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Discussions

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Interactive comment on "A small volume multiplexed pumping system for automated, high frequency water chemistry measurements in volume-limited applications" *by* Bryan M. Maxwell et al.

Bryan M. Maxwell et al.

bmmaxwel@ncsu.edu

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Major comments: No major comments.

Discussion paper Specific comments:

1.Although the well names (S.In.Mid, S.In.side, etc) used in the manuscript are understandable, but I found it very difficult to follow when I am trying to interpret the data plots. I often need to stop and recall the exact meaning of each name. So I strongly suggest the authors to replace the well names. Maybe S1- S4 for the wells in shallower

depth and D1-D4 for the welss in deeper depth.

Response : Corrected wells names to D1-D4 and S1-S4 for shallow and deep wells, as well as edited the references to them in Sec. 3.1 – 3.2

2.Page 5, Line 27-29. "The results show that without a DI rinse. . . by at least four times Vcuvette to make . . .". Is this correct? Because the p = 0.236 for 10x Vcuvette, which suggest negligible difference after 10 times purge, right?

Response : This is correct, and thank you for catching this. This has been corrected in the manuscript. "the cuvette must be rinsed with the current sample by at least ten times Vcuvette to make cuvette contamination by previous sample negligible"

3.Page 8, Line 13, determination of NO3- with optical methods should be detailed either in the manuscript or in the supporting information.

Response : In Sec. 2.3, the following edits were made : "The spectrophotometer's estimates of NO3- based on the absorbance fingerprint (method detailed further in Supporting Information) were used to quantify contamination."

In the Supporting Information, the following paragraph was added to clarify the optical method for estimating nitrate from absorbance.

The s::can spectro::lyser (s::canTM, Vienna, Austria) was used for the optical measurement of NO3- 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 NO3- were used to determine source/cross contamination due to the probe's low coefficient of variance for NO3- measurements and ability to detect small changes in NO3- concentration. Measurement of NO3- 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 NO3- 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.

4.Page 10, Line 33, should be "referred to as Sediment mesocosms"

Response : Corrected to include "referred to as Sediment mesocosms". Same with "Control mesocosms."

5.Although it is stated as small-volume sampling, it usually withdrew tens of milliliters of water, which might not be a big problem for overlying water. But the volume is relatively large when this device is applied to extract porewater from porous media, for example in the case of sediments. This could be a limitation for the implementation of the system designed. Also as a suggestion for the authors to improve the system in the future, maybe rhizon in situ samplers (Seeberg-Elverfeldt et al., 2005 Limnol. Oceanogr: Method 3, 2005, 361-371) could be included into the system as the fine pores on the sampler preclude the suction of fine particles (diameter > 0.2 μm).

Response : the following edits were made in Sec. 5.1, detailing the system limitations. "The volume-limited applications presented include sampling an overlying water column and porewater in coarse woodchips. Porewater sampling in fine soils or sediments may be more restrictive and will result in a larger sphere of influence around the sampling point. While the minimum volume required for measurement using the MPS is

small (∼7 mL) and comparable to other small volume sediment samplers (e.g. Rhizon in situ samplers, Seeberg-Elverfeldt et al., 2005), bi-directional pumping from multiple sources by the MPS requires closer to 10-15 mL to reduce cross contamination for accurate solute measurement. Sampling of fine soils with low hydraulic conductivity using the MPS can be aided by the use of small diameter sampling wells similar to those described in Sec. 3.1."

6.Many typos such as "PTFE", "through" should be corrected.

Response : corrected several typos of "though" instead of "through". The authors are unclear for the typo of PFTE, as this is the commonly used abbreviation for polytetrafluoroethylene tubing.

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