

***Processes that Affect the Chemistry  
and Transport of Contaminants  
in the Subsurface: An Overview***

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# *What are special challenges of soil/groundwater pollution*

- Air pollution (urban), **response time,  $t \sim$  days**
- Surface water pollution
  - Rivers,  **$t \sim$  weeks – months** (unless problem is associated with sediments)
  - Lakes,  **$t \sim$  months – years** (unless problem is associated with sediments)
- Sediments/soils/groundwater,  **$t \sim$  years to centuries**  
(transport limitations)

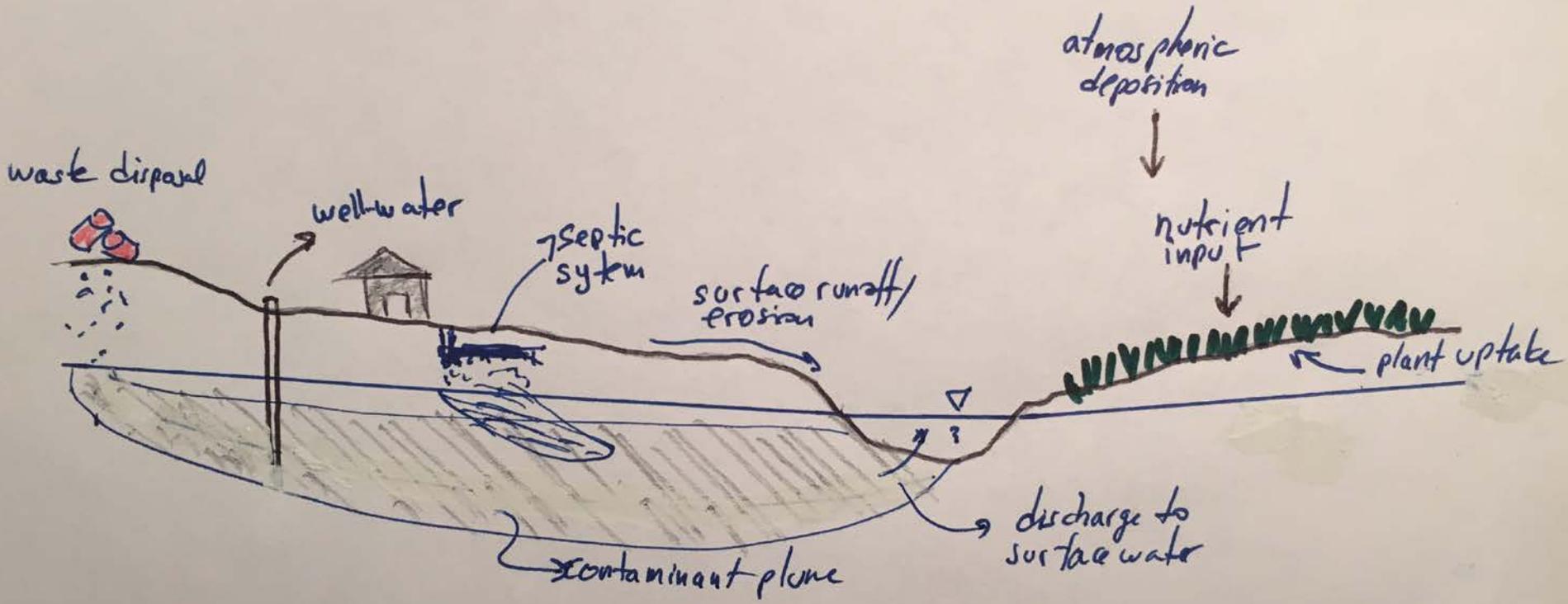
**Short  $t$**  → address source

**Long  $t$**  → address source and need treatment

## *How extensive is the problem?*

- **Regional** → agricultural soils, many kilometers of river sediments. Usually, but not always, low concentrations.
- **Site specific** → spills, waste disposal, industrial activity (manufacturing...), urban, septic systems. Most times high concentrations above drinking water levels.

# Exposure pathways



For drinking water wells, for example, ~15% of US population depends on private wells.  
~ 23% of these wells contains at least one contaminant at levels of potential health concern.

<https://water.usgs.gov/edu/gw-well-contamination.html>

# *Processes that affect the fate, and transport of subsurface contaminants*

- **Immobilization** (sorption, precipitation).
- **Mobilization** (formation of soluble complexes, dissolution).
- **Reaction** (mineralization [fast/slow], formation of stable intermediates, change in chemical speciation).

# Sorption

- $K_d, K_p [=] \left( \frac{\text{mass of compound sorbed}}{\text{mass of soil}} \right) / \left( \frac{\text{mass of compound in solution}}{\text{volume of solution}} \right)$
- **Ionic species** (e.g., trace metals): Ion exchange process, but since it is affected by other ions and pH it is best described via a surface complexation model.  $K_d$
- $K_d = f(\text{pH, presence of other ions, T, etc.})$
- **Low solubility organics**: Partition into the organic fraction of soil.  $K_p$  is proportional to fraction of soil organic carbon ( $f_{OC}$ ) and to the compound's octanol water partitioning ( $K_{OW}$ ) (or inversely proportional to its solubility).  $K_p$
- $K_p \sim 0.63 f_{OC} K_{OW} = K_{OC} f_{OC}$

# Why do we need to quantify sorption?

- $$v_{pollutant} = \frac{v_{water}}{(1 + \frac{K_{pd} \delta}{\theta})}$$

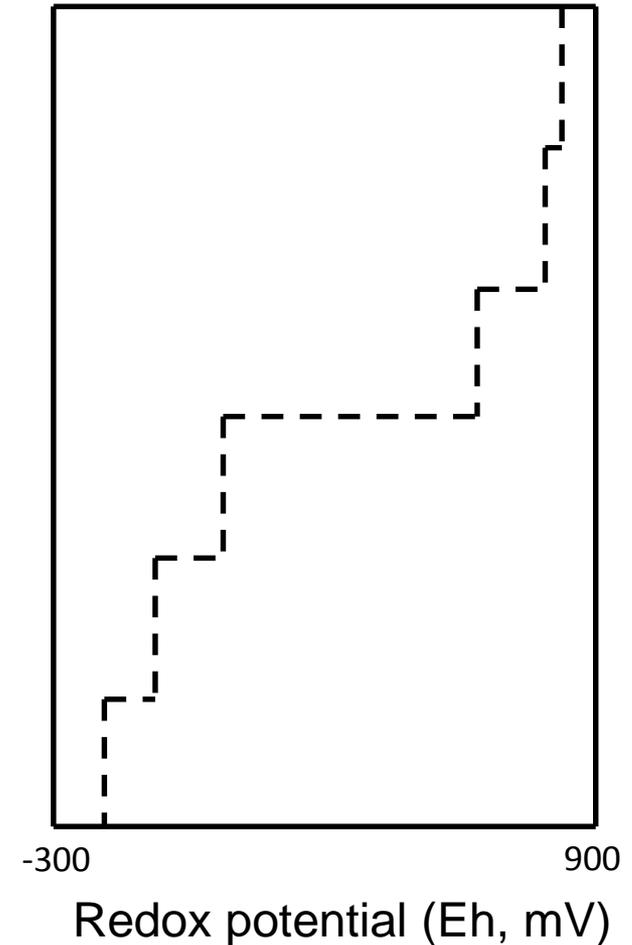
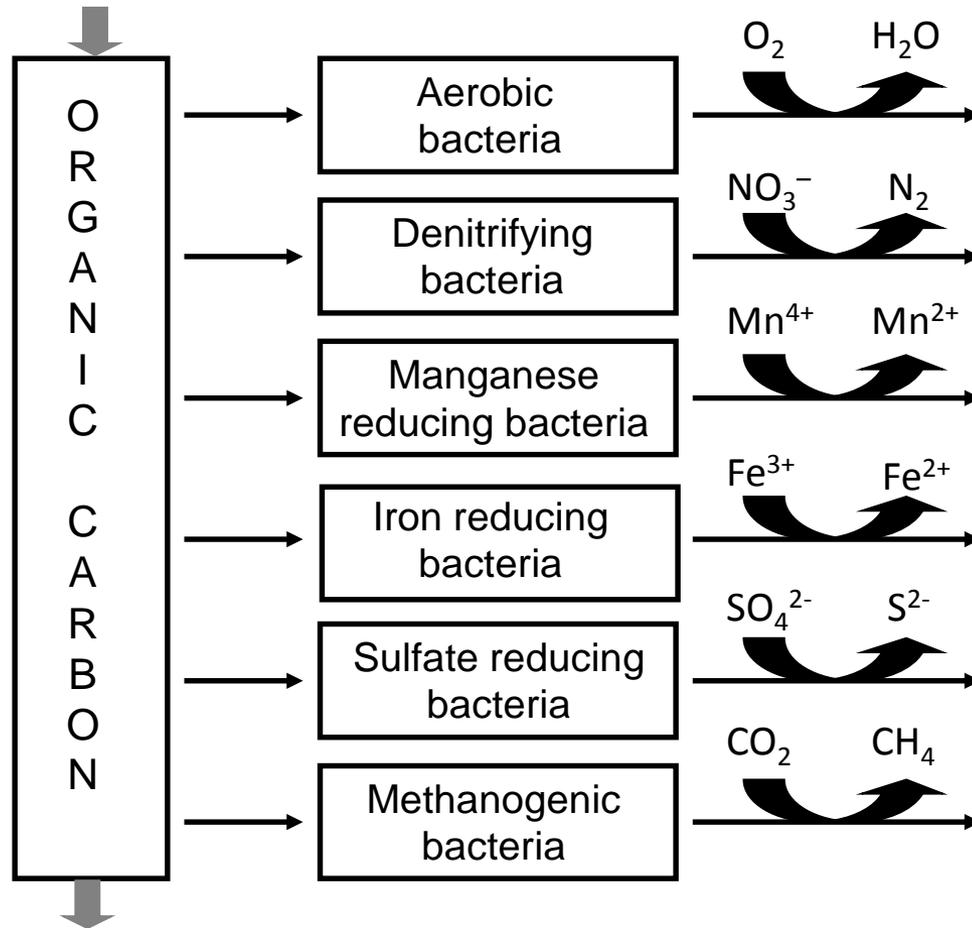
$\delta$  = bulk density,  $\theta$  = porosity

- When only the fraction of a contaminant in the dissolved phase reacts (e.g., many biodegradation processes), the bulk reaction rate,  $r = \frac{r_{dissolved\ phase}}{(1 + \frac{K_{pd} \delta}{\theta})}$

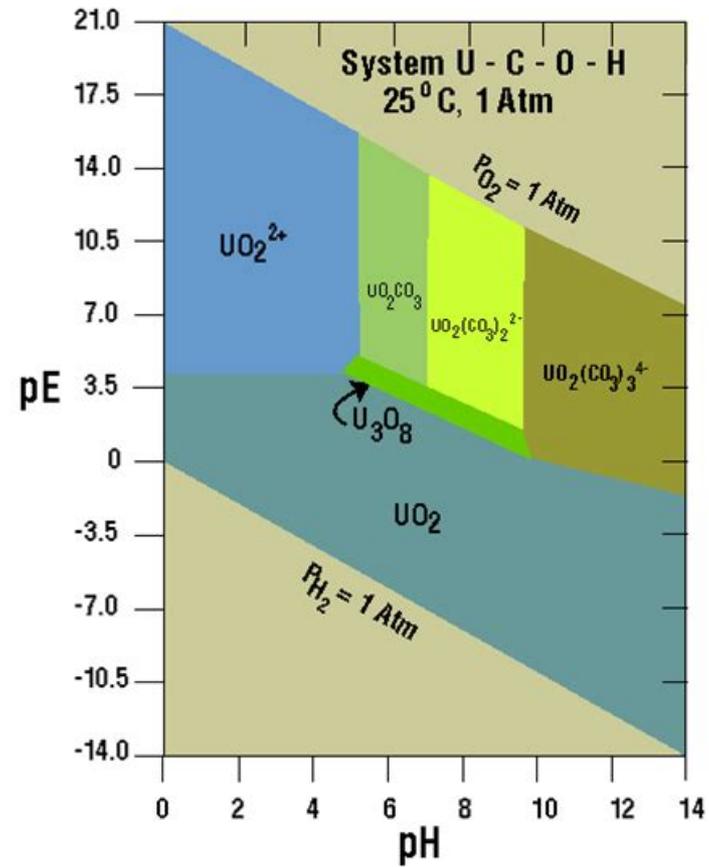
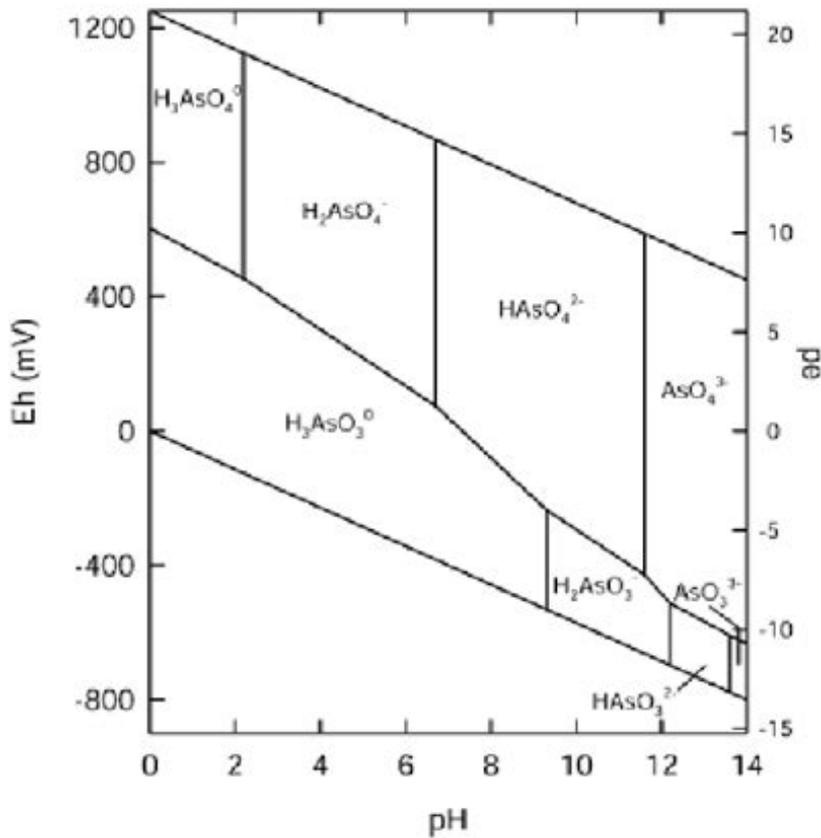
# Biology drives groundwater redox conditions.

## Sequential utilization of major electron acceptors

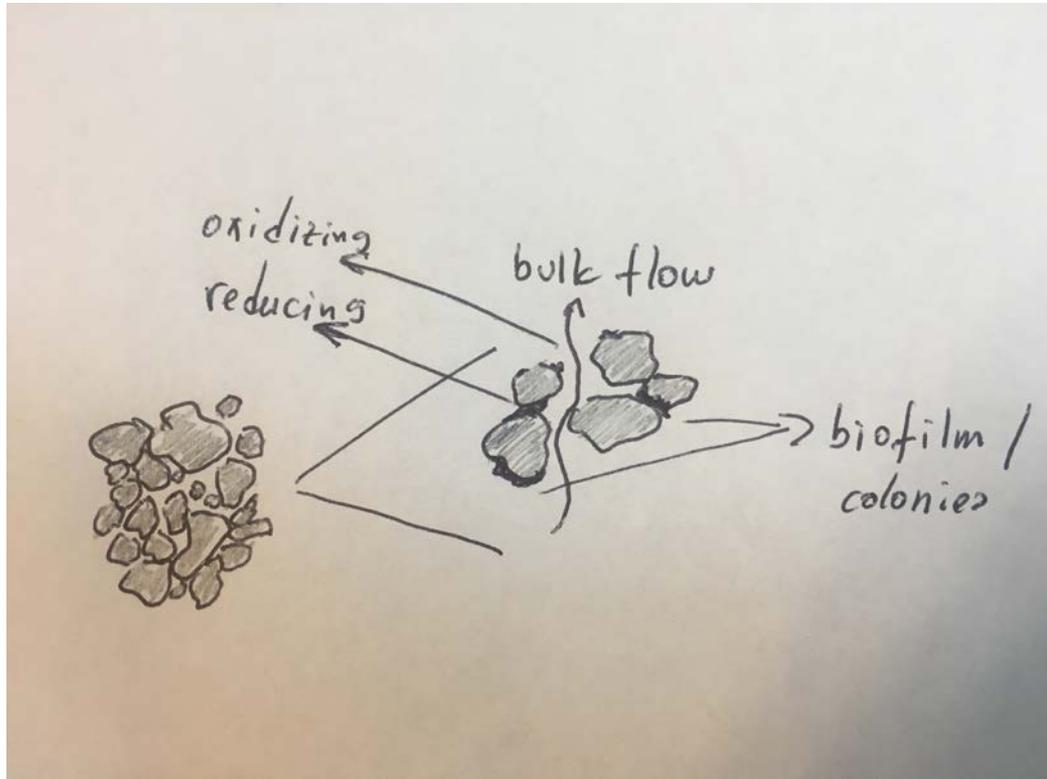
water flow



# Speciation at equilibrium is driven by the redox conditions in soils/groundwater



# *Soil heterogeneity can make chemistry difficult to interpret*



Sampling is biased towards water in major flow paths.

Transport in some pores can be diffusion limited while in others governed by advection.

Large range in redox conditions is possible at the pore-scale.

# *Direct/indirect bio-immobilization of trace metals/metalloids/radionuclides, etc.*

- Iron reduction

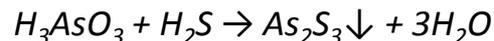
Heterotrophs (e.g. *Geobacter sp.*):  $CH_2O + 4Fe(OH) + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11 H_2O$

Autotrophs (Feammox):  $3Fe_2O_3 \cdot 0.5H_2O + 10H^+ + NH_4^+ \rightarrow 6Fe^{2+} + 8.5H_2O + NO_2^-$

under either iron reduction:  $U(VI) \rightarrow U(IV) \downarrow$

- Sulfate Reduction

Heterotrophs:  $CH_2O + 0.5 SO_4^{2-} + 0.5 H^+ \rightarrow CO_2 + 0.5 HS^- + H_2O$



# *Mobilization of contaminants*

- Oxidation/reduction to more mobile forms. Example: U(IV) is rapidly oxidized to U(VI) in the presence of dissolved oxygen (DO) or  $\text{NO}_2^-$ . Or oxidation of MeS phases in the presence of DO.
- Formation of inorganic complexes (change from anion to cation or vice versa). Example:  $\text{UO}_2^{2+}$  in the presence of carbonate and/or as a function of the pH can form many complexes:  
e.g.  $(\text{UO}_2)^{2+}$ ,  $(\text{UO}_2)_2\text{OH}^+$ ,  $(\text{UO}_2)_2\text{CO}_3^{2-}$ ,  $(\text{UO}_2)_2\text{CO}_3^{4-}$ , ...
- Complexation of metals (e.g.  $\text{Me}^{2+}$ ) with organic matter.  
Minimal observed  $\text{Me}^{2+}$  precipitation with  $\text{HS}^-$  in the presence of high dissolved organic carbon in sulfidic wetland soils. (El Bishlawi et al., 2013 doi:

10.1016/j.ecoleng.2013.06.018.)

# *Biodegradation of organic contaminants*

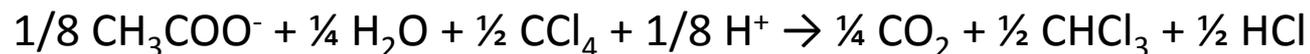
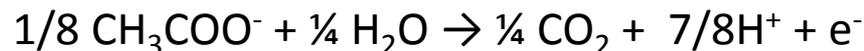
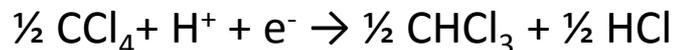
Bacteria population in soils is high  $\sim 10^8$  cells/gr of soil.

Compound may be biodegradable but not degrading. Something is missing:

- Electron acceptor is missing:

$O_2$ ,  $NO_3^-$ , Fe(III), ...

- Electron donor is missing:



- Concentration is too low (specially when there are no alternate organic C source).
- Concentration is too high (toxicity).

# Biodegradation - continued

Compound is biodegradable but something is missing:

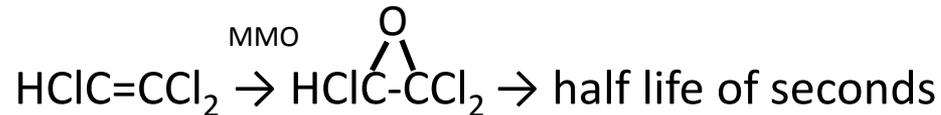
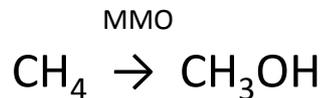
- Trace nutrients

N, P, trace elements, pH

- Specific Bacteria

Dehalogenator - i.e. *Rhodococcus sp.*

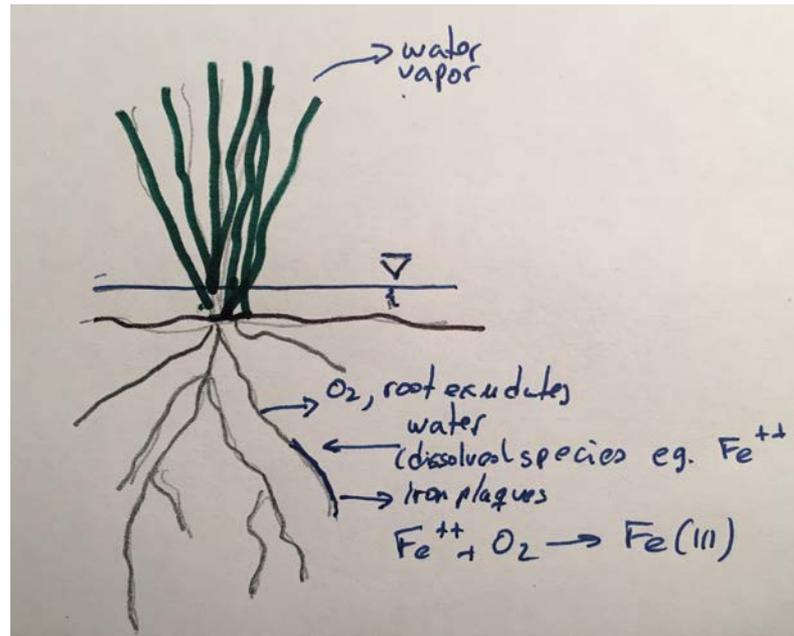
- Inducer



=> Supply CH<sub>4</sub> to induce the production of MMO (aerobic conditions)

# Roots affect chemical processes in surrounding soils (rhizosphere)

- Roots release exudates and siderophores.
- Root turnover provides organic C and N, etc.
- Roots alter water flux (and in unsaturated soils soil moisture) due to plant transpiration.
- Wetland plant roots: Release oxygen into pore-water, causing reduced species to oxidize [Fe(III) plaque formation on root surfaces].



# Iron oxides on root surfaces

Mesocosm experiments followed by XANES analysis have shown that U is immobilized in the Fe(III) phase on the root surface mostly as U(VI) and remains stable during dry periods when soil becomes unsaturated.

Gilson et al., 2015. doi: 10.1021/acs.est.5b02957.

Although As(V) sorbs strongly onto Fe(III) oxides, mesocosm experiments, varying Fe content in soils and  $\text{SO}_4^{2-}$  loading showed that As speciation, retention in soil, and accumulation in plants was mainly controlled by  $\text{SO}_4^{2-}$ .

XANES analysis showed that increasing the  $\text{SO}_4^{2-}$  concentrations from 0.1 mM to 5 mM resulted 1.5 times more As accumulation in soils, 30 times more in roots, and a 49% decrease in leaves.

Zhang et al., 2017. doi: 10.1016/j.jhazmat.2016.06.022



Image taken by Peter Jaffe

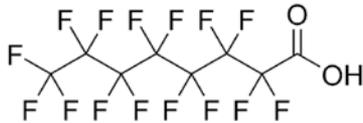


Image from Kaplan et al., DOI: 10.1021/acs.est.5b05165

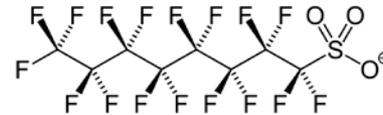
# Example of emerging challenges

## Polyfluoroalkyl substances (PFASs)

Perfluorooctanoic Acid (PFOA)



Perfluorooctyl Sulfonate (PFOS)



Makes products resistant to water/grease stains. Used in the production of carpets, clothing, packaging for food, cookware, etc. Also used for **fire fighting at airfields**.

PFASs are very stable in the environment.

PFOS and PFOA have been found in the blood samples of the general human population and wildlife.

PFOS and PFOA are toxic to laboratory animals.

PFOS and PFOA may cause cancer.

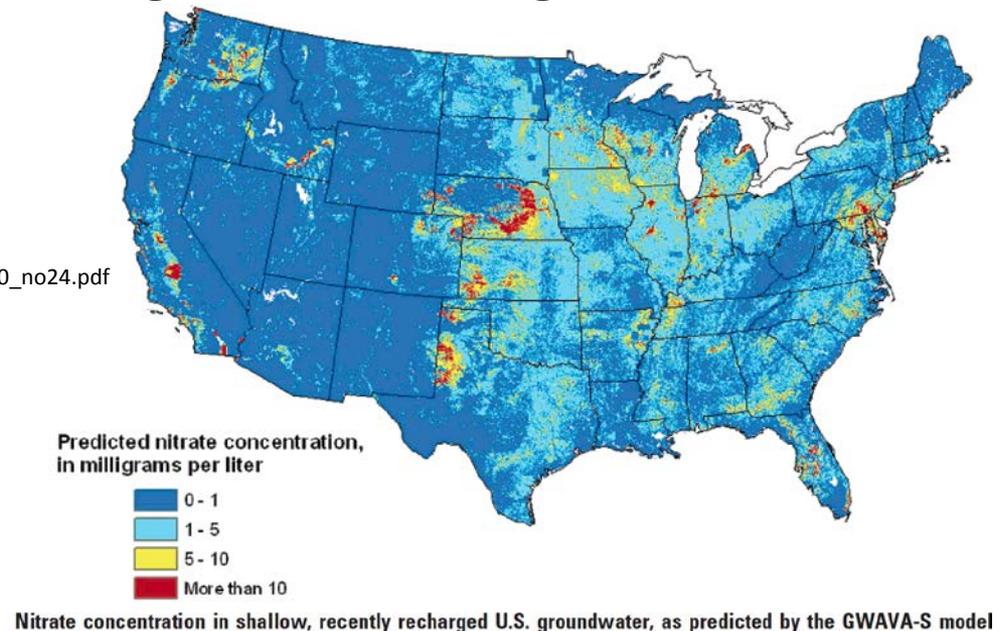
Concentrations in groundwater can be high. PFOA ~ 10<sup>4</sup>, PFOS ~ 10<sup>5</sup> ppt. Specially where firefighting foam was applied (i.e. near airports, military installations, etc.) [https://www.ewg.org/interactive-maps/2017\\_pfa/index.php#.WpLgkmaZOWY](https://www.ewg.org/interactive-maps/2017_pfa/index.php#.WpLgkmaZOWY)

Property affecting transport in groundwater	EPA Health Advisory Concentration Levels (µg/l)			
	PFOS	PFOA		
Water solubility (mg/l)	680	9.5 X 10 <sup>3</sup>		
Organic carbon partition coefficient (K <sub>oc</sub> )	2.57	2.06		
	<b>Year</b>	<b>PFOA</b>	<b>PFOS</b>	
	<b>2002</b>	150	-	
	<b>2006</b>	0.5	-	
	<b>2009</b>	0.4	0.2	
	<b>2016</b>	0.07*	0.07*	* Individual or combined
	<b>NJ</b>	0.04		
	<b>MN</b>	0.035		
	<b>VT</b>	0.02		

# *Excess N loading to watersheds*

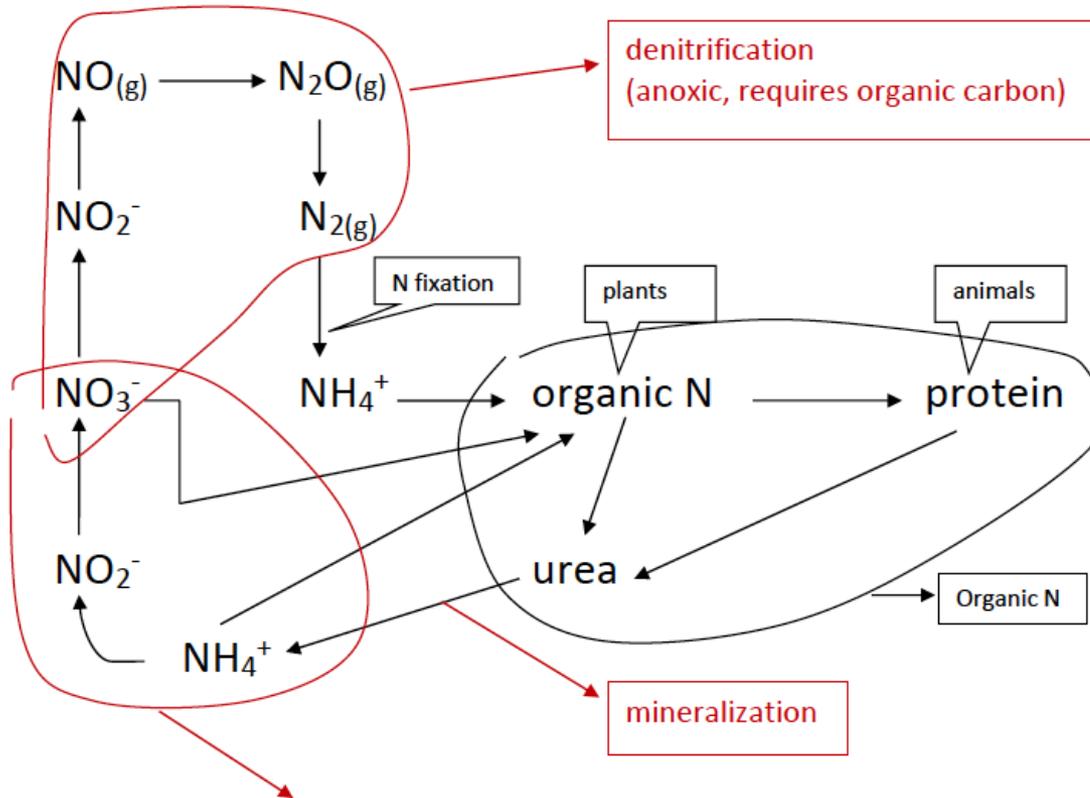
- Yearly mass of synthetically fixed N (Haber-Bosh) is similar to naturally fixed N.
- EPA's limit for  $\text{NO}_3^-$  in drinking water = 10 mg/l.

[https://water.usgs.gov/nawqa/nutrients/pubs/est\\_v40\\_no24/est\\_v40\\_no24.pdf](https://water.usgs.gov/nawqa/nutrients/pubs/est_v40_no24/est_v40_no24.pdf)



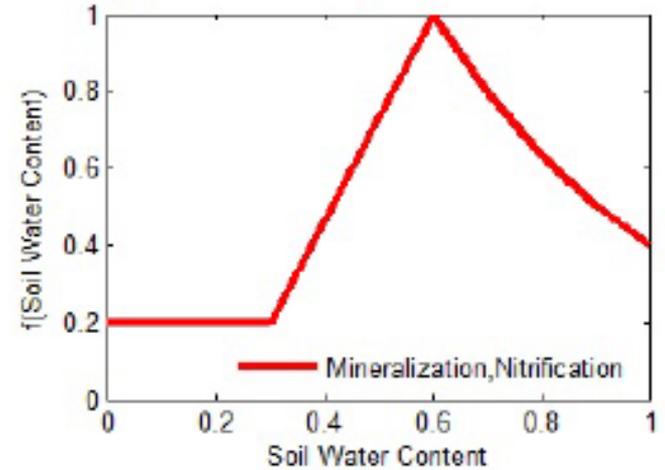
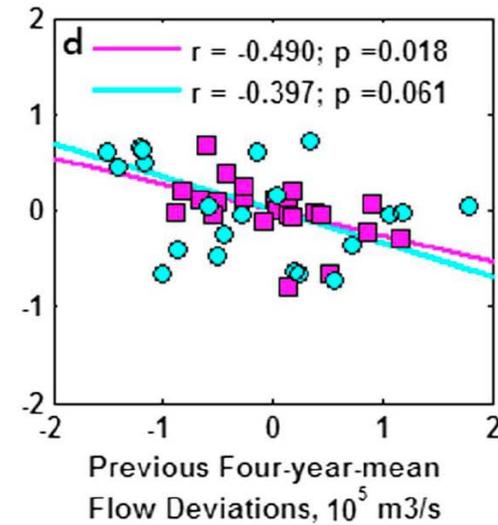
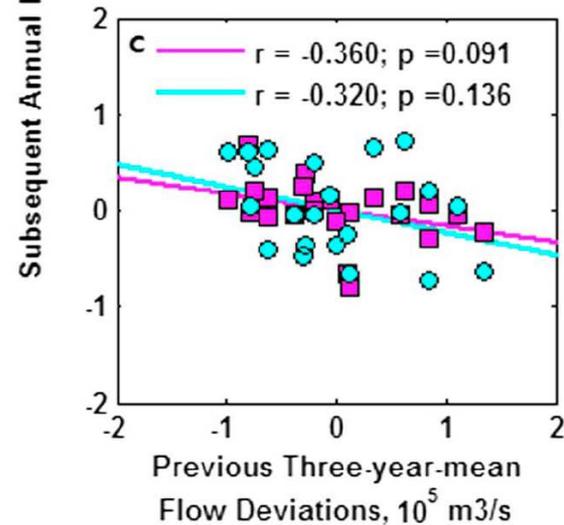
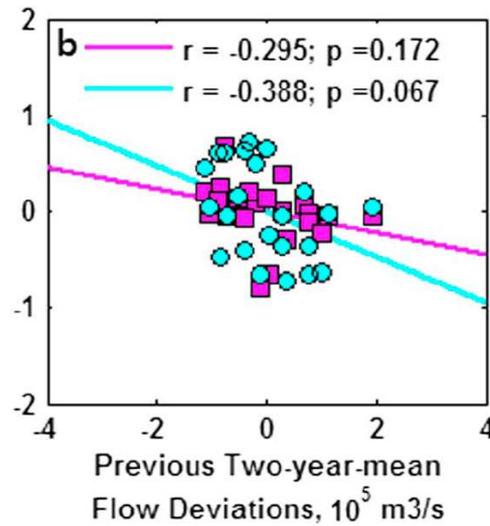
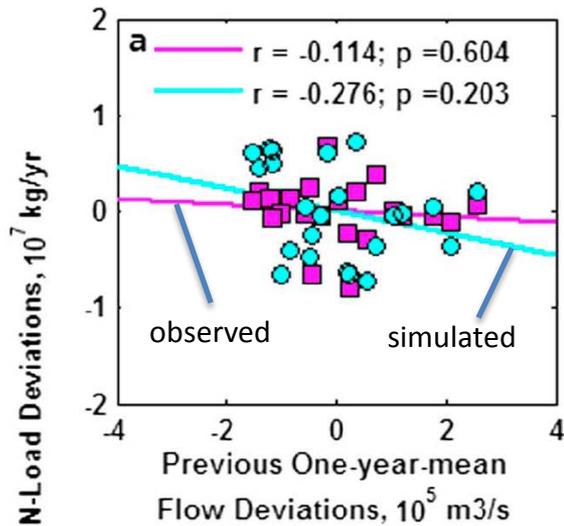
- Oceans are N limited, hence excess N loads lead to significant eutrophication in estuaries and near-shore environment.

# Simplified N cycle schematic

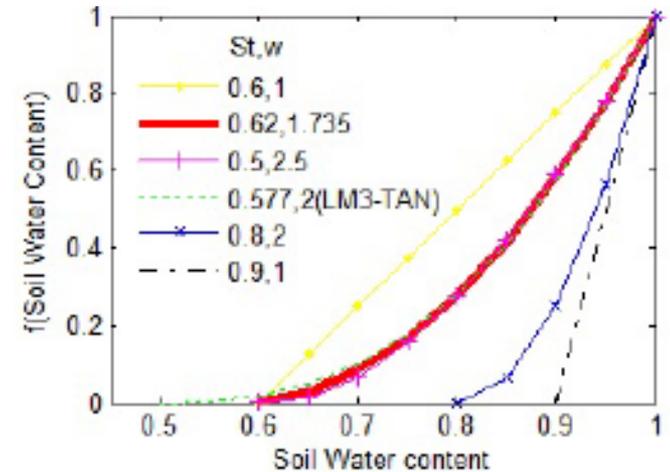


Nitrification: does not require organic carbon AOA,  
 AOB:  $\text{NH}_4^+ + \text{O}_2$  oxic  
 Anammox:  $\text{NH}_4^+ + \text{NO}_2^-$  anoxic  
 Feammox:  $\text{NH}_4^+ + \text{Fe(III)}$  anaerobic, Fe-reducing

# Nitrogen at the watershed-scale: Susquehanna River



Correction factor for mineralization/nitrification rates



Correction factor for denitrification rates

## *Challenges to describe watershed-scale chemical transformations (e.g. N)*

- How do we characterize redox conditions at the watershed (hectare) scale?
- How important are anoxic  $\text{NH}_4^+$  (Anammox, Feammox) oxidation processes at the watershed scale?
- What are groundwater/surface water interactions?

# ***Major advances made and gaps remaining***

*(most certainty an incomplete and biased list)*

- We can reliably predict abiotic dynamics of most inorganic species and their transport in soil. Chemical speciation modeling has advanced significantly.
- Many developments in analytical/imaging methods (e.g., XANES, microscopy,...) provide detailed insights into chemical speciation, distribution of specific elements on soil surfaces, etc.
- Many advances in understanding biodegradation, but it is harder to predict all possible transformations that might happen to an external input of specific pollutants.
- We do understand physical limitations that affect reaction and transport, but they are hard to quantify in real soils.
- Surprisingly, we still get surprised when new molecules turn out to be a soil/groundwater contamination problem.