

A Comparison of Two Collectors for Monitoring Precipitation Chemistry

Victoria R. Kelly · Kathleen C. Weathers ·
Gary M. Lovett · Gene E. Likens

Received: 15 February 2011 / Accepted: 3 August 2011
© Springer Science+Business Media B.V. 2011

Abstract Comparison of event-based precipitation collected during 1 year showed that samples from a Yankee Environmental Systems collector had significantly higher volume, higher concentrations, and higher deposition of all ions analyzed except PO_4^{3-} and NH_4^+ compared to samples collected simultaneously with an Aerochem Metrics collector.

Keywords Precipitation chemistry · Acid rain · Acid deposition · pH · Ammonium · Nitrate · Sulfate

1 Article

The efficiency of precipitation collectors can affect the concentrations and measured deposition of acidic and other components of rain and snow (Claassen and Halm 1995a, 1995b). For example, higher chemical concentrations have been measured in early stages of precipitation events and during light precipitation (Seymour and Stout 1983; Lim et al. 1991; Claassen and Halm 1995b; Radojevic and Lim 1995; Khare et al. 1996; Minoura and Iwasaka 1996, 1997; Tanner and Wong 1997; Pryor et al. 2007). Thus, automatic precipitation collectors that do not collect early stages

of a rain event, or light precipitation, can underestimate concentration and total deposition of important solutes. Several automated collectors are used at sampling locations throughout the USA. In this study, we compared the collection efficiency and chemistry of samples collected using an Aerochem Metrics (AM) sampler, which is used extensively throughout the National Atmospheric Deposition Program network and elsewhere in the USA, with the newer Yankee Environmental Systems (YES) sampler. The two collectors are similar in that they both have a moisture sensor that causes a motor to remove a cover from a collection bucket at the beginning of a precipitation event. The YES collector has a more sensitive wetness sensor and a faster motor, which are the two components that most affect collector efficiency. In addition, the YES collector differs from the AM collector in placement of the cover during precipitation events; the YES collector cover is below the bucket opening, whereas the AM collector cover is beside the bucket opening. Thus, the cover could be a source of splash contamination in AM samples, but not in YES samples.

Paired precipitation samples were collected using one AM and one YES sampler for 1 year between September 2008 and August 2009. The two collectors were located side-by-side about 3 m from each other in an open, flat field at the Cary Institute of Ecosystem Studies in southeastern New York, USA (N 41.78, W 073.74). With the exception of PVC bird

V. R. Kelly (✉) · K. C. Weathers · G. M. Lovett ·
G. E. Likens
Cary Institute of Ecosystem Studies,
PO Box AB, Millbrook, NY 12545, USA
e-mail: kellyv@caryinstitute.org

perches, there were no trees or structures within 25 m of the samplers. The bird perches were located about 3 m from the collectors. In total, 130 precipitation events were collected from each collector and 94 events were analyzed for this study; 36 events were eliminated from this comparison because of debris, bird feces, or other forms of visible contamination in the samples. The precipitation types included rain (71 events, 76% of the annual volume), snow (12 events, 6% of the volume), or mixed rain and snow (11 events, 19% of the volume). Samples were collected on an event basis; an event was defined as continuous precipitation that had not been interrupted by more than 6 h. Occasionally, events were combined into one sample because it was not possible to collect the sample before another event began. For this analysis, we refer to each event as a sample. At the end of each event, the samples were collected, weighed, transferred to clean, labeled sample bottles, and analyzed at the Cary Institute of Ecosystem Studies Analytical Laboratory for pH, SO_4^{2-} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Cl^- . A 60-ml aliquot of sample was preserved with two drops of chloroform and refrigerated (sensu Weathers et al. 1988). This aliquot was analyzed for NH_4^+ , NO_3^- , and PO_4^{3-} . The NH_4^+ and PO_4^{3-} concentrations were analyzed using an Alpkem Flow Solution III or Lachat QuikChem 8000 FIA, SO_4^{2-} , Cl^- , and NO_3^- were analyzed using a Dionex 500 DX Ion Chromatograph, K^+ and Na^+ were analyzed using a PerkinElmer AAnalyst 300 Atomic Absorption Spectrometer, and Ca^{2+} and Mg^{2+} were analyzed using a Leeman Labs Profile ICP. Precipitation volume was determined using a Geonor precipitation gauge model T-200B at a co-located US Climate Reference Network station. Total annual volume of precipitation measured for the samples that we compared was 105.5 cm. Collector volume was calculated by dividing the total mass of water collected by the opening area of the collection bucket. Collector efficiency was calculated by dividing the collector volume by the precipitation volume determined using the Geonor gauge. Nonparametric paired sample Wilcoxon signed-rank tests were computed using SAS for Windows, Version 9.2 to test for differences between the two collectors.

Overall, the YES sampler collected significantly more precipitation (102.3 cm, 97.0% of measured)

than the AM collector (101.9 cm, 96.6% of measured) and, with the exception of PO_4^{3-} and NH_4^+ the concentrations and deposition of inorganic ions were consistently and significantly higher in the YES samples than the AM samples (Table 1). There was no significant difference in PO_4^{3-} and NH_4^+ concentration and deposition between the two collectors. Using a YES sampler feature that allowed examination of the status of the sensor and cover during a precipitation event, comparison of beginning and ending times of several events between the Geonor rain gauge and the YES sensor and cover indicated that the YES collector was open during light precipitation both at the beginning and end of these events. This feature was not available on the AM collector. Concentrations of inorganic ions are often higher during the initial and light stages of precipitation events (Seymour and Stout 1983; Lim et al. 1991; Claassen and Halm 1995b; Radojevic and Lim 1995; Khare et al. 1996; Minoura and Iwasaka 1996; Pryor et al. 2007), which could explain the higher concentrations and volume in the YES samples. The difference between sulfate concentrations from the YES and the AM sampler was higher for low-volume events than high-volume events (Fig. 1), indicating that concentrations in YES samples were higher than AM samples during light precipitation.

The number of samples that contained insects, bird feces, or particles was higher for the YES collector. Nine YES samples had bird feces, while no AM samples did. Bird feces contamination was eliminated after we provided alternative perches for birds near the collectors. Twenty-one YES samples had insects in them, compared to six AM samples. Large particles such as leaves and other debris from nearby vegetation as well as pollen and dust are usually washed out of the air during the onset of precipitation. The more sensitive YES collector often contained organic debris that the AM collector did not. We eliminated all sample pairs from analysis for this comparison if they contained visible debris or other visible contamination. Thus, the difference in concentrations between the samplers in this comparison was not due to visible contamination. The sensitivity of the moisture sensor on the YES sampler is adjustable, which could reduce contamination of samples, but could also likely reduce the efficiency of collection of light rain. We

Table 1 Volume (centimeter), volume-weighted means (VWM) with ranges in parentheses (microequivalent per liter) and total deposition (microequivalent per hectare) of ions in precipitation collected using an Aerochem Metrics (AM) and a Yankee

Environmental Systems (YES) collector at the Cary Institute of Ecosystem Studies, Millbrook, NY during 1 year from September 2008 to August 2009

Collector	VWM ($\mu\text{eq/L}$)			Deposition ($\mu\text{eq/ha}$)		
	AM	YES	p value	AM	YES	p value
Ca^{2+}	2.12 (0.25–29.4)	2.48 (0.25–46.4)	<0.001	216	253	<0.001
Mg^{2+}	1.24 (0.41–14.8)	1.40 (0.41–18.1)	<0.001	127	143	<0.001
Na^+	2.89 (0.22–62.6)	3.57 (0.22–79.6)	<0.001	295	364	<0.001
K^+	0.27 (0.13–1.79)	0.36 (0.13–5.37)	<0.001	28	37	0.001
NH_4^+	7.41 (0.55–61.5)	7.61 (0.55–77.6)	0.06	757	779	0.17
H^+	23.36 (0.18–160.9)	24.45 (0.18–189.0)	<0.001	2,466	2,578	<0.001
NO_3^-	13.55 (1.94–80.0)	14.59 (2.10–93.5)	<0.001	1,385	1,494	<0.001
SO_4^{2-}	16.69 (3.33–87.2)	17.74 (3.33–110.4)	<0.001	1,674	1,780	<0.001
Cl^-	4.01 (0.28–69.7)	4.75 (0.28–82.6)	<0.001	409	484	<0.001
PO_4^{3-}	0.068 (0.032–0.290)	0.064 (0.032–0.284)	0.18	7.0	6.6	0.08
Volume collected	101.9 cm	102.3 cm	0.01			

P values are from a Wilcoxon, signed-rank test of paired samples ($n=94$ events)

cannot rule out the possibility that the differences in chemistry were due to contamination that was not visible or to dry deposition. However, examination of open and close cycles for the YES sampler for some of the events revealed that, although the sampler sometimes cycled open and closed during the beginning and end of events, it remained open during

steady precipitation and closed during dry periods, so dry deposition seems unlikely to be a major factor for samples collected with the YES sampler.

Neither collector was 100% efficient in collecting total precipitation compared to independent measures using a Geonor gauge. In fact, the difference between the collectors (0.4 cm of precipitation) was smaller than the difference between each collector and the independent measure. Nonetheless, the total deposition estimated using the YES collector was 5–8% higher than deposition estimated using the AM collector for the ions H^+ , NO_3^- , and SO_4^{2-} , but for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Cl^- , the difference ranged from 12% to 27%. While the differences in concentration and deposition were small for 1 year, consistent positive differences over a longer time period may represent important ecosystem inputs that are missed using an AM collector. On the other hand, the YES collectors are more subject to contamination by birds if some other effective mechanism of controlling them is not used (e.g., perches), and collect more debris, probably in the initial minutes of an event. The pro of the YES collector is improved efficiency, especially for light precipita-

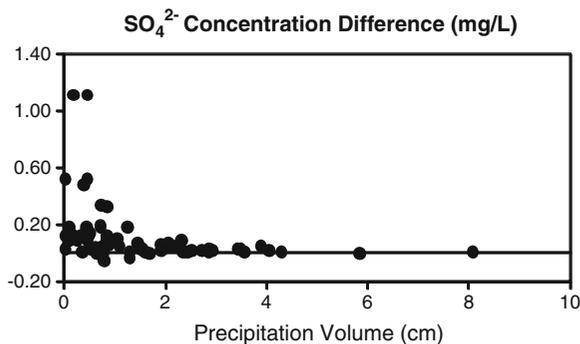


Fig. 1 Difference (YES sulfate concentration–AM sulfate concentration) between sulfate concentrations (milligrams per liter) in samples collected from the YES and samples collected from the AM sampler versus precipitation volume (centimeter) at the Cary Institute of Ecosystem Studies, Millbrook, NY, USA during 1 year from September 2008 to August 2009

tion. The con is a greater potential for contamination, which should be addressed in further development of this instrument.

Acknowledgments Funds for this study were provided solely by the Cary Institute of Ecosystem Studies; no funds were received from YES or any outside entity for this study. We thank the staff of the Rachel L. Carson, analytical facility at the Cary Institute of Ecosystem Studies for chemical analysis of samples, Donald Buso and Thomas Butler for comments on an earlier version of the manuscript. This is a contribution to the program of the Cary Institute of Ecosystem Studies.

References

- Claassen, H. C., & Halm, D. R. (1995a). A possible deficiency in estimates of wet deposition obtained from data generated by the NADP/NTN network. *Atmospheric Environment*, *29*, 437–448.
- Claassen, H. C., & Halm, D. R. (1995b). Performance-characteristics fo an automated wet deposition collector and possible effect on computed annual deposition. *Atmospheric Environment*, *29*, 1021–1026.
- Khare, P., Kapoor, S., Kulshrestha, U. C., Saxena, A., Kumar, N., Kumari, K. M., et al. (1996). Variation in ionic composition of precipitation collected by sequential sampling. *Environmental Technology*, *17*, 637–642.
- Lim, B., Jickells, T. D., & Davies, T. D. (1991). Sequential sampling of particles, major ions and total trace-metals in wet deposition. *Atmospheric Environment Part a-General Topics*, *25*, 745–762.
- Minoura, H., & Iwasaka, Y. (1996). Rapid change in nitrate and sulfate concentrations observed in early stage of precipitation and their deposition processes. *Journal of Atmospheric Chemistry*, *24*, 39–55.
- Minoura, H., & Iwasaka, Y. (1997). Ion concentration changes observed in drizzling rains. *Atmospheric Research*, *45*, 165–182.
- Pryor, S. C., Spaulding, A. M., & Rauwolf, H. (2007). Evolution of the concentration of inorganic ions during the initial stages of precipitation events. *Water, Air, and Soil Pollution*, *180*, 3–10.
- Radojevic, M., & Lim, L. H. (1995). Short-term variation in the concentration of selected ions within individual tropical rainstorms. *Water, Air, and Soil Pollution*, *85*, 2363–2368.
- Seymour, M. D., & Stout, T. (1983). Observations on the chemical-composition of rain using short sampling times during a single event. *Atmospheric Environment*, *17*, 1483–1487.
- Tanner, P. A., & Wong, A. Y. S. (1997). Atmospheric gases, particulates and rainfall concentrations during summer rain events. *International Journal of Environmental Analytical Chemistry*, *67*, 185–202.
- Weathers, K. C., Likens, G. E., Bormann, F. H., Bicknell, S. H., Bormann, B. T., Daube, B. C. Jr., et al. (1988). Cloudwater chemistry from ten sites in North America. *Environmental Science and Technology*, *22*, 1018–1026.