Science of the Total Environment 514 (2015) 250–260

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Steep spatial gradients of volcanic and marine sulfur in Hawaiian rainfall and ecosystems

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HIGHLIGHTS

- Sources of sulfur in Hawaiian ecosystems were investigated via sulfur isotopes.
- Basalt, sea-salt, volcanic and marine biogenic emissions have distinct isotope ratios.
- Atmospheric deposition sources of sulfur dominated all but one site investigated.
- Steep gradients of marine vs. volcanic atmospheric deposition were found.
- Gradients occurred with distance to the coast and elevation.

ARTICLE INFO

Article history:
Received 8 September 2014
Received in revised form 14 January 2015
Accepted 1 February 2015
Available online xxxx

Editor: Eddy Y. Zeng

Keywords:
Atmospheric deposition
Coastal environment
Sea-salt
Sulfur isotopes
Volcanic emissions

ABSTRACT

Sulfur, a nutrient required by terrestrial ecosystems, is likely to be regulated by atmospheric processes in well-drained, upland settings because of its low concentration in most bedrock and generally poor retention by inorganic reactions within soils. Environmental controls on sulfur sources in unpolluted ecosystems have seldom been investigated in detail, even though the possibility of sulfur limiting primary production is much greater where atmospheric deposition of anthropogenic sulfur is low. Here we measure sulfur isotopic compositions of soils, vegetation and bulk atmospheric deposition from the Hawaiian Islands for the purpose of tracing sources of ecosystem sulfur. Hawaiian lava has a mantle-derived sulfur isotopic composition (δ^{34}S VCDT) of −0.8‰. Bulk deposition on the island of Maui had a δ^{34}S VCDT that varied temporally, spanned a range from +8.2 to +19.7‰, and reflected isotopic mixing from three sources: sea-salt (+21.1‰), marine biogenic emissions (+15.6‰), and volcanic emissions from active vents on Kilauea Volcano (+0.8‰). A straightforward, weathering-driven transition in ecosystem sulfur sources could be interpreted in the shift from relatively low (0.0 to +2.7‰) to relatively high (+17.8 to +19.3‰) soil δ^{34}S values along a 0.3 to 4100 ka soil age-gradient, and similar patterns in associated vegetation. However, sub-kilometer scale spatial variation in soil sulfur isotopic composition was found along soil transects assumed by age and mass balance to be dominated by atmospheric sulfur inputs. Soil sulfur isotopic compositions ranged from +8.1 to +20.3‰ and generally decreased with increasing elevation (0–2000 m), distance from the coast (0–12 km), and annual rainfall (180–5000 mm). Such trends reflect the spatial variation in marine versus volcanic inputs from atmospheric deposition. Broadly, these results illustrate how the sources and magnitude of atmospheric deposition can exert controls over ecosystem sulfur biogeochemistry across relatively small spatial scales.

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1. Introduction

Sulfur is essential for plant growth and therefore the functioning of ecosystems, but many aspects of sulfur cycling and biogeochemistry set it apart from other nutrients. Concentrations of sulfur in most bedrock parent materials of soils are low (Migdisov et al., 1983), and most primary mineral hosts are rapidly weathered (Doner and Lynn, 1989). Sulfate is the dominant inorganic form of sulfur in well-drained soils where reducing conditions are not sustained (Freney and Williams, 1983) and it is easily leached by excess water. As a result, in many well-drained, upland settings, ecosystem sulfur is dominantly supplied as sulfate in atmospheric deposition (Bern and Townsend, 2008; Hasan et al., 1970; Tisdale et al., 1986; Yi-Balan et al., 2014). Of the forms of sulfur retained in soils, organic forms usually dominate in surface soil (Freney and Williams, 1983; Houle

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http://dx.doi.org/10.1016/j.scitotenv.2015.02.001
0048-9697/Published by Elsevier B.V.

and Carignan, 1992; Tanikawa et al., 2014). Below the surface, sulfate can be retained by sorption (Harrison et al., 1989; Hasan et al., 1970) and less commonly by precipitation in secondary sulfate minerals (Delfosse et al., 2005; Mayer et al., 2001). Sulfur has six oxidation states, and inorganic sulfur compounds of oxidation states lower than +6 might occur in reducing microsites or during temporary reducing conditions but are generally considered negligible in well-drained, upland soils (Freney and Williams, 1983).

Sulfur availability can limit primary production, but this fact is both better recognized and more problematic in agriculture because of the export of sulfur by crop removal (Tisdale et al., 1986). Even in agriculture, the commonality of sulfur limitation is often masked by nitrogen and phosphorus fertilizers that contain incidental sulfur (Scherer, 2001). The patterns of sulfur limitation in agriculture correlate generally with atmospheric deposition rates (McGrath and Zhao, 1995). In coastal settings and locations downwind from anthropogenic activities like fossil fuel burning, sulfur limitation is less likely; inland areas and zones where greater rainfall promotes greater leaching are more likely to experience sulfur deficiency (Tisdale et al., 1986). In undisturbed ecosystems, atmospheric deposition in excess of demand should result in rapid 'flow-through' losses of sulfur (Likens et al., 2002), whereas if demand exceeds atmospheric deposition, more efficient recycling should result.

Much of the research on ecosystem sulfur sources and biogeochemistry has focused upon sites impacted by anthropogenic sulfur deposition and ecosystem acidification because this was a widespread problem, though it is now generally declining (Houle and Carignan, 1992; Likens and Bormann, 1974; Mitchell et al., 2001; Novák et al., 1996). Less research has been done on sulfur sources in relatively unpolluted ecosystems (Yi-Balan et al., 2014). In this study, sulfur isotopes are used to trace the mixing of natural sulfur sources of volcanic (basalt and vent emissions) and marine (sea-salt and biogenic) origin in Hawaiian atmospheric deposition and ecosystems. Bulk deposition from three sites on the island of Maui provides insight into the composition and variability of atmospheric deposition. The sulfur isotopic composition of lichens has been used to trace the composition of atmospheric deposition (Wadleigh, 2003) and two samples of lichen from the northern end of Hawaii Island are used for the same purpose here. Strontium isotopes are used to confirm lichen dependence on atmospheric inputs. Soil and vegetation from sites comprising an age-gradient, differing in volcanic substrate age from 0.3 to 4100 ka but otherwise similar, are used to examine the idea that progressive weathering and element leaching drives ecosystems to depend on atmospheric sulfur inputs. Transects are used to evaluate the importance of elevation, rainfall, and distance to the coast relative to ecosystem sulfur sources. Wide ranges in the sulfur isotopic composition of Hawaiian soils and crops have been observed (Mizota and Sasaki, 1996; Rodrigues et al., 2011), and there is potential for sulfur limitation in Hawaiian agriculture (Hasan et al., 1970; Hue et al., 1990). The results presented here shed light on the role of spatial gradients of atmospheric sulfur deposition on such patterns, and suggest that similar gradients exist in other coastal settings.

2. Materials and methods

2.1. Bulk deposition sampling

Bulk deposition (rainfall plus dry deposition) was collected at three locations on the island of Maui (Fig. 1). All three locations were co-located with U.S. Geological Survey (USGS) rain gaging sites. The first site was at West Wailuaiki Stream near Keanae (USGS 16518000), located at 20.81436°N, 156.14297°W at 472 m asl and about 3.0 km from the coast. West Wailuaiki is on the wetter windward side of Maui and averages 5000 mm of annual rainfall. The second site was at Oheo Gulch at a dam near Kipahulu (USGS 16501200), located at 20.66837°N, 156.05222°W, 128 m asl, and about 1.2 km from the coast. Oheo Gulch is on the southeastern corner of Maui and averages 2800 mm of annual rainfall. The third site was at Kepuni Gulch (USGS 203721156151601) located at 20.61950°N, 156.25189°W, 226 m asl, and about 1.5 km from the coast. Kepuni Gulch is on the dry, leeward side of Maui and averages 530 mm of annual rainfall.

Bulk deposition was collected by means of plastic funnels covered with nylon screening material connected via plastic tubing to polyethylene reservoirs. The reservoirs were protected from sunlight inside stream gage equipment boxes. All collector materials were soaked overnight in, and then thoroughly rinsed with, 18 MΩ/cm water. Samples were collected from the reservoirs in acid-washed, 18 MΩ/cm water-rinsed, polyethylene bottles approximately once every two months from September 2007 to December 2009. Samples were shipped to Denver, Colorado and then kept frozen until analysis.

2.2. Soil and vegetation sampling

Soil samples analyzed for this study were obtained from previous studies' archives or by resampling sites from those studies. The soil samples fall into two categories. First is a series of soil depth profiles collected from substrates spanning a gradient of ages (0.3, 20, 150, 1400, 4100 ka), and therefore time for soil development, along the island chain (Fig. 1; Table 1). At each site the soils are derived from basaltic volcanic material with a reasonably similar chemistry, are colonized by similar vegetation dominated by *Metrosideros polymorpha*, have similar climate with approximately 2500 mm annual rainfall, and have low gradient topography that minimizes gains or losses by erosion (Vitousek et al., 1997). Two samples of *M. polymorpha* leaves from canopy emergent trees were collected at each site.

The second category consists of shallow soil collected along transects of elevation, rainfall and distance from the coast, but developed on lava flows of a common age (Fig. 1; Table 1). In most cases, a single 0–30 cm-depth integrated sample was taken, but in some cases samples representing one or more A horizons from similar depths were analyzed. From the Kohala Peninsula on the northern end of the island of Hawaii, 22 samples were analyzed from two transects on Hawi volcanics, assigned an age of approximately 150 ka (Vitousek et al., 2004). Supplementing those are samples from another three sites on the Hawi volcanics, assigned an age of 170 ka (Chadwick et al., 2003). Together, the transects span elevations from 160 to 1150 m, annual rainfall from 180 to 2500 mm, and distances from the coast of 1.7 to 9.4 km. Also from the island of Hawaii, 21 soil samples from two transects on the 350 ka Pololu volcanics were analyzed (Vitousek et al., 2004). Together, the transects span elevations from 13 to 569 m, annual rainfall from 626 to 1829 mm, and distances from the coast of 0.1 to 7.0 km. Estimates of annual rainfall come from Giambelluca et al. (2013). To expand the range covered by these transects, we analyzed two samples of soil (12–20 and 38–43 cm) from another site on the Pololu volcanics at 1800 m elevation, 3500 mm annual rainfall, and at 11.6 km from the coast (Marin-Spiotta et al., 2011). In addition to the soil, samples of the epiphytic cyanolichens *Pseudocyphellaria crocata* and *Flavoparmelia caperata* collected from the 3500 mm rainfall site in March of 2008 were also analyzed.

Soils from transects on the south flank of Haleakala Volcano on the island of Maui were also analyzed (Fig. 1; Table 1). The samples were initially collected as part of an investigation of environmental constraints on Polynesian agriculture (Kirch et al., 2004). From 53 ka flows of the Hana volcanics (Sherrod et al., 2003), nine samples spanning an elevation range from 152 to 790 m, annual rainfall from 545 to 780 mm, and distance from the coast of 0.7 to 4.0 km were analyzed. From 226 ka flows of the Kula volcanics (Sherrod et al., 2003), 13 samples spanning an elevation range from 154 to 2126 m, annual rainfall from 757 to 885 mm, and distances from the coast of 0.7 to 8.3 km were analyzed.

Finally, soils from three sites on the 5000 ka Na'Pali member of the Waimea Canyon Basalt on the island of Kauai were analyzed (Chadwick