Diurnal Variations in Urban Stream Chemistry

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Background

Long-term trends in nitrogen, carbon and pH contribute to water quality issues such as eutrophication, hypoxia, and acidification. However, less is known regarding their dynamics over day and night cycles related to whole stream metabolism. Most of the information on carbon, nitrogen and pH in streams comes from discrete grab samples rather than continuous samples taken throughout full diurnal cycles. Diurnal cycles in urban stream chemistry are driven by metabolic processes such as primary production (photosynthesis) and respiration (organic matter decomposition). Stream metabolism is affected by factors such as nutrient availability, temperature, and physical stream characteristics.

Hypothesis

Carbon quantity and form (organic carbon *vs.* inorganic carbon) show diurnal variations in an urban stream across seasons due to stream metabolism (evidence as changes in diurnal O_2).

H_0: There is no diurnal variation in carbon and nitrogen in an urban stream across seasons.

Methods

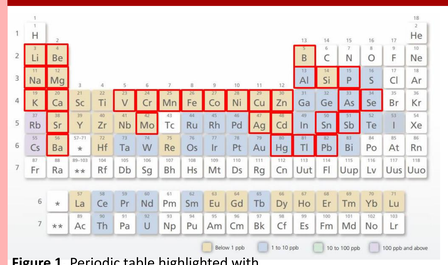


Figure 1. Periodic table highlighted with elements analyzed by the ICPE-9800. Elements analyzed were in concentrations higher than minimum detection limits.

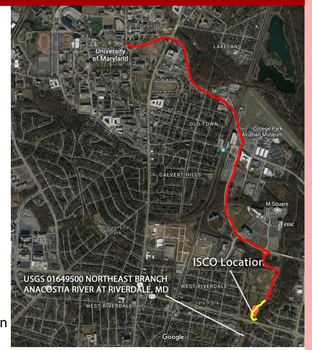


Figure 2. Site location with the ISCO deployment site and USGS Water Data station marked relative to UMD.

Automated samplers, ISCOS, were used to collect water samples. Initially samples were to be collected every 30 minutes over 24 hours, the fall sample set was collected in this manner. To better visualize a diurnal cycle, two periods were collected for the winter sample set. Samples were collected to be analyzed with an Shimadzu TOC-L and a Shimadzu ICPE-9800. After samples were collected, the samples were filtered to extend sample lifetime and to be able to be analyzed with the TOC-L. Samples were acidified in order to analyze concentrations of various elements (Figure 1) by the ICPE-9800. Site selected was the Northeast Branch of the Anacostia River (Figure 2) which is a USGS Water Data gauging station which also gauges dissolved oxygen, specific conductance and pH.

Results

Data was normalized by subtracting each elements mean and then dividing by the standard deviation. The majority of elements analyzed did not show any diurnal pattern. Most elements did demonstrate a diurnal cycle. The fall data set demonstrated a diurnal cycle for DOC and had sporadic elemental concentrations, which could be attributed to the delay in analysis. The spring data set also demonstrated a diurnal DOC signal.

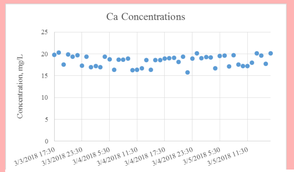
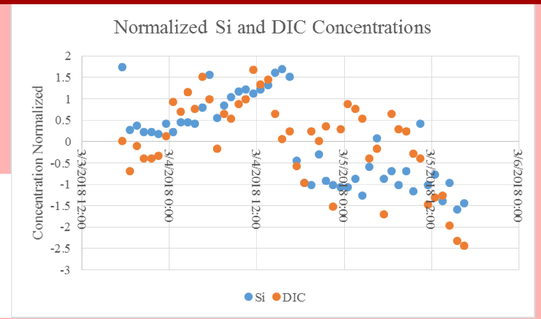


Figure 4. Plot of calcium concentrations from the winter data set. Ca is not bioactive and does not demonstrate a diurnal signal.

Figure 8. Dissolved inorganic carbon (DIC) and Si show similar shapes when normalized. The similar shapes may be attributed to weathering.



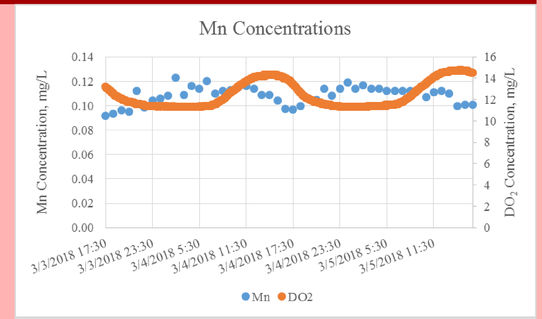
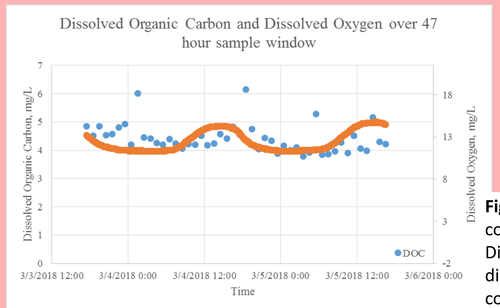


Figure 9. Antimony concentrations from the fall sample set. Concentrations jumped from less than 0.1 ppm to about 1.5 ppm and then back to around 0.1 ppm. This could be attributed to sampling error or contamination.



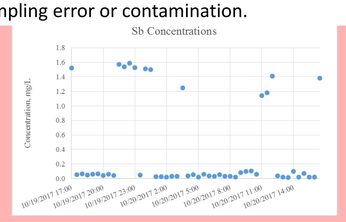


Figure 5. Dissolved organic carbon (DOC) concentrations from the winter sample set. Diurnal cycle can be seen by comparing to dissolved oxygen concentrations. DOC concentration lags two hours behind DO_2.

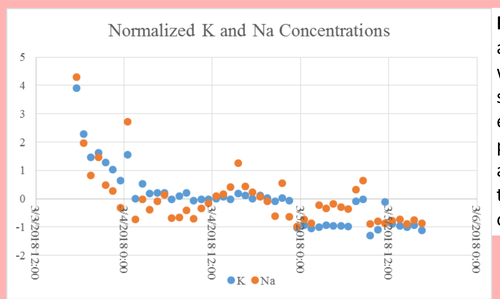


Figure 6. Plot of normalized potassium and sodium concentrations from the winter data set. There was a winter storm a few days prior which may explain the decrease in sodium and potassium concentrations. Potassium and sodium are used in road salt so their similar shape could be indicative of leftover road salt runoff.

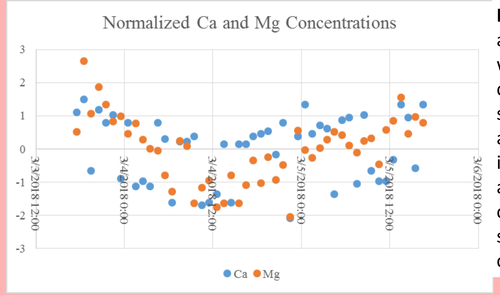
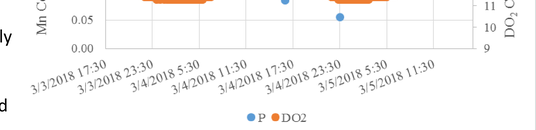


Figure 7. Plots of normalized calcium and magnesium concentration from the winter data set. The data does not contain a diurnal signal but the two show similar shapes. Both Ca and Mg are elements present in concrete. Mg is in a majority of rocks used in aggregate and Ca is used as an admixture in concrete. Ca and Mg show a similar shape and both may be linked to concrete weathering.

Figure 10. Both manganese and phosphorus concentrations demonstrate a diurnal cycle. Manganese appears to be inversely related to dissolved oxygen and influenced by redox. Phosphorus exhibits a diurnal cycle as it is used in stream metabolism and is also influenced by redox conditions.



Conclusion

Dissolved oxygen can be compared to dissolved organic carbon. The concentrations have similar shapes with a lag time of two hours. Diurnal variations of organic carbon can vary as much as 20%. Dissolved inorganic carbon is also similar and exhibits a diurnal cycle. There are not many elements that exhibit a diurnal cycle. Manganese and phosphorus exhibited a diurnal cycle whereas Na and Ca did not.

This study demonstrates for an urban stream that most elements do not exhibit a diurnal cycle. Diurnal cycles would indicate that that element would be included and influenced by stream metabolism. Manganese, iron and phosphorus are elements that exhibited a diurnal cycle which is because the elements are affected by stream metabolism. Changes in dissolved oxygen affects redox conditions and allows for an element such as Fe to be consumed. The lack of a diurnal cycle affirms that most elements in urban streams are not affected by stream metabolism and affected by some other factor such as weathering. This study showed that DIC and Si, K and Na, Ca and Mg each are linked and show similar patterns between each pair.

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