Stream chemistry in five Rhode River subwatersheds, Maryland, USA, 1974-2023

Methods details

**Sites**

Table 1. Watershed locations and drainage areas.

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| --- | --- | --- | --- |
| Weir Number | Latitude | Longitude | Drainage area (ha) |
| W101 | -76.55766000 | 38.89061000 | 226 |
| W102 | -76.56444000 | 38.88806000 | 192 |
| W103 | -76.56913000 | 38.88936000 | 253 |
| W109 | -76.55371389 | 38.86896667 | 16.3 |
| W110 | -76.55362000 | 38.88398000 | 6.3 |

**Sample collection**

Water samples were composited and volume-integrated, then promptly collected and returned to the laboratory. A Stevens, model 61R, flow meter actuated the sampling of an aliquot for pre-determined flow thresholds. The water sample was drawn from the stream channel upstream of the weir and split samples were deposited into two plastic containers: one was pretreated with 20 mL of 18 N sulfuric acid to prevent biological or enzymic activity during storage, while the other was not acidified. From 1974-2004, samples were collected every one week, and after 2004, sampling frequency varied among weirs from weekly to monthly depending on programmatic needs and funding. After collection samples were either analyzed immediately or stored at 4°C. When flow was too low to obtain an integrated sample for analysis, spot samples were analyzed. Grab samples were also collected at the time of integrated sample collection for analysis of pH, conductivity, alkalinity, and anion concentrations.

**Lab analyses**

Stream samples were analyzed for various parameters. The parameters collected and analysis methods changed through the record period. The most complete record is for sediment, nitrogen, and phosphorus. While many measurements were discontinued from this record in 2013, these measurements were continued as part of the mercury watershed monitoring program and can be found elsewhere.

Total suspended sediment

The concentration of total suspended solids (TSS) was measured by filtering unpreserved samples through prewashed, preweighed Millipore 0.45 um filters, drying at 60 °C,

and reweighing. See (Correll et al. 1999a).

pH

pH was measured on whole grab water samples using a pH meter in the lab. These measurements were discontinued in 2013.

Conductivity

Specific conductivity was measured on whole grab water samples using a benchtop YSI Model 32 conductance meter. These measurements were discontinued in 2013.

Alkalinity

Alkalinity was measured on whole grab water samples using sulfuric acid titration Standard Method 2320 B (19th Ed.). These measurements were discontinued in 2013.

Nitrogen

Nitrogen (as nitrate, ammonium, and total Kjeldahl Nitrogen) was measured on samples collected from the acidified carboy, samples for nitrate and ammonium were filtered prior to analysis. Nitrate (NO3) was measured using cadmium reduction, ammonium was measured using hypochlorite digestion, and TKN was determined using Kjeldahl digestions. Methods are detailed in (Correll et al. 1999c). Total nitrogen was calculated as the sum of TKN and nitrate, and organic nitrogen was calculated as the difference between TKN and ammonium. Total nitrogen was measured on whole water samples directly through persulfate digestion for a subset of samples between 2019 and 2023. The alkaline persulfate digest (USGS 2003) was modified with borate buffer (D’Elia et al 1977) to allow analysis of sulfuric-acid-acidified samples.

Phosphorus

Phosphorus was measured on samples from the acidified carboy. Total phosphorus was measured on whole water samples using perchloric digestion, and phosphate was measured on filtered water samples using molybdate reaction. Details are provided in (Correll et al. 1999b). Organic phosphorus was calculated as the difference between TP and phosphate. Total phosphorus was measured on whole water samples directly through persulfate digestion for a subset of samples between 2019 and 2023. The alkaline persulfate digest (USGS 2003) was modified with borate buffer (D’Elia et al 1977) to allow analysis of sulfuric-acid-acidified samples.

Organic Carbon

Organic carbon was measured as chemical oxygen demand by colorimetry on whole water samples. Details are provided in (Correll et al. 2000). COD measurements were discontinued in 2017.

Silicate

Orthosilicate was measured on filtered, unacidified samples by reaction with ammonium molybdate. Details are provided in (Correll et al. 2000).

Anions

Chloride and sulfate were measured on filtered grab samples from 1981-2013 using ion chromatography.

**References**

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