

We thank the reviewers for their constructive comments. We have addressed each comment below, with the reviewer comment in black followed by our response in blue. We have also appended an updated manuscript after our responses with all changes highlighted.

Referee #1

This manuscript prepared by Hennigan et al. represents a novel study to provide insights into the impact of pH on the light absorptivity of atmospheric Brown Carbon (BrC). Through measurement of actual cloudwater samples, they have demonstrated that the light absorptivity of water-soluble BrC in cloudwater samples is highly pH dependent. While pH dependence of BrC absorptivity has been shown to some degree by previous studies, this work is the first to provide systematic insights into this phenomenon. BrC belongs to a class of short-lived climate forcers that has uncertain radiative effects and atmospheric lifetime. Meanwhile, a changing pH in cloud and fog water in North America and Europe has been reported. These facts make the current work highly relevant and important. The manuscript is very well written and should be considered for publication in ACP. I have the following comments and questions for the authors. I only have one major comment, with the rest considered minor or technical.

Major comment

- Generally, I think the manuscript can benefit from a little more discussion regarding potential mechanisms via which the observed pH dependence is attained. In Line 335, the authors mention hydrophobic organic acid. Do we expect this magnitude of changes in absorbance when the pH swing across their pKa value(s)? Have any previous studies on Suwanee River samples discussed how DOM exhibits pH dependence? I think such a mechanism is important in connecting a few key observations/conclusions in the manuscript: Ageing of BB aerosol, relative changes in absorption spectra, etc.

We agree with the reviewer's comment that more discussion of the underlying mechanisms is warranted. We have added the following text to the Discussion, (lines 294 – 304):

“The results in this study suggest that aromatic carboxylic acids and phenolic compounds, including nitrophenols, are primarily responsible for the observed pH-dependent optical properties. Phenols and aromatic carboxylic acids are major contributors to atmospheric BrC (Laskin et al., 2015). Prior studies have shown that aromatic carboxylic acids contribute most to the pH-dependence below pH 7 while phenols are most responsible above pH 7 (Schendorf et al., 2019; Qin et al., 2022). Our results also suggest that phenols are primarily responsible for the observed dependence of AAE on pH (**Figure 6**). AAE only varied with pH above pH 7, consistent with phenolic pKa values that are typically in the 7 – 10 range. The wavelength-dependent enhancements with increasing pH shown in **Figure 7** also point to the influence of phenols because the shape and magnitude of the enhancements become much more prominent above pH 7.”

We also point the reviewer to several points in the manuscript where we discuss other studies that have observed a relationship between pH and BrC, including: lines 232 – 237 (updated manuscript line numbers), lines 273 – 276, and lines 356 – 367.

Minor comments

- As the authors pointed out themselves, aerosol liquid water represents a highly concentrated medium that is not considered ideal aqueous solution. Are acid-base equilibria, hence BrC absorption, differ in non-ideal solutions compared to ideal aqueous solutions? I do not know the answer. I am just asking.

This question has never been explored for atmospheric BrC; however, the effects of ionic strength on optical properties of BrC in aquatic and terrestrial environments (termed “chromophoric DOM”) has been investigated (e.g., see Gao et al. (2015)). It is likely that ionic strength also affects BrC optical properties in aerosols and clouds, but it would be speculation at this point. This is a new topic of research that our group is pursuing.

- I wonder if the pH dependence observed in the current work is repeatable. In other words, if the authors would acidify the solution but then basify it again (or vice versa), do you expect the absorptivity to follow the same pH-dependence?

For a variety of different humic substances, including Suwannee River Humic Acid and Suwannee River Fulvic Acid, Schendorf et al. (2019) observed that the spectral changes with pH are completely reversible. This is consistent with aromatic carboxylic acids and phenols being the moieties primarily responsible for the pH-dependence we observe. We have added the following to the text (line 184 – 185) “Based on the results of Schendorf et al. (2019), we expect the observed pH-dependence to be reversible, although this was not verified experimentally.”

- Related to my previous comment, certain aqueous-phase reactions (e.g., hydrolysis) and equilibria (imine formation) are acid and/or base-catalyzed. Is there any chance that acidifying or basifying the sample induces any irreversible artifact to the composition?

This is an excellent question. In theory – yes – pH changes could induce irreversible reactions of chromophoric WSOC in our cloud samples. However, we believe this is unlikely to occur in our samples because the LWCC measurements occur so soon after the pH adjustment (within a few minutes). Therefore, there is likely not enough time for any such reactions to proceed very far. To address this point, we have added the following text to line 129 – 130: “The sample was injected into the LWCC within minutes of the pH adjustment, minimizing the time for any acid-catalyzed reactions of BrC chromophores to occur.”

- The authors mentioned that this study ignores water-insoluble BrC chromophores. Do the authors think water-insoluble chromophores also exhibit pH dependence? They do not dissolve or interact with water very much. I do not know the answer. I am just asking.

This is a very tricky question. The reason is that pH can be defined in non-aqueous media, such as organic solvents, but the pH scale between different solvents (including water) does not directly transfer (Himmel et al., 2010). To our knowledge, pH of the non-aqueous phase of

atmospheric organic aerosols has never been measured or estimated - given the complexity of OA in atmospheric particles, this would be quite daunting. Therefore, it is quite difficult to speculate about the potential pH behavior, given how little is known about the acidity of the non-aqueous phase of atmospheric OA.

- Page 5. It seems that the LWCC measurement was intentionally done using two channels, one to record absorbance and the other to track light source stability. How is this approach more advantageous compared to a single-channel measurement? I have seen previous studies using only one channel.

We implemented this measurement detail at the recommendation of Dr. Lelia Hawkins (personal communication). In our studies, our light sources have been extremely stable across many months of use. Eventually, the bulbs will have to be replaced so this measurement configuration will help us catch any changes early and without significant troubleshooting. However, we have not needed to apply any measurement corrections due to light source fluctuations to-date.

- Line 215. "The present results suggest that one such change not previously reported is that atmospheric ageing reduces the sensitivity of biomass burning BrC optical properties to pH ". I feel like this sentence is an overstatement and would ask the authors to consider relaxing the statement. I don't think the results really suggested it. It is the authors' speculation.

We agree with the reviewer's suggestion. We have edited the sentence so that it now reads: "The present results suggest that atmospheric ageing may reduce the sensitivity of biomass burning BrC optical properties to pH, though future studies are needed to substantiate this finding through investigations that provide for controlled ageing conditions."

- Line 254. "Therefore, measurements of BrC in aqueous environments need to include and report pH in order to facilitate interstudy comparisons and to assess the climate forcing effects of BrC." I agree with the authors and also believe that this is one of the most important implications they are making from this manuscript. Given that the authors demonstrated that the pH dependence also varies from sample to sample. Shouldn't we report absorbance at least two pH to constrain the slope? This may or may not always be feasible, but I wanted to hear the reviewer's ideas.

The reviewer is correct that reported absorbance values should include two pH levels, where possible. We have added the following to the text: "Further, optical properties of water-soluble BrC in aqueous environments should be measured at two pH levels, when feasible, to enable translation to other conditions in the atmosphere."

- Discussion related to Figure 7. I think it would be beneficial if the authors could include a little discussion on what functional groups are likely (or unlikely) contributing to the observed relative spectral change. E.g., carbonyl is not likely contributing due to minimal changes at around 300 nm.

See our reply to this reviewer's major comment above.

Technical Comment

- I feel like the use of Figure X and Fig. X is inconsistent throughout the manuscript.

To be consistent we have now used 'Figure X' throughout the manuscript.

Referee #3

This paper describes observations of the absorption characteristics of brown carbon in cloud water samples obtained from orographic clouds at Whiteface Mountain. Recent work has demonstrated that brown carbon absorption is highly pH dependent, however, the number of studies that report optical properties in aqueous samples as a function of pH is limited. Furthermore, the majority of these studies have analysed aerosol samples in aqueous solution but cloudwater is more dilute, typically has a higher pH and therefore demonstrates stronger absorption. However, to date few studies exist. This work presents such a set of observations. The work is well described and the methods carefully detailed in the paper. The results are carefully described and logically presented and the authors have provided a well considered and detailed discussion, comparing their results with those of other studies and discussing the ramifications of their work. Overall, this is a well presented paper that is of merit scientifically and offers some new results and important insight. I have some small suggestions that the authors should address, but these are minor.

Line 46-49: “Unlike BC and dust, which are removed from the atmosphere only through wet and dry deposition, it also undergoes chemical losses initiated by oxidants and direct photolysis (collectively termed bleaching), that can rapidly diminish its light absorbing properties (Hems and Abbatt, 2018)”. This sentence needs a re-word. The processes discussed for BrC are in addition to the physical processes controlling BC and dust.

The sentence has been reworded so that it now reads: “Like BC and dust, BrC is removed from the atmosphere through wet and dry deposition; however, BrC also undergoes chemical losses initiated by oxidants and direct photolysis (collectively termed bleaching) that can rapidly diminish its light absorbing properties (Hems and Abbatt, 2018).”

It is worth emphasising in the introduction as well as in the conclusions that many studies only focus on the optical properties of brown carbon under dry conditions and also that multiple studies considered absorption at ambient humidity have not reported the aerosol pH at which the determinations have been made.

This is an excellent point. The effects of drying on the optical properties of BrC are unknown; however, the transition of pH as ambient particles are dried, as occurs with many widely used aerosol measurement systems, will change the water-soluble BrC absorption. We have added the following text to the Discussion: “These results also inform measurements of BrC that are not conducted in aqueous matrices. For example, experimental approaches such as cavity ringdown spectroscopy (CRDS), photoacoustic spectrometry (PAS), and aethalometry are frequently used to measure total BrC, not just the water-soluble fraction (Liu et al., 2015). Non-filter based approaches, including CRDS and PAS, typically dry the air sample before measurement

(Washenfelder et al., 2013; Lack et al., 2012). It is unclear how the optical properties of chromophoric WSOC change as the particles transition from ambient conditions, where they often contain liquid water, to the dry environment within the instrument. Our results suggest that the water-soluble BrC compounds that exhibit a pH dependence will also exhibit different absorbance behaviors transitioning from an aqueous to non-aqueous phase state, though this topic should be explored in detail in the future.”

Line 95-97: How were non-precipitating clouds selected?

Schwab et al. (2016) indicates that cloud water collection occurs when: “the heated grid rain sensor must indicate that no rain is present, to assure that samples are from non-precipitating clouds.”

Line 147-149 and table 1: “with the exception that Ca^{2+} and Mg^{2+} concentrations were excluded because a decadal analysis of WFM cloud composition revealed that these species likely derive predominantly from coarse particles” If these cations are predominately in the coarse mode, which anions correspond to the coarse mode? How can it be discounted that the Na^+ , Cl^- and NO_3^- do not have a significant coarse mode contribution? What role would this play on the aerosol pH calculation?

Lawrence et al. (2023) have a very detailed discussion and analysis of this point – see especially their Section 6.3. While the reviewer correctly points out that other species are present in the coarse mode, as well, their imbalance between number and mass fractions is not nearly as disparate as it is for Ca^{2+} and Mg^{2+} . Lawrence et al. show convincingly that Ca^{2+} and Mg^{2+} , likely balanced with unmeasured species like carbonate, are overrepresented in the cloud water compared to the aerosol.

Line 155-159: To what extent does the Mountain affect airflow and therefore the ability of HYSPLIT capture the airmass history accurately?

We agree with the reviewer that this could be a concern for the 1-2 hours immediately before sampling. However, because our trajectory analysis extended backwards for 144 hours, the uncertainty imposed by the orographic effects should be relatively minor overall.

Lines 195-196: The authors comment on the greater variability in their results compared to the aerosol measurements of Phillips et al and suggest this may be due to ageing of air masses at the sample site. Another plausible explanation is that the activation characteristics of the aerosol are a source of variability. Unlike Phillips et al, who studied aerosol, the cloud water samples only observe activated aerosols. Since this is a strong function of both the aerosol size distribution and the updraft velocity and BrC is likely to be prevalent in the unactivated aerosol, greater variability may be induced in the observations. This is worth commentary.

We agree with the reviewer that the activated fraction of BrC-containing particles has importance for the pH of the aqueous environment and optical properties of BrC - see our reply to the next comment and our addition to the text. However, in this case, Phillips et al. (2017) have collected ambient aerosols onto filters and extracted the BrC in water, and filtered the

extracts. Therefore, their study also only considered the water-soluble fraction of BrC, similar to ours.

Lines 280-284: This discussion also implies that it is also important to quantify the available activated fraction of BrC from a range of important sources as a function of age.

The reviewer brings up an excellent point. To our knowledge, no studies have examined the activated fraction of BrC, but this is certainly worth exploring in light of our present results. We have added the following text to this discussion:

“The activated fraction of BrC has, to our knowledge, never before been explored but also affects the radiative forcing of BrC in aerosols and clouds.”

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pH-Dependence of Brown Carbon Optical Properties in Cloud Water

Christopher J. Hennigan¹, Michael McKee¹, Vikram Pratap¹, Bryanna Boegner¹, Jasper Reno¹, Lucia Garcia¹, Madison McLaren¹, Sara M. Lance²

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¹Department of Chemical, Biochemical and Environmental Engineering, University of Maryland, Baltimore County, Baltimore, 21250, USA

²Atmospheric Sciences Research Center (ASRC), University at Albany, Albany, 12226, USA

10 *Correspondence to:* Christopher J. Hennigan (hennigan@umbc.edu)

Abstract. Light-absorbing organic species present in aerosols, collectively called brown carbon (BrC), contribute important but highly uncertain effects on climate. Clouds likely represent a significant medium for secondary BrC production and for bleaching reactions, though the relative importance of formation and loss processes in clouds is unknown at present. The acidity (or pH) of atmospheric particles and clouds affects the optical properties of BrC and bleaching rates. Given the wide variability of pH in the atmosphere (pH in particles and clouds ranges from -1 to 8), the optical properties of BrC and its bleaching behavior are expected to vary significantly, and the link between pH and BrC is yet another uncertainty in attempts to constrain its climate forcing effects. In this work, we characterize the pH-dependence of BrC optical properties – including light absorption at 365 nm (Abs_{365}), mass absorption coefficient (MAC_{365}), and the absorption Ångström exponent (AAE) – in bulk cloud water sampled from the summit of Whiteface Mountain, NY. In all samples ($n = 17$), Abs_{365} and MAC_{365} increased linearly with increasing pH, highlighting the importance of reporting pH in studies of BrC in aqueous media. There was strong variability in the sensitivity of Abs_{365} to pH, with normalized slopes that ranged from 5.1% to 17.2% per pH unit. The normalized slope decreased strongly with increasing cloud water $[K^+]$, suggesting that the non-biomass burning BrC has optical properties that are more sensitive to pH than BrC associated with biomass burning. AAE also showed a distinct pH-dependence, as it was relatively flat between pH 1.5 – 5, then decreased significantly above pH 5. The cloud water composition was used to inform thermodynamic predictions of aerosol pH upwind/downwind of Whiteface Mountain and the subsequent changes in BrC optical properties. Overall, these results show that,

30 in addition to secondary BrC production, photobleaching, and the altitudinal distribution, the climate forcing of BrC is quite strongly affected by its pH-dependent absorption.

1 Introduction

Light-absorbing organic compounds, or chromophores, in particulate matter are collectively referred to as brown carbon (BrC). BrC exhibits a strong spectral dependence whereby the absorption efficiency
35 increases as wavelength decreases (Lack and Cappa, 2010; Kirchstetter et al., 2004). The light absorbing properties of BrC – both the absorption efficiency at a given wavelength and the wavelength-dependence – vary considerably in the atmosphere (Saleh, 2020). This variability in optical properties is due to the multitude of different organic compounds that contribute to BrC (Laskin et al., 2015). Regionally, the radiative forcing of BrC can represent an important component in the direct effect of aerosols on the
40 radiative balance (Zhang et al., 2017). However, the global climate forcing attributed to BrC is largely unconstrained at present due to the chemical complexity and widely variable optical properties; global climate models predict a net warming effect from BrC but estimates of the direct radiative forcing vary by almost a factor of 20 (from $+0.03 \text{ W m}^{-2}$ up to $+0.57 \text{ W m}^{-2}$) (Saleh, 2020).

45 BrC is different from other absorbing aerosols, dust and black carbon (BC), because it has prominent primary and secondary sources (Laskin et al., 2015). Like BC and dust, BrC is removed from the atmosphere through wet and dry deposition; however, BrC also undergoes chemical losses initiated by oxidants and direct photolysis (collectively termed bleaching) that can rapidly diminish its light
50 absorbing properties (Hems and Abbatt, 2018). Multiphase atmospheric processes, including those in clouds, play a key role in the life cycle of BrC, as they can facilitate production or loss, depending on the conditions (Hems and Abbatt, 2018; Laskin et al., 2015; Schnitzler and Abbatt, 2018; Zhao et al., 2015; Lee et al., 2014; Yu et al., 2016; Lin et al., 2015). Many laboratory studies have investigated BrC formation and loss using cloud water mimics (e.g., Powelson et al., 2014; De Haan et al., 2018) but few using real atmospheric cloud water samples. This represents a key knowledge gap in understanding the
55 temporal and spatial distribution of BrC and its effects on climate.

The acidity (or pH) of aerosols and clouds has tremendous importance for numerous atmospheric processes and for associated environmental effects (Pye et al., 2020). This includes an effect of pH on the radiative forcing of BrC compounds. pH affects the light-absorbing properties of many organic
60 compounds in aqueous media (Baes and Bloom, 1990). Aerosol samples collected in the southeastern U.S. showed pronounced pH-dependent absorbance spectra (Phillips et al., 2017). This was observed for both background ambient samples and those that had been influenced by biomass burning emissions. The increase in absorbance with increasing pH suggests that carboxylic acids and phenols contributed significantly to BrC in this study (Phillips et al., 2017). A similar study found that the aqueous extracts
65 of biomass burning aerosols exhibited a strong spectral dependence with pH (Cai et al., 2018). Further, pH had an important effect on the evolution of BrC bleaching in photolysis experiments conducted with the aqueous aerosol extracts (Cai et al., 2018). This is expected because many aqueous reaction rates are pH-dependent (Pye et al., 2020; Tilgner et al., 2021).

70 The pH of atmospheric particles, cloud, and fog droplets spans a wide dynamic range, from approximately -1 in highly acidic particles up to 8 in clouds containing alkaline components (Shah et al., 2020; Pye et al., 2020). Therefore, the optical properties of BrC and its bleaching behavior are expected to vary significantly in the atmosphere, as well. The pH-dependence of BrC absorbance and bleaching may be especially dynamic in cloud cycles because the pH of CCN particles can increase by 3-4 pH units when
75 they activate and form cloud droplets or decrease by the same amount when they transition from cloud droplets back to aqueous particles (Rusumdar et al., 2020). This suggests that the light absorbing properties of chromophores may be dramatically different in clouds compared to the properties of the same compounds in aqueous haze particles. In addition to in-cloud BrC transformations due to secondary formation and bleaching, changes in BrC absorbance with pH need to be characterized in order to
80 understand the impact of clouds on BrC.

The purpose of this study is to characterize the pH-dependence of BrC optical properties in cloud water samples collected at Whiteface Mountain, NY (WFM). The samples were collected over two summers and have diverse chemical composition and back trajectories, suggesting a variety of source influences

85 and airmass ageing. The analysis of BrC optical properties is paired with aerosol thermodynamic equilibrium modeling and cloud water composition measurements to calculate the aerosol liquid water content and pH of aerosols upwind of WFM. Using the measured pH-dependence of BrC optical properties, the modeled aerosol pH upwind of WFM informs changes to BrC radiative forcing in the atmosphere.

90 **2 Materials and Methods**

Cloud water samples were collected at the summit of Whiteface Mountain, NY (latitude N44°21'58" and longitude W 73°54'10", 1483 m a.s.l.) during the summers of 2018 and 2019. The site has been used continuously for atmospheric chemistry and cloud research for more than three decades (Mohnen and Kadlec, 1989). Procedures for cloud water collection and chemical analysis have been described in
95 detail before (Lance et al., 2020; Schwab et al., 2016; Lawrence et al., 2023). Briefly, cloud water collection occurred via a passive Mohnen omni-directional sampler when non-precipitating liquid clouds were present under select meteorological conditions. The collected cloud water was refrigerated (4°C), and analyzed for inorganic ionic species, organic acids, pH, conductivity, and total organic carbon (TOC) content. A subset of the samples was syringe filtered (0.45 µm) prior to analysis and thus, the analyzed
100 organics represents WSOC instead of TOC (Lance et al., 2020). The remaining sample volume was frozen (-20°C) for further analysis. Some of these frozen samples were packed in dry ice and shipped overnight to the University of Maryland, Baltimore County for BrC analysis.

In this study, BrC is operationally defined as the water-soluble organic carbon compounds that absorb
105 light in the 300 – 500 nm wavelength range. Many chromophores are found in the atmosphere that are insoluble or are soluble in other solvents (e.g., methanol) (Jiang et al., 2022; Zeng et al., 2020; Zhang et al., 2013). For the cloud water samples that were filtered, and since no additional organics were added, our analyses neglect any chromophores that are insoluble in water or soluble in other solvents (e.g., methanol), which can be 40-50% of BrC globally (Zeng et al., 2020). Absorbance spectra of cloud water
110 samples at each pH were recorded based on the method described previously (Pratap et al., 2020). A liquid waveguide capillary cell (LWCC, World Precision Instruments) with 50 cm path length was

coupled via fiber optic cables to a light source (200 – 1600 nm, Ocean Insight DH-mini) and two spectrometers, one to record absorbance spectra (FLAME-S, Ocean Optics) and one to continuously monitor the light source stability (STS-VIS, Ocean Insight). An automated syringe pump (model C3000, TriContinent Scientific) delivered the pH-adjusted cloud water sample to the LWCC, which was thoroughly rinsed with DI water ($>18.2 \text{ M}\Omega \cdot \text{cm}$) in between each sample. Absorbance spectra from 300 – 500 nm were recorded every 3 seconds and averaged over 4 minutes. Mass absorption coefficients at 365 nm ($\text{MAC}_{365}, \text{m}^2 \text{g}^{-1}$) were calculated according to Saleh (2020). The absorbance spectra from 300 – 500 nm were fit with an exponential function (Igor Pro, WaveMetrics) to calculate the absorption Ångström exponent at each pH (AAE_{pH}).

The optical properties of each cloud water sample were measured at pH from 11 to 1.5. Following the approach of Phillips et al. (2017), sample pH was cycled from 2 to 11 to avoid potential hysteresis effects prior to the optical measurements. The cloud water sample was adjusted to pH 11 using 1.0 M NaOH (Fisher Scientific). Downward pH adjustments of ~ 1 pH unit were made through additions of 0.1 M and 3.0 M HCl (Fisher Scientific). pH was measured using an Orion Star A211 meter with Ross Ultra pH Electrode (Orion 8103BNUWP). The actual pH after NaOH and HCl additions was variable and depended on the cloud water composition (Table 1). Therefore, the actual pH at each step was recorded and used for the analyses. After the pH stabilized, approximately 1 mL of the cloud water sample was injected into the LWCC to fill the LWCC sample loop and tubing void volumes. The sample was injected into the LWCC within minutes of the pH adjustment, minimizing the time for any acid-catalyzed reactions of BrC chromophores to occur. The optical measurements accounted for the small diluting effects of the NaOH and HCl additions. Initially, these pH titrations and optical analyses were performed in duplicate on each cloud water sample; however, a high degree of repeatability was observed (Figure 1), so subsequent samples were only analyzed once to conserve the limited sample volumes. QA/QC on the experimental procedure was run using the full range of pH adjustments to DI water. The DI water at all pH levels showed absorbance values approximately 2 orders of magnitude lower than the cloud water samples and often below the system limit of detection: No background adjustments were made to the cloud sample measurements. Cloud water samples were also compared to Suwannee River Natural

140 Organic Matter (SR-NOM, International Humic Substances Society), a well-characterized material that has similarities to BrC sampled in the atmosphere (Green et al., 2015; Graber and Rudich, 2006).

Back trajectories for each cloud water sample were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, (Stein et al., 2015)). Following the approach of
145 Lawrence et al. (2021), 6-day back trajectories were initiated at each hour of cloud water sampling using meteorology from the North American Regional Reanalysis (NARR) 32 km x 32 km. Output from the HYSPLIT model included the air mass location and altitude, as well as meteorological parameters. The temperature (T) and relative humidity (RH) output from HYSPLIT were used as inputs to the ISORROPIA-II aerosol thermodynamic equilibrium model (Fountoukis and Nenes, 2007). The inorganic ionic
150 composition of the cloud water samples was used for the ISORROPIA-II model input, with the exception that Ca^{2+} and Mg^{2+} concentrations were excluded because a decadal analysis of WFM cloud composition revealed that these species likely derive predominantly from coarse particles (Lawrence et al., 2023). To provide an estimate of fine aerosol pH along the back trajectory, ISORROPIA-II was run in forward mode with solids formation suppressed (i.e., metastable) according to Pye et al. (2020). We note that this
155 approach assumes a constant chemical composition along the entire 6-day back trajectory, which is clearly not realistic. However, this exercise shows pH variations along the back trajectory that may arise solely from the changes in T and RH as air mass altitude and position changes. In many locations, T and RH exert a greater influence on fine aerosol pH than composition, like sulfate and ammonium (Battaglia et al., 2017; Zheng et al., 2020; Tao and Murphy, 2021). Therefore, this exercise, while not accurate in
160 predicting the actual fine aerosol pH along the back trajectory, does reflect the magnitude of pH variability that may be expected as air masses were transported to WFM and how they compared to the cloud water pH.

3 Results

An overview of the cloud water samples analysed for this study is presented in **Table 1**. The cloud liquid
165 water content ranged from 0.26 g m⁻³ to 0.87 g m⁻³ (median 0.53 g m⁻³) and the temperature ranged from 7.2 °C to 21.0 °C (median 17.2 °C). Cloud water composition also showed quite a bit of variability: pH

ranged from 4.27 to 6.41 (median 4.70). TOC concentrations in the cloud water varied by more than an order of magnitude, from 106 μM to 1770 μM (median 505 μM). Amongst the inorganic ionic species measured, NH_4^+ had the highest median concentration (58.3 μM), followed by NO_3^- (32.5 μM), SO_4^{2-} (22.0 μM), and Cl^- (19.0 μM). In a prior study at WFM, Cook et al. (2017) found that K^+ concentrations exceeded 0.04 mg L^{-1} (1 μM) in cloud water samples influenced by fire emissions. In the present study, 12 of the 17 samples had K^+ concentrations above 0.04 mg L^{-1} , suggesting fire emissions had an important impact on cloud water composition. This is supported by the linear correlation between K^+ and TOC concentrations ($R^2 = 0.62$) in our samples and prior studies at WFM observing frequent influence of fire emissions on cloud water samples during the summer (Lance et al., 2020; Lee et al., 2022).

The distribution of MAC_{365} values at pH 4 is shown in **Figure 2**. MAC_{365} values at pH 4 ranged from 0.12 $\text{m}^2 \text{g}^{-1}$ up to 0.68 $\text{m}^2 \text{g}^{-1}$ (median of 0.34 $\text{m}^2 \text{g}^{-1}$). The median MAC_{365} value for WFM cloud water samples was similar to the value observed for Suwannee River NOM (0.30, green hatched bar in Fig. 2). A key feature of the BrC optical properties in our samples was the strong pH-dependence of absorption, as illustrated in Fig. 1 for duplicate analyses of sample 1922801. All samples showed a positive linear relationship, as absorption (and MAC) increased with increasing pH. This result is consistent with observations of BrC in ambient aerosols sampled in Georgia, including under conditions of biomass burning influence (Phillips et al., 2017). Based on the results of Schendorf et al. (2019), we expect the observed pH-dependence to be reversible, although this was not verified experimentally.

Although a positive linear relationship between MAC_{365} and pH was observed in all samples, there was considerable variation in the slope of this relationship for different cloud water samples (**Figure 3** and **Table 2**). Each sample's absorbance at 365 nm (Abs_{365}) at each pH was normalised to the sample Abs_{365} at pH 1.5. The slope of the normalized Abs_{365} vs. pH is a measure of how much BrC absorption changes for each pH unit change. The lowest relative slope was observed for sample 1822702 (slope of 0.051), which indicates the Abs_{365} varied by 5.1% per pH unit. Thus, a change of 6 pH units would only change the BrC absorption at 365 nm for this sample by $\sim 30\%$. The highest relative slope was observed for sample 1920702 (17.2% change in Abs_{365} per pH unit), where a 6 pH unit change would result in greater

195 than a factor of two change for the BrC absorption at 365 nm. The results in **Figure 3** are contrasted with results from Phillips et al. (2017), where slopes of 8% and 13% per pH unit were observed for BrC sampled in ambient aerosols uninfluenced and significantly influenced by biomass burning, respectively (solid red and green lines in **Figure 3**). The sensitivity of Abs₃₆₅ to pH observed in WFM samples was similar to that of SR-NOM (thick dashed black line in **Figure 3**), which had a slope of 10.7% per pH unit.
200 The greater variability observed in our study may be due to the ageing of air masses sampled at WFM and more diverse source influences, which is discussed in detail below.

Variability in the response of BrC absorption to changes in pH was likely influenced by BrC sources. **Figure 4** shows the relationship between the normalized slope from Fig. 3 and the cloud water K⁺
205 concentration. There was a clear decreasing trend in the sensitivity of BrC absorption to pH as [K⁺] increased. As discussed above, [K⁺] in WFM cloud water samples was used to identify biomass burning influence (Cook et al., 2017). The results in **Figure 4** suggest that aged biomass burning samples have less sensitivity to pH than ambient samples uninfluenced (or only lightly influenced) by biomass burning. This contrasts the results of a prior study that observed samples heavily influenced by fresh biomass
210 burning emissions showed higher sensitivity of BrC absorption to pH (Phillips et al., 2017). The apparent discrepancy between the results in Fig. 4 and those in Phillips et al. (2017) is likely due to atmospheric ageing. Phillip et al. (2017) sampled under conditions when large fires were burning relatively close to the sampling site, suggesting that the emissions were fresh. By contrast, fires burning in the western U.S. and Canada undergo transport of days (typically 3 – 7 days) before sampling at WFM (Cook et al., 2017;
215 Lance et al., 2020). Changes in BrC optical properties as biomass burning emissions age in the atmosphere are well documented (Saleh et al., 2013; Laskin et al., 2015; Forrister et al., 2015). Photobleaching and secondary BrC production alter the MAC and AAE of primary biomass burning emissions, though the timescale for these changes varies widely in the atmosphere and remains a major uncertainty in better representing BrC in global models (Saleh, 2020). The present results suggest that
220 atmospheric ageing may reduce the sensitivity of biomass burning BrC optical properties to pH, though future studies are needed to substantiate this finding through investigations that provide for controlled ageing conditions.

Similar to the MAC_{365} , the absorption Ångström exponent showed wide variability across the cloud water
225 samples (**Figure 5** and **Table 2**). The AAE_5 ranged from 4.63 (sample 1822702) to 7.09 (sample
1818204). AAE_5 values of cloud water samples were systematically higher than the SR-NOM, which
had an AAE_5 of 3.39 (green hatched bar in **Figure 5**). AAE_5 values indicate three samples (1822702,
1920004, and 1817601) were ‘moderately absorptive’ ($2.5 < AAE < 5$), while the remainder were ‘weakly
absorptive’ ($5 < AAE < 8$) according to the optical bins defined by Saleh (2020). The AAE values also
230 showed a distinct pH dependence. **Figure 6** shows the mean AAE values for WFM cloud water samples
as a function of pH. For pH 1.5 – 5, there was not much variation in AAE with pH; however, AAE
decreased significantly above pH 7. The results in Figure 6 are consistent with the results of Qin et al.
(2022b), who characterized water-soluble BrC in Beijing and observed a non-linear relationship between
AAE and pH, with significant reductions in AAE at $pH > 6$. This is likely due to chromophores with pKa
235 values above 6. For weakly acidic and moderately basic BrC chromophores, changes in pH below pH 6
impart only minor changes to the acid-base equilibrium and thus the spectral dependence on pH. Above
pH 6, BrC speciation becomes more sensitive to pH variations, resulting in changes to AAE in this range.

The optical properties of BrC are highly variable, reflecting the chemical diversity of atmospheric organic
240 compounds that absorb light (Laskin et al., 2015). In general, as BrC becomes more highly oxidized (and
thus water-soluble), BrC absorption efficiency weakens and AAE increases (Saleh, 2020). The optical
properties of BrC in WFM samples were broadly consistent with the findings in other locations. For
example, the AAE values of WSOC sampled in cloud water at Mt. Tianjing, China ranged from 5.37 –
6.31 during a study where cloud water composition was strongly influenced by biomass burning (blue
245 hatched bar in **Figure 5**, (Guo et al., 2022)). Water-soluble BrC extracted from $PM_{2.5}$ samples exhibited
average AAE values of 6.6 – 6.8 in Beijing and 4.8 – 7.3 in other cities in China (Qin et al., 2022a; Wu
et al., 2020), while water-soluble $PM_{2.5}$ extracts at various locations in India had AAE values of 5.1 – 5.3
(Kirillova et al., 2014; Srinivas et al., 2016). In the U.S., water-soluble organic carbon had mean AAE
values of 7.6 in Los Angeles (Zhang et al., 2013) and 6.0 – 8.3 in Atlanta, depending on the time of year
250 (Hecobian et al., 2010). In the Atmospheric Tomography Missions (ATom-2, ATom-3, and ATom-4)

aircraft studies probing global aerosol compositions, water-soluble BrC exhibited mean AAE values of 4.1 – 6.5 (red patterned bars in **Figure 5**; (Zeng et al., 2020)). There was not an apparent trend in the geographic distribution of AAE, though there was an altitudinal dependence, with lowest AAE values observed at the highest (10 – 13 km) and lowest altitudes (< 1 km) (Zeng et al., 2020).

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A comparison of the present results to other studies brings up a critical point: Most of the prior studies did not report the pH of the aqueous extracts or the pH-dependence of absorption or AAE. The results in Figures 1, 3, and 6 show that the optical properties of atmospheric water-soluble BrC depend strongly on pH. Therefore, measurements of BrC in aqueous environments need to include and report pH in order to
260 facilitate interstudy comparisons and to assess the climate forcing effects of BrC. **Further, optical properties of water-soluble BrC in aqueous environments should be measured at two pH levels, when feasible, to enable translation to other conditions in the atmosphere.**

In addition to the changes in Abs_{365} (and MAC_{365}) and AAE with pH, the relative absorption changed
265 with wavelength at each pH, as well. **Figure 7** shows the absorption at a given pH relative to the absorption at pH 1.5 averaged over all cloud water samples. There was a clear wavelength-dependence of the absorption enhancements with increasing pH. At $pH < 6$, there was a minor increase in absorption from 300 nm up to 340 nm. The mean absorbance spectra below pH 6 were relatively flat from 340 nm up to 400 nm, declined gradually to a minimum around 450 nm, then gradually increased up to 500 nm.
270 Above pH 7, mean absorbance spectra showed a steady increase from 300 nm – 380 nm, peak absorption relative to pH 1.5 at 380 – 400 nm, followed by a similar decline and minimum at ~450 nm. Comparison to other studies reveals both similarities and differences in the wavelength-dependent variations with pH shown in **Figure 7**. For example, in a study characterizing the effects of pH on water-soluble BrC aerosols in Beijing, there was a similar wavelength-dependence to the absorption enhancement we observed in
275 **Figure 7** (Qin et al., 2022a); however, the magnitude of the absorption enhancement at 400 nm relative to pH 1.5 was higher in WFM cloud water at each pH level.

4 Discussion

Our results have important implications for understanding BrC in the atmosphere. It is imperative that studies reporting the optical properties of water-soluble BrC – whether in aerosol extracts, cloud, or fog water – also report the pH at which the measurements were conducted. The *in situ* aerosol pH (ranging from -1 to 8) may be dramatically different from the pH of dilute aqueous extract solutions (most likely in the range of pH 4 to 6). This will facilitate more accurate comparisons between studies. Cloud cycling, with the accompanying 2 – 3 pH unit step changes, results in BrC absorption efficiency changes of 10% – 50% for the WFM samples. Particle composition and changes in meteorology also change aerosol pH, such that BrC compounds may experience variability of 5 - 6 pH units over their atmospheric lifetime. Our results suggest that these pH changes dramatically change the climate forcing effects of BrC. Aerosols are usually more acidic than clouds, so BrC exhibits stronger absorption in clouds than in aerosols. The activated fraction of BrC has, to our knowledge, never before been explored but also affects the radiative forcing of BrC in aerosols and clouds. Therefore, in addition to factors that have been considered, such as the altitudinal distribution of BrC (Zhang et al., 2017), accurately constraining the climate forcing effects of BrC requires accounting for the sensitivity to pH.

The results in this study suggest that aromatic carboxylic acids and phenolic compounds, including nitrophenols, are primarily responsible for the observed pH-dependent optical properties. Phenols and aromatic carboxylic acids are major contributors to atmospheric BrC (Laskin et al., 2015). Prior studies have shown that aromatic carboxylic acids contribute most to the pH-dependence below pH 7 while phenols are most responsible above pH 7 (Schendorf et al., 2019; Qin et al., 2022c). Our results also suggest that phenols are primarily responsible for the observed dependence of AAE on pH (Figure 6). AAE only varied with pH above pH 7, consistent with phenolic pKa values that are typically in the 7 – 10 range. The wavelength-dependent enhancements with increasing pH shown in Figure 7 also point to the influence of phenols because the shape and magnitude of the enhancements become much more prominent above pH 7.

305 The variability in BrC absorption due to pH is illustrated in **Figure 8**, which shows back trajectories corresponding to each cloud water sample analysed in this study. The 6-day back trajectories are coloured by the Abs_{365} along the trajectory normalized to the Abs_{365} for cloud water conditions. The relative Abs_{365} changes in Figure 8 are based upon the changes in pH along the back trajectories as well as the sensitivity of absorption to pH for each sample (normalized slope in Table 2). For all samples, the maximum Abs_{365} occurs in-cloud because the pH is systematically higher than in particles due to the effect of dilution. The predicted changes range from minor to major, depending on the sample. The mean normalized Abs_{365} among all trajectories was 0.637 (median 0.661), indicating a $\sim 1/3$ reduction in BrC absorption in the aerosols relative to the cloud water. As described above, aerosol pH modelled along the back trajectory was computed using the cloud water composition so it only accounts for changes in T and RH. Although these factors have a major effect on pH (Tao and Murphy, 2019), the actual pH along the back trajectories will differ due to changes in aerosol composition. Abs_{365} will further change if secondary BrC production or bleaching occurs during transport to WFM. Therefore, the results in **Figure 8** serve only as a guide to illustrate the magnitude of BrC absorbance changes that may occur in the atmosphere due to changes in pH associated with changes in T and RH. **Figure 8** also illustrates the diversity of sources influencing the cloud water samples, consistent with the variable cloud water composition discussed above. The trajectories collectively show marine, clean arctic, biogenic, and polluted continental air mass origins. We attempted to correlate BrC optical properties with the trajectory analyses; however, this was inconclusive because of the small number of trajectories originating in some regions.

325 These results also inform measurements of BrC that are not conducted in aqueous matrices. For example, experimental approaches such as cavity ringdown spectroscopy (CRDS), photoacoustic spectrometry (PAS), and aethalometry are frequently used to measure total BrC, not just the water-soluble fraction (Liu et al., 2015). Non-filter based approaches, including CRDS and PAS, typically dry the air sample before measurement (Washenfeller et al., 2013; Lack et al., 2012). It is unclear how the optical properties of chromophoric WSOC change as the particles transition from ambient conditions, where they often contain liquid water, to the dry environment within the instrument. Our results suggest that the water-soluble BrC compounds that exhibit a pH dependence will also exhibit different absorbance behaviours

transitioning from an aqueous to non-aqueous phase state, though this topic should be explored in detail in the future.

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BrC compounds are likely to encounter liquid water during much of their time in the atmosphere and water-soluble chromophores can dissolve or partially dissolve in the aqueous fraction (Zhang et al., 2012; Pye et al., 2018). Therefore, the optical properties of BrC are not static, but evolve in space and time. Secondary BrC formation and photobleaching contribute to these dynamic changes. Our results show that changing pH, which can be due to changing inorganic aerosol composition, changing T and RH, also contribute to changing BrC optical properties that may be as - or more - impactful as these other processes.

Our results indicate that pH is a key parameter that may dramatically change the radiative forcing of water-soluble BrC relative to insoluble BrC. Water-soluble BrC makes a variable contribution to the overall light absorption. Guo et al. (2022) found that water-soluble BrC contributed approximately half of the Abs_{370} in cloud droplet residuals sampled at Mt. Tianjing, China, and Zeng et al. (2020) estimated that the water-soluble fraction of BrC was approximately half of the total BrC in the ATom aircraft studies characterizing the global distribution of aerosol composition and concentration. However, our results show that changes in aerosol and cloud water pH will clearly change the climate forcing of water-soluble BrC relative to the total. Changes in composition, aerosol and cloud processes (e.g., cloud activation or drying), and meteorology (temperature and RH) strongly affect pH (Pye et al., 2020). Therefore, the contribution of water-soluble BrC to total BrC radiative forcing will change in time and space, as well.

The WFM cloud water samples showed similarities with Suwannee River NOM. Specifically, the MAC at pH 4 (Fig. 2) and the normalized slope of Abs_{365} vs. pH (Fig. 3) for SR-NOM were both very close to the median WFM cloud water samples. More broadly, Schendorf et al. (2019) characterized the pH effects on optical properties of five different humic substances isolated from aquatic and terrestrial systems and found similar behaviour to our cloud water samples, as absorption increased with increasing pH, though the wavelength-dependence and spectral characteristics differed between different samples. Our WFM cloud water samples were most similar to their analysis of Suwannee River fulvic and humic

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acids (Schendorf et al., 2019), materials that contain hydrophobic organic acids isolated from the SR-NOM we analysed (<https://humic-substances.org/>, last accessed 24-Feb-2023). It is now well known that chemical and physical characteristics of atmospheric organic matter – especially the light-absorbing fraction – bear similarities to organic material found in aquatic and terrestrial systems (Kalberer et al., 2004; Graber and Rudich, 2006). The present results build upon this body of work and support the use of these materials, which are abundant and commercially available, as surrogates for further studies into the pH-dependent optical properties of atmospheric BrC.

Turnock et al. (2019) analysed changes in aerosol radiative forcing due to cloud water pH. Their study considered the effects of pH on the aqueous oxidation of SO₂ in clouds and how this changed global particle size distributions. Ultimately, their model predicted stronger aerosol radiative forcing at higher cloud water pH because of enhanced SO₂ oxidation to sulphate in clouds and the resulting reduction in gas-phase production of H₂SO₄ (Turnock et al., 2019). Our results show that changes in cloud water pH also affect the climate forcing of aerosols through effects on BrC absorption. Increasing pH increased the absorption efficiency of BrC for all cloud water samples analysed. Because BrC absorption is sensitive to pH, photolysis rates (i.e., photobleaching) are sensitive to pH, as well. For example, Zhao et al. (2015) observed a factor of ~2 increase in the photolysis rate of a nitrophenol (4-nitrocatechol) going from pH 3 to pH 5. Another study observed an increase in the photolysis rates of nitrophenols (guaiacol, catechol, and 5-nitroguaiacol) with decreasing pH (Yang et al., 2023). Therefore, cloud and aerosol pH affect the lifetime of BrC compounds, which further affects their climate forcing.

Finally, our measurements were conducted on liquid cloud samples, so these results are limited to aqueous environments. Aerosol liquid water, while often abundant, is also highly variable in the atmosphere (Nguyen et al., 2016). Aqueous aerosols contain orders of magnitude less water than cloud droplets, so organic solutes rapidly transition between highly concentrated and dilute environments during cloud cycling. Organic compounds in atmospheric particles span a very wide range of water solubilities, including compounds measured in the water-soluble fraction (i.e., as WSOC) (Psichoudaki and Pandis, 2013). Changes in liquid water content cause organic aerosols to undergo various phase transitions,

including liquid-liquid phase separation and transition to highly viscous “glassy” states (Reid et al., 2018).
390 Acidity can be defined in non-aqueous media, though the pH scale as a measure of solution acidity does
not directly transfer between different solvents (Himmel et al., 2018). Therefore, our results do not inform
the optical properties of BrC in non-aqueous environments; however, future studies should address this
question. These results reflect the optical properties of organic compounds dissolved in cloud water at
their time of sampling under the environmental conditions given in Table 1; a different distribution of
395 solubility would likely change the measured optical properties, as well.

Data Availability

All data presented in this work are published in Tables 1 and 2. Any data not published, e.g., raw spectra,
are available upon request.

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Author Contributions

C. Hennigan: Conceptualization, Methodology, Resources, Funding acquisition, Supervision, Writing –
Original Draft, Writing – Review & Editing. M. McKee: Methodology, Validation, Formal analysis,
Writing – Review & Editing, Visualization. V. Pratap: Methodology, Validation, Formal analysis,
405 Writing – Review & Editing, Visualization. B. Boegner: Methodology, Validation, Formal analysis,
Writing – Review & Editing, Visualization. J. Reno: Methodology, Validation, Formal analysis, Writing
– Review & Editing, Visualization. L. Garcia: Methodology, Validation, Formal analysis, Writing –
Review & Editing, Visualization. M. McLaren: Methodology, Validation, Formal analysis, Writing –
Review & Editing, Visualization. S. Lance: Methodology, Resources, Writing – Original Draft, Writing
410 – Review & Editing.

Competing Interests

The authors declare no competing financial interests.

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425 opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York.

Table 1: Overview of the cloud water composition for samples collected from the summit of Whiteface Mountain and analysed for this study.

Sample ID	Date	Cloud sampling duration (hr)	Cloud LWC (g/m ³)	Temp. (°C)	pH	TOC (µmol/L)
1817601	25-Jun-2018	4.7	0.51	7.2		439.3
1818204*	1-Jul-2018	10.9	0.66	19.0	4.51	988.3
1818205*	1-Jul-2018	3.8	0.33	19.0	4.57	1770
1820401	23-Jul-2018	4.95	0.40	17.7	4.60	206.1
1820702	26-Jul-2018	6.3	0.75	15.2	4.64	106
1821005	29-Jul-2018	11.1	0.87	11.5	4.88	216
1821301	1-Aug-2018	7.4	0.36	15.2	4.27	498.2
1822701	15-Aug-2018	2.1	0.55	17.2	4.62	869.2
1822702	15-Aug-2018	2.1	0.55	17.2		732.1
1822901	17-Aug-2018	5.8	0.72	15.8	4.76	311.4
1823805	26-Aug-2018	7.4	0.78	13.8	5.35	801.8
1920004*	19-Jul-2019	11.3	0.57	18.9	5.18	512.3
1921102*	30-Jul-2019	1.9	0.27	21.0	6.41	1323.3
1922202*	10-Aug-2019	10.8	0.50	15.0	5.38	344.6
1922801*	16-Aug-2019	6.8	0.51	18.3	4.28	540
1926801	25-Sept-2019	2.9	0.26	16.7	5.18	385

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Sample ID	[Na ⁺] (µM)	[K ⁺] (µM)	[NH ₄ ⁺] (µM)	[Ca ²⁺] (µM)	[Mg ²⁺] (µM)	[Cl ⁻] (µM)	[NO ₃ ⁻] (µM)	[SO ₄ ²⁻] (µM)
1817601	0.9	1.0	20.0	1.0	0.4	25.7	11.3	14.9
1818204*	5.7	2.0	510.0	23.0	5.3	46.8	93.5	67.0
1818205*	10.0	3.1	908.9	28.2	8.2	57.3	125.0	102.4
1820401	31.3	1.3	14.4	3.5	2.5	28.5	21.3	10.5
1820702		0.8	20.0	2.0	0.8	13.8	24.4	9.9
1821005	1.3	0.5	10.6	3.2	1.2	22.6	6.1	6.7
1821301	13.9	1.5	52.2	7.5	2.1	22.3		21.8
1822701	7.0	3.1	141.1	21.5	4.9	18.9	40.5	22.3
1822702	0.4	2.6	80.0	19.2	4.9	19.2	35.6	21.4

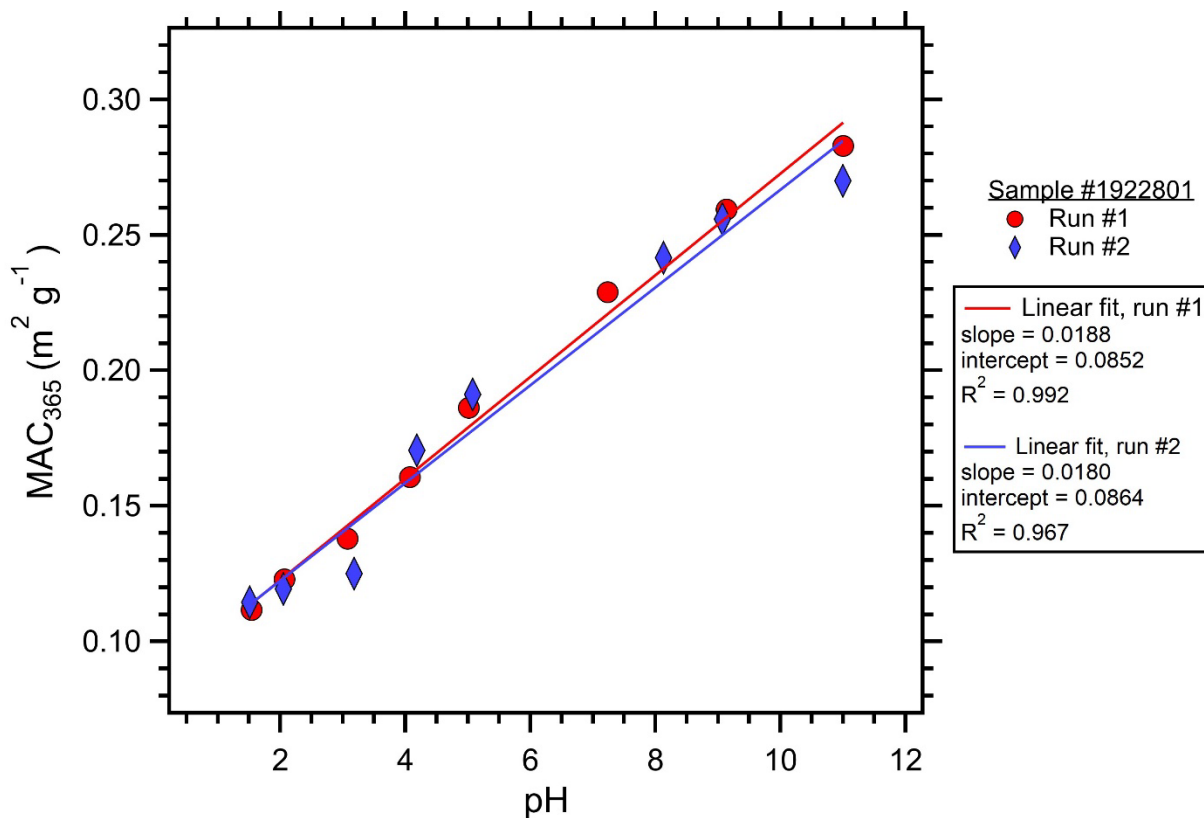
1822901	1.3	2.3	60.0	13.0	3.7	0.8	37.7	25.2
1823805	13.0	2.6	141.7	39.2	13.6	3.7	69.7	32.8
1920004*	2.6	1.8	38.9	11.5	2.5	24.3	25.8	13.1
1921102*	3.0	4.6	248.3	94.6	11.9	1.7	158.5	85.7
1922202*	2.6	1.8	56.7	10.2	2.5	9.9	29.4	22.9
1922801*	2.6	2.0	96.7	10.7	4.1	9.9	90.6	30.3
1926801			9.4			5.4	10.6	7.9

*Denotes samples that were syringe-filtered (0.45 μm); thus the TOC reported is actually WSOC for these samples.

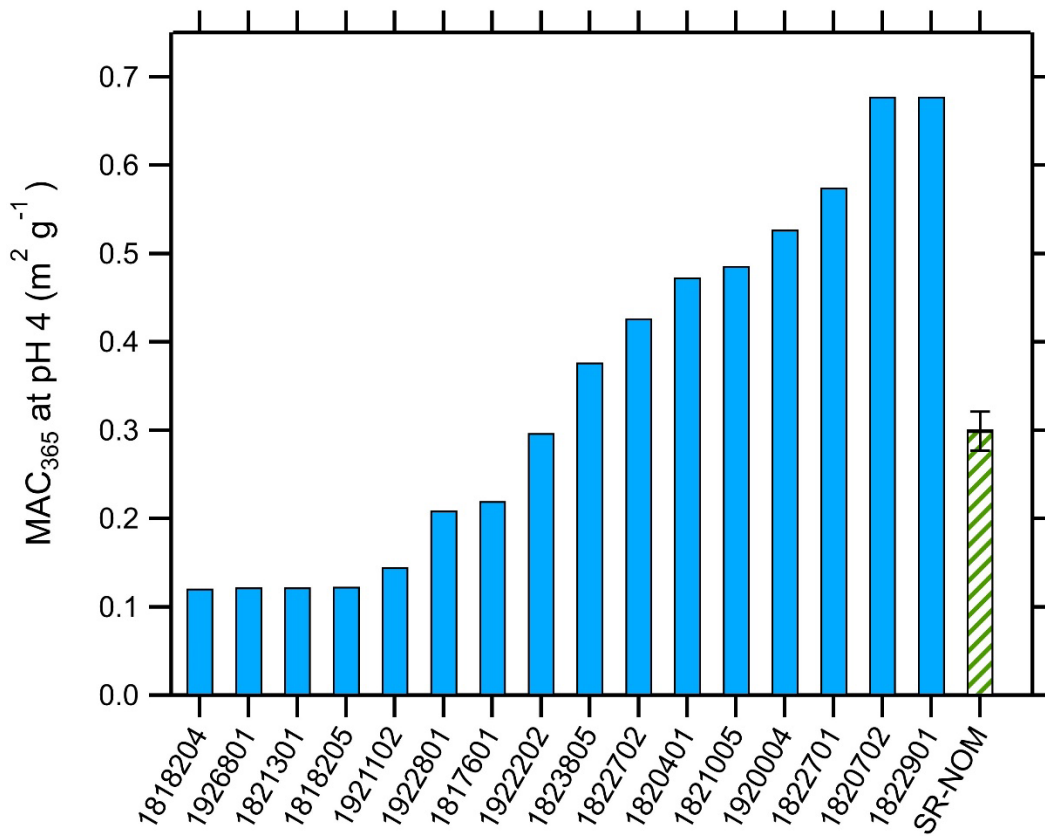
Table 2: Summary of key optical properties for cloud water samples.

Sample ID	MAC ₃₆₅ (m ² g ⁻¹)	*Normalized slope Abs ₃₆₅ vs. pH	AAE ₂	AAE ₅	AAE ₉
1817601	0.220	0.171	5.49	4.96	4.53
1818204	0.121	0.066	7.59	7.09	4.43
1818205	0.123	0.070	6.86	6.50	4.81
1820401	0.473	0.146	5.66	6.16	6.22
1820702	0.678	0.172	-	-	-
1821005	0.486	0.109	5.94	6.41	5.01
1821301	0.122	0.154	6.20	5.79	6.08
1822701	0.575	0.058	6.23	6.00	5.19
1822702	0.427	0.051	4.53	4.63	4.77
1822901	0.678	0.093	6.13	5.76	5.08
1823805	0.377	0.054	5.84	5.32	4.13
1920004	0.527	0.087	4.83	4.80	5.09
1921102	0.145	0.055	6.56	6.45	5.63
1922202	0.297	0.083	6.15	6.02	5.11
1922801	0.209	0.163	6.70	6.43	6.25
1926801	0.122	0.139	6.07	5.66	5.44

435 *Slope determined as Abs₃₆₅(pH)/Abs₃₆₅(pH 1.5) vs. pH for each sample (see Fig. 3)

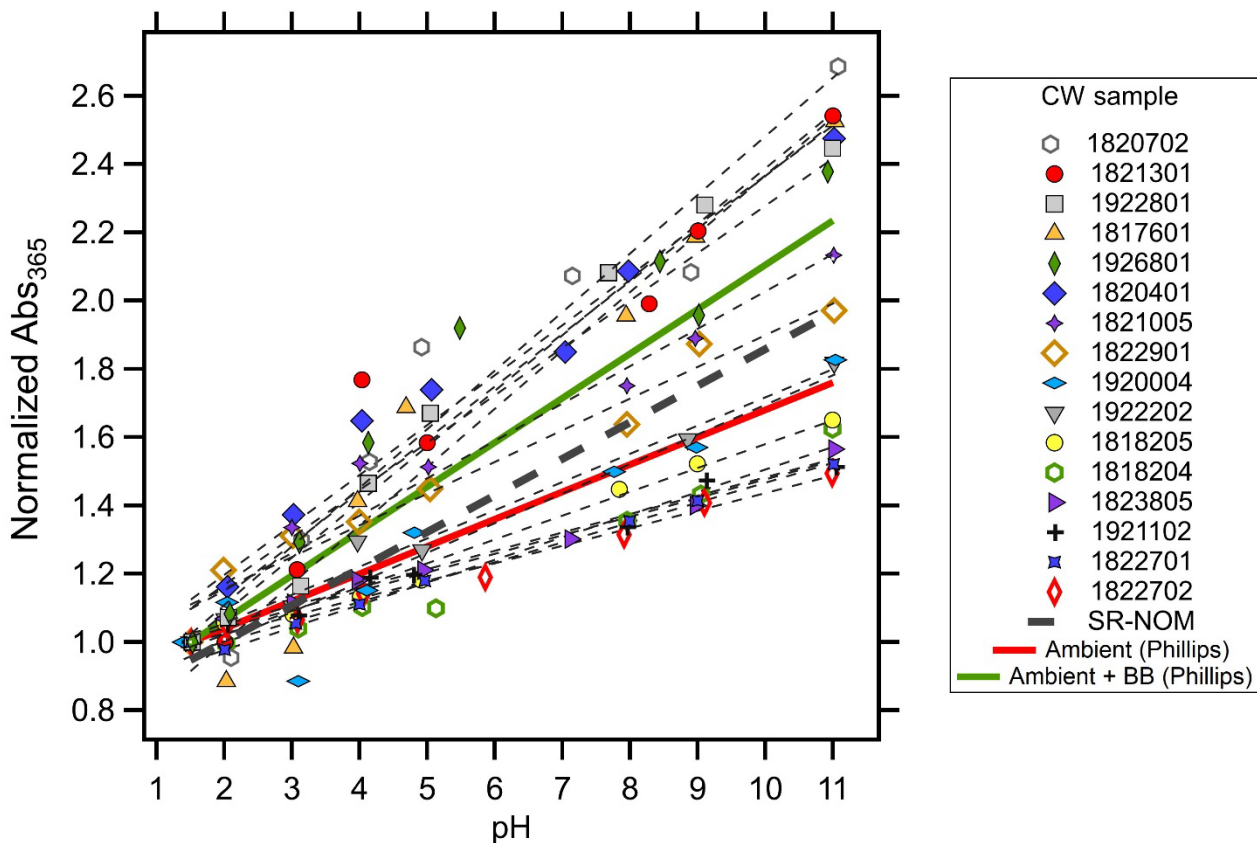


440 **Figure 1:** Duplicate measurements of MAC_{365} as a function of pH for cloud water sample #1922801. The slope, intercept, and coefficient of variation (R^2) showed excellent repeatability for the analyses run for the same sample on different days. WSOC for this sample was $540 \mu\text{M}$, close to the median value of $505 \mu\text{M}$ observed for this study.



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Figure 2: Average mass absorption coefficient measured at 365 nm (MAC₃₆₅) and pH 4 for cloud water samples (solid blue bars) and Suwannee River natural organic matter (hatched green bar).



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Figure 3: Normalized absorbance at 365 nm ($Abs_{365}(pH)/Abs_{365}(pH\ 1.5)$) versus pH for all cloud water samples analyzed in this study. Lines of best fit (least squares linear regression) for each cloud water sample are shown as the thin dotted lines. Comparison to BrC sampled in ambient aerosols both influenced and uninfluenced by biomass burning are shown with the solid green and red lines, respectively, both from Phillips et al. (2017). Mean behaviour of Suwannee River NOM shown with the thick dashed black line.

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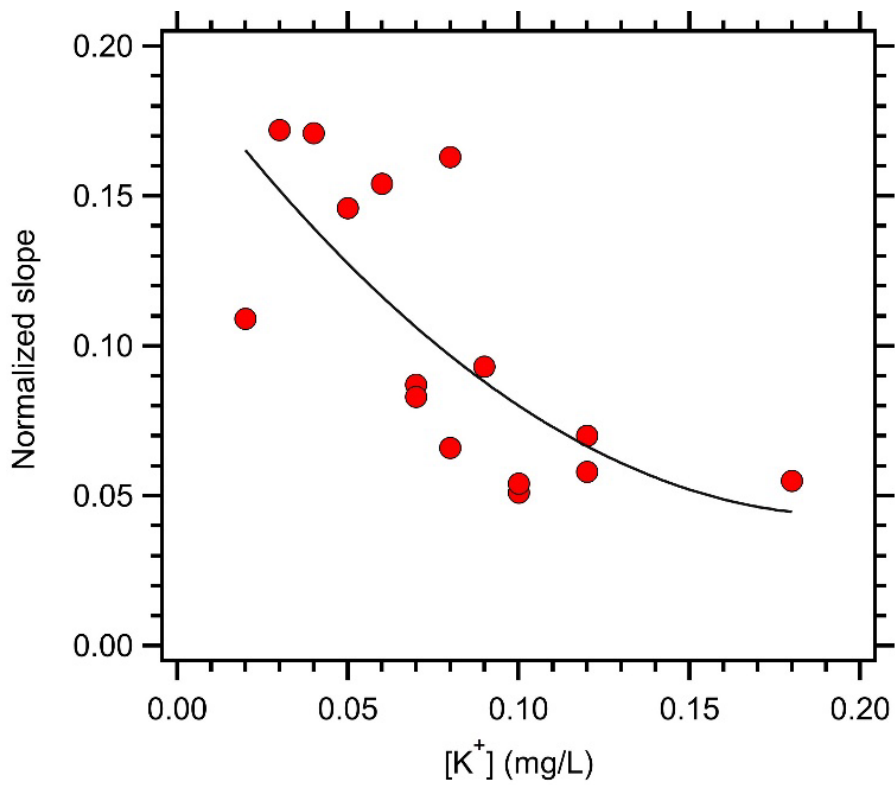


Figure 4: Relationship between the normalized slope of Abs₃₆₅ vs. pH (from Table 2) and the cloud water K⁺ concentration.

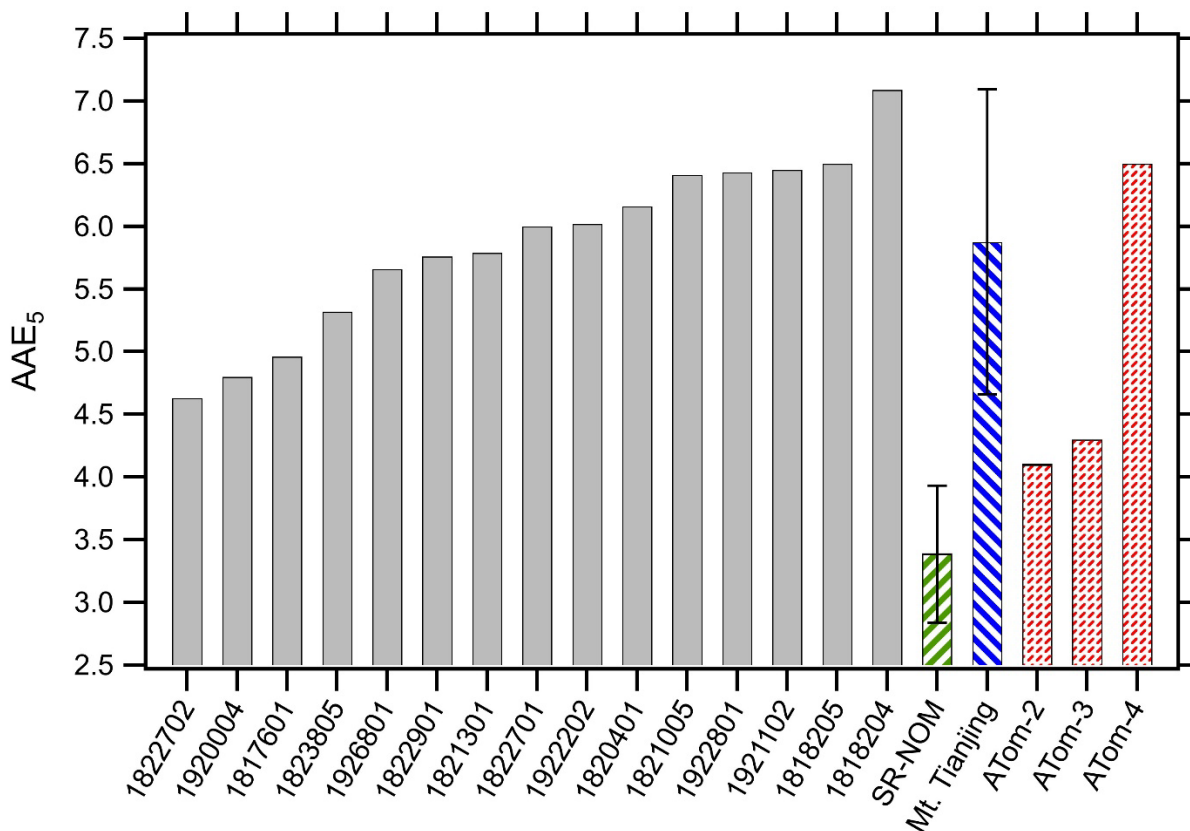


Figure 5: Distribution of absorption Ångström exponent values at pH 5 (AAE₅) for cloud water samples (solid bars), Suwannee River Natural Organic Matter (green hatched bar), cloud water samples from Mt. Tianjing, China (blue hatched bar, mean value $\pm 1\sigma$ reported from Guo et al., 2022 for WSOC), and mean values from the ATom aircraft missions (red patterned bars, from Zeng et al., GRL, 2020). Note, the pH corresponding to the AAE values from Mt. Tianjing and ATom missions were not specified.

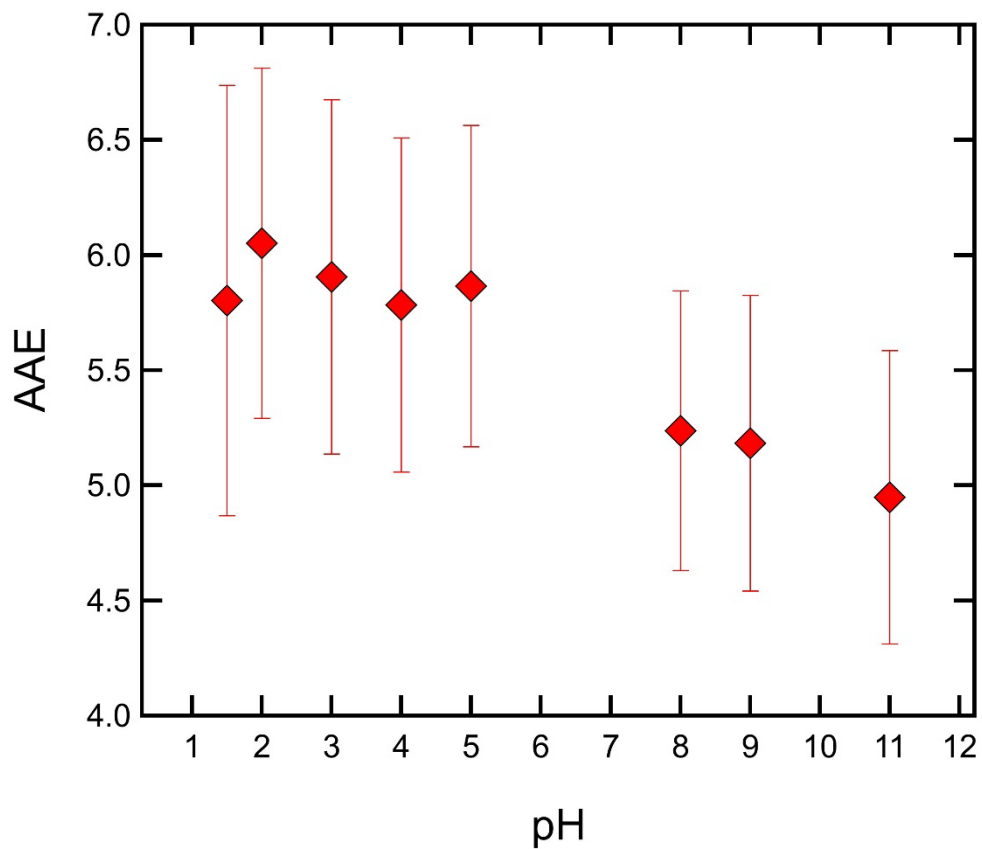


Figure 6: Mean absorption Ångström exponent value for all cloud water samples as a function of pH. Error bars represent $\pm 1\sigma$.

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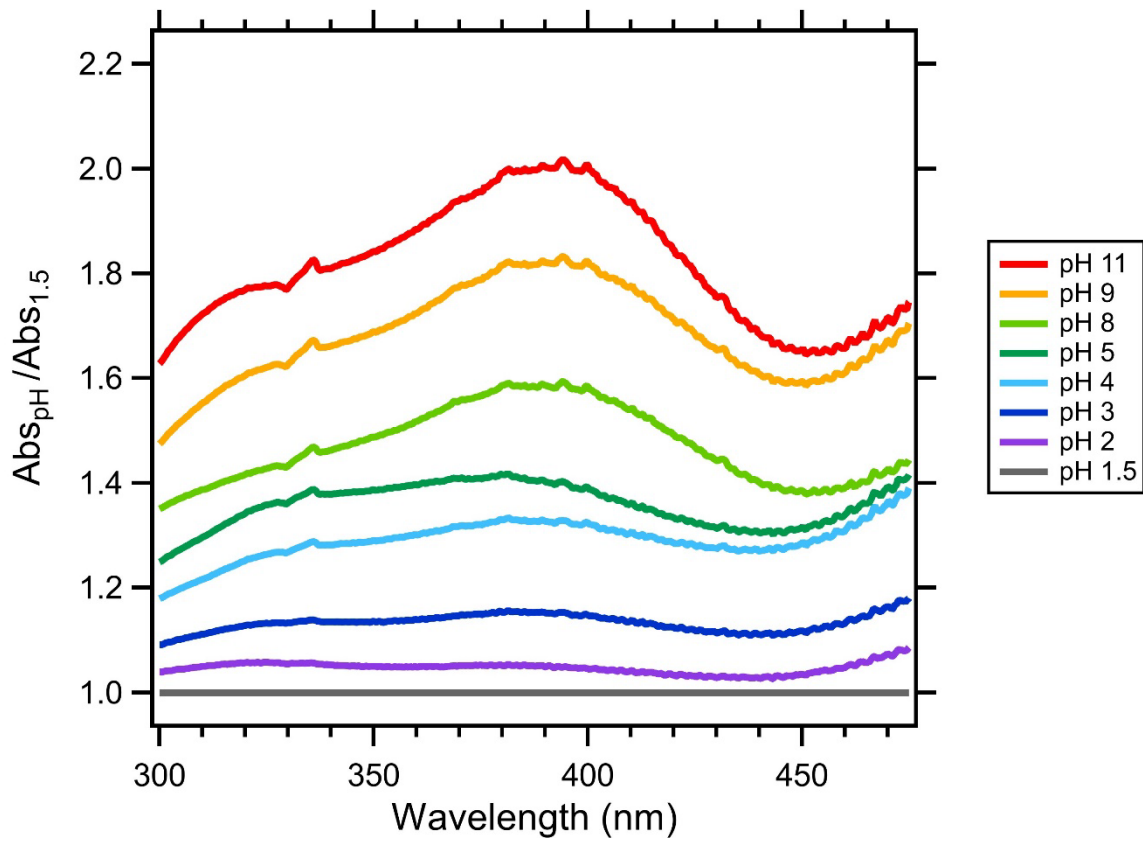
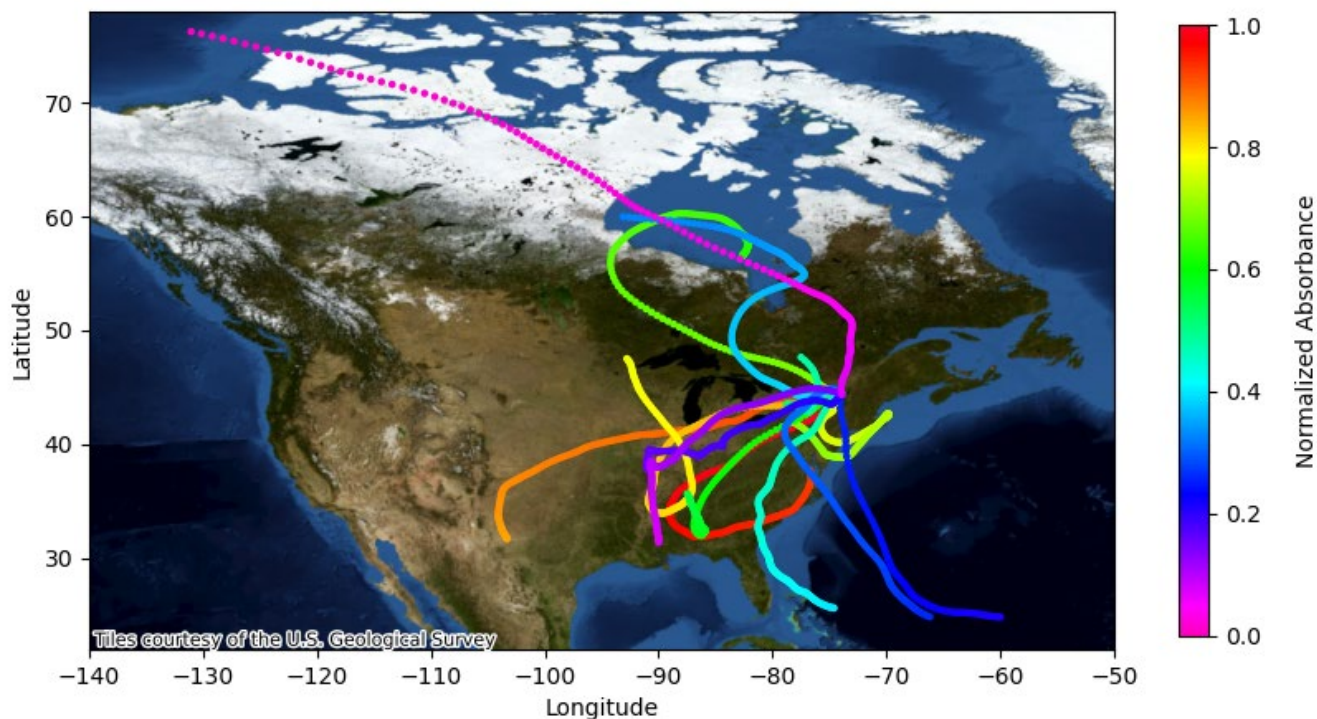


Figure 7: Mean absorption at a given pH relative to the absorption at pH 1.5 as a function of wavelength
 480 for all cloud water samples.



485 **Figure 8:** Map showing 6-day back trajectories for cloud water samples. Trajectories are coloured according to the relative BrC absorption at 365 nm (Abs_{365}) based upon the slopes (Table 2 and Fig. 3) and aerosol pH modelled along the back trajectory by ISORROPIA-II. The thermodynamic calculations assume constant aerosol composition along the back trajectory and only account for differences in pH based on T and RH.

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