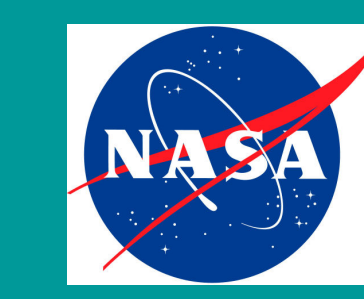


Examining controls on dissolved organic carbon quantity and quality in large U.S. rivers

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Introduction

- Dissolved organic carbon (DOC) – organic carbon fraction passing through a 0.45 μm filter
- DOC quality – a measure which quantifies the nature of the heterogeneous molecular assemblage that makes up DOC
 - Specific ultraviolet absorbance (SUVA)
 - UVA at 254nm normalized to DOC concentration
 - SUVA is a measure of aromaticity (Weishaar et al., 2003)
 - Labile or refractory DOC
 - More or less easily metabolized by heterotrophs, - typically determined by bioassay
- DOC quantity is important, but without understanding quality as well, its utility in many applications is limited:
 - Coastal carbon cycle analyses (Gattuso et al., 1998)
 - Management of estuaries (Lehtoranta et al., 2009)
 - Drinking water quality (Siddiqui et al, 1997)
- History of terrestrial DOC begins with the death, senescence, or exudation of terrestrial plant organic material and deposition as detritus
 - Most labile organic compounds are decomposed and transformed at the surface leaving refractory compounds known as humus
 - Both labile and refractory organic material dissolved in interstitial water and exported to streams and rivers
 - Soil carbon timescales are longer than for riverine DOC – thus what is considered labile in soil may be refractory in rivers
- **Research Question 1: Wetland cover and hydrology are important controls on DOC load and concentration in small watersheds, but do these controls remain evident at large watershed scales, despite in-stream processes?**
- **Research Question 2: Can some of these same watershed-scale controls also explain variability in DOC quality (as measured by SUVA), or is quality independent of wetland-cover and hydrology?**

Methods

- Analysis of samples from 17 rivers (NASQAN)
 - National Stream Water Accounting Network
 - Periods of measurement from 2004 to 2010
 - Catchments heterogeneous and sampling stations located near the mouth of each river, upstream of tidal influence (Fig. 1)
 - Quality determined by measuring SUVA-254 (specific ultraviolet absorbance at 254nm)
 - Daily discharge data procured from the USGS National Water Information System
 - Wetland cover ascertained by GIS analysis of the National Landcover Database

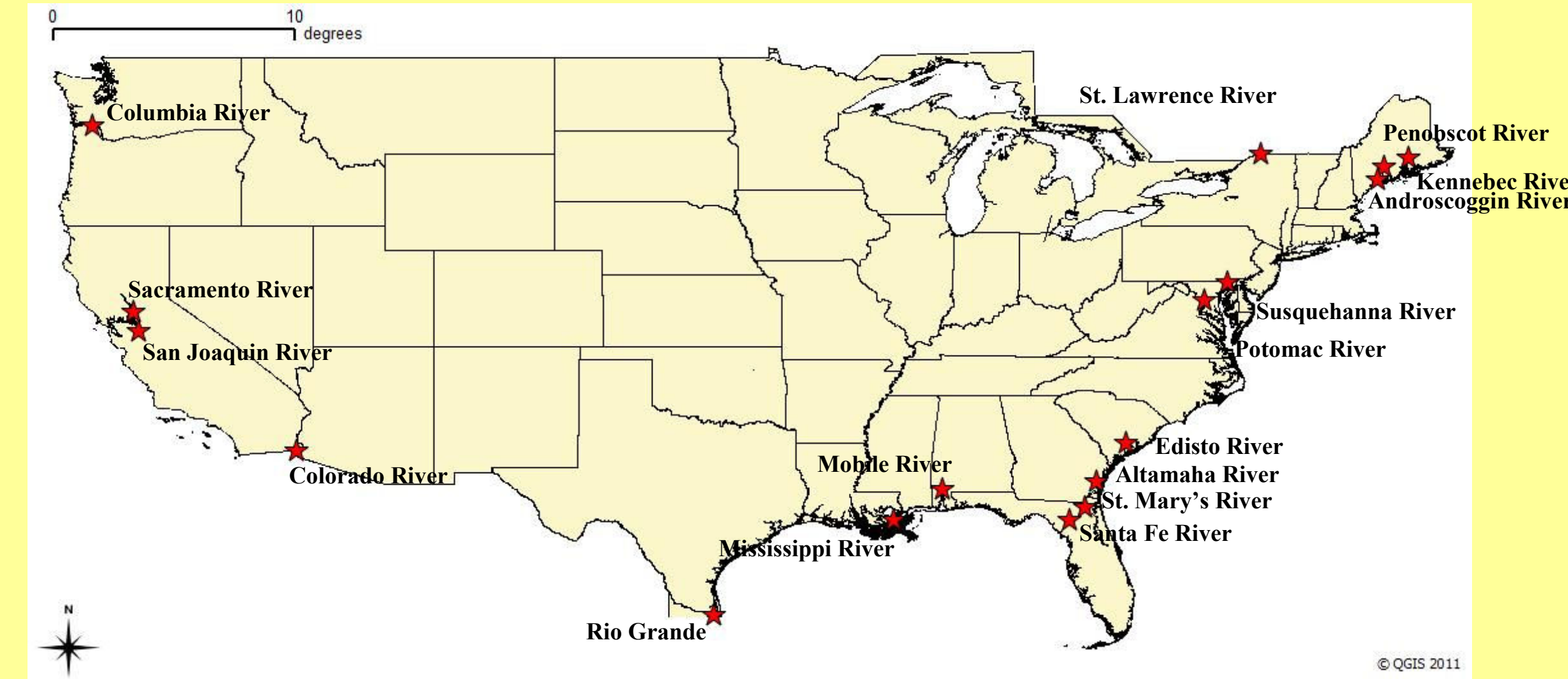


Figure 1. Map of stations

- LoadRunner, front end to USGS's LOADEST, used to estimate daily and mean annual bulk DOC and SUVA (Fig. 2)
 - Incorporates discharge, seasonality, and concentration, to parameterize multiple-regression models to find the best fit
 - Resulting daily concentration estimates combined with daily discharge data enabled estimation of annual DOC flux and

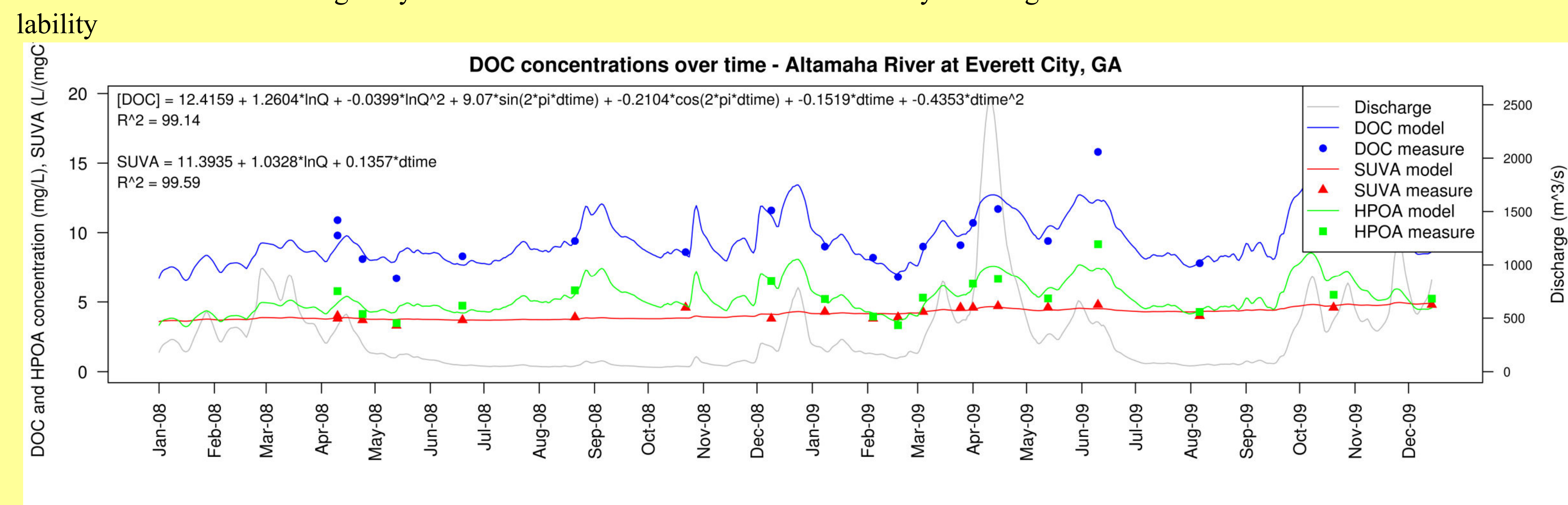


Figure 2. Timeseries of discharge (grey), bulk DOC concentration (blue), SUVA (red), and HPOA concentration (green) for the Altamaha River in Georgia. Points represent field measurements while curves represent multiple-regression models fitted by LoadRunner.

Insights on DOC quality...

- **SUVA variability is not explained by runoff (Fig. 3)**
- **SUVA variability is explained well by wetlands (Fig. 4)**
 - Quality of DOC is strongly influenced by its source
- **Two outliers exist: St. Lawrence and Colorado river**
 - large 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**

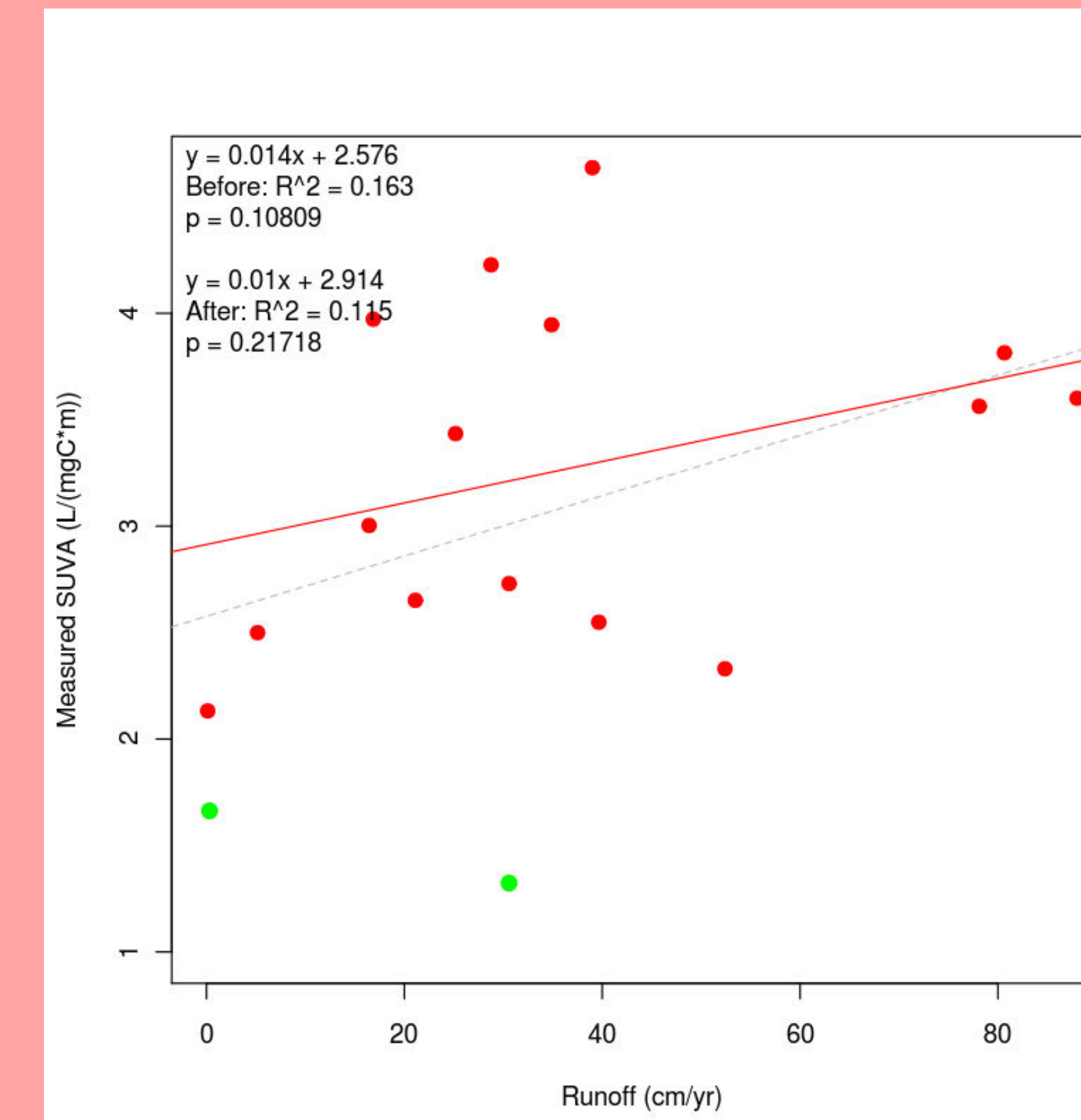


Figure 3. Linear regressions representing the relationship between SUVA and runoff before (grey dotted) and after (red) the removal of two outliers (green).

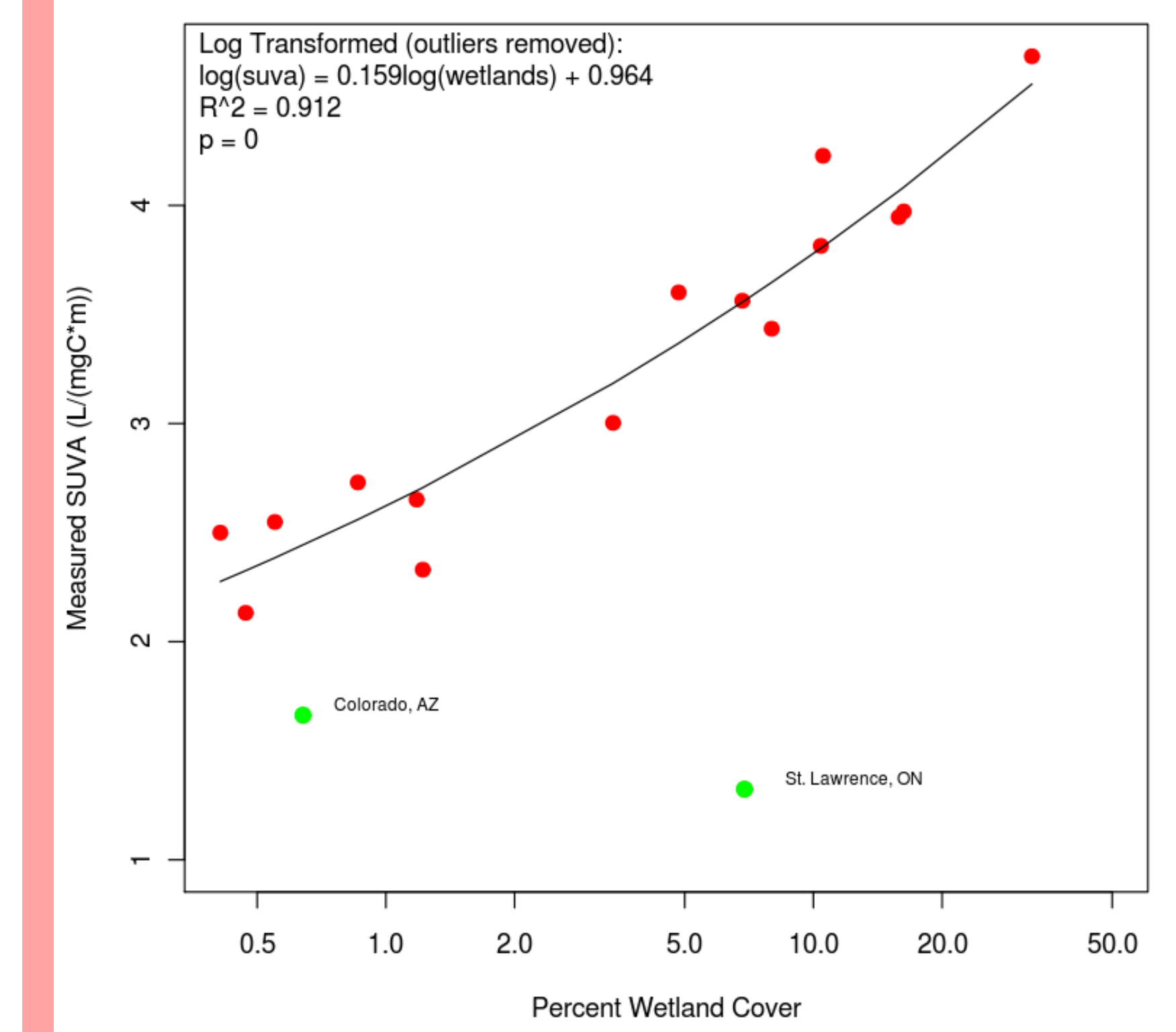


Figure 4. Linear regression representing the relationship between the natural log of SUVA and the natural log of percent wetland-cover after the removal of two outliers (green).

Basin-scale Controls on DOC quantity

- **As in small basins, we found a positive correlation between mean annual DOC flux and both mean annual runoff and a basin's percent-wetland coverage (Figs. 5 & 6)**
 - Further analysis revealed that these two predictor variables explained 99% of variability in a multiple regression
- Because DOC flux is inherently controlled by discharge (flux = Q*conc), we also examined whether these variables were useful in predicting raw DOC concentration
 - **Using wetland-cover, runoff, and mean latitude we explained 98% of variability in DOC concentration (Fig. 7)**

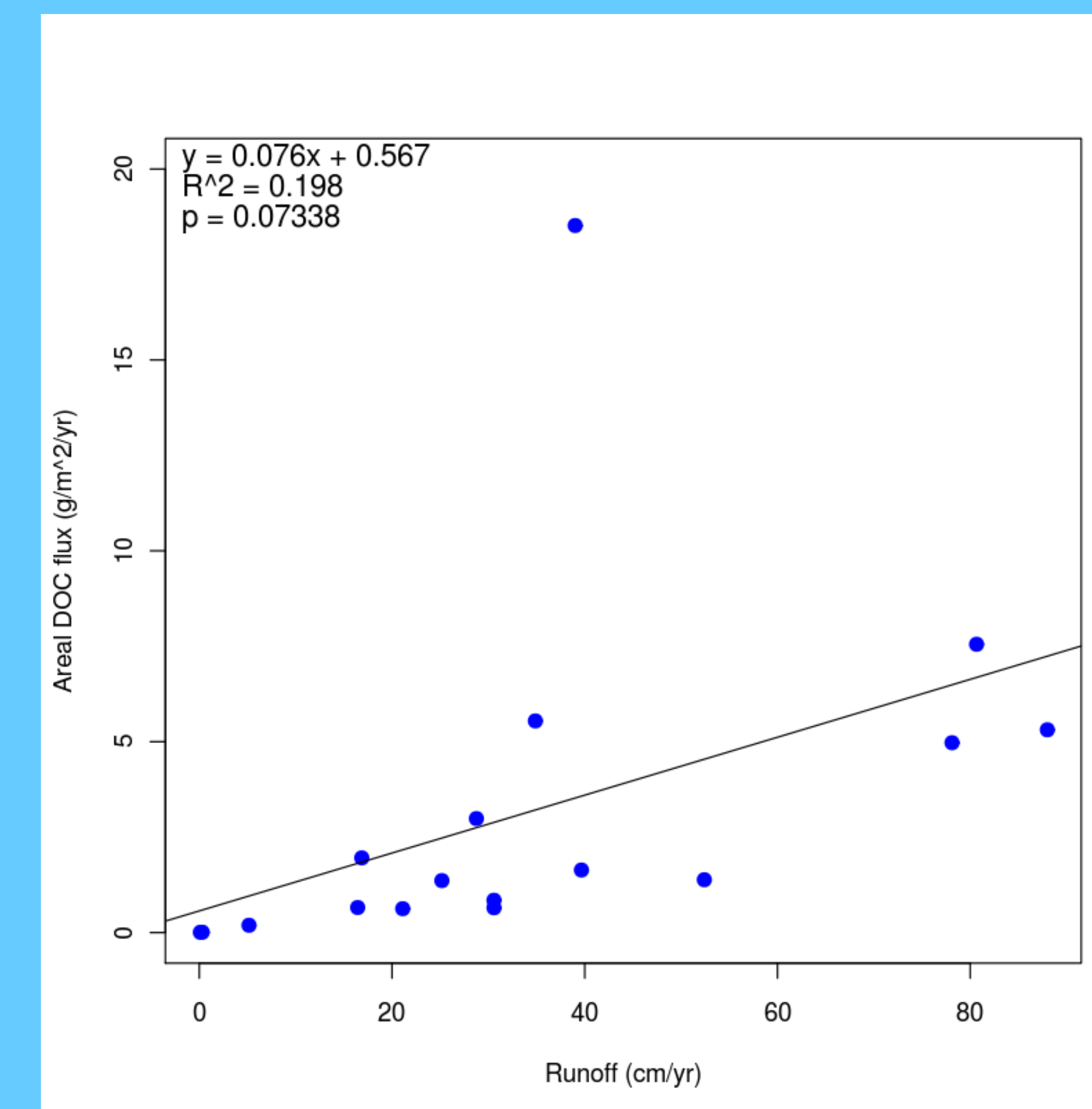


Figure 5. Linear regression representing the relationship between DOC flux and runoff

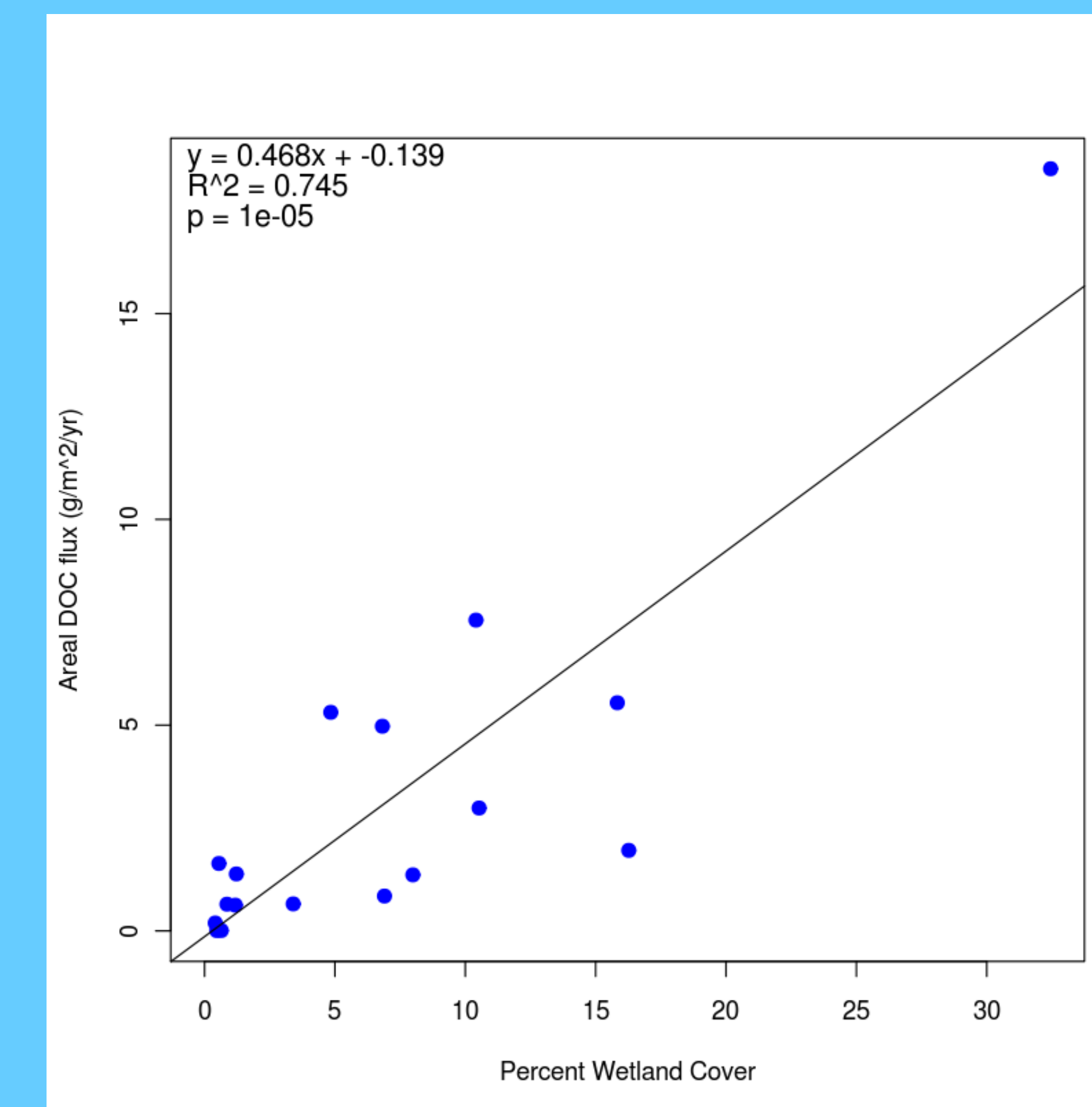


Figure 6. Linear regression representing the relationship between DOC flux and percent wetland cover

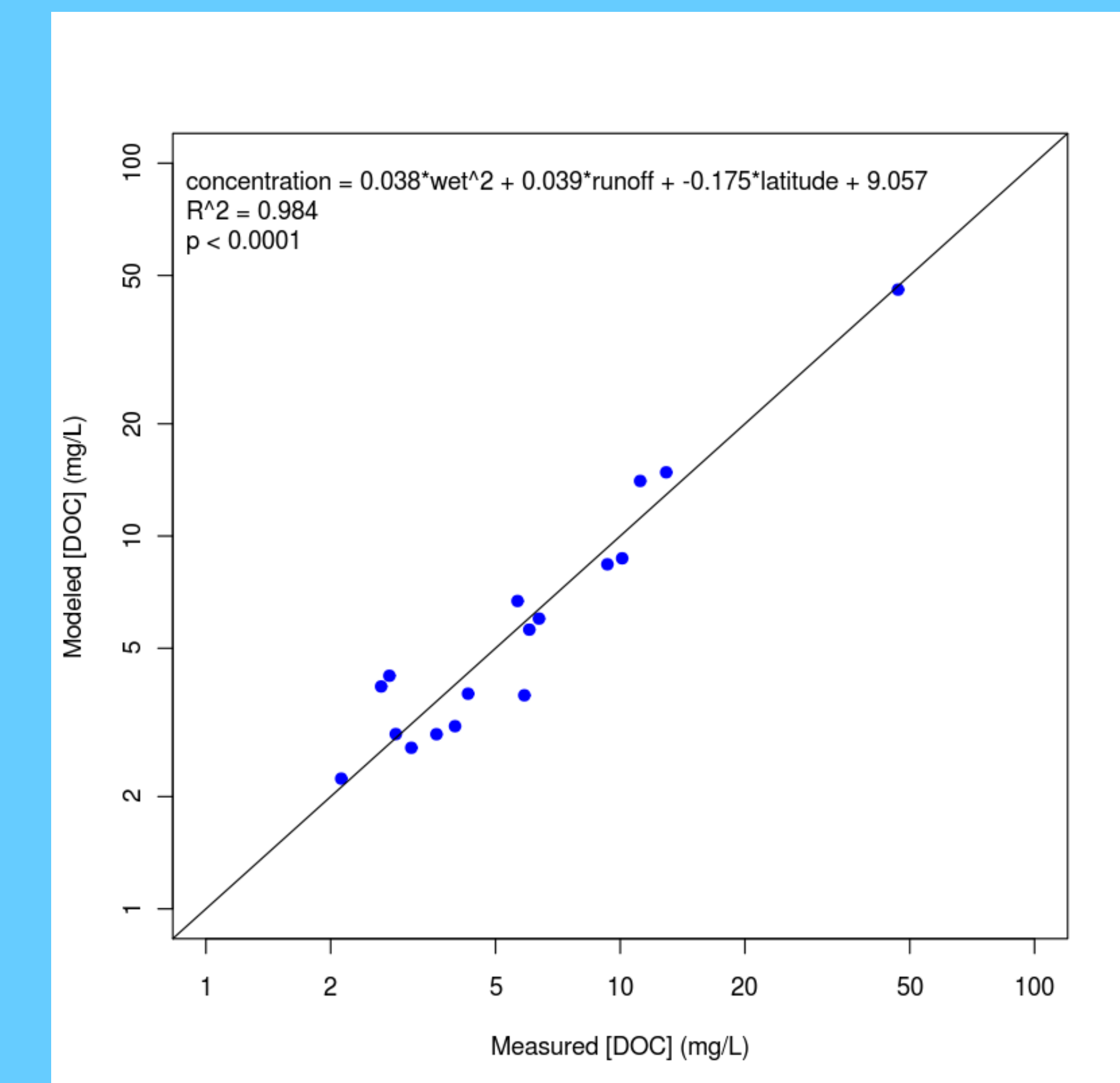


Figure 7. Discharge-weighted mean annual DOC concentration vs. modeled DOC concentration. Line is 1:1.

Conclusions and Future Work

- These results indicate that similar processes control DOC flux and concentration in large rivers and in small rivers – positive response to wetlands and runoff
- Although wetland-cover adequately explains SUVA variability in large basins, future studies should seek to elucidate whether these relationships are important in small basins
 - A significant difference in the nature of this relationship will indicate that transformations occur in-stream
 - Care should be taken to ensure that algogenic DOC quality is fully understood in any future studies
- These results may prove useful in the development of DOC loading algorithms for use in continental-scale modeling
 - SUVA to segregate DOC into quality pools
 - Wealth of SUVA data available through the USGS

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