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journal homepage: www.elsevier.com/locate/envpolTrends in bromide wet deposition concentrations in the contiguous United States, 2001–2016[☆]

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ABSTRACT

Bromide (Br^-) and other solute concentration data from wet deposition samples collected and analyzed by the National Atmospheric Deposition Program (NADP) from 2001 to 2016, were statistically analyzed for trends both geographically and temporally by precipitation type. Analysis was limited to NADP sites in the contiguous 48 United States. The Br^- concentrations for this time period had a high number of values censored at the detection limits with greater than 86 percent of sample concentrations below analytical detection. Bromide was more frequently detected at NADP sites in coastal regions. Analysis using specialized statistical techniques for censored data revealed that Br^- concentrations varied by precipitation type with higher concentrations usually observed in liquid versus precipitation containing snow. Negative temporal trends in Br^- wet deposition concentrations were observed at a majority of NADP sites; approximately 25 percent of these trend values were statistically significant at less than 0.05 to 0.10 significance levels. Potential causes for the negative trends were explored, including annual and seasonal changes in precipitation depth, reduced emissions of methyl bromide (CH_3Br) from coastal wetlands, and declining industrial use of bromine compounds. The results indicate that Br^- in non-coastal wet-deposition comes mainly from long-range transport, not local sources. Correlations between Br^- , chloride, and nitrate concentrations also were evaluated.

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1. Introduction

Production and industrial use of brominated hydrocarbons such as methyl bromide (CH_3Br), halons, and other ozone-depleting substances have been greatly reduced or eliminated in countries party to the amended and adjusted Montreal Protocol, resulting in measured decreases of these compounds in ambient air (UNEP, 2006; Maione et al., 2013; Carpenter et al., 2014). Decreases in atmospheric CH_3Br concentration have returned the natural oceanic source: oceanic sink ratio to near parity (Carpenter et al., 2014). Coastal wetlands have also been shown to emit biogenically produced methyl halides, including CH_3Br and methyl chloride (CH_3Cl) (Rhew et al., 2000; Schaefer et al., 2007). Therefore, loss of coastal

wetlands, primarily due to inundation from sea level rise (Dahl, 2011; Cahoon and Guntenspergen, 2010; Kennish, 2001), could also cause decreasing CH_3Br emissions. In addition, emission of CH_3Br from biomass burning, both natural and human-caused, has been shown to increase in regions experiencing drought and/or undergoing agricultural expansion (Andreae et al., 1996; Mano and Meinrat, 1994). Because solute concentrations in wet deposition are proportional to pollutant concentrations in tropospheric ambient air (Record et al., 1982), wet deposited bromide (Br^-) was considered as a potential indicator of changing brominated halocarbon emissions from natural and industrial sources.

The National Atmospheric Deposition Program (NADP) has monitored the concentrations of wet deposition solutes in the U.S. since 1978 for assessment of air pollution controls and the effects of air pollution deposited to the landscape (NADP, 2015b). In 2009, the NADP added Br^- to its routine analytical schedules for its National Trends Network (NTN) and Atmospheric Integrated Research Monitoring Network (AIRMoN) (NADP, 2010), primarily because Br^-

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is a component of chemical emissions that are important reactants in catalyzed ozone (O_3) destruction (McCauley et al., 1999; Orlando, 2003; Singh and Kanakidou, 1993; Federal Register, 1993) and mercury (Hg) and nitrogen dioxide (NO_2) oxidation (Obrist et al., 2011; Roos-Barracough et al., 2002; Orlando, 2003). This current study inventoried the NTN and AIRMoN Br^- concentration data collected from 2009 to 2016, and augmented the inventory with data from archived NTN samples collected 2001–2009.

This study investigated the presence of trends in NADP Br^- concentration and determined whether the trends are consistent with decreases in brominated hydrocarbon emissions from both natural and industrial sources measured and implied by others (Singh and Kanakidou, 1993; Gan et al., 1998; Rhew et al., 2000; Maione et al., 2013; Carpenter et al., 2014). The NADP Br^- concentration data were statistically evaluated for seasonal characteristics, including differences between solid and liquid precipitation types. The data were also evaluated for temporal trends, correlation with other wet-deposition analytes, sources of natural and anthropogenic CH_3Br emissions, and regional variation with respect to trends in precipitation depth and intensity.

2. Materials

Since 2009, the NTN has included approximately 250 sites in the contiguous U.S., which is the focus of this study. Sites in Alaska, Puerto Rico, U.S. Virgin Islands, and Argentina are not included in this study. Weekly composite NADP/NTN “wet-only deposition” samples were collected with Aerochem Metrics model 301 and N-CON model ADS 00–120 collectors¹ (NADP, 2015a). The NTN samples were removed from the collectors every Tuesday morning and decanted from plastic collector buckets into 1-L volume Nalgene bottles (NADP, 2015a). The AIRMoN samples were collected in the same way, but the buckets were lined with clean-room grade plastic bags beginning in October 2014. Important differences with AIRMoN sampling include refrigeration after collection, daily sample removal when precipitation occurs, and analysis without prior filtration. NTN samples are filtered (0.45- μm polyethersulfone). All NADP NTN and AIRMoN samples are shipped to the NADP Central Analytical Laboratory (CAL) in Champaign, Illinois, where they are analyzed for: calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-), Br^- , nitrate (NO_3^-), sulfate (SO_4^{2-}), orthophosphate (PO_4^{3-}), pH, and specific conductance. Given sufficient volume, split samples are stored in a refrigerated archive for at least 5 years for additional uses and analyses by request. Collector buckets and sample bottles are reused after being washed in laboratory washers using only deionized water. Sampling supplies are tested for cleanliness with respect to NADP analytes and bagged in cleanroom-grade plastic bags prior to field deployment (Gartman, 2016).

Archived NTN samples collected during the March–September growing seasons of 2001–2009, in states where CH_3Br was used for agricultural purposes, were analyzed to augment the data set for this study. The archived samples were analyzed to provide a longer record of Br^- deposition to investigate potential links between agricultural emissions of CH_3Br and Br^- in precipitation. No NADP sites were established specifically for this study. Data for existing sites, including both currently active and inactive, were used.

Data for this study are available from the NADP at <http://nadp.sws.uiuc.edu/data/NTN/> and <http://nadp.sws.uiuc.edu/data/MDN/>, but Br^- data are available by contacting the NADP Database Manager (<http://nadp.sws.uiuc.edu/NADP/contacts.aspx>). Unrounded

laboratory instrument values for sample analyte concentrations were obtained directly from the CAL database on August 10, 2016 because Br^- results were not available from the NADP web site (<http://nadp.isws.illinois.edu/NTN/>). Concentrations were multiplied by analytical dilution factors, and then values below the annually reported detection limits were qualified as censored. Data for event-based wet deposition samples collected at 7 AIRMoN sites were also obtained for the period July 2009–June 2016. The AIRMoN data were analyzed separately from the NTN data because AIRMoN samples are collected on a daily event basis whereas NTN samples are collected as weekly composite samples.

NADP data are quality assured by internal and external programs which are documented on the NADP web site: <http://nadp.sws.uiuc.edu/QA/> and <http://nadp.sws.uiuc.edu/lib/>. Analytical procedures for NTN and AIRMoN samples are available on the CAL web site: http://nadp.sws.uiuc.edu/cal/analytical_capabilities.html. Data obtained for this study were evaluated for completeness and consistency.

Only samples with sufficient volume for analysis (sample type “W”) and acceptable NADP quality rating codes of “A” and “B” were used. Sample results with missing Br^- values were not included. Samples with Br^- values of “0” (zero) indicate no Br^- was quantified by the analytical method, and these values were considered to be valid measurements below the analytical detection limits of 0.004–0.005 mg/L. In the final data set, zeros were expressed as censored values, and quantified Br^- values were censored by the applicable detection limit, which is calculated and reported annually by NADP. No substitutions were made for data values less than the detection limits for statistical analysis. The final data set consisted of 71,718 NTN samples and 1997 AIRMoN samples, with 86.5 percent and 91 percent of the Br^- concentration values reported less than the detection limits (censored), respectively. Censored data values are identified as such by statistical calculations using the NADA package in R-Project version 3.3.1 software (R Development Core Team, 2013, <https://cran.r-project.org/web/packages/NADA/NADA.pdf>) without substitution or elimination of any values.

To accompany the measurement of weekly wet-deposition concentrations, precipitation depth is continuously recorded by rain gages at all NADP wet-deposition monitoring sites. Precipitation-depth data are monitored and corrected by the NADP Program Office for variability and bias caused by infrequent false positive gage measurements. Every gage and its data are inspected weekly, and gages are independently tested and recalibrated when necessary and at least every 3 years. The continuous records are summed by day, season, and year, and the data are evaluated for completeness. Only records with less than 11 percent invalid or missing data (i.e. 90 percent complete) were used to estimate site-specific trends in annual and seasonal precipitation depth. Site-specific precipitation data were not adjusted for elevation, wind, or any climatic effects.

Site-specific, annual precipitation-weighted mean concentration (in mg/L) and total deposition (in kilograms per hectare, kg/ha) values were spatially interpolated by an inverse distance weighting method by the NADP (<http://nadp.sws.uiuc.edu/ntn/annualmapsByYear.aspx>, accessed June 29, 2017). Annual raster data for Cl^- were obtained from this source, accessed June 29, 2017, to estimate Br^- deposition as described below.

3. Methods

3.1. Non-detects

Evaluation of this dataset, which included a high percentage of samples with Br^- detected below the detection limit (greater than

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