Examining controls on dissolved organic carbon quantity and quality in U.S. rivers

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Introduction

- Dissolved organic carbon (DOC) in rivers is a critical component of the global carbon cycle and both its quantity and quality are important parameters in numerous fields of study, from water quality to coastal oceanography.

- DOC quantity in rivers can be studied in terms of either flux or concentration – both are important:
  - Flux of DOC from the continents to the ocean is a crucial parameter in fields of study like the global carbon cycle and coastal eutrophication
  - Concentration is more important when investigating fields like photochemistry and microbial ecology

- DOC quality – composition of the heterogeneous assemblage of organic molecules that makes up DOC
  - Specific ultraviolet absorbance ($SUVA_{254}$): UV absorbance at 254nm normalized to DOC concentration
    - Measure of aromaticity (Weishaar et al., 2003)
  - Quality drives reactivity – biological remineralization, photochemistry, and pollutant complexing and transport

- Both large and small basins are important to study: large basin DOC flux represents the sum of all terrestrial biogeochemical influence, while small headwater basins provide something closer to an unprocessed endmember

- Question 1: Are the same relationships that are reported in the literature between watershed-scale characteristics and DOC quantity among small basins also observable among large and continental-scale rivers?

- Question 2: Can some of these same watershed-scale characteristics also explain variability in DOC quality in terms of $SUVA_{254}$, or is quality independent of characteristics like wetland-cover and hydrology?

- Question 3: What drives DOC quantity and quality variability in time among small basins? Are these drivers remotely observable, enabling us to predict DOC variability in ungauged systems?

Methods

- Analysis of 17 large rivers in the National Stream Quality Accounting Network (NASQAN)
  - DOC concentration and $SUVA_{254}$ samples taken from 2002 to 2010
  - Catchments heterogeneous and sampling stations located near the mouth of each river, upstream of tidal influence (Fig. 1).
  - Daily discharge data procured from the USGS National Water Information System
  - Wetland coverage from GIS analysis of the National Land Cover Dataset (NLCD)
  - LoadRunner, front end to USGS's LOADEST, used to estimate mean-annual [DOC] and SUVA

Figure 1. Map of large-river stations

- Analysis of approximately 2000 small streams in the USGS National Water Information System (NWIS)
  - Daily discharge (Q), discrete [DOC] and $SUVA_{254}$, and site information (lat/long) downloaded from the NWIS
    - In order to compare among basins, runoff (RO) was caclulated as discharge/basin area
  - Basins were < 100km^2, heterogeneous, and distributed throughout the United States
  - Landcover data for each station was derived from accumulated upstream NLCD values in the stream-network of the National Hydrography Dataset (NHDplus)
  - Contributing watersheds for each gauging station delineated using the NHDplus BasinDelineator tool
  - Mean daily MODIS indices were calculated for each of the delineated watersheds
    - Enhanced Vegetation Index (EVI), Land Surface Water Index (LSWI), Gross Primary Production (GPP)
  - Hydrograph divided into baseflow and stormflow following Eckhardt (2005)
    - As an indicator of stormflow intensity, we calculated S_R as the ratio of stormflow to total discharge
  - Mean antecedent values of Q, S_R, EVI, LSWI, and GPP calculated over 2, 4, 8, 16, 32, 64, and 128 days.

DOC in Large Rivers

- DOC concentration and $SUVA_{254}$ were strongly correlated with the percent wetland-cover of the watershed.

- Two outliers existed: St. Lawrence and Colorado rivers
  - large lakes or impoundments upstream of mouth
  - very low SUVA is associated with algogenic DOC (Henderson 2008) rather than a terrestrial signal

- This indicates that mean annual DOC quality, in terms of SUVA, can be explained by wetland-cover in large basins receiving minimal algogenic contribution to the DOC pool

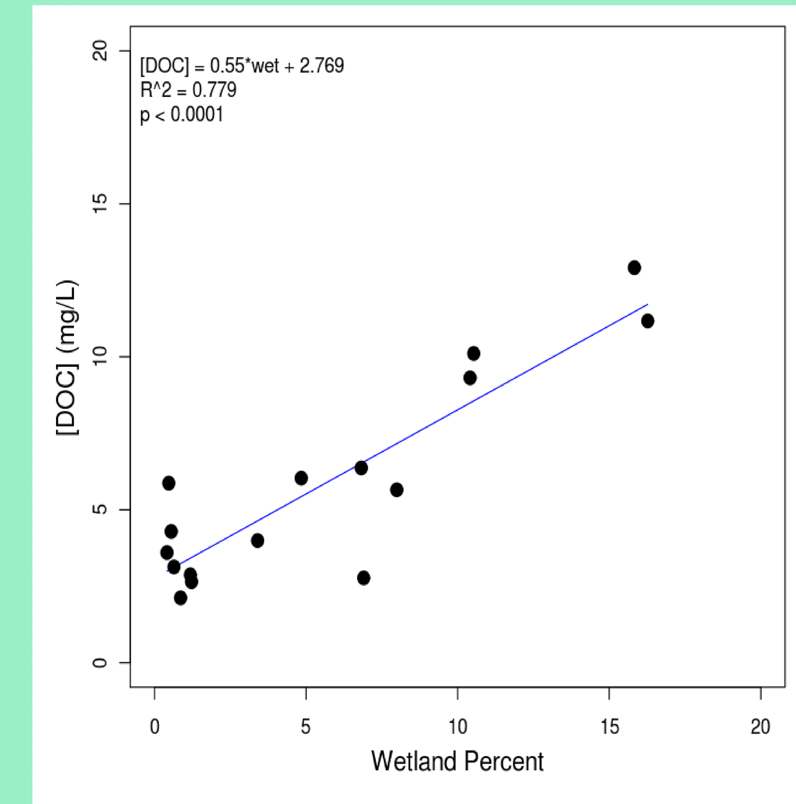

Figure 3. Linear regressions representing the relationship between DOC concentration and percent wetland-cover.

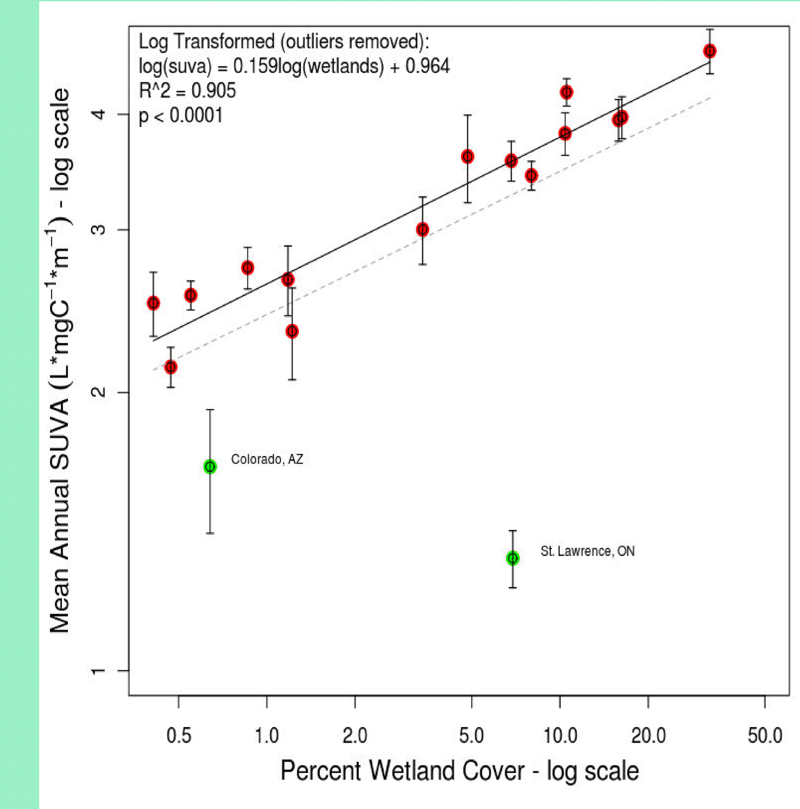

Figure 4. Linear regression for the relationship between the natural log of SUVA and the natural log of % wetland-cover before (dotted grey line) and after (black line) the removal of two outliers (green points).

DOC in Small Streams

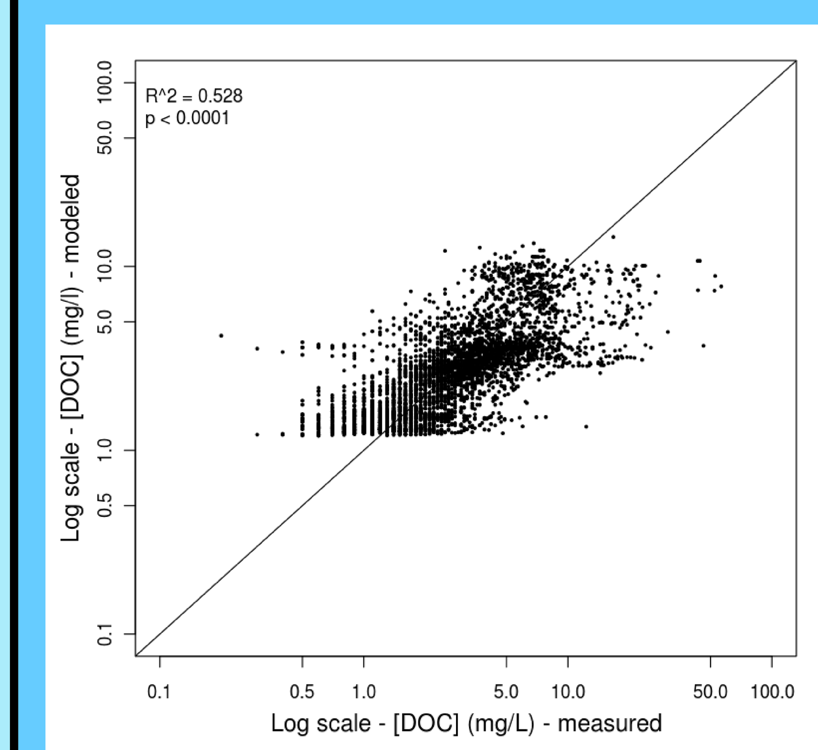

Figure 4. Multiple linear regression for the relationship between [DOC] and basin attributes – line is 1:1

- We evaluated a series of potential drivers of [DOC]:
  - Across basins, the S_R was the hydrological parameter most able to explain [DOC] variability
  - Mean EVI, GPP, and LSWI were intercorrelated and able to explain [DOC] variability
    - GPP was most normally distributed; its 64-day antecedent was best correlated with [DOC]
  - Coniferous forest (L_F) and herbaceous wetland cover (L_W) explained [DOC] variability
  - Multple regression developed for [DOC] across all basins (Figure 4):

$$\ln([DOC]) \sim S_R + GPP_{64day} + \ln(L_F) + \ln(L_W)$$

  - Some basins were well described by the model (Figure 5) and others were not (Figure 6)
  - Differences among basin types or in basin characteristics that may have led to this divergence have not yet been identified and are the subject of continuing work

- We also evaluated basin-scale characteristics as potential drivers of $SUVA_{254}$
  - Several time-varying parameters, such as MODIS indices, were significant, but explained less than 2% of variability in $SUVA_{254}$
  - Of drivers we investigated, variability in $SUVA_{254}$ was best explained by wetland-cover
    - Wetland cover does not vary within basins and is thus limited to describing basin-mean $SUVA_{254}$ (Figure 7)

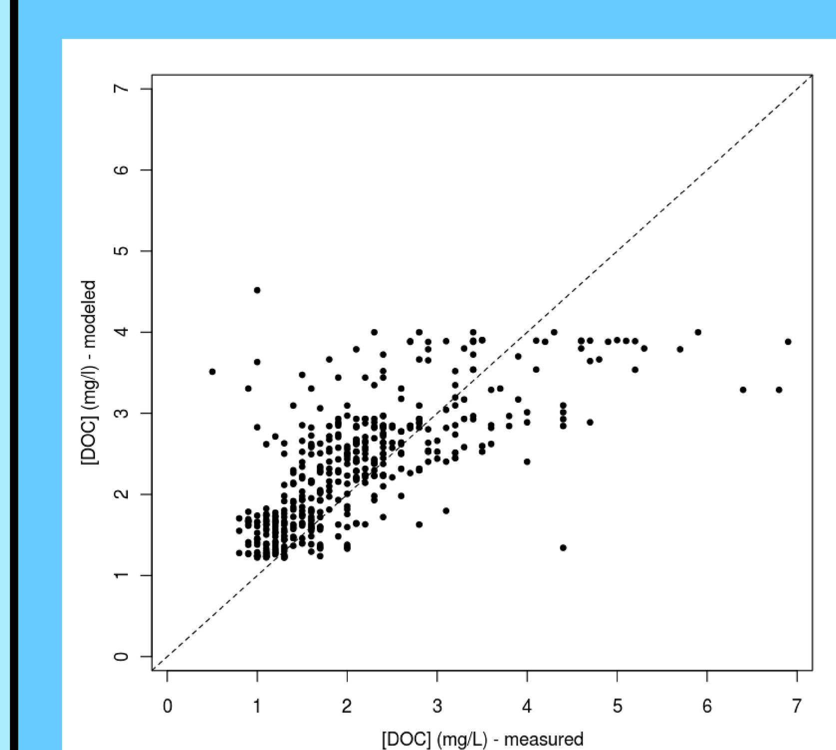

Figure 5. Measured vs. modeled [DOC] for site 01422747 in Walton, NY – line is 1:1

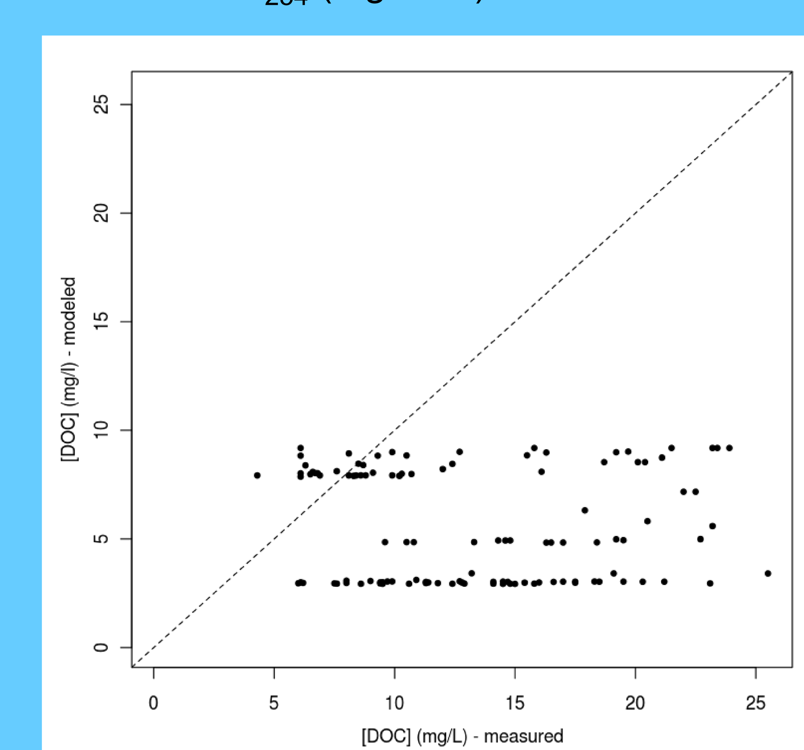

Figure 6. Measured vs. modeled [DOC] for site 01466500 in Byrne State Forest, NJ – line is 1:1

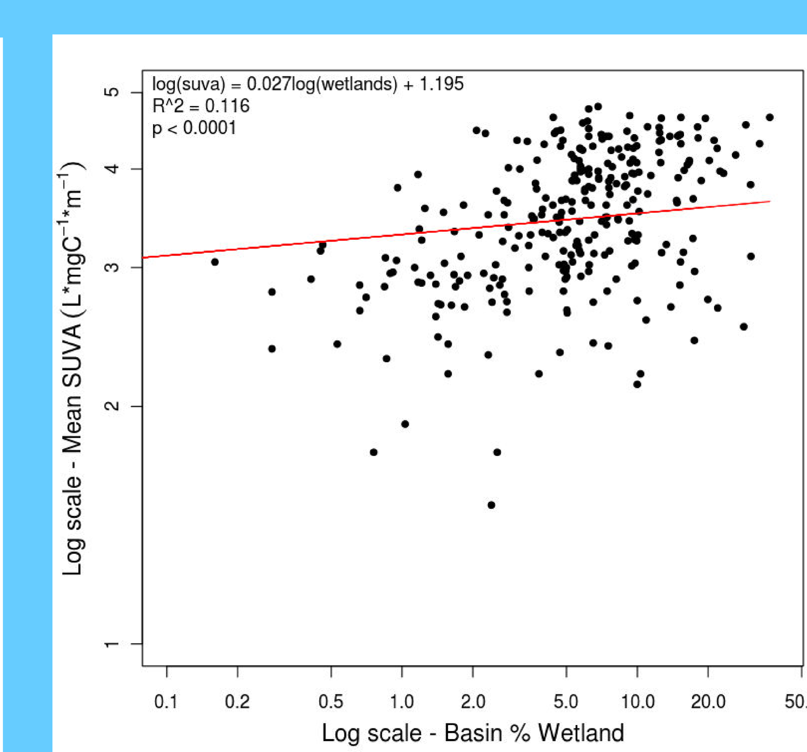

Figure 7. Linear regression representing the relationship between mean $SUVA_{254}$ and % wetland-cover of a basin

Conclusions and Future Work

- These results indicate that similar processes control DOC quality and concentration in large rivers and in small rivers – strong positive [DOC] and $SUVA_{254}$ response to wetland-cover
  - Results also suggest that stormflow is an important driver of [DOC] variability in time
  - Remotely sensed characteristics, like antecedent GPP can improve prediction of [DOC] variability

- No remotely sensed or hydrological basin characteristics appear to drive temporal variability in $SUVA_{254}$
  - Wetland-cover explains some variability in mean-annual $SUVA_{254}$, but future work should seek to identify processes that drive $SUVA_{254}$ variability in time

- Results will also be useful in the development of DOC loading algorithms for use in continental-scale modeling
  - Enable the estimation of DOC flux from ungauged rivers to the coastal ocean

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