GMOS TRAIN

ICMGP 2024
CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY
CAPE TOWN INTERNATIONAL CONVENTION CENTRE

Stockholm University

Formation of **Refractory Methylmercury pools** by particle adsorption

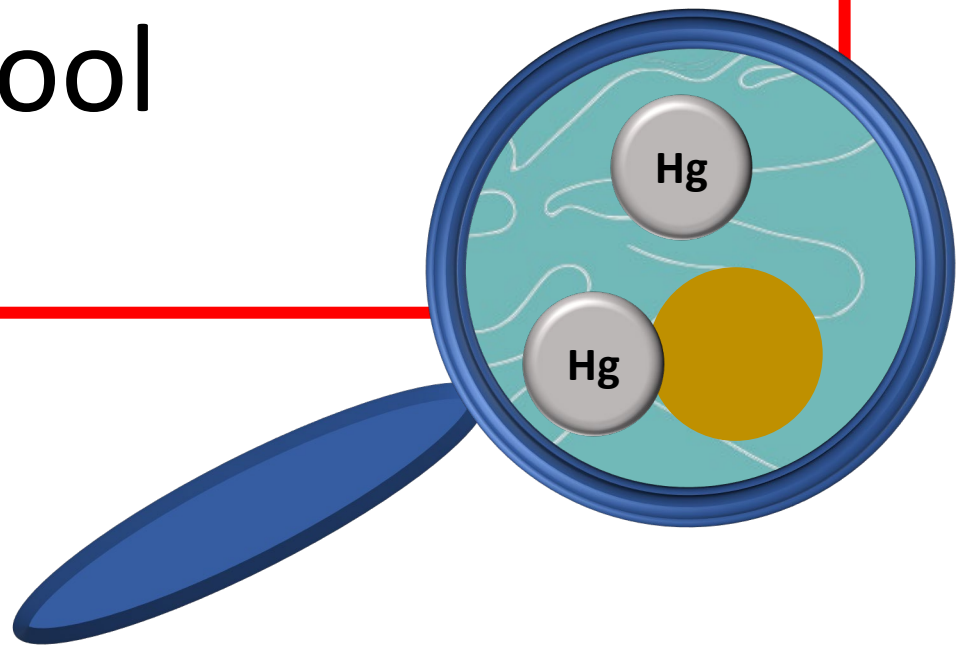
Sonja Gindorf, Abhinav Bharadwaj Tirunaghari , Sofi Jonsson

23.07.2024, ICMGP Cape Town



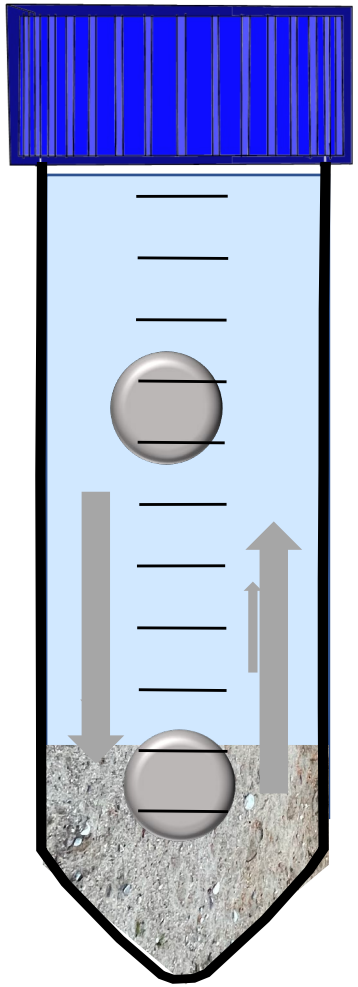
This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

Up to **85% of MMHg** adsorbing to terrestrial particles enters the refractory pool



Experimental setup

Incubation



1. 0.5 – 1 g soil
2. 50 mL water
3. Pre-Equilibration 24 hours
4. Addition of 10 ng $MM^{201}Hg$
5. Adsorption incubation 48 hours
6. Water exchange
7. (re-)Desorption incubation 8 weeks

Conditions:
10 °C climate chamber

Rotation at 1 rpm

Experimental Setup

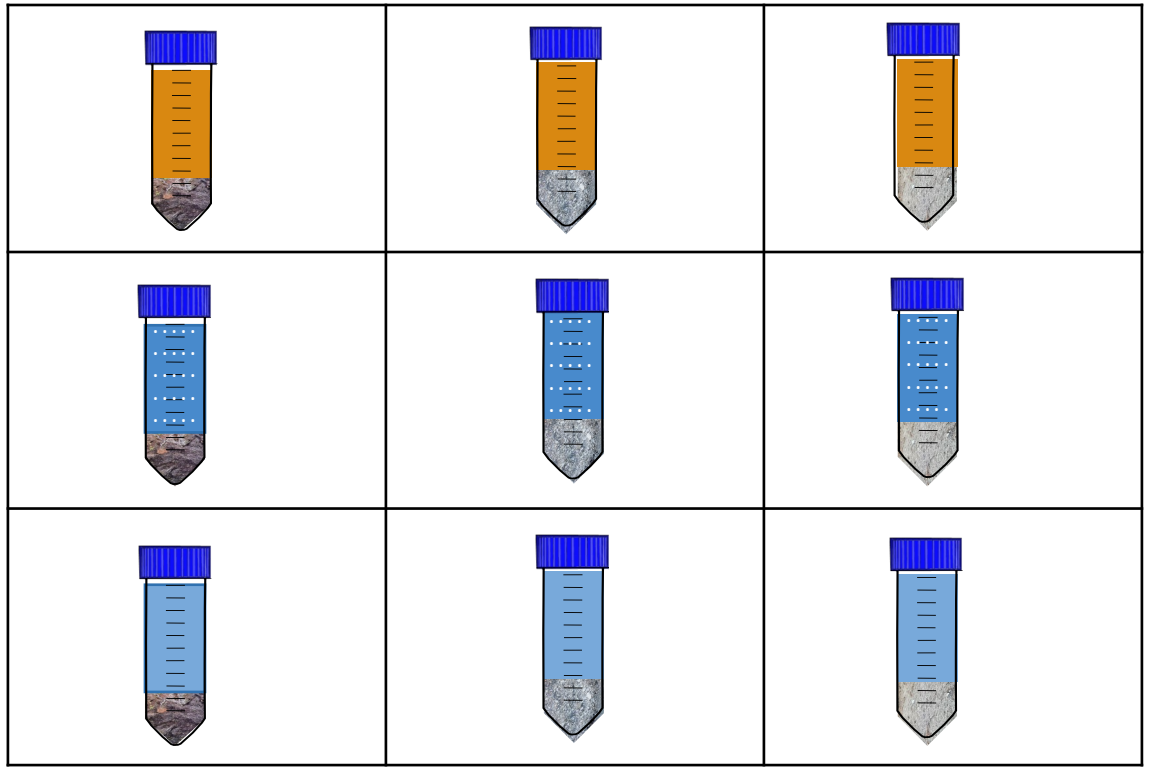
The Samples

Soils

Peat High OC	**Stream mineral** low OC	**Mineral** low OC
		

Waters

Pond High DOC	
Fjord Low DOC, high salinity	
Stream Low DOC, Low salinity	



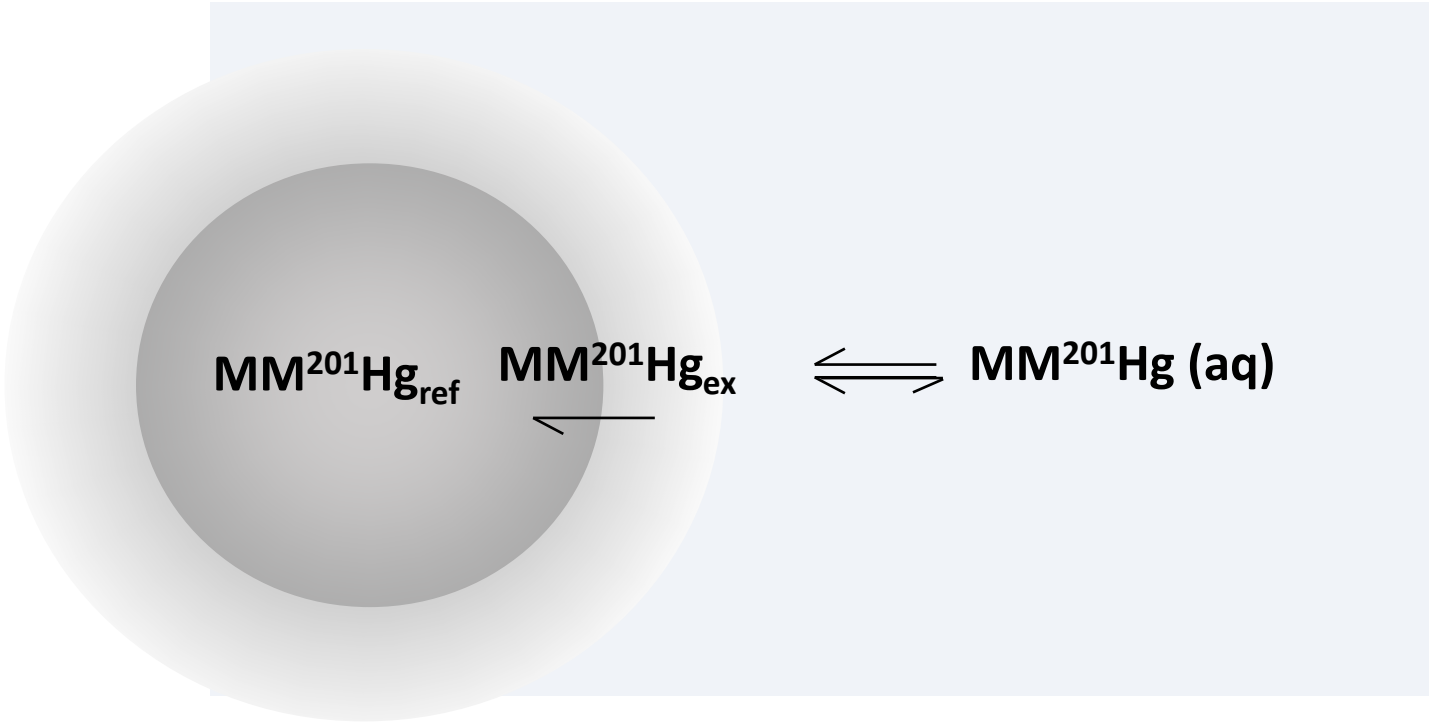
7 timepoints adsorption

7 timepoints desorption

Triplicates for last timepoints

MMHg adsorption (48h)

Experimental Approach

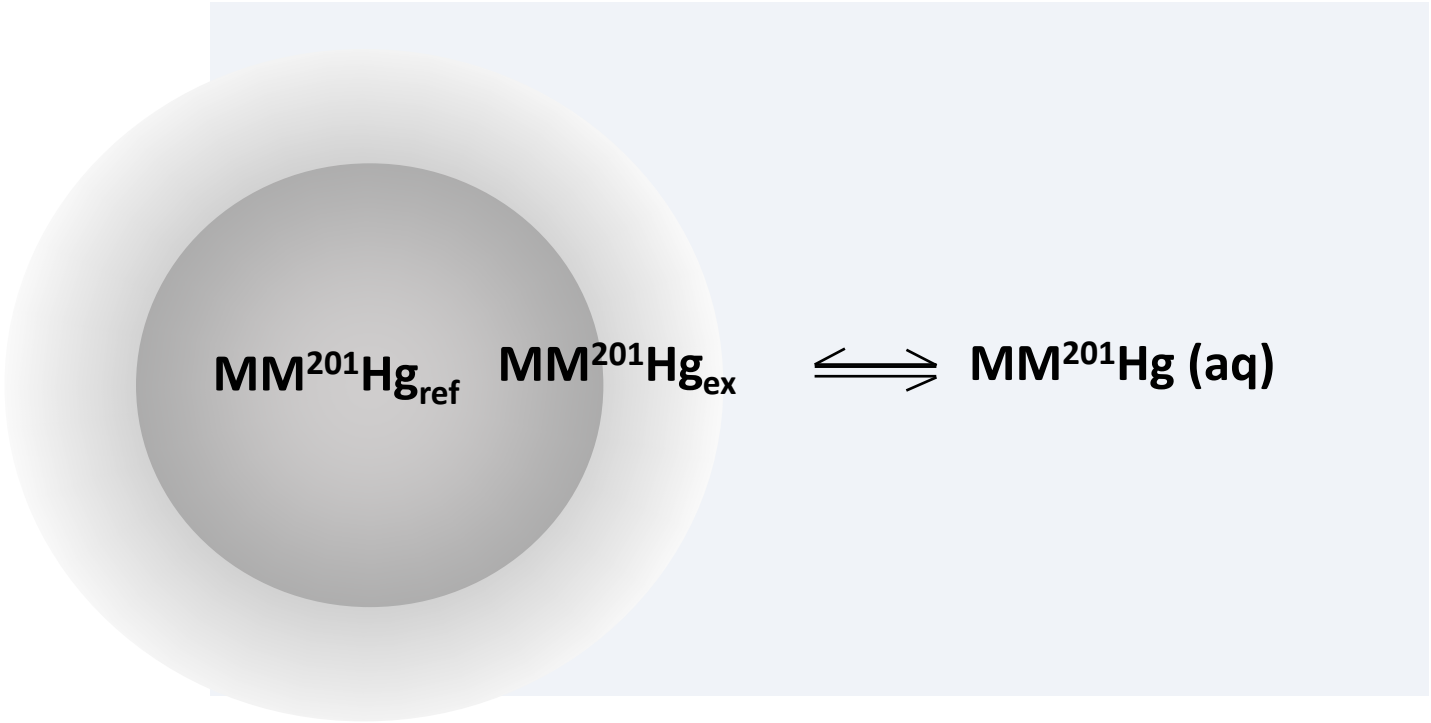


K_A Solid-to-Water Partitioning Coefficient for the **adsorption step**

$$K_A = \frac{[MMHg]_{solid\ phase}}{[MMHg]_{aqueous\ phase}}$$

MMHg (re-)desorption (8 weeks)

Experimental Approach



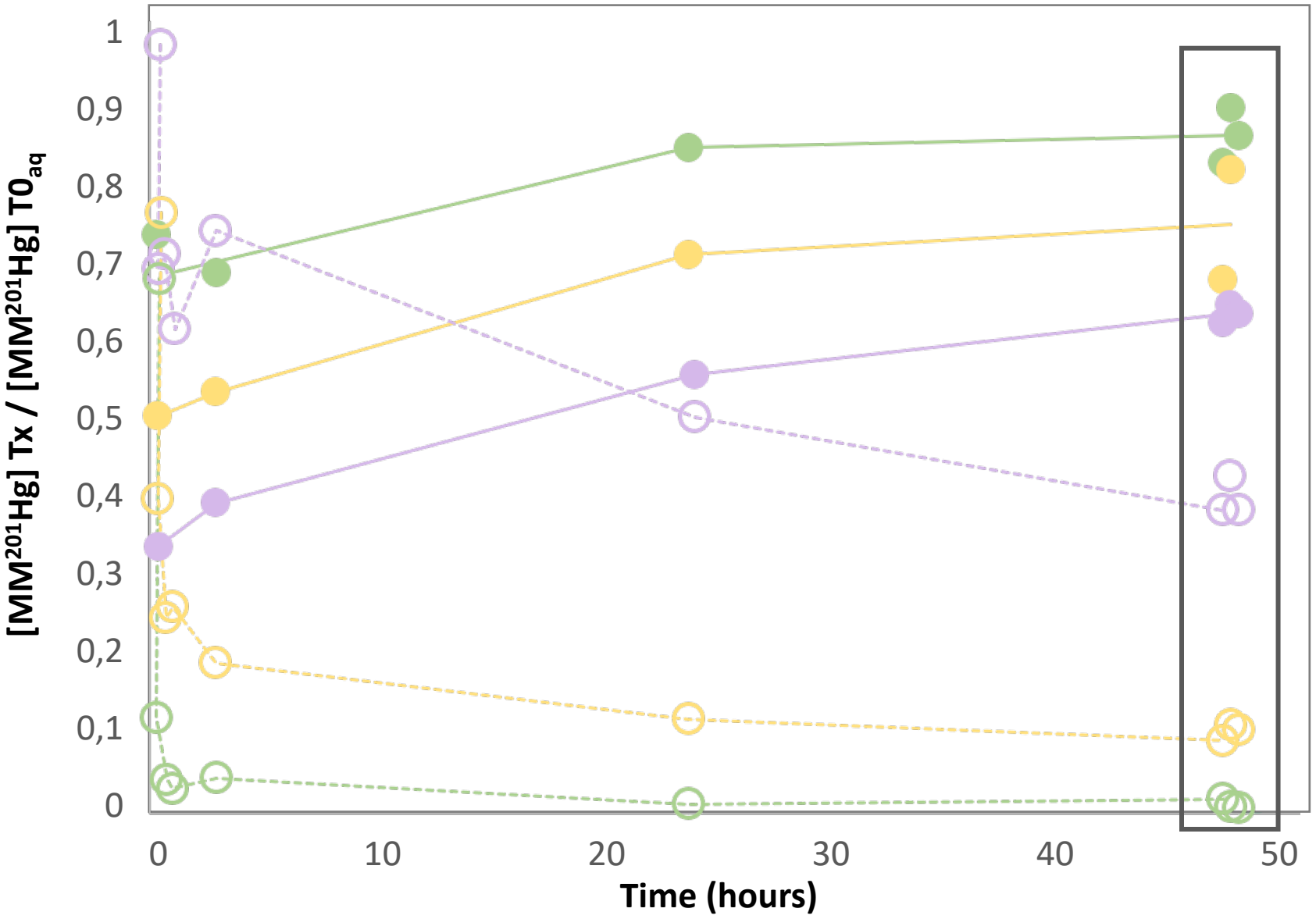
K_D Solid-to-Water Partitioning Coefficient for the **(re-)desorption step**

$$K_D = \frac{[MMHg]_{solid\ phase}}{[MMHg]_{aqueous\ phase}}$$

RESULTS

MMHg adsorption kinetics (48h)

$$kA = \frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}}$$



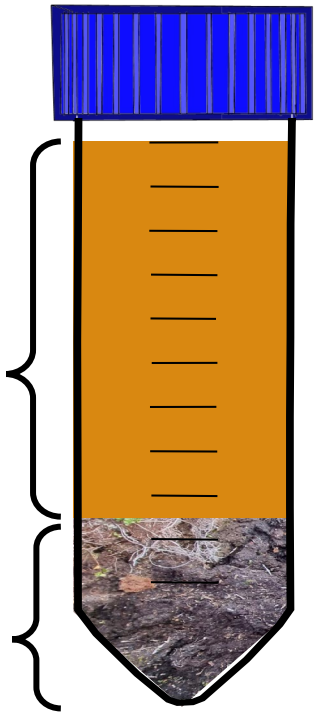
Fjord

Stream

Pond

Aqueous

Solid

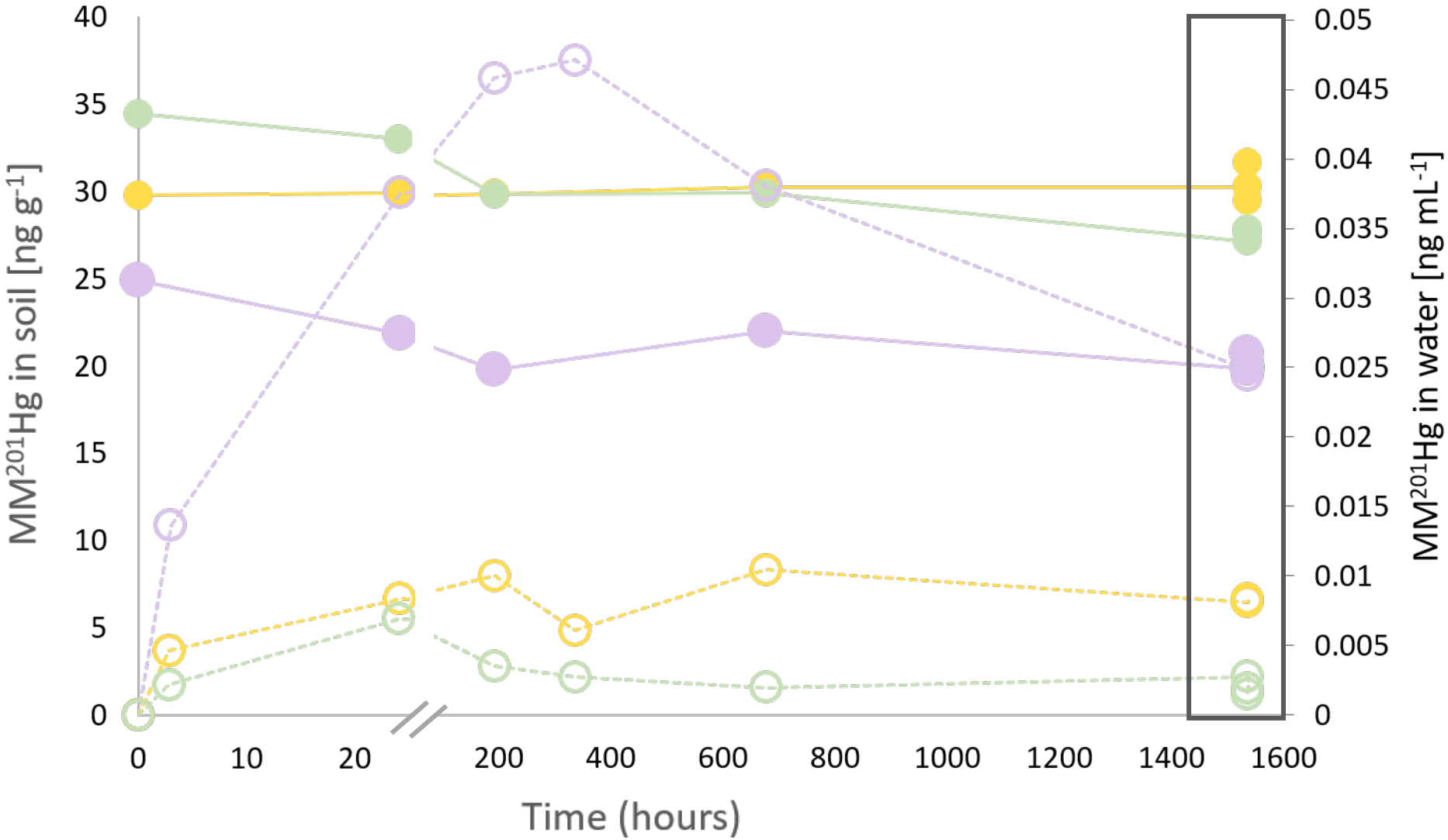


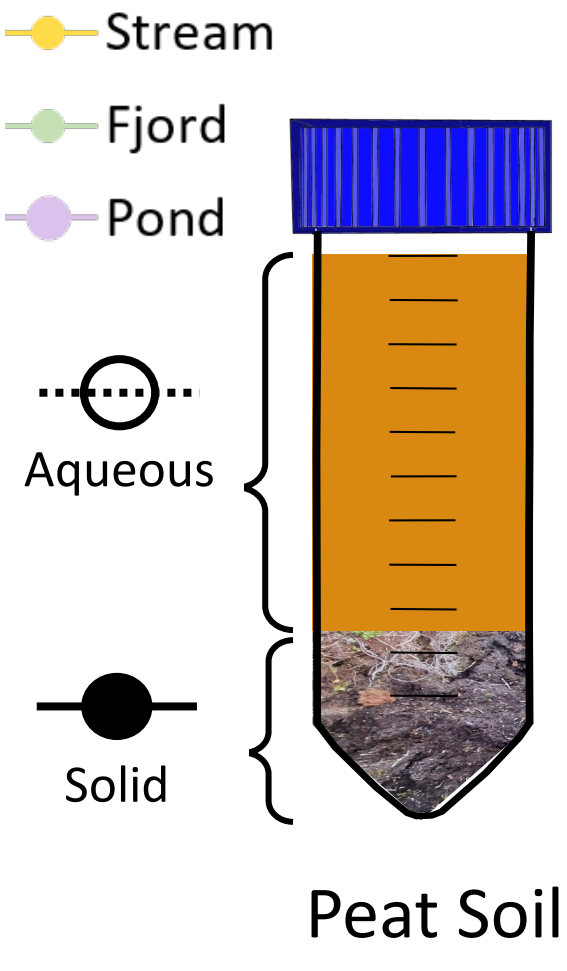
Peat Soil

RESULTS

MMHg Desorption kinetics (8 weeks)

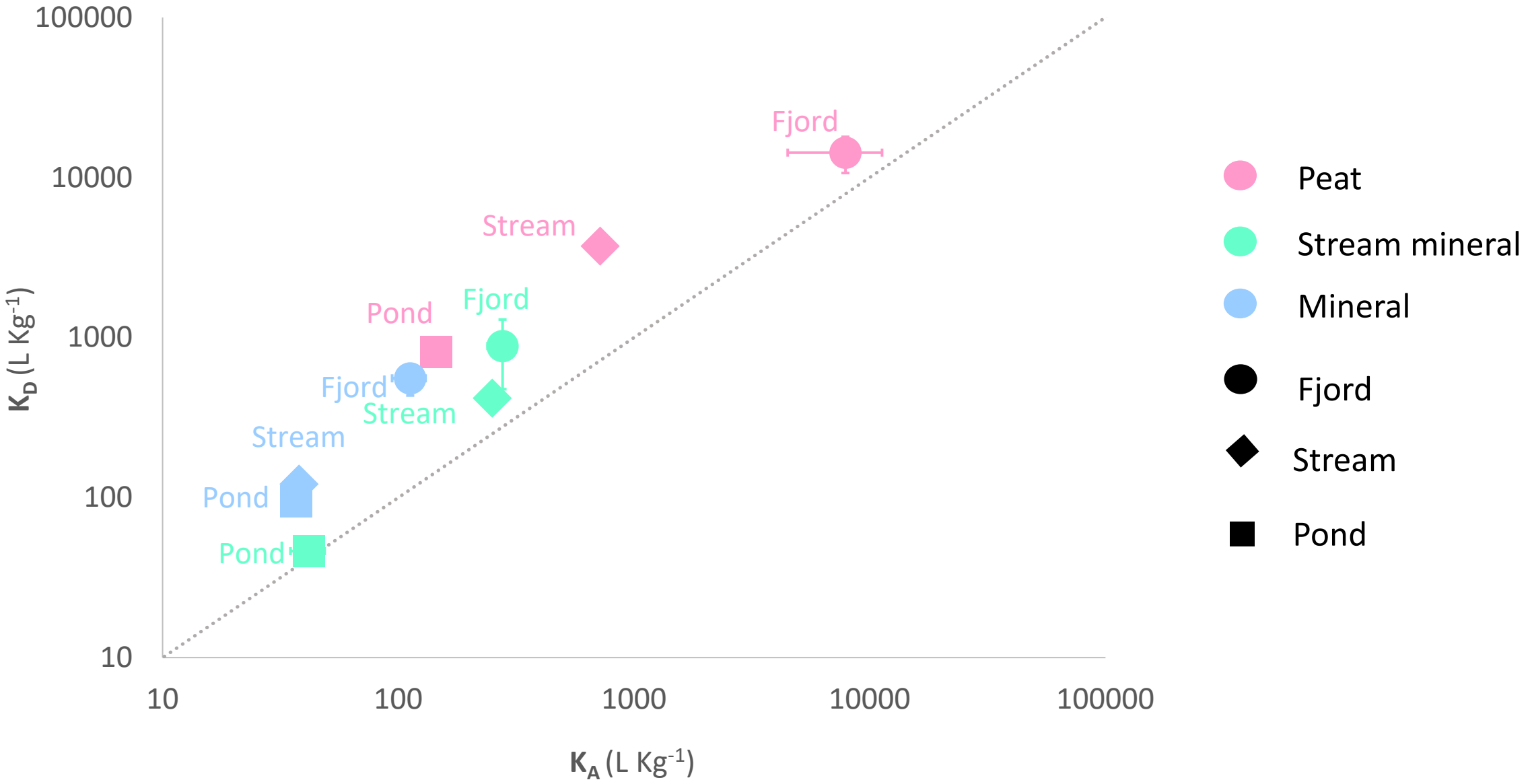
$$kD = \frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}}$$



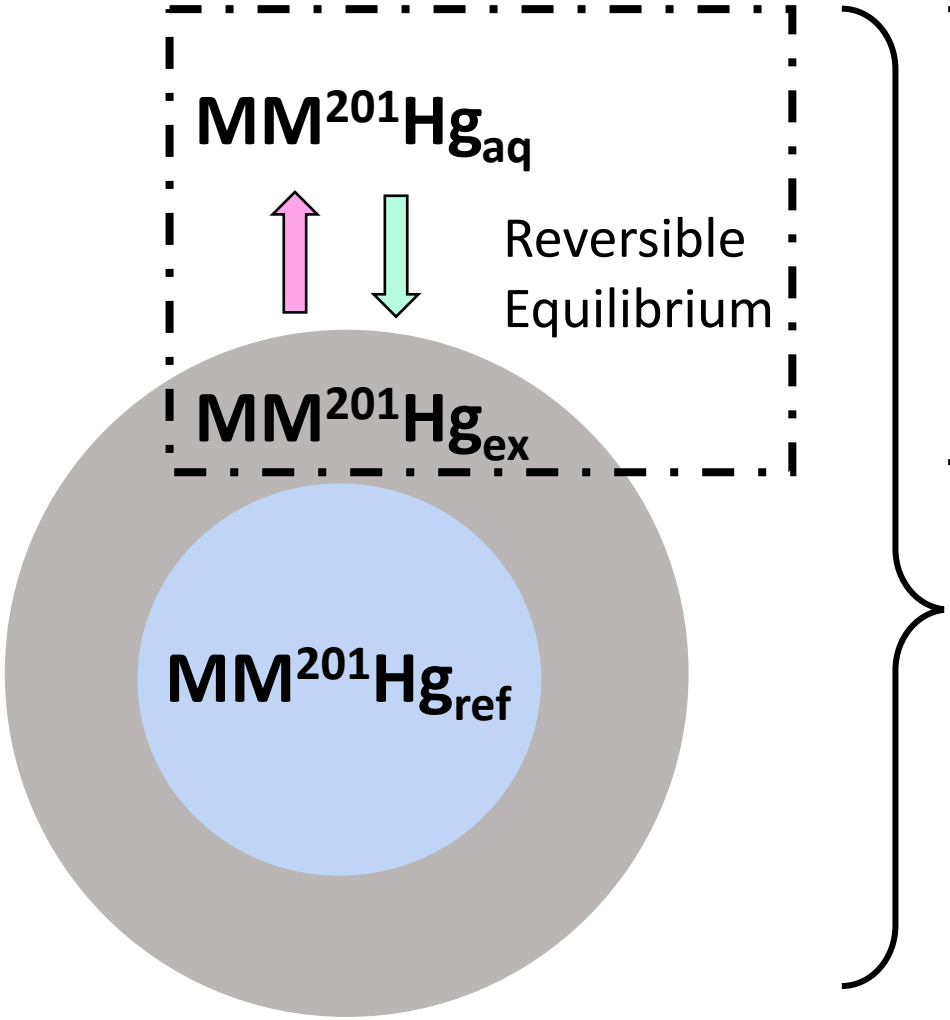


Relationship between MMHg adsorption and desorption

RESULTS



Calculation refractory pools



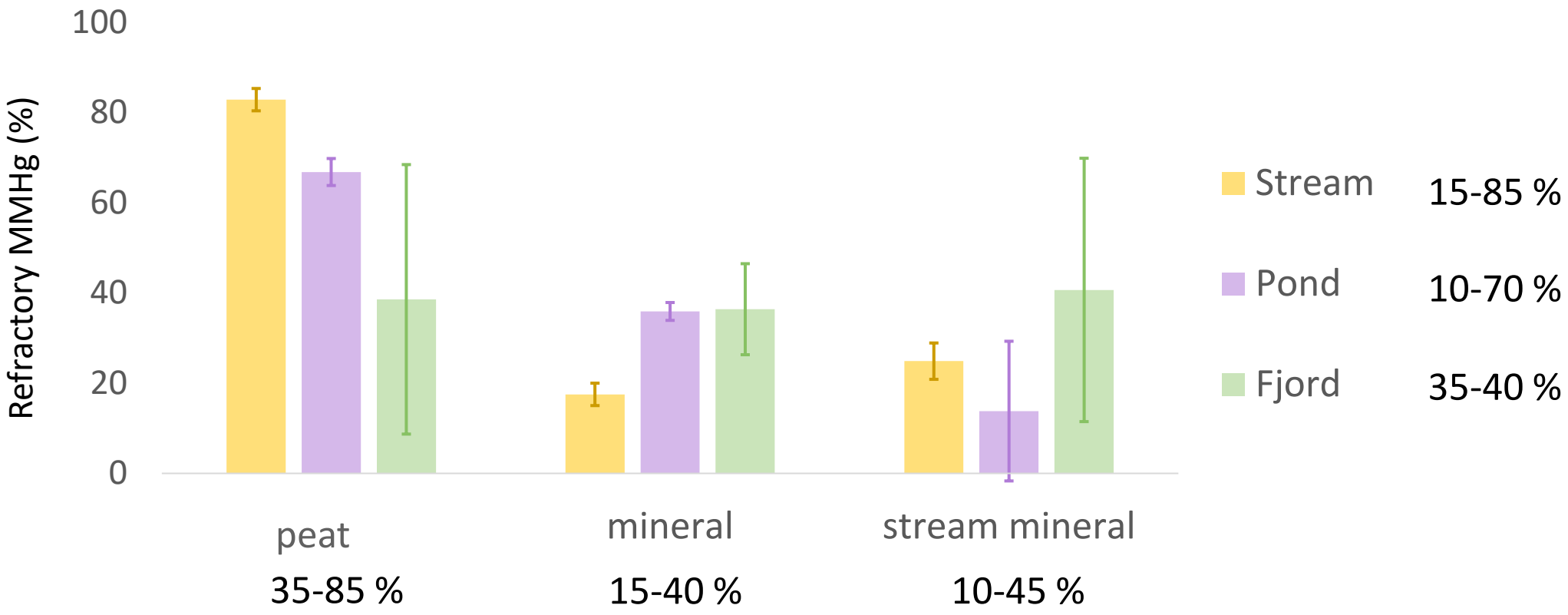
$$K_A = \frac{[MM^{201}Hg]_{ex}}{[MM^{201}Hg]_{aq}}$$

$$K_D = \frac{[MM^{201}Hg]_{ex} + [MM^{201}Hg]_{ref}}{[MM^{201}Hg]_{aq}}$$

$$[MM^{201}Hg]_{ref} = (K_D - K_A) * [MM^{201}Hg]_{aq}$$

ref refractory ex exchangeable aq aqueous

Refractory MMHg pools



Key messages

- Refractory pools were formed for all particles and waters tested
- Particle characteristics and water physico-chemical properties are important for the formation of refractory MMHg pools
- These results can help to improve modelling the fate of terrestrial Hg transported to aquatic systems



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THANK YOU

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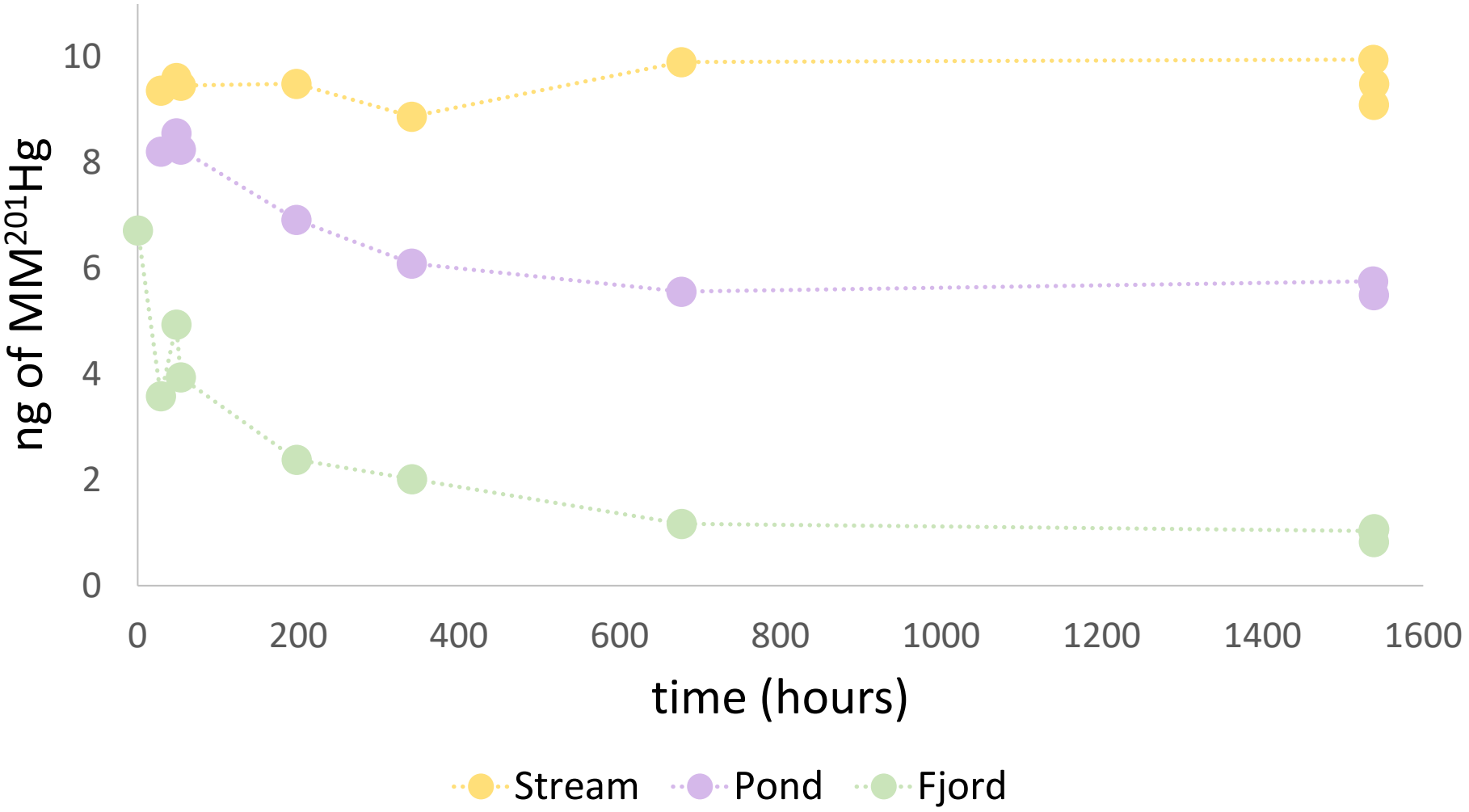
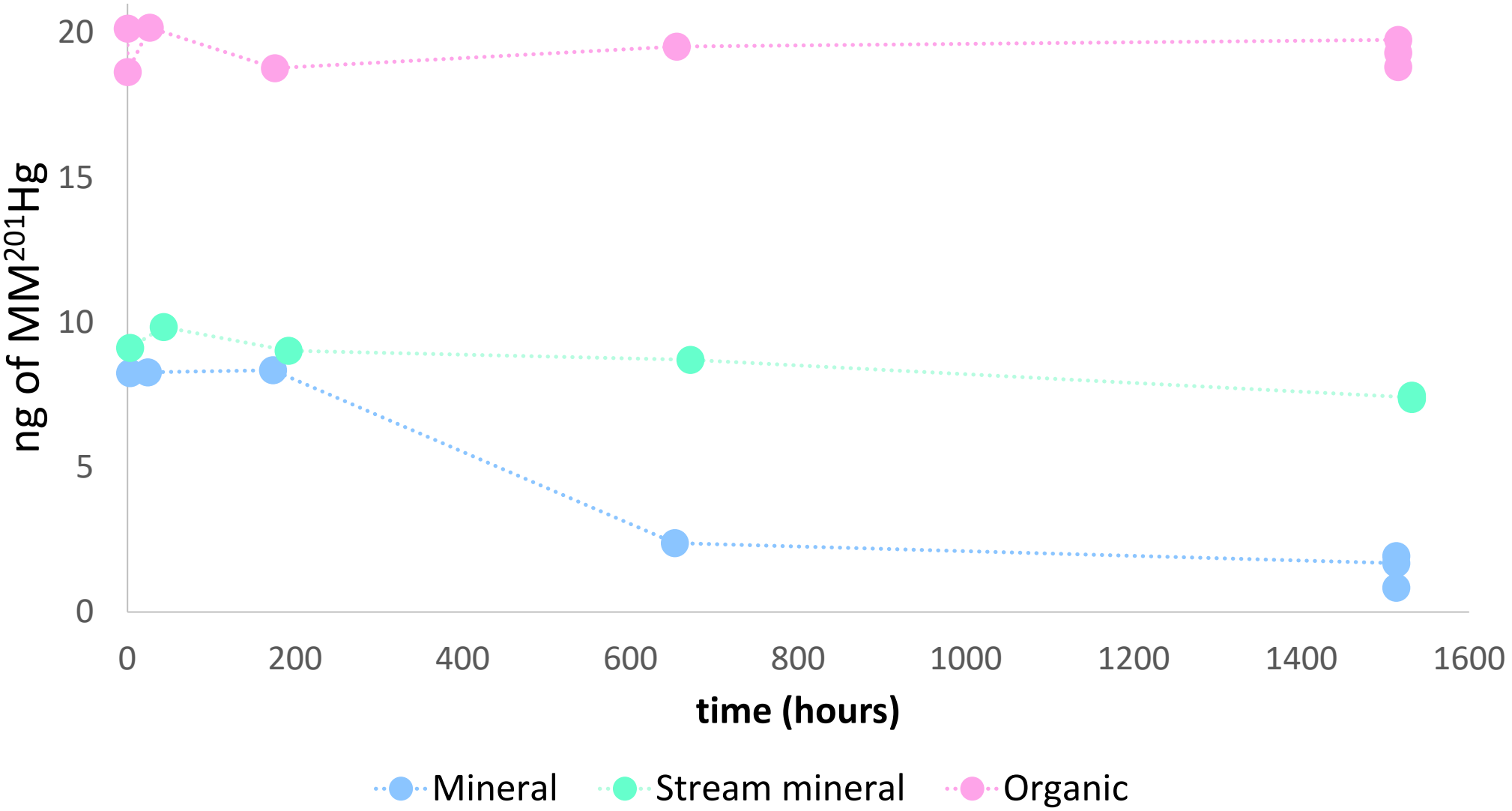
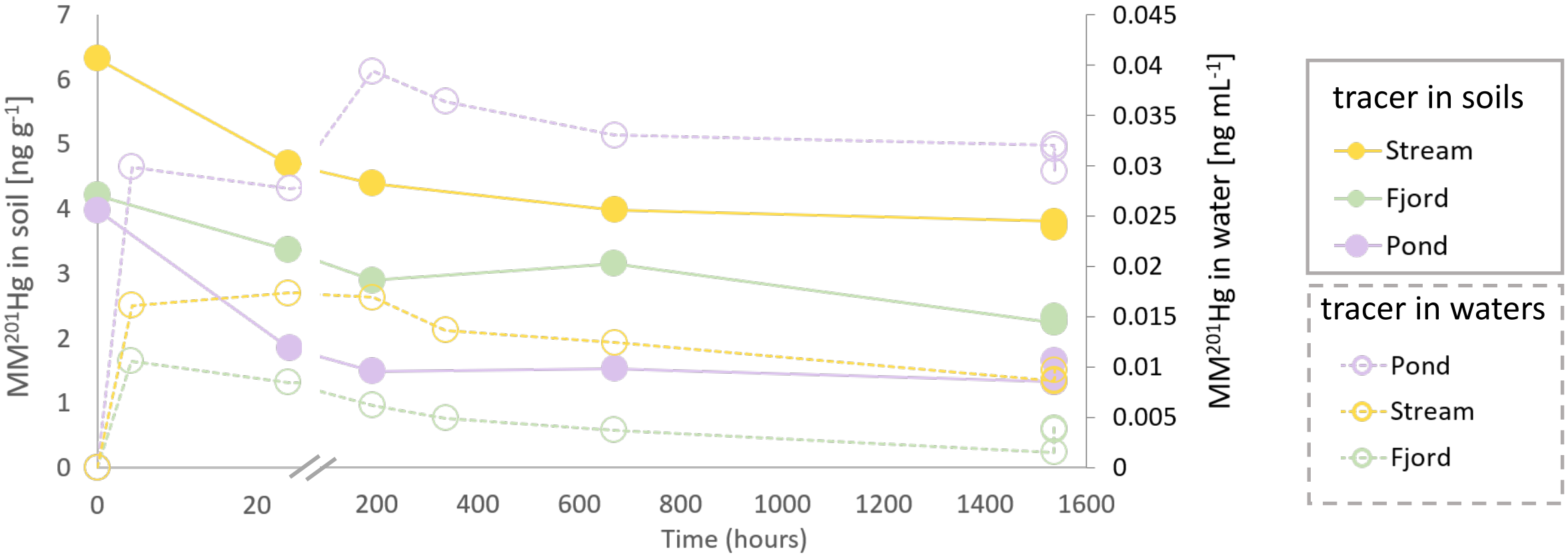
Demethylation / loss of tracer in water



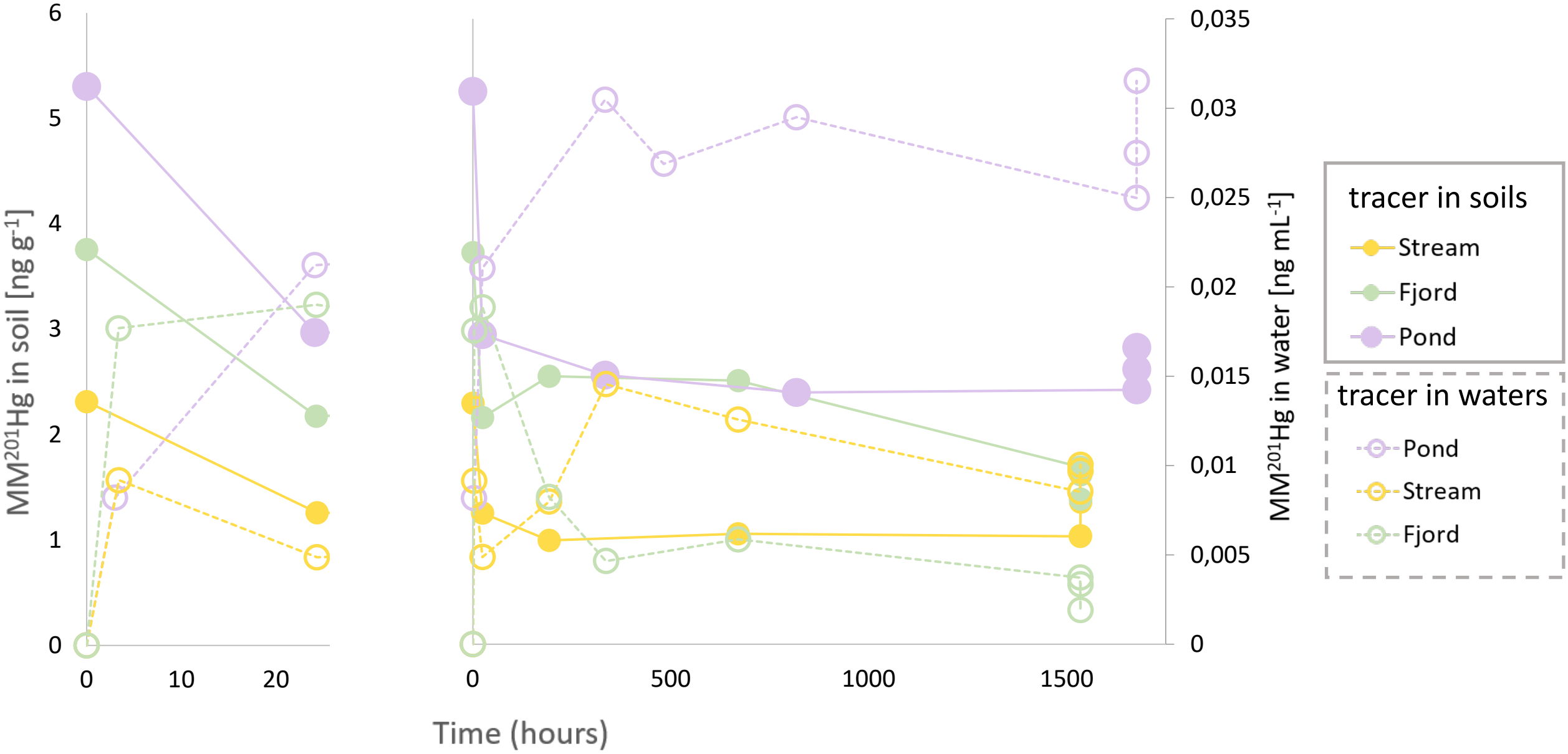
Demethylation / loss of tracer in soil



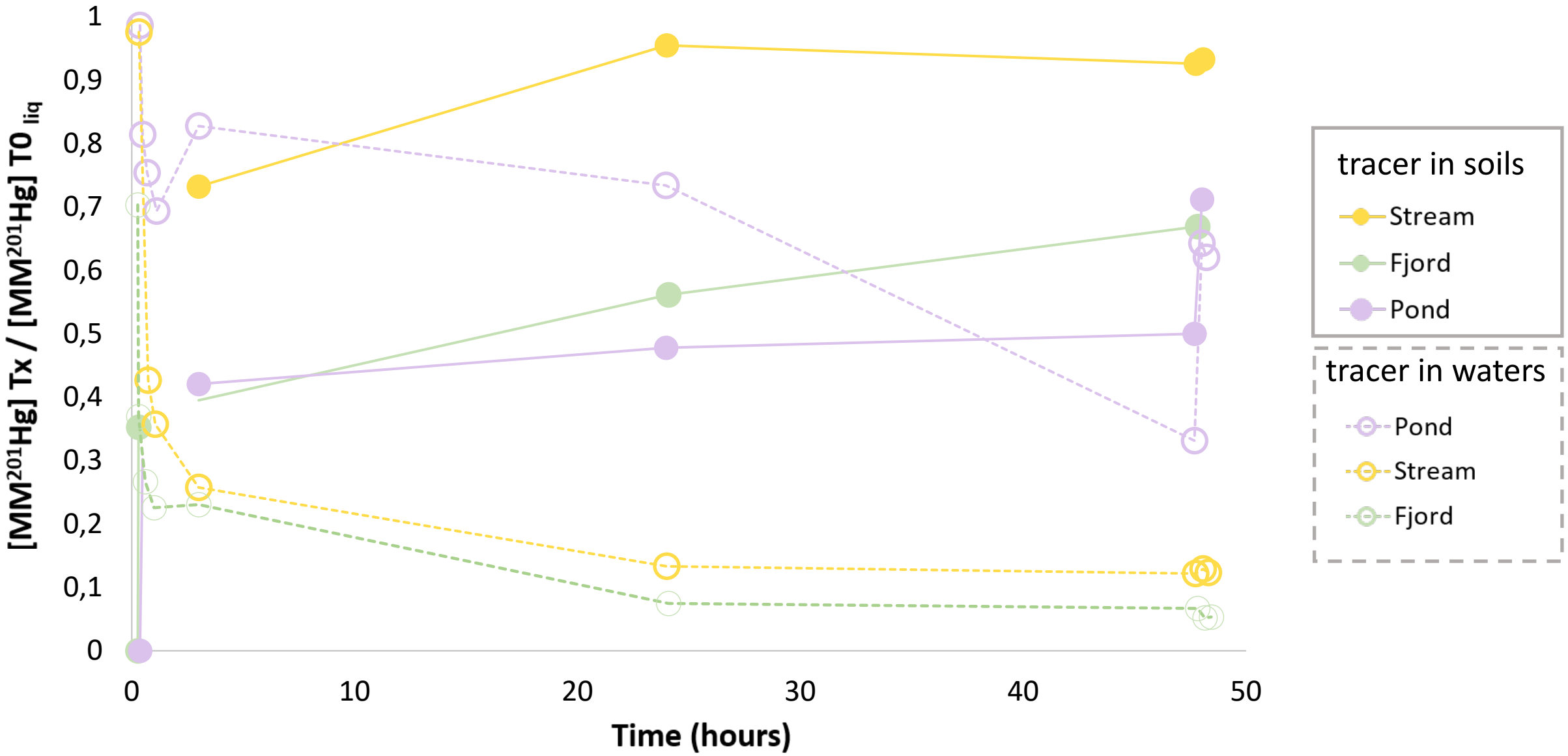
Desorption Stream Mineral Soil



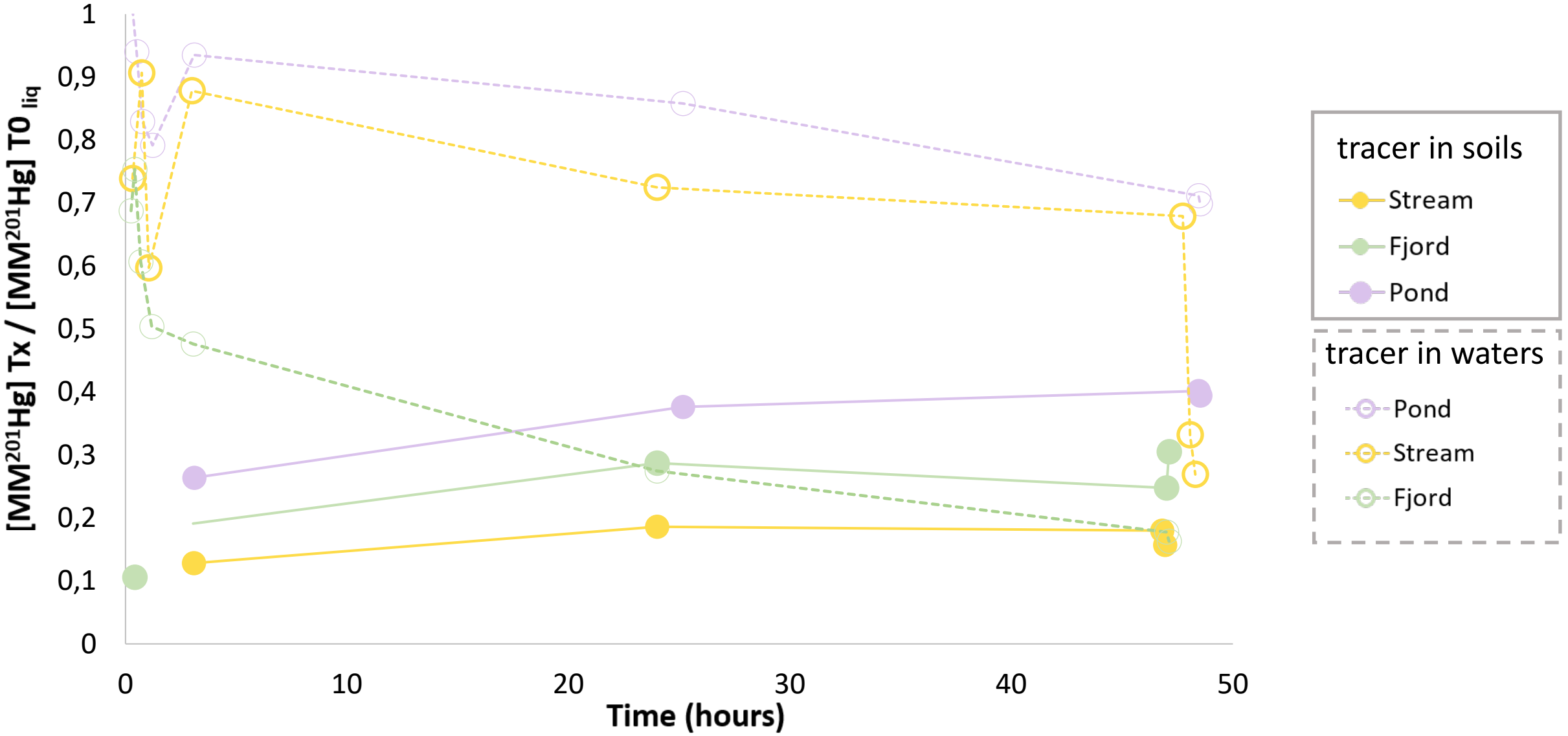
Desorption Mineral Soil

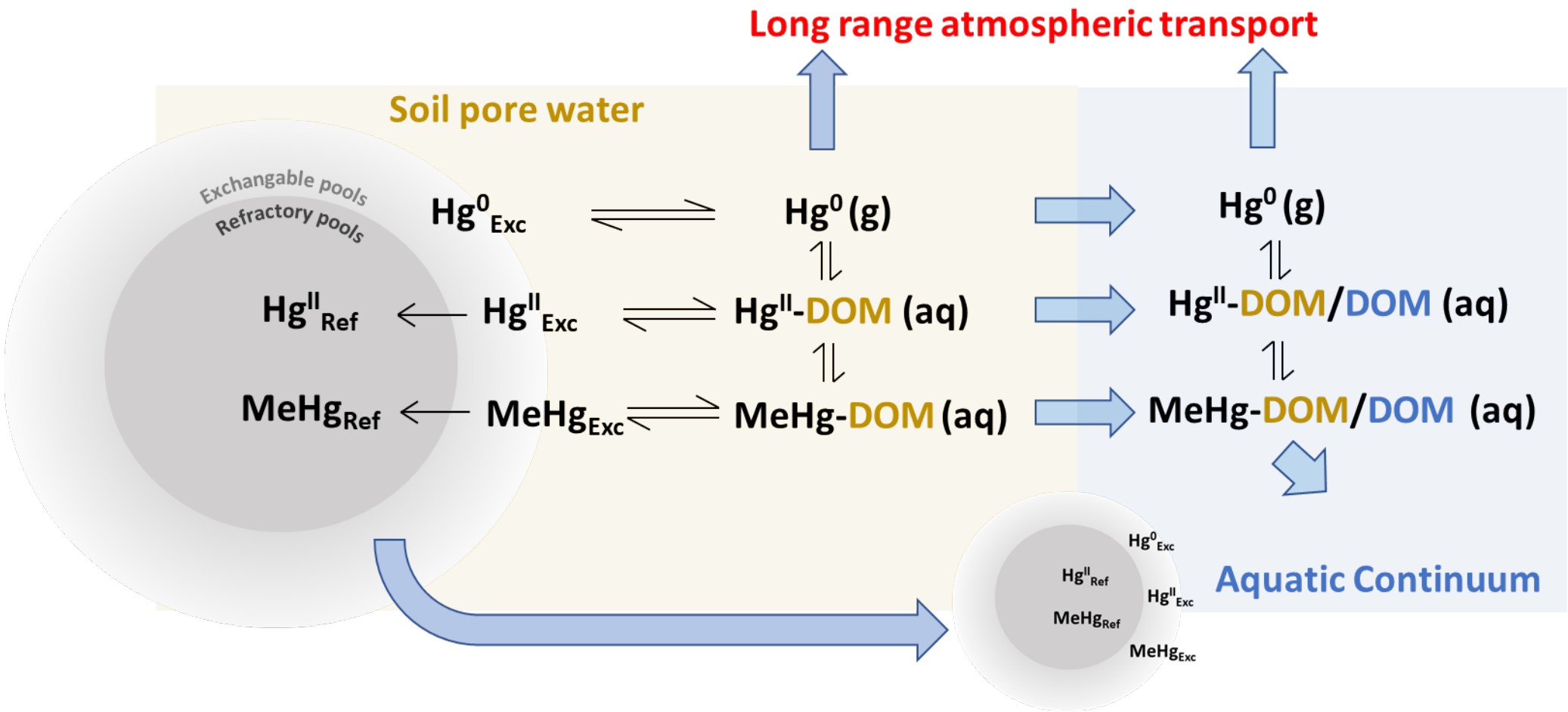


Adsorption Stream Mineral Soil



Adsorption mineral soil




Long range atmospheric transport
Soil pore water
Exchangable pools
Refractory pools
Hg^0_{Exc}
Hg^0 (g)
Hg^0 (g)
Hg^{II}_{Ref}
Hg^{II}_{Exc}
Hg^{II}-DOM (aq)
Hg^{II}-DOM/DOM (aq)
$MeHg_{Ref}$
$MeHg_{Exc}$
MeHg-DOM (aq)
MeHg-DOM/DOM (aq)
Hg^0_{Exc}
Hg^{II}_{Ref}
Hg^{II}_{Exc}
$MeHg_{Ref}$
$MeHg_{Exc}$
Aquatic Continuum

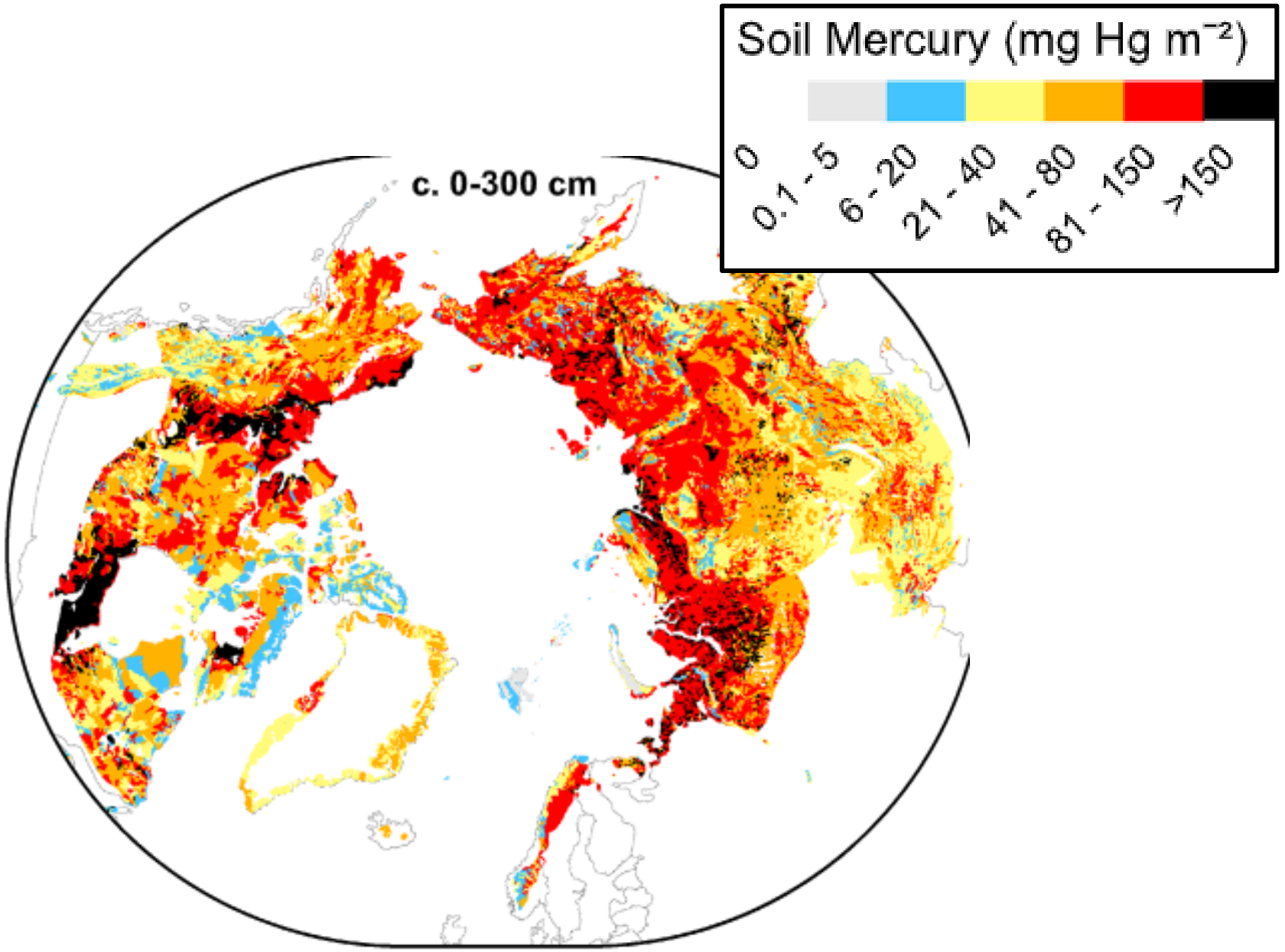
% refractory	Peat	Stream mineral	Mineral
fjord	38.57	40.65	36.38
stream	82.81	24.87	17.51
pond	66.78	13.80	35.88

Peat

Mineral

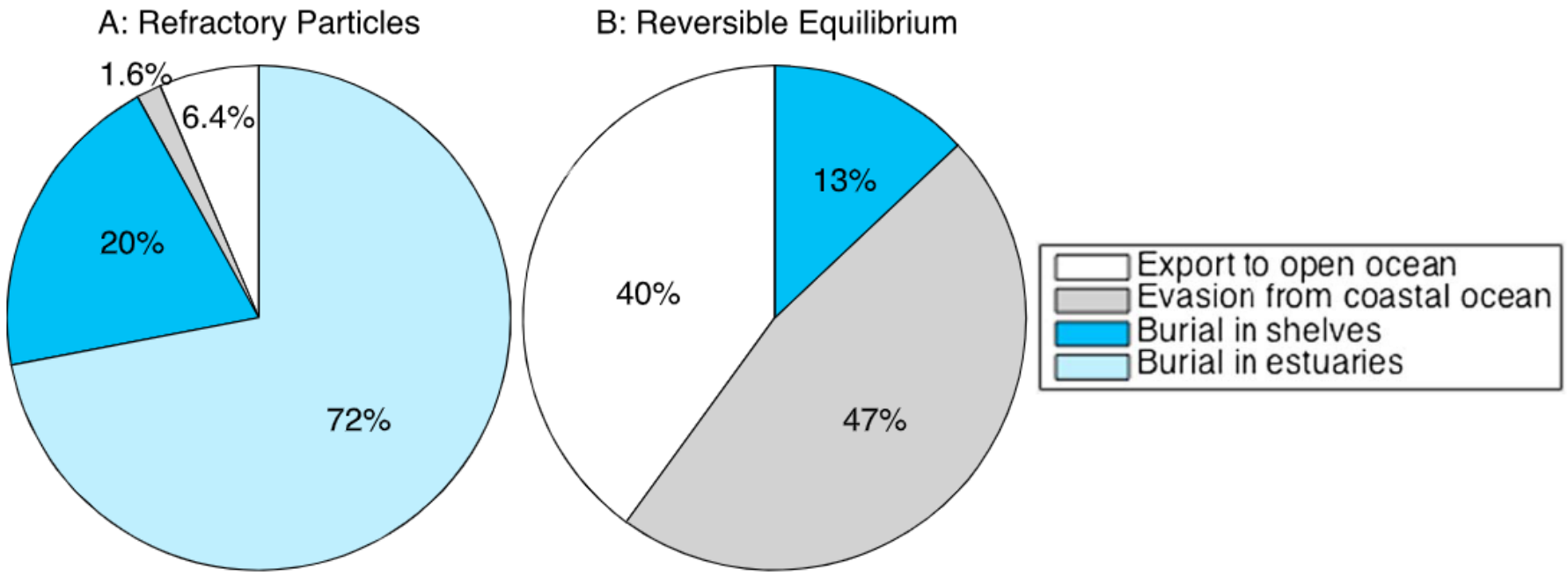
Stream Mineral

Charlotte Haugk

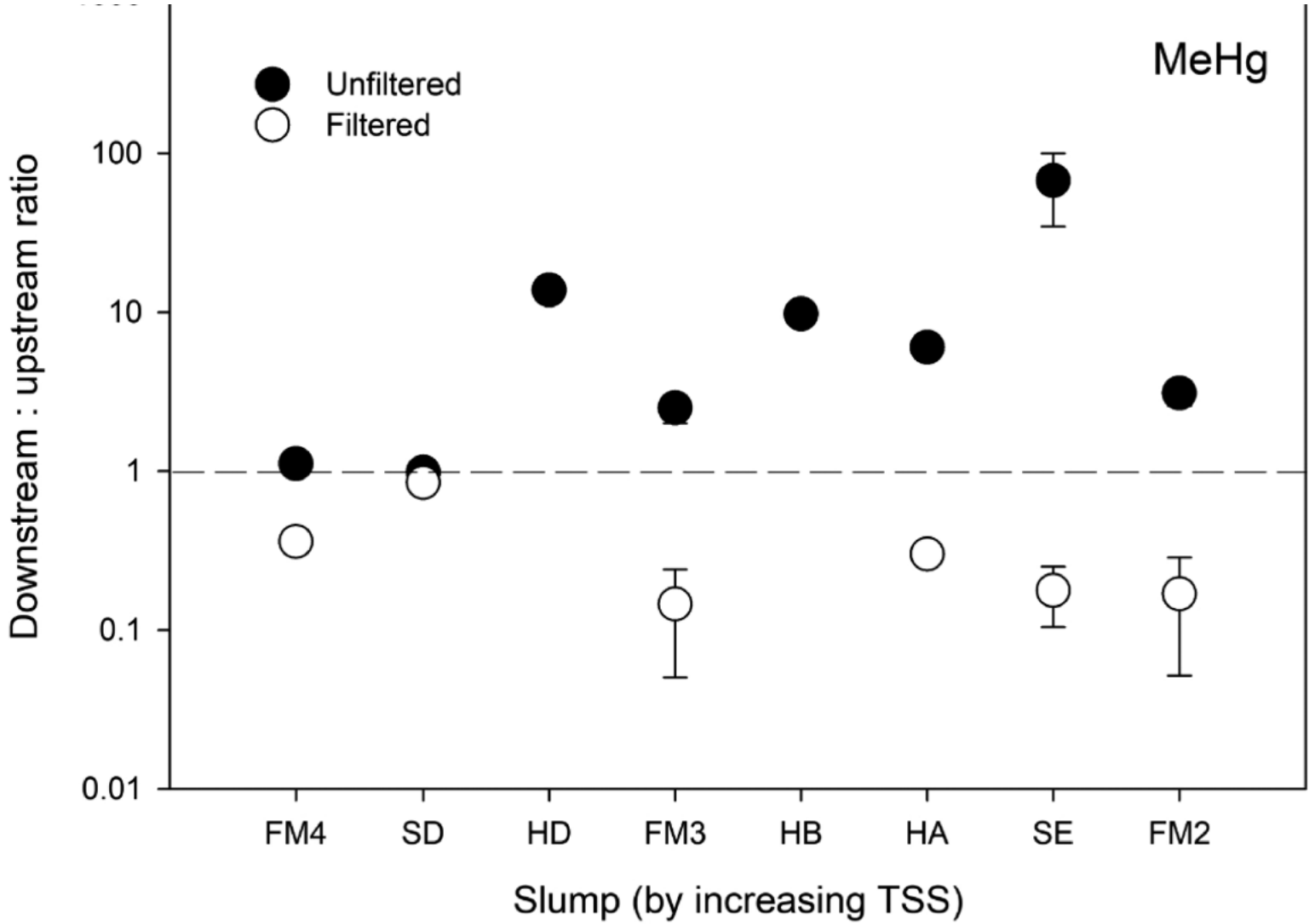


Schuster, P.F., Schaefer, K.M., Aiken, G.R., Antweiler, R.C., Dewild, J.F., Gryziec, J.D., Gusmeroli, A., Hugelius, G., Jafarov, E., Krabbenhoft, D.P., Liu, L., Herman-Mercer, N., Mu, C., Roth, D.A., Schaefer, T., Striegl, R.G., Wickland, K.P., Zhang, T., 2018. Permafrost Stores a Globally Significant Amount of Mercury. Geophys. Res. Lett. 45, 1463–1471. https://doi.org/10.1002/2017GL075571

The importance of refractory Hg

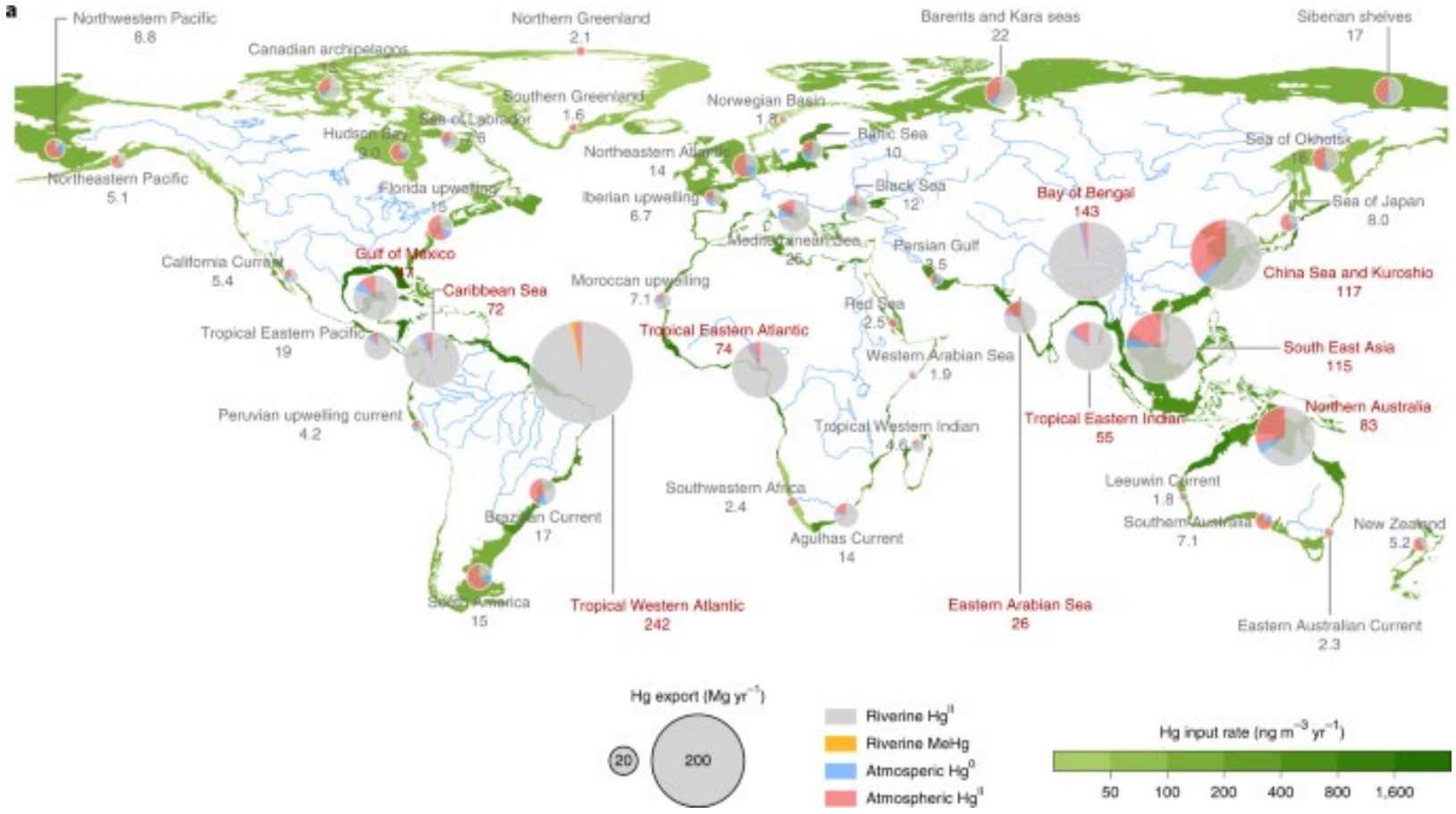


Zhang, Y., Jacob, D.J., Dutkiewicz, S., Amos, H.M., Long, M.S., Sunderland, E.M., 2015. Biogeochemical drivers of the fate of riverine mercury discharged to the global and Arctic oceans. Global Biogeochem. Cycles 29, 854–864. https://doi.org/10.1002/2015GB005124



St Pierre, K.A., Zolkos, S., Shakil, S., Tank, S.E., St Louis, V.L., Kokelj, S. V., 2018. Unprecedented Increases in Total and Methyl Mercury Concentrations Downstream of Retrogressive Thaw Slumps in the Western Canadian Arctic. Environ. Sci. Technol. 52, 14099–14109. https://doi.org/10.1021/acs.est.8b05348

Rivers as the largest source of mercury to coastal oceans worldwide



Liu, M., Zhang, Q., Maavara, T., Liu, S., Wang, X., Raymond, P.A., 2021. Rivers as the largest source of mercury to coastal oceans worldwide. Nat. Geosci. 14. https://doi.org/10.1038/s41561-021-00793-2

Calculation refractory pools

$$Refractory\ pool\ (\%) = \frac{\text{Refractory } [MM^{201}Hg]_{solid}}{\text{T0 desorption } [MM^{201}Hg]_{solid}} * 100$$

Calculation of refractory MeHg pools (step III)

APPROACH

MeHg adsoption (step I)

$MM^{201}Hg_{ref}$ $MM^{201}Hg_{exc}$ $\Longleftarrow$ $MM^{201}Hg\text{-}R$ (aq)

$$K_A = \frac{[MMHg]_{solid\ phase}}{[MMHg]_{aqueous\ phase}} \Rightarrow [MMHg]_{solid\ phase} = MM^{201}Hg_{exc} \Rightarrow K_A = \frac{[MM^{201}Hg]_{exc}}{[MMHg]_{aq\ STEP\ I}}$$

MeHg desoption (step II)

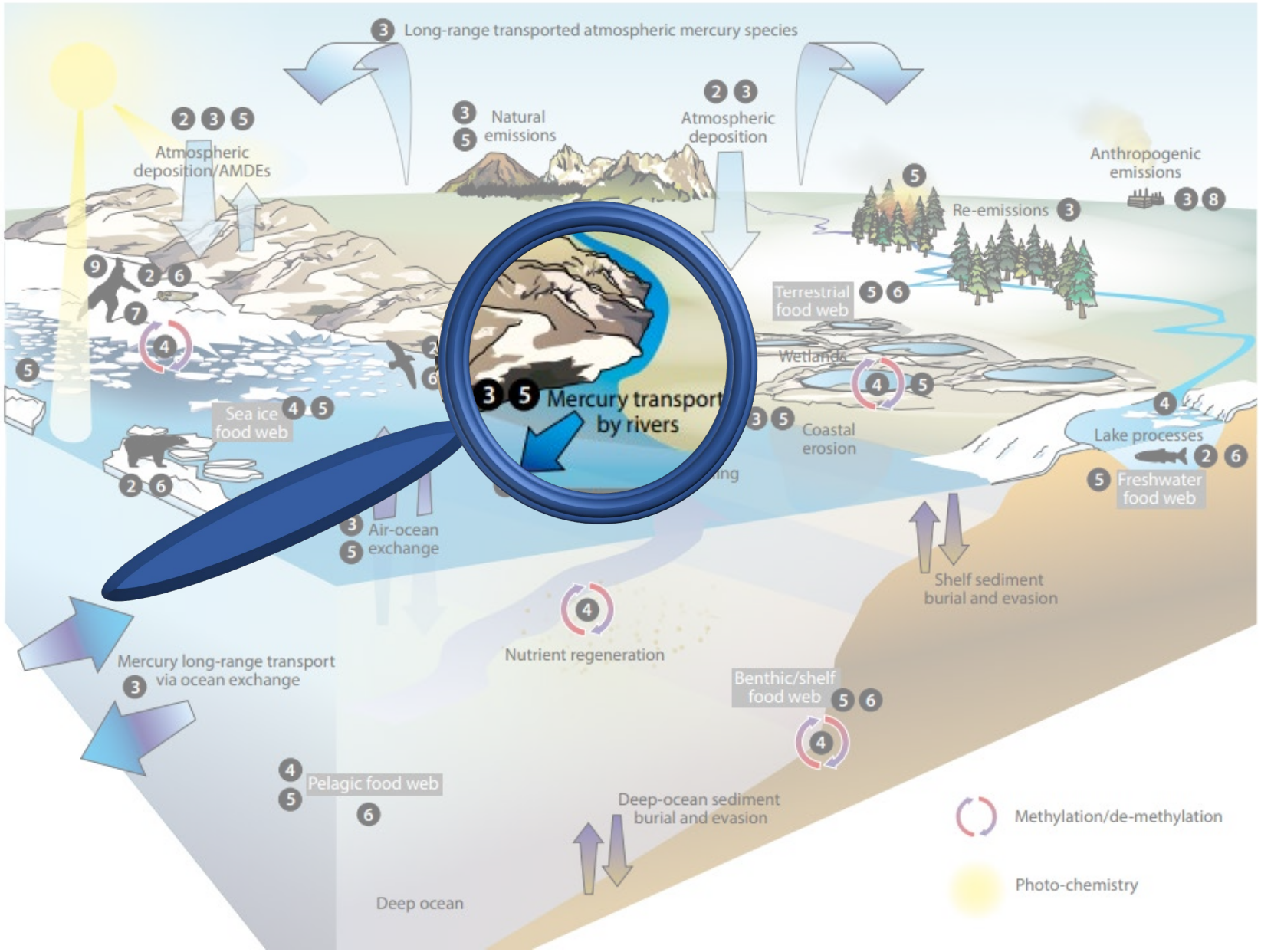
$MM^{201}Hg_{ref}$ $MM^{201}Hg_{exc}$ $\Longrightarrow$ $MM^{201}Hg\text{-}R$ (aq)

$$K_D = \frac{[MMHg]_{solid\ phase}}{[MMHg]_{aqueous\ phase}} \Rightarrow K_D = \frac{[MM^{201}Hg_{ref}] + [MM^{201}Hg_{exc}]}{[MMHg]_{aq\ STEP\ II}}$$

$$\Rightarrow [MMHg]_{solid\ phase} = [MM^{201}Hg_{ref}] + [MM^{201}Hg_{exc}]$$

Refractory pools ($[MM^{201}Hg_{ref}]$)

$$K_D = \frac{[MM^{201}Hg_{ref}]}{[MMHg]_{aq.\ STEP\ II}} + K_A$$

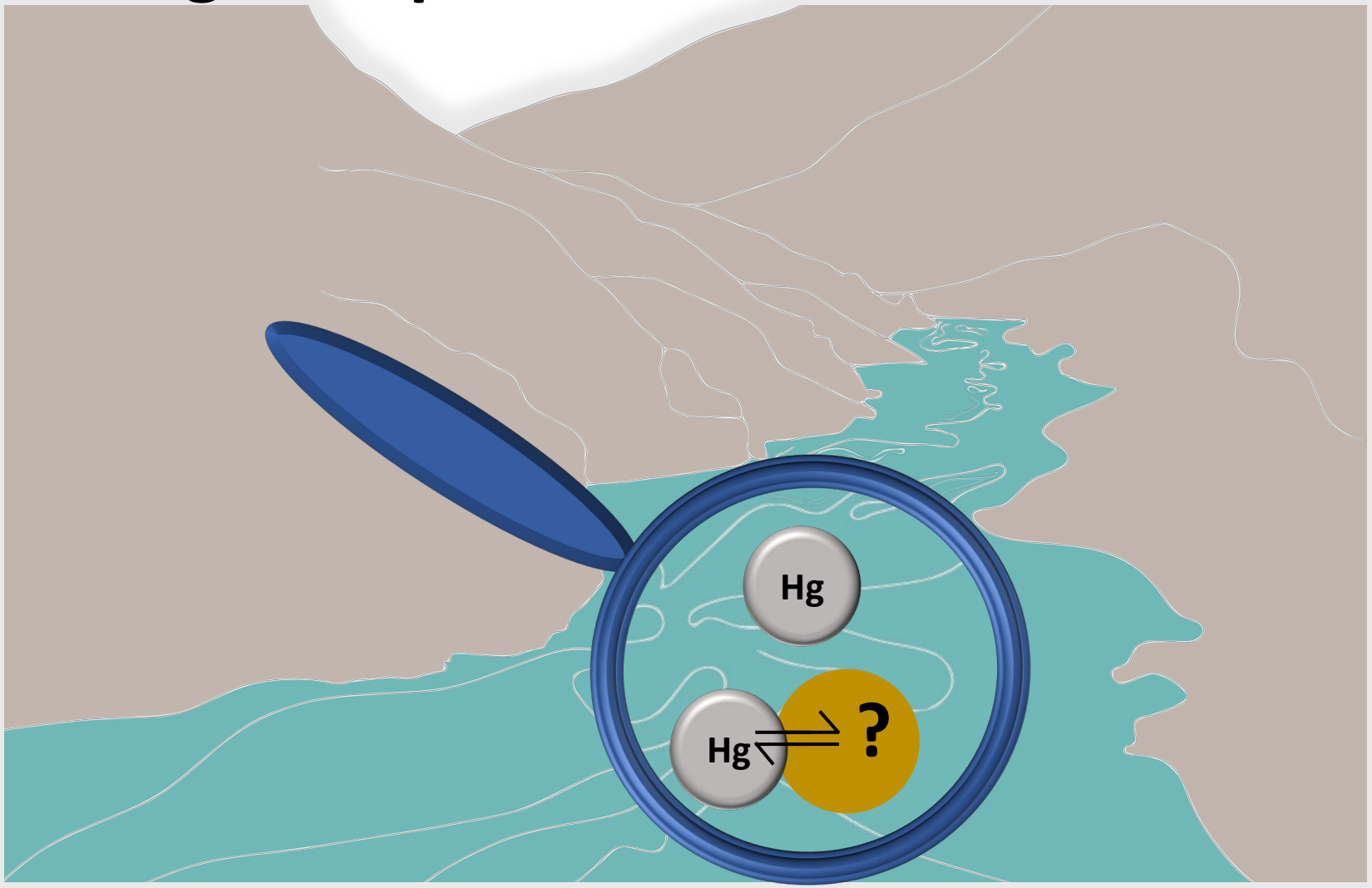


AMAP, 2021. AMAP Assessment 2021: Mercury in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Tromsø, Norway. 324 pp

Story line idea

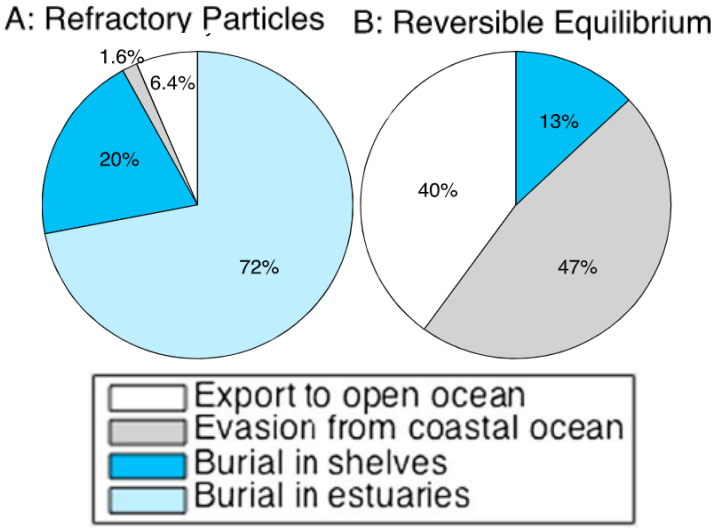
- As we all know mmhg is a concern in seafood (???% of which is) caught in coastal areas
- However there are still a lot of factors unknown regarding the entrance of MMHg at the base of marine food webs
- Rivers are the main source of Hg and MMHg to coastal oceans globally and the majority is particle bound
- To understand the fate of this Hg (and in this talk I will focus on MMHg) in the ocean one important aspect to take into consideration is the refractory fraction of the MMHg transported from the terrestrial to the marine environment (Zhang study & explain)
- So the idea is that if MMHg adsorbs to a particle, some of it will not be available to desorb again – that is the refractory pool here whereas there is also an exchangeable pool which represents the MMHg that can desorb back into the pore water depending on the equilibrium

Formation of refractory MMHg pools during transport



Rivers are an important source of marine (MM)Hg (Liu et al. 2021)

Landscape features and soil characteristics can impact binding (St Pierre et al. 2018)



(Zhang et al. 2015)

Particle remineralization as the major source of dissolved Hg in deep ocean (Lamborg et al. 2016)

Liu, M., Zhang, Q., Maavara, T., Liu, S., Wang, X., Raymond, P.A., 2021. Rivers as the largest source of mercury to coastal oceans worldwide. Nat. Geosci. 14. https://doi.org/10.1038/s41561-021-00793-2
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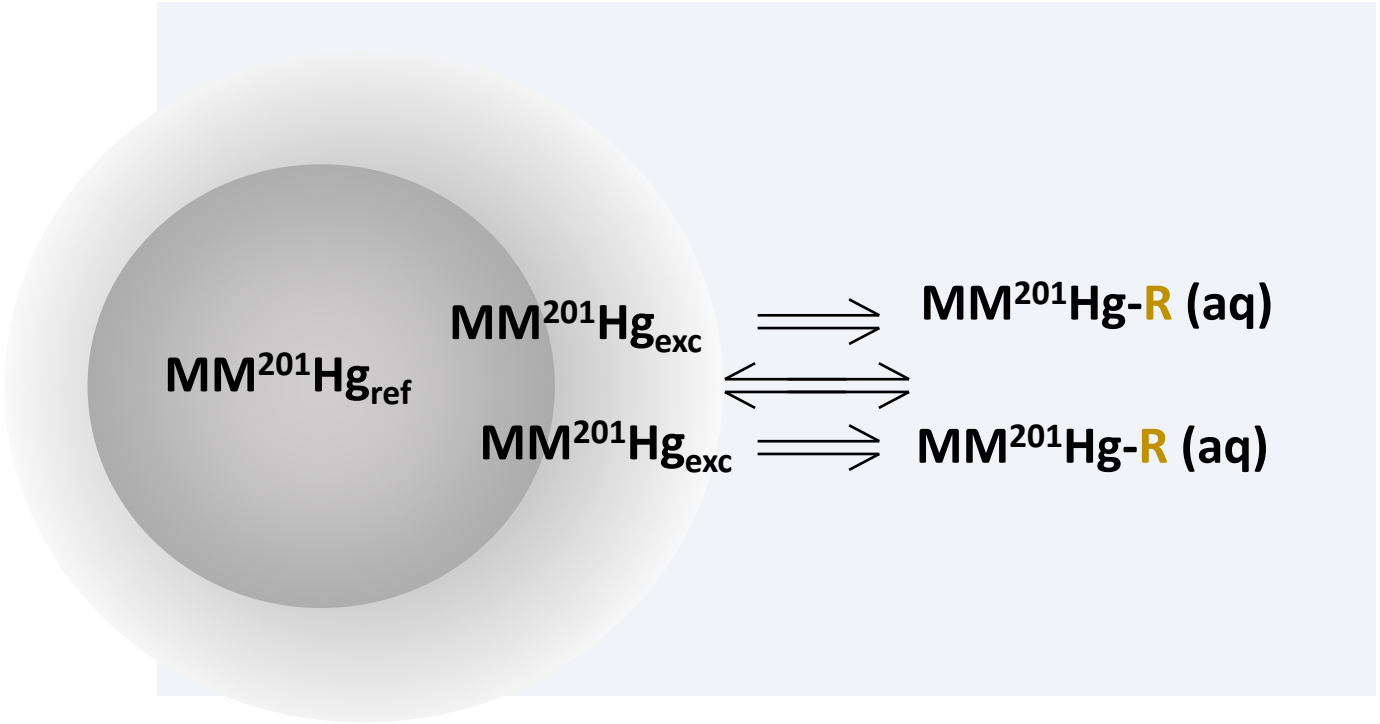
Lamborg, C.H., Hammerschmidt, C.R., Bowman, K.L., 2016. An examination of the role of particles in oceanic mercury cycling. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 374. https://doi.org/10.1098/rsta.2015.0297

Why is the arctic relevant

- Thawing perfmafrost expected to release a lot of stored Hg
- Due to wet conditions methylation hot spots ??
- Refractory pools in the arctic are expected to be much lower in arctic rivers compared to lower latitudes & play a critical role for How available this remobilized (MM)Hg is to end up in marine food webs

Step II. MeHg Desorption (8 weeks)

Approach



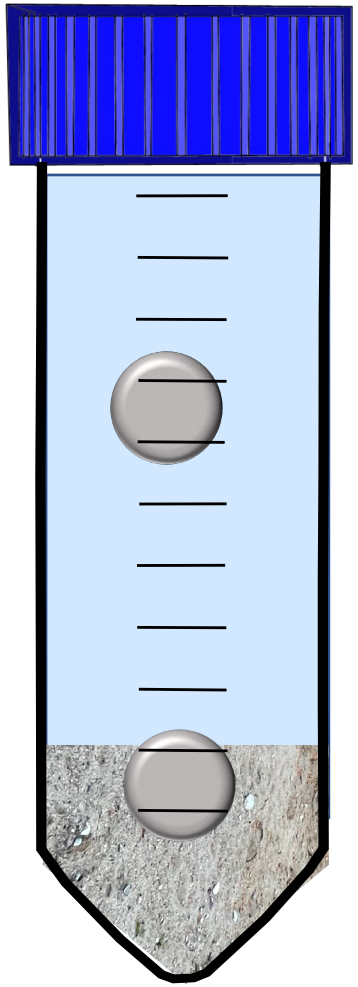
K_A Solid-to-Water Partitioning Coefficient for the **adsorption step**

K_D Solid-to-Water Partitioning Coefficient for the **desorption step**

$$K_D = \frac{[MMHg]_{solid\ phase}}{[MMHg]_{aqueous\ phase}}$$

Experimental setup

Incubation



1. 0.5 – 1 g soil

2. 50 mL water

3. Pre-Equilibration 24 hours

4. Addition of 10 ng $MM^{201}Hg$

5. Adsorption incubation
48 hours

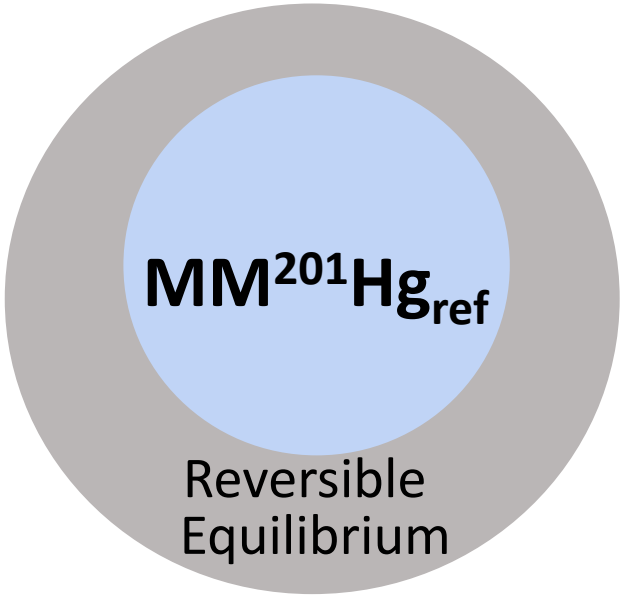
6. Water exchange

7. (re-)Desorption incubation
8 weeks

Conditions:
10 °C climate chamber

Rotation at 1 rpm

Calculation refractory pools



$$kA = \frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}}$$

At equilibrium of the adsorption phase

$$kD = \frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}}$$

At equilibrium of the desorption phase

$$kD = \frac{\text{ReversibleEquilibrium } [MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}} + \frac{\text{Refractory } [MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}}$$

$$kD - kA = \frac{\text{Refractory } [MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{liquid}}$$

$$\text{Refractory } [MM^{201}Hg]_{solid} = (kD - kA) * [MM^{201}Hg]_{liquid}$$

Calculation refractory pools

$$kA = \frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{aq}}$$

At equilibrium of the adsorption phase

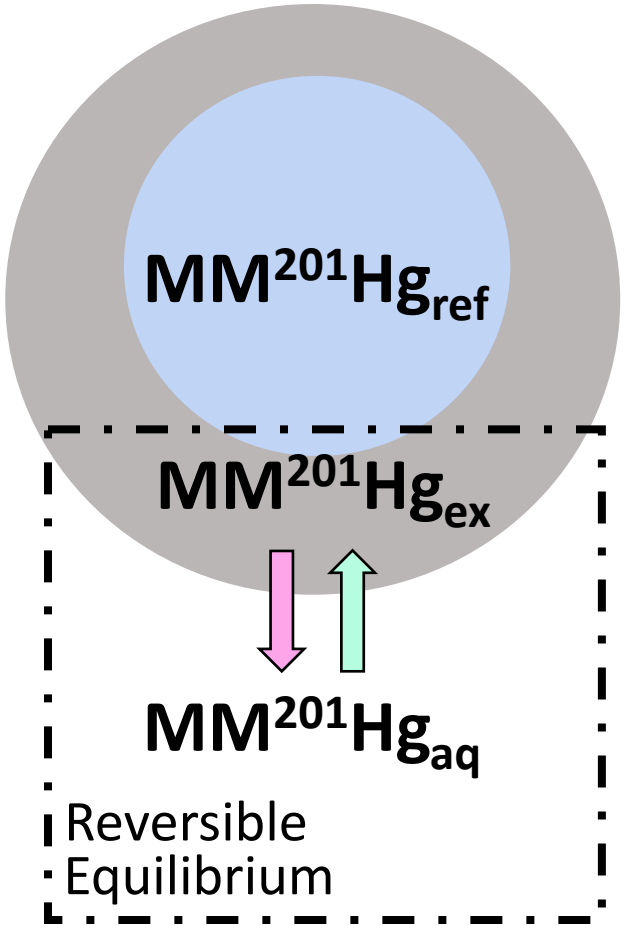
$$kD = \frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{aq}}$$

At equilibrium of the desorption phase

$$kD = \underbrace{\frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{aq}}}_{\text{Reversible Equilibrium}} + \underbrace{\frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{aq}}}_{\text{Refractory}}$$

$$kD - kA = \underbrace{\frac{[MM^{201}Hg]_{solid}}{[MM^{201}Hg]_{aq}}}_{\text{Refractory}}$$

$$\underbrace{[MM^{201}Hg]_{solid}}_{\text{Refractory}} = (kD - kA) * [MM^{201}Hg]_{aq}$$



ref	refractory
ex	exchangeable
aq	aqueous