

Habilitation à Diriger des Recherches

L'étude de la variabilité des hydrosystèmes hétérogènes au
moyen des traceurs environnementaux dans un contexte de
changement global

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Éducation et emploi

Hydrogéologue, Hydrochimiste

Emplois

2013-actuel	Chercheur - IRD, UMR G-eau, Montpellier
2010-2013	Lecturer (MCF) - Université de James Cook, Australie
2007-2010	Chercheur - Université de James Cook, Australie
2003-2006	Chercheur - Universités de Monash et de Melbourne, Australie

Formations

2003	Ph.D. (Doctorat) - Université de Melbourne, Australie
1998	Bachelor of Science (Honours) - Université de Melbourne, Australie

Recherche

Comment peut-on améliorer notre compréhension de la variabilité des hydrosystèmes hétérogènes à partir des traceurs environnementaux ?

Forçage intrinsèque

i. Hétérogénéités géologiques

Forçages externes

ii. Fluctuations climatiques

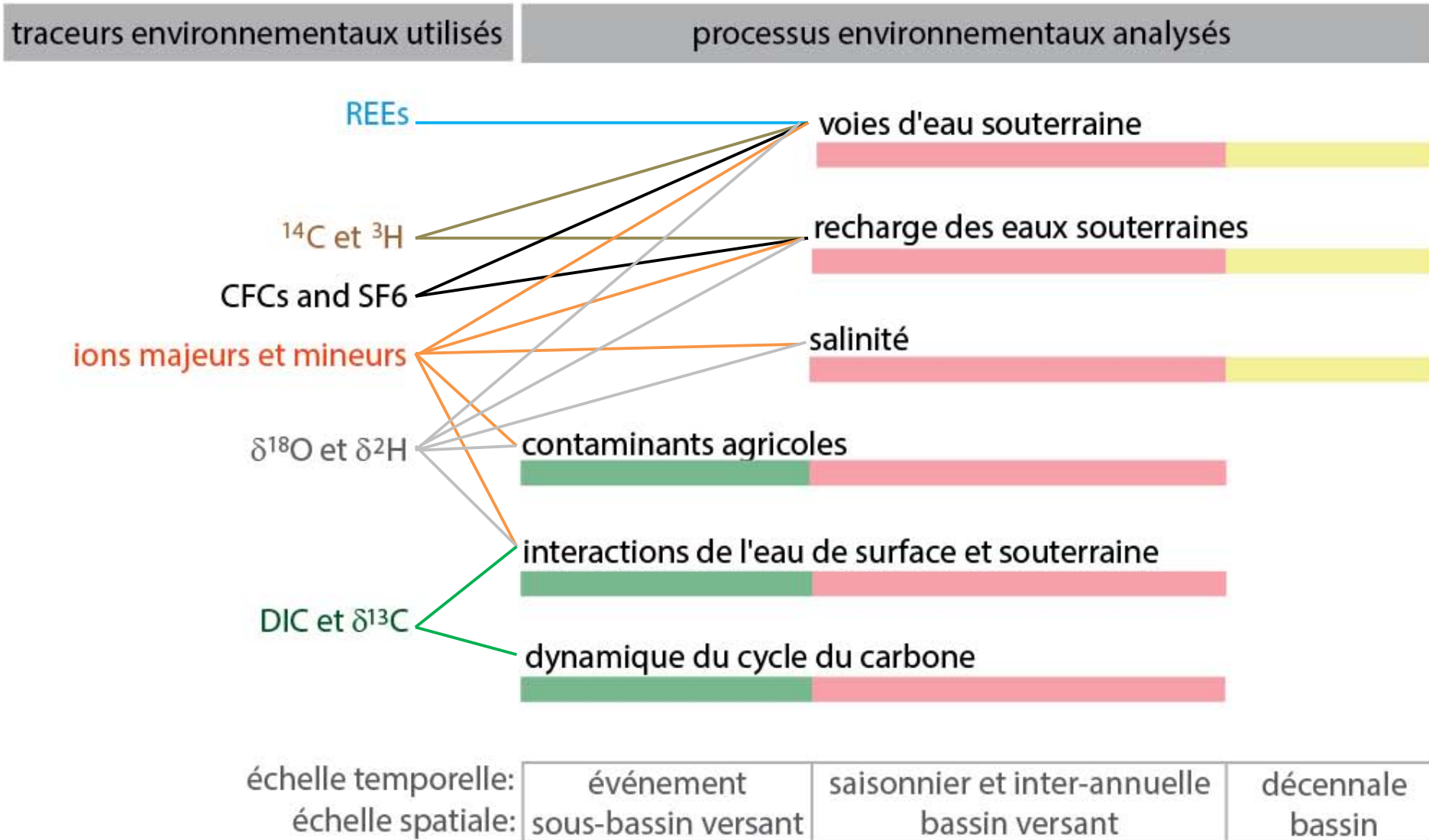
iii. Pressions anthropiques

Etudes de cas

- Problématiques
- Conditions environnementales
- Echelles espace-temps

Quels sont les traceurs adaptés au site ?

Approche : Traceurs Environnementaux



Etudes de cas



Scheu Creek

Transport des contaminants pendant un événement pluvieux

Corangamite Catchment

Impacts de la sécheresse sur la qualité de l'eau

Lake Eyre Basin

Recharge par les plaines d'inondation

Murray Groundwater Basin

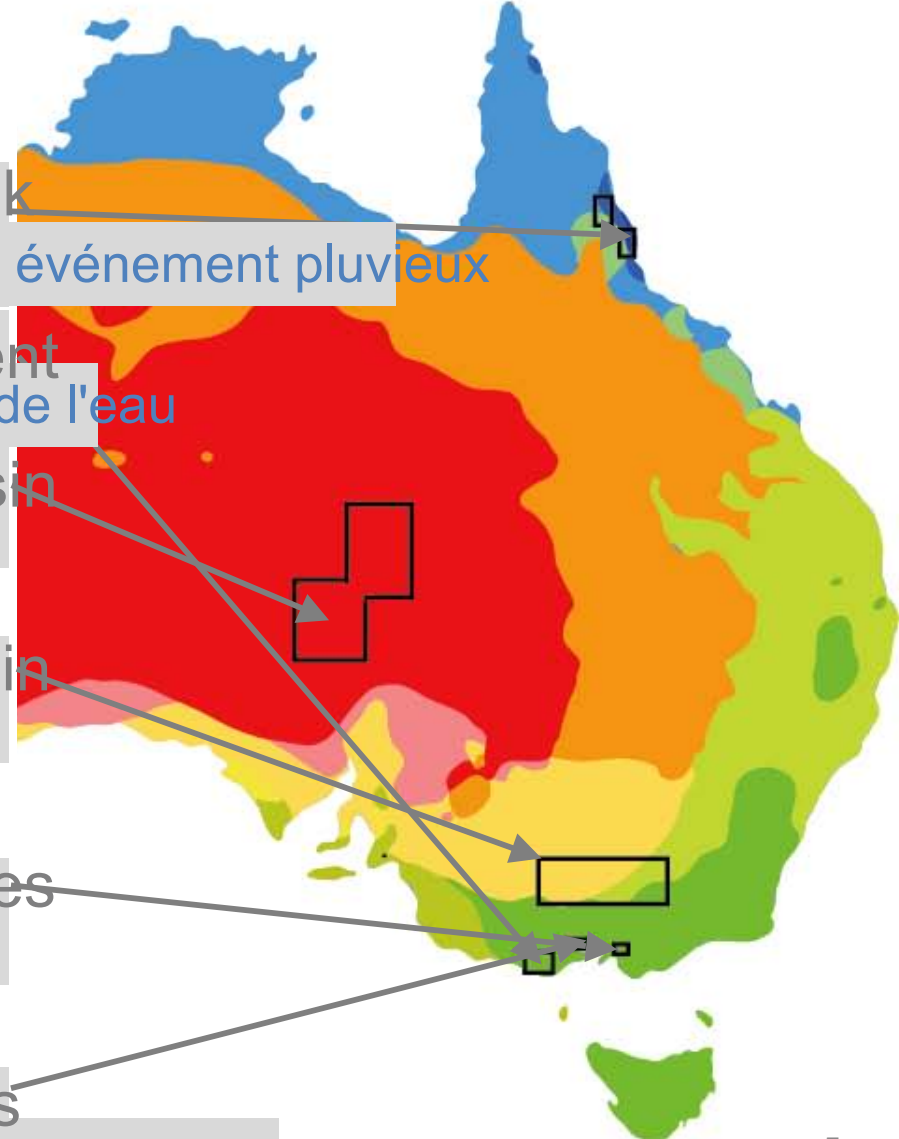
Contrôles de salinité

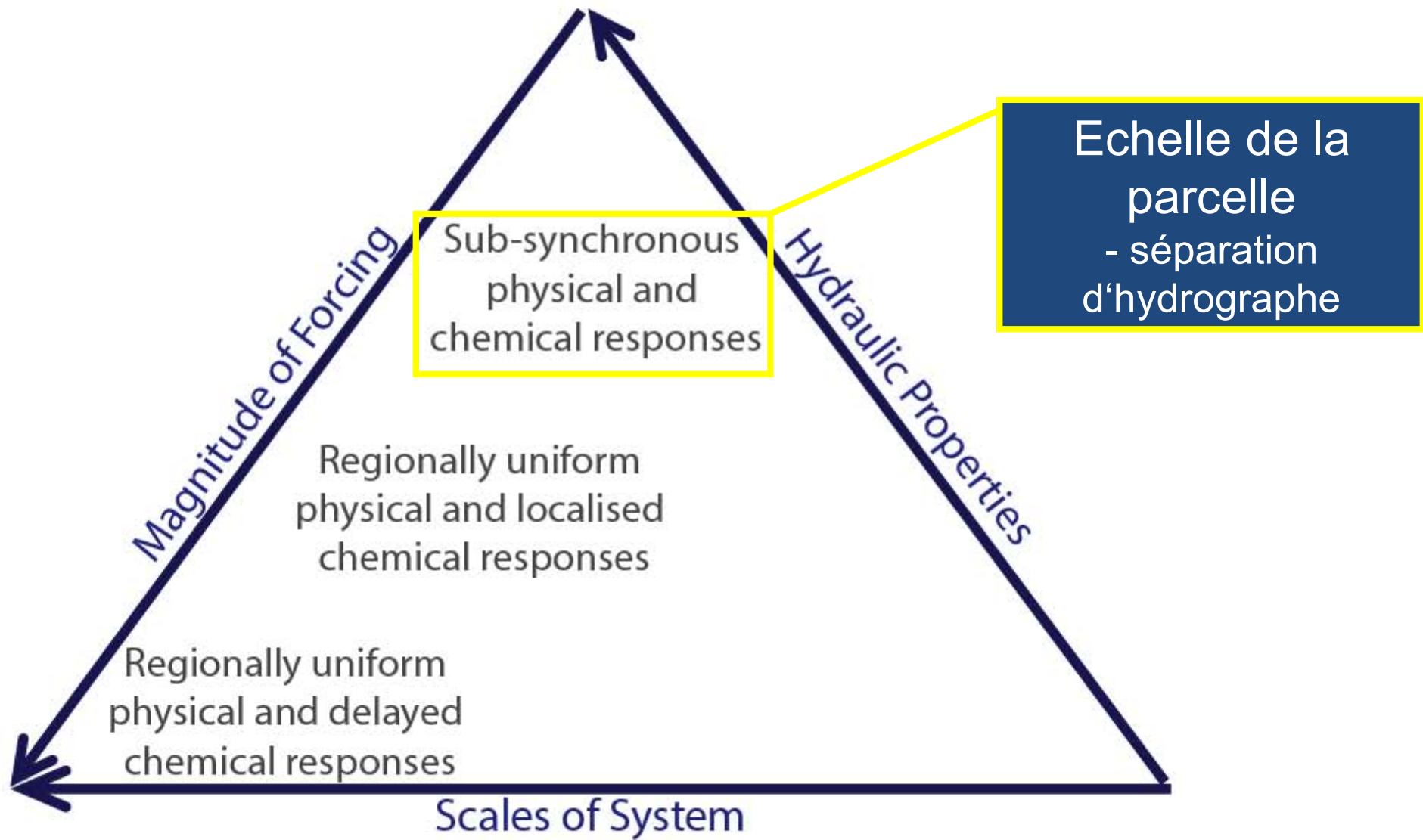
Dandenong Ranges

Mélange dans des aquifères fracturés

Mineral Springs

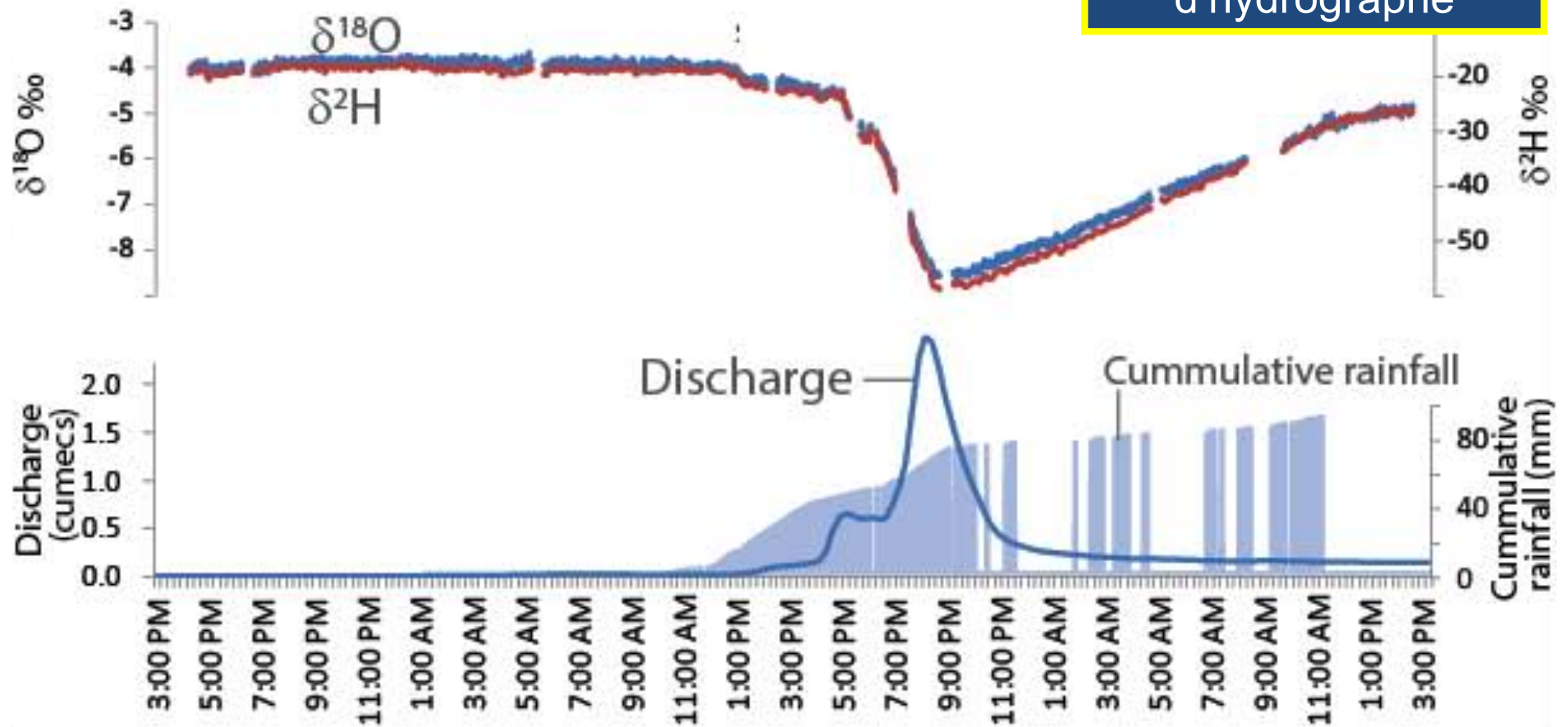
Ecoulements profonds dans les aquifères fracturés

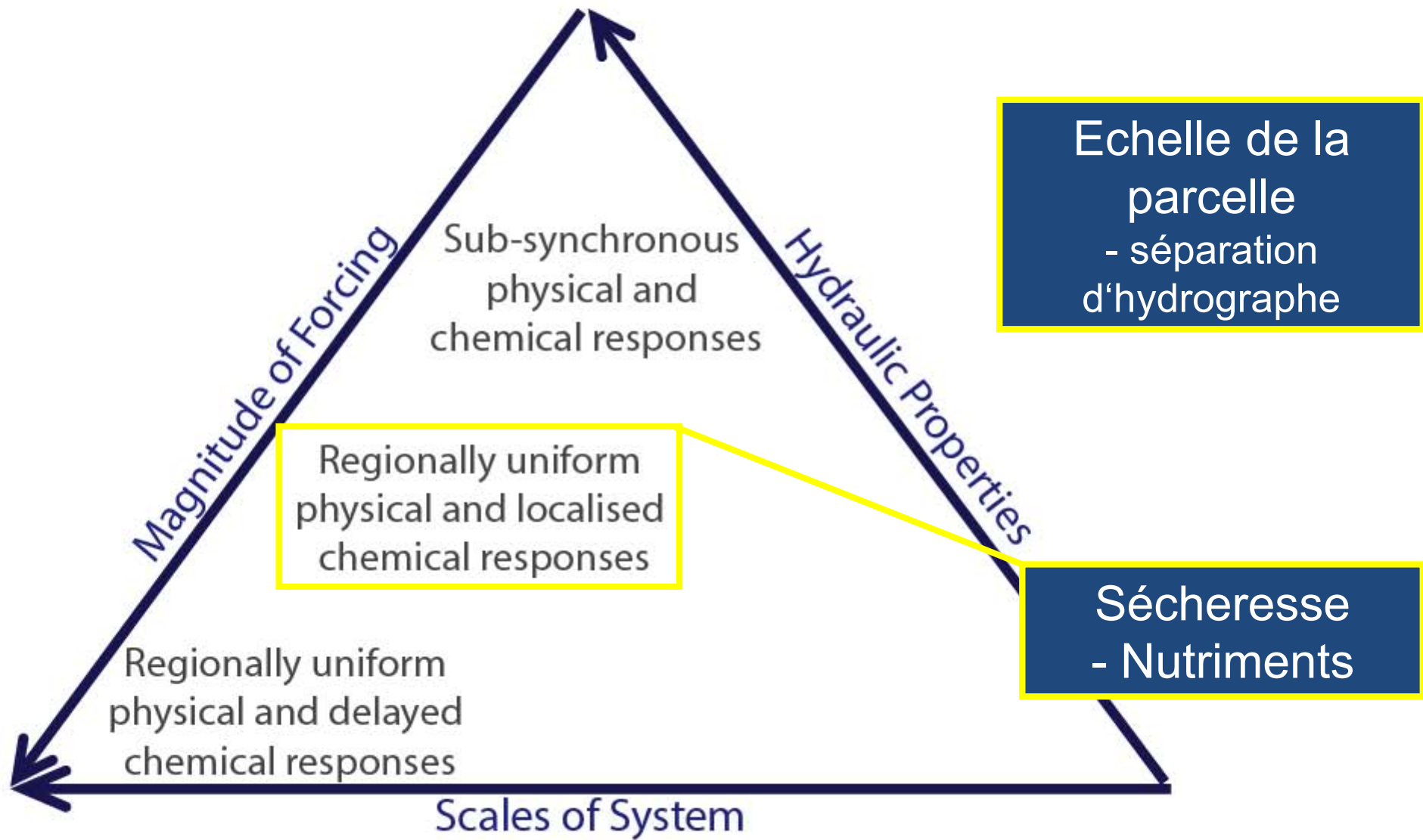


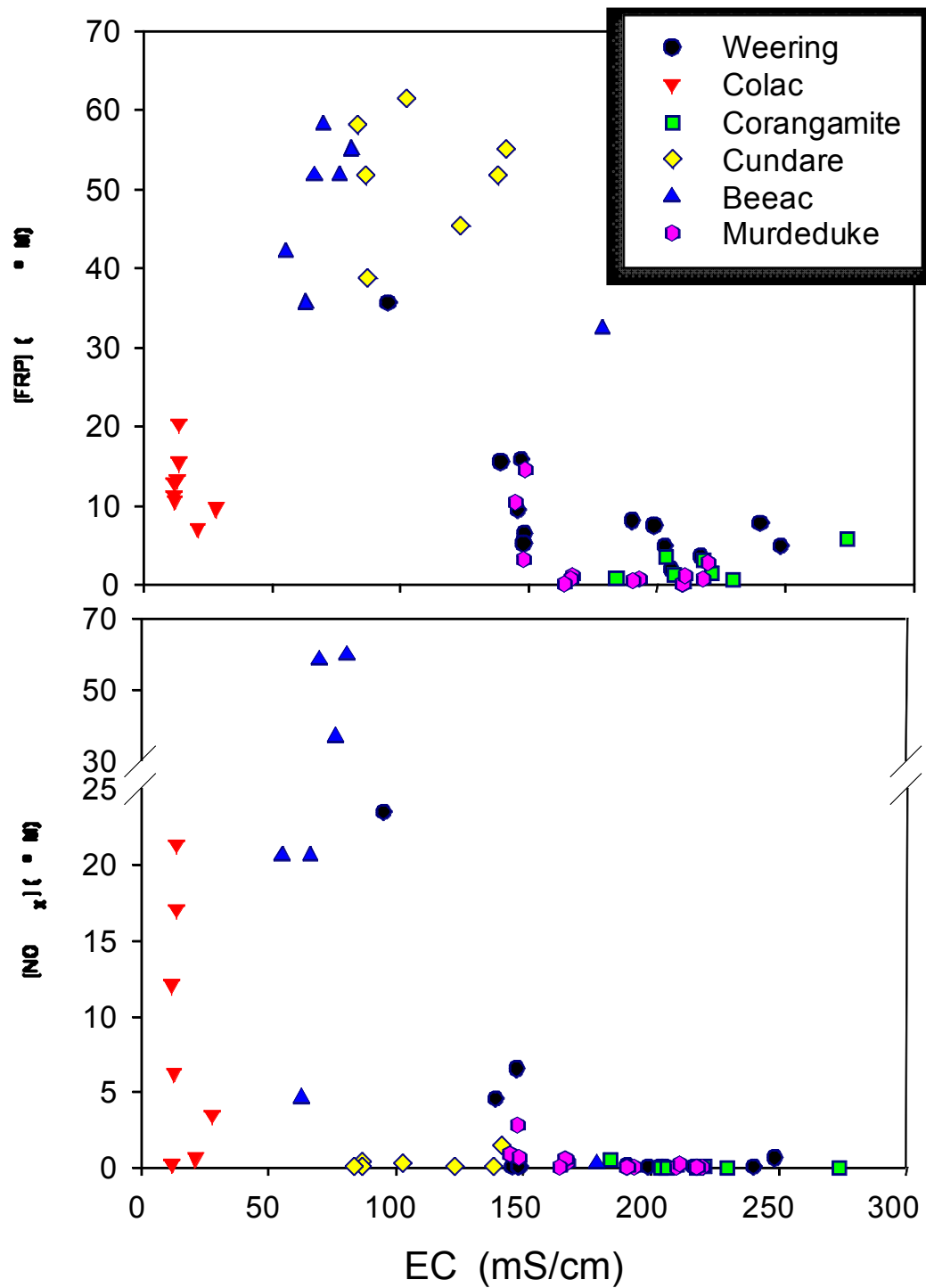


Synthèse des forçages externes

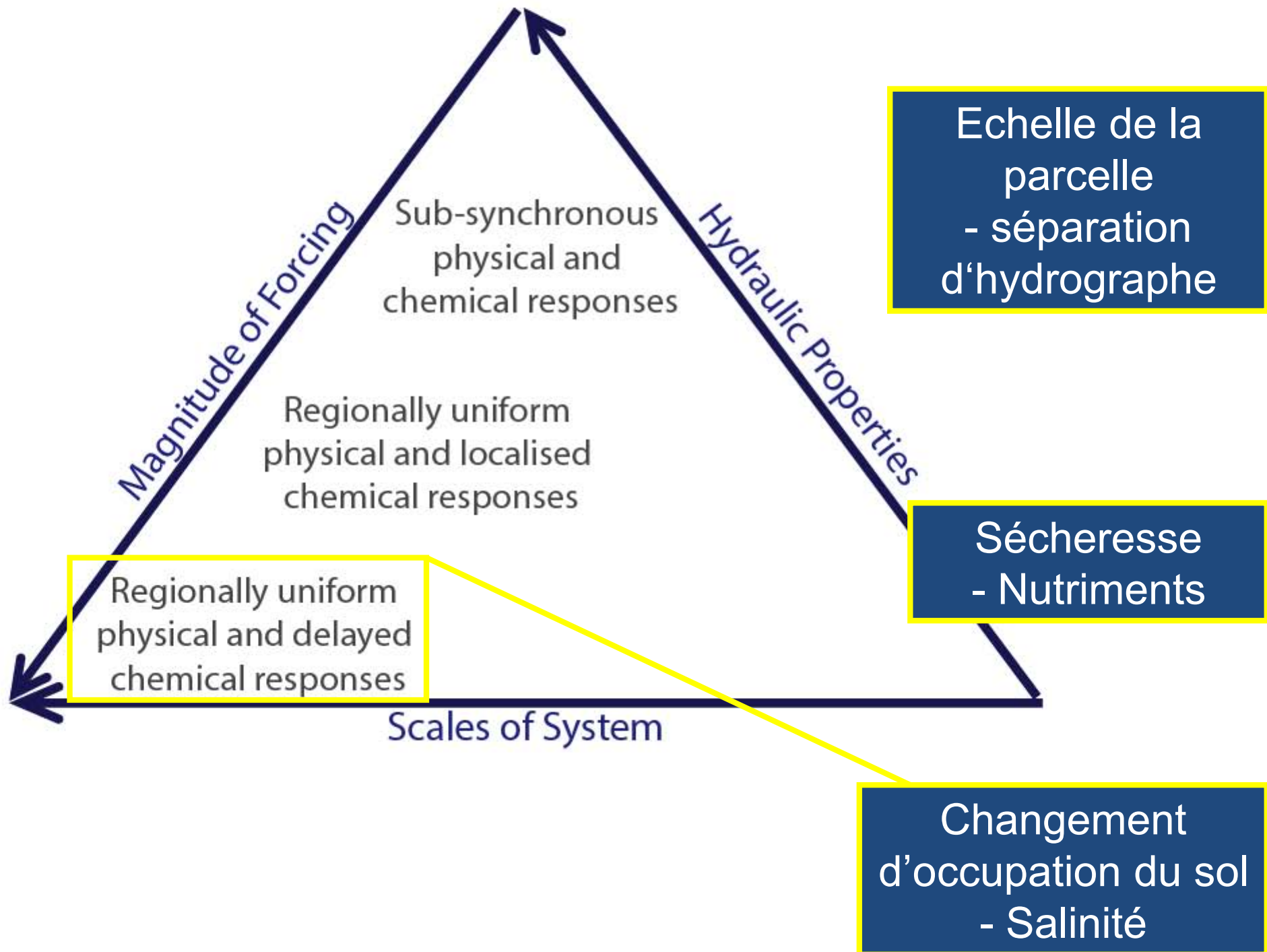
Echelle de la
parcelle
- séparation
d'hydrographe

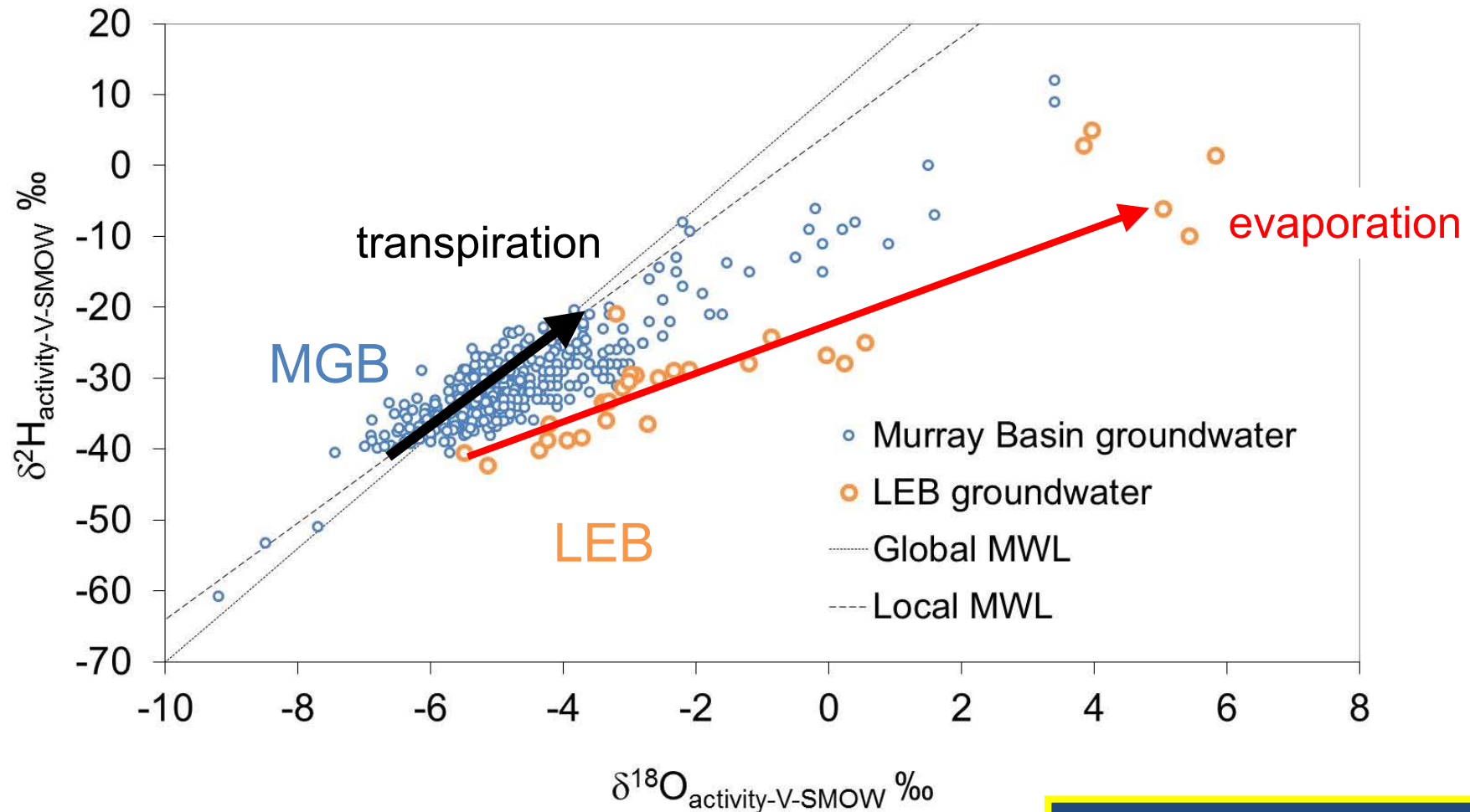






Sécheresse
- Nutriments

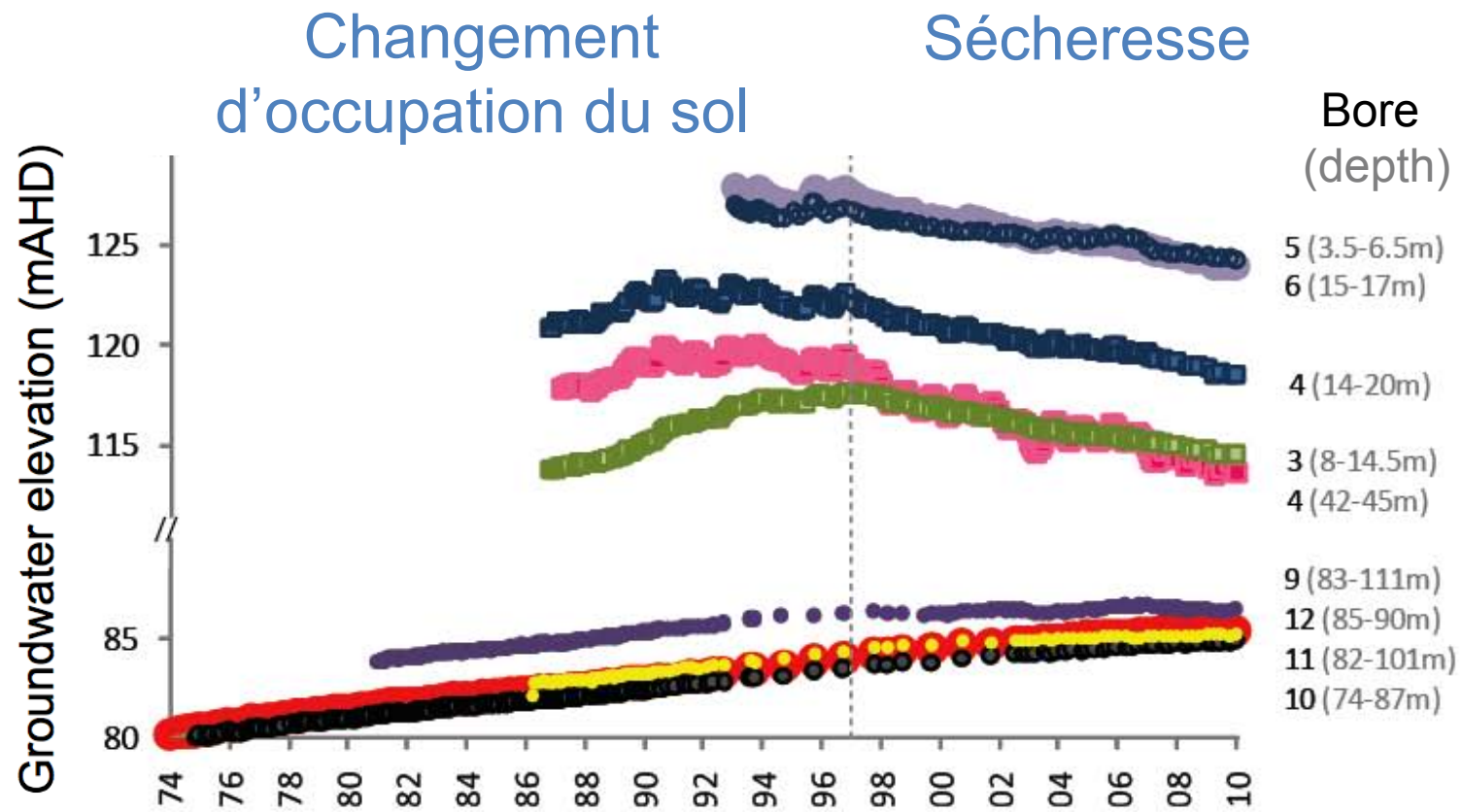




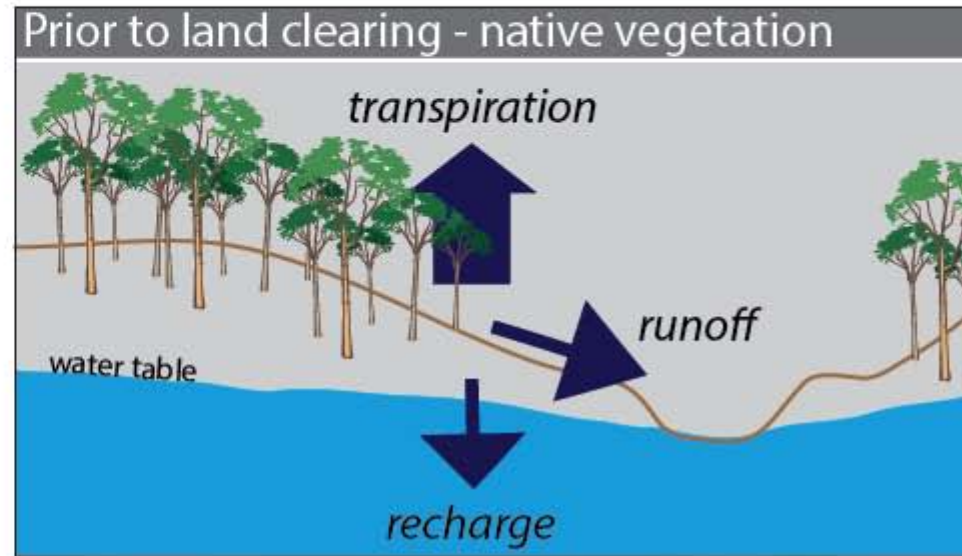
- Transpiration des eaux souterraines dans le MGB (semi-aride)

Changement
d'occupation du
sol

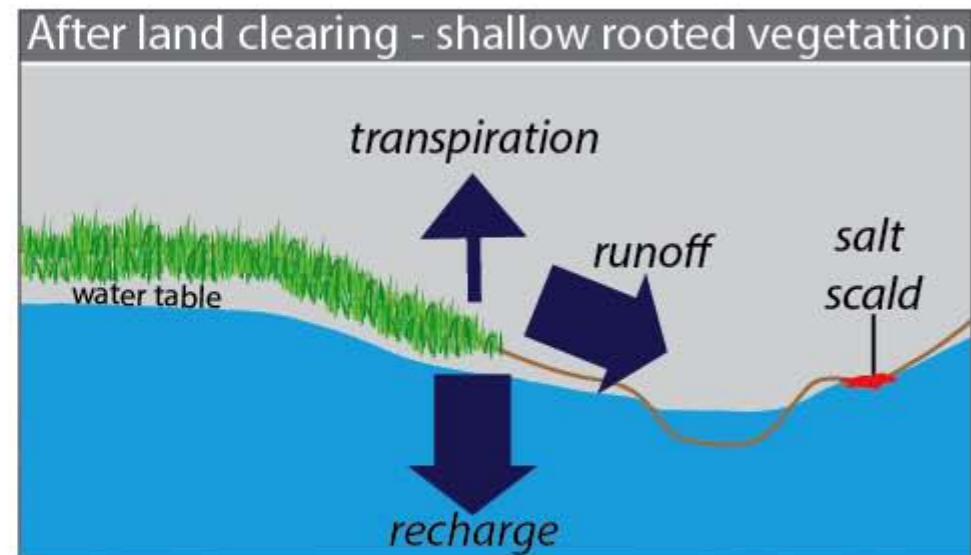
- Évaporation des eaux souterraines dans le LEB (aride)

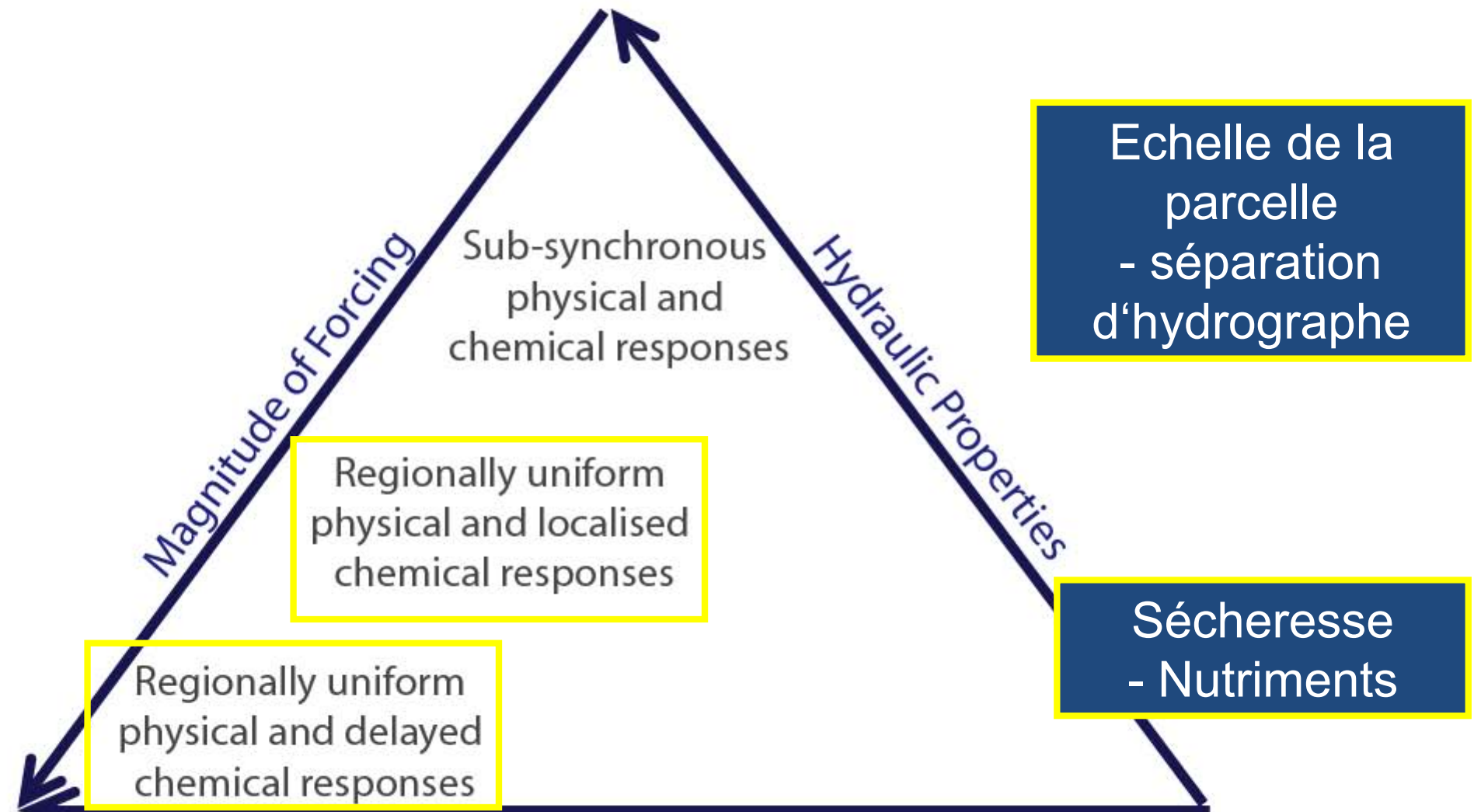


Transpiration :
système **avant**
changement
d'occupation du sol



Augmentation du niveau des
nappes :
système **après** changement
d'occupation du sol
(pratiques agricoles
européennes)





Défis

- Distinguer forçages actuels et historiques effet sur la qualité de l'eau
- Utilisation de traceurs environnementaux pour contraindre les processus physiques dans les hydrosystèmes

Avantages

Chimie peut mettre en évidence les processus historiques importants que le système physique actuel ne représente plus

Utilisez les leçons apprises dans ces hydrosystèmes

- i. Échelles et forçages multiples
- ii. Représentativité des données
- iii. Traceurs multiples
- iv. Les systèmes régionaux



Projets de recherche actuels et futurs

Datation des eaux souterraines

-> Fonctionnement hydrologique : Niger, Australie

Hydrosystèmes fortement modifiées

-> Irrigation : Senegal, Maroc

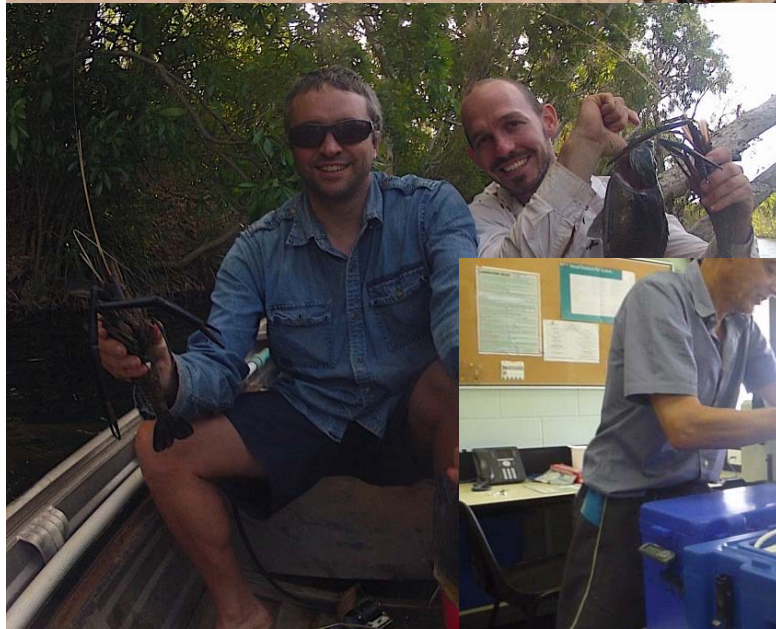
-> Transport de contaminants agricoles : Australie, France

-> Fonctionnement du continuum eau-sol-plante sous conditions climatiques extremes : France

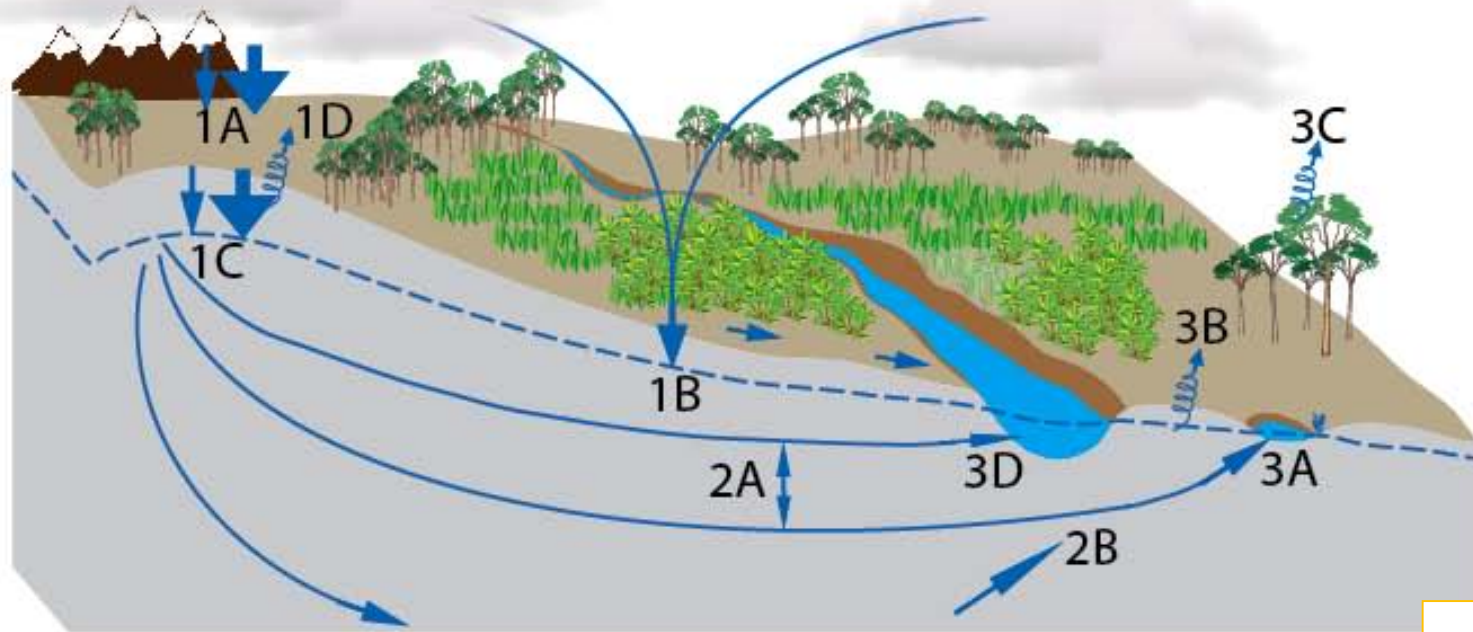
Australian Research Council
Victorian Mineral Waters Commission
Corangamite Catchment Management Authority
National Groundwater Centre



Thanks



1. Research Retrospective



1. Recharge

- A. rainfall intensity and seasonal rainfall ($\delta^{18}\text{O}$, $\delta^2\text{H}$)
- B. rainfall origin ($\delta^{18}\text{O}$, $\delta^2\text{H}$)
- C. via dual porosity (^3H , ^{14}C)
- D. evaporation during recharge ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

- recent (CFCs, SF6)
- paleo ($\delta^{18}\text{O}$, $\delta^2\text{H}$, ^{14}C)

2. Flow Pathways

- A. mixing (majors, CFCs, ^{14}C)
- B. deep groundwater flow ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

- origin of solutes ($\delta^{13}\text{C}$, majors/trace)
- controls on salinity ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Cl/Br, majors)

3. Discharge

- A. to lakes (Cl/Br, Cl)
- B. via evaporation ($\delta^{18}\text{O}$, $\delta^2\text{H}$)
- C. via transpiration ($\delta^{18}\text{O}$, $\delta^2\text{H}$)
- D. to rivers ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Si)

- transfer of inorganic carbon (DIC, $\delta^{13}\text{C}$) and contaminants (nutrients, herbicides, pesticides)

physical

chemical

Study area	Climate	Mean annual rainfall (mm)	Terrain	Dominant geology	Dominant land use	Hydrosystem process studied
Mineral Springs*	temperate oceanic	880	valleys and base of hillslope	basalt and sediments	grazing and dryland cropping	spring water origins and flow pathways
Dandenong Ranges*	temperate oceanic	600 - 1200	highlands	basalt and marine sediments	horticulture	recharge processes, groundwater flow in fractured aquifers
Corangamite Catchment*	temperate oceanic	730	plains	basalt, and alluvial sands and clays	grazing and dryland cropping	drought impacts on water quality
Glenelg Hopkins Catchment	temperate oceanic	550	plains	basalt, and alluvial sands and clays	grazing and dryland cropping	groundwater and lakes interactions
Murray Groundwater Basin*	cold semi-arid	400–600	plains	paleochannels, and alluvial sands and clays	grazing and dryland cropping	salinity processes and groundwater pathways
Lake Eyre Basin*	warm desert	140-260	plains	sand, clay and sandstone	grazing	salinity and recharge processes
South Johnstone (Scheu Creek)*	monsoon	3500	base of hillslope	basalt and sediments	sugar cane	groundwater and creek interactions, transport of contaminants and DIC
Atika Creek Catchment*	monsoon	1990	base of hillslope	mudstone siltstone	forested	transport of DIC
Mitchell River Basin*	monsoon and tropical savanna	1600	highlands and plains	sediments and igneous intrusive	forested and grazing	recharge origins, groundwater and river interactions, transport of DIC
Cape York Springs	tropical savanna	1900	valleys and base of hillslope	sandstones, bauxites, ferricrete, sand	forested and grazing	spring water origins

Environmental tracer sampling regime

Increasing study area	Number of sampling sites	Temporal resolution
Scheu Creek	6	hourly over 2 days; creek continuous (1 min)
Atika Creek	2	hourly over 2 days; creek continuous (15 min)
Dandenong Ranges	14	4 seasons (over 2 years)
Glenelg Hopkins Catchment	11	3 seasons (over 1 year)
Mitchell River Basin	13	weekly-monthly (over one year)
Mineral Springs	34	monthly (over 4 months)
Corangamite Catchment	6	monthly (over 2 years)
Cape York Springs	10	once
Murray Groundwater Basin	440	once
Lake Eyre Basin	36	3 seasons (over 1 year)

CFCs

Processes impacting CFCs

Recharge conditions

- CFC solubility is affected by recharge temperature
- Excess air effect; enrichment of CFC-12 relative to CFC-11 during dissolution of air bubbles that are trapped in the unsaturated zone

Aquifer and groundwater chemistry

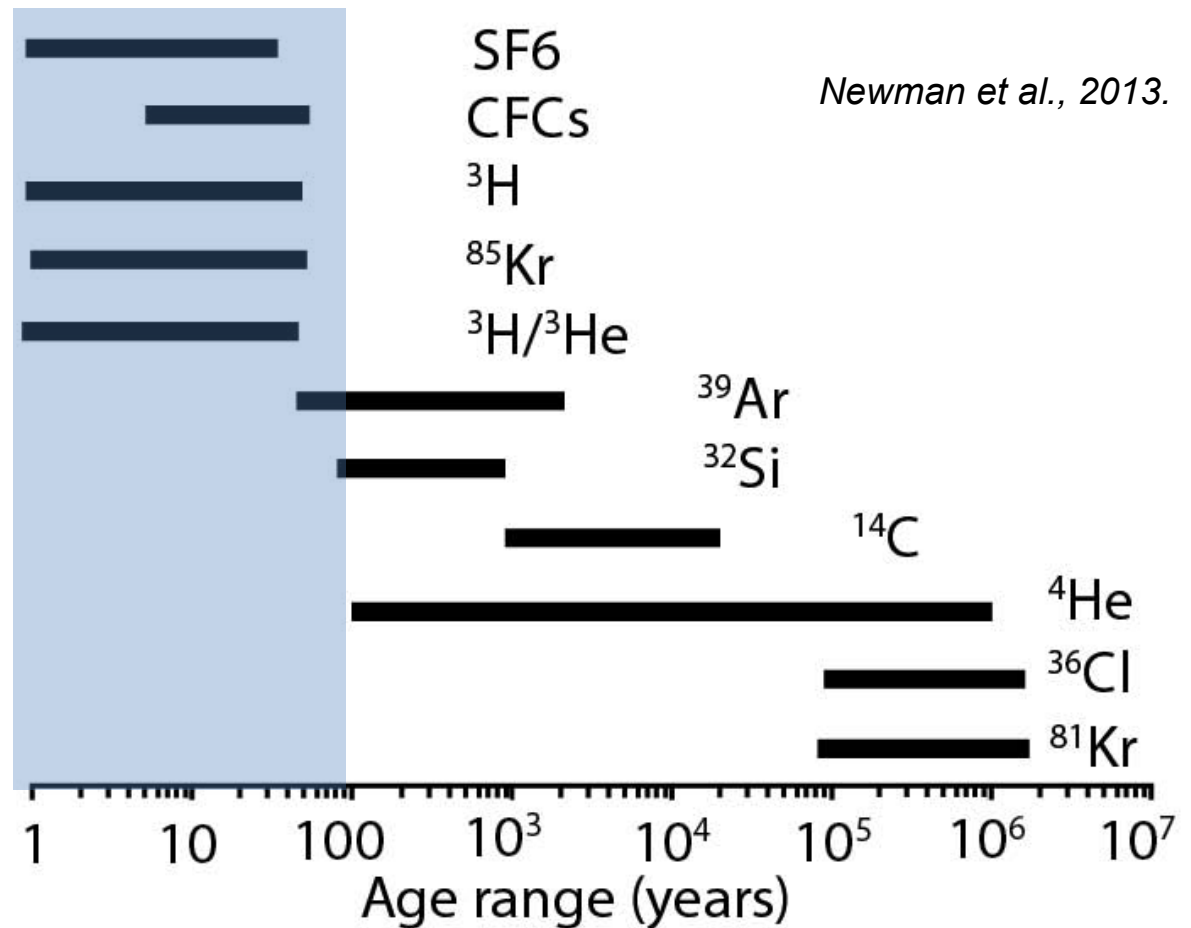
- In organic-rich aquifers sorbtion onto organic and mineral surfaces; increases in CFC-12 to CFC-11 and CFC-13
- Anaerobic microbial degradation; rapid loss of CFC-11 and CFC-13 compared with CFC-12
- In industrial and urban regions CFC contamination

During flow

- Vertical velocity and connectivity of fracture networks
- Mixing between fracture and matrix waters
- Solute diffusion effects

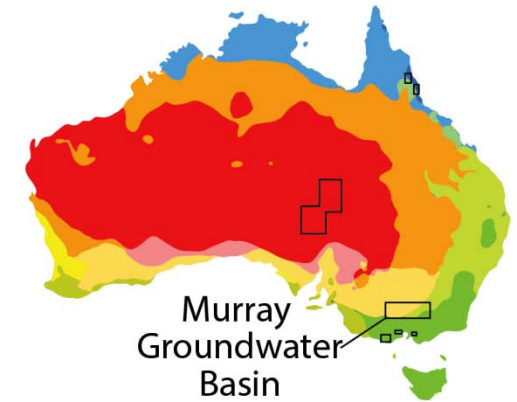
Improvements to CFC dating

- Other dating tracers
- Noble gases to correct for excess air
- Environmental tracers to identify mixing effects
- Solute modelling to identify diffusive transport effects



14C

Mixing in alluvial aquifers – Murray Groundwater Basin



Questions

Investigation of heterogeneous geological controls on inter-aquifer mixing

Approach

^{14}C

- Part of a greater research project which incorporates ^{14}C with $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in MGB ($\sim 100\,000\text{ km}^2$)

Management Links

Water resource sustainability in a large agricultural basin

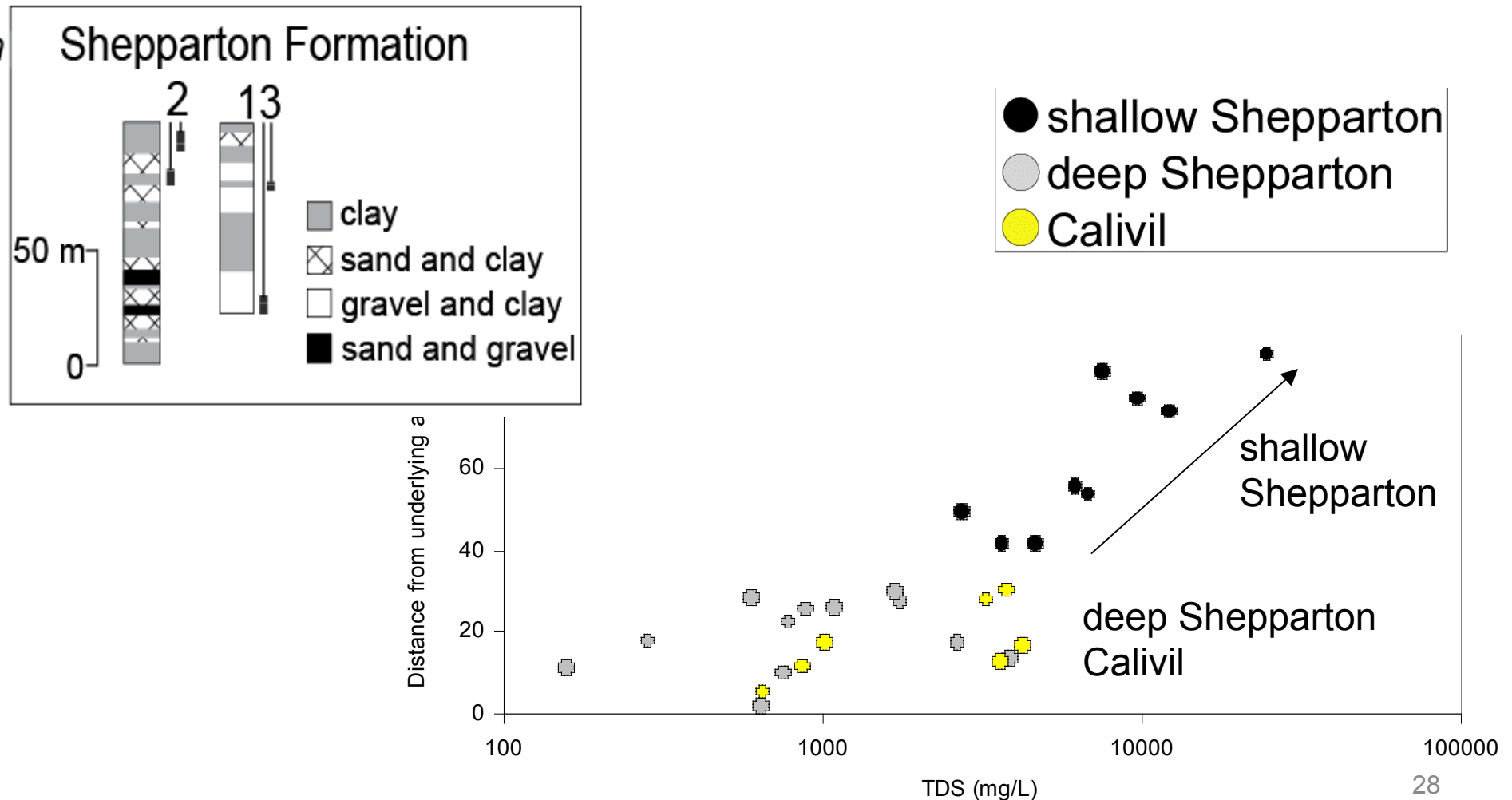
Funding

ARC

Cartwright, I., Weaver, T.R., Cendón, D.I., Fifield, L.K., Tweed, S.O., Petrides B., Swane, I. 2012. Constraining groundwater flow, residence times, inter-aquifer mixing, and aquifer properties using environmental isotopes in the southeast Murray Basin, Australia. *Applied Geochemistry*, 27, 1698-1709.

Mixing in alluvial aquifers - Murray Groundwater Basin

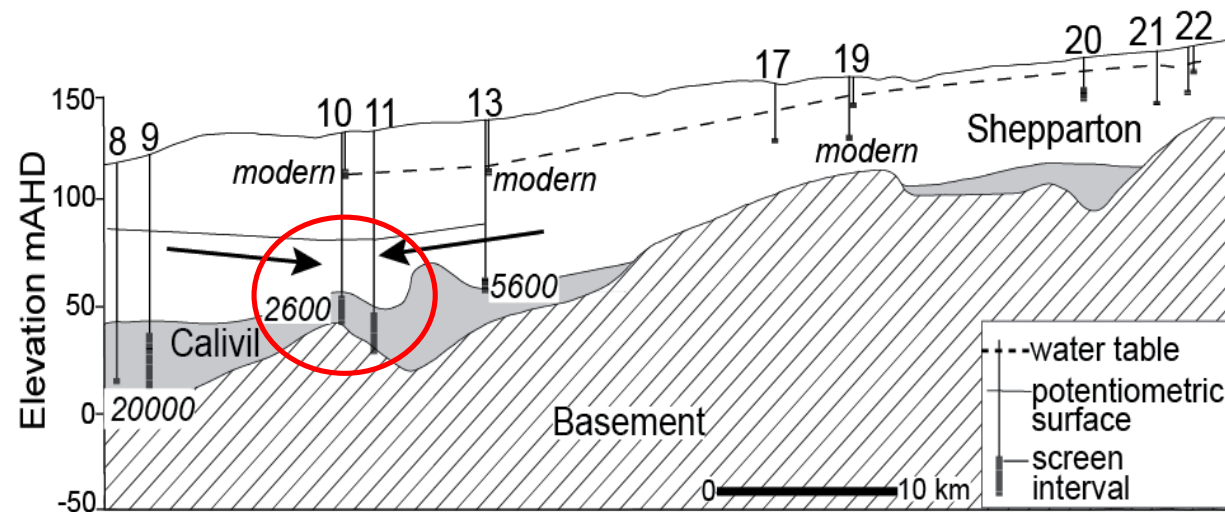
- Deeper aquifers: fresher (TDS: 160 - 4,250 mg/L)
- Shallower aquifers: more saline (TDS: 2,180 - 24,700 mg/L)



Mixing in alluvial aquifers - Murray Groundwater Basin

^{14}C

- 7 to 101 pmC
- Groundwater < 30m depth: modern recharge
- Groundwater 66-109 m: 2600-20000 years
- ^{14}C - areas of infiltration from the shallower system



Mixing in alluvial aquifers - Murray Groundwater Basin

$\delta^{18}\text{O}$ and $\delta^2\text{H}$

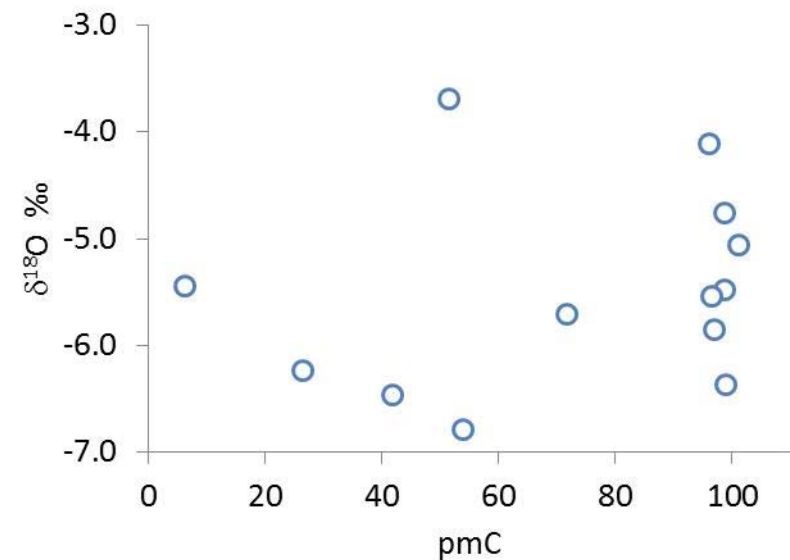
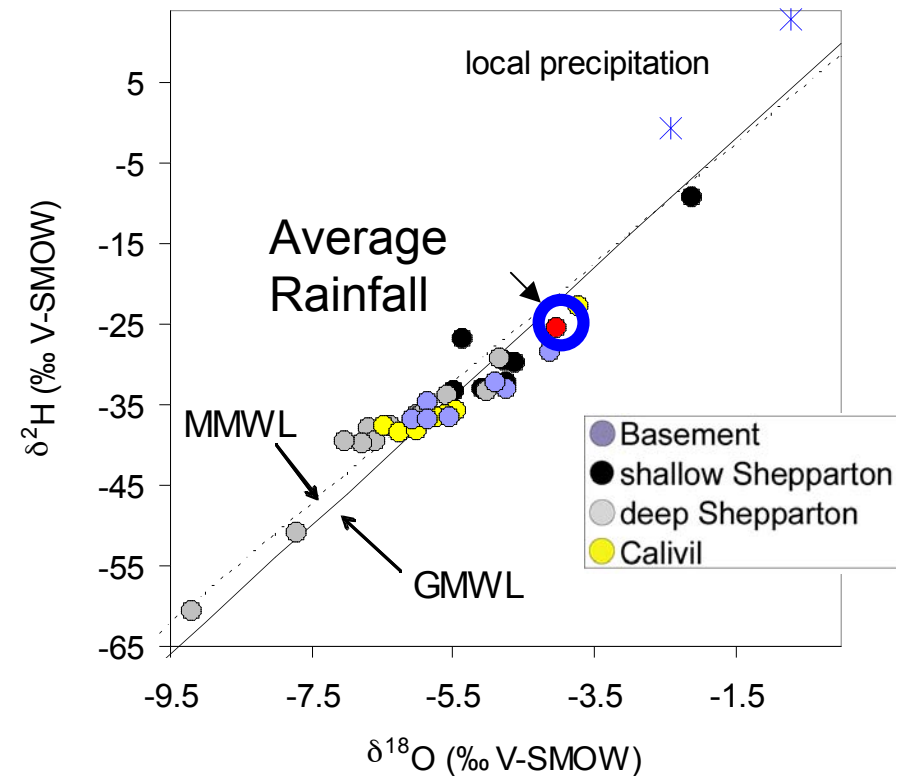
No correlation with ^{14}C age

-> Older and younger groundwater
recharged under similar conditions

or

-> Other factors effecting ^{14}C age

- Errors in ^{14}C correction
- Mixing
- Diffusion



Mixing in alluvial aquifers - Murray Groundwater Basin

¹⁴C

Qualitatively infer groundwater mixing between two aquifers of complex alluvial deposits

- across MGB: significant inter-aquifer mixing



Mixing in alluvial aquifers - Murray Groundwater Basin

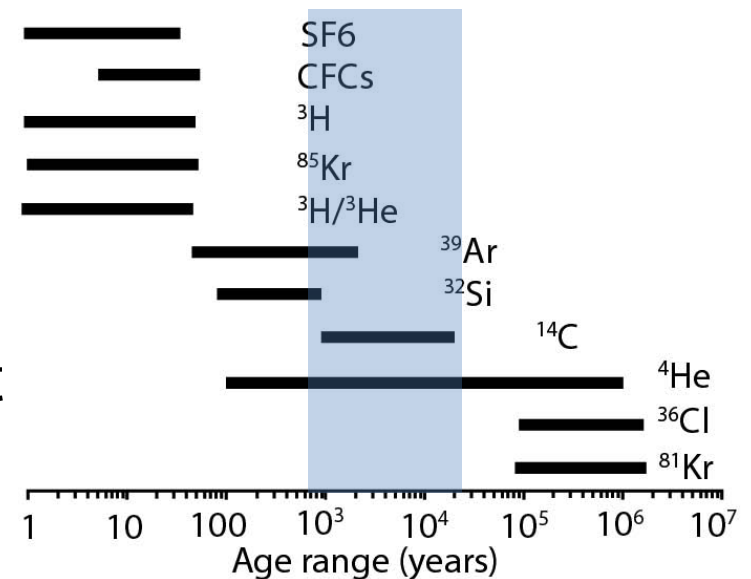
Challenges in calculating the residence time of water using ^{14}C

- Determination of the initial ^{14}C content, A_0 ; infiltrating water is isolated from unsaturated zone ^{14}C reservoir
- Mixing between waters
- Diffusive transport
- Heterogeneous geochemical reactions in aquifer
 - Dissolution of carbonate minerals or organic material from the aquifer matrix;
 - Deep-seated CO_2 from volcanic activity;
 - CH_4 generated via the breakdown of organic material in the aquifer matrix

Mixing in alluvial aquifers - Murray Groundwater Basin

To overcome these challenges

- Multiple tracers of similar timeframes
- Environmental tracers to explore mixing
- Solute models to explore diffusion affect
- Correct for geochemical reactions;



- Dissolution of carbonates corrected using dilution factor (q)
 - Measured $\delta^{13}\text{C}$ of groundwater -16.6 to -8.8 ‰ V-PDB
 - Estimate of $\delta^{13}\text{C}$ of calcite dissolved 0‰ V-PDB
 - Estimate of $\delta^{13}\text{C}$ of soil -23‰ V-PDB
 - Estimate of recharge pH

^{14}C correction

Heterogeneous dissolution of carbonates corrected using dilution factor (q)

$$t = -8267 \times \ln\left(\frac{a_t {}^{14}\text{C}}{q \times a_o {}^{14}\text{C}}\right)$$

-8267 is the decay constant, a_t is the activity after some time, and a_o is the initial activity

$$q_{\delta^{13}\text{C}} = \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{carb}}}{\delta^{13}\text{C}_{\text{rech}} - \delta^{13}\text{C}_{\text{carb}}}$$

$\delta^{13}\text{C}_{\text{DIC}}$ is groundwater -16.6 to -8.8 ‰ V-PDB, $\delta^{13}\text{C}_{\text{carb}}$ is calcite dissolved ~ 0‰ V-PDB

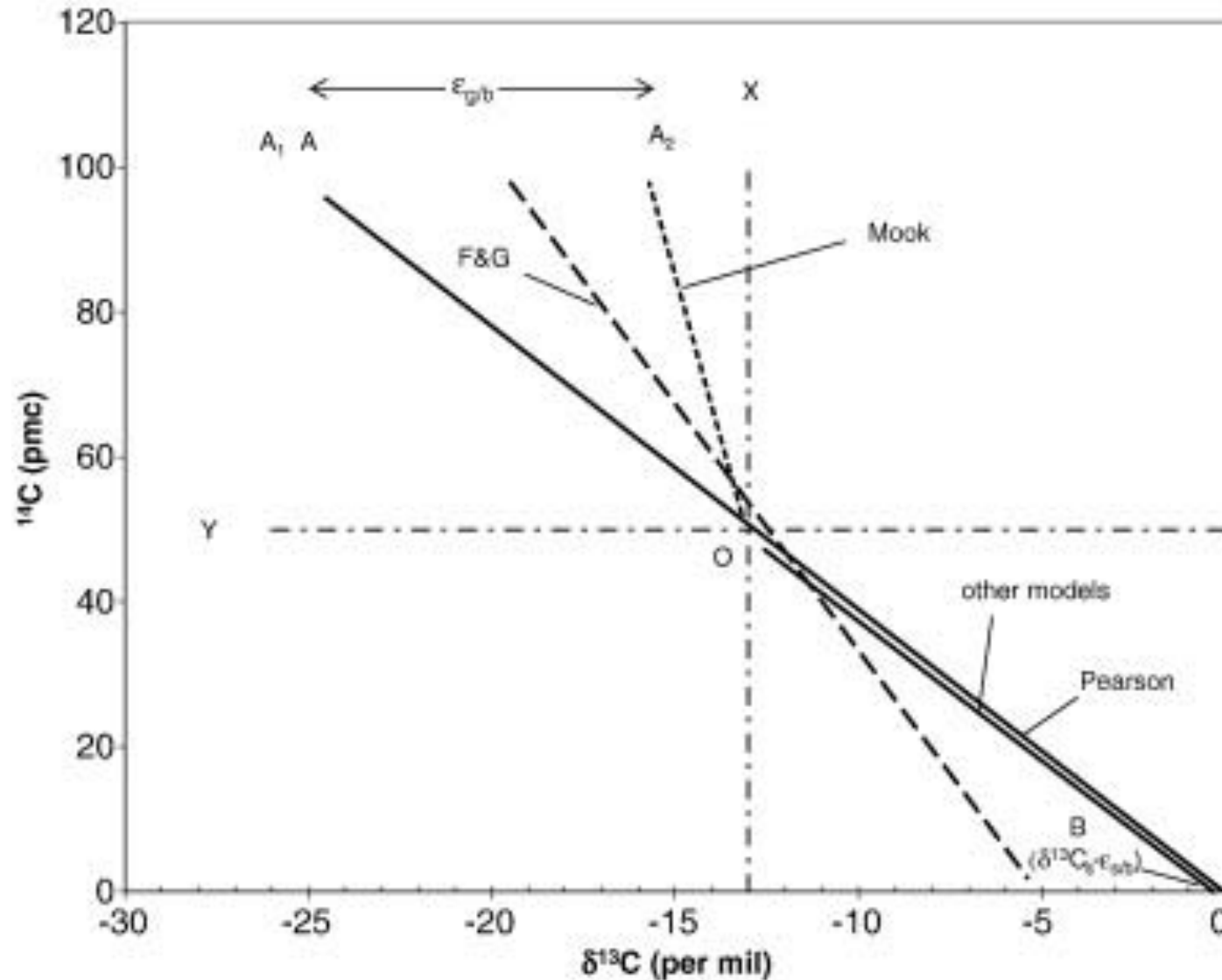
$$\delta^{13}\text{C}_{\text{rech}} = \delta^{13}\text{C}_{\text{soil}} + \epsilon^{13}\text{C}_{\text{DIC}-\text{CO}_2(\text{soil})}$$

$\delta^{13}\text{C}$ of soil ~ -23‰ V-PDB

enrichment between soil CO_2 and aqueous carbon ~ 2.4-8.5 ‰ V-PDB

- Recharge pH assumed
- Estimates of soil and calcite $\delta^{13}\text{C}$ values

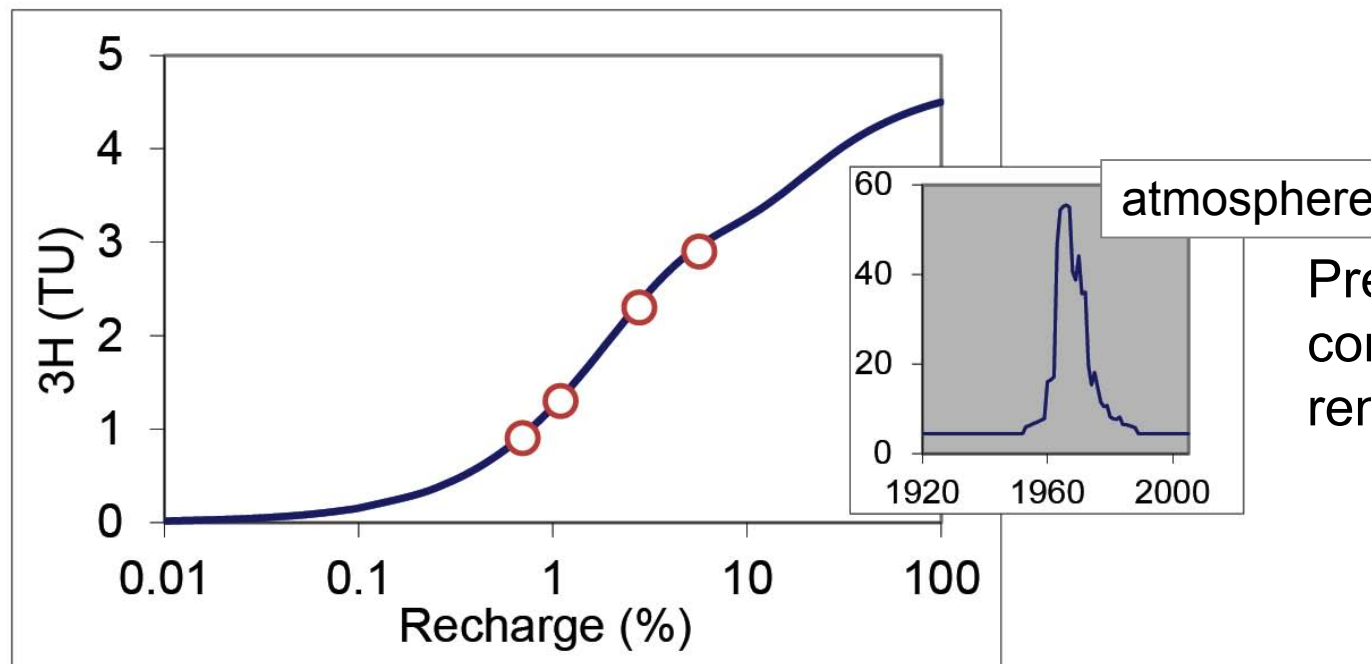
Han and Plummer, 2013.



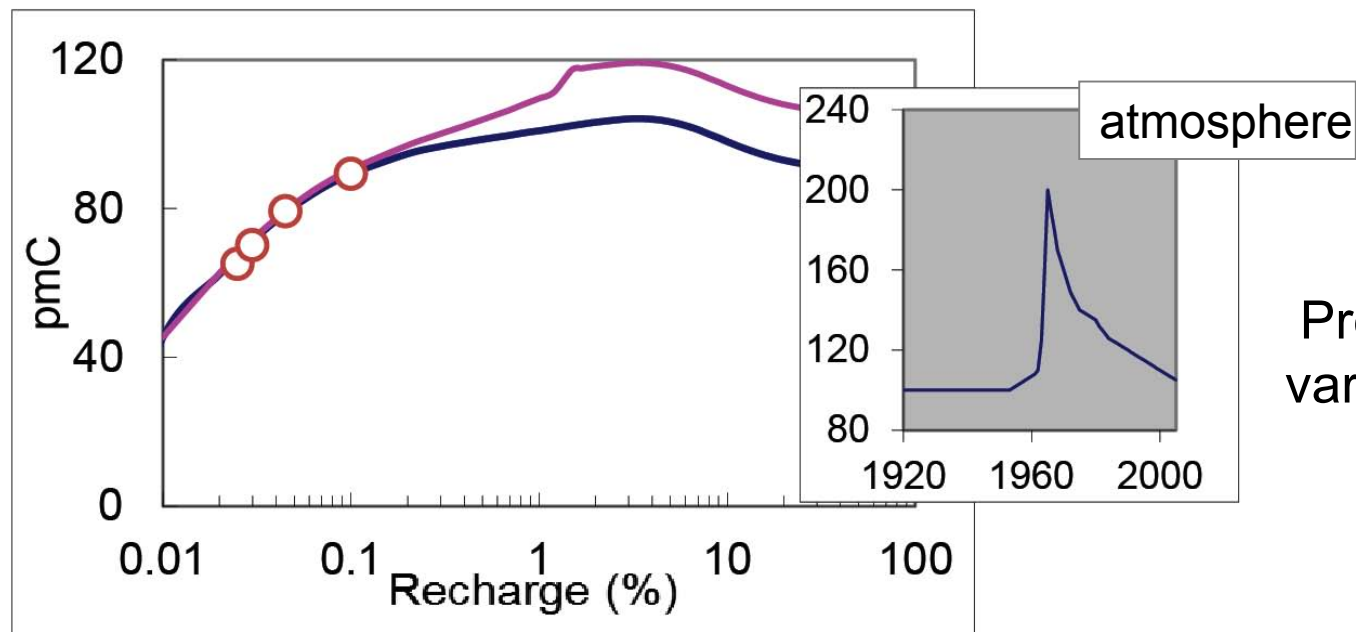
Models represented in the relationship of ^{14}C vs. $\delta^{13}\text{C}$. Points A, A1 and A2 represent isotopic composition of gaseous soil CO_2 , dissolved CO_2 in water and HCO_3^- . Line O–B represents simulated values from the models of Wigley (1976), Evans et al. (1979), and Eichinger (1983). Pearson's model is shown by the line that connects the origin and A (or A₁). X and Y represent 0.5 $\delta^{13}\text{C}$ and 0.5 ^{14}C respectively.

^3H and ^{14}C covariance curve

- Co-variance of ^3H contents and ^{14}C activities for expected values in recharge areas
- Renewal rate (R_n); percentage of aquifer replenished each year by recharge
- Recharge rates relate to renewal rates via the aquifer thickness (b) and porosity (n):
 $R = R_n b n$
- Calculations assume that pre-atmospheric nuclear test precipitation had the same ^3H concentration as modern precipitation in Melbourne (~4.5 TU)
- Use of ^{14}C to define renewal rates is complicated by the dissolution of old carbon from the aquifer matrix.
 - Simple assumption that 15% of carbon was derived from the aquifer

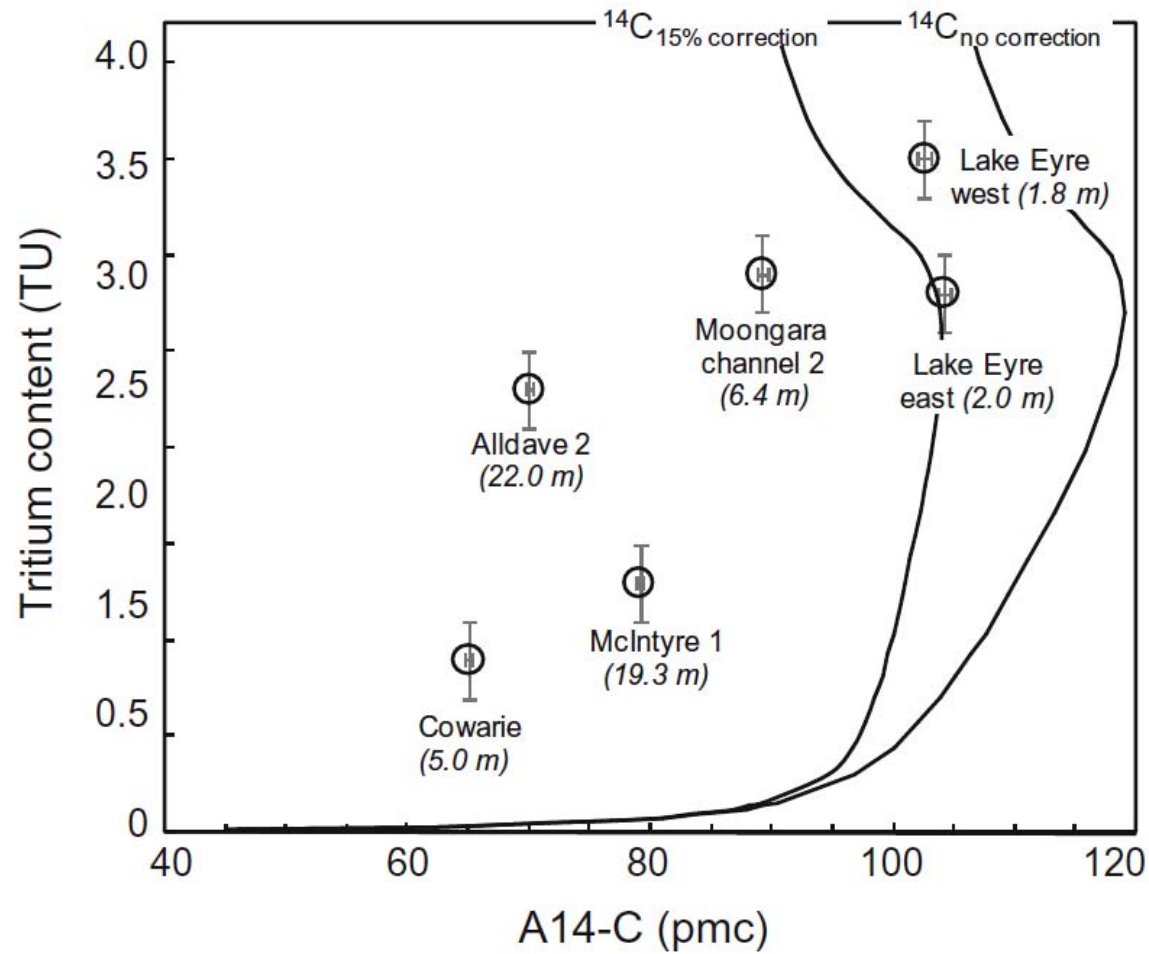


Predicted ^3H concentration for various renewal rates



Predicted ^{14}C activity for various renewal rates

^3H and ^{14}C covariance curve



REEs

Mixing in fractured rock aquifers

- Dandenong Ranges

Question

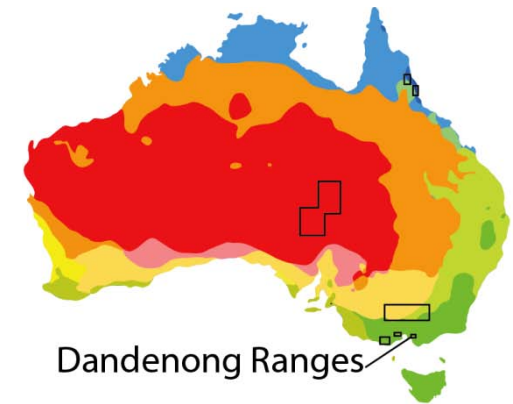
In fractured rock aquifers extent of inter-aquifer mixing?

Approach

Major ions, CFC-11, CFC-12, and REEs

Management link

Aquifer vulnerability to intensive farming



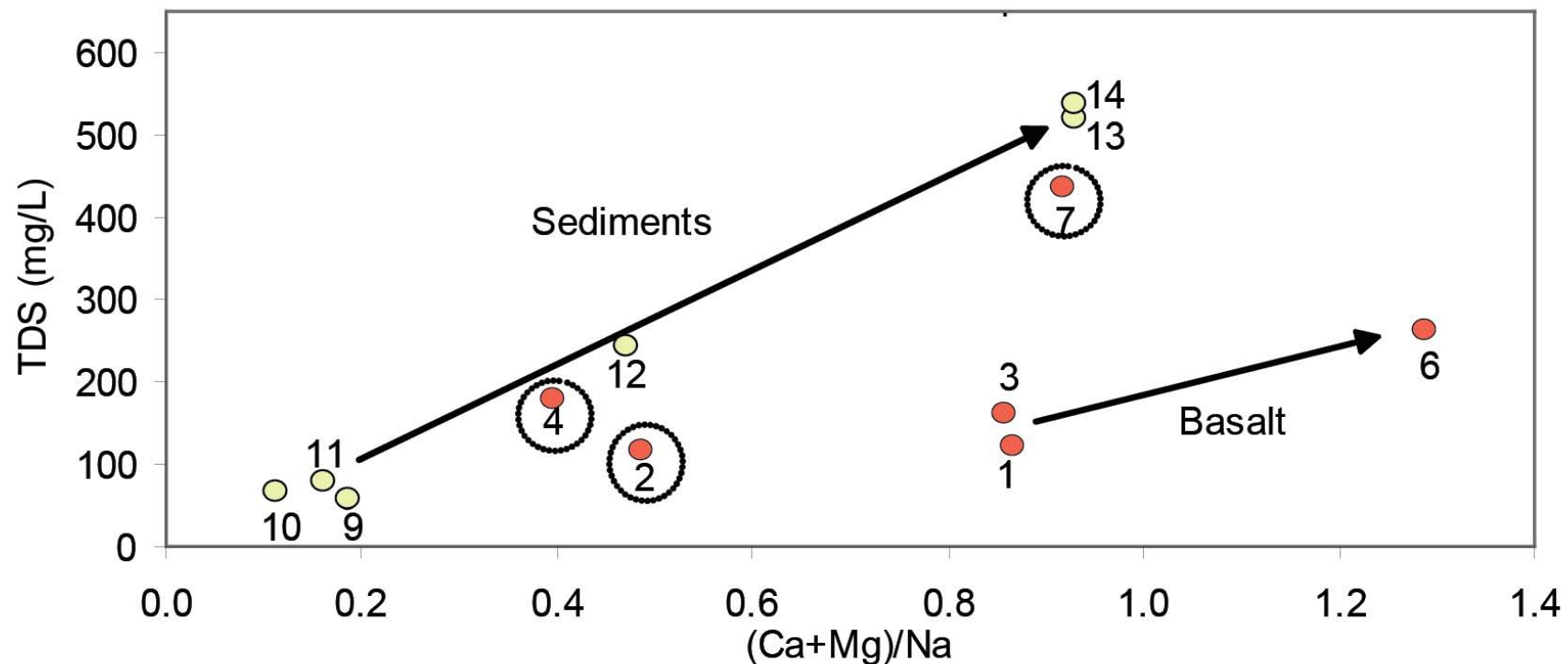
Tweed S.O., Weaver T.R., Cartwright I., 2005. Distinguishing groundwater flow paths in different fractured-rock aquifers using groundwater chemistry: Dandenong Ranges, southeast Australia. *Hydrogeology Journal* 13(5-6); 771-786

Tweed S.O., Weaver T.R., Cartwright I., Schaefer, B., 2006. Behaviour of rare earth elements in groundwater during flow and mixing in fractured rock aquifers. An example from the Dandenong Ranges, southeast Australia. *Chemical Geology* 234

Mixing in fractured rock aquifers - Dandenong Ranges

Major ion concentrations increase along groundwater flow paths

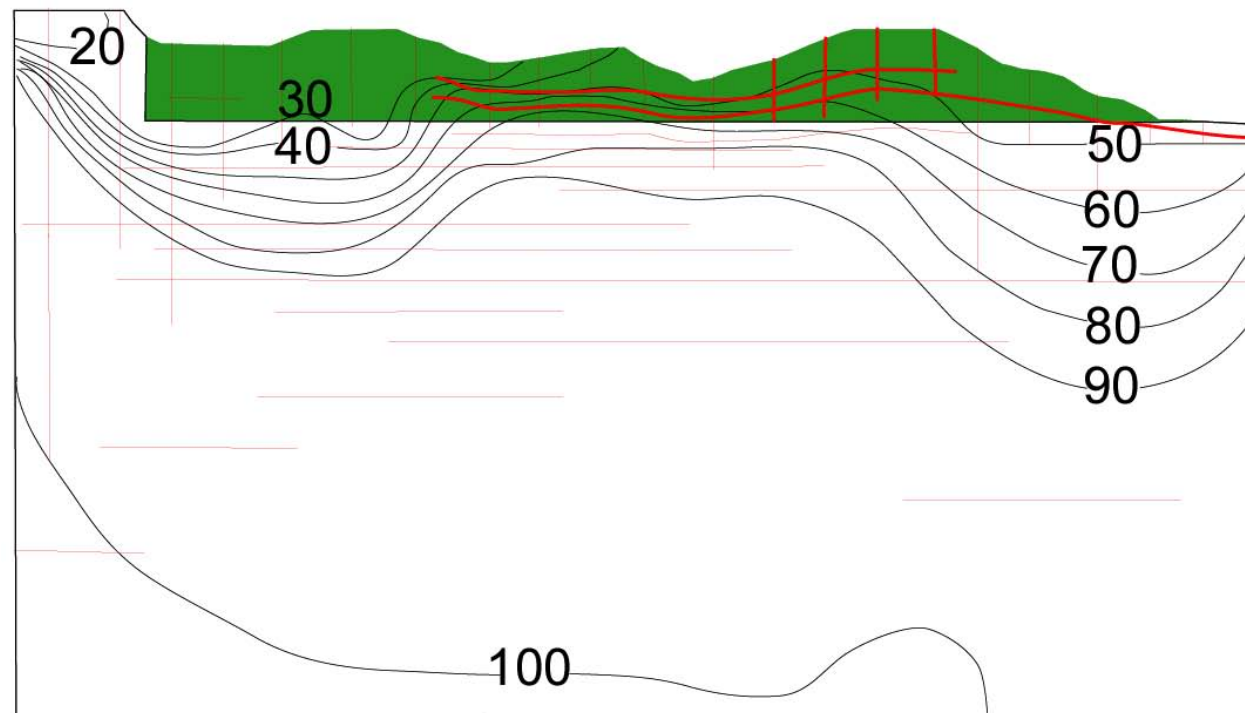
- Olivine and plagioclase dissolution
- Basalt aquifer - increases in Mg, Si and Ca to Na concentrations
- Mixing between groundwater from the basalt and sedimentary aquifers



Mixing in fractured rock aquifers - Dandenong Ranges

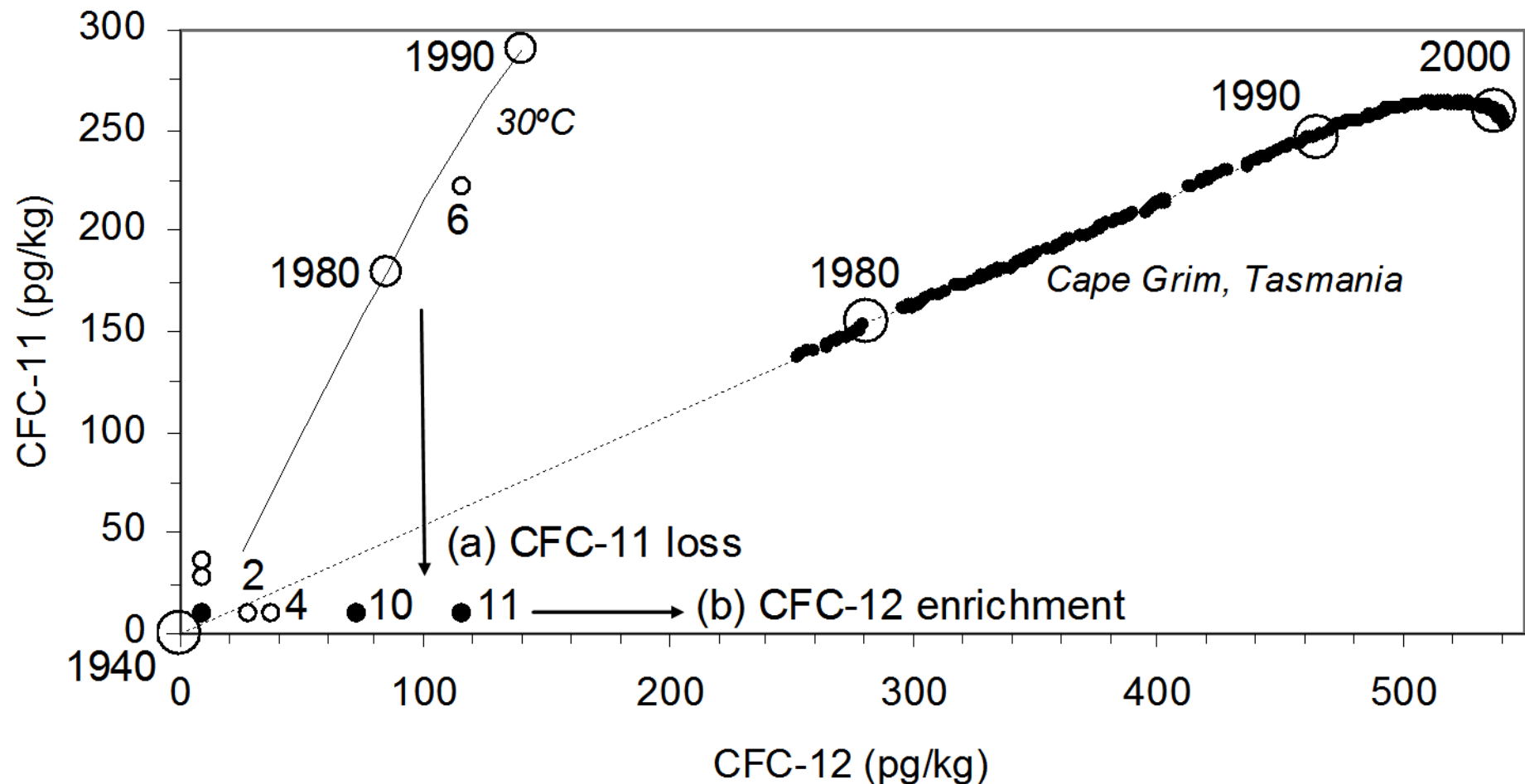
Physically based model (FRAC3DVS)

- Construct conceptual model for fracture flow pathways and mixing



Mixing in fractured rock aquifers - Dandenong Ranges

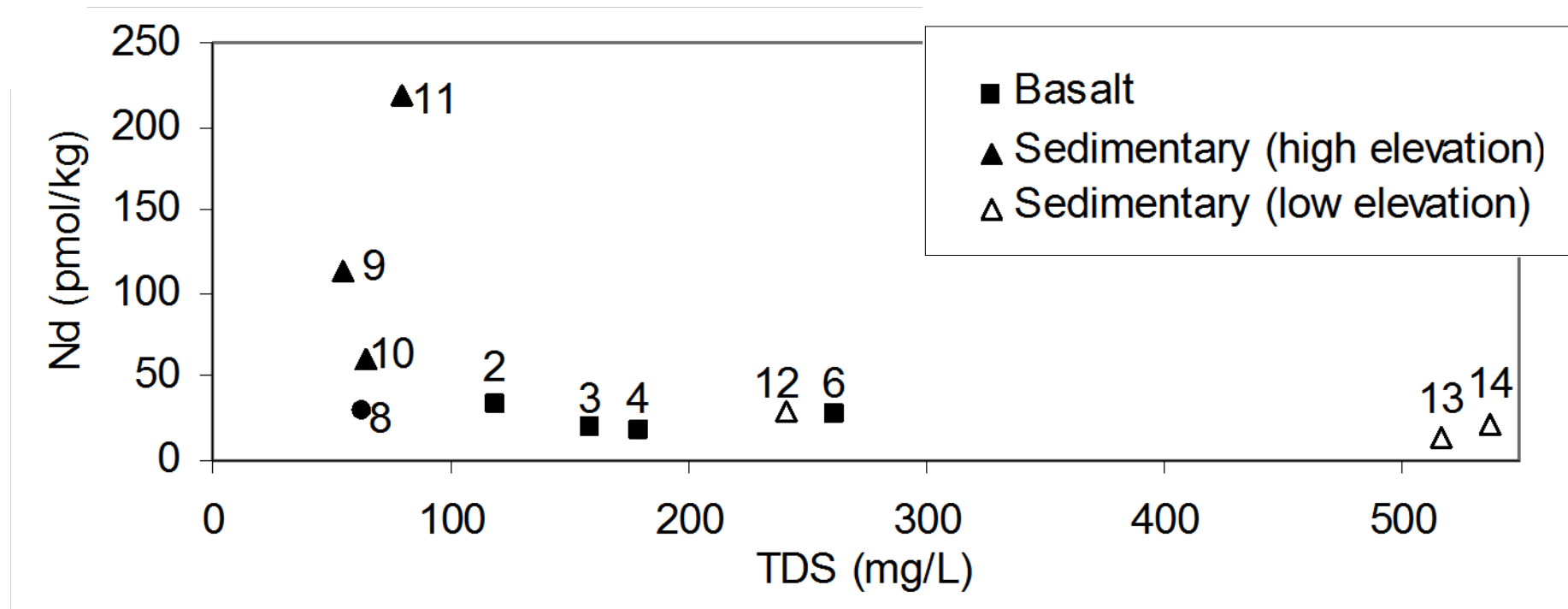
CFCs less successful indicators of groundwater processes



Mixing in fractured rock aquifers - Dandenong Ranges

REEs less successful indicators of groundwater processes

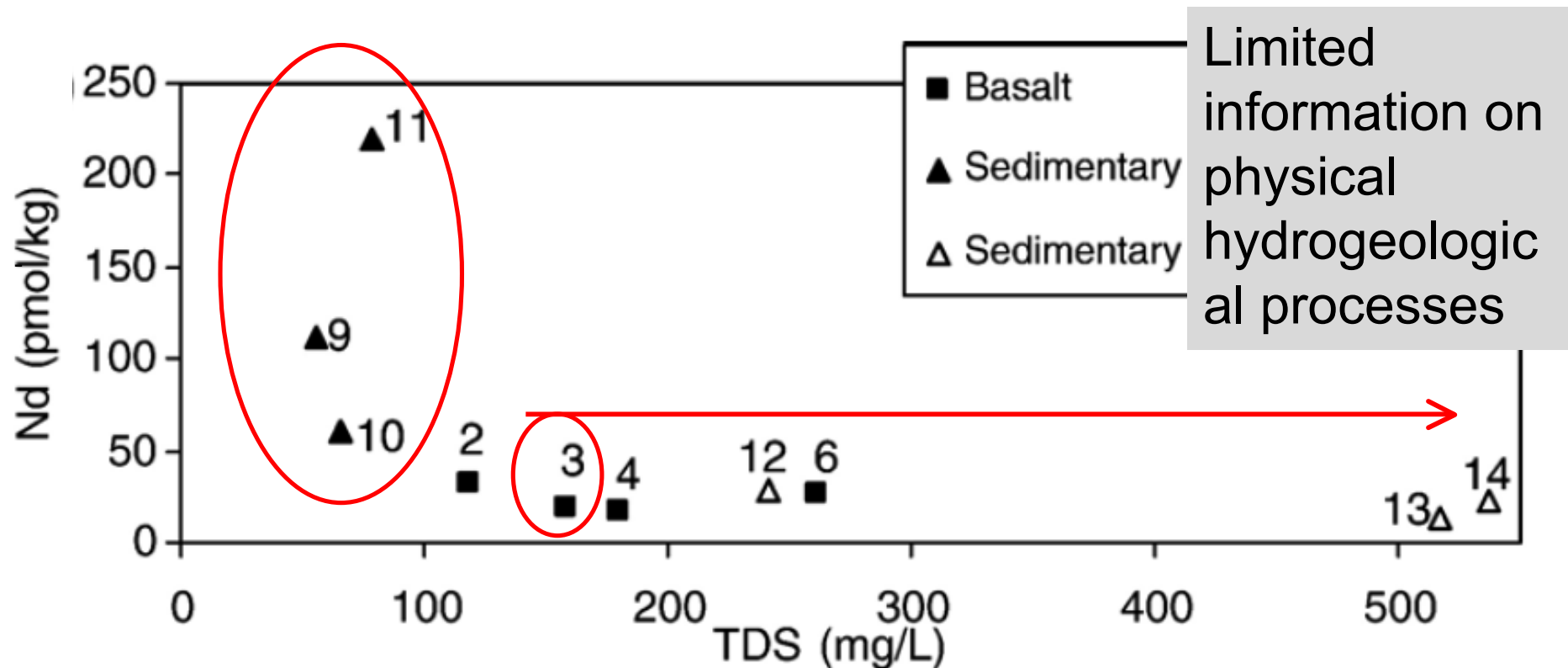
- Did not accumulate with increased flow
- Did not reflect mixing between basalt and sedimentary aquifers



Mixing in fractured rock aquifers - Dandenong Ranges

REEs

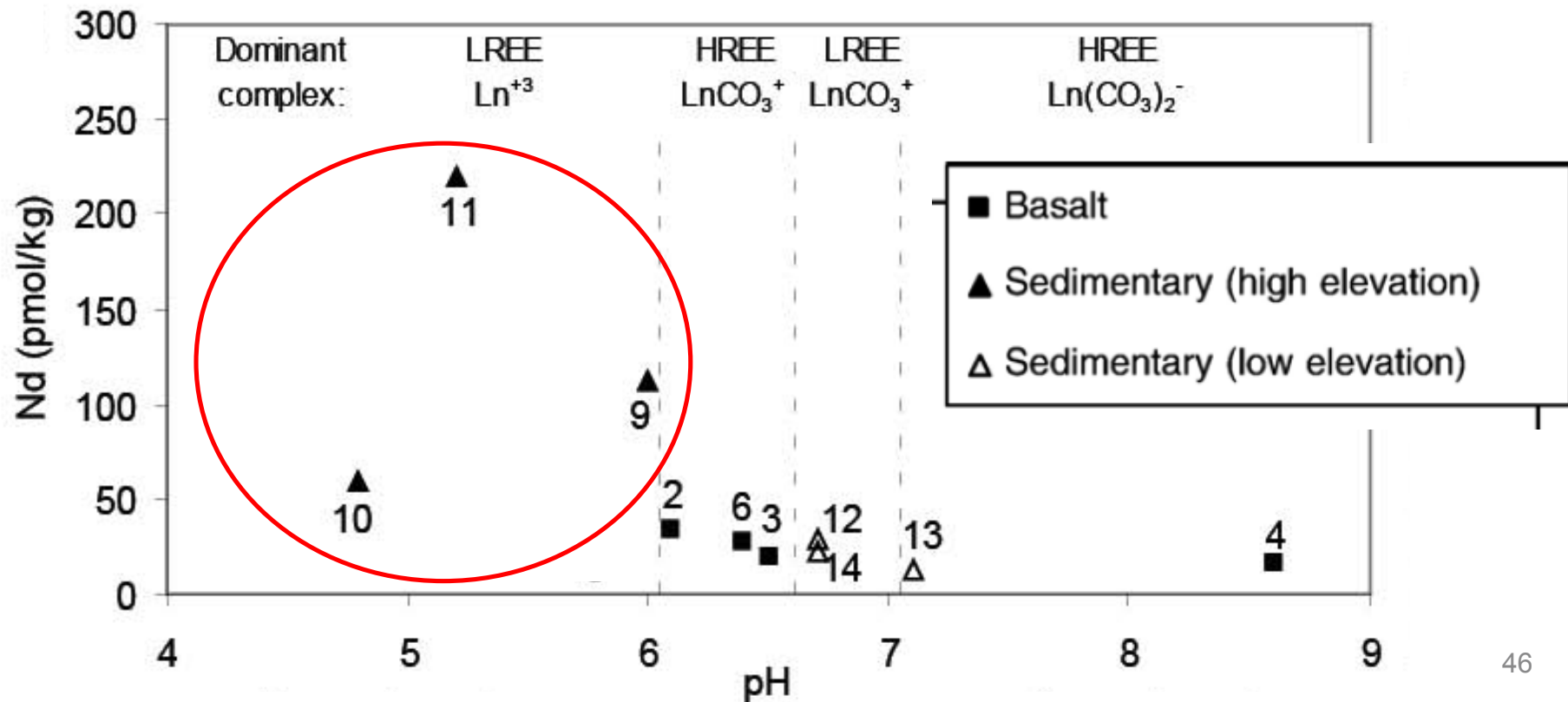
- Early-stage REE mobilisation in sedimentary aquifer
- Lower concentrations in recharge areas of basalt aquifer
- REE concentrations remain relatively constant along groundwater flow paths in basalt and sedimentary aquifers



Mixing in fractured rock aquifers - Dandenong Ranges

REEs

Early-stage REE mobilisation in sedimentary aquifer with low pH values (pH < 6)

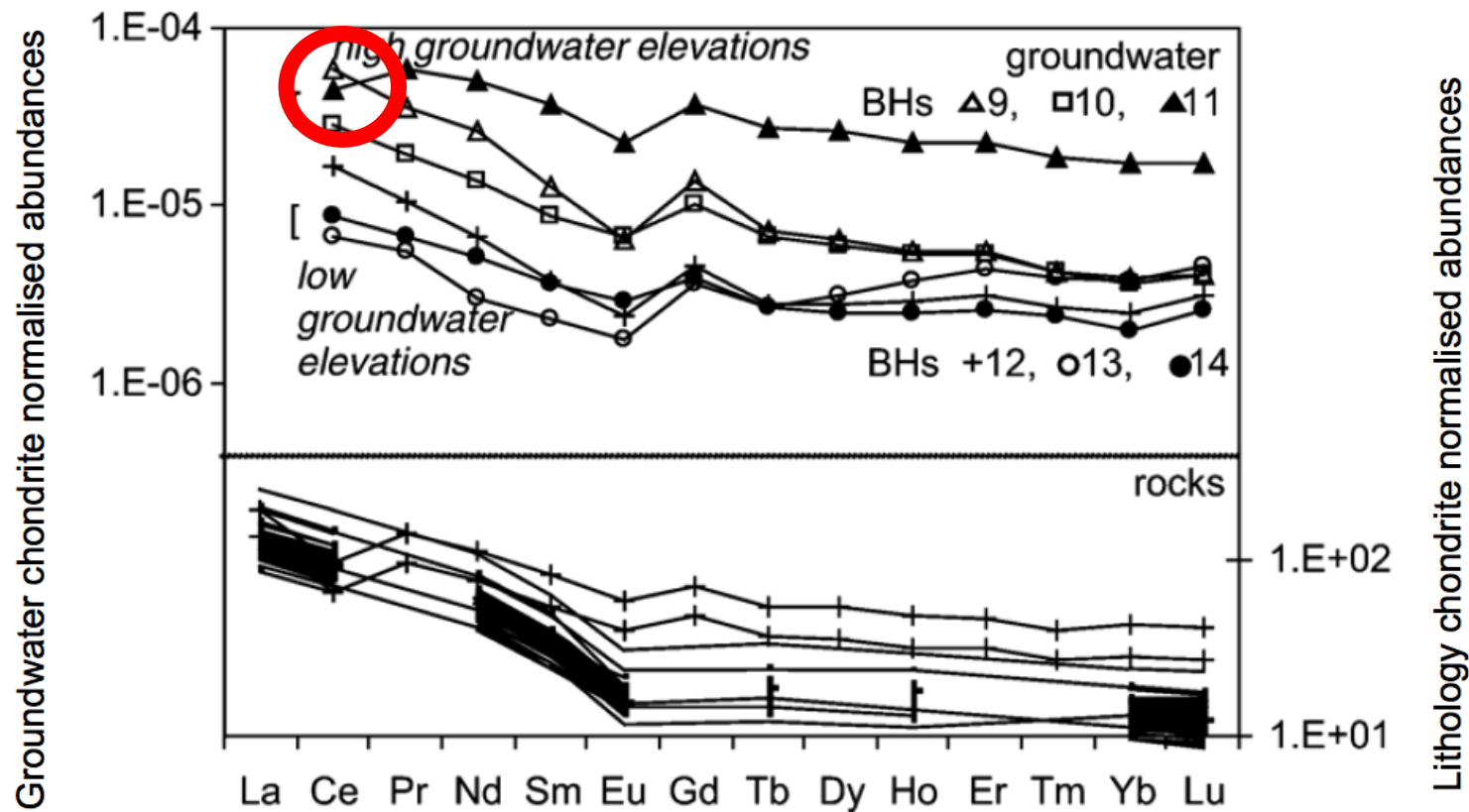


Mixing in fractured rock aquifers - Dandenong Ranges

REEs

Recharge sedimentary:

- localised source heterogeneity affected REE patterns and concentrations

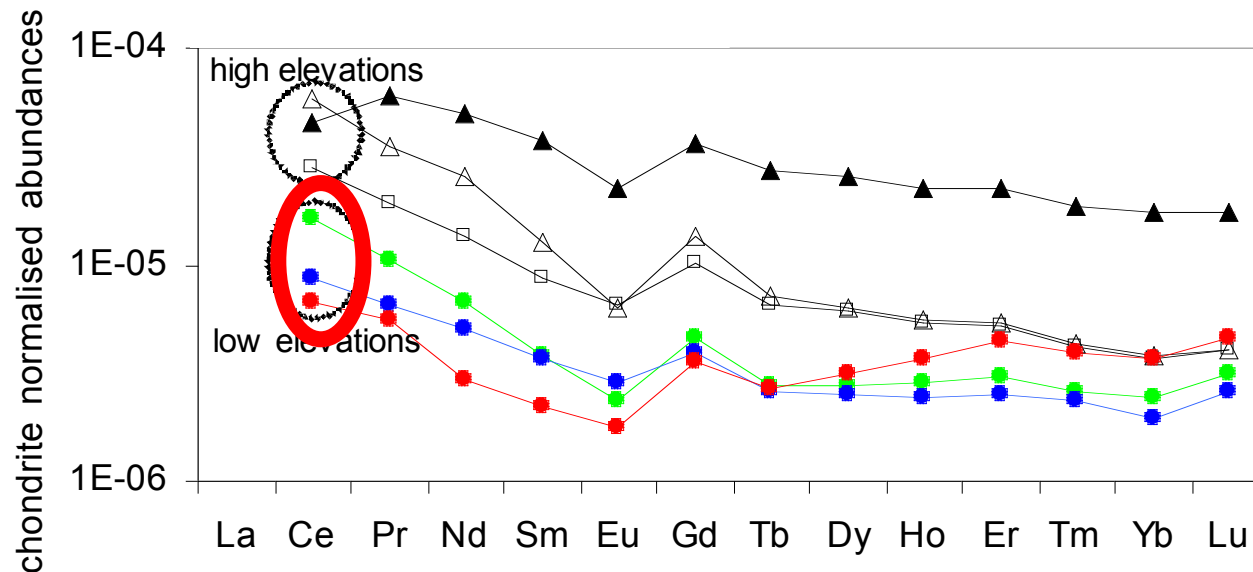


Mixing in fractured rock aquifers - Dandenong Ranges

REEs

Increased flow via sediments

- lower REE concentrations and variation in patterns due to sorption or co-precipitation



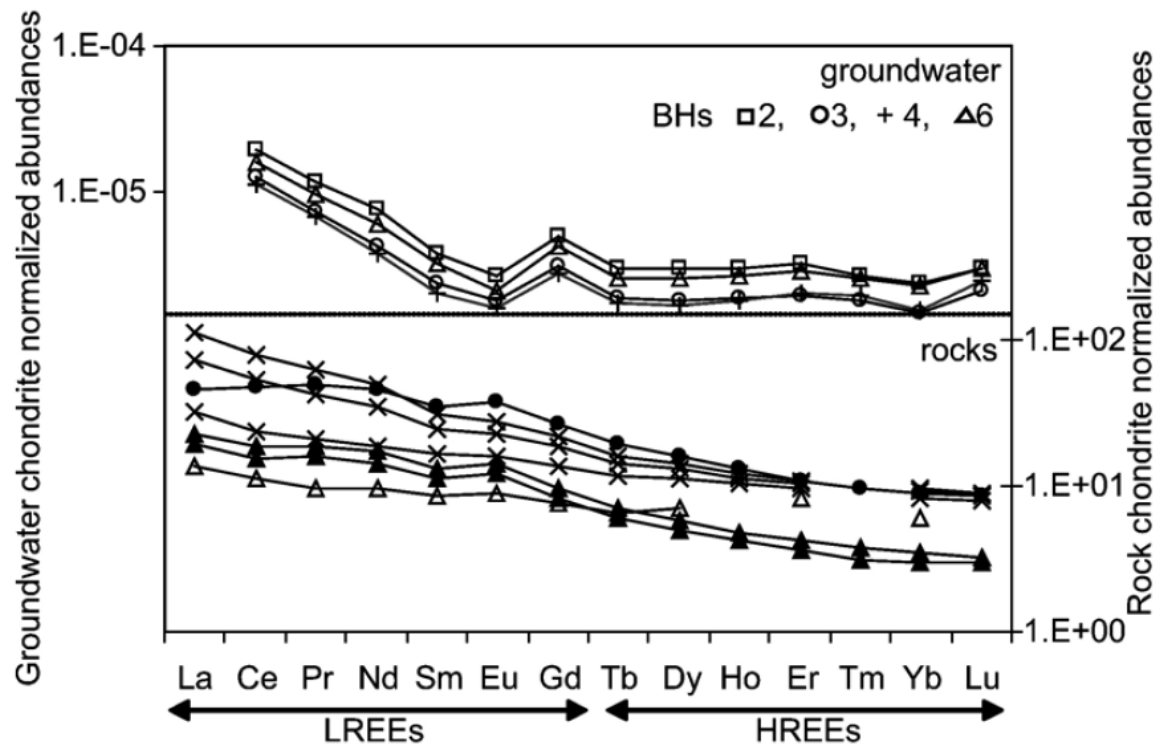
Mixing in fractured rock aquifers - Dandenong Ranges

REEs

Flow via basalt aquifer

Low REEs concentrations (pH values 6.1 - 8.6)

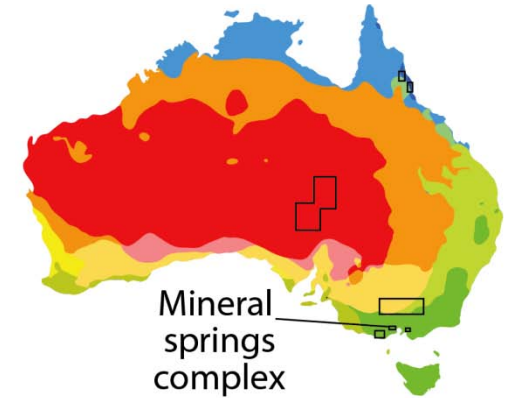
- Almost identical REE patterns and concentrations in basalt aquifer groundwater do not reflect mixing with groundwater from the sedimentary aquifer, or REE removal via sorption or co-precipitation



Mineral springs

Deep flow in fractured rock aquifers

– Mineral Springs



Question

Origins of waters and gas (CO_2) in naturally effervescent mineral spring waters?

Approach

$\delta^{13}\text{C}_{\text{CO}_2}$ values of gas emissions, and $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}_{\text{DIC}}$ of the spring waters

Management link

Protection of this popular tourist destination



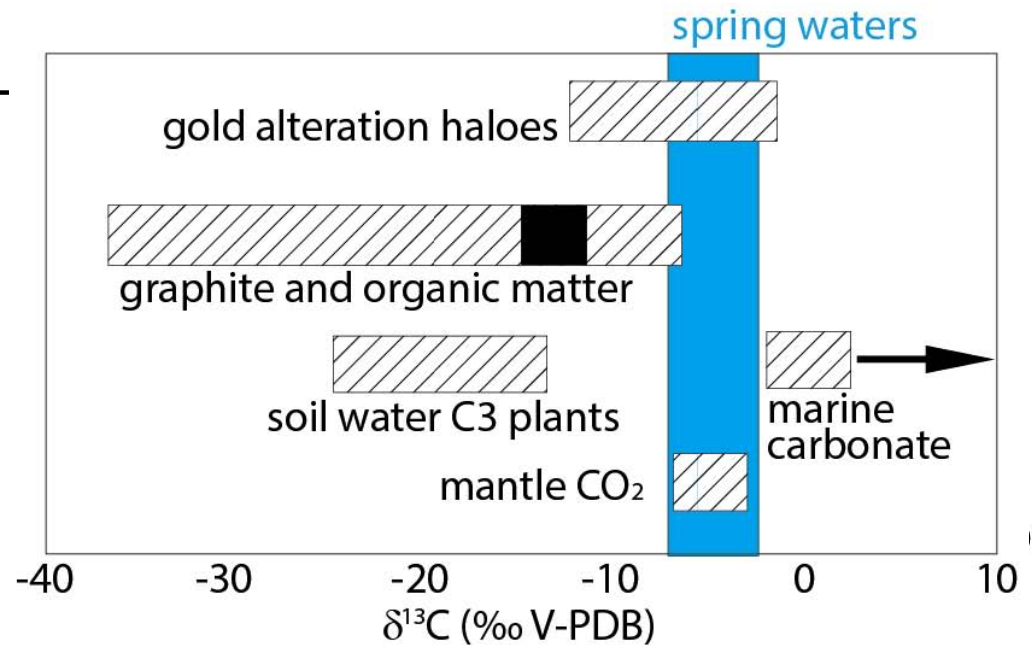
Cartwright I., Weaver T., Tweed S., Ahearne D., Cooper M., Czapnik K., Tranter J., 2002. Stable isotope geochemistry of cold CO_2 -bearing mineral spring waters, Daylesford, Victoria, Australia: sources of gas and water and links with waning volcanism. *Chemical Geology* 185: 71–84

Circulation of deep groundwater flow – Mineral Springs

Up to 2500 mg/L CO₂ and 2650 mg/L HCO₃

$\delta^{13}\text{C}$ - DIC sources

- Spring water $\delta^{13}\text{C}$
-5.9 to -0.1 ‰
- Gold veins
-13 to -2 ‰ – minor presence
- Magmatic CO₂
-6 to -3 ‰
 - Correlation between spring abundance and eruption points



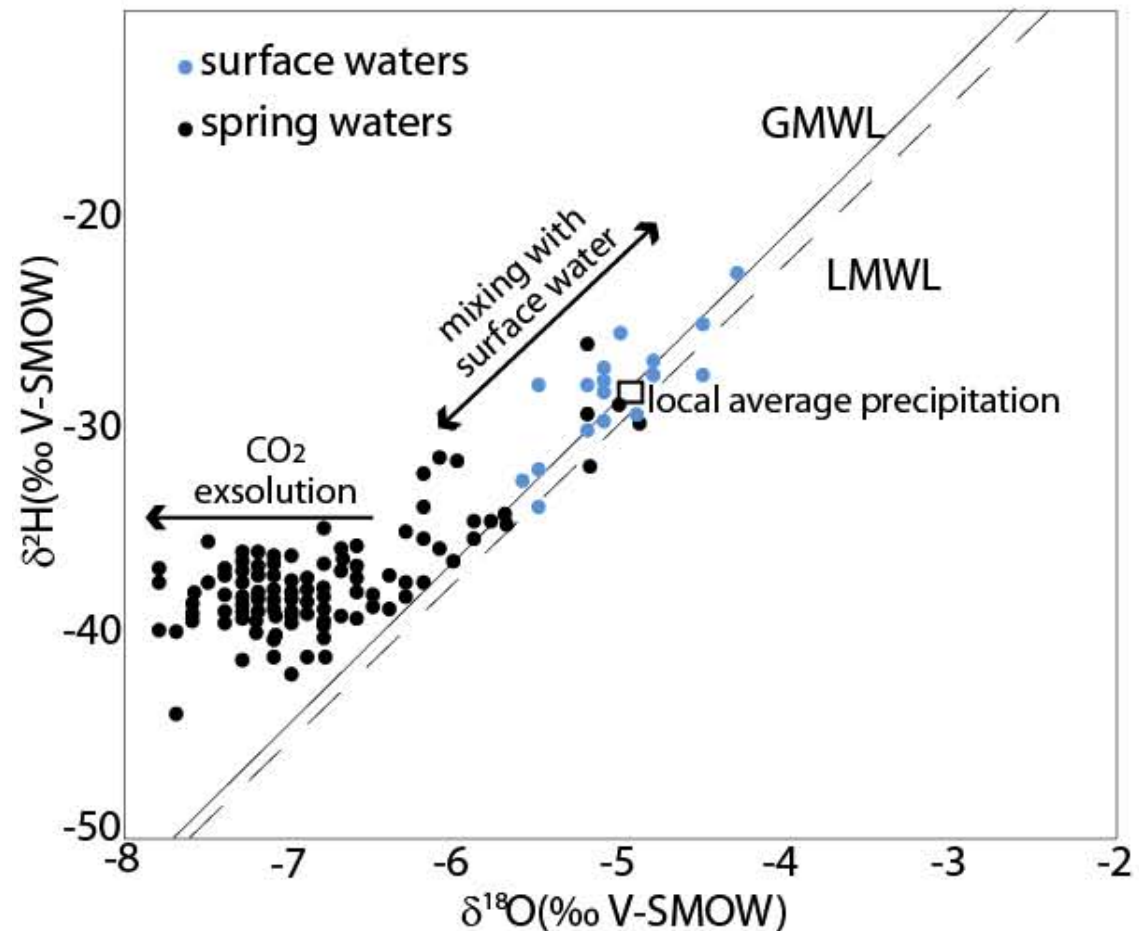
Other major ions

- Controlled by water–rock interactions in different fracture flow paths

Circulation of deep groundwater flow – Mineral Springs

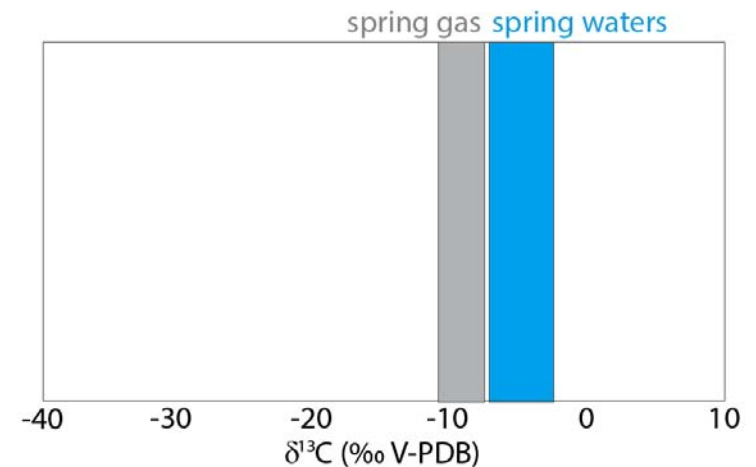
$\delta^{18}\text{O}$ and $\delta^2\text{H}$

- Low $\delta^2\text{H}$ values not explained by modern rainfall recharge
- Springs recharged under colder climatic conditions (~3.5 to 3.0 ka BP)



Circulation of deep groundwater flow – Mineral Springs

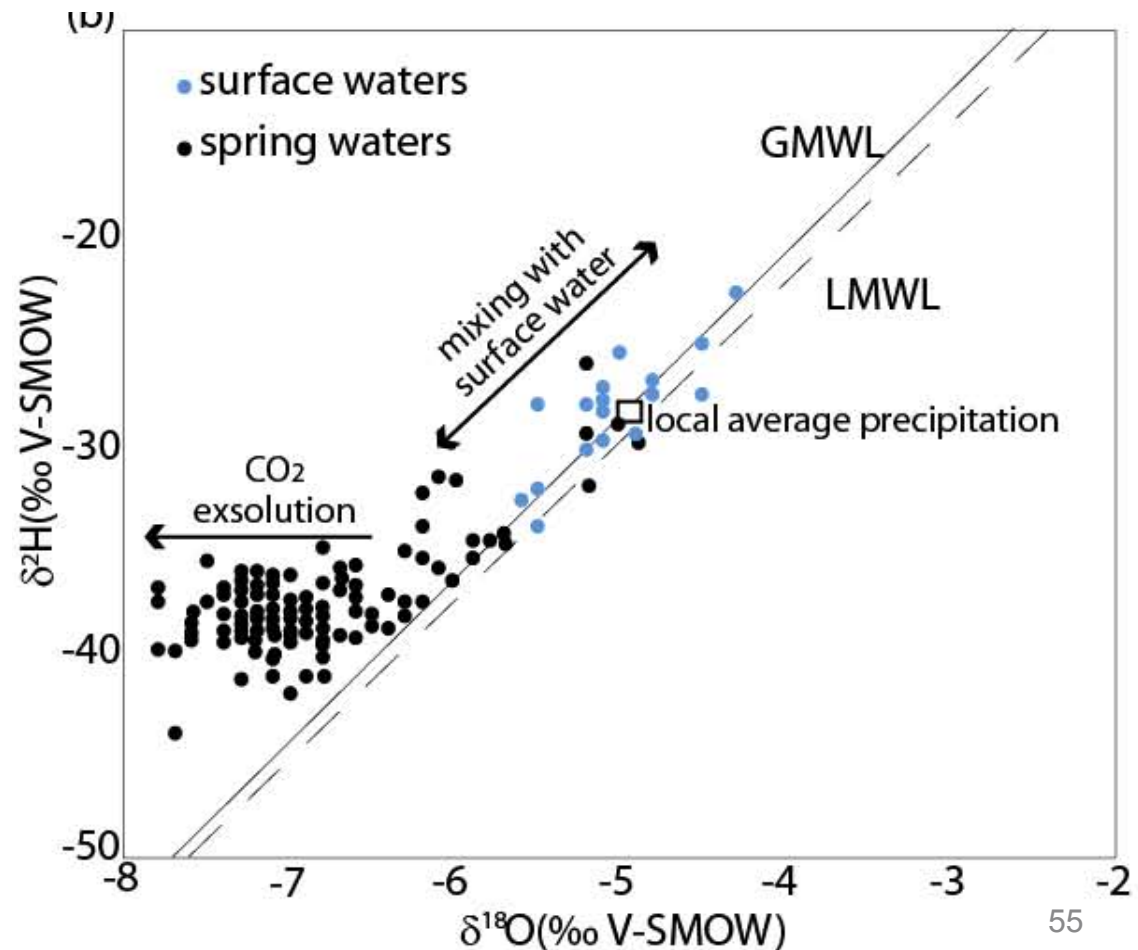
- Up to 2516 mg/L CO_2 and 2648 mg/L HCO_3^-
- $\delta^{13}\text{C}_{\text{CO}_2}$ of gas emissions : -10.6 to -7.0 ‰
- $\delta^{13}\text{C}_{\text{DIC}}$ of spring waters: -5.9 to -0.1 ‰
- Difference in $\delta^{13}\text{C}_{\text{CO}_2}$ of gas and $\delta^{13}\text{C}_{\text{DIC}}$ of the spring waters ($\delta^{13}\text{C}_{(\text{DIC}-\text{CO}_2)}$): 3–8‰
- Predicted difference: 1 – 7‰ (at 10–50°C and pH 5.8–6.9)
 - CO_2 is in approximate isotopic equilibrium with the DIC; part of a single mineral water–gas system



- Spring water $\delta^{13}\text{C}$ values function of
 - relative amount of CO_2 and DIC
 - $\delta^{13}\text{C}$ values of each of these components
 - not possible to measure the proportions of these two components

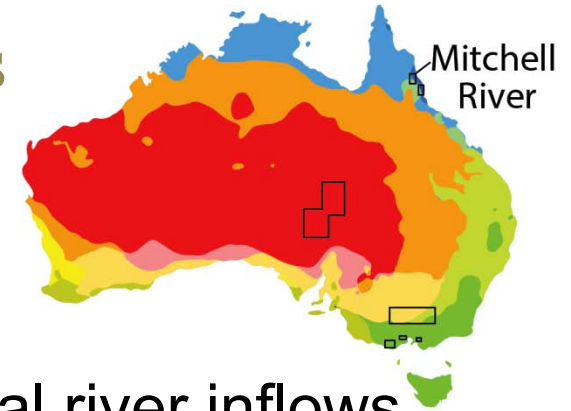
Circulation of deep groundwater flow – Mineral Springs

- Mineral springs $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values lie to the left of meteoric water lines
 - As spring waters are transported to the surface the CO_2 exsolves which lowers $\delta^{18}\text{O}$



Mitchell 18O and DIC

Seasonal inflows from wet versus dry tropics – Mitchell River



Questions

Seasonal variations in the provenance of tropical river inflows

Approach

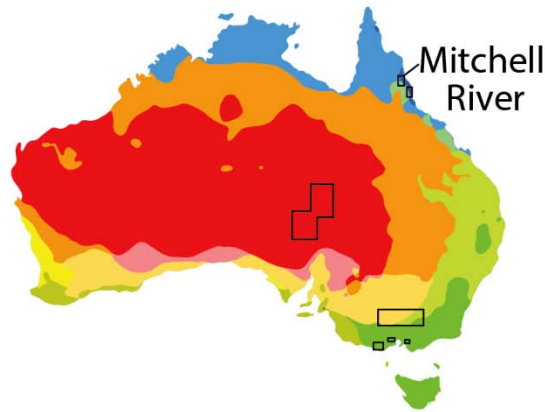
$\delta^{18}\text{O}$ as a tracer of rainfall provenance

Funding

ARC and National Centre for Groundwater Research and Training (NCGRT)

Management links

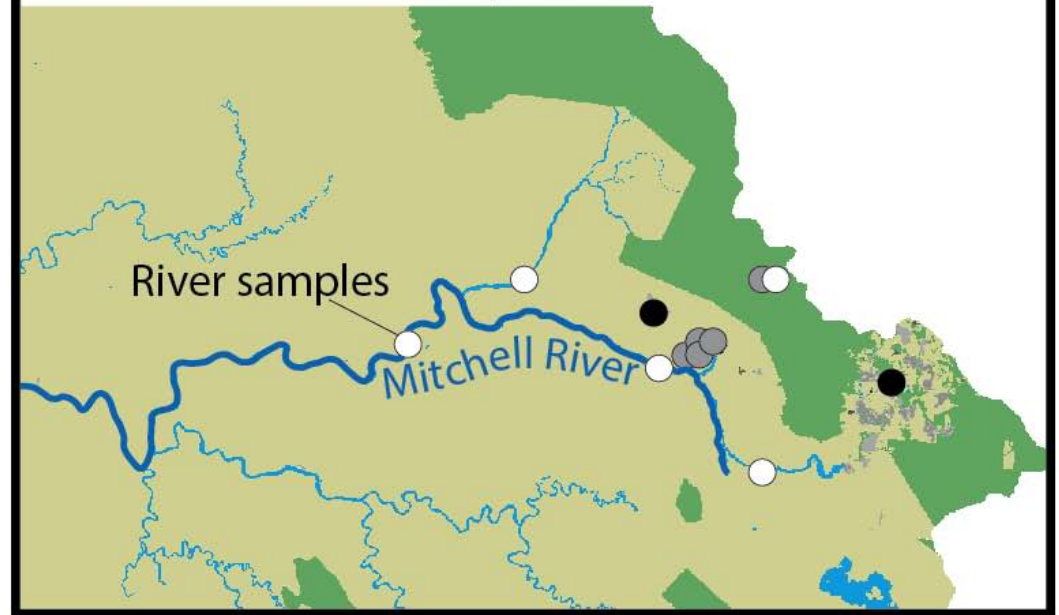
Protection of tropical river ecosystems and water resources



Mitchell
River

Land cover and sample locations

10km



River samples

Mitchell River

Wet tropics

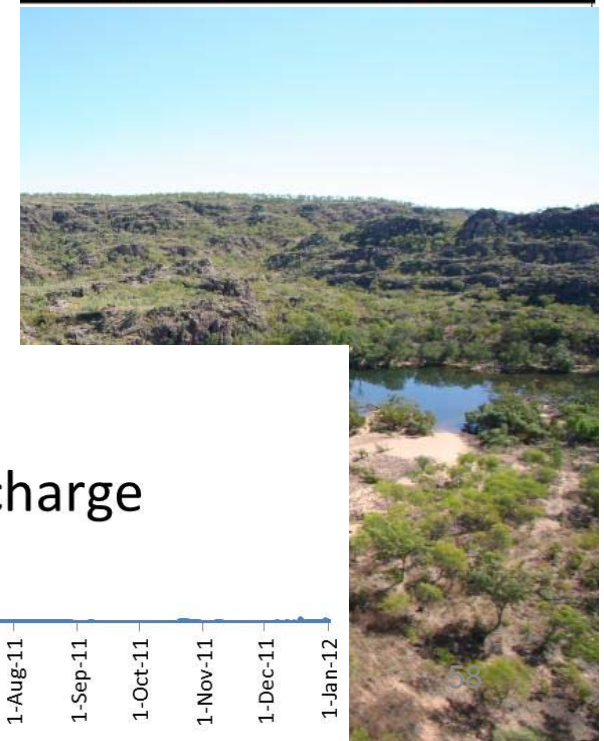
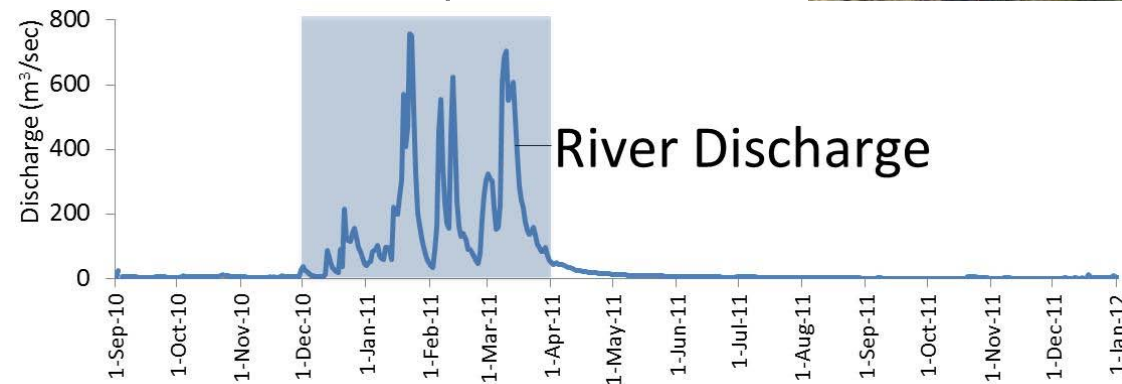
- rainforest
- annual rainfall ~ 1600 mm/yr
- mountains

Dry tropics

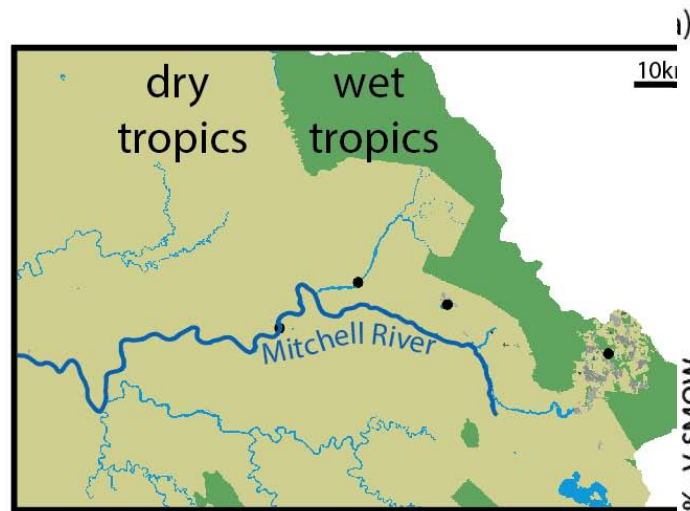
- savanna vegetation
- annual rainfall ~ 900 mm/yr

Rivers

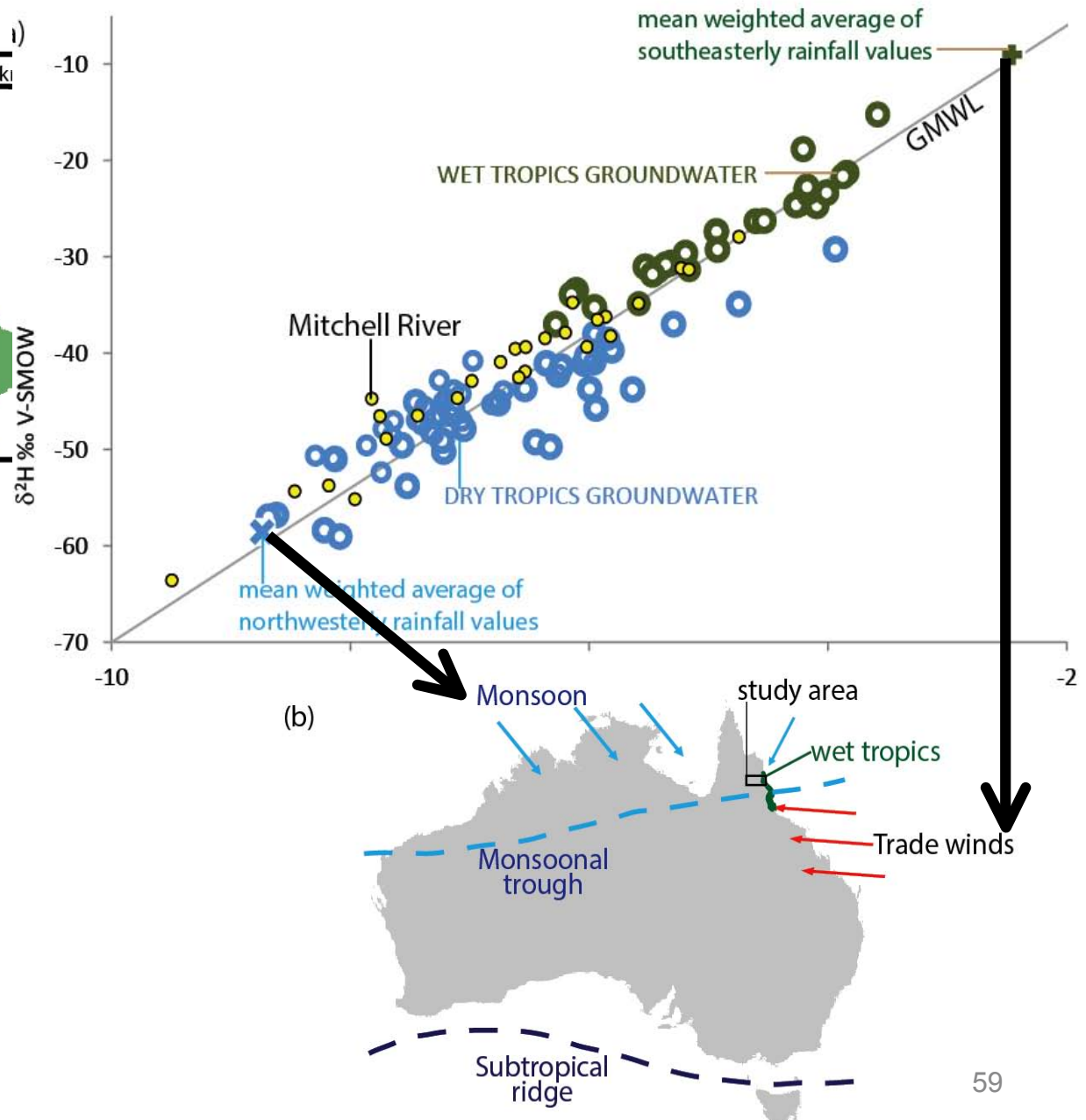
- high wet season flow
- low dry season flow; limited rainfall (<5% of



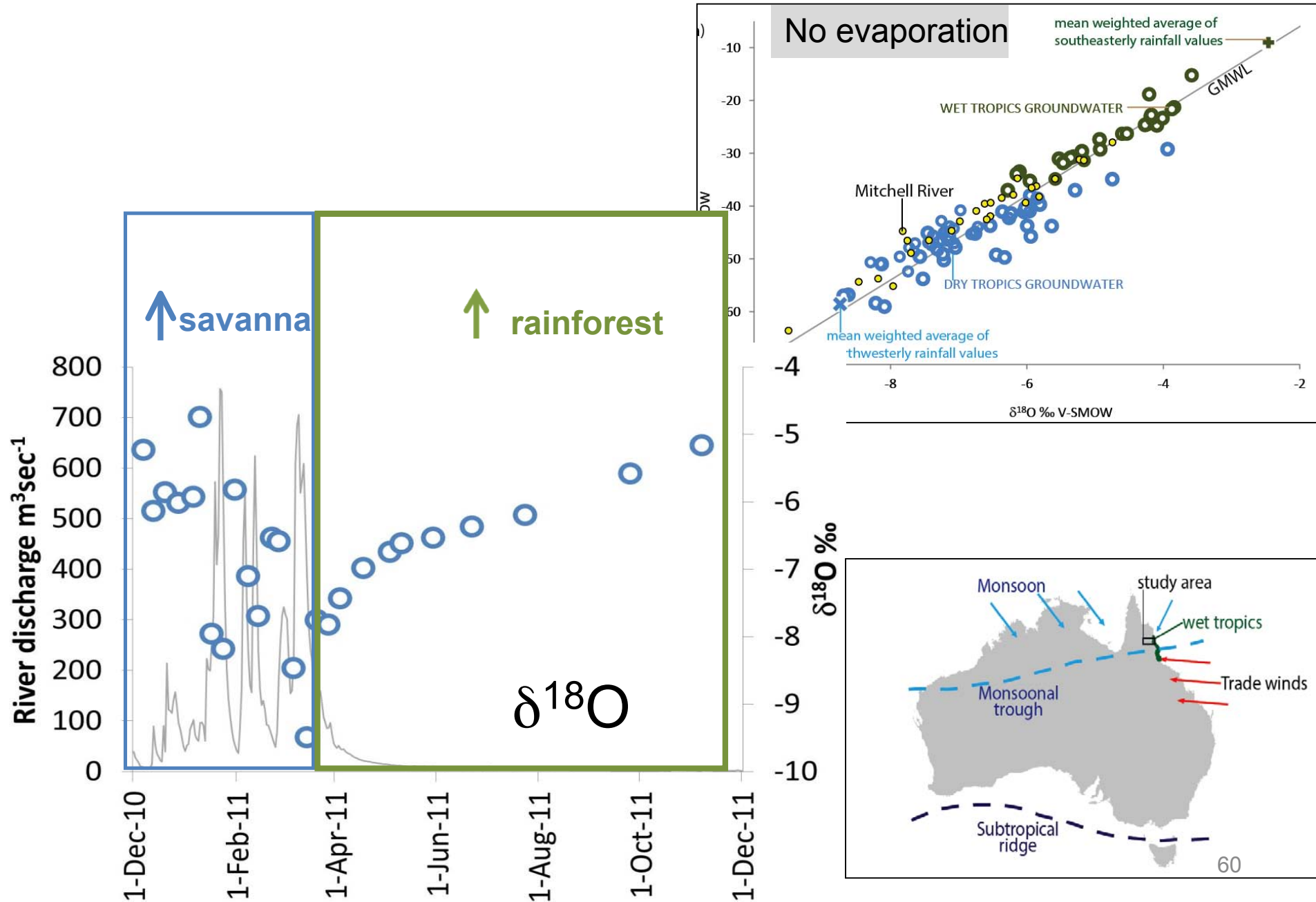
Seasonal inflows from wet versus dry tropics – Mitchell River



Rainfall provenance



Seasonal inflows from wet versus dry tropics – Mitchell River



Seasonal inflows from wet versus dry tropics – Mitchell River

$\delta^{18}\text{O}$

Information on a river - remote and logistically difficult to sample during the tropical wet seasons

Wet season

Relative increase in inflows from savanna

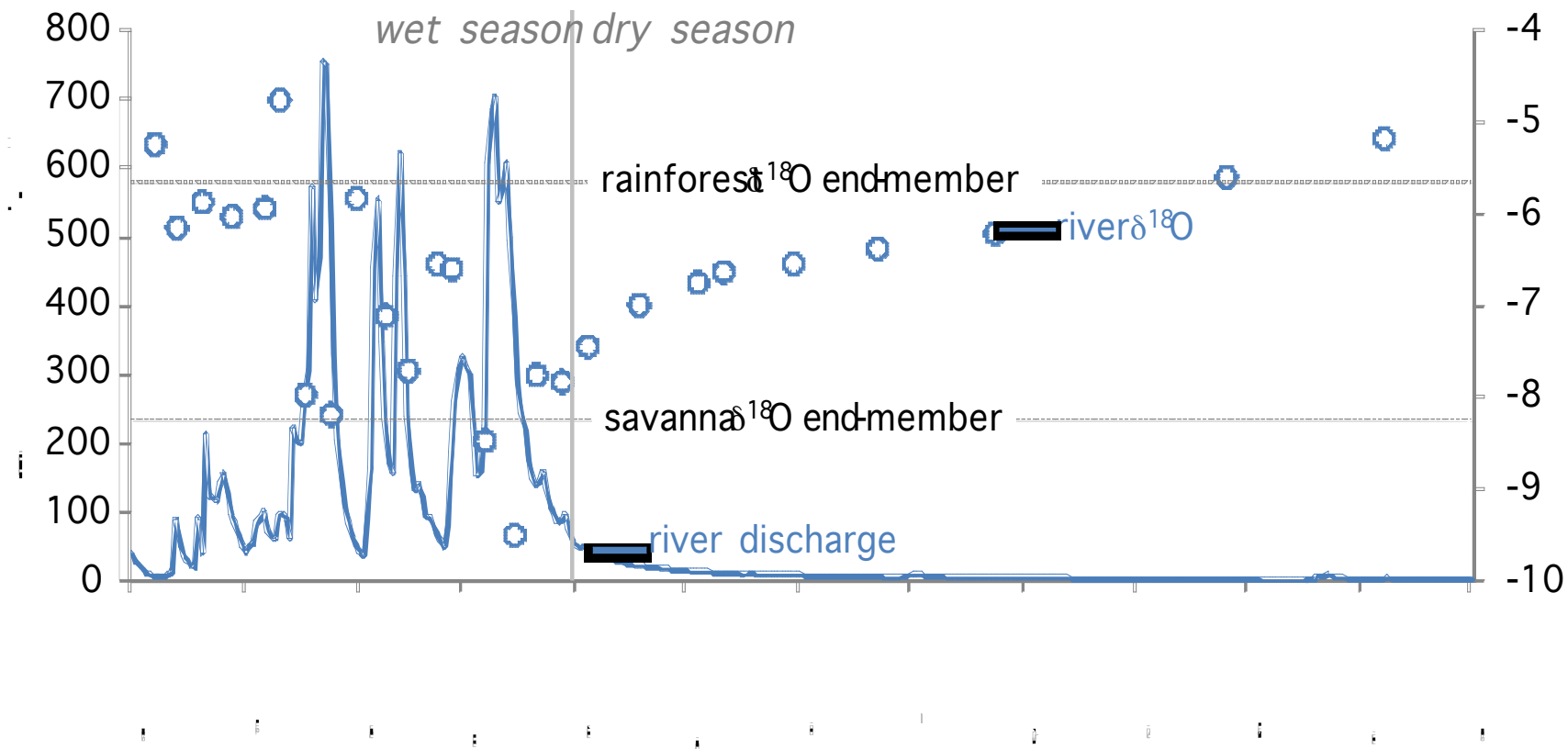
Dry season

Relative increase in inflows from rainforest

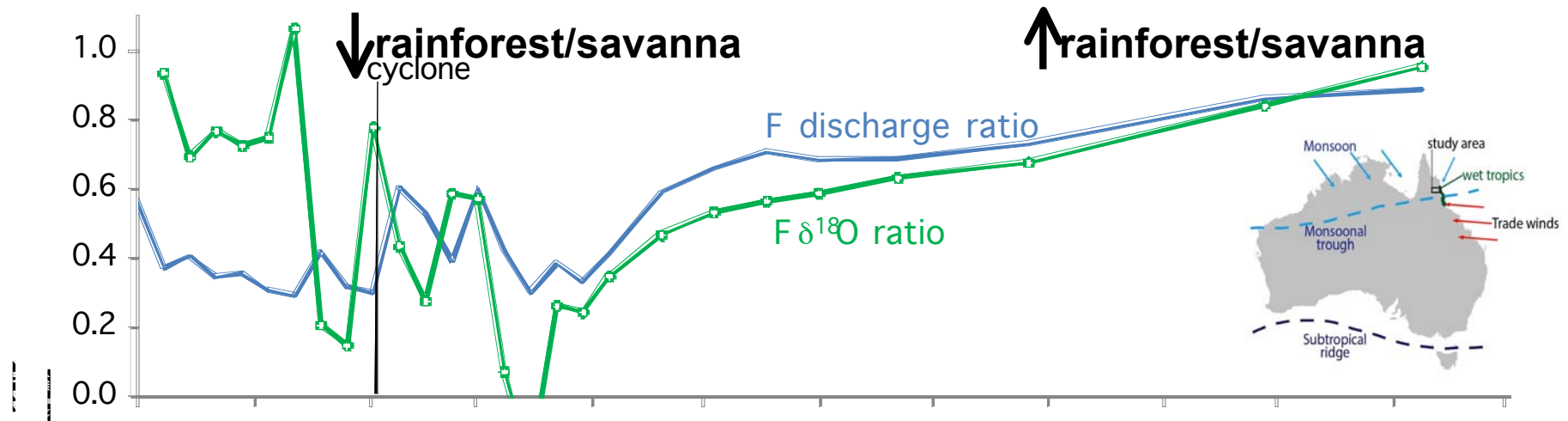


Improvements to component models

Use of constant end-members; dynamic end-members more likely; large variations in tropical rainfall



Seasonal inflows from wet versus dry tropics – Mitchell River



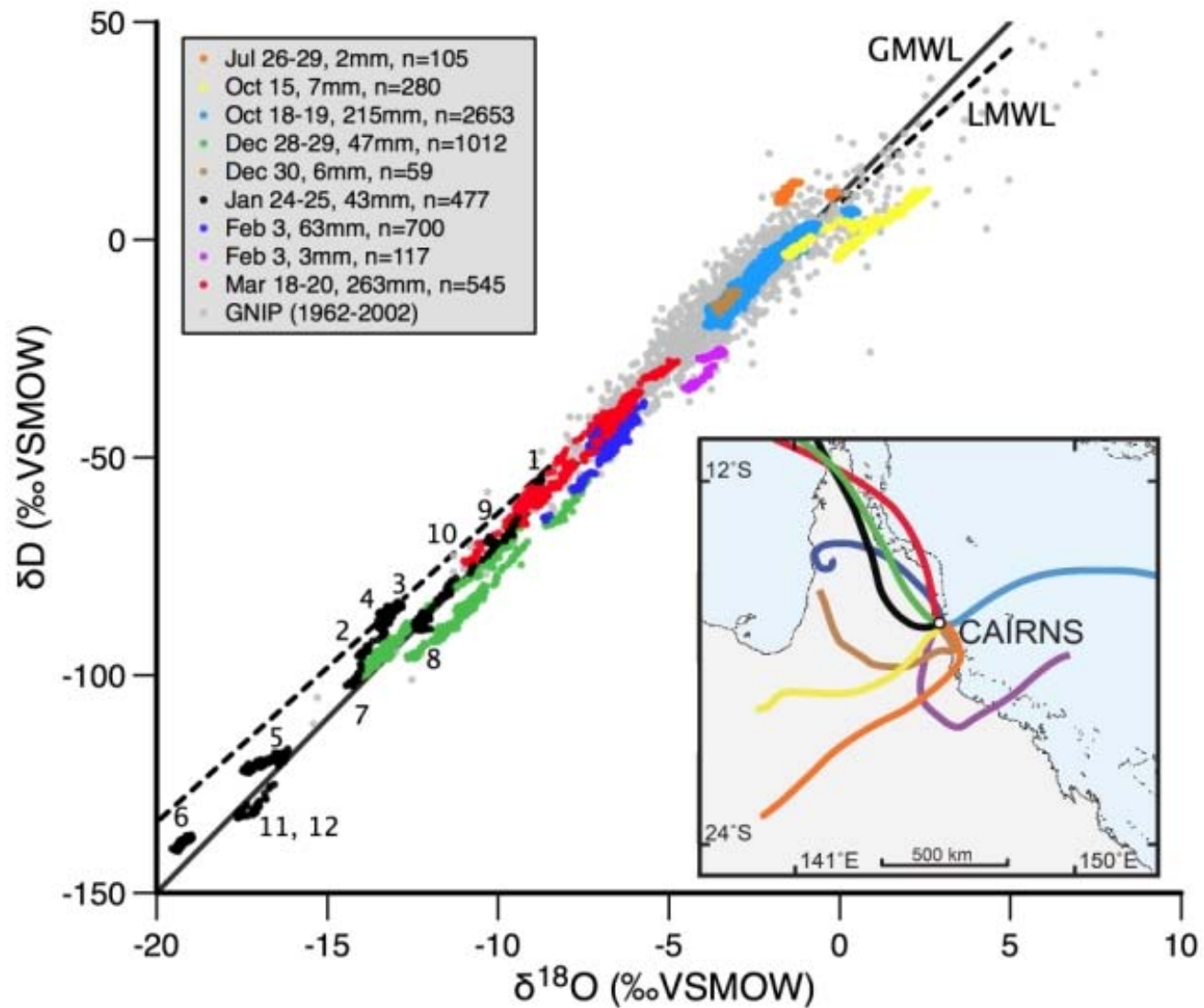
Fraction (F) of inputs from the rainforest to total river discharge is solved using $\delta^{18}\text{O}$ end-member for the savanna ($\delta^{18}\text{O}_{(\text{SAV})}$), rainforested highlands ($\delta^{18}\text{O}_{(\text{RF})}$), and the measured river $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{(\text{R})}$):

$$F = \frac{\delta^{18}\text{O}_{(\text{R})} - \delta^{18}\text{O}_{(\text{SAV})}}{\delta^{18}\text{O}_{(\text{RF})} - \delta^{18}\text{O}_{(\text{SAV})}}$$

Compared with a mixing fraction of river discharge (F_Q), calculated using the gauged discharge data from Rifle Creek (Q_{RIF} – increased rainforest), McLeod River (Q_{MCL} – increased rainforest) and Mitchell River (Q_{MIT} – mix savanna and rainforest):

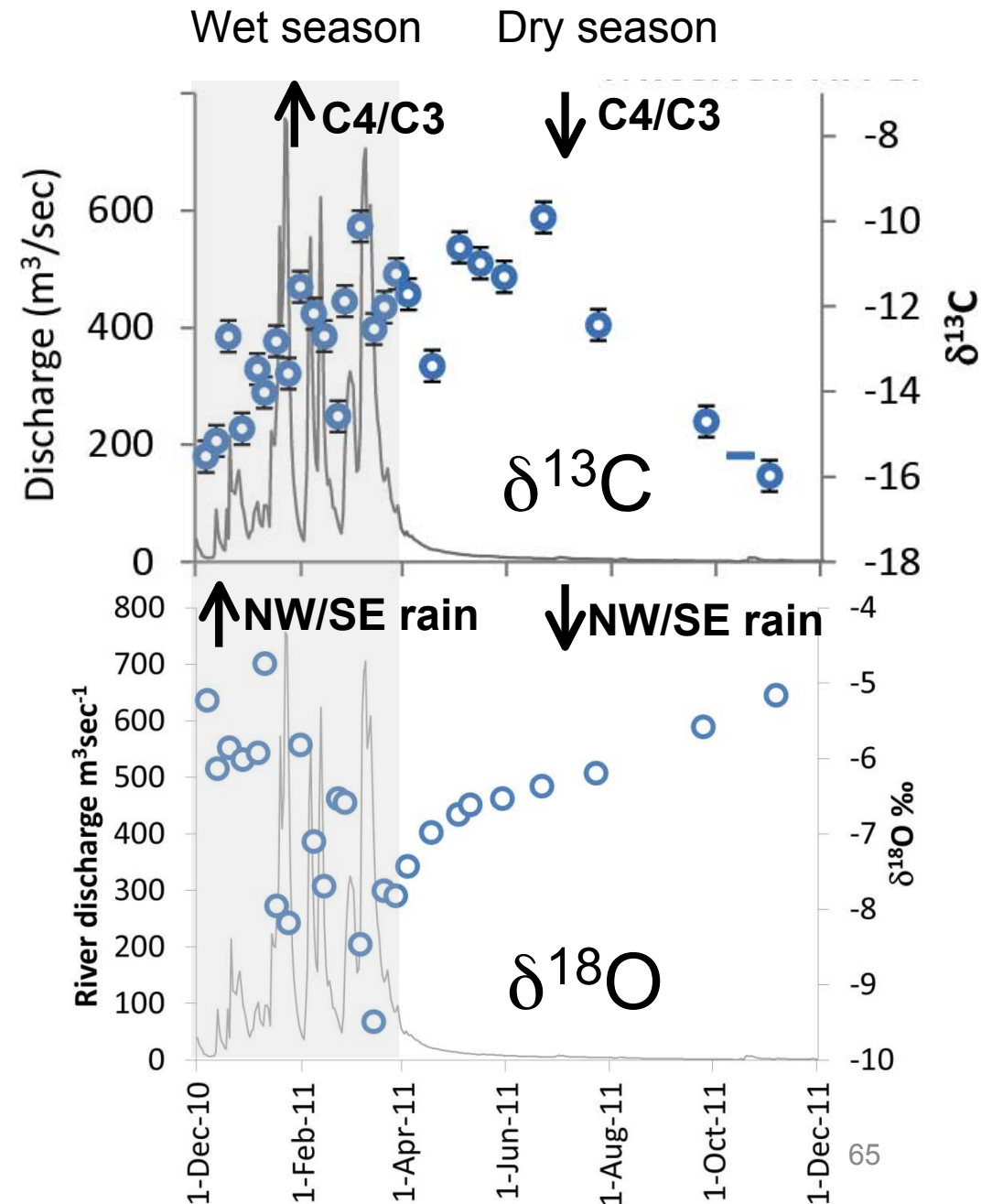
$$F_Q = \frac{Q_{\text{RIF}} + Q_{\text{MCL}}}{Q_{\text{MIT}}}$$

Tropical rainfall

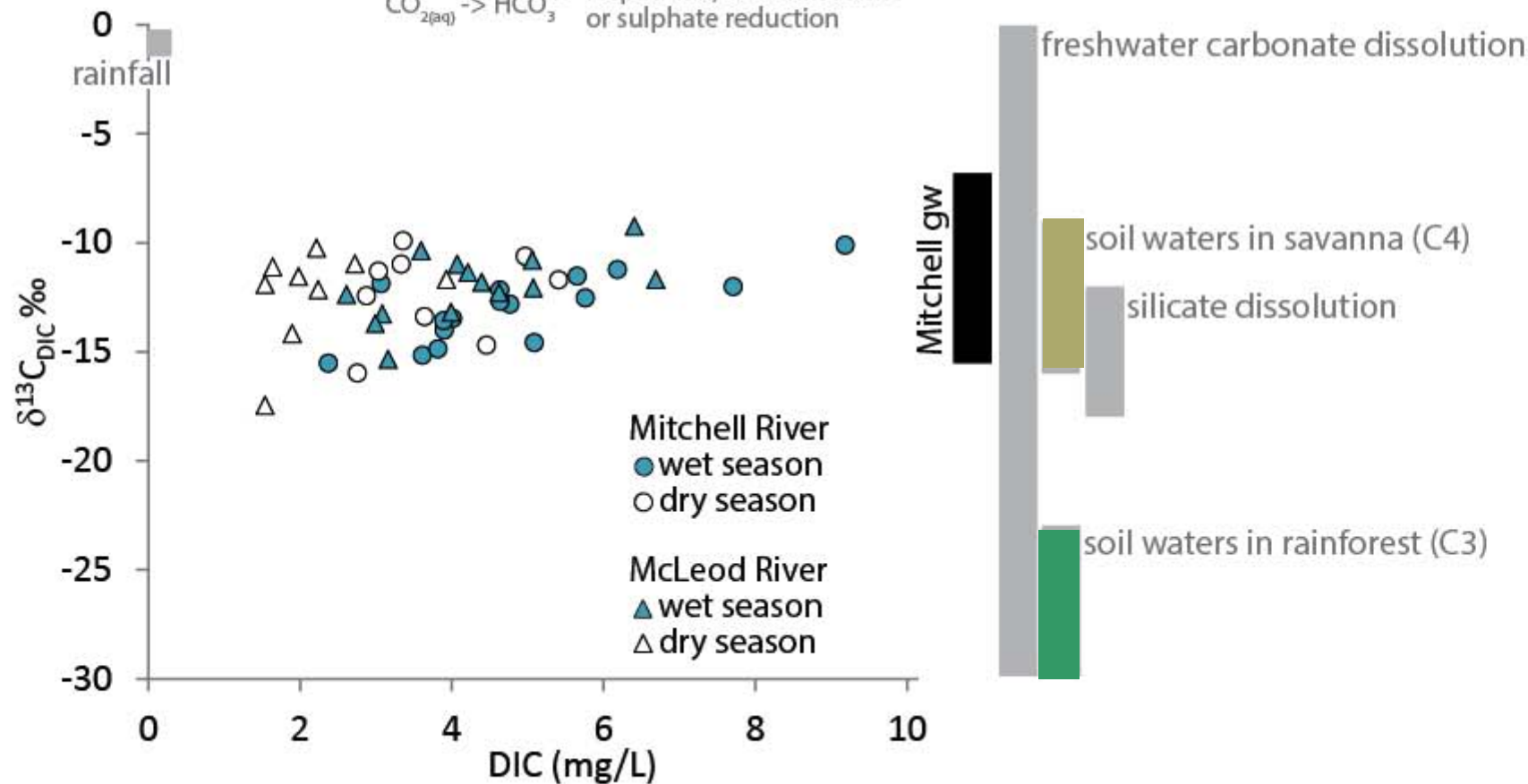
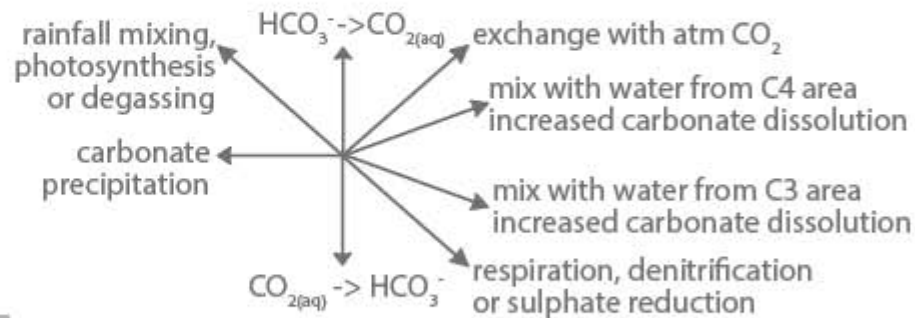
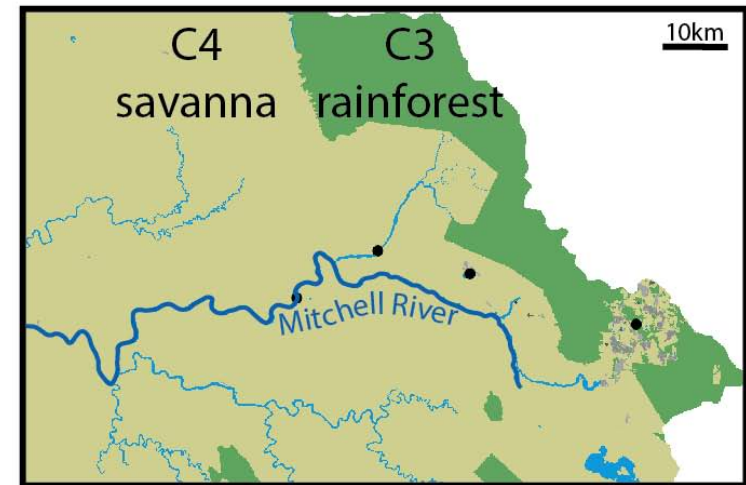


Results – $\delta^{18}\text{O}$

- Wet season
 - Relative increase in inflows from savanna
- Dry season
 - Relative increase in inflows from rainforest



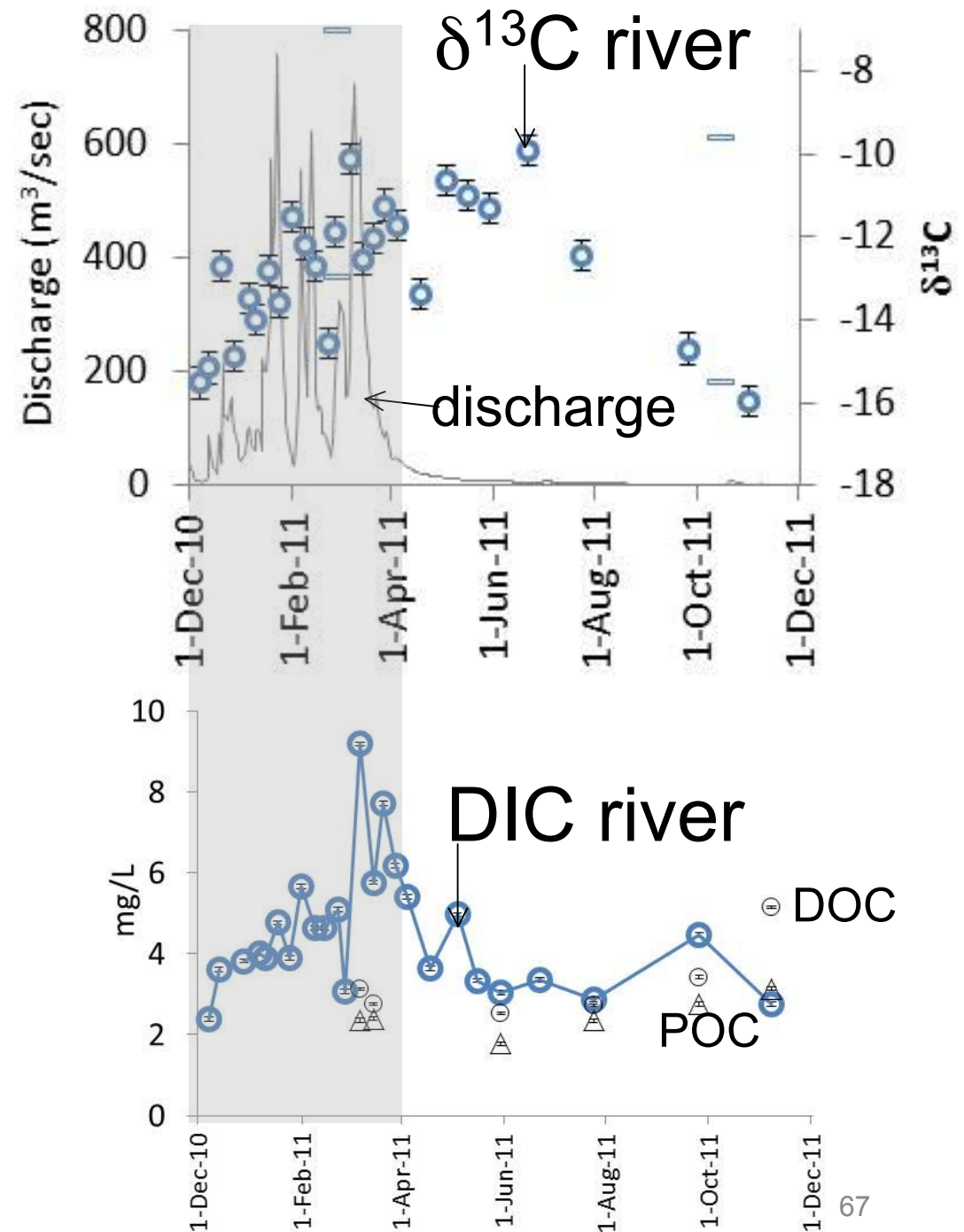
$\delta^{13}\text{C}$ – vegetation provenance



Results - DIC

- Wet season – increase in $\delta^{13}\text{C}$
- Dry season – decrease in $\delta^{13}\text{C}$
- Wet season – increase in DIC;
-> groundwater
- Dry season – decrease in DIC

-> high wet season DIC export



Results - diurnal DIC

- inverse trends between DO and DIC values
- inverse trends between $\delta^{13}\text{C}$ and DIC values

Daylight:

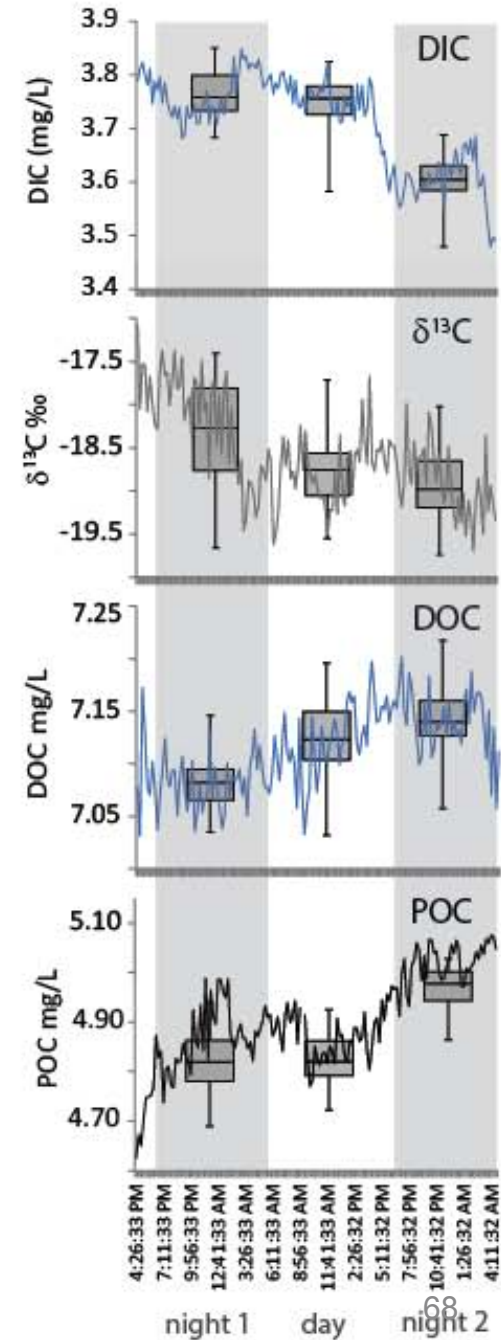
- photosynthesis

Night:

- Respiration

-> Compared with seasonal changes the diurnal variations are relatively minor

max DIC change – diel: 0.27 mg/L
– seasonal: 6.81 mg/L



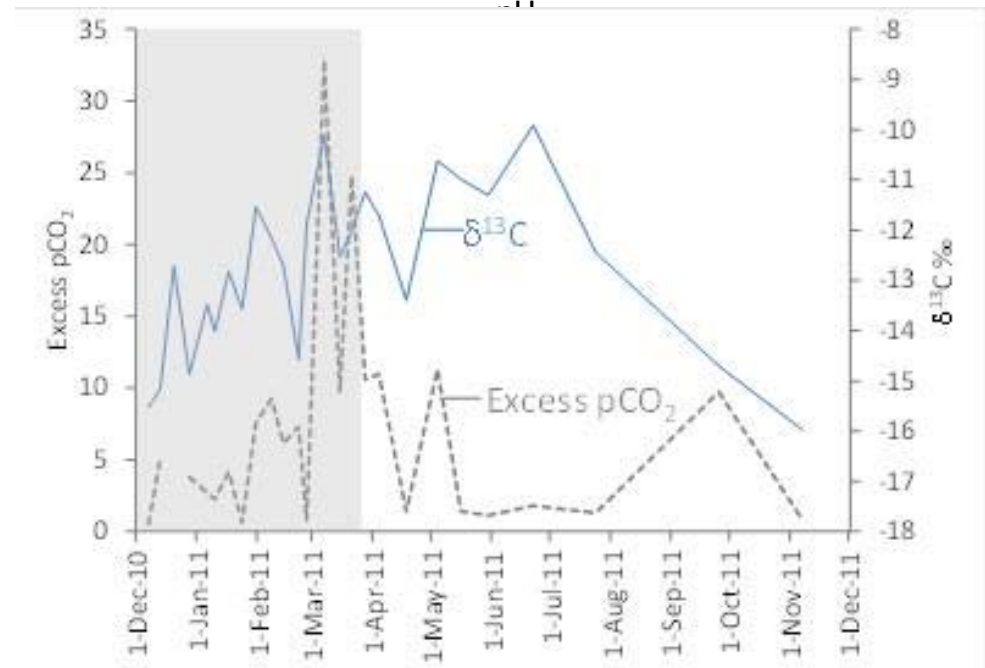
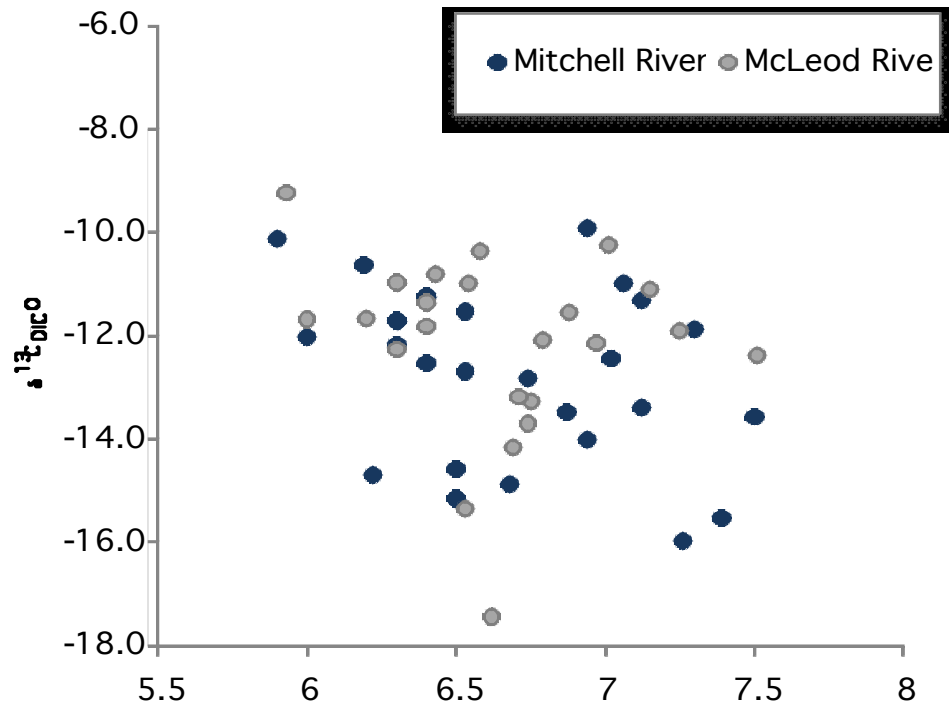
120 11 004 01

Seasonal DIC

Respiration \neq corresponding increases in DIC and $\delta^{13}\text{C}$

Photosynthesis \sim no increase in pH with declines in DIC or increases in $\delta^{13}\text{C}$ (potential dry season affects)

Degassing \sim increase in excess $p\text{CO}_2$ and $\delta^{13}\text{C}$ during wet season; but SI show water is undersaturated with respect to CO_{2g} and DIC data do not show corresponding declines in concentrations



Seasonal DIC

Speciation ~ pH values

-5.90 to 7.50 wet season

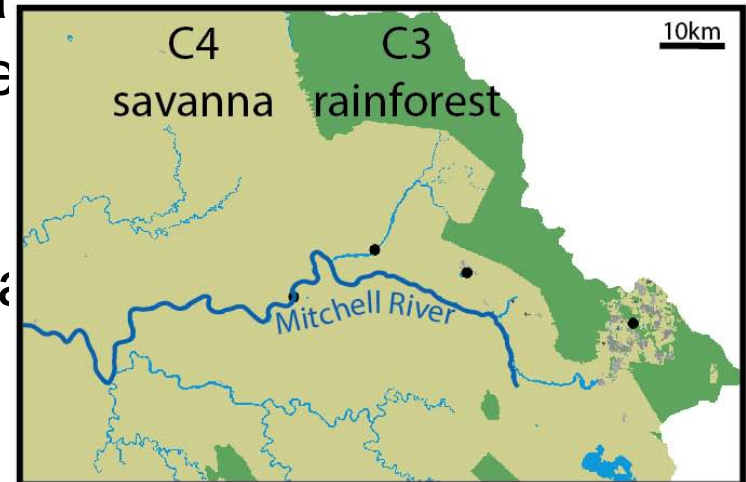
-6.19 to 7.26 dry season

-speciation between $\text{CO}_{2(\text{aq})}$ and HCO_3^- ;

-trends in pH and $\delta^{13}\text{C}$ values indicate a weak inverse relationship

Geochemical reactions ~ SIs indicate that the rivers are undersaturated with respect to calcite, aragonite and dolomite; potentially increase DIC concentration

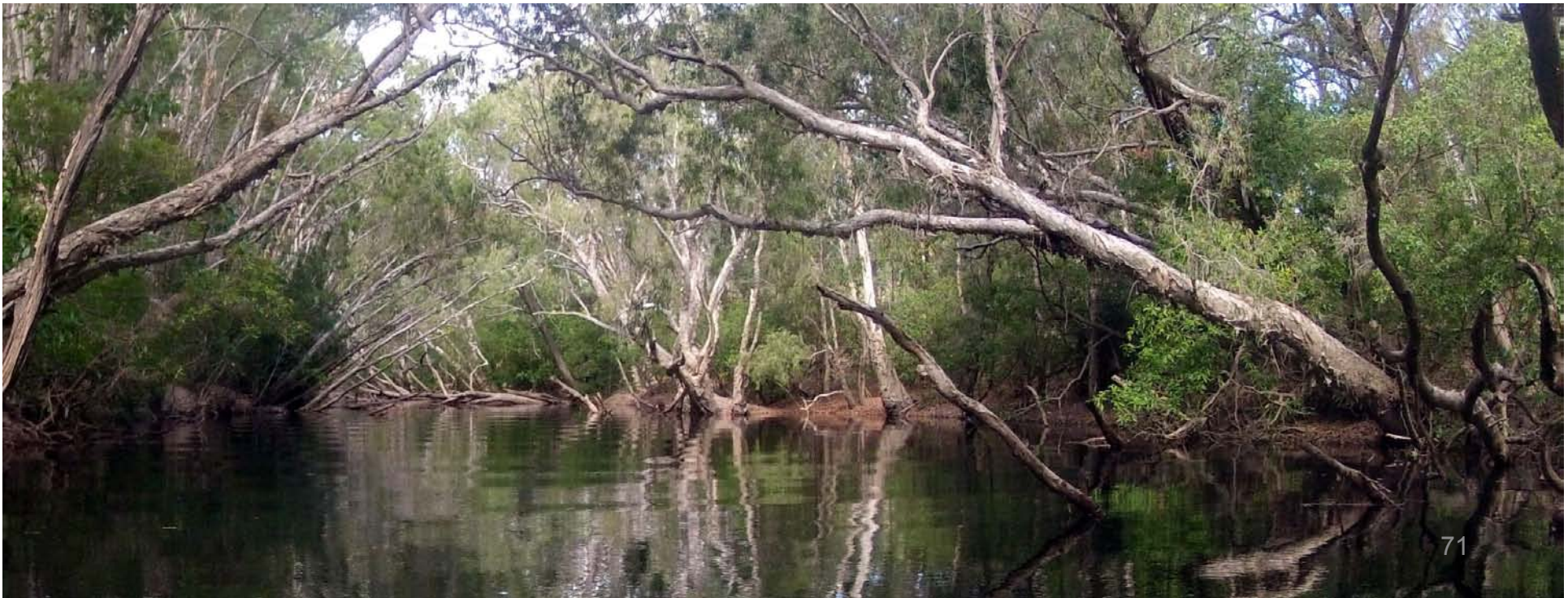
Mixing with waters from C3 and C4 areas



Where there are

- distinct river discharge changes from the wet to the dry season
- distinct spatial variations in C3 and C4 vegetation

DIC and $\delta^{13}\text{C}$ are indicators of river inflows

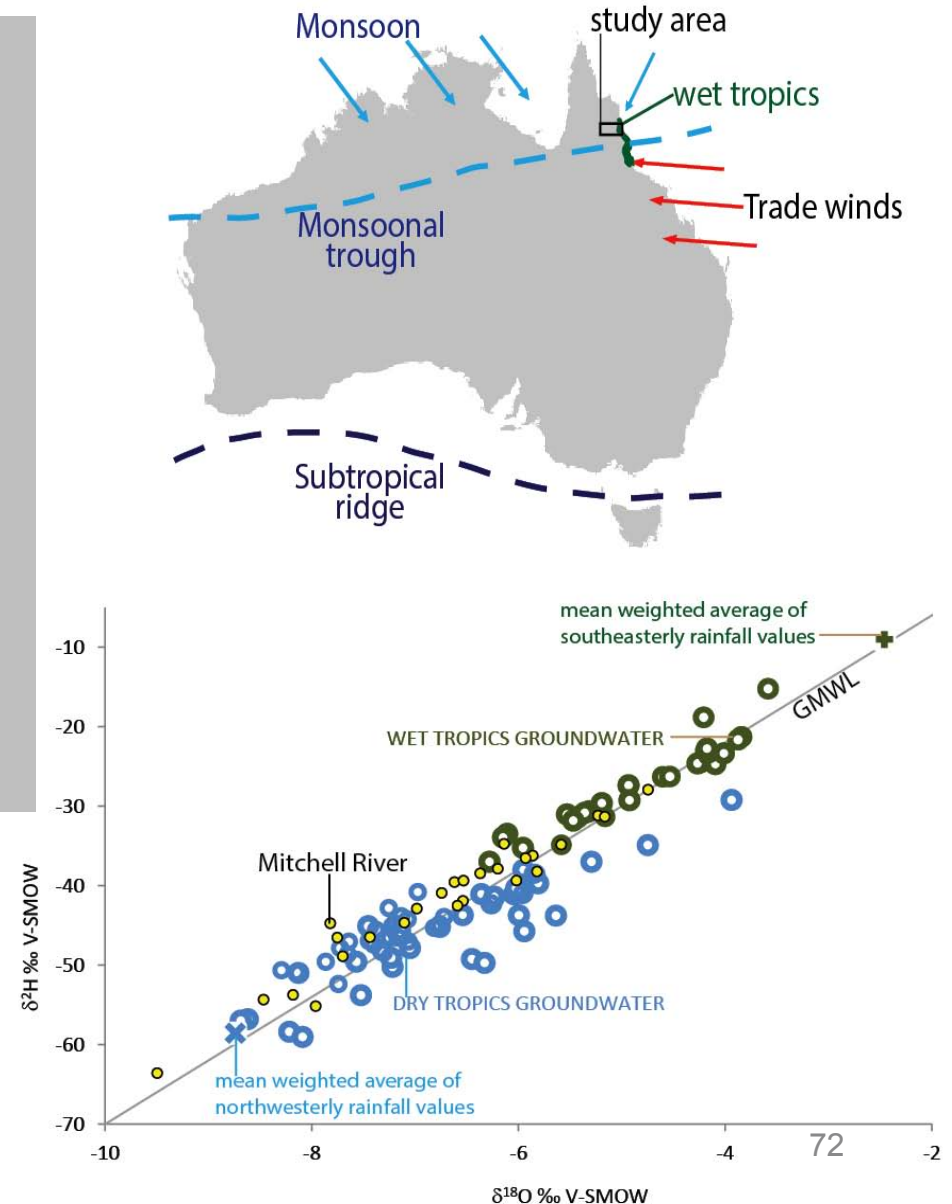


Improvements to component models

To improve :

Explore origin of isotopic differences in rainfall systems; just due to continental fall out or due to weather system differences?

e.g. atmospheric moisture residence time (e.g. Aggarwal et ., 2012)



LEB

Floodwater recharge – Lake Eyre Basin

Question

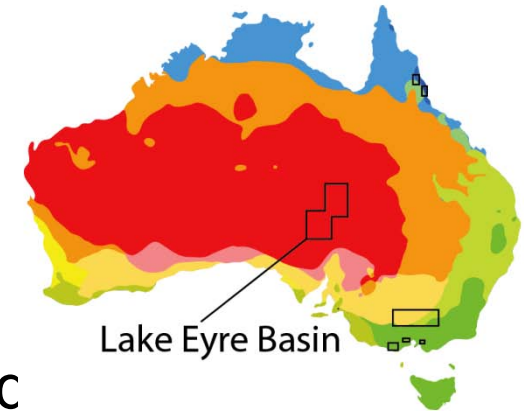
Groundwater recharge from the intermittent flood
(average annual rainfall 150 mm/yr)

Approach

$\delta^{18}\text{O}$, $\delta^2\text{H}$, ^{14}C and ^3H - groundwater recharge processes

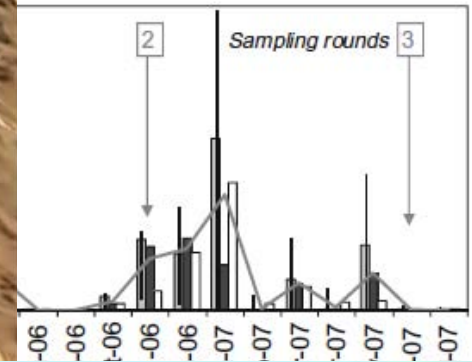
Management link

Arid system hydrogeological processes



Tweed, S., Leblanc, M., Cartwright, I., Favreau, G., Leduc, C., 2011. Arid zone groundwater recharge and salinisation processes; an example from the Lake Eyre Basin, Australia, *Journal of Hydrology*, 408, 257-275

basin



Floodwater recharge – Lake Eyre Basin

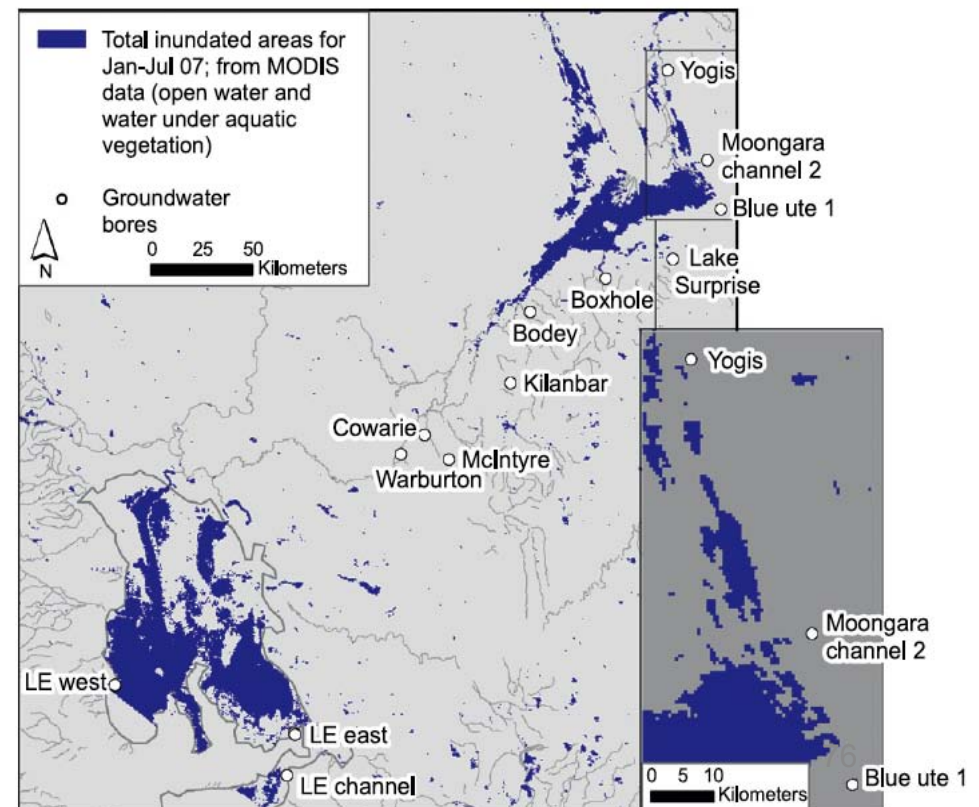
Groundwater chemistry before and after flood

- Groundwater TDS contents
 - before: 6,800-140,000 mg/L
 - after: 8,100-100,000 mg/L
- Groundwater $\delta^2\text{H}_{\text{activity}}$
 - before: -41 to 3 ‰
 - after: -42 to 5 ‰

No evidence of a significant recharge event from floodwaters

Either

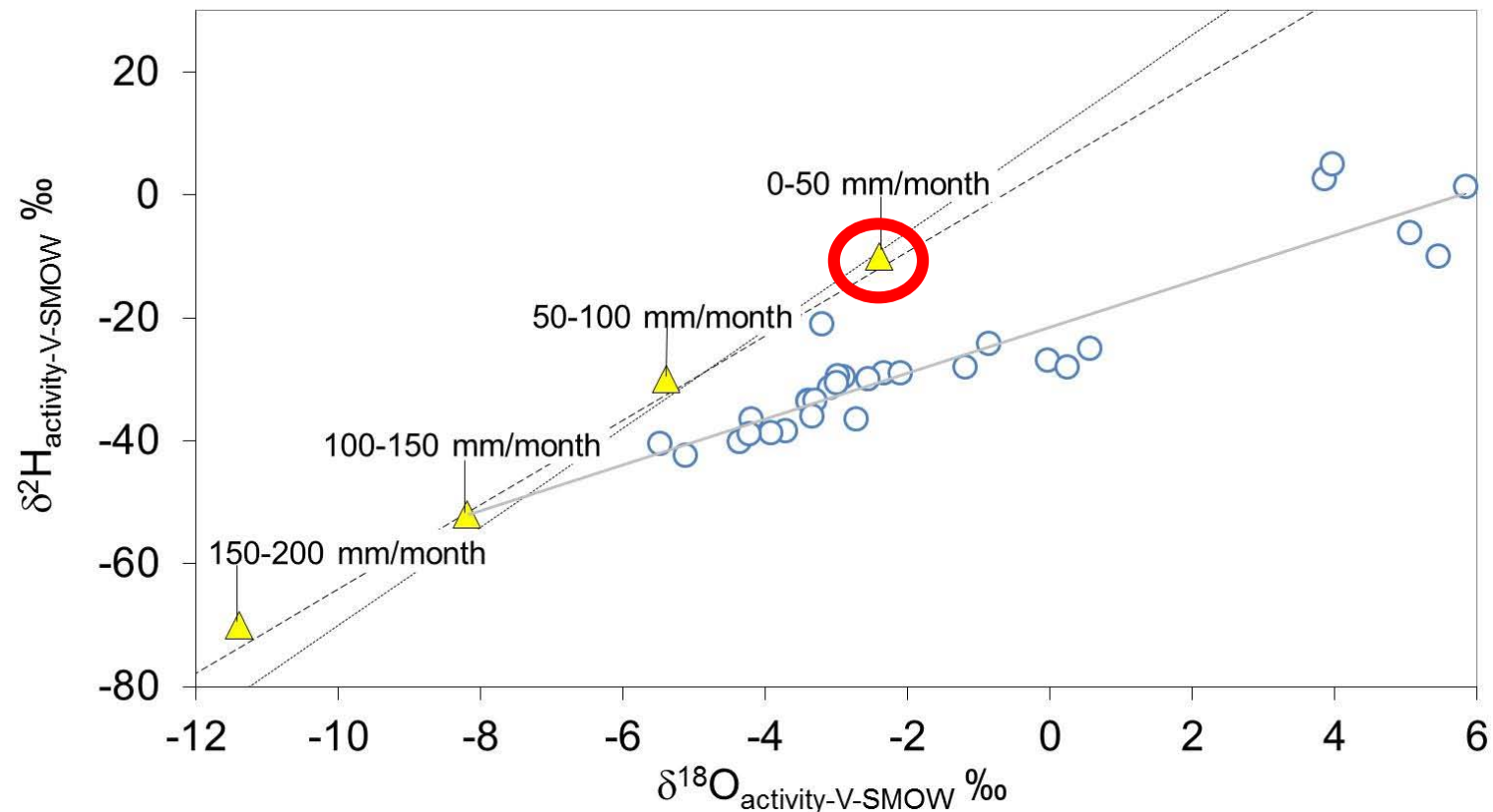
- (1) Transit times are slow
 - 6 months between flood and sampling;
- (2) Volume of infiltrating water is low
 - change in chemistry is minimal



Floodwater recharge – Lake Eyre Basin

$\delta^{18}\text{O}$, $\delta^2\text{H}$ - long-term recharge processes

- Linearly interpolated isotope values for groundwater
- Corresponding rainfall levels are ~ 100-150 mm/month
- Highest average monthly rainfall is 33 mm (Jan)
- Groundwater recharge from local rainfall is not a regular occurrence



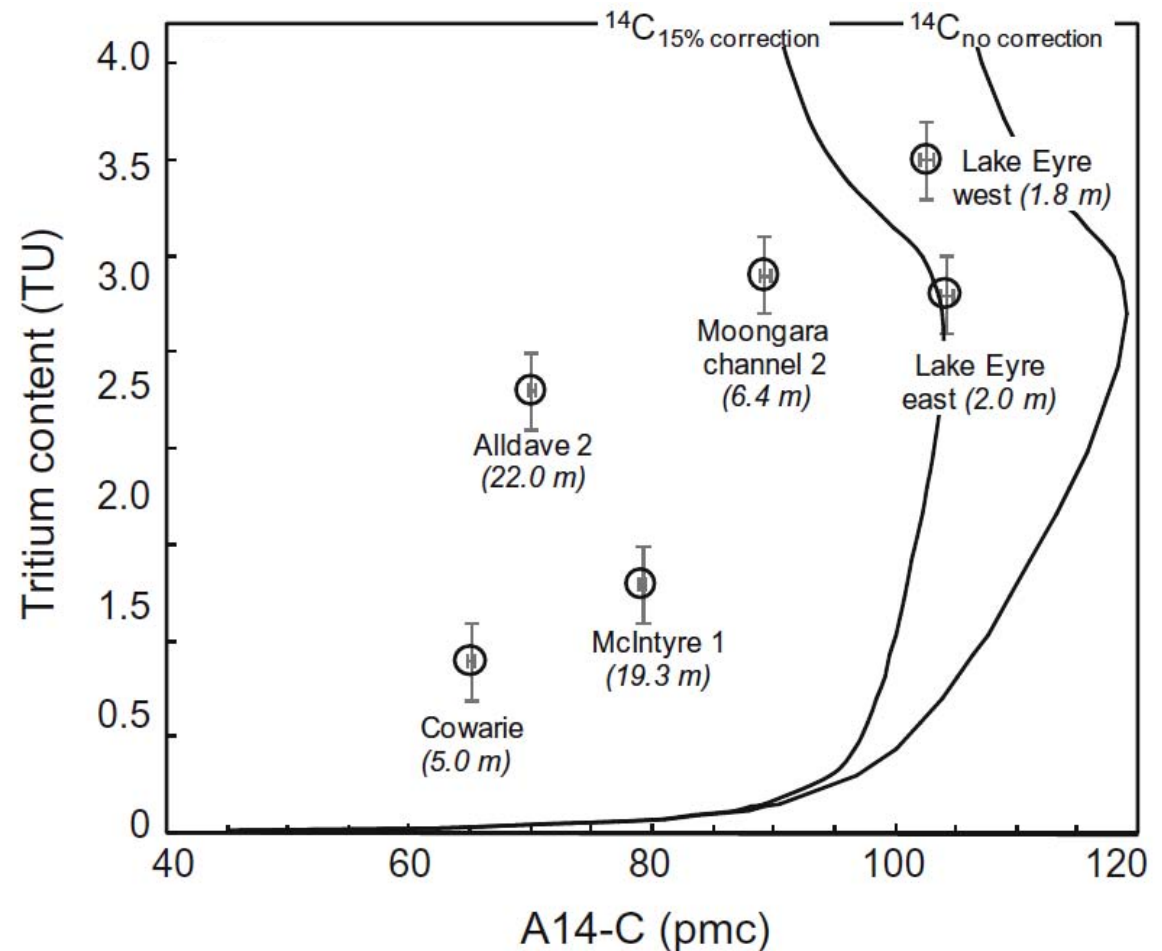
Floodwater recharge – Lake Eyre Basin

^{14}C and ^3H

- ^{14}C (65.1–104.2 pmC) and ^3H (0.9–3.5 TU)
- mixing between younger water and older water

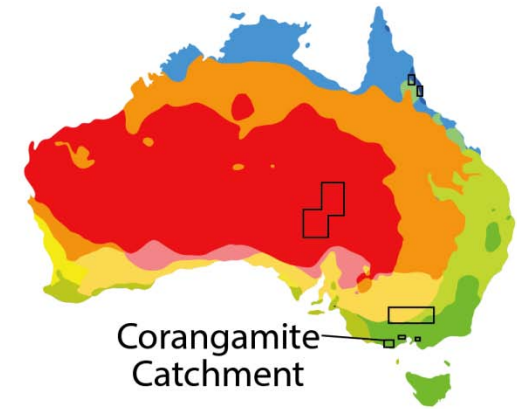
Dual porosity recharge

- cracking clays
- Fractured sandstone and shale aquifers



Corangamite drought

Drought impacts on water quality – Corangamite Lakes



Question

Impacts of drought on nutrient concentrations in groundwater through-flow lakes?

Approach

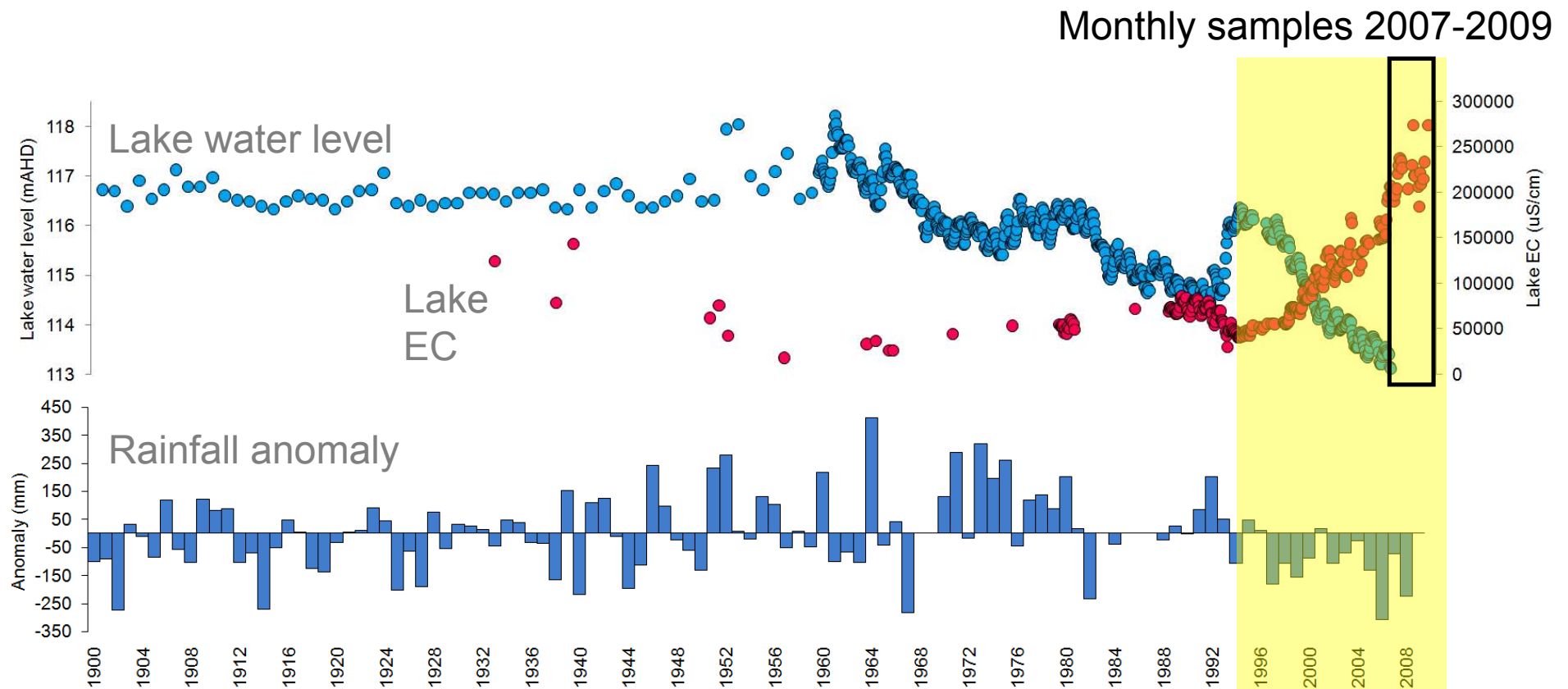
Major ions and nutrient concentrations

Management link

Ecologically important (Ramsar sites) lakes

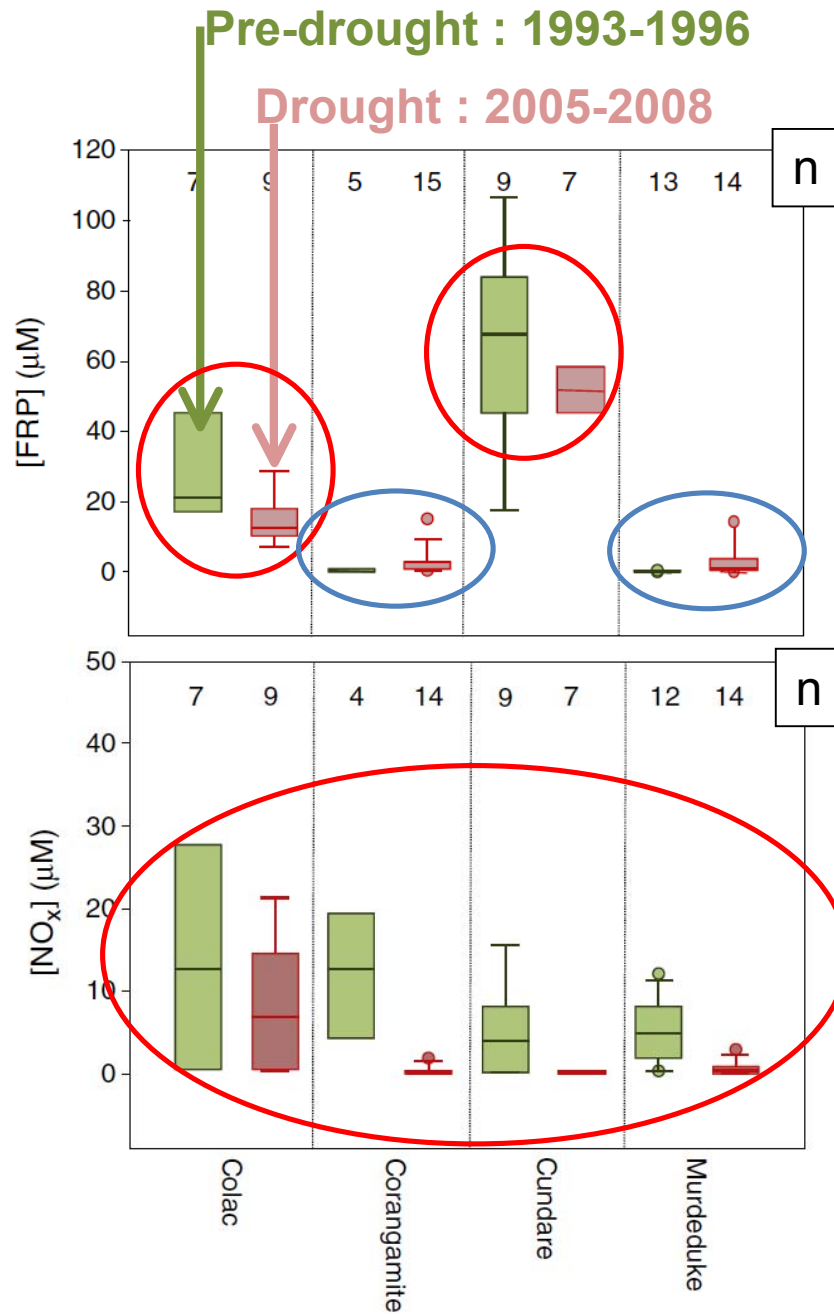


Drought: 1997 - 2011



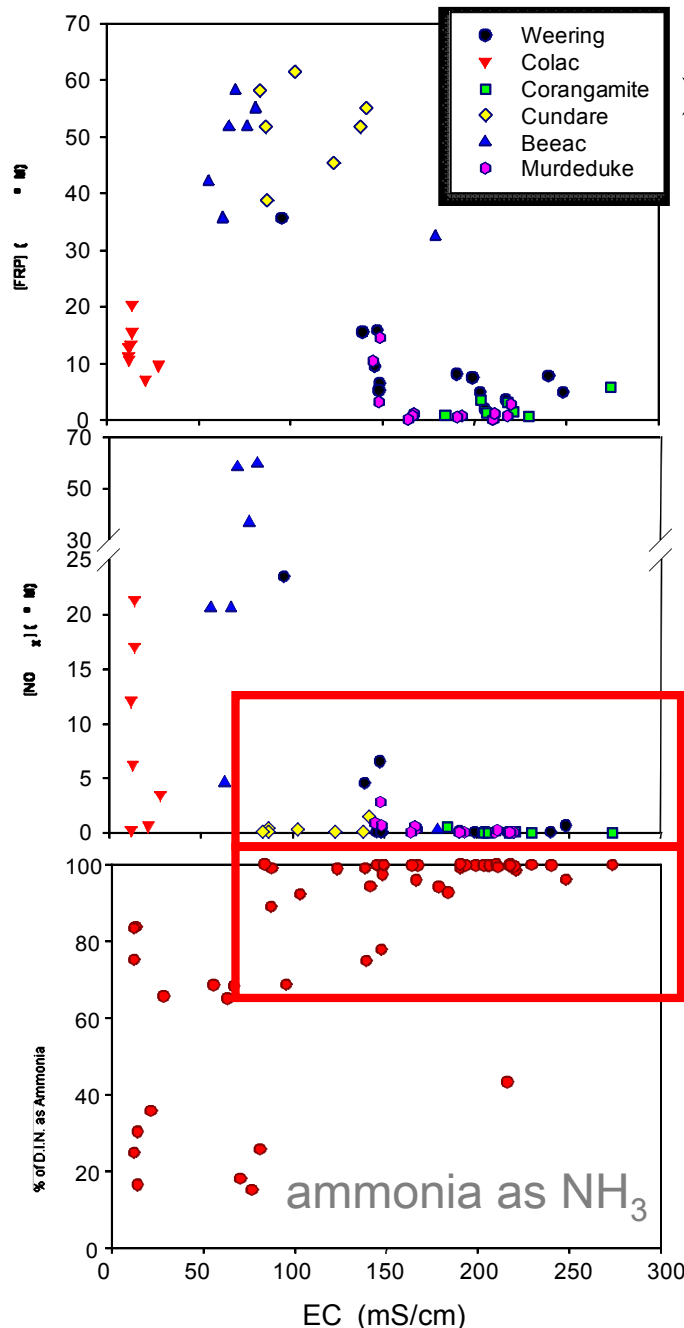
	1900-1937	1939-1959	1960-1993	1994-2009
Max change in water level (m)	↓ 0.7	↑ 1.7	↓ 3.6	↓ 3.2
Max change in EC (mS/cm)		↑ 120	↑ 52	↑ 220

Trends in changes in nutrients from pre-drought to drought?



- Decrease in phosphate
- Minor increase in phosphate
- Decrease in NOx

Trends in changes in nutrients with lake salinity?

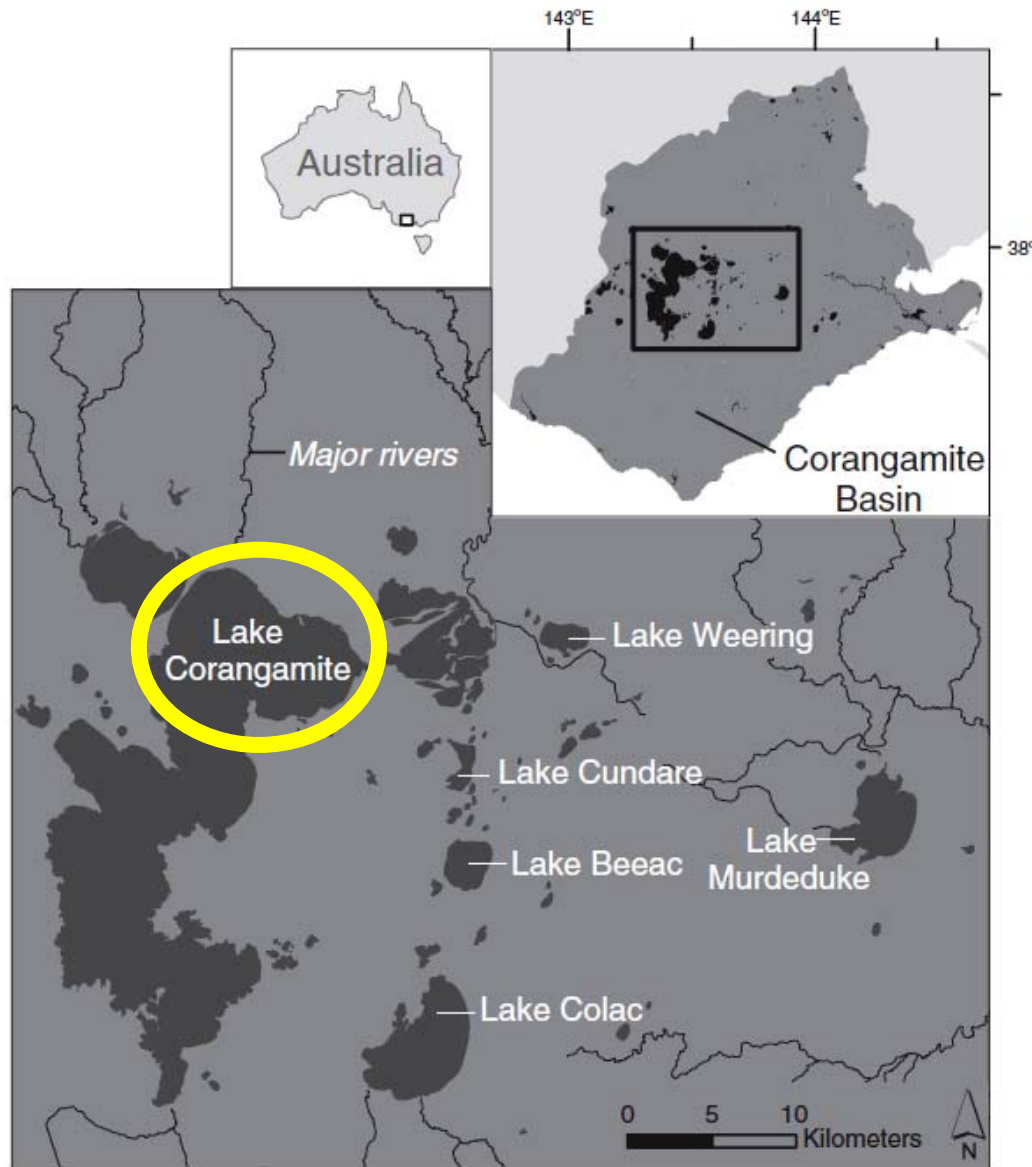


➤ FRP is largely determined by the individual lake (and sources) rather than the salinity

➤ EC < 100 mS/cm, greater NO_x variability

➤ EC > 100 mS/cm, NO_x concentrations low

➤ EC > 100 mS/cm, almost all of the D.I.N. is NH₃



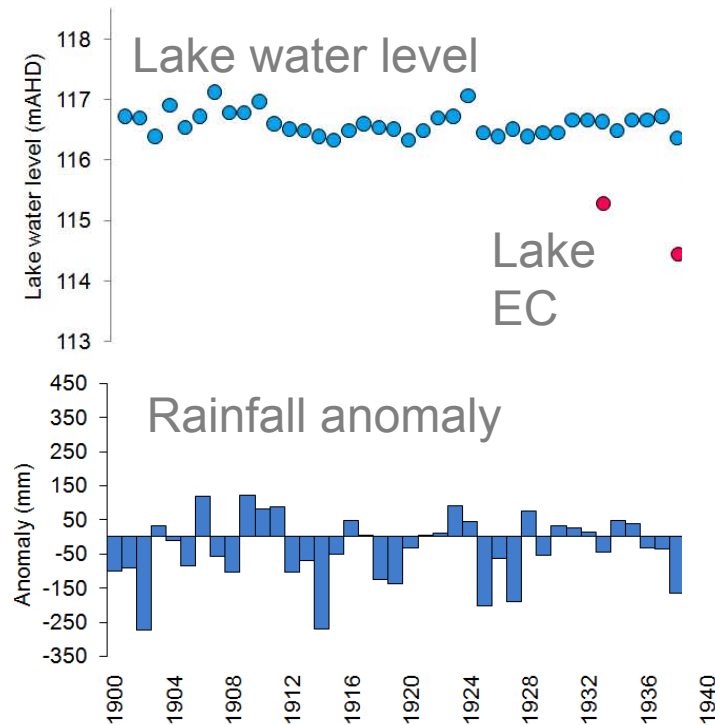
6 Lakes

- mostly shallow (< 6 m)
- Range in sizes
 - 0.13 to 241 km²
- Mostly saline
 - up to > 400 mS/cm

Drought in context
e.g. Lake Corangamite

1900-1938: low rainfall

European settlement expansion 1830s - early 1900s



	1900-1937
Max change in water level (m)	↓ 0.7
Max change in EC (mS/cm)	

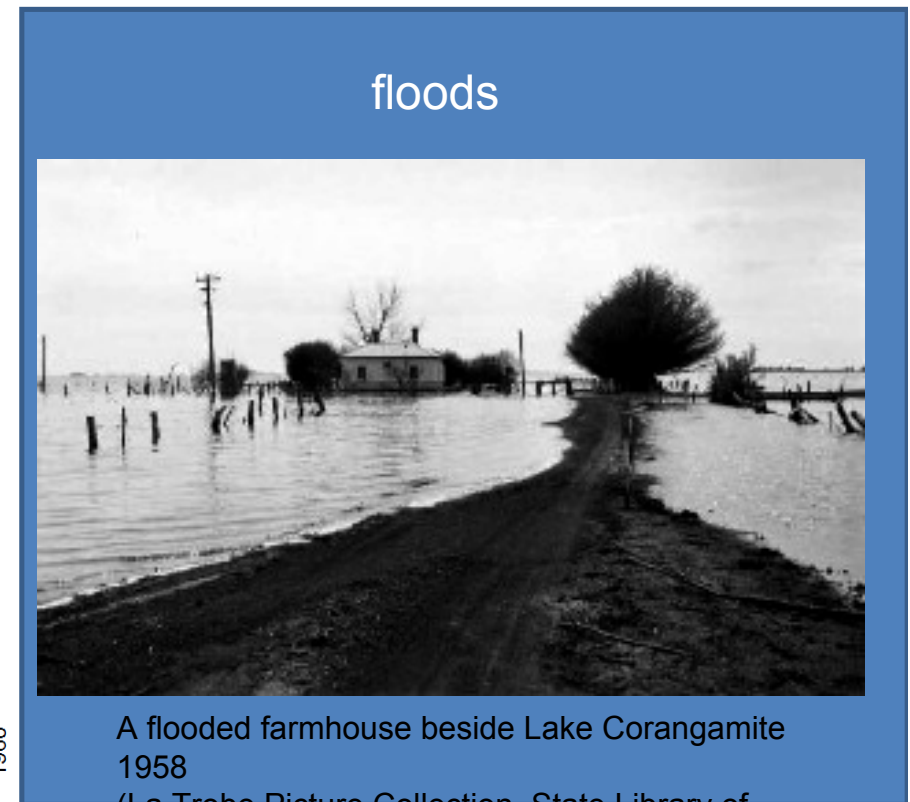
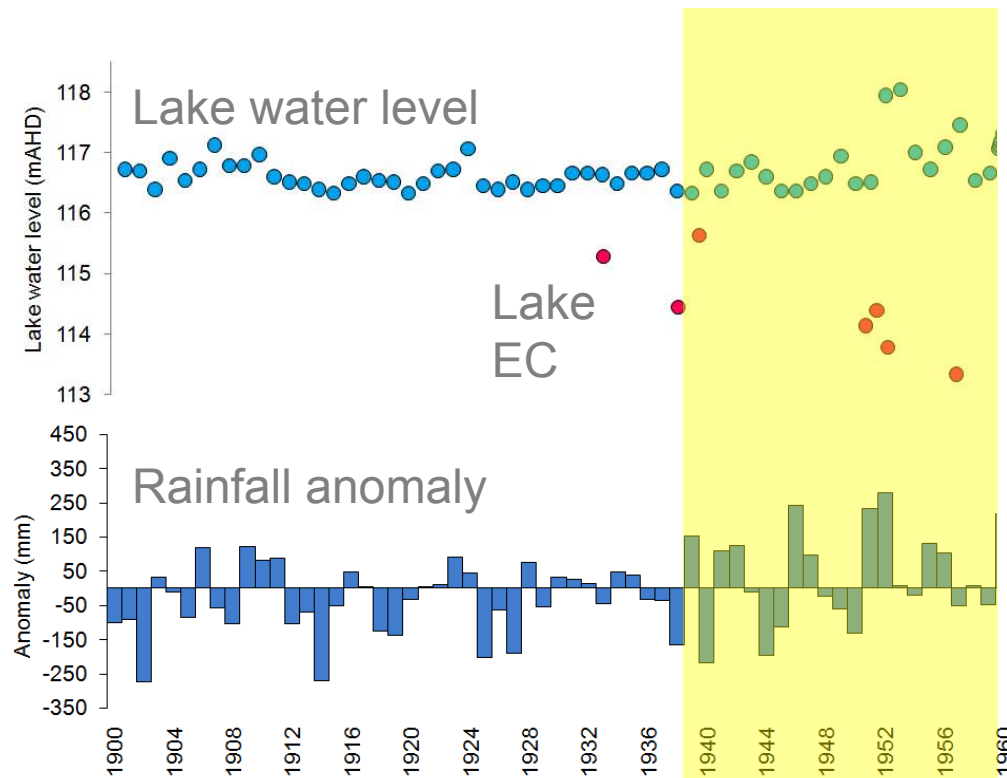
Lake Corangamite takes its name from the Colijon tribe word koraiyn, meaning bitter or salty

EC: 78 -124 mS/cm (1933-38)



Salt beside Lake Corangamite, c. 1920
(La Trobe Picture Collection, State Library of Victoria).

1939-1959: increased rainfall

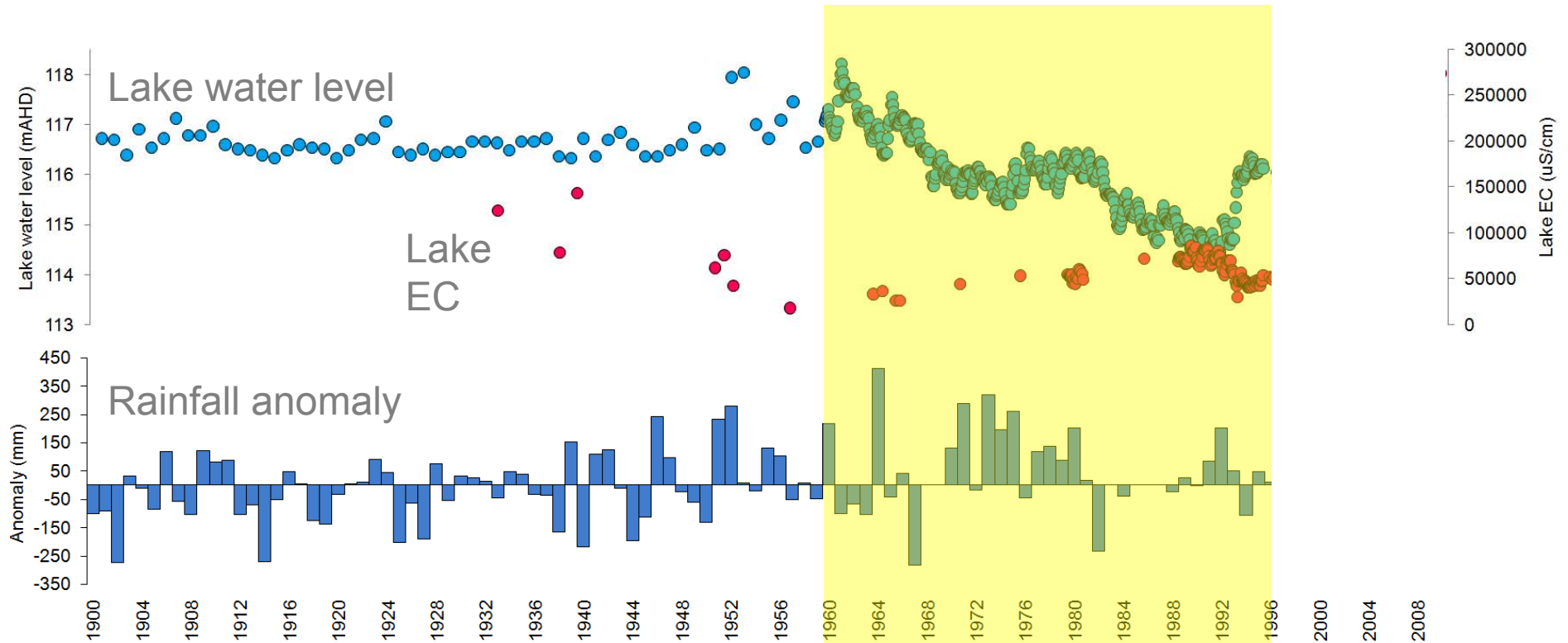


A flooded farmhouse beside Lake Corangamite 1958
 (La Trobe Picture Collection, State Library of Victoria).

	1900-1937	1939-1959
Max change in water level (m)	↓ 0.7	↑ 1.7
Max change in EC (mS/cm)		120

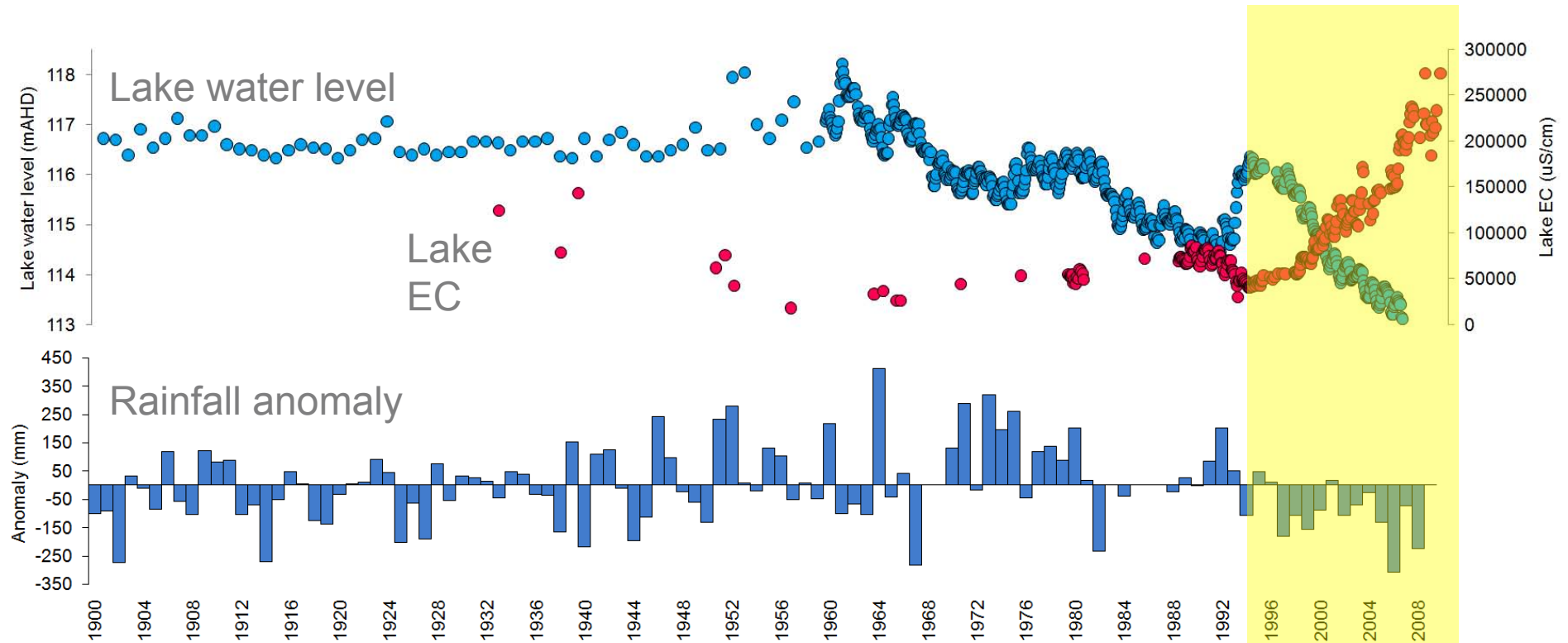
1960-1996: water diversion

Changes in lake biota; affected bird species



	1900-1937	1939-1959	1960-1993
Max change in water level (m)	↓ 0.7	↑ 1.7	↓ 3.6
Max change in EC (mS/cm)		↑ 120	↑ 52

1994 - present: drought



	1900-1937	1939-1959	1960-1993	1994-2009
Max change in water level (m)	↓ 0.7	↑ 1.7	↓ 3.6	↓ 3.2
Max change in EC (mS/cm)		↑ 120	↑ 52	↑ 220

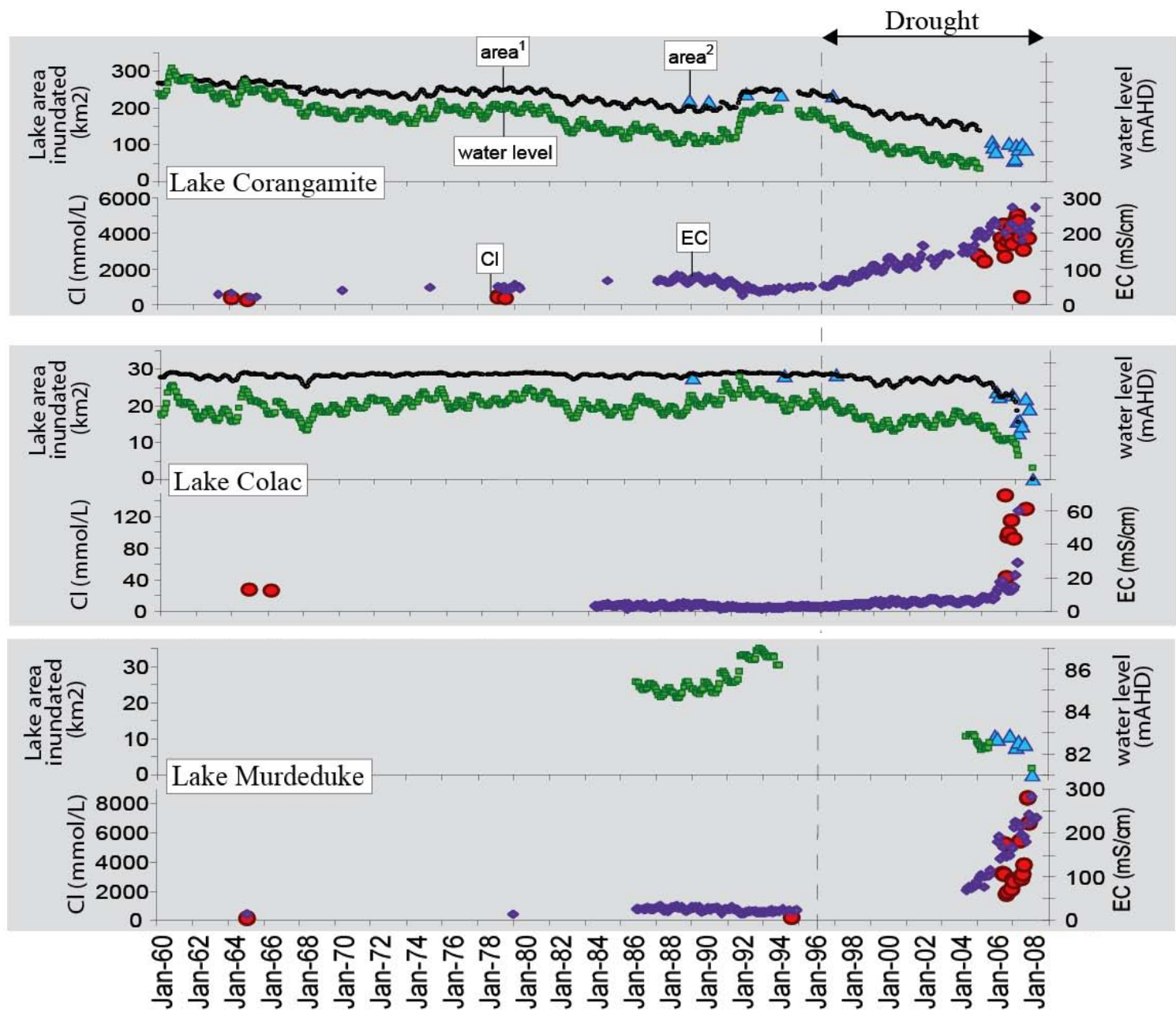
Agriculture surrounding lakes

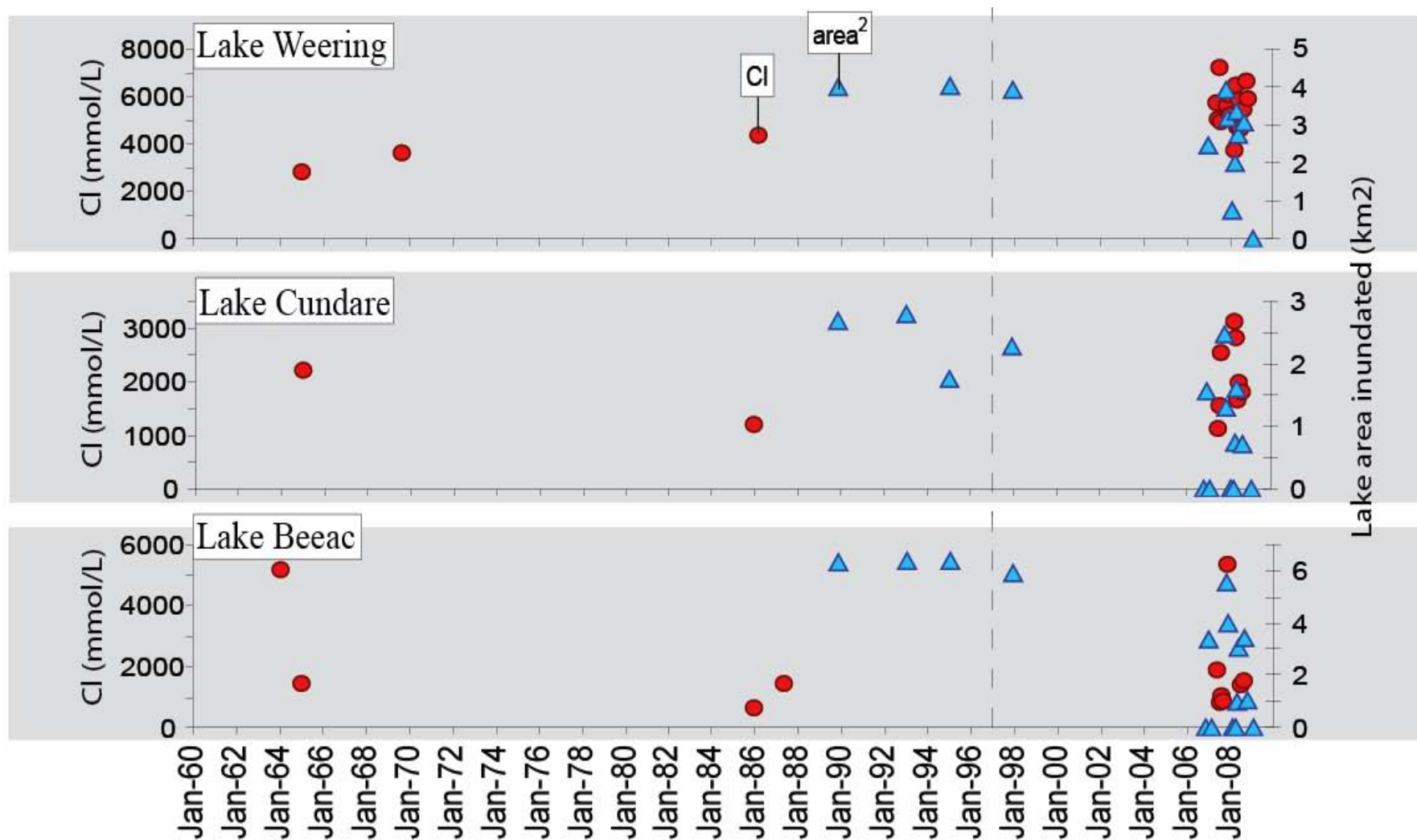


Sensitive to climatic variability...

Drought – increased EC

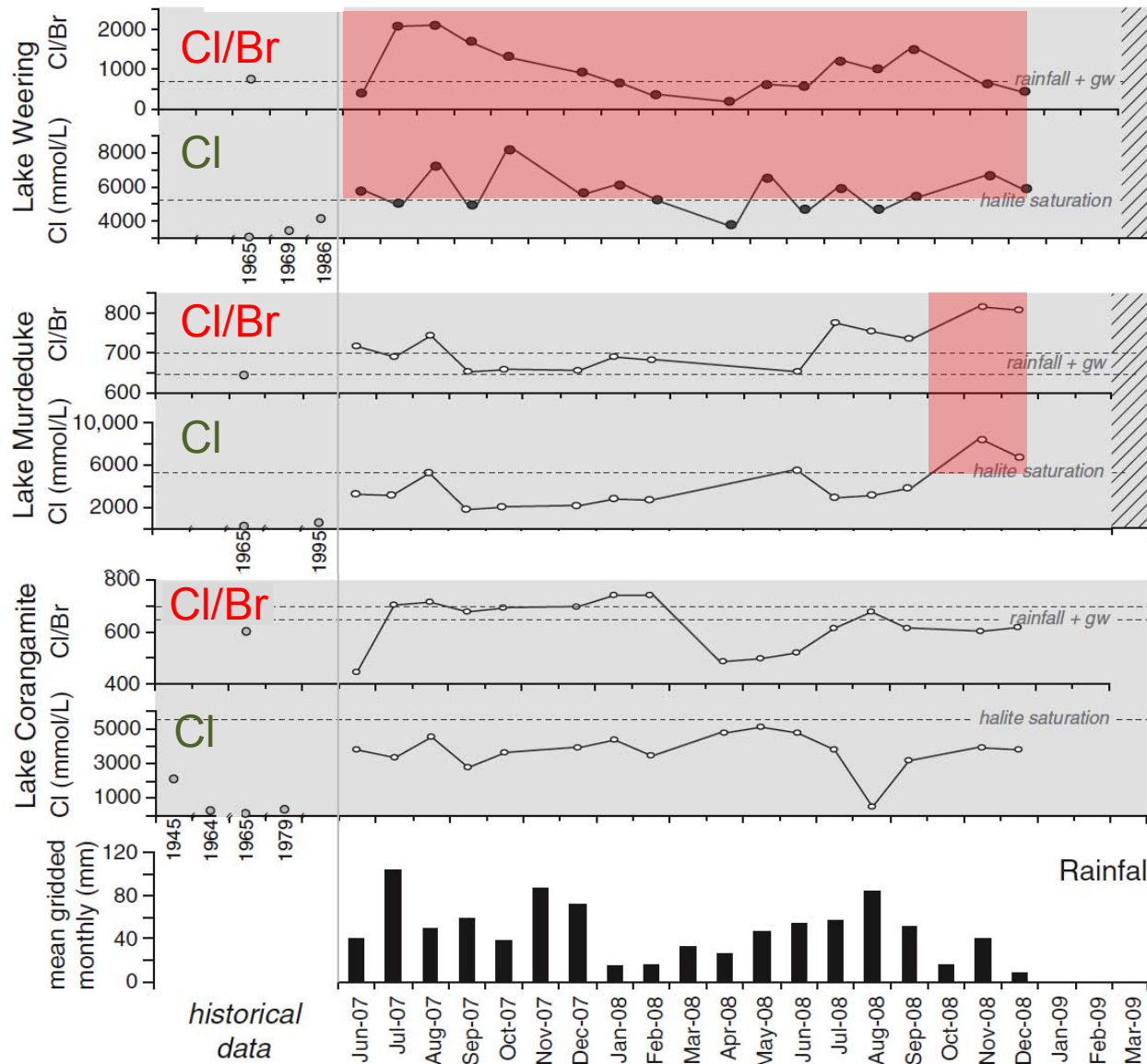






Multi-year drought impacts on water quality – Corangamite Lakes

Varied responses in salinity processes to drought

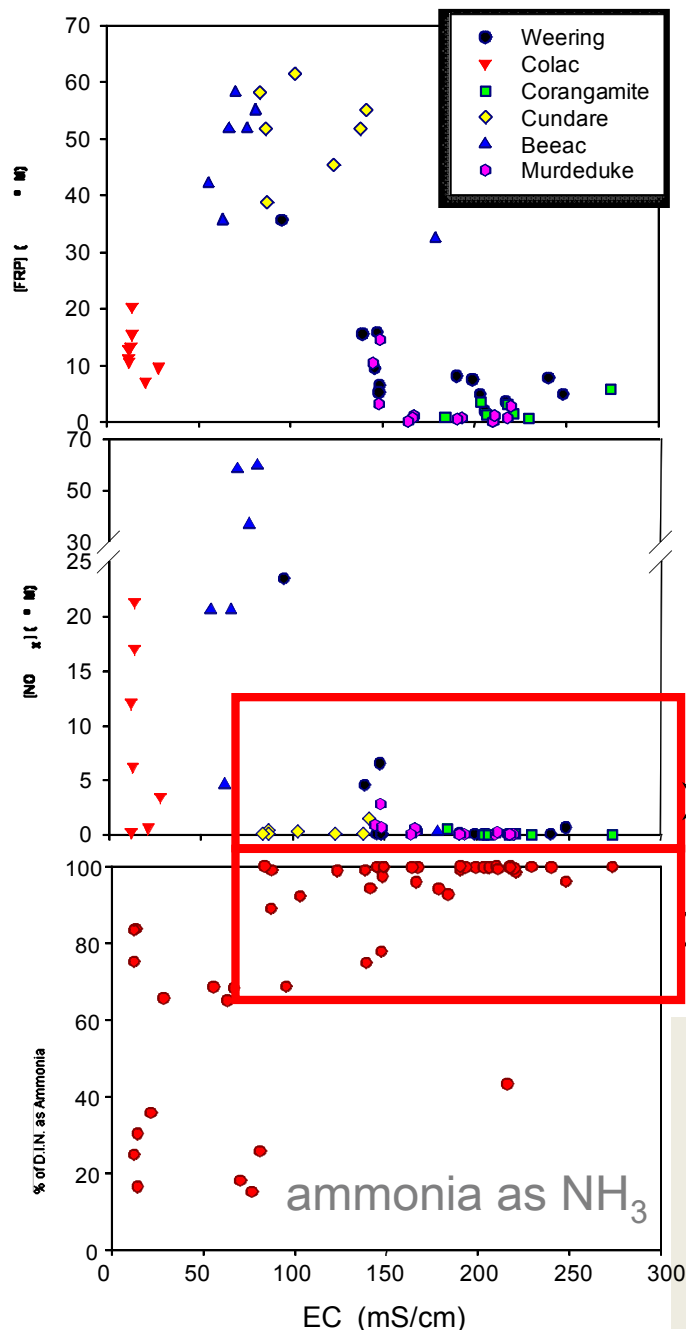


- Pre-drought: evaporation
- Drought: Halite precipitation and dissolution

- Saturated with respect to halite
- Increase in Cl/Br ratios
- Increase influence of halite precipitation and dissolution

- No change

Trends in changes in nutrients with lake salinity?



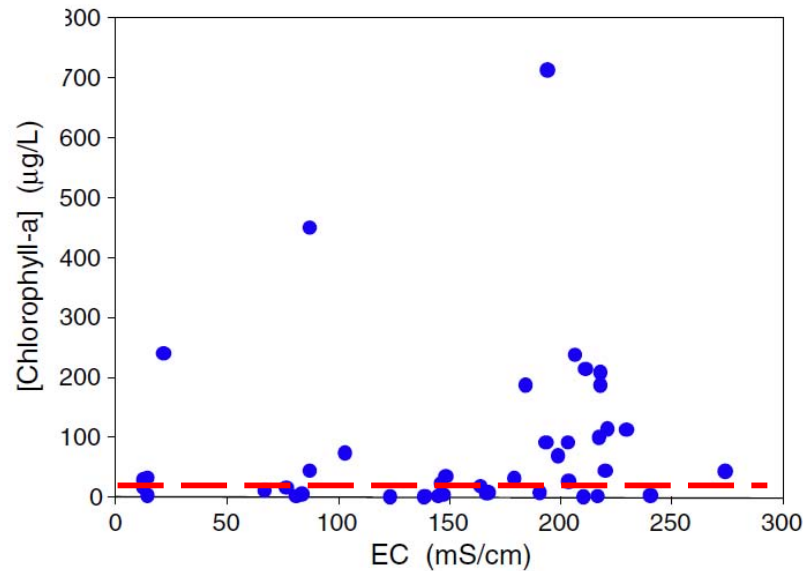
➤ NO_x variations are driven not by salinity increases but by other biogeochemical processes

➤ EC > 100 mS/cm, almost all of the D.I.N. is NH₃ (pH 7.5 - 9.6)

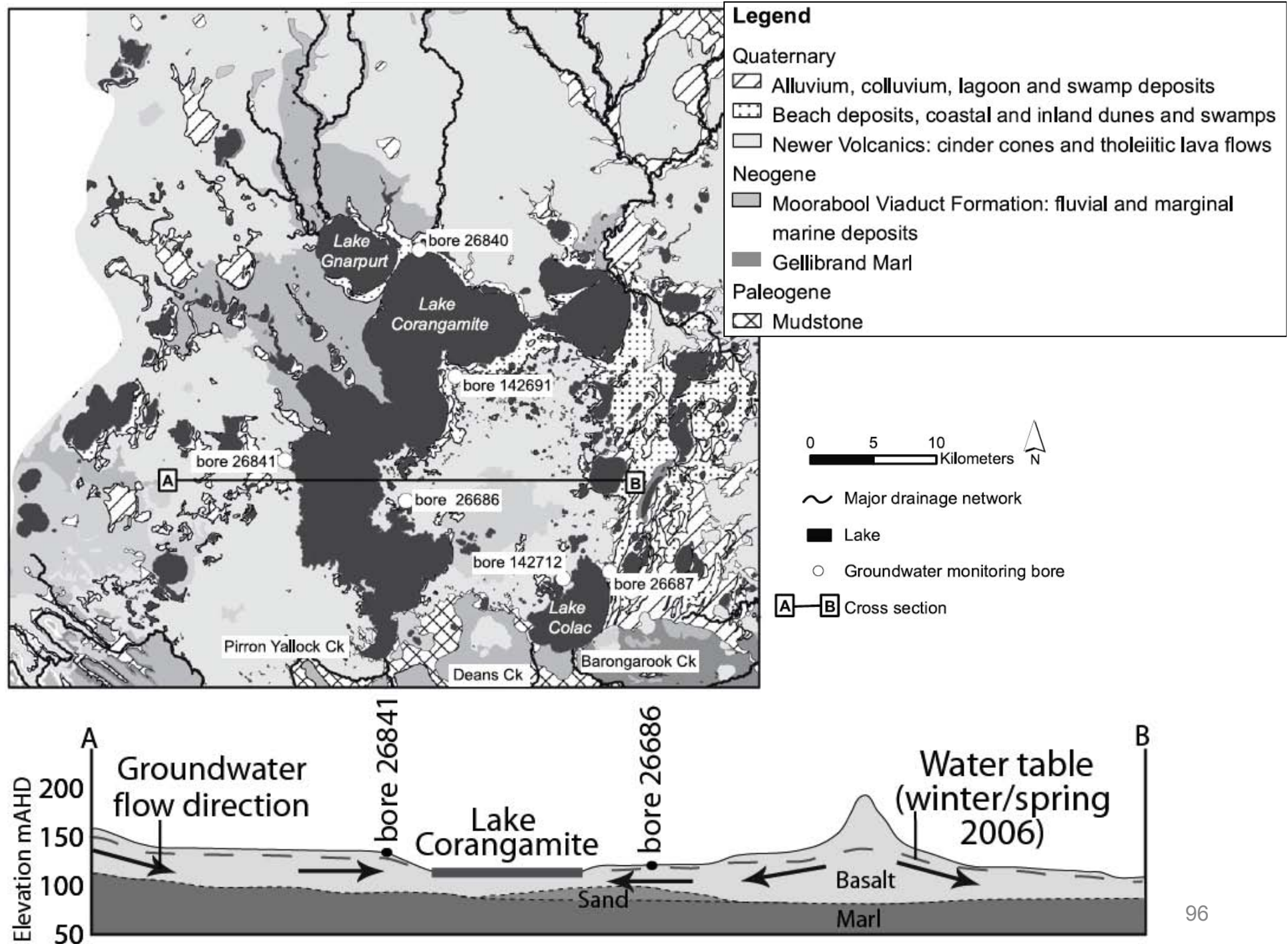
➤ NH₃ can be toxic to a wide range of organisms at high concentrations

- high concentrations of Na⁺ can displace NH₄⁺ bound to negatively charged suspended particles
- nitrification (of NH₄⁺ to NO₃⁻) is suppressed due to the inability of ammonia oxidizing bacteria to function under hypersaline conditions

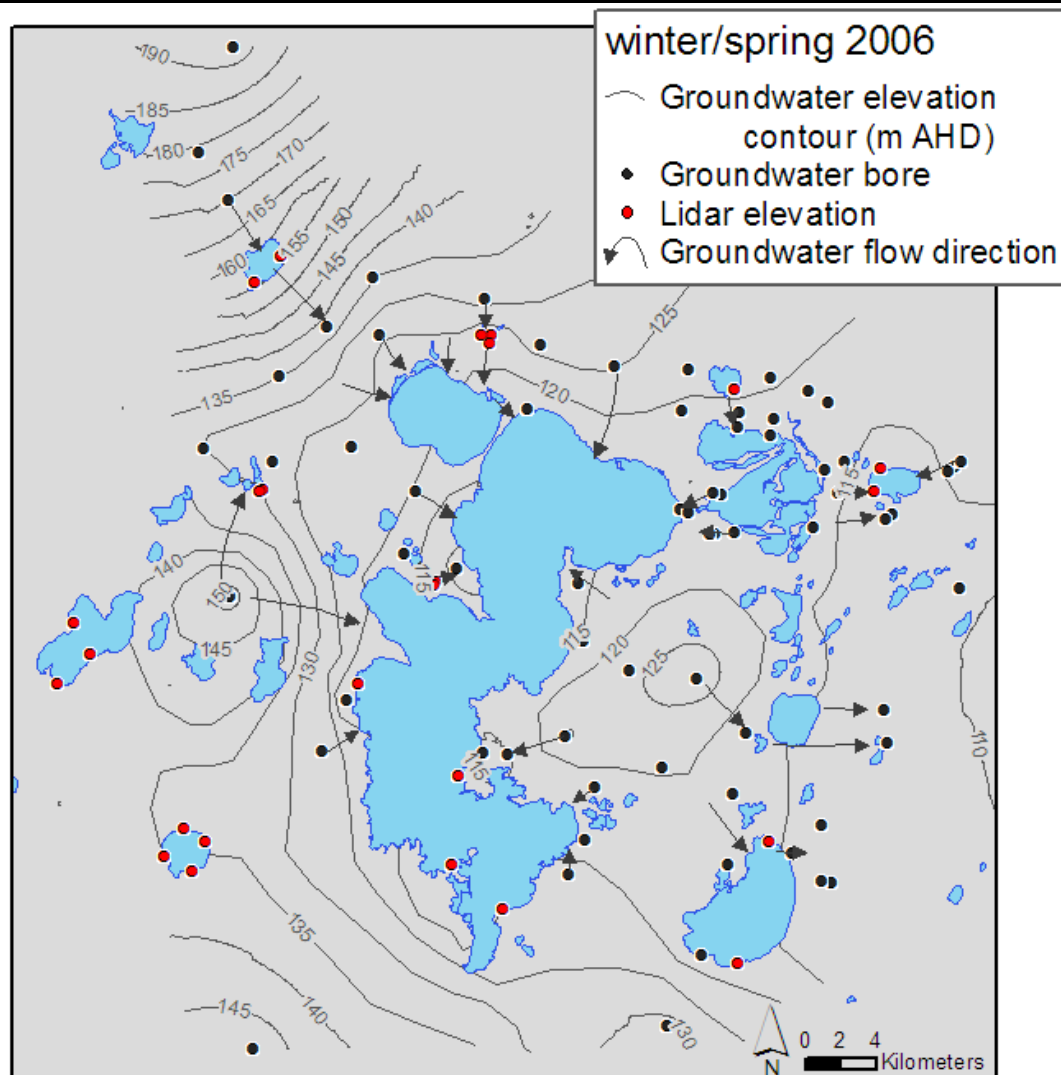
Trends in changes in nutrients with lake salinity?



- At various times during the drought, each lake exceeds the 8 µg/L government trigger level
- EC ~ 200 mS/cm: high chlorophyll-a concentrations
- High salinities not constraining algal growth



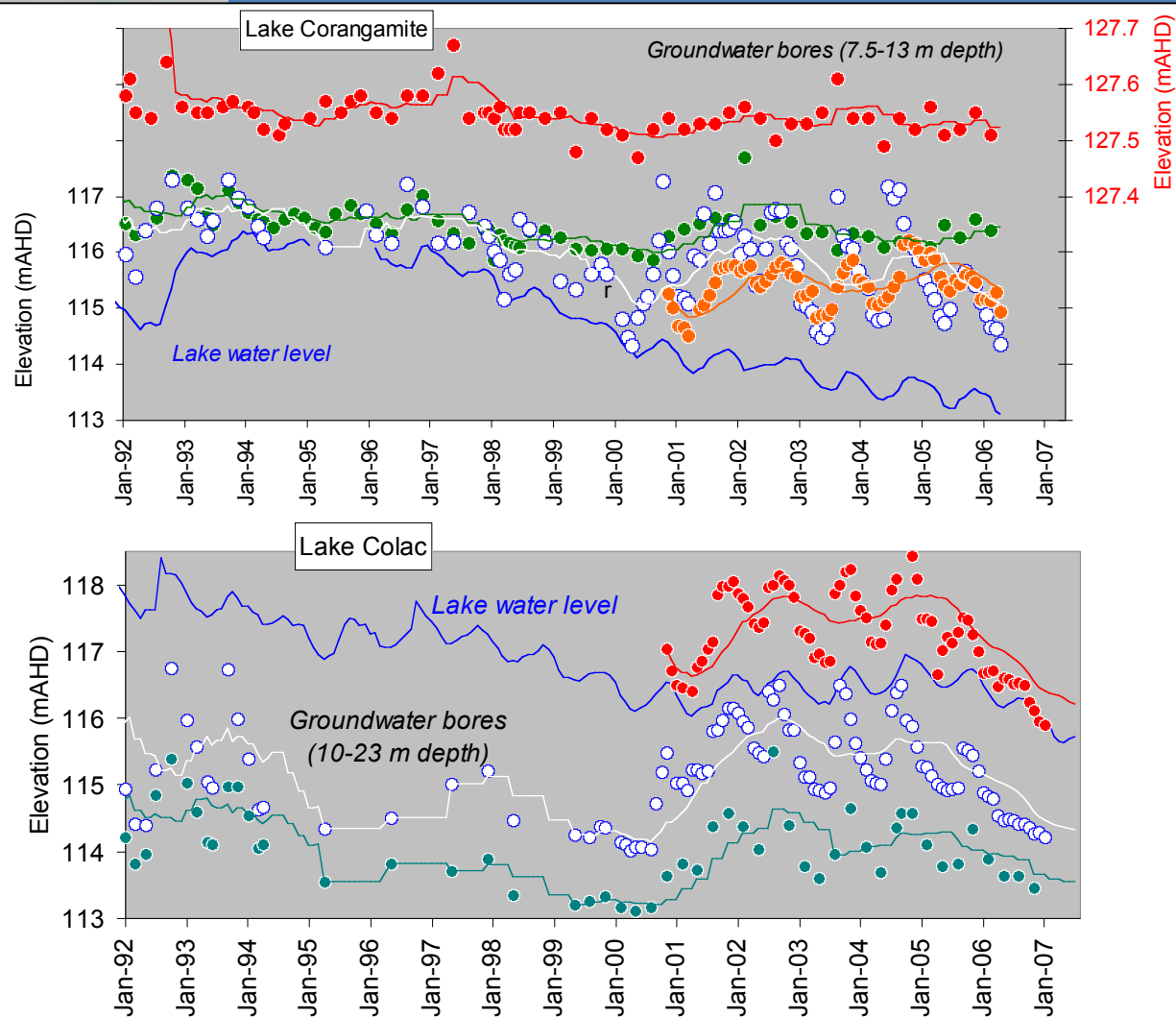
Temporal variation groundwater and lakes



Pre-drought (1992) vs. Drought (2006)

- Regional groundwater flow to the east
- Water table during drought is lower on average by
 - 0.73 m in summer/autumn
 - 1.24 m in winter/spring

Temporal variation groundwater and lakes



Lake levels decrease at a more rapid rate than the groundwater levels

–hydraulic gradients between groundwater and lakes have changed

–No reversals

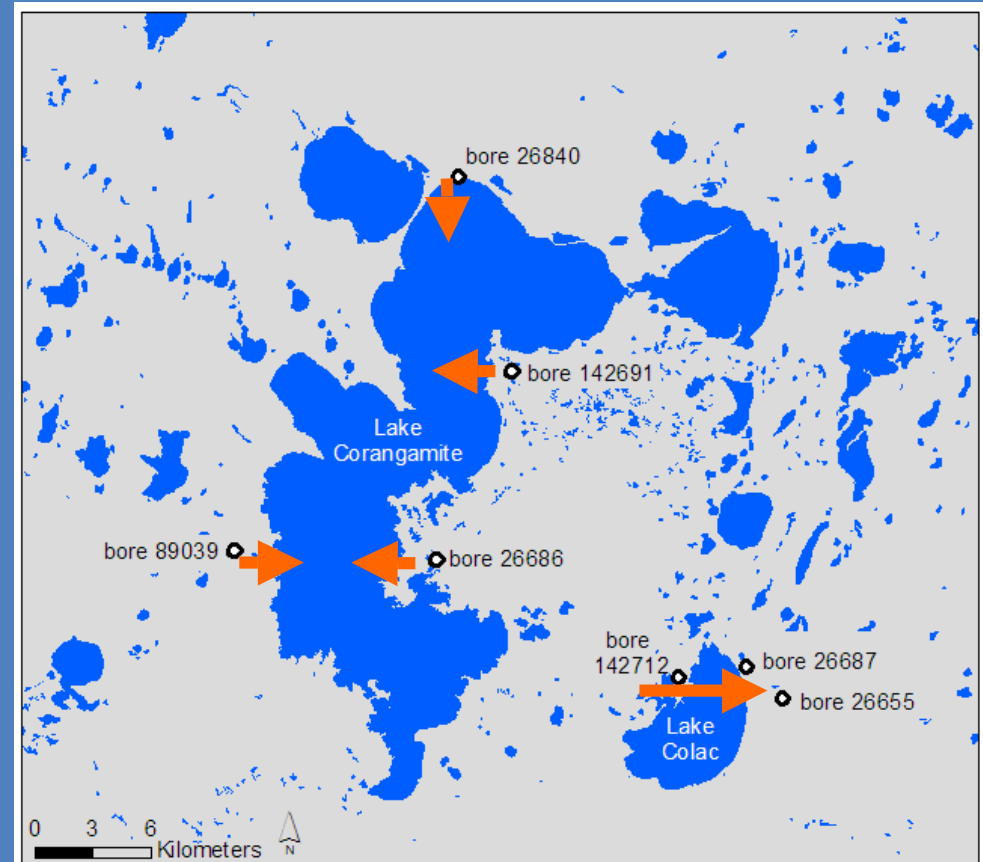
- Lake Corangamite remains a discharge lake
- Lake Colac remains a throughflow lake

Temporal variation groundwater and lakes

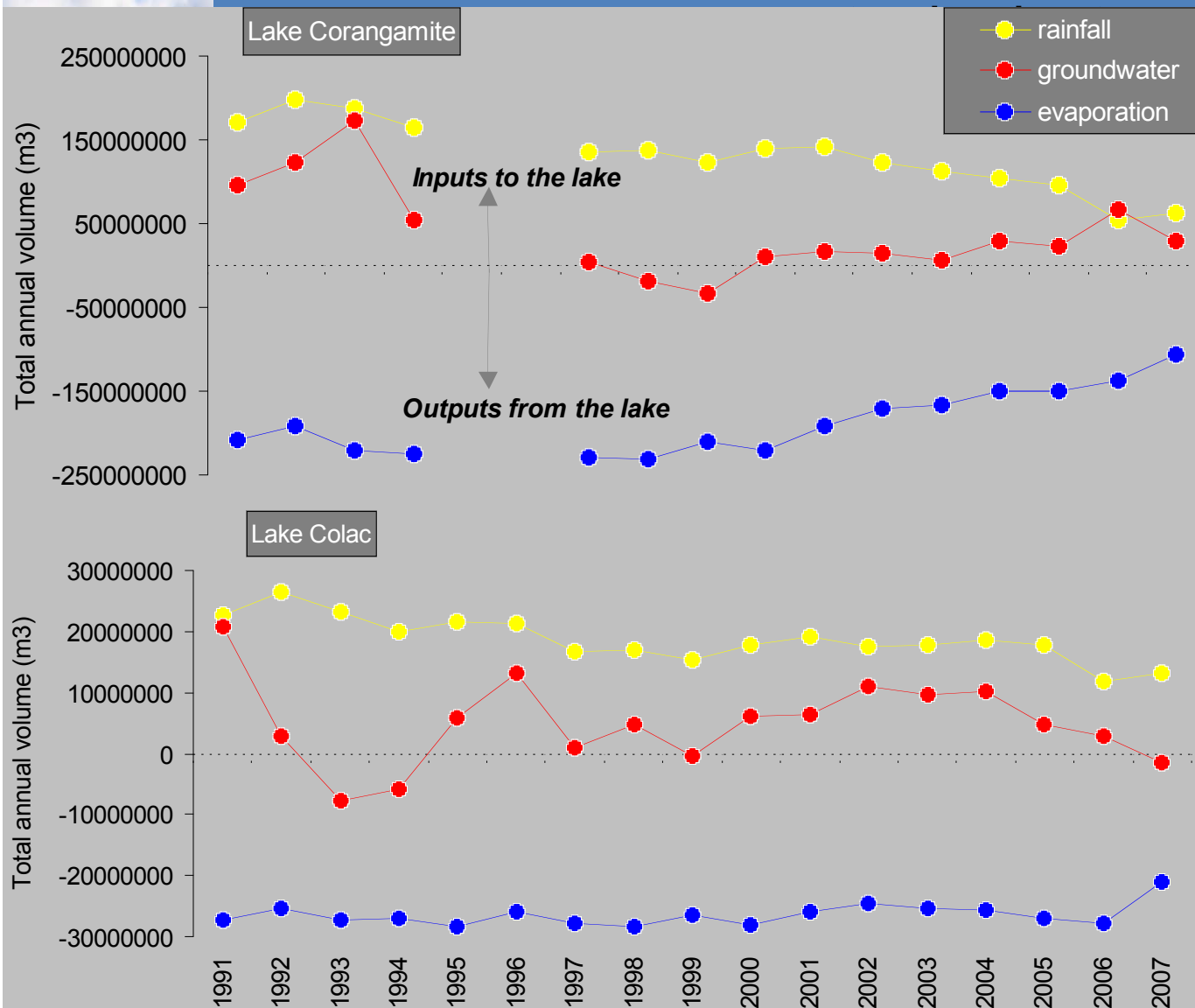
Limitation

- Point data: insufficient distribution of monitored groundwater bores surrounding lakes

..water budget



Temporal variation

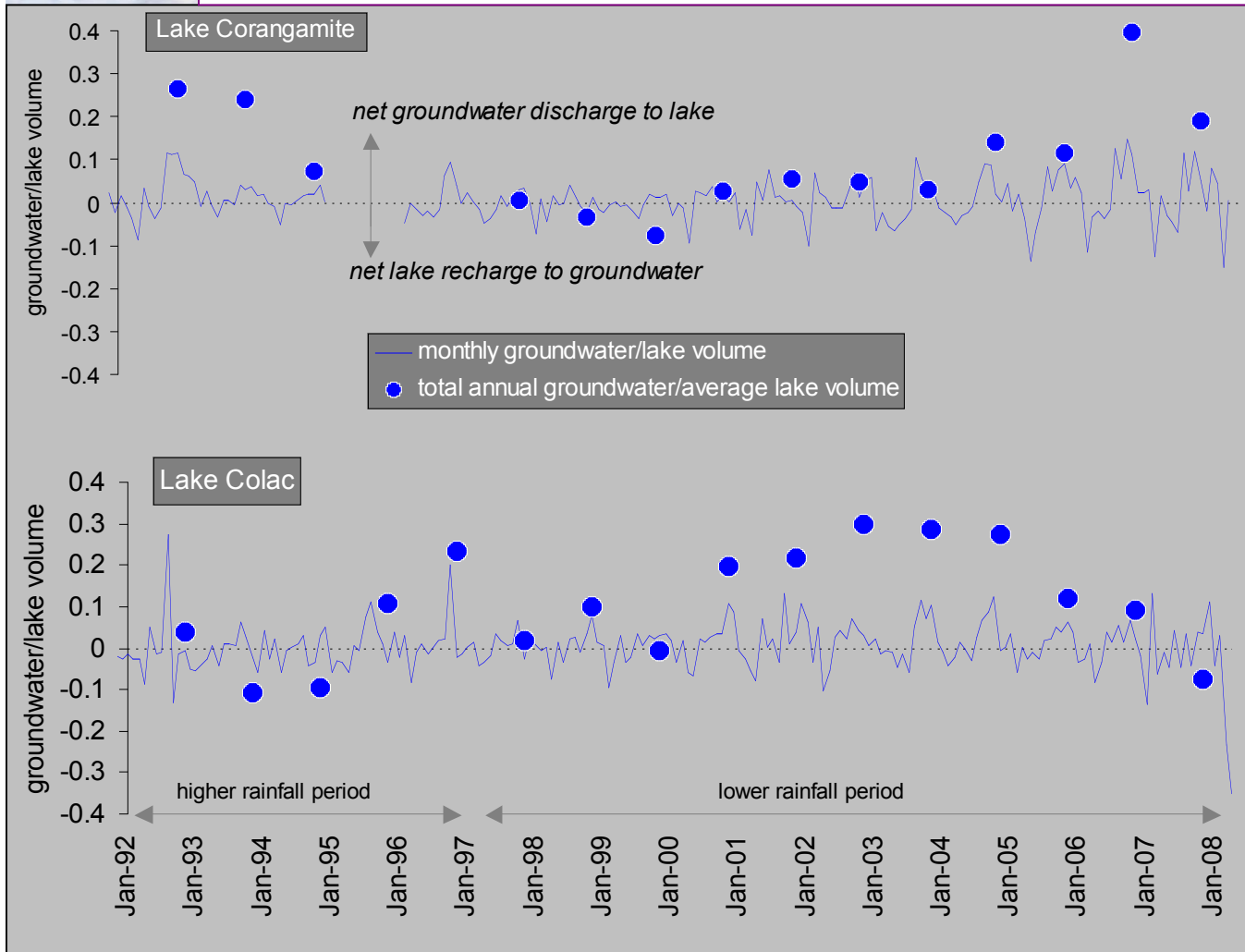


- Water in lakes from rainfall
- Reduced rainfall
- No decrease in groundwater discharge
- No increase in evaporation

Reduced rainfall controlling declines in lake levels

Temporal variation water budget

varying responses in groundwater-lakes interaction to drought stress



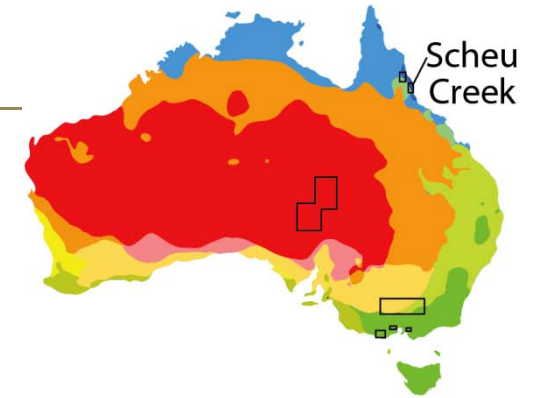
- Seasonal fluctuations
- Discharge decrease during wetter period
- Discharge increase during drought

- Seasonal fluctuations
- Discharge increase and then decrease during drought

Tweed, S., Leblanc, M., Cartwright, I. 2009. Groundwater-surface water interaction and the impact of a multi-year drought on lakes condition in south-east Australia. *Journal of Hydrology*, 379(1-2): 41-53.

High resolution $\delta^{18}\text{O}$ and $\delta^2\text{H}$

Contaminant transport during rainfall events – Scheu Creek



Question

High temporal resolution analysis of hydrological processes in a wet tropics?
(average annual rainfall 3000 mm/yr)

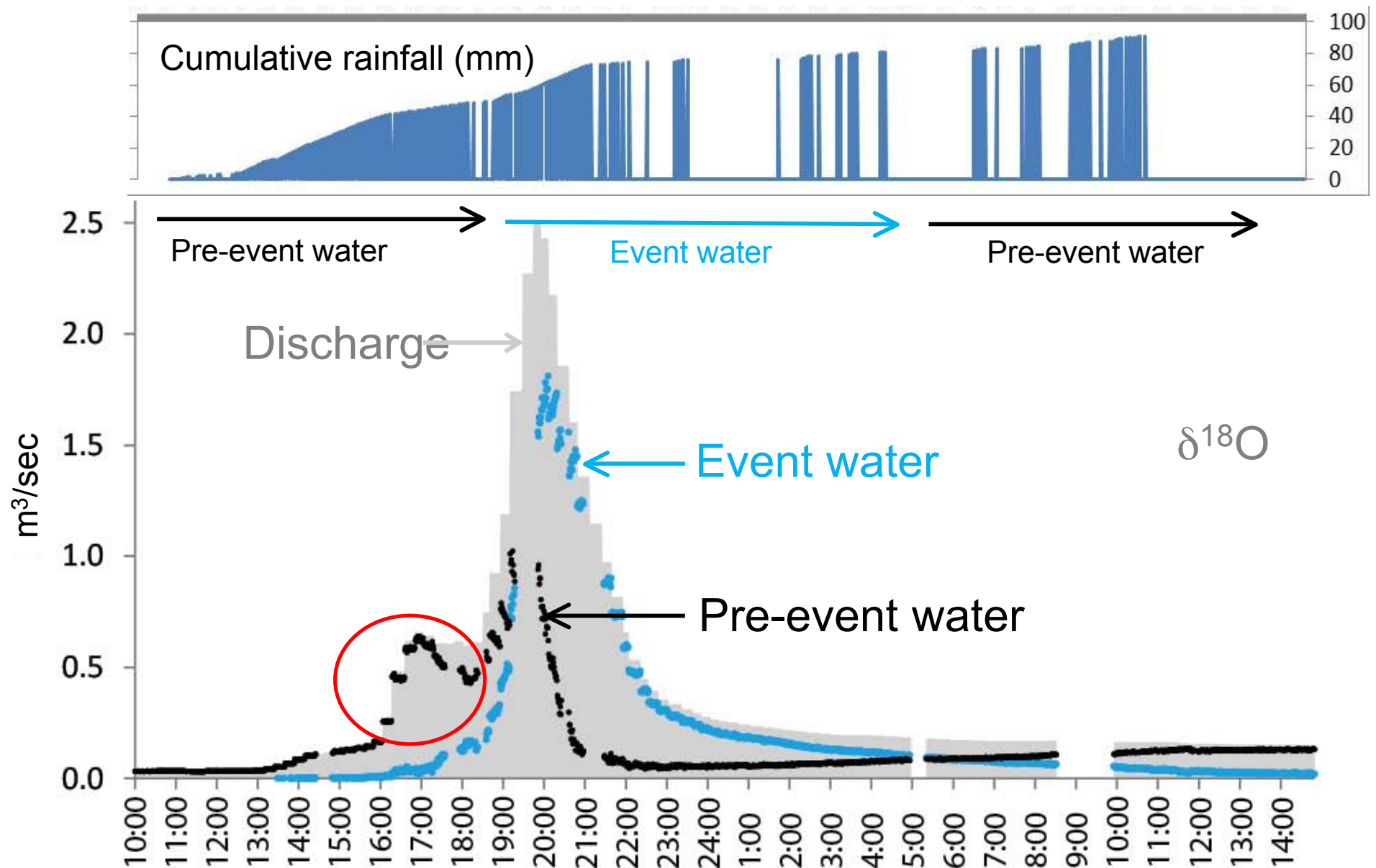
Approach

- $\delta^{18}\text{O}$, $\delta^2\text{H}$ and major ions to study river inflows
- Contaminant concentrations

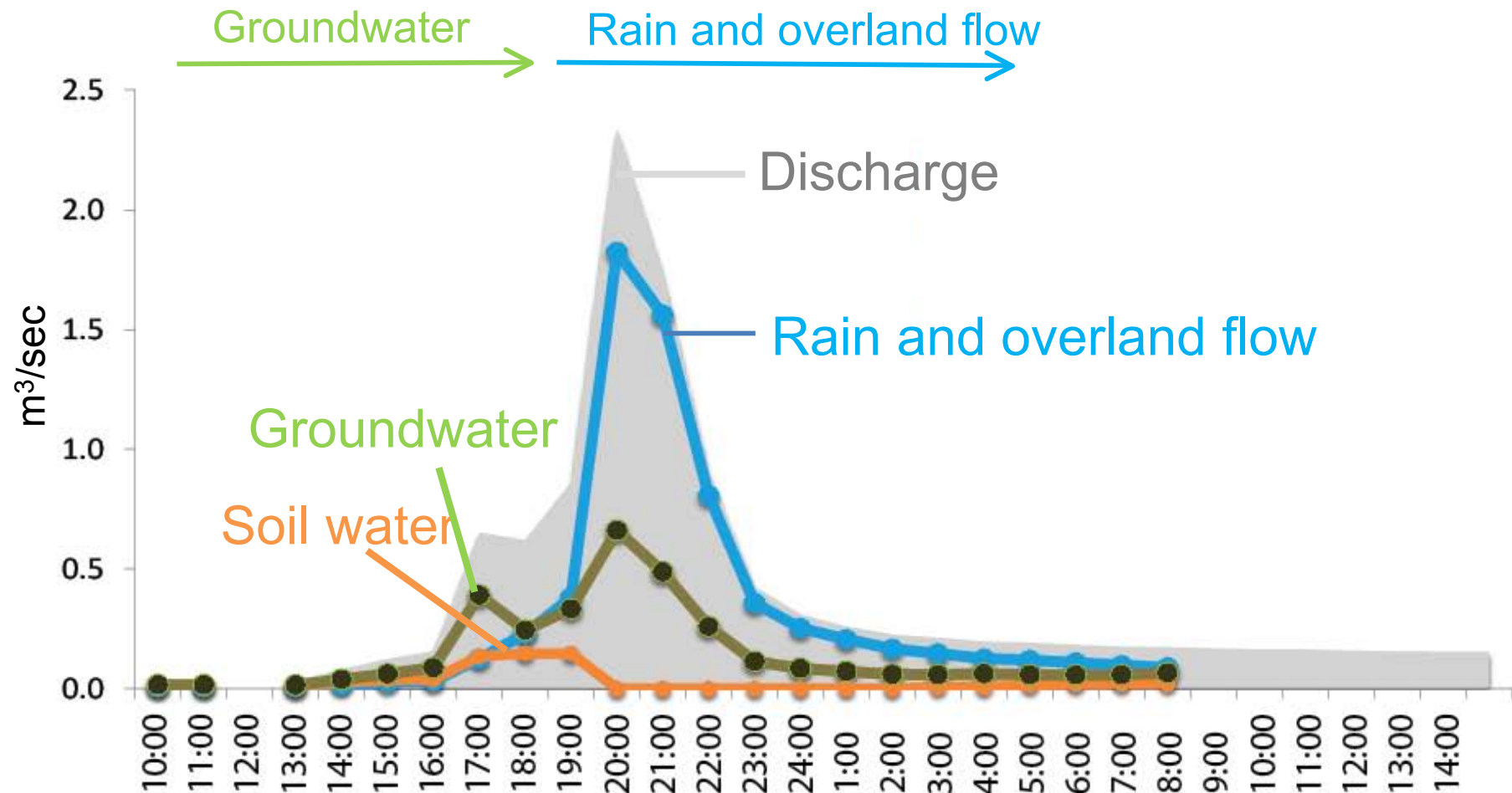
Management Link

Protection of the Great Barrier Reef from the transfer of contaminants



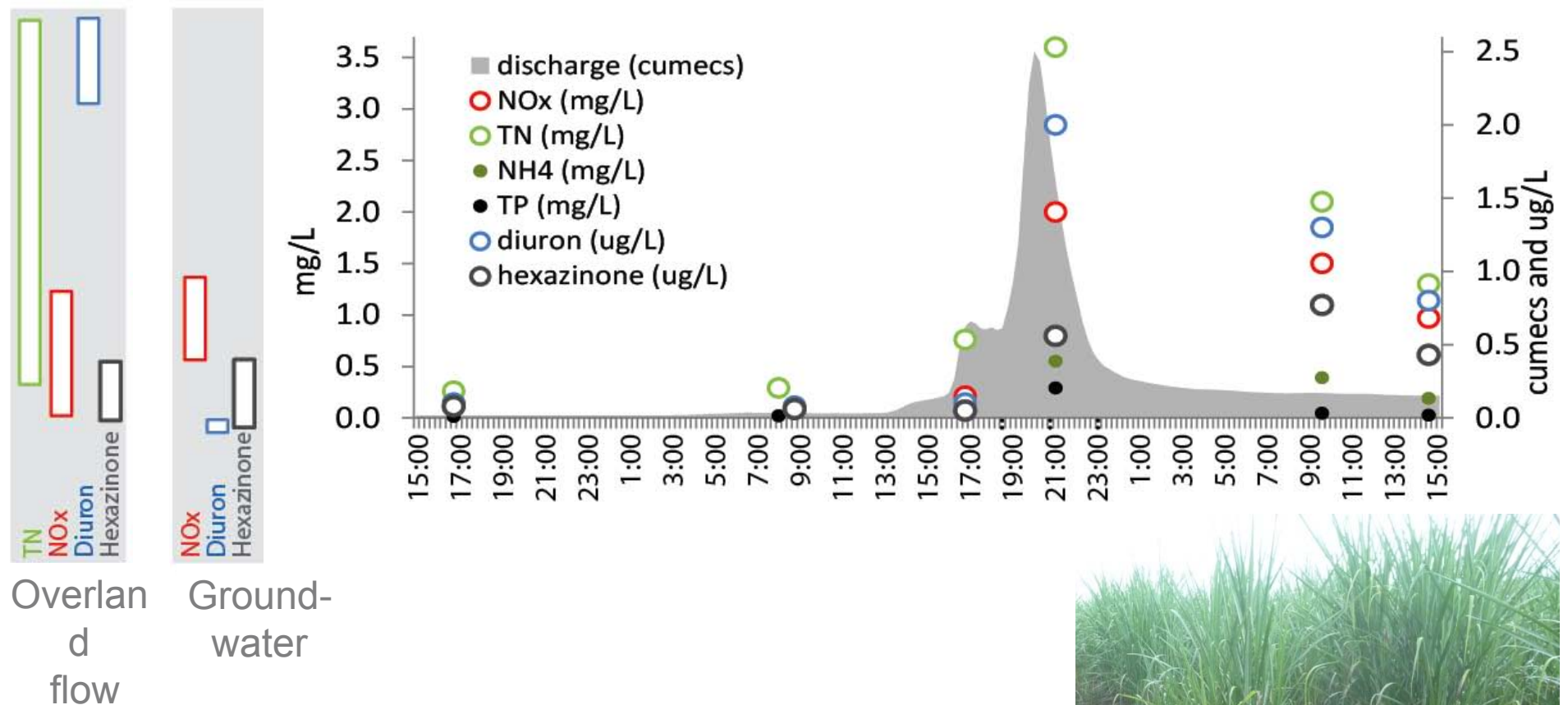


Subsurface system rapidly responds to changes



- Pre-event water: groundwater inflows
- Peak creek discharge: rain and overland flow

Contaminant transport during rainfall events – Scheu Creek

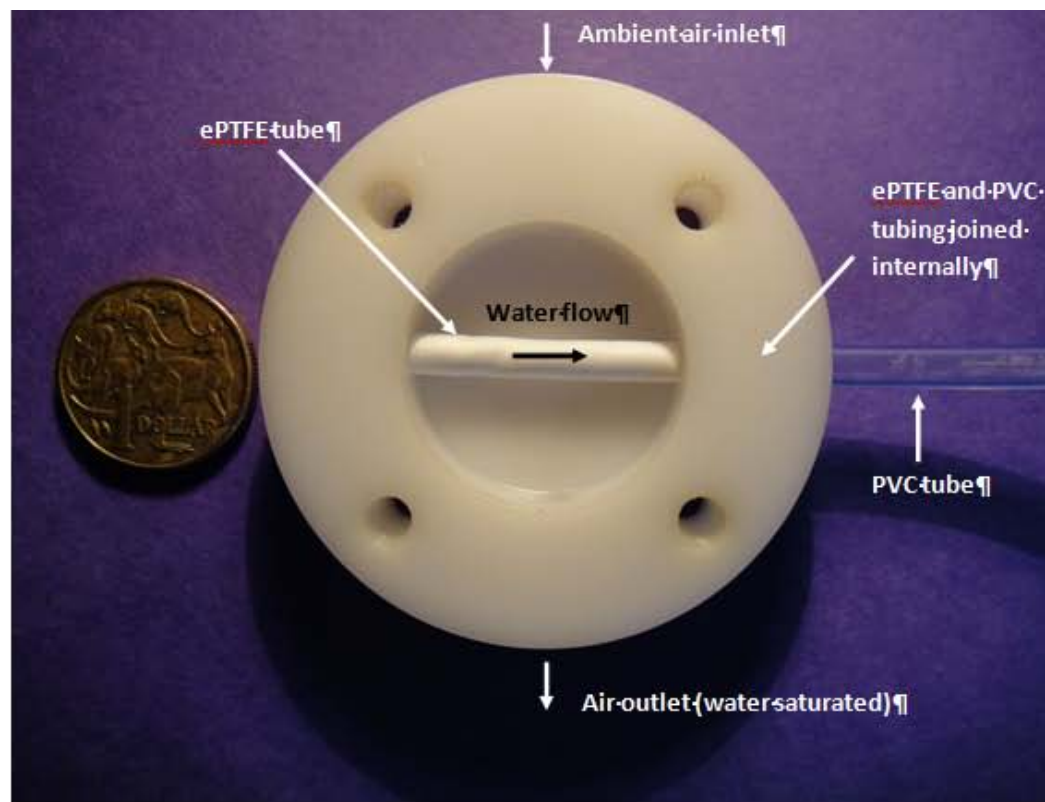


- Higher contaminant concentrations in overland flow
- Dominant flow pathway for contaminants via overland flow

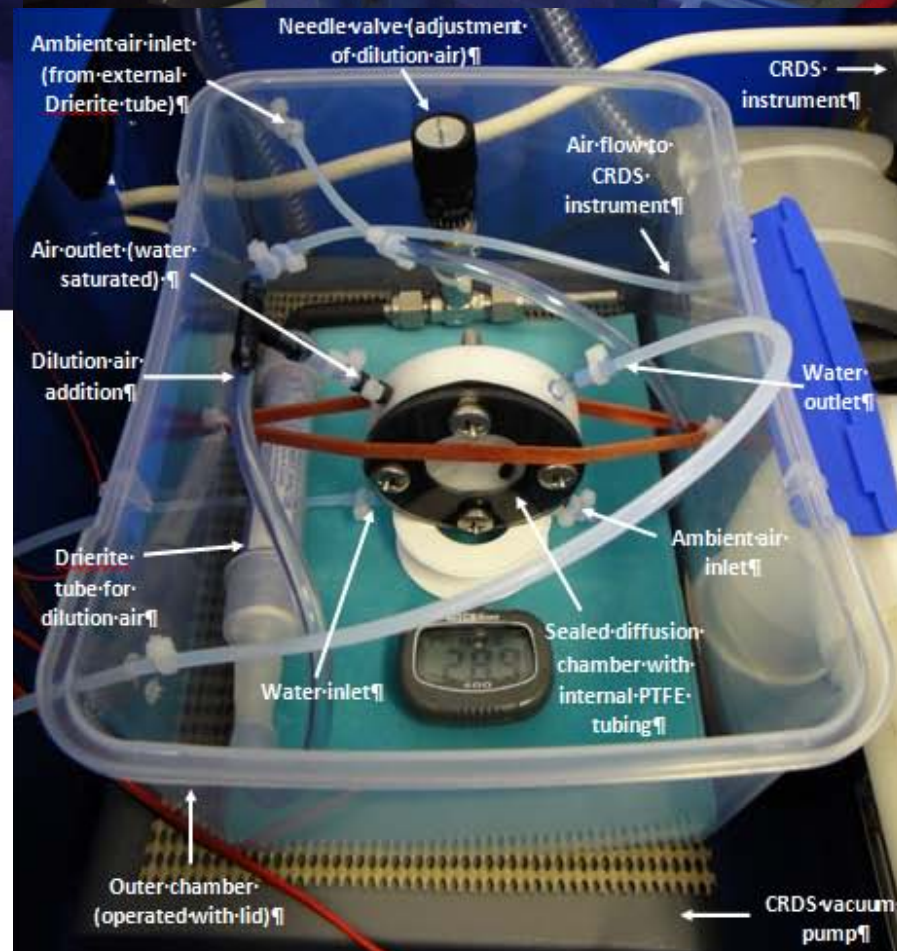
Diffusion Sampling-CRDS (DS-CRDS)

- Analysis of $\delta^{18}\text{O}$ and δD values by Cavity Ring-Down Spectrometry (CRDS)
- Diffusion sampling device utilises expanded PolyTetraFluoroEthylene (ePTFE) tubing developed for medical applications
- Diffusion through porous ePTFE tubing delivers water vapour continuously from a liquid water source
- Precision for an integration period of 3 min
SD = 0.1 % for $\delta^{18}\text{O}$
SD = 0.3 % for δD



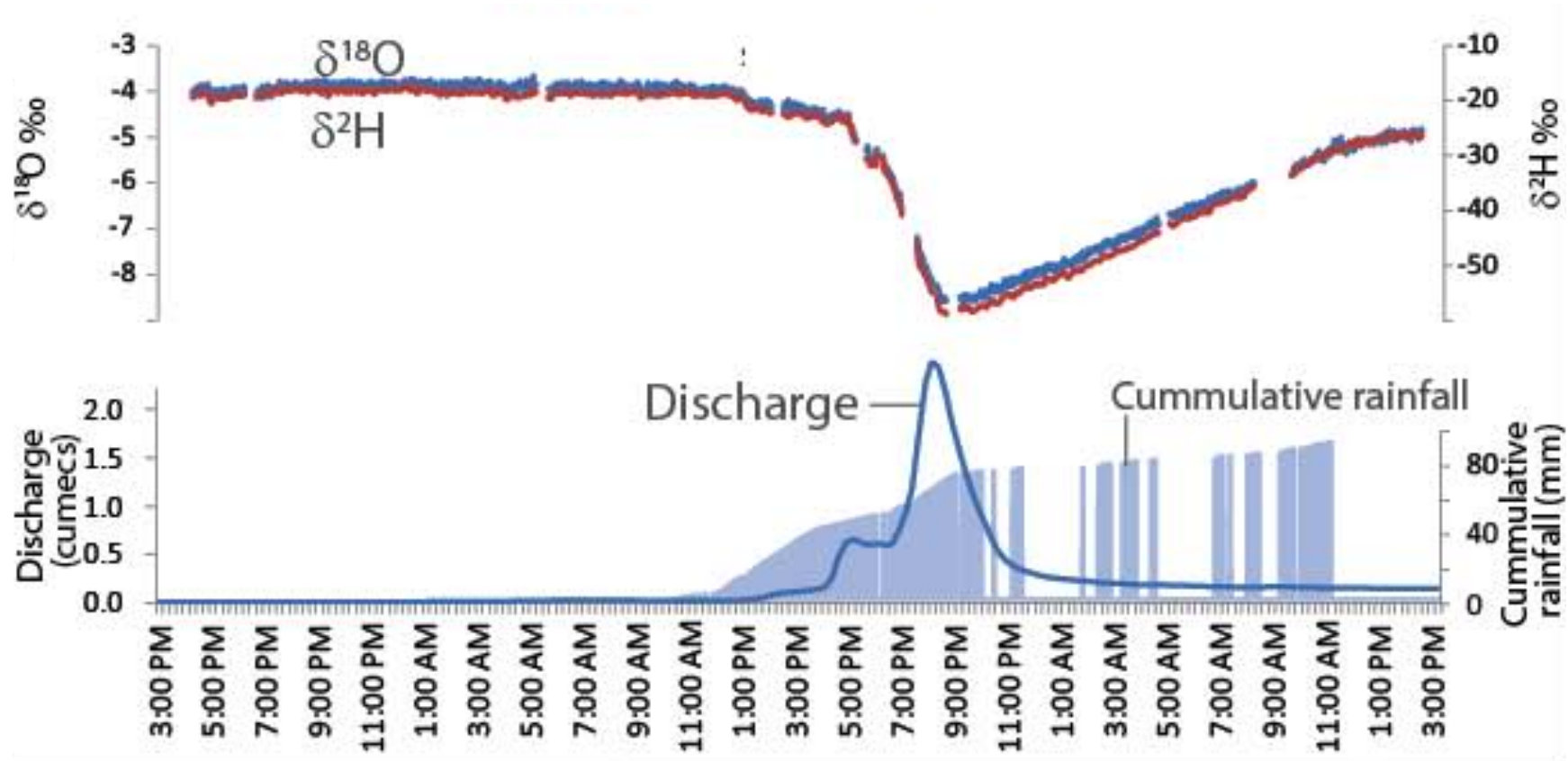


Inner diffusion chamber disassembled (seal and front plate removed)

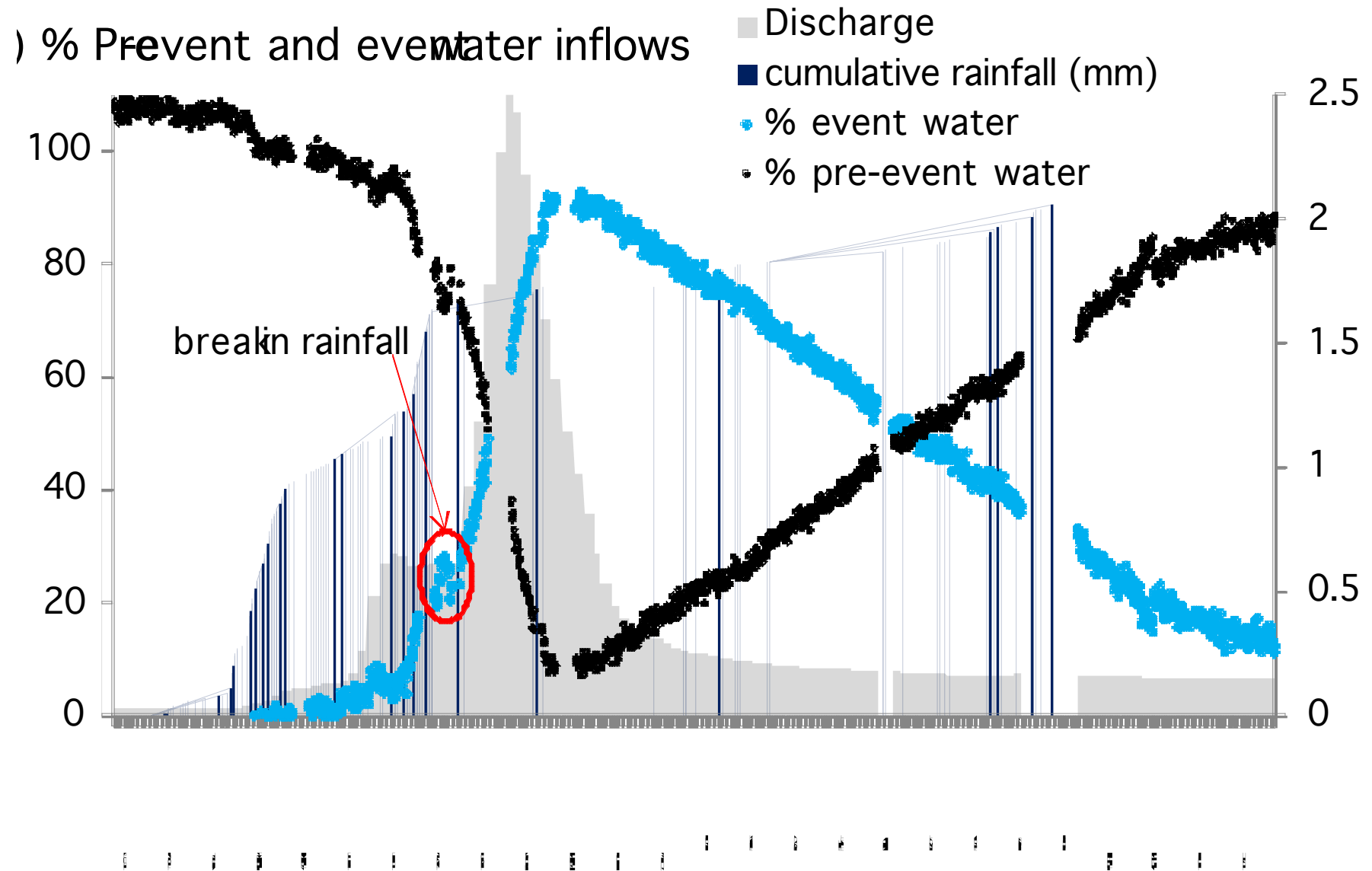


Munksgaard et al., Rapid Commun. Mass Spectrom.
2011, 25, 3706–3712

Contaminant transport during rainfall events – Scheu Creek



- $\delta^{18}\text{O}$ and $\delta^2\text{H}$: rapid changes in processes, one minute intervals
- Maximum time difference between the peak discharge and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of 10 minutes



Rainfall stopped; decline in inflows from event water compared with pre-event water of 7% over 7 minutes

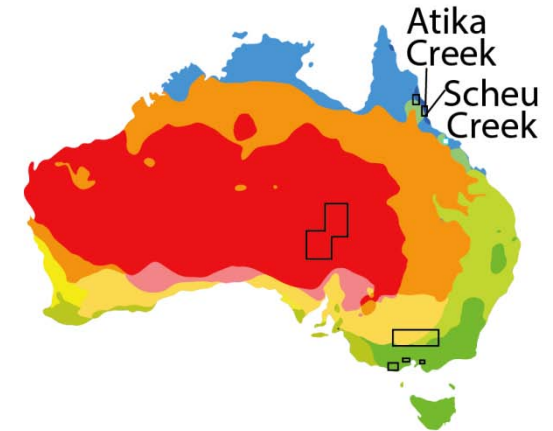
High resolution $\delta^{13}\text{C}$ and DIC

High resolution $\delta^{13}\text{C}$ and DIC

- Isotopic Continuous Dissolved Inorganic Carbon Analyser (ISO-CADICA)
- Acidifies water and utilises ePTFE tubing to measure DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ values
- Accuracy approaching that of IRMS analysis
- Bass et al. (2012) ISO-CADICA: Isotopic – continuous, automated dissolved inorganic carbon analyser. Rapid Communications in Mass Spectrometry, Vol. 26(6), 639–644.

Atika and Scheu Creek

Carbon transport during rainfall events – Scheu Creek and Atika Creek



Question

Links between C transfers and land cover

Approach

High temporal resolution DIC concentrations and $\delta^{13}\text{C}$ values during a storm event - pristine rainforest and cultivated sub-catchments

Funding

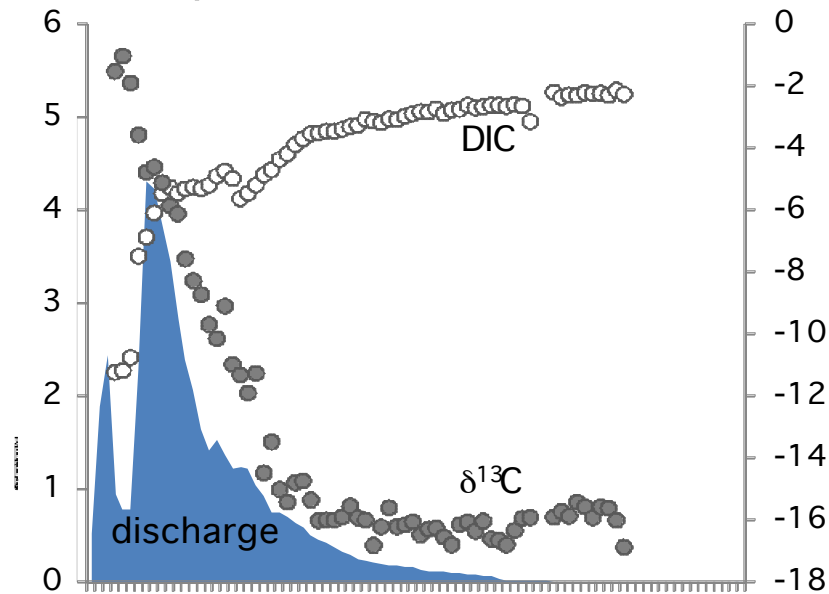
ARC and NCGRT

Management Links

Ecologically important in first-order streams

Bass, A., Munksgaard, N., Leblanc, M., Tweed, S., and Bird, M. 2014. Contrasting carbon export dynamics of human impacted and pristine tropical catchments in response to a short-lived discharge event. *Hydrological*

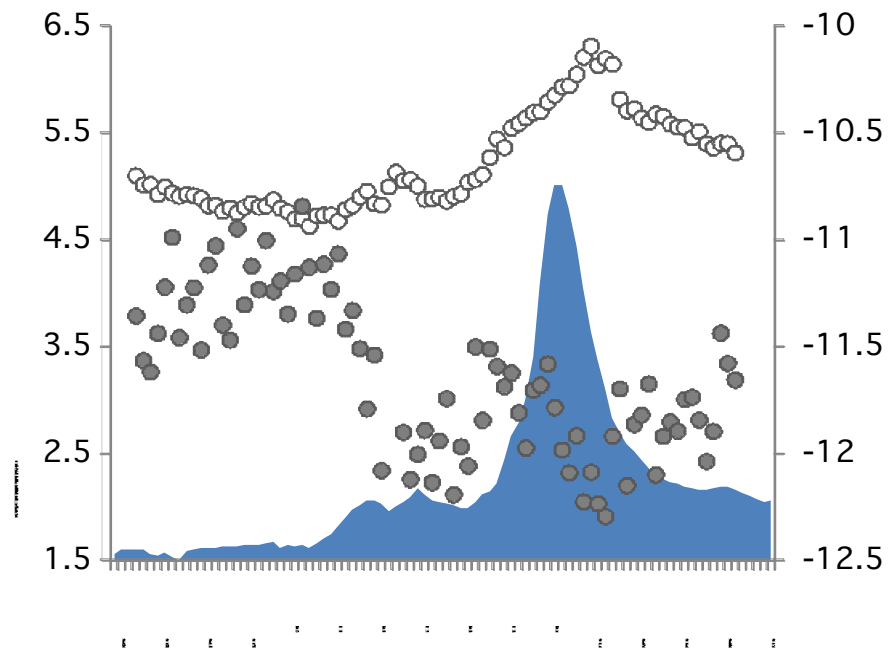
Atika Creekp pristine rainforest



Rainforest

- $\delta^{13}\text{C}$ values with high variation (16‰)
- $\delta^{13}\text{C}$ - high component of rainwater input at the start of the storm, with increases in C3-derived DIC
- DIC values that increased after storm event

Scheu Creepkultivated land

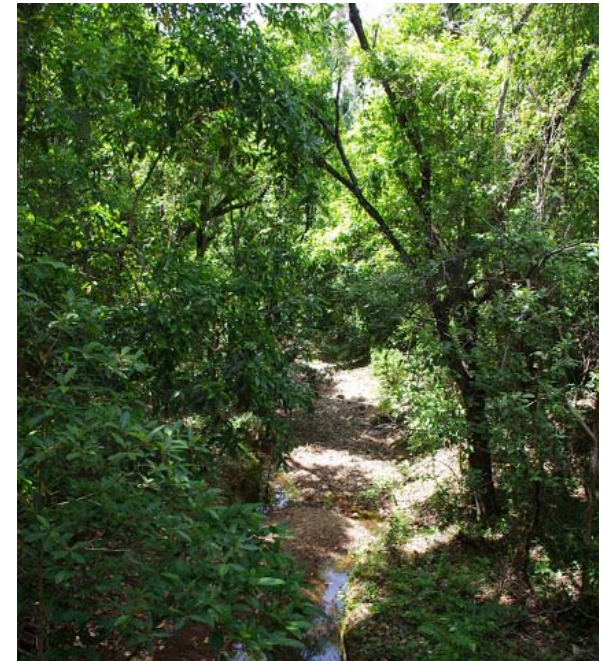


Cultivated

- $\delta^{13}\text{C}$ values with less variation (<2‰)
- $\delta^{13}\text{C}$ - dominate source of DIC is from C4 sources
- DIC values that decreased after storm event

Carbon transport during rainfall events – Scheu Creek and Atika Creek

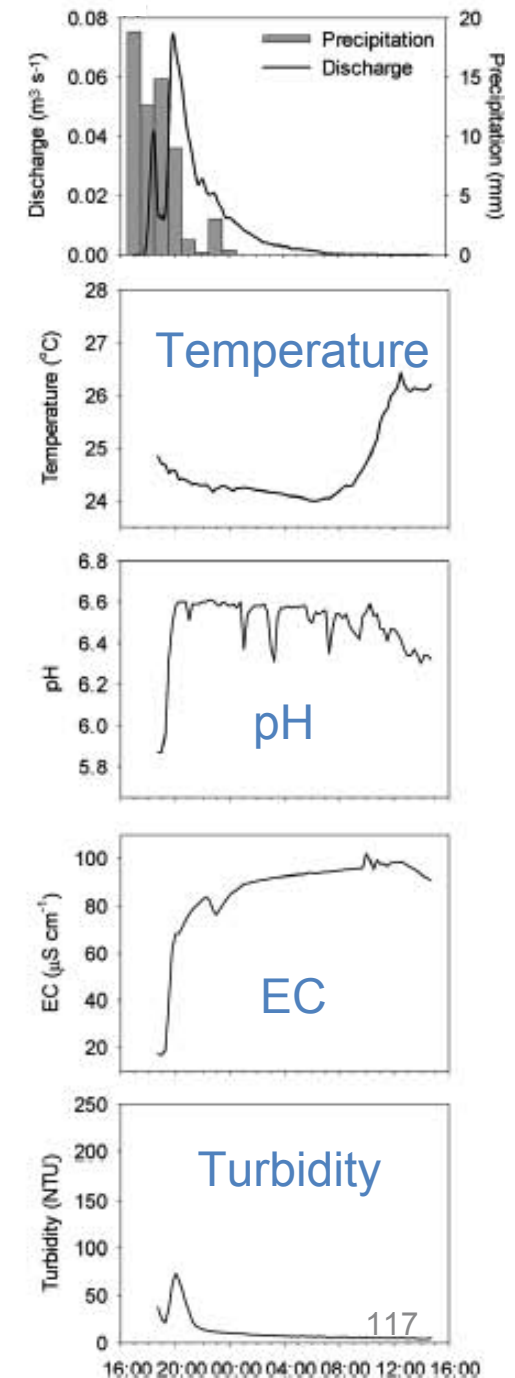
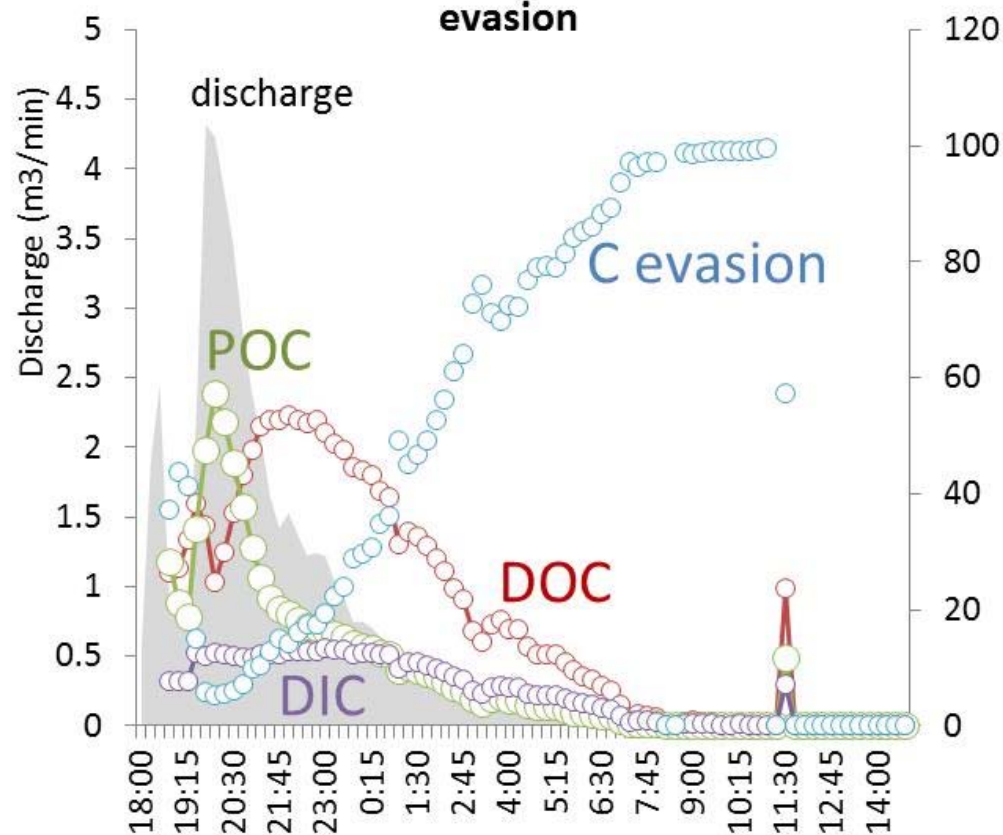
- Deployment of newly developed field equipment;
Isotopic Continuous Dissolved Inorganic Carbon Analyser (ISO-CADICA; Bass et al., 2012)
- Measure $\delta^{13}\text{C}$ and DIC values at high temporal resolution



Atika Creek

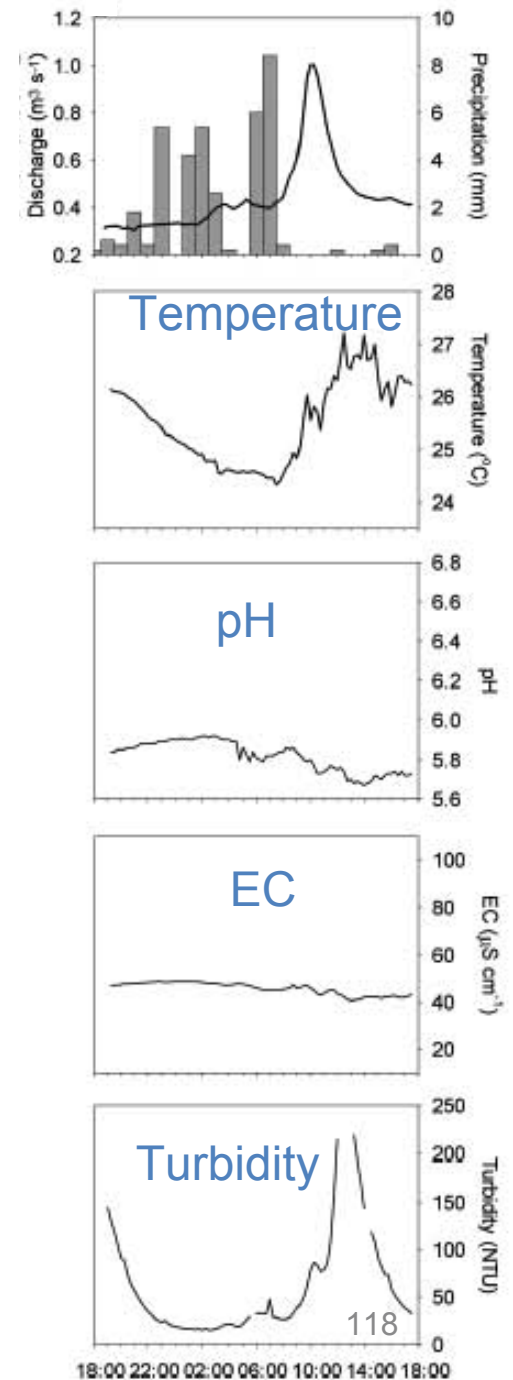
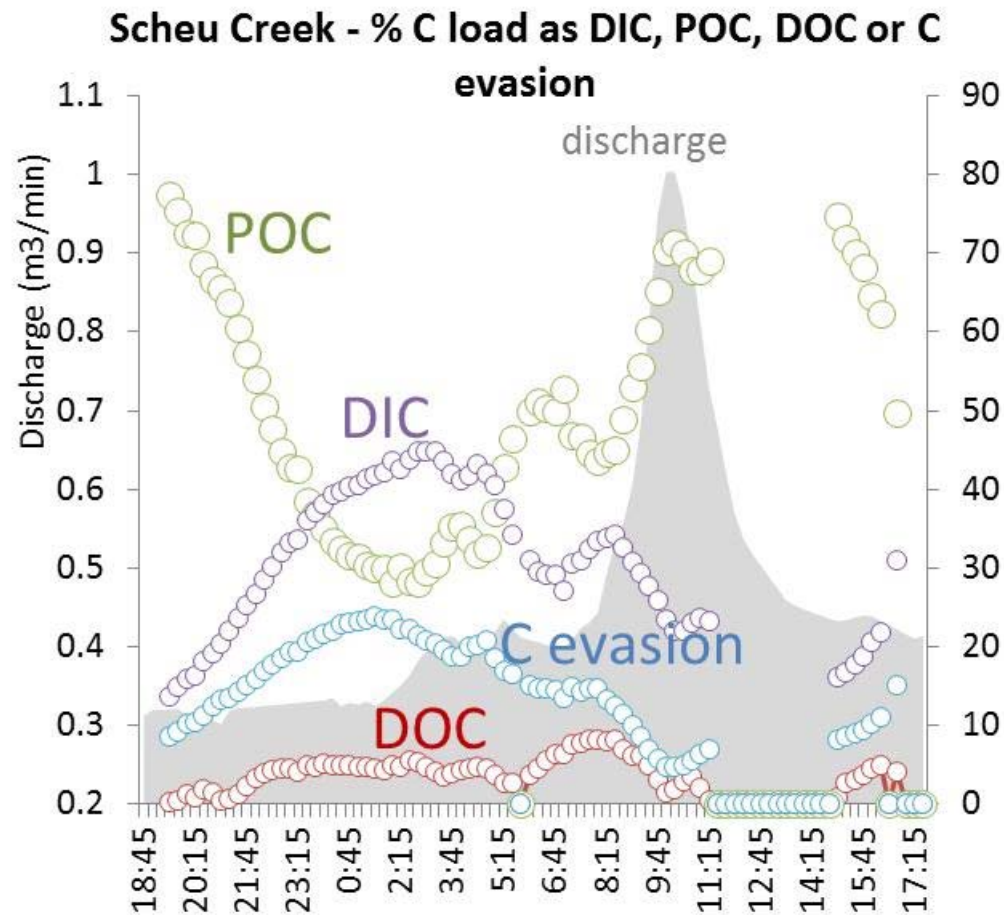
- Large initial variation
- DOC and POC concentrations higher than other rainforest studies - prolonged dry period preceding the study
- over 85% of C exported during baseflow is through vertical evasion to the atmosphere

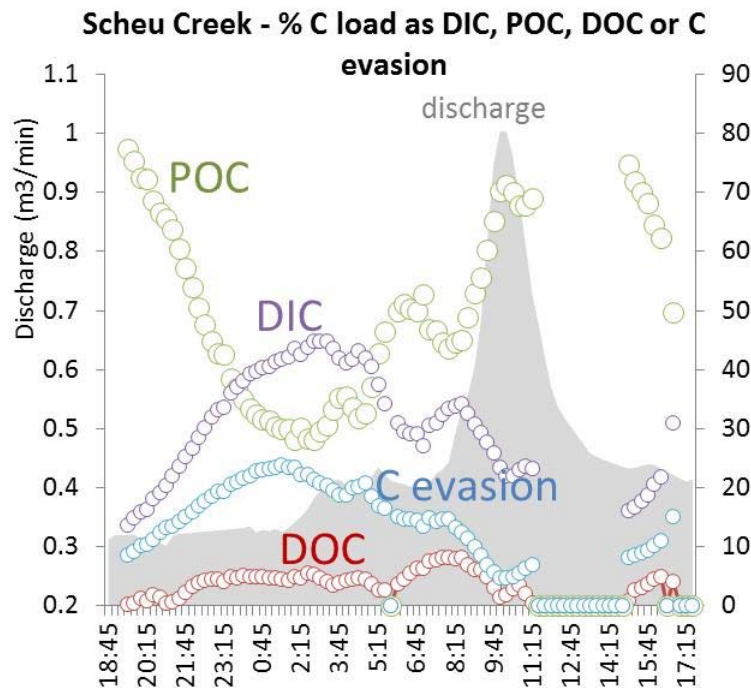
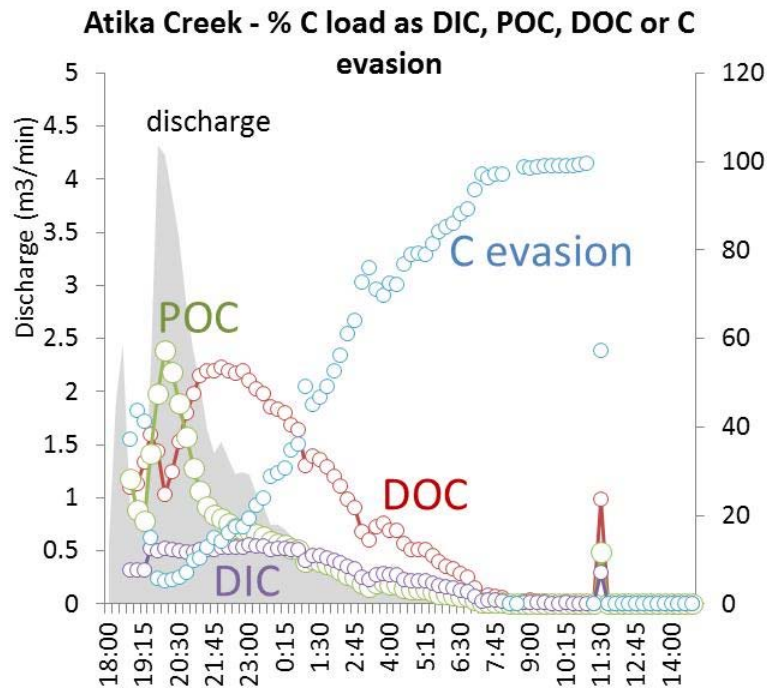
Atika Creek - % C load as DIC, POC, DOC or C evasion



Scheu Creek

- Stable chemistry
- High POC and DIC concentrations
- Low C evasion to the atmosphere





Differences

Initial conditions

- SC: flow prior to event
- AC: initially dry; explanation for initially extreme variations in hydrochemical parameters

Influence of land cover

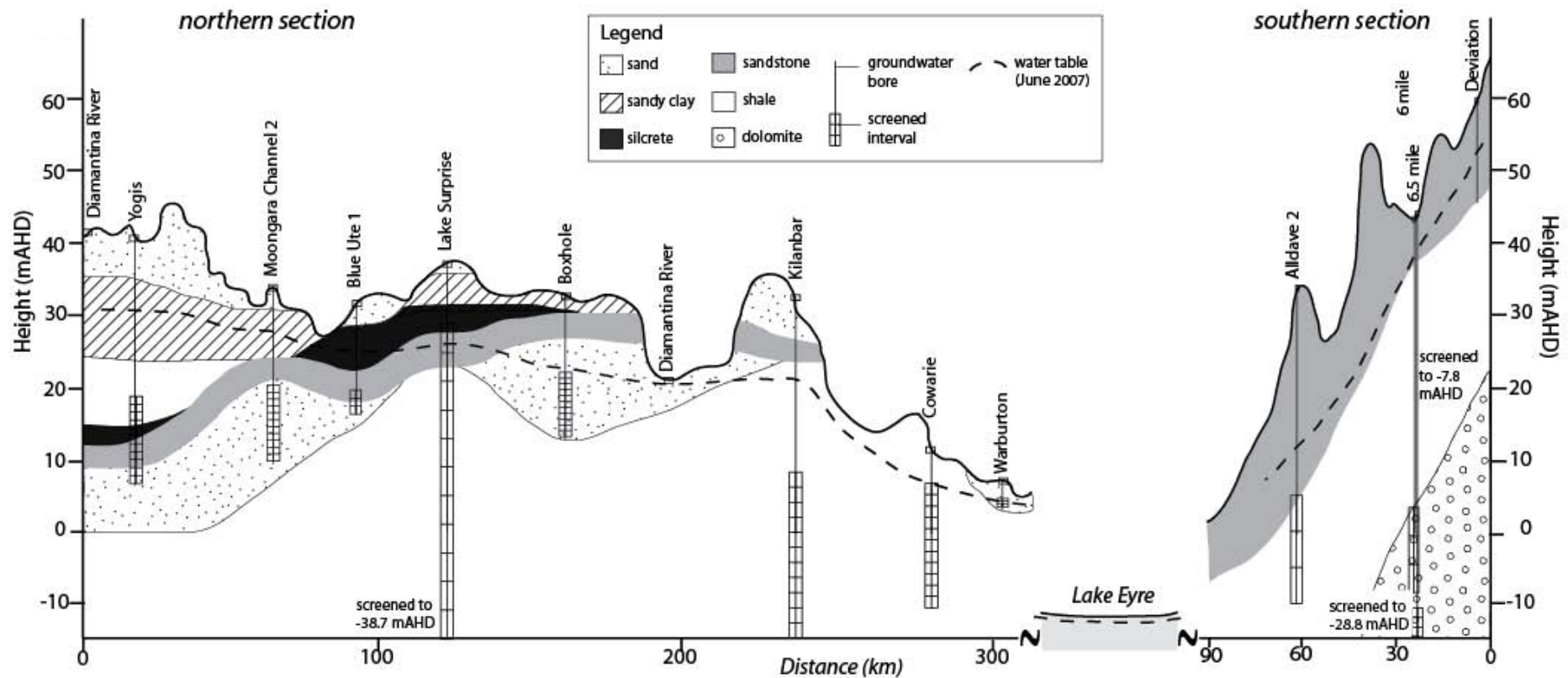
- POC concentration higher in SC
- DOC showed little significant change with increasing discharge in SC due to high clay content; adsorption

Interaction with groundwater

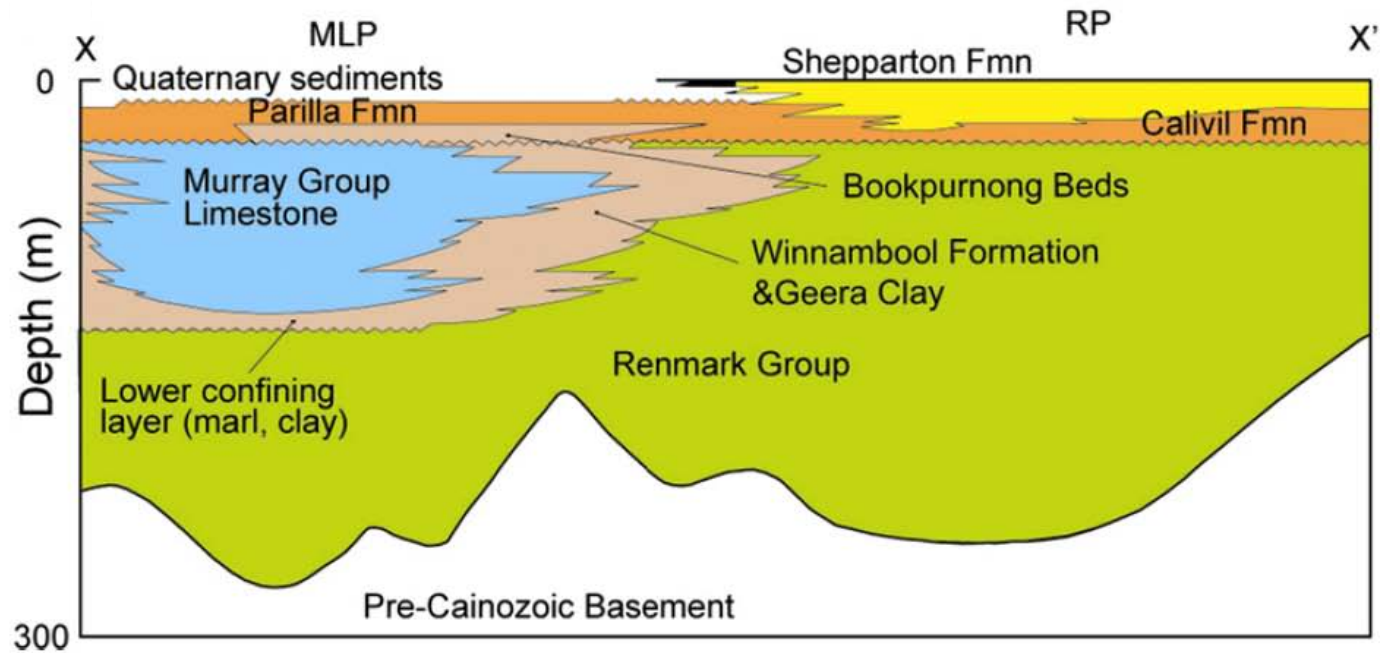
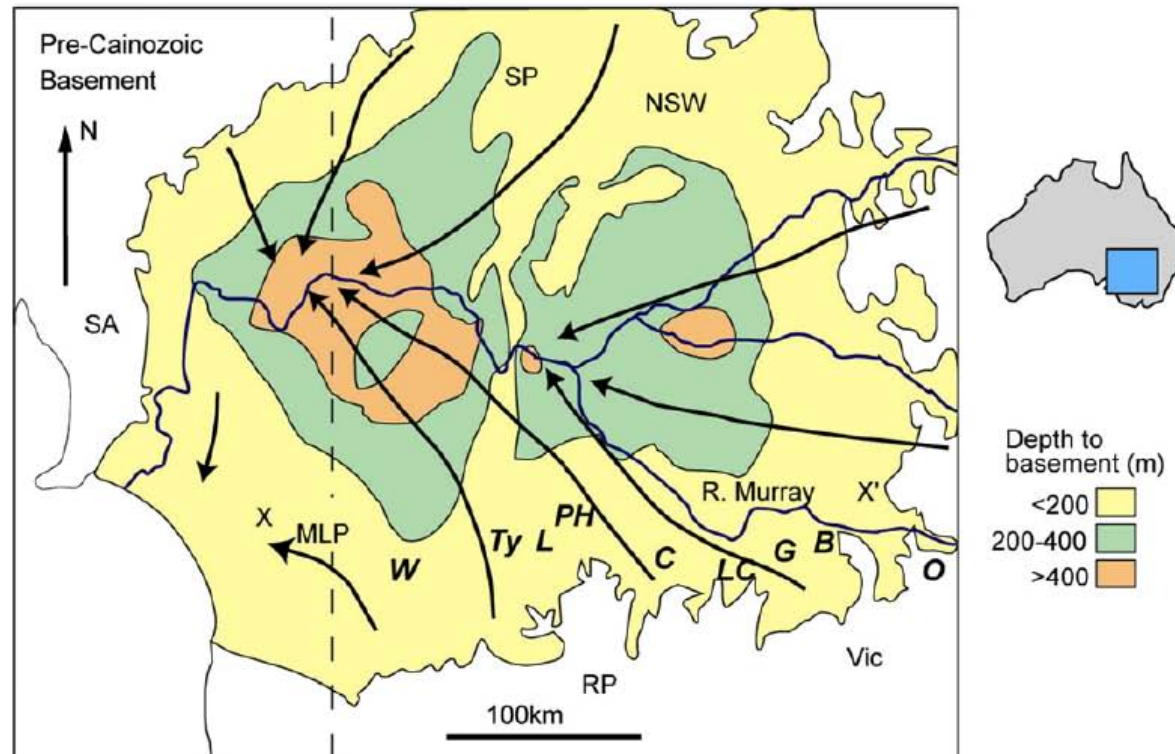
- SC increase in DIC concentration correlates to period of increased groundwater or soil water

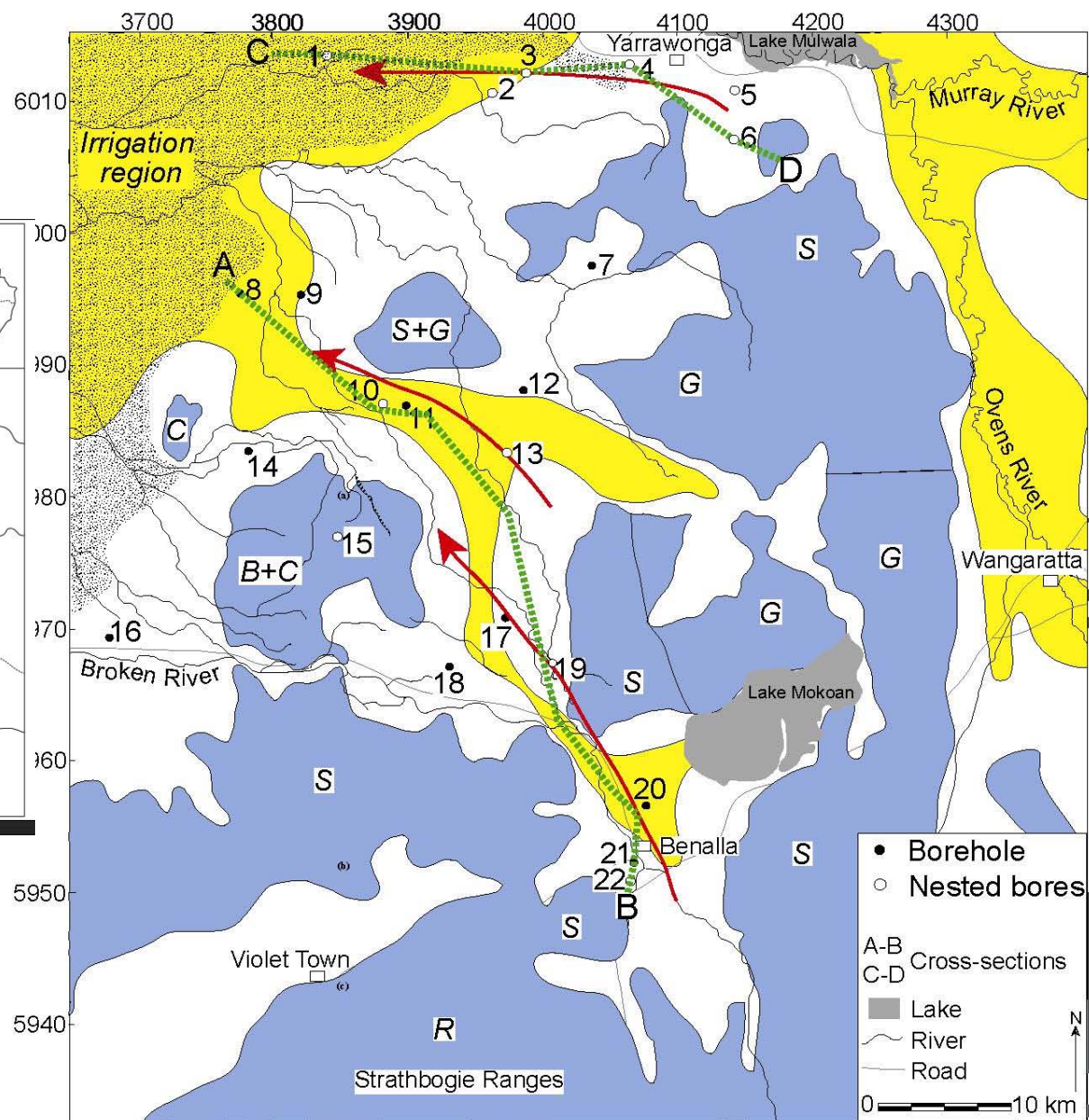
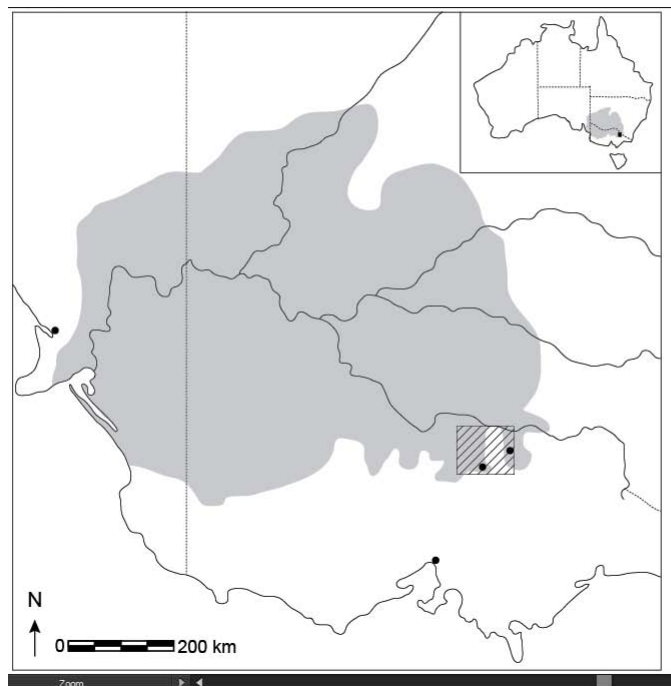
MGB and LEB

LEB geological cross-section



MGB





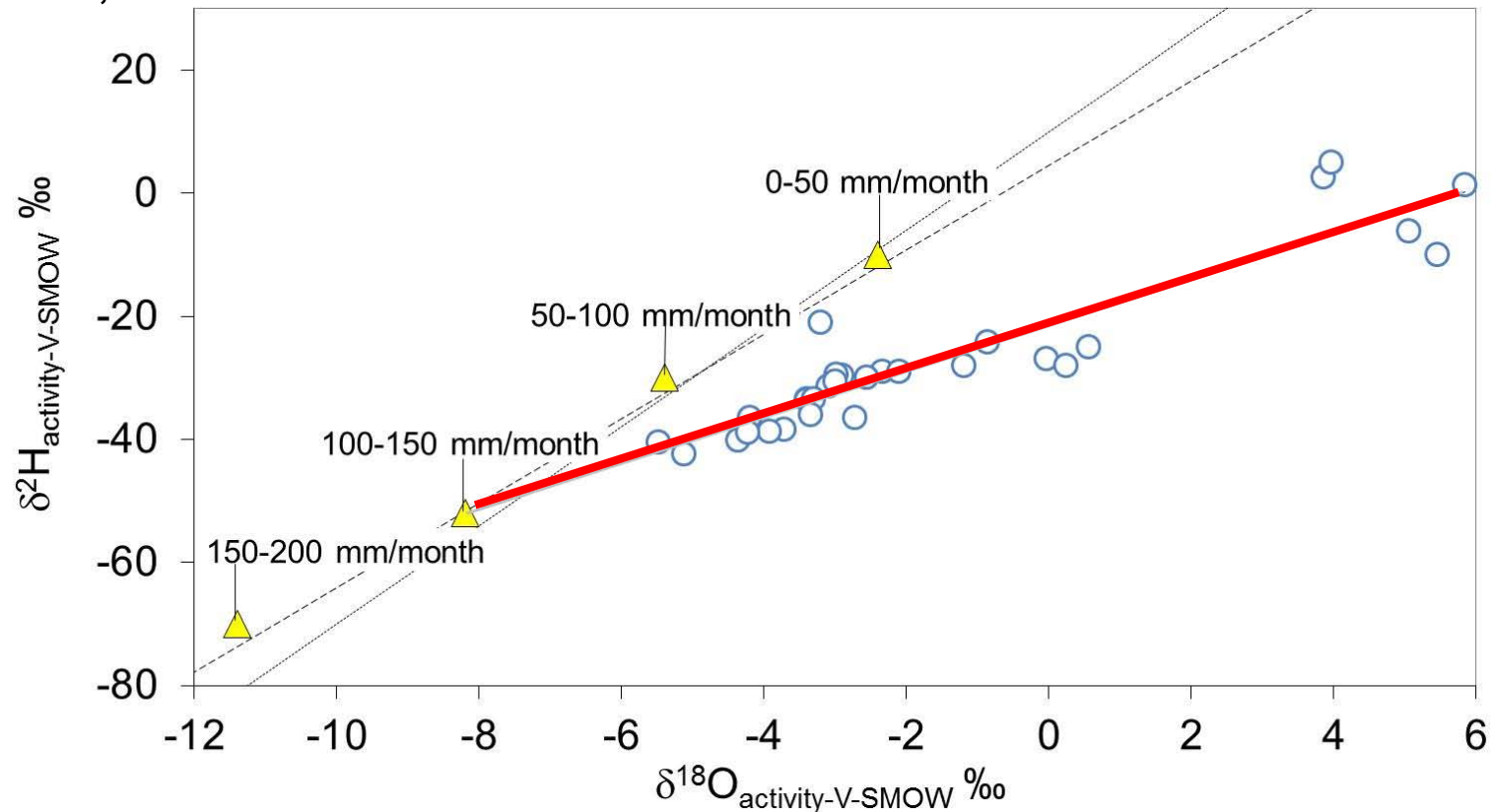
- Shepparton Formation
- Calivil Formation (underlying Shepparton Formation)
- Basement outcrop: basalt (B), granite (G), sandstone (S), chert (C), rhyodacite (R)
- Groundwater flow directions in the Shepparton aquifer

Lake Eyre Basin

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ – long-term recharge processes

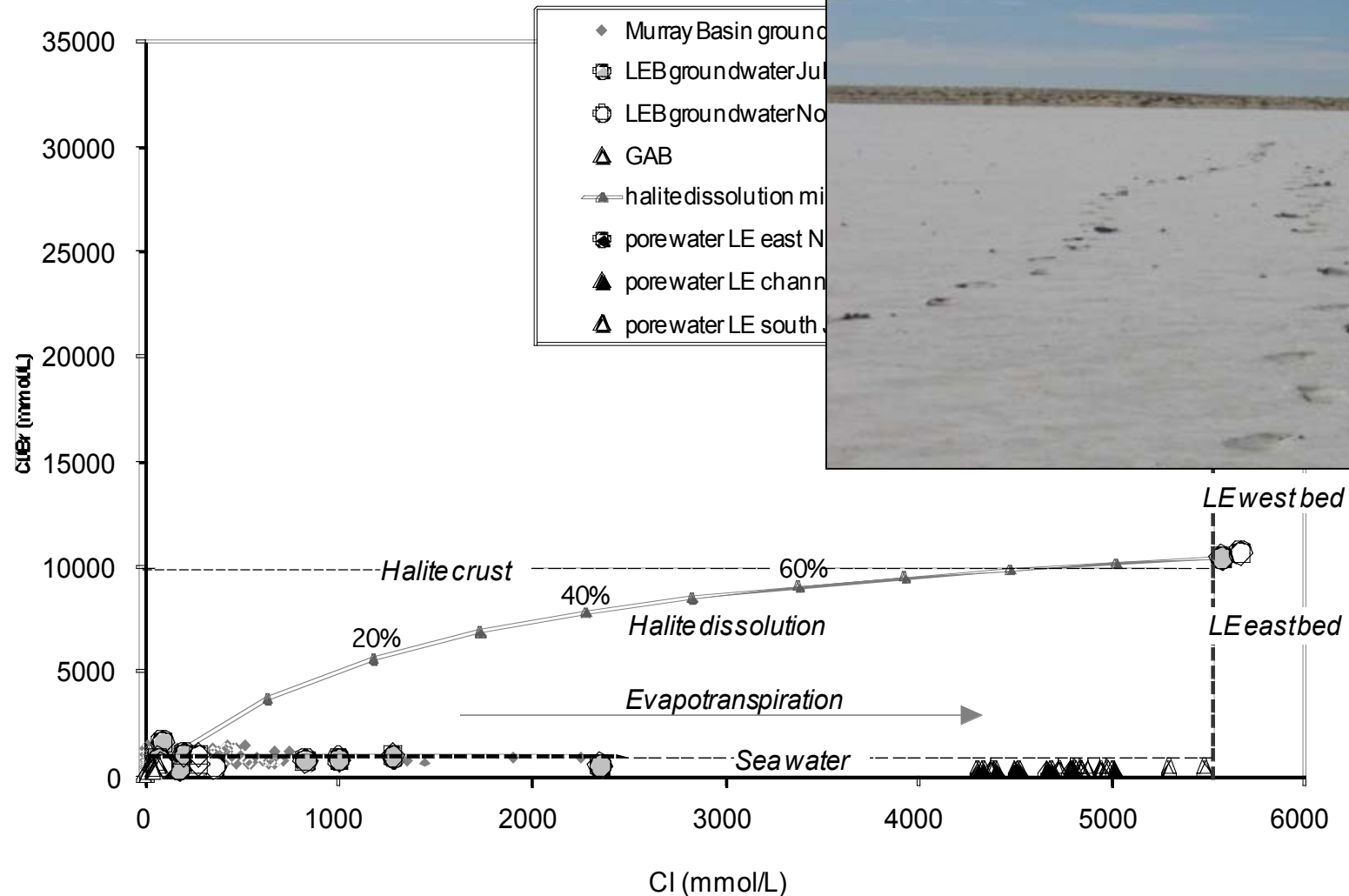
- Evaporation slope low (2.97)
- Evaporation from surface water or water table (4-6)

-> Water evaporated in the dry unsaturated zone – not from floodwaters;

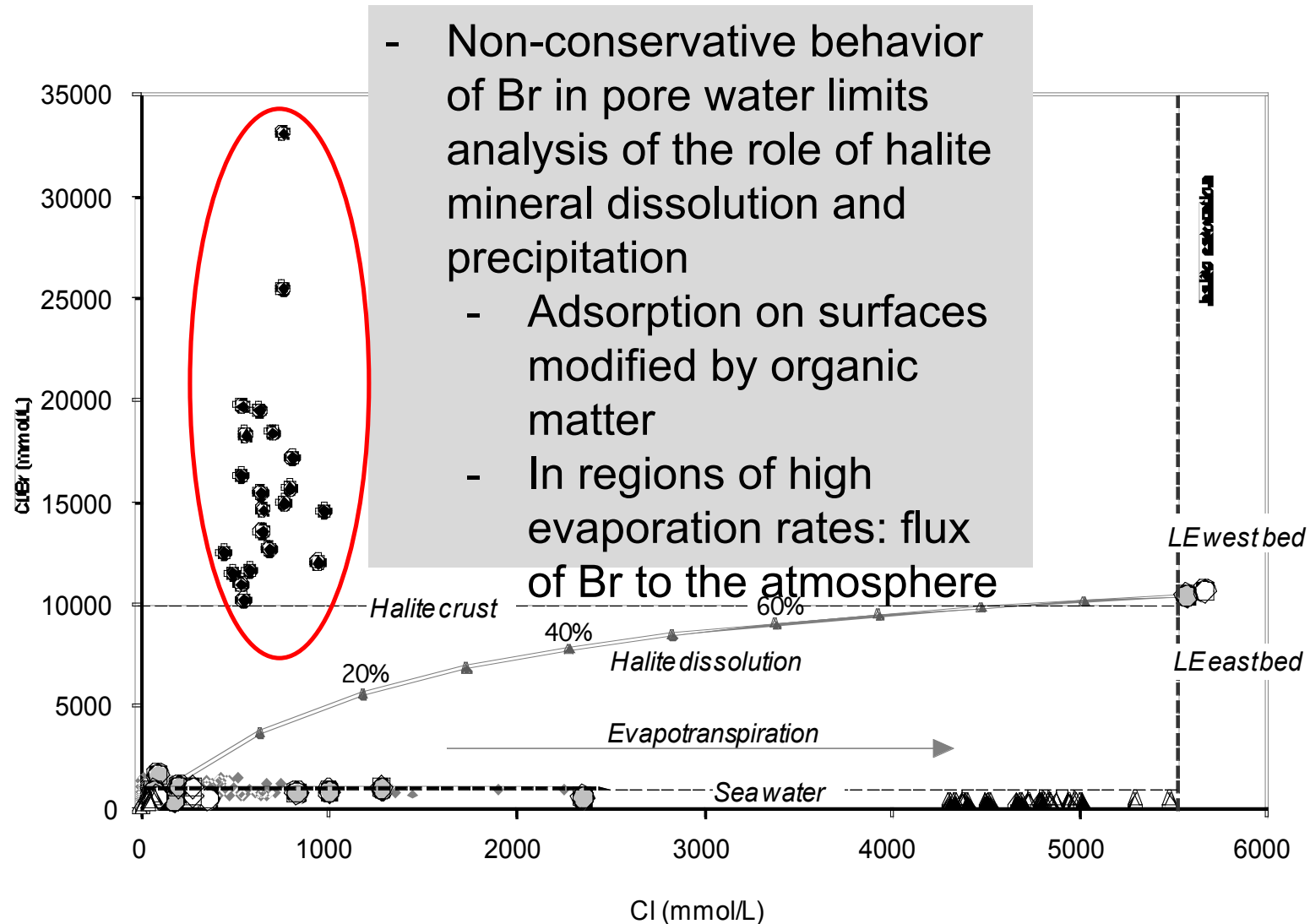


Salinity Controls – Murray Groundwater Basin and Lake Eyre Basin

Cl/Br ratios constant with increasing Cl concentrations: evaporation and/or transpiration

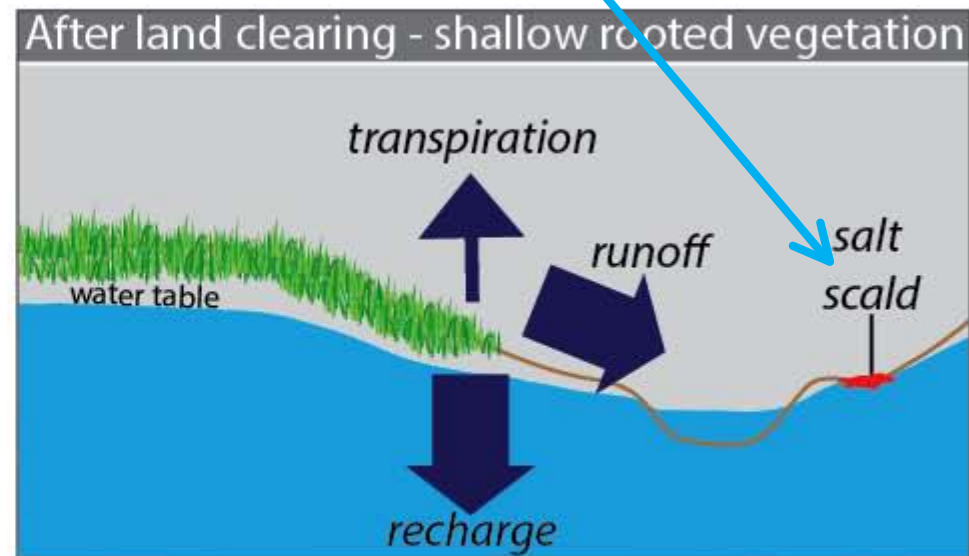
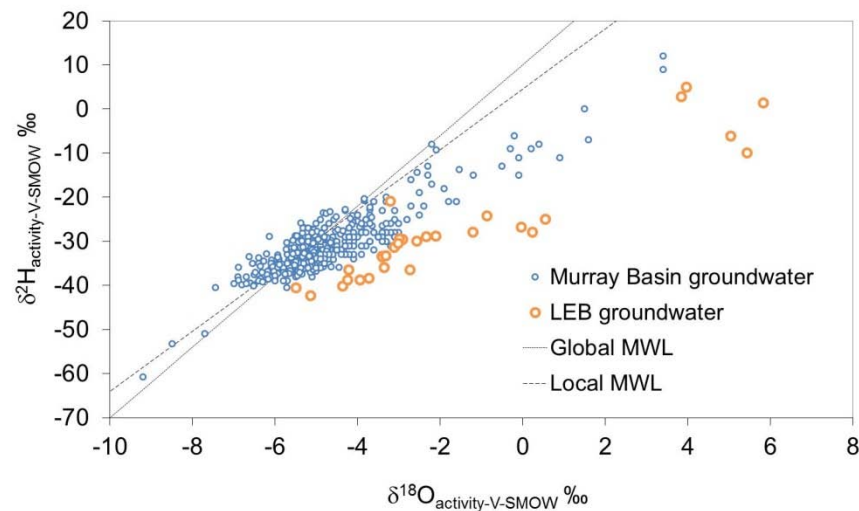


Salinity Controls – Murray Groundwater Basin and Lake Eyre Basin

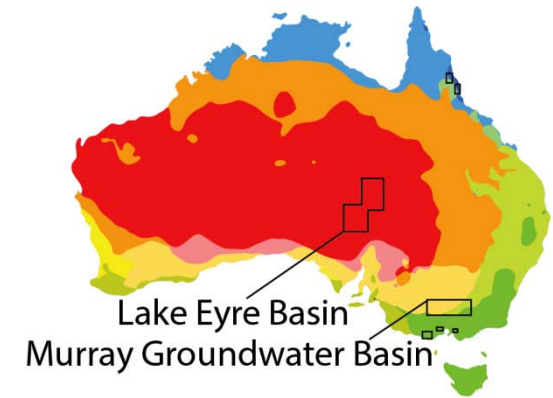


Salinity Controls – MGB

Localised secondary salinity –
evaporation and cyclic evaporite
dissolution



Salinity controls – Murray Groundwater Basin (MGB) and Lake Eyre Basin (LEB)



Question

Salinity processes in two basins; LEB and MGB?

Approach:

Groundwater Cl/Br ratios, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data

Management Link

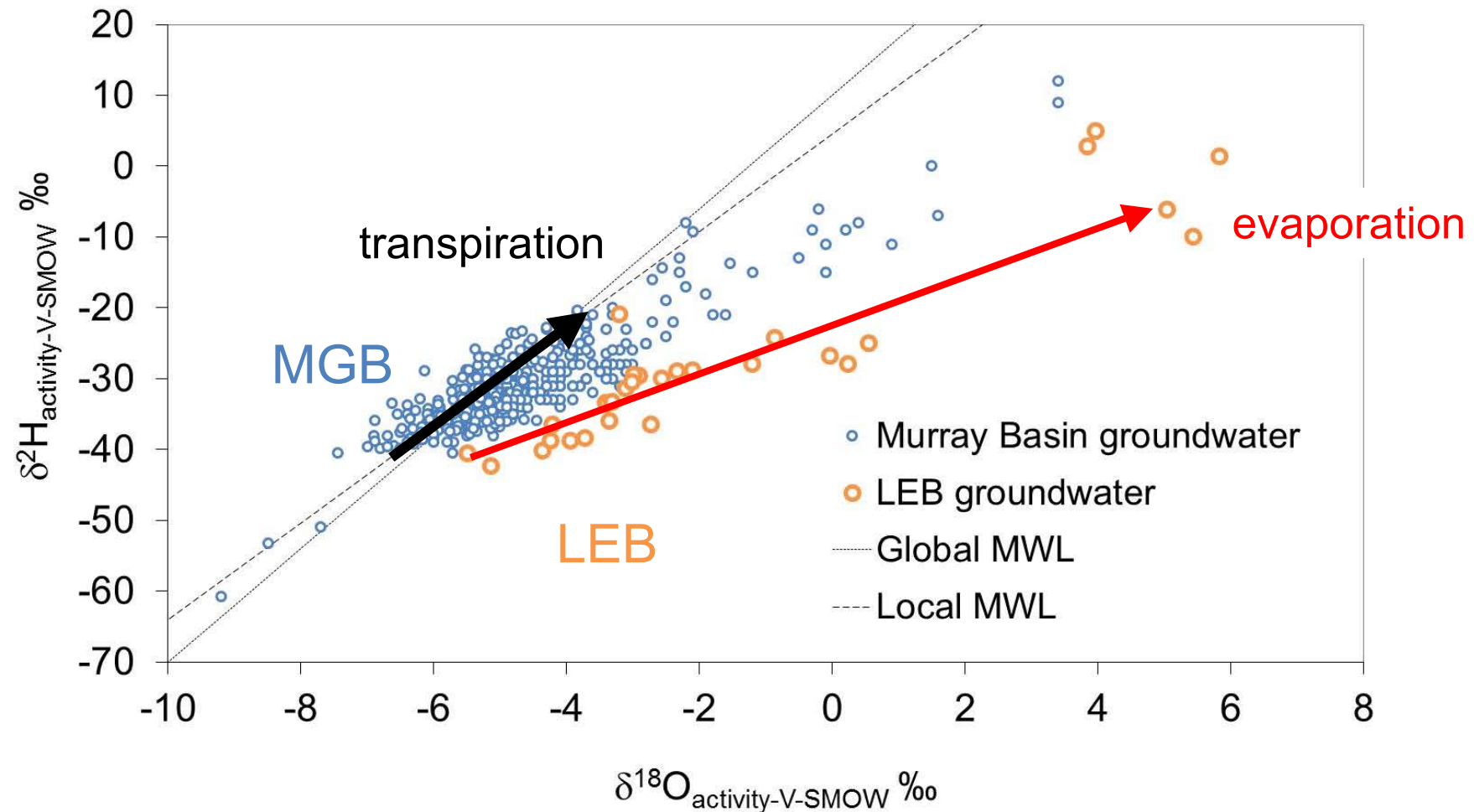
Controls on salinity in more
intensively cultivated MGB



Tweed, S., Leblanc, M., Cartwright, I., Favreau, G., Leduc, C., 2011. Arid zone groundwater recharge and salinisation processes; an example from the Lake Eyre Basin, Australia, *Journal of Hydrology*, 408, 257-275

Cartwright, I., Weaver, T.R., Cendón, D.I., Fifield, L.K., Tweed, S.O., Petrides B., Swane, I. 2012. Constraining groundwater flow, residence times, inter-aquifer mixing, and aquifer properties using environmental isotopes in the southeast Murray Basin, Australia. *Applied Geochemistry*, 27, 1698-1709.

Salinity Controls – MGB and LEB



- Transpiration of groundwater in semi-arid MGB
- Evaporation of groundwater in arid LEB

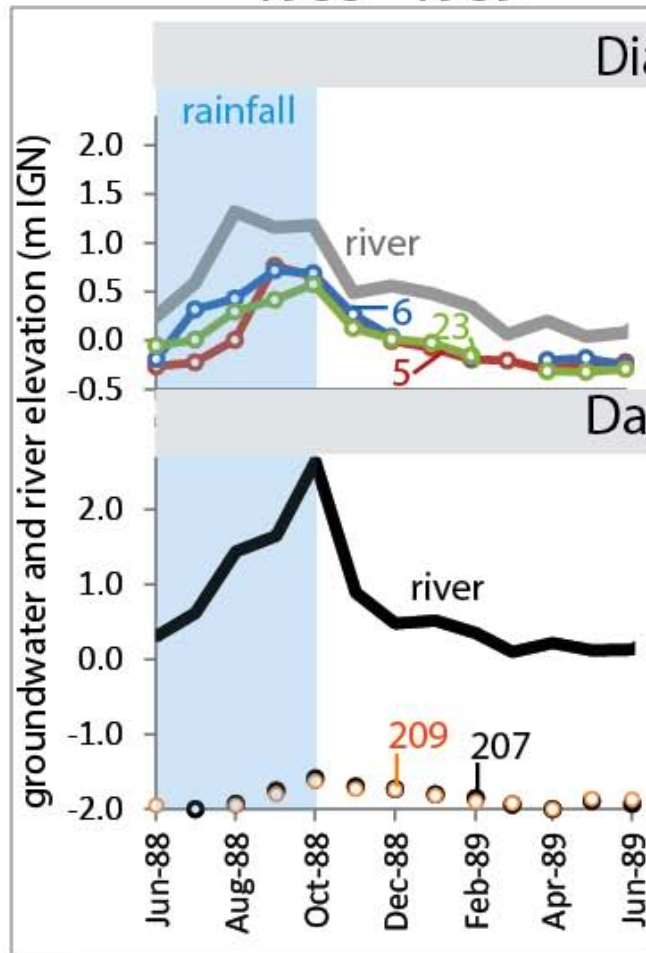
Senegal example

Example : Senegal Delta

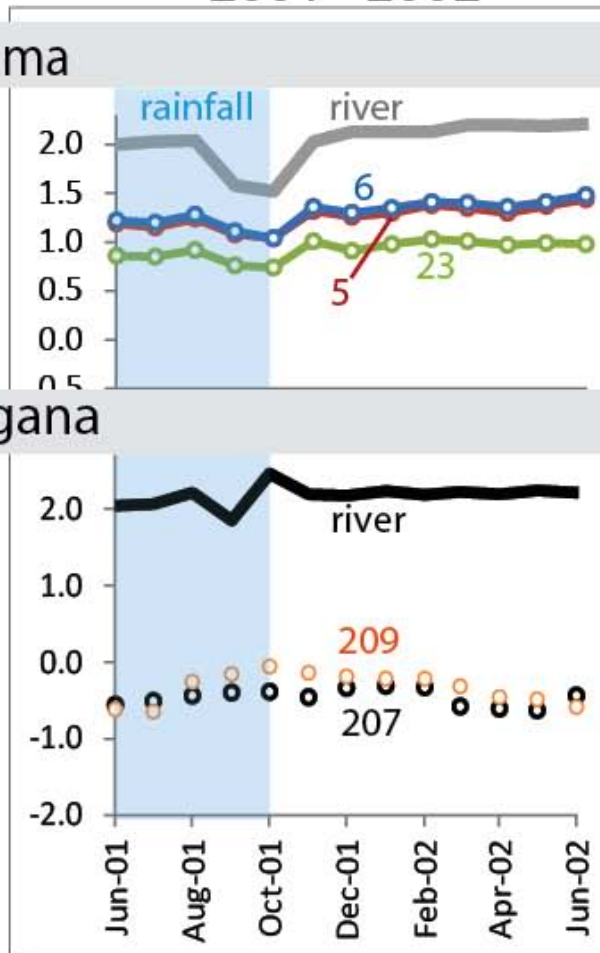
Non-uniform physical hydrosystem response to multiple changes

Groundwater close to river

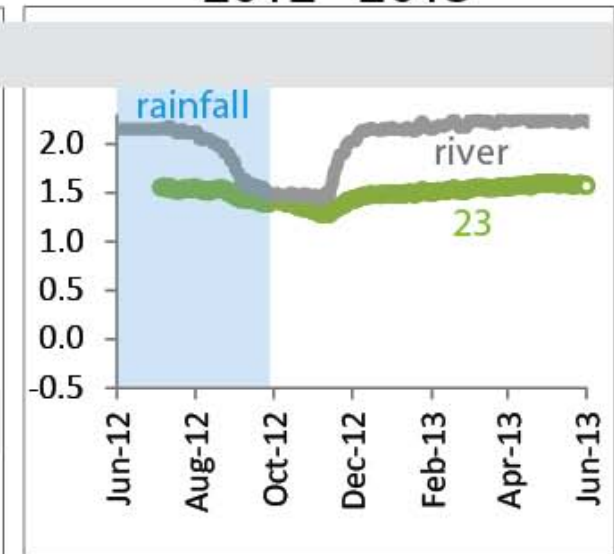
Seasonal hydrographs
1988 - 1989



2001 - 2002



2012 - 2013

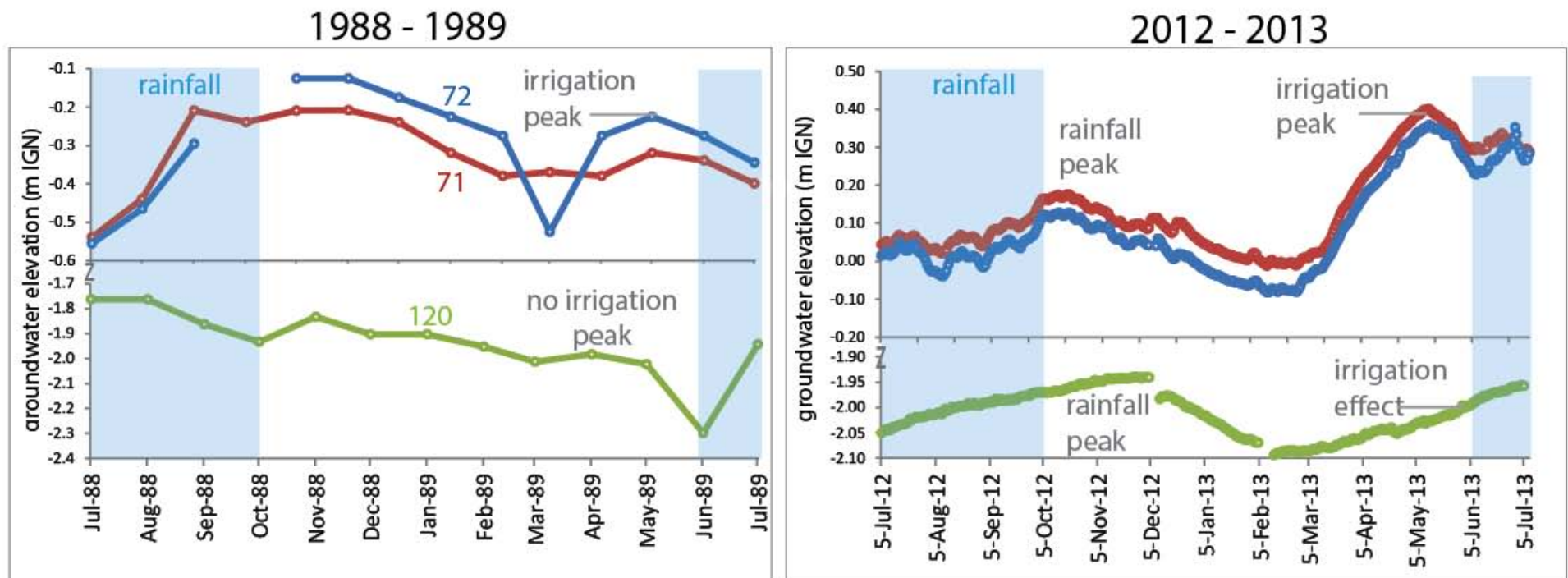


Example : Senegal Delta

Non-uniform physical hydrosystem response to multiple changes

Groundwater in irrigated area

Seasonal hydrographs



Multiple controls on salinity in irrigated systems

Multiple environmental tracers

- Age of groundwater

dating tracers

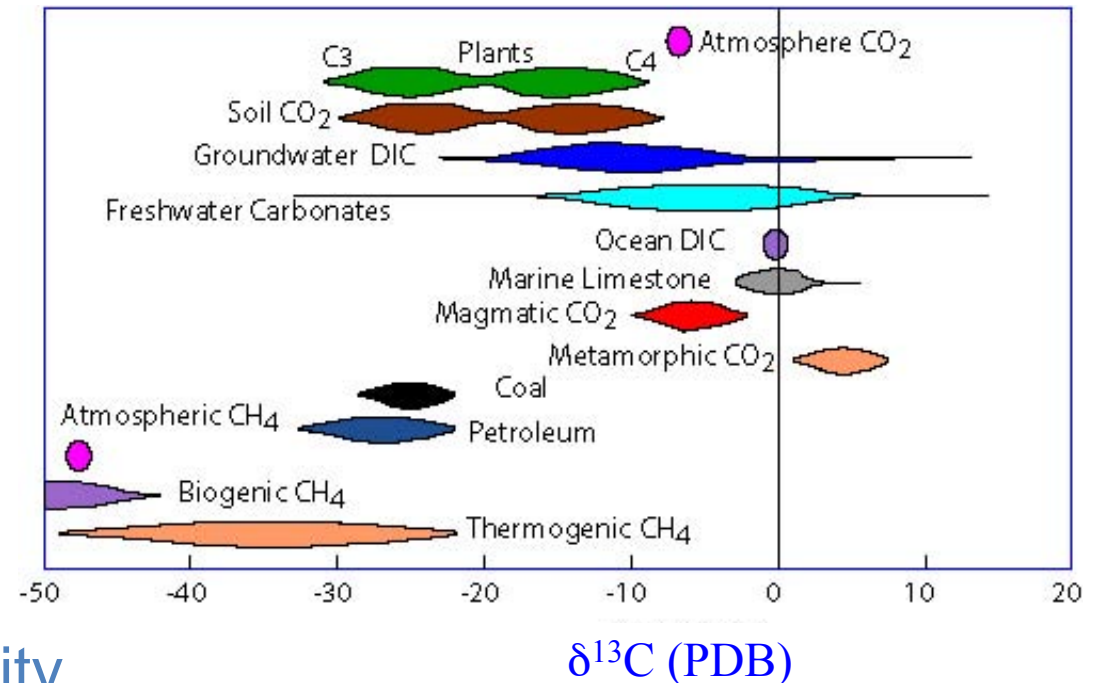
- Origin of water

$\delta^{18}\text{O}$, $\delta^2\text{H}$ / tropical rainfall

$\delta^{13}\text{C}$ – marine

- Dominant control on salinity

Na/Cl and Cl/Br ratios, $\delta^{18}\text{O}$, $\delta^2\text{H}$



Project approaches

Groundwater ages: Interpretation within the hydrogeochemical system

1. Environmental tracers:
identify mixing processes



2. Dating tracers:
selective analysis of multiple dating tracers



3. Dating tracers:
sorption, degradation, contamination, terrigenous sources, excess air



4. Matrix diffusion model:
affects of diffusion on dating tracer concentrations
parallel-plate (Sudicky and Frind, 1981), circular sectioned (Harrington et al., 2007)



5. Quantify dynamics of local and regional groundwater systems:
dating and environmental tracer data, with physical data in numerical models
HydroGeoSphere (Therrien and Sudicky, 1996), KARST (Jourde et al., 2013)



Projects 2 and 3

Groundwater C transfers

Stores of C?

- Spatial variations in groundwater C stores and contributions to rivers

Transfers of C?

- Comparison between seasonal and event scale processes
 - High temporal resolution $\delta^{13}\text{C}$, DIC, $\delta^{18}\text{O}$ and $\delta^2\text{H}$;
 - ISO-CADICA
 - DS-CRDS

- Variations in ages of groundwater transferring DIC to rivers

Impacts of land cover change on C transfers?

- Timeframes for anthropogenic forcings to impact on DIC transfers

Can we differentiate impacts from multiple forcings on water quality?

1. Potential impacts of different forcings

Transects of shallow zone/local processes over multiple land uses

Origins of solutes

- Environmental tracers coupled with land cover/use history

Fluxes of solutes

- Renewal rates long-term (dating tracers)
- Renewal rates event-scale (environmental tracers)

Groundwater
ages

High temporal resolution $\delta^{18}\text{O}$ and $\delta^2\text{H}$; DS-CRDS

2. Propagation of forcings through regional system

Time lag between forcing and impact on chemistry

Groundwater
ages

3. Evolution of solute through local and regional system

Mixing (environmental tracers)

Biogeochemical controls (environmental tracers)

Groundwater
ages

Challenges in using environmental tracers to investigate variabilities

- i. Multiple scales and forcings
- ii. Data representivity
- iii. Multiple tracers
- iv. Regional systems

Challenges in using environmental tracers to investigate variabilities

i. Multiple scales and forcings

Retrospective

Most studies
conducted at different
sites

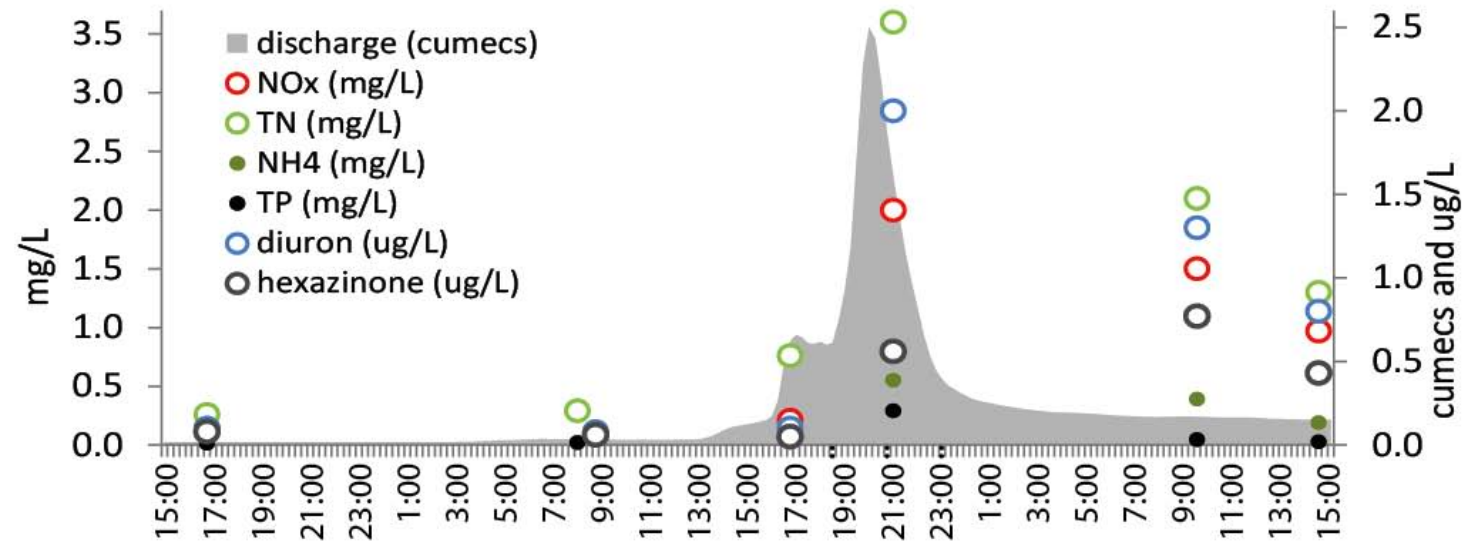
Scales

Contaminant
transfers

- Event
- Seasonal?

Challenges in using environmental tracers to investigate variabilities

Scheu creek event scale

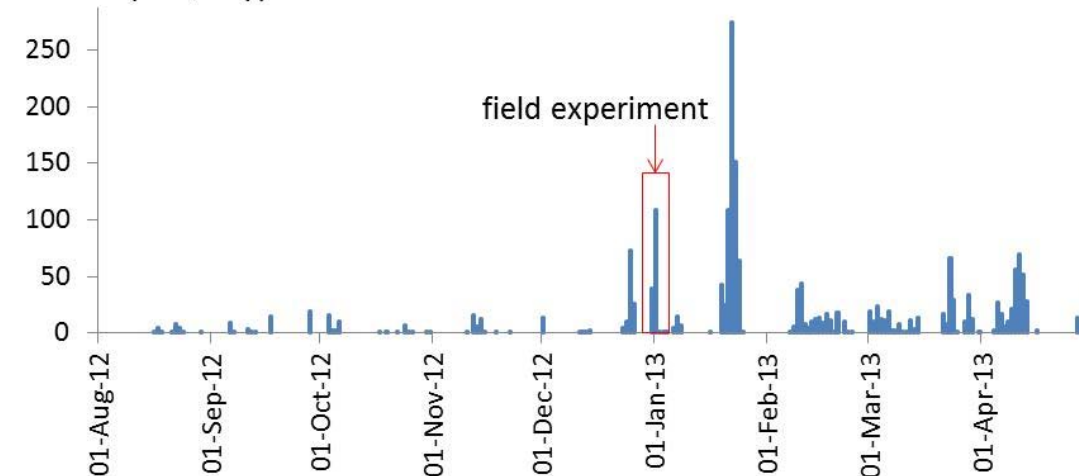


Scales

Contaminant
transfers

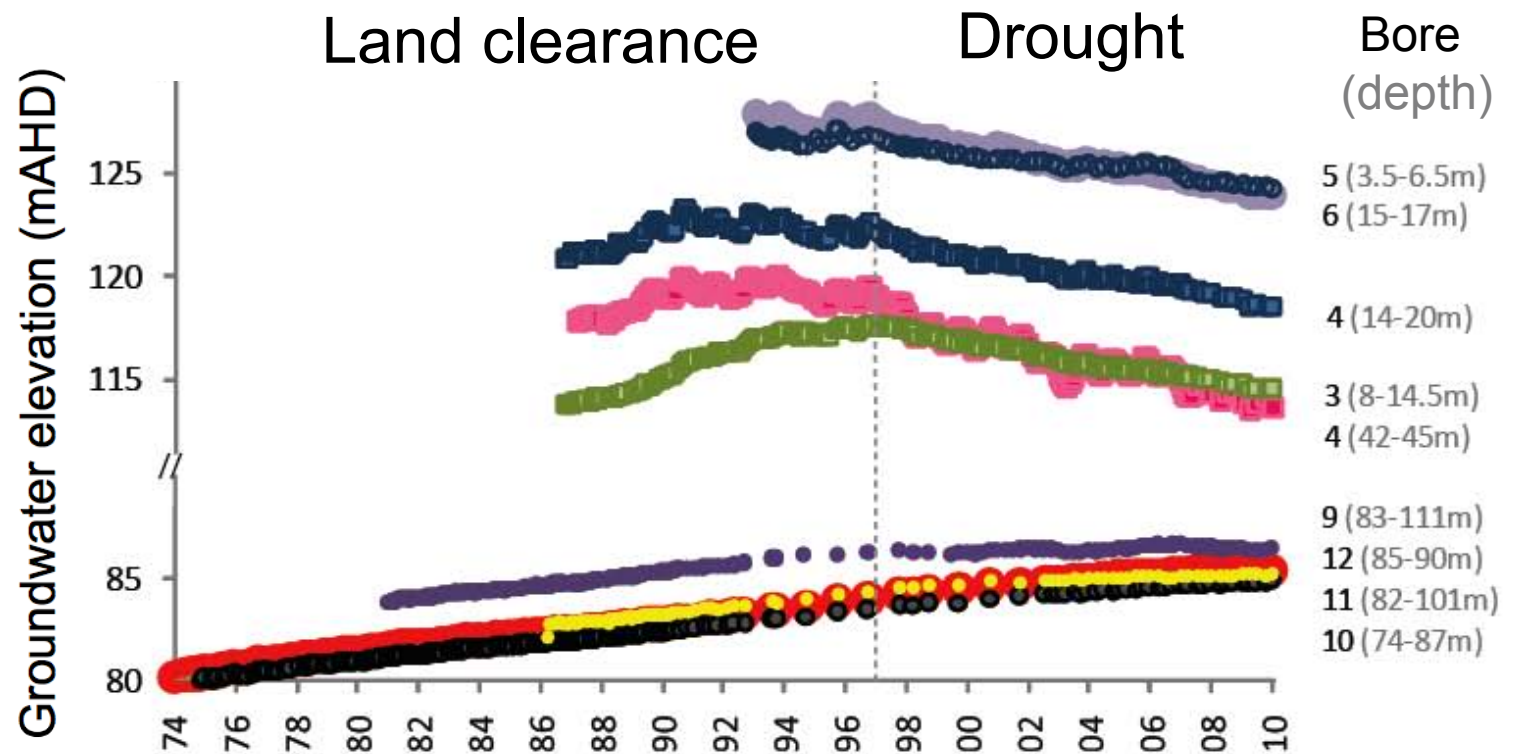
- Event
- Seasonal?

Rainfall (mm/day)



Challenges in using environmental tracers to investigate variabilities

Murray Groundwater Basin



Forcings

Effects on salinity

- Land clearance
- Drought ?

Challenges in using environmental tracers to investigate variabilities

i. Multiple scales and forcings

Retrospective

Most studies conducted at different sites

Scales

Contaminant transfers

- Event
- Seasonal

Forcings

Effects on salinity

- Land clearance
- Drought

Prospective

One site

- Multiple scales
- Multiple forcings

Impacts of forcing propagating through the hydrosystem

Challenges in using environmental tracers to investigate variabilities

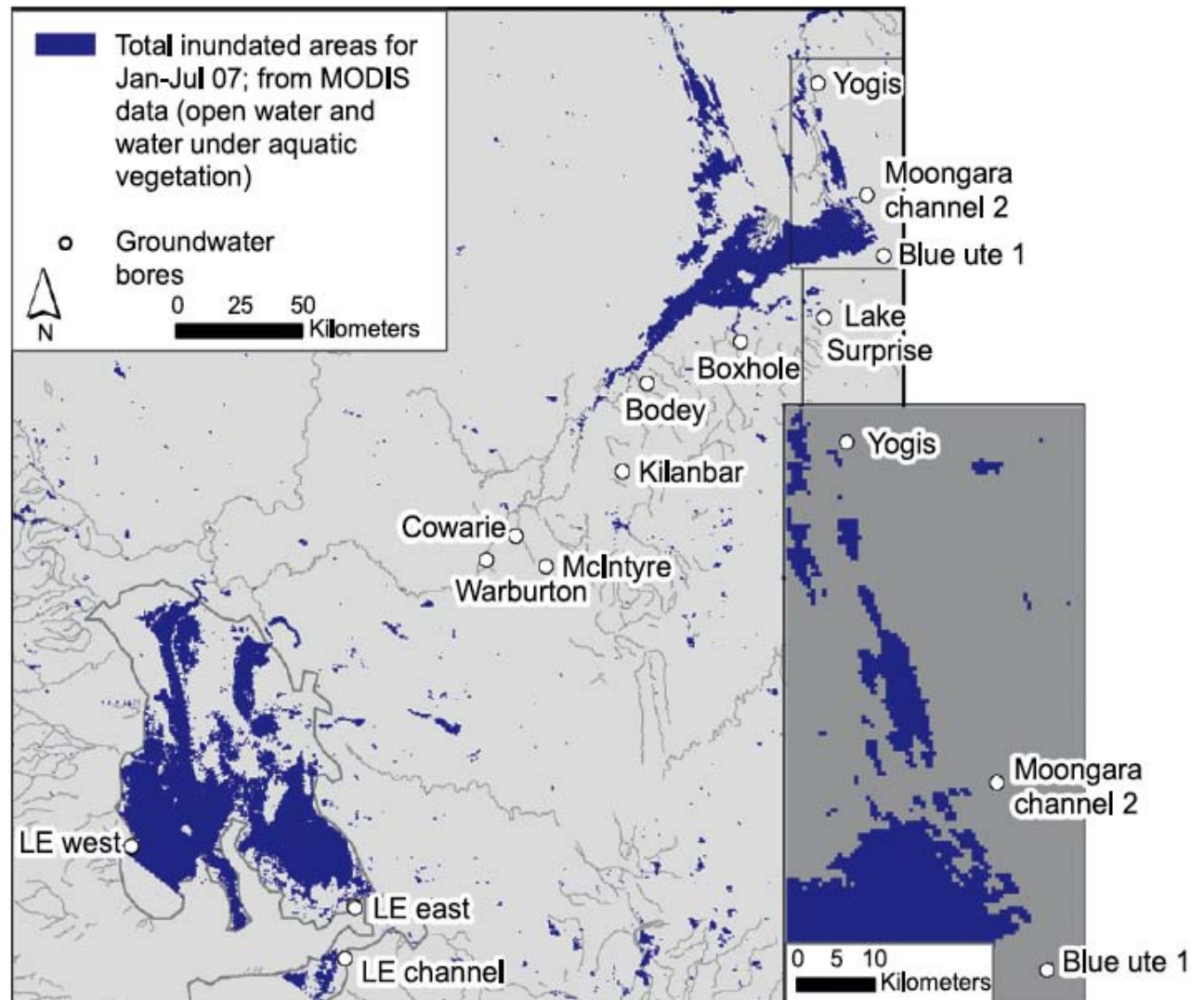
ii. Data representivity

Lake Eyre Basin

Retrospective

Space

Insufficient data to represent floodwater recharge



Challenges in using environmental tracers to investigate variabilities

ii. Data representivity

Retrospective

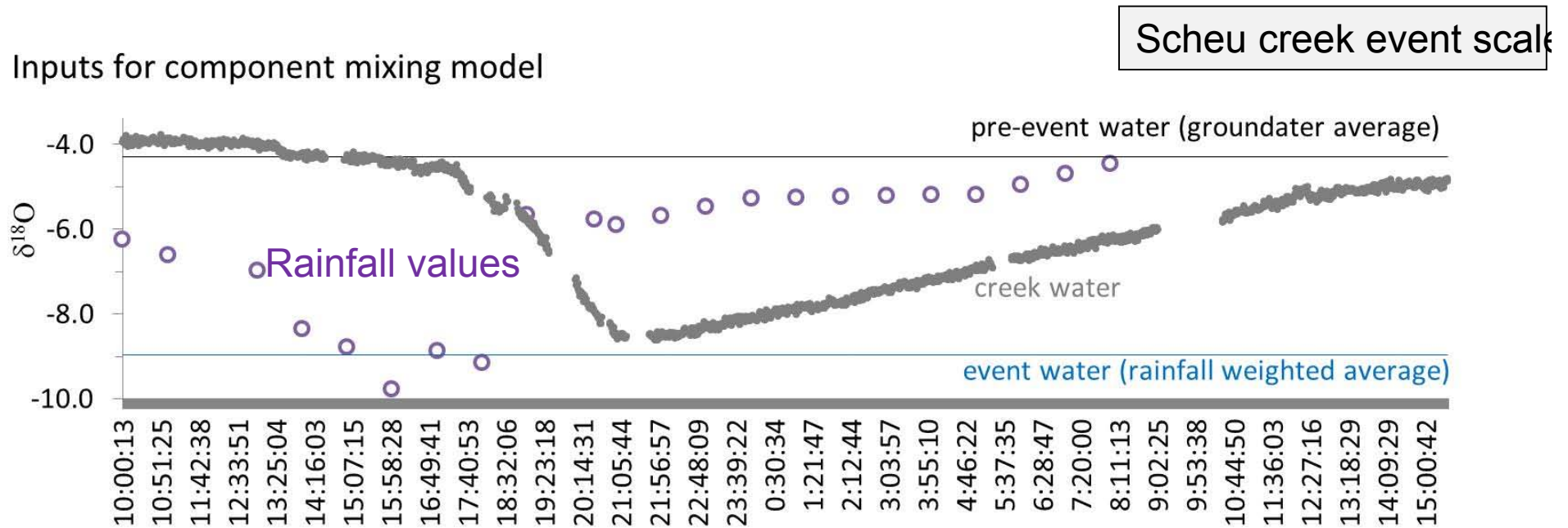
Space

Insufficient data to represent floodwater recharge

Time

Component mixing models: constant end-members

Challenges in using environmental tracers to investigate variabilities



Time

Component mixing
models: constant end-
members

Challenges in using environmental tracers to investigate variabilities

ii. Data representativity

Retrospective

Space

Insufficient data to represent floodwater recharge

Time

Component mixing models: constant end-members

Prospective

➤ Optimum sample frequency and density

➤ Dynamic end-members in models

Challenges in using environmental tracers to investigate variabilities

iii. Multiple tracers

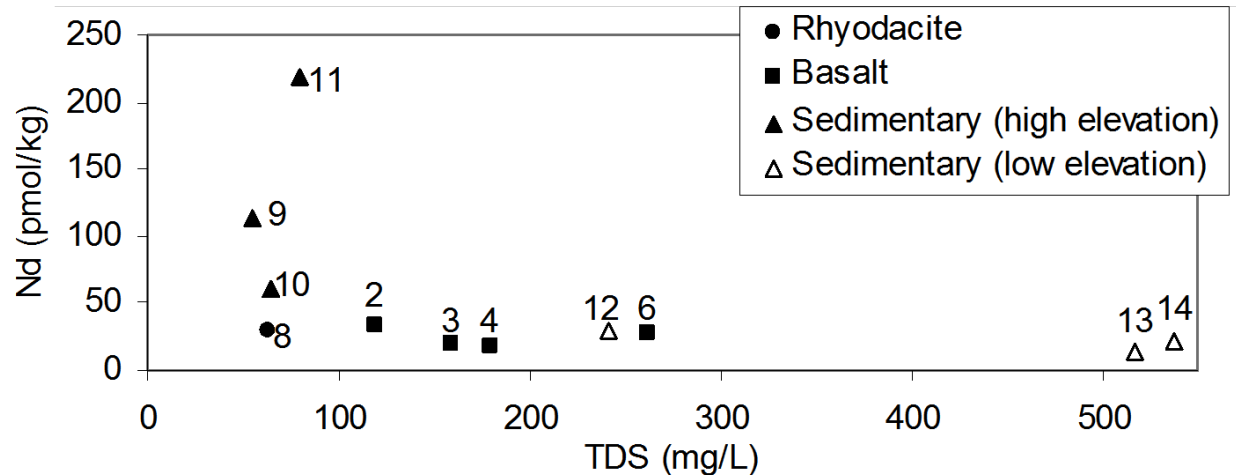
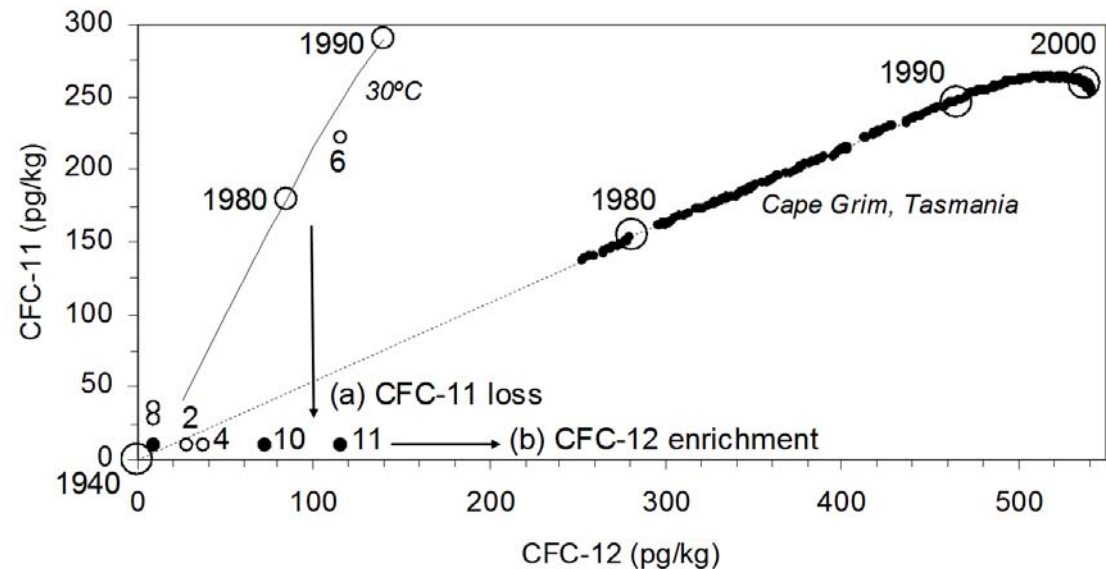
Retrospective

Suite of tracers

(1) Suitability to process

(2) Known mechanisms controlling solutes

Dandenong Range



Challenges in using environmental tracers to investigate variabilities

iii. Multiple tracers

Retrospective

Suite of tracers

(1) Suitability to process

(2) Known mechanisms controlling solutes

Prospective

Selective Analysis

Less expensive tracers to understand geological controls on mixing in system

Targeted tracers

-> Dating tracers

-> Contaminants

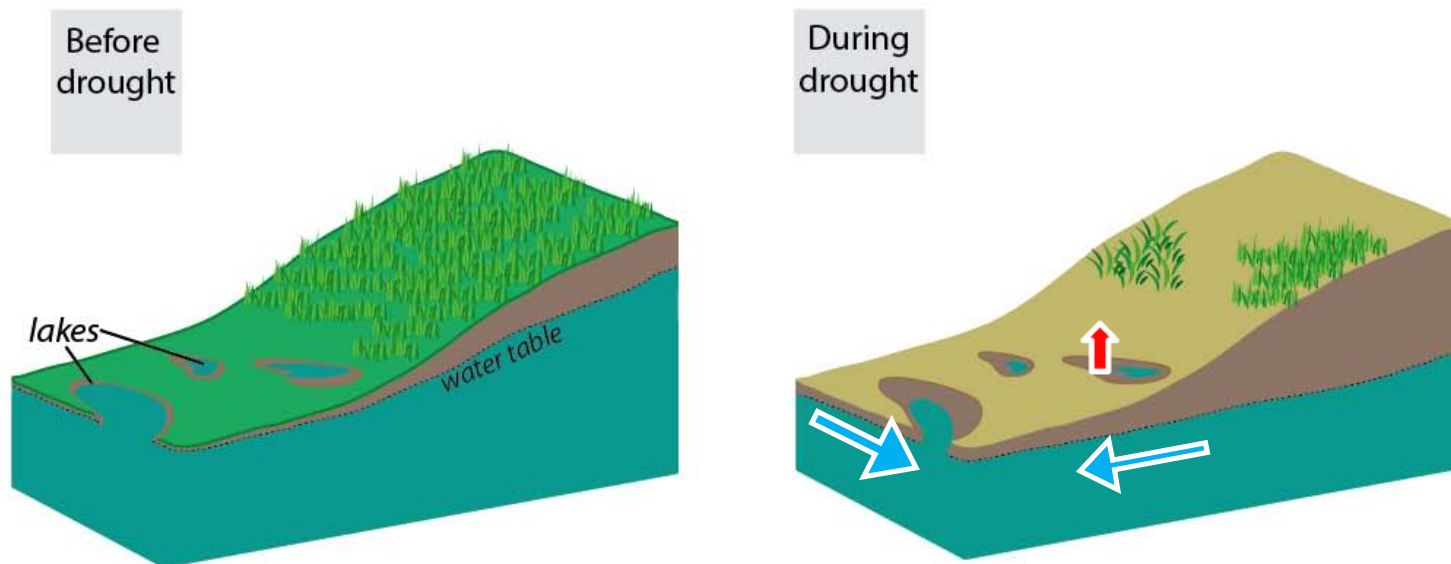
Challenges in using environmental tracers to investigate variabilities

iv. Regional systems

Retrospective

Impacts on chemical system

- Localised - Drought (Corangamite: 13,000 km²)



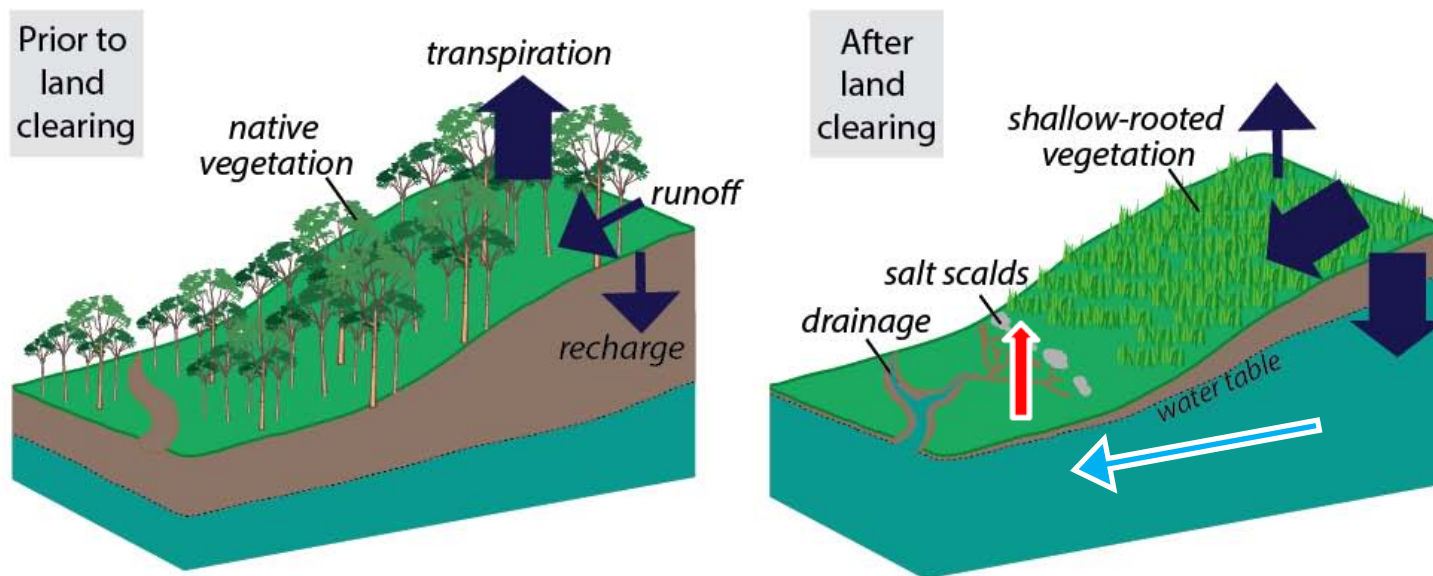
Challenges in using environmental tracers to investigate variabilities

iv. Regional systems

Retrospective

Impacts on chemical system

- Localised - Drought (Corangamite: 13,000 km²)
- Delayed - Land clearance (MGB: 300,000 km²)



Challenges in using environmental tracers to investigate variabilities

iv. Regional systems

Retrospective

Impacts on chemical system

- Localised - Drought (Corangamite: 13,000 km²)
- Delayed - Land clearance (MGB: 300,000 km²)

Prospective

Challenges

- Distinguishing current versus historical forcings impacting water quality
- Using environmental tracers to constrain physical hydrosystem processes

Advantages

- Chemistry can highlight significant historical processes that the current physical system no longer represents

1. Groundwater ages

Builds on research in Australia and current research at IRD
(Wankama catchment SW Niger)

Importance

- Water resources quantity assessments
 - Groundwater renewal rates and sustainable yield
- Water resources quality assessments
 - Fluxes and evolution of contaminants
- Impact of forcings assessments
 - Time lag for chemical system response

Challenges in measuring groundwater ages are amplified in heterogeneous systems (e.g. McCallum et al., 2013)

1. Tracer specific processes: sorption, degradation, terrigenous sources, contamination

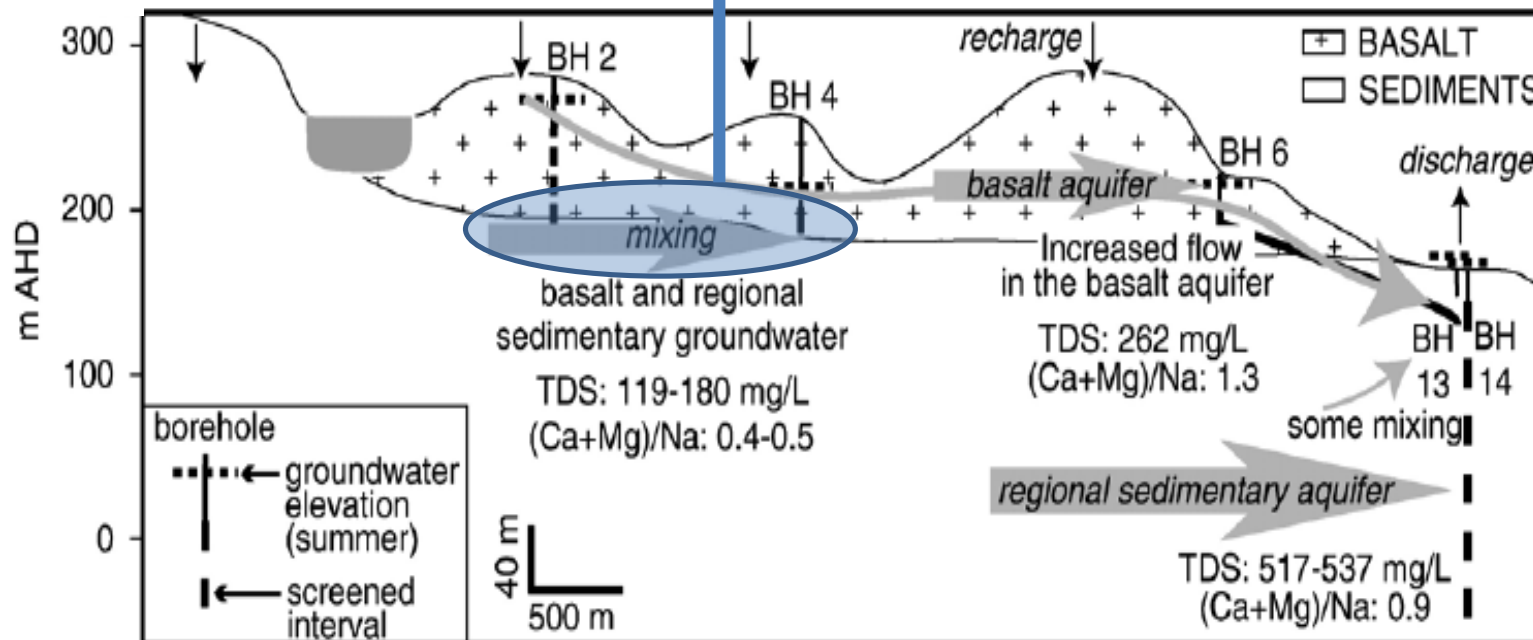
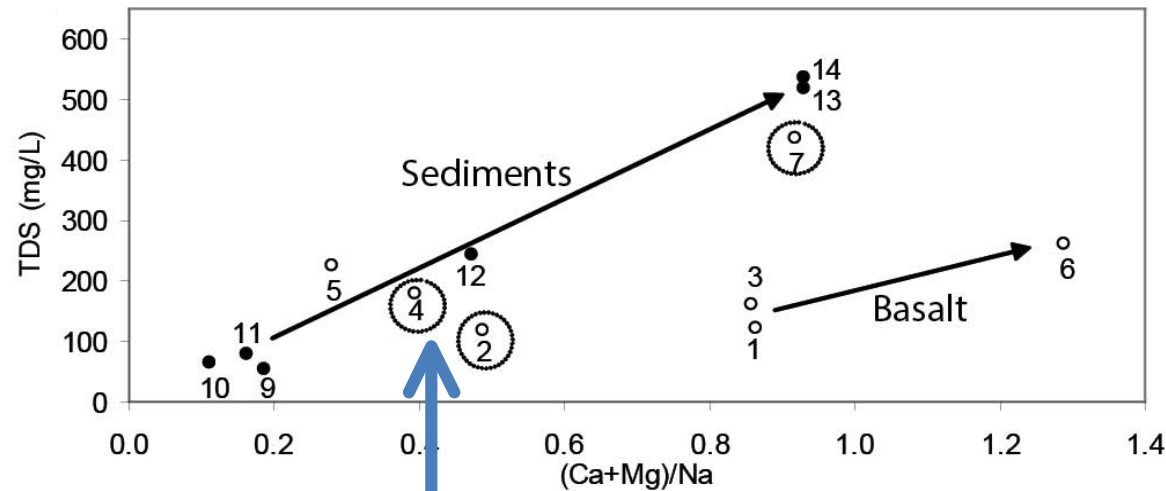
2. Excess air effect

3. Mixing - **average age of mixed waters**

4. Solute diffusive transport – **in dual porosity systems**

Example 1. Mixing between fracture rock aquifers

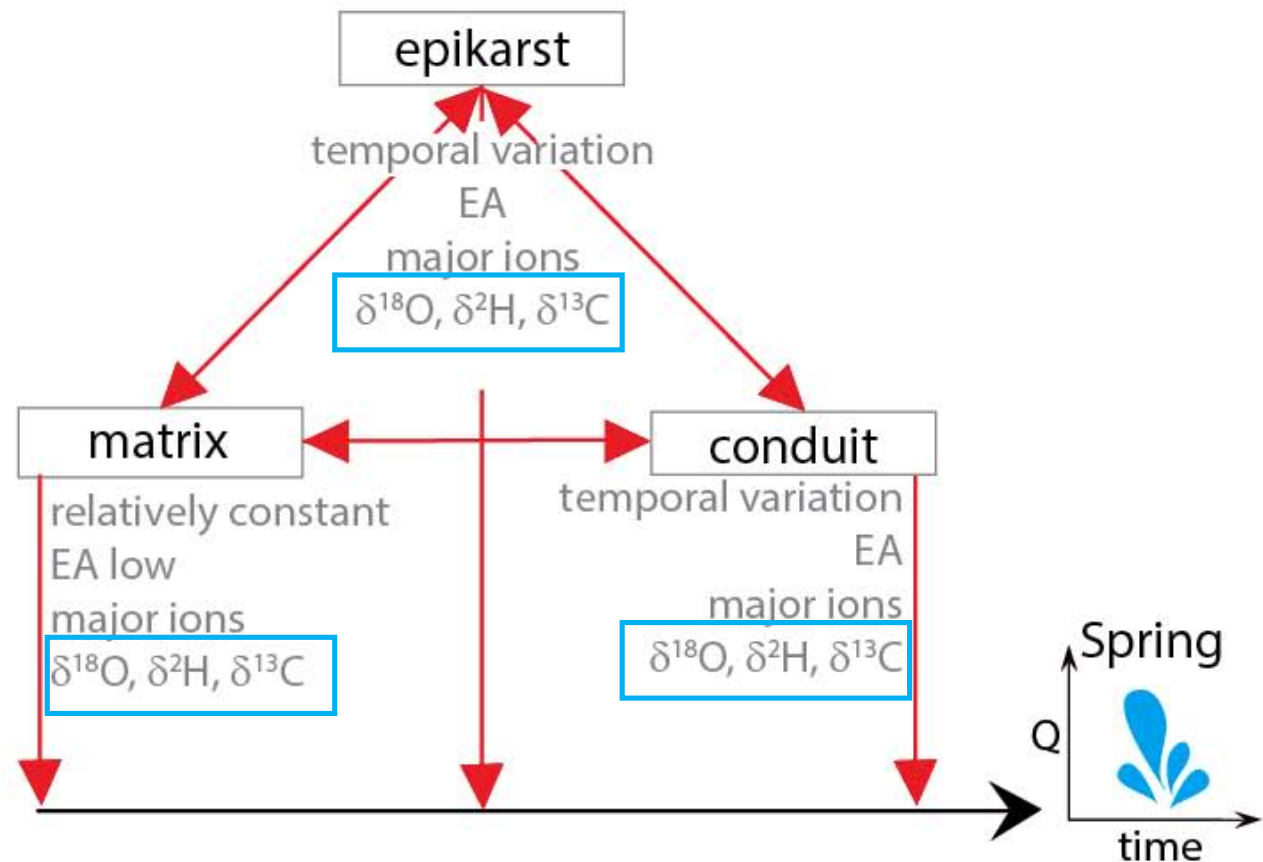
-major ions



Sources of karst waters to springs – storm events (e.g. de Montety, 2013)

-> Mixing processes?

-> Impacts of diffusive transport?



Analysis of temporal variations in mixing between different flow pathways during storm events

2. Groundwater C transfers

Builds on previous research in Australia

Importance

Linked water and carbon cycling

Knowledge gaps

Role of groundwater in the transfer of carbon from terrestrial catchments

- Stores of C
- Transfers of C
- Impacts of land cover change on C transfers

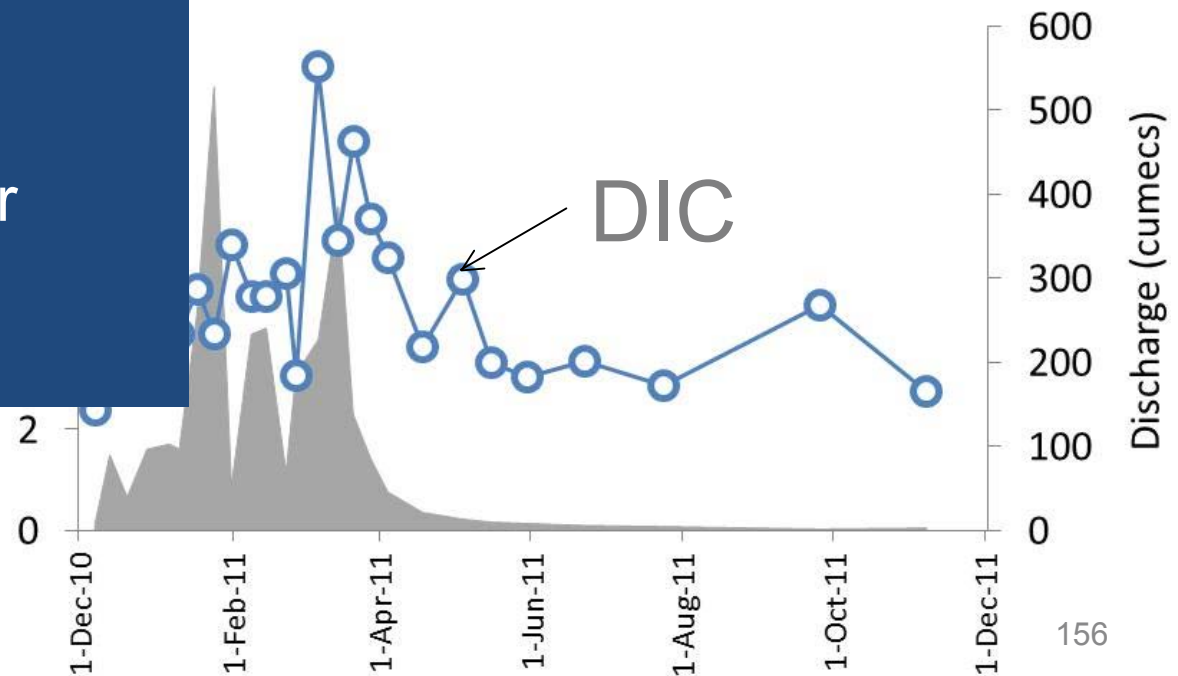
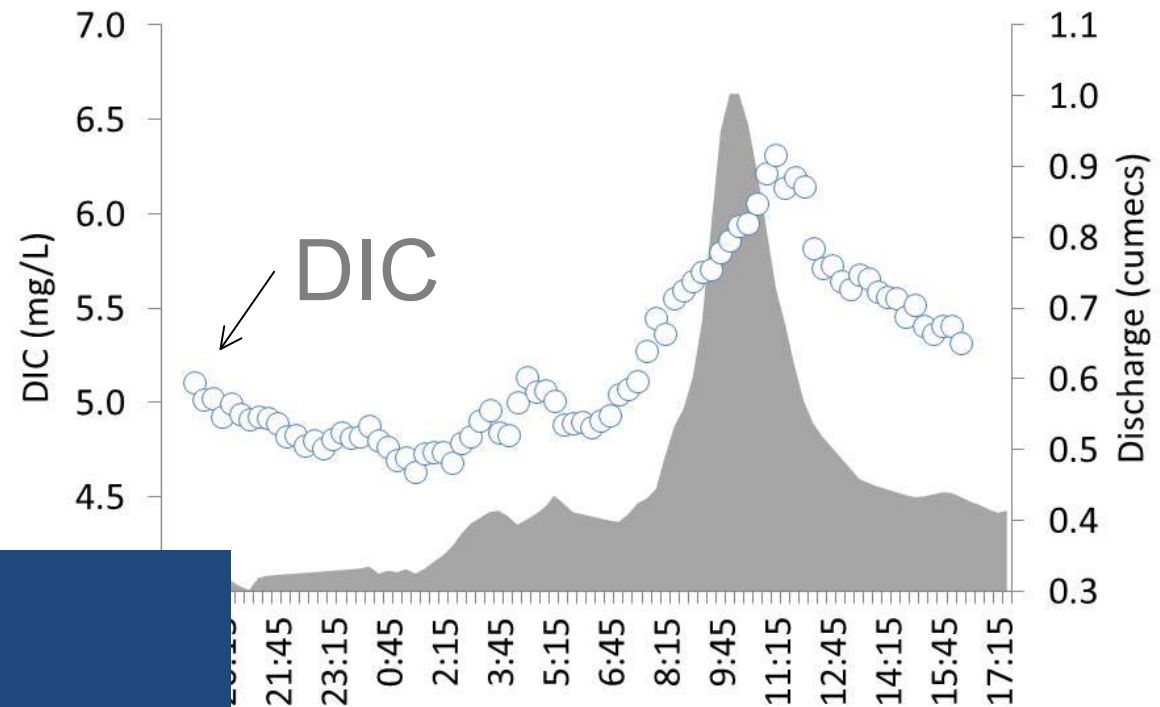
Groundwater C transfers

Event scale

- > Stores of C?
- > Transfers of C?
- > Impacts of land cover change on C transfers?

Seasonal scale

86% of the annual carbon load over a 4 month period



3. Heavily modified hydrosystems

Builds on current research at IRD (irrigated areas in lower Senegal Delta, Haouz Plain Morocco, and Crau Plain France)

Importance

Food and water security

Challenges

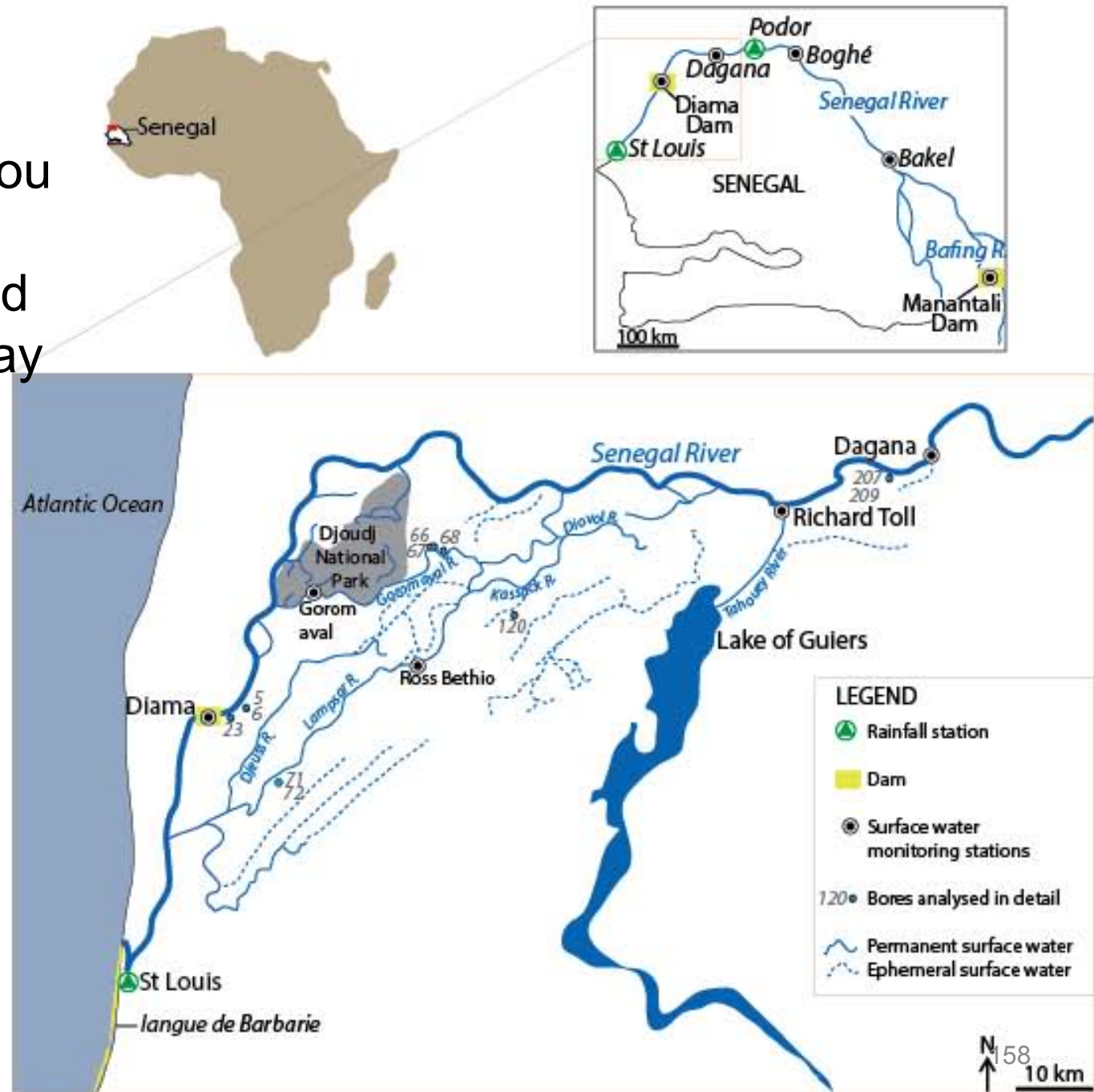
Chemical system can reflect current or prior conditions

Question

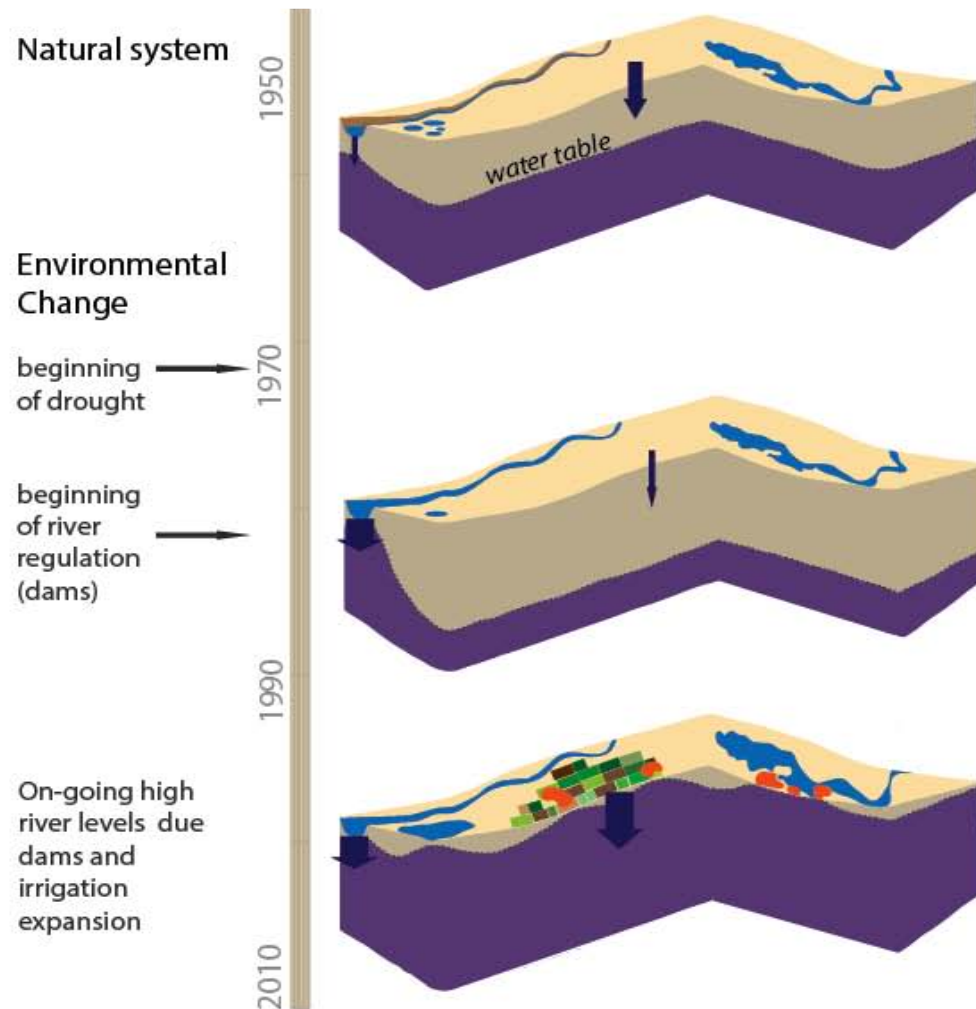
Can we differentiate impacts from multiple forcings on water quantity and quality?

Example: Senegal Delta

- Heterogeneous aquifer:
disconnected sand and clay
lenses
- Multiple forcings



Physical hydrosystem changes



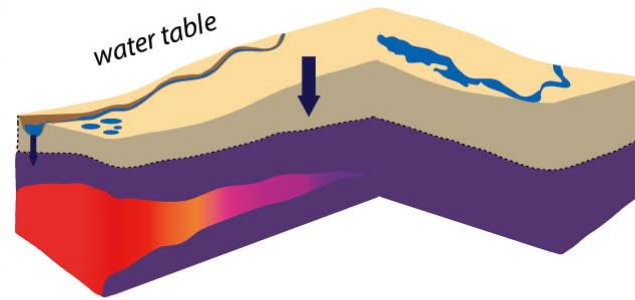
1970s

- Drought
- Start of dams regulating Senegal River
- Start of irrigation expansion

-> Non-uniform physical

Marine
transgression

Quaternary



-> Impacts of different
forcings?

-> Propagation of forcings?

-> Evolution of solute?

- sea water transgressions

↑ salinity

- Drought

Reduced recharge

↑ salinity

Lower water tables

↓ salinity

- Dams regulating the River

Increased river recharge ↓ salinity

- Irrigation

Increased recharge

↓ salinity

Water table close to the surface

↑ salinity¹⁶⁰

On-going high
river levels due
dams and
irrigation
expansion

199

2010

