

**NPS / Multi Agency Critical Loads Project**  
**Steady-State Critical Loads and Exceedance for Terrestrial and Aquatic Ecosystems in**  
**the Northeastern United States**

**Appendix Technical Document 4b**  
**DOC correction to the ANC limit required to insure that a Critical Load represents a**  
**desired target pH**

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**DOC correction of the ANC limit for the Eastern Critical Loads Project**

In order to calculate a critical load, a critical threshold condition must be established with respect to a biogeochemical metric that can be modeled and which is associated with ecosystem health or the condition of key organisms in an ecosystem (ICP Mapping Manual 2004, Henriksen and Posch 2001). For aquatic ecosystems subject to acidification by sulfur and nitrogen, the parameter most often related to the condition of key organism and aquatic ecosystem health is pH (ICP Mapping Manual, 2004, Dupont et al. 2005). For historical reasons – due primarily to the complications associated with DOC (discussed below) a target pH critical threshold has been translated to a corresponding value of the acid neutralizing capacity termed the ANC limit (see discussion in Dupont et al. 2005). This is done because the charge-balance form of the acid neutralizing capacity (see Morel and Hering 1993) is simpler to model than pH in a steady-state context with limited data (ICP Mapping Manual 2004). Often, previous aquatic critical loads studies were restricted to limited landscape conditions or regions with roughly similar DOC concentrations. These prior studies (e.g. Dupont et al. 2005) make an assumption of an average DOC effect on pH relative the charge balance ANC. Because the Northeastern US region experiences a wide range of DOC concentrations in surface waters, the former approach is not practical for comprehensive regional aquatic critical loads modeling.

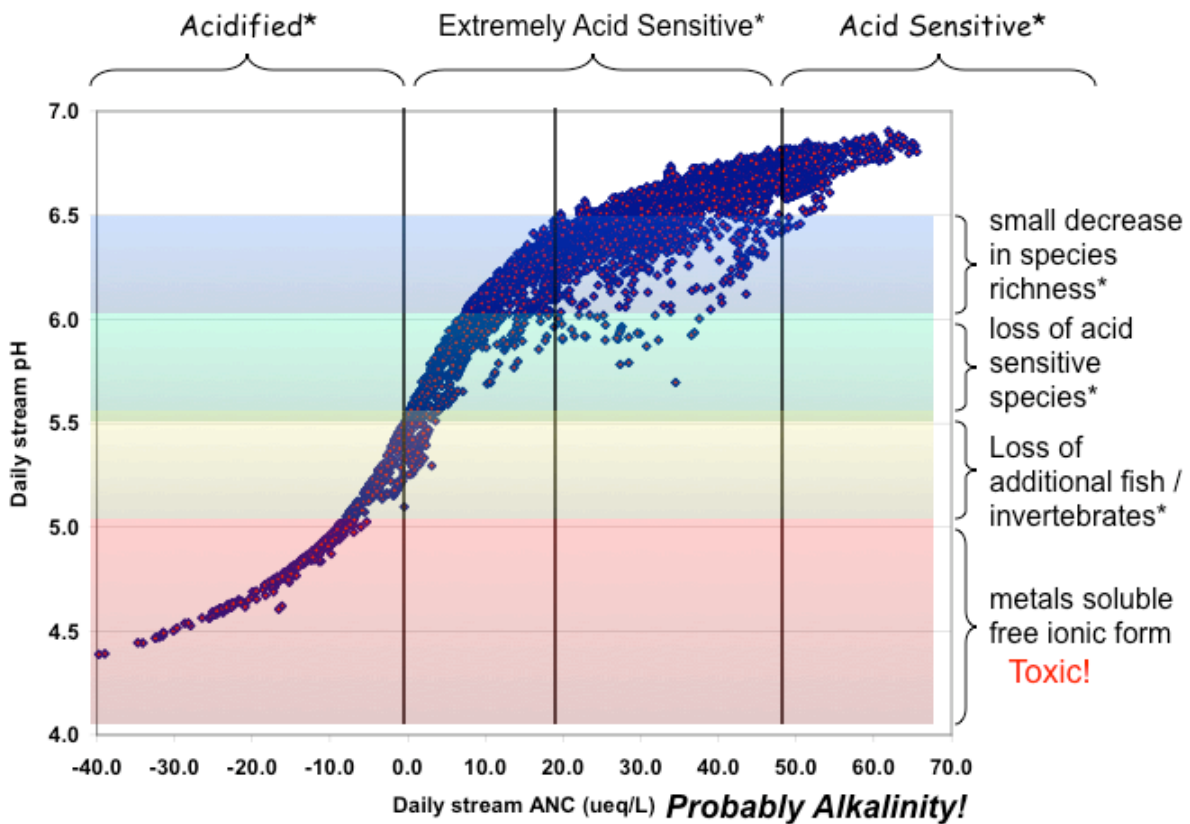
The aquatic critical loads analysis in this project employs two versions of the steady state simple mass balance model (ICP Mapping Manual 2004),

$$\begin{aligned}\text{CL (S+N Acidity)} &= \text{BC}_0 - \text{ANC}_{\text{limit}} \\ &= Q * ([\text{BC}]_0 - [\text{ANC}]_{\text{limit}}).\end{aligned}$$

As many biological effects have been linked to pH and pH-mediated processes (Lynch, personal communication project conference call June 15 2009), ANC serves as a proxy for pH in the CL analysis (Figure 1). A selection of an ANC<sub>limit</sub> includes an implied pH target associated with that level of ANC *in a specific surface water system*.

ANC in the context of the steady-state simple mass balance models (ICP Mapping Manual 2004) is **the charge-balance ANC** (CBANC) not alkalinity (ALK).

The pH conditions in surface waters are not as tightly correlated with the CBANC as they are with ALK. Aquatic pH is significantly influenced by DOC and DIC (Figure 2). DOC and DIC effects are operationally included in ALK. In the project area of interest (NY and New England) there is a large range of DOC values in surface waters, thus the CBANC<sub>limit</sub> must be adjusted to reflect the influence of DOC.

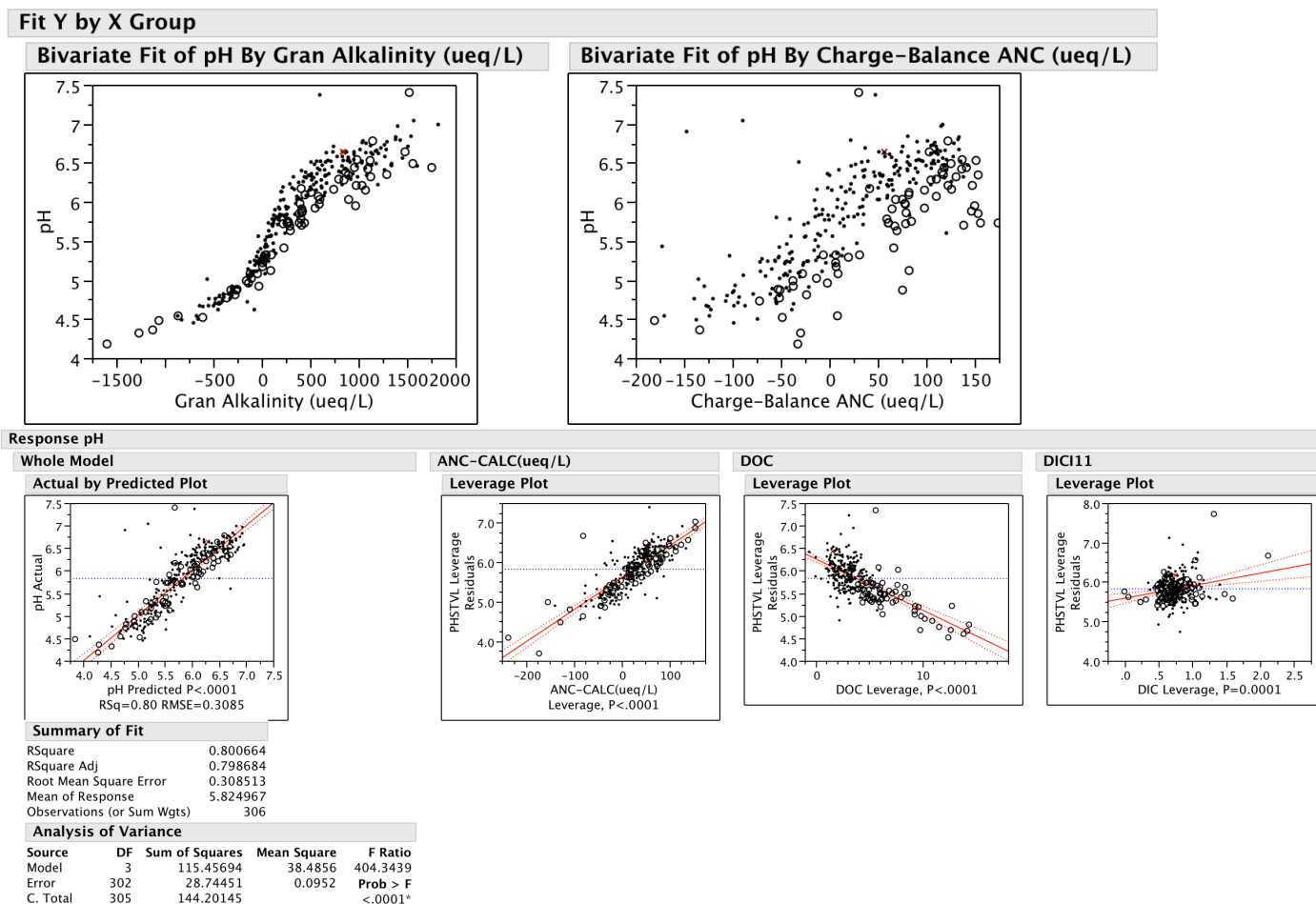


Slide: Tamara Blett, NPS / Multi-agency CL Working Group

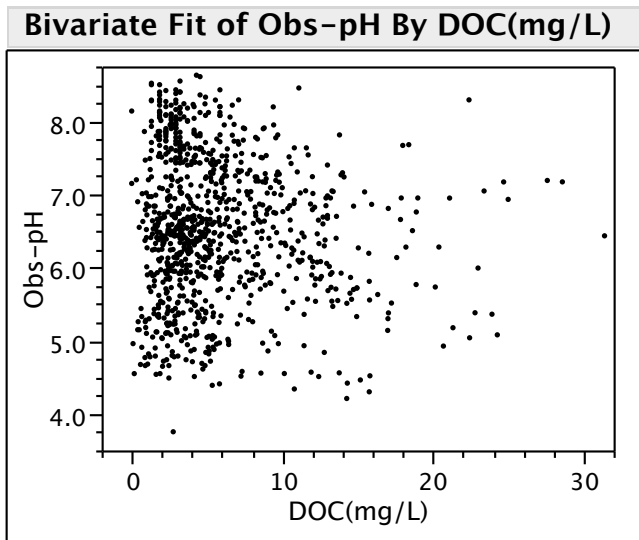
\*Baker et al. 1990

**Figure 1.** Relationship between pH and ecological effects showing the correspondence between pH and the Alkalinity – often loosely referred to (see figure caption) as ANC or acid neutralizing capacity. Alkalinity “ANC” and charge-balance ANC are different entities (see Morel and Hering 1993).

The relationship between DOC, pH and CBANC in waters representative of the project domain was investigated using the EPA ELS surface water data set for NY and New England. These data reveal that pH is strongly influenced by DOC (Figure 2, see also Morel and Hering 1993). Despite a general relationship of decreasing pH with increasing DOC (Figure 2) high pH conditions can exist where DOC is very high and low pH when DOC is low (Figure 3). Thus, a higher CBANC<sub>limit</sub> must be set for DOC rich waters than for low DOC waters to insure a given target pH is attained (Figures 4 and 5).



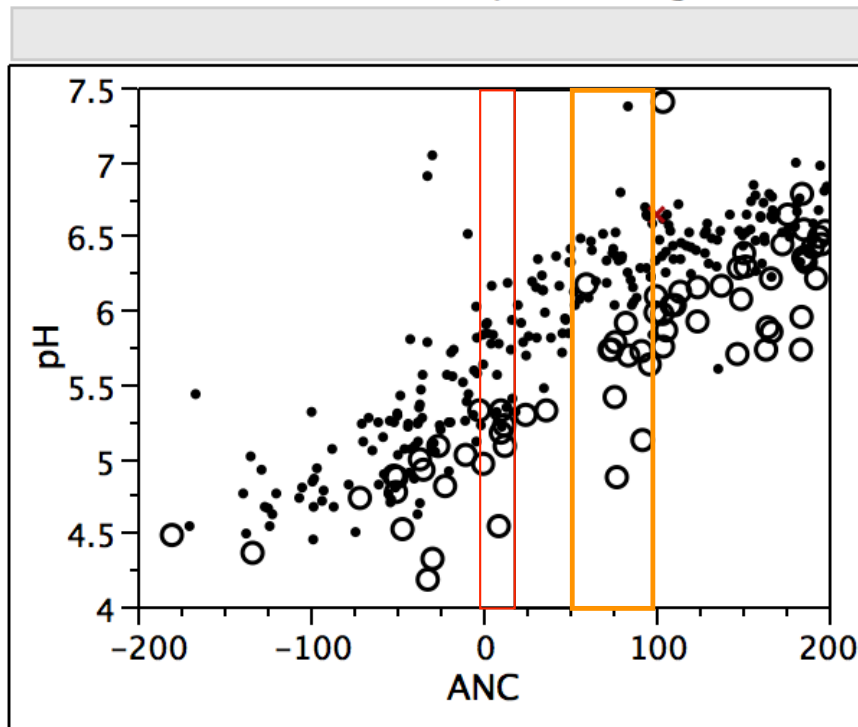
**Figure 2.** The relationships between pH and Alkalinity and charge-balance ANC (top). Regression model for pH as a function of CBANC, DOC and DIC (bottom).



**Figure 3.** Observed pH vs. observed DOC in training site sample. Note that high DOC does not always imply low pH. There are many observations of high-DOC, high-pH waters. Similarly, high DOC is not a prerequisite for a condition of low pH.

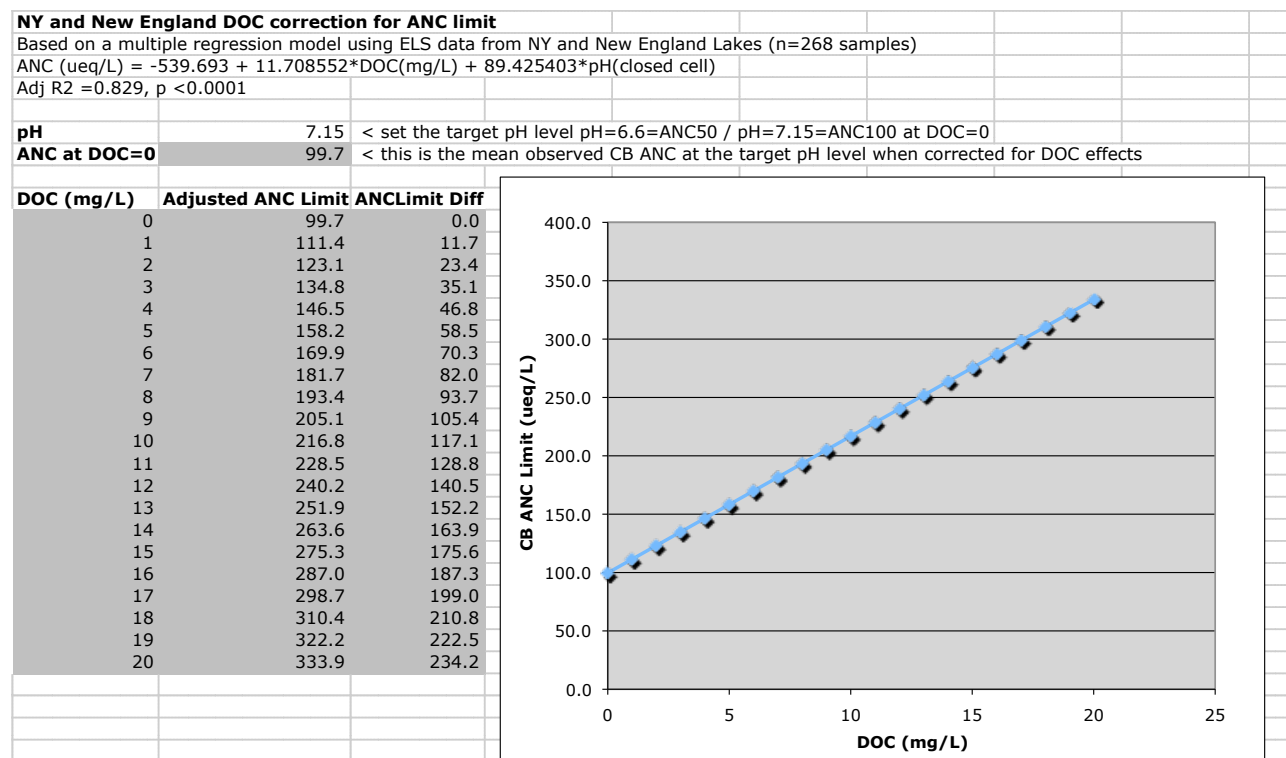
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Data Table=EasternLakesSurveyData4-Region1-ANCLT200



**Figure 4.** Different CBANC values are associated with a given pH depending the DOC content of surface waters. Open circles are high DOC waters.

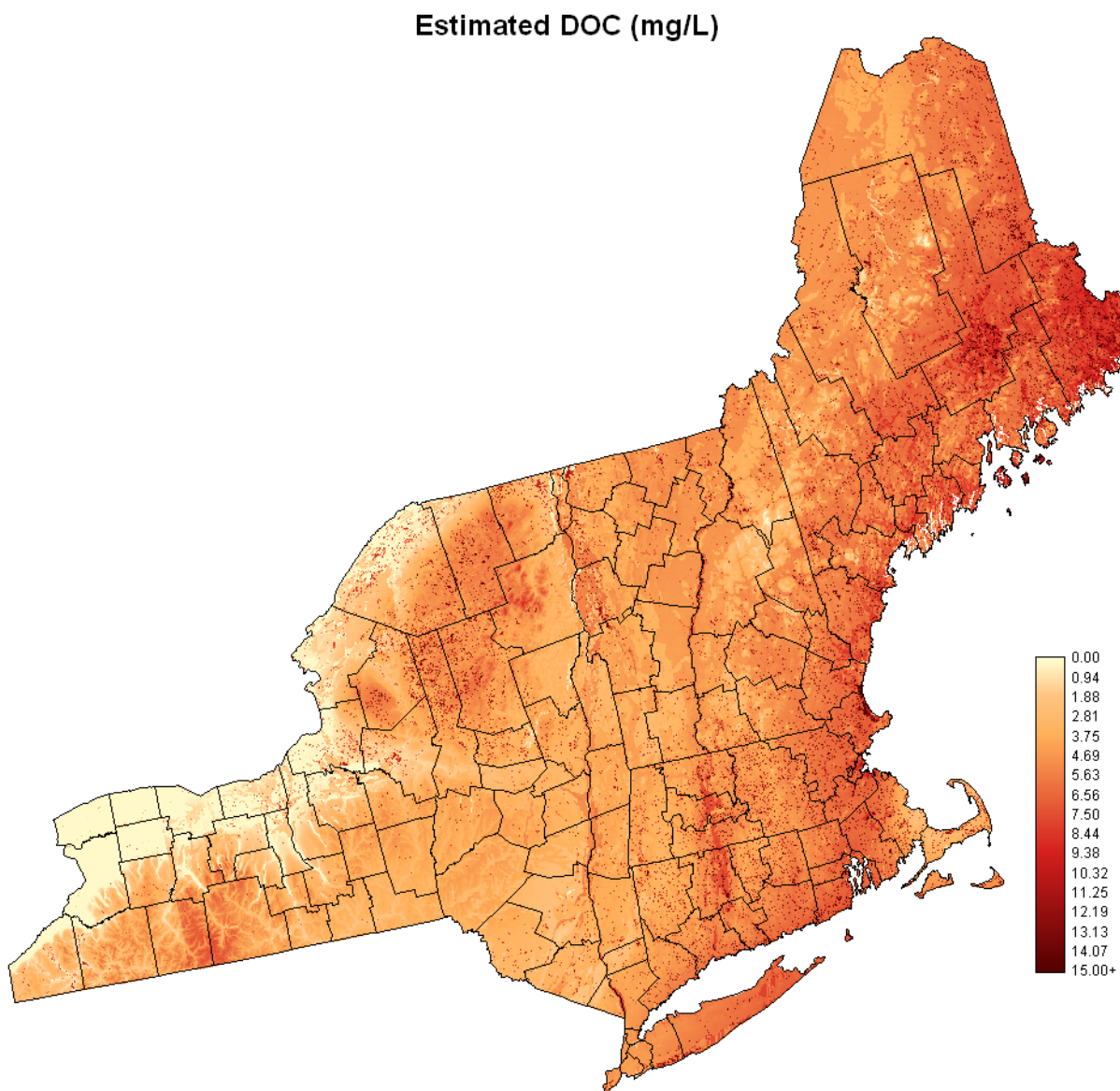
A regression model relating pH, CBANC, and DOC can be used to establish an empirical adjustment factor for the  $CBANC_{limit}$  that is representative of conditions in NY and New England waters. The model (Figure 5) explains 83% of the pH variance in sampled surface waters. While this adjustment model will not perfectly protect all water bodies with respect to the target pH, it is a rational approach to DOC correction for regional modeling. For surface waters of particular concern or sensitivity, and where adequate data exist, a specific correction can be developed.



**Figure 5.** Example of DOC adjustments to the  $CBANC_{limit}$  to attain a desired pH target in NY and New England. In this example the target pH is 6.6. At DOC=0 mg/L the appropriate  $CBANC_{limit}$  would be 50.5 ueq/L. At DOC = 5 mg/L the appropriate  $CBANC_{limit}$  would be 109 ueq/L. At DOC = 10 mg/L the appropriate  $CBANC_{limit}$  would be 168 ueq/L.

## Regional Estimates of DOC concentrations

In order to generate regional estimates of aquatic critical loads for all surface waters, it is first necessary to have regional estimates of DOC concentrations in all surface waters. DOC concentrations in the region (from measured surface water samples) ranged from 0 to 25 mg/L. The DOC concentration is required for calculating the DOC-adjusted value of the charge-balance  $ANC_{limit}$  associated with the scenario target pH (see figure 5 and text above). All available project data layers were systematically explored to search for good predictors for DOC concentrations in the training sites. Figure 6 shows the best empirical model for surface water DOC concentrations obtained from available data.



**Figure 6.** Regional estimate of surface water dissolved organic carbon (DOC) concentration.

The empirical model used to estimate surface water DOC concentrations is shown below. Sensible predictor variables such as wetland parameters, surficial material type, latitude, longitude, and elevation entered the model. DOC is in units of mg C / L. See NPSCL-TD3-NY-Terrestrial-CL.pdf and NPSCL-TD4-Aquatic-CL.pdf for more information on data layers used as input for this model. Observed DOC concentrations at the training sites varied widely across the landscape and were not very amenable to modeling with available data layers. The best model was only able to explain less than 50% of variance in observed DOC concentrations (Figure 7). Given the very strong dependence of the  $ANC_{limit}$  on DOC (see discussion above), the regional estimates of surface water DOC concentrations (Figure 6) were used in aquatic critical loads modeling despite the modest predictive ability of the model. As sensible broad regional (gradients from coast to interior and north to south) as well as local (elevation dependent, surficial materials dependence) patterns were well represented in the model, use of this layer reduces the uncertainty in aquatic critical loads estimates relative to the case where DOC is completely ignored or represented by an average value.

$$\begin{aligned}
 \text{DOC} = & 52.25 \\
 & - 0.1823 * \text{Latitude (in decimal degrees)} \\
 & + 0.5122 * \text{Longitude (in decimal degrees)} \\
 & - 0.00257413 * \text{Elevation (in meters of the target grid cell)} \\
 & + (\text{Longitude} + 71.51153) * ((\text{Elevation} - 291.40) * -0.0036331) \\
 & + ((\text{Elevation} - 291.40) * (\text{Latitude} - 43.91869) * 0.00341242) \\
 & - 9.2055 * \text{Flow-averaged Atmospheric Deposition of Cl (keq/ha/y)} \\
 & + 3.252 * \text{Flow-averaged Wetland fraction} \\
 & - 0.3997 * \log(\text{Flow-averaged Percent Clay})
 \end{aligned}$$

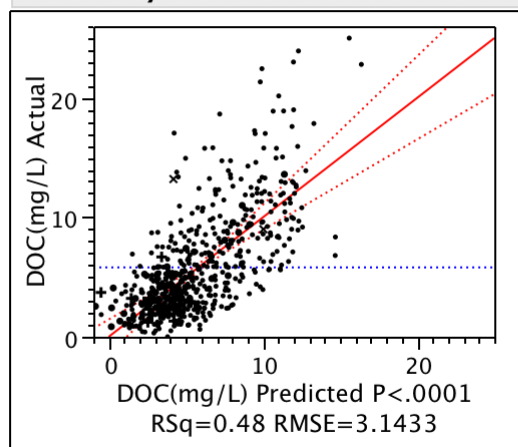
If the surficial material mapped is:

Calcareous Rocks - 1.08  
 Coarse-grained stratified sediment + 0.49  
 Fine-grained stratified sediment + 2.50  
 Thick till + 0.79  
 Thin or patchy till - 0.39  
 Organic-rich sediment + 0.26  
 Water (geologic data unknown) - 2.57

If the cell is classified in the NLCD as wetland then + 3.85 otherwise for non-wetland cells - 1.65

If the cell is classified in the NLCD as water then if the number of grid cells contributing to the target cell is > 10,000 then -0.75, otherwise - 1.30



**Response DOC(mg/L)****Actual by Predicted Plot****Summary of Fit**

RSquare	0.475484
RSquare Adj	0.457783
Root Mean Square Error	3.143252
Mean of Response	5.804496
Observations (or Sum Wgts)	583

**Analysis of Variance**

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	19	5042.483	265.394	26.8616
Error	563	5562.457	9.880	<b>Prob &gt; F</b>
C. Total	582	10604.940		<.0001*

**Figure 7.** Predictive ability of the regional surface water DOC estimate. Observed values are from the training site data set described in NPSCL-TD4-Aquatic-CL.pdf.