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# Volcano fixes nitrogen into plant-available forms

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**Abstract.** Hawaiian montane ecosystems developing on recent tephra deposits contain more fixed nitrogen than conventional sources can explain. Heath and Huebert (1999) demonstrated that cloud water interception is the mechanism by which this extra nitrogen is deposited, but could not identify its source. We show here that atmospheric dinitrogen is fixed at the surface of active lava flows, producing concentrations of NO which are higher than those found in most urban rush hour air pollution. Over a period of hours this NO is blown away from the island and oxidized to nitrate. Interruptions in the trade wind flow can return this nitrate to the island to be deposited in cloud water. Thus, fixation on active lava flows is able to provide nitrogen to developing ecosystems on flows emplaced earlier.

## Introduction

In the course of measuring atmospheric inputs of N into a Hawaiian montane forest, Heath and Huebert (1999) found that occasional collections of cloud water contained very high concentrations of nitrate (10–15 mg $NO_3^-$ N $l^{-1}$). These high concentrations only occurred in about 20% of the collections, but they accounted for 60% of the annual N input via cloud water. This input of fixed N is biologically significant; forest growth is limited by N supply in young volcanic sites (Vitousek et al. 1997) and overall cloud water nitrogen input to this site is 8-fold greater than the input of N via rainfall, dry deposition, and biological N fixation combined (Heath & Huebert 1999; Vitousek 1994).

Studies elsewhere (Weathers et al. 1988; Vong et al. 1997) indicate that cloud water often is enriched relative to the same ions in precipitation, but the source for the occasional high nitrate concentrations that we observed was not obvious. The Hawaiian Islands are among the most remote ecosystems on Earth; while traces of anthropogenic fixed N have been detected there, they rarely exceed 0.2 ppbv N (molar mixing ratio) in the free troposphere (Lee et al. 1994) and are even smaller in the marine boundary layer (Huebert & Lazrus 1980). Assuming a cloud liquid water content of 0.1 g $H_2O$ $m^{-3}$, the elevated cloud water nitrate that Heath and Huebert reported is equivalent to 3 ppbv of $NO_x$ (NO plus $NO_2$) in the atmosphere. This is at least two orders of magnitude higher than typical tropical Pacific $NO_x$ concentrations (Torres & Thompson 1993).

Some of the Heath and Huebert's (1999) high nitrate samples also contained elevated levels of sulfate. The largest sulfate source on Hawaii is Kilauea Volcano, which has been in a nearly constant state of eruption since mid-1986. This suggests that the source may be volcanic. Previous studies have not reported elevated $NO_3^-$ in volcanic plumes (Lazrus et al. 1979). Hobbs et al. (1991), however, found small amounts of the precursor gas $NO_x$ downwind of Mount Redoubt, Alaska, and Bandy et al. (1982) detected NO above background levels in the Mt. St. Helen's plume. During a study at the Mauna Loa Observatory (MLO), Hübler et al. (1992) considered the possibility that hot lava could fix nitrogen that might interfere with their study of free tropospheric nitrogen oxides. However, their instrument (which was insensitive to sodium nitrate particles) was unable to detect any volcanic contribution, even in upslope flow (MLO is situated above Kilauea, at an altitude of 3400 m).

Here we show that the source of elevated nitrate in Heath and Huebert's (1999) cloud water is thermal fixation of atmospheric $N_2$ by hot, active lava surfaces. The volcano itself fixes the N that hastens the revegetation of young lava flows.

## Meteorological analysis

We analyzed winds to find the source of high cloudwater nitrate and sulfate levels. Trade winds (brisk winds from 20–40° azimuth as measured at a nearby air quality monitoring site within Hawaii Volcanoes National Park) usually blow volcanic fume, including $SO_2$ and sulfate aerosol released from Pu‘u ‘O‘o vent to the southwest, away from our cloudwater sampling site (Figure 1). However, when the azimuth is 105 to 115°, Pu‘u ‘O‘o and the lava tube system that transports the mostly degassed, molten lava from the vent to the ocean comprise a 9 km long arc of volcanic influence 14 to 25 km upwind of our cloud water collection site. The fact that some high nitrate samples did not contain elevated sulfate implies that Pu‘u ‘O‘o itself was not a major source of fixed nitrogen found in this study.

Cloudwater nitrate concentrations varied systematically with respect to recorded winds. During the 17 stable trade wind samples, cloud water nitrate

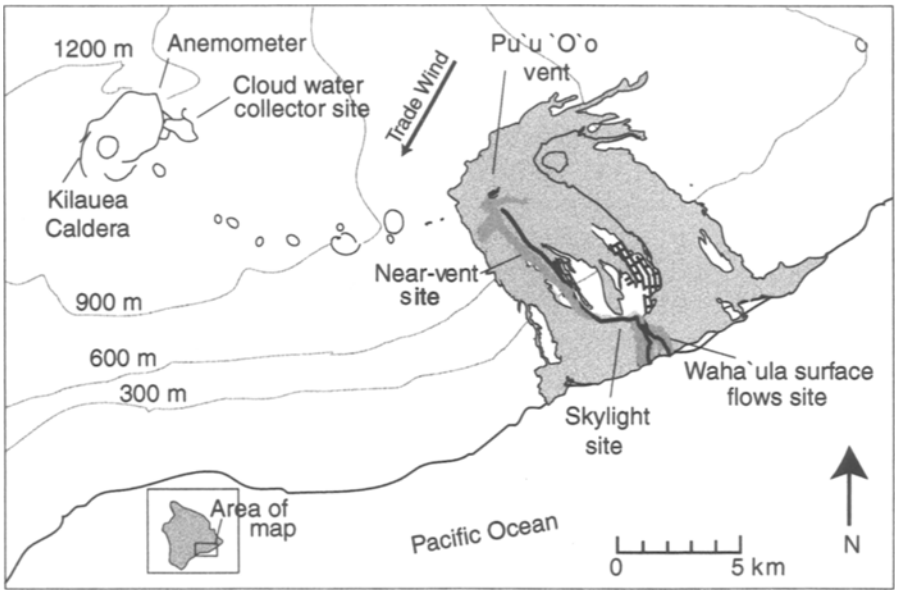

*Figure 1.* Map of the study area. Darkened regions on the right are surface flows from the Pu‘u ‘O‘o vent. The trade winds usually carry gases from these flows well to the south of our cloudwater collector site at Thurston Lava Tube. Our wind data is from an anemometer located on the northestern edge of Kilauea Caldera. Map by U.S. Geological Survey.

concentrations were below 2 mg N $l^{-1}$ (Figure 2). In contrast, all four high nitrate samples were collected during or just after departures from stable trades. Figure 2 shows the influence of profound trade wind disruptions. The x-axis of this figure (2) is the maximum change in the 6 hour average wind direction between successive 6 hour periods for the two days prior to the collection of each cloud water sample. It is evident that while a large change in wind direction is a necessary condition, it is not sufficient by itself to ensure that high nitrate will be observed. Deposition will depend also on a) the direction of the wind shifts; and b) the nature of upwind volcanic activity.

Three of these samples followed Kona (weak southerly) winds, that caused volcanogenic material to accumulate to the east and north of Hawaii; when the northeast trades resumed they pushed the material back to our site. Satellite images (J. Porter, pers. comm.) confirm this behavior for volcanic haze (vog) particles during and after kona winds. The fourth high nitrate sample was taken when kona winds interrupted a long period of trades, returning material that had moved to the south and west of the island.

Simply on the basis of transport, then, volcanic influence could explain the high nitrate concentrations we found in cloudwater. However, a transport

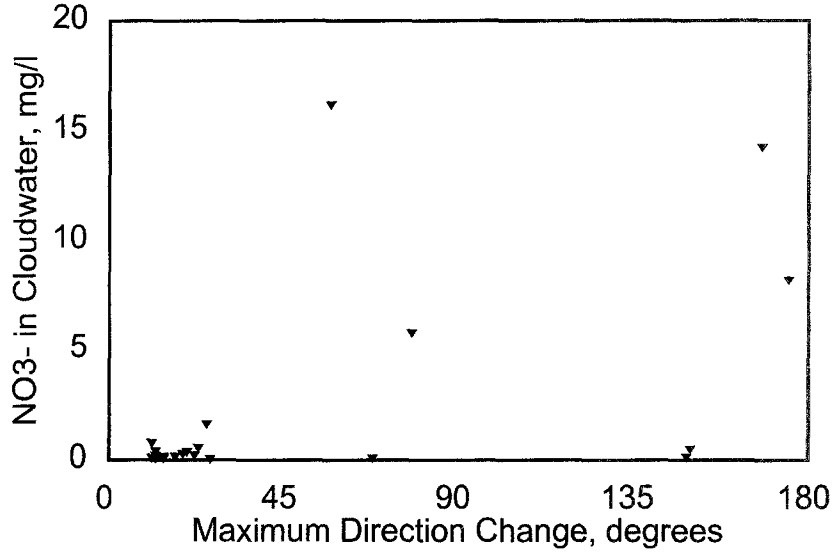

*Figure 2.* Cloud water nitrate as a function of the stability of wind direction. The x-axis is the maximum change in 6 hour vector-averaged wind direction between successive 6 hour periods in the 2 days preceding the collection of each cloud water sample.

pathway alone cannot establish that the volcano fixed the N we found in cloudwater. A formation mechanism also must be identified.

## Thermal fixation of atmospheric dinitrogen

Volcanoes could be expected to produce NO by thermal fixation of atmospheric dinitrogen, just as it is fixed in automobile engines:

$$N_2 + O_2 \rightleftarrows 2\,NO.$$

This equilibrium lies far to the left at ambient temperatures, but at elevated temperatures it shifts slightly to the right, forming trace amounts of NO ($K_{eq} = 4.69 \exp\{-21{,}600/RT\}$ with $R = 1.99$ cal/molK) (Seinfeld 1986). At 1000 °C the equilibrium NO concentration is 372,000 ppbv, while at 1100 °C it is 692,000 ppbv. Thus, the 1145–1155 °C temperatures of molten lava could generate substantial NO. However, the amount of NO formed is probably limited by kinetics rather than the thermodynamic equilibrium. Seinfeld (1986) gives the forward rate for the above reaction as

$$\frac{d[NO]}{dt} = 1.161 \times 10^3 \exp(-135,000/RT)[N_2][O_2]^{1/2}$$
$$(\mathrm{cm}^3\ \mathrm{molecule}^{-1})^{1/2}\ \mathrm{sec}^{-1}$$

*Table 1.* NO concentrations from LMA-3 and sampling conditions.

| Date | NO, ppbv | Location and conditions |
|---|---|---|
| 7–18–97 | <1 | Ambient air clear of sources |
| 7–18–97 | 5 to >100 | Near Pu'u 'O'o vent: 2 m above surface; 1–2 km downwind of active pahoehoe flow. High concentration persisted for several minutes, then disappeared. |
| 1–28–98 | <1 | Ambient air clear of sources |
| 1–28–98 | 1–86 | Active surface flows near Waha'ula, <20 cm from various incandescent spots on pahoehoe; 31 minute average: 18 ppbv (Saltzman average: 23 ppbv) |
| 1–28–98 | 1–>170 | Active surface flows near Waha'ula, <20 cm from various incandescent spots on pahoehoe; 18 minute average: 53 ppbv (Saltzman average: 59 ppbv) |
| 1–28–98 | 1–22 | Several meters downwind of 80 m elevation skylight and several cm above the ground surface; 21 minute average: 9 ppbv |

in air. At 1100 °C and ambient pressures of $O_2$ and $N_2$, it should take about 2 minutes to generate 100 ppbv of NO. It would take several hours for a significant fraction of this NO to be oxidized to $NO_2$ and then $NO_3^-$ (Logan 1983), so measurements close to the NO source would be unlikely to detect appreciable $NO_3^-$.

## Measurements of NO at active lava flows

We conducted a preliminary assessment of Kilauea as a source of fixed N by measuring the concentration of NO near active flows from the Pu'u 'O'o vent. Using a portable chemiluminescent $NO_2$ analyzer (Scintrex LMA-3 with an NO to $NO_2$ converter (Kelly et al. 1990)) we found concentrations of >100 ppbv in air that had blown across an active pahoehoe lava flow that was 1–2 km upwind (Table 1). Momentarily removing the NO to $NO_2$ converter dropped the signal to zero, confirming that the analyte was indeed NO. After several minutes of stable concentrations >100 ppbv, the concentrations returned to ambient values of <1 ppbv NO, presumably because of changes in wind direction. For comparison, the average summertime morning rush hour (NO + $NO_2$) concentrations in 20 major US urban areas is less than 100 ppb (NRC 1991).

During a follow-up field visit, we confirmed the presence of NO using two independent analytical methods: the LMA-3 analyzer, as before, and the Saltzman wet chemical method (Stern 1968). Both methods sampled from a single Teflon tube, with a thermocouple attached to the end for measuring air temperatures near the molten lava surface. Between the sampling tube and the analyzers we placed a base-impregnated filter to minimize interference by $SO_2$. Surface temperatures of the toe of the advancing pahoehoe flow that we sampled were in the range of 1000–1100 °C.

We used the continuous readout of the LMA-3 to search for NO sources by moving the sampling inlet among potential NO source regions. Our time-averaged samples thus contain contributions from a variety of molten and cooled areas on the active surface flow. At these sampling locations we found concentrations in the range of 1 to >170 ppbv NO (Table 1). The average values during two half-hour samples were 18 and 53 ppbv. Concentrations were highest when the inlet tube was closest to molten lava, especially in locations that had some protection from brisk surface winds. During the first two samples the averaged real time values from the LMA-3 were within 20% of the chemically-integrated Saltzman values (Table 1), which further confirmed the identity of the analyte as NO.

We also sampled fume coming through the collapsed roof (skylight) of an active lava tube. The tube fume, however, contained sufficient $SO_2$ to exceed the buffering capacity of our impregnated filter, which invalidated the Saltzman data for that sample. We encountered lower concentrations of NO directly downwind of the skylight than near surface flows, but we were unable to sample air inside the skylight opening because our Teflon inlet tube could not tolerate sustained temperatures above 300 °C. The highest tube fume concentrations came from the hottest air (~500 °C). Although measured concentrations varied considerably, sampling closer to molten lava always caused the NO concentration to rise, confirming that these hot surfaces are the source of the NO we observed.

## Discussion

Based on these observations it is clear that atmospheric dinitrogen is fixed thermally at the surface of molten lava, forming NO in concentrations of tens to greater than 170 ppbv. We expect that a‘a and sheet pahoehoe lava flows, because of their high surface areas, as well as vigorous fountaining events, should produce even higher ambient NO concentrations.

Since active surface flows can be located as much as several km away and hundreds of m below Pu‘u ‘O‘o vent, the main sources of NO and $SO_2$ can be spatially distinct from each other. This fact explains why our cloud water samples with high nitrate were not always accompanied by high sulfate concentrations.

A fraction of the NO produced at molten lava surfaces (limited by the ambient ozone concentration of 10–20 ppbv) should react with ozone within a few minutes, completely consuming the ozone and forming an equivalent concentration of $NO_2$. The remaining NO will be oxidized more slowly as additional ozone mixes into the plume. While some $NO_2$ may dry deposit to vegetation immediately downwind, the majority of the fixed nitrogen probably blows off the island before it can be converted to nitrate. During periods of changes in wind direction, however, the plume can be returned to the island after much of the conversion to nitrate has taken place. When this air is lifted to the ca 1200 m elevation of our sampling site, clouds often form, dissolving the resulting nitrate in cloudwater. The interception of this cloudwater by vegetation supplies more than half of the fixed nitrogen that supports plant growth in these developing ecosystems (Heath and Huebert 1999).

This is clearly a case in which the dynamics of an ecosystem are enhanced by a geological process. Such intimate linkages of biological and geological cycles demonstrate the importance of multi-disciplinary studies to understand the workings of the Earth system. While Kilauea volcano covers land with new lava flows, destroying vegetation and pushing ecosystems towards a developing, N limited state, it also fixes and thereby supplies plant-usable N. In geologic history, there have been large areas of the Earth that have been covered by basaltic lava flows (Coffin & Eldholm 1994) and could have been affected by similar processes. The importance of this process should be investigated in other volcanic situations.

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