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Spatial and Temporal Patterns in Atmospheric Deposition of Dissolved Organic Carbon

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Abstract Atmospheric deposition of dissolved organic carbon (DOC) to terrestrial ecosystems is a small, but rarely studied component of the global carbon (C) cycle. Emissions of volatile organic compounds (VOC) and organic particulates are the sources of atmospheric C and deposition represents a major pathway for the removal of organic C from the atmosphere. Here, we evaluate the spatial and temporal patterns of DOC deposition using 70 data sets at least one year in length ranging from 40° south to 66° north latitude. Globally, the median DOC concentration in bulk deposition was 1.7 mg L^{-1}. The DOC concentrations were significantly higher in tropical (<25°) latitudes compared to temperate (>25°) latitudes. DOC deposition was significantly higher in the tropics because of both higher DOC concentrations and precipitation. Using the global median or latitudinal specific DOC concentrations leads to a calculated global deposition of 202 or 295 Tg C yr^{-1} respectively. Many sites exhibited seasonal variability in DOC concentration. At temperate sites, DOC concentrations were higher during the growing season; at tropical sites, DOC concentrations were higher during the dry season. Thirteen of the thirty-four long-term (>10 years) data sets showed significant declines in DOC concentration over time with the others showing no significant change. Based on the magnitude and timing of the various sources of organic C to the atmosphere, biogenic VOCs likely explain the latitudinal pattern and the seasonal pattern at temperate latitudes while decreases in anthropogenic emissions are the most likely explanation for the declines in DOC concentration.

Plain Language Summary Dissolved organic carbon (DOC) is ubiquitous in precipitation. However, the geographic and temporal patterns in terrestrial ecosystems are not well established. We analyzed 70 data sets of DOC from rainfall collectors sampled for at least a year to examine these patterns and relate them to possible sources of the carbon. The combination of higher concentrations of DOC and more precipitation resulted in greater DOC deposition at low latitude sites. Some sites had strongly seasonal patterns in DOC concentration while others had similar concentrations year round. The most noticeable seasonal pattern was that the mid-latitude sites had the highest concentrations during the summer months. The latitudinal and seasonal patterns of DOC deposition best matched with the pattern of emissions of organic compounds from plants to the atmosphere suggesting plant emissions are the dominant source of DOC to ecosystems. The temporal trends from sites with at least 10 years of data suggest declining DOC concentrations, especially in the mid-latitudes. These declines are consistent with declines in anthropogenic emissions of organic compounds to the atmosphere over this time period. It is essential to document the patterns and changing amounts of DOC and other compounds in precipitation to understand the effects on terrestrial ecosystems.

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1. Introduction

Atmospheric deposition is a catch-all term for the physical transfer of particulate and dissolved materials and trace gases back to Earth's surface. While the magnitude of atmospheric deposition is often small compared to other parts of global elemental cycles, fluxes from the atmosphere to Earth's surface can have many important consequences for ecosystems. In some cases, these fluxes are largely natural, such as iron deposition to the ocean (Jickells et al., 2005) or nutrient inputs to tropical forests from dust (Okin et al., 2004). In other cases, atmospheric fluxes are anthropogenic compounds such as polychlorinated biphenyls deposition in the Arctic (Hung et al., 2005). In many cases, the deposition is naturally occurring, but the human activity has dramatically altered the magnitude and chemical composition of the flux, such as nitrogen deposition (Galloway, 2003), acid deposition (Lajtha & Jones, 2013), and ozone deposition (Lamarque et al., 2005). Although deposition from the atmosphere is recognized as a key component of most global elemental cycles, it is often ignored in studies of carbon (C) cycling (Schlesinger & Bernhardt, 2013).

It is widely known that organic compounds from biogenic and anthropogenic sources are emitted to the atmosphere, transported and transformed there, and deposited back to Earth's surface (Bidleman, 1988). One consequence of this wide range of sources is that dissolved organic carbon (DOC) is ubiquitous in precipitation. It has been suggested that precipitation provides a relatively small, but highly labile, input of organic carbon to both terrestrial (McDowell & Likens, 1988) and ocean (Willey et al., 2000) ecosystems. In terrestrial ecosystems this flux encounters the plant canopy first, where the phyllosphere community is typically C limited (Lindow & Brandl, 2003). In more remote terrestrial regions, DOC can also be the major source of acidity in precipitation (Andreae et al., 1988; Galloway et al., 1982; Likens et al., 1987). Human activity is likely changing the composition, magnitude, and spatial distribution of C inputs to terrestrial ecosystems. Before we can understand the importance of DOC deposition on ecosystems, we must know its spatial and temporal patterns.

Organic carbon deposition has been measured on varying temporal scales with multiple collection and analysis methods (Iavorivska et al., 2016). In some cases, only deposition during precipitation events is measured (wet-only sampling) while in many cases a mixture of wet and dry deposition is measured with a permanently open collector (bulk sampling). The magnitude of the transfer of organic C compounds in precipitation to the surface is a function of concentrations in the atmosphere, the washout ratio (which depends on the chemical properties of the compounds such as Henry's Law constant), and the partitioning between the vapor and particulate phase (Bidleman, 1988). Therefore high-concentration, highly soluble compounds, such as low molecular weight organic acids and aldehydes, would be expected to have the highest concentrations in precipitation. For example, Kieber et al. (2002) found formate and acetate concentrations of ~1 µM, which accounted for almost 10% of the total DOC. While the exact chemical composition of DOC in precipitation is unknown, there are several factors that affect site-specific DOC concentration, including air mass origin (Avery et al., 2006) and anthropogenic activities such as biomass burning (Coelho et al., 2008). Because the sources of C are often also sources of other elements, DOC concentration in precipitation has been found to be correlated with the concentration of many other inorganic constituents including mercury (Åkerblom et al., 2015; Boy et al., 2008).

The published global estimates of the global annual C flux based on precipitation samples are similar, ~400 Tg C yr^{-1} (Willey et al., 2000) and ~200 Tg C yr^{-1} (Raymond, 2005). Similarly, a global simulation model predicts almost 300 Tg C yr^{-1} (Safieddine & Heald, 2017). Although this C flux is two orders of magnitude lower than photosynthetic fluxes, it is of similar magnitude to the reported 400 Tg C yr^{-1} for the global riverine flux of DOC to the ocean (Schlesinger & Bernhardt, 2013). The estimate by Willey et al. (2000) was based on data from 16 sites at which between 1 and 205 measurements were made, typically over the course of less than one year, while the Raymond (2005) estimate is based on isotopic analysis of even fewer samples from a single site. The site level data compiled by Iavorivska et al. (2016) highlighted the spatial variability in DOC concentration and fluxes and the large difference between marine (0.92 mg L^{-1}) and continental (2.87 mg L^{-1}) concentrations but did not examine temporal variability. At the global scale, the spatial and temporal patterns of DOC in deposition are still underexplored.

Temporal patterns in site-level DOC have been reported for scattered locations around the world with different sampling frequency, sample collection and analysis methodologies, and study duration. Within a site, there is a negative exponential relationship between the DOC concentration and precipitation amount (Arisci et al., 2012; Pan et al., 2010). These authors suggest that this relationship means that dilution of DOC occurs

during high rainfall events, but also report that individual small rainfall events can have DOC concentrations of over 50 mg C L^{-1}. Many sites report predictable seasonal variation (Arisci et al., 2012; Boy et al., 2008; Jian-fen et al., 2005; Liu & Sheu, 2003; Mladenov et al., 2012; Verstraeten et al., 2014), but there are also some sites with little seasonal variation (Eklund et al., 1997). The interannual trends in DOC concentration are not consistent across studies: increases (Verstraeten et al., 2014), decreases (Willey et al., 2006), and no significant change (Vanguelova et al., 2010) have all been reported. Variability in terrestrial DOC deposition has been observed from precipitation samples (Iavorivska et al., 2016), while modeled data for the oceans suggest strong latitudinal and longitudinal patterns in the flux of DOC (Jurado et al., 2008).

Atmospheric C deposition may play an underappreciated role in ecosystem dynamics, given that it appears to contain a large fraction of low-molecular weight material that may be readily bioavailable. The goal of this study was to evaluate the spatial and temporal patterns in the concentration and fluxes of DOC at terrestrial sites across the globe and the underlying causes of these patterns, which is a fundamental step in evaluating the role of atmospheric deposition in terrestrial carbon cycling. We examined latitudinal patterns as well as seasonal cycles and interannual trends in DOC concentrations by focusing on data sets with at least one full year of samples. Finally, we searched for dilution effects of DOC in precipitation and examined the relationship between DOC and other major cations and anions in precipitation.

2. Methods

The database of DOC measurements in precipitation began with a search of the literature in the ISI Web of Science online database (http://isiknowledge.com/). However, because we found relatively few data sets using the search terms "DOC" and "precipitation" we supplemented the published data sets by contacting researchers who might be measuring DOC in precipitation. We asked if they had any data and if they knew anyone who had any data that encompassed at least 1 year of DOC in precipitation. The database includes 70 data sets from around the globe with data at least at monthly frequency for at least one complete year (Table S1). These data sets included nine publicly available data sets (Fredriksen & Johnson, 2019; Matt et al., 2021; McDowell. 2021; Sebestyen et al., 2020), 18 unpublished data sets, and 44 data sets described in the cited publications listed in Table S1. While this database is extensive, there are likely other published and unpublished data sets that are not included. For example, DOC is currently one of the mandatory parameters in International Co-operative Program on Assessment and Monitoring of Air Pollution Effects on Forests (http://icp-forests.net/page/data-requests). At four sites the chemistry was collected only as wet deposition, at 62 sites bulk deposition chemistry was collected, and at two sites both bulk and wet deposition were collected side by side for a total of 70 data sets. The sampling frequency included event-based, weekly, biweekly, and monthly sampling and the duration ranged from one to 21 years. We did not control for any differences in the method of filtering of the samples or differences in the analytical methods for measuring DOC because we could not control for these differences in the statistical analysis. In one case, the samples were unfiltered. Further, many studies do not include this information, so we strongly encourage future studies to make these methodological distinctions clear. Precipitation was always measured independently from the volume in the sample for chemistry. In addition to DOC, we also compiled the available data from these sites for the solutes measured by the United States National Atmospheric Deposition Program: calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), and chloride (Cl) along with hydrogen (H) reported as pH.

Prior to any analysis, all the data sets were converted, if necessary, to a monthly volume weighted mean (VWM) concentration for all solutes and a monthly total precipitation by summing the products of the concentration and precipitation volume for each sample during that month and dividing by the precipitation volume. Similarly, this process was repeated using the monthly samples to calculate an annual VWM. The annual deposition for each site was calculated by multiplying the annual VWM concentration and the average annual precipitation. Most sites were missing DOC concentrations for less than 10% of precipitation samples, but no adjustments were made to the annual deposition for missing data. The global flux (kg ha^{-1}) was calculated in two ways: (a) the product of the median global VWM DOC concentration from bulk collectors and the global average precipitation and (b) the area-weighted sum of the median tropical (<25°N or S) VWM DOC concentration and average tropical precipitation plus the median temperate (>25°N or S) VWM DOC concentration and average temperate precipitation. The precipitation data were 1° gridded data from Schneider et al. (2020). As different sources reported values as deposition (Tg) or flux (kg ha^{-1}), we used a global land extent of 13 billion ha and an ocean extent of 36 billion ha.

Relationships among sites and within sites between DOC concentration and the concentration of other solutes were examined by calculating Pearson product moment correlations using the monthly values. Data were log transformed as necessary to meet the assumptions of correlation. At the site level, we evaluated the binomial probability of the number of positive and negative relationships between DOC and each solute regardless of whether the correlation was significant. We investigated whether there was a power law relationship between DOC concentration and precipitation at the sites where precipitation was collected weekly, analogous to the concentration-discharge relationship that has been evaluated in rivers (Godsey et al., 2009). Within each site, we fit a power function ($C = aQ^b$ where a and b are constants) to the relationship of weekly solute concentrations (C) and precipitation amounts (Q). A log-log slope (b-value) of -1 indicates perfect dilution while a b-value of zero indicates that solute concentrations are independent of the water flux. The b-value was compared between temperate and tropical sites with a t-test.

We examined the frequency distribution of the VWM concentrations of each solute as well as the DOC deposition. We examined seasonal patterns at individual sites determining the month with the highest mean DOC concentration. Differences in DOC concentration between tropical ($<25°$N or S) and temperate ($>25°$N or S) sites were tested with a one-way ANOVA.

For data sets with at least 10 years of data, we used the Seasonal Mann-Kendall Test (SMK) in Matlab (Kendall, 1975; Mann, 1945) to determine statistically significant temporal trends in DOC concentration across sites. The SMK analysis is a non-parametric test that detects monotonic trends in the data accounting for seasonality. We defined the seasons to be January–March, April–June, July–September, and October through December.

For all statistical tests, significance was determined as $p < 0.05$.

3. Results

The latitude of the 70 sites ranged from 40°S to 66°N with precipitation ranging from approximately 550 to 4,000 mm (Table S1). The annual VWM DOC concentrations varied from 0.3 to 9.7 mg C L^{-1} with a median of 1.7 for bulk deposition collectors (Figure 1). The DOC concentrations, as well as those of all other solutes, tended to be positively skewed. The range in annual C flux was 8–132 kg C ha^{-1} yr^{-1}, with a median of 18 kg C ha^{-1}. Similar to the concentration data, the DOC deposition was positively skewed with a mean of 27 kg C ha^{-1} (Figure 2).

Both wet and bulk deposition sites were included in this study, but the limited number of wet deposition sites precluded any comparisons between collection methods. However, at two sites both wet and bulk deposition were measured side by side. At Calhoun Forest in the southeastern United States the DOC concentrations were twice as high in bulk deposition compared to wet deposition while at El Verde in Puerto Rico, the bulk deposition was almost four times as high as wet deposition (Table 1). This represents the largest increase in the ratio of bulk to wet suggesting that dry deposition is most important for DOC. At El Verde, the other solutes were close to a 1:1 ratio with the notable exception of NH$_4$ and NO$_3$, which were twice as high in wet deposition compared to bulk deposition. In contrast, at Calhoun, NO$_3$, SO$_4$, and Na, were similar in concentration, as was pH, in the two collector types, but the concentrations of all the other solutes were two to six times higher in bulk deposition.

The annual VWM DOC concentration was significantly positively associated with the concentrations of Ca ($r = 0.44$) and K ($r = 0.49$), and significantly negatively associated with pH ($r = -0.33$) and Na ($r = -0.30$) using sites with bulk collectors as replicates (Figure 3). Within a site, the correlations of DOC with other solutes were more consistent. Over 90% of the sites had positive correlations between DOC and Ca, K, SO$_4$, NH$_4$, and NO$_3$ and almost 70% of the sites had a positive correlation between DOC and Mg; based on the binomial probabilities this pattern was not due to chance. The relationships between DOC and pH, Na, and Cl were about equally split between positive and negative correlations.

Tropical and temperate sites differed in both the concentration and seasonal variability of DOC. There were strong latitudinal patterns in annual DOC concentrations (Figure 4). The mean DOC concentrations from bulk collectors were significantly higher at tropical sites (3.6 ± 0.73 mg C L^{-1}) compared to temperate sites (1.7 ± 0.10) ($p < 0.0001$). Similarly, the mean ($\pm$SE) annual C deposition in bulk collectors was significantly higher in the tropics (70 ± 10 kg C ha^{-1} yr^{-1}) compared to temperate sites (19 ± 1.3 kg C ha^{-1} yr^{-1}) ($p < 0.0001$). In part this is due to the significantly higher average measured precipitation in tropical (2,300 mm yr^{-1}) compared to temperate
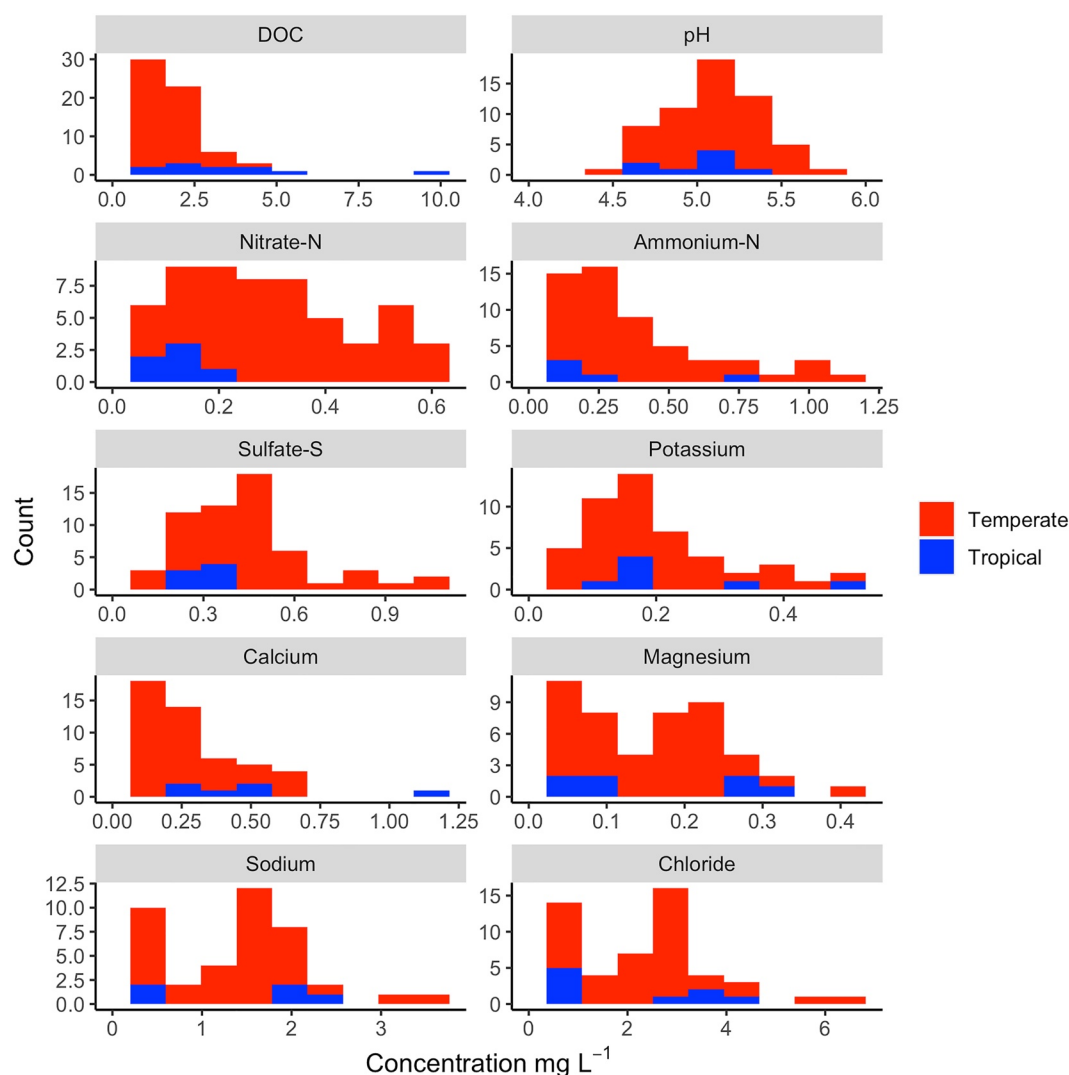
Figure 1. Histogram of annual volume weighted mean concentration for all solutes (mg L^{-1}) and pH by site for bulk deposition sites. DOC = dissolved organic carbon.

(1,200 mm yr^{-1}) sites. At both tropical and temperate sites with highly seasonal precipitation, the monthly DOC concentration was strongly negatively related to the amount of precipitation (Figures 5a and 5c). However, at sites without a pronounced dry season, the temperate sites had stronger seasonality in DOC concentration than the tropical sites. For example, at Cone Pond, New Hampshire a temperate site in the United States, there was a clear summer maximum with the monthly DOC concentration almost 4 times the minimum monthly VWM concentration (Figure 5d). In contrast, the bulk collector at a tropical site in El Verde, Puerto Rico had a smaller difference between the minimum and maximum monthly DOC concentration and lacked a seasonal pattern in DOC concentration (Figure 5c). The timing of the maximum also differed between temperate and tropical sites. Temperate sites had the highest DOC concentrations in July while tropical sites had the highest monthly concentration evenly distributed throughout the year (Figure 6).

Focusing on sites with weekly precipitation sampling, there was evidence for some dilution of all the solutes. The Bisley, Puerto Rico site is shown as an example for DOC. There is a significant negative relationship that is linear on a log-log scale with a slope (*b*-value) from the power law relationship of −0.50 (Figure 7). Across all sites the median *b*-value for the various dissolved constituents ranged from −0.26 for Ca to −0.49 for DOC (Table 2). The *b*-value was significantly lower in temperate than tropical sites (Figure 8, $p < 0.005$).
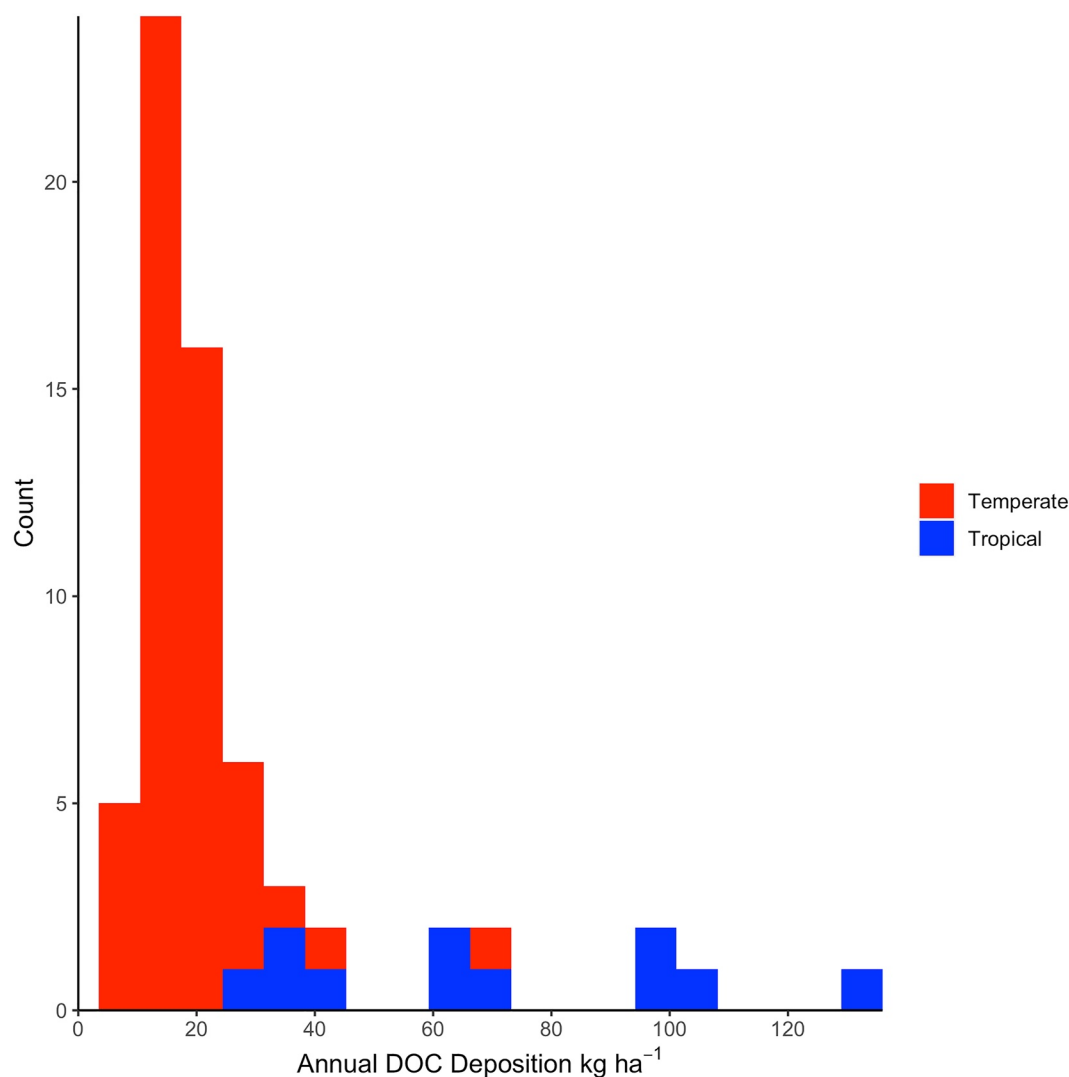
Figure 2. Histogram of annual dissolved organic carbon (DOC) deposition (kg ha^{-1}) by site for sites with bulk deposition collectors.

Thirteen out of the 34 sites with records longer than 10 years had a significant trend in DOC concentration over time, all negative. The significant Sen's slopes ranged from -0.008 to -0.170 mg C L^{-1} yr^{-1} (Figure 9). There were relatively few long-term data sets for the tropics, but the variability in the magnitude of the slopes was greater at the temperate sites.

4. Discussion

4.1. Global Estimates of DOC in Precipitation

The global organic C deposition budget can be estimated using a variety of approaches (Table 3). One set of bottom-up approaches used measured DOC in precipitation and extrapolated up to a global estimate by multiplying an average concentration by a total water flux. Often, the number of sites is quite small. The estimates for terrestrial deposition have ranged from 101 (Raymond, 2005) to 299 (Willey et al., 2000) to 442 Tg C yr^{-1} (Iavorivska et al., 2016) corresponding to an average flux of DOC of 7.7–23–34 kg C ha^{-1}, respectively. Using a spatially gridded precipitation data set, our median DOC concentration of 1.7 mg L^{-1} results in annual deposition of 202 Tg C yr^{-1} or an average flux of 17 kg C ha^{-1}. One problem with these estimates may be spatial distribution of the sampling. In the present study DOC concentrations and deposition were significantly higher in tropical

Table 1

Ratio of Volume Weighted Mean (VWM) Concentrations of Wet: Bulk Collectors for Each Solute at the Two Sites, El Verde in Puerto Rico and Calhoun Forest in the Southeastern United States, Where Both Types of Precipitation Collector Were Measured Side by Side

	El Verde	Calhoun
DOC	0.31	0.54
Na	0.88	0.73
K	0.80	0.15
Ca	0.77	0.22
Mg	0.84	0.33
NH_4-N	1.80	0.36
NO_3-N	1.85	0.88
SO_4-S	0.95	0.81
Cl	0.92	0.55
H	0.92	1.62

Note. At each site, samples from both collection types were filtered prior to analysis. Ratios less than one represent enrichment of solutes associated with collection of dryfall in an open container. Ratios greater than one suggest consumption or transformation of biologically active materials during the interval between the precipitation event and the collection and processing of samples. DOC = dissolved organic carbon.

than temperate sites. In addition, the precipitation is much higher in the tropical (1,367 mm yr^{-1}) than temperate (571 mm yr^{-1}) latitudes. The previous estimate by Raymond (2005) only used data from one mid-latitude site while the estimate by Willey et al. (2000) used a mixture of temperate and tropical sites. These authors suggested that the wet deposition of 46 kg C ha^{-1} yr^{-1} for Manaus in the Brazilian Amazon is an outlier. However, similarly high values have been subsequently measured throughout Brazil, especially in areas with high biomass burning (Coelho et al., 2008). The deposition in Manaus would be below the mean value of 60 kg C ha^{-1} yr^{-1} for bulk deposition in the tropical sites included in the present study. The data set in Iavorivska et al. (2016) included many more tropical sites than the other two studies and reported a much higher concentration of DOC, but included sites without at least one full year of data. Therefore, using a global average concentration based on a data set skewed toward temperate sites would underestimate the deposition since the concentrations are significantly higher at the tropical sites. Given the greater concentration of DOC measured in bulk adjacent to wet deposition collectors, it appears important to take the dry deposition account in these calculations (Table 1).

The atmospheric deposition of organic C can also be calculated with a top-down approach by partitioning the fate of global emissions of organic C to (a) oxidation to carbon dioxide and (b) dry and wet deposition on an annual basis. Using this approach, (Goldstein & Galbally, 2007) estimated that the 1,300 Tg C yr^{-1} of volatile organic compounds (VOC) emissions resulted in 305–645 Tg C yr^{-1} of dry and wet deposition. Similarly, a simulation model estimated that the ∼1,000 Tg C yr^{-1} in the atmosphere from global annual emission of non-methane organic C emissions resulted in the deposition of 259 Tg C yr^{-1} on land and 230 Tg C yr^{-1} to the ocean (Kanakidou et al., 2012).

4.2. Spatial Patterns of DOC Deposition

By comparing the magnitude as well as the spatial and temporal patterns of emissions to deposition, we can begin to evaluate the drivers that appear to affect DOC deposition. While many sources likely contribute DOC to precipitation to some degree at every location, we explore which of these sources can explain the observed patterns in DOC deposition. The major patterns are (a) higher DOC concentrations at tropical sites compared to temperate sites (Figure 4), and (b) higher DOC concentrations in the growing season at temperate sites (Figure 6). While there is some uncertainty in the mass of the various emissions of organic C to the atmosphere, the spatial and temporal patterns are better constrained. The major potential sources of DOC are (a) primary particulates consisting of primary biological particles (PBPs) and from biomass burning, fossil fuel combustion, dust, and sea salt organic aerosols, all of which vary in their solubility, and (b) emissions of VOC from biomass burning, anthropogenic emissions, and biogenic emissions. Of the global models reported by Kanakidou et al. (2012), the biogenic VOC emissions typically account for ∼80% of the total gaseous emissions of organic C to the atmosphere.

Global models suggest that primary particulates are likely a minor source of DOC in deposition at a global scale because of their relatively low contribution (28–269 Tg C yr^{-1}) to atmospheric organic C combined with their low (10%–50%) solubility, but the uncertainty in these estimates is high (Kanakidou et al., 2012). Dust emissions are most important in the subtropics, particularly North Africa and the Arabian Peninsula (Tegen & Fung, 1994), but our data set does not include this region. If we assume a global dust flux of 1,000–2,000 Tg yr^{-1} (Jickells et al., 2005) and an organic C content of 3.5% (Jurado et al., 2008), organic C in dust would be ∼53 Tg C yr^{-1}. However, most (∼90%) of this C would be present as insoluble forms, which would not contribute to DOC deposition (Kanakidou et al., 2012). Sea salt aerosol emission is highest in high latitudes and lower in tropical latitudes (Spada et al., 2013), once again the opposite of the observed patterns. Further, modeled emissions of primary marine organic aerosol are relatively low, less than 10 Tg yr^{-1} (Meskhidze et al., 2011). The PBPs are the biggest source of uncertainty. A review of biogenic aerosols reported high variability in the annual emissions ranging
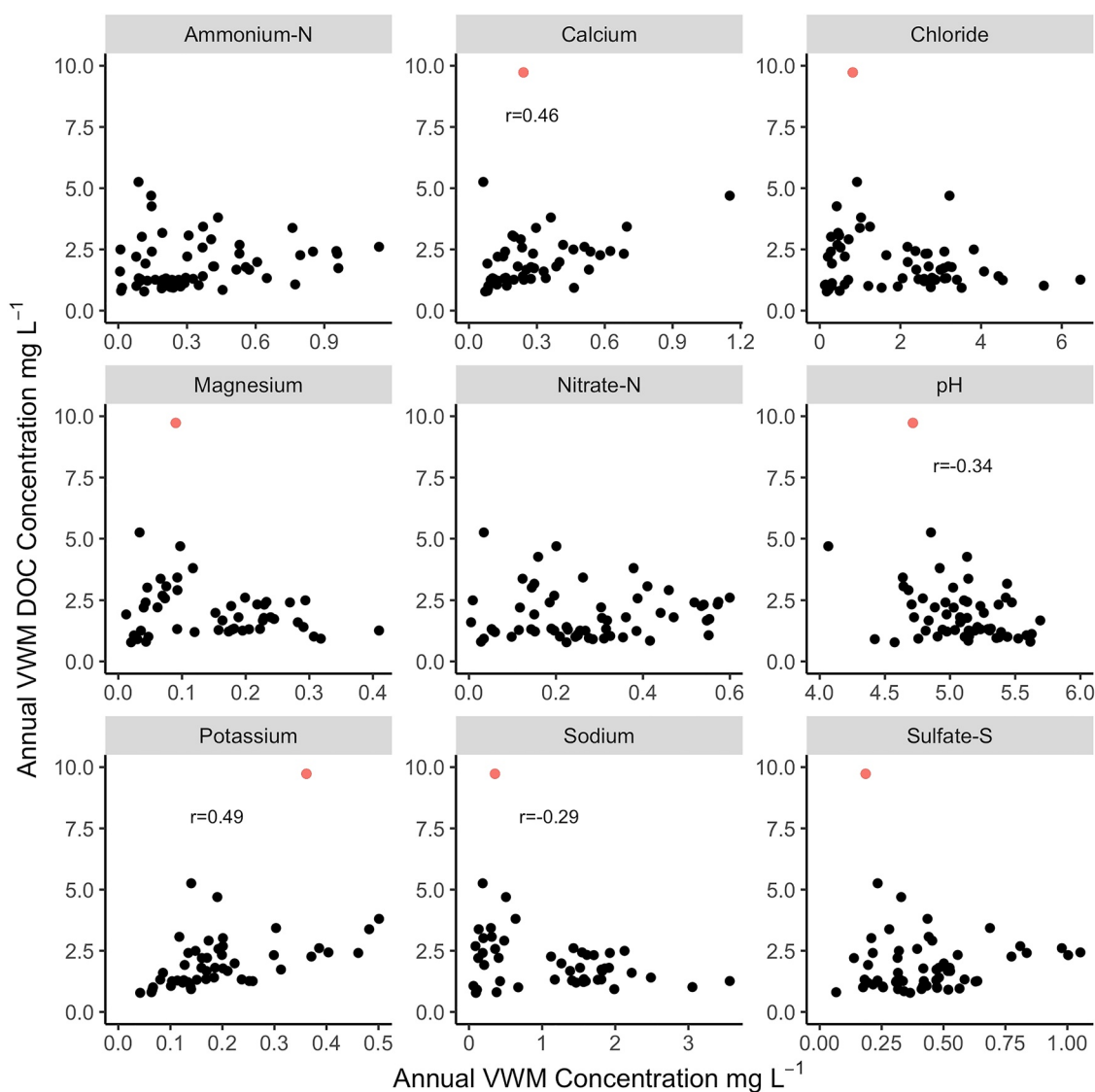
Figure 3. Relationship between volume weighted mean dissolved organic carbon (DOC) concentration and concentration of other solutes and pH with filled circles representing sites. Correlations were significant for potassium, calcium, ammonium, nitrate, sulfate, and pH. The site with the highest DOC, shown in red, was excluded from the analysis because it was an outlier for most solutes.

from <10 to 1,000 Tg yr^{-1} or <5 to 500 Tg C yr^{-1} assuming that these particulates are 50% C by mass (Després et al., 2012). These particulates include bacterial cells, fungal spores, and pollen, but may also include a large amount of plant fragments (Jaenicke, 2005). Pollen can likely be ruled out as the main cause of the global patterns of precipitation DOC as most tropical pollen is not wind dispersed. There is more overlap in the timing of pollen release and the seasonal DOC patterns in temperate systems, and it is clearly a source of soluble phosphorus in deposition, but it is less clear that it is a source of soluble C (Doskey & Ugoagwu, 1989). Further, the increase of DOC in temperate systems lasts for the whole growing season, not just during the short window early in summer when pollen appears to have the most effect on deposition chemistry (Anttila et al., 1995). In the tropics, fungal spores may be the major source of PBPs, but once again, their importance as a source of soluble C in deposition is not well established (Elbert et al., 2007). Thus, we cannot rule out PBPs as an important source of DOC in precipitation, but the magnitude of the emissions, the solubility of the materials, and the temporal and spatial patterns suggest they are not the dominant source.

Gaseous emissions of VOCs dominate the potential sources of DOC deposition. Anthropogenic emissions, including fossil fuel combustion, biofuel combustion, industrial processes and waste management, contribute
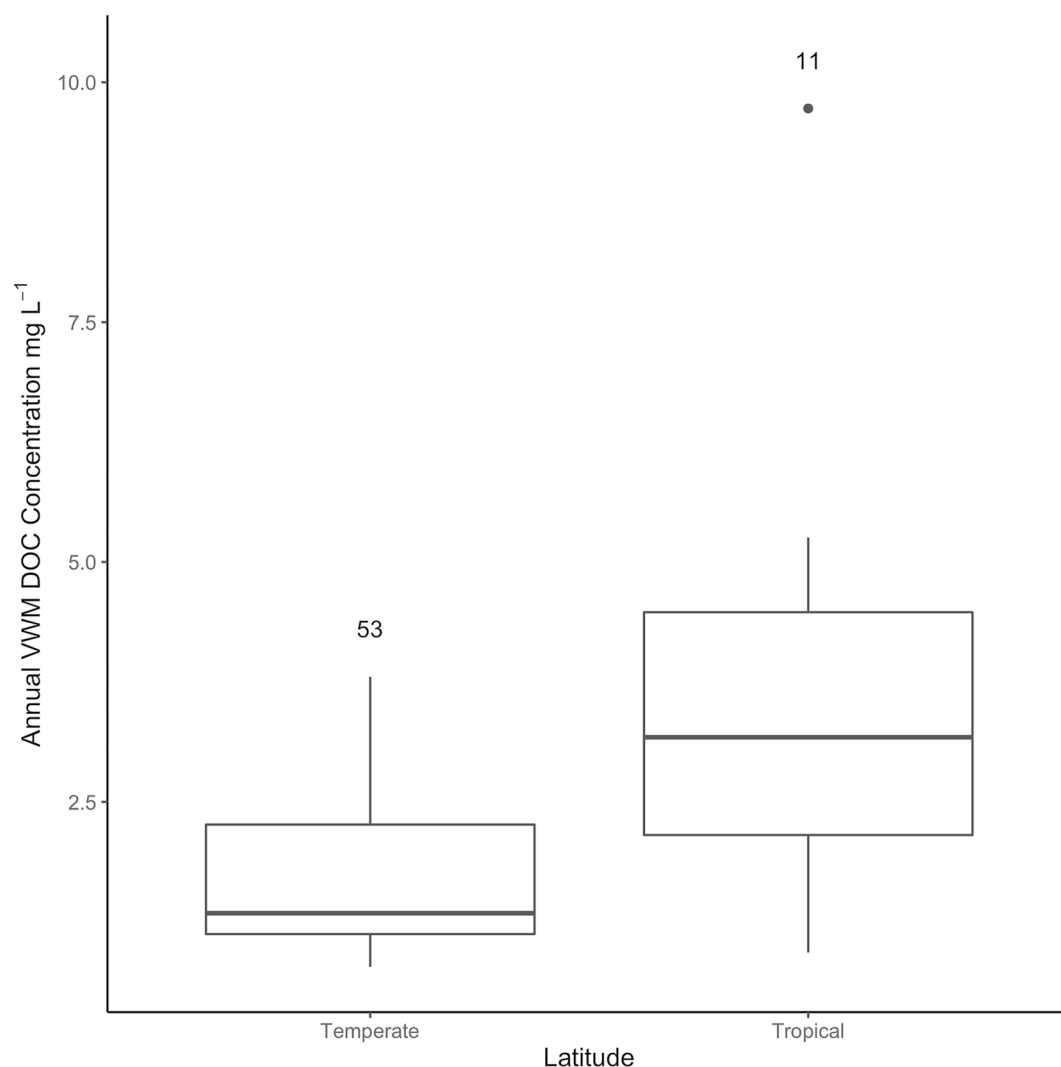
Figure 4. Boxplot of site-level volume weighted mean (VWM) dissolved organic carbon (DOC) concentration at sites with bulk deposition collectors at temperate (>25°) or tropical (<25°). The central line is the median, the upper and lower edges of box are 75th and 25th percentile, the whiskers are the whole range, excluding outliers, and points are outliers. Numbers above the boxplots are the count of sites in each boxplot.

~100 Tg C yr^{-1} to the atmosphere (Reimann & Lewis, 2007). However, the vast majority of these emissions are from the mid-latitude northern hemisphere and not the tropics (Piccot et al., 1992). Biomass burning is concentrated at low latitudes with high interannual variability related to drought with annual emissions on average 1,900–2,500 Tg C yr^{-1} (Randerson et al., 2012; van der Werf et al., 2010). Only a small fraction of the C emitted from biomass burning is in the form of VOCs. Recent estimates suggest emissions of ~350 Tg C yr^{-1} as VOCs from biomass burning globally assuming VOCs are 70% *C* (Akagi et al., 2011; Yokelson et al., 2008), much higher than earlier estimates of only 70 Tg C yr^{-1} (Andreae & Merlet, 2001). Similar to biomass burning, terrestrial biogenic VOC emissions are concentrated at low latitudes with half of all emissions from tropical woodlands (Guenther et al., 1995). The output from MEGAN, a global biogenic VOC emission model, suggests on average 760 Tg C yr^{-1} with relatively small (<30%) interannual variability in emissions; these modeled emissions were greatest in the tropics, especially south of the equator, and are highly seasonal in the temperate zone (Sindelarova et al., 2014). Based on a simple regression, 22% of the variance in annual DOC deposition could be predicted by the biogenic VOC emissions estimated by the MEGAN model for the coordinates of the studies included in this analysis. Given the global magnitude of their emissions and their maxima at low latitudes, biomass burning and biogenic VOCs likely represent the dominant sources of precipitation DOC.
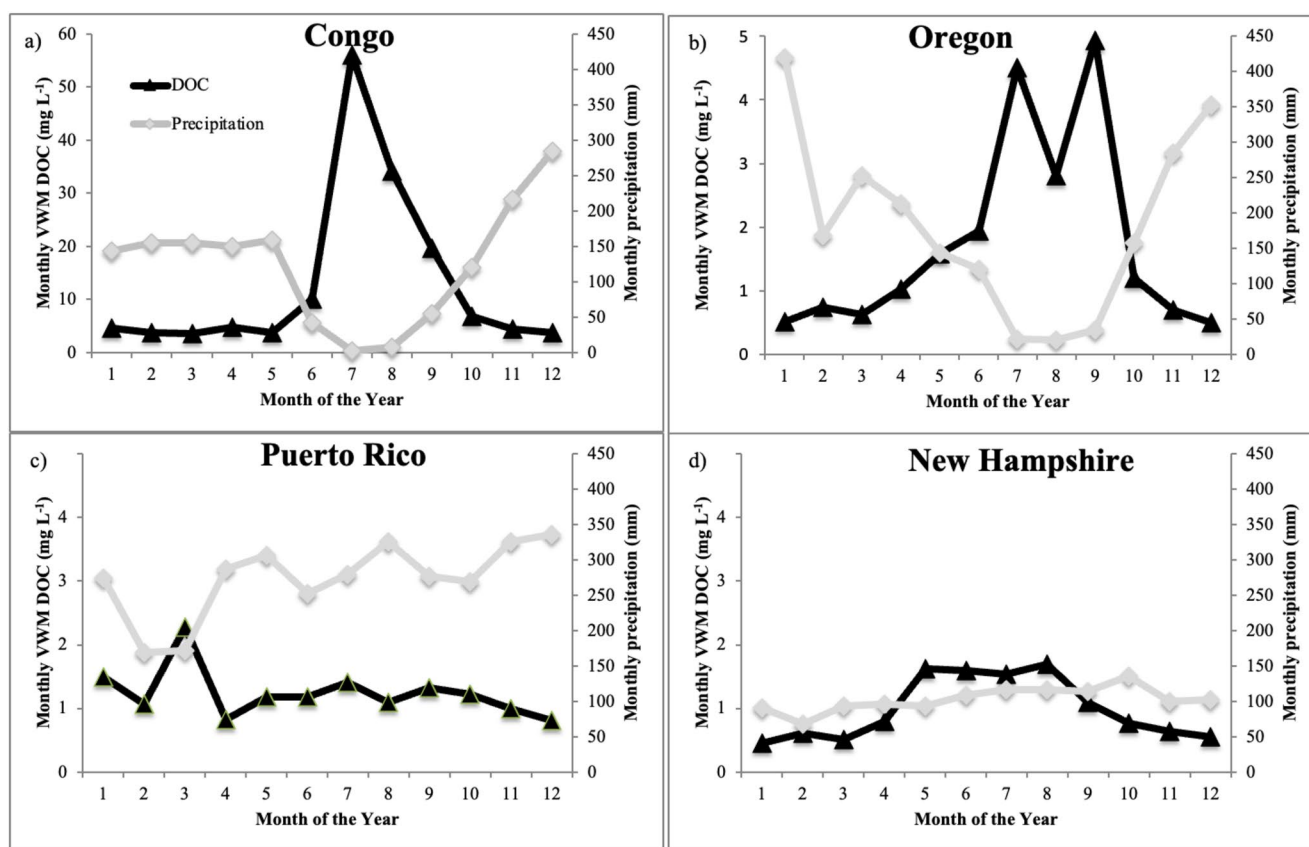
Figure 5. Volume weighted mean (VWM) monthly dissolved organic carbon (DOC) concentrations in bulk deposition and monthly precipitation for two tropical (a, c) and temperate (b, d) and strongly seasonal (a, b) and weakly seasonal (c, d) in terms of precipitation. Further information about these sites is available in Table S1. Both vertical axes are scaled the same on all plots except for VWM DOC concentrations in plot a.

4.3. Temporal Patterns of DOC Deposition

Most sites exhibited one of two types of seasonality in the concentration of DOC. First, seasonally dry tropical and temperate sites had relatively low DOC concentrations during the wet season and relatively high DOC concentrations during the dry season (Figures 5a and 5b). The simplest explanation for the seasonality of DOC concentration is dilution of DOC in precipitation, but changes in sources, like the timing of biomass burning, may also play a role. In terms of DOC deposition, the seasonality is less distinct as the high DOC concentration and low precipitation in the dry season is approximately balanced by the low DOC concentration and high precipitation in the wet season. Second, many temperate sites, without strong seasonality in precipitation, had DOC concentrations twice as high during the growing season (Figure 5d). At these latitudes, increased biogenic VOC emissions are the most likely cause of this pattern as the seasonality of the VOC emissions and the deposition of C are similar. Other potential sources are either relatively small at these latitudes (e.g., biomass burning) or not strongly seasonal (e.g., industrial emissions). Finally, the only sites without seasonality were the wet tropical sites without a strong dry season (Figure 5c). In addition, there may be offsetting seasonality of the major sources of DOC. While there is strong seasonality in both biomass burning and biogenic VOC emissions in tropical latitudes, the seasonal patterns are opposite. That is, biomass burning tends to be highest in the hemisphere's dry season and biogenic emissions are highest during the hemisphere's wet season (Sindelarova et al., 2014; van der Werf et al., 2010).
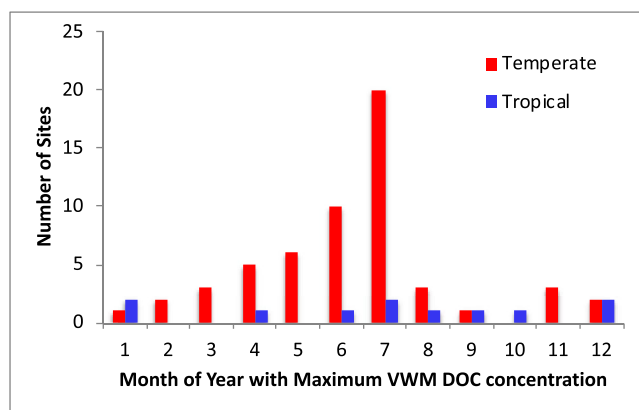

Figure 6. Histogram of the monthly maximum site-level volume weighted mean (VWM) dissolved organic carbon (DOC) concentration for tropical and temperate sites.
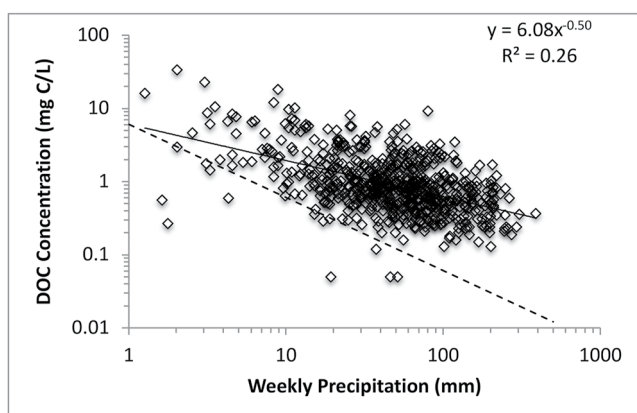
Figure 7. Relationship between volume weighted mean dissolved organic carbon (DOC) concentration and precipitation depth for weekly samples at the Bisley site in Puerto Rico shown on a log-log scale. The solid line represents the best fit power function. The dashed line represents the line with the same *a*-value, but with a *b*-value of −1 indicating perfect dilution.

There are relatively few published long-term data sets with temporal trends in DOC deposition. A decline in DOC at a single site in North Carolina of ∼0.05 mg C L^{-1} yr^{-1} has been reported (Willey et al., 2006). In that study, the decrease in DOC in precipitation was associated with a decrease in small organic acids (formic, acetic, oxalic) that are either emitted directly or are the oxidative breakdown products of other anthropogenic emissions, particularly vehicle exhaust. The decline at the North Carolina site was in the middle of the range of the trends for the sites in the present study. Twelve out of 31 temperate sites, located in western Europe and the United States, and one out of four tropical sites with long-term data (>10 years) had significant trends in DOC concentration, all negative ranging from −0.008 to −0.170 mg C L^{-1} yr^{-1} (Figure 9). Of the factors described earlier, this temporal pattern seems to correspond most to the decline of industrial emissions in Europe and North America (USEPA, 2018). There is high regional variability in biomass burning annually, but no trends in recent global emissions (van der Werf et al., 2010). There is no indication that emissions of any other type are changing either.

4.4. DOC and Other Solutes

The relationships between DOC and other solutes can also provide some clues about the sources of DOC (Figure 3). Using wet deposition data, there are strong associations among ions associated with sea salt (Na and Cl) and acid deposition from fossil fuel burning (NH_4, NO_3, SO_4, H), but more complicated patterns with Ca, Mg, and K (Hooper & Peters, 1989). The average Cl:Na and Mg:Na ratios (in microequivalents) across all sites were 1.14 and 0.23, very close to the ratios in seawater: 1.16 and 0.23 (USDOE, 1994). It appears that sea salt aerosols are thus the dominant source of Na, Cl, and Mg to precipitation. None of these ions were strongly associated with DOC in precipitation. In contrast, the average K:Na and Ca:Na ratios were 0.08 and 0.25 in deposition compared to 0.02 and 0.04 in seawater. Potassium concentrations are high in particles emitted from biomass burning (Reid et al., 2005), but can also be emitted in organic aerosols from plants (Pöhlker et al., 2012) and fungi (Zhang et al., 2015). Because the spatial patterns of both biomass burning and biogenic emissions were similar to those of DOC, it is conceivable that these were also sources of K. Calcium deposition is typically associated with dust deposition and increased human disturbance to arid areas (Brahney et al., 2013). However, long-distance transport of North African dust to the Caribbean and South America is known to be a major source of elements, including Ca (McClintock et al., 2019). It is surprising that Ca was the ion most strongly correlated with DOC across sites as it is unclear what source would provide both Ca and DOC, but not other cations. The high frequency of within-site correlations of DOC with NO_3, NH_4, and SO_4 suggests that fossil fuel combustion is at least periodically a source of DOC. However, Boy et al. (2008) found that NO_3 and NH_4 were the ions most strongly associated with DOC at a remote site in the Amazon far from fossil fuel emissions.

Positive relationships between DOC and Ca, Mg, NO_3, NH_4, or SO_4 were observed within sites and also among sites for Ca and Mg. Air masses from different source regions can lead to precipitation events with different chemistries within sites. For example, Avery et al. (2006) found significant differences in organic acid concentrations in precipitation related to the direction of the back trajectory of the storm. Similarly,

Table 2
Values for b Parameter of the Power Law Relationship Between for Solute Concentration (C) and Precipitation (Q) for all Sites With Weekly Data

	DOC	Na	K	Ca	Mg	NH_4-N	NO_3-N	SO_4-S	Cl
Median	−0.49	−0.37	−0.34	−0.26	−0.28	−0.35	−0.43	−0.31	−0.30
Max	−0.10	0.07	−0.06	0.06	0.06	−0.05	0.02	−0.02	0.15
Minimum	−0.61	−0.58	−0.47	−0.71	−0.59	−0.61	−0.92	−0.48	−0.69

Note. A value of −1 indicates perfect dilution and a value of 0 indicates chemostasis. DOC = dissolved organic carbon.
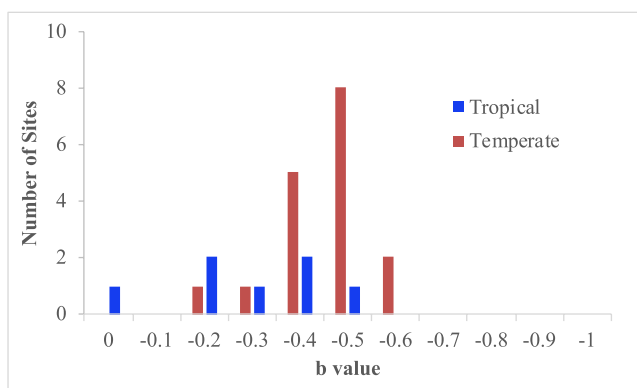
Figure 8. Histogram of the *b*-value from the power function ($C = aQ^b$) where *C* is dissolved organic carbon concentration and *Q* is precipitation depth for the 24 data sets with weekly measurements. A value of −1 indicates perfect dilution and a value of 0 indicates chemostasis.

Willey et al. (2006) reported significantly more acidic rainfall in storms from continental sources compared to marine sources. The similarity in the relationships among ions within and among sites indicates that the same factors control variability in precipitation chemistry at both scales. Analysis of carbon isotopes can also provide some clues about the sources of DOC in precipitation. Using ^{13}C and ^{14}C, the contribution from fossil fuels, marine sources, and terrestrial sources can be partitioned. At a coastal site in Alaska, the DOC in deposition was dominated by fossil fuel sources (Fellman et al., 2015). In contrast, a coastal site in Connecticut was dominated by modern marine and terrestrial carbon sources on average (Raymond, 2005). However, individual rain events were highly variable ranging from 0% to 80% modern terrestrial carbon.

The intermediate *b*-values from the concentration-precipitation relationship correspond to partial dilution of the DOC and inorganic solutes in precipitation (Figure 8). The partial dilution suggests that there is some type of limitation to the production of DOC in precipitation such that some dilution at high volume occurs. Changes in solute concentrations during precipitation events have been observed, but the causes can be difficult to pinpoint because the dissolved constituents can be incorporated by within-cloud or below-cloud scavenging or advection (Beverland & Crowther, 1992). There is not a consistent pattern of DOC concentration over time in storm events, but the middle of the storm tends to have the lowest concentrations (Iavorivska et al., 2017). The DOC concentration can reflect multiple possible source areas containing gases and aerosols that can be incorporated in precipitation as well as changes in the rate of precipitation over time. However, the intermediate *b*-value in the atmosphere suggests that there is a reservoir of DOC in the atmosphere that can be replenished at relatively short time scales similar to what occurs in tropical rivers in high rainfall areas (Shanley et al., 2011).

5. Conclusions

The global DOC deposition based on the current study is generally consistent with previous global estimates. However, the strong latitudinal pattern in our global data set, with concentrations 2*x*, deposition 3.5*x*, and precipitation 2.4*x* greater at the tropical sites suggests that using a global average concentration with existing data sets and a global precipitation flux would underestimate the global deposition flux. Given the higher fluxes and low number of samples included in this study from the tropics, it is important to increase the sampling density at low latitude sites to improve our understanding of the spatial patterns. Further, the strong seasonal patterns highlight the necessity of collecting samples year-round. The high concentrations in the tropics are consistent with the higher biogenic VOC emissions at these latitudes, but biomass burning is also highest at these latitudes. The seasonal maximum DOC concentration in temperate latitudes is also consistent with the timing of biogenic VOC emissions, but biological particulates may also play a role. The long-term decreasing trends in DOC concentrations observed throughout the northern hemisphere are consistent with the decline of anthropogenic VOC emissions in developed countries. The various changes in precipitation chemistry over the last century because of human activities have resulted in changes in ecosystem nutrient dynamics (Groffman et al., 2018). As precipitation chemistry continues to change, the role of DOC in ecosystem processes needs to be examined in terms of precipitation pH, chemistry of labile C, and interactions with other solutes.
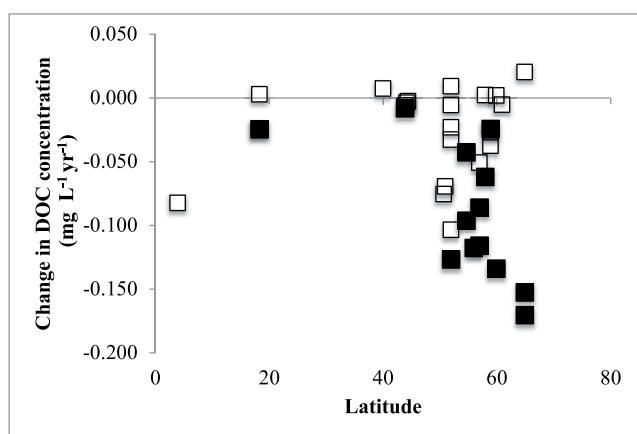
Figure 9. Long-term trends in dissolved organic carbon (DOC) concentration by latitude in the northern hemisphere (no long-term sites were located in the southern hemisphere). Square symbols represent the annual change in DOC concentration over time (Sen's slope) calculated for the long-term (>10 years) data sets examine with the Seasonal Mann Kendall tests. Filled symbols represent sites with significant trends and open symbols represent sites with non-significant trends.

Table 3
Published Values of Annual Global, Terrestrial and Marine Deposition and Flux of Carbon From the Atmosphere to Earth's Surface

Study	Method	Terrestrial flux (kg ha^{-1})	Terrestrial deposition (Tg)	Marine flux (kg ha^{-1})	Marine deposition (Tg)	Global deposition (Tg)
Willey et al. (2000)	Measurements	23	299[a]	2.5[b]	90	389
Raymond (2005)	Measurements	7.7[a]	101	3.5[b]	127	228
Iavorivska et al. (2016)	Measurements	34	442[a]			
Kanakidou et al. (2012)	Model	22[a]	282			
Jurado et al. (2008)	Model			6.8[b]	246	
Safieddine and Heald (2017)[c]	Model	14	188	2.4[b]	85	273
Goldstein and Galbally (2007)	Mass balance					475[d]
This study – global	Measurements	17	202[a]			
This study – latitudinal	Measurements	23	295[a]			

Note. The estimates for this study were calculated with the annual 2011–2019 precipitation from Schneider et al. (2020) using (a) the global median bulk collector volume weighted mean (VWM) dissolved organic carbon (DOC) concentration multiplied by the global average precipitation and (b) the sum of the median volume weighted mean DOC concentration for the latitude zones (<25° or >25°) multiplied by average latitudinal precipitation.
[a]Calculated using a global land area of 13 billion ha. [b]Calculated using a global ocean area of 36 billion ha. [c]Wet deposition only. [d]Calculated as the mean of the reported range.

Data Availability Statement

Support for collection of individual data sets is described in the references that describe the data sources. The survey to contact researchers by email to find appropriate data sets was organized and implemented by the University of New Hampshire and was not conducted on behalf of the U.S. Geological Survey. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. While many of the data sets used in this study are already publicly accessible, all data used in this study are available at https://doi.org/10.6073/pasta/6b32f4ea012a6068106736d886546441.

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