Nitrate contamination of shallow groundwater in Alberta

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Introduction

- Providing sufficient amounts of high-quality water is of key importance for Alberta's economic future development.

- In regions of Alberta where surface water is fully allocated, the question arises to what extent groundwater can be used to supplement the availability of high-quality water to sustain current and future economic growth.

- Groundwater also frequently contributes to the water balance of lakes and may be a source of nutrients such as nitrate.

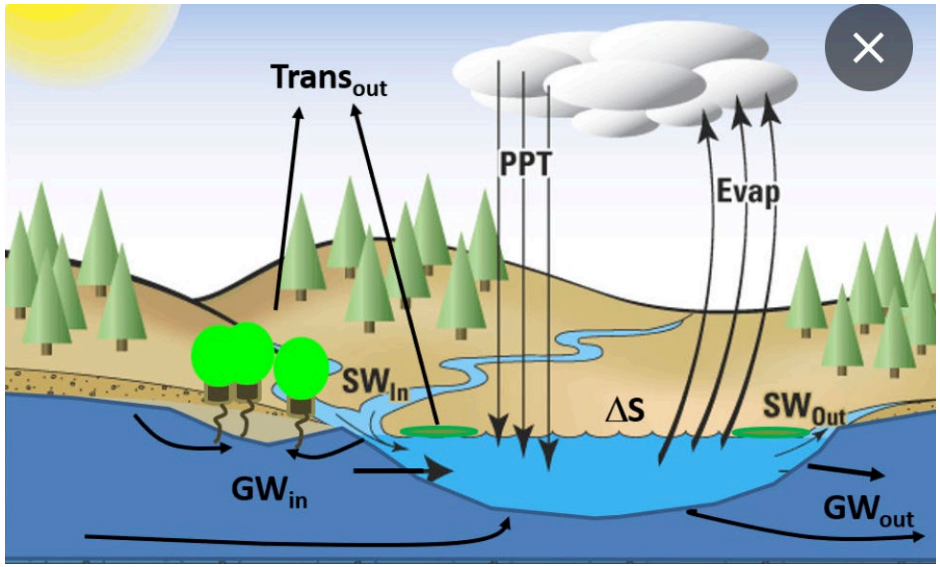

Figure: Water budget components of a flow-through lake (from: Woessner, 2020)

Introduction

- Knowledge about the quality of Alberta's groundwater is still in its infancy

- Key questions include:
  - what natural processes control groundwater quality?
  - are there regional patterns?
  - are there any noticeable anthropogenic impacts on groundwater quality (e.g., nitrate)?

- If so, do nutrients in groundwater affect surface waters including lakes?

Figure: Lake in British Columbia affected by excess nutrient loading

Objectives

- To summarize the current understanding of groundwater quality in Alberta on a province-wide scale
- Review the occurrence of nitrate in Alberta groundwater
- Determine the sources of groundwater nitrate
- Evaluate the fate of nitrate in groundwater dependent on redox environment

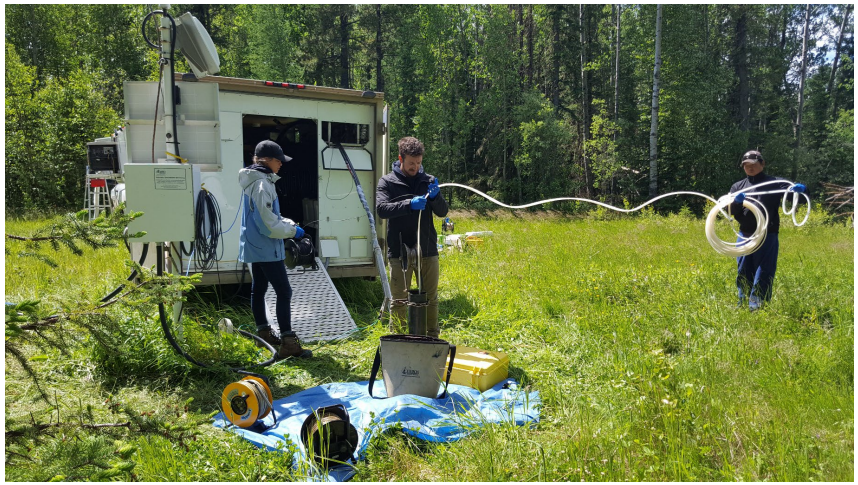

Figure: Groundwater sampling conducted by a team from Alberta Environment & Parks (AEP)

Groundwater Quality in Alberta
Data Sources

- Groundwater samples for water quality assessment have been collected by various government programs including AHS, GOWN, BWWT, AWWID, AGI and others for several decades;

- We have amalgamated groundwater quality data from 5 major sources and conducted a rigorous QA/QC analysis

- Over 131,000 groundwater samples are represented in the unified data base

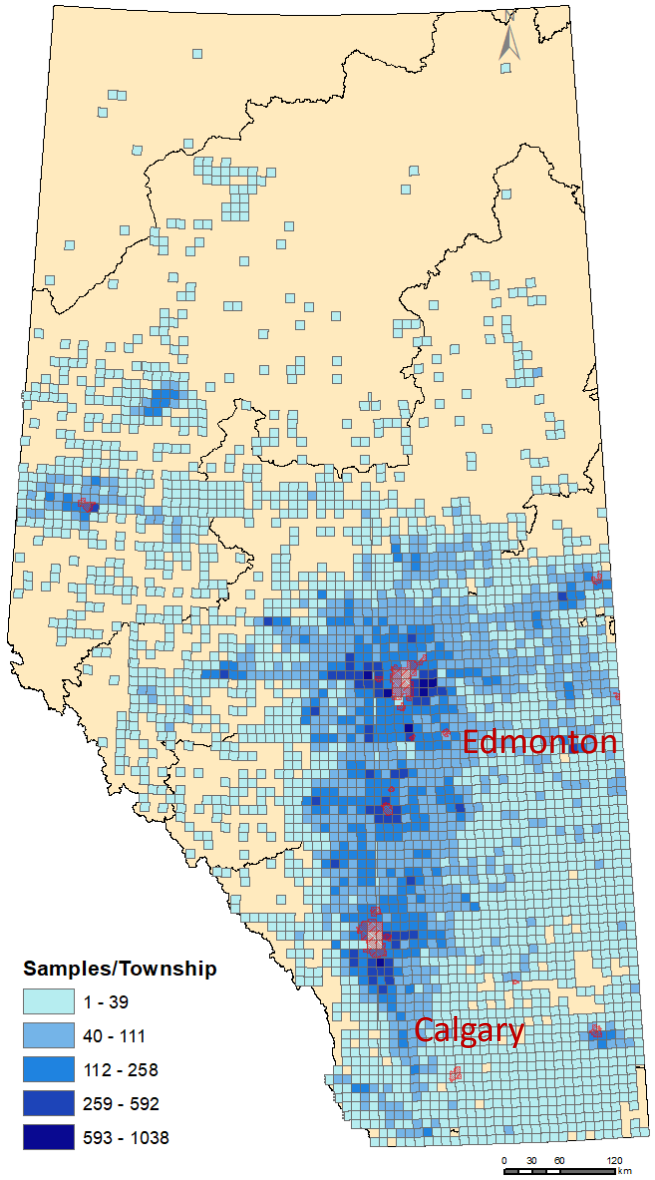

Figure: Number of groundwater quality Samples per township in unified database

Groundwater Quality in Alberta

Parameters

Field Parameters:	temperature, pH, dissolved O_2, (EC, ORP)
Major cations:	Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}
Major anions:	HCO_3^{-}, SO_4^{2-}, Cl^{-}
Nutrients:	NO_3^{-}, NH_4^{+}, PO_4^{3-}
Minor and trace elements:	*e.g.,* F, Mn, Fe, As, Se many others
Dissolved & free gases:	methane *(*CH_4), ethane (C_2H_6) etc.
Stable isotope compositions	water, DIC, nitrate, sulfate, methane
Age-dating	tritium, C-14, Kr-81: select samples only

> 50 parameters per sample;
→ more than 6 million parameters

> 130.000 samples passing QA/QC tests (electroneutrality)

Groundwater Quality in Alberta
Total Dissolved Solids (TDS)

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TDS = sum of major cations (**Ca^{2+}, Mg^{2+}, Na^{+}**) and major anions (**HCO_3^-, SO_4^{2-}, Cl^-**) measured in mg/L

Indicates **salinity** of the groundwater:

< 1000 mg/L freshwater: 65%
1000-4000 mg/L: 34%
> 4,000 mg/L saline gw: 1%

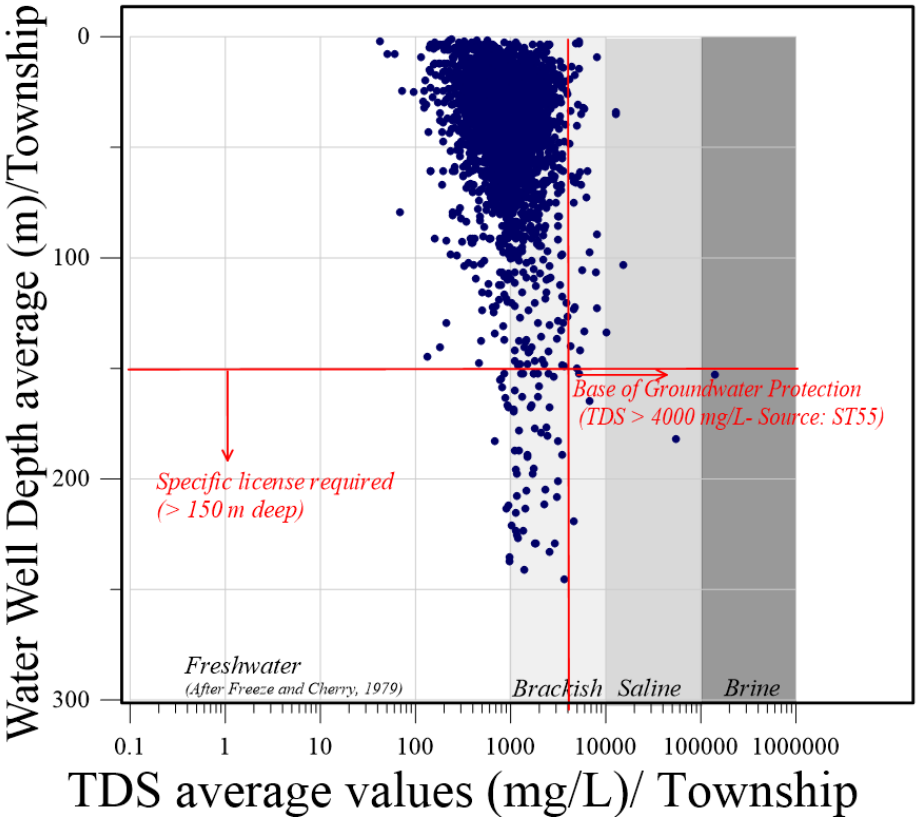

Figure: Average TDS contents of groundwater versus average well depth per township

Groundwater Quality in Alberta

Major groundwater types

Ca (Mg) – HCO_3 water type

→ carbonate dissolution

→ freshly recharged

Na – HCO_3 water type

--> More evolved/older groundwater

Na – HCO_3/SO_4 water type

→ Evolved and mixed groundwater

Na – Cl water type

--> Saline water type

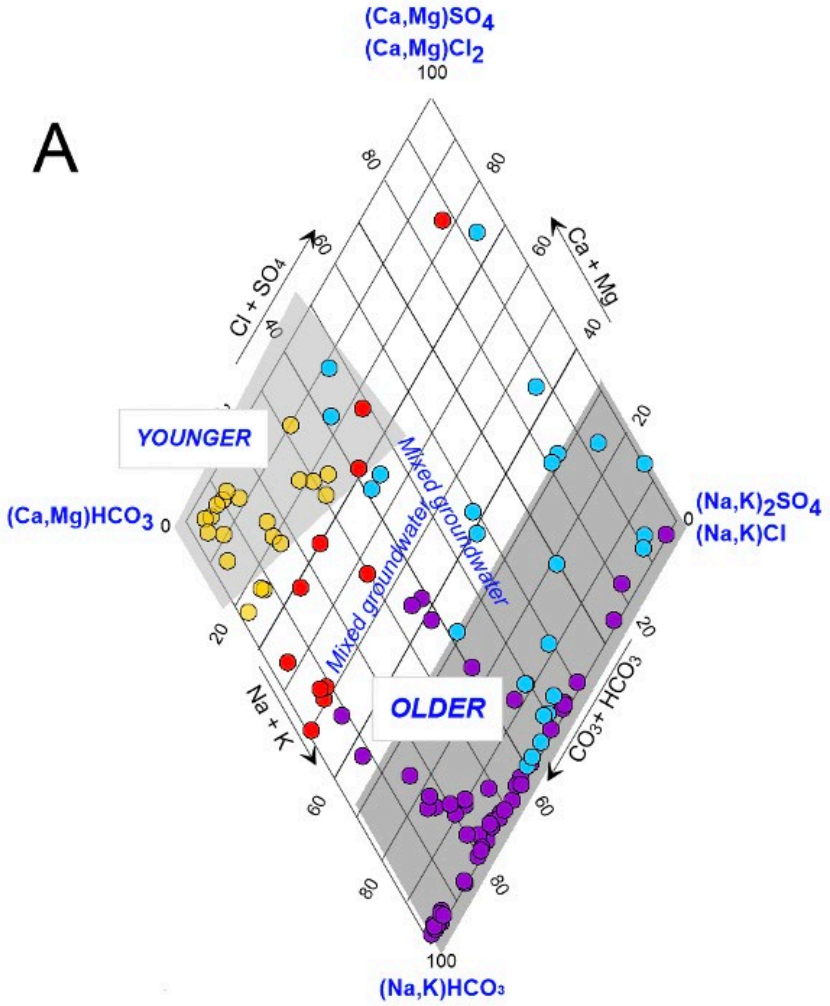

Figure: Piper diagram showing key groundwater types

Groundwater Quality in Alberta
Groundwater types and salinity trends

Groups	Dominant water-type	Average TDS (mg/L)	Percentage
Alkaline earth - HCO_3	Ca-Mg-HCO_3	418	15%
Na-HCO_3	Na-HCO_3	799	48%
Na- mixed anions	Na-HCO_3-SO_4	1298	27%
Na-SO_4	Na-SO_4	2311	9%
Na-Cl	Na-Cl	3363	2%

Regional Groundwater Quality in Alberta
Total dissolved solids (TDS)

- Low TDS mainly in western foothills region;
- Elevated TDS especially in SE corner of the province

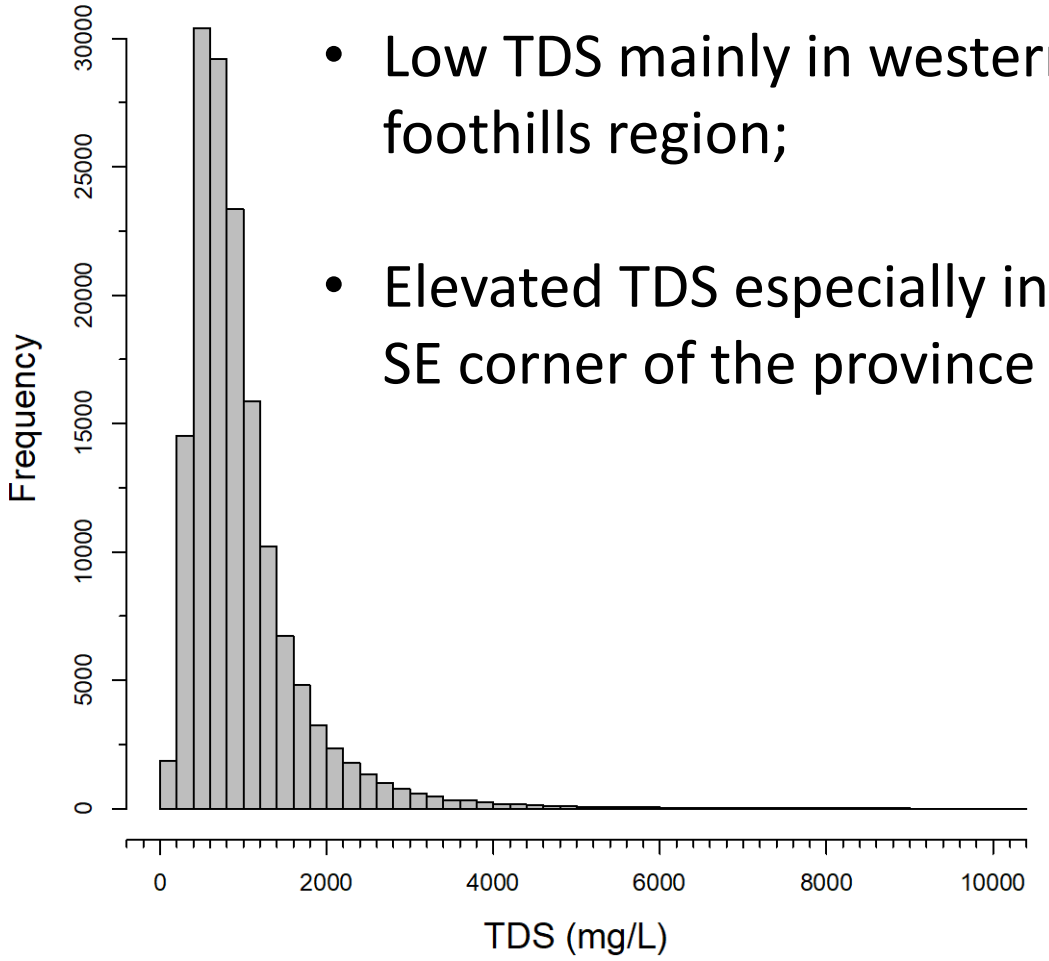

Figure: Frequency distribution of TDS contents in groundwater

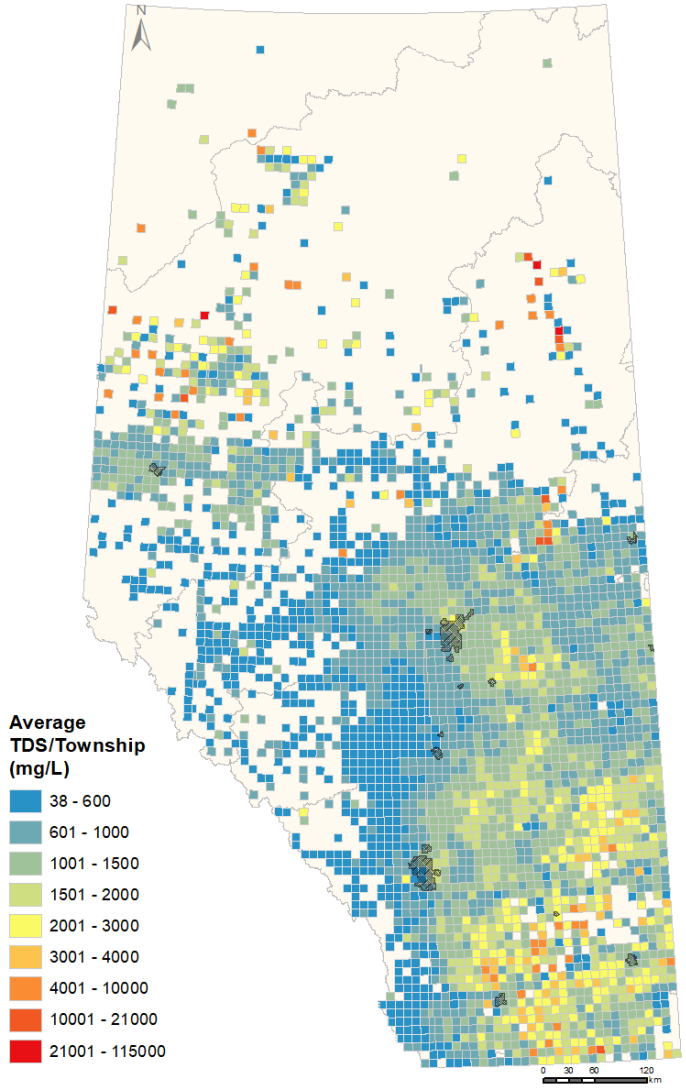

Figure: Regional map of average TDS contents in groundwater per township

Regional Groundwater Quality in Alberta

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Ca

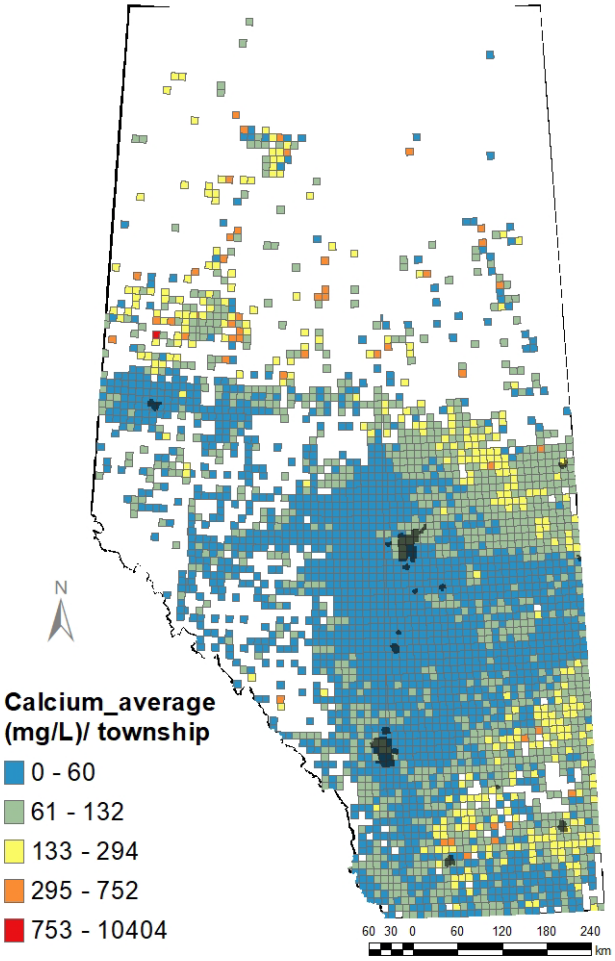

Figure: Regional map of average Ca concentrations in groundwater per township

Na

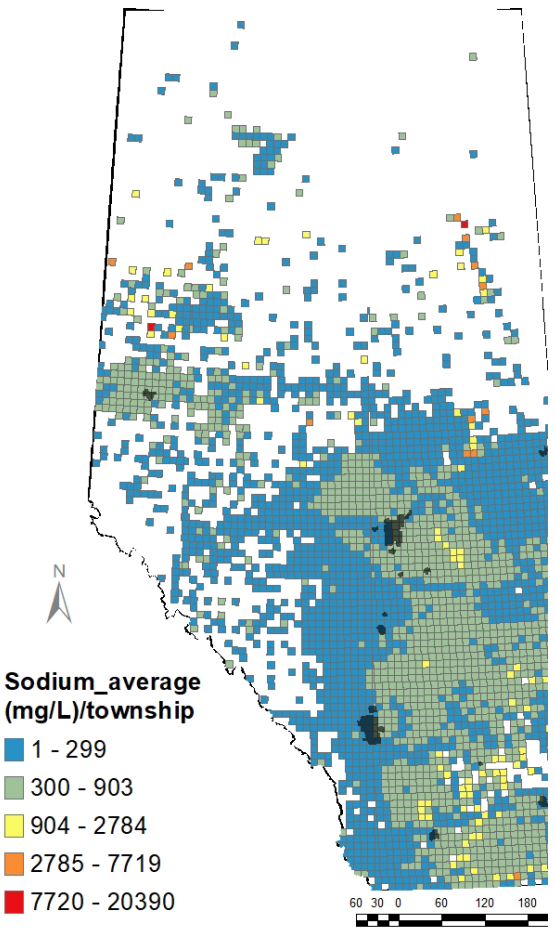

Figure: Regional map of average Na concentrations in groundwater per township

HCO_3^-

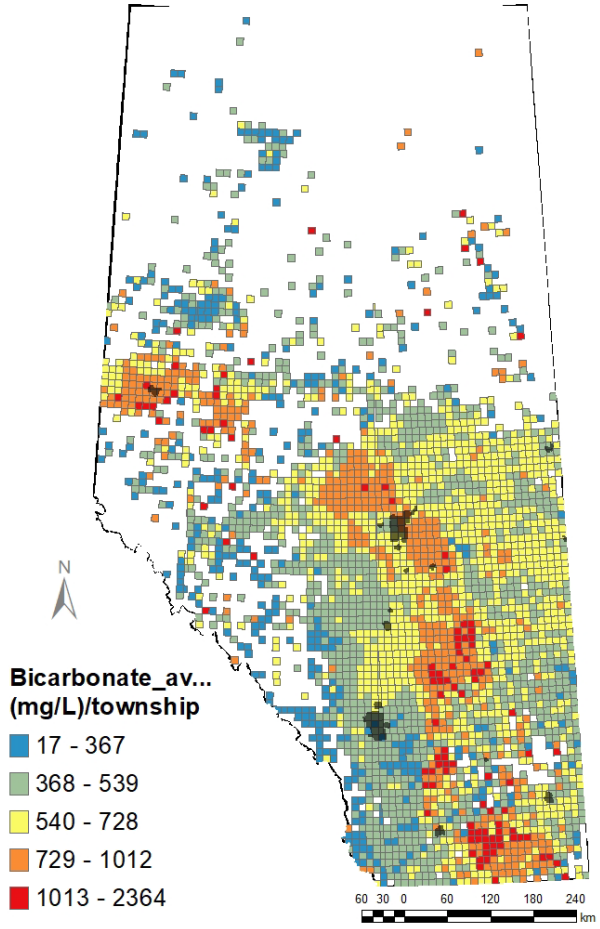

Figure: Regional map of average HCO_3^- concentrations in groundwater per township

Regional Groundwater Quality in Alberta
Nitrate

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- Excessive nitrate is a concern in drinking water (e.g., health effects such as blue baby syndrome, among others)

- WHO and Health Canada require < 10 mg/L NO_3-N in drinking water (= maximum allowable concentration or MAC)
- Excessive nutrients including nitrate can cause eutrophication in surface waters
- Hypoxia (low oxygen) in coastal waters → fish kills

Figure: Eutrophication in irrigation canals in Alberta and Lake Winnipeg, Manitoba

Alberta: Nitrate in Groundwater

- Reviewed circa 90,000 groundwater quality records
- In 65% of groundwater samples, nitrate is below the detection limit
- The maximum allowable concentration (MAC) of 10 mg/L for nitrate-N is exceeded in 3% of samples

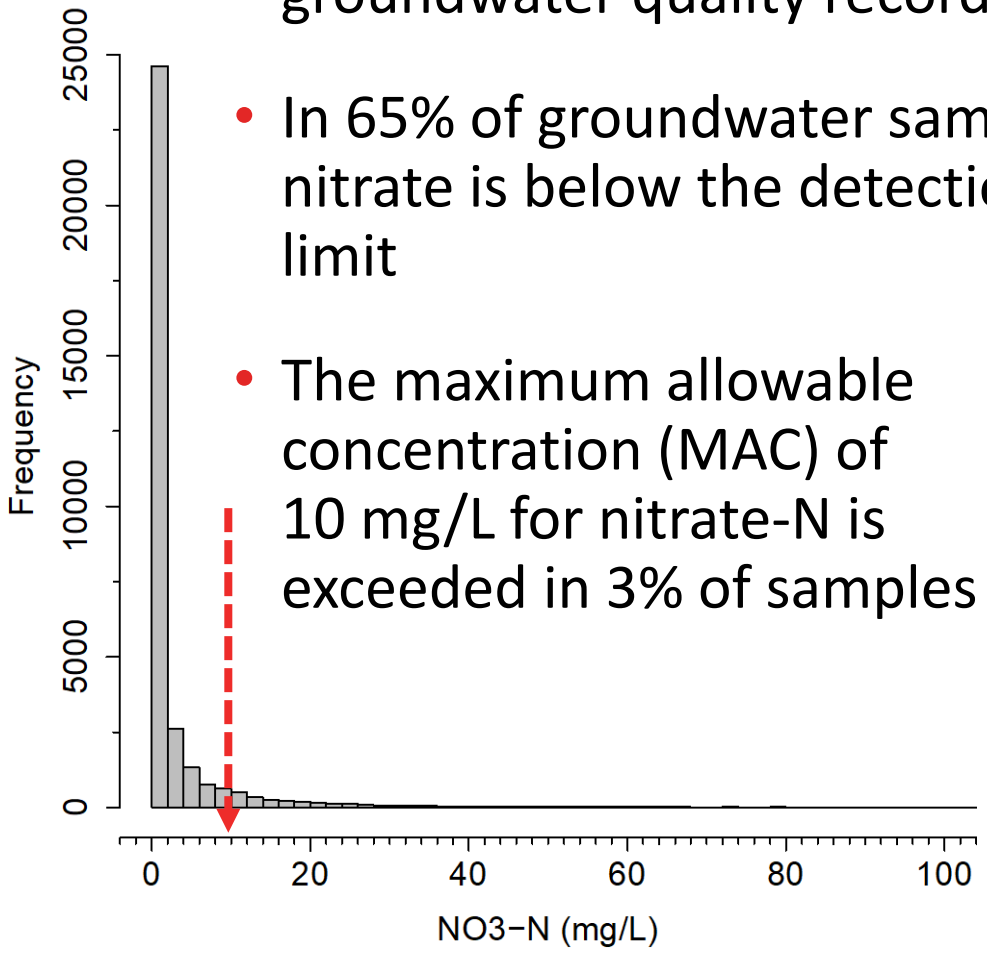

Figure: Frequency distribution of NO_3-N concentrations in groundwater

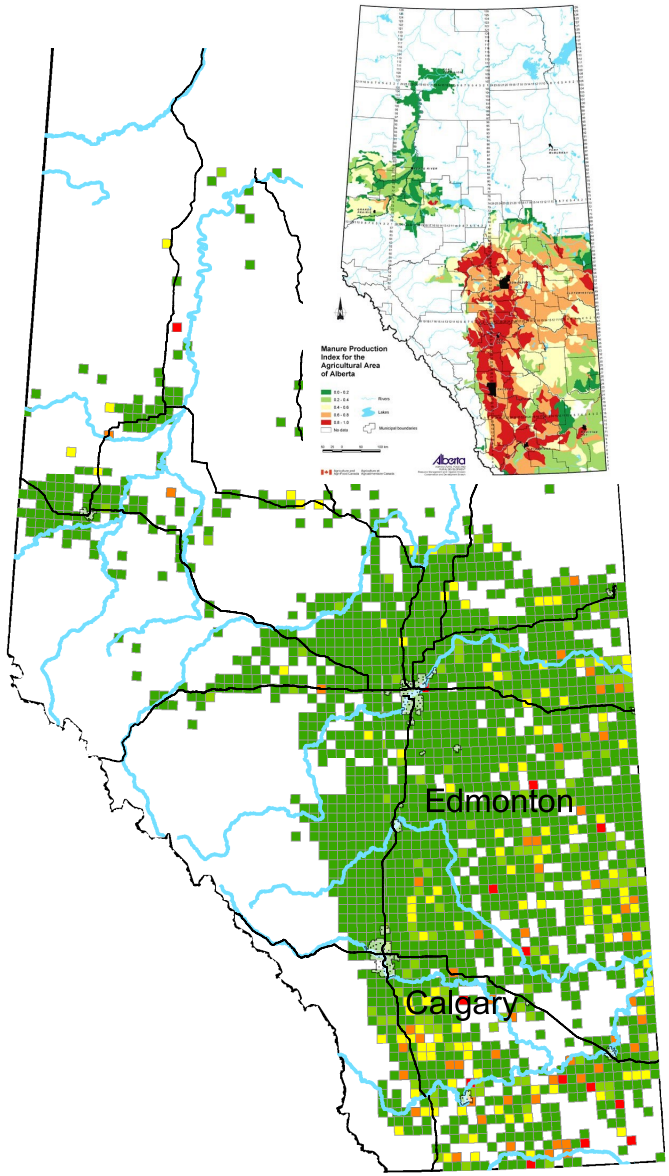

Figure: Map of average NO_3-N concentrations in groundwater per township

Alberta: Nitrate in Groundwater vs. depth

- Elevated nitrate concentrations predominantly observed in:
  - shallow groundwater (<50 m)
  - areas with agricultural landuse

→ How can we identify the sources of nitrate in groundwater?

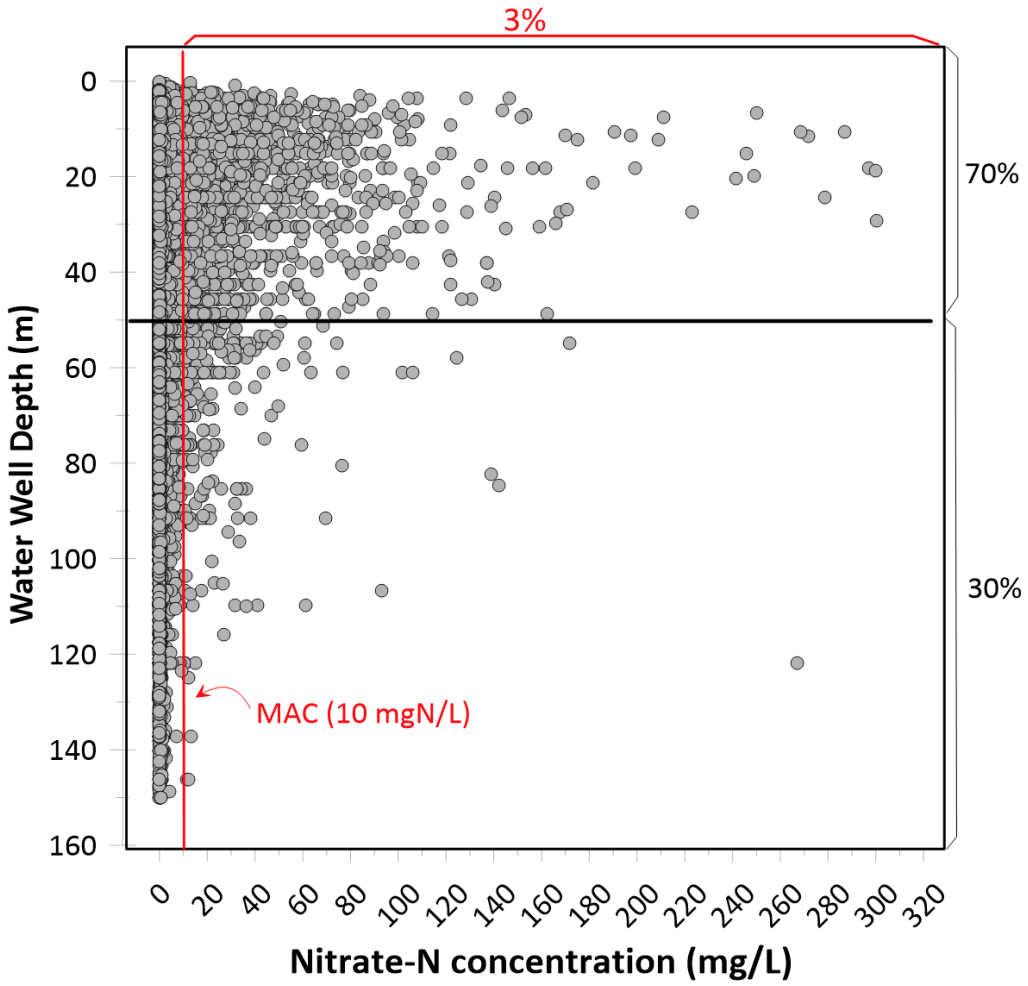

Figure: Nitrate-N concentrations in Alberta groundwater versus well depth

Sources of Nitrate in Alberta Groundwater

Potential Nitrate Sources

- Atmospheric deposition
- nitrification in soils
  ($N_{org} \rightarrow NO_3^-$)
- synthetic fertilizers
- manure (e.g., from cattle)
- waste water effluents and septic systems

Sources of Nitrate in Alberta Groundwater
Stable Isotope Ratio Measurements

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Isotopic composition by isotope ratio mass spectrometry

$$\delta^{15}N\ [‰] = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard}}{(^{15}N/^{14}N)_{standard}} \times 1000$$

$$\delta^{18}O\ [‰] = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \times 1000$$

Sources of Nitrate in Alberta Groundwater

Isotopic Fingerprinting of Nitrate Sources

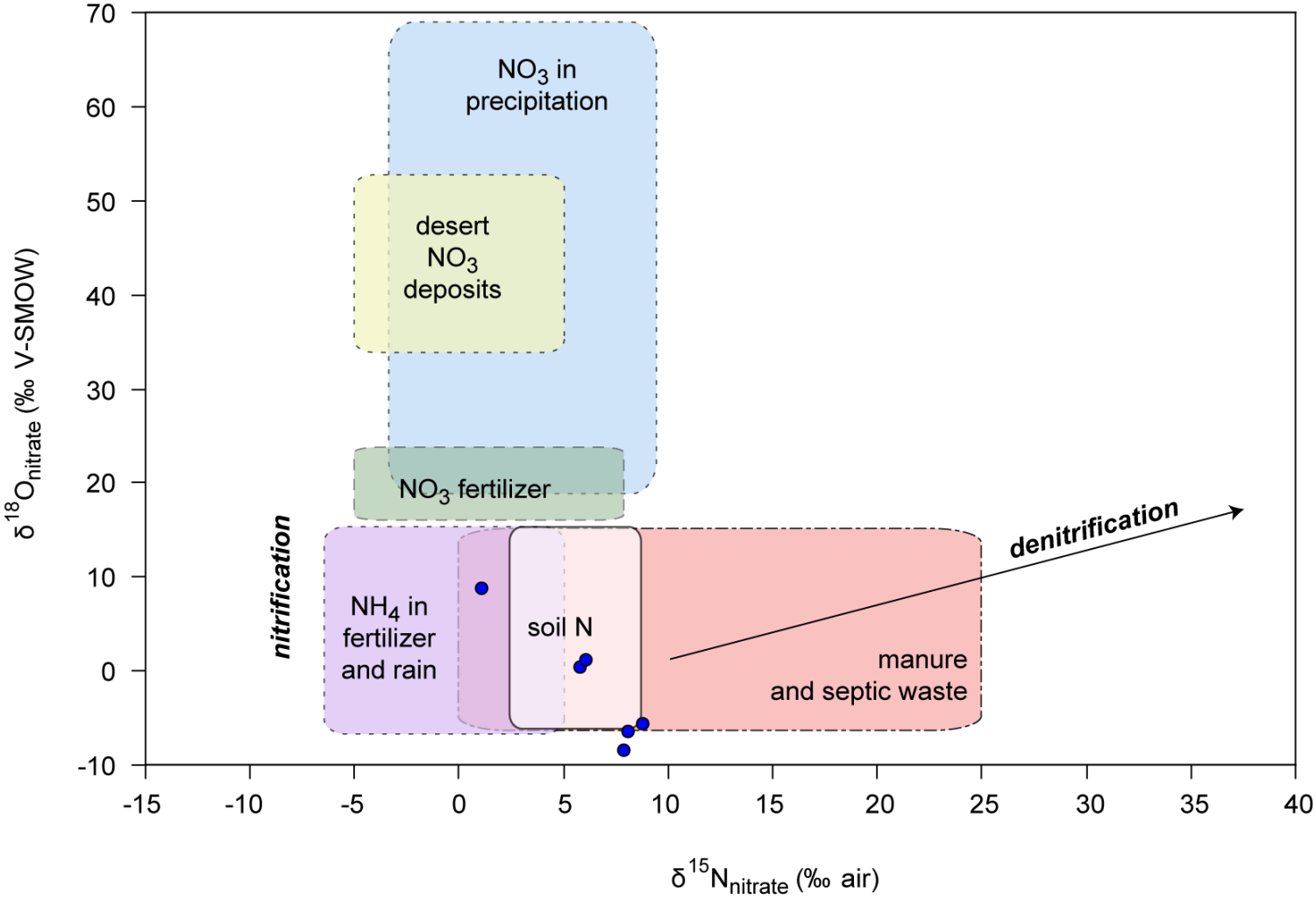

Figure: Isotopic composition of nitrate derived from different sources (from Kendall et al., 2007)

GOWN High-Quality Sampling Reveals sources and fate of nitrate

- Isotope analyses reveal that groundwater nitrate is frequently derived from manure
- In some cases, NO_3^- is derived from nitrification of soil organic N supplemented by urea and NH_4-based fertilizers
- Similar observations have been made in many other case studies in other countries or provinces

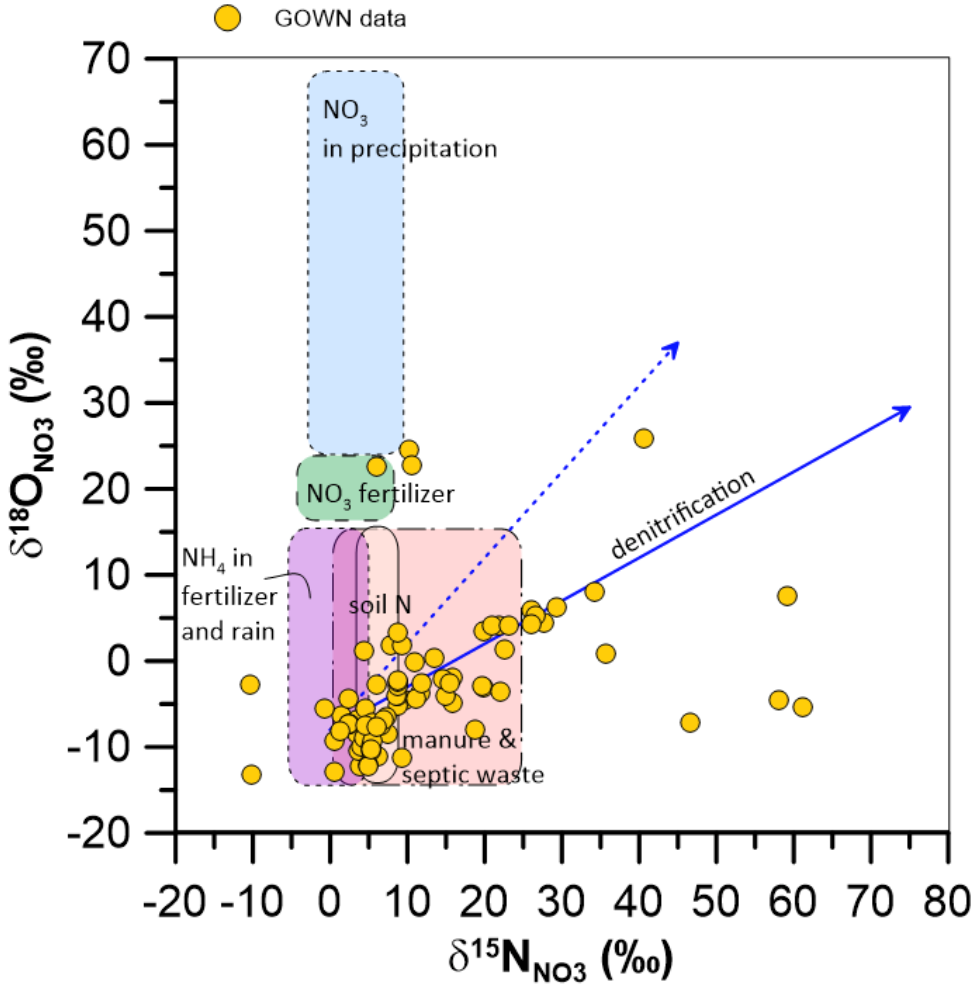

Figure: Isotopic composition of groundwater nitrate in samples from Alberta's Groundwater Observation Network (GOWN)

Sources of Nitrate in Alberta Groundwater

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- **Key Observations**

  - where groundwater nitrate occurs in high concentrations, the nitrate seems to be derived from agricultural sources (often manure-derived)

  - the majority of groundwater samples do not contain nitrate

Figure: Application of manure is solid and liquid forms

Groundwater Quality in Alberta
Redox Zones & and the Redox Ladder

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- As groundwater migrates away from the recharge zones, a systematic redox sequence is observed:

  - **post-oxic zone**
    (dissolved oxygen is first consumed, then nitrate is "denitrified")

  - **sulfidic zone** (H_2S produced)

  - **methanic zone** (CH_4 produced)

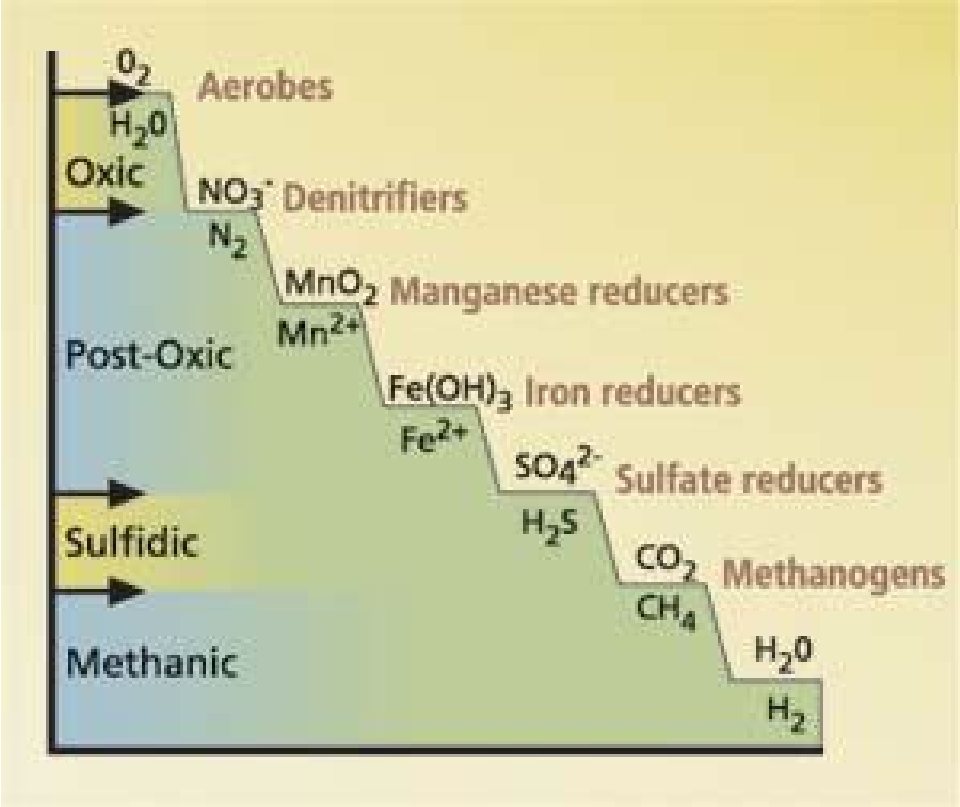

Figure: The redox ladder concept

Processes that Remove Nitrate from Groundwater

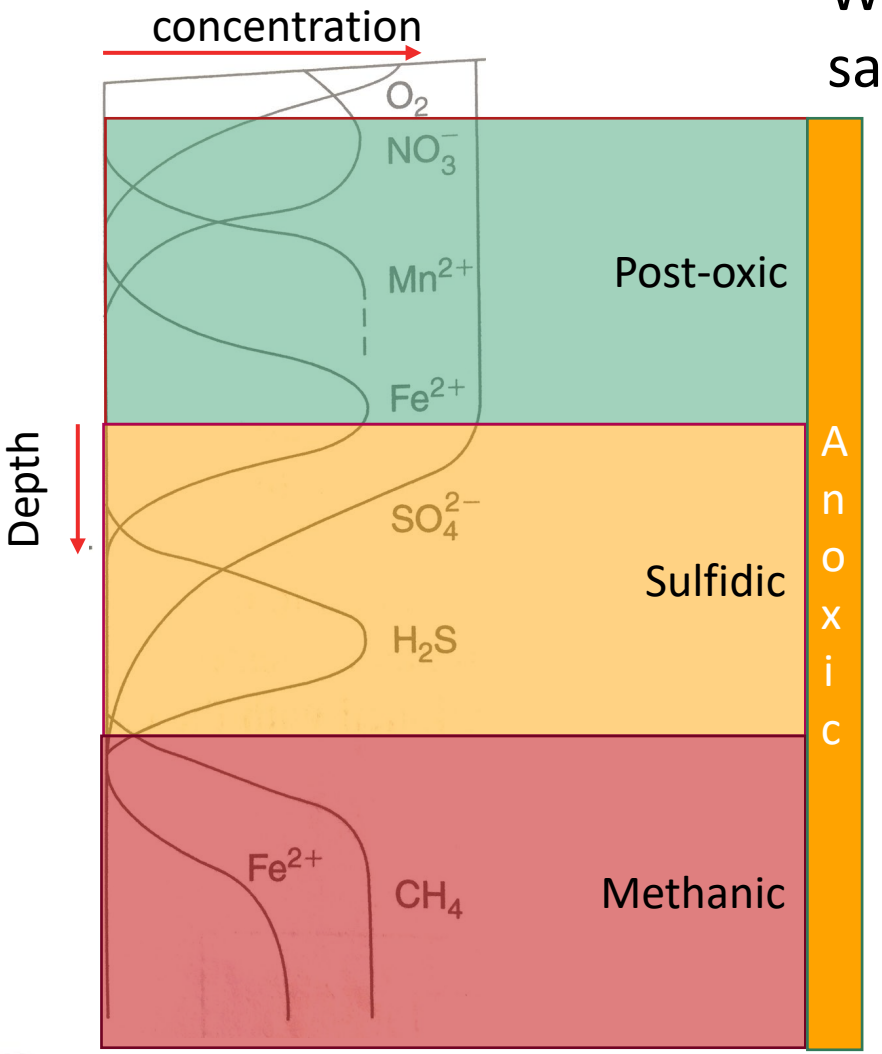

Figure: Groundwater redox zones

Why do 66% of Alberta's groundwater samples not contain nitrate?

→ gw is often too reducing

- oxic-anoxic mixture: 11%
- post-oxic: 21%
- anoxic mixture zones: 9 %

- sulfidic: 11%

- methanic: 49%

Conclusions

- Knowledge about aquifers in Alberta and the quality of the groundwater they contain is slowly emerging
- The chemical composition of groundwater is naturally evolving in space and time
- Anthropogenic impacts from agricultural activities are apparent in elevated concentrations of nitrate, often derived from manure
- Much of Alberta's groundwater is quite reducing; in these aquifers, denitrification is an effective nitrate removal process

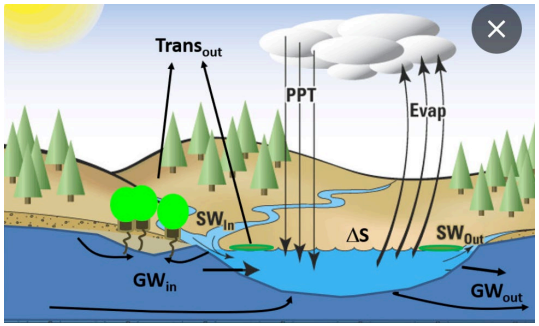

Figure: Water budget components of a flow-through lake (from: Woessner, 2020)

- To what extent groundwater (and its nutrients) impact lakes in Alberta needs to be evaluated on a case by case basis

Acknowledgements

Contact: bmayer@ucalgary.ca

Regional Groundwater Quality in Alberta
Redox Zones & and the Redox Ladder

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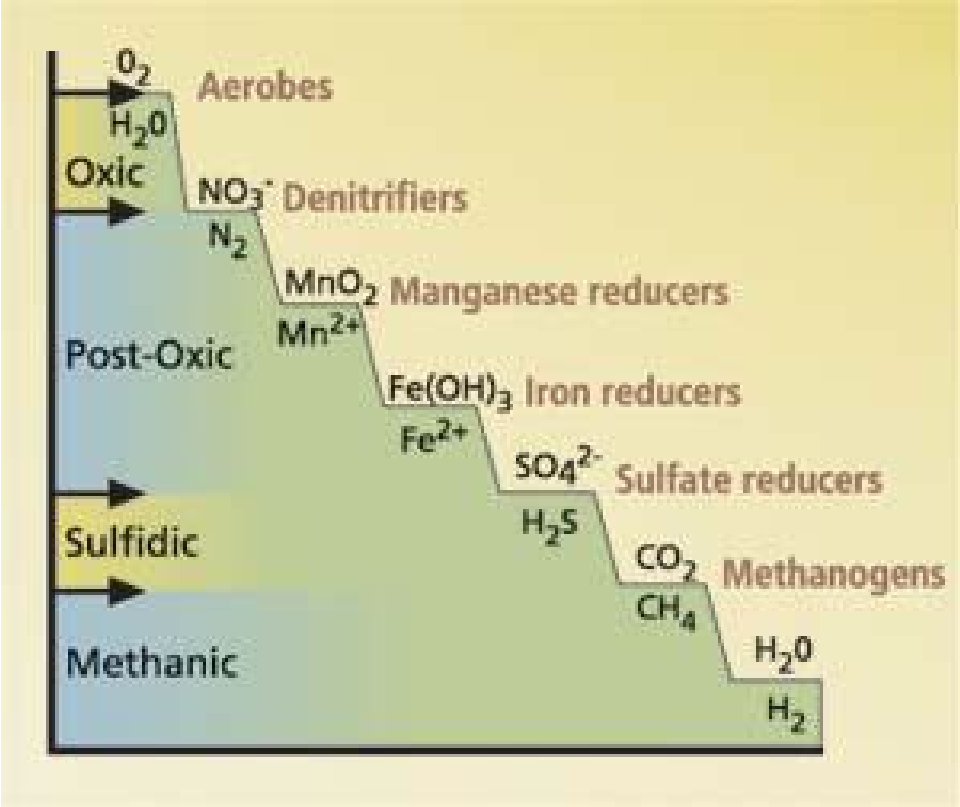
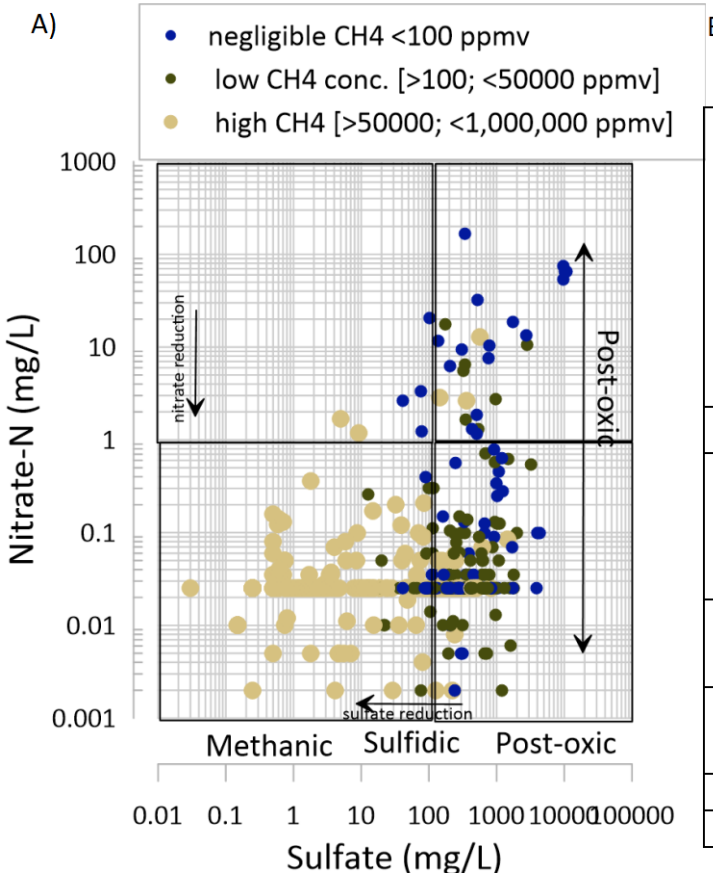


Figure: The redox ladder concept

Regional Groundwater Quality in Alberta
Groundwater redox zones were classified

A)



B)

Criteria used for assigning redox categories to groundwater in CLC area: identifying dominant ongoing redox process(es)				Oxygen	Nitrate	Manganese	Iron	Sulfate
			Threshold [mg/L]	1.0	1.0	0.04	0.2	100-400
General	Redox processes		Abbreviation					
Post-oxic	NO_3-reducing	Mixed process (NO_3-reducing/sulfate reducing or NO3reducing +pyrite oxidation)	NO_3red or NO_3red-SO_4red	<	≥	<	<	≥
Anoxic	Mn(IV)-reducing	Methanic	Mn(IV)red or CH4fm	<	<	≥	<	<
Anoxic	Fe(III)-reducing	Methanic	Fe(III)red or CH4fm	<	<	<	≥	<
Anoxic	SO_4-reducing		SO_4red	<	<	<	<	≥
Anoxic	Methanic		CH_4fm	<	<	<	<	<

Figure 2: Redox zone delineations based on A) nitrate-sulfate-methane diagrams, and B) criteria used for assigning redox categories and probable dominant redox processes based on water chemistry threshold data.