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A small-volume multiplexed pumping system for automated, high-frequency water chemistry measurements in volume-limited applications

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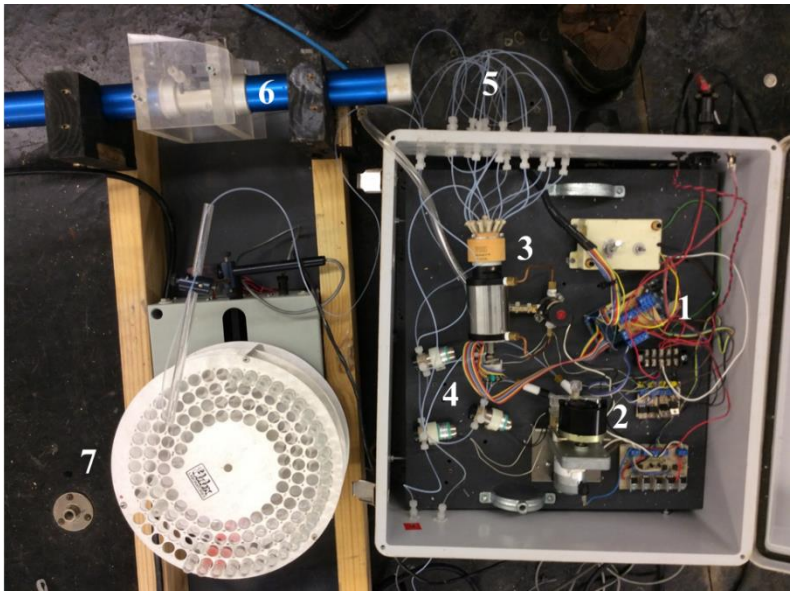
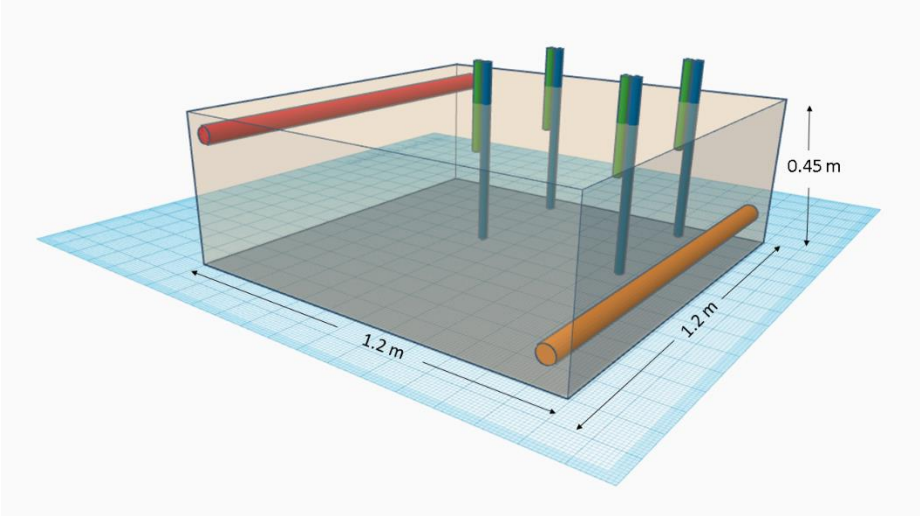
Optical methods for estimating NO_3^- concentrations

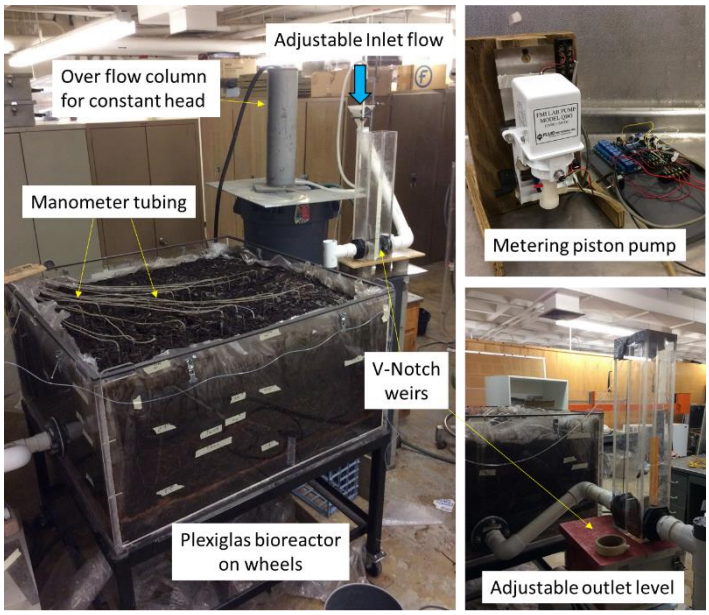
The s::can spectro::lyser (s::can^{TM}, Vienna, Austria) was used for the optical measurement of NO_3^- concentrations during the source and cross contamination trials (Sec. 2.3.1 and 2.3.2), as well as the woodchip bioreactor and stream mesocosm applications. The probe's estimates for NO_3^- were used to determine source/cross contamination due to the probe's low coefficient of variance for NO_3^- measurements and ability to detect small changes in NO_3^- concentration. Measurement of NO_3^- by the spectrophotometer is made possible by the principle of Behr's law and measuring the absorbance of a water volume over the 200 – 750 nm range. The resulting absorbance fingerprint provides absolute absorbance values at each 2.5 nm interval, with NO_3^- showing an absorbance peak at 200-205 nm. The spectrophotometer was configured for the 4 mm pathlength cuvette by changing the measurement pathlength of the spectrophotometer, and a baseline using deionized water was set using the manufacturer's specifications. While the spectro::lyser provides estimates of NO_3^- concentrations based on the manufacturer's global calibration, a local calibration is often recommended, particularly as the presence of organic matter absorbing at UV wavelengths can interfere with measurement of nitrate. During the cross and source contamination, the global calibration of the probe was used. In the bioreactor and stream applications, a local calibration was performed using PLSR methods detailed further in Etheridge et al. (2014). The R package *pls* was used to construct a model using the 240 raw absorbance values as predictors for the lab samples analyzed for NO_3^- by the NCSU Environmental Analysis Lab.



Supplemental Figure 1 – Photo of the small volume multiplexer with 1) Arduino control board, 2) bidirectional peristaltic pump, 3) 12 port air-actuated valve, 4) 3 way valve manifold, 5) 0.9 mm ID PFTE tubing, 6) s::can spectrophotometer with housing for 1.1 mL, 4 mm path length cuvette, and 7) fractional volume collector (optional).



Supplemental Figure 2 – Diagram of lab bioreactor at NCSU facility. Eight sampling wells were located in four well pairs placed at 20.9 and 41.9 cm depth, at 55.9 and 100.2 cm from the inlet, and in transects along the centerline of flow and 21.6 cm from left sidewall. Shallow and deep wells are shown in green and blue, respectively. Flow was diagonal downflow from the inlet header (red) to the outlet header (orange).



Supplemental Figure 3 – Photo of the lab bioreactor at the NCSU facility using V-notch weirs to measure flow, overflow constant head column for uniform flow, the metering piston pump for KNO_3 additions, and an adjustable outlet weir to stop flow or drain bioreactor.

Supplemental Figure 4 – Photo of the small volume MPS being deployed in the Sand section of Goldsboro stream. Four open-bottom Sediment mesocosms were inserted into the stream bottom and a fifth closed-bottom Control mesocosm was used as a baseline for nitrate fluxes occurring in the water column. The small volume MPS sampled each mesocosm every 6 min for a 36 min data interval on each mesocosm.

Supplemental Figure 5 – Photo of the small volume MPS being deployed in the Muck section of Goldsboro stream. Recirculating pumps were installed on the mesocosm sidewall to mimic advective flow of the stream.

Supplemental Figure 6 – Photo of the small volume MPS being deployed in the Muck section of Goldsboro stream. Emergent vegetation along the banks during March trials resulted in large variability in nitrate decreases over the 24 h experiment.