Evaluation of an in situ UV-Vis spectrophotometer for high frequency measurements of dissolved organic carbon and nitrate concentrations

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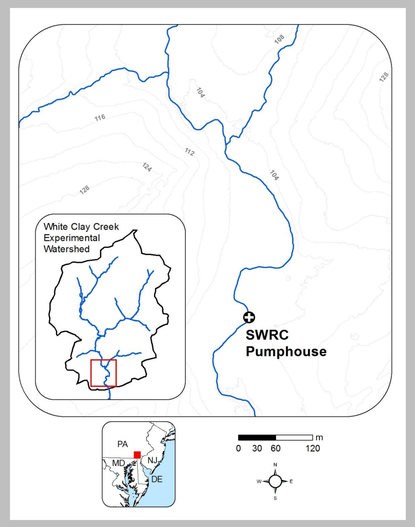
Introduction

- There exist several critical indicators of water quality in streams and watersheds, including dissolved organic carbon (DOC) and nitrate.
- An in situ UV-Vis spectrophotometer was installed in White Clay Creek, Christina River Basin CZO, to capture fluctuations in these parameters at a high frequency.

Study Site



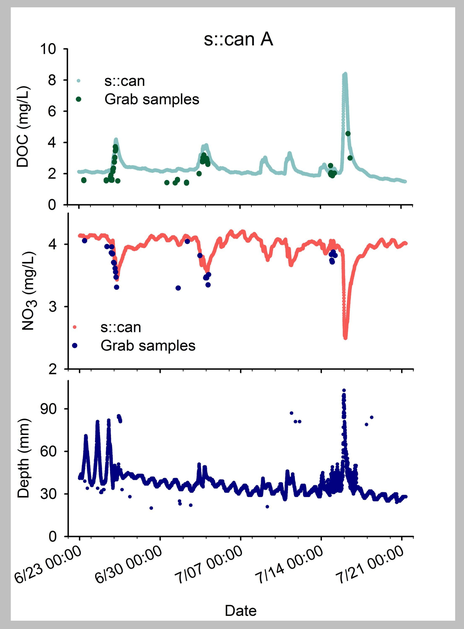
- Samples were collected from White Clay Creek at the Stroud Water Research Center pumphouse, located in the Christina River Basin.
- The pumphouse site is located in a forested section of the creek.

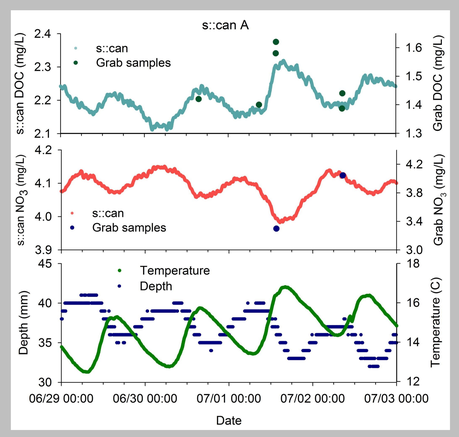
Methods

- Three s::can spectro::lyser probes took continuous measurements of a full UV-Vis spectrum at four minute time intervals, and used a built-in algorithm to determine DOC, nitrate, and turbidity.
- DOC, nitrate, and total suspended solids were measured in discrete samples collected at the pumphouse during baseflow and storms.
- The s::cans were manually cleaned with oxalic acid and HCl at varying time intervals, and an automatic air stream every six hours.
- DOC and nitrate measurements by the s::can were processed using locally weighted scatterplot smoothing and outlier removal. This method was used to smooth points and correct for drift due to biofilm accumulation.

Results

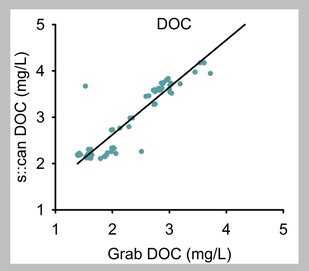
- During periods of high rainfall, DOC concentrations significantly increased, while nitrate decreased.
- All s::cans captured similar dynamics in DOC and nitrate, but DOC levels were offset from one another.
- Each s::can exceeded concentrations in laboratory measurements of DOC and nitrate. They had a precision of 0.05 mg/L for both DOC and nitrate, which is significantly larger than the repeatability of discrete samples, 0.01 mg/L.
- Biofilm accumulated on the s::can daily; cleaning the window caused measured DOC concentrations to decrease, but did not affect nitrate.

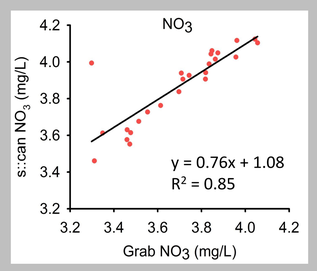




- The s::can captured dynamics that occur on a diel basis. DOC concentrations exhibited a recurring peak at approximately 1700 and a trough at 0500. Nitrate concentrations showed an inverse pattern to DOC, and both parameters varied by approximately 0.1 mg/L between peaks and troughs.

- A high R^2 between s::can and lab values was seen for both DOC and nitrate, indicating a correlation between the two measurement methods.





Conclusions

- In this study, the s::can probes were installed using the built-in algorithm for determination of DOC. It may be useful to either use the local calibration provided by the manufacturer, or manually calibrate collected data using a multiple linear regression model.
- Diel variations in DOC and nitrate correspond to fluctuations in temperature and water depth, so it is most likely that variations in these parameters are due to evapotranspiration in the riparian zone[1]. This mechanism decreases stream input from groundwater low in DOC and high in nitrate[2].
- During periods of high growth in summer months, the s::can must be cleaned frequently enough to reduce interference from biofilm accumulation.

Future Work

- An s::can will be used in the laboratory to allow for varied solute concentrations and provide flexibility in determining the relationship between the s::can and laboratory measurements.
- Cleaning methods will continue to be studied to develop the most efficient procedure and cleaning frequency.
- Multiple linear regression models will be used to derive a more accurate site-specific calibration of the s::can.

References

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- (2) Sawyer, A. H.; Kaplan, L. A.; Lazareva, O.; Michael, H. A. Hydrologic dynamics and geochemical responses within a floodplain aquifer and hyporheic zone during Hurricane Sandy. Water Resour. Res. *2014*, **50**, *4877-4892.*

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