Precipitation chemistry at the Smithsonian Environmental Research Center, Maryland, USA 1981-2022

Methods Details

Precipitation sampling locations and sampling equipment

The locations and instrumentation for precipitation chemistry have changed over time. Both sampling locations are on the SERC main campus, within Watershed 101.

From 1973-2001, precipitation samples were collected from a weather station positioned 13 m off the ground at 38o 53’18’’ N, 76 o 33’ 17” S. Precipitation samples were collected in an Aerochem Metrics model 301 automated sampler which opened only during wet fall events. From 2002-present, precipitation samples have been collected from the top of the SERC meteorology tower, 40 m above the ground above the tree canopy (38o 53’ 20” N, 76 o 33’ 20” S). From 2002-2020, precipitation samples were collected for each event using the Aerochem Metrics automated sampler. From 2020 onwards, precipitation samples have been collected weekly (Tuesday ± 1 day) to match Mercury Deposition Sampling (MD00) frequency at this site.

From 1981-2020, samples were collected by event. After each event of more than 0.5 cm of precipitation, the samples were collected, and the samplers were cleaned. Events of less than 0.5 cm were generally combined with samples from subsequent events (Jordan et al., 1995). From 2020 onwards Aerochem samples were checked weekly and collected and processed if any volume is present.

Rain sample processing:

Aerochem samples were collected in a 2 mm industrial polyethylene bag, replaced each sampling with a clean bag. Once collected, the weight and volume of the sample were recorded in the lab.

A portion of the raw rainwater was used for conductivity, pH, and acidity measurements. Conductivity was measured using a YSI benchtop probe after bringing the sample to 25°C in water bath. pH was measured using a freshly calibrated pH meter at 25°C. The sample was then subsequently titrated with 0.1M sodium hydroxide until a pH of 9 was reached and volume recorded. Base was then continually added incrementally until a pH of 11 was reached. An aliquot of unfiltered sample was refrigerated for TN and TP analysis.

A portion of the rain sample was filtered through a 0.45 um MCE membrane 47 mm diameter Millipore filter (HAWP04700) using acid-washed glassware. Filtrate aliquots were refrigerated for anion (Cl, NO3, SO4) and ortho-phosphate analyses. A 50-ml aliquot was preserved with 0.5 mL of 50% Trace Metals Grade HCl for cation analyses by ICP-OES (since 2014). A 60 ml aliquot was frozen (since 2018) for NH4 analysis.

Precipitation volume measurement methods

* 1973-2001 Weather station on top of the old SERC silo, 13m height
  + Precipitation volume was measured daily with a standard weather-bureau manual rain gauge. However, if more than one event-based sample was collected for analysis between manual rain gauge readings, the precipitation volume for each event was estimated with a Belfort weight-recording rain gauge.(David L Correll et al., 1999; Jordan et al., 1995)
* 2002-2007 SERC meteorology tower, 40 m above tree canopy
  + Manual rain gage as above
* 2007-present SERC meteorology tower, 40 m above tree canopy
  + NOAH IV electronic/gravimetric gage, part of Mercury Deposition Network MD00 site, backed up by a manual rain gage.

**Lab analyses**

The number of parameters and the analytical techniques have changed through time. These are summarized in Table 1. Methodological details are provided in Jordan et al. (1995). Samples were measured either on whole water samples, or samples filtered through 0.45 um Millipore filters. (D. L. Correll et al., 1999a, 1999b; Higman & Correll, 1982)

Table 1. Summary of precipitation chemistry analytes, sample processing (whether on filtered or whole samples) and start and end dates for analysis methods. Methods details are provided in (Jordan et al. 1995). Filtration was through a 0.45 um MCE membrane 47 mm diameter Millipore filter (HAWP04700).

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| **Analyte** | **Sample processing** | **Start** | **End** | **Technique** |
| Conductivity | whole | 1983 | 2022 | YSI conductivity meter in the lab, 25 C |
| NO2- | filtered | 2000 | 2021 | Ion chromatography |
| NO3- | filtered | 1973 | 1981 | Cadmium reduction |
| 1982 | 1985 | Ion chromatography |
| 1985 | 1987 | Automated colorimetry |
| 1987 | 2022 | Ion chromatography |
| NH4+ | filtered | 1977 | 2019 | Hypochlorite oxidation |
| 2019 | 2022 | Alkaline phenol and hypochlorite reaction |
| TKN | whole | 1973 | 2014 | Kjeldahl digestion |
| TP | whole | 1973 | 2015 | Perchloric digestion |
| PO4- | filtered | 1979 | 1991 | Molybdate reaction |
| 1991 | 2020 | Ion chromatography |
| Organic C | whole | 1974 | 2015 | Chemical oxygen demand by titration |
| Na+ | filtered | 1981 | 2002 | Atomic absorption |
| K+ | filtered | 1981 | 2002 | Atomic absorption |
| Mg2+ | filtered | 1981 | 2002 | Atomic absorption |
| Ca2+ | filtered | 1981 | 2002 | Atomic absorption |
| Cl- | filtered | 1981 | 2022 | Ion chromatography |
| SO4- | filtered | 1981 | 1985 | Ion chromatography |
| 1985 | 1987 | Automated colorimetry |
| 1987 | 2022 | Ion chromatography |
| F- | filtered | 1996 | 2019 | Ion chromatography |
| pH | whole | 1974 | 2022 | pH meter, low ionic strength electrode |
| ANC | whole | 1985 | 2022 | Gran titration with 0.1m NaOH |

**References**

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