A sudden increase in the concentration of dissolved organic carbon in precipitation at a northeastern US forest

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Abstract

The oxidation of organic matter from fuel combustion or vegetation emissions into organic acids is a major source of dissolved organic carbon (DOC) in precipitation. Long-term measurements of DOC in precipitation are rare, but the existing records mostly show decreases due to reduction in fuel combustion. Here, we show a recent, sudden increase in precipitation DOC concentration in a 27-year record from the Hubbard Brook Experimental Forest (HBEF) in northern New Hampshire, U.S.A. Starting in 2010, mean annual DOC concentration increased from about 80 to 130 μmol L^{-1} in 2022. No other solutes in precipitation showed a similar, sudden change. The weekly DOC concentration was not clearly related to the 72-hour air mass trajectory characteristics or changes in trajectories. We assessed the feasibility of multiple possible causes for the DOC increase, including an increase in biogenic volatile organic compound (BVOC) emissions from the forest or from forest fires, changes in oxidation processes in the troposphere, and

changes in gas-phase solubility due to increasing pH in precipitation. Further study of sudden changes in BVOC emissions in the region, possible causes and air quality effects are warranted.

Key Points

- Dissolved organic carbon (DOC) in bulk deposition drastically increased over the recent decade at a long-term research forest.
- The cation-to-anion charge balance suggested the presence of an unmeasured anion, indicating that the DOC could from organic acids.
- Possible causes of the DOC increase include enhanced biogenic volatile organic compound emissions or their oxidation and dissolution.

Introduction

Organic carbon (OC) in the atmosphere is common and can play an important role in tropospheric chemistry (Heald et al. 2008, Heald and Kroll 2020) and precipitation formation processes (Yu 2000, Sun and Ariya 2006). The primary sources of OC are emissions from fossil fuel combustion, biomass burning, and the production of biogenic volatile organic compounds (BVOCs) emitted from plants and soils (e.g., Saarikoski et al. 2008, Sindelarova et al. 2014, US EPA 2023). Emissions of OC can undergo oxidation by reactions with O_3, the OH radical, NO_x or SO_2 resulting in new secondary OC species. In particular the OH radical associated with OC play a major role in determining the oxidation potential of the atmosphere (Lelieveld et al. 2016). Products from the oxidation of BVOCs include organic acids (Link et al. 2021), which can be scavenged by precipitation and become a large source of dissolved organic carbon (DOC) in atmospheric deposition (Iavorivska et al. 2016). Organic acids have long been recognized as an important source of anions in precipitation (Likens et al. 1983).

The amount of DOC in precipitation is typically small relative to other parts of terrestrial ecosystem carbon budgets (e.g., Fahey et al. 2005). Atmospheric deposition of DOC ranges from 7.7 to 34 kg C ha^{-1} yr^{-1} (Liptzin et al. 2022) compared to ecosystem gross primary productivity and respiration fluxes on the order of thousands of kg ha^{-1} yr^{-1} (Zheng et al. 2020, Tagesson et al. 2024). Concentrations of dissolved organic carbon in precipitation tend to be higher in the tropics and lower in northern latitudes, and concentrations over the ocean are lower than on terrestrial sources (Liptzin et al. 2022). Although the amount of DOC in precipitation is small relative to other ecosystem carbon fluxes, changes in precipitation DOC concentrations may provide insight into changing atmospheric and ecosystem processes.

Few long-term records of atmospheric DOC deposition exist (Liptzin et al. 2022). National networks of atmospheric deposition do not include DOC as a routinely analyzed solute (Lamb and Bowersox 2000). The trends at individual sites reported by Liptzin et al. (2022) showed some trends in DOC concentration over time, which were mostly declines, likely associated with decreasing fuel combustion. A site in the northeastern U.S. has shown increasing total OC in atmospheric deposition (Lawrence et al. 2023). One of the longest-running datasets of DOC in pre-

cipitation in the United States is from the Hubbard Brook Experimental Forest in New Hampshire, where weekly measurements have been made at one bulk deposition station since 1995, and two additional stations since 2013 (HBWatER 2023). In this study we evaluate trends in DOC bulk deposition and examine other constituents in precipitation that may provide insight into long-term changes in atmospheric chemistry or forest ecosystem processes.

Methods

Site Description

The Hubbard Brook Experimental Forest (HBEF) is a 3500-ha research reserve in the White Mountains of central New Hampshire in the northeastern U.S. (43°56'N, 71°45'W). The climate at the site is cool, humid, and continental; the mean minimum daily temperature in January is -9 °C and the mean maximum daily temperature in July is 18 °C (Campbell et al. 2021). Mean annual precipitation is 1400 mm which is distributed evenly throughout the year. About a third of precipitation falls as snow, and there is typically a continuous snowpack that on average persists from late December until mid-April. The forest cover type is predominantly northern hardwood (sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), and yellow birch (*Betula alleghaniensis*)), with some spruce-fir (red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*)) at higher elevations.

Sample Collection and Handling

Concentrations of major solutes in precipitation have been monitored at the HBEF since 1963 (HBWatER 2024). Analysis of DOC in precipitation started later, beginning in 1995 at one location on a south-facing slope and in 2013 at two additional locations: one on a north-facing slope (RG23) and the other at the US Forest Service headquarters building (RG22). In this analysis, we used the portion of the chemistry record when DOC data were available (1995-2022). In 2017, precipitation chemistry sampling on the south-facing slope was moved from RG11 to RG1, a distance of 811 m. A comparison of major solutes between the two collectors indicated no significant difference (Buso 2000). All chemistry collectors used in this study are within 7 km of each other and range in elevation from 255-668 m.

At the HBEF, precipitation samples for chemical analysis are collected weekly in bulk collectors that are continuously open to the atmosphere (see Buso et al. 2000). Chemical concentrations obtained from bulk collectors are comparable to concentrations from a wet-only collector associated with the National Trends Network (https://nadp.slh.wisc.edu/networks/national-trends-network/) based on an analysis of major solutes at the HBEF (Martin et al. 2000), however analysis of DOC was not included in this comparison. The bulk collector used during the warmer months, when precipitation falls mostly as rain, consists of a high-density polyethylene (HDPE) funnel connected by tubing to a sample bottle housed in a container that shields sample water from sunlight. The tubing has a loop that partially fills with water and serves as a vapor barrier to minimize evaporation. A plug of acid-washed polyfill is placed in the neck of the funnel to keep debris out of the sample bottle. During winter, when precipitation falls mostly as snow, samples for precipitation chemistry are collected with an open-top HDPE bucket. Samples containing frozen water are brought to the lab, melted at room temperature, and poured into bottles for chemical analysis. Thus, each sample is frozen for less than one week before it is retrieved from the field. Both types of collectors deployed in the field are replaced weekly with collectors that have been cleaned and acid washed.

Precipitation chemistry collectors are collocated with weight-recording rain gages for measuring precipitation volume (USDA Forest Service 2024). The chemistry collectors and rain gages are mounted 2 m above the ground in a clearing where vegetation is removed approximately every 3 years so that no portion of the surrounding canopy intersects a 45-degree angle from the rims upward (Buso et al. 2000). The resulting vegetation in the clearing is dominated by raspberry (*Rubus ideaus*) and hayscented fern (*Dennstaedtia punctilobula)*, which are also major understory species that emerge after forest disturbance at the HBEF (Hughes and Fahey 1991). Precipitation volume was measured with a mechanical Belfort Universal Precipitation Gage (5-780 model) until 2011, when it was replaced with an electronic, ETI Instruments rain gage (NOAH IV model). The older rain gage model produced a continuous record of precipitation on a strip chart that was collected weekly. These strip charts were recently digitized to extract precipitation volume at 15-minute intervals, which matches the interval of the new, electronic gage to provide a complete record of 15-minute data.

Chemical analyses were performed at the U.S. Forest Service Laboratory in Durham, New Hampshire, except for pH, which was measured with a benchtop pH meter (Thermo Scientific, Orion 3-Star) at the Hubbard Brook Experimental Forest laboratory on the same day samples were collected. Samples were filtered with a pre-combusted glass-fiber filter (0.7 μm nominal pore size) and stored frozen prior to analysis, except for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and Si, for which an aliquot was poured off and refrigerated. Samples were analyzed for SO_4^{2-}, NO_3^{-} and Cl^{-} using ion chromatography (Metrohm 761); NH_4^{+} with automated colorimetry (SmartChem AQ2 Discrete Analyzer); Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and Si with inductively coupled plasma optical emission spectroscopy (Agilent 730); and DOC and total dissolved nitrogen (TDN) using high-temperature catalytic oxidation (Shimadzu TOC-VCSH analyzer). The Ca, Mg, Na, and K measurements were of dissolved elements, not the ions, however we assumed that they were in ionic form. Dissolved organic nitrogen (DON) was determined by subtracting NO_3^{-} and NH_4^{+} from TDN. Filtration for DOC began on March 7, 2005. A comparison of 37 filtered and unfiltered samples during 2005 showed that filtered samples were 6.7 μmol L^{-1} higher on average; we report the unfiltered values as DOC in the current study. More detailed field and analytical procedures can be found in Buso et al. (2000) and method quantification and detection limits are in USDA Forest Service (2019). We use data from the National Atmospheric Deposition Program station at the HBEF (site NH02) to compare the total cation-to-anion charge balance in wet deposition with results from our bulk deposition samples (National Atmospheric Deposition Program, 2022).

Air Mass Trajectory Analysis

We used the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al. 2015) to evaluate whether changing weather patterns could explain the recent increase in DOC at the HBEF. The precipitation chemistry collector on the south-facing slope was used as the endpoint to calculate 72-hour backward trajectories for air masses 500 m above ground level, which is thought to be representative of in-cloud processes and has been used in previous studies of atmospheric transport of DOC (Mead et al. 2013, Siudek et al. 2015). Since precipitation for chemical analysis is collected weekly at the HBEF, samples can include water from multiple storms. For this analysis, we only evaluated weekly chemistry that was associated with one discrete storm so that we could reliably match a DOC concentration with an air mass trajectory (n=351). An event was defined

as a period of continuous precipitation lasting for six or more hours and totaling at least 6.35 mm (0.25 inch) of total precipitation. The event end-dates, to the nearest 15-minute interval, were used to calculate the backward trajectory with the HYSPLIT model.

We performed a k-means cluster analysis to group HYSPLIT trajectories (Hartigan and Wong 1979, Cui et al. 2021). Independent variables were the latitude, longitude, and distance from the HBEF for each hour in the 72-hour trajectory. The number of clusters was plotted against their explained variance and the lowest number that corresponded to the optimal inflection point on the plot determined the number used in the analysis. In this case, the optimal number of clusters was five. We calculated the total trajectory distance traveled, and the distance over land and water (ocean or freshwater) for each 72-hour trajectory using the *sf* and *lwgeom* packages in R (Pebesma 2018, Pebesma 2021, Pebesma and Bivand 2023).

Statistical Analyses

The seasonality in DOC concentrations was assessed using ANOVA tests with Tukey HSD *post hoc* tests. Data from the entire record were used to first assess which months were statistically distinct from one another. The presence of trends in time series was quantified using the Kendall test within the cor.test() function in base R. A breakpoint analysis of the DOC bulk deposition concentration using the *segmented* package in R (Muggeo 2016) was used to identify when DOC began increasing. This included a Davies test to determine whether there was a significant breakpoint and if a breakpoint was indicated, the year when the breakpoint occurred was identified. The data were separated into two groups, prior to and after that breakpoint, and then the differences between DOC concentrations in the two groups and across months were assessed using an ANOVA with a Tukey HSD *post hoc* test. The difference in DOC concentration across the different air mass trajectory clusters was assessed with an ANOVA test.

Comparison of DOC Trends with Other Solutes and Atmospheric Variables

The time series of other solutes in bulk deposition, atmospheric water vapor pressure, ozone, and reactive nitrogen (N; NO_3^- + NH_4^+ + HNO_3) dry deposition were compared with the DOC concentration time series to develop new hypotheses about mechanisms responsible for changes in the DOC concentration. Average daily vapor pressure was calculated from air temperature and

relative humidity, which were measured with a Campbell Scientific Inc. 201 digital sensor at the RG 22 site (USDA Forest Service 2023). Ozone was measured at a CASTNET site about 100 m away from RG 22 using a continuous UV ozone analyzer (Bloomer et al. 2010). Dry deposition of reactive N (sum of N in NO_3, NH_4, and HNO_3) was estimated by measuring reactive N concentration from filter packs and modeling deposition velocities (Clarke et al. 1997). The annual average during April to October was calculated for each variable, since that was the period when DOC concentration in precipitation was highest, exhibited the greatest long-term change, and thus when we were most interested in other solute and environmental changes.

Calculating the Effect of pH on Organic Acid Solubility in Precipitation

The solubility of organic acids in precipitation is a function of pH, which could be important at the HBEF since precipitation pH has markedly increased since the 1990s (Fuss et al. 2015). We evaluated that effect using Henry's law for estimating the concentration of non-disassociated aqueous organic acids:

$$[HA] = p\, k_H \quad (1)$$

where [HA] is the concentration of a non-disassociated organic acid (molar), p is the partial pressure for the gas phase of that organic acid (atm), and k_H is the Henry constant for that organic acid (mol L^{-1} atm^{-1}). We estimated the disassociated aqueous organic acids using the equilibrium constant (K_a) for an organic acid (HA):

$$K_a = [H^+][A^-]/[HA] \quad (2)$$

where Ka is the equilibrium constant for the organic acid, $[H^+]$ is the concentration of the hydrogen ion, and $[A^-]$ is the concentration of the conjugate base. Combining the non-disassociated and disassociated (rearrange equation 2 for A^-) components results in an equation for the total aqueous concentration (C_{tot}):

$$C_{tot} = p\, k_H\, (1 + K_a/[H^+]). \quad (3)$$

We used our measured volume weighted H^+ concentration in bulk deposition and assumed a K_a of 1.74×10^{-5} M for acetic acid and 1.78×10^{-4} M for formic acid (Khare et al. 1999), at 25 °C, to estimate the theoretical change in the concentration of organic acids in precipitation due to a change in H^+. We assumed no change in the partial pressure of the organic acid in the atmosphere since we were estimating the % change that was theoretically possible given a change in

225 H^+. We calculated the theoretical change for acetic and formic acid since they are abundant in the
226 troposphere above forests (Link et al. 2020).
227
228
229 **Results**
230 Mean annual DOC concentration ranged around 50 to 80 μmol L^{-1} from 1996 to 2012 with nota-
231 ble spikes in 2000 and 2004, followed by an increase to about 130 μmol L^{-1} by 2018 and has re-
232 mained at that level through 2022 (Figure 1). The DOC concentration increase was similarly ob-
233 served in precipitation collected at the two other bulk deposition collectors. A breakpoint analy-
234 sis identified a significant change in slope of the DOC concentration time series in 2010 (± SE of
235 1.4 years; Davies test p=0.0001). DOC concentration was negatively related to storm precipita-
236 tion amount in log-log space across all months (Figure 2).
237
238 The DOC concentration had strong seasonality with the highest concentrations in the summer,
239 peaking in August, and the lowest concentrations in the winter (Figure 3a). There are six statisti-
240 cally distinct month groupings of DOC concentrations. After the 2009 breakpoint in DOC con-
241 centration, most months had a higher average DOC concentration, however only August, Sep-
242 tember, and October were significantly higher at the α=0.05 level (Figure 3b).
243
244 The air mass trajectories fell into clusters that were largely associated with the direction from
245 which they approached (Figure 4a). Trajectory clusters 1 through 5 had a median azimuth direc-
246 tion of 202°, 76°, 258°, 328°, and 295°, respectively. Trajectory clusters 1 through 5 had a me-
247 dian distance from the HBEF of 345, 814, 782, 781, and 1183 km, respectively. Thus, Cluster 2
248 was notable because it was a more easterly trajectory, and Clusters 1 and 5 are notable for being
249 substantially shorter and longer, respectively, than the other trajectory clusters. Clusters 3 and 4
250 were typical lengths but approached from the west and north, respectively. Even with clear dif-
251 ferences in the characteristics of each group, the ANOVA showed no difference in DOC concen-
252 tration among the clusters (p=0.58; Figure 4b). The DOC concentration was, however, negatively
253 related to air mass trajectory length and positively related to the fraction over land (Spearman
254 rho=-0.11, p=0.04; and rho=0.14, p=0.01, respectively).
255

Other solutes and atmospheric factors provided context for how atmospheric chemistry changed during the past three decades. Acid anions (SO_4^{2-} and NO_3^-), NH_4^+, and H^+ decreased over time (Figure 5; Table 1). K^+, Ca^{2+}, and Mg^{2+} were variable with no clear change during the DOC increase. Na^+ and Cl^- increased significantly, although this increase was not as clear as the acid anions. The molar Na:Cl ratio was mostly around 0.8 except for an unexplained spike in 2013 that declined in the subsequent two years. The molar DOC:DON ratio was around 20 prior to 2010 and then increased to around 40 thereafter. The anion:cation ratio (cations are Na^+, K^+, Ca^{2+}, NH_4^+, H^+, and Mg^{2+}; anions are SO_4^{2-}, Cl^-, and NO_3^-) was within 10% of 1 prior to 2013, and then suddenly decreased, demonstrating an approximately 25% anion deficit from 2013 onwards. This change in the balance of cations and anions was also apparent in wet deposition collected at the NADP network site, showing a more gradual change towards an unmeasured anion starting around 2010 (Figure 6). Average April to October DOC concentration was significantly negatively correlated with SO_4^{2-} and H^+ and positively correlated with Na^+ and Cl^- (Table 1). The calculated changes in aqueous acetate and formate concentrations in precipitation suggested a 69% and 122% increase between 2010 and 2022, respectively, given changes in H^+. The concentration of volume-weighted H^+ concentration over the April-October interval was 15.8 μmol/L in 2010 and 6.8 μmol/L in 2022. Other atmospheric factors that potentially could impact the oxidation of BVOCs in the atmosphere showed notable changes. Water vapor pressure increased, while ozone and dry N deposition decreased (Figure 7).

Discussion

The abrupt increase in bulk deposition DOC concentration at the HBEF was surprising and challenging to explain. The change in anion-cation balance after 2012 is coincident with the initiation of the DOC increase and suggests that organic anions are an important component of precipitation chemistry, presumably in the form of dissociated organic acids, which have been previously recognized in atmospheric deposition at the HBEF (Likens et al. 1983) and other forested sites (Schaefer et al. 1989, Williams and Melack 1991, Link et al. 2020). The measured anion-cation balance after 2012 showed a discrepancy that accounted for ~25% of the total anions. If the unmeasured anions were derived from organic acids, the proportion would be similar to the 25-30% of total anion composition from acetic and formic acid measured at a Sierra Nevada forested site

(Williams and Melack 1991). Below, we discuss different possible causes of the DOC concentration increase and their likelihood.

It is not clear whether our observed increase in DOC concentration is a local phenomenon or part of a larger-scale change, since published data on trends in DOC atmospheric deposition are limited. Past studies that documented changes in atmospheric deposition of DOC have shown decreases, mostly associated with reduction in fossil fuel combustion (Willey et al. 2011, Cao et al. 2022, Liptzin et al. 2022). We do not think that the DOC increase at the HBEF is associated with an increase in fossil fuel-related sources of organic carbon, since inorganic acid anions associated with fossil fuel combustion (e.g., SO_4^{2-}, NO_3^-) have substantially decreased over time. One site in the northeastern U.S. has shown an increase in the concentration of total organic carbon (TOC) in precipitation that is of similar timing and magnitude as the increase in DOC observed at the HBEF (Lawrence et al. 2023). Lawrence and colleagues also show a change in the cation-anion balance towards unmeasured anions, show that the TOC is a source of acids, and demonstrate that regional smoke events have higher deposition of TOC, thus hypothesizing that their trend could be driven by increasing fire activity in upwind areas. We do not think that an increase in smoke deposition is the driver of our observed increase in DOC concentrations since smoke tends to contain elevated concentrations of Ca^{2+}, K^+, and NO_3^-, which have not increased with DOC at the HBEF (Evans et al. 2021, Boyer et al. 2022). Further, a notable regional smoke deposition event occurred during the summer of 2002, causing an increase in aerosol organic carbon and other elements including K^+ (DeBell et al. 2004), but did not cause a clear spike in our measured DOC at the HBEF (Figures 1 and 5). We cannot fully exclude the hypothesis that fire could impact our increase in DOC concentration since fires emit VOCs that can be transported across North America (de Gouw et al. 2006, Ciccioli et al. 2014), which could increase DOC while having a minimal impact on other solutes. Also, smoldering fires have lower K^+ concentrations than flaming fires (Allen and Miguel 1995), so there are fire conditions that could result in higher DOC without elevated inorganic analytes.

While smoke could be a source of the DOC increase, other possible sources of DOC can be considered unlikely causes of the DOC concentration increase because they contain other analytes that would have also increased. Dust can be a source of DOC (de Vicente 2012). However dust is

317 a major source of Ca^{2+} in the atmosphere to the extent that it has caused regional increases in
318 Ca^{2+} deposition in the western U.S. (Brahney et al. 2013). Pollen can be a source of DOC (Rösel
319 et al. 2012), however it is also a source of phosphorus, nitrogen, and K^{+} (Lee et al. 1996). Insects
320 could introduce DOC to the deposition collectors, but they contain other ions like Ca^{2+} that
321 would increase if they were the source of DOC (Dube et al. 2000).
322
323 We do not see evidence that the DOC concentration increase is associated with changes in rain-
324 out processes or air mass source area changes. Rainout of DOC is an important mechanism that
325 controls the concentration of DOC in precipitation (Iavorivska et al. 2016). However, precipita-
326 tion is increasing at the HBEF (Campbell et al. 2021), which would result in decreases in DOC
327 concentrations due to dilution or more frequent removal. As a result, we do not think that
328 changes in precipitation amount are the cause of the DOC concentration increase. Further, pre-
329 cipitation at the HBEF has increased gradually over the long-term, rather than a recent marked
330 increase like DOC concentration. The trajectory analysis suggests that the increase in DOC con-
331 centration over time is not due to atmospheric transport changes, since there is no clear differ-
332 ence in DOC concentrations between the trajectory clusters that we tested.
333
334 Biogenic VOCs are a source of DOC that would not result in increases other analytes in precipi-
335 tation and thus are a possible source of the observed increase in DOC concentration. BVOCs are
336 emitted into the atmosphere by many tree species (Harley et al. 1999, Helmig et al. 1999). Com-
337 mon BVOCs from temperate forests include isoprene and monoterpenes (Nguyen et al. 2015),
338 which are precursors to organic acids in the atmosphere (Link et al. 2021). The generation of
339 DOC from BVOCs involves dissolution of gaseous BVOCs or forming secondary organic aero-
340 sols and then wet-scavenging (Safieddine and Heald, 2017). The seasonality of DOC concentra-
341 tion that we observed is similar to the phenology of the forest canopy at the HBEF (Richardson
342 et al. 2006), and the long-term increase was mostly driven by increases during the late summer,
343 suggesting that the DOC increase could be related to an increase in BVOC production by the for-
344 est at the HBEF or the surrounding region. This pattern is consistent with previous studies that
345 have monitored DOC concentrations seasonally and attributed the seasonality of DOC deposition
346 to BVOC emissions from terrestrial ecosystems (Willey et al. 2000, Siudek et al. 2015). Further,
347 terrestrial ecosystems can contribute up to 80% of OC in precipitation based on isotopic evidence

(Raymond 2005). Organic acids in the troposphere above forests are generally derived from BVOCs (Link et al. 2020) and thus it is likely that the seasonality and the increase of DOC is associated with BVOC production, oxidation to organic acids and peroxides, and rainout at the HBEF. If the source of organic carbon is BVOCs, multiple studies have shown that local BVOC emissions can result in local organic acid production (Nguyen et al. 2015). However, if BVOCs are the source of the DOC it is not clear why their production would increase in a sustained manner. We think that it is reasonable to hypothesize that the increase in DOC concentration at the HBEF is related to increases in BVOCs, but further work is needed to test this hypothesis.

Whether there has been a change in BVOCs emissions or not, a change in tropospheric oxidation dynamics could cause higher DOC in bulk deposition. Atmospheric oxidants such as O_3 and reactive N have been decreasing over time at the HBEF, raising questions about whether the increase in the DOC concentration in precipitation might be associated with a decrease in the oxidation of BVOCs leading to an increase in organic acids and peroxides and ultimately DOC. Ozone and nitrogen oxides are precursors of OH radical (Lelieveld et al. 2016), which is a major oxidant of BVOCs into organic acids (Link et al. 2021). Atmospheric water vapor pressure also increased, which could have a positive effect on BVOC oxidation (e.g., Anglada et al. 2017). However, changes in these factors may not necessarily be evidence of a change in the OH radical abundance in the atmosphere (and thus the oxidation potential) due to the relatively stable OH abundance from OH recycling (Lelieveld et al. 2016). The oxidation of isoprene has been demonstrated to occur in low N environments like the Amazon rainforest (Paulot et al. 2009) and is a likely cause of high concentrations of organic acids over forests (Link et al. 2020). The pathways for BVOC oxidation in low NO_x environments can result in greater production of water-soluble secondary aerosols (Shrivastava et al. 2017). Therefore, while there were significant changes in variables that are OH sources, this might not result in a step change of the oxidation potential of the lower troposphere at the HBEF that would result in a sudden, sustained increase in DOC concentration.

Our calculated potential increase in aqueous acetate and formate in precipitation due to the decrease in H^+ was similar in magnitude to the changes in DOC that we observed. This pattern sug-

gests that it is feasible that the increase in DOC is due to a change in the solubility of organic acids in the troposphere. Our calculations assumed no change in the partial pressure of acetic and formic acid during this period, however, if there were a change, we would hypothesize that the partial pressure would have increased, due to our hypothesis that BVOCs have increased. The lack of change in DOC from 1990 to 2010 a period when H^+ in precipitation decreased considerable, however, challenges the suggestion that this increase is entirely due to decreased H^+ (Figure 5e).

If the increase in DOC concentration in bulk deposition is due to an increase in BVOC emissions, we hypothesize that this response could be caused by an increase in forest photosynthesis or a heat stress response. The rate of BVOC flux can be attributed to changes in internal leaf biochemical processes in response to environmental stimuli or stressors (Lantz et al. 2019). Isoprene is associated with photosynthesis, particularly signaling the production of compounds involved in plant growth and stress tolerance (Monson et al. 2020); therefore, an increase in gross primary productivity (GPP) of the forest would increase a local isoprene atmospheric flux (Guenther et al. 2006). This increase would align well with two observations from the HBEF that have suggested an increase in GPP beginning between 2010-2015: (1) increased evapotranspiration beyond what could be explained by atmospheric drying potential (Green et al. 2021), and (2) a sudden large increase in soil respiration (Mann et al. 2024, Possinger et al., 2025). Additional considerations would include climatic stresses such as drought and heat (Ferracci et al. 2020). Shallow soil moisture has been declining at the HBEF (Green et al. 2021; Wilson et al. 2025), however, this condition has not likely been dry enough to cause persistent moisture stress. Plus, trees at the HBEF can access water from deeper soil water when surface soil water availability declines (Harrison et al. 2020). The rate of air temperature increase has increased considerably in late summer and early autumn months at the HBEF (Supplemental Figure 1), potentially increasing heat stress on trees might be the cause of increases in BVOC emissions and DOC concentration in precipitation. The July summer air temperature at the HBEF increased from about 18°C in 2010 to about 20°C in 2022, which would result in a 22% increase in BVOC emissions according to the McKinney et al. (2011) model of the temperature dependence of monoterpene emissions at Harvard Forest in Massachusetts. This pattern suggests that the temperature effect would not produce a large enough increase in monoterpene emissions to result in a doubling of DOC as

observed without some other mechanism in play, such as the increase in organic matter solubility.

Mechanical stresses such as herbivory or pest damage can stimulate BVOC plant-atmospheric fluxes (Ghimire et al. 2022) and thus should be considered as playing a role in the increase in DOC deposition at the HBEF. There was a high wind event in 2013 that damaged the forest canopy in areas of the HBEF (Battles et al. 2017); however the forest damage was concentrated in specific areas of the HBEF valley. We observed the sustained increase in DOC concentration in all three collectors that included one at the head of the valley that was 4 km from the concentrated forest damage. We are not aware of any sustained, valley-wide mechanical stress that started at the HBEF in the 2010-2015 period. An increase of BVOC emissions can result from changes in forest composition (Harley et al. 1999), leaf anatomy (Schollert et al. 2015), or leaf age (Baldocchi et al. 1995), but changes in BVOC emissions associated with these would happen gradually.

Additional research is needed to understand the cause of the increase in DOC concentration at the HBEF and whether this is part of a larger scale phenomenon. Future measurements of organic anions in bulk deposition are needed to understand the composition of the DOC. Detailed modeling of organic acid production in the troposphere has proven helpful in understanding how VOC emissions are transformed into organic acids and transported to Whiteface Mountain in New York (Lawrence et al. 2024). Similar modeling focused on the HBEF during the 2000-2020 increase in DOC bulk deposition could help address hypotheses related to changing oxidation potential or pathways in the troposphere. Additionally, modeling BVOC forest emissions would help us test whether forest warming or other environmental changes would be predicted to increase BVOC emissions, as has been applied globally (Shen et al. 2019; Wang et al. 2024). Remote sensing data of atmospheric BVOCs concentrations should be explored to see if they support the hypothesis that BVOC emissions have increased suddenly and the spatial extent of any increase (Wells et al. 2022). Finally, more long-term observations of DOC deposition are needed to understand changes like we observed. DOC is not often included as an analyte in atmospheric deposition monitoring; adding it could contribute better information about the changing organic chemistry of the troposphere.

Conclusion

We observed a sudden doubling of DOC concentration of precipitation between 2010 and 2022 at the HBEF that was not associated with changes in concentrations of other solutes or air mass trajectory changes. Given the available evidence, we hypothesize that the increase in precipitation DOC concentration was primarily due to either an increase in BVOC emissions from the forest at the HBEF, since this would cause an increase in DOC but not other solutes, or an increase in dissolution of gas phase organic carbon due to higher pH and lower nitrogen concentrations. Given other, recent changes at the HBEF associated with sudden changes in the carbon cycle, we further hypothesize that an increase in BVOC emissions could be caused by an increase in forest photosynthesis or a heat stress response to recent increases in late summer and early autumn air temperatures. These hypotheses warrant further investigation.

Open Research

All data used in this analysis are publicly available. Precipitation bulk deposition chemistry data are available at the Environmental Data Initiative (Hubbard Brook Watershed Ecosystem Record 2004). Water vapor pressure data are available at the Environmental Data Initiative (USDA Forest Service 2023). Daily and 15-minute precipitation data are available at the Environmental Data Initiative (USDA Forest Service 2024a, 2024b). Ozone and nitrogen dry deposition are available through the CASTNET Network (U.S. Environmental Protection Agency 2024). Wet deposition data are available through the National Atmospheric Deposition Program (NADP 2022).

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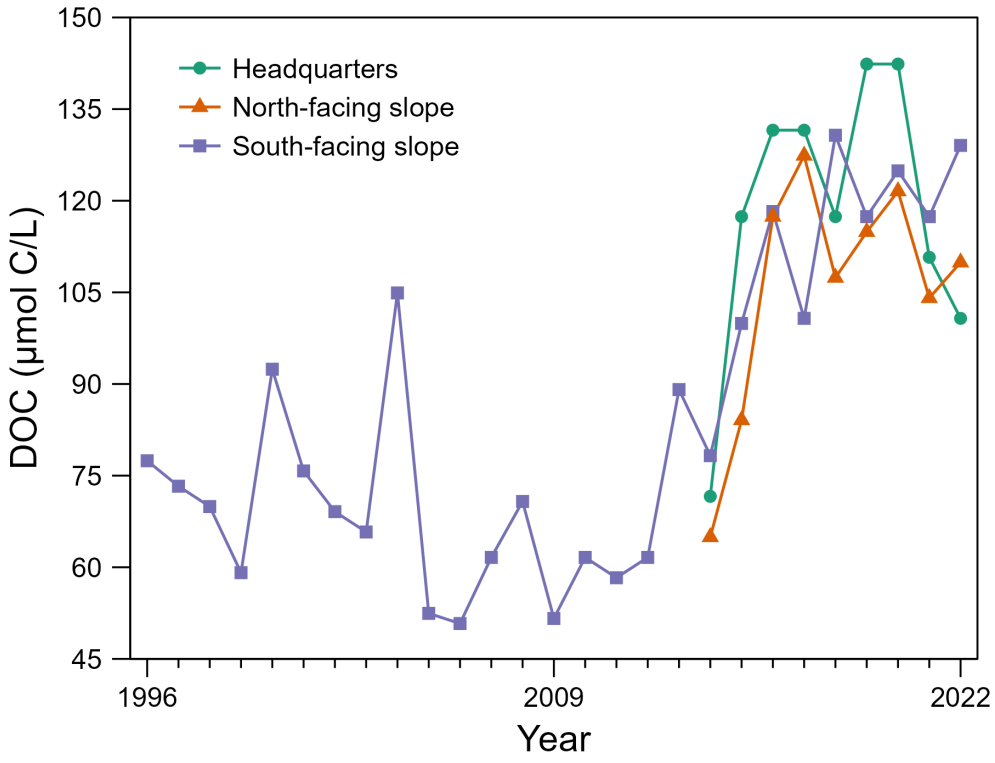
Table

Table 1. Summary of trends in the annual growing season (April to October) volume weighted concentration from 1996 to 2023 using the Kendall trend test, and the Spearman correlation between solutes and DOC. Bolded values indicate a significant result at the α=0.05 level.

	Temporal Trend	**Correlation with DOC**
Solute	**Kendall τ**	**Spearman ρ**
Ca^{2+}	0.02	0.37
Mg^{2+}	-0.00	0.30
K^{+}	0.07	0.30
Na^{+}	**0.36**	**0.63**
H^{+}	**-0.87**	**-0.43**
NH_4^{+}	**-0.45**	-0.09
SO_4^{2-}	**-0.85**	**-0.47**
NO_3^{-}	**-0.66**	-0.20
Cl^{-}	**0.45**	**0.70**
DON	-0.21	-0.23
DOC	**0.36**	NA

Figures

Figure 1. Mean annual volume-weighted DOC concentration in bulk precipitation at three sites at the Hubbard Brook Experimental Forest. The record from the south-facing slope is from RG1 and RG11, the north-facing slope is from RG23, and from the headquarters site is RG22.



837 **Figure 2.** Monthly relationships between bulk precipitation amount and the
838 concentration of DOC on a weekly basis over the period of record at Hubbard Brook.
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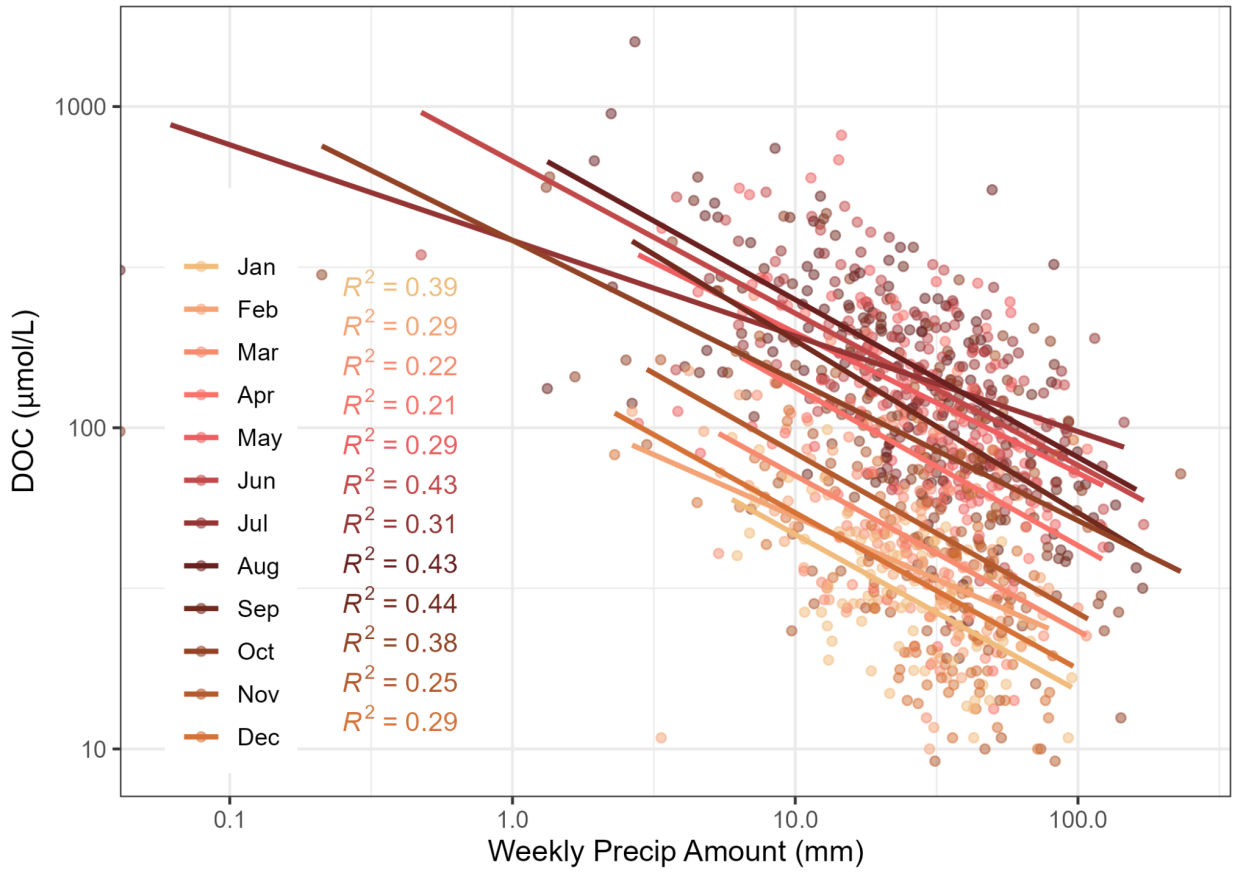

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Figure 3. The seasonality of DOC during the 1995 to 2022 record from the south-facing collectors shows significant monthly differences (panel *a*). The letters above each box in panel *a* indicate the unique group, as indicated by the Tukey HSD *post hoc* test. The data were then split using the 2009 breakpoint in the time series and the months were compared (panel *b*). The stars in panel *b* indicate significant changes before and after 2009.

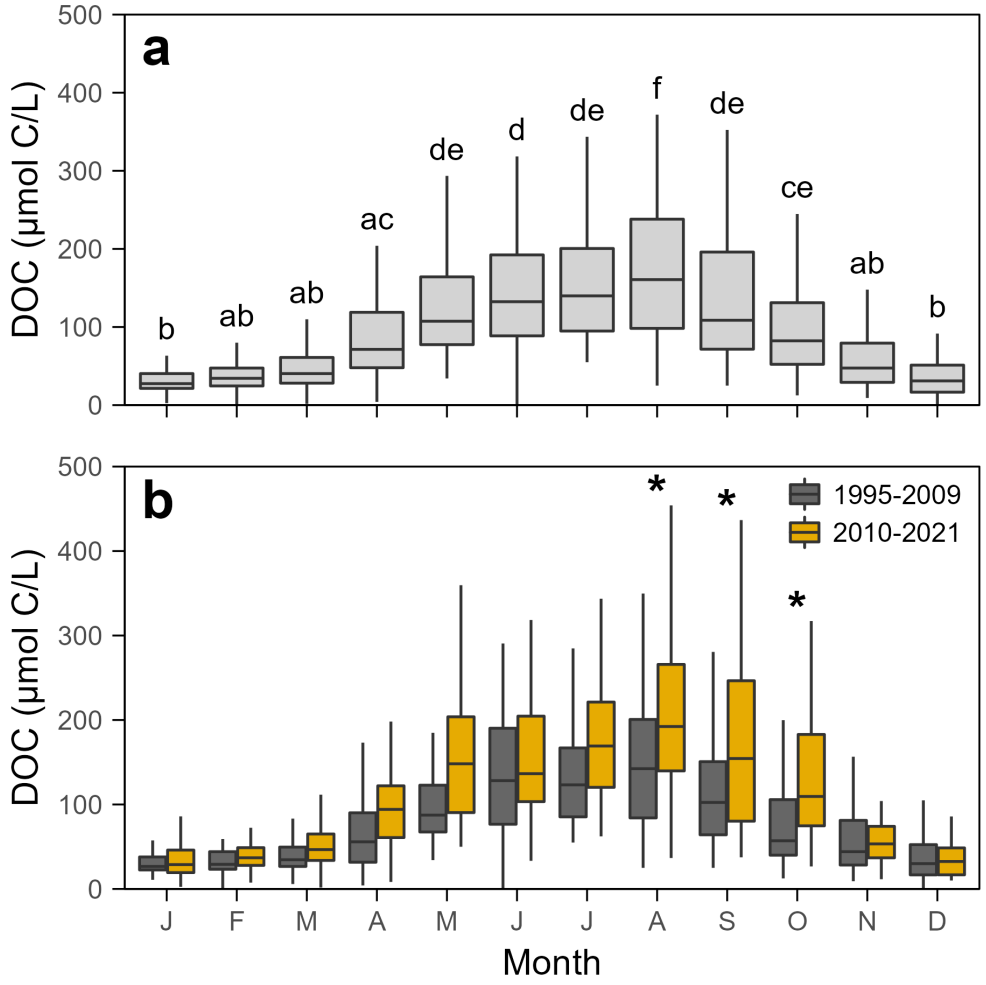
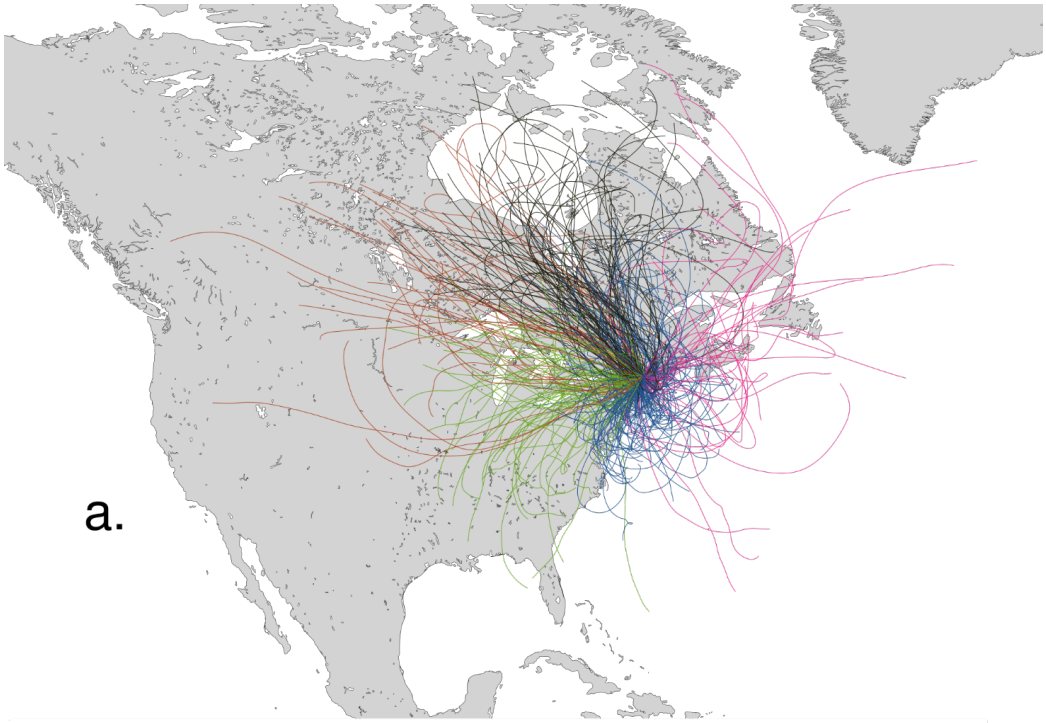


Figure 4. Air mass trajectories from the HYSPLIT model for April to October storm events (panel a). A comparison of the DOC in these trajectories suggests no difference in their concentrations (ANOVA p=0.58; panel b).



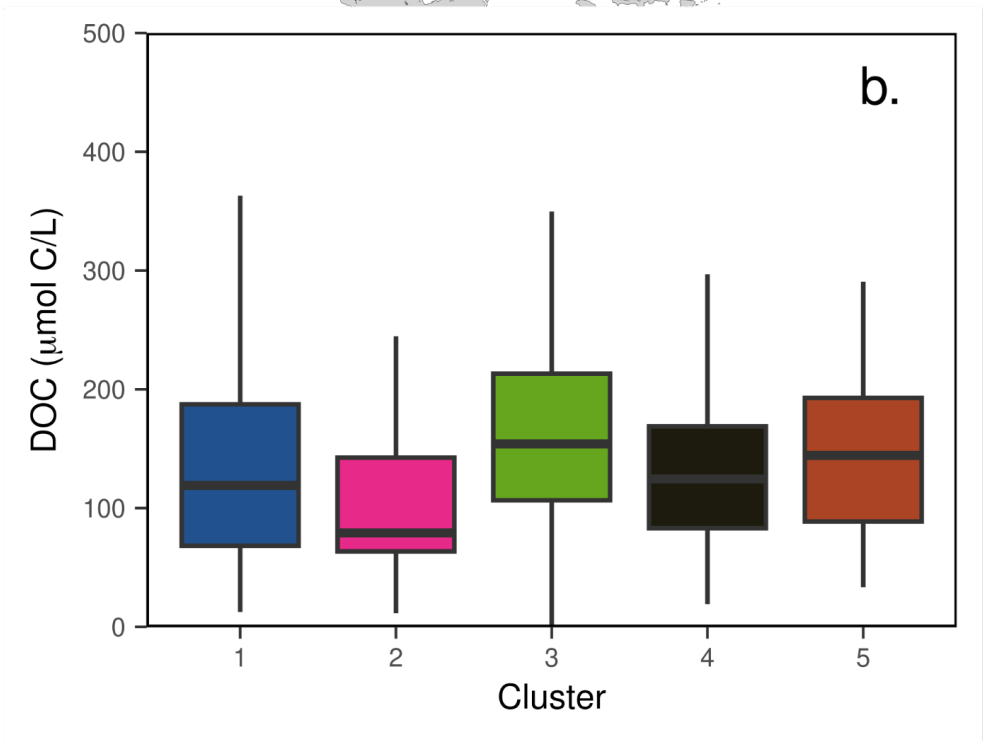


Figure 5. Mean April to October volume-weighted concentrations of solutes in precipitation for the collector on the south-facing slope at the Hubbard Brook Experimental Forest. The ratio of anions to cations (p) is the sum of anions (NO_3^-, SO_4^{2-}, Cl^-) divided by the sum of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+, NH_4^+) calculated in microequivalents per liter. The Na:Cl (panel m) and DOC:DON (panel l) ratios are reported as molar ratios.

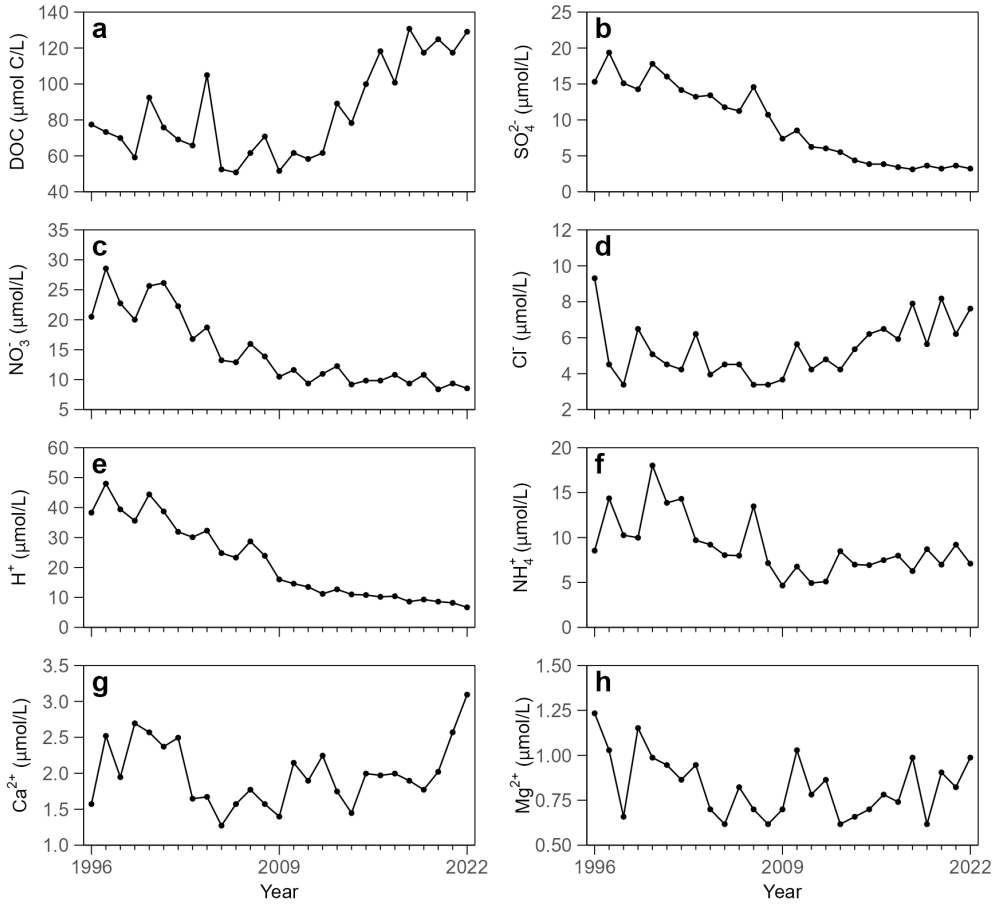
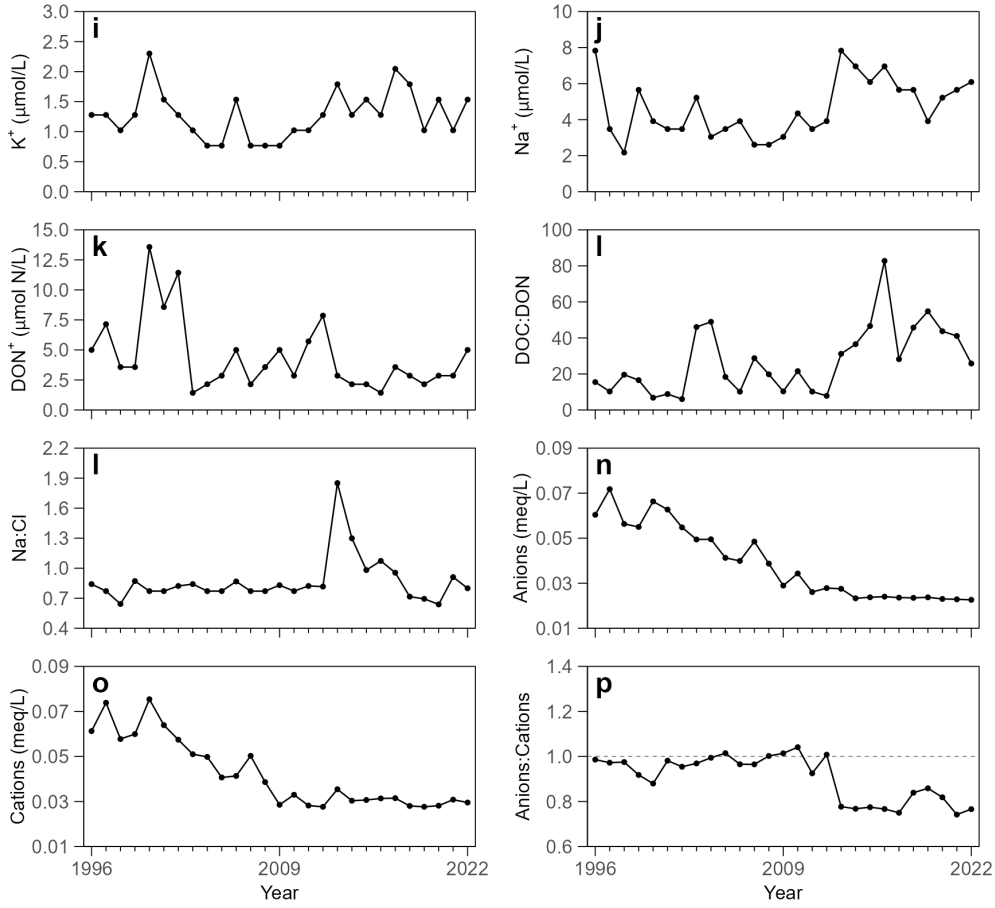


Figure 5. (continued)



868 **Figure 6.** Change in the charge balance (total cations minus total anions) in wet
869 deposition at Hubbard Brook from the National Atmospheric Deposition Program site.
870 Summer refers to the April to October period and winter is November to March.
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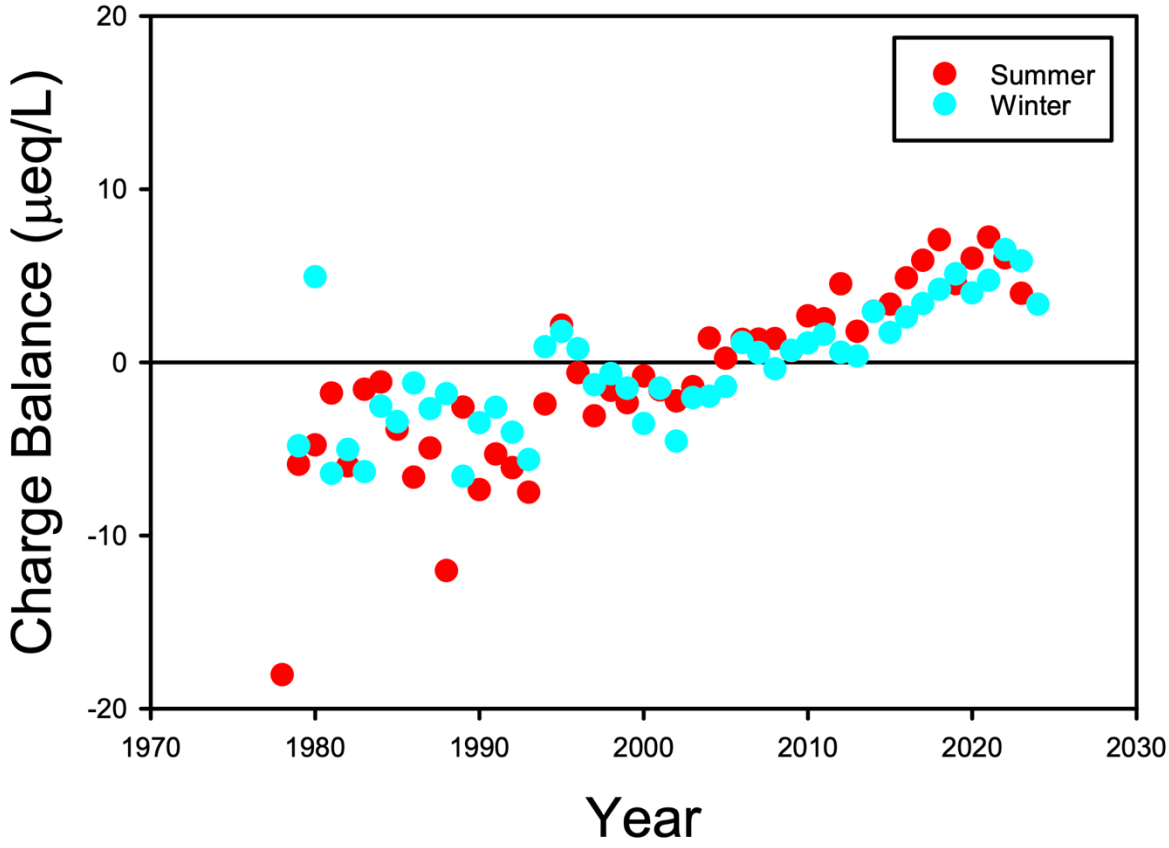

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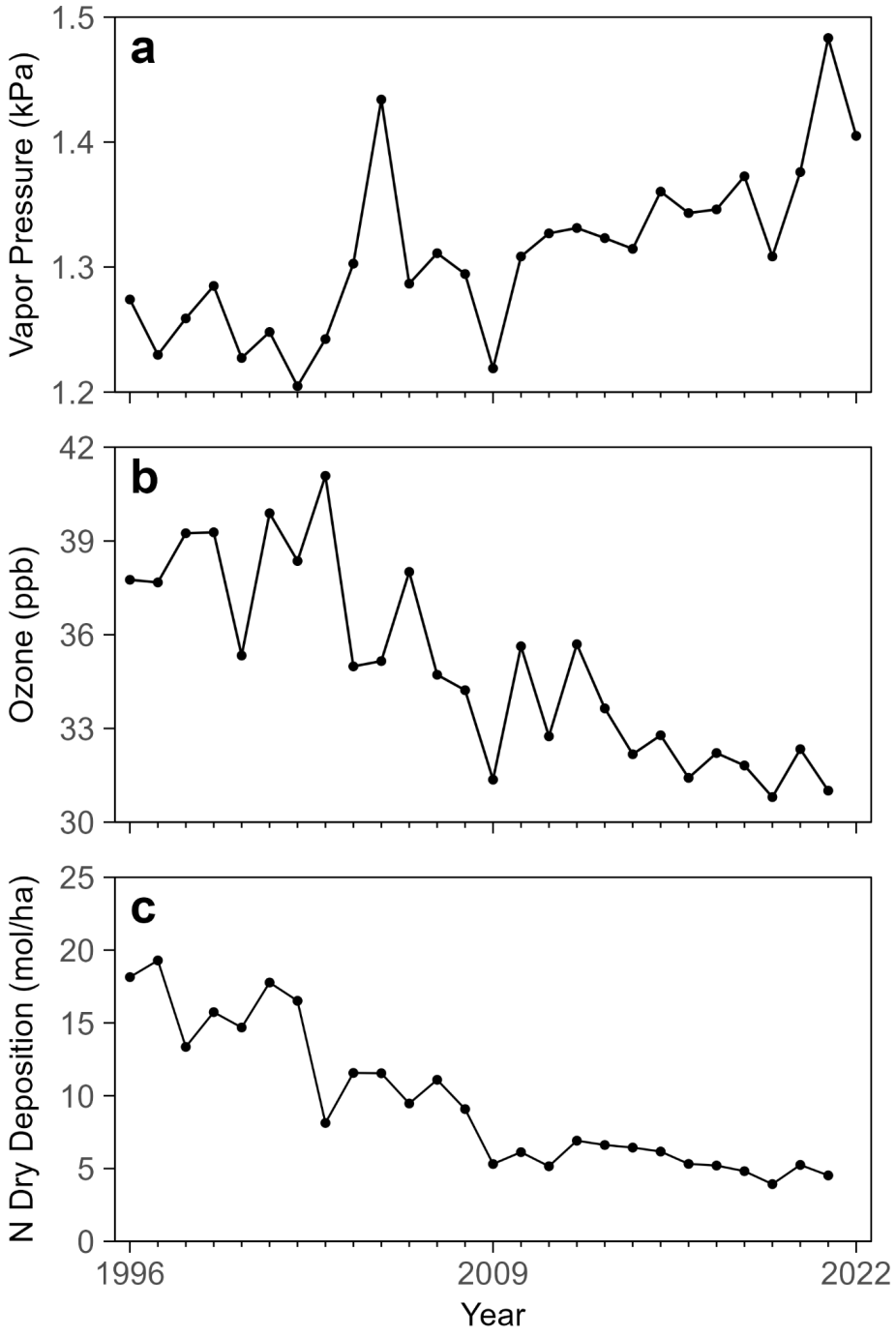
875 **Figure 7.** Time series of variables that are related to organic matter oxidation in the
876 atmosphere: a) mean water vapor pressure, b) mean ozone, and c) mean dry
877 deposition of reactive N. The mean from April to October, when DOC concentrations are
878 highest, is shown.



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Supplemental Information

Supplemental Methods

The mean daily air temperature from three stations at different locations (Stations 1, 14, and 23;) within the Hubbard Brook Experimental Forest were averaged and the mean monthly air temperature was calculated and shown in Supplemental Figure 1.

USDA Forest Service, Northern Research Station. 2024. Hubbard Brook Experimental Forest: Daily Temperature Record, 1955 - present ver 14. Environmental Data Initiative. https://doi.org/10.6073/pasta/67395641442370b21198973fb553def5.

Supplemental Figure 1. Mean monthly air temperature at the Hubbard Brook Experimental Forest.