High-Frequency, Field-Deployable Isotope Analyzer for Hydrological Applications

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Outline

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• Very High-Frequency Water Isotope Measurements
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  • Time-Resolved Liquid Water Isotope Measurements
Technical Overview

Conventional Absorption Spectrometry

Beers Law: \( \frac{\Delta I}{I_o} = 1 - \exp(-\alpha L_{\text{eff}}) \)

- \( \Delta I/I_o \) = fractional change in laser intensity
- \( L_{\text{eff}} \) = effective optical path length
- \( \alpha(\lambda) \) = absorption coefficient, \( S \ P \chi(\lambda) \)
- \( S \) = absorption line strength
- \( \chi \) = mixing ratio (mole fraction)
- \( P \) = total pressure

- 1st principles measurement of species' concentration
- Different isotopes absorb at different wavelengths
- Measure molecules directly - no need for sample conversion
- Narrow linewidth laser provides extraordinary selectivity
Technical Overview
Absorption Spectrum of Water

- Mid-infrared region strongly absorbs, but is hardware limited
- Near-infrared region is readily accessible but weak absorptions
- Select isolated, proximate near-IR absorption features for isotope studies
Technical Overview

Off-Axis Integrated Cavity Output Spectroscopy

- Optical cavity provides pathlength enhancement of $L_{\text{eff}} = L / (1-R)$
- Typical $R = 99.99\%$, $L_{\text{eff}} = 10,000$ meters
- Allows for the highly accurate measurement of very weak absorptions
- Extraordinarily robust - alignment insensitivity, telecom components
- Field-deployable, autonomous operation, no sample preparation
- Can measure stable isotopes of water, carbon dioxide, methane, etc...

![Diagram of gas inlet, gas outlet, diode laser, lens, detector, and data collection and analysis system.](image)
Technical Overview
Experimental Setup

- Gas Input
- Fiber Launch
- Detector
- Output Mirror
- Lens
- P & T Gauge
- Gas Outlet
- Fiber-Coupled DFB Diode Laser
- High-Finesse Optical Cavity
**Technical Overview**

**Measured Cavity-Enhanced Spectrum of Water**

- Measure [HOD], [H\(^{16}\)OH], [H\(^{18}\)OH] → D/H, \( ^{18}O/^{16}O \)
- Simultaneously measure both isotopes in a single laser scan
- High signal-to-noise ratio → precise isotope ratio determination
- Well characterized transitions

\[ \lambda \sim 1390 \text{ nm} \]

Injected Volume = 920 nL

![Graph showing cavity-enhanced spectrum of water with peaks at H\(^{16}\)OH, H\(^{18}\)OH, and HOD]
High-Frequency LWIA
Conventional LGR Liquid Water Isotope Analyzer

- Measure δ¹⁸O and δD of liquid water to better than ±0.2 ‰ and ±0.6 ‰
- Approximately 30 unknown samples per day
- Widely used in hydrology, geology, and medical laboratories worldwide
High-Frequency LWIA

Laboratory Test Data

- Conventional LWIA requires 250 seconds/injection → 30 unknowns/day
- Improved gas conductance, evaporation, and data analysis to increase speed
- High-Frequency LWIA requires < 86 seconds/injection → 134 unknowns/day
- Measurement Precision: $\delta^{18}O$ and $\deltaD$ to within ±0.06 ‰ and ±0.30 ‰ (1σ)
- Accuracy verified by direct comparison to IRMS for widely varying samples
Deploy a High-Frequency LWIA for Continuous Isotope Measurements of Rain & Streams
High-Frequency LWIA
H. J. A. Deployment - Location

- Deployed in a gauging station at ~ 1 km² Watershed #1 in the H.J. Andrews
- Small propane heater in station to prevent freezing
- Enclosures to prevent debris from entering instrument or autosampler
- Collocated measurements of temperature, wind speed, rainfall, and humidity
- 4 week deployment: 3/5/09 - 4/3/09
Injection tray allows external water sources to be interfaced to autosampler
Submersible pump pushes 31 mL/s against 3 m of head
Open split to feed and filter ~ 10 mL/min through the tray
Precipitation (snow/rain) gravity-sampled from a rooftop 576 in² funnel
Both flows passed through inline stainless steel filters to remove particulates
High-Frequency LWIA
H. J. A. Deployment – 4 Major Storms

- 4 major rain events: 3/15/09, 3/25/09, 3/29/09, 4/2/09
- Amount of rainfall per storm ranged from 32 - 111 mm
High-Frequency LWIA
H. J. A. Deployment - 3/15/09 Storm

- 40 stream and 40 rain samples/day
- Large excursion in rainfall isotope ratio
- No change in stream isotope ratio
  - "Old Water Paradox"
    - Pressure Pulse (flow) = immediate
    - Water stored in watershed for years
- Precipitation dynamics
- "Grab" samples every 12 - 24 hours
- Periodic servicing - septum, filters, stds
High-Frequency LWIA

H. J. A. Deployment – LMWL for 3 Rain Events

- Continuous, high-frequency data throughout long-term deployment
- Examine individual storm events
- Very limited previous studies involved using “grab” samples
High-Frequency LWIA
Rain on Snow Studies - Objective

• Rain on snow is the flood-producing runoff generation method in the Pacific Northwest
• How does rain mix with snow within the melting pack to deliver water to the ground?
• Use distinct isotopes of rain, snow, and runoff to help determine melting dynamics
• Work performed with Professor McDonnell (OSU)
High-Frequency LWIA
Rain on Snow Studies – Experimental Method

- Snow Core: 200 mm diameter, 125 mm of water equivalent, 1512 g, from HJA Watershed #7
- “Rainfall”: 10 mm/hr, 22 minute pulses spaced 1 hour apart... by a professional “rainmaker”
- Eluted water gravity-sampled into high-frequency Liquid Water Isotope Analyzer
- Analyzer sequence: 6 injections of std, 18 injections of eluted water (first 2 discarded)
- Minimal sample memory effects – each injection treated as individual analysis (no averaging)
- Measurement every 2 minutes with $\delta^{18}$O and $\delta$D precisions of ±0.22 ‰ and ±0.8 ‰ (no averaging)
High-Frequency LWIA
Rain on Snow Studies - Preliminary Results

- Gaps due to measurements of water standards
- Over 5 hour run, 41% of the total snow water equivalent lost due to melting
- Initially, rainfall dominates water passing through core (> 80%)
- End of the experiment → eluted water is ~ 60% rain water, 40% snow melt
- High-frequency dynamics? Modeling efforts underway by McDonnell Group
- Measurements verified by comparison to “grab” samples
Field-Deployable WVIA

Cavity-Enhanced Spectrum

Less Sample, Higher Pressure → Better cavity and improved data analysis
Field-Deployable WVIA

Water Vapor Isotopic Standard Source

- QUANTITATIVE evaporation with controlled water and dry air flows
- Water vapor isotope standard with controlled humidity (3000 - 30000 ppmv)
- Allows WVIA to rapidly switch between reference and sample (like LWIA)
Field-Deployable WVIA

Laboratory Test Data - Precision

$\delta^{18}O$ and $\delta D$ to $\pm 0.3 \%$ and $\pm 1.2 \%$ in 10 seconds
Field-Deployable WVIA

Laboratory Test Data - Accuracy

Accurate over natural water range (VSMOW → SLAP)
Field-Deployable WVIA

Laboratory Test Data - Thermal Stability

Stable from 5 - 45 °C
Field-Deployable WVIA

Laboratory Test Data - Concentration Invariance

No concentration dependence from 3000 - 25000 ppmv H₂O
Field-Deployable WVIA

Deployment at Sherman Island - Experiment

- Deployed at Sherman Island, CA with Todd Dawson’s group (UC Berkeley)
- Housed in mobile laboratory and interfaced to existing flux tower setup
- Instrument operated at a 2 Hz data rate for over 48 hours continuously
- Automatic, periodic calibration using Water Vapor Isotopic Standard Source
Field-Deployable WVIA

Deployment at Sherman Island - Raw Data

- $\text{H}_2\text{O}$ (ppmv)
- $\delta^{18}\text{O}(\%)$
- $\delta\text{D}(\%)$

Time (hours)
Field-Deployable WVIA
Deployment at Sherman Island - LMWL

\[ \delta D = 8 \times \delta^{18}O + 10 \text{ (GMWL)} \]
\[ \delta D = 6.4 \times \delta^{18}O - 15.5 \]
Field-Deployable WVIA Deployment at Mauna Loa

- 25 days of continuous water vapor isotope measurements at 0.1 Hz
- Vapor concentration fluctuates between 500 - 15000 ppmv as atmospheric boundary layer moves
- Isotope ratio changes with boundary layer movement - sampling ocean air and Antarctic air
- Will incorporate these measurements into global circulation models
Very High Frequency Measurements

Water Vapor Isotope Flux

\[ \delta^{18}\text{O} \text{ (‰)} \]

\[ \delta D \text{ (‰)} \]

\[ [\text{H}_2\text{O}] \text{ (ppmv)} \]

\( \tau_{1/e} = 0.18(2) \text{ seconds} \)

\( \tau_{1/e} = 0.26(2) \text{ seconds} \)

\( \tau_{1/e} = 0.18(1) \text{ seconds} \)

5 Hz Measurements \( \rightarrow \) Eddy Flux Technique
Very High Frequency Measurements
Liquid Water Isotopes

Measure liquid samples every 3 minutes...

\( \tau_{1/e} = 36.7 \text{ seconds} \)

\( \tau_{1/e} = 37.5 \text{ seconds} \)
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Relevant Publications/Posters


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Thank you!