Tracing water sources and greenhouse gases using field-based stable isotope techniques

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Overview:

1. Stable isotopes
   What are they? How do we measure them?

2. Oxygen and Hydrogen isotopes in water
   Tracing the hydrological cycle
   Agricultural water use

3. Carbon isotopes in Carbon Dioxide and Methane
   Tracing greenhouse gas emissions
Stable isotopes

- Physical and chemical properties vary slightly between isotopes
  - Example: \( \text{H}_2\text{^{18}O} \) has lower vapour pressure than \( \text{H}_2\text{^{16}O} \)

- Isotopes ‘fractionate’ between different compounds or physical forms
  - Example: water vapour has a lower \( ^{18}\text{O}/^{16}\text{O} \) ratio than liquid water
  - Example: \( \text{CO}_2 \) resired from grasses and trees have different \( ^{13}\text{C}/^{12}\text{C} \) ratios

- \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) carry isotopic ‘fingerprints’ and can be traced from their source

\[
\delta^{^{13}\text{C}}_{\text{Sample}} = \left\{ \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Reference}}} - 1 \right\} \times 1000
\]
Isotope analysis

The past:
Laboratory bound mass spectrometry
Specialist staff required
Discrete samples only

The future:
Laser spectroscopy
Mobile, field capable
Simple operation
Continuous analysis

Advantage: Greater temporal and spatial resolution at reduced cost
Field-based isotope measurements
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Tracing water sources

Moisture Source $\rightarrow$ Rainfall $\rightarrow$ Soil water $\rightarrow$ Groundwater $\rightarrow$ Rivers $\rightarrow$ Vegetation
O- and H-isotopes in the water cycle
Annual O-isotope composition of precipitation
...but event-based and seasonal variations in O- and H-isotope composition of rainfall are large → discrete events can be traced in the hydrological cycle!
Continuous monitoring of stream $\delta^{18}O$ and $\delta^2H$ and stormflow hydrograph separation using laser spectrometry in an agricultural catchment
Hydrograph separation of storm flow
AN036: Water Stable Isotope Technique to Determine Evapotranspiration Partitioning

Plant transpired H_2O has δ^{18}O ≈ δ^{18}O soil H_2O

Soil evaporated H_2O has δ^{18}O < δ^{18}O soil H_2O (liquid-vapour fractionation)
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Mobile detection of methane using an isotope spectrometer

### Greenhouse gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration (ppm)</th>
<th>Warming factor (100 yr)</th>
<th>Warming contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>≈400</td>
<td>1</td>
<td>≈9-26%</td>
</tr>
<tr>
<td>CH₄</td>
<td>≈2</td>
<td>25</td>
<td>≈4-9%</td>
</tr>
<tr>
<td>N₂O</td>
<td>≈0.3</td>
<td>298</td>
<td>?</td>
</tr>
</tbody>
</table>
Measurement of $^{13}\text{C}/^{12}\text{C}$ in CH$_4$ helps distinguish coal seam and microbial (farming) gas sources.
Accounting for natural emissions: soil and plant respiration (CO$_2$)
CO₂ emissions from two forest systems measured using a mobile isotope spectrometer interfaced with GPS

Rainforest / Eucalyptus transition, 40 km forest track (2 hours), continuous measurement integrated at 2 min intervals
Conclusions - relevance to remote area monitoring:

• Laser spectroscopy allows field-based isotope analysis of water and greenhouse gasses

• High temporal and spatial resolution - reactive sampling/analysis - low cost

• Highly versatile instruments – can interface with project-specific sampling modules

CDU’s present capabilities in field-based stable isotope analyses:

1. Continuous analysis of \(^2\text{H}/\text{H}\) and \(^{18}\text{O}/^{16}\text{O}\) in water vapour, rainfall, river water, seawater...

2. Continuous analysis of \(^{13}\text{C}/^{12}\text{C}\) isotope ratio in \(\text{CO}_2\) – including analysis of \(\text{CO}_2\) and \(\text{CH}_4\) concentration