De l’intérêt et de la difficulté d’extraire l’ammonium de diverses matrices environnementales

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Where does N come from in alpine regions?

$N = N_{org} + NH_4^+ + NO_3^-$

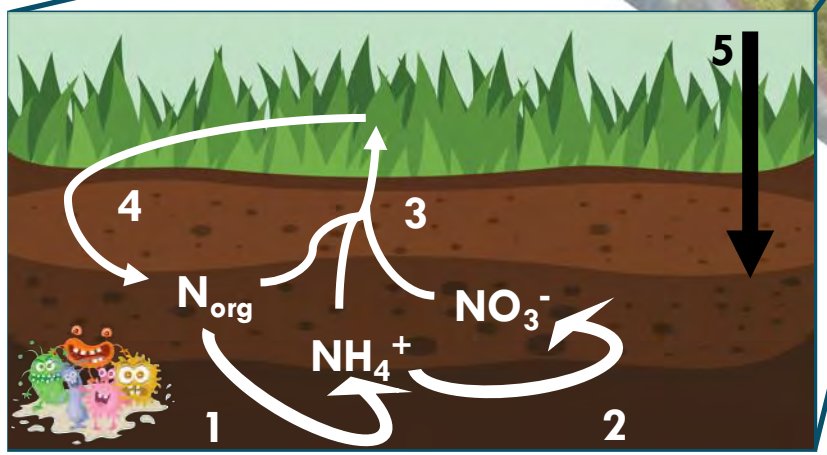
nitrate

ammonium

Atmospheric deposition

Glaciers and snow melt

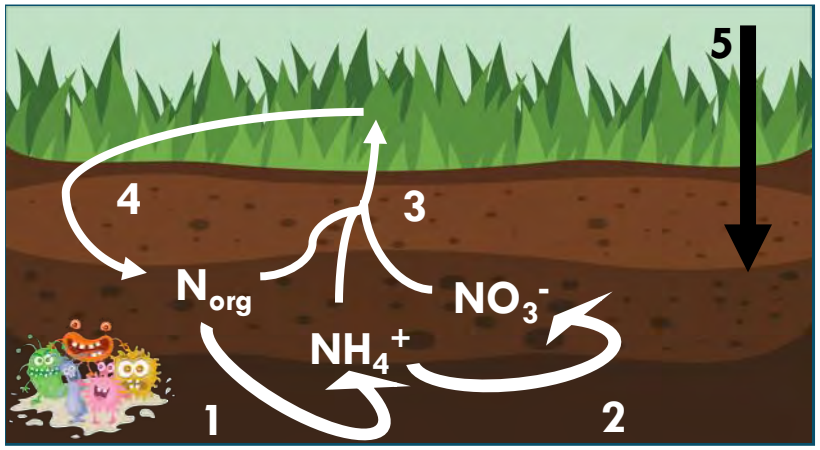
Microbial production



1 Mineralization
2 Nitrification
3 Plant uptake
4 Litter decomposition
5 N_2-fixation

Pastoralism and tourism

Isotopic analysis of NO_3^- using $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$



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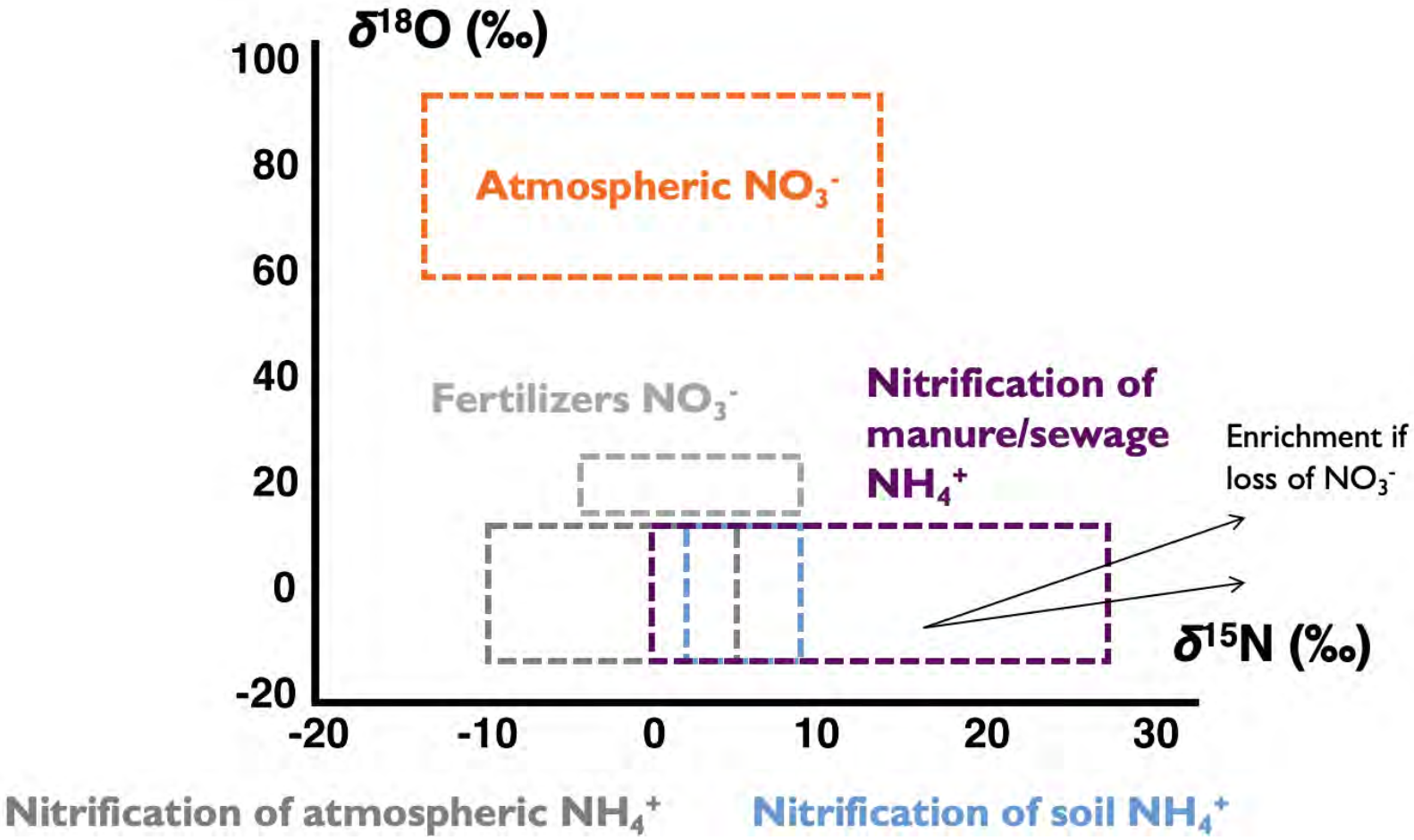
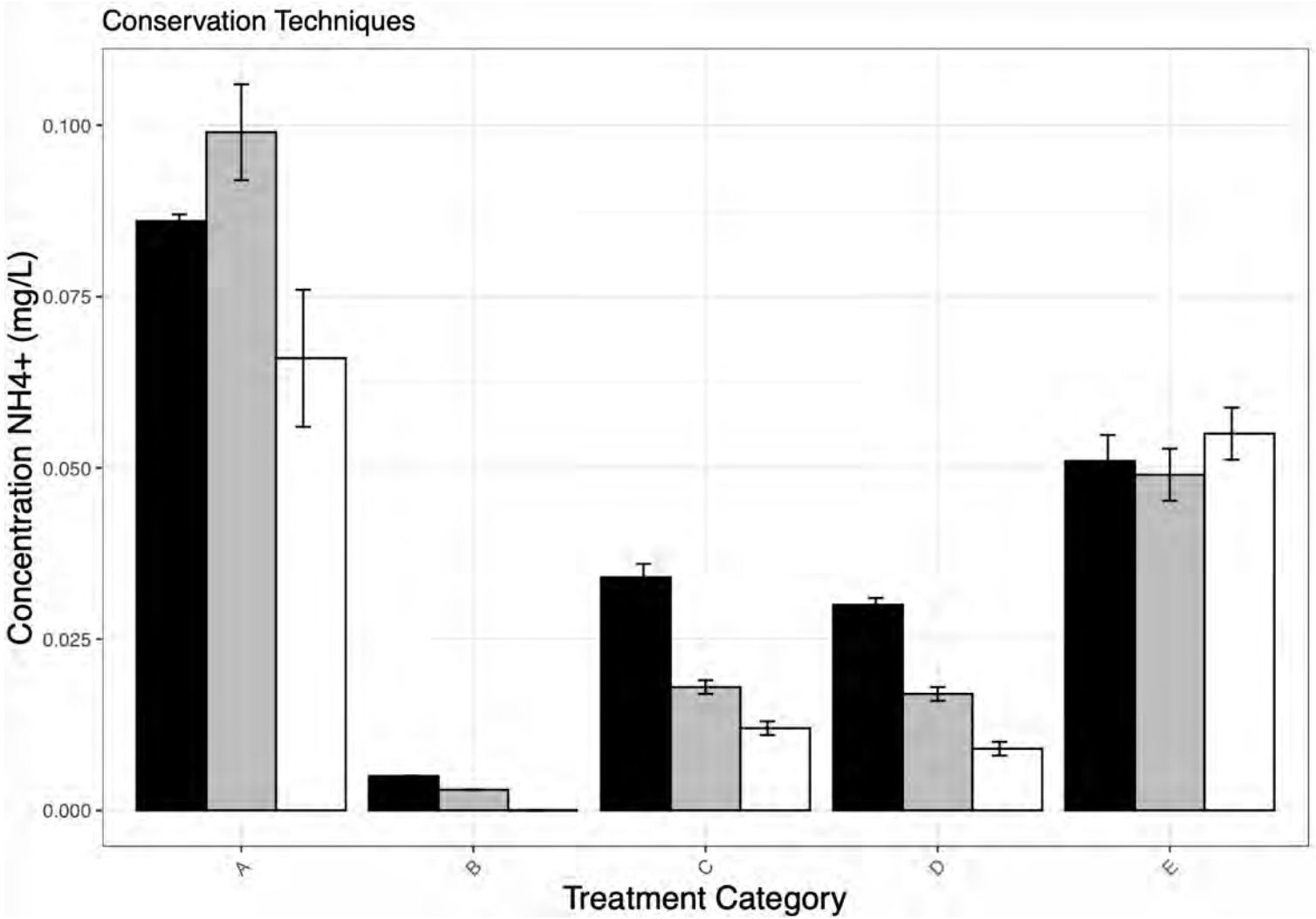


Isotopic analysis of $NH4^+$ using $\delta^{15}N$

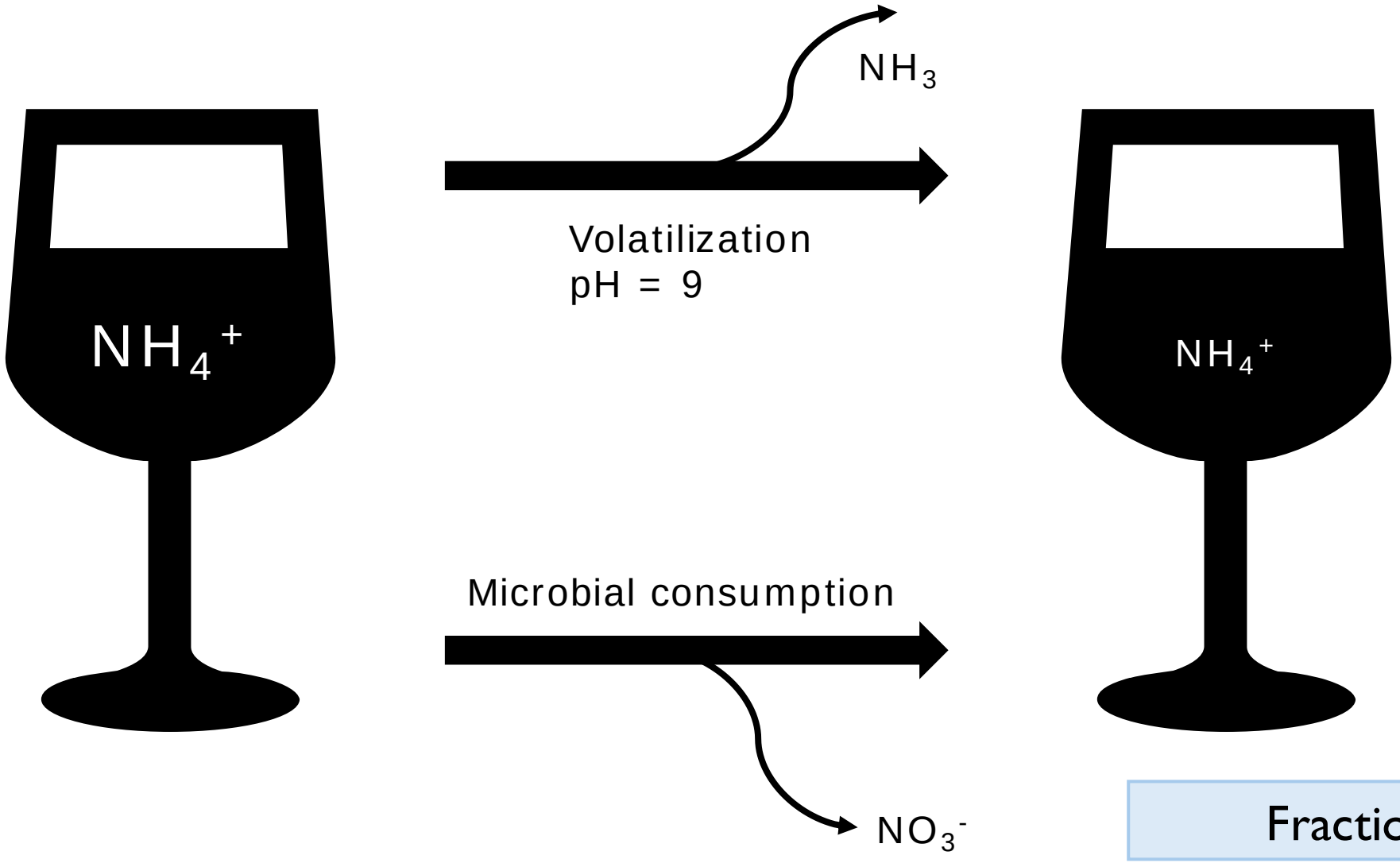
Extraction and conservation of NH_4^+ in water (© Maria Page)

Filtration at 0.45µm = not good enough at low concentration



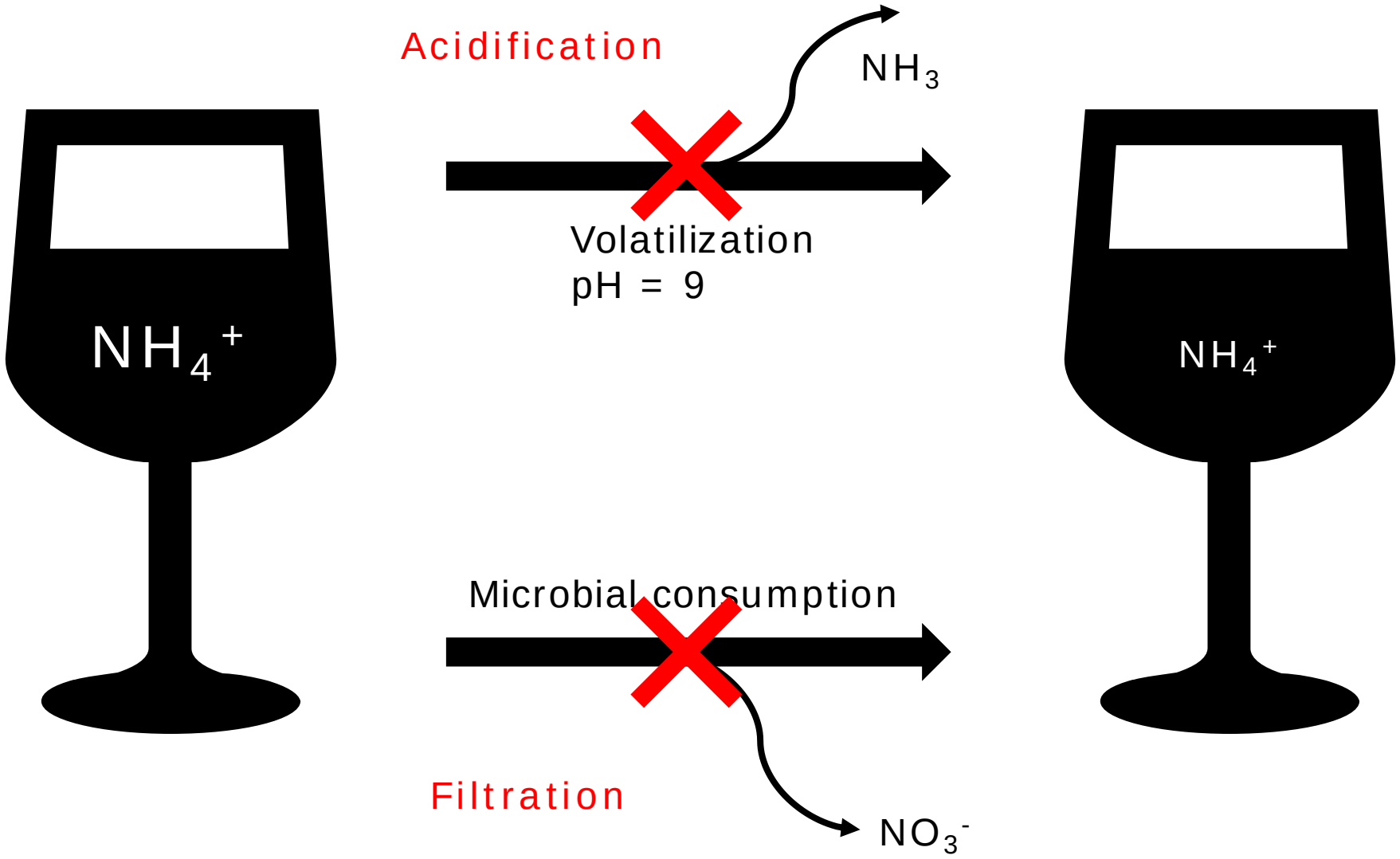
TreatmentCategory	Treatment
A	Immediate analysis
B	1 week at 4C
C	1 week in freezer, unfrozen at 4C
D	1 week in freezer, unfrozen at room temp
E	1 month in freezer, unfrozen at 4C

Extraction and conservation of NH_4^+ in water



Fractionation!!!

Extraction and conservation of NH_4^+ in water



Extraction and conservation of NH_4^+ in water

How do we filter?

The EPA methods state that samples must be preserved with sulfuric acid immediately upon collection, and that once preserved, samples can remain at 4 C for up to 28 d.

Extraction and conservation of NH_4^+ in water

How do we filter?

LIMNOLOGY and OCEANOGRAPHY: METHODS

ASLO

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Effects of filtration timing and pore size on measured nutrient concentrations in environmental water samples

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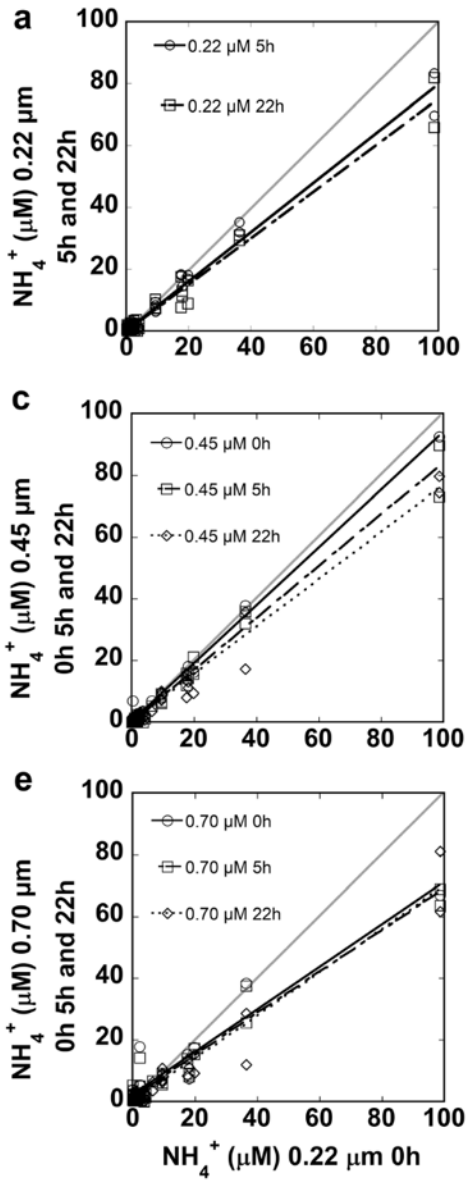
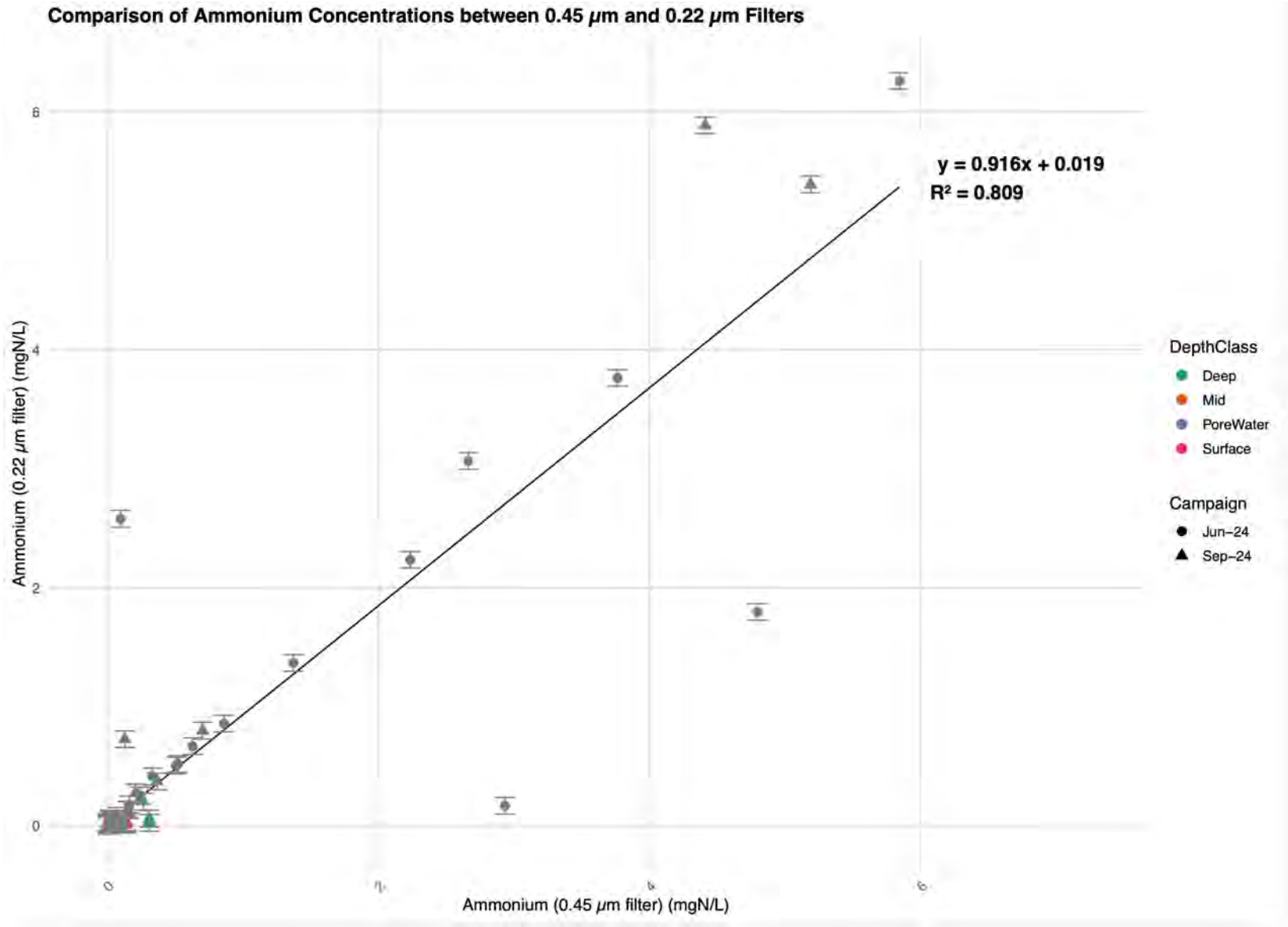
Better to filter at 0.2µm in the field!



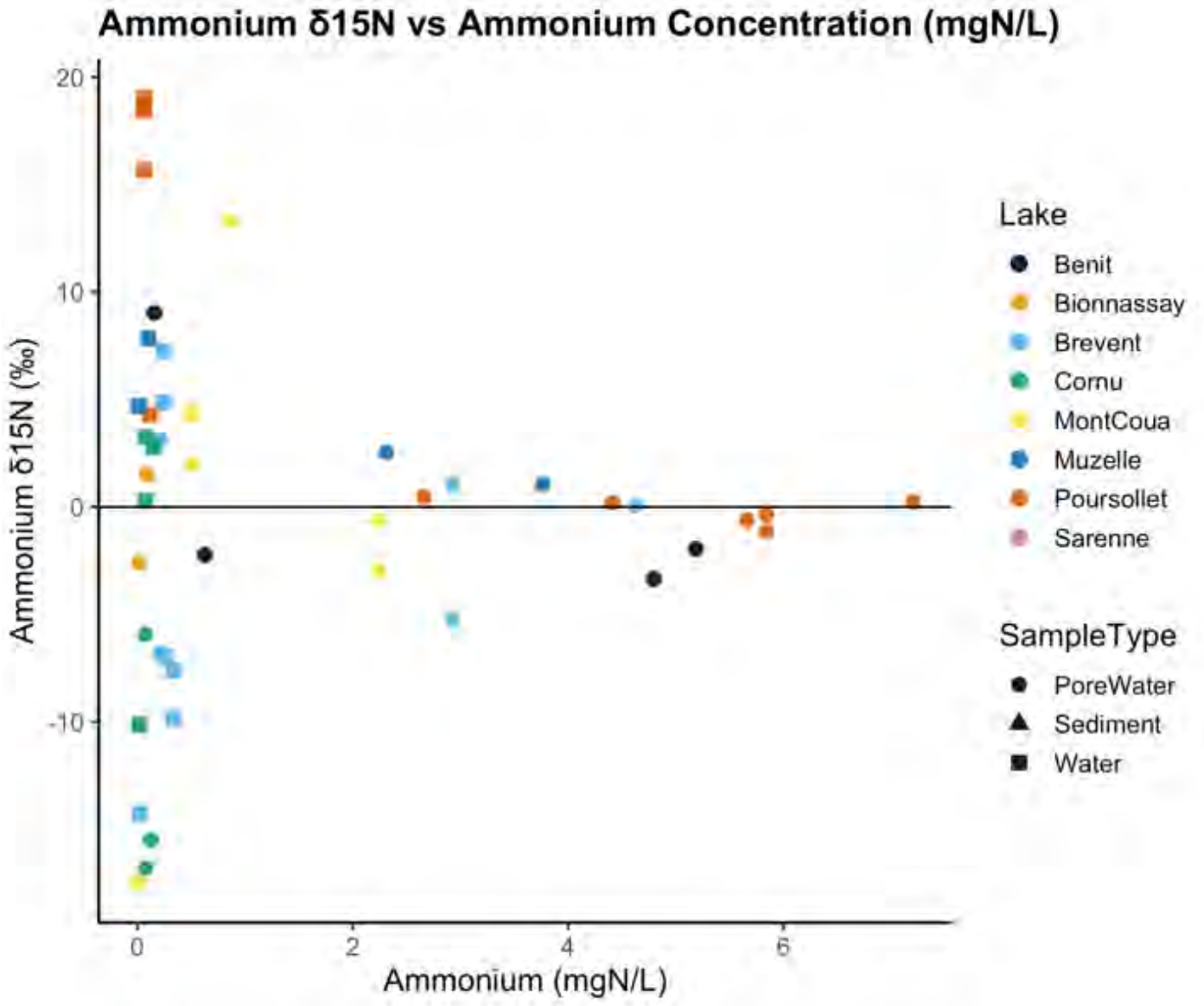
Extraction and conservation of NH_4^+ in water (© Maria Page)

Filtration at 0.45µm = good enough at higher concentration?

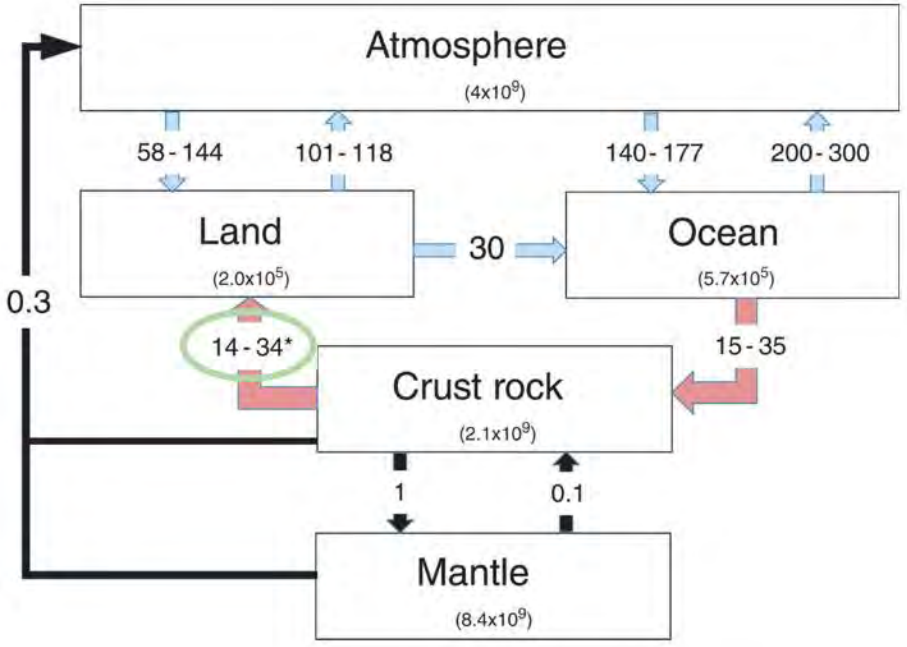


Extraction and conservation of NH_4^+ in water (© Maria Page)

How do we interpret this?
Filtration at 0.2µm + acidification

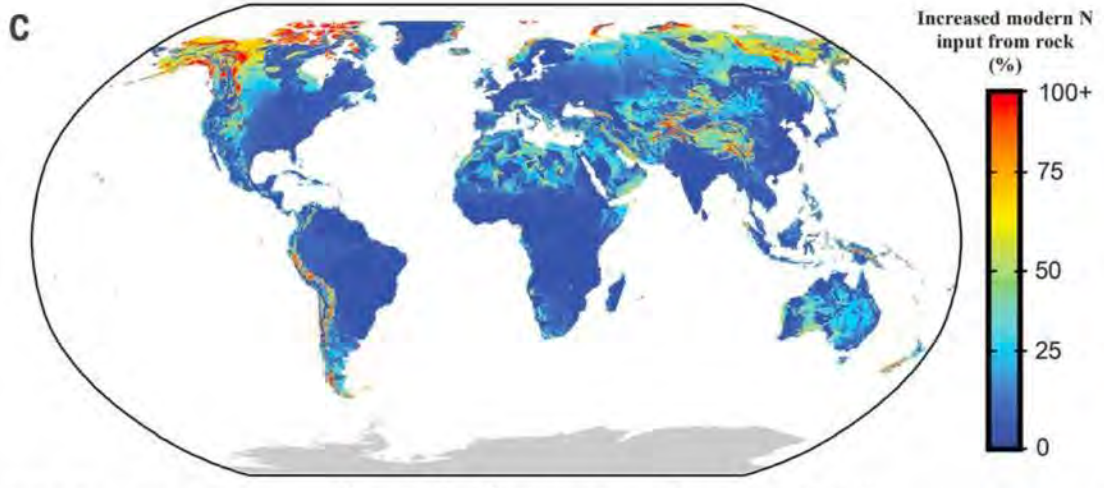


A petrogenic source of nitrogen ?



Preindustrial planetary N cycle. *Houlton et al. (2018)*
Fluxes: Tg y^{-1}, Reservoirs: Tg

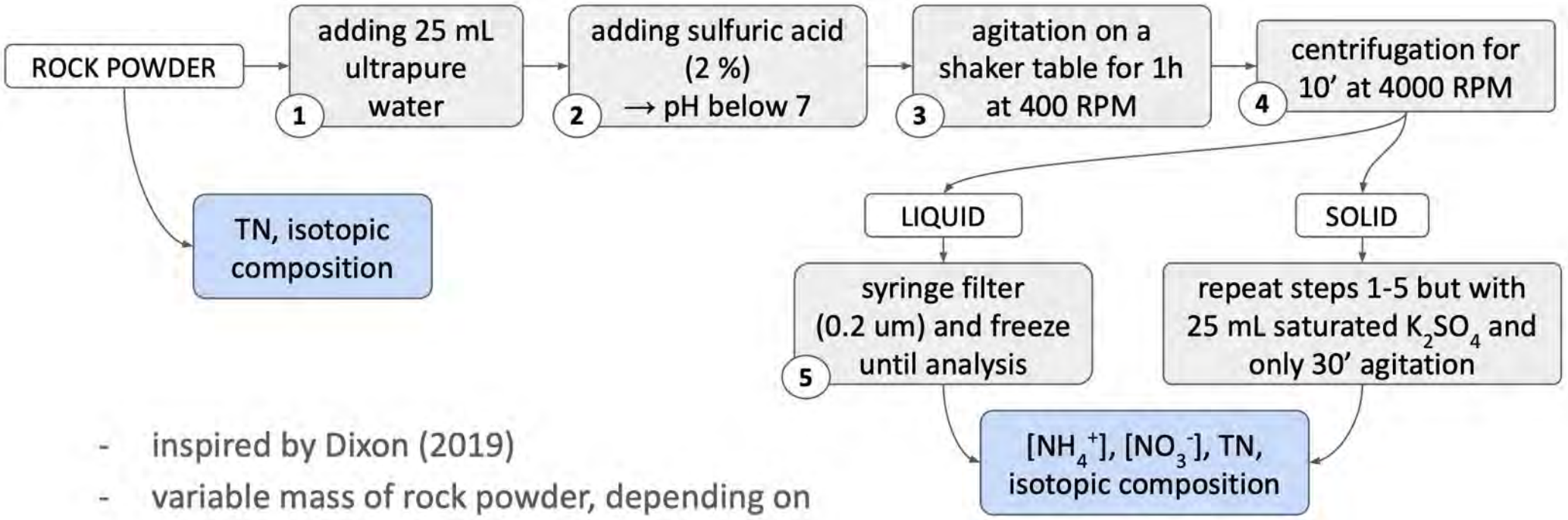
- completing the planetary N cycle by a crust ⇒ land term to reach balance (Holloway et al., 1998 and Houlton et al., 2018)
- mountainous regions : high alteration, N-limited ecosystems imply a more likely geogenic N source



N weathering map. *Houlton et al. (2018)*

Extraction and conservation of NH_4^+ in rocks (© Jil D'Erceville)

Leaching experiments

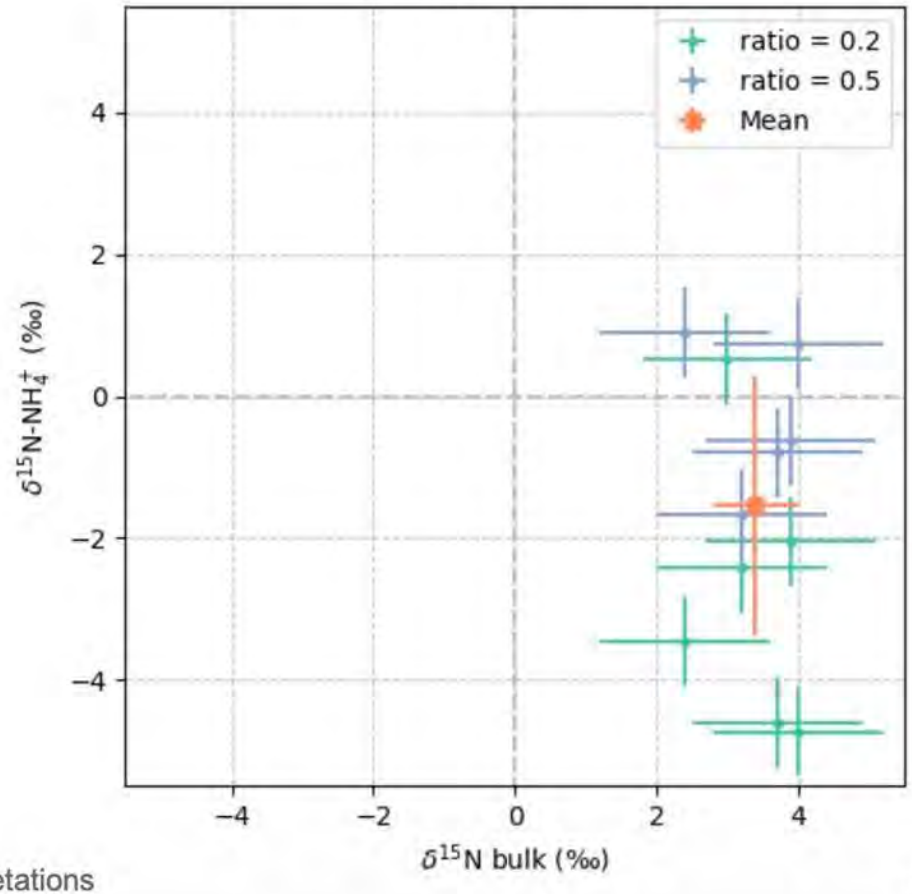


- inspired by Dixon (2019)
- variable mass of rock powder, depending on the rock/matrix ratio

Tracing ammonium

- no clear correlation
- shift from $\delta^{15}N$ in the bulk (between 2.4 and 4 ‰) and in leached ammonium (between -4.7 and 0.9 ‰)
- possible causes:
  - other forms of nitrogen have a different $\delta^{15}N$
  - $\delta^{15}N$ in adsorbed NH_4^+ is higher (Dixon, 2019)

Comparison of $\delta^{15}N$ in the bulk and in leached ammonium.

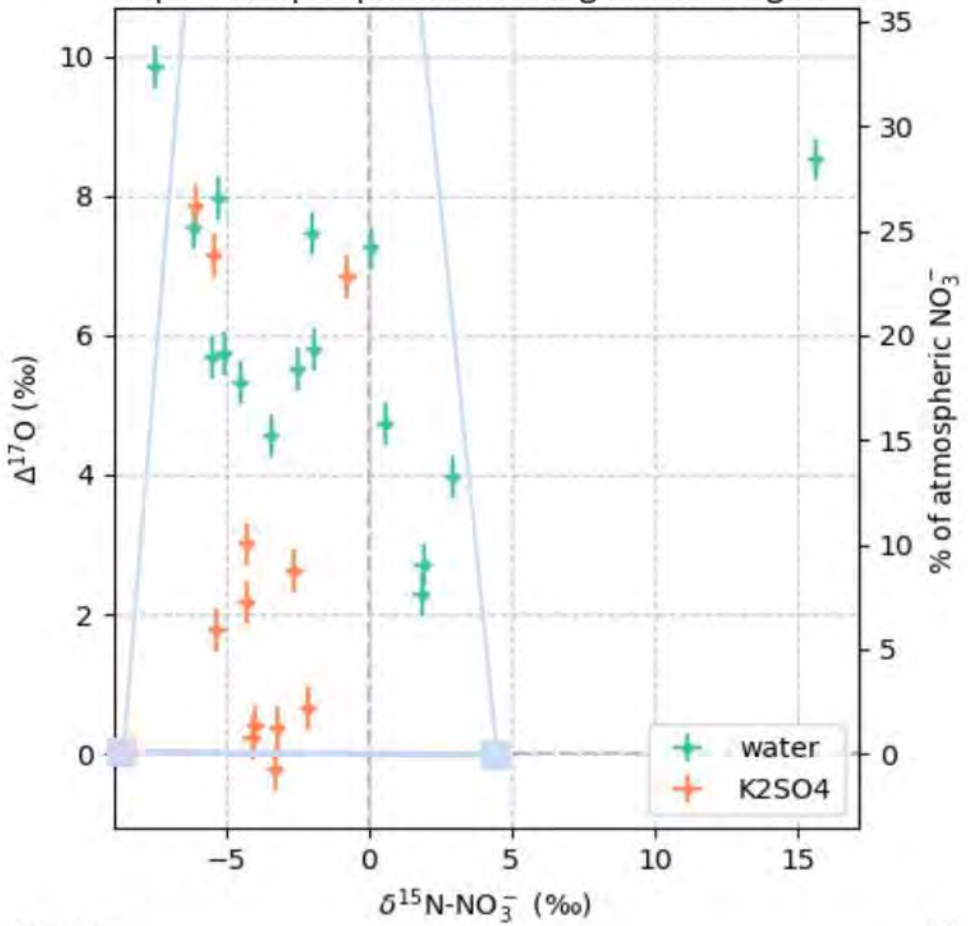


Tracing nitrate

- $\Delta^{17}O$ above 0 ‰ : atmospheric nitrate
- likely to have nitrate contamination from the tubes and/or the K_2SO_4
- mixed with nitrified "soil" ammonium: probably geogenic ammonium which was nitrified

→ try with cleaner K_2SO_4 and better quality centrifuge tubes

Triple isotopes plot illustrating nitrate origin.

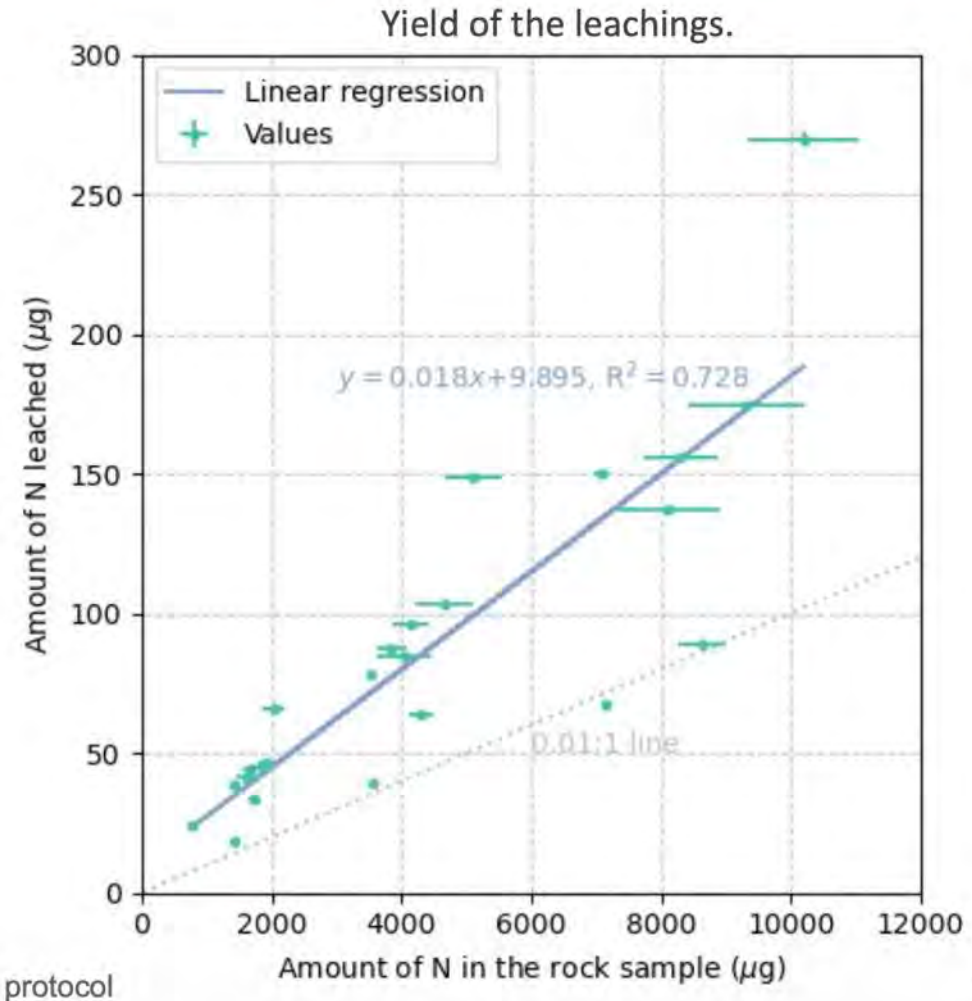


Yield of the leachings

- around 1.8 % in average
- stable, no matter the rock sample or the ratio

→ **more leachings could improve the yield**

(Laize-Générat et al., 2024)

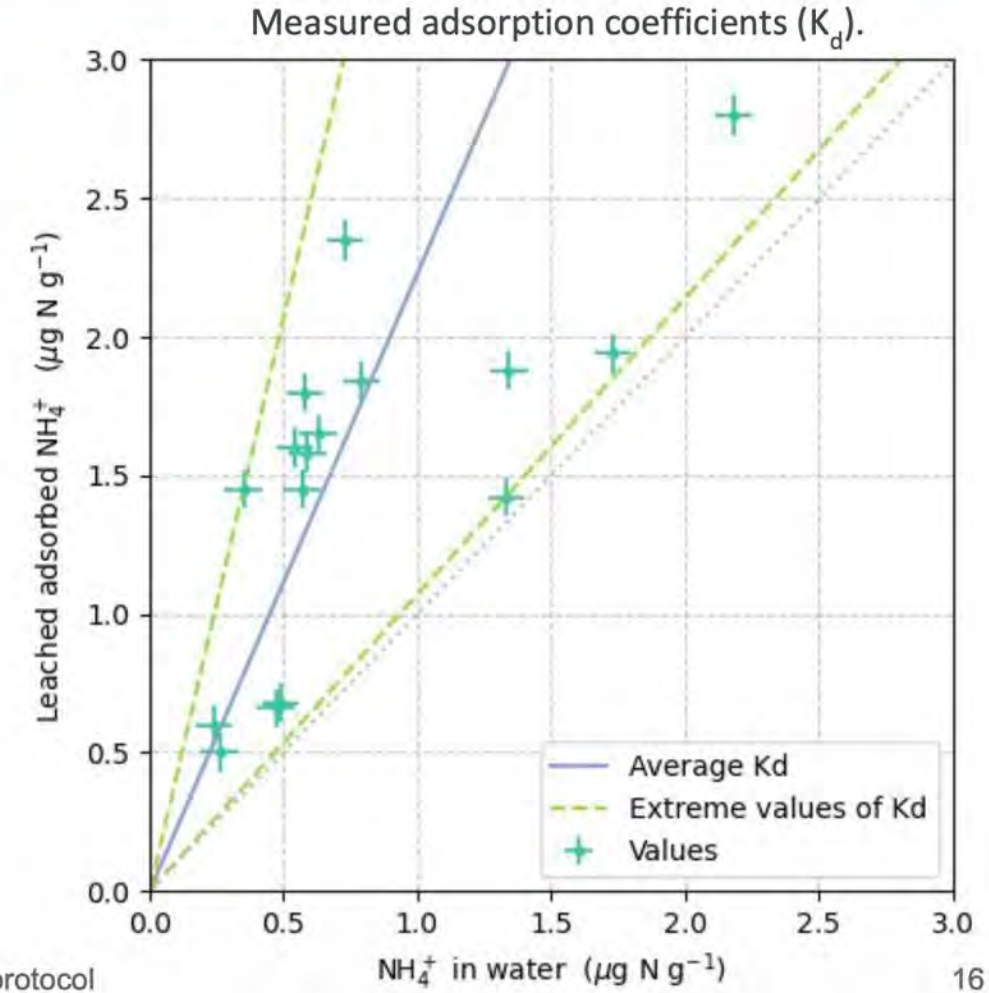


Recovery of adsorbed ammonium

$$K_d = \frac{\text{adsorbed ammonium } (\mu g\ N\ g^{-1})}{\text{ammonium in solution } (\mu g\ N\ g^{-1})}$$

- ratio between ammonium leached in K_2SO_4 and in water between 1 and 4 (average 2.2)
- Dixon's values : between 5 and 12 for sedimentary rocks
- KCl instead of K_2SO_4

→ **try with KCl to see if better yield and K_d**



Extraction and conservation of NH_4^+ in rocks

What are the next steps?