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# Characterization of Pyroclastic Deposits and Pre-eruptive Soils following the 2008 Eruption of Kasatochi Island Volcano, Alaska

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#### Abstract

The 7-8 August 2008 eruption of Kasatochi Island volcano blanketed the island in newly generated pyroclastic deposits and deposited ash into the ocean and onto nearby islands. Concentrations of water soluble Fe, Cu, and Zn determined from a 1:20 deionized water leachate of the ash were sufficient to provide short-term fertilization of the surface ocean. The 2008 pyroclastic deposits were thicker in concavities at bases of steeper slopes and thinner on steep slopes and ridge crests. By summer 2009, secondary erosion had exposed the pre-eruption soils along gulley walls and in gully bottoms on the southern and eastern slopes, respectively. Topographic and microtopographic position altered the depositional patterns of the pyroclastic flows and resulted in pre-eruption soils being buried by as little as 1 m of ash. The different erosion patterns gave rise to three surfaces on which future ecosystems will likely develop: largely pre-eruptive soils; fresh pyroclastic deposits influenced by shallowly buried, pre-eruptive soil; and thick (>1 m) pyroclastic deposits. As expected, the chemical composition differed between the pyroclastic deposits and the pre-eruptive soils. Pre-eruptive soils hold stocks of C and N important for establishing biota that are lacking in the fresh pyroclastic deposits. The pyroclastic deposits are a source for P and K but have negligible nutrient holding capacity, making these elements vulnerable to leaching loss. Consequently, the preeruption soils may also represent an important long-term P and K source.

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# Introduction

The Kasatochi Island volcano erupted on 7–8 August 2008. The eruption produced an aerosol cloud rich in sulfur (Martinsson et al., 2009), deposited pyroclastic fall (ash) into the ocean and onto the islands southwest of Kasatochi, and covered the island in coarse and fine pyroclastic deposits (Scott et al., 2010 [this issue]). Reconnaissance observations in late August 2008 confirmed that pyroclastic-flow deposits completely covered the island and extended the shoreline seaward by about 400 m (Scott et al., 2010 [this issue]). It appeared that none of the pre-eruptive terrestrial ecosystem had survived. In late summer 2008 a large-scale phytoplankton bloom in the NE Pacific Ocean was reported and the release of bio-available iron from the pyroclastic fall produced during the eruption of Kasatochi is suspected to have contributed to this event (Langmann et al., 2010).

The fine particles are an important sink for volatile sulfate, halogens, and metals that are thus removed from the atmosphere during volcanic eruptions (Mather and Pyle, 2003; Delmelle et al., 2007). The sulfate, halogens, and metals can be released when the particles are exposed to water. These water-soluble constituents are readily available for biotic uptake and may be innocuous, injurious, or advantageous to the ecosystem (Hinkley and Smith, 1987; Cronin et al., 1998). In the short term, bio-available trace metals from volcanic ash may stimulate phytoplankton growth in the surface ocean (Duggen et al., 2007, 2009), affect plant fertility (Cronin et al., 1998), and pose hazards to terrestrial and aquatic ecosystems (Cronin et al., 1998; Witham et al., 2005).

The long-term effects on and recovery of the terrestrial ecosystem following major eruptions depend both on the characteristics of the newly deposited substrate and on remnants of former ecosystem (legacies) that survived (Dale et al., 2005). In the terrestrial system, the fresh pyroclastic deposits are parent material from which future soils will develop, yet these deposits may lack essential nutrients for plant re-establishment (Zobel and Antos, 1997). In contrast, pre-eruption soils that were not buried or are exposed during erosion can be an important pre-eruption ecosystem legacy. Such soils can provide important nutrients, seeds, and roots for plant regeneration (Turner et al., 1998; Dale et al., 2005; Swanson and Major, 2005).

In 2009, the U.S. Geological Survey (USGS), the U.S. Fish and Wildlife Service (USFWS), and the University of Alaska, Fairbanks, initiated an ecosystem study to document the acute, short-term impacts of the 2008 Kasatochi eruption and establish a quantitative baseline for future comparisons. As part of this effort we present (1) a field assessment of the preservation of preeruption soils and the environments in which they are preserved and exposed, and (2) an initial characterization of pyroclastic deposits and the buried pre-eruption soils.

#### Materials and Methods

SITES AND SAMPLING

During a brief visit to Kasatochi Island in late August 2008, bulk grab samples of the newly deposited pyroclastic surge and fall deposits were collected from the north and west sides of the island (Fig. 1). At this time, only about 1 to 2 m of the pyroclastic sequence was exposed and the deposits were sampled from within

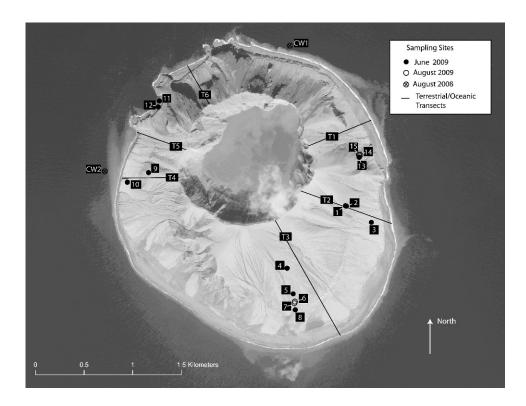


FIGURE 1. Site locations for the 2008 and 2009 samples. Not shown are the locations of a fishing boat from which a sample of the 2008 tephra fall was taken or the grab sample collected near site 13 by William Scott. The boat was approximately 13 km southwest of the island. The sample was collected the following day when the boat returned to port. The base image is from April 2009. Erosion of pyroclastic deposits between 2008 and 2009 place the 2008 sites in the water.

the upper 1 m of the pyroclastic deposits (Christopher Waythomas, written communication). In addition to these on-island samples, a pyroclastic (ash) fall sample was obtained from a fishing boat that was approximately 13 km southwest of the island on 7 August when it experienced heavy fall from the eruption. About a day later when the boat returned to harbor, the sample was collected from the boat's deck by its owner and sent to the Alaska Volcano Observatory. Hereafter these samples will be referred to as the 2008 samples.

In 2009, six transect lines were delineated to integrate the oceanic, intertidal, and terrestrial components of the study. During two separate field efforts (June and August 2009), sites were selected on or near three of these transect lines (T2, T3, and T4; Fig. 1). Along these transects, the site locations were subject to access constraints. Additional characterization sites (14 and 15) were established on the east side of the island (Fig. 1). At the characterization sites, pits of approximately 1.5 m  $\times$  1 m wide  $\times$ 1 m deep were hand dug unless an impenetrable layer was encountered above 1 m depth; the exposed strata were described and cored for bulk density (BD) and sampled for chemical analysis according to USDA procedure (Survey Staff, 1996; Schoeneberger et al., 2002). The samples taken at sites 11 and 12 were grab samples collected from the base of the eroding pyroclastic deposits that now cover what was an auklet nesting colony. This deposit corresponds to the pyroclastic material from early in the eruption (Scott et al., 2010 [this issue]). A displaced organic soil fragment was collected on the east side of the island (site 13), and an additional grab sample of the early pyroclastic deposits was collected by William Scott from the island's east side near site 13.

## SAMPLE ANALYSIS

The 2008 samples were sent to the USGS Mineral Resource laboratories in Denver, Colorado, where they were dried and sieved to <2 mm through nylon sieves. Aqueous extractions were conducted on the <2 mm fraction of the 2008 samples using the USGS Field Leach Test (FLT; Hageman, 2007). For this

procedure, we followed the prescribed 1:20 leaching solid:leachant ratio using 6.25 g sample:125 mL deionized water with a 5 minute shaking time. After settling for 10 minutes, unfiltered aliquots of the leachate were analyzed for pH and specific conductance. For each sample, aliquots of the filtrate were collected and preserved for anionic and cationic composition analysis. Samples for cationic analysis by inductively coupled mass spectrometry (ICP-MS) were preserved by acidification with ultra-pure nitric acid (HNO<sub>3</sub>). Filtered, un-acidified aliquots for anion and alkalinity analysis were preserved by refrigeration. Analysis for Cl<sup>-</sup>, F<sup>-</sup>, NO<sup>-</sup><sub>3</sub> and SO<sub>4</sub><sup>2-</sup> was conducted using ion chromatography (IC).

The 2009 pyroclastic deposit and pre-eruption soil samples were transported back to the laboratory and refrigerated before air-drying for analysis. Soils and pyroclastic deposit samples were analyzed by the Palmer Plant and Soils Analysis Laboratory of the University of Alaska Fairbanks. All analyses were performed according to the USDA-NRCS procedure (Soil Survey Laboratory Staff, 1996) unless specified. Cation exchange capacity was determined by leaching the soil with neutral 1 M ammonium acetate solution with NH<sub>4</sub><sup>+</sup> retained by the soil determined by steam distillation and titration. Extractable cations (K, Ca, Mg, and Na) were extracted with neutral 1 M ammonium acetate and cation concentrations quantified by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). Total C and N were determined by high-temperature ignition using a LECO CHNanalyzer. Total P and S were determined by ICP-AES on perchloric acid digests of samples. Plant-available forms of the three main macronutrients were obtained on air-dried samples and quantified colorimetrically for N (extracted with 2 M KCl), P (Mehlich-3), and by ICP-AES for K (1 M ammonium acetate) (Keeney and Nelson, 1982; Michaelson and Ping, 1986; Soil Survey Laboratory Staff, 1996). The N, P, and K extracted by the 2 M KCl, Mehlich-3, and 1 M ammonium acetate extracts, respectively, are considered to be indices of plant-available nutrients. Stocks of available nutrients for a horizon were estimated on an areal basis for pre-eruption soils and pyroclastic deposits by: (% element concentration/100) × BD g cm<sup>-3</sup> soil

horizon  $\times$  cm thickness of horizon  $\times$  10<sup>4</sup> = g available N, P, or K m<sup>-2</sup>. The stocks of the individual horizons then were summed for the pyroclastic deposits or for those of the residual soil horizons observed in sampling pits. The pH was determined on a saturated paste. BD was determined by dividing the 105 °C ovendried weight of core samples by the volume (cm<sup>3</sup>) of the core.

#### STATISTICAL ANALYSIS

Summary statistics were calculated using Minitab. Correlations among the major ions determined in the 2008 leachates were performed using the Kendal Tau macro for Minitab available at http://www.minitab.com. Comparison of medians between the group of all pyroclastic samples (N=66) and the group of all preeruption soil samples (N=20) collected in 2009 were performed using the Mann-Whitney test available in Minitab. For constituents with censored values, statistical analyses (median and Mann-Whitney tests) were calculated and performed with procedures for censored data (Helsel, 2005) using the macros for Minitab available at http://www.practicalstats.com/nada/.

# **Results**

#### SITE OBSERVATIONS

Pyroclastic deposits from the 2008 eruption dominated the pits excavated at the characterization sites along the southeastern (T2) and western (T4) transects and at sites 4, 5, and 7 along the southern (T3) transect (Fig. 1). Site 7 (Fig. 2A) is a typical substrate profile found in the characterization pits at these sites. These profiles were characterized by varying thickness of finegrained pyroclastic deposits (horizons C1 and C2, seen in the upper 40 cm of Fig. 2A) overlying coarser deposits (horizons C3–C9). The transition between the upper finer and lower coarser deposits presented a barrier to infiltration and resulted in saturation or supersaturation of the material between 5 and 30 cm.

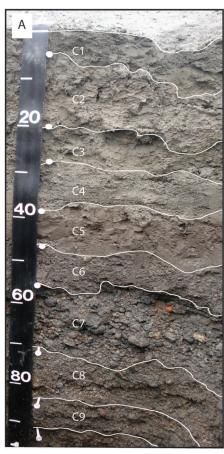
In June 2009, exposures of in-place, pre-eruption soil were observed along the former sea bluff on the south side of the island (site 8; Fig. 2B), while displaced organic soil fragments were found at the base of the cliffs west of the south bluff (not sampled) and on the slope on the east side of the island (site 13). By August 2009, gully erosion had exposed additional pre-eruption soil surfaces in the gully walls along the south transect. A trench dug perpendicular to an erosion gully exposed pre-eruption soils along its profile (site 6; Fig. 2C). On the eastern slopes, erosion had removed the overlying pyroclastic deposits and exposed, but not yet bisected, the pre-eruptive soils (site 14), while several centimeters of pyroclastic deposits (horizons C1 and C2) still covered these surfaces in other locations (site 15; Fig. 2D). The pre-eruption soils at three sites were buried <1 m by fine pyroclastic material (Figs. 2B-2C; sites 6, 8, and 15) and the coarser grain material found in the lower profiles of the pits consisting only of pyroclastic deposits (Fig. 2A) was absent in profiles with pre-eruptive soils. Although the sites received varying amounts of eruptive deposits, general observations can be made regarding the pre-eruptive soils. The pre-eruption soils developed in fine tephra (loamy to sandy loam materials) deposits of about 40 to 60 cm and about 10 cm on southern (Figs. 2B, 2C) and eastern slopes (Fig. 2D), respectively. Pre-eruption soils showed well-developed Bw horizons (accumulation of sesquioxides) to 80 cm on southern slopes (sites 6 and 8; Figs. 2b, 2c), compared to only 20 cm on eastern slopes (sites 14 and 15; Fig. 2D). Depths of finer-grained pyroclastic deposits from this eruption were consistent with the relative thickness of the older surfaces.

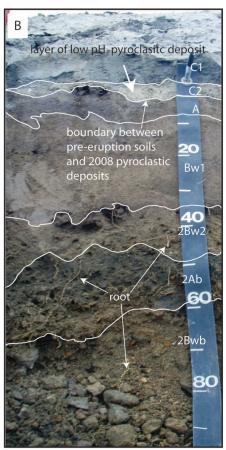
There were several modifications in the surface morphology of the pre-eruptive surface horizons due to both the character and erosive force of the new deposition. The organic horizons of the pre-eruptive soils were observed in pit profiles at sites 6, 14, and 15, but not at site 8. The organic horizons were about 2–8 cm thick and were composed of highly decomposed (sapric; horizon Oa; Fig. 2D), fibrous and partially decomposed (hemic) material (horizon Oi/Oe; Fig. 2D). Where present, the fibrous surface layer was obviously compressed by the new deposits on top (Fig. 2D). This organic horizon was probably a few centimeters thicker prior to burial. Being more fibrous in nature, the upper few centimeters of the organic horizons were infiltrated by the new pyroclastic deposits. Fine sand, silt, and clay-sized material filled the upper organic horizon on all surfaces, and even rock fragments were occasionally found embedded in the buried organic horizons at sites 14 and 15. The pre-eruptive organic horizon was broken or missing in some areas due to the erosive force of the new deposition and post-eruption erosion (Figs. 2B-2D). Occasional pieces of the pre-eruption organic mat were found mixed and deposited with pyroclastic material on lower slopes and alluvial fans. The pre-eruptive soil surface was relatively smooth along the former south-bluff exposure (Fig. 2B), and wavy on the steeper slope positions (Figs. 2C-2D).

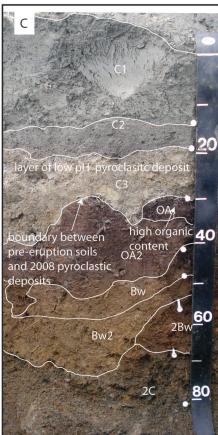
# CHEMICAL CHARACTERISTICS: PYROCLASTIC DEPOSITS AND PRE-ERUPTION SOILS

Water soluble constituents are generally considered readily bioavailable, and aqueous extractions contain the water-soluble constituents that may leach from the pyroclastic deposits following an eruption. The leachate pH of the 2008 samples ranged from mildly acidic to alkaline (pH 6-8.2; Table 1). As expected in volcanic ash leachates,  $SO_4^{\ 2^-}$  and  $Cl^-$  were the most abundant anions. The pH and concentrations of many elements in the leachates of the collected-wet island samples were higher than those in the leachate of the collected-dry boat sample, suggesting chemical reactions between the island sample and rainwater. The interaction resulted in the neutralization of sorbed/precipitated acid species, hydrolysis of alumino-silicates in the tephra, and release of elements such as Al, Ca, K, Mg, Na, and Si. Copper, Ni, Mn, Se, and Zn were detected in all leachates. Iron was detected in one leachate. Although the 2008 sample set is small, strong correlations were found between sulfate and both the alkali (Na, K, Li) and alkali-earth (Ca, Mg, Sr) metals (Kendels Tau range 0.8–1, corresponding p-value 0.09–0.03). Strong correlation among these elements is common in volcanic ash leachates and indicates that the sulfate is present as alkali metal and/or alkali earth salts (Smith et al., 1983). A pervasive white precipitate was noted on the surface of the pyroclastic deposits, especially at the footslope terminus of deposits near the new beach bluffs in both 2008 and 2009. The 2008 leachates from the island samples were near or above saturation with gypsum (ion actively product [IAP]/ gypsum solubility [K<sub>sp</sub>] range of 0.9-4.5), suggesting that the gypsum may be precipitating.

Pyroclastic samples collected from the characterization sites in 2009 ranged from extremely acidic to slightly alkaline (pH 3.50–7.5; Table 2). The extremely acidic conditions in the 2009 samples were found in the samples of the pyroclastic material from early in the eruption (sites 11, 12, and grab sample near site 13) and the pyroclastic deposits immediately above the pre-eruptive soil surface (pH 3.50–4.07). The median bulk density, pH, and total-base cation (TBC) of the pyroclastic samples are significantly higher than those of the pre-eruptive soils (Table 2). The TBC







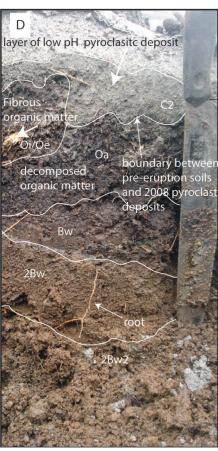


FIGURE 2. Field photos of selected 2009 characterization pits. (A) Horizon sequence for a profile without shallowly (<1 m) buried soils. (B-D) Profiles for pits in which shallowly buried soils were found. White lines demarcate distinctive horizons with differences in either color, texture, or material (Shoeneberger et al., 2002). At all sites with pre-eruptive soils in the profile, roots were seen throughout the soil sequence. (A) Typical sequence of the 2008 pyroclastic deposits found in pits without shallowly buried pre-eruption soils in the profile. Contact between the fine pyroclastic material and the coarse material below is seen at about 30 cm at this site (site 7). (B) Sequence of the 2008 pyroclastic deposits overlying the pre-eruptive soil along the former sea bluff, site 8. This site had a relatively smooth boundary between overlaying 2008 pyroclastic deposits and pre-eruptive soils. No organic horizons were identified at this site. Note that the zero mark of this tape is set at the boundary between the 2008 pyroclastic deposits and the underlying soils. The depth of the pyroclastic deposits was 11 cm. (C) Sequence of the 2008 pyroclastic deposits overlying the pre-eruptive soil along the south slope, site 6. Boundary with the overlying pyroclastic material is wavy; a discontinuous organic horizon is seen between 30 and 35 cm. (D) Sequence of the 2008 pyroclastic deposits overlying the pre-eruptive soils on the eastern slope, site 15. Fibrous and decomposed organic horizons are visible in the profile. The knife blade from shank to point of burial is 16.5 cm.

TABLE 1

Composition of the water-soluble constituents in a 1:20 mixture of Kasatochi Island pyroclastic material to distilled water for samples collected in August 2008 from Kasatochi Island (shaded) and fishing boat (unshaded).

|   | Boat    | Kasatochi Island samples      |                     |          |  |  |  |  |
|---|---------|-------------------------------|---------------------|----------|--|--|--|--|
| Map No.   | sample  | CW2                           | CW1                 | CW1      |  |  |  |  |
| Sample depth  | Surface | Surface                       | Upper 10 cm         | 50–60 cm |  |  |  |  |
| Field condition   | Dry     | Wet/clayey                    | Moist, agglomeratic | Moist    |  |  |  |  |
| Deposit type  | Fall    | Surge and Fall Surge and Fall |                     | Surge    |  |  |  |  |
| pH  | 6       | 7.8                           | 7.8                 |          |  |  |  |  |
| (the following concentrations are in $mg\ kg^{-1}$ ash) |         |                               |                     |          |  |  |  |  |
| Cl  | 1430    | 4308                          | 2322                | 1200     |  |  |  |  |
| F   | <1.6    | <1.6                          | 6.7                 | <1.6     |  |  |  |  |
| $NO_3$  | 16      | 54                            | 28                  | 6        |  |  |  |  |
| SO <sub>4</sub> (IC)                                    | 3482    | 11274                         | 7536                |          |  |  |  |  |
| Ca  | 1572    | 4820 2700                     |                     | 2060     |  |  |  |  |
| K   | 197     | 506                           | 320                 | 306      |  |  |  |  |
| Mg  | 104     | 332                           | 230                 | 79       |  |  |  |  |
| Na  | 650     | NA                            | 1288                | 788      |  |  |  |  |
| Al  | < 0.04  | 0.16                          | 0.23                | 0.18     |  |  |  |  |
| Co  | 0.06    | 0.03                          | 0.007               | 0.004    |  |  |  |  |
| Cu  | 0.10    | 0.07                          | 0.02                | 0.04     |  |  |  |  |
| Fe  | <1      | 3.62                          | <1                  | <1       |  |  |  |  |
| Ni  | 0.13    | 0.42                          | 0.07                | 0.05     |  |  |  |  |
| Se  | 0.04    | 0.13                          | 0.12                | 0.13     |  |  |  |  |
| $SiO_2$   | <4      | 16                            | 26                  | 10       |  |  |  |  |
| Zn  | 0.41    | 0.13                          | 0.02                | 0.08     |  |  |  |  |

concentration of both the pyroclastic deposits and the soils is dominated by calcium (Table 2). In the pyroclastic material, TBC concentration ranged from 5.4 to 44 cmole  $\rm kg^{-1}$  (median TBC = 25.2 cmole  $\rm kg^{-1}$ ), while the cation exchange capacity (CEC) ranged from 0.9 to 10 cmole  $\rm kg^{-1}$  (median CEC = 6.2 cmole  $\rm kg^{-1}$ ). The TBC exceeds the CEC, indicating that there is an excess of

base-cations relative to the number of exchange sites available. Calculation of the excess base-cations within the pyroclastic deposits indicates that between 33 and 92% of the base-cations measured were present in solution and not on exchange sites. Excess TBC was not found in the pre-eruption soils. Median concentrations of Ca, K, and S were significantly higher in the pyroclastic samples, while median Na, C, available P, and NH<sub>4</sub>-N were significantly higher in pre-eruption soils (Table 2). Available N, and total C and N stocks were higher in the pre-eruptive soils than the overlaying pyroclastic deposits (Table 3). Available N and P stocks in the pyroclastic deposits ranged from <0.01 to  $0.77 \text{ g N m}^{-2}$ , and from  $0.17 \text{ to } 3.78 \text{ g P m}^{-2}$ , while available N and P in the pre-eruption soils contained 1.38 to 5.86 g N m<sup>-2</sup> and 2.18 to 6.00 g P m<sup>-2</sup>, respectively. Total C and N stocks of the pyroclastics ranged from 0.13 to 0.50 kg m<sup>-2</sup> and from <0.01 to 0.01 kg m<sup>-2</sup>, respectively. The pyroclastic deposits contained higher amounts of total S compared to underlying soils and were higher in available K and total P at sites 6 and 15. Available K stocks in the pyroclastic deposits ranged from 31 to 79 g m<sup>-2</sup>, total P from 0.064 to 0.187 kg  $\mathrm{m}^{-2}$ , and total S from 1.20 to 2.82 kg  $\mathrm{m}^{-2}$ compared to soil stocks of 8–138 kg m $^{-2}$ , 0.011–0.136 kg m $^{-2}$ , and  $0.04-0.56 \text{ kg m}^{-2}$ , respectively.

# **Discussion**

#### BURIAL AND EXPOSURE OF PRE-ERUPTION SOILS

Spatial patterns are important to successional sequences following disturbances (Turner et al., 1998; Dale et al., 2005), and both deposition heterogeneity and secondary erosion contribute to the mosaic of post-eruption surfaces (Turner et al., 1998; Swanson and Major, 2005). In volcanic eruptions the accumulation of pyroclastic surge and flow deposits is typically less, while post-eruption erosion is more on ridges and steeper slopes than on flatter slopes and hollows (Wilson and Houghton, 2000; Swanson

TABLE 2
Summary statistics for pyroclastic and pre-eruption soil samples collected in June and August, 2009. The p-values for the Mann-Whitney test for significant difference between the median of the pyroclastic and soil groups are also given. Shaded cells indicate the properties for which the median of the pyroclastic deposits is significantly greater than the pre-eruption soils.

|                              |                            | Pyroclastic $N = 66$ |        |       |            | <i>p</i> -value  Mann-Whitney |      |             |
|------------------------------|----------------------------|----------------------|--------|-------|------------|-------------------------------|------|-------------|
|                              |                            |                      |        |       |            |                               |      |             |
|                              |                            | Range                | Median | IQR** | Range      | Median                        | IQR  | comparisons |
| bulk density *               |                            | 1.53-1.78            | 1.5    | 0.25  | 0.13-1.39  | 0.87                          | 1.04 | 0.00        |
| pH                           |                            | 3.5-7.5              | 6.9    | 0.35  | 4.0-6.0    | 5.13                          | 0.83 | 0.00        |
| CEC                          | cmole kg <sup>-1</sup> *** | 0.9-10               | 6.2    | 4.7   | 0.6-35     | 5.6                           | 16.1 | 0.79        |
| Ca                           | cmole kg <sup>-1</sup>     | 4.0-42.3             | 23.8   | 14.6  | 0.5-21.2   | 4.1                           | 13   | 0.00        |
| K                            | cmole kg <sup>-1</sup>     | 0.17 - 1.1           | 0.49   | 0.3   | 0.05-1.7   | 0.24                          | 0.3  | 0.00        |
| Mg                           | cmole kg <sup>-1</sup>     | 0.28-3.4             | 0.81   | 0.44  | 0.23 - 8.2 | 0.67                          | 1.23 | 0.38        |
| Na                           | cmole kg <sup>-1</sup>     | 0.19-11              | 0.28   | 0.29  | 0.25-6.1   | 0.53                          | 0.7  | 0.00        |
| Total base cations           | cmole kg <sup>-1</sup>     | 5.4-44               | 25.2   | 13.6  | 1.2-33     | 5.8                           | 15   | 0.00        |
| total C                      | $\rm g~kg^{-1}$            | 0.2 - 1.9            | 0.8    | 0.6   | 0.9-196    | 11.2                          | 72.4 | 0.00        |
| total P                      | $\rm g~kg^{-1}$            | 0.2 - 0.4            | 0.4    | 0.1   | 0.2-0.8    | 0.3                           | 0.4  | 0.44        |
| total S                      | $\rm g~kg^{-1}$            | 1.8-15.1             | 7.5    | 4.9   | 0.5-9.8    | 0.9                           | 2.5  | 0.00        |
| total N                      | $\rm g~kg^{-1}$            | < 0.1-0.1            | < 0.1  | _     | < 0.1-13.4 | 0.8                           | 0.39 | 0.00        |
| available P                  | ${\rm mg~kg^{-1}}$         | <1.0-37              | <1     | _     | 1.0-170    | 16.6                          | 50.5 | 0.00        |
| available NH <sub>4</sub> -N | mg kg <sup>-1</sup>        | <1.0-9.0             | <1     | _     | <1.0-196   | 6.1                           | 10.3 | 0.00        |
| available NO <sub>3</sub> -N | $mg kg^{-1}$               | <1.0                 | _      | _     | <1-19.5    | _                             | _    | _           |

<sup>\*</sup> The number of bulk density samples are 38 and 16 for pyroclastic samples and soils, respectively.

<sup>\*\*</sup> Interquartile range.

<sup>\*\*\*</sup> cmole kg<sup>-1</sup> is an SI concentration unit typically used in reporting total base cation concentrations. Conversion to mg/kg is done by (cmole kg<sup>-1</sup>) \* (atomic weight/equivalents of charge) \* 10.

<sup>-</sup>Not calculated due to the extent of censoring of the data.

TABLE 3

Nutrient stocks in pyroclastic and pre-eruptive soils. Stocks of available (N—nitrogen, P—phosphorus, and K—potassium), and total nutrients (C—carbon, N—nitrogen, P—phosphorus, and S—sulfur). For site 14 the pre-eruptive soil was exposed and no recent pyroclastic material was present so stocks are calculated only for pre-eruptive soils.

| Site Horizon <sup>†</sup> | Material <sup>††</sup> | Horizon depth (cm) | Available                           |                           |     | Total |            |                        |      |  |
|---------------------------|------------------------|--------------------|-------------------------------------|---------------------------|-----|-------|------------|------------------------|------|--|
|                           |                        |                    | N                                   | P<br>(g m <sup>-2</sup> ) | K   | С     | N<br>(kg r | P<br>n <sup>-2</sup> ) | S    |  |
| site 6 <sup>†††</sup>     |                        |                    |                                     |                           |     |       |            |                        |      |  |
| C1                        | Pyroclastic            | 0-14               | < 0.01                              | 0.96                      | 57  | 0.22  | < 0.01     | 0.096                  | 1.99 |  |
| C2                        | Pyroclastic            | 14-19              | < 0.01                              | 0.68                      | 5   | 0.14  | 0.01       | 0.030                  | 0.23 |  |
| C3                        | Pyroclastic            | 19-30              | 0.77                                | 1.07                      | 17  | 0.14  | < 0.01     | 0.061                  | 0.60 |  |
| OA1                       | Soil                   | 30-32              | 0.36                                | 0.39                      | 1   | 0.52  | 0.04       | 0.003                  | 0.01 |  |
| OA2                       | Soil                   | 32-40              | 2.06                                | 1.79                      | 7   | 1.96  | 0.11       | 0.008                  | 0.03 |  |
| Total                     | Pyroclastic            | 30                 | 0.77                                | 2.71                      | 79  | 0.50  | 0.01       | 0.187                  | 2.82 |  |
| Total                     | Soil                   | 10                 | 2.42                                | 2.18                      | 8   | 2.48  | 0.15       | 0.011                  | 0.04 |  |
| site 8                    |                        |                    |                                     |                           |     |       |            |                        |      |  |
| C1                        | Pyroclastic            | 0–7                | < 0.01                              | < 0.01                    | 42  | 0.05  | < 0.01     | 0.045                  | 1.12 |  |
| C2                        | Pyroclastic            | 7–11               | 0.04                                | 0.17                      | 6   | 0.08  | < 0.01     | 0.019                  | 0.08 |  |
| A                         | Soil                   | 11–14              | 0.75                                | 0.52                      | 7   | 0.52  | 0.04       | 0.009                  | 0.03 |  |
| Bw1                       | Soil                   | 14-44              | 3.66                                | 0.34                      | 56  | 4.43  | 0.3        | 0.067                  | 0.30 |  |
| 2Bw2                      | Soil                   | 44–58              | 1.15                                | 0.19                      | 37  | 2.08  | 0.12       | 0.045                  | 0.15 |  |
| 2Ab                       | Soil                   | 58-69              | 0.30                                | 0.45                      | 11  | 0.53  | < 0.01     | 0.030                  | 0.08 |  |
| 2Bwb                      | Soil                   | 69–91              | < 0.01                              | 1.21                      | 27  | 1.21  | < 0.01     | 0.060                  | 0.24 |  |
| Total                     | Pyroclastic            | 11                 | 0.04                                | 0.17                      | 48  | 0.13  | < 0.01     | 0.064                  | 1.20 |  |
| Total                     | Soil                   | 80                 | 5.86                                | 2.71                      | 138 | 8.77  | 0.46       | 0.211                  | 0.56 |  |
| site 14                   |                        |                    |                                     |                           |     |       |            |                        |      |  |
| Oa                        | Soil                   | 0–2                | 0.2                                 | 0.60                      | 1   | 1.00  | 0.06       | 0.004                  | 0.01 |  |
| Oi/Oe                     | Soil                   | 2–5                | 0.22                                | 0.84                      | 2   | 1.00  | 0.05       | 0.008                  | 0.13 |  |
| Bw                        | Soil                   | 5–8                | 0.25                                | 0.71                      | 3   | 0.41  | 0.01       | 0.008                  | 0.03 |  |
| 2Bw                       | Soil                   | 8-20               | 0.50                                | 1.67                      | 7   | 0.90  | < 0.01     | 0.033                  | 0.12 |  |
| 2Bw2                      | Soil                   | 20-50              | 0.83                                | 2.09                      | 13  | 1.34  | 0.04       | 0.083                  | 0.25 |  |
| Total                     | Pyroclastic            | 0                  | $NP^{\dagger\dagger\dagger\dagger}$ | NP                        | NP  | NP    | NP         | NP                     | NP   |  |
| Total                     | Soil                   | 50                 | 2.01                                | 5.91                      | 25  | 4.65  | 0.17       | 0.136                  | 0.54 |  |
| site 15                   |                        |                    |                                     |                           |     |       |            |                        |      |  |
| C1                        | Pyroclastic            | 0-30               | < 0.01                              | 1.20                      | 19  | 0.19  | < 0.01     | 0.069                  | 1.32 |  |
| C2                        | Pyroclastic            | 30-60              | < 0.01                              | 2.58                      | 12  | 0.21  | < 0.01     | 0.069                  | 0.41 |  |
| Oi/Oe                     | Soil                   | 60-62              | 0.09                                | 0.40                      | 1   | 0.36  | 0.02       | 0.005                  | 0.08 |  |
| Oa                        | Soil                   | 62–68              | 0.32                                | 0.87                      | 1   | 2.32  | 0.16       | 0.01                   | 0.04 |  |
| Bw                        | Soil                   | 68-74              | 0.33                                | 0.74                      | 2   | 0.31  | 0.02       | 0.011                  | 0.03 |  |
| 2Bw                       | Soil                   | 74–84              | 0.36                                | 1.44                      | 6   | 0.49  | 0.03       | 0.027                  | 0.08 |  |
| 2Bw2                      | Soil                   | 84-101             | 0.28                                | 2.55                      | 12  | 0.27  | < 0.01     | 0.028                  | 0.13 |  |
| Total                     | Pyroclastic            | 60                 | < 0.01                              | 3.78                      | 31  | 0.40  | < 0.01     | 0.138                  | 1.73 |  |
| Total                     | Soil                   | 41                 | 1.38                                | 6.00                      | 22  | 3.75  | 0.23       | 0.081                  | 0.36 |  |

<sup>†</sup> Soil horizons described according to Schoeneberger (2002).

and Major, 2005). On Kasatochi, in-place, pre-eruption soils were found on the southern and eastern slopes of the island. All sites with shallowly buried (<1 m) soils were on slopes greater than 40%, and lacked the thick deposits of coarse material found in pits consisting only of pyroclastic deposits (Figs. 2A-2D). The topographic position of these sites likely precluded the deposition of the coarser pyroclastic materials that would have buried the pre-eruptive soils more deeply. Microtopography also influenced the thickness and sequence of the pyroclastic deposits. Despite their close proximity (approximately 100 m), different pit profiles were observed at sites 6, 7, and 8. Site 7 is located at the base of a steep slope and only pyroclastic deposits were found in the profile (Fig. 2A). Sites 6 and 8 are located on a small steep slope and a ridge crest, respectively, and pre-eruption soils were only thinly covered by fine pyroclastic deposits (Figs. 2B and 2C). The presence of the low pH material at sites 6 and 8, coupled with the lack of coarser deposits, suggests that only material from early and late in the eruption was preserved at these sites (Scott et al., 2010 [this issue]). Microtopographic controls on the burial depths of pre-eruption soils have been found after other eruptions (Swanson and Major, 2005). Where and how deep the pre-eruptive soils were buried during the 2008 eruptions was controlled, in part, by the pre-eruption topography and microtopography of Kasatochi.

Along the southern transect, erosion bisected the pre-eruption soils and exposed them in the gully walls. On the steeper eastern slopes, mass wasting exposed the buried soil in the gully bottoms. Following volcanic eruptions, initial erosion rates are typically high but decrease as more stable geomorphic surfaces develop (Collins and Dunne, 1986). Development of a stable geomorphology often precedes revegetation due to exposure of pre-eruption soils and less erodible substrates, formation of a stable rill network, and increased surface infiltration (Collins and Dunne,

<sup>††</sup> Material of horizons: Pyroclastic = August 2008 eruptive deposit, Soil = pre-August 2008 surface soil.

<sup>†††</sup> Lower B horizons shown in Figure 2 were not sampled.

 $<sup>^{\</sup>dagger\dagger\dagger\dagger}$  NP = not present.

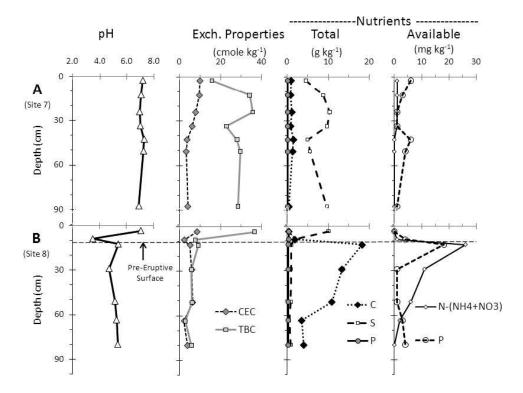


FIGURE 3. Depth profiles showing typical changes in soil properties (pH; exchange properties: CEC-cation exchange capacity, TBC-total base cations; total nutrients: C-carbon, Pphosphorus, S-sulfur; and Available nutrients: N-nitrogen, Pphosphorus) with depth for (A) a typical pyroclastic dominated site (site 7), and (B) a site with preeruption soils in the pit profile (site 8). (Dashed line at 11 cm corresponds to the depth of the overlying pyroclastic deposits across all plots. Note that the zero line for this plot has been adjusted relative to Fig. 2A so that zero is at the ground surface.)

1986; Tsuyuzaki and Haruki, 2008). Initial erosion of the pyroclastic deposits on Kasatochi occurred rapidly (Waythomas et al., 2010 [this issue]) and increased the number and size of erosion features (rills, gullies); a coarsening of the surface was noted between June and August 2009 (B. Wang, personal observation). We do not yet know how quickly the surface of Kasatochi will stabilize. Nonetheless, based on these early observations, differing erosion patterns gave rise to three surfaces on which the ecological systems will likely develop; one on what is largely the pre-eruptive soils; one on fresh pyroclastic deposits but influenced by shallowly buried pre-eruptive soil; and one on the thick (>1 m) pyroclastic deposits.

## CHEMICAL COMPOSITION OF PYROCLASTIC DEPOSITS AND PRE-ERUPTION SOILS

Following major ecosystem disturbance, the distribution of different surfaces leads to a gradient of successional states (Turner et al., 1998; Halvorson, 2005). Pyroclastic deposits typically have low concentrations of important plant nutrients, such as C, N, and P, while supplying other major, minor, and trace nutrients, such as SO<sub>4</sub><sup>2-</sup>, K, and Se (Dahlgren et al., 1997; Zobel and Antos, 1997; Cronin et al., 1998; Vitousek, 1999; Halvorson, 2005). At Kasatochi, total C and N, and available N and P concentrations were significantly lower, while Ca, K, and total S (probably as sulfate) were significantly higher in the pyroclastic deposits than the soils (Table 2). Compositional differences between the pyroclastic deposits and the pre-eruptive soils on Kasatochi led to distinctive chemical profiles with depth for the sites with preeruption soils versus those without (Fig. 3). Characteristics of profiles dominated by the pyroclastic material (Fig. 3A) are: (1) pH, total C, and P, and available N concentrations that are relatively invariant with depth; (2) a maximum in TBC and sulfur concentrations between 15 and 35 cm depth; and (3) TBC concentration in excess of the CEC throughout the profile. In contrast, pits with buried pre-eruptive soils (Fig. 3B) exhibited (1) a sharp decrease in pH with depth within the overlaying pyroclastic layers followed by a pH increase in the pre-eruptive soil, (2) elevated sulfur and TBC concentrations in the pyroclastic material that decreased rapidly in the pre-eruption soils, and (3) total C and P, and available-N and P concentrations that rise sharply at the contact between the pyroclastic/pre-eruption soils then decrease downward through the pre-eruptive soil horizons. The sharp decrease in the pH of the pyroclastic layer immediately above the pre-eruption soil surface was striking in that it was not observed in the pits dominated by pyroclastic deposits. The pH values in these layers (pH 3.5-4.0) are commensurate with the pH of the pyroclastic samples from early in the eruption (sites 11 and 12 and a sample near site 13; pH 3.7, 3.7, and 4.3, respectively). We consider the low pH material in pits with buried pre-eruptive soils to be the pyroclastic material from early in the eruption. The preservation of the early eruptive, low pH material at these sites suggests that it "stuck" and resisted erosion, as if it were cohesive from a mud component as suggested by Scott et al. (2010 [this issue]).

In addition to major elements important to plant growth, minor and trace elements can leach from volcanic ash in sufficient concentrations to cause short-term fertilization of surface oceans (Duggen et al., 2007). An iron concentration of 3.6 mg kg<sup>-1</sup> was detected in one Kasatochi leachate, and Cu and Zn were present in all leachates at concentrations ranging from 0.02 to 0.1 and 0.02 to 0.41 mg kg<sup>-1</sup>, respectively. Concentrations of these trace elements in this magnitude have the potential to provide short-term oceanic fertilization (Duggen et al., 2009) without, as in the case of Cu, resulting in toxicity (Duggen et al., 2007). Because the Kasatochi samples were exposed to moisture during and after deposition they are not ideal samples for evaluating the potential for oceanic fertilization. Nonetheless, these data support the assertion that a large-scale phytoplankton bloom in the NE Pacific Ocean in October 2008 (Langmann et al., 2010) was due, in part, to soluble iron and other trace elements derived from the Kasatochi ash.

As the soil ecosystem develops the interaction between the abiotic and biotic components will, over time, result in soil compositional changes (Tansley, 1935; Singer and Munns, 1987;

Halvorson, 2005). N-fixation, organic debris from plants, and bird guano are potential sources of nutrients to the developing soils on Kasatochi (Erskine et al., 1998; Maron et al., 2006; Halvorson, 2005). Though nutrient concentrations describe the immediate amount available to biota at the soil particle level and relate to ease of nutrient uptake, nutrient stocks describe the nutrient amounts on the landscape that can contribute to the nutrient cycle. Because of density differences between the pyroclastic material and pre-eruption soils, comparisons of the relative landscape contributions of the two substrates are made on stock values and not on concentrations. Additionally, stock calculations should be used to evaluate changes in soil nutrients with time. Comparison of the stocks of important plant nutrients (Table 3) indicate that the pre-eruptive soils are an important source for total C and N, and, to a lesser degree, P and K. The pyroclastic deposits are a source for total S and available K. However, the newly deposited pyroclastics are low in nutrient holding capacity, as indicated by the low CEC, and much of the S, P, and K stocks in the new deposits are soluble and subject to translocation within the developing soil profile and to loss by leaching (Dahlgren et al., 1997). The upper horizons of the pre-eruptive soils hold sufficient levels of available P and K to support plant growth and establishment (Michaelson and Ping, 1990). Pre-eruptive soils with their higher nutrient holding capacity will likely be a more stable, long-term source of plant nutrients than the pyroclastic deposits. Because of the differences in nutrients between the pyroclastic and pre-eruption soils, the different surfaces discussed above will likely have differing influences on the establishment of plant communities (Talbot et al., 2010 [this issue]; Zobel and Antos, 1997; Turner et al., 1998).

# Summary

Iron, Cu, and Zn concentrations detected in Kasatochi leachates were sufficient for these trace elements to provide short-term marine fertilization. These findings lend support to the assertion that a large-scale phytoplankton bloom in the NE Pacific Ocean in October 2008 was due, in part, to soluble iron and other trace-element nutrients released from the deposition of Kasatochi ash (Langmann et al., 2010). Compositional differences between the pre-eruptive soils and the newly deposited material could influence the recovery of Kasatochi's terrestrial ecosystem. The pyroclastic material is a source for total S, available P, and available K, but these nutrients are vulnerable to leaching due to their high mobility within the soil and the low CEC of these materials. Pre-eruptive soils will be an important source for total C and N, and available P and K may become more important as the highly soluble P and K of the pyroclastic deposits are leached over time. All sites where pre-eruptive soils were found were on slopes steeper than 40%. The pyroclastic flow characteristics (sequence and intensity), secondary erosion and deposition, and topographic position on slopes were important determinants in the preservation of in-place, pre-eruption soils on Kasatochi. Pre-eruption soils were exposed on the gully bottoms on the eastern slopes, and gully walls along the southern slopes. The different erosion patterns gave rise to three surfaces upon which biological communities will likely develop: pre-eruptive soils; new pyroclastic deposits that are influenced by shallowly buried pre-eruptive soil; and thick (>1 m), new pyroclastic deposits. Further study and characterization of both the pyroclastic deposits and the preeruption soils, and continued evaluation of Kasatochi's terrestrial ecosystem recovery will provide insights into the longer-term nutrient sources and dynamics, solute transport, and biotic community development.

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