Investigation of Black Carbon Wet Deposition to the United States from National Atmospheric Deposition Network Samples

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ABSTRACT

Black carbon (BC) aerosols from burning biomass, fossil fuels, and waste are transported over large distances in the Earth's atmosphere, absorbing sunlight, altering climate, and impacting air quality. These aerosols are relatively short-lived in the troposphere and are returned to the surface by wet and dry deposition processes. Although wet deposition is considered the primary mechanism for removing BC from the atmosphere, published data is exceptionally scarce. In this study, we investigated the feasibility of determining BC wet deposition on a national/international scale using samples from the US National Atmospheric Deposition Program (NADP). The study investigated BC concentrations in precipitation by single-particle laser-induced incandescence (SP2). From October 26th to December 1st, 2020, we analyzed 478 NADP wet deposition samples from 209 locations, including sites in the United States, Canada and US territories, Puerto Rico, and the US Virgin Islands. Wet deposition BC concentrations varied from less than 0.3 µg L⁻¹ to 38.7 µg L⁻¹ with a median of 3.50 µg L⁻¹. Associated BC wet deposition fluxes ranged from near zero to 9.1 g ha⁻¹ wk⁻¹, with a median of 0.87 g ha⁻¹ wk⁻¹. An analysis of the spatial variability indicated a pattern of higher BC deposition through the central United States consistent with BC transport from biomass burning during the sampling period.

Keywords: Black carbon, Wet deposition, National Atmospheric Deposition Program, Precipitation chemistry

1 INTRODUCTION

Black carbon aerosols (BC) are a by-product of the incomplete combustion of biomass, fossil fuels, and other carbon-based materials and are the primary light-absorbing particles in the atmosphere (Bond et al., 2013; Tiwari et al., 2016). These aerosols have a significant impact on the Earth’s radiation budget and climate (Ramanathan and Carmichael, 2008; Takemura and Uchida, 2011; Bond et al., 2013; Lee et al., 2013; Fierce et al., 2015) and are a significant component of PM₂.₅ air pollution affecting human health (Janssen et al., 2011). BC has a mean atmospheric residence time that is relatively short, typically ranging from a few days to a few weeks (Lee et al., 2013). This residence time is too short for BC to become well-mixed in the atmosphere resulting in spatiotemporal fluctuations due to source emissions, atmospheric circulation, and dry and wet deposition processes (Zhang et al., 2015b; Kanaya et al., 2016; Chiloane et al., 2017; Zhang et al., 2019).

Ground and airborne-based BC studies, satellite aerosol observations, and chemical transport modeling studies suggest that wet deposition is the primary sink for BC aerosols, accounting for
~80% of the total deposition to the Earth’s surface (Liu and Matsui, 2021; Mori et al., 2021; Barret et al., 2019; Wu et al., 2018; Schwarz et al., 2006). However, modeled estimates of BC concentrations are highly uncertain, with order of magnitude differences between simulated estimates and observations, particularly over remote regions (Eckhardt et al., 2023; Liu and Matsui, 2021; Schill et al., 2020). The parameterization of BC wet deposition processes and BC aging in the atmosphere are considered key sources of uncertainty in modeled BC estimates (Liu and Matsui, 2021; Wang et al., 2018b). BC aging processes include the build-up of surface coatings on BC aerosols, mixing with other aerosols (internal and external), the formation of oxygen-containing functional groups by partial oxidation of the BC surface and structural changes (Liu et al., 2020; Riemer et al., 2010; Rojas et al., 2015; Wang et al., 2018a). The transformation of initially hydrophobic BC particles to hydrophilic BC is a key feature of these processes (Liu et al., 2013; Liu et al., 2020; Sadiq et al., 2015; Zhang et al., 2015a; Choi et al., 2020), which in turn affects BC’s interaction with water, its removal by wet deposition and atmospheric residence time (Kanaya et al., 2016; Yang et al., 2019).

Few studies have quantified BC in wet deposition despite its importance to BC’s atmospheric residence time and spatial variability. The lack of BC wet deposition data is likely due to the analytical challenges of quantifying BC in water (Torres et al., 2014). A recent literature review of BC in wet deposition (Barrett et al., 2019) found sporadic data for only 42 unique sites globally and only three in the United States (US). Of the sites in the US, there is only one site (Hadley et al., 2010) with data within the past thirty-six years and little data for the past ten years (Torres et al., 2014). Published data from Arctic ice cores (McConnell et al., 2007; McConnell and Edwards, 2008; Zdanowicz et al., 2018) show the human impact of fossil fuel combustion on BC deposition in the remote northern hemisphere and its spatial variability. These historical records show a decreasing trend in BC after the 1950s, which may be associated with air quality legislation in the US and Europe and possibly decadal changes in atmospheric transport (Mao et al., 2016; Zdanowicz et al., 2018; Kang et al., 2020). However, recent extreme wildfire seasons in North America (Jaffe et al., 2020) and Siberia and observational and modeling studies of fire weather suggest that wildfire BC emissions will likely increase in the future (Jains et al., 2022; Ohata et al., 2021; Viera et al., 2016).

To address the exceptional gap in BC wet deposition data, we investigated whether the US National Atmospheric Deposition Program (NADP) National Trend Network (NTN) could be used to monitor BC in wet deposition. The NADP has been operating since 1978 and has a large spatial network of sites spanning the United States (including the US territories of Puerto Rico and the US Virgin Islands) with additional sites in Canada. As part of the study, we investigated the feasibility of analyzing NTN samples for BC by two different methods (single-particle laser-induced incandescence and thermal-optical analysis), including a study of BC contamination and losses from NTN sampling equipment and collection variability from collocated automated wet deposition samplers. From October 26th to December 1st, 2020, 478 wet deposition samples from 209 NTN sites were analyzed to investigate spatial variability using NADP modeling methods.

2 METHODS

2.1 Wet Deposition Samples

Wet deposition samples used to investigate spatial variability and BC analysis procedures were collected from NADP NTN network sites from October 26th to December 1st, 2020. These samples were analyzed primarily by single-particle intracavity laser-induced incandescence (SP2), determining refractory BC (rBC) particles. This form of BC is the carbon mass determined by laser-induced incandescence with a vaporization/boiling temperature of ~4000 K (Lack et al., 2014). A subset of the NTN samples (79) with volumes greater than 400 mL were analyzed for elemental carbon (EC) by the thermal-optical analysis (TOA) of quartz filter sub-samples. TOA EC is defined as BC, which oxidizes at temperatures > 340°C (Lack et al., 2014). These two methods have several differences. For example, the SP2 method determines the carbon mass of single particles in a defined mass range (0.3 fg–80 fg) and does not require the capture of particles by filtration. The TOA method requires the capture of particles on a filter but may determine heavier EC masses (as part of the bulk analysis) than the SP2 rBC analysis. The method intercomparison focused on
determining the feasibility of implementing the analyses at a monitoring network scale, determining if detection limits were sufficient, and investigating differences due to large EC particle capture on the filters.

Samples used to investigate losses to NADP sampling equipment and variability between automatic wet deposition samplers were collected in August and September 2021 (S2) from Madison, Wisconsin, USA, and analyzed by SP2.

2.1.1 NADP NTN wet deposition samples for method development and spatial variability study

Fig. 1 shows the locations of two hundred and two NADP National Trend Network (NTN) site locations (for locations, see Table S1) used to collect weekly wet deposition samples from October 26th to December 1st, 2020. A total of 478 samples were collected from the sites on a weekly basis in clean high-density polyethylene (HDPE) plastic buckets (29-cm diameter) by automated wet deposition samplers, including N-CON ADS and ACM Model 301 atmospheric deposition samplers (N-CON Systems Co. Inc., GA, USA; Aerochem Metrics, Inc.) following NADP standard operational procedures (SOPs, https://nadp.slh.wisc.edu/networks/national-trends-network/). When wet deposition was present, NADP staff weighed the HDPE buckets and transferred the contents to 1-L Nalgene low-density polyethylene (LDPE) wide-mouth bottles and sealed them in polyethylene bags prior to shipping them to the NADP at the Wisconsin State Laboratory of Hygiene (WSLH), University of Wisconsin-Madison (UW-Madison). The NADP NTN network classifies wet deposition samples as quality A, B, and C. Only samples with quality ranking A or B (see Supplemental S1, Table S2) were used in the study. The NTN samples were comprised of 449 samples from US sites (199 sites), 23 samples from Canadian sites (8 sites), and 6 samples from sites in the US territories (4 from Puerto Rico and two from the US Virgin Islands). The NADP characterizes sites as Isolated (I), Rural (R), Suburban (S), Urban (U), and others (see Fig. S1). Most of the samples studied (∼82%) were from isolated and rural sites. The elevation of the sites included 20 sites at ≥ 2400 m (AMSL) and 189 sites areas below 1000 m.

Fig. 1. Locations of NTN sampling sites included in 2020 study. Site coordinates and elevations are given in supplemental materials Table S1.
2.1.2 Wet deposition samples for investigating automatic sampler variability and losses to sampling equipment

The study collected a total of 13 wet deposition samples in Madison, WI, in August and September 2021 to examine the recovery of BC from NADP wet deposition buckets and 1-L Nalgene shipping bottles and to assess the variability between co-located automated wet deposition samplers. Eleven samples were collected from an NADP site (Eagle Heights test site, see Supplemental S2) in Madison, WI, using three collocated automated samplers, which included two NCON NTN wet deposition samplers and one ACM NTN wet deposition sampler. The two NCON IDs were NCON2 and NCONS, and the ACM sampler ID was KJ1. Of these samples, five were single-event samples collected within 24 hours of a wet deposition event. The event samples were used to investigate losses of rBC to the sampler buckets and shipping bottles over one week. The remaining 12 Eagle Heights samples were collected from the site weekly to investigate variability in rBC collected by different automatic samplers using NADP NTN procedures. In addition to the Eagle Heights samples, we manually collected one sample (single event sample) using an NADP wet deposition bucket at a non-NADP site in Madison, WI (Supplemental S2). In this case, an NADP bucket was fixed to a pole, and the bucket lid was removed by hand at the beginning of a precipitation event.

2.2 Cleaning Procedures

2.2.1 Wet deposition buckets and shipment bottles

NADP NTN wet deposition buckets and 1-L wide-mouth Nalgene bottles used to collect and transport wet deposition samples were precleaned following NADP NTN cleaning procedures at the WSLH NADP laboratory at UW-Madison. Briefly, the cleaning procedure included rinsing with ultrapure water (RO, > 18 MΩ), overnight soaking in 1% Citrajet® (Alconox Inc., for new buckets + lids only), rinsing with RO, cleaning with 3% hydrogen peroxide solution (10 minute sit time), and cleaning in a RO supplied industrial dishwasher (no chemicals, total time = 20 minutes, 2 × 4-minute rinse cycles at room temperature and 2 × 6-minute rinse cycles at 50°C). After the dishwasher step, the containers were rinsed with RO, placed inside a clean air bench (HEPA), and allowed to dry before being sealed in clean LDPE bags.

2.2.2 Cleaning of labware and Quartz fiber filters

Glassware used for the BC SP2 and TOA analysis was cleaned by: 1. Rinsing with RO followed by scrubbing and soaking in a 1% solution of Citranox® (Alconox Inc.) and RO water for 30 minutes; 2. Baking in a furnace at 450°C for 8 hours (covered with aluminum foil); and 3. Rinsing with RO water, followed by acetone (AR grade), in a fume hood before use. Two 25-mm all-glass vacuum filtration systems were used to prepare samples for EC analysis. The filter systems were prepared using the method described above daily, but during the day, they were cleaned in between samples by rinsing them multiple times with RO water followed by acetone. Quartz fiber filters (QF, 25 mm, Pallflex®, Pall Corporation, USA) used for TOA were prepared by covering the filters with aluminum foil and baking them in a furnace at 550°C for 15 hours.

2.3 Sample Preparation

On arrival at WSLH, NADP NTN network samples were shaken and sub-sampled for NADP analytes by decanting from the 1-L Nalgene bottles. The remainder of the 1-L Nalgene bottle sample was sonicated for 10 minutes in an ultrasonic bath before SP2 analysis. Samples containing more than 500 mL were filtered for TOA EC after SP2 analysis (See schematic in Fig. 2). TOA filtration consisted of pouring 400 mL of sample from the 1-L Nalgene bottle into a 25-mm quartz filter all-glass vacuum filtration assembly. The system included a 300 mL funnel and a sinter glass support with a filtration area of 2.1 cm². After filtration, the filters were carefully removed from the apparatus using clean stainless-steel tweezers (cleaned with acetone) and placed in a clean aluminum foil-lined petri dish. The filters in the Petri dishes were dried overnight in a large glass desiccator before being sealed with Teflon tape and stored in a freezer. Prior to analysis, a 1-cm² sub-sample was removed from the filter with a clean stainless-steel punch and transferred to the TOA instrument for analysis. The 400 mL sample volume used for the TOA analysis was based on sample volume availability and the TOA EC detection limit (~0.2 micrograms C, µg). Assuming a
100% EC capture by a filter (25 mm diameter), and a 1-cm² TOA filter subsample, the TOA EC detection limit translates to a concentration of ~1.1 µg L⁻¹ EC. The TOA preparation method did not use a coagulant to increase EC filter capture (Torres et al., 2014) since this would have precluded investigating whether large EC particles (which exceed the SP2 mass range) were present. We did not attempt to stack filters (Hadley et al., 2010) to investigate the penetration of EC particles through the filter as we determined this would not be feasible for larger sample numbers.

The Madison, WI, samples from 2021 included rBC recovery and collocated wet deposition samples. Recovery samples were collected within 24 hours of a wet deposition event and analyzed by SP2 directly from the buckets or poured into 1-L Nalgene bottles and analyzed from the bottle. These samples were collected following NTN standard procedures, with the exception that NADP staff did not decant other aliquots from the 1-L Nalgene bottles prior to SP2 analysis. EC analyses were not performed on these samples.

2.4 Analysis of BC by Liquid to Aerosol SP2 (SP2) and EC by TOA

2.4.1 SP2 aqueous rBC analysis

All samples were analyzed at the University of Wisconsin Madison Water Science and Engineering Laboratory (WSEL) for refractory black carbon (rBC) using a single-particle soot photometer (SP2, Droplet Measurement Technologies, Boulder, Colorado). The SP2 estimates the rBC mass (as carbon) of individual aerosol particles (masses ranging from 0.3 to 80 fg) based on the peak amplitude of incandescent light (and estimated temperature) emitted from particles passing through an intracavity Nd: YAG laser at 1064 nm (Stephens et al., 2003; Schwarz et al., 2006; Moteki and Kondo, 2007, 2010; Moteki, 2023). While typically employed for atmospheric rBC analysis, other studies have combined this method with desolvating nebulizers to quantify rBC in liquid samples (McConnell et al., 2007; Zdanowicz et al., 2018; Sterle et al., 2013; Bisiaux et al., 2011; Mori et al., 2021). For the wet deposition analysis, a custom-built desolvating spray chamber (see Supplemental S3) fitted with a pneumatic nebulizer (Glass Expansion, Seaspray U series nebulizer - 0.4 mL min⁻¹, ARG07US504) was used to aerosolize and separate rBC particles from water samples before introduction to the SP2. Standards comprised of fullerene soot (S3) dispersed in a solution of RO water and ammonia hydroxide (NH₄OH, 20 µM) were used to quantify rBC concentrations by external calibration. The SP2 method had a detection limit (DL, 3 σ) of ~0.03 µg L⁻¹ and a linear response from 0.03 µg L⁻¹ to ~70 µg L⁻¹. Samples were introduced to the SP2 desolvation system using Teflon PFA capillary tubing pumped using a peristaltic pump at ~0.4 mL min⁻¹. Full details of the SP2 analysis are given in S3.
2.4.2 Analysis of wet deposition EC by TOA

TOA analysis of EC was performed on 79 NADP NTN samples at Wisconsin State Laboratory of Hygiene (WSHL) using a Sunset Lab Laboratory Organic Carbon Elemental Carbon Analyzer (Sunset Laboratories Inc., Tigard, OR, USA) following the National Institute for Occupational Safety and Health (NIOSH) 5040 method (Birch, 2002). Briefly, the method determines organic carbon (OC) and EC on quartz filters by exposing a 1-cm² filter subsample to a thermal ramp in an inert atmosphere (helium, He) followed by a thermal ramp in an oxidizing atmosphere (He, oxygen mixture, He/O2). In the ideal case, OC species are emitted during the He stage and detected by a flame ionization detector (FID). During the He/O2 stage, EC is combusted and determined by FID after converting EC carbon dioxide (CO2) to methane (CH4). However, some OC typically pyrolyzes during the inert He stage and forms EC on the filter. Pyrolysis EC is subtracted from the total EC using a laser-based optical system to monitor the filter samples (filter) optical properties (transmittance or reflectance). The EC on the filter before pyrolysis is determined as the EC quantified after the filter’s optical properties return to the pre-pyrolysis state (split point). The EC detection limit for the method is estimated at ~0.2 µg EC cm⁻² of filter (Sunset Laboratories Inc.).

2.5 Contamination/Loss of rBC from NADP Sampling Containers

We conducted a series of leaching and recovery (see Supplemental S4 and S5) experiments to examine rBC contamination from NADP containers and the loss of rBC to these containers. For the leaching experiments, we filled seven NADP buckets to a depth of 1.5 inches and seven 1-L Nalgene bottles to 500 mL with RO water, based on average precipitation volumes collected in both containers. We directly measured rBC concentrations on the first day (t = 0) and then again after a week (t = 7 days). We chose a seven-day interval assuming that NADP buckets would be deployed on samplers for one week and shipment to WSLH could take up to a week.

To investigate rBC recovery from NADP NTN containers, we collected wet deposition buckets (or Nalgene bottles filled from them) within 24 hours following a wet deposition event. These samples were analyzed directly from the respective containers by SP2. The study comprised five bucket samples and eight bottle samples. We obtained three bucket samples from the NADP Eagle Heights site automatic wet deposition samplers and manually collected two in Madison, WI, by mounting the buckets on a large 5 ft PVC pole and removing the bucket lids by hand during rain events. We re-analyzed these samples after seven days to simulate NADP collection and shipping procedures. The rBC recovery was calculated as the percentage difference between the initial and seven-day rBC concentrations.

2.6 Estimation of BC Wet Deposition

Weekly and monthly rBC deposition was estimated from rBC concentrations and precipitation amounts. Precipitation amounts were from rain gauges or bucket precipitation volumes (mL) for samples with missing rain gauge data. Bucket precipitation volumes were converted to inches of precipitation by dividing the sample volume by a factor of 1724.406 (the NADP bucket surface area of 678.9 cm² multiplied by 2.54 cm per inch). Weekly rBC wet deposition in grams per hectare per week was calculated by Eq. (1).

\[
rBC_{\text{wet dep.}} \, (\text{g ha}^{-1} \text{wk}^{-1}) = rBC \, (\mu g \text{ L}^{-1}) \times \text{weekly precip (inches)} \times 0.254
\]  

(1)

Monthly rBC deposition as grams per hectare per month was calculated from the precipitation weighted mean (weighted mean hereafter) rBC concentration using Eq. (2) and Eq. (3).

\[
\bar{x}_w = \frac{\sum_{i=1}^{n} (x_i \times w_i)}{\sum_{i=1}^{n} w_i}
\]

(2)

\[
rBC_{\text{wet dep.}} \, (\text{g ha}^{-1} \text{mth}^{-1}) = rBC_{\bar{x}_w} \, (\mu g \text{ L}^{-1}) \times \text{monthly precip (inches)} \times 0.254
\]

(3)
2.7 Interpolation Maps for BC Wet Deposition Data

As part of the study, we applied the spatial interpolation models used by NADP to investigate the wet deposition of other chemical species (Latysh and Wetherbee, 2011). This method is used to account for topographic influences on precipitation which can lead to an underestimation of wet deposition in high-elevation areas. Using monthly weighted mean rBC concentrations from October 26th to December 1st, 2020, we interpolated (inverse distance weighted) the site-weighted mean concentrations to a spatial grid matching the Parameter-elevation Relationships on Independent Slopes Model (PRISM; Daly et al., 2015) dataset grid points. Wet deposition was calculated from interpolated weighted mean concentrations and the PRISM precipitation amounts following the methods described in Latysh and Wetherbee (2011) according to Eq. (4).

\[
\text{rBC}_{\text{wet dep.}} \text{ (g ha}^{-1} \text{ mth}^{-1}) = \text{rBC}_{\text{grid}} (\mu\text{g L}^{-1}) \times \text{monthly precip}_{\text{PRISM}} \text{ (cm)} \times 0.1
\]  

(4)

3 RESULTS AND DISCUSSION

3.1 Assessment of rBC Procedural Blanks, Loss to NADP Sampling Containers and Variability between Auto-wet Deposition Samplers

We conducted procedural blanks (RO water) and wet deposition recovery experiments (described in 2.5) for the NADP wet-dep buckets and shipping containers. All the procedural blanks (seven buckets and seven bottles) were found to be at or below the SP2 rBC method detection limits (~0.03 µg L^{-1}) and comparable to the RO water used to prepare the blanks. The recovery experiments determined rBC in buckets and bottles within 24 hours of a rain event and ~one week later. Recoveries of rBC from the NADP buckets and bottles are shown in Table 1. The bucket rBC recoveries ranged from 104 to 56 %, with four of the five buckets recoveries ≥ 84%. The bottle recoveries ranged from 118 to 82%, with a mean bottle recovery of 95%.

Figs. 3(a–c) and Table S6 shows data from the collocated wet deposition samplers. Relative standard deviations in precipitation mass ranged from 2 to 4%, while rBC concentrations and wet deposition fluxes ranged from ~2.5 to 11% and ~1 to 11%, respectively. Apart from one ACM sampler (ID = KJ1) sample from September 1st, 2021, the results show no discernible difference between the NCON and ACM samplers. From the study, we conclude that the rBC RSD resulting from variations in the automatic samplers and rBC analysis is at most ~11%.

3.2 Comparison of the Liquid to Aerosol SP2 BC Method with TOA EC Determination

Approximately ~80% of the published BC wet deposition data (Barrett et al., 2019) was determined

Table 1. Recovery of rBC from the NADP buckets and bottles.

<table>
<thead>
<tr>
<th>Start date</th>
<th>ID</th>
<th>Sampler</th>
<th>Initial concentration (µg L^{-1})</th>
<th>Final concentration (µg L^{-1})</th>
<th>Difference (µg L^{-1})</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/22/21</td>
<td>Bucket5</td>
<td>By hand</td>
<td>9.9</td>
<td>5.5</td>
<td>4.4</td>
<td>55.56</td>
</tr>
<tr>
<td>9/3/21</td>
<td>Bucket4</td>
<td>By hand</td>
<td>15.8</td>
<td>13.3</td>
<td>2.5</td>
<td>84</td>
</tr>
<tr>
<td>9/7/21</td>
<td>Bucket3</td>
<td>NCON2</td>
<td>90.5</td>
<td>49</td>
<td>41.5</td>
<td>95</td>
</tr>
<tr>
<td>9/7/21</td>
<td>Bucket1</td>
<td>NCON5</td>
<td>84.5</td>
<td>87.2</td>
<td>2.7</td>
<td>96</td>
</tr>
<tr>
<td>8/24/21</td>
<td>Bottle1</td>
<td>NCON5</td>
<td>4.9</td>
<td>4.9</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>8/24/21</td>
<td>Bottle3</td>
<td>KJJ1</td>
<td>5</td>
<td>5.9</td>
<td>0.9</td>
<td>118</td>
</tr>
<tr>
<td>8/24/21</td>
<td>Bottle2</td>
<td>NCON2</td>
<td>5.1</td>
<td>5.9</td>
<td>0.8</td>
<td>115.69</td>
</tr>
<tr>
<td>9/1/21</td>
<td>Bottle8</td>
<td>NCON2</td>
<td>13.4</td>
<td>11</td>
<td>2.4</td>
<td>82.09</td>
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<td>9/1/21</td>
<td>Bottle7</td>
<td>NCON5</td>
<td>14.6</td>
<td>12.6</td>
<td>2</td>
<td>86.3</td>
</tr>
<tr>
<td>9/1/21</td>
<td>Bottle6</td>
<td>KJJ1</td>
<td>16.6</td>
<td>14.6</td>
<td>2</td>
<td>87.95</td>
</tr>
<tr>
<td>9/5/21</td>
<td>Bottle4</td>
<td>KJJ1</td>
<td>20.9</td>
<td>17.3</td>
<td>3.6</td>
<td>82.78</td>
</tr>
<tr>
<td>9/5/21</td>
<td>Bottle5</td>
<td>NCON2</td>
<td>22.6</td>
<td>20.2</td>
<td>2.4</td>
<td>89.38</td>
</tr>
</tbody>
</table>
Fig. 3. Variability of three collocated automatic wet deposition samplers: (a) precipitation; (b) rBC concentration; and (c) rBC wet deposition flux.

using TOA. As part of the study, we conducted an inter-instrumental comparison between TOA EC and the SP2 rBC for 79 samples with water volumes (≥ 500 mL). Thirty-three (~42%) of the 79 samples were below or equal to the TOA EC detection limit (~1.1 µg L⁻¹) and excluded from the dataset. Fig. 4(a) shows density plots for rBC and EC in the remaining 46 samples. The EC and rBC concentration distributions were long-tailed with maximum EC and rBC concentrations of 44.1 and 44 µg L⁻¹, respectively. The SP2 rBC data had a median value of 3.5 µg L⁻¹ and a broader density peak compared to TOA EC, which had a lower median concentration of 2.1 µg L⁻¹. Fig. 4(b) shows a scatterplot of rBC versus EC concentrations. An ordinary least squares regression of rBC ~EC and estimates of Cook’s distance statistics (Cook, 1979; Aguinis et al., 2013) were used to identify extreme outliers (OT1 and OT2, Fig. 3(b)) before applying a robust linear regression. To investigate the relationship between rBC and EC, we applied robust linear regressions (Yohai et al., 1991, Cran R, robustbase :: lmrob) to the data with the outliers included and excluded. With the outliers
Fig. 4. Comparison of SP2 rBC and TOA EC. (a) Density plots for rBC and EC data. Dashed lines are median values. (b) Comparison of EC and rBC data. Ot1 and Ot2 are extreme outliers identified by Cooks distance. Robust linear regression lines are shown with the outliers included (dashed orange) and excluded (dashed blue). These regression lines are comparable. The dashed grey line represents a one-to-one relationship between rBC and EC.

included, the robust linear regression had a slope of 1.88 (P = 3.08e-09), an intercept of ~0.30, and an adjusted $r^2$ of 0.64 ($n = 46$). The data predominately show higher concentrations for SP2 rBC compared to TOA EC.

The TOA EC filtration method used a single filter to capture the EC, and the higher SP2 rBC concentrations likely result from an under-catch of EC by the filter. Torres et al. (2014) found low EC capture efficiencies (~10%) and reported large discrepancies in the literature for EC collection by quartz fiber filters. The study found that coagulant additives such as ammonium dihydrogen phosphate are required to increase filter capture by aggregating EC. The single filter used in the current study is likely missing a percentage of the wet deposition EC particles, like Torres et al. (2014). However, the filter may also catch larger EC particles, which the SP2 rBC method would only partially quantify, given its single-particle upper rBC mass limit of ~80 fg. Outlier OT2 from Fig. 4(b) had a much higher EC concentration than rBC and may be an example of large EC particles captured by the filter. Overall, the two measurements agreed within a factor of ~two, with the TOA-EC likely under-catch an unknown percentage of the total EC. The Torres et al. (2014) study suggests that adding a coagulant is necessary for the method to be quantitative, increasing the time and labor required for analysis. Furthermore, the large sample volumes (> 400 mL) required are currently out of reach for routine analysis by the NADP NTN monitoring network.

3.3 NADP rBC Wet Deposition Concentrations and Fluxes from October 26th to December 1st, 2020

We detected rBC in all but one NTN sample with a concentration below the detection limit of 0.03 µg L$^{-1}$. Excluding this sample, NTN rBC concentrations varied from 0.33 µg L$^{-1}$ to 38.7 µg L$^{-1}$ with a median of 3.58 µg L$^{-1}$, a mean of 5.57 µg L$^{-1}$ and an interquartile range from 1.73 µg L$^{-1}$ to 7.52 µg L$^{-1}$ (Fig. 5(b)). In comparison the highest rBC concentration found in the network was ~50% of the maximum rBC reported in Beijing wet deposition (78.9 µg L$^{-1}$) by Lei et al. (2023) using a similar analysis method. The mean weekly rBC concentrations were comparable to the mean EC wet deposition concentrations of 5.3 to 6.9 µg L$^{-1}$ reported by Hadley et al. (2010) for snowfall and rain in California, USA, using a stacked filter, TOA analysis method.
Weekly rBC wet deposition fluxes were estimated using Eq. (1) and ranged from 0.02 to 9.09 g rBC ha\(^{-1}\) wk\(^{-1}\). The median and mean fluxes were 0.88 and 1.33 g rBC ha\(^{-1}\) wk\(^{-1}\), with an interquartile range from 0.44 to 1.73 g rBC ha\(^{-1}\) wk\(^{-1}\) (Fig. 5(c)). Approximately monthly (October 26th–December 1st) precipitation weighted mean rBC concentrations were calculated (from the weekly rBC concentrations, Eq. (2)). The monthly rBC concentrations ranged from 0.1 to 35 µg L\(^{-1}\) with a median and mean of 3.6 µg L\(^{-1}\) and 5 µg L\(^{-1}\), respectively. The corresponding monthly rBC wet deposition fluxes (estimated using Eq. (3)) ranged from 0.02 g rBC ha\(^{-1}\) to 20 g rBC ha\(^{-1}\) with a median and mean of 2.3 and 3.0 g rBC ha\(^{-1}\), respectively.

### 3.4 NADP rBC Spatial Variability

To investigate the spatial variability of rBC in the contiguous US, we interpolated (inverse distance) the October 26th to December 1st weighted mean rBC concentrations to the PRISM precipitation grid and estimated gridded wet deposition fluxes using Eq. (4). We created isopleth maps of the gridded weighted mean rBC concentrations, rBC wet deposition, and PRISM precipitation totals (Figs. 6, 7, and 8). The rBC concentration map (Fig. 6) reveals a northeasterly band of relatively higher rBC concentrations (5–35 µg L\(^{-1}\)) from Arizona to Texas, extending into Northern Dakota, the Great Lakes, Ohio, and northern regions of Pennsylvania, New York, and Vermont. The highest weighted mean (interpolated) rBC concentrations were found near site NE99, south of North Platte, Nebraska (35 µg L\(^{-1}\)), and at site NM07 near the Bandelier Monument in New Mexico (27 µg L\(^{-1}\)). The rBC data for these sites were from single events with relatively low precipitation amounts. The sharp concentration contours around NE99 and NM07 (Fig. 6) are likely due to the surrounding sites having averaged values from multiple events. For example, a relatively high rBC concentration (20 µg L\(^{-1}\)) was found at a second Nebraska site (NE15) for the same week as the NE99 and NM07 samples. However, the monthly weighted mean for this site is 6 µg L\(^{-1}\). Longer time intervals (seasonal to annual) are required to create concentration maps with robust statistics and interpretable spatial variability. This limitation does not apply to the interpolated rBC wet deposition, as the data represents a summation of wet deposition over the sampling period.

A map of the interpolated rBC wet deposition is shown in Fig. 7 and the PRISM precipitation data used to estimate the wet deposition in Fig. 8. The map features a band of relatively high rBC deposition (> 7 g ha\(^{-1}\)) that stretches northeasterly from Oklahoma to New York. The highest deposition rates occurred in northern Arkansas (site AR16, ~28 g ha\(^{-1}\)), Southeastern Missouri.
Fig. 6. Contiguous US monthly weighted (precipitation) mean rBC concentrations from NADP NTN sites, October 26th to December 1st, 2020. Mean NTN rBC concentrations were interpolated (inverse distance) to PRISM precipitation grid cells. Interpolated rBC concentrations in µg L⁻¹ are shown to the left of NTN site locations.

Fig. 7. Contiguous US monthly rBC wet deposition from October 26th to December 1st 2020. rBC deposition amounts were calculated from interpolated monthly rBC weighted mean (precipitation) concentrations and PRISM precipitation data. rBC wet deposition amounts in g ha⁻¹ are shown adjacent to NADP NTN sites.
Fig. 8. PRISM gridded precipitation totals from October 26th to December 1st 2020. The precipitation data was used to convert monthly precipitation weighted mean rBC concentrations to rBC wet deposition. The mapped precipitation is shown using a semi-log scale. PRISM Climate Group, Oregon State University, https://prism.oregonstate.edu, data created 19th May 2021, accessed 1 October 2022.

(site MO05, ~29 g ha⁻¹), and New York adjacent to Lake Erie and Lake Ontario (site NY10 and NY99, 30 g ha⁻¹ and 19 g ha⁻¹, respectively). Additionally, we found localized regions of higher rBC deposition at sites in northern New Mexico, southern Colorado, and Washington. The prominent band of rBC wet deposition shown over northern Arkansas and Southern Missouri (sites AR16 and MO05) is associated with widespread biomass burning emissions (Fig. S6) from Arkansas, Mississippi, Louisiana, Alabama, and Georgia from November 17th to November 22nd (as determined by NASA Merra-2 BC biomass burning emission rate estimates; GMAO, 2015) and precipitation on November 22nd. Hysplit (Stein et al., 2015; Rolph et al., 2017) back trajectories (from November 22nd) for sites MO05 and AR16 show air parcels (Fig. S7) from Alabama, Mississippi and Louisiana traveling west over the Gulf of Mexico and northeast through Texas to the sites. Fire-emitted carbon monoxide (CO) and surface PM2.5 aerosols forecasts from November 18th to November 21st (NCAR WRF-CHEM) show comparable transport features to the Hysplit trajectories suggesting transport of biomass burning emissions. Regions of higher rBC wet deposition to sites in Washington, New Mexico, and Colorado show a similar association with biomass burning emissions, atmospheric transport, and precipitation. Anthropogenic rBC emissions from non-biomass sources may also have been present in the wet deposition (Fig. S6). However, these sources are expected to remain relatively constant during the sampling period and would be highest adjacent to large cities. During November 2020, wildfires in the contiguous US burned a record 994,338 acres, approximately four times the burned area average from 2000 to 2020 (NCEI, 2020). While these wildfires likely contributed to the observed spatial deposition pattern, prescribed burning in the south-central and south-eastern states may have also contributed significant amounts of BC (Jaffe et al., 2020). The study was conducted after the typical June to October wildfire season, associated with the Western USA, Great Plains, Rocky Mountains, and Canada. A similar study conducted during these months may show higher BC wet deposition rates and different spatial variability.
4 CONCLUSIONS

BC emissions, atmospheric transport, and deposition profoundly impact climate, ecosystems, and human health. Understanding these impacts is becoming increasingly important as the Earth warms and wildfires increase in intensity and duration (Carnicer et al., 2022). Little BC wet deposition data exists to inform aerosol models, and to our knowledge, there are no data from a large-scale monitoring network. This study investigated the feasibility of monitoring rBC in wet deposition on a national scale using the US NADP national trends network. Based on this research, we conclude the following:

• Wet deposition rBC samples can be collected reliably by the NADP NTN network with reasonable recoveries and combined automated wet deposition sampling system and analysis RSDs of up to ~11%.
• NADP NTN network monitoring of BC should be as rBC analyzed by SP2 as the TOA EC analysis method requires too much sample volume, and significant uncertainties remain for EC filter capture efficiency.
• Wet deposition rBC concentrations and fluxes were determined at 209 sites 478 samples in the continental US, Canada and Puerto Rico, and the US Virgin Islands from October 26th to December 1st, 2020.
• The major spatial pattern of rBC wet deposition fluxes observed was consistent with biomass burning emissions (prescribed burning and wildfires) and atmospheric transport as represented in fire emission inventories and atmospheric back trajectories.
• Long-term monitoring studies of rBC in wet deposition are needed to improve modeling estimates of atmospheric transport and impacts on climate.

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SUPPLEMENTARY MATERIAL

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