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Contrasting wet deposition composition between three diverse islands and coastal North American sites

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Abstract

This study examined spatial variations of precipitation accumulation and chemistry for six sites located on the West and East Coasts of the U.S., and one site each on the islands of Hawaii, Bermuda, and Luzon of the Philippines (specifically Manila). The nine coastal sites ranged widely in both mean annual precipitation accumulation, ranging from 40 cm (Mauna Loa, Hawaii) to 275 cm (Washington), and in terms of monthly profiles. The three island sites represented the extremes of differences in terms of chemical profiles, with Bermuda having the highest overall ion concentrations driven mainly by sea salt, Hawaii having the highest SO_4^{2-} mass fractions due to the nearby influence of volcanic SO_2 emissions and mid-tropospheric transport of anthropogenic pollution, and Manila exhibiting the highest concentration of non-marine ions (NH_4^+ non-sea salt [nss] SO_4^{2-} , nss Ca^{2+} , NO_3^- , nss K^+ , nss Na^+ , nss Mg^{2+}) linked to anthropogenic, biomass burning, and crustal emissions. The Manila site exhibited the most variability in composition throughout the year due to shifting wind directions and having diverse regional and local pollutant sources. In contrast to the three island sites, the North American continental sites exhibited less variability in precipitation composition with sea salt being the most abundant constituent followed by some

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

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combination of SO_4^{2-} , NO_3^- , and NH_4^+ . The mean-annual pH values ranged from 4.88 (South Carolina) to 5.40 (central California) with NH_4^+ exhibiting the highest neutralization factors for all sites except Bermuda where dust tracer species (nss Ca^{2+}) exhibited enhanced values. The results of this study highlight the sensitivity of wet deposition chemistry to regional considerations, elevation, time of year, and atmospheric circulations.

Graphical Abstract

Keywords

Precipitation chemistry; Wet deposition; Acidity; Neutralization factor; CAMP²Ex; ACTIVATE

1. Introduction

Precipitation chemistry is routinely measured in different global regions as a way to understand sources, transport, and sinks of pollutants. Aerosol particles serve as the cloud condensation nuclei (CCN) upon which droplets form, which after subsequent growth produce precipitation. The majority of particulate compounds emitted to the atmosphere or formed from chemical reactions have an atmospheric residence time typically ranging from 3 to 10 days depending on their size and composition (Andreae and Rosenfeld, 2008), with wet deposition being a primary sink for those that are soluble or non-volatile (Keene et al., 2015). Falling precipitation can also scavenge pollutants on the path towards the surface (Ahmady-Birgani et al., 2020; Chatterjee et al., 2010; MacDonald et al., 2018). Long-term global records of species from wet deposition provide insight into numerous phenomena such as acid rain (Likens and Bormann, 1974; Likens et al., 1972), improvements in air quality owing to regulatory activities (Feng et al., 2019; Keene et al., 2014), impacts on ecosystems such as fertilization and acidification of water bodies and soil and biodiversity reduction (Johansen et al., 2019; Likens, 2013), and deleterious impacts on public health (Likens, 2013).

Studies examining long-term trends in wet deposition chemistry highlight competing effects between regulatory activities, urbanization and economic development, and changes in natural emissions, meteorology, and transport patterns (Keene et al., 2015; Yao and Zhang, 2019; Zhou et al., 2019). The following three examples showcase this complexity. Measurements at Mt. Rainer in Washington (U.S.) between 1989 and 2015 showed that sulfate SO_4^{2-} , nitrate (NO_3^-), and protons peaked in the early 2000s and then decreased significantly, concomitant with an increase in pH (5.2–5.6) governed largely by emission regulations of stationary sources that resulted in reductions of major acidic ions such as non-

sea salt (nss) SO_4^{2-} and NO_3^- (Johansen et al., 2019). In contrast, wet deposition over South China exhibited a decrease in pH since the 1980s up to 2009, assisted in part by rapid economic development and thus increasing levels of nss SO_4^{2-} and NO_3^- (Zhou et al., 2019). Data between 1989 and 2009 at Bermuda revealed an increasing trend in ammonium (NH_4^+), speculated to be due to more ammonia (NH_3) emissions from nearby continents (Keene et al., 2014).

Aside from regional differences, there are important seasonal differences at individual locations impacting wet deposition chemistry. For example, dry and wet seasons in South America exhibit significant variability in species amounts based on precipitation patterns and differences in atmospheric circulation (Andreae et al., 1990; Forti and Moreiranordemann, 1991; Hendry et al., 1984; Talbot et al., 1990; Veneklaas, 1990). Pre-monsoon periods exhibited higher ionic concentrations and pH as compared to monsoon periods at a high altitude site in the central Himalaya region (Nainital), owing to more natural aerosols (i.e., dust) in the former period (Bisht et al., 2017). Precipitation in Northeast India was shown to have more influence from marine sources during monsoon periods in contrast to non-marine sources in non-monsoonal periods (Garaga et al., 2019). Data for the island of Puerto Rico revealed more SO_4^{2-} and NO_3^- during winter periods owing to North American transport associated with cold front periods, while summertime periods coincided with higher levels of Ca^{2+} , Mg^{2+} , and K^+ linked to Saharan dust (Mcdowell et al., 1990).

The goal of this work is to extend upon past works with a broader view of wet deposition chemical data between diverse regions as a function of time of year. The regions are characterized by different atmospheric circulation patterns, regional emissions sources, and meteorology. The unique aspect of this work is the combination of sites examined, including the understudied Philippines, and the use of relatively recent data as compared to older reports for many of these sites. This paper addresses the following topics, in order, for each studied region: monthly profiles of (i) precipitation accumulation and (ii) pH; speciated ion concentration profiles and mass fractions over (iii) annual and (iv) monthly scales; and (v) seasonal neutralization factor analysis.

2. Methods

2.1. Data description

Nine total sites were investigated in this work (Fig. 1) as a way to contrast wet deposition data for locations with varying meteorological, topographic, and pollution characteristics. Table 1 summarizes details related to the nine sites, which are classified into three subgroups based on geophysical considerations: islands (HI00, BTT, MM), U.S. West Coast (WA14, CA45, CA42), and U.S. East Coast (NJ00, SC05, FL11). Data were examined between 2007 and 2016 for all stations except Bermuda (January 1989–February 1997 and July 2006–June 2009) and Mauna Loa, Hawaii (June 1980–September 1993). This work is focused only on liquid rain and excludes frozen precipitation.

Precipitation data for seven out of nine sites were retrieved from the National Atmospheric Deposition Program (NADP) National Trends Network (NTN) database (<http://nadp.slh.wisc.edu/data/ntn/>). The NADP/NTN network was established in 1983 to monitor spatial and temporal trends of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} concentrations and pH in wet deposition in the U.S. (See et al., 1989). A Belfort B5–780 rain-gauge (daily resolution) and Aerochem Metrics 301 precipitation collector (ACM) were operated in parallel at each NADP/NTN site. For the ACM, weekly samples were collected (Tuesday to Tuesday) and sent to the Central Analytical Laboratory (CAL) at the Wisconsin State Laboratory of Hygiene (WSLH) for data analysis, entry, verification, and screening (<http://nadp.slh.wisc.edu/NTN/>). Details associated with quality control and quality assurance (QA/QC) are provided elsewhere (NADP, 2014; See et al., 1989). Major ions were speciated and quantified using ion chromatography (IC).

Precipitation samples from Metro Manila (MM) were collected as part of the Acid Deposition Monitoring Network in East Asia (EANET) (<https://www.eanet.asia/>). EANET was established to determine acid deposition trends among East Asian countries. Wet deposition samples were collected weekly at the Manila Observatory (14.64° N, 121.08° E) with a wet-only sampler and transported in ice-cold containers to the Environmental Management Bureau Laboratory for subsequent analysis of pH, electrical conductivity, and ion concentrations using methods adopted from the NADP/NTN (Viernes and Laciste, 2013). QA/QC procedures were carried out in all stages of the monitoring activities including assurance that cation-anion charge balances and intercomparisons between measured and calculated conductivities adhered to established criteria (EANET, 2016; Viernes and Laciste, 2013). Note that rainfall data was unavailable as precipitation samples from MM were only collected for chemical analysis. For subsequent calculations described in Section 2.2.1, rainfall amount was obtained at the same coordinate point of the Manila Observatory using the Precipitation Estimation from Remotely Sensed Information using Artificial Neural Networks – Cloud Classification System (PERSIANN-CCS; Hong et al., 2004; Nguyen et al., 2018) dataset available from the Center for Hydrometeorology and Remote Sensing (CHRS) at the University of California Irvine Data Portal (<http://chrsdata.eng.uci.edu>; Nguyen et al., 2019).

Lastly, wet deposition data from Bermuda are based on measurements conducted as part of the Atmosphere/Ocean Chemistry Experiment (AEROCE), as summarized by previous work (Keene et al., 2014, 2015). Daily measurements were conducted at Tudor Hill Atmospheric Observatory using pre-cleaned buckets attached to an automated collector (Galloway et al., 1993). Samples were sterilized with chloroform (CHCl_3) and kept refrigerated until analysis at the University of Virginia. Data relevant to this study include pH and ions, similar to the other eight sites, and are based on techniques summarized elsewhere including IC for ions and electrode and meter for pH (Keene et al., 2015; Moody et al., 2014). Precipitation amount was derived from measurements with a bulk rain gauge. Data from two time periods (January 1989–February 1997 and July 2006–June 2009) were collectively used in this study to enhance statistics rather than just presenting results calculated from the most recent period.

A cautionary note in comparing results between the different monitoring stations using different techniques and protocols is that NH_4^+ is not conserved in samples that are not immediately sterilized or frozen such as with weekly NADP samples (Keene et al., 2002).

2.2. Calculations

2.2.1. Volume-weighted mean concentrations and standard errors—Volume-weighted mean concentration (VMC) and standard error of VMC calculations were obtained using Eqs. (1) and (2), respectively:

$$C = \frac{\sum_{i=1}^n C_i P_i}{\sum_{i=1}^n P_i} \quad (1)$$

$$E = \sqrt{\frac{\sum_{i=1}^n P_i (C_i - C)^2}{n \sum_{i=1}^n P_i}} \quad (2)$$

where C_i is the concentration ($\mu\text{eq L}^{-1}$ or mg L^{-1}) of a species for sample i and C is the VMC ($\mu\text{eq L}^{-1}$ or mg L^{-1}) over samples $i = 1 - n$; P_i is the amount of precipitation (mm) coinciding with sample i ; and n is the total number of samples for the averaging time scale of interest (i.e., month, seasonal, annual). E is the standard error ($\mu\text{eq L}^{-1}$ or mg L^{-1}) of the corresponding VMC (Miller, 1974). Subsequent references to pH values correspond to VMC of H^+ expressed as pH (Li et al., 2020; Meng et al., 2019; Zhang et al., 2020).

2.2.2. Non-sea salt concentrations—The contribution of nss and ss fractions of Na^+ , Ca^{2+} , K^+ , Mg^{2+} , and SO_4^{2-} were determined by simultaneously solving Eq. (3)–(9) following an established method (AzadiAghdam et al., 2019). This technique takes into account that dust is a non-negligible source of Na^+ (Berner and Berner, 1996; Farren et al., 2019; Shapiro et al., 2007), which is the common reference species for sea salt relying on the assumption that sea salt is the exclusive source for that species. The equations below rely on established mass ratios between constituents in crustal matter and/or pure sea water. Examples of such ratios include $\text{Ca}^{2+}:\text{Na}^+$ in crustal matter and sea water being 1.78 and 0.038, respectively (Bowen, 1979), and the $\text{Mg}^{2+}:\text{Na}^+$ ratio in sea water being 0.121 (Seinfeld and Pandis, 2016). The ss fraction of K^+ , Mg^{2+} , and SO_4^{2-} was obtained by subtracting the nss fraction from the measured concentration of that species. We note there is uncertainty with this method rooted in ratios used for crustal matter, which are more variable based on region as compared to sea water.

$$\text{ss Na}^+ = \text{Na}^+ - \text{nss Na}^+ \quad (3)$$

$$\text{nss Na}^+ = \text{nss Ca}^{2+} \times \left(\frac{\text{nss Na}^+}{\text{nss Ca}^{2+}} \right)_{\text{crustal}} \quad (4)$$

$$\text{nss Ca}^{2+} = \text{Ca}^{2+} - \text{ss Ca}^{2+} \quad (5)$$

$$\text{ss Ca}^{2+} = \text{ss Na}^+ \times \left(\frac{\text{Ca}^{2+}}{\text{Na}^+} \right)_{\text{sea water}} \quad (6)$$

$$\text{nss K}^+ = \text{K}^+ - 0.037 \times \text{ss Na}^+ \quad (7)$$

$$\text{nss SO}_4^{2-} = \text{SO}_4^{2-} - 0.253 \times \text{ss Na}^+ \quad (8)$$

$$\text{nss Mg}^{2+} = \text{Mg}^{2+} - 0.121 \times \text{ss Na}^+ \quad (9)$$

2.2.3. Neutralization factor— SO_2 and NO_x are emitted into the atmosphere by a variety of anthropogenic sources, which undergo reactions to form nss SO_4^{2-} and NO_3^- , respectively. The latter two species have been largely responsible for acid rain in different global regions such as the Western (Liljestrand and Morgan, 1978) and Northeastern U.S. (Cogbill and Likens, 1974; Driscoll et al., 2001; Sorooshian et al., 2020), and Europe (Oden, 1976). Base ions such as NH_4^+ and Ca^{2+} act as neutralization compounds to buffer acid precipitation. As a way to quantify the relative importance and magnitude of neutralization by different base ions, neutralization factors (NF) are typically quantified to represent neutralization capacity of alkaline ions present in precipitation (Kulshrestha et al., 1995):

$$\text{NF} = \frac{X}{\text{nss SO}_4^{2-} + \text{NO}_3^-} \quad (10)$$

where X ($\mu\text{eq L}^{-1}$) is the concentration of nss Ca^{2+} , nss Mg^{2+} , nss K^+ , and NH_4^+ ; the two species in the denominator are also concentrations in units of $\mu\text{eq L}^{-1}$. The NF values of the four selected ions in this study for identifying neutralization effects are likely overestimated for the MM site due to the missing contribution of undetermined anions in the denominator such as organic acids and bicarbonate.

2.3. Site descriptions

The nine total sites chosen in this study represent sites that are from different geographic areas (Fig. 1). Three islands are chosen that vary greatly in terms of topography and the degree of anthropogenic and natural influences. The six coastal sites associated with continental North America provide a useful contrast with the island sites and with each other as well owing to latitudinal differences. Important features of each site are highlighted next.

2.3.1. Islands—Mauna Loa is located on the south-central part of the island of Hawaii, which is the most southeastern island within the chain of Hawaiian Islands. The site is adjacent to Mauna Loa crater. The site is characterized by rocky terrain with scattered

vegetation with a resident population of ~140,000 living mainly near the coast. This site is important in this study because of its high elevation (3399 m ASL) as topographical features can impact wet deposition chemistry. For instance, measurements based at the Carpathian Mountain chain in Romania showed that there was blockage of transported aerosols, such as sea spray, as confirmed by a lack of correlation between commonly linked sea salt species such as Mg^{2+} and Na^+ (Szep et al., 2018). Mauna Loa's high altitude reduces the influence of short lived pollutants from near the surface such as primary marine aerosols (Keene et al., 2015). In addition to the remoteness of this site yielding minimal anthropogenic influence, the site is additionally devoid of local biogenic influence owing to the lack of vegetation, but instead is influenced by volcanic emissions enriched with SO_2 (Luria et al., 1992).

Remote islands without complex topography provide a useful contrast with more polluted regions as has been demonstrated by an extensive body of literature for the remote island of Bermuda (Altieri et al., 2013; Galloway et al., 1982, 1988, 1989; Keene et al., 2014; Moody and Galloway, 1988). Here we use data from the Tudor Hill Atmospheric Observatory (51 m ASL) at Bermuda, which is positioned on the southwest coast of Bermuda. Located about ~1000 km east of Cape Hatteras, North Carolina, the island hosts a population of ~64,000 as of 2016 (Government of Bermuda, 2019). The Bermuda-Azores High is the major feature over the Western North Atlantic Ocean that drives most of the flow climatology impacting the island, with frontal and convective storms being most responsible for Bermuda's precipitation (Galloway et al., 1993). Transported pollution to Bermuda (e.g., North American anthropogenic emissions and associated reaction products) is thought to outweigh the influence of local pollution from the island (Galloway et al., 1988; Keene et al., 2014). As noted by Keene et al. (2015), local sources include emissions from tourism (e.g., cruise ships) and power production by a fuel oil turbine, with limited influence from industry. The impact of upwind pollution sources are dependent on seasonal atmospheric circulation patterns, resulting in impact from North America, Europe, Africa, and the central North Atlantic Ocean (Keene et al., 2015).

Metro Manila is the capital of the Philippines and the country's largest megacity, hosting the majority of economic activity and a population of ~12.88 million (Authority, 2015). Precipitation was sampled from February 2007 to December 2016 at the Manila Observatory (87 m ASL) on the Ateneo de Manila University campus in Quezon City, which is characterized by pollutants of varying types from multiple sources, such as biomass burning, vehicles, and industry (Alas et al., 2018; Braun et al., 2020; Cohen et al., 2009; Cruz et al., 2019; Kecorius et al., 2017). The Southwest Monsoon season (May–October) is associated with southwesterly flow, more rain, and extensive biomass burning upwind of Luzon over the Maritime Continent (Cayanan et al., 2011; Cruz et al., 2013; Hilario et al., 2020b; Reid et al., 2013; Villafuerte et al., 2014; Xian et al., 2013). Cruz et al. (2019) showed with size-resolved aerosol measurements and positive matrix factorization modeling that five predominant pollution sources during the Southwest Monsoon include aged aerosol, sea salt, combustion, waste processing, and vehicular/resuspended dust. The period of time between November and April coincides with a dry season with more northeasterly winds (Bagtasa et al., 2018; Chang et al., 2005; Cruz et al., 2013; Moron et al., 2009), including influence from both East Asia and local burning activities (Hilario et al., 2020b, 2020c).

2.3.2. U.S. West Coast—Data were used from three sites along the U.S. West Coast, with one in Washington and two in California. The Olympic National Park-Hoh Ranger Station (WA14, 176 m ASL) is located in the northwestern part of Washington. This site is ~100 km northwest of the state capital city of Seattle, which is the largest city in the state occupying 217.3 km² of land that hosts a population of 744,955 (U.S. Census Bureau, 2018). The Hopland (CA45, 253 m ASL) site is in northern California, situated in a small town called Hopland within Mendocino County. Tanbark Flat (CA42, 853 m ASL) is in southern California, approximately ~35 km northeast of Los Angeles, and has a population of 3,990,456 (U.S. Census Bureau, 2018). This site is at much higher elevation than the other two sites on the West Coast since it is part of the San Gabriel Mountains. These three sites are impacted by a range of sources including marine emissions, shipping, crustal sources, wildfires and wood burning, transportation, and agricultural, anthropogenic, and biogenic emissions (Kim and Hopke, 2008; Ryerson et al., 2013; Sorooshian et al., 2019; Wang et al., 2014).

2.3.3. U.S. East Coast—Similar to the U.S. West Coast, three sites are used with fairly uniform latitudinal spacing across the U.S. East Coast. The Edwin B. Forsythe National Wildlife Refuge site (NJ00, 2 m ASL) is located in southern New Jersey along the Atlantic Ocean coast by Atlantic City, which has a population of 37,804 (U.S. Census Bureau, 2018). It is also to the east and south of major populated metropolitan cities including Philadelphia (1,584,138 population) and New York City (8,398,748 population) (U.S. Census Bureau, 2018), respectively. The Cape Romain National Wildlife Refuge site (SC05, 1 m ASL) is in southeast South Carolina along the Atlantic coast. The nearest urban area is the capital city of Charleston to its southeast with a population of 136,208 (U.S. Census Bureau, 2018). The Everglades National Park Research Center site (FL11, 2 m ASL) is at the southern tip of Florida near the city of Miami, which has a population of 470,914 (U.S. Census Bureau, 2018). The same set of sources impacting the West Coast generally apply to the East Coast (Hand et al., 2012b, 2019) with notable features being more influence from African dust (Aldhaif et al., 2020; Zuidema et al., 2019), enhanced agricultural burning (especially in the Southeast) (Sevimoglu and Rogge, 2019; Shingler et al., 2016), and extensive power plant emissions that have actually been reduced over time since the early 1990s leading to SO₄²⁻ reductions (Hand et al., 2012a).

3. Results and discussion

3.1. Monthly precipitation accumulation

Monthly profiles of precipitation accumulation reveal the influence of meteorology impacting the different regions examined (Fig. 2). The sites on the U.S. West (WA14, CA45, CA42) and East Coasts (NJ00, SC05, FL11) exhibit nearly opposite annual profiles. The West Coast sites were characterized by higher precipitation accumulation in the winter months (December–January–February, DJF) and the lowest values in the summer months (June–July–August, JJA). This is consistent with the highest (lowest) cloud fractions and the lowest (highest) temperatures in the DJF (JJA) season along the West Coast spatially coincident with these sampling sites (Sorooshian et al., 2015). Extratropical cyclones from the Pacific Ocean provide the majority of rain to these sites, especially in the form of

wintertime atmospheric rivers (Dettinger et al., 2011; Gershunov et al., 2019). In contrast, East Coast precipitation accumulation tended to be lower in the cool winter season as compared to warmer summer and fall months. Coastal extratropical cyclones provide significant precipitation in winter months in the northern part of the East Coast, which is why the NJ00 site exhibits high variability in rain amount in the DJF season, with a relatively high value in December. In warmer months, mesoscale convective systems and also tropical cyclones from the south provide rain to the East Coast, especially at the FL11 site (226 ± 104 mm month⁻¹ in the JJA season).

The three island sites exhibited different precipitation profiles. The HI00 site in Hawaii recorded the lowest amount of year-round rain among the three islands (402 ± 253 mm) and exhibited a monthly profile resembling that of the U.S. West Coast with highest accumulation in the winter, due to wintertime Pacific Ocean storm systems. The BTT site in Bermuda had the highest mean-annual amount of accumulation (2688 ± 3743 mm) with most rain between May and October (i.e., up to 380 ± 722 mm in May). As noted already, frontal and convective systems are responsible for most of the rain at Bermuda (Galloway et al., 1993). Lastly, the MM site in Metro Manila exhibited a fair amount of monthly variability in rain (14 ± 29 mm month⁻¹ to 466 ± 288 mm month⁻¹) owing to it having dry and wet seasons. Rain at the MM site is driven by a combination of multi-scale phenomena such as typhoons (Bagtasa, 2017), the Asian monsoon system (Akasaka et al., 2007; Chang et al., 2005; Hilario et al., 2020d; Matsumoto et al., 2020), the Madden-Julian Oscillation (Maloney and Hartmann, 2001; Pullen et al., 2015), and the El Niño Southern Oscillation (ENSO) (Cruz et al., 2013; Jose et al., 1996). Precipitation was enhanced in the wet season with maximum precipitation occurring in July (395 ± 327 mm), August (289 ± 196 mm), September (466 ± 288 mm), and October (266 ± 144 mm) due to the influence of the Southwest Monsoon. Compared with WA14 (2746 ± 713 mm), rain accumulation is substantially decreased at the CA42 (463 ± 215 mm) and HI00 (402 ± 253 mm) sites, suggesting the influence of elevation.

3.2. Monthly pH

The monthly pH profile of wet deposition is next summarized to show how it varies within an annual cycle and between regions. While comparisons are made between sites based on VMC of H⁺, the standard deviations in measured pH (Table 2) were large between sites, reducing the statistical significance between differences in mean values. The discussion focuses on VMC values of pH although Table 2 additionally reports basic statistics for measured pH without applying Eq. (1). A pH threshold of 5.6 is often used as a threshold to distinguish acid rain (pH < 5.6) as this value signifies deionized water being in equilibrium with CO₂ (Charlson and Rodhe, 1982; Das et al., 2005; Roy et al., 2016; Xing et al., 2017); however, the collected samples are never truly pure water owing to droplet activation of CCN. Furthermore, the 5.6 value should be used with caution owing to the sensitivity of rain acidity to factors such as geographic variability in water, sulfur, and nitrogen cycles (Charlson and Rodhe, 1982).

The West Coast sites varied in monthly pH patterns with mean annual pH values ranging from 5.32 (CA42) to 5.40 (CA45). The northernmost site (WA14) exhibited the highest

(lowest) pH in winter (summer) months. Similarly, the two sites in California exhibited higher seasonal pH values in DJF (CA45: 5.42) and/or MAM (CA42: 5.28–5.36). The East Coast sites were characterized by more acidic wet deposition than the West Coast. This is not surprising as the northeastern states in particular have a long history of suffering from acidification of precipitation due to combustion of fossil fuel associated with industrial and human activities (Galloway et al., 1976; Likens and Bormann, 1974; Likens et al., 1972). FL11 had the highest mean-annual pH among the East Coast sites (5.09), while SC05 had the lowest pH of all nine sites (4.88). The two northernmost East Coast sites tended to exhibit a bimodal annual pH profile with high pH values in the MAM and SON seasons, with FL11 exhibiting higher pH values between October and January (5.17–5.30).

The three island sites exhibited relatively similar mean-annual pH values: Bermuda = 4.94; MM = 4.95; HI00 = 4.99. When comparing the two time periods that Bermuda had available data, the mean pH values were 4.92 (1989–1997) and 4.96 (2006–2009). Using the same dataset, Keene et al. (2014) showed a statistically significant decrease in volume-weighted average concentrations of H^+ when sampling under conditions of westerly flow from eastern North America, attributed to decreased emissions of SO_2 over North America. That this site exhibited nearly the lowest pH among the various regions studied highlights the vulnerability of this remote island to upwind continental emissions. The MM site exhibited the largest monthly variability likely due to a diversity of regional sources and the wide range of meteorological conditions it experiences including shifts in predominant wind directions in different seasons (Braun et al., 2020; Cruz et al., 2019). More broadly, two of the three island sites (HI00 and MM) exhibited the most monthly variability in pH as compared to the continental sites. A plausible explanation is that without the stabilizing background of continental emissions, these islands may be more sensitive to seasonally dependent changes in atmospheric circulation that are accompanied by varying air masses differing in composition.

3.3. Composition

3.3.1. Charge balance analysis—Charge balance statistics are first provided for the cumulative ion data at each site (Fig. 3), with a slope of unity indicative of a perfect balance. All sites except HI00 and MM exhibited charge balance slopes close to unity (0.99–1.09) with r^2 values of the best-fit lines being 0.88 and higher. The HI00 site exhibited a slope of 1.17 but had a reduced value of r^2 (0.66) owing to scatter in data points. The slopes above unity point to anion deficits, which are not uncommon and attributed to species that are not measured routinely by wet deposition networks such as carboxylic acids (e.g., formate, acetate) and the bicarbonate ion (Akpo et al., 2015; Hontoria et al., 2003; Keene et al., 2015; Williams and Melack, 1991; Yang et al., 2012; Zhang et al., 1996).

The charge balance at MM requires discussion owing to its unusually high slope of 3.54. According to the World Meteorological Organization (WMO) Data Quality Objectives (WMO, 2004), acceptable ion differences (%) should not exceed 60% for total anion and cation charges $50 \mu\text{eq L}^{-1}$, and furthermore should not exceed 10% for total charges exceeding $500 \mu\text{eq L}^{-1}$. While the methods and quality assurance details were already noted (EANET, 2016; Viernes and Laciste, 2013), speculations unrelated to poor data quality are

offered here. The WMO report indicates that regions with basic rain experience issues with undetected organic substances and especially the bicarbonate ion; as the measured pH at MM was the highest of all sites according to Table 2 (6.30 ± 0.85), this site presumably has significant influence from bicarbonate that may contribute to the anion deficit. There could also be extensive amounts of organics unaccounted for in the measurements, including especially carboxylic acids. Past work for the Manila region has pointed to the substantial fraction of particulate mass unaccounted for by water-soluble ions including inorganic species and select elements and organic acids (Cruz et al., 2019); they showed that approximately 70% of the bulk aerosol mass ($< 0.056 \mu\text{m}$) went unaccounted for, pointing to a substantial amount of anions potentially undetected that may be associated with the large deficit shown in Fig. 3. As will be shown, the MM site was impacted perhaps the most by biomass burning, and carboxylic acids are an important constituent in such emissions (Gao et al., 2003; Mardi et al., 2018; Reid et al., 1998).

3.3.2. Mean annual profile—For a broader view of how wet deposition composition varies between the nine sites, annual-mean ion mass fractions (in percentages) are next summarized to highlight sites that had particularly strong features. Results in Fig. 4 do not resolve constituents into ss and nss fractions and are based on relative amounts of the native ion concentrations (units of mg L^{-1}) without having applied Eq. (3)–9. The HI00 site had the highest SO_4^{2-} mass fraction (69.5%) of all sites. This is partly attributed to the influence of the nearby Mauna Loa crater that emits SO_2 (Luria et al., 1992). As the site is at very high altitude, it is not as directly influenced by surface marine emissions of dimethylsulfide, which is a precursor to nss SO_4^{2-} , as compared to many of the other sites and especially the other two islands. Instead, the HI00 site is impacted by natural and anthropogenic species transported over long distances in the mid-troposphere (Miller et al., 1984; Miller and Yoshinaga, 1981), including nss SO_4^{2-} and ions associated with Asian dust (Shaw, 1980) such as Ca^{2+} .

The MM site was next in terms of the highest SO_4^{2-} mass fraction (25.4%), owing especially to nearby combustion sources emitting SO_2 (Cruz et al., 2019). Of note is that biofuel combustion, especially peat burning, is a significant source of SO_4^{2-} in the region stemming from sources in areas such as Borneo, Sumatra, and New Guinea (Ikegami et al., 2001; Reid et al., 2013). The MM site exhibited the highest NH_4^+ mass fraction of any site (24.1%). Recent work has shown that a major source of NH_4^+ impacting the Metro Manila region is long-range transport from East Asia, in addition to biomass burning plumes transported from the Maritime Continent (Braun et al., 2020; Hilario et al., 2020a). The MM site also had the highest K^+ mass fraction of all sites (7.4%), which is a biomass burning tracer species (e.g., Artaxo et al., 1994; Farren et al., 2019; Reid et al., 2005; Savoie and Prospero, 1980; Wonaschutz et al., 2011). A recent study pointed to the correlation between K^+ and SO_4^{2-} in the Manila area and attributed it to the existence of K_2SO_4 (Bagtasa and Yuan, 2020), which can be derived from aged smoke as KCl reacts with S-bearing constituents in fire emissions (Li et al., 2003). Therefore, biomass burning was an especially

important source at MM (Braun et al., 2020; Cruz et al., 2019), with chemical signatures evident in the sampled wet deposition.

The BTT site in Bermuda was distinct in its profile owing to the largest combined contribution from Na^+ and Cl^- (82.9%) followed by WA14 (76.0%). This result is due to its remote nature and low elevation as compared to the other two island sites. The highest NO_3^- mass fractions were observed at CA42 (26.7%), likely due to nitric acid (HNO_3) from sources such as biomass burning, agriculture, shipping, and urban emissions that either partition directly to drops, form salts with acids such as sulfuric acid (H_2SO_4), or partition to sea salt or dust particles (Dadashazar et al., 2019; Maudlin et al., 2015; Prabhakar et al., 2014). In contrast to the three islands and U.S. West Coast sites, the U.S. East coast sites exhibited the most similarity to one another in terms of mean annual mass fraction profile. There were relatively comparable contributions from SO_4^{2-} , NO_3^- , Cl^- , and Na^+ .

3.3.3. Monthly trends—The previous section pointed to the distinct features impacting the various sites, and now those results are resolved into monthly averages for concentrations and mass fractions (Fig. 5), while also separating ss and nss fractions for sea salt constituents (Na^+ , Ca^{2+} , SO_4^{2-} , K^+ , Mg^{2+}). References below to sea salt represent the sum of ss Na^+ , ss Ca^{2+} , ss SO_4^{2-} , ss K^+ , ss Mg^{2+} , and Cl^- .

The three island sites exhibited very different compositional profiles. The island site with the lowest mean-annual cumulative ion concentration was HI00 ($20.93 \pm 31.99 \mu\text{eq L}^{-1}$). HI00 was distinct in its higher mass fraction of nss SO_4^{2-} that was fairly consistent and dominant year-round (~60%), driven in part by volcanic SO_2 emissions (Luria et al., 1992) and mid-tropospheric transport of pollution from continental sources such as from Asia (Miller and Yoshinaga, 1981). In sharp contrast to HI00, the BTT site in Bermuda exhibited higher overall ion concentrations in the DJF season ($1234.85 \pm 4673.05 \mu\text{eq L}^{-1}$), and the monthly profile of mass fractions clearly shows the dominance of sea salt (86–97%). The next most abundant constituents in terms of mass fraction were nss SO_4^{2-} (1–4%) and NO_3^- (0–3%), which contributed more to the overall mass fraction between May and September. The BTT site had the highest overall mean-annual concentration of all ions ($404.28 \pm 1519.74 \mu\text{eq L}^{-1}$) of any site, driven mainly by the high sea salt concentrations. This is indicative of the key role that sea salt plays in aerosol-cloud interactions over the WNAO in terms of activating into droplets that eventually become rain drops.

After the BTT site, the MM site had the next highest mean-annual cumulative ion concentration ($313.46 \pm 412.38 \mu\text{eq L}^{-1}$) out of all nine sites. This site was unique in terms of having the highest concentration of ions stemming from non-marine sources (NH_4^+ , nss SO_4^{2-} , nss Ca^{2+} , NO_3^- , nss K^+ , nss Na^+ , nss Mg^{2+}) including anthropogenic, biomass burning, and crustal emissions. In contrast to HI00 and BTT sites that were dominated by nss SO_4^{2-} and sea salt, respectively, MM exhibited more variability during the year driven by diverse sources and changing wind directions (Braun et al., 2020; Cruz et al., 2019). Note that Fig. 5 shows data for only 9 months as the other months suffered from negative

concentrations for at least one species when using Eq. (3)–(9); in contrast, Fig. S1 shows MM results when applying a different calculation method described in Fig. S1 caption to allow for an examination of all 12 months. Based on Fig. S1, mass fractions in the dry season months (November–April) were dominated by NH_4^+ (37%), nss SO_4^{2-} (18%), and NO_3^- (18%) in contrast to the wet season (May–October) that exhibited enhanced levels of nss SO_4^{2-} (27%) but decreased levels of NH_4^+ (18%) and NO_3^- (16%). The enhanced nss SO_4^{2-} is thought to be at least partly due to extensive peat burning and biomass burning plume transport from areas to the southwest of Manila such as Borneo and Sumatra (Reid et al., 2013). This site exhibited the highest mean-annual mass fraction for nss K^+ (7%), suggestive of the highest relative influence from biomass burning as compared to other sites. There was little difference in the mass fraction of nss K^+ between dry (9%) and wet (6%) seasons.

For the U.S. West Coast sites, mean-annual ion concentrations were $59.51 \pm 76.75 \mu\text{eq L}^{-1}$ and $38.71 \pm 24.04 \mu\text{eq L}^{-1}$ for WA14 and CA45, respectively, with a sharper increase at the southernmost site of CA42 ($84.06 \pm 78.75 \mu\text{eq L}^{-1}$). Of the three West Coast sites, the WA14 site exhibited the highest levels of sea salt with a mean-annual mass fraction of 82%, and a seasonal range from 45% in JJA to 88% in DJF. The summertime (JJA) was marked by an enhancement in mass fractions of nss SO_4^{2-} (23%), NO_3^- (21%), and NH_4^+ (6%), partly driven by an increase in photochemical activity and wildfires (Dadashazar et al., 2019; Johansen et al., 2019). For the other two sites in California, the mass fraction profiles across different months were fairly similar and different from WA14 in that there were relatively higher year-round mass fractions for NO_3^- , nss SO_4^{2-} , and NH_4^+ . The CA42 site stood out in terms of the highest mass fraction for NO_3^- on an annual basis (~30%) owing to presumably more abundant sources of its precursor HNO_3 .

In contrast to the U.S. West Coast, the three East Coast sites exhibited more internal consistency with regard to overall ionic concentrations and mass fraction profiles across all months. More specifically, the mean-annual total ion concentrations for NJ00, SC05, and FL11 were $116.56 \pm 88.30 \mu\text{eq L}^{-1}$, $83.89 \pm 48.01 \mu\text{eq L}^{-1}$, and $94.41 \pm 63.27 \mu\text{eq L}^{-1}$, respectively. The most abundant constituent based on mass fraction was sea salt (range of mean-monthly values: 48–50%), followed by either nss SO_4^{2-} (18–23%) or NO_3^- (19–20%).

3.4. Acid neutralization

The regional differences in rainwater acidity and intensity of neutralization by different basic components in rainwater can be illustrated by the following examples. Approximately 64% and 87% of all rain events in the monsoon and non-monsoon seasons in Northeast India were considered acidic (based on having $\text{pH} < 5.6$) owing to high levels of SO_4^{2-} and NO_3^- and poor neutralization capacity by crustal species (Mg^{2+} , Ca^{2+} , K^+) (Garaga et al., 2019). In contrast, rain on the Aegean coast of Turkey was noted to have a mean pH of 5.6, with extensive neutralization of acids by NH_3 from fertilizer use, with less contribution by calcium carbonate (CaCO_3) from resuspended soil (Almomani et al., 1995). In North China,

Ca^{2+} derived from crustal dust was the most dominant neutralization agent ($\text{NF} = 1.35 \pm 0.72$) in rain (Xu et al., 2020), whereas rain in Eastern Romania was mainly neutralized by NH_4^+ (NF : 0.26–3.94) from agriculture and biomass burning (Szep et al., 2019). Also, precipitation pH decreased as a function of elevation from sea level (5.2) to above 2500 m (4.3) on the island of Hawaii mainly due to long-range transport of acidic compounds in the upper atmosphere (Miller et al., 1984; Miller and Yoshinaga, 1981); moreover, they showed that sea-salt derived alkaline species such as Mg^{2+} and Na^+ decreased with elevation and therefore their neutralization effect was not prominent at higher elevations.

Neutralization factor values were quantified for each site as a function of season (Table 3). The cation exhibiting the highest overall NF values for all sites was NH_4^+ , except for BTT, indicating that of the measured ions, NH_4^+ was most responsible for neutralization. The WA14 and MM sites had especially high NFs for NH_4^+ . Specifically, MM had seasonal mean values between 0.84 (JJA) and 5.59 (DJF), whereas those for WA14 were between 0.52 (JJA) and 1.48 (SON). Five sites exhibited their highest NF values for NH_4^+ in DJF, with three others peaking in SON (WA14, NJ00, SC05), and the last being in JJA (CA45).

The BTT site was unique in that nss Ca^{2+} , rather than NH_4^+ , exhibited higher NF values for three of four seasons with a range between 0.29 (JJA) and 0.40 (MAM), albeit the differences per season between nss Ca^{2+} and NH_4^+ are quite small (< 0.10). An important source of nss Ca^{2+} is transported dust such as from northern Africa (Arimoto et al., 1992, 1995; Muhs et al., 2012), which can neutralize nss SO_4^{2-} and NO_3^- . For the other sites, the second most impactful neutralization agent was nss Ca^{2+} with seasonal average values ranging from 0.11 to 0.50. A wide body of work has associated Ca^{2+} in wet deposition with dust, including over Africa (Akpo et al., 2015; Bonnail et al., 2018), Asia (Cao et al., 2009; Qiao et al., 2015; Wu et al., 2016; Yang et al., 2005) and North America (Dadashazar et al., 2019; Sorooshian et al., 2013).

The impact of nss K^+ on the neutralization of precipitation acidity was relatively low for all sites (0.01–0.38), with the highest values being for MM (0.13–0.38). The influence of biomass burning at the MM site is also highlighted by how it was the only site where nss K^+ exhibited comparable NF values to nss Ca^{2+} and nss Mg^{2+} .

For context, NFs for other regions (i.e., China, Indonesia, Russia, Japan, Jordan, India) based on similar methods and units as this study were 0.05–0.54 for K^+ , 0.09–3.2 for Ca^{2+} , 0.19–1.5 for NH_4^+ , and 0.01–0.89 for Mg^{2+} (Das et al., 2005; Garaga et al., 2019; Lu et al., 2011; Xing et al., 2017; Xu et al., 2020; Yang et al., 2012). Values from the current study mostly fall in these ranges except for the minimum value for nss K^+ being 0.01 (HI00 and BTT), and the maximum of NH_4^+ being 5.59 (MM).

4. Conclusions

Multi-year wet deposition data were analyzed at nine different coastal sites to examine spatial and monthly variations in precipitation accumulation and chemical composition for understanding emissions, transport, and deposition of pollutants in coastal environments.

The three islands were exemplary in demonstrating the sensitivity of precipitation composition to meteorology, sources, elevation, and atmospheric circulation at different times of the year. For instance, the Manila site was distinct in exhibiting the most monthly variability in composition due to shifting wind directions and the wide diversity of sources impacting the region including biomass burning, continental pollution, and dust, which is supported by the highest concentration of ions (i.e., NH_4^+ , nss SO_4^{2-} , nss Ca^{2+} , NO_3^- , nss K^+ , nss Na^+ , nss Mg^{2+}) measured at this site. Influenced largely by sea salt, the Bermuda site was characterized by the highest overall ion concentrations and a low mean-annual pH value, the latter of which is influenced by upwind continental pollution (e.g., nss SO_4^{2-}) from areas such as North America. Bermuda was also vulnerable to the impact of dust as evident by the high NF values for nss Ca^{2+} , exceeding those of NH_4^+ as a function of season. The Hawaii site featured the lowest mass fraction of sea salt owing to its high elevation (i.e., 3399 m ASL) cutting off influence from surface marine sources. The Hawaii site had the highest mass fraction of nss SO_4^{2-} , which can be linked to the nearby volcanic emissions of SO_2 and long-range transport in the mid-troposphere.

The U.S. West and East Coasts exhibited contrasting monthly precipitation profiles, in which the highest monthly precipitation occurred in winter and summer, respectively. Different from the island sites, the continental U.S. sites generally exhibited less month-to-month variability in precipitation chemistry and acidity. Notable results were that the southernmost California site exhibited the highest NO_3^- mass fraction of ~30% owing to presumably abundant sources of HNO_3 . The wet deposition at the East Coast sites were more acidic than the West Coast, while the FL11 site had the highest pH of the East Coast sites, presumably assisted by transport of African dust and alkaline ions associated with it.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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HIGHLIGHTS

- Bermuda exhibited the highest ion concentrations due to sea salt.
- Anthropogenic and biomass burning tracer levels were the highest at Manila.
- Mauna Loa's high SO₄ fraction due to mid-tropospheric transport and volcanic emissions.
- North American continental sites had less monthly variability than the islands.
- Ammonium had the highest neutralization capacity at all sites except Bermuda (Ca²⁺).

Fig. 1.

Geographic location of the nine study sites from which wet deposition data were analyzed. HI00 is a NADP/NTN station at Mauna Loa, Hawaii; NJ00, SC05, and FL11 are NADP/NTN stations along the U.S. East Coast; WA14, CA42, and CA45 are NADP/NTN stations along the U.S. West Coast. Tudor Hill Atmospheric Observatory (BTT) and Metro Manila (MM) are sampling sites located in Bermuda and Luzon, Philippines, respectively.

Fig. 2.

Monthly average precipitation (blue bars) and volume-weighted mean pH (black markers) from the nine study sites over the periods described in Table 1. Although pH is shown with precipitation accumulation, no relationship between the two parameters is suggested.

Fig. 3.

Charge balance summary of each station based on their respective cumulative datasets based on time periods shown in Table 1. An outlier point was removed at WA14 for 11–August 18, 2015 and at FL11 for 13–April 19, 2016.

Fig. 4. Chemical mass fraction percentages of ions in precipitation collected at the Mauna Loa (HI00), the U.S. West Coast (WA14, CA45, and CA42), the U.S. East Coast (NJ00, SC05, and FL11), Tudor Hill Atmospheric Observatory at Bermuda (BTT), and Metro Manila (MM). Mass fractions were calculated using volume-weighted mean concentrations in unit of mg L^{-1} .

Fig. 5.

Monthly profiles of weekly volume-weighted mean concentration ($\mu\text{eq L}^{-1}$) and mass fraction of precipitation species. Similar to Fig. 4, mass fractions were calculated using volume-weighted mean concentrations in unit of mg L^{-1} . Months with missing data are due to a combination of dry conditions (CA45 and CA42) and, in the case of MM, limitations associated with Eq. (3)–(9) yielding negative values for some nss species, which were discarded from the analysis. Fig. S1 shows MM results for all months without applying Eq. (3)–(9).

Table 1

Geographic details associated with the nine study sites and the date range of data used in this work. Samples analyzed in this study were based on liquid precipitation samples and excludes influence of frozen precipitation. Precipitation data are based on years that had a full 12 months of data.

Program	Site	Lat/Lon(°)	Altitude (m ASL)	Time Period	Number of Samples	Annual Precipitation (mm)
NADP/NTN	Olympic National Park-Hoh Ranger Station (WA14)	47.86/-123.93	176	January 2007 - December 2016	321	2746
NADP/NTN	Hopland (CA45)	39.00/-123.93	253	January 2007 - December 2016	221	758
NADP/NTN	Tanbark Flat (CA42)	34.21/-117.76	853	January 2007 - December 2016	158	463
NADP/NTN	Edwin B. Forsythe National Wildlife Refuge (NJ00)	39.47/-74.43	2	January 2007 - December 2016	319	994
NADP/NTN	Cape Romain National Wildlife Refuge (SC05)	32.94/-79.66	1	January 2007 - December 2016	361	1261
NADP/NTN	Everglades National Park Research Center (FL11)	25.39/-80.68	2	January 2007 - December 2016	374	1450
NADP/NTN	Mauna Loa (HI00)	19.54/-155.58	3399	June 1980 - September 1993	291	402
AEROCE	Tudor Hill, Bermuda (BTT)	32.27/-64.87	51	January 1989 - February 1997, July 2006 - June 2009	953	2688
EANET	Metro Manila, Philippines (MM)	14.64/-121.08	87	February 2007 - December 2016	285	1996

Table 2

Summary of pH and major ions ($\mu\text{eq L}^{-1}$) in rainwater for weekly/event-based samples collected from different study sites. Listed are the volume-weighted mean concentrations (VMC), in addition to the arithmetic mean, standard deviation, minimum, maximum, and median concentrations.

	pH	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
HI00									
VMC	4.99	1.15	0.80	0.17	2.19	1.46	1.10	2.14	12.35
Mean $\pm$ std dev	5.42 $\pm$ 0.74	5.10 $\pm$ 9.34	3.39 $\pm$ 7.84	0.75 $\pm$ 2.84	13.96 $\pm$ 67.99	3.23 $\pm$ 5.97	2.43 $\pm$ 3.02	7.47 $\pm$ 13.16	25.86 $\pm$ 49.34
Min/Max	2.39/7.24	0.50/75.00	0.25/85.67	0.05/38.92	0.13/820.87	0.56/47.22	0.32/20.81	0.56/132.39	0.83/610.42
Median	5.44	2.00	1.08	0.13	3.61	1.11	1.29	3.38	13.13
BTT									
VMC	4.94	12.73	53.67	5.22	239.14	3.57	5.38	277.38	34.45
Mean $\pm$ std dev	4.92 $\pm$ 0.38	17.36 $\pm$ 43.72	69.20 $\pm$ 179.08	6.61 $\pm$ 18.56	305.11 $\pm$ 879.47	4.62 $\pm$ 5.93	8.34 $\pm$ 9.39	358.71 $\pm$ 1041.25	47.35 $\pm$ 106.76
Min/Max	3.23/1.09	0.10/823.35	1.73/3640.48	0.08/332.48	6.09/16670.29	0.11/50.34	0.11/76.42	8.35/19891.06	1.31/942.33
Median	4.93	7.14	26.86	2.66	116.75	2.68	5.31	136.84	23.69
MM									
VMC	4.95	33.81	13.06	17.60	21.79	124.91	24.95	25.82	46.74
Mean $\pm$ std dev	6.30 $\pm$ 0.85	57.66 $\pm$ 99.11	23.19 $\pm$ 45.78	43.68 $\pm$ 144.26	40.31 $\pm$ 116.95	253.26 $\pm$ 879.40	33.99 $\pm$ 59.03	48.75 $\pm$ 145.90	71.71 $\pm$ 117.60
Min/Max	2.99/8.57	1.50/877.69	0.41/309.42	0.26/1537.54	3.35/1739.89	0.61/11006.10	0.27/520.92	3.78/2126.94	9.24/1088.90
Median	6.35	28.94	9.34	7.42	19.53	52.99	19.92	22.06	42.06
WA14									
VMC	5.36	1.92	5.57	0.69	25.05	2.23	1.42	29.31	5.16
Mean $\pm$ std dev	5.30 $\pm$ 0.19	2.25 $\pm$ 3.39	4.48 $\pm$ 6.73	0.72 $\pm$ 0.84	19.53 $\pm$ 29.79	3.34 $\pm$ 13.99	2.85 $\pm$ 6.90	24.96 $\pm$ 50.83	6.50 $\pm$ 7.65
Min/Max	4.59/6.48	0.20/53.80	0.08/54.17	0.05/7.13	0.13/247.00	0.22/234.78	0.15/111.05	0.39/694.37	0.38/91.38
Median	5.34	1.65	2.25	0.46	9.59	0.94	1.58	11.32	5.13
CA45									
VMC	5.40	1.59	2.88	0.51	12.85	2.88	2.61	15.03	3.71
Mean $\pm$ std dev	5.39 $\pm$ 0.21	3.16 $\pm$ 6.45	2.81 $\pm$ 2.79	0.64 $\pm$ 0.80	11.11 $\pm$ 11.16	6.92 $\pm$ 18.31	6.17 $\pm$ 13.48	13.06 $\pm$ 13.06	5.79 $\pm$ 8.32
Min/Max	4.86/6.47	0.15/65.20	0.08/17.42	0.05/9.00	0.04/70.91	0.33/214.83	0.74/125.47	0.25/80.56	0.29/83.06
Median	5.39	1.85	2.00	0.41	7.17	2.50	2.79	8.28	4.04
CA42									
VMC	5.32	3.68	3.97	0.62	16.67	11.17	10.29	18.90	7.38

	pH	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
Mean ± std dev	5.30 ± 0.49	10.36 ± 23.03	6.87 ± 10.75	1.18 ± 43.74	25.82 ± 43.74	27.01 ± 28.27	30.89 ± 37.08	28.12 ± 46.64	15.10 ± 17.81
Min/Max	3.90/6.89	0.45/238.75	0.08/106.33	0.13/432.70	0.1/432.70	1.28/161.22	1.98/248.97	0.31/458.17	0.88/128.60
Median	5.34	4.05	3.92	12.70	12.70	16.69	17.33	14.10	8.93
NJ00									
VMC	4.93	4.93	4.96	1.55	37.49	12.88	10.98	43.73	18.90
Mean ± std dev	5.00 ± 0.45	5.00 ± 0.45	6.26 ± 9.40	1.90 ± 3.71	34.03 ± 40.93	16.35 ± 16.09	15.89 ± 14.25	40.11 ± 46.96	23.51 ± 20.58
Min/Max	3.76/6.47	3.76/6.47	0.33/71.50	0.05/53.44	0.57/314.87	0.44/108.00	1.00/115.71	1.18/361.75	1.46/202.56
Median	4.99	4.99	5.00	1.08	17.22	11.61	11.77	20.85	18.19
SC05									
VMC	4.88	3.61	5.47	0.81	23.19	6.02	8.22	27.46	14.69
Mean ± std dev	4.88 ± 0.29	5.62 ± 5.85	6.85 ± 7.97	0.99 ± 0.91	28.34 ± 34.60	7.17 ± 8.67	11.82 ± 8.67	33.30 ± 39.64	19.01 ± 14.34
Min/Max	4.09/5.91	0.85/70.60	0.25/79.58	0.05/7.67	0.57/333.13	0.76/61.03	0.76/61.03	0.99/409.41	3.02/129.44
Median	4.87	3.90	4.42	0.72	17.74	9.97	9.97	21.92	15.10
FL11									
VMC	5.09	5.76	5.80	1.93	23.57	7.88	8.47	27.46	13.54
Mean ± std dev	5.21 ± 0.49	10.23 ± 12.84	11.59 ± 16.48	2.86 ± 4.69	48.33 ± 73.77	12.01 ± 8.37	11.94 ± 83.44	55.47 ± 83.44	20.64 ± 16.41
Min/Max	4.17/6.92	0.90/148.80	0.58/180.00	0.13/46.03	4.30/809.39	0.11/57.24	5.21/918.85	5.21/918.85	1.44/125.10
Median	5.10	6.80	6.58	1.31	25.00	10.05	24.49	29.49	16.04

Table 3

Neutralization factor results for the four seasons at each site: DJF, MAM, JJA, SON refer to December–February (winter), March–May (spring), June–August (summer), and September–November (fall), respectively.

	Season	HI00	BTT	MM	WA14	CA45	CA42	NJ00	SC05	FL11
nss Ca^{2+}	DJF	0.22	0.36	0.50	0.36	0.23	0.13	0.13	0.12	0.25
	MAM	0.13	0.40	0.42	0.30	0.33	0.24	0.17	0.17	0.23
	JJA	0.13	0.29	0.43	0.13	0.11	0.18	0.14	0.14	0.29
	SON	0.17	0.34	0.38	0.21	0.19	0.18	0.18	0.16	0.24
nss Mg^{2+}	DJF	0.07	0.20	0.21	0.07	0.11	0.02	0.03	0.02	0.07
	MAM	0.06	0.11	0.12	0.07	0.06	0.05	0.04	0.04	0.04
	JJA	0.06	0.05	0.12	0.03	0.04	0.05	0.05	0.03	0.06
	SON	0.08	0.19	0.21	0.05	0.04	0.05	0.04	0.04	0.09
nss K^+	DJF	0.03	0.03	0.38	0.04	0.08	0.02	0.02	0.02	0.24
	MAM	0.02	0.01	0.13	0.04	0.07	0.03	0.05	0.04	0.05
	JJA	0.02	0.01	0.15	0.04	0.08	0.02	0.06	0.02	0.08
	SON	0.02	0.13	0.33	0.04	0.04	0.02	0.07	0.02	0.27
NH_4^+	DJF	0.49	0.38	5.59	1.40	0.80	1.05	0.34	0.34	0.59
	MAM	0.24	0.33	1.18	0.73	0.58	0.66	0.68	0.50	0.55
	JJA	0.19	0.23	0.84	0.52	0.82	0.73	0.52	0.24	0.36
	SON	0.23	0.24	1.84	1.48	0.43	0.77	0.72	0.61	0.36