Distribution of carbon in Catskills soils and production of DOC

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Dissolved Organic Carbon (DOC)

- Naturally occurring
  - Derived from leaching of organic matter in soils and litter in stream and lake beds.
  - Plant, animal and microbial sources.
- Highly variable in composition
  - Due to wide range of source materials.
  - "Weak acid polyelectrolytes".
    - —COOH and >—OH functional groups are weakly acidic.
    - Dissociate to $—COO^-$ and $>—O^-$ as pH increases.
- Important biogeochemical driver
  - Acid-base chemistry.
  - Trace metal transport.
  - Ecological function (talks to follow).

DOC and Disinfection By-products

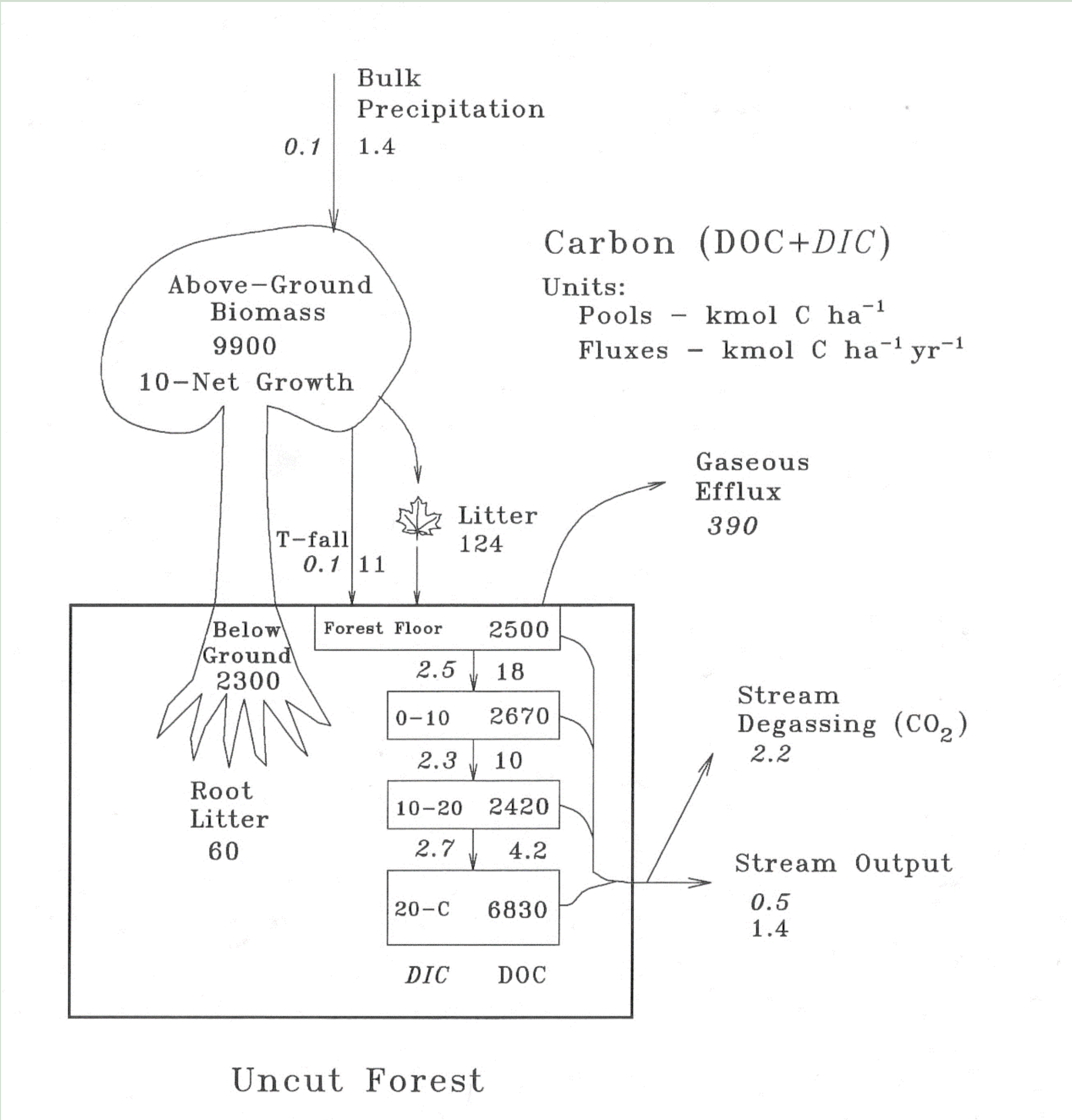
Oxidation of DOC can produce byproducts that are carcinogenic:

Table 1. Disinfectants and Associated Disinfection By-products

Disinfectant	Disinfectant By-product
Chlorine (e.g. gas, sodium hypochlorite, tablets, OSEC)	Trihalomethanes, Haloacetic Acids, Chloramines[1], Chlorinated Acetic Acids, Halogentated Acetonitriles, Chloral Hydrate, Chlorophenols, MX[2], bromate[3], chloropicrin, halofurans, bromohydrins.
Chlorine Dioxide	Chlorite, Chlorate and Chloride.
Ozone	Bromate, Formaldehyde, Aldehydes, Hydrogen Peroxides, Bromomethanes.
Chloramines	Dichloramines, Trichloramines, Cyanogen Chloride, Chloral Hydrate.

https://www.epa.ie

DOC in the Forest Carbon Cycle



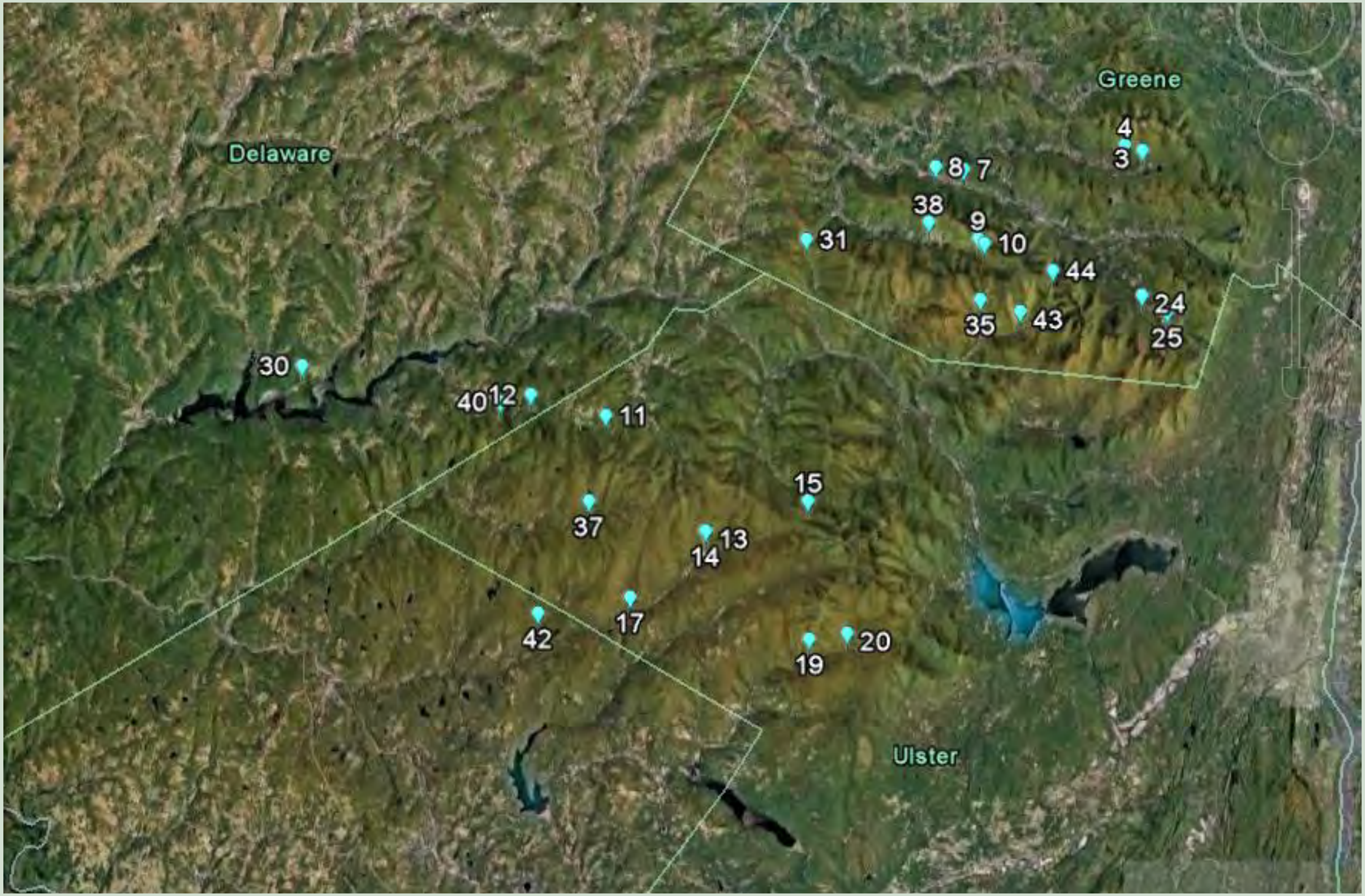
Hubbard Brook Experimental Forest, NH

Johnson et al. (1995)

Sampling Sites

Twenty-five headwater catchments:

- Selected from sites studied by Lovett et al. (2000)

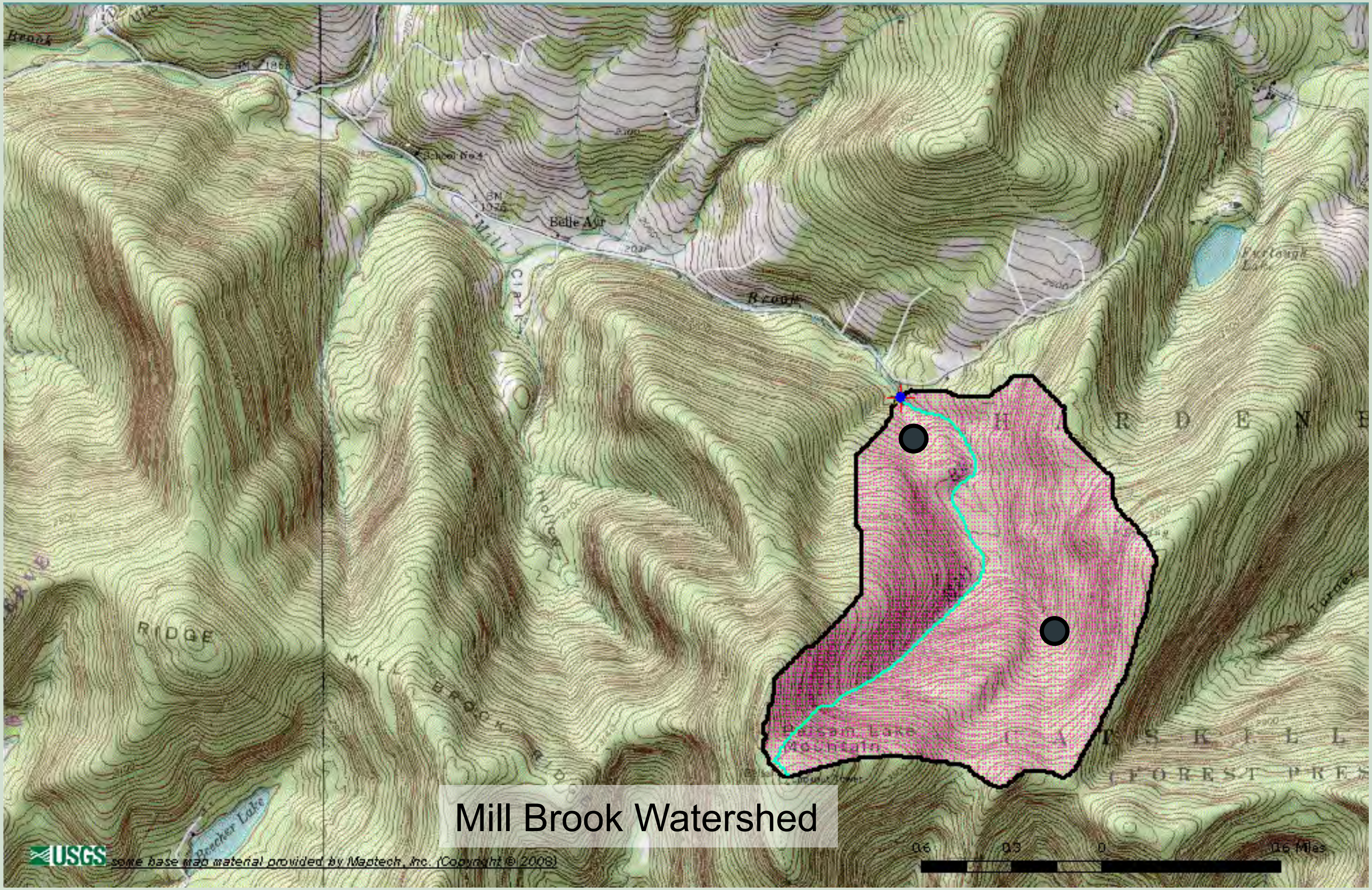


Site Selection for Soil Sampling

In each watershed:

- One site near stream sampling location.
- One site at elevation approximately half-way between stream sampling site and watershed divide.
- Total = 50 pits [25 watersheds x 2 pits]
  - Sample sites that actually have soil
  - Sample range of forest types
  - State land – low probability of land-use change

Soil Sampling Site Selection



Sampling Method

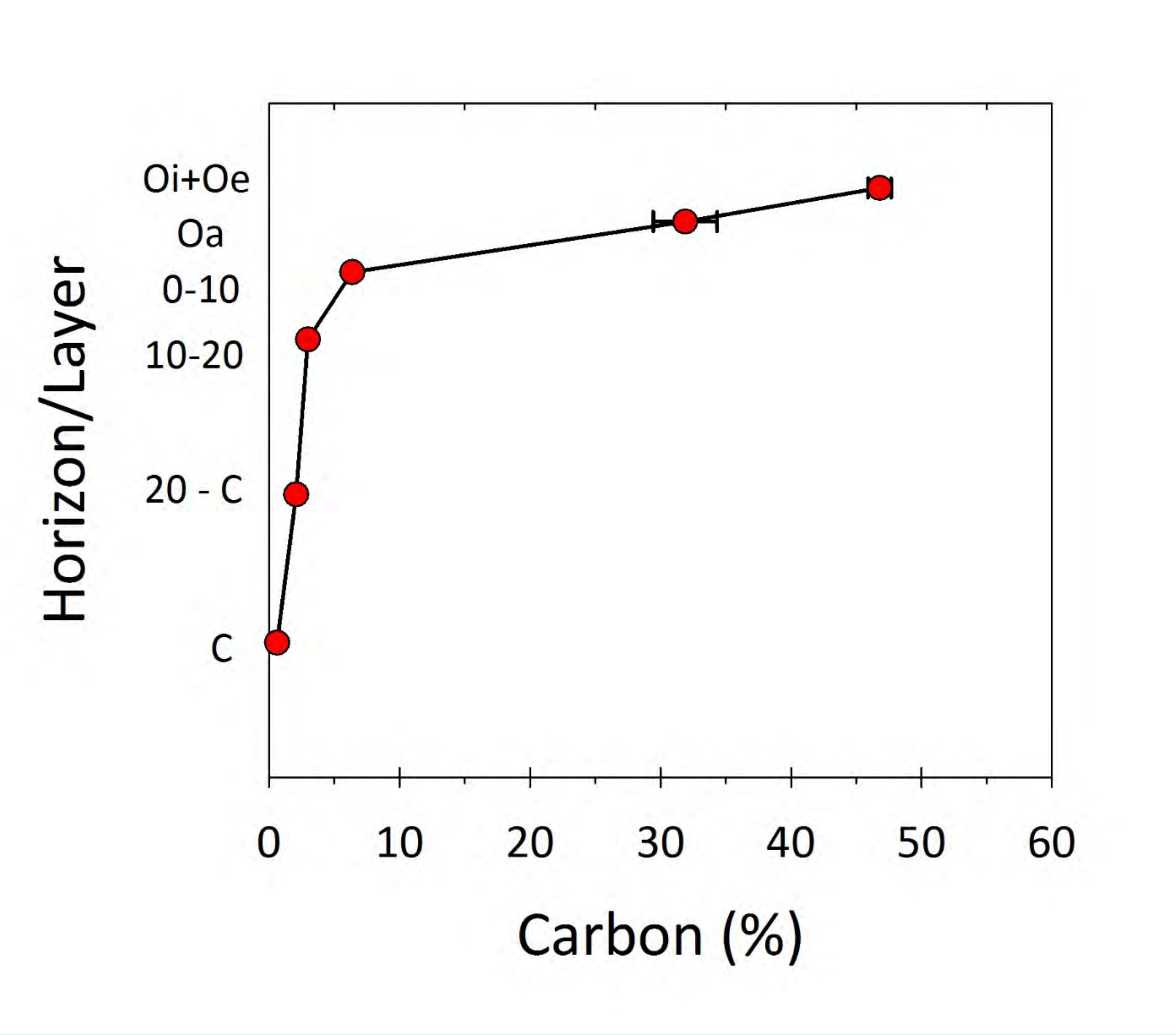
"Quantitative" soil pits

Sampling Method

"Quantitative" soil pits:

- Direct measurement of soil mass (kg m^{-2})
- Calculate soil chemical pools
- Layers sampled:
  - + Oi+Oe
  - + Oa/A
  - + Mineral soil by depth increment: 0-10 cm, 10-20, 20-C

Soil Carbon Profile



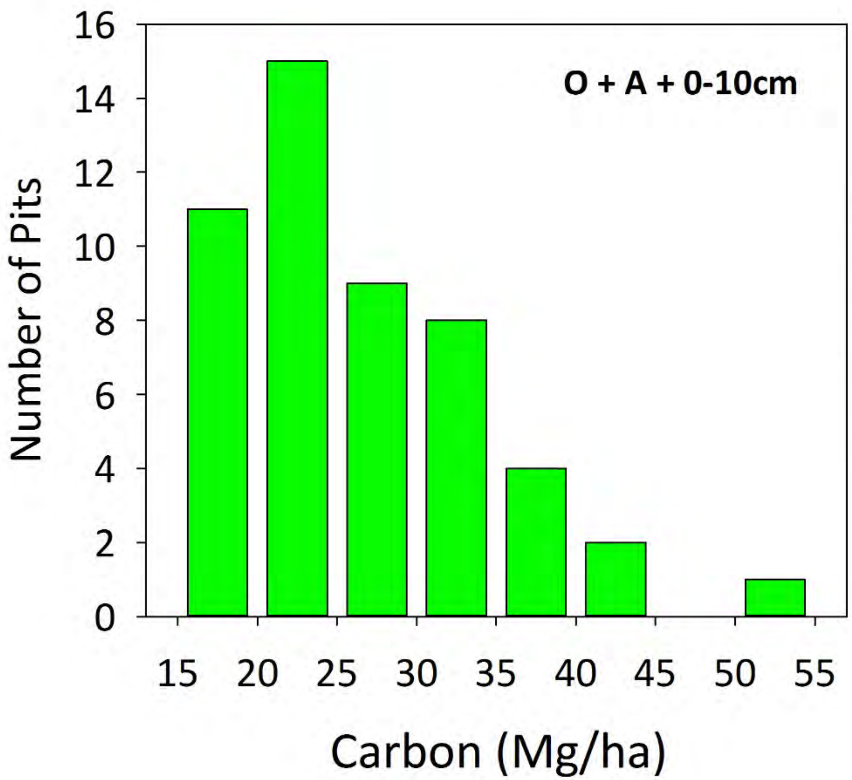
Soil Carbon Pools in Catskills Soils

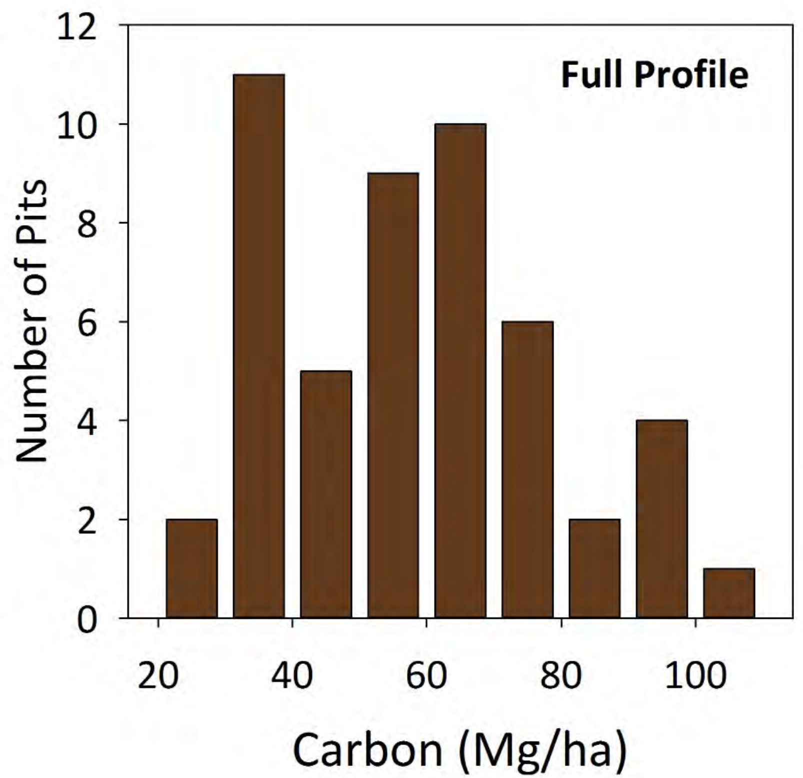
Horizon/Layer	Soil Carbon ($Mg\ ha^{-1}$)	Soil Nitrogen ($Mg\ ha^{-1}$)	C:N Ratio
Oi+Oe	6.6	0.34	19.8
Oa/A	1.5	0.08	17.0
0-10 cm	17.8	1.16	16.1
10-20 cm	11.1	0.80	13.9
20 cm – C Horizon	21.2	1.53	13.4
Total	**58.2**	**3.91**	**14.9**

Soil Carbon Distribution

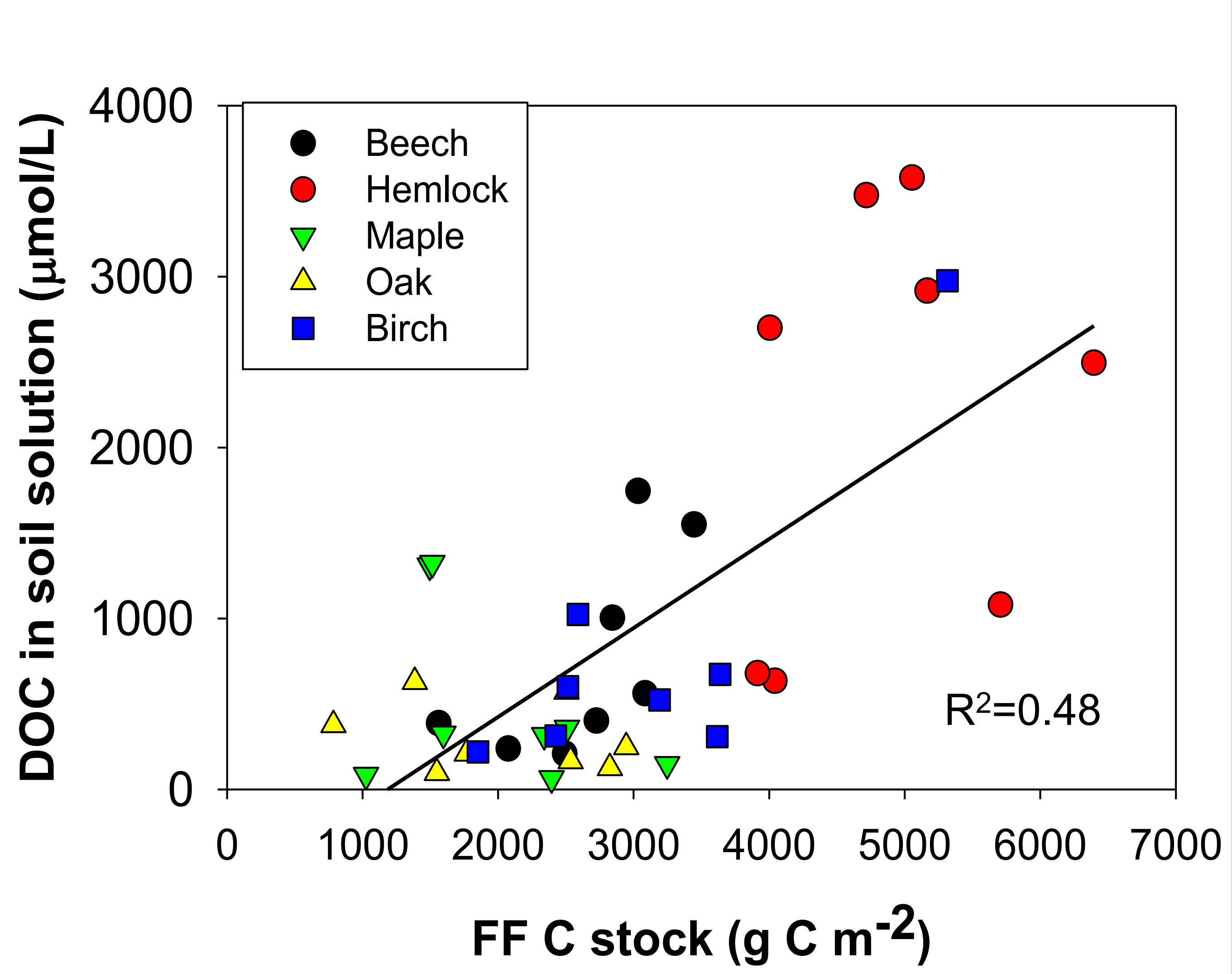
Mean: 26.0
Median: 24.3
Std. Dev.: 8.2

Mean: 58.5
Median: 57.7
Std. Dev.: 20.6





DOC in soil solution is correlated with forest floor C stock…

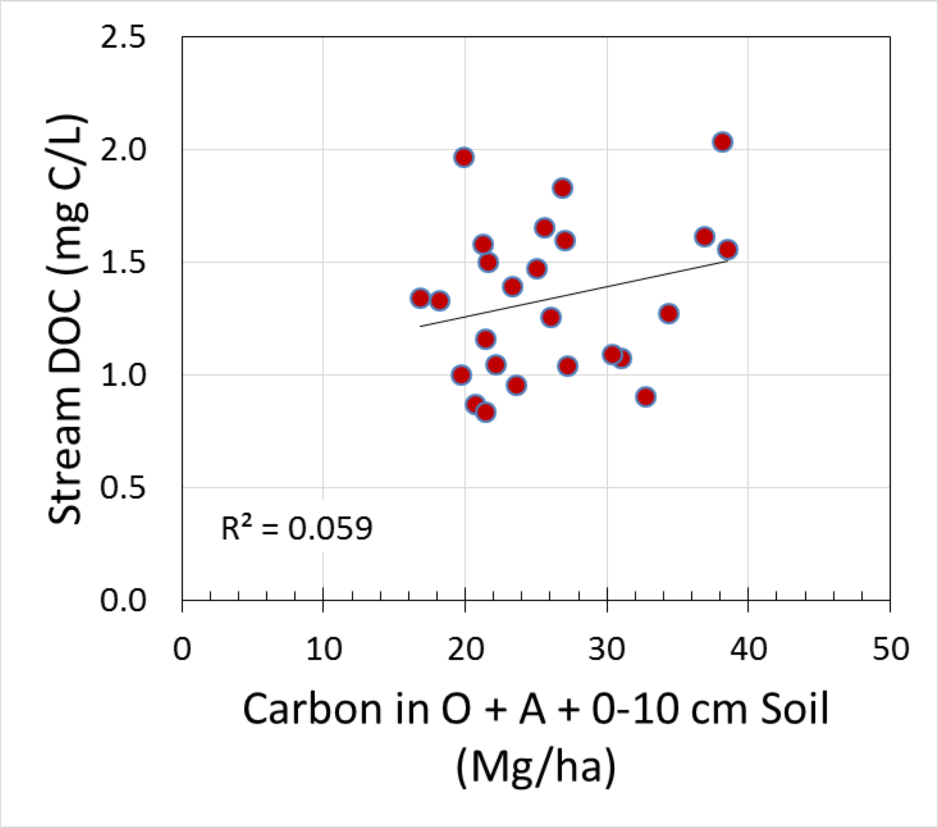


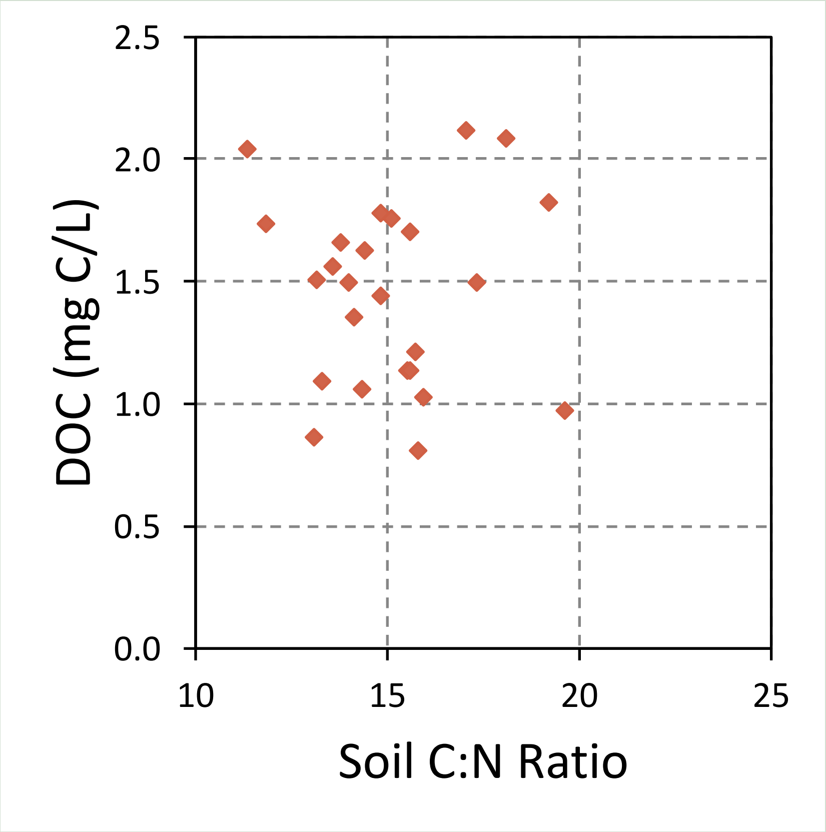
- Single-species plots
- Tension lysimeters in lower B horizon.

Lovett et al. (2013)

…But Stream DOC is Not Related to Soil C

- Soil Data: 2011
- Stream Data: 2010-2013





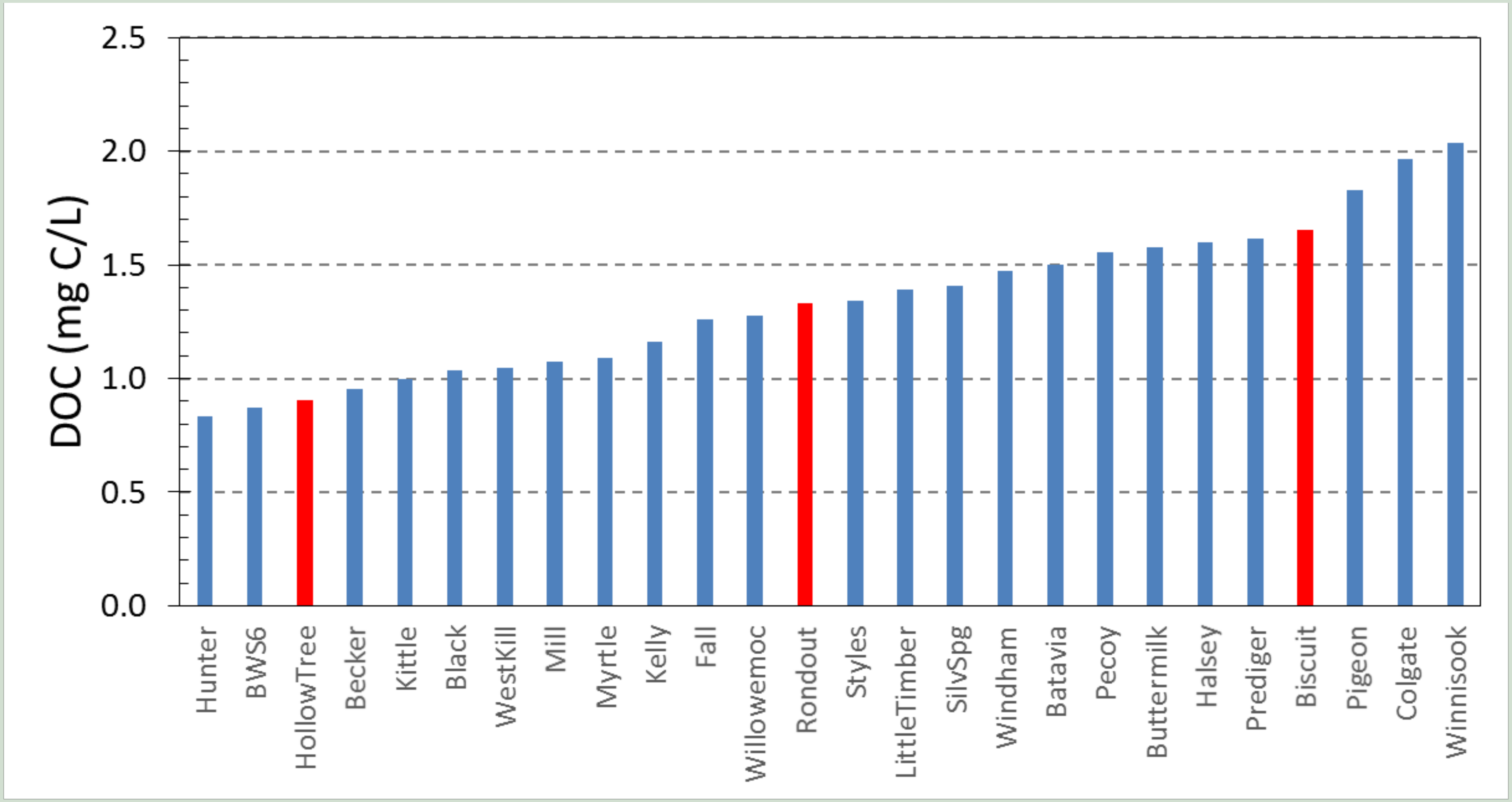
Factors Influencing DOC Release

- Ionic strength
  - DOC is fundamentally *hydrophobic.* Ions in solution make DOC more soluble through interactions with polar and ionizable functional groups in DOC.
- Solution pH
  1. As pH increases, negative charge of DOC increases.
  2. As pH increases, positive charge of soil adsorption sites decreases.

Mean DOC in 26 Catskills Streams

6/2010 - 7/2013

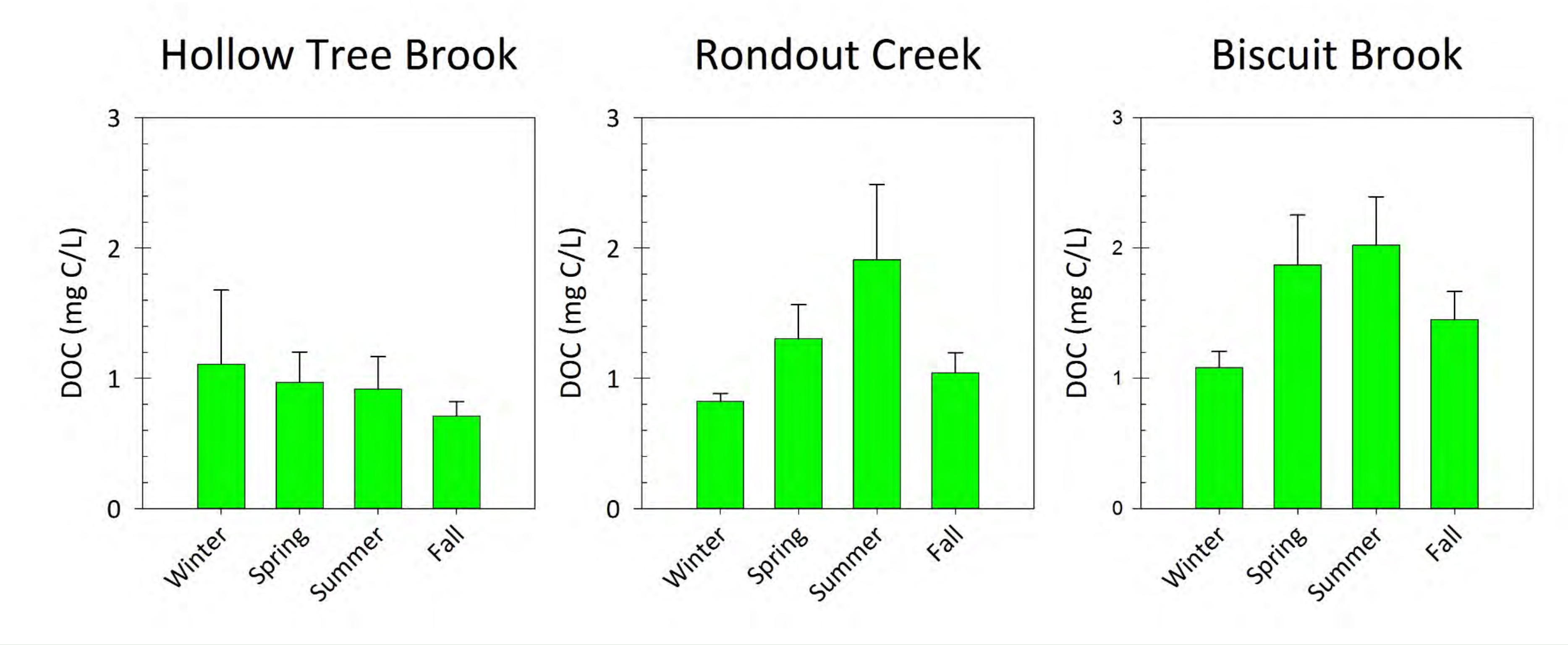
Monthly Sampling (when flowing)



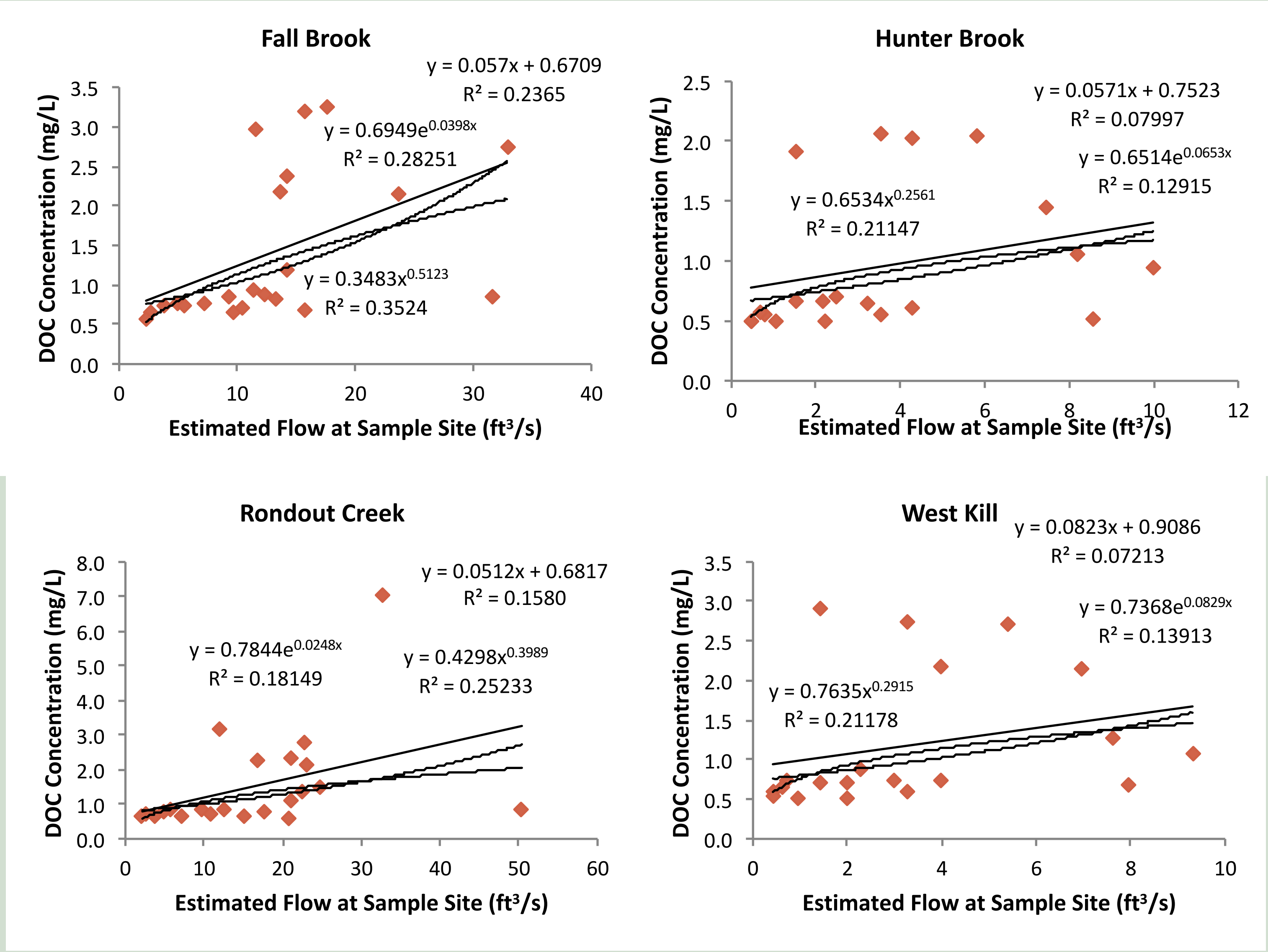
Seasonal Patterns in Stream DOC

6/2010 - 7/2013

Monthly Sampling (when flowing)

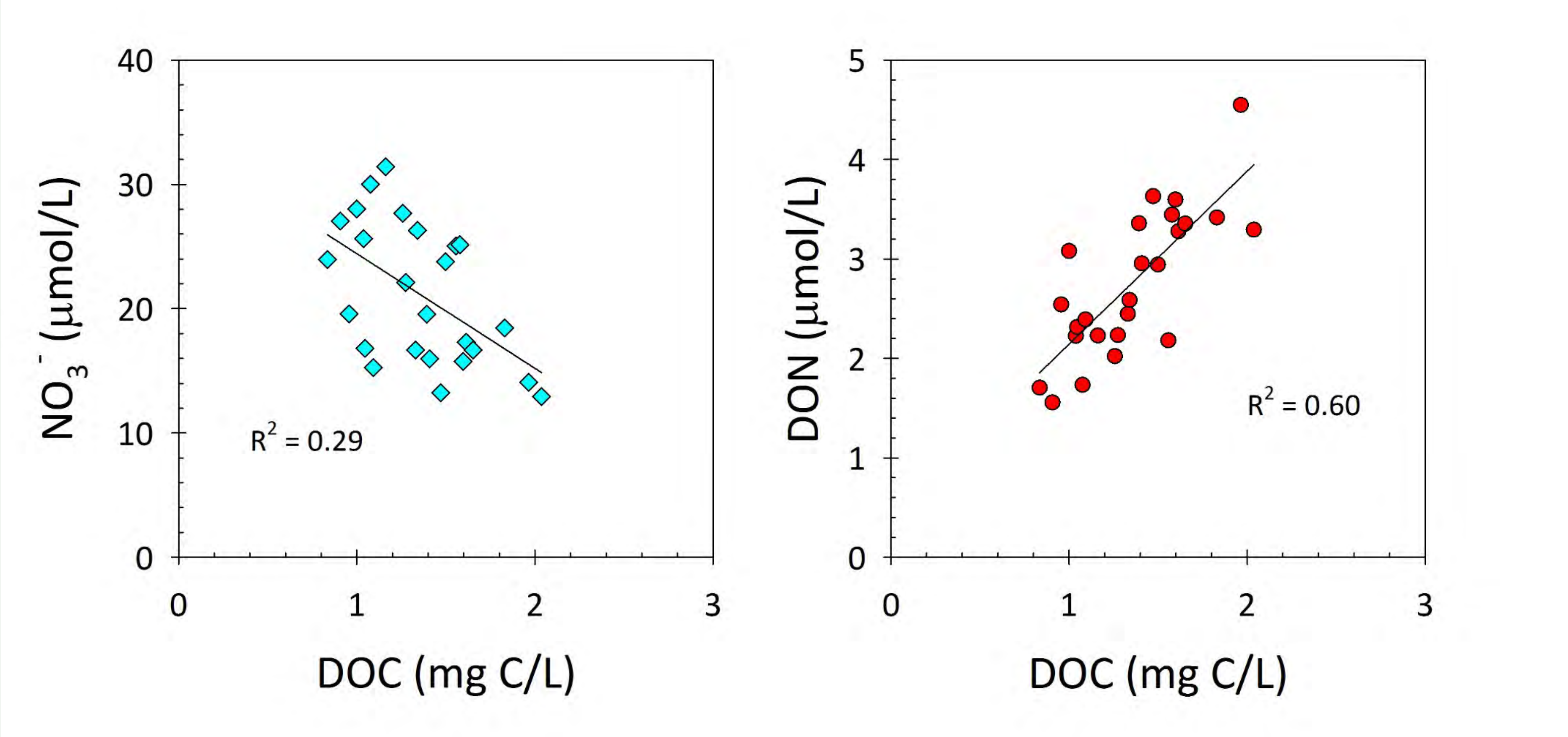


DOC is Only Weakly Related to Flow



Gianfagna (2013 - Thesis)

DOC Linkages to Stream N

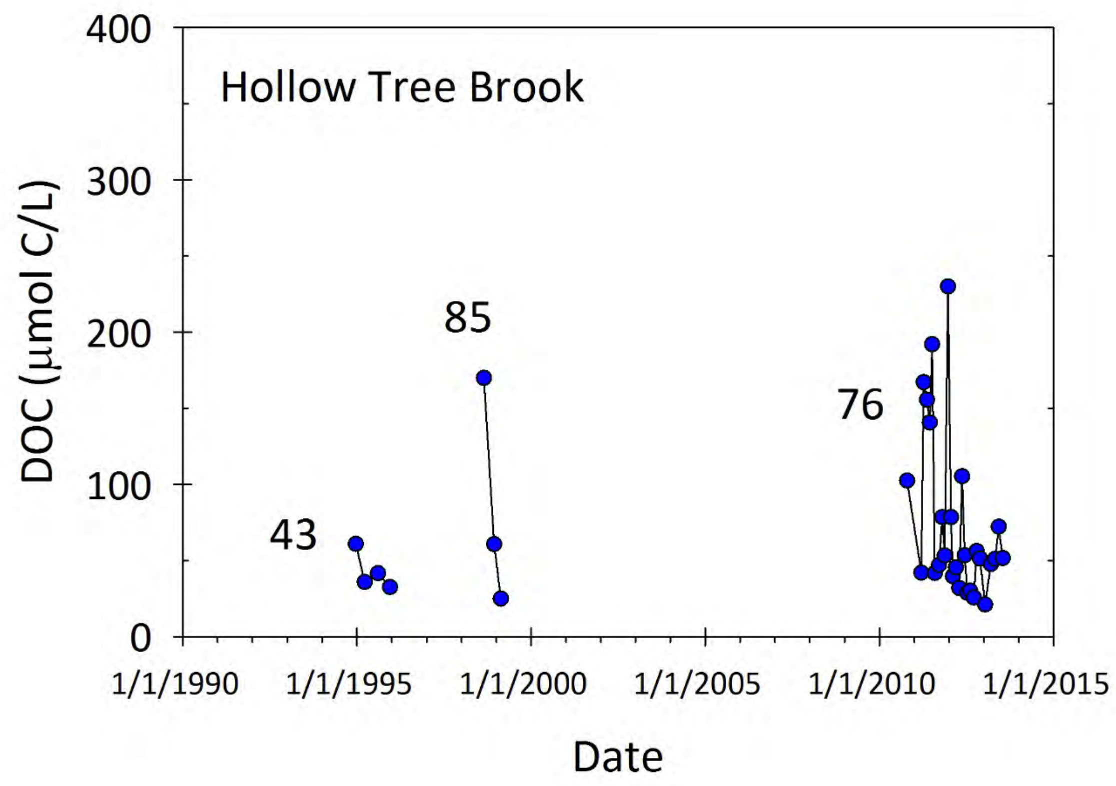


Is DOC Increasing in Catskills Streams?

Factors Influencing DOC Release:

- Ionic strength – Decreasing → Should *DECREASE DOC*
- Solution pH – Increasing → Should *INCREASE DOC*

Long-Term Changes in Stream DOC



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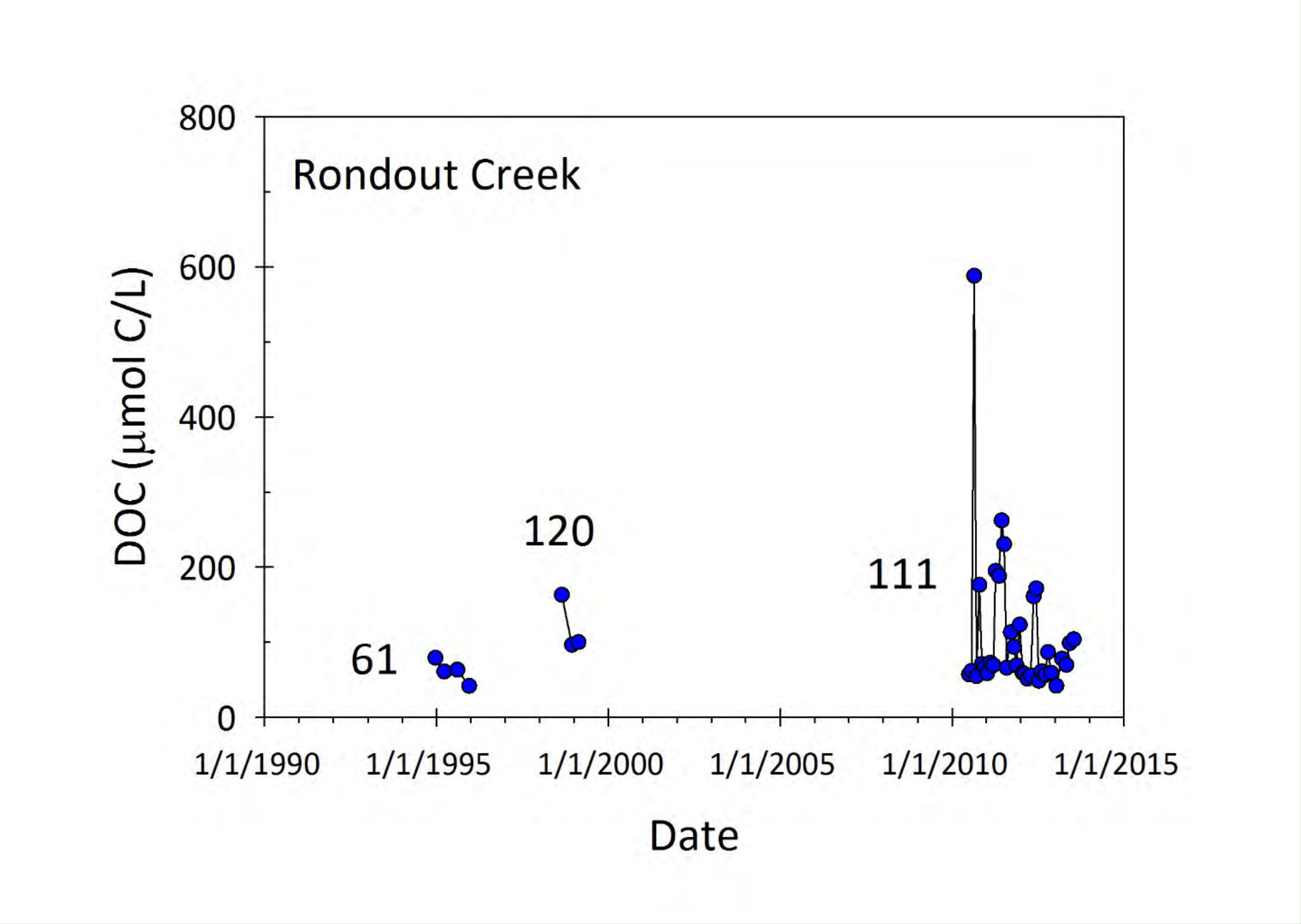

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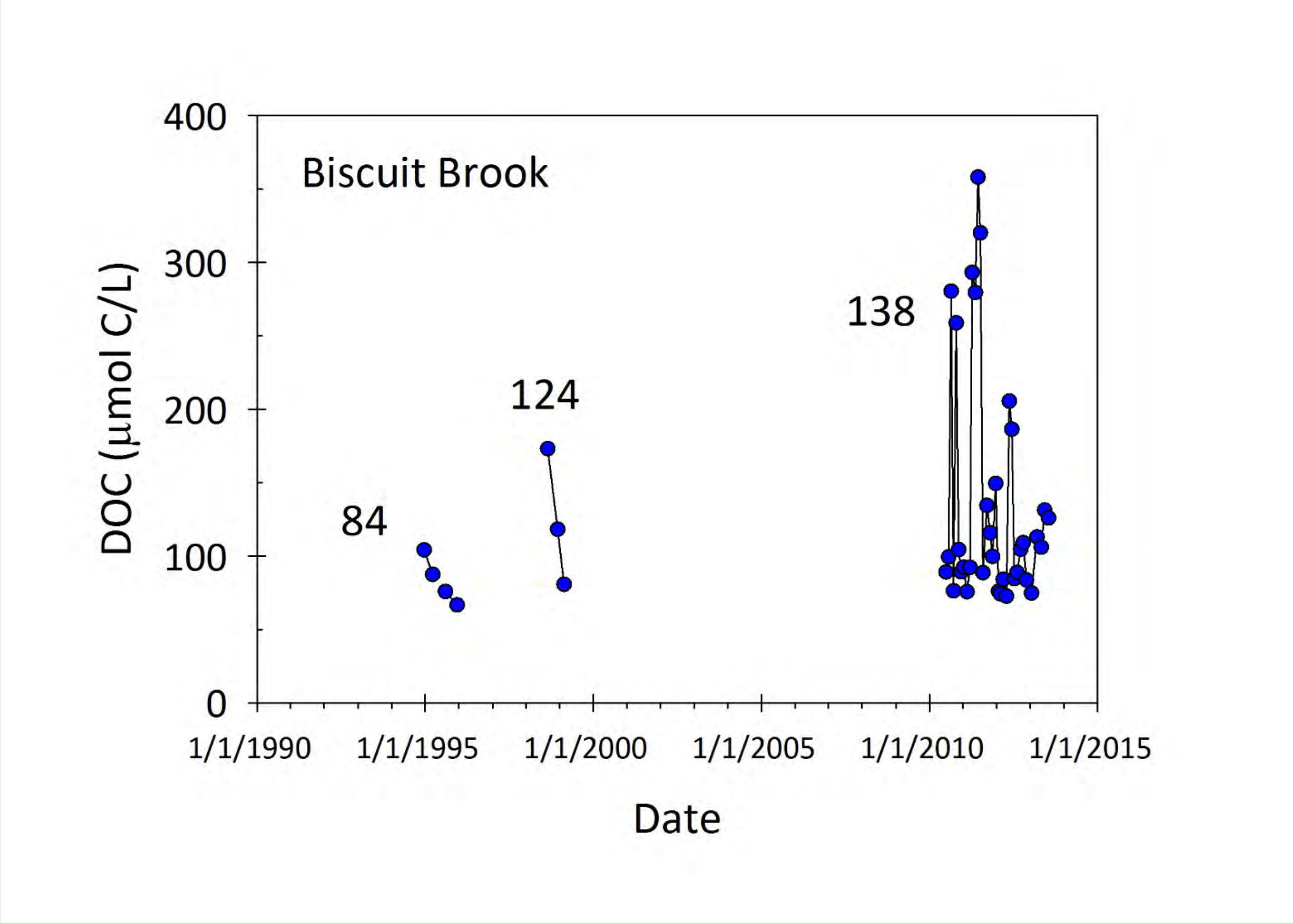

Conclusions

- DOC is produced by leaching soil C, especially from forest floor soils.
- DOC concentrations in Catskills streams are remarkably uniform. There is more temporal variation in individual streams than total variation among the 26 sample streams.
- DOC concentrations in 26 Catskills streams appear to be increasing, consistent with increasing pH and with other studies in Europe and North America.
- (Further) DOC increases in stream waters could result in compliance issues related to disinfection byproducts.