

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

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Remote environmental
monitoring techniques



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

^1H 1.00794 99.985% Stable	^2H 2.0141 0.015% Stable	^3H $t_{1/2} = 12.32\text{yrs}$ Cosmogenic/ anthropogenic
^{16}O 15.9949 99.76% Stable	^{17}O 16.9991 0.04% Stable	^{18}O 17.9991 0.20% Stable
^{12}C 12.00000 98.89% Stable	^{13}C 13.00335 1.11% Stable	^{14}C 14.0 $t_{1/2} = 5715\text{yrs}$ Radioactive Cosmogenic/ anthropogenic

$$\delta^{13}\text{C}_{\text{Sample}} = \left\{ \left(\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Reference}}} - 1 \right) * 1000 \right.$$

- Physical and chemical properties vary slightly between isotopes
 - Example: H_2^{18}O has lower vapour pressure than H_2^{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: CO_2 respired from grasses and trees have different $^{13}\text{C}/^{12}\text{C}$ ratios
- H_2O and CO_2 carry isotopic 'fingerprints' and can be traced from their source

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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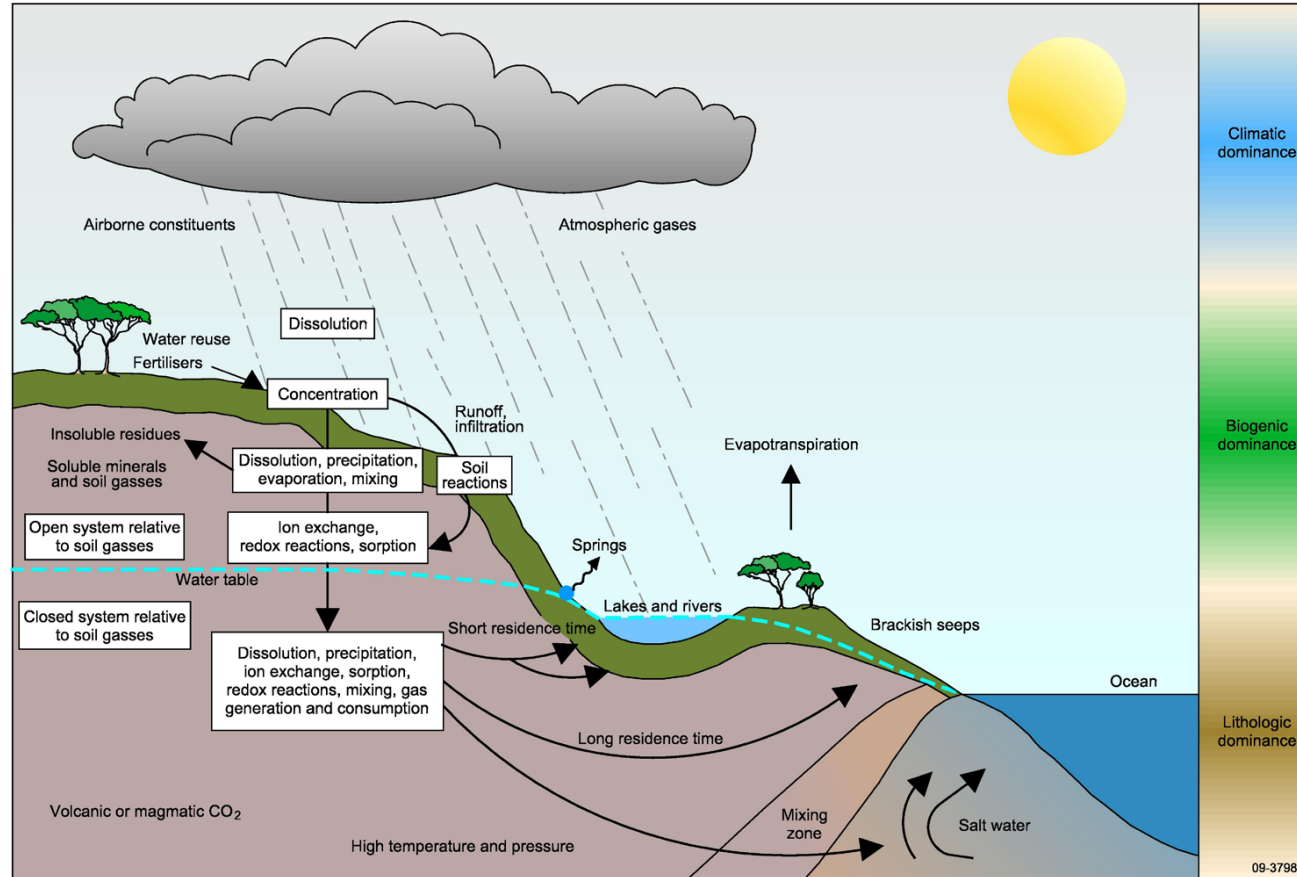
Tracing the hydrological cycle

Agricultural water use

3. Carbon isotopes in Carbon Dioxide and Methane

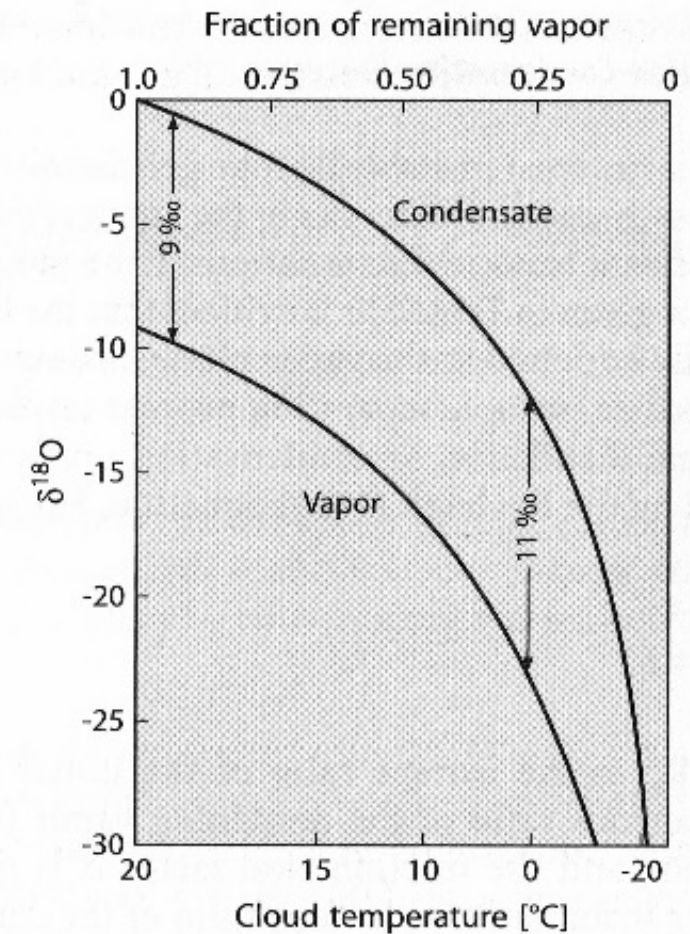
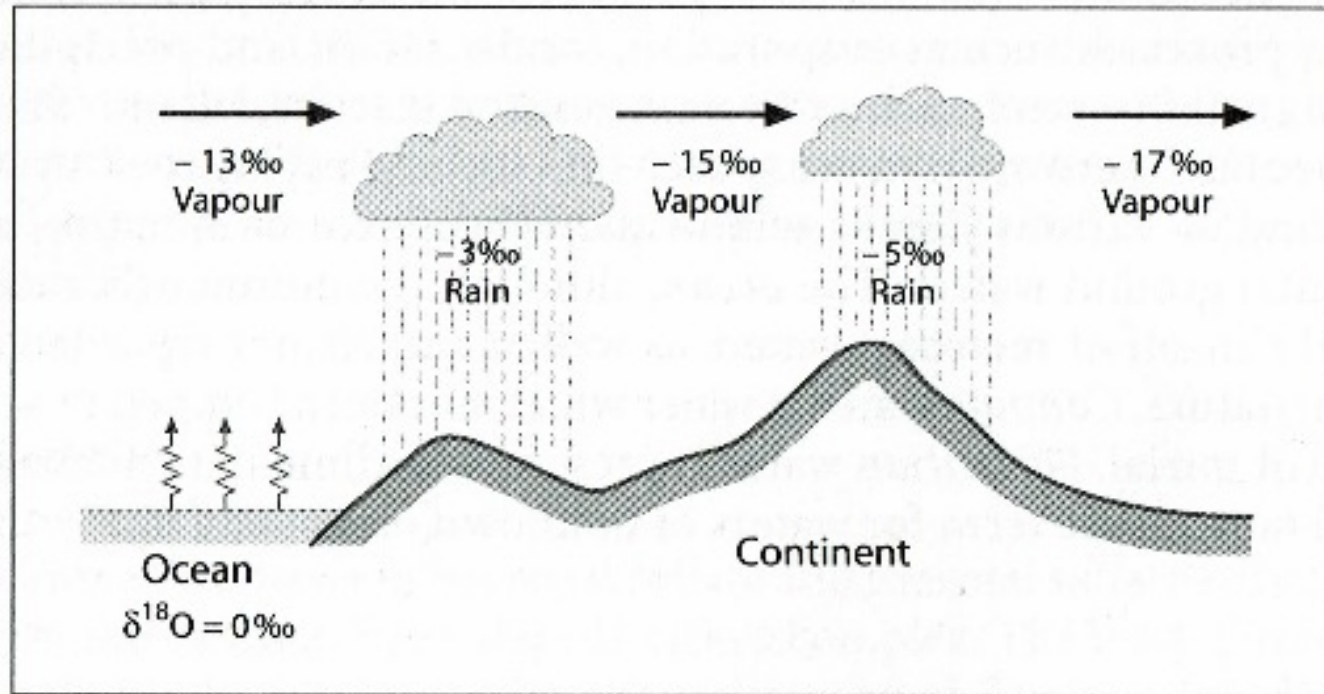
Tracing greenhouse gas emissions

Tracing water sources

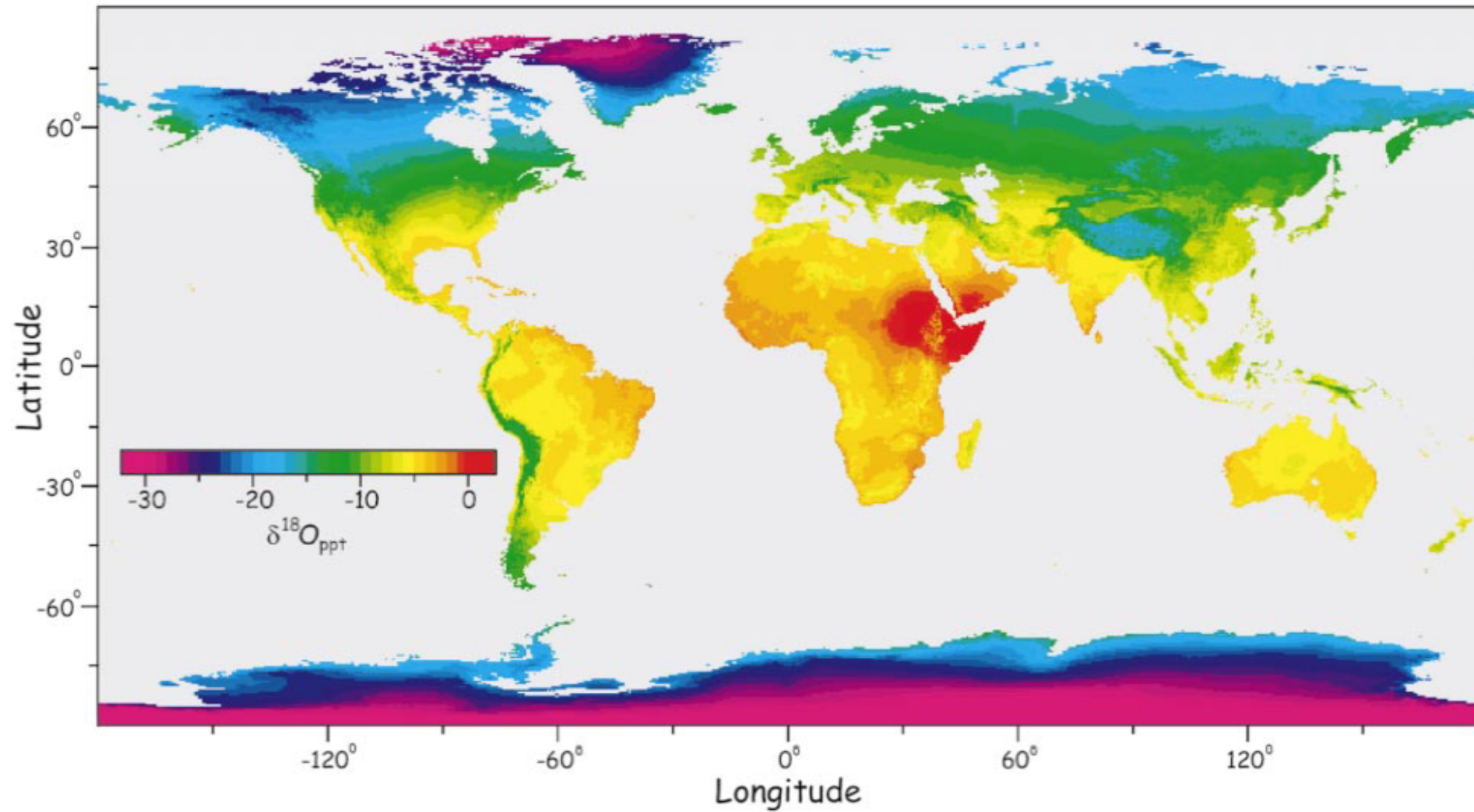


Moisture Source → Rainfall → Soil water → Groundwater → Rivers
→ Vegetation

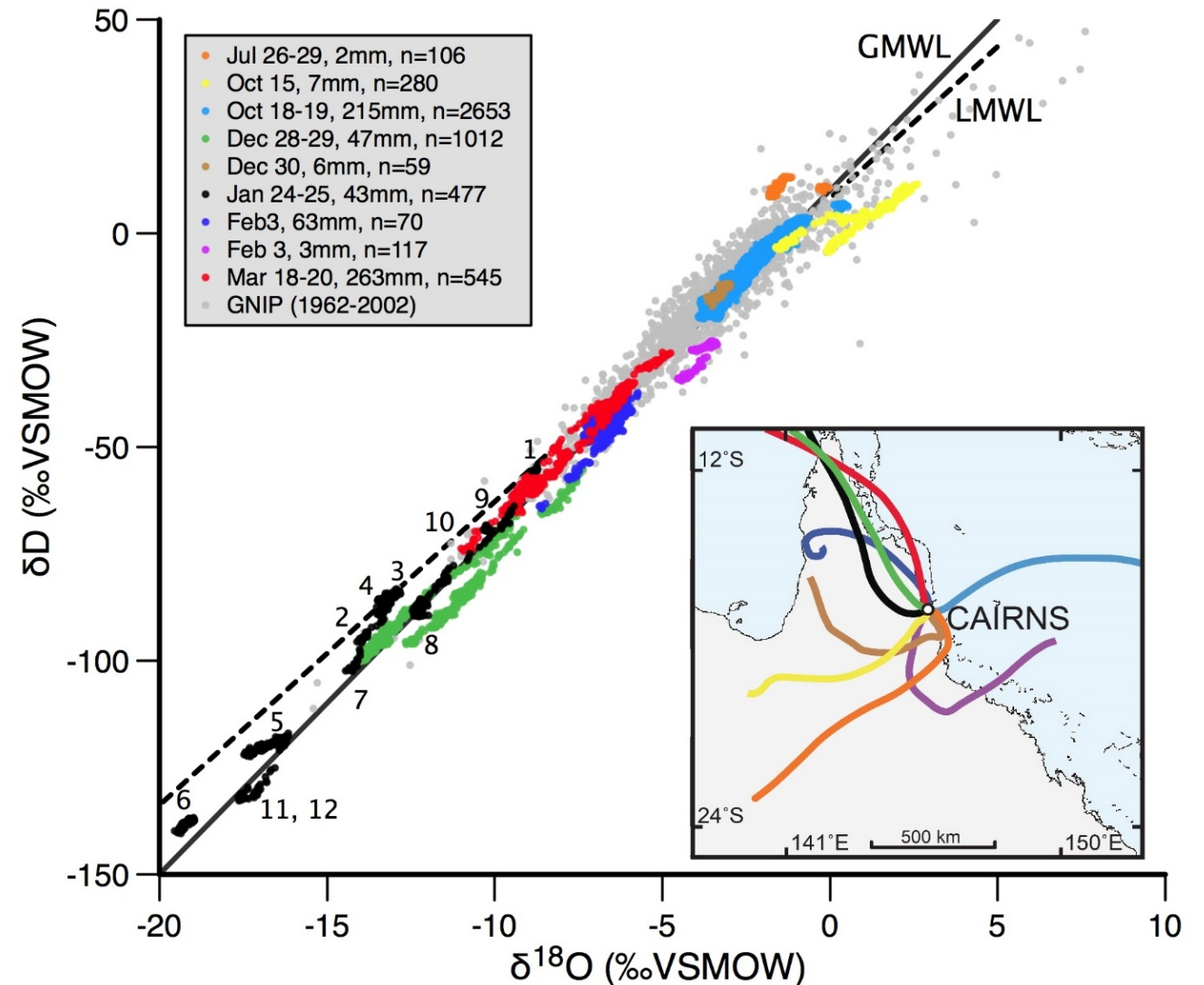
O- and H-isotopes in the water cycle



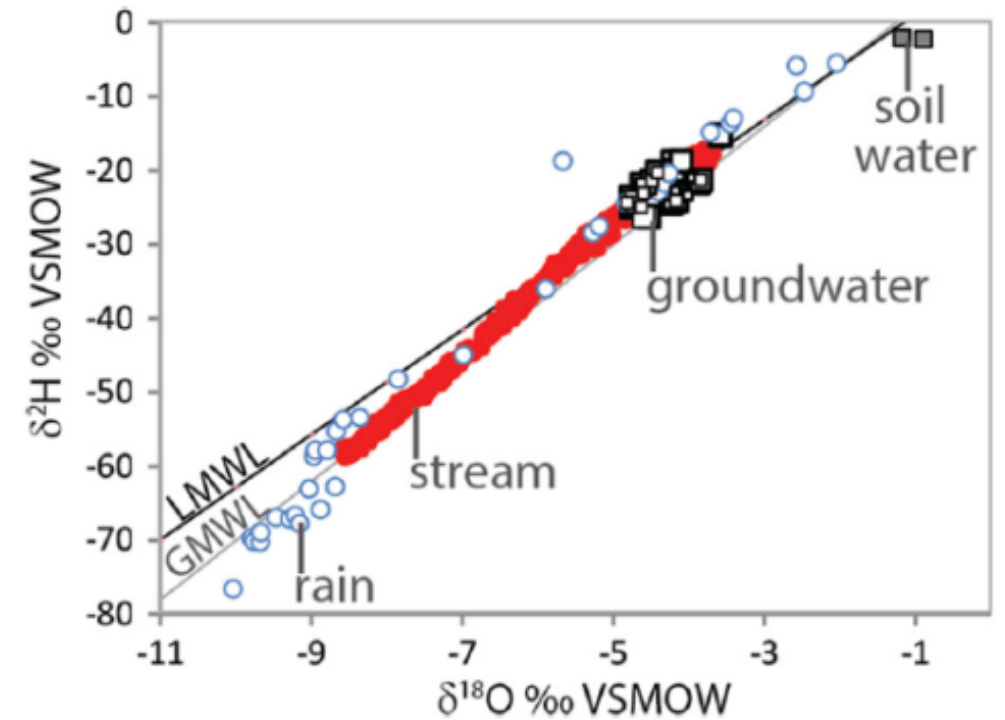
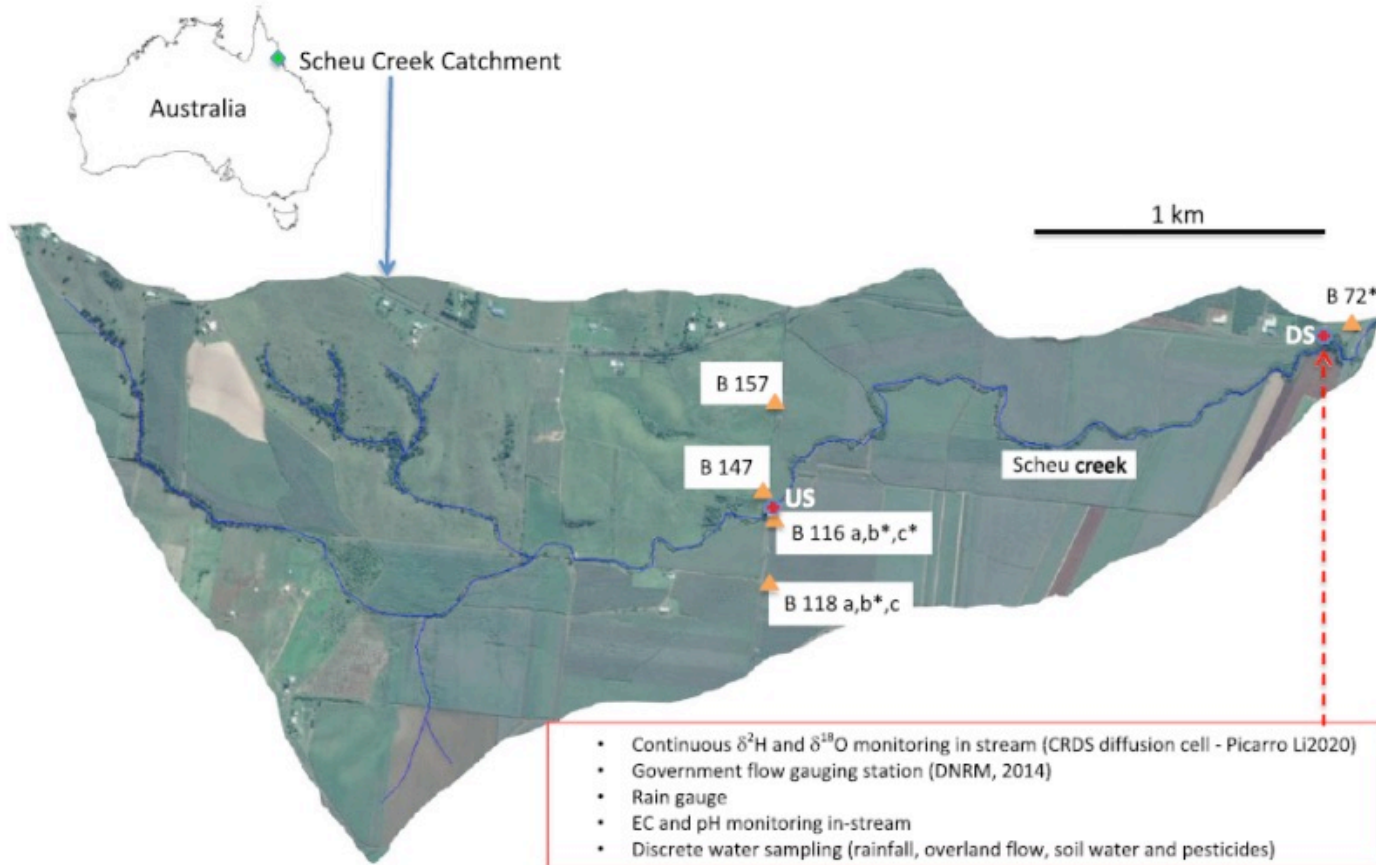
Annual O-isotope composition of precipitation



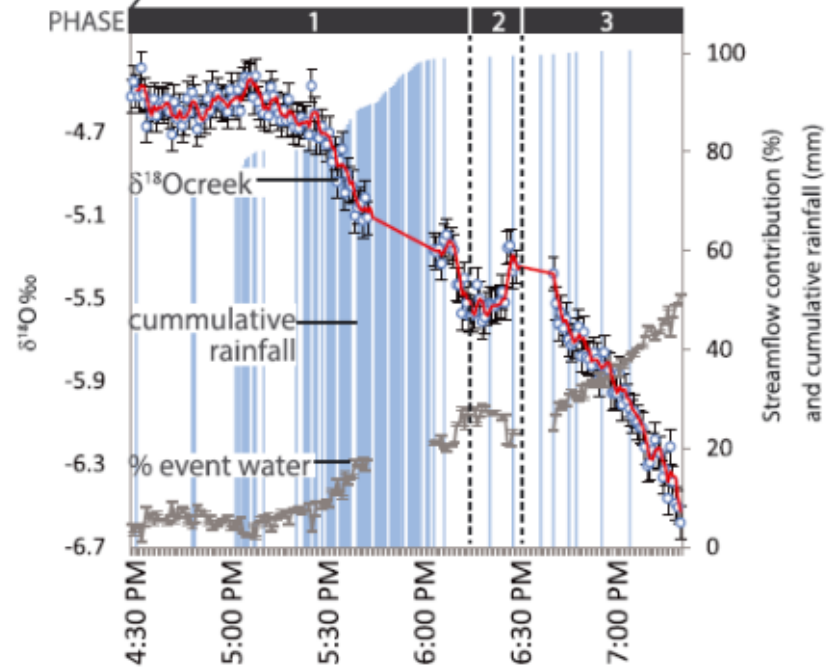
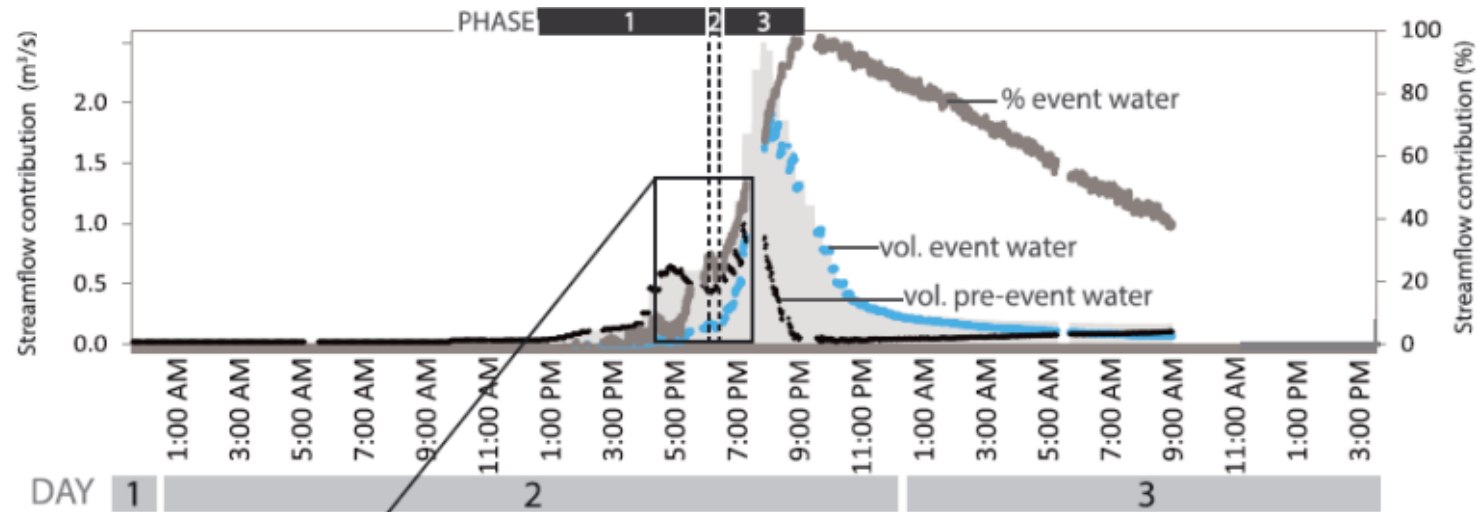
...but event-based and seasonal variations in O- and H-isotope composition of rainfall are large → discrete events can be traced in the hydrological cycle !



Continuous monitoring of stream $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and stormflow hydrograph separation using laser spectrometry in an agricultural catchment

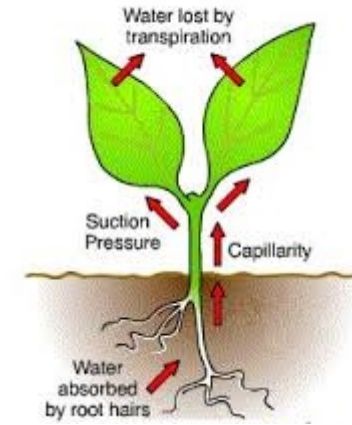
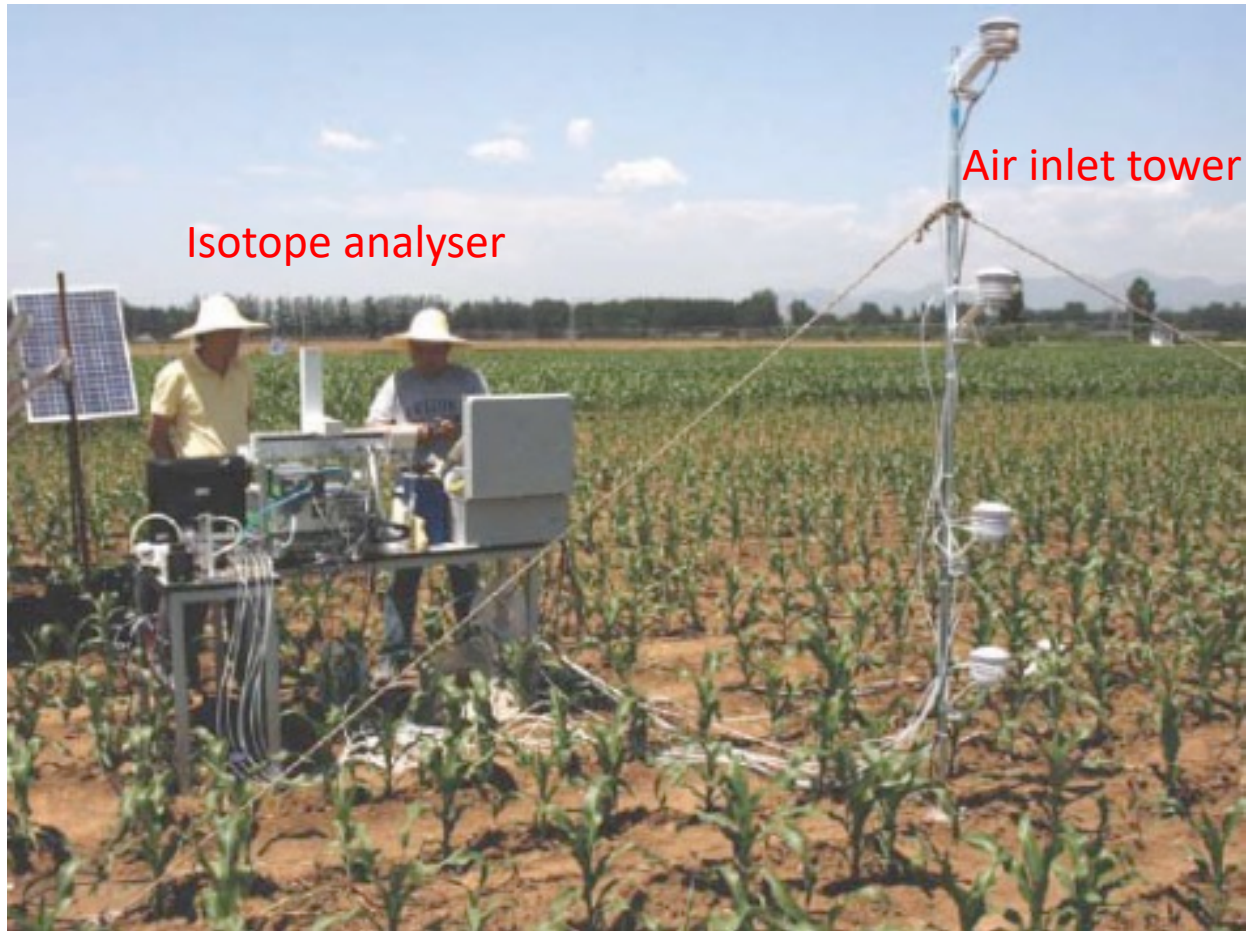


Hydrograph separation of storm flow



PICARRO

AN036: Water Stable Isotope Technique to Determine Evapotranspiration Partitioning



Plant transpired H_2O has $\delta^{18}\text{O} \approx \delta^{18}\text{O}$ soil H_2O

Soil evaporated H_2O has $\delta^{18}\text{O} < \delta^{18}\text{O}$ soil H_2O
(liquid-vapour fractionation)



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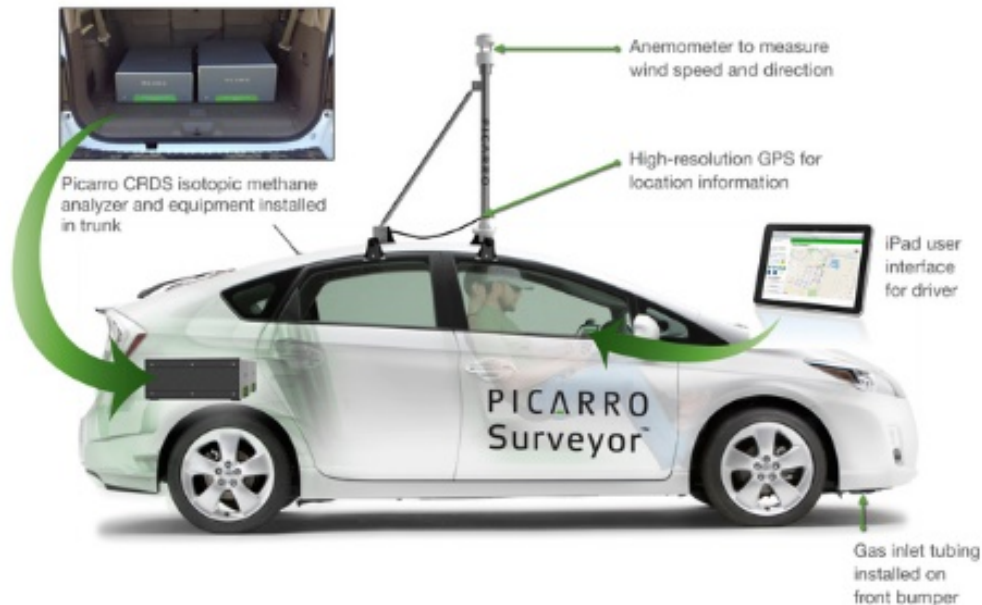
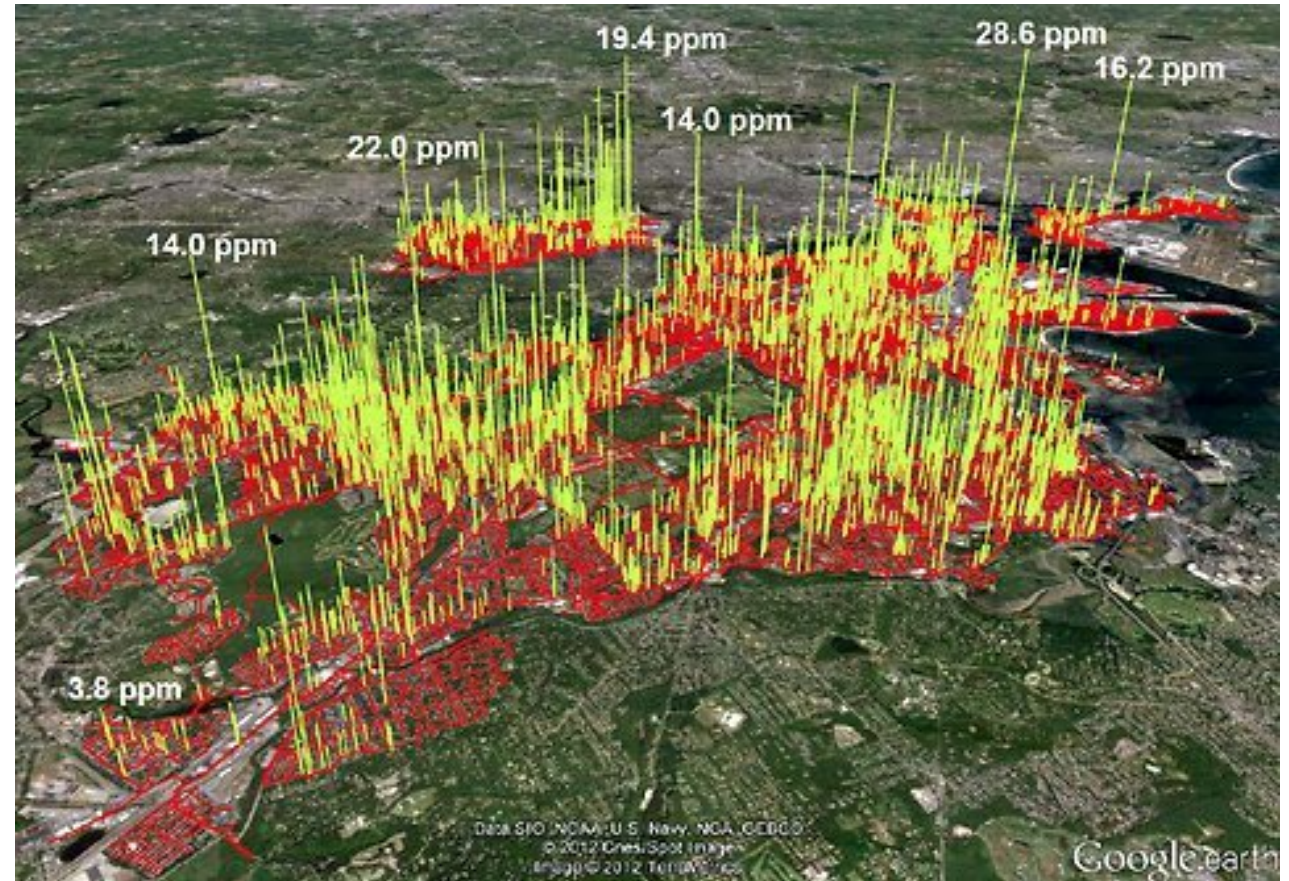
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Mobile detection of methane using an isotope spectrometer

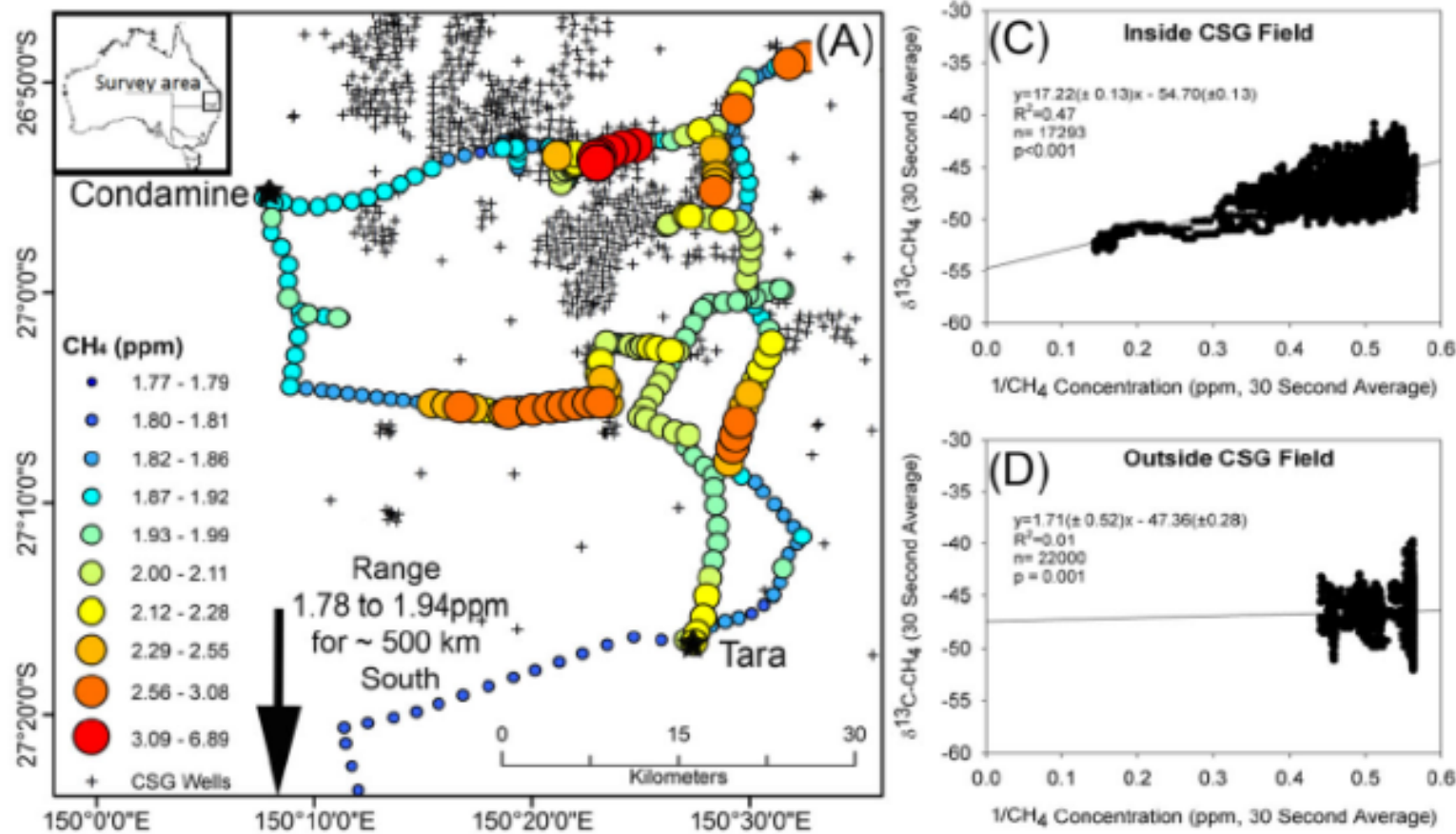
Greenhouse gasses

Gas	Concentration (ppm)	Warming factor (100 yr)	Warming contribution
CO ₂	≈400	1	≈9-26%
CH ₄	≈2	25	≈4-9%
N ₂ O	≈0.3	298	?

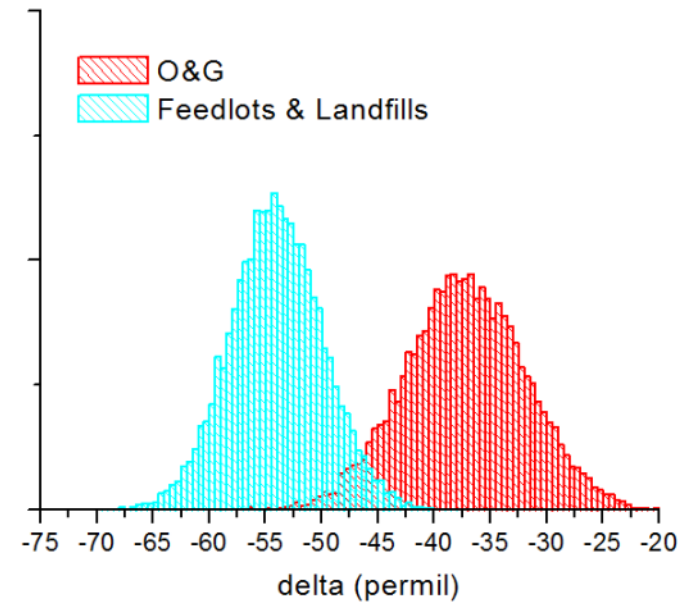


Mapping Methane and Carbon Dioxide Concentrations and $\delta^{13}\text{C}$ Values in the Atmosphere of Two Australian Coal Seam Gas Fields

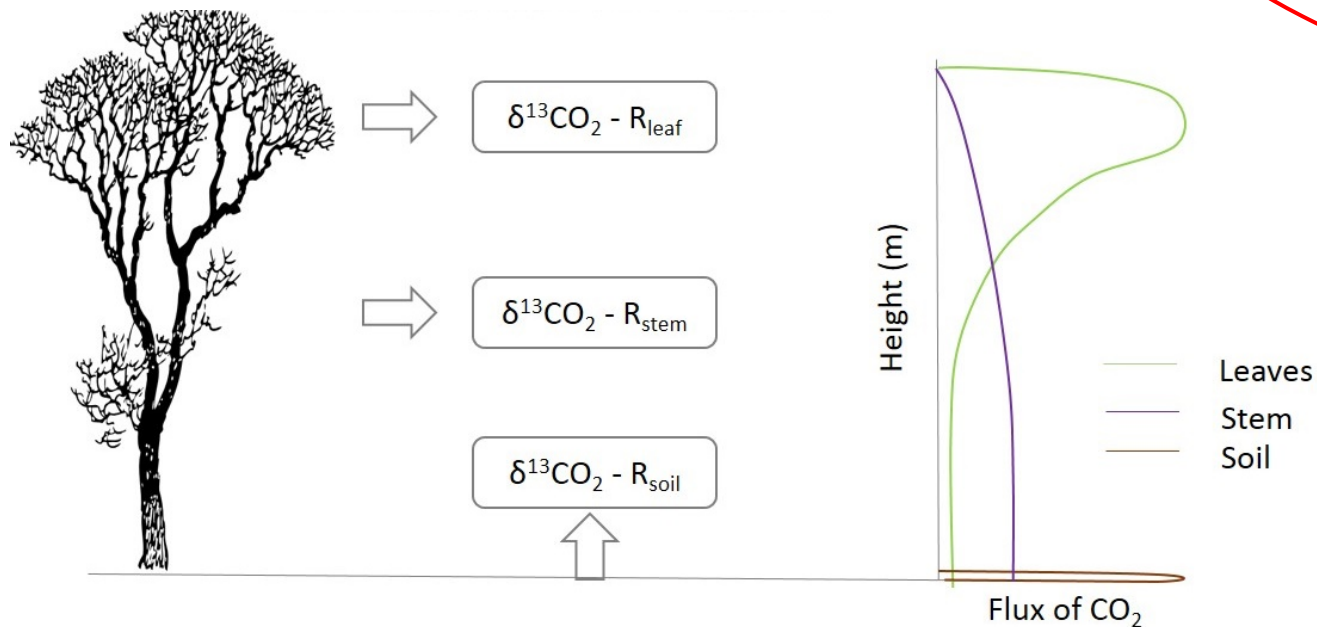
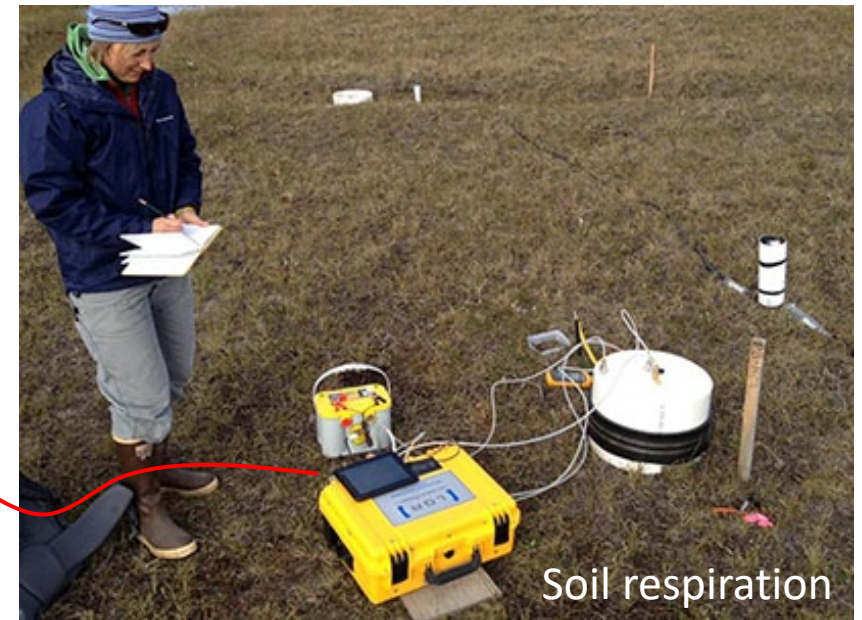
Damien T. Maher • Isaac R. Santos • Douglas R. Tait



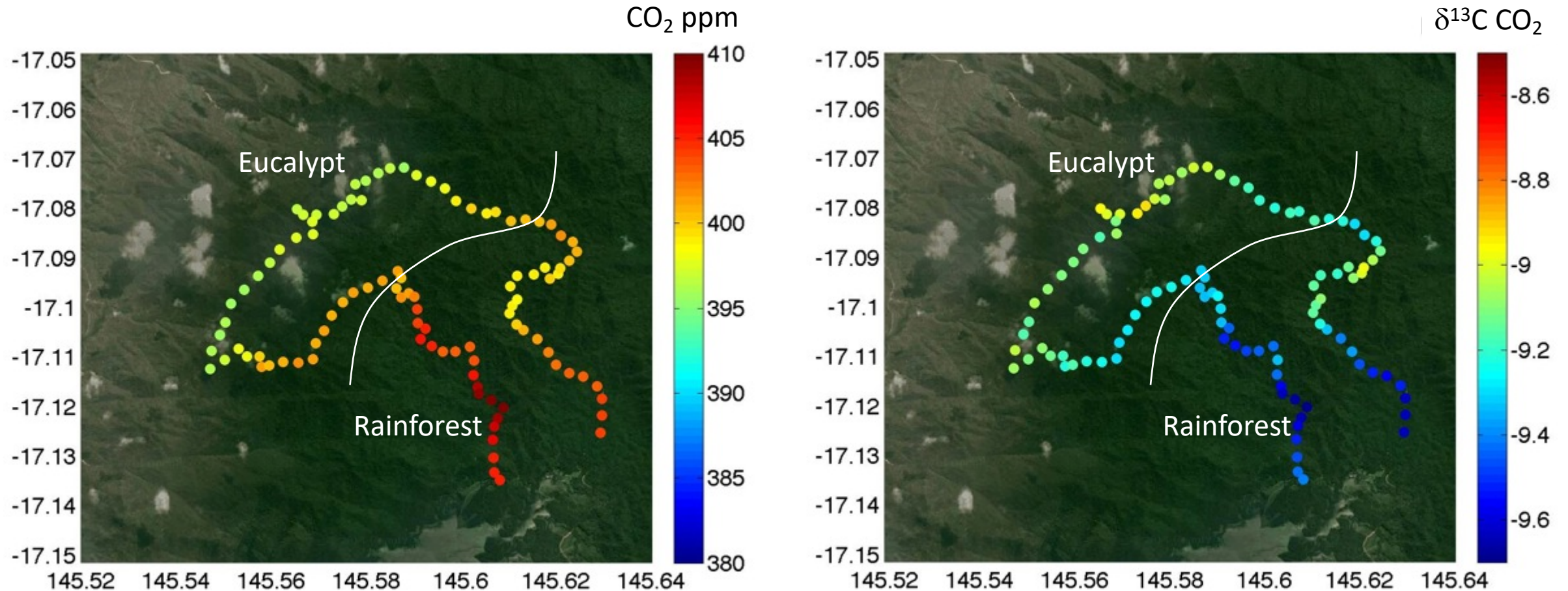
Measurement of $^{13}\text{C}/^{12}\text{C}$ in CH_4 helps distinguish coal seam and microbial (farming) gas sources



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 $^2\text{H}/^1\text{H}$ 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 CO_2 – including analysis of CO_2 and CH_4 concentration