

Methods note · Land and freshwater

When dissolved-carbon concentration and export diverge

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Fictional author and institute · Editorial demonstration, not peer reviewed

ABSTRACT

Dissolved organic carbon concentration and annual river export can move in opposite directions because transport depends on water volume and the timing of chemistry. This methods note combines published Arctic river sampling evidence, load-estimation guidance, and uncertainty principles. It defines the dissolved fraction and river-section boundary, explains concentration–discharge covariance, and distinguishes sampled, time-weighted, and flow-weighted summaries. Fictional calculations demonstrate both the bias from multiplying separate means and a year with declining concentration but increasing export. The note examines seasonal coverage, station alignment, calibration limits, and correlated prediction errors. It does not estimate Arctic carbon emissions or identify the age and fate of exported carbon. Its practical implication is to publish water volume, carbon mass, sampling support, and reconstruction assumptions together before interpreting an annual change.

Keywords: dissolved organic carbon · river export · discharge covariance · flow weighting · seasonal sampling

A source-based editorial text, not a report of original Still North research. Examples and imagery are illustrative.

The annual question hidden inside a bottle

An increase in dissolved organic carbon concentration does not necessarily mean that a catchment exports more dissolved carbon during the year. The river might carry less water, its high concentrations might occur mainly at low flow, or the sampling schedule might have shifted towards a different season. Conversely, a wetter year can export more carbon even while its average sampled concentration falls. The important analytical question is how concentration and water transport vary together through the period being assessed.

This methods note synthesises the seasonal sampling and load modelling described by Holmes and colleagues for six large Arctic rivers, the US Geological Survey's LOADEST documentation, and measurement-uncertainty guidance. It considers dissolved organic carbon, abbreviated DOC, crossing a defined river section. It does not estimate Arctic emissions, identify carbon age, or infer ecological harm from colour. Every numerical river in the worked examples is fictional. Published studies supply the methodological evidence, not results attributed to the demonstration institute.

Define the substance, boundary, and interval

DOC is an operationally defined fraction, separated from larger particles by a stated filtration procedure and quantified through carbon analysis. The filter, preservation, holding time, analytical method, blanks, and reporting units matter when combining records. A change in method can alter what enters the dissolved category. A river's brown colour may help motivate sampling, but is not itself a universal carbon-concentration measurement. Optical properties depend on composition as well as amount.

Export through a section is obtained by integrating concentration multiplied by discharge through time. With concentration in milligrams of carbon per litre and discharge in cubic metres per second, their product is grams of carbon per second. Summing that transport over compatible intervals gives a mass. Dividing the mass by catchment area gives an areal yield, which is useful for comparing differently sized basins but does not remove differences in runoff or source material.

The boundary is as important as the arithmetic. Carbon passing an upstream station may be stored, transformed, or supplemented before reaching an estuary. Export to a coastal zone is not identical to delivery unchanged to the open ocean. DOC export is also not equivalent to immediate carbon dioxide emission. Some carbon may be respired, buried, retained, or transported onwards. Those fates require additional evidence beyond the river-section budget.

Why the average of concentrations can mislead

The mean of concentration multiplied by discharge is not generally the product of their separate means. It also contains their covariance. When high concentrations coincide with high flows, multiplying ordinary time-average concentration by total water volume underestimates transport. When the relationship is negative, that shortcut can overestimate it. An arithmetic mean of irregular grab samples creates a further problem: it reflects the sampling schedule, not necessarily equal intervals of time or equal volumes of water.

Holmes and colleagues deliberately sampled contrasting hydrological seasons, including winter low flow and spring high flow. Their analysis showed strong seasonal differences within rivers and differences between rivers.

The transferable finding is not one universal seasonal curve. It is that constituent-specific seasonality and discharge must be represented together. A summer-access programme cannot assume that its chemistry describes the annual mixture merely because its laboratory measurements are precise.

Worked example: equal duration, unequal transport

Fictional worked example. Consider two equally long periods. During the first, DOC concentration is 2 milligrams per litre and discharge is 1 cubic metre per second. During the second, concentration is 10 milligrams per litre and discharge is 9 cubic metres per second. The two instantaneous carbon fluxes are therefore 2 and 90 grams per second. Their equal-duration mean is 46 grams per second.

The ordinary mean concentration is 6 milligrams per litre, and mean discharge is 5 cubic metres per second. Multiplying these gives only 30 grams per second, about 35% below the correct equal-duration mean flux. The discrepancy is not a conversion error. It arises because the shortcut loses the positive association between concentration and flow. A flow-weighted mean concentration would be 9.2 milligrams per litre and would recover the transport when multiplied by mean discharge.

Now compare two hypothetical whole years. Year A passes 10 million cubic metres with a flow-weighted DOC concentration of 8 milligrams per litre, exporting 80 tonnes of carbon. Year B passes 16 million cubic metres with a flow-weighted concentration of 6 milligrams per litre, exporting 96 tonnes. Concentration falls by 25%, but export rises by 20%. These values demonstrate a possible relationship, not a forecast of northern rivers. Neither year establishes why the carbon concentration changed.

Estimate the missing concentration history carefully

Continuous discharge is often available more densely than chemistry. A load model uses sampled concentrations and explanatory variables to estimate the concentration or load during unsampled intervals. The [LOADEST](#) report describes regression approaches using streamflow, time, and additional variables, along with diagnostics and methods for censored observations. The existence of a model does not make sparse sampling representative. Its calibration still needs relevant conditions.

At minimum, inspect the distribution of chemistry samples across discharge, season, and year. A model calibrated only on falling flows may fail on the rising freshet. A relationship fitted before a major landscape disturbance may not remain valid afterwards. Concentration at the same discharge can differ with flow path, antecedent wetness, and material availability. Adding a seasonal term can represent a recurring pattern, but cannot guarantee that an unprecedented event follows it.

Validation should challenge the transport estimate, not merely reproduce the calibration scatter. Holding out a whole event or year is often more informative than randomly splitting closely neighbouring samples, which can leave similar conditions on both sides of the split. Compare modelled and sampled concentrations by flow

range, examine residuals over time, and report how much annual load occurs outside the sampled range. A good overall fit can conceal poor performance during the few intervals that carry most carbon.

Align the water and chemistry

Discharge and chemistry stations may occupy different sections. Travel time, tributary inputs, floodplain exchange, and changing catchment area can then matter. Holmes and colleagues explicitly considered offsets between some sampling and gauging locations. A local project should not copy their numerical assumptions without testing whether its river, distances, and flow conditions support them. Matching a bottle timestamp to an unshifted downstream hydrograph can pair different water parcels.

Uncertainty also enters through discharge ratings, especially under ice or at poorly constrained high stages. Concentration precision is only one part of the export budget. Errors in high-flow discharge can affect a large fraction of the annual total. Filtration changes or contaminated blanks can introduce systematic differences that repeated sampling alone will not average away. Retain raw chemistry, flags, discharge versions, station locations, and the model specification with the published estimate.

NIST's uncertainty guidance provides the relevant principle: combine contributions with their sensitivities and covariance, rather than assuming every input error is independent. For annual river export, temporal model errors can be correlated across many consecutive intervals. Treating every predicted day as an independent measurement can generate implausibly narrow uncertainty. Model-structure and missing-season limitations should remain explicit even when no defensible probability distribution can be assigned to them.

Separate transport change from source attribution

A higher DOC yield can result from more runoff, a different concentration-flow relationship, or both. A useful decomposition can compare actual annual export with a flow-normalised calculation under a common hydrological distribution. That is a model-based diagnostic, not a replacement for the actual mass transported. Its interpretation depends on whether the concentration model captures changing seasonality and whether the reference distribution remains appropriate.

Attribution requires further tests. Thaw can change flow paths, but so can rainfall, drainage, vegetation, and channel connection. DOC concentration alone does not identify the proportion derived from old permafrost carbon. Isotopic and compositional measurements may constrain sources, with their own mixing assumptions. Nor does an increasing river export establish a net loss of the entire terrestrial carbon stock without accounting for other inputs, outputs, and storage changes.

Limits and a defensible annual statement

The six large rivers in the cited synthesis are not direct analogues for every small tundra stream. Large basins mix broad climates and long travel paths, while a small catchment may respond sharply to one storm or thaw feature. The worked arithmetic assumes representative

section concentrations and exact intervals. Real estimates require field methods, uncertainty assessment, and sampling plans appropriate to the channel and safe access.

A defensible annual statement therefore gives both water volume and carbon mass, identifies the dissolved fraction and station boundary, and states how unsampled periods were estimated. Report ordinary sampled concentration only for the purpose it actually serves. The useful conclusion is not that concentration is unimportant. It is that concentration describes composition, while export describes movement, and their relationship is a measurable part of the question rather than an assumption to hide.

References

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