Using stable isotopes of water to characterize the hydrological cycle in a northern Minnesota black spruce-sphagnum bog forest

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Introduction

Spatial and temporal variation in isotopic ratios of hydrogen ($^{2}H/^{1}H$ or D/H) and oxygen ($^{18}O/^{16}O$) in surface water allows characterization of the hydrological cycle in terrestrial ecosystems. Processes such as evaporation, precipitation, uptake of water by roots and vertical or lateral mixing of source water all affect hydrogen (δD) and oxygen ($\delta^{18}O$) isotopic ratios.

Climate change will increase temperature and CO_2 levels affecting evaporation and plant water use. We can track the effects of changes in temperature and CO_2 on the hydrological cycle by monitoring δD and $\delta^{18}O$ in source water.

The objectives of this study included: calibrating the Picarro L1102-i Isotopic Liquid Water Analyzer, developing and verifying a working procedure for this instrument, and analyzing baseline water samples from a field site that will be subjected to climate change treatments.

Site Description

Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) project:

- Exploration of the ecological response to various temperature increases and elevated concentrations of atmospheric carbon dioxide
- Experimental work conducted on the southern margin of the boreal peatland forest, which is considered especially at risk due to impending climate change
- The 8.1 h ombrotrophic *Picea mariana-Sphagnum* bog forest is located in the USDA Forest Service Marcell Experimental Forest in northern Minnesota
- Climate change manipulations will take place in open-top enclosures subjecting the environment to various levels of warming and CO_2 exposure

Visit: http://mnspruce.ornl.gov/ for more information

Methods

Calibration of Instrument

•The Picarro L1102-i simultaneously measures the isotopic ratios of hydrogen (D/H) and oxygen ($^{18}O/^{16}O$) using Wavelength-Scanned Cavity Ring-down Spectroscopy.

•Calibration is done by comparing the reference values to measured values of three International Atomic Energy Agency (IAEA) standards:

Primary Standard	$\delta^{18}O$ Reference Value	δD Reference Value
VSMOW2	0	0
GISP	-24.78	-189.5
SLAP2	-55.5	-427.5

Picarro Method Settings

Needle Penetration

Site	Depth (mm)
Evaporator	44.5
Waste 1	10.0
Waste 2	40.0
Wash 1	44.3
Wash 2	40.0

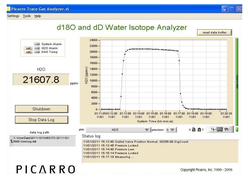
Method Picarro

Name	Setting
Cycle	LC-Inj
Syringe	5 µL
Samp Vol	4.5 µL
Air Vol	0 nL
Pre Cln Slv1	0
Pre Cln Slv2	0
Pre Cln Sp1	2
Fill Speed	500 nL/s
Fill Strokes	1
Pullup Del	5.0 s
Inject to	Vaporizer
Inject Sp	1.0 µL/s
Pre Inj Del	2.0 s
Pst Inj Del	2.0 s
Pst Cln Slv1	0
Pst Cln Slv2	2
Vlv Cln Slv1	0
Vlv Cln Slv2	0

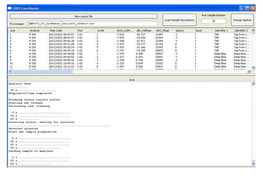
Stable Isotopic Analysis

- Test samplers nested at 0.0, 0.25, 0.5, 1.0, 2.0 and 3.0 m from the surface of the hollow were used to collect water samples from the bog
- Each sample run on the instrument was compared to internal standards and expressed as negative δ values (δD and $\delta^{18}O$):

Internal Standard	Average Normalized $\delta^{18}O$	Average Normalized δD
Deep Blue	-0.14	-0.16
DI	-8.42	-47.67
Mountain (MTN)	-21.37	-159.57
Hollow	-13.38	--94.94



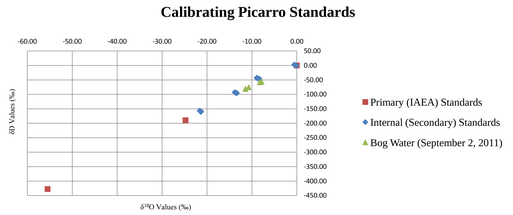
Water Content on Graphical User Interface



Raw Output File from Coordinator

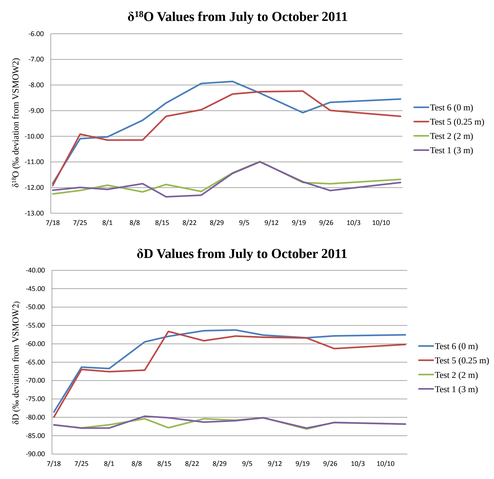
Results

Standards and Calibration



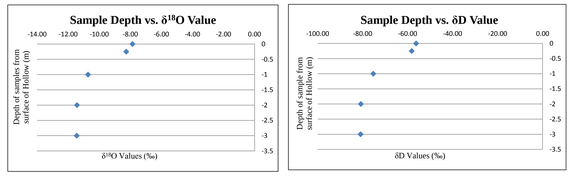
Primary standards were used to calibrate internal standards, which are run daily. The Picarro is extremely precise. For each secondary standard shown above, there are actually 9 separate points on the graph, nearly impossible to distinguish from one another due to instrumental precision.

Temporal Variation in Isotopic Ratios



$\delta^{18}O$ and δD values for more than 40 bog samples taken from July to October. Over time, waters near the surface of the bog (<0.25 m) have become increasingly enriched, while deeper water (>2 m) displayed no such pattern.

Spatial Variation in Isotopic Ratios



$\delta^{18}O$ and δD values for samples taken on September 2, 2011 from 0, 0.25, 1, 2 and 3 meters below the surface of the hollow. Deeper water was more depleted in both $\delta^{18}O$ and δD than the surface water. This pattern was maintained for depth analysis on all sampling days.

Aerial photograph of the landscape around the S-1 bog

Conclusions

Conclusions

Following calibration, the instrument yielded isotopic ratio results with:

•An average standard error of <0.05 ‰ for $\delta^{18}O$ and <0.15 ‰ for δD

•An average standard deviation of <0.06 ‰ for $\delta^{18}O$ and <0.3 ‰ for δD

Temporal Variation:

•Shallow surface waters (<0.25 m) have become enriched over the three month period from July to October

•Deeper water (>2 m) isotopic ratios have remained relatively stable

Spatial Variation:

•In terms of depth below the bog, the deeper the surface water, the more depleted the isotopic ratios of oxygen and hydrogen

Relevant References

1. *Picarro L1102-i Analyzer User's Guide,* Picarro Inc., Sunnyvale, CA, 2009.
2. *Picarro Community* [Online]. Available: http://www.picarro.com/community/picarro_community/
3. P. Gupta. (2009, April). Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology. *Rapid Commun. Mass Spectrom.* [Online]. 23, 2534-2542. Available: http://onlinelibrary.wiley.com/doi/10.1002/rcm.4100/full

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