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Cloudwater deposition as a source of fixed nitrogen in a Hawaiian montane forest

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Abstract. Precipitation, dry deposition, and cloud water deposition of fixed nitrogen (nitrate and ammonium ions) were measured on the Island of Hawaii. The first two were small N inputs, averaging 0.6±0.2 and 0.15±0.08 kg N ha^{-1} yr^{-1} respectively. We estimate cloud water deposition to be 8–22 kg inorganic N ha^{-1} yr^{-1}. If an estimate of organic N is included, it may be as high as 50 kg N ha^{-1} yr^{-1}. Additionally, cloud water deposition is of hydrological significance as it comprised 37% of the total water input. Cloud water interception was certainly lower in the past, as the developing ecosystem would have had less collection surface area.

Cloud water samples that were associated with volcanic haze events were very concentrated in NO_3^- and constituted 60% of the annual cloud water N deposition. This NO_3^- probably originated from atmospheric N fixed thermally at the hot lava surface or from an interaction between lava and the ocean. If volcanically influenced samples are excluded from the analysis, the resulting cloud water deposition would have been 4–9 kg N ha^{-1} yr^{-1}. The Pacific Ocean and Kilauea volcano may have a profound impact on the development of this terrestrial ecosystem, as sources of fixed nitrogen.

Introduction

The deposition of cloud droplets containing fixed nitrogen to vegetation can be a significant contributor to the nitrogen budget of an ecosystem. Cloudwater nitrate deposition (also referred to in the literature as occult deposition and horizontal precipitation) has been identified as a major contributor to acidification of high altitude forests in northeastern North America (Lovett et al. 1982; Weathers et al. 1988a, b; Vong et al. 1991). In unpolluted ecosystems there have been fewer studies, but Asbury et al. (1994) and Weathers and Likens (1997) have measured cloudwater fixed nitrogen concentrations in relatively remote locations and conclude that it may be a significant N source for those ecosystems.

The island of Hawaii has two volcanos, Kilauea and Mauna Loa, that have both been active in recent times. The occurrence of lava flows of known dates over different elevation, moisture, and temperature gradients makes this a unique spot to study primary succession and ecosystem development, making it a focus of numerous biological and ecological studies (Vitousek et al. 1983; Vitousek & Walker 1989; Vitousek et al. 1992; Vitousek et al. 1993; Aplet & Vitousek 1994; Crews et al. 1995; Raich et al. 1997). In a budget of fixed N for a site near the Thurston Lava Tube, it was determined that the amount of fixed N in the soil (NH_4^+, NO_3^-, and organic N) divided by the substrate age is substantially greater than the yearly N input via biological N fixation. If the N input was constant with time, a 33 kg N ha^{-1} yr^{-1} input is required, whereas biological N fixers presently account for only 1.2 kg N ha^{-1} yr^{-1} (Crews et al. 1995). This means that other fixed N sources on average total 32 kg N ha^{-1} yr^{-1}.

We evaluated whether atmospheric deposition, particularly cloud water deposition, could contribute part of this unaccounted-for N input. The Thurston site is on the windward flank of Kilauea at a location where orographic clouds are often at ground level, making deposition to the surface possible. In a study of rain and cloud water deposition on the windward slopes the Kohala Mountains on the island of Hawaii, Juvik and Nullet (1993) measured a cloud water input that was 406% of the rainfall for the period studied. Ionic concentrations are often higher in cloud water than precipitation (Weathers et al. 1988a; Vong et al. 1997) so that a significant ionic flux is likely to accompany this water deposition (Lovett & Kinsman 1990). While measuring the chemical composition of cloud water is relatively straightforward (Hering et al. 1987), quantifying the water deposition is considerably more difficult (Lovett & Kinsman 1990; Lovett 1994).

To assess the atmospheric sources of fixed N at the Thurston Lava Tube, we measured dry deposition (using filter packs and meteorologically-derived deposition velocities) and precipitation deposition (with a wet-only collector) from October of 1993 to June of 1996. Between June of 1995 and June of 1996 we also continuously measured parameters from which we could compute cloudwater volume deposition using a hydrologic balance approach and intermittently measured cloudwater chemistry with an active-string cloudwater collector. From these we could calculate the cloudwater input of N to our site. We limit our focus here to quantifying nitrogen deposition in cloud water, and leave the details of cloud water nitrogen chemistry (Cape et al. 1997) for a later paper.

Methods

Precipitation, dry deposition, and cloud water chemistry were all measured in a clearing at approximately 1190 m elevation near the Thurston Lava Tube in the Hawaii Volcano National Park. The only conceivable non-volcanic pollution sources are lightly-used park roads 1 or more km from the site and mostly downwind (during trade winds). The throughfall and stemflow collectors were located in the forest about 2 km to the southeast, at very nearly the same elevation. The forest is dominated by a 12–16 m-tall canopy of *Metrosideros polymorpha*, with *Coprosma ochracea* and *Ilex anomala* in the subcanopy and a tree-fern layer dominated by *Cibotium glaucum*.

Precipitation deposition

Weekly collections of precipitation for chemical analysis were made using an Aerochemetrics wet-only rain collector (Chan et al. 1984). The buckets were rinsed and soaked repeatedly in DI before use. Samples were fixed with chloroform, refrigerated, and analyzed for nitrate and ammonium using ion chromatography (Dionex 300 Series) within two months. The same analytical techniques were used for both rain and cloud water samples: anion analyses were performed with an OmniPac Pax-500 column, a gradient elution (from 5 to 28.75 mM NaOH/5% methanol), and a 25 mM H_2SO_4 autoregenerant in a micromembrane suppressor. Cations were analyzed with an IonPac CS-10 column, 20 mM HCl/2 mM DL-2,3-diaminopropionic acid eluant and 0.1 M tetrabutylammonium hydroxide autoregenerant in a micromembrane suppressor. The weekly buckets were weighed to determine rain water volume until June of 1995, when a Campbell Scientific, Inc. TE525 tipping bucket rain gage was installed at the site to obtain a continuous time-resolved record of rainfall.

Dry deposition

Dry deposition estimates were made using weekly day and night filter packs (Lee et al. 1994) mounted under a rain shield and deposition velocities computed from observed wind speeds and wind-direction variation (Hicks et al. 1987). Samples were analyzed for nitrate and ammonium using ion chromatography. A Campbell Scientific, Inc. data logger was programmed to shut the filter pump off whenever the Aerochemetrics rain collector was open or when the relative humidity (RH), as measured by a Vaisala temperature and RH probe, was above 95%. This "dry-only" sampling was intended to reduce contamination of the filters by rain, light drizzle, and fog. An RM Young propeller-vane anemometer was used to measure two parameters used

in the deposition velocity calculations: the wind speed and sigma theta, the variability of the wind direction.

Cloud water deposition

Cloud water volume. To evaluate the cloud water volume deposited, we used the hydrologic balance method of Juvik and Nullet (1993). They employed the following equation, where the water inputs to the system are on the left.

$$R + CW = TF + SF + CS + E \quad (1)$$

Here R, the rainfall amount, and CW, the amount of cloud water deposition, are set equal to the sum of the possible fates of the water: throughfall (TF – water that drips off the vegetation), stemflow (SF – water that runs down the vegetation), canopy storage (CS – the amount of water necessary to saturate the dry vegetation so that TF and SF can occur), and evaporation (E). Thus, the cloudwater deposition is

$$CW = TF + SF + CS + E - R \quad (2)$$

Although representative sampling may be difficult (due to questions about the placement of collectors in the forest), TF and SF are easily measured (Juvik & Nullet 1993; Likens & Eaton 1970; Reynolds & Neal 1991). During events that result in measurable TF, the relative humidity is generally high enough that E is likely to be insignificant. We used Juvik and Nullett's (1993) value of CS, which had been estimated in a nearby forest from events where there was rain, but no cloud water deposition. The throughfall amount was measured continuously with four 7 m pieces of 2.54 cm aluminum angle. These were arranged with the open parts facing upward so that they create troughs (Juvik & Nullet 1993) in a x-pattern and were between 1 and 2 m above the ground. Throughfall was measured and CW calculated for all 277 events on the continuous datalogger record. Weekly-integrated stemflow was measured from January to June of 1995 on 6 trees using collectors made from galvanized steel sheet metal wrapped around the stems to form a funnel and sealed with plumbers' putty. Rainfall outside the forest was measured by a tipping bucket rain gage, so that we could directly relate individual rainfall and throughfall events. No chemical analysis was done on the throughfall or stemflow water.

Chemistry. Cloud water samples were collected intermittently (the collector was not automated, so an operator had to be present to collect cloud water for chemical analysis) with an active string (0.05 cm diameter FEP Teflon)

CASC cloud water collector after the design of Daube et al. (1987). The 50% size cut was just under 5 μm. String cartridges were cleaned by agitating in nonionic detergent, rinsing repeatedly, and then soaking in DI water for several days. The collector was turned on and sampling was started when a cloud was visibly present. Every two hours that the cloud persisted the sample bottle was changed. Cloud water was collected on 1 to 4 days every month from May through the end October 1995 and from January to June 1996. The majority of the samples were collected between 6 PM and 3 AM, as those were the cloudiest times.

Results

Precipitation deposition

Precipitation for 1993 to 1996 was 2480, 3300, 1630, and 2180 mm respectively. The total yearly deposition of N in rainfall for 1993 to 1996 was 0.7±0.1, 0.6±0.3, 0.5±0.2, and 0.5±0.1 kg N ha^{-1} yr^{-1} respectively (Table 1). This accounts for only 2–3% of the previously unidentified N input. While the total amount of precipitation can almost halve from one year to the next, the amount of N deposited was remarkably consistent. The relative amounts of NO_3^- and NH_4^+ in precipitation also vary little from year to year with NO_3^-/NH_4^+ molar ratios of 1.7, 1.0, 1.5, and 1.1 for 1993 to 1996 respectively.

Dry deposition

The amount of time that an individual day or night filter was exposed varied from week to week according to how much "dry" time there was in the sampling period. The deposition velocity (V_d) for nitric acid gas (HNO_3) was calculated by the method of Hicks et al. (1987) which uses an estimate of atmospheric turbulence to infer V_d. V_d was multiplied by the weekly atmospheric HNO_3 concentration to derive the dry flux.

The dry deposition of HNO_3 for 1994 to 1996 was 0.04±0.05, 0.2±0.1, and 0.2±0.1 kg N ha^{-1} yr^{-1} respectively (Table 1). This accounted for only 0.1–0.6% of the unidentified N input. Atmospheric concentrations of N species from 1994 to 1996 in ng N m^{-3} were 28±7, 54±7, and 14±7 for HNO_3 (Table 1), 126±14, 224±28, and 54±14 for particulate NO_3^-, and 126±14, 70±7, and 98±14 for particulate NH_4^+.

To estimate the importance of particulate N deposition, we assumed an aerosol deposition velocity of 0.1 cm s^{-1} (Duce et al. 1991). This would yield a total particulate N deposition of 0.02, 0.05, and 0.04 kg N ha^{-1} yr^{-1} for 1994 to 1996. Even if particulate deposition were twice or three times as large as our estimate, it would still contribute little to the total yearly N input.

Table 1. Chemical concentrations, atmospheric deposition rates, N deposition values, and standard errors. Dry deposition fluxes are calculated from 104 samples per year, while we collected 52 precipitation samples each year. We collected cloudwater from 4 "vog" events and 18 non-"vog" events, out of 277 cloud water events during the year of cloudwater measurements. The means for dry deposition and precipitation are for multiple years, but we have only a single year's data for cloud water deposition.

Type of deposition →		Dry	Cloud water		Precipitation	
		HNO_3 (ng N m^3)	Non-"vog" (μg N l^{-1})	"Vog" (μg N l^{-1})	NH_4^+ (μg N l^{-1})	NO_3^- (μg N l^{-1})
Chemical concentration	1993	NA	NA	NA	15	25
	1994	28	NA	NA	19	19
	1995	42	NA	NA	19	29
	1996	14	360	10900	27	31
	Mean	28 ± 11	360 ± 60	10900 ± 1500	20 ± 4	26 ± 5
		(cm s^{-1})		(mm yr^{-1})		(mm yr^{-1})
Deposition rate	1993	NA		NA		2480
	1994	0.8		NA		3300
	1995	0.7		NA		1630
	1996	1.2		1130		2180
	Mean	0.9 ± 0.5		1130 ± 570		2400 ± 240
		(kg N ha^{-1} yr^{-1})		(kg N ha^{-1} yr^{-1})		(kg N ha^{-1} yr^{-1})
Total N deposition	1993	NA		NA		0.7 ± 0.1
	1994	0.04 ± 0.05		NA		0.6 ± 0.3
	1995	0.2 ± 0.1		NA		0.5 ± 0.2
	1996	0.2 ± 0.1		15 ± 7		0.5 ± 0.1
	Mean	0.15 ± 0.08		15 ± 7		0.6 ± 0.2

It is not surprising that dry deposition is so small at this site given that it was so seldom dry. There was no rain and the relative humidity was below 95% during only 38% of the daytime hours and 3% of the nighttime hours.

Cloud water deposition

The SF was consistently near 25% of TF for the half year we measured it weekly, so we assumed it to be 25% of TF for all events. However, this estimate represents a lower limit of the true SF amount, as several samples overflowed their collection containers. The actual CW is therefore slightly larger than what we calculate. We use a scaled version of Juvik and Nullet's (1993) CS_{max} in our calculations (Heath 1996), even though the forest at our

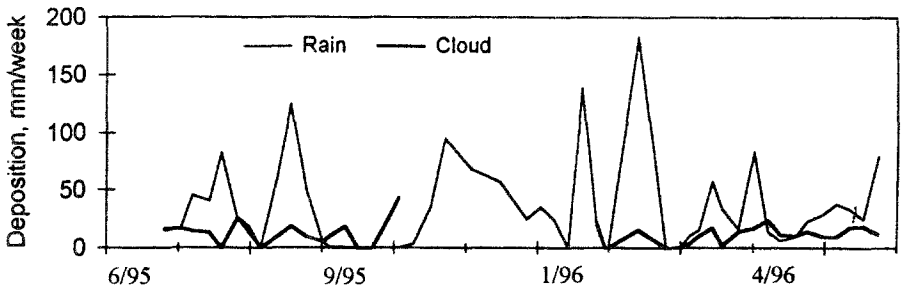

Figure 1. Weekly sums of the cloud water and rain deposition amounts for 1995 to 1996 near Thurston Lava Tube. The gap during the winter months is due to a data logger failure.

site is somewhat taller than the *Sophora chrysophylla* one which they studied. If throughfall events were separated by 6 or more hours of sunshine, we used their 3.8 mm for CS. For shorter dry periods we used a fraction of their value, depending on the time the canopy had to dry out. Weekly sums of cloud water and rain volume were similar in about half the cases, with rainfall exceeding cloudwater in all but a few of the remaining weeks (Figure 1). The R total for the simultaneous sampling periods was 1900 mm yr^{-1} and the CW total was 1130 mm yr^{-1}, which is 37% of R + CW.

Concentrations of N, particularly of NO_3^-, varied considerably from one event to another (Figure 2 and Table 2). If the very concentrated samples are excluded, the average concentration of N was 370 μg N l^{-1}. There are events, however, where the amount of N was as high as 17000 μg N l^{-1}. During the lower concentration events the NO_3^-/NH_4^+ ratio was between 0.6 and 6, with a mean of 2.3, whereas during the high concentration events it was as high as 76, with a mean of 21. The elevated non-seasalt sulfate (NSS) values (corrected for seasalt using sodium) indicate that during those times we were sampling H_2SO_4 in the fume from Kilauea volcano. The elevated Na^+values (as high as 290 mg l^{-1}) in some of the events with high NO_3^- point to a significant marine influence in these samples.

The very concentrated cloudwater samples were all collected during "vog" (the haze when winds blow volcanic fumes from the currently-active Pu'u O'o vent back towards land) or "laze" (the fumes that result when molten lava enters the ocean) episodes. The wind speeds are often low at these times so that the very acidic fumes stagnate over the Volcano Park and surrounding areas.

Although we measured the water input amounts for most of the year, chemical samples were collected only occasionally because they required personnel to be on site. Because the concentration of N in CW was so variable, several approaches were used to estimate the actual cloud deposition (Heath 1996). The method that we consider to be our best estimate computes

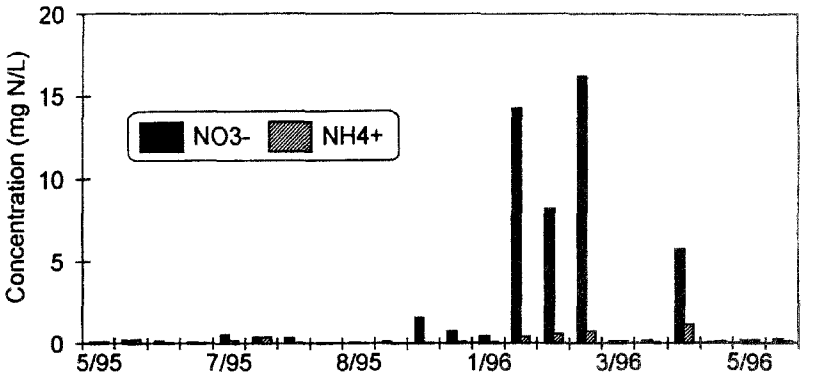

Figure 2. Chemistry of cloud water during 22 cloud events in 1995 and 1996 near Thurston Lava Tube.

Table 2. Solute concentrations measured in 22 individual cloud events

Date	NO_3 ug N L^{-1}	NH_4 ug N L^{-1}	NSS mg L^{-1}	Na mg L^{-1}
05/21/95	101	118	1	4
06/21/95	202	251	2	9
06/21/95	153	51	2	6
06/22/95	66	29	5	1
07/13/95	540	172	nd	2
08/09/95	410	390	4	5
08/12/95	350	29	4	10
08/12/95	43	6	0	1
08/14/95	75	33	1	1
08/16/95	120	51	1	2
09/25/95	1610	73	nd	2
10/25/95	760	112	nd	4
01/28/96	480	97	nd	1
01/30/96	14200	430	7	60
02/11/96	8200	610	29	8
02/13/96	16200	780	57	290
03/24/96	126	134	170	2
04/15/96	154	80	2	2
05/05/96	5800	1160	153	82
05/15/96	68	129	15	2
05/30/96	204	208	4	4
06/03/96	260	117	4	4

CW chemical deposition by multiplying the N concentration in cloud water for an event by the water input for that event for only those samples for which both types of data are available. From this we then calculate an average chemical deposition amount per event. The resulting average deposition per event was 0.054 kg N ha^{-1} $event^{-1}$ for the 22 events sampled. If this average were valid for all 277 events yr^{-1}, the N deposition would have been 15±7 kg N ha^{-1} yr^{-1}. CW deposition of inorganic N ions then would account for 47% of the unidentified N input, by far the largest identified source. Of this 15±7 kg N ha^{-1} yr^{-1}, about 60% was deposited during volcanic haze events.

Discussion

Magnitude of precipitation inputs

Our wet deposition data are similar to previous measurements at this site. On the opposite side of Kilauea Iki Crater near Halema'uma'u, Vitousek and Walker (1989) measured 3.8 kg N ha^{-1} yr^{-1} in precipitation. Using bulk funnel samplers, they measured organic N and inorganic NO_3^- and NH_4^+. About 70% of the fixed N was organic. Their inorganic N input of 1.1 kg N ha^{-1} yr^{-1} is similar to the 0.6 kg N ha^{-1} yr^{-1} we measured. This also implies that the total precipitation N flux may be significantly greater than our estimate, due to our omission of organic N.

Harding and Miller (1982) also used bulk samplers to collect precipitation near the Vitousek and Walker site. Although they did not report deposition totals, their 18 μg NO_3^- N l^{-1} concentration would result in 0.4 kg N ha^{-1} yr^{-1} using our average annual precipitation rate. This is in good agreement with the 0.3 kg ha^{-1} yr^{-1} NO_3^--N we found.

N in precipitation was a small input at this site. Since we omitted organic N, our estimate is a lower limit, although the total N in wet deposition is still likely to be small. If we had a similar ratio of organic to inorganic N as found by Vitousek and Walker (1989), precipitation deposition would still only contribute about 2 kg N ha^{-1} yr^{-1}. Although the amount of precipitation varies substantially from year to year, the N deposition is relatively constant.

Magnitude of dry deposition input

Like precipitation, dry N deposition was small at this site (0.15±0.08 kg N ha^{-1} yr^{-1}), accounting for 1% of the total atmospheric deposition and 0.5–0.7% of the unaccounted-for N input. This is not surprising, given that our criteria for "dry" conditions (a closed rain collector and RH below 95%) were met only about 20% of the time. It is likely that we have somewhat

underestimated the time available for dry deposition, as the sensor of the Vaisala RH probe had a tendency to become wetted during cloud events. Even if we were to assume that the time for dry deposition was double what we measured and that particulate NO_3^- and NH_4^+ and NH_3 vapor deposition were equal to HNO_3 deposition, the implied yearly N dry deposition would still be only 0.6 kg N ha^{-1} yr^{-1}, the smallest atmospheric input we measured. Driving the aerodynamic resistance to zero (as might be appropriate on rough terrain) also cannot make this flux significant: there is simply too little nitric acid vapor.

Cloud water deposition

Comparison with other measurements

Although we know of no other measurements of cloud water chemical composition in Hawaii, Huebert (unpublished data) measured 840 μg N l^{-1} as NO_3^- and NH_4^+ in the cloud water in clean marine air off the coast of Los Angeles. There are reports of measurements in other unpolluted regions: Asbury et al. (1994) measured 910 μg N l^{-1} in the cloud water of a marine-influenced montane forest in Puerto Rico; Weathers and Likens (1997) found an average inorganic N of just under 1000 μg N l^{-1} (70% as NH_4^+) in Southern Chile; and Vong et al. (1997) found about 600 μg N l^{-1} (33% as NH_4^+) in clean marine air in Washington state. While our non-"vog" samples are more dilute than these, averaging 360 μg N l^{-1}, the "vog" samples are considerably more concentrated, averaging almost 11,000 μg N l^{-1}. In fact, the "vog" clouds sampled contained more N than many continental clouds (Collett Jr et al. 1990; Weathers et al. 1988a; Weathers et al. 1988b).

Juvik and Perriera (1973) made cloud water interception measurements at a location slightly higher in elevation, but in the same general vicinity as our site over a 7-month period. They measured fog interception rates which were 49% of rainfall during the winter months; in the summer this rose to 66%. While the rainfall for the period of our measurements was only slightly below typical values at 1190 mm, our CW interception rate was 59% of the rainfall, and is still in good agreement with Juvik and Perriera.

Measurement uncertainties

Because of the difficulty in measuring cloud water deposition, there is considerable uncertainty in our estimates. We are confident that the ambient chemical concentrations were within 5% of what we measured (based on the accuracy of our IC analyses), but we could only measure composition intermittently. We have no way of knowing how representative our samples are of the whole year's chemical concentrations, so we tripled the concentration

uncertainty to 15%. We did sample at somewhat regular intervals, suggesting that we approximated the true range and frequency of concentrations.

The spatial variability of TF contributes to the uncertainty in the cloud water input measurements. The troughs we used to collect throughfall have a total collection area of 0.9 m^2, which we use to represent the entire forest. To evaluate the sampling uncertainty of TF, we isolated each collector for several weeks from the other three. The differences between each individual trough and the mean of the other three averaged 13%. The troughs are long (14 m in both directions) and are arranged in an x-pattern, so they are continuously collecting throughfall over a scale that is large relative to the scale of any of the vegetation. This should make them more representative than a set of discreet collectors, but the uncertainty due to trough placement is obvious. We may also underestimate cloud inputs because some of the smaller ferns are too near the ground to be included in our throughfall measurements. We estimate the uncertainty in the SF observations, which are based on measurements from 6 trees, as −30% to +100%. For our assumption that Juvik and Nullet's (1993) CS_{max} of 3.8 mm applies to our site, we assume an uncertainty of ±50%. The propagated uncertainties from all these sources amount to 50% of the deposition flux (Table 1).

The "vog" cloud water samples were so concentrated in NO_3^- that even at very low cloud water interception rates they represent a substantial N source. The 8–22 kg N ha^{-1} yr^{-1} cloudwater input we estimated would be our largest measured N input to this site even if our estimate were double the actual value. There is little doubt that we have identified one of the most important pathways by which N enters this N-limited ecosystem.

Sources of NO_3^- in "vog" and "laze"

The concentrations of oxidized nitrogen in this cloudwater are an order of magnitude or more above what one would expect in a remote region. If the liquid water content of the clouds was 0.1 g H_2O m^{-3}, a fairly conservative value, the 16 mg N l^{-1} sample would correspond to about 3 ppb (molar mixing ratio) of NO_3^-. Typical NO_3^- concentrations measured in the free troposphere at the Mauna Loa Observatory (Lee et al. 1994) rarely exceed 0.2 ppb, and boundary layer concentrations are much smaller still (Huebert & Lazrus 1980). Since the trade winds do not pass over populated areas before they arrive at the Thurston site, the source of this elevated NO_3^- must be natural.

Many active volcanos have either molten lava pools or areas where lava is exposed to the atmosphere. The very high temperatures of the freshly exposed surface, around 1100 °C for Kilauean lava, could allow for the conversion of some atmospheric N_2 to NO. In otherwise clean air, it would take at least

several hours for the NO to then be oxidized to the NO_3^- that we measure. NO can be oxidized to NO_2 by ozone in minutes. However, using rate constants from Finlayson-Pitts and Pitts (1986) and assuming 20 ppbv O_3 and 5×10^6 OH cm^{-3}, we conclude that the lifetime of NO_2 against OH reaction is over 2 hours, while that for the nighttime oxidation of NO_2 by O_3 to form NO_3 radical (which then has several more steps to become nitric acid) is more than 12 hours. This slow conversion means that most of the thermally-fixed NO would leave the area before being converted to NO_3^- under typical trade winds of 20 km/hr.

Our own measurements in various volcano plumes (Lazrus et al. 1979) indicated that NO_3^- concentrations at crater rims are usually below detection limits, indicating that either fixation was not occurring at appreciable rates or the NO that was produced had not yet been oxidized to NO_3^- near the vent. For these reasons, we were surprised to find such high concentrations of NO_3^- in the volcano-influenced cloud water we sampled. One of the characteristics of the "vog" episodes, however, is that the wind speeds were very low (<0.5 to 4 m/s), so that the air stagnated over the Hawaii Volcanos National Park and surrounding areas. During the two highest-concentration events, the wind direction changed from its usual 25–30° azimuth to 80–95°, so plumes from the Pu'u O'o vent and the point of lava entry into the ocean were coming almost directly to our Thurston sampling site. Under these low wind conditions there would be enough time for some of the NO to be oxidized to HNO_3. This probable source of the elevated NO_3^- is under further study.

It is also possible that some of the NO_3^- in the cloud water is due to the volcanic "laze". "Laze" contains high concentrations of hydrochloric acid as well as concentrated, dehydrated sea water (Sutton & Elias 1996), but we are unaware of any inorganic N measurements in "laze". Could sea water N be the source of our high NO_3^-? Values for NO_3^- and NH_4^+ in coastal Hawaiian sea waters are generally around 7 and 0.7 μg N l^{-1} respectively, and total dissolved N (including organic N) is generally between 70 and 140 μg N l^{-1} (Steve Dollar, pers. comm.). Eppley (1992) measured 7 μg N l^{-1} particulate N in the open Pacific Ocean slightly south of Hawaii. Coastal values for particulate N may be slightly higher. As the coastal waters are injected into the atmosphere in this very violent process, presumably all of this fixed N will be carried with it. The maximum N/Na mass ratio in seawater is thus about 10^{-5}, which is far less than the 0.01 to 0.24 we found in cloud water. Clearly the ocean alone cannot account for the elevated NO_3^- we observed. Nonetheless, the high Na^+ values (as high as 286 mg l^{-1}) in some "vog" samples suggest that there are times when there is marine influence.

Implications for N budget

Cloud water deposition is by far the largest atmospheric N input to this site, accounting for 96% of the total. Additionally, cloud water is of hydrological significance, as it was 37% of the total water input (R + CW). Cloud water appears to be especially significant in providing the "missing N" input proposed by Vitousek and Walker (1989). While our estimate of inorganic N deposition from cloud water does not account for the entire 33 kg N ha^{-1} yr^{-1}, it is by far the largest identified fraction of it, accounting for 47%. Additionally, our estimate of cloud water input is likely to be a lower limit to the true N deposition, as organic N measurements were not made. Vitousek and Walker (1989) found that 70% of the N in the rain they measured was in the form of organic N. If there were a similar amount in our cloud water, cloud water deposition of N could be as high as 50 kg N ha^{-1} yr^{-1}. However, if only the non-"vog" events (that caused 40% of the N-deposition) contained this much organic N, the non-"vog" total would be 20±10 kg N ha^{-1} yr^{-1}. Adding back the 9±5 kg N ha^{-1} yr^{-1} from "vog" events would put the total at 29±15 kg N ha^{-1} yr^{-1}, in the range of the average unexplained source. Clearly the presence or absence of organic N in cloud events of various types warrants further study.

Although cloud water is the major source of N deposition under present conditions, the actual atmospheric input through time is difficult to assess. (The same is true for biological N fixation, of course.) The efficiency with which an ecosystem intercepts cloud water is a strong function of its structure and the structure will change significantly throughout ecosystem development from barren lava to the present forest. Likewise, if either thermal fixation of atmospheric N or the sea water "laze" N is the source of the elevated NO_3^- levels during "vog" events, the strength of this source over time would depend on the eruption history of the volcanos. During massive eruptions there may have been large pulses of N entering the atmosphere and depositing to vegetation growing on earlier flows, provided they are present in areas which frequently experience ground level clouds.

Our results suggest that the ocean and the volcano may directly affect the development of this terrestrial ecosystem. While it has long been known that terrestrial runoff affects coastal waters, in this situation the reverse may be true. Although volcanos may have negative effects on surrounding ecosystems, in this case they may actually provide a mechanism to resupply nutrients. In either case, volcanic activity at this unique location may be the source of the largest identified nitrogen input to this ecosystem.

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