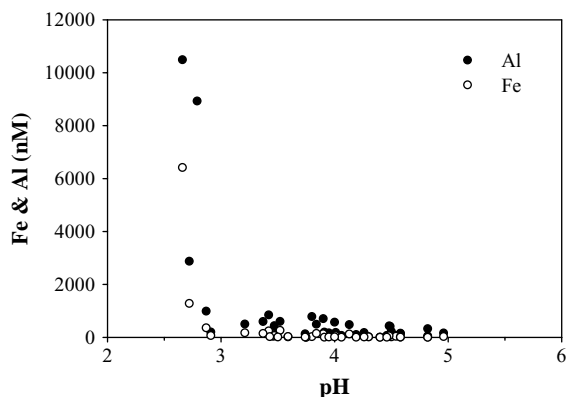


Fig. 1. Al (dark circles) and Fe (open circles) versus pH in individual CW samples collected at Volcano National Park.

trajectory analyses of several samples measured during the week of 1<sup>st</sup>–4<sup>th</sup> May, 1999 (CW 12,199–12,499). Back trajectories of air masses sampled on 1<sup>st</sup> and 4<sup>th</sup> May clearly indicate that they had passed directly over the Pu'u 'O'o vent, whereas air masses sampled on 2 and 3rd May did not (Carrillo et al., 2002b). Comparison of data from these 4 d shows a factor of 10 increase in Fe and Al CW concentrations in the Pu'u 'O'o affected samples along with a factor of 10–100 increase in NSS  $\text{SO}_4^{2-}$ , a factor of 10 increase in  $\text{F}^-$ , and a large decrease in pH from  $\sim 3.7$ – $\sim 2.7$  (Table 2). A further indication of a volcanic influence in our elevated CW Fe and Al samples is apparent from the close relationship found between  $\text{F}^-$  and NSS  $\text{SO}_4^{2-}$ , indexes of volcanic activity (Bluth et al., 1993; De Angelis and Legrand, 1994; Allen et al., 2000), and Fe and Al concentrations (e.g. Fig. 2).

A third indication of potential volcanic influence is the molar Al/Fe ratio. The molar Al/Fe ratio determined in aerosol samples at the Mauna Loa Observatory (3.4 km above sea level) which is also located on the island of Hawaii is  $\sim 3.5$  (Perry et al., 1999). During periods when Mauna Loa samples contain greater quantities of anthropogenically impacted aerosols from Asia (March–May), this ratio decreases to  $\sim 3.0$ . At Eniwetok Atoll (closest available data) the Al/Fe molar ratio measured in precipitation is  $\sim 4.4$  (Arimoto et al.,

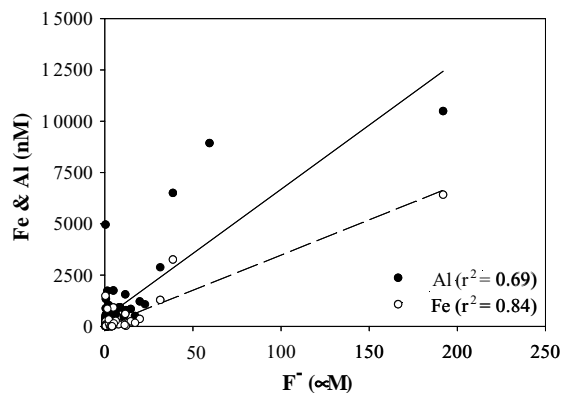


Fig. 2.  $\text{F}^-$  versus Al (dark circles) and Fe (open circles) concentrations in individual CW samples collected at Volcanoes National Park. Linear regression (solid line is for Al and dashed line is for Fe) for Al has an  $r^2 = 0.69$  and Fe has an  $r^2 = 0.84$ . A similar relationship is found between NSS  $\text{SO}_4^{2-}$  and Al and Fe (both have an  $r^2 = 0.68$ ).

1985), while the molar Al/Fe ratio measured in sea level aerosols is 3.3 (based on dry season, April–May, when maximum fluxes occur, Duce et al., 1983).

In this study, the CW Al/Fe ratios varied widely with ratios  $> 10$  occurring when Fe concentrations decreased below  $\sim 30$  nM Fe (Fig. 3). We believe that much of the ratio variability below 30 nM Fe is due to blank issues (median blank = 11 nM Fe) as none of our measurements have been 'blank' corrected. Similarly high molar Al/Fe ratios occur at Al concentrations  $< 900$  nM Al, 20 times the median Al blank of 49 nM Al. As a result, any blank correction below 30 nM Fe results in large ratio errors. Removing those samples with Fe concentrations  $< 30$  nM, we determine an average molar Al/Fe ratio of 4.3 (this ratio drops to 3.8 if we further remove one high ratio event, Al/Fe = 21, CW08799b), similar to that measured for aerosols and precipitation in the North Pacific. However, closer examination reveals that as Fe and Al concentrations increase, the molar ratio of Al/Fe decreases below 3 (Fig. 3), and this is reflected in the volume weighted average Al/Fe molar ratio of 2.2. While this is lower than that found for aerosols and

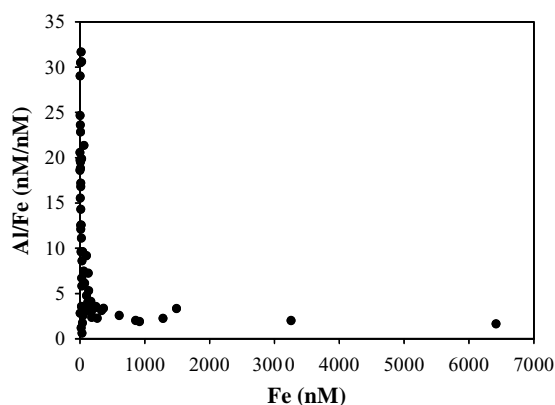


Fig. 3. Molar Al/Fe ratios versus Fe concentrations (nM) in individual CW samples collected at Volcanoes National Park.

precipitation, our volume weighted CW Al/Fe ratio is similar to the Al/Fe ratio of 1.8 determined by DeCarlo and Spencer (1995) for Hawaiian basalts, detrital sediments, and their weathering products. In addition, the molar Al/Fe ratio measured within the aerosol cloud produced at the lava ocean entry point is 1.2 (Sansone et al., 2002). Given the low Al/Fe ratios found in CW, it appears that other sources of Al and Fe dominate the CW flux when Fe and Al concentrations are high.

As noted earlier, the lack of major industrial centers on the island of Hawaii minimizes local anthropogenic influences (e.g. Carrillo and Huebert, 2002). However, long-range transport of anthropogenically influenced air masses, particularly from Asia, have been well documented at Mauna Loa, Enewetok, and at Hawaii Volcanoes National Park. These effects are seasonal and are not sufficient to explain the high variability in concentrations documented in this study (Duce et al., 1983; Perry et al., 1999; Carrillo et al., 2002a,b).

We can make a minimum estimate of the volcanic influence on Fe and Al deposition at our study site by distinguishing between volcanically and less or non-volcanically impacted events. We consider this to be a minimum estimate as it is possible that the Kilauea Volcano is always influencing Al and Fe CW deposition at our site. We identified volcanically influenced CW events using three criteria: visible volcanic influence, wind direction, and CW  $F^-$  concentrations. During this study, there were a number of periods when the sampling site was enveloped in a volcanic haze or “vog” (Sutton and Elias, 1993). Vog formation arises from the conversion of  $SO_2$  degassed from the eruption site to  $SO_4^{2-}$  aerosols. It is easily detectable by the sulfuric smell, eye and skin irritation, and a decrease in visibility to sometimes less than 10 m. The presence or absence of vog was subjectively noted during each CW event. Wind direction and speed were continuously

monitored at our sampling site. During periods of reduced trade wind activity, winds often blew directly from the currently active Pu’u ’O’o vent over our sampling area and we considered those samples to have been potentially influenced by volcanic activity as well.

As stated earlier, there is a clear relationship between CW  $F^-$  and high CW Al and Fe concentrations at our site.  $F^-$  is produced from both coal burning and volcanic activity (e.g. Symonds et al., 1988; De Angelis and Legrand, 1994) and while the Hawaiian Islands are far removed from anthropogenic sources, there may be a background level of  $F^-$  deposition that is associated with both natural and anthropogenic sources from Asia (e.g. Wilkening et al., 2000). Although limited, CW analyses of  $F^-$  in a relatively unpolluted regions ranges from 36 to 84  $\mu M$   $F^-$  (Jiries, 2001; Fisak et al., 2002). The  $F^-$  concentrations measured in this study, however, only had a median concentration of 1.7  $\mu M$   $F^-$  and ranged from < 0.5 to 191.4  $\mu M$   $F^-$  (Table 2). As a result, we chose a 5  $\mu M$   $F^-$  threshold that included most of the samples that we had subjectively identified earlier as having been influenced by volcanic activity. Out of the 26 events measured, 7 were identified as having a volcanic influence.

Volcanically influenced CW samples had median  $F^-$ , Al, and Fe sample concentrations of 11.4  $\mu M$   $F^-$ , 913 nM Al, and 209 nM Fe. In contrast, non-volcanically influenced CW samples had median concentrations that were significantly lower, 1  $\mu M$   $F^-$ , 211 nM Al, and 24 nM Fe (*t*-test  $p_{Al} = 0.0001$ ,  $p_{Fe} = 0.001$ ). We used a volume weighted average concentration to determine the Fe and Al flux from every measured event. Although volcanically impacted events accounted for only 43 mm of the total fog water deposition (12% of the events in which Fe and Al concentrations were measured), they accounted for 42% of the measured CW Al deposition (e.g. 135  $\mu mol$   $Al m^{-2}$  vs. a total of 319  $\mu mol$   $Al m^{-2}$ ) and 61% of the CW Fe deposition (e.g. 75  $\mu mol$   $Fe m^{-2}$  vs. a total of 124  $\mu mol$   $Fe m^{-2}$ ). Furthermore, the average ratio of Al/Fe in volcanic versus non-volcanic events was 1.9 versus 3.3. It is important to note that the higher Al/Fe ratios determined during non-volcanic events are closer to the ratio we would expect from atmospheric deposition of dust from non-local sources in the North Pacific (e.g. Duce et al., 1983; Arimoto et al., 1985; Perry et al., 1999). Again, we acknowledge that this is a minimum estimate of the volcanic influence at our site as our criteria may have missed more subtle volcanically impacted events.

We can determine the non-volcanic CW Fe and Al flux to Volcanoes National Park using the two estimation methods described previously. Using the volume weighted method, CW Al and Fe deposition decreases by 11% and 39%, respectively, to 1.23  $mmol$   $Al m^{-2} yr^{-1}$  and 0.32  $mmol$   $Fe m^{-2} yr^{-1}$ . Using non-volcanic median CW concentrations, however, decreases

the CW Al and Fe deposition flux by 31% and 67%, respectively, to  $0.43 \text{ mmol Al m}^{-2} \text{ yr}^{-1}$  and  $0.05 \text{ mmol Fe m}^{-2} \text{ yr}^{-1}$ .

We can determine the relative importance of CW Fe and Al deposition to the Hawaiian Islands by comparing it to that delivered via dust. Using an average mineral aerosol deposition rate to Oahu of  $0.12 \mu\text{g cm}^{-2} \text{ d}^{-1}$  (Uematsu et al., 1985), and a crustal abundance of Fe and Al of 5.63% and 8.23% (Lide, 2000), respectively, we can determine that the average Fe and Al aerosol deposition to our study site is  $\sim 0.44 \text{ mmol Fe m}^{-2} \text{ yr}^{-1}$  and  $1.34 \text{ mmol Al m}^{-2} \text{ yr}^{-1}$ . This suggests that non-volcanically impacted Fe and Al CW deposition contributes 11–48% of the total deposition (Dust + CW) to the island of Hawaii.

## 5. Summary

We measured CW concentrations of total dissolvable Fe and Al in 60 samples spanning 26 individual CW events throughout 1999 in Hawaii Volcanoes National Park on the island of Hawaii. Al and Fe concentrations varied dramatically both within and between individual events, with Al concentrations ranging from 8 to 10,489 nM, with a median of 344 nM and Fe concentrations ranging from < 1 to 6419 nM with a median of 32 nM. CW deposition fluxes for Fe and Al ranged from  $0.15\text{--}0.52 \text{ mmol Fe m}^{-2} \text{ yr}^{-1}$  and  $0.62\text{--}1.35 \text{ mmol Al m}^{-2} \text{ yr}^{-1}$ , depending on whether we estimated deposition using the median concentration or a volume weighted average scaled to total water deposition. Although the Fe and Al median concentrations are among the lowest ever measured in CW, the wide variability in concentrations suggested that volcanic activity from Kilauea Volcano, rather than an anthropogenic source, contributed to elevated trace metal concentrations in some samples. We separated volcanic versus non-volcanic influences using wind direction, the presence or absence of vog, and  $\text{F}^-$  concentrations. Using these criteria, we determined that volcanic activity may contribute at least 42% and 61% of the measured CW Al and Fe deposition, with volcanic activity having a larger influence on Fe than Al.

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## References

- Allen, A.G., Baxter, P.J., Ottley, C.J., 2000. Gas and particle emissions from Soufrière Hills Volcano, Montserrat, West Indies: characterization and health hazard assessment. *Bulletin of Volcanology* 62, 8–19.
- Arimoto, R., Duce, R.A., Ray, B.J., Unni, C.K., 1985. Atmospheric trace elements at Enewetak Atoll: 2. Transport to the ocean by wet and dry deposition. *Journal of Geophysical Research* 90, 2391–2408.
- Azvedo, J., Morgan, D.L., 1974. Fog precipitation in coastal California forests. *Ecology* 55, 1135–1141.
- Behra, P., Sigg, L., 1990. Evidence of redox cycling of iron in atmospheric water droplets. *Nature* 344, 419–421.
- Bergin, M.H., Jaffrezo, J.L., Davidson, C.I., Caldow, R., Dibb, J., 1994. Fluxes of chemical species to the Greenland ice sheet at Summit by fog and dry deposition. *Geochimica et Cosmochimica Acta* 58, 3207–3215.
- Bluth, G.J.S., Schnetzler, Krueger, A.J., Walter, A.S., 1993. The contribution of explosive volcanism to global atmospheric sulfur dioxide concentrations. *Nature*, 366, 327–329.
- Bridges, K.S., Jickells, T.D., Davies, T.D., Zeman, Z., Hunova, I., 2002. Aerosol, precipitation and cloudwater chemistry observations on the Czech Krusne Hory plateau adjacent to a heavily industrialized valley. *Atmospheric Environment* 36, 353–360.
- Carrillo, J.H., Huebert, B.J., 2002. Fog interception in Hawaii calculated with a water balance: results and uncertainties. *Land Use and Water Resources Research*, submitted for publication.
- Carrillo, J.H., Huebert, B.J., Glantner, M., Sigman, D.M., 2002a. Atmospheric deposition of inorganic and organic nitrogen and base cations in Hawaii. *Global Biogeochemical Cycles*, 16(4), 1076, doi: 10.1029/2002GB001892.
- Carrillo, J.H., Huebert, B.J., Stevens, D., Reynes A., 2002b. Volcanically produced nitrogen in Hawaii. *Global Biogeochemical Cycles*, submitted for publication.
- Chadwick, O.A., Derry, L.A., Vitousek, P.M., Huebert, B.J., Hedin, L.O., 1999. Changing sources of nutrients during four million years of ecosystem development. *Nature* 397, 491–497.
- Cini, R., Prodi, F., Santachiara, G., Porcu, F., Bellandi, S., Stortini, A.M., Oppo, C., Udisti, R., Pantani, F., 2002. Chemical characterization of cloud episodes at a ridge site in Tuscan Appennines, Italy. *Atmospheric Research* 61, 311–334.
- Collet Jr., J.L., Oberholzer, B., Staehelin, J., 1993. Cloud chemistry at Mt. Rigi, Switzerland: dependence on drop size and relationship to precipitation chemistry. *Atmospheric Environment* 27, 33–42.
- Collett Jr., J.L., Hoag, K.J., Sherman, D.E., Bator, A., Richards, L.W., 1999. Spatial and temporal variations in San Joaquin Valley fog chemistry. *Atmospheric Environment* 33, 129–140.
- Crowe, B.M., Finnegan, D.L., Zoller, W.H., Boynton, W.V., 1987. Trace element geochemistry of volcanic gases and particles from 1983–1984 eruptive episodes of Kilauea volcano. *Journal of Geophysical Research* 92, 13708–13714.
- Daube, B.C., Kimball, K.D., Lamar, P.A., Weathers, K.C., 1987. Two ground-level cloud water sample designs which reduce rain contamination. *Atmospheric Environment* 21, 893–900.

- Dawson, T.E., 1998. Fog in the California redwood forest: ecosystem inputs and use by plants. *Oecologia* 117, 476–485.
- De Angelis, M., Legrand, M., 1994. Origins and variations of fluoride in Greenland precipitation. *Journal of Geophysical Research* 99, 1157–1172.
- DeCarlo, E.H., Spencer, K.J., 1995. Records of lead and other heavy inputs to sediments of the Ala Wai Canal, Oahu, Hawaii. *Pacific Science* 49, 471–491.
- Dollard, G.J., Unsworth, M.H., Harve, M.J., 1983. Pollutant transfer in upland regions by occult precipitation. *Nature* 302, 241–243.
- Duce, R.A., Arimoto, R., Ray, B.J., Unni, C.K., Harder, P.J., 1983. Atmospheric trace elements at Enewetok Atoll. *Journal of Geophysical Research* 88, 5321–5342.
- Erel, Y., Pehkonen, S.O., Hoffman, M.R., 1993. Redox chemistry of iron in fog and stratus clouds. *Journal of Geophysical Research* 98, 18423–18434.
- Fisak, J., Tesar, M., Rezacova, D., Elias, V., Weignerova, V., Fottova, D., 2002. Pollutant concentrations in fog and low cloud water at selected sites of the Czech Republic. *Atmospheric Environment* 64, 75–87.
- Foster, P., 2001. The potential negative impacts of global climate change on tropical montane cloud forests. *Earth-Science Reviews* 55, 73–106.
- Ghauri, B.M., Mirza, M.I., Richter, R., Dutkiewicz, V.A., Rusheed, A., Khan, A.R., Husain, L., 2001. Composition of aerosols and cloud water at a remote mountain site (2.8 kms) in Pakistan. *Chemosphere* 3, 51–63.
- Giambelluca, T.W., Schroeder, T.A., 1998. Climate. In: Juvik, S.P., Juvik, J.O., Paradise, T.R. (Eds.), *Atlas of Hawaii*. University of Hawaii Press, Mililani, Hawaii.
- Heath, J.A., Huebert, B.J., 1999. Cloud water deposition as a source of fixed nitrogen in a Hawaiian montane forest. *Biogeochemistry* 44, 119–134.
- Herckes, P., Wortham, H., Mirabel, P., 2002a. Cloud water deposition at a high-elevation site in the Vosges Mountains (France). *The Science of the Total Environment* 296, 59–75.
- Herckes, P., Wortham, H., Mirabel, P., Millet, M., 2002b. Evolution of fogwater composition in Strasbourg (France) from 1990 to 1999. *Atmospheric Research* 64, 53–62.
- Hicks, B.B., Baldocci, D.D., Hosker, R.P., Hutchison, B.A., Matt, D.R., McMillen, R.T., Satterfield, L.C., 1985. On the use of monitored air concentrations to infer dry deposition. NOAA Technical Memorandum ERL ARL-141, Air Resources Laboratory.
- Jacob, D.J., Waldman, J.M., Munger, J.W., Hoffman, M.R., 1985. Chemical composition of fogwater collected along the California coast. *Environmental Science Technology* 19, 730–735.
- Jickells, T.D., Davies, T.D., Tranter, M., Landsberger, S., Jarvis, K., Abrahams, P., 1992. Trace elements in snow samples from the Scottish Highlands: sources and dissolved/particulate distributions. *Atmospheric Environment* 26, 393–401.
- Jiries, A., 2001. Chemical composition of dew in Amman, Jordan. *Atmospheric Research* 57, 261–268.
- Juvik, J.O., Nullet, D., 1993. Relationships between rainfall, cloud-water interception, and canopy throughfall in a Hawaiian montane forest. In: Hamilton, L.S., Scatena, F.N. (Eds.), *Tropical Montane Cloud Forests*. East-West Center, Honolulu, HI, pp. 102–114.
- Khwaja, H.A., Brudnoy, S., Husain, L., 1995. Chemical characterization of three summer cloud episodes at Whiteface Mountain. *Chemosphere* 31, 3357–3381.
- Larrain, H., Velasquez, F., Cereceda, P., Espejo, R., Pinto, R., Osses, P., Schemenauer, R.S., 2002. Fog measurements at the site “Falde Verde” north of Chanaral compared with other fog stations of Chile. *Atmospheric Research* 64, 273–284.
- Lide, D.R., 2000. *CRC Handbook of Chemistry and Physics*, 80th Edition, 1999–2000. CRC Press, Boca Raton, FL.
- Lovett, G.M., Reiners, W.A., Olson, R.K., 1982. Cloud droplet deposition in subalpine balsam fir forests: Hydrological and chemical inputs. *Science* 218, 1303–1304.
- Lovett, G.M., 1984. Rates and mechanisms of cloud water deposition to a subalpine basalm fir forest. *Atmospheric Environment* 18, 361–371.
- Lovett, G.M., Kinsman, J., 1990. Atmospheric deposition to high-elevation systems. *Atmospheric Environment* 24, 2767–2786.
- Measures, C.I., Yuan, J., Resing, J.A., 1995. Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. *Marine Chemistry* 50, 3–12.
- Miller, E.K., Friedland, A.J., 1999. Atmospheric pollutants and trace gases. *Journal of Environmental Quality* 28, 270–277.
- Monteith, J.L., 1965. *Evaporation and environment*. The state and movement of water in living organisms. Symposium of the Society of Experimental Biology: No 19. Vol. 19, pp. 205–234.
- Munger, J.W., Waldman, J.M., Jacob, D.J., Hofman, M.R., 1983. Fogwater chemistry in an urban atmosphere. *Journal of Geophysical Research* 88, 5109–5132.
- Nadkarni, N.M., Solano, R., 2002. Potential effects of climate change on canopy communities in a tropical cloud forest: an experimental approach. *Oecologia* 131, 580–586.
- Naughton, J.J., Lewis, V.A., Hammond, D., 1974. The chemistry of sublimates collected directly from lava fountains at Kilauea Volcano, Hawaii. *Geochimica et Cosmochimica Acta* 38, 1679–1690.
- Perry, K.D., Cahill, T.A., Schnell, R.C., Harris, J.M., 1999. Long-range transport of anthropogenic aerosols to the National Oceanic and Atmospheric Administration baseline station at Mauna Loa Observatory, Hawaii. *Journal of Geophysical Research* 104, 18521–18533.
- Plessow, K., Acker, K., Heinrichs, H., Moller, D., 2001. Time study of trace elements and major ions during two cloud events at the Mt. Brocken. *Atmospheric Environment* 35, 367–378.
- Pounds, A., Fogden, M.P.L., Campbell, J.H., 1999. Biological response to climate change on a tropical mountain. *Nature* 398, 611–615.
- Resing, J., Measures, C.I., 1994. Fluorometric determination of Al in seawater by FIA with in-line preconcentration. *Analytical Chemistry* 66, 4105–4111.
- Sansone, F.J., Benitez-Nelson, C.R., DeCarlo, E.H., Resing, J.A., Vink, S.M., Heath, J.A., Huebert, B.J., 2002. Geochemistry of atmospheric aerosols generated from lava-seawater interactions. *Geophysical Research Letters* 29, 49–1, 49–4, 10.1029/2001GL013882.
- Sedlak, D.L., Hoigné, J., David, M.M., Colville, R.N., Seyffer, E., Acker, K., Wieprecht, W., Lind, J.A., Fuzzi, S., 1997. The cloudwater chemistry of iron and copper at Great Dun Fell. *Atmospheric Environment* 31, 2515–2526.

- Sutton, J., Elias, T., 1993. Volcanic gases create air pollution on the Island of Hawaii. *Earthquakes and Volcanoes* 24, 179–196.
- Symonds, R.B., Rose, W.I., Redd, M.H., 1988. Contribution of Cl and F-bearing species to the atmosphere by volcanoes. *Nature* 334, 145–148.
- Uematsu, M.R., Duce, A., Prospero, J.M., 1985. Deposition of atmospheric mineral particles to the North Pacific Ocean. *Journal of Atmospheric Chemistry* 3, 123–138.
- Vitousek, P.M., Gerrish, G., Turner, D.R., Walker, L.R., Mueller-Dombois, D., 1995. Litterfall and nutrient cycling in four Hawaiian montane rainforests. *Journal of Tropical Ecology* 11, 189–203.
- Vogelmann, H.W., 1973. Fog precipitation in the cloud forests of eastern Mexico. *BioScience* 23, 96–100.
- Waldman, J.M., Munger, J.W., Jacob, D.J., Flagan, R.C., Morgan, J.J., Hoffman, M.R., 1982. Chemical composition of acid fog. *Science* 218, 677–680.
- Watanabe, K., Ishizaka, Y., Takenaka, C., 2001. Chemical characteristics of cloud water over the Japan Sea and the Northwestern Pacific Ocean near the central part of Japan: Airborne measurements. *Atmospheric Environment* 35, 645–655.
- Weathers, K.C., Likens, G.E., 1997. Clouds in southern Chile: an important source of nitrogen to nitrogen-limited ecosystems? *Environmental Science and Technology* 31, 210–213.
- Weathers, K.C., Likens, G.E., Bormann, F.H., Eaton, J.S., Bowden, W.B., Andersen, J.L., Cass, D.A., Galloway, J.N., Keene, W.C., Kimball, K.D., Huth, P., Smiley, D., 1986. A regional acidic cloud/fog water event in the eastern United States. *Nature* 319, 657–658.
- Weathers, K.C., Likens, G.E., Bormann, F.H., Bicknell, S.H., Bormann, B.T., Daube, B.C., Eaton, J.S., Galloway, J.N., Keene, W.C., Kimball, K.D., McDowell, W.H., Siccama, T.G., Smiley, D., Tarrant, R.A., 1988. Cloudwater chemistry from ten sites in North America. *Environmental Science Technology* 22, 1018–1026.
- Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloud water inputs of nitrogen to forest ecosystems in southern Chile: forms, fluxes, and sources. *Ecosystems* 3, 590–595.
- Wilkening, K.E., Barrie, L.A., Engle, M., 2000. Atmospheric science. : Trans-Pacific air pollution 290, 65–67.
- Wrzesinsky, Th., Klemm, O., 2000. Summertime fog chemistry at a mountainous site in central Europe. *Atmospheric Environment* 34, 1487–1496.