MULTI-PRONGED APPROACH TO ELUCIDATE NITRATE ATTENUATION IN SHALLOW GROUNDWATER

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MEASURE. MODEL. MANAGE.

Nitrate attenuation

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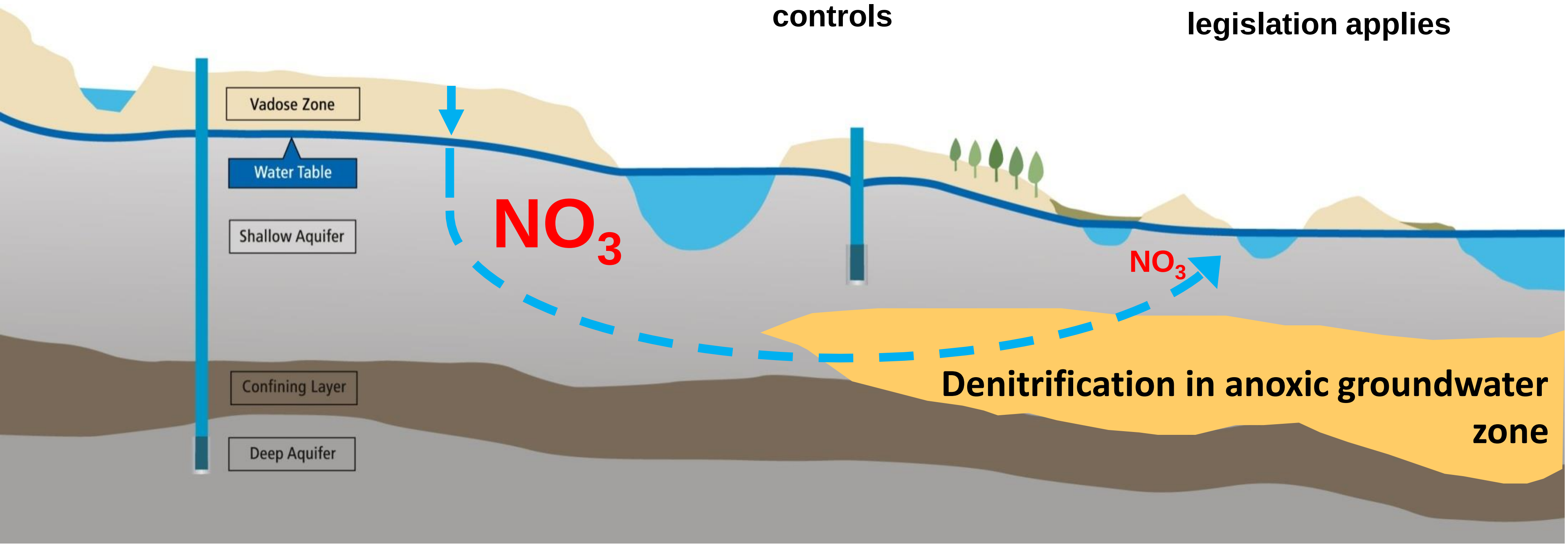
Source
Root zone losses

Transfer
Hydrological and biogeochemical controls

Impact
Surface waters to which most environmental legislation applies



Example of a groundwater flow path

Multi-pronged approach to elucidate nitrate attenuation

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Groundwater monitoring

- **Redox assignment**
- **Nitrate isotopes**
  Clague et al., 2015
- **Excess N_2**
- **Age-dating**

Field experiments

Push-pull tests
(location of denitrification activity)

Slug and tracer tests
(hydraulic conductivity, flow paths)

Lab experiments

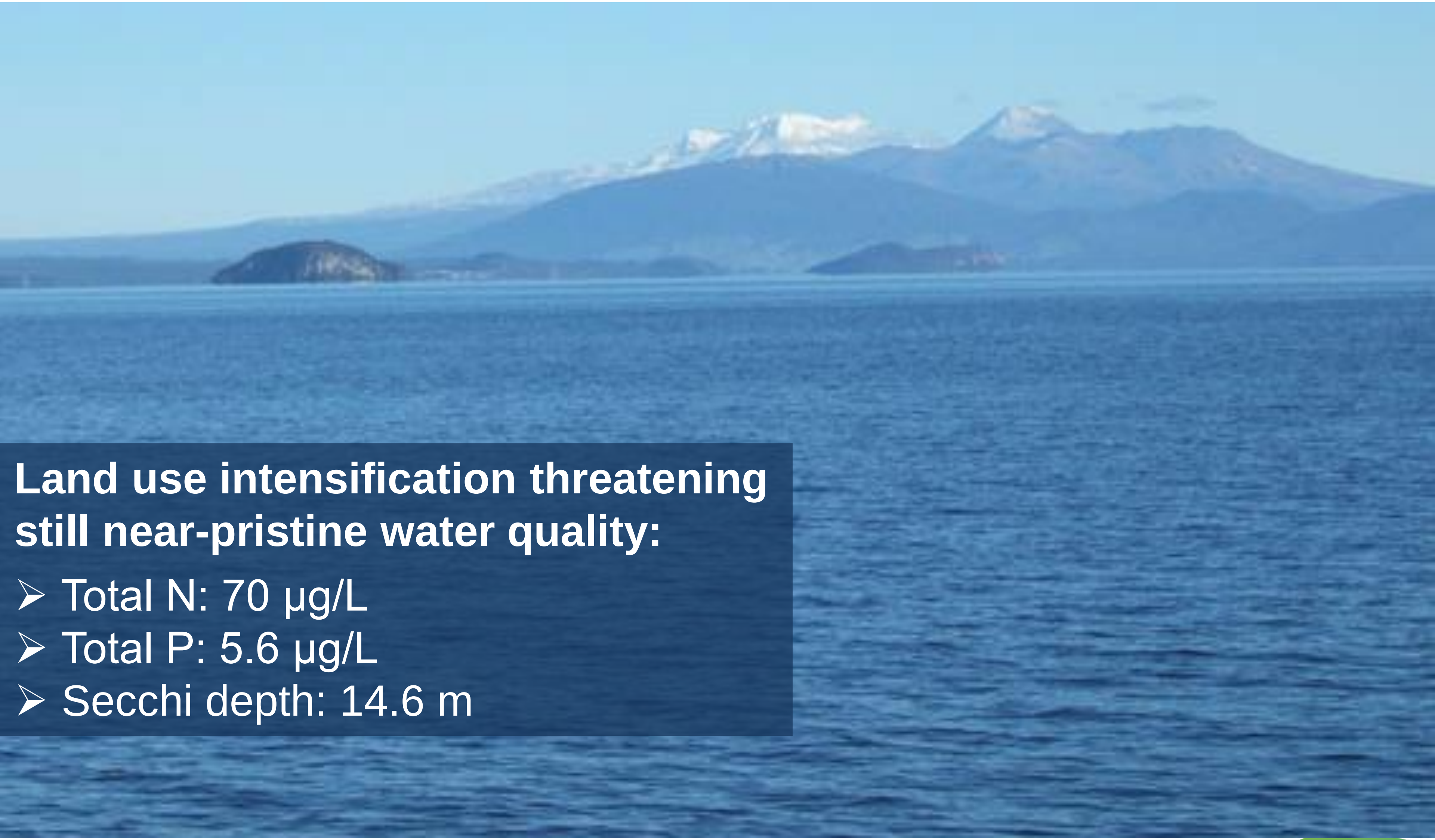
Incubation exp.
(electron donors, microbial capacity),
Clague et al., 2013 + 2015

Synthesis

supported by modelling

Woodward et al., 2013 + 2015

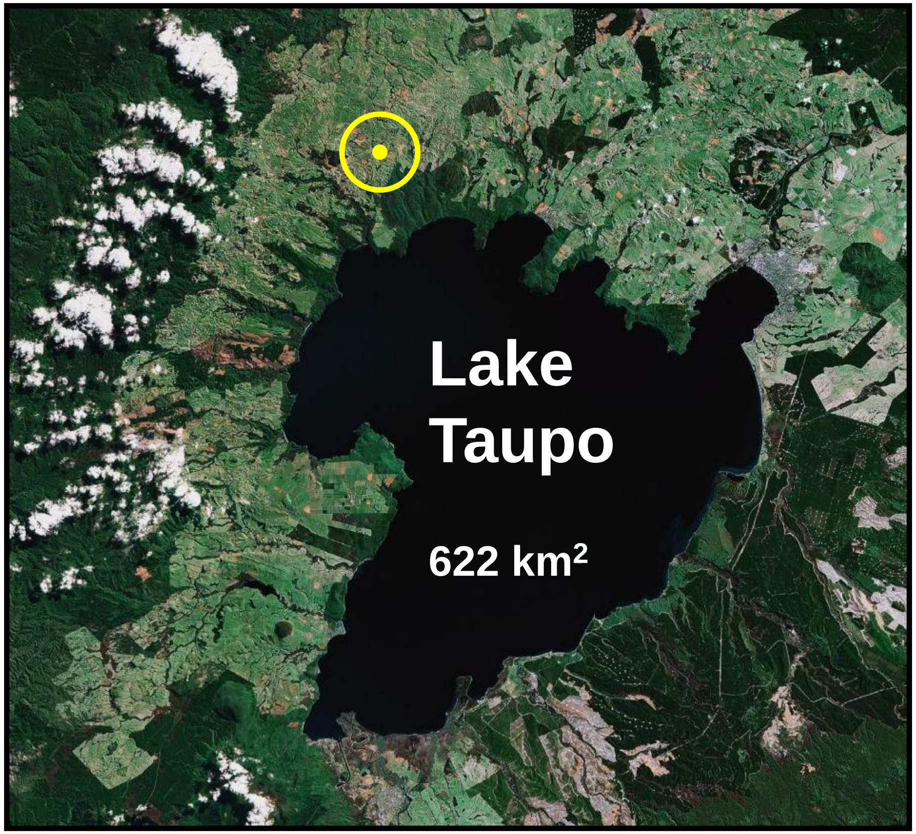
Lake Taupo catchment

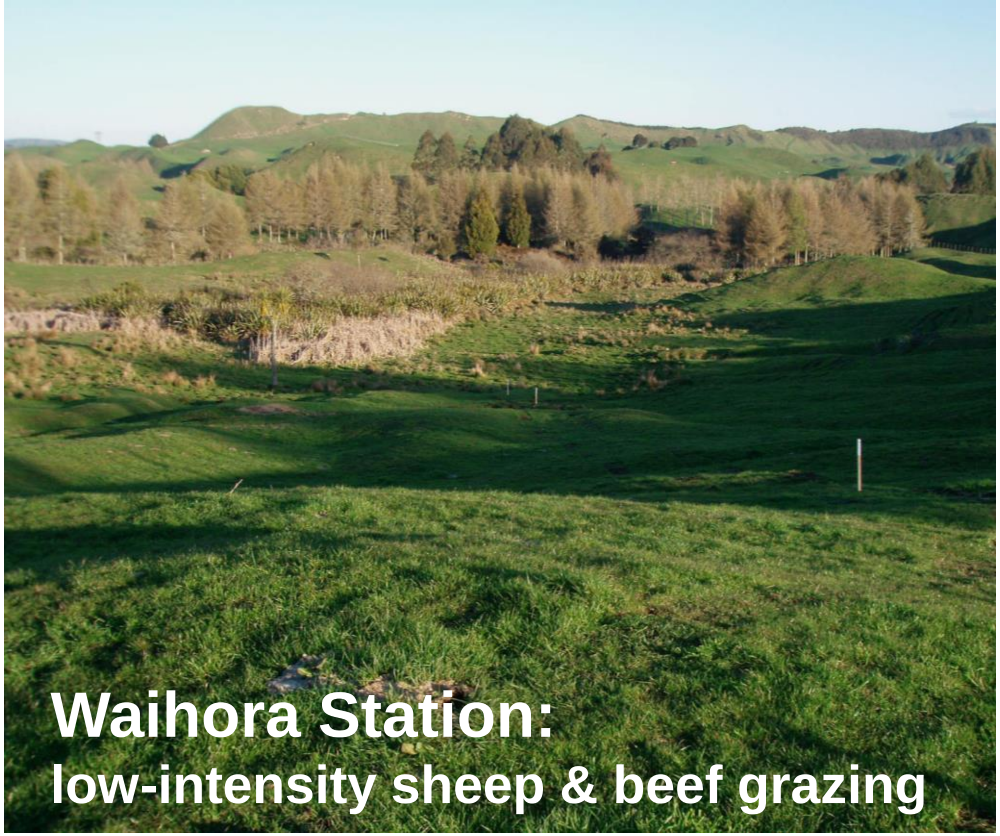


Land use intensification threatening still near-pristine water quality:

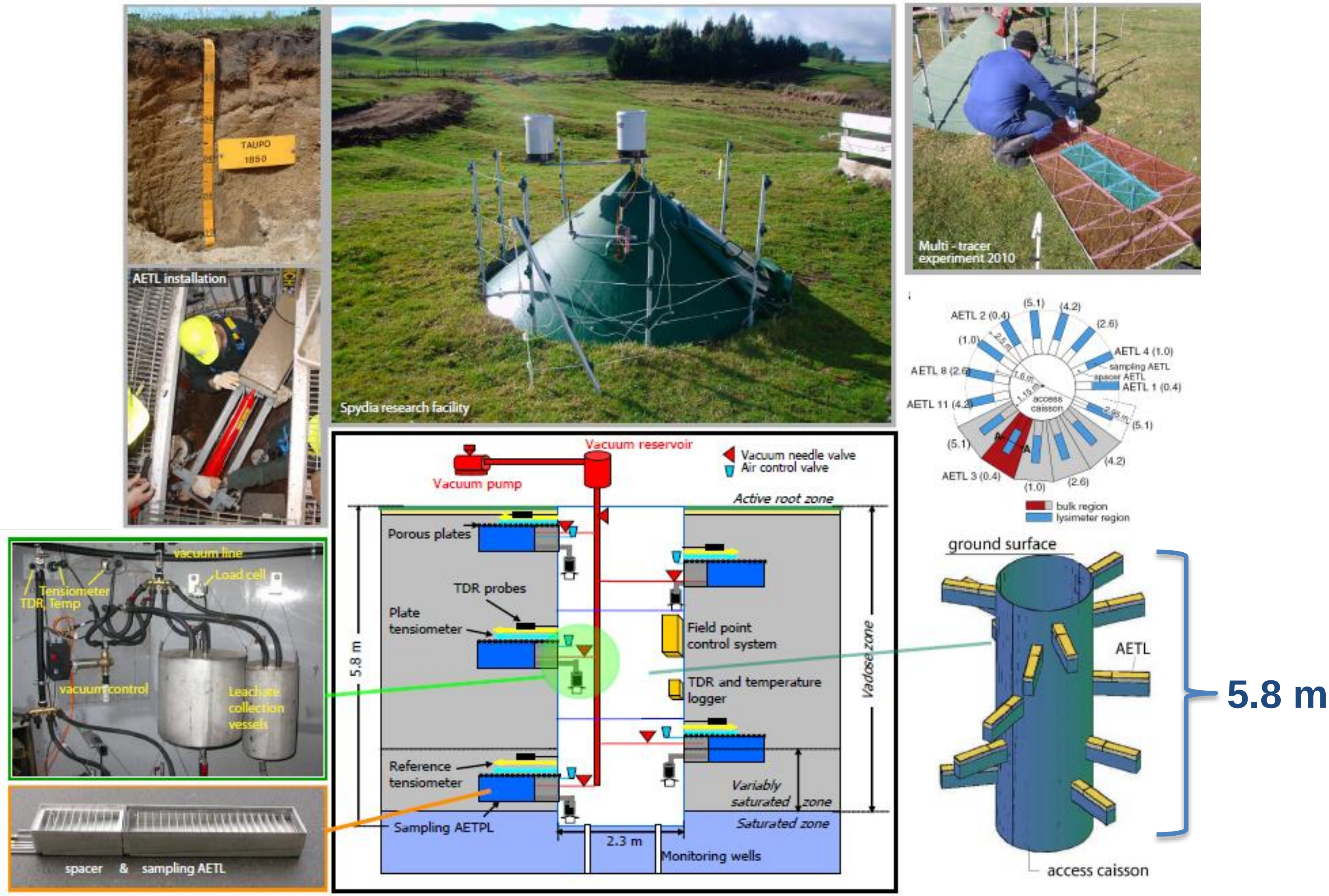
- Total N: 70 µg/L
- Total P: 5.6 µg/L
- Secchi depth: 14.6 m

Field site: Waihora Station





Vadose zone research: Spydia



Barkle et al., 2011, 2014a, 2014b
Wöhling et al., 2009, 2012

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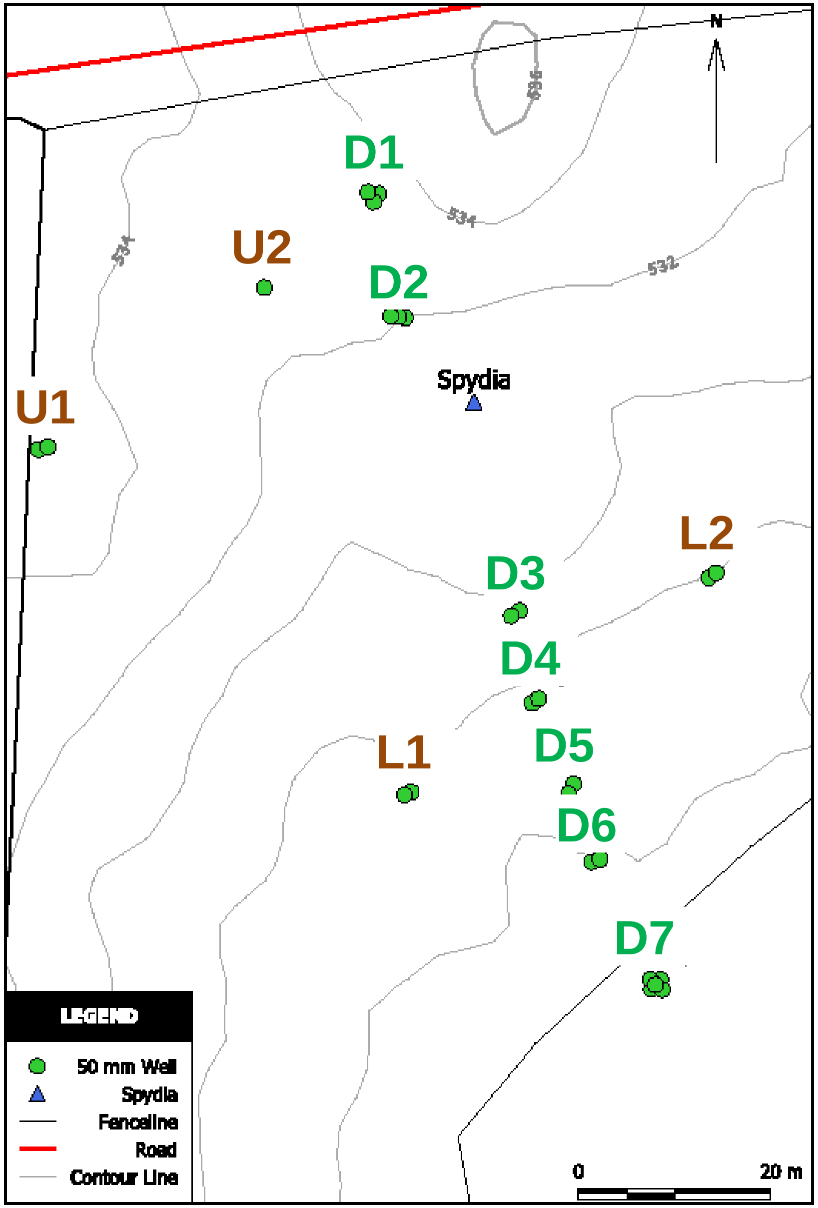
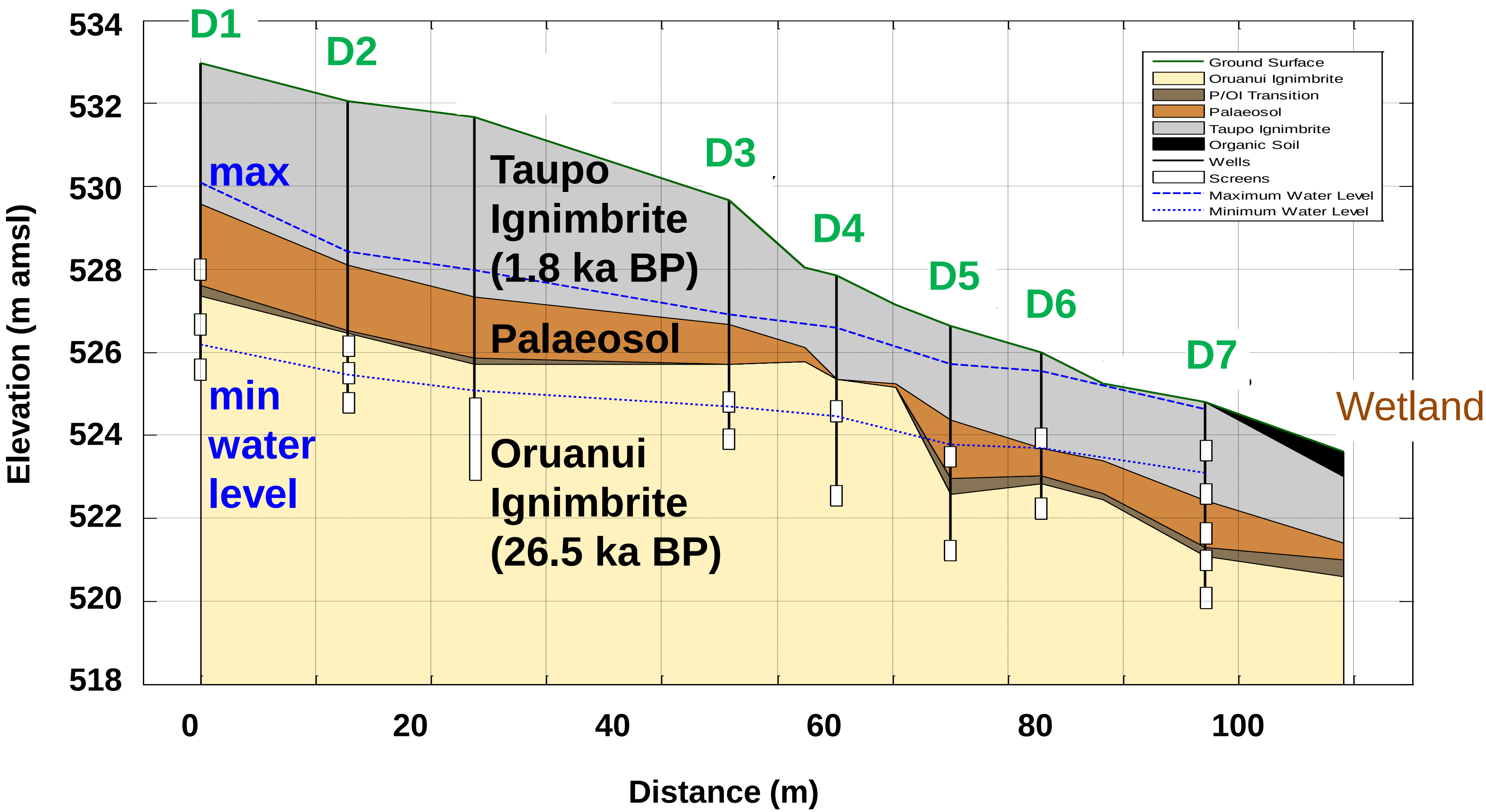
Groundwater monitoring



Waihora well field

- 11 multilevel well clusters on a hillslope (approx. 6000 m²)
- 2 – 5 screens per cluster
- Well depths: 1.5 to 9 m
- Screen max. 5 m below water table
- **Downslope transect (D)**
- **Upper (U) and lower (L) perpendicular MLW clusters**

Downslope well transect (D)



Multi-pronged approach to elucidate nitrate attenuation

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Redox assignment:
Ecological succession

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Decreasing energy yield

Aerobic Decomposition

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

Heterotrophic Denitrification

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O$$

Manganese (IV) Reduction

$$CH_2O + 2MnO_2 + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + 2H_2O$$

Ferric Iron (III) Reduction

$$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O$$

Sulfate Reduction

$$2\ CH_2O + SO_4^{2-} \rightarrow HS^- + 2\ HCO_3^- + H^+$$

Methane Generation

$$2CH_2O + H_2O \rightarrow CH_4 + HCO_3^- + H^+$$

oxic

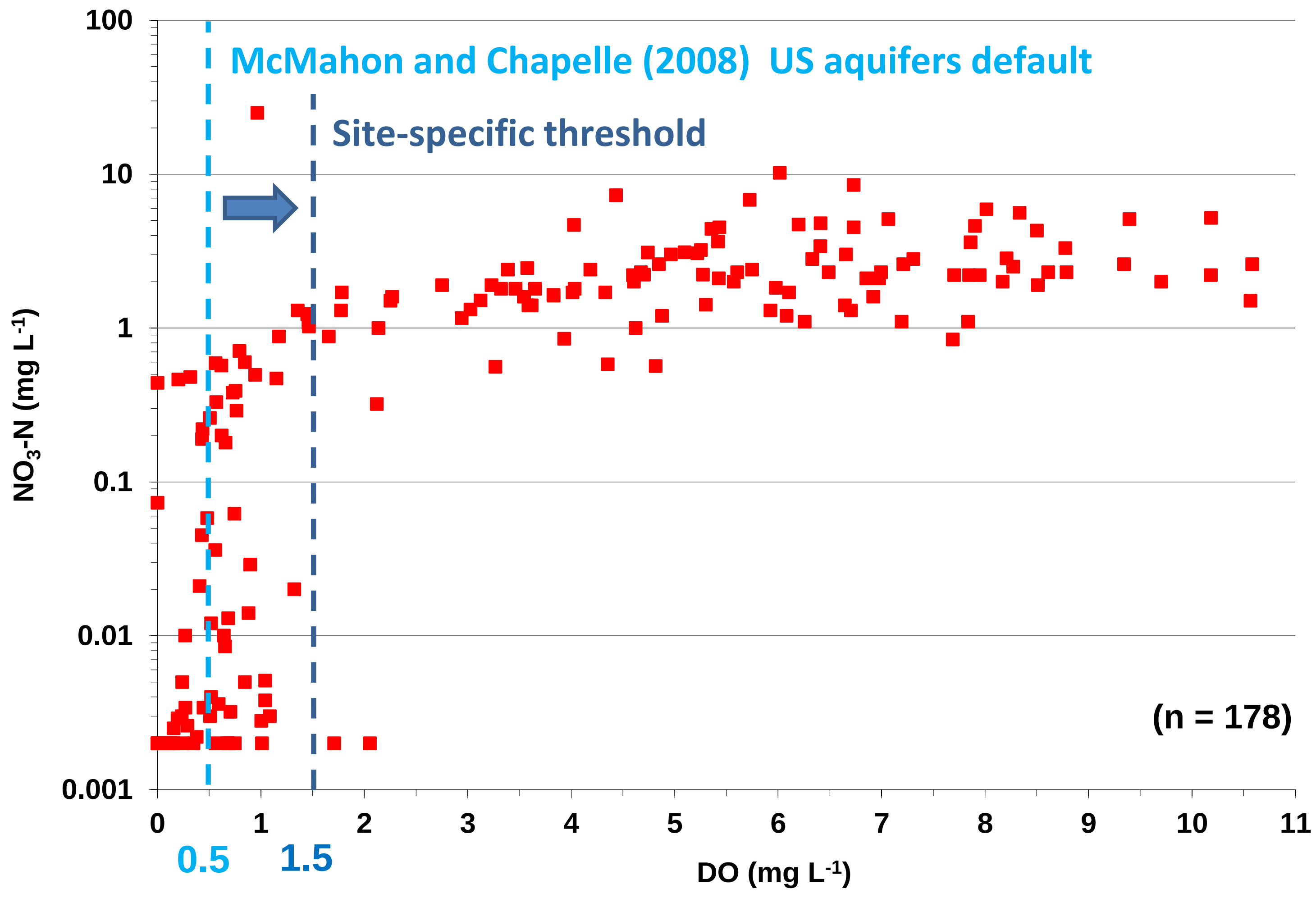
anoxic

Redox assignment:
Classification scheme

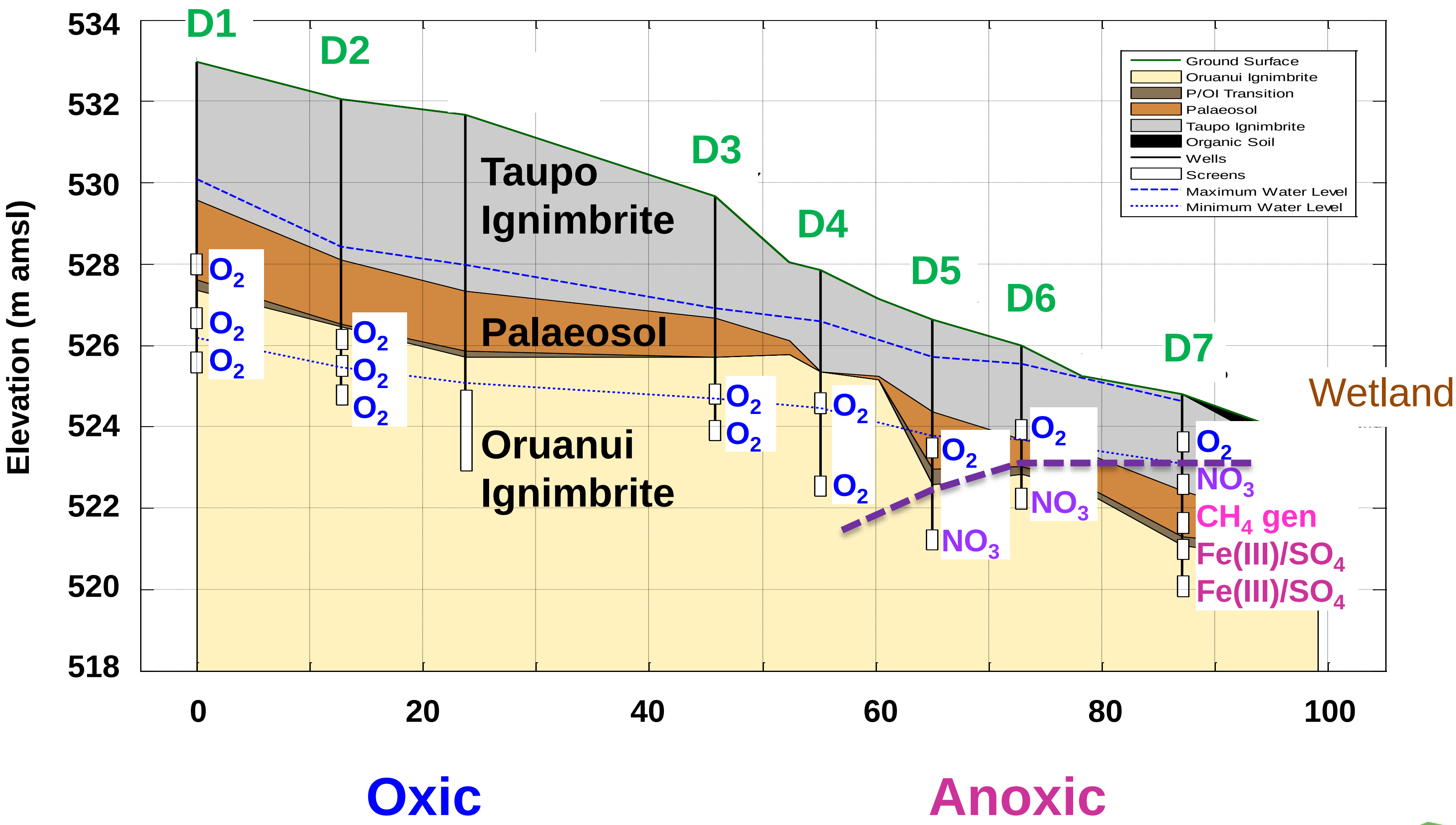
McMahon and Chapelle (2008)						
		Criteria for inferring process from water-quality data				
		US default thresholds				
Redox category	**Redox process**	**DO (mg/L)**	**Nitrate-N (mg/L)**	**Manganese (mg/L)**	**Iron (mg/L)**	**Sulfate (mg/L)**
Oxic	**O2**	≥0.5	—	<0.05	<0.1	—
Suboxic	**Suboxic**	<0.5	<0.5	<0.05	<0.1	—
Anoxic	**NO3**	<0.5	≥0.5	<0.05	<0.1	—
Anoxic	**Mn(IV)**	<0.5	<0.5	≥0.05	<0.1	—
Anoxic	**Fe(III)/SO4**	<0.5	<0.5	—	≥0.1	≥0.5
Anoxic	**Fe(III)**	<0.5	<0.5	—	≥0.1	≥0.5
Mixed(anoxic)	**Fe(III)-SO4**	<0.5	<0.5	—	≥0.1	≥0.5
Anoxic	**SO4**	<0.5	<0.5	—	≥0.1	≥0.5
Anoxic	**CH4gen**	<0.5	<0.5	—	≥0.1	<0.5
		Site-specific thresholds				
		1.5	**0.1**	**0.3**	**0.4**	**4.0**

- **Default thresholds *'broadly applicable to regional US aquifer systems'***
- **Site-specific thresholds used where indicated by own data**

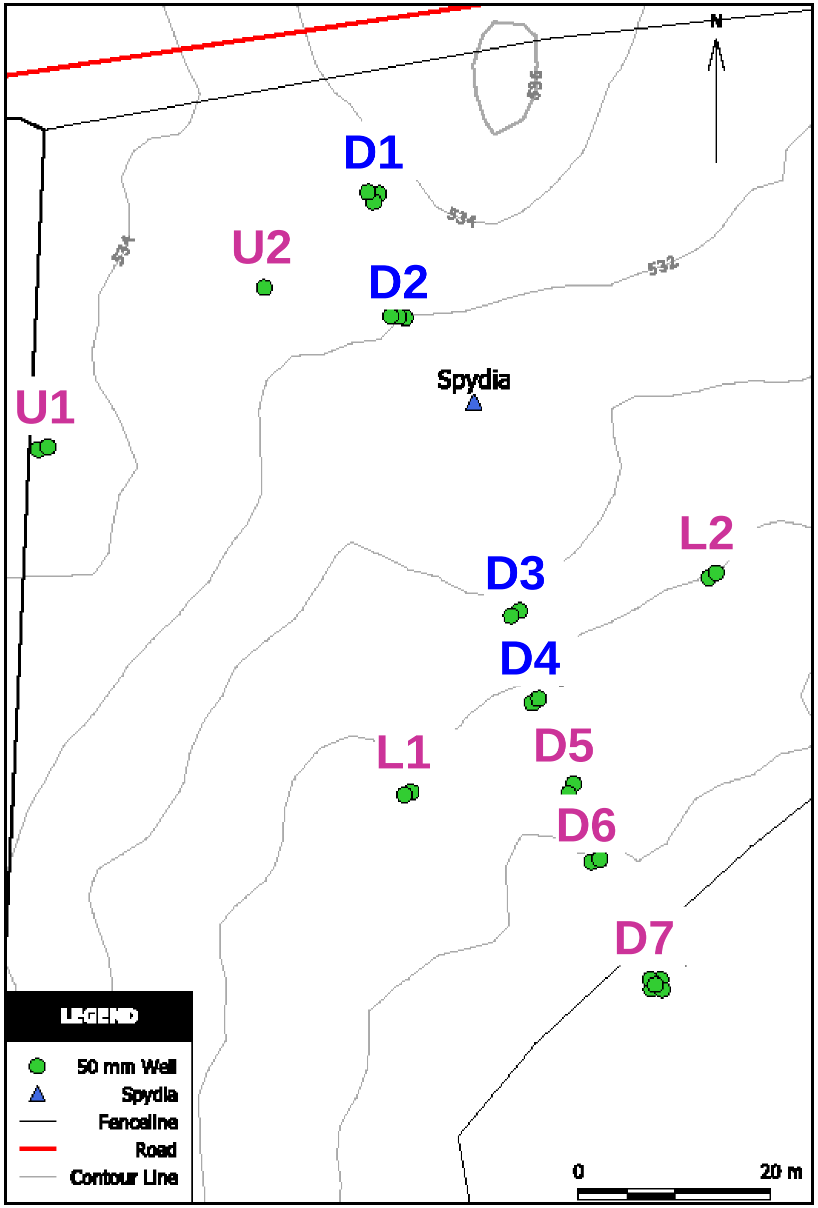
Redox assignment:
Site-specific thresholds



Redox assignment:
Downslope well transect (D)



Redox assignment: Well field

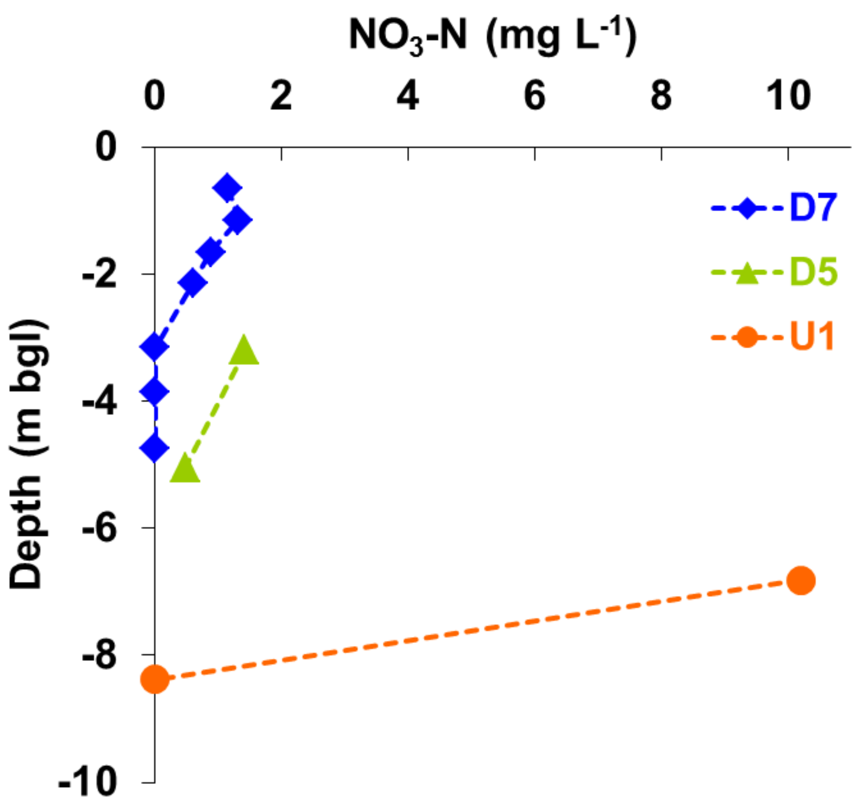


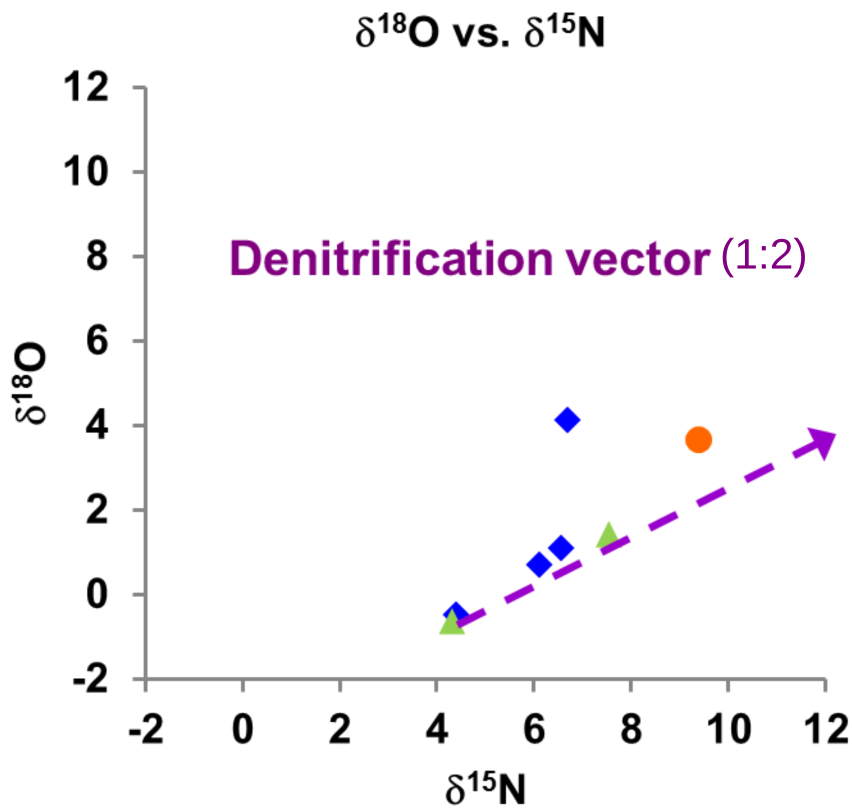
Vertical redox gradients common

- **Oxic** groundwater throughout investigated depth range at 4 MLW clusters
- **Anoxic** groundwater underlying **oxic** groundwater at 7 of the 11 MLW clusters

➔ **Substantial denitrification potential**

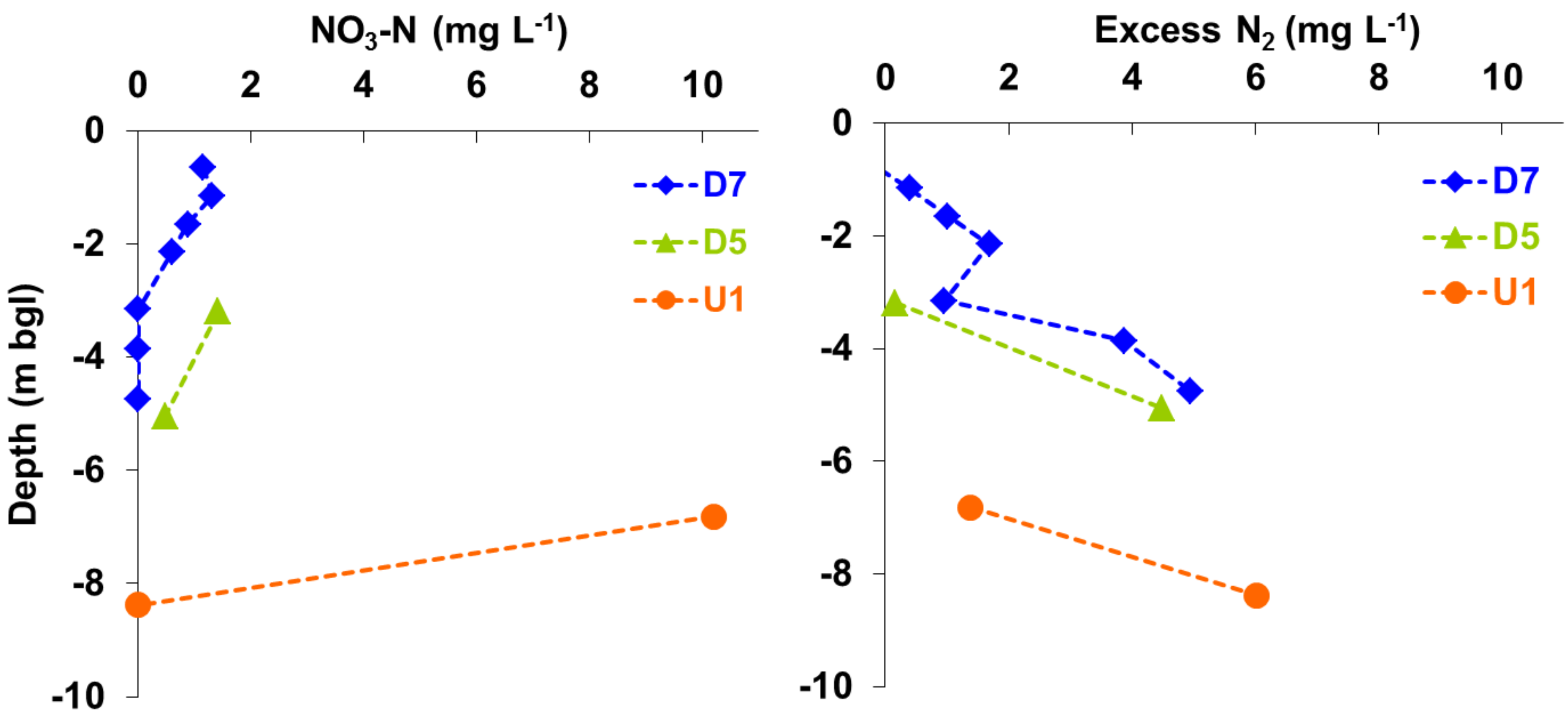
Nitrate isotopes:
Evidence for denitrification?





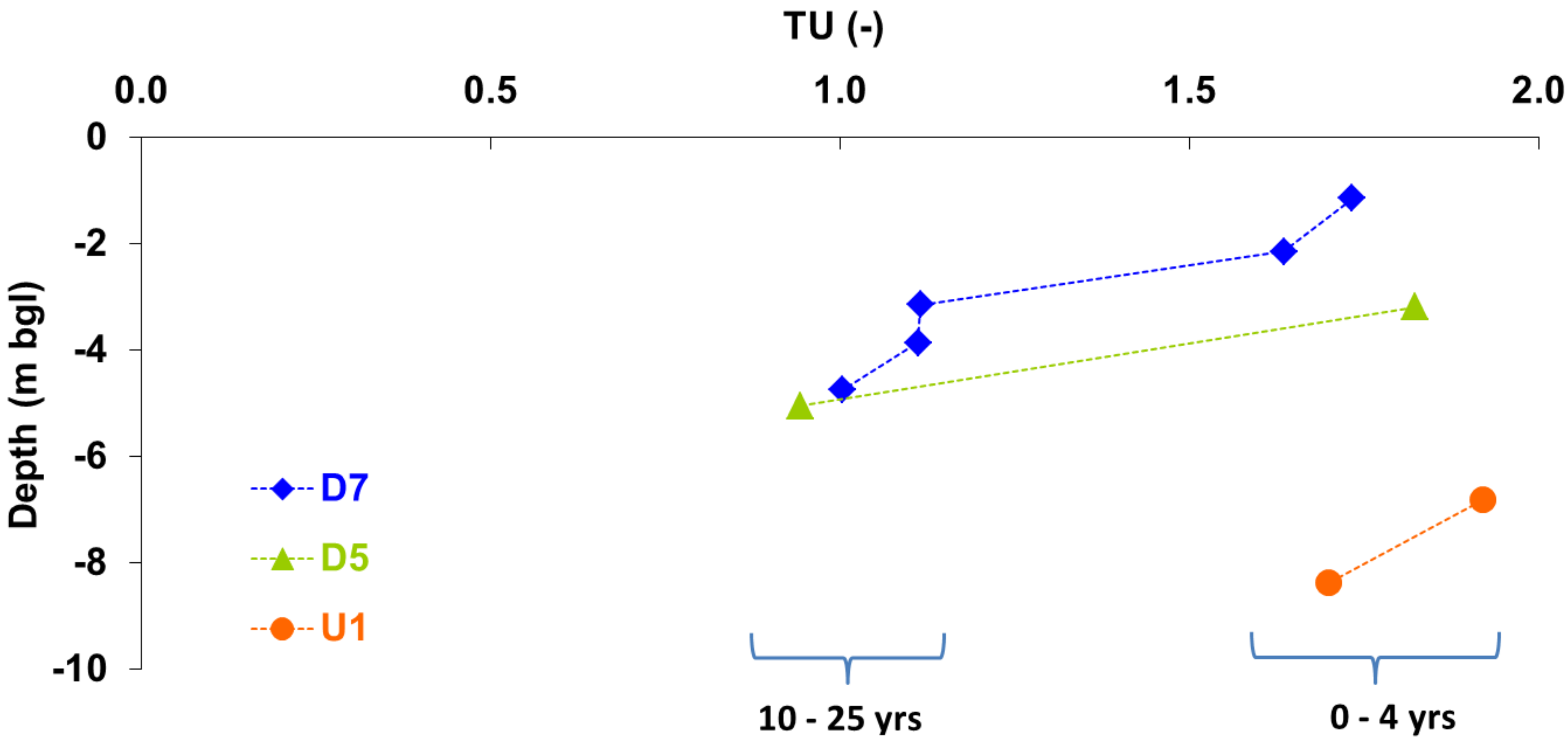
- Some data indicate denitrification
- Challenges: variability, measurement uncertainty at low concentrations, insufficient N mass (c.f. Clague et al., 2015)

Excess N_2:
Evidence for denitrification?



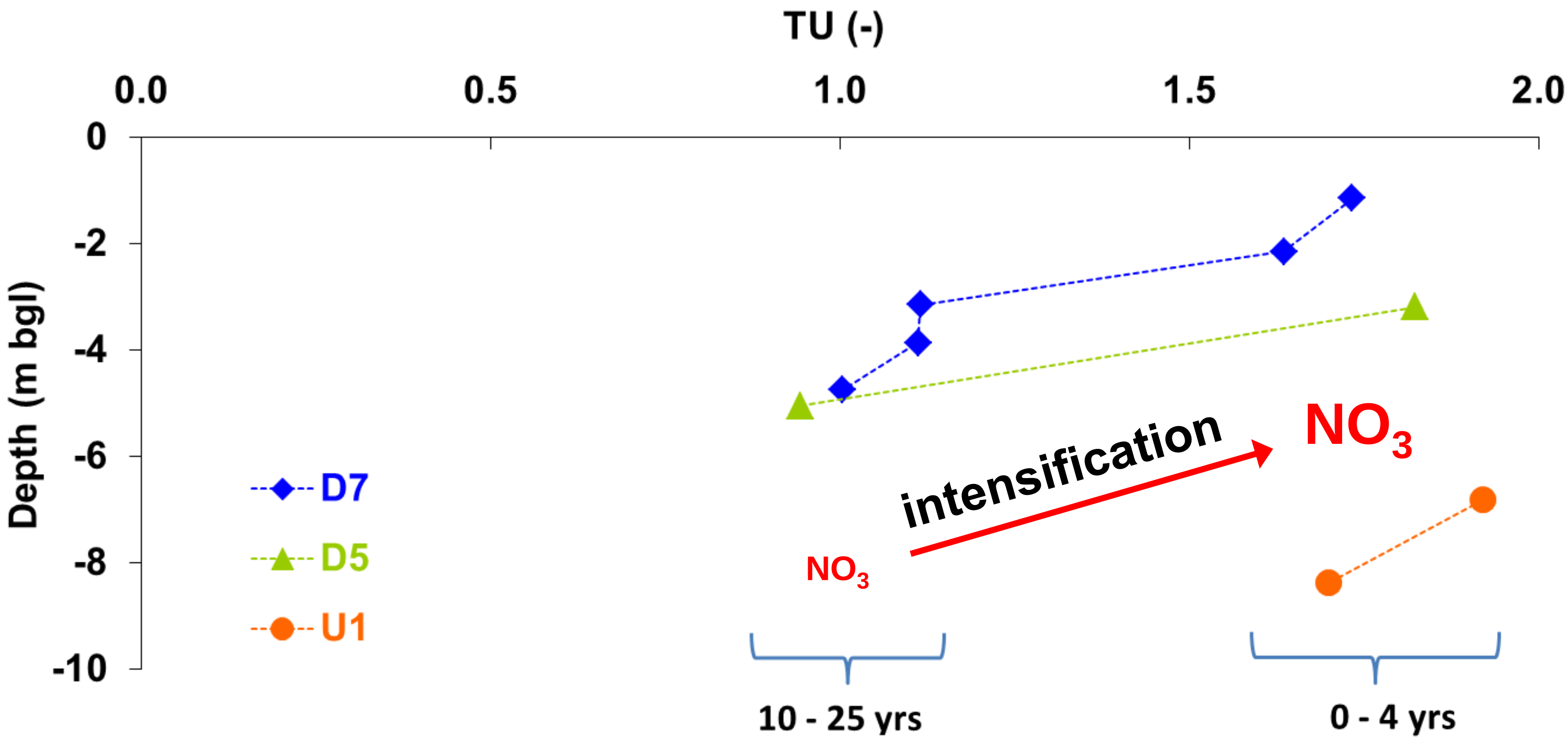
- Excess N_2 increase concurrent with NO_3-N decrease
- Challenges: uncertainty, effect of lateral flow paths, temporal variation of nitrate inputs
- Improvement: additional neon measurements

Age-dating: Tritium-based MRTs



- Subsurface Mean Residence Times (MRTs) derived from tritium
- Exponential-piston flow model with 50% mixing applied

Age-dating: Multiple benefits



- Land use history: minimum nitrate conc. of land surface recharge
- Hydrology: impeded vertical flow through Palaeosols
- Redox : oxic conditions restricted to young water

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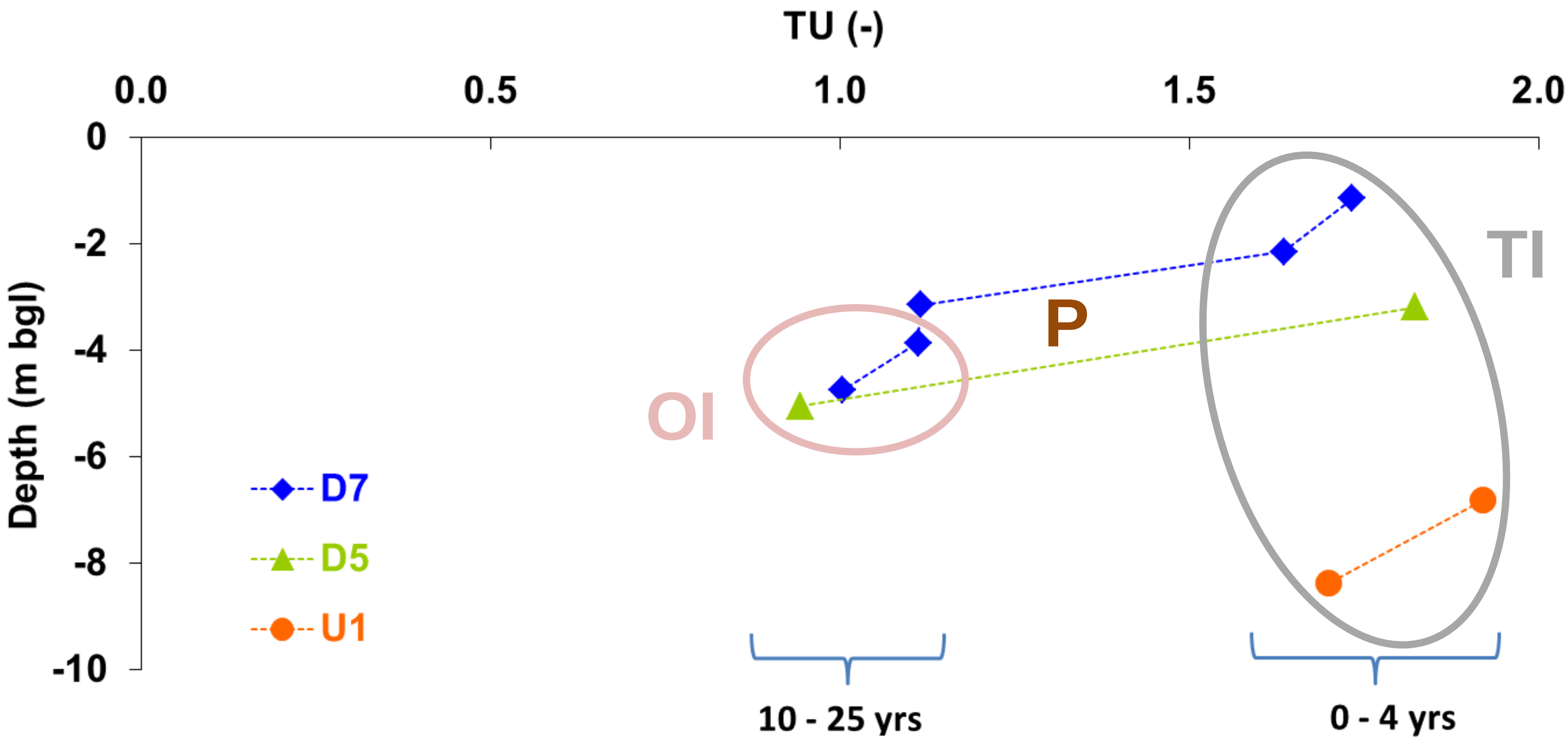

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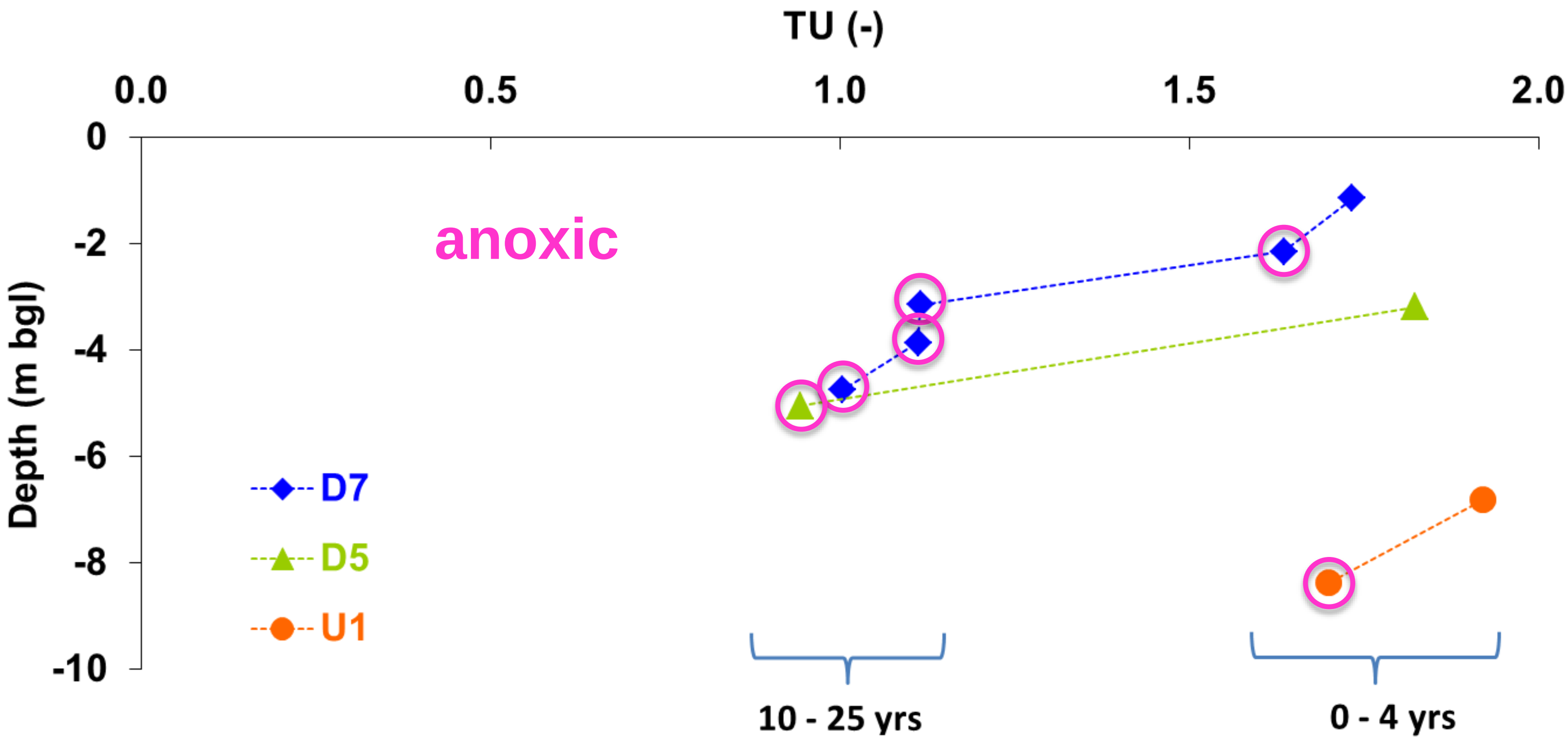

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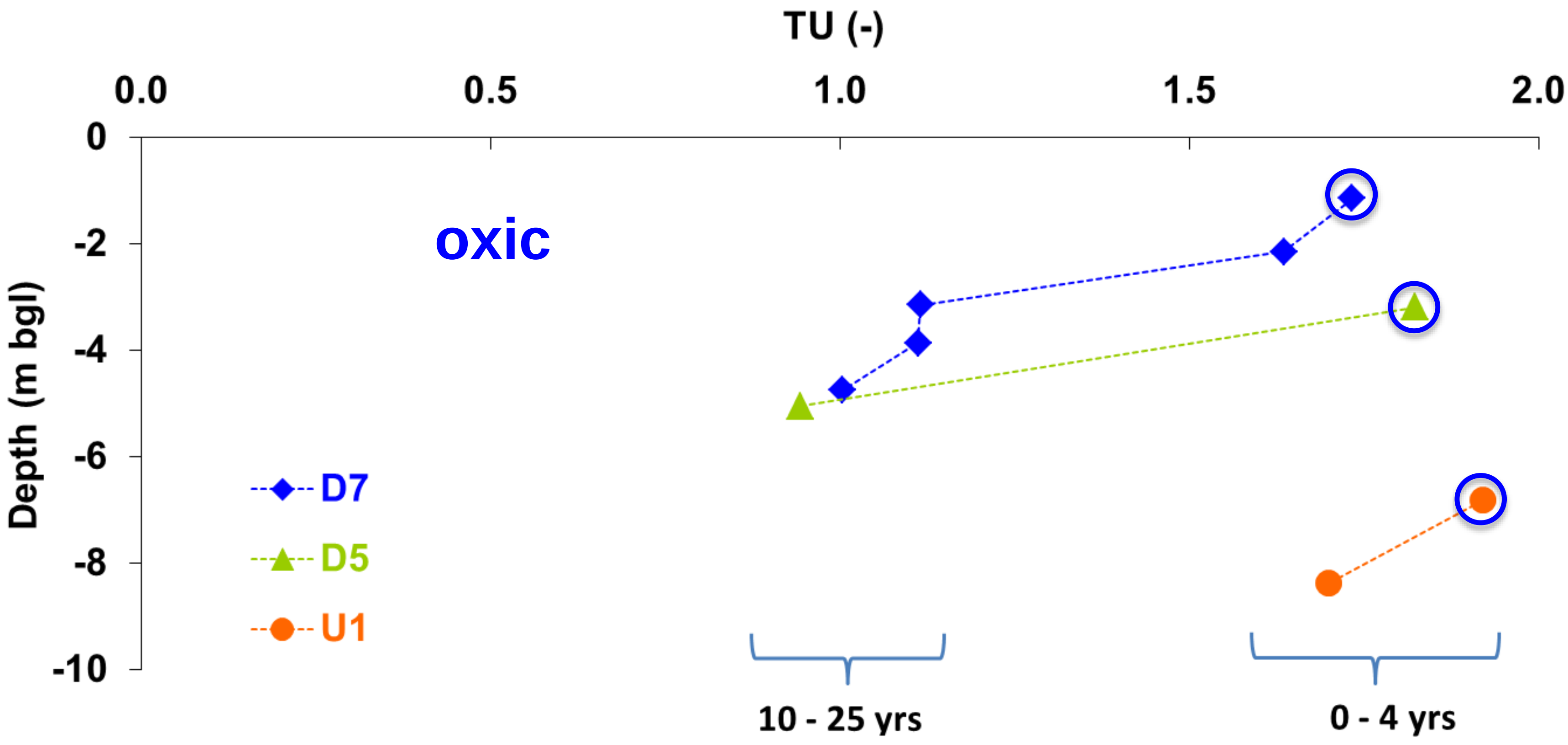

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Multi-pronged approach to elucidate nitrate attenuation

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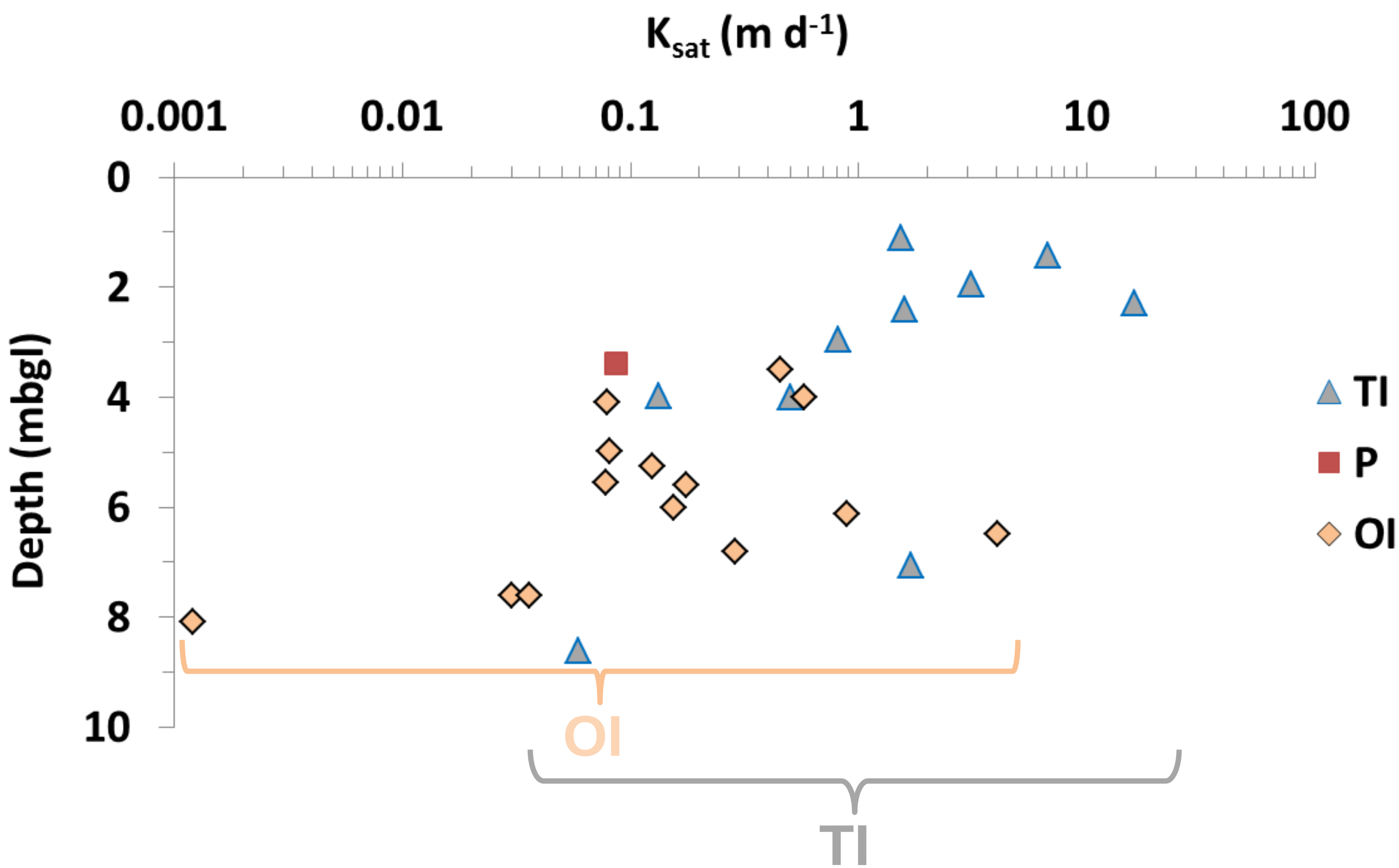
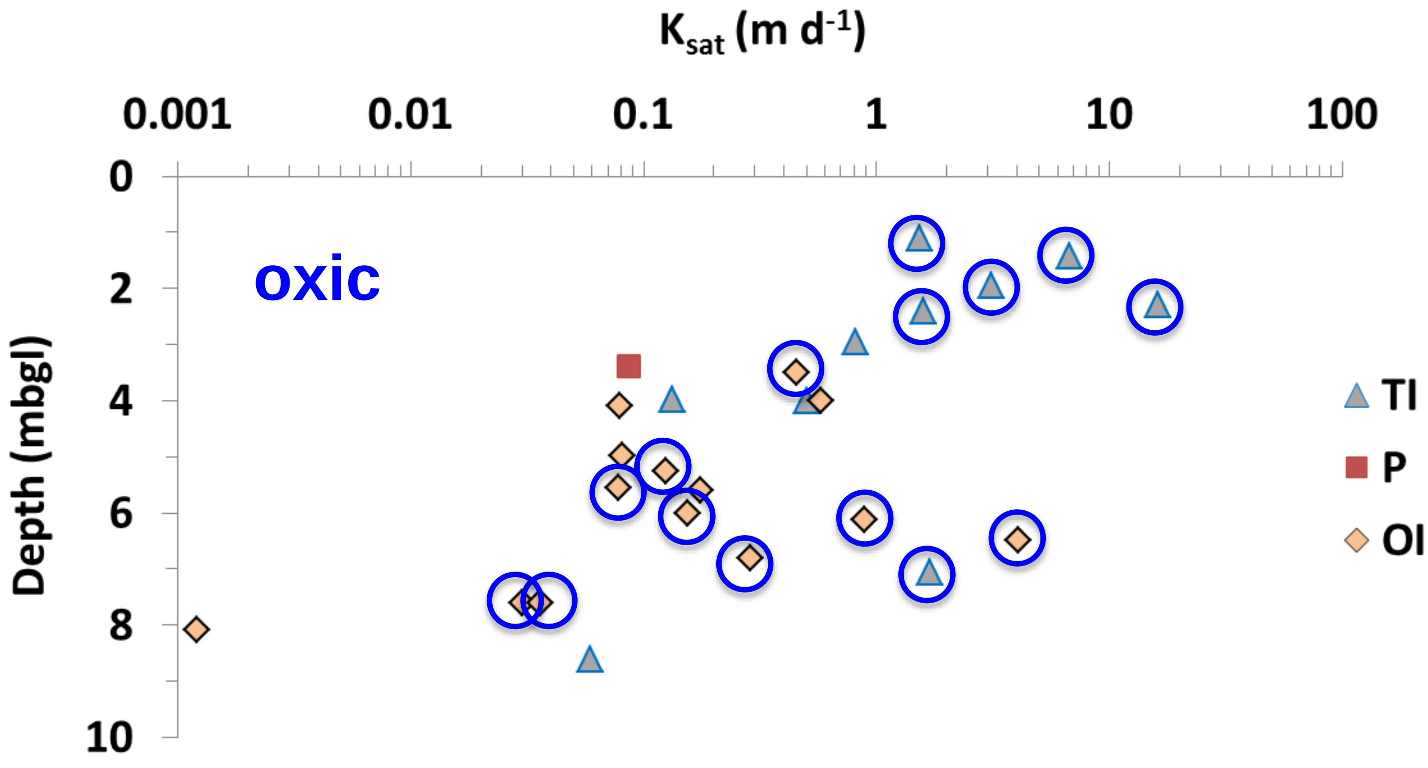
Slug tests:
In situ hydraulic conductivity



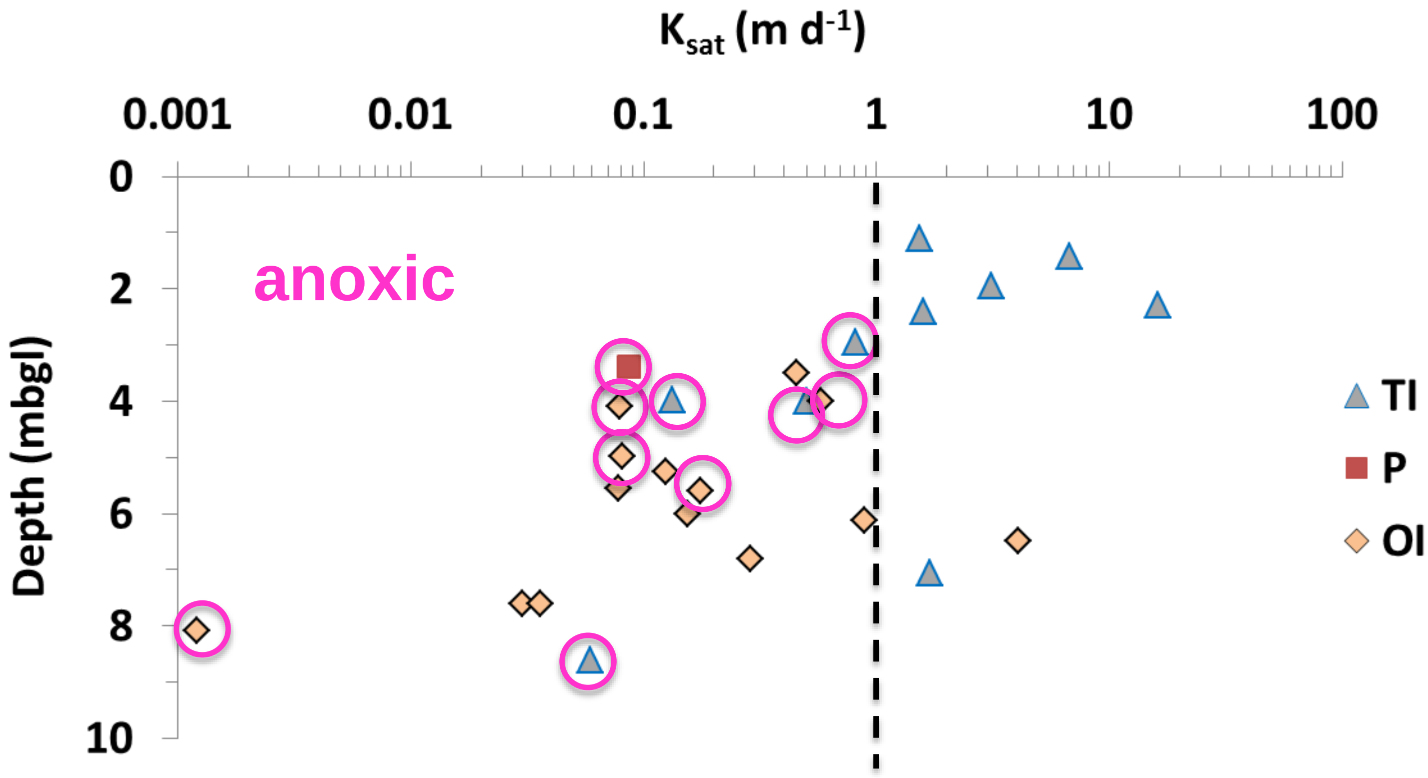
- ➢ Ksat in TI tends to be greater than in OI, but substantial variation
- ➢ Ksat generally decreasing with depth

Slug tests:
In situ hydraulic conductivity



- Oxic groundwater observed nearly across the entire Ksat range

Slug tests:
In situ hydraulic conductivity



- Anoxic groundwater observed at Ksat up to 1 m d^{-1}

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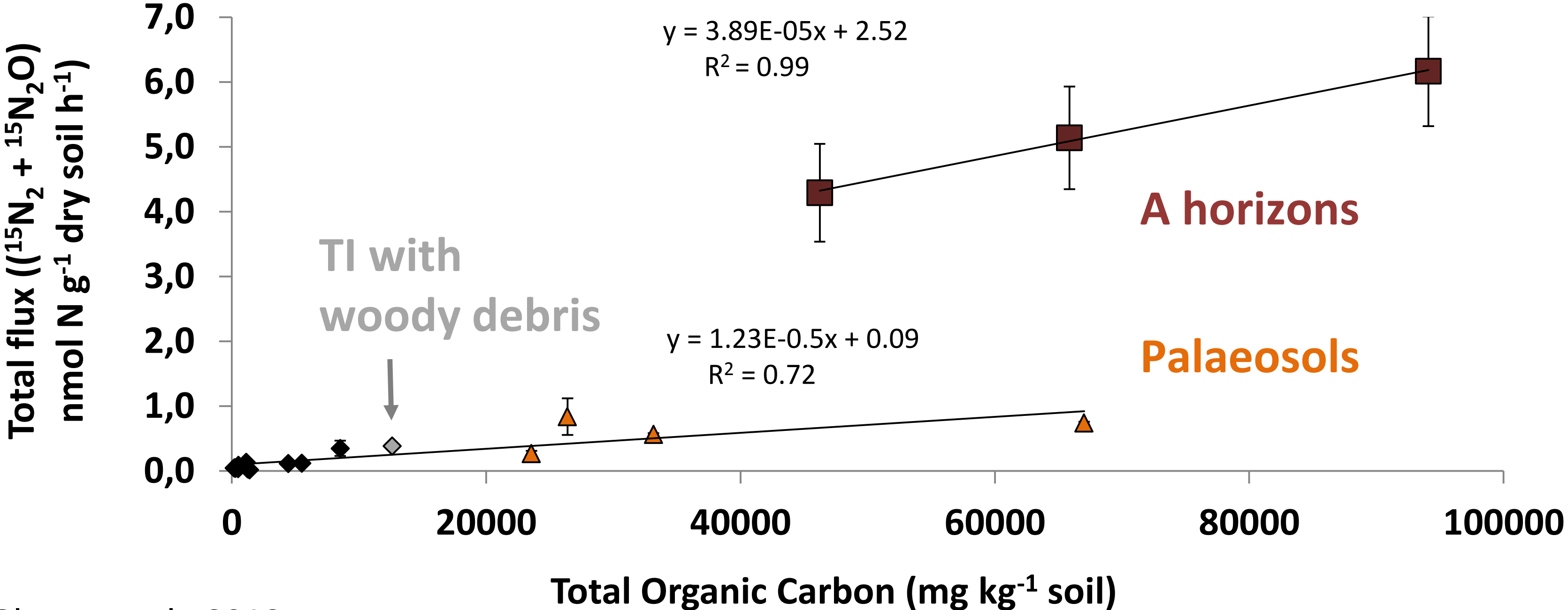
Lab incubations:
Electron donor identification



Clague et al., 2013

- Palaeosols (and woody debris) fuelling denitrification
- Lower rates than in A horizon: C quality, microbial constraints
- Rates still high enough to attenuate root zone losses

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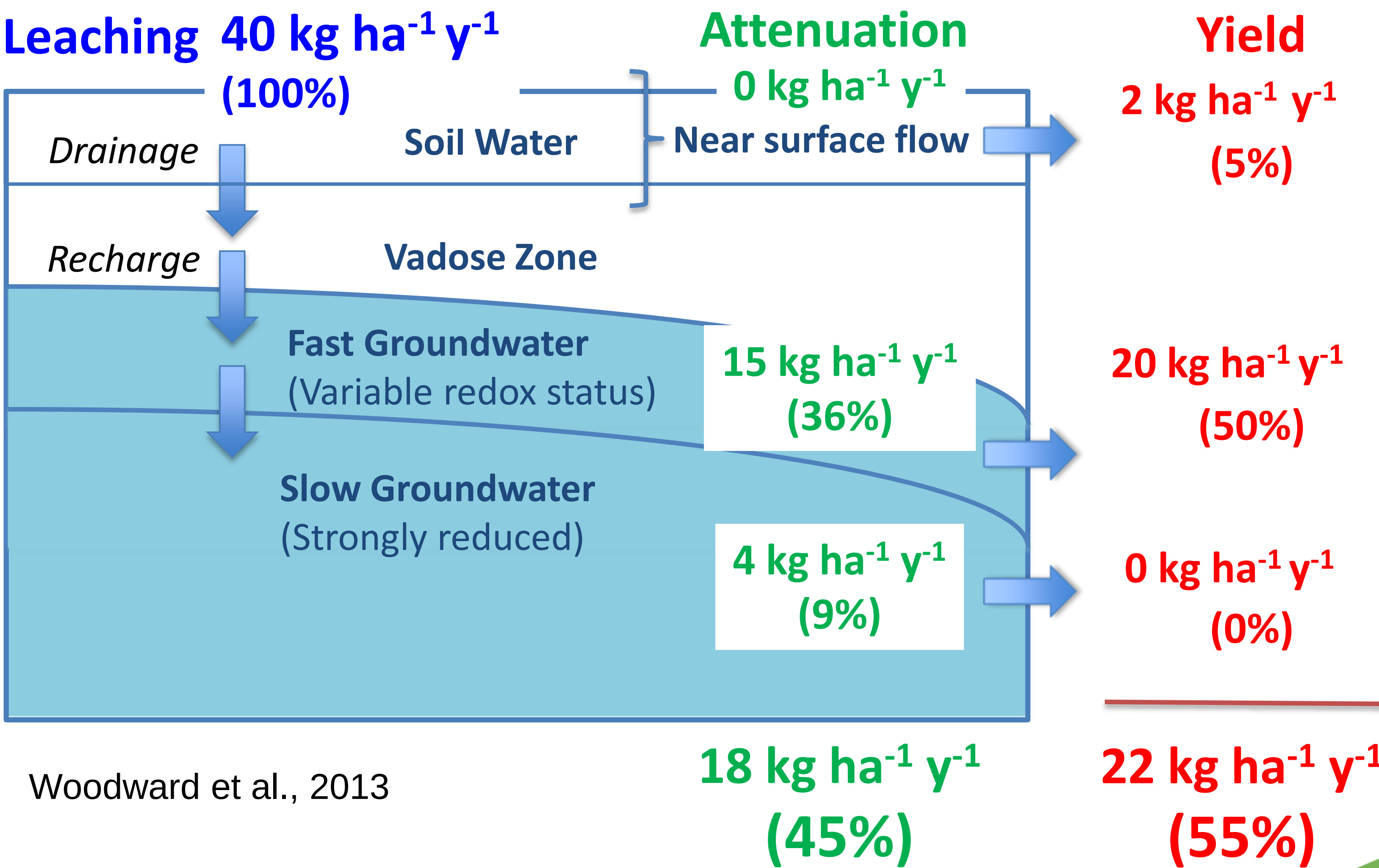
Synthesis: Toenepi catchment

15 km², intensive dairying



Woodward et al., 2013

THANK YOU

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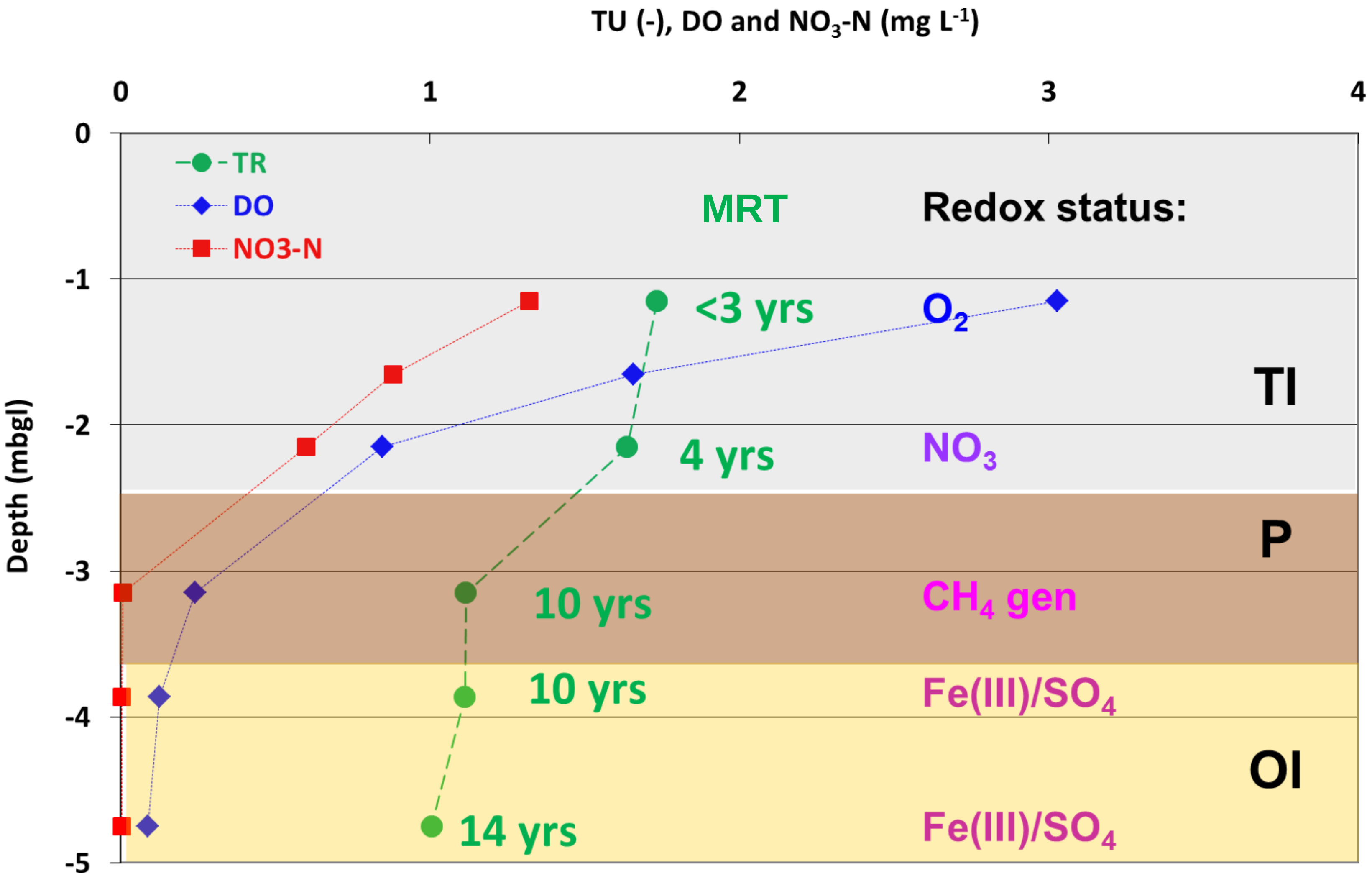
MEASURE. MODEL. MANAGE.

Age-dating: Chemistry vs. MRT



Pragmatic starting point for resource users/managers:

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