Using Water Isotopes to Assess Fresh Fuel to High Arctic Ponds

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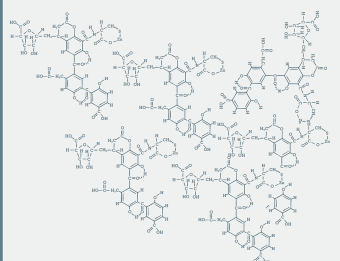
INTRODUCTION

Arctic Ponds

- Northern environments are characterized by an abundance of ponds and lakes
- Can act as biogeochemical hotspots and are important sites for nutrient cycling
- These systems are sensitive to a warming climate



Dissolved Organic Matter (DOM)

- Found in many aquatic and terrestrial ecosystems
- Comprised of thousands of different molecules
  - ~50% is carbon
- Important for aquatic health & drinking water quality
  - Absorbs sunlight in surface waters
  - Energy source for microbes
  - Complexes with and mobilizes heavy metals
  - Primary determinant of drinking water treatment cost

DOM, Ponds, and a Changing Climate

- Sunlight is an important determinant of DOM fate in arctic environments[1]
- *Photolysis* (degradation by sunlight) of DOM can influence:
  - how easily DOM is used as a fuel source (i.e. microbial degradation and mercury methylation; carbon cycling)
  - loss of carbon via greenhouse gases (CO_2 or CH_4)

However, using long-term experiments to understand the fate of DOM via photolytic degradation can be laborious and economically intensive. Ponds and lakes offer an opportunity to observe how DOM changes without having to run experiments on long time scales

OBJECTIVE

Can stable water isotopes of ponds within a high Arctic catchment be used as an indicator of photolytic DOM degradation?

We hypothesize that ponds with stable water isotope signatures representative of evaporative systems will contain less 'fresh' DOM compositions, unlike flow-through systems, due to longer sunlight and enhanced photolytic degradation of DOM.

FIELD SITE

Lake Hazen Watershed, Quttinirpaaq National Park, NU

FIG 1: Field photo of the study site with locations of sampled ponds and Skeleton (SK) Lake. Photo is directed towards the NE.

- Semi-desert climate in the high Arctic with a number of well characterized ponds
- Watershed has history of scientific study (productivity estimates, mercury cycling, greenhouse gas emissions)

TABLE 1: Morphology and general chemistry of four ponds and SK Lake[2]. Chemistry represents averaged data during the growing seasons of 2005 and 2007-2012.

	Surface Area (ha)	Max Depth (m)	TDS (umol/L)	TDN (umol/L)	Chl a (ug/L)
Pond 3	0.04	0.8	485	113	0.9
Pond 12	0.2	1.9	1060	86	1.1
Pond 10	2.5	2.4	934	121	2.4
Pond 16	0.7	2.1	328	24	0.3
Skeleton Lake	1.9	4.7	317	22	0.5

METHODS

Field Sampling

- Four ponds and Skeleton (SK) Lake
  - Sampled July 1, July 17, and Aug 1
- Samples were filtered in-field to 0.45µm
- Measured temperature, electrical conductivity, dissolved total and inorganic nitrogen

Photolysis Experiment

- Determine how photolysis influences DOM concentration and composition
- Samples taken from SK Lake and adjacent subsurface (~20cm below surface)
- Filtered to 0.45µm and placed in tedlar bags
  - 1:1 ratio of water to air
- Left in direct sunlight for 14 days
- Measured sunlight over course of experiment
  - Hoskin Scientific QS5 PAR Quantum Sensor
- Measured change in DOM concentration and composition over time

Laboratory Analysis

Stable isotopes of water (OA-ICOS)
- $\delta^{18}O$-H_2O; δ^2H-H_2O

DOM concentration (Shimadzu TOC Analyzer)
- Concentration of dissolved organic carbon

DOM composition

Absorbance (Cary 100 UV-Vis Spectrophotometer)
- SUVA (specific UV-abs at 255nm)
  related to UV-absorbing components in DOM
- Sr (slope ratio)
  inversely related to bulk DOM molecular weight

Size-exclusion Chromatography (LC-OCD)
- HS (proportion of humic substances)
  proportion of large molecular weight components

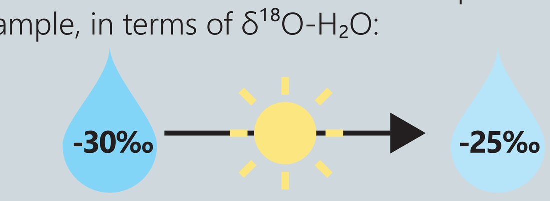
Elemental Ratio
- DOC:DON
  related to lability and DOM source

A Brief Primer to Stable Isotopes

Isotope: an element with the same number of protons and electrons, but different number of neutrons

Compare ratio of isotopes in sample to known standard
For water: $^{16}O/^{18}O$ or $^{1}H/^{2}H$
δ (‰) = (R_{sample} / $R_{standard}$ - 1)×1000

Differences in δ values hint at sources or processes. For example, in terms of $\delta^{18}O$-H_2O:



RESULTS - FIELD MEASUREMENTS

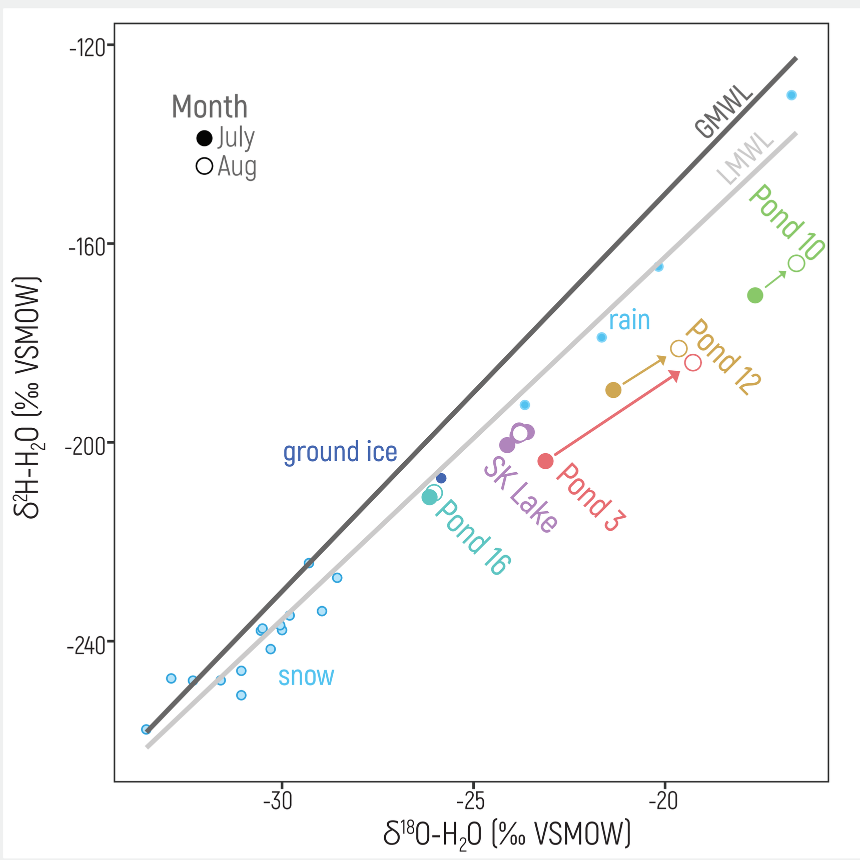


FIG 2: Stable isotopes of water from sampled ponds and precipitation. Dark line represents the Global Meteoric Water Line (GMWL) while the light-grey line represents the Local Meteoric Water Line (LMWL) obtained from snow and rain samples from our study site. Four ponds and Skeleton Lake are plotted, showing the evolution of isotopic signatures among sites and over the summer.

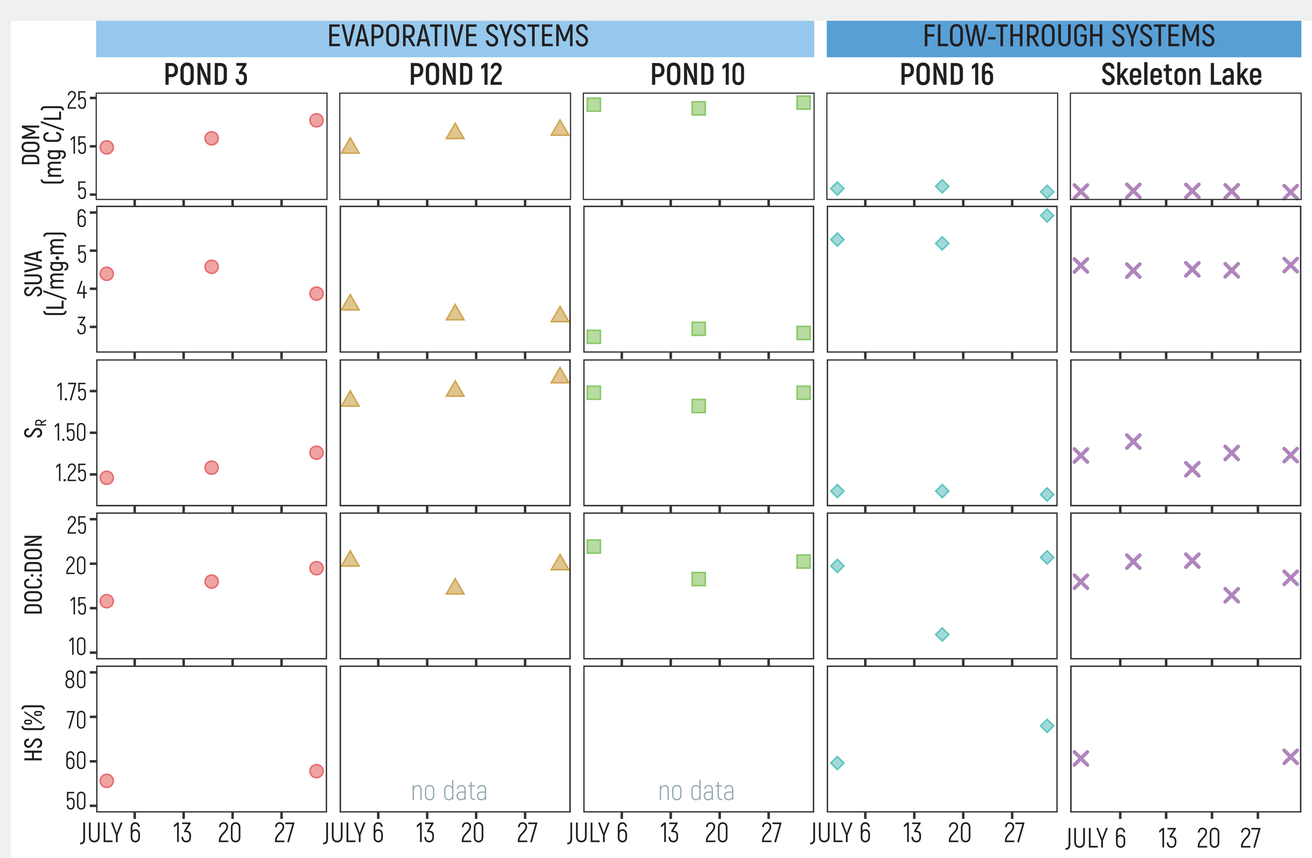


FIG 3: Dissolved organic matter (DOM) concentration and composition for the evaporative (Ponds 3, 12, & 10) and flow-through systems (Pond 16 & SK Lake) over the course of the summer. Composition was measured as specific UV-absorbance at 255nm (SUVA), slope ratio (Sr), organic carbon to nitrogen (DOC:DON), and proportion of humic substances (HS). Flow-through systems appear to have consistent properties across the catchment (DOM of 6 mg/L and SUVA ~5 L/(mg·m)).

What did we find?

Stable isotopes illustrate different flow regimes
- Evaporative ponds become more positive over season
- Flow-through systems show little change
- Different stages of evaporation are observed when comparing isotopic signatures of ponds
- Ponds plot along a local evaporation line with water source close to that of snow

Differences in stable isotopes relate to DOM
- Flow-through ponds contain similar DOM concentrations and compositions to each other
- Surface waters with more positive $\delta^{18}O$-H_2O have:
  - higher DOM concentrations
  - More low-molecular weight DOM with lower capacity to absorb UV

These results show DOM concentration and composition differs across ponds in the Lake Hazen Watershed, and relate to $\delta^{18}O$-H_2O value of ponds. Ponds with more water lost to evaporation also have higher DOM concentrations. Flow-through systems appear to have consistent properties (DOM of 6 mg/L and SUVA ~5 L/(mg m)) over the summer.

RESULTS - PHOTOLYSIS EXPERIMENT

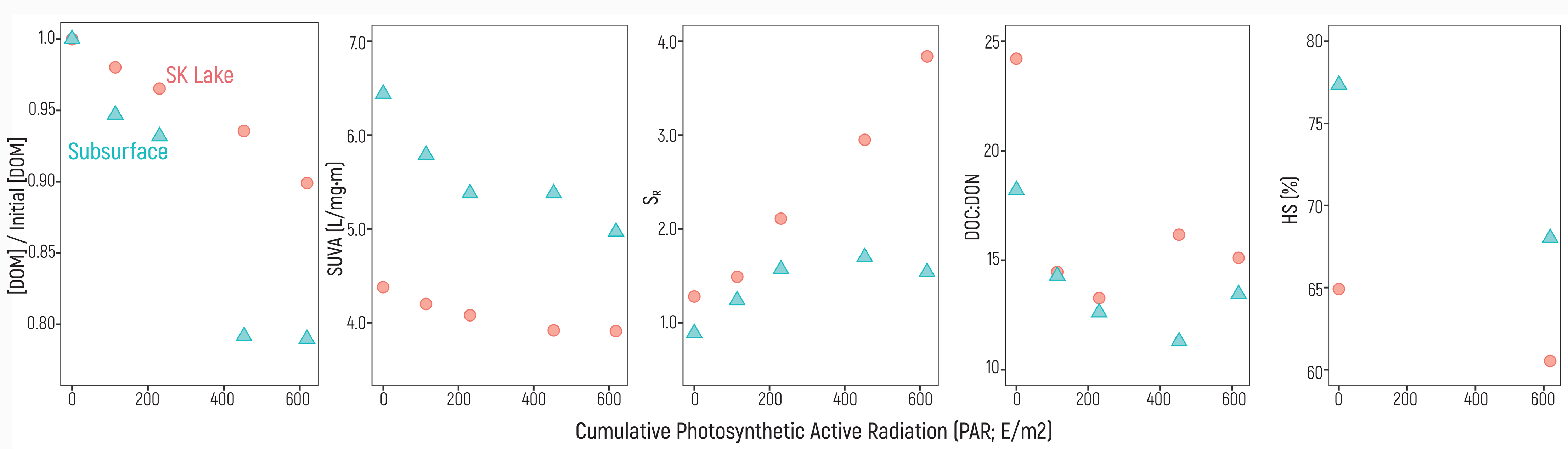


FIG 4: DOM from SK Lake (red circles) and nearby subsurface (blue triangles) exposed to sunlight at Lake Hazen, NU. Changes to DOM quantity and composition were measured over the course of the 14-day experiment. Changes to DOM concentration are plotted as proportion from initial concentrations (SK Lake: 6.05 mg C/L; subsurface: 5.28 mg C/L). Composition was measured as specific UV-absorbance at 255nm (SUVA), slope ratio (Sr), organic carbon to nitrogen (DOC:DON), and proportion of humic substances (HS). Amount of sunlight recieved by the samples was measured as cumulative PAR (E/m²).

What did the experiment identify?

DOM degrades following a 1st-Order Reaction:

$$\frac{DOM}{DOM_0} = e^{-k(PAR)}$$

Rate for SK Lake (k): -1.6 x10 ^{4} m²/E
Rate for SK Subsurface (k): -4.2 x 10 ^{4} m²/E

Photolysis leads to:
- Lower molecular weight DOM
- Lower capacity to absorb UV
- Lower DOC:DON ratios

We provide a range of photolytic DOM degradation rates for high Arctic systems. Further, similar changes to DOM composition occur in each sample, suggesting a predictability in photolytic fate of DOM.

Assuming the watershed recieves ~4500 E/m² in a summer[2], 50 to 85% of 'fresh' DOM input into surface waters will be photolysed.

PAIRING FIELD & EXPERIMENT RESULTS

Agreement between Field and Experimental Results

Although photolysis results in a net loss of DOM, ponds showed higher DOM concentrations with more evaporation. This suggests the accumulation of recalcitrant (not easily degraded) DOM, and is further supported by measures of DOM composition. Photolysis leads to lower DOC:DON (Fig 4), but higher DOC:DON were found in the field suggesting there may be internal cycling of DOM or *in-situ* production. However, previous microbial DOM degradation studies from the same sites found little change over time. Hence, photolysis is the dominant driver of DOM fate in this high Arctic watershed.

Water Residence Time (τ)

Isotope Mass Balance can be used to understand DOM dynamics
- evaporation to input ratio (E/I) indicates fraction lost by evaporation
- can use E/I to find water residence time for each system
- assumptions: rain input is negligible to the overall signature of the pond, average relative humidity is 0.65[2], annual evaporation is 100 mm/yr[4]
- using equations as outlined by Gibson et al. 2016

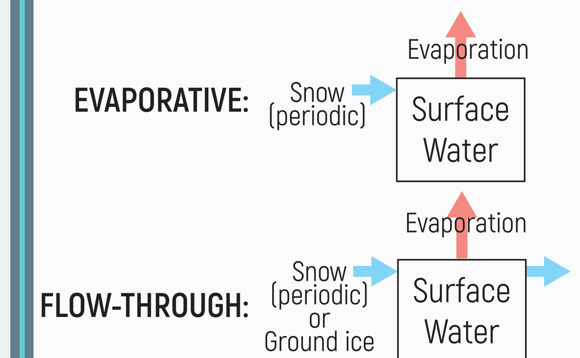


TABLE 2: Evaporation to input ratio (E/I) and water residence time (τ) calculated using an isotope mass balance[3]

	E/I	τ (years)
Pond 3	0.18	0.55
Pond 12	0.25	2.03
Pond 10	0.45	4.95
Pond 16	0.02	0.22
Skeleton Lake	0.07	1.4

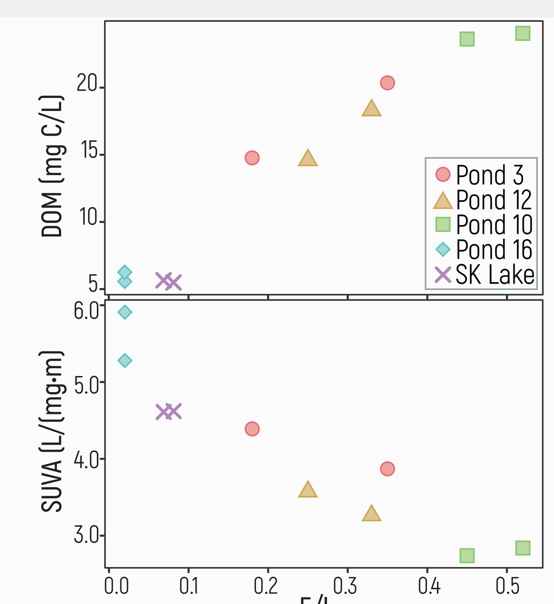


FIG 5: DOM concentration and SUVA values for each pond versus evaporation to input ratio (E/I) calculated from an isotopic mass balance[3].

CONCLUSIONS

Stable isotopes of water can be used as a proxy for photolytic degradation of DOM
- aids in determining overall lability (ease of degradation)
- can assess overall composition using photolytic degradation rates obtained from the experiment and stable isotopes of water in the catchment

In terms of drinking water and aquatic health, the amount of time DOM is exposed to sunlight will dictate its overall composition and subsequent reactivity
- Measures of DOM composition are in agreement with photolytic degradation experiments
- Changes to composition suggest photolysis is a key determinant of overall DOM 'quality'

Future work could assess the microbial lability of photolysed DOM in these high Arctic watersheds

Acknowledgments

A big thank you to Richard Elgood, Janessa Zheng, Justin Harbin, Dr. Monica Tudorancea, Kyra St. Pierre, Dr. Vince St. Louis, Craig Emmerton, Jennifer Hickman, Erin MacDonald, Sarah Indris, Jenn Mead, Sarah Sine, Amanda Bichel, Parks Canada, and the organizations listed below:

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