

Predicting DOC response to reductions in acid deposition

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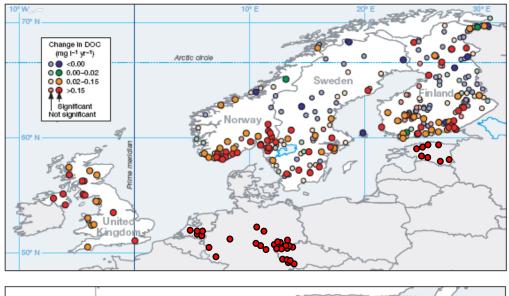
With particular thanks to:

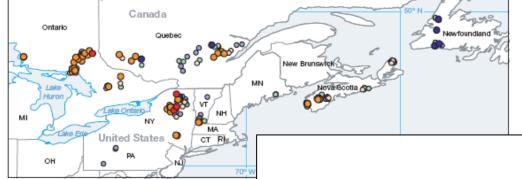
Peter Henrys, Jakub Hruška, Heleen De Wit, Pavel Krám, Iain Malcolm, Filip Moldan, Gloria Pereira, Antii Räike, John Stoddard & Chris Evans





Hemispheric scale increase in Dissolved Organic Carbon (DOC) over recent decades







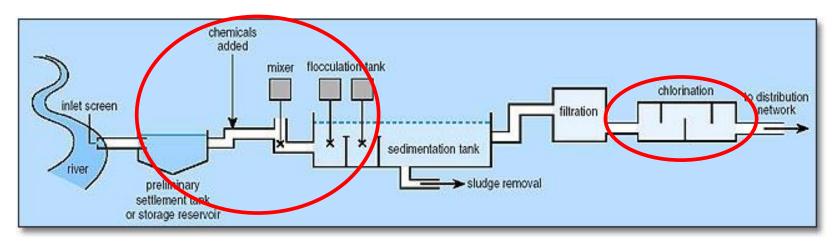


Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry

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Economics of Dissolved Organic Matter (DOM)

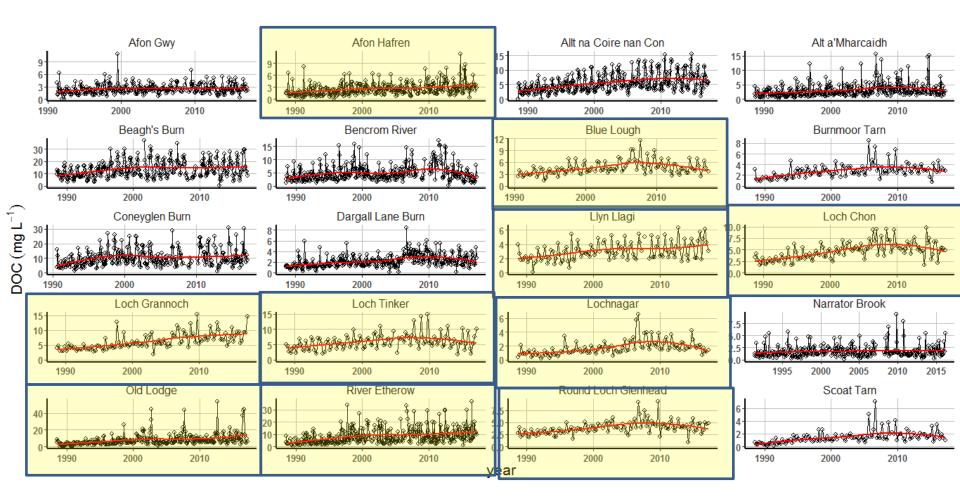
- Upland catchments with organic-rich soils provide 70% of UK drinking water (Defra, 2011)
- DOM + chlorination = Trihalomethanes (THMs)



- DOM removal for typical plant (processing 60 ML/day)
 = £480K per year. (NEA, 2010)
- Scaled up for 70% UK population (150 litres/person)
 £50 million per year



Continuing or flattening out in the UK?







Industry needs to know what will happen next

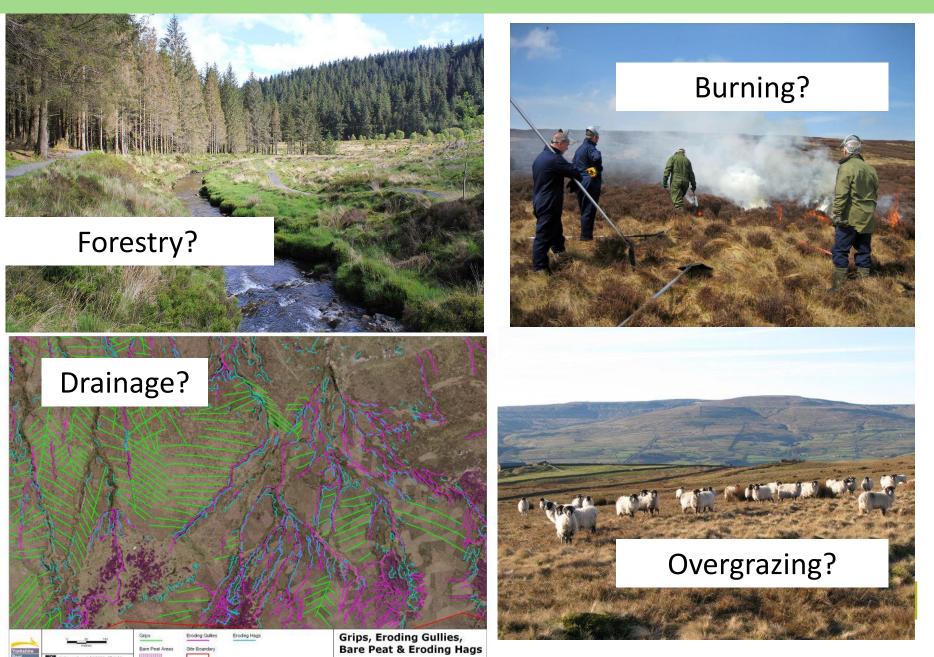
in order to:

- Identify water treatment plants most at risk of exceeding threshold concentrations
- Plan for future coagulant use
- Determine potential to intervene at catchment level

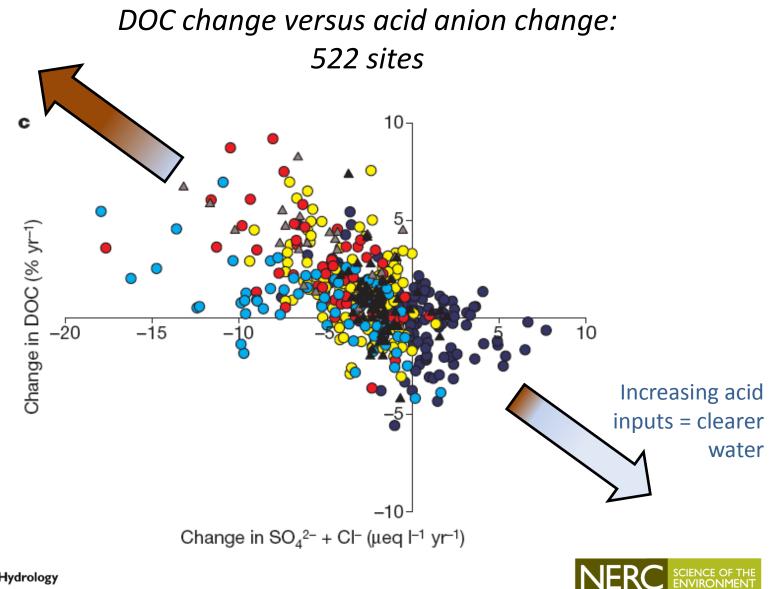




Would it help to control.....?



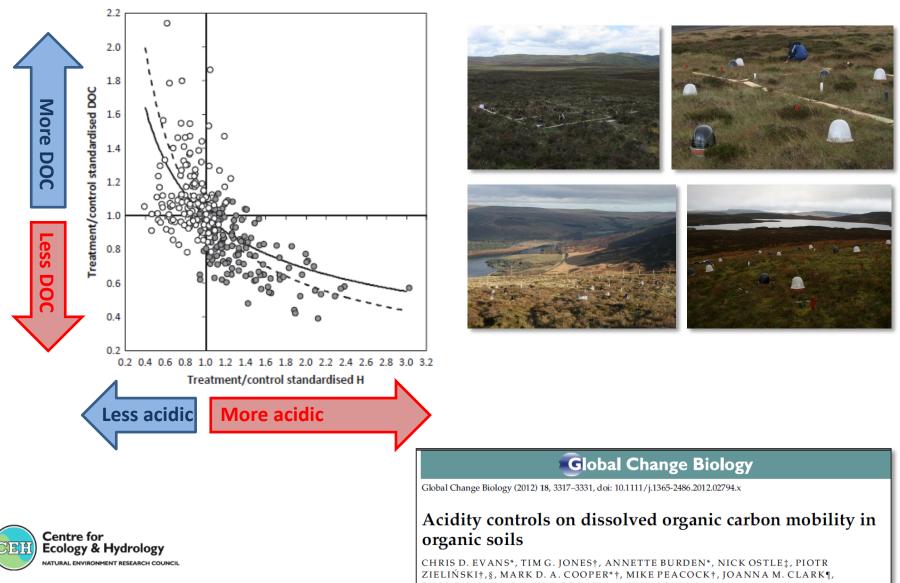
DOC trends linked to trends in acid anions



Centre for Ecology & Hydrology NATURAL ENVIRONMENT RESEARCH COUNCIL

Monteith et al., Nature 2007

and soil acidity



FILIP OULEHLE* ||, DAVID COOPER* and CHRIS FREEMAN†

.....and ionic strength of runoff

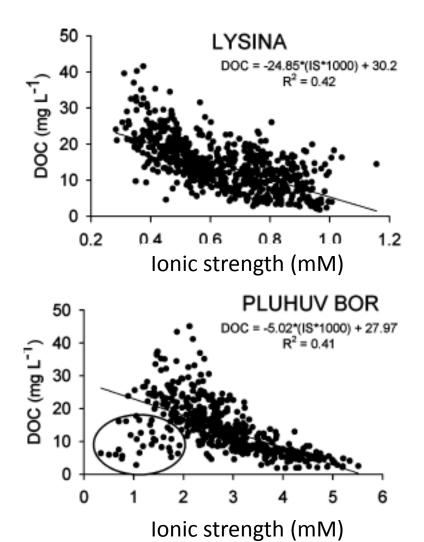


Increased Dissolved Organic Carbon (DOC) in Central European Streams is Driven by Reductions <u>in Ionic</u> <u>Strength</u> Rather than Climate Change or Decreasing Acidity

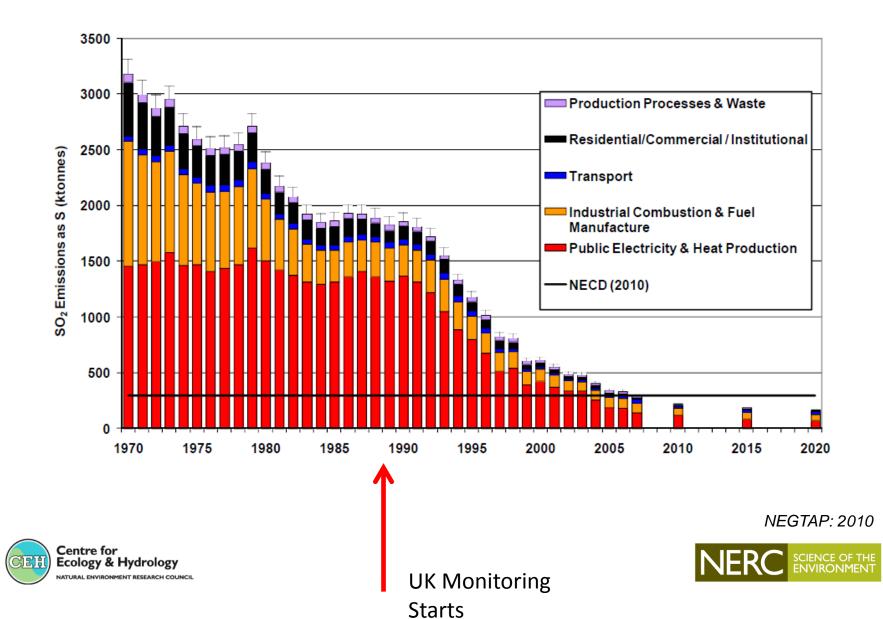
JAKUB HRUŠKA,*,[†] PAVEL KRÁM,[†] WILLIAM H. MCDOWELL,[‡] AND FILIP OULEHLE[†]

Czech Geological Survey, Klárov 3, 118 21, Prague 1, Czech Republic, and Department of Natural Resources and the Environment, University of New Hampshire, Durham, New Hampshire 03824

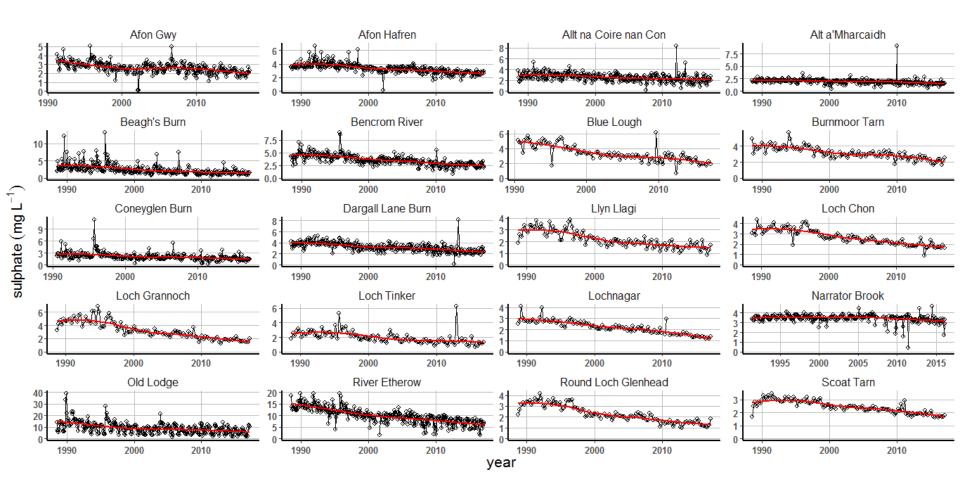
$$IS = 0.5 \text{ x } \Sigma_i c_i Z_i^2$$



Last few decades - huge reduction in UK sulphur emissions and sulphur deposition



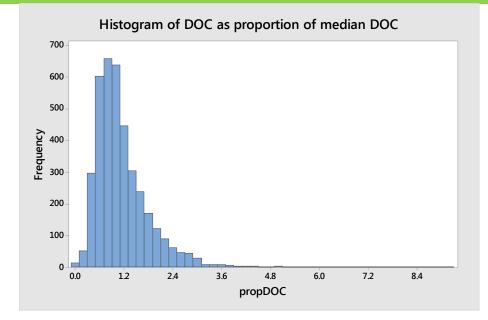
Lagged response in surface water sulphate. Concentrations continue to trend downwards at several sites







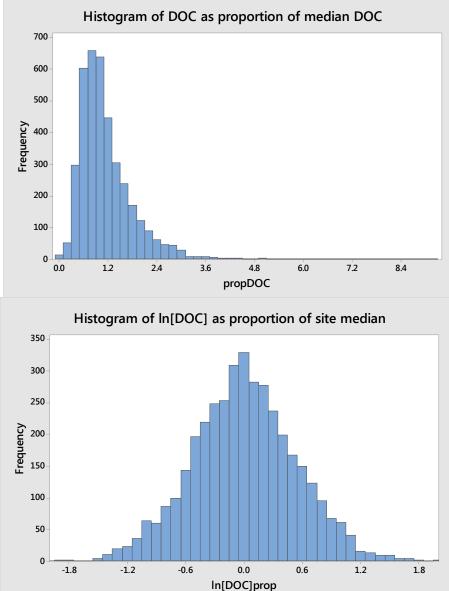
UK DOC data (20 sites, 3700 data points) transformed to: proportion of site median DOC







UK DOC data transformed to: proportion of site median.....and then logged (In DOC_{prop})







What hydrochemical variables best explain variation in $In \ DOC_{prop}$?

Candidates

- SO₄²⁻ concentration
- Cl⁻ concentration
- Sum Acid Anions (SAA) $(SO_4^{2-} + CI^- + NO_3^{-})$
- ANC (Sum Base Cations Sum Acid Anions)
- Ionic strength (IS) $IS = 0.5 \ x \ \Sigma_i c_i Z_i^2$

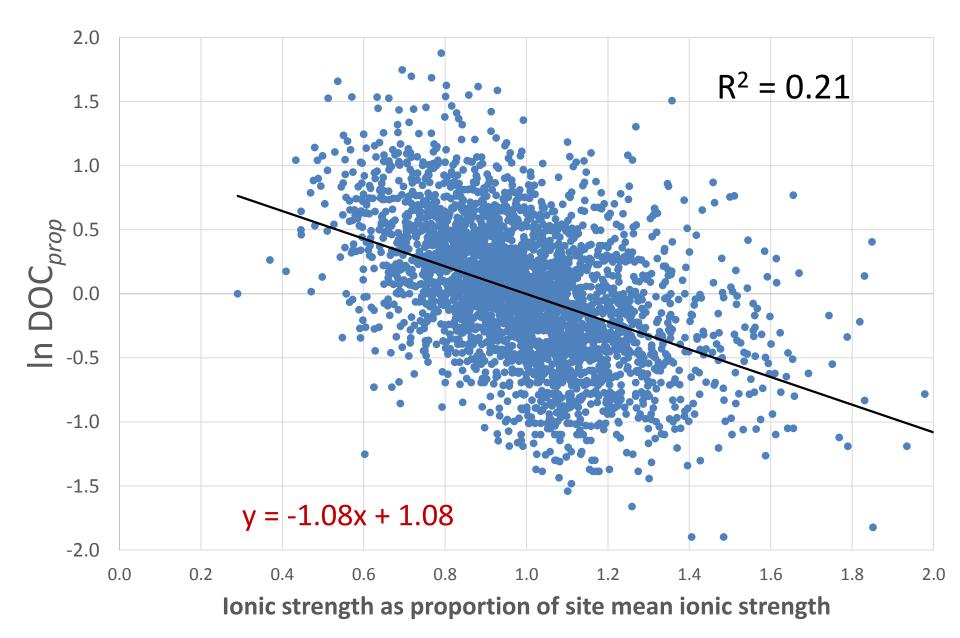
Expressed as:

- Absolute concentrations
- Difference from site mean concentration
- Proportion of site mean concentration





$In DOC_{prop} = 1 - Ionic strength_{prop}$



Model refined by site-specific calibration

site *i* time *t*

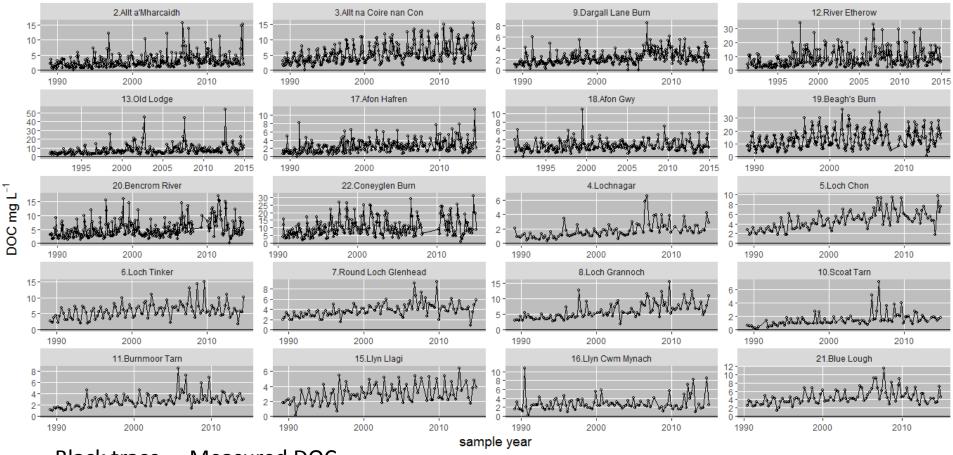
$$\ln DOC_{prop(i,t)} = f - f^* IS_{prop(i,t)}$$

$$DOC_{(i,t)} = DOC\bar{x}_{(i)}.e^{(f - f*ISprop(i,t))}$$

Where f = site-specific IS – DOC calibrated constant Ranging from 1 - 3 depending on base-flow index



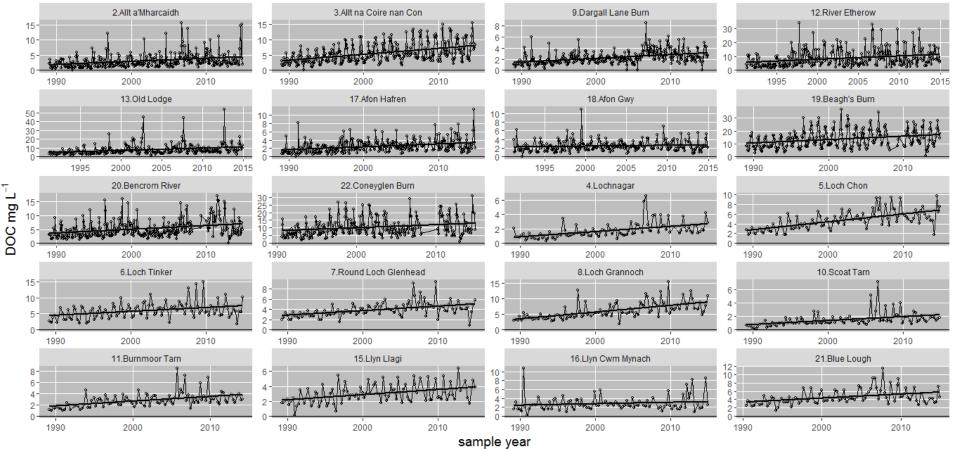




Black trace = Measured DOC



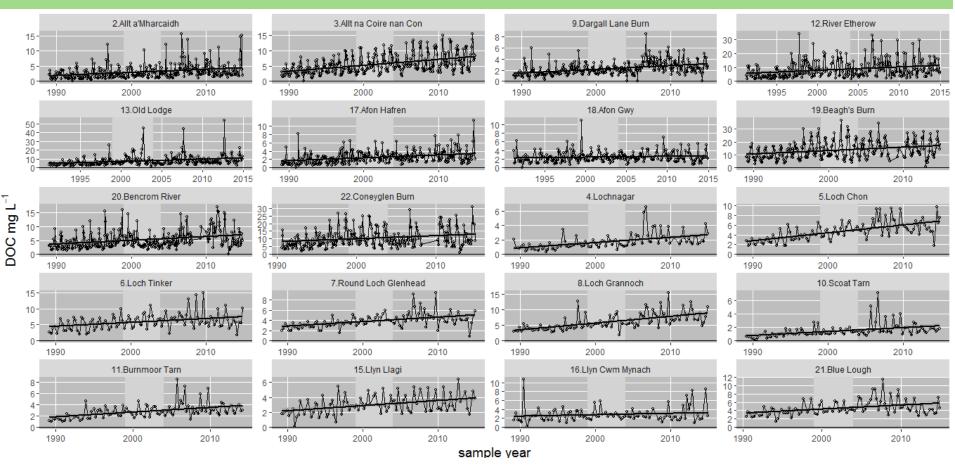




Black trace = Measured DOC Black line = linear DOC trend

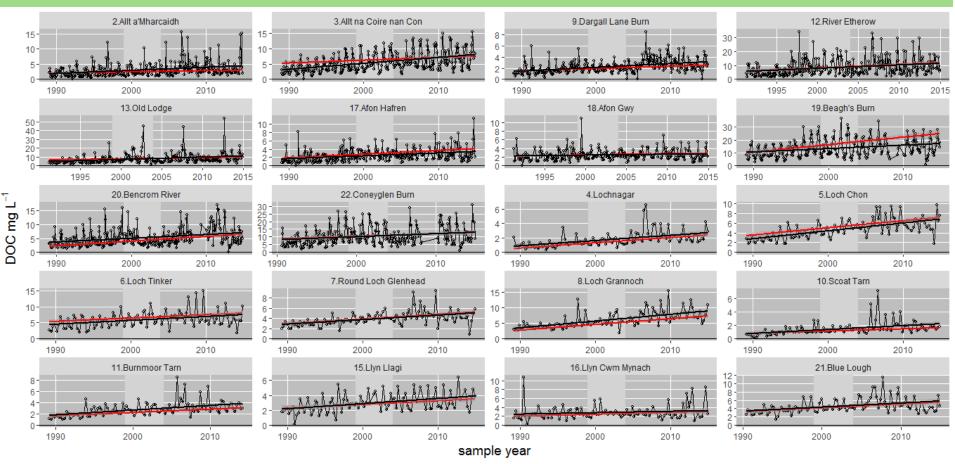






Black trace = Measured DOC Black line = linear DOC trend Light grey hatching = DOC vs IS calibration period

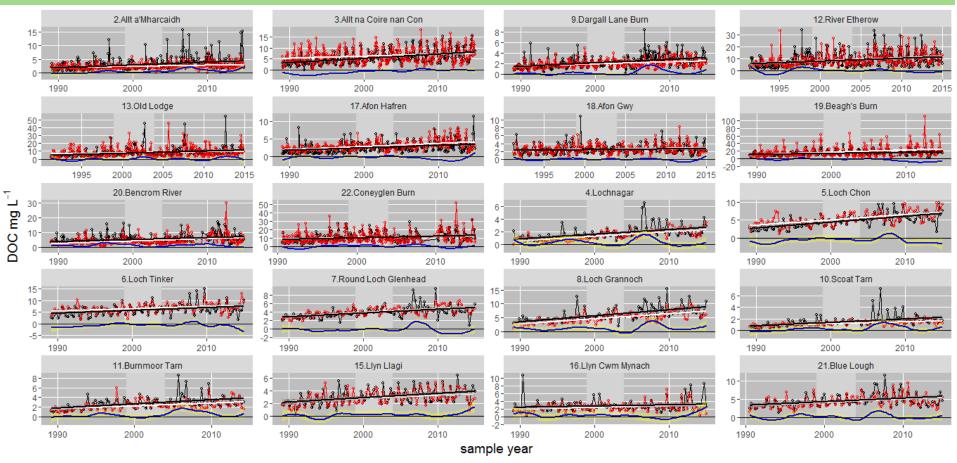




Black trace = Measured DOC Black line = linear DOC trend Red line = linear modelled DOC trend



Model including fixed seasonal component



Black trace = Measured DOC Black line = linear DOC trend white line = linear modelled DOC trend



Predicting the moving DOC baseline

- If we have access to:
 - 1. short-term runs of DOC and IS or conductivity data to calibrate f
 - 2. current non-marine sulphate concentration
 - 3. knowledge of regional non-marine sulphate trend
- We can then:
 - Predict how IS will respond to further declines in non-marine sulphate
 - And hence the DOC response





summary

- For a wide range of surface waters logged DOC concentrations vary in inverse proportion to change in ionic strength
- Relationships are similar across sites but vary depending on base flow contribution
- Relationships likely reflect effects of variation in soil acidity on soil organic matter solubility
- Potential to apply relationship to predict likely future behaviour of the DOC baseline in response to expected further reductions in IS
- This provides a framework against which we can then attempt to superimpose catchment-specific effects (e.g. land use manipulations).



