SERDP

GUIDE BOOKLET

A Mechanistic Understanding of PFAS in Source Zones: Characterization and Control

PFAS Mass Estimator - PFAS Retention by Source-Zone Soils: Practical Knowledge for Remedial Program Managers

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The objective of the attached Technology Transition Product is to provide site managers with a simple model for estimating PFAS mass retained based on publicly available information on soils at their sites.

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Controls on PFAS fate and transport: a practical guide for site assessments

1. Introduction

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Pertinent* questions

What chemical–physical **properties are** most **useful** in predicting fate and transport for PFAS?

What patterns emerge that can be used to develop empirical models to estimate environmental fate and transport?

**adopted from Table 1 in Guelfo et al. 2021. Environmental Toxicology and Chemistry, 40 (12), 3234–3260*

Overall goal

Provide a practitioner-oriented guide in support of the management of PFAS Source Zones, with three major outcomes:

1.) Know how different PFAS interact with different constituents of the solid Source Zone Matrix

2.) Use mechanistic insight to estimate odds for retention, release and transport

3.) Know where to find publicly available data that support the above outcomes

Definition

A **source zone** is defined by three major components:

1.) The physicochemical properties of the xenobiotic **compound** or, aggravating the issue, the compound **mix** that has been introduced

2.) The ability of the source zone to retain or release the contaminant class in question, here called **matrix** properties

3.) The abundance and chemical properties of the aqueous phase, usually the soil solution or the ground water that permeates the source zone (= **solvent** properties)

Consequence

The retention and release of PFAS from Source Zones results from the interplay between three major system components:

1. Compound,
2. Matrix, and
3. Solvent

Interactions between system components can be assessed based on information about component properties

Background, continued

During this project, our team examined controls on PFAS retention and release in soil horizons from Wurtsmith Air Force Base

The activity generated a predictive model for PFAS retention:

$$\boldsymbol{Percent\ Mass\ retained} = \{[0.204 * \boldsymbol{Molar\ Mass}] + [0.318 * \boldsymbol{Mass\ Fluorine}] + [c * \boldsymbol{Nitrogens}] + Z\} \pm 16.2$$

$$c = [3.5 * \boldsymbol{FeOx}] + [89.7 * \%\boldsymbol{OC}] + 22.7$$

$$Z = [0.12 * \boldsymbol{S.A._{BET}}] - 146$$

(More detailed discussion of the model to follow)

Conceptual approach

Guided by this example of a predictive model, we will, in the following,

I. for the three major system* components
- contaminant (PFAS);
- matrix (Soil or sediment) and
- solvent (H_2O),

provide parameterizations that are relevant for PFAS retention in the source zone

II. derive mechanisms of interaction and

III. demonstrate application of the above for site assessments

**We use the chemical term "system" synonymously with the engineering term "source zone"*

Background

One deliverable from the (recently completed) Research Project
“A mechanistic Understanding of PFAS in Source Zones: Characterization and Control”
[Lead-PI: Dr Jennifer Field] was a technical transfer activity aiming

“to allow site managers to use published soil and site information to better understand the fate of PFAS in the soils and sediments at their sites”

Accordingly, the product presented here uses insights from current research to point practioners at information sources that will allow them to connect the dots between PFAS molecular properties, site properties and expected contaminant behavior in source zones

Three major system **components** (with relevant **features**)

Elements of PFAS Source Zone functionality			
Sorbate (PFAS in AFFF, n = 34 in our study)	Sorbent (Environmental matrix = soil or sediment)		Solvent ($H_2O \pm$ NAPL)
	Mineral Phase	Organic Phase	
1. **Fluorocarbon chain**: - voluminous - negligible vdW-bonding capacity - hydrophobic - lipophobic 2. **Amphiphilicity**: - anionic - cationic (infrequent) - zwitterionic 3. **Hydrocarbon sidechain**: - smaller diameter than fluorocarbon sidechain - usually associated with zwitterions - capable of vdW-interactions	1. **Permanent negative surface charge**, pH-independent (Phyllosilicates, Manganese oxides) 2. **Variable** (= positive or negative) **surface charge, pH dependent** (Fe and Al-oxides and hydroxides, poorly crystalline alumino-silicates) 3. **Surfaces without charge**, expressing hydrophobicity (Pyrophyllite, talc)	1. **Hydrophobic, nonpolar moieties** (lignocellulose, cutin, suberin, cell wall lipids, etc.) 2. Functional groups that are **electrically neutral, but polar** (alcoholic OH) 3. Oxygen containing, **ionizable functional groups** (COOH → COO^-; pH dependent) 4. **Frequent amphiphilicity**, extent increasing with progressing decomposition stage	1. **pH** = concentration of H_3O^+ 2. **Concentration of electrolytes** (Na^+; Cl^- etc.) 3. **Valence of electrolytes** (Ca^{++} vs K^+) 4. Concentration of **dissolved organic matter** (polar or negatively charged) 5. Presence of **liquid hydrocarbon solvents** (i.e., Jet Fuel)

Mechanisms of interaction are numerous

In our system of PFAS molecules, porous matrix and nonpolar solvent, numerous **interactions** between the three system components (contaminant, matrix, solvent) may occur, such as

- Partial solvation (formation of a cavity in the solvent surrounding the molecule)
- Electrostatic attraction and repulsion (between opposing and like charges, respectively)
- Van der Waals (= short distance) bonding (**not** applicable to fluorocarbon sidechain)
- Self-assembly of amphiphiles into supramolecular aggregates (Micelles in solvent, hemimicelles at surfaces)
- Hydrophobic exclusion (entropic segregation of nonpolar/hydrophobic compounds
- Other mechanisms

Never forget the solvent: Water (H_2O)

All of the interactions listed above depend on the status of the solvent (H_2O):

- The proton concentration or **pH**, because protons (H^+) determine the ionization state of organic functional groups associated with the contaminant and the solubility of background electrolytes

- The **type and concentration of background electrolytes** (Ca^{++}; Al^{+++}, others) available for cation bridging and to balance matrix surface charges

- The polarity of the solvent H_2O, enabling the entropy driven process called **hydrophobic exclusion**, i.e., the dictate of the second law of thermodynamics ("entropy must be maximized") to force all nonpolar compounds (organic and mineral) solvated in an aqueous phase into close association with each other

Goal: convey ability to assess risk

Answer a question of the kind:

How would retention and eventual transport of PFLA applied with AFFF differ between Travis AFB* (CA) and Jacksonville NAS** (FL) ?

*low organic matter content, high clay content, abundance of the mineral smectite, high CEC, pH above 6.5, moderately well drained, low saturated hydraulic conductivity, well aerated (oxidizing conditions)

**high organic matter content, very low clay content, 90% quartz, very low CEC, pH between 3.5 and 6, poorly drained, very high saturated hydraulic conductivity, reducing below 64 cm

Generalized ambition

Considering the system components listed above, we can express our task as:

- Assess the probabilities for accumulation and loss of a large group of relatively low molecular weight, fluorinated organic compounds from a
- porous system that is
- composed of solids with variable surface characteristics and
- filled with a polar solvent of variable composition

Controls on PFAS fate and transport: a practical guide for site assessments

2. Contaminant properties

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Empirical finding

When our team examined controls on PFAS retention and release in soil horizons from Wurtsmith Air Force Base, we found this relationship:

$$\boldsymbol{Percent\ Mass\ retained} = \{[0.204 * \boldsymbol{Molar\ Mass}] + [0.318 * \boldsymbol{Mass\ Fluorine}] + [c * \boldsymbol{Nitrogens}] + Z\} \pm 16.2$$

$$c = [3.5 * \boldsymbol{FeOx}] + [89.7 * \%\boldsymbol{OC}] + 22.7$$

$$Z = [0.12 * \boldsymbol{S.A._{BET}}] - 146$$

Of the parameters isolated, those labeled in **green** are contaminant properties

Verbalization

When we investigated the retention of dozens of PFAS by a soil, we found that, across many different PFAS compounds

- the “size” (molecular mass) of the molecule,

- the proportion (molecular mass) of fluorine atoms in that molecule, and

- the number of N atoms in the PFAS compound

were the contaminant properties or features that correlated with the mass retained

This begs the question: **why** were these features good predictor variables ?

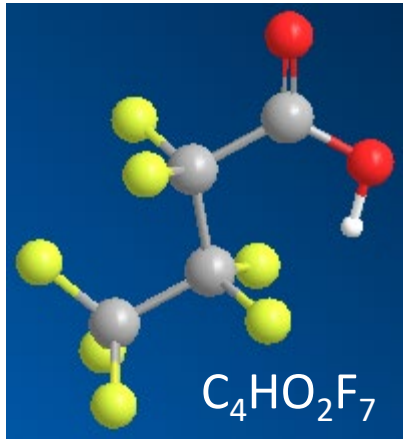
Inference drawn

→Retention of a PFAS compound that is relatively large overall, has a large fluorocarbon sidechain and one or more N atoms will be strong !

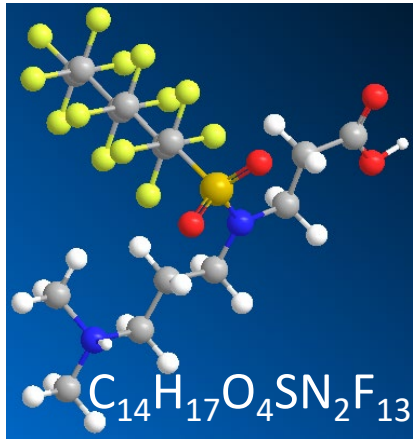
→ Conversely, a PFAS compound that is relatively small overall, has only a minor fluorocarbon sidechain and no N atoms in its structure will not be significantly retained.

Molecular variability in PFAS

Model parameters visualized through comparison of two PFAS

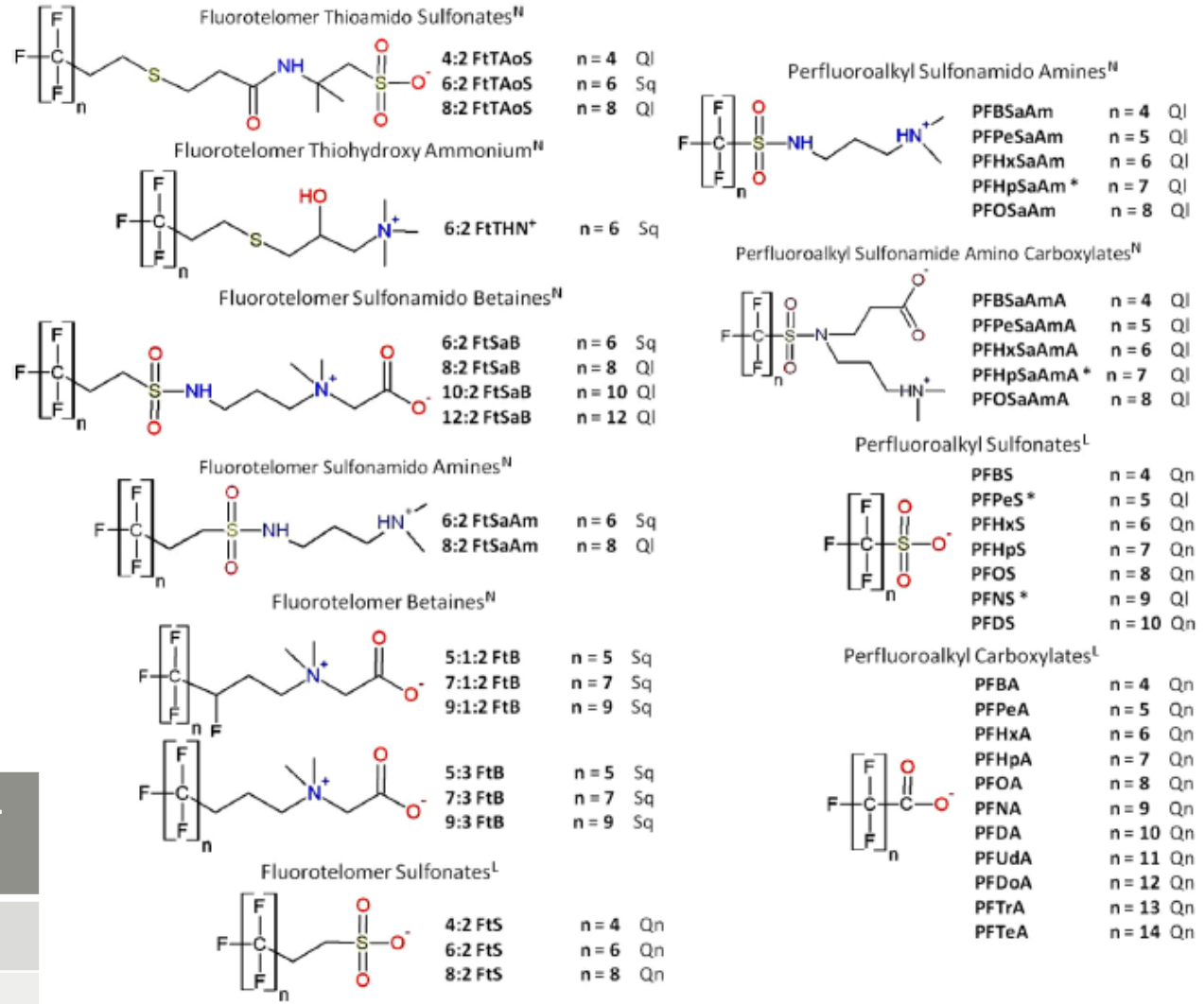


PFBA



AmPr-FHxSA-PrA

Parameter	PFBA	AmPr-FHxSA-PrA
Total Mol. Mass *(g Mol^{-1})*	214	556
Mass Fluorine *(g Mol^{-1})*	133	247
# N atoms *(integer)*	0	2



Backe et al 2013 ES&T 47, 5226-5234

The mechanisms behind the parameters

The following slides will make a brief attempt to deduce the mechanisms behind the correlations seen.

We will also discuss molecular properties that are not among our three dominant molecular features, but that we need to consider in order to understand the importance of matrix properties.

PFAS **functional** varieties

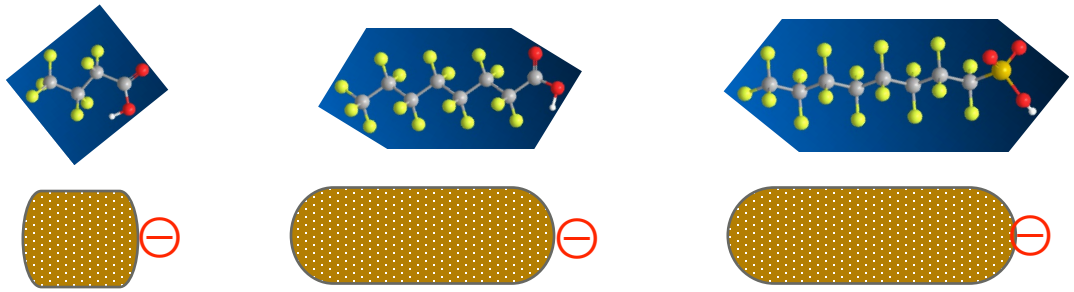
Fluorocarbon sidechain

Hydrocarbon sidechain

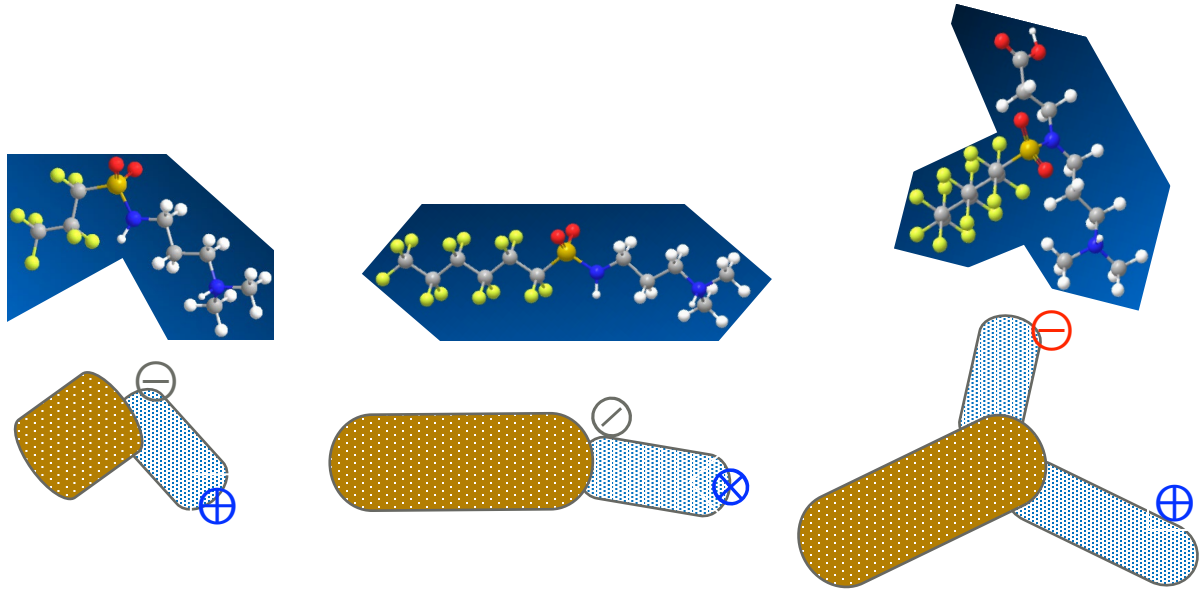
Positive charge ($-NH^+$)

Negative charge (-COO^-; -SO_3^-)

Negative charge (=N^-) in neutral to alkaline environments only



PFBA **PFOA** **PFOS**



AmPr-FPrSA **AmPr-FHxSA** **AmPr-FHxSA-PrA**

Empirical predictors in context

To understand **how** the three PFAS-compound features

M_{total} = overall molecular mass; [g Mol^{-1}]

$M_{fluorine}$ = mass of fluorine atoms; [g Mol^{-1}] and

$\#_N$ = number of nitrogens; [integer]

are mechanistically involved in retention of PFAS by the solid matrix, we briefly recapitulate modes of interaction between organic compounds and sorbent surfaces

Fundamentals

Simplifying, we can distinguish three basic ways how an organic sorbate can attach to (or be forced to associate with) a sorbent surface in an aqueous system (where polar water is the solvent):

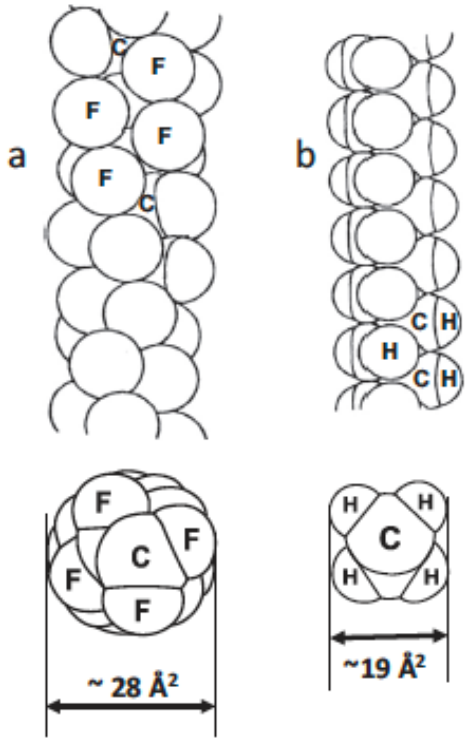
1. Attraction through Van der Waals forces (VdW forces are very weak and of extremely short range. They are additive and hence gain importance for **large** adsorbates. They operate between **all** molecules if they can come close enough to each other)

2. Electrostatic attraction (represents forces between nearby atoms and molecules that are of opposite charge or of opposite polarity → positive charge attracts negative charge, like charges repel each other)

3. Hydrophobic exclusion (the tendency of nonpolar molecules or functional groups, such as hydrocarbon chains, to associate with each other or with nonpolar surfaces because polar water molecules prefer to interact with each other and not with hydrophobic compounds)

Fundamentals – the uniqueness of fluorocarbons

The fluorocarbon sidechain is unique in two ways

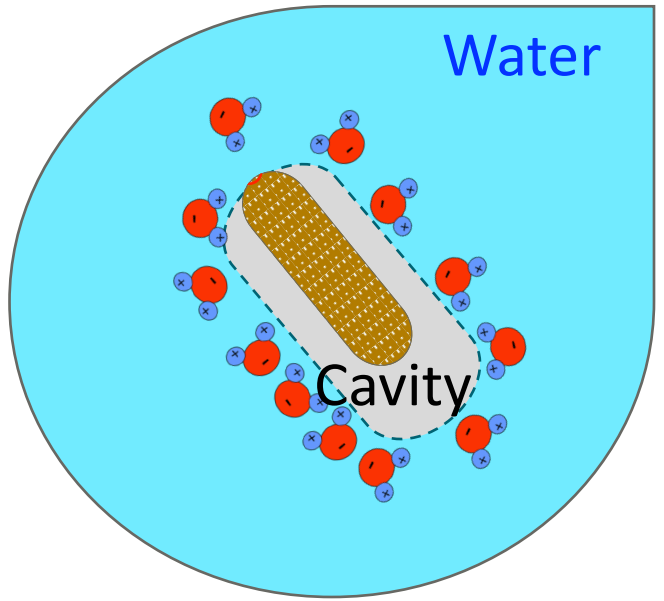


F-alkyl (a) vs. H-alkyl (b) chain and their cross sections. From Krafft and Ries (2009)

1. Van der Waals forces are extremely weak (the bonding mechanism that allows all molecules to weakly attract each other if they come close enough is not available for fluorocarbons, making them **extremely hydrophobic**)

2. Fluorocarbon sidechains are big (they need extra room to partition into a condensed phase such as water)

→ Fluorocarbons require an extra large **cavity** to partition into water, and this is **energetically unfavorable**



The Goss/Bronner* rules for fluorocarbons

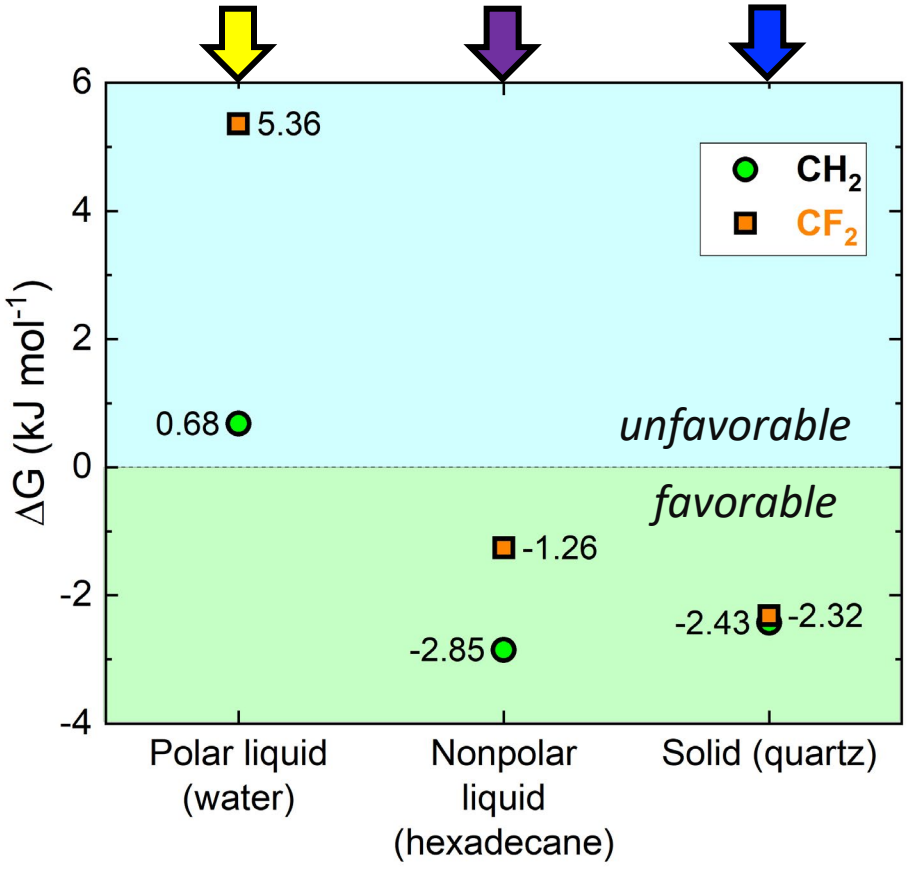
a) Partitioning between the gas phase and a condensed phase (air - water) will shift to the gas phase for the fluorinated compound **due to the large volume** (of the fluorinated part) **that causes a high energy expense for cavity formation** (in the condensed phase). The extent of this **effect will increase with the degree of fluorination** and with the cohesive energy of the condensed phase

(b) The partitioning between two condensed phases (water-NAPL) will shift toward the phase with the lower cohesive energy (NAPL) because of the **lower energy expense to make a cavity in the less cohesive phase**. This effect **will increase with the degree of fluorination** and with the difference in the cohesive energy of the condensed phases

(c) Adsorption on surfaces will be unaffected because **no cavity formation is possible** in the solid phase and the van der Waals interaction remains unaltered.

*Goss KU and G Bronner. J. Phys. Chem. A 2006, 110, 9518-9522

Fluorocarbon vs hydrocarbon



Data from Table 2 in Goss KU and G Bronner. J. Phys. Chem. A 2006, 110, 9518-9522

Goss & Bronner show that both, CH_2 and CF_2 fragments will only partition into liquid water when energy is provided (positive ΔG), with CF_2 requiring almost **8 times as much** energy to make that happen, compared to CH_2

For the less cohesive Non-Aqueous Phase Liquid hexadecane (NAPL), partitioning is favorable for both species (negative ΔG), although less so for CF_2

In an aqueous system, both CH_2 and CF_2 will willingly (negative ΔG) and to the same extent associate with an uncharged mineral surface (quartz)

Note: in this case, only the hydrocarbon can benefit from some VdW bonding, mostly they are both being "pushed" towards that surface

Consequence

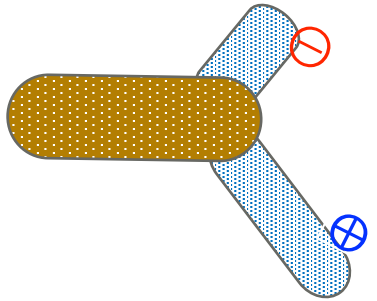
Quote: “ Extreme hydrophobicity, along with lipophobicity, and rod-like, rigid F-chain shape endow fluorinated surfactants with a powerful driving force for segregation and self-assembly into discrete supramolecular constructs and thin interfacial films”

Krafft & Ries 2015 Chemosphere 129 4-19

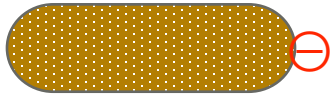
→ Note that, since free energies of adsorption to mineral surfaces are near identical (compare previous slide) for both CH_2 and CF_2, there will be strong competition between hydrocarbon and fluorocarbon phases for mineral surface sites in cases where both are introduced to the system (such as with commercial AFFF formulations)

Not quite done: The contribution of the N

At his point, we have mechanistic explanations for the importance of



M_{total} (overall molecular mass) = a large hydrophobic molecule will be subject to strong hydrophobic exclusion, but will be able to attach to a surface through VdW forces (i) if it comes close enough and (ii) has a hydrocarbon segment



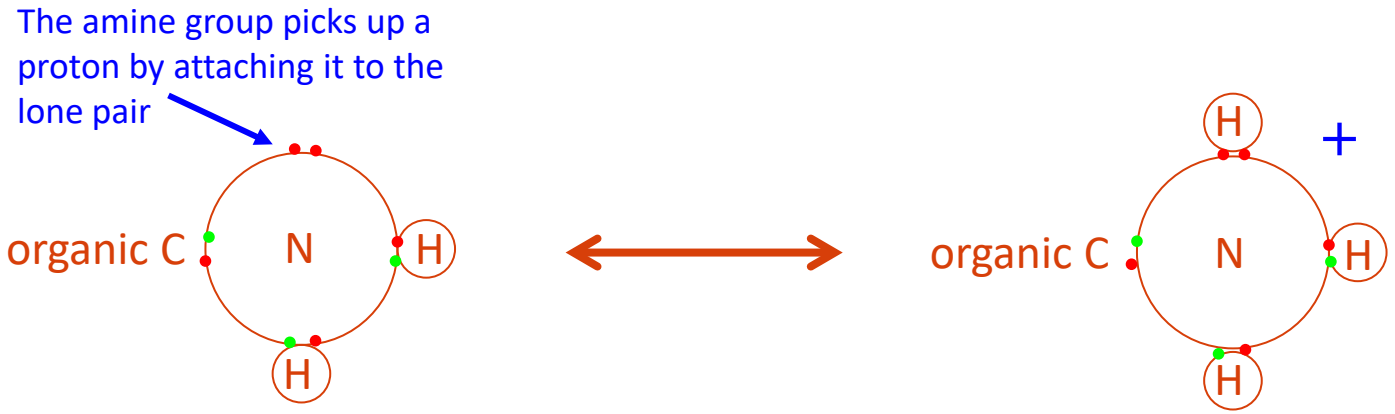
$M_{fluorine}$ (mass of fluorine atoms) = a large fluorocarbon sidechain increases the intensity at which an organic compound will be expelled from a polar liquid phase. The phase boundary will be the only way to go.

$\#_N$ = Nitrogen can develop positive charge. This allows for electrostatic attraction to a negative charge (in special cases, the N can develop negative charge as well)

Why can the N do that?

In organic molecules, **Nitrogen is the major provider of positively charged functional groups**. This is because it has a "lone pair" of electrons, which allow it to pick up an extra hydrogen ion = proton

organic C-NH_2 + H^+ ⟷ R-NH_3^+



Amine groups tend to be quite willing to accept protons. Thus they are generally protonated = carry positive charge in acidic (= proton rich) soil environments.

The importance of pH

When the N can become charged upon acceptance of a proton (H^+), then it follows that there have to be protons around for this to happen. Proton concentration is measured as pH (reminder: the lower the pH value, the higher the proton concentration).

Depending on its molecular environment, the N can as well loose that proton.

The **pKa** value of a functional group tells us at what proton concentration (pH) that group has a 50% likelihood of being protonated (If the pH drops below the pKa, the group will be protonated, if it rises above, the group will loose the proton)

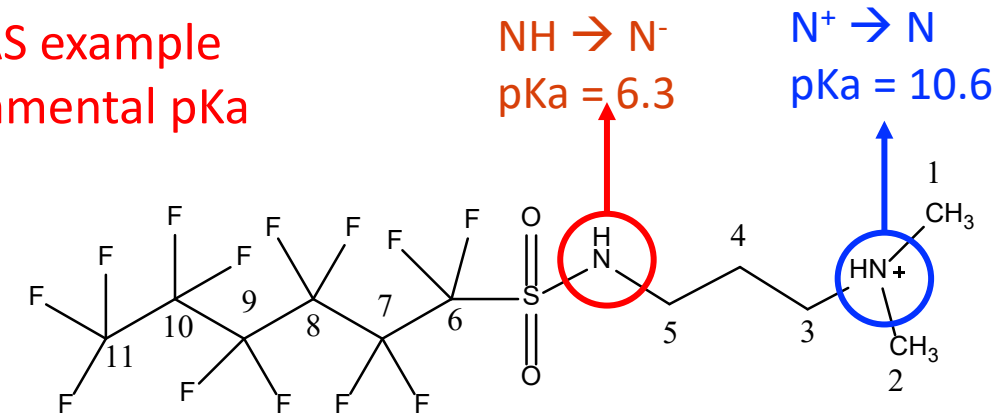
The oxygen containing functional groups in PFAS (-COOH; SO_3^-) all have pKa values well below the environmental pH range of pH 3.5 - 8, which means they are deprotonated and hence negatively charged at environmental pH

Back to the N

The majority of amine functional groups in PFAS tend to have pKa values above the environmental pH-range (pH 3.5 - 8), and are hence protonated = carry **positive charge**

But exceptions are known: the secondary amine in the PFAS example chosen here has a pKa of 6.3, which falls inside the environmental pKa range.

Accordingly, this N will carry no charge as long as it is protonated (in this case, the number of negative charges surrounding the N is balanced by the number of Protons in its nucleus) but when the environmental pH rises above 6.3 (as it is known to do in source zones of arid land areas), this N will loose its proton and develop **negative charge**, making the compound amphoteric or a "zwitterion"



AmPr-FHxSA

N-dimethyl ammonio propyl perfluorohexane sulfonamide

$C_{11}H_{13}O_2SN_2F_{13}$

484 Da

Summary

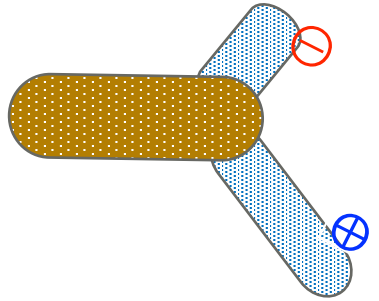
The three molecular features identified as predictor variables for PFAS retention **(M_{total}; $M_{fluorine}$, # of Nitrogens)** can be mechanistically linked to all three major modes of sorbate – sorbent attachment to environmental matrices:

1. Attraction through Van der Waals forces (very weak)
2. Electrostatic attraction (relatively strong)
3. Hydrophobic exclusion (no bonding, just an association)

Variation of PFAS structure will favor or disfavor one or more of these mechanisms

The strength of retention will necessarily also depend on **matrix properties** (availability of hydrophobic surfaces, opposing charges) and on the **properties of the aqueous phase** (pH etc.)

Summary: PFAS functionalities



Fluorocarbon sidechain	Extremely weak VdW forces and lack of charge, i.e. neither able to associate with water nor with oily and fatty compounds
Hydrocarbon sidechain	"normal" VdW forces, unable to associate with water, but partitions readily among oily and fatty compounds
⊕ **Positive charge (≡ NH^+)**	Can attract ion of opposite (= negative) charge, may engage in hydrogen bonding and can attract polar water molecules
⊖ **Negative charge (-COO^-; -SO_3^-)**	Can attract ion of opposite (= positive) charge, may engage in hydrogen bonding and can attract polar water molecules
⊖ **Negative charge (=N^-) in neutral to alkaline environments only**	Same as above, exact dissociation state at natural pH (4-8) not well known but assumed to carry negative charge at pH ≫ 6

Afterthought

As we have seen, the process of hydrophobic exclusion plays a major role in PFAS attachment to environmental matrices.

To enable this process, the system needs to contain the polar solvent water (H_2O)

Because there is no actual bonding involved here, this insight allows us to predict that any compound associated with a matrix surface because of hydrophobic exclusion **will become detached** when the system dries out!

→ **Watch out for wet-dry cycles in source zones!**

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3. Matrix properties

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Empirical model, second part

Restating our model for the description of PFAS retention at Wurtsmith Air Force Base, this time emphasizing the parameters representing the environmental matrix

$$\boldsymbol{Percent\ Mass\ retained} = \{[0.204 * \boldsymbol{Molar\ Mass}] + [0.318 * \boldsymbol{Mass\ Fluorine}] + [c * \boldsymbol{Nitrogens}] + Z\} \pm 16.2$$

$$c = [3.5 * \boldsymbol{Fe_o}] + [89.7 * \%\boldsymbol{OC}] + 22.7$$

$$Z = [0.12 * \boldsymbol{SA_{BET}}] - 146$$

Verbalization

When we investigated the retention of PFAS by an environmental matrix, we found that, across many different matrix properties

- the content of oxalate extractable iron (Fe_o)

- the content of organic carbon (OC) and

- the specific surface area as measured through the BET N_2 method

were the matrix features that correlated significantly with the mass of PFAS retained

Inference drawn

→ An environmental matrix that has high levels of natural organic matter combined with a large BET-N_2 specific surface area (by mass), together with an abundance of oxalate extractable Fe will be particularly good at retaining PFAS

→ Translated in to plain speak: a soil high in organic matter and clay/silt sized particles that are coated by poorly crystalline iron oxide phases will be particularly good at retaining PFAS

As with our contaminant features, this begs the question: **why** were these features good predictor variables ?

Inference illustrated

PFAS retention: strong

Organic matter

high ← → low

50 cm vs 5 cm

Oxalate extractable Fe

high ← → very low

bright brown vs pale gray

Specific surface area:

high ← → very low

silt loam vs sand

PFAS retention: weak

The mechanisms behind the parameters

The following slides will make a brief attempt to deduce the mechanisms behind the correlations seen.

We will also discuss molecular properties that are not among our three dominant molecular features, but that we need to consider in order to understand interactions with fluorinated contaminants.

Empirical predictors in context

To understand **how** the three Matrix features

OC = mass of organic carbon [% weight, dry soil]

BET-N_2 Surface Area (**SA**) = area of mineral surfaces measured through adsorption of Nitrogen gas [m^2 g^{-1} soil] and

Fe_o = oxalate extractable iron [% weight, dry soil]

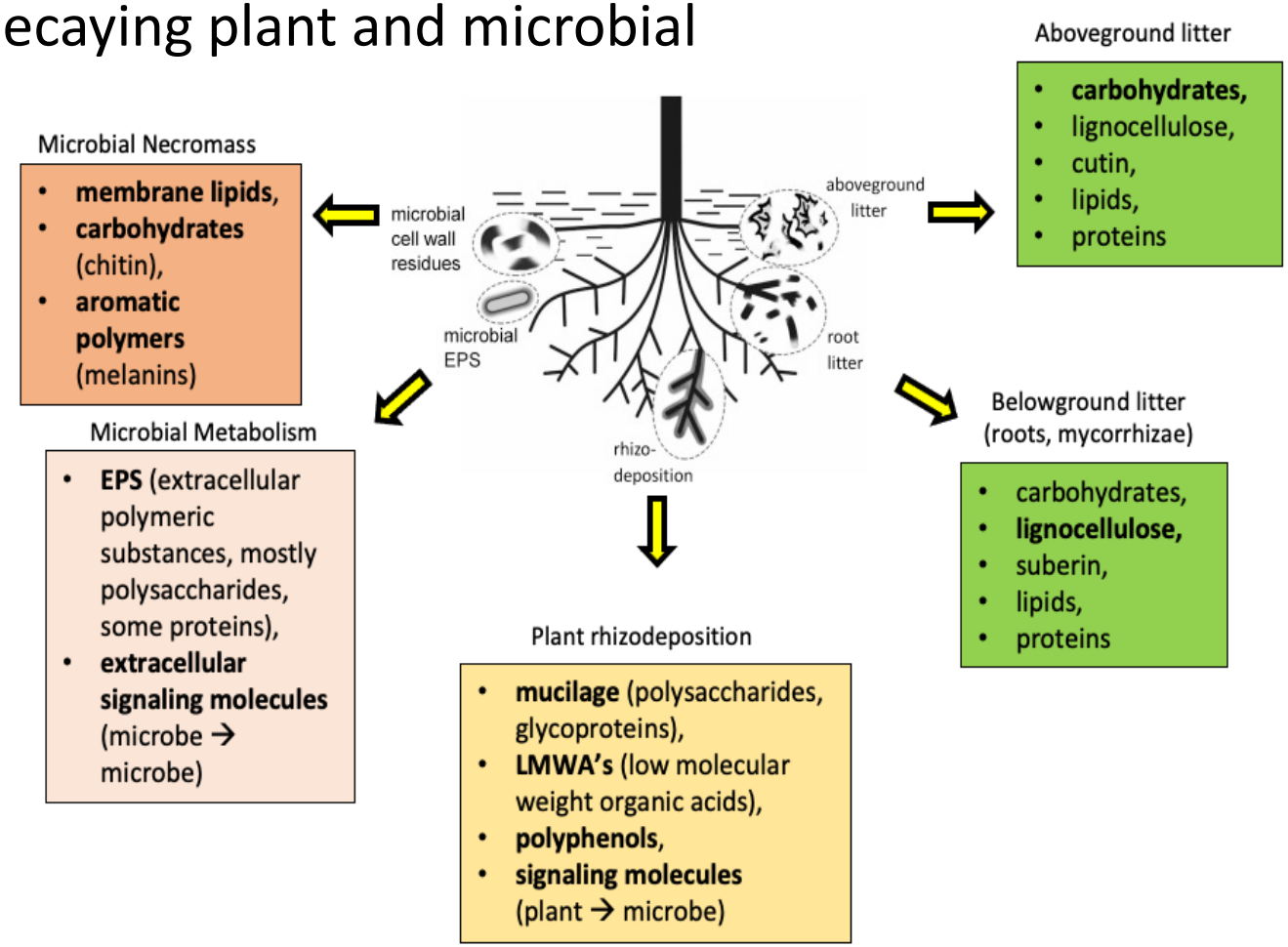
are mechanistically involved in retention of PFAS by the solid matrix, we briefly recapitulate the types of solid phases and their associated surface properties

Solid matrix part one: Soil **O**rganic **M**atter

Natural organic matter derives from decaying plant and microbial tissue

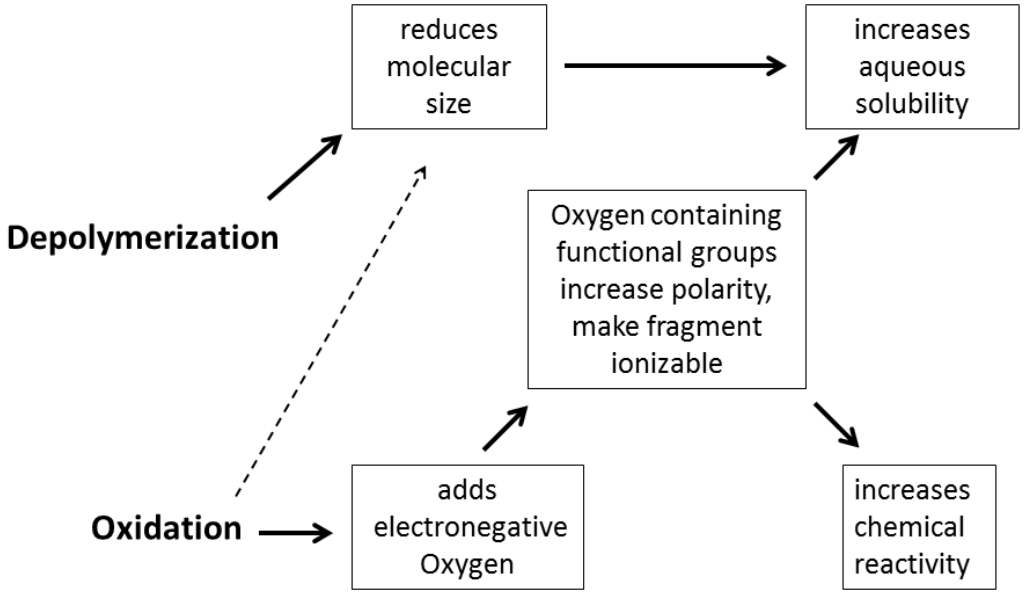
Organic tissues and debris/litters are initially hydrophobic (leaves and roots do not dissolve in the rain)

Accordingly, the solid organic phase initially contains abundant molecular compounds with hydrophobic characteristics



Functionalization through decay

Oxidative depolymerisation (performed by microbial exoenzymes) **adds oxygen containing functional groups** (such as COOH) to organic biomacromolecules.



*Decay sequence from **dead plant material (brown**, left) to amorphous "**humus" (black** and on the right)*

This reduces molecular size and turns previously nonpolar biomacromolecules into smaller, amphiphilic, surfactant like compounds with the ability to ionize.

OM has hydrophobic and hydrophilic features

The organic phase in soils starts out as plant litter which is **overwhelmingly nonpolar.**

Through oxidative degradation, ionizable **COOH groups** (negative charge!) are added, endowing the organic phase with ability to engage in electrostatic interactions

This process is responsible for the high **Cation Exchange Capacity (CEC)** of a well-decayed organic phase

The more advanced the decay, the greater the negative charge associated with and contributed by the organic phase = the greater the CEC contributed by OM

The organic phase is multifunctional

At any time, the organic phase in soil will contribute variable proportions of both, nonpolar (hydrophobic) **and** polar/anionic functionality. The relative importance of these functionalities depends on:

→ the degradation state of the OM. Fresh **(brownish) litter** will be largely nonpolar/hydrophobic, while OM in an advanced stage of decomposition **(blackish)** will be decorated with abundant ionizable COO^- groups and will have only minor proportions of hydrophobic functionalities left

→ soil pH, with proton concentration controlling the extent to which carboxylic groups are dissociated (many carboxyl groups in soil organic matter have pKa values in the vicinity of 4.5, i.e. they require a soil pH above 4.5 to assume anionic functionality = the form COO^-)

OM and PFAS retention – quite a few options

- non-polar, hydrophobic moieties in OM allow for some partitioning of **surfactant-like PFAS** into such OM

- anionic functional groups [**-COO^{-}**] allow for electrostatic attraction of polar heads of **cationic PFAS**

- in the presence of multivalent cations (Mg^{++}; Ca^{++}), anionic functional groups [**-COO^{-}**] may engage in cation bridging* with **anionic PFAS**

*Cation bridging: **Organic R – COO^{-} ---$^{+}$Ca^{+}---$^{-}$OOC-PFAS**

OM and PFAS retention

Clearly, OM offers multiple opportunities for PFAS to associate

Constraints are the varying proportions of hydrophobic versus polar/anionic moieties, pH, and the availability of bridging, multivalent cations (Ca^{++}, Mg^{++})

But **generally, OM is pretty good at retaining PFAS** ! *Compare Higgins and Luthy 2006. ES&T 40:7251-7256.*

→ Traditional K_{OC} and K_{OW} partitioning coefficients do not capture the complexity of PFAS retention by OM ! *Compare Sigmund et al. 2022. ES&T 56:4702-4710*

Solid matrix part two: Mineral matter

Specific surface area and oxalate extractable Fe are properties of the mineral matrix

Specific surface area is **capacitative** metric and quantifies the space available for adsorption processes

Oxalate extractable Fe is a **qualitative** metric and indicates the presence of reactive, poorly crystalline Fe-oxides that can develop **positive charge** at environmental pH

Two kinds of minerals: primary and secondary

Primary minerals are those that crystallize out of molten magma, examples are feldspar, quartz, mica, olivine
These tend to have **large particle size, low to negligible surface reactivity and low specific surface area**

Secondary or soil minerals are those that crystallise out of the weathering products of primary minerals, such as phyllosilicate **clays**, Fe, Al, Mn – **oxides** and short range aluminosilicates
These tend to have **colloidal size, high to extremely high surface reactivity and high to very high specific surface area**

Note: **Primary minerals** dominate in the sand and silt particle size fractions and **are** usually **inherited**, **secondary minerals** dominate the clay size fraction and **are** typically **made in the soil** = crystallize out of solution or transform out of certain precursors

Soil minerals

(incomplete)

Charge column: reactivity information

Surface area column: capacitative information

*Kleber, M., et al. Nat Rev Earth Environ **2,** 402–421 (2021).*

Crystal structure

SiO_4 tetrahedron
MO_4 tetrahedron (M = Al, Fe)
MO_6 octahedron (M = Al, Fe, Mg, Mn)

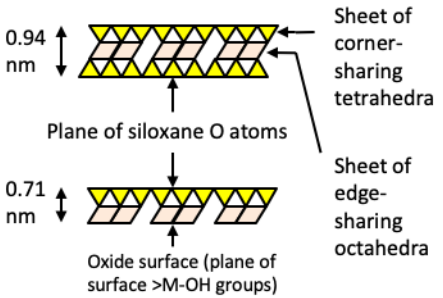
Charge (σ, $mmol_c\ g^{-1}$)

Area (a_s, $m^2\ g^{-1}$)

Size and shape

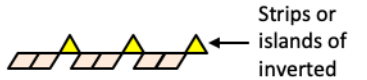
Phyllosilicates

2:1 layer type
illite ≥ smectite ≥ vermiculite ≥ …

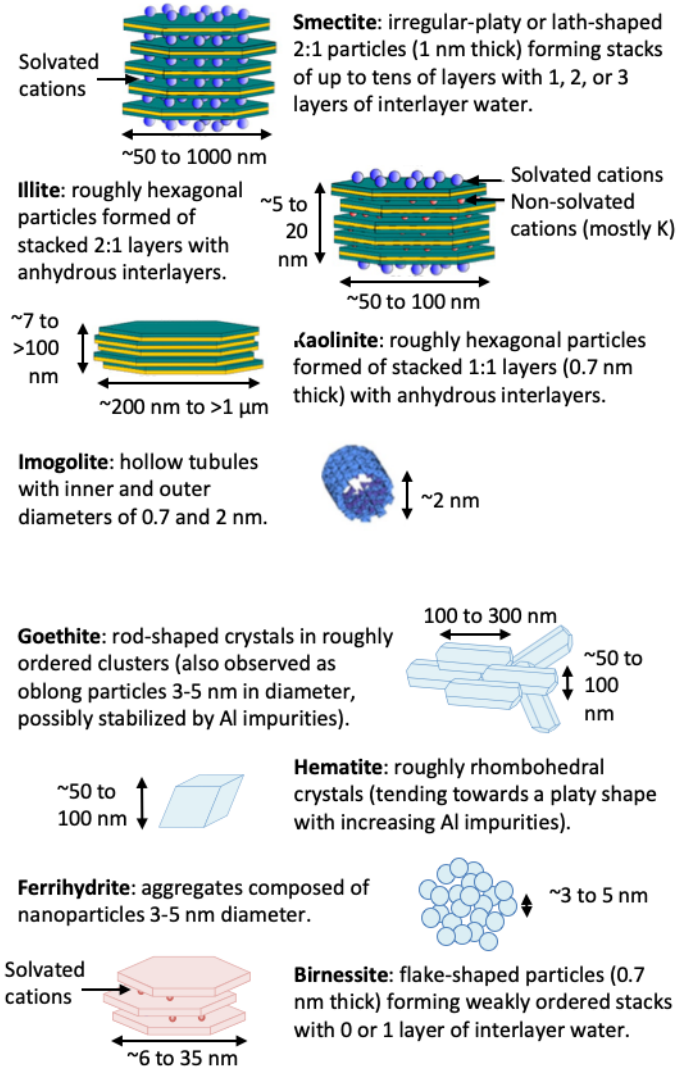


1:1 layer type
kaolinite

Modulated phyllosilicates
imogolite, 'allophane'



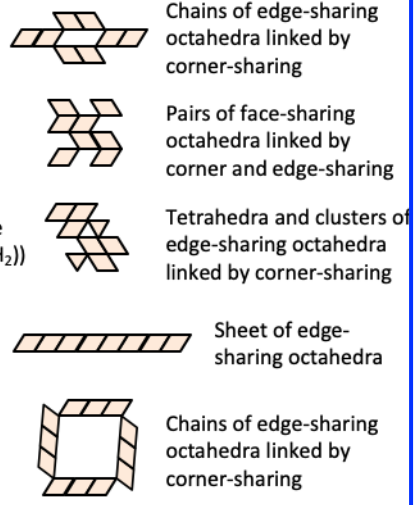
	Charge (σ, $mmol_c\ g^{-1}$)	Area (a_s, $m^2\ g^{-1}$)
Smectite: -0.7 to -1.2	Smectite: 740 to 780	
Illite: -0.16 to -0.22	Illite: 20 to 200	
Kaolinite: 0 to -0.02	Kaolinite: 7 to 80	
Imogolite: 0.1 to 0.5	Imogolite: 600 to 900	
Allophane: 0 to -1.0	Allophane: 700 to 900	



Metal oxides

Fe oxides
goethite > hematite ≥ ferrihydrite > …

Mn oxides
birnessite > todorokite > …



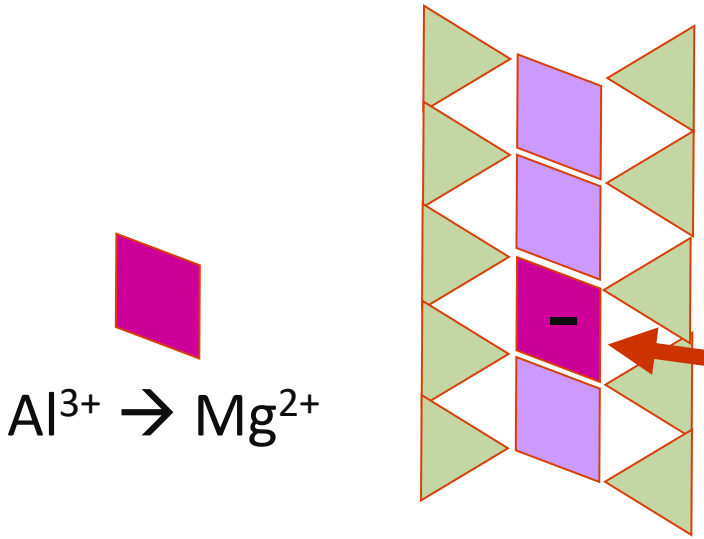
	Charge (σ, $mmol_c\ g^{-1}$)	Area (a_s, $m^2\ g^{-1}$)
Goethite: 0 to 0.15	Goethite: 40 to 90	
Hematite: 0 to 0.02	Hematite: 10 to 35	
Ferrihydrite: 0 to 1.3	Ferrihydrite: 200 to 800	
Birnessite: -1.3 to -2.8	Birnessite: 1200	
Todorokite: -0.15	Todorokite: ~1200	

Mineral surface fundamentals: two kinds of charge

The symbol for a charge = *q*

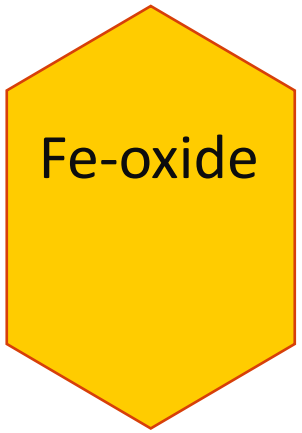
σ = charge density = C m^{-2}

The unit of charge = Coulomb (C)



structural charge, *independent of pH, called **permanent** charge*

<u>Majority</u> (by mass) of soil minerals carry **negative** charge



-OH + H^+

$-OH_2^+$

net proton charge, *changes with proton concentration = pH, historically called **variable** charge*

Fe, Al - minerals with single coordinated OH groups can develop **positive** charge, depending on pH

Mineral surface archetypes

At this point, we have identified two functional types of mineral surfaces:

1.) Minerals with permanent negative charge (making up the majority of secondary minerals by mass)

2.) Minerals with variable, pH dependent charge (can develop positive charge, contributing a minor part of secondary minerals by mass but, because of their extraordinary reactivity and huge surface area, have disproportional functional relevance)

But there is a third functional category of great relevance to the retention of PFAS:

3.) Mineral surfaces lacking any surface charge and thus having significant hydrophobic functionality

Surfaces without charge: PFAS solvated

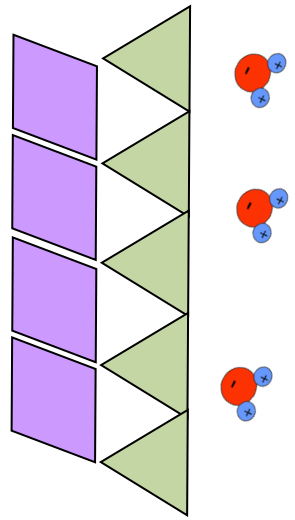
Al,Mg-octahedron

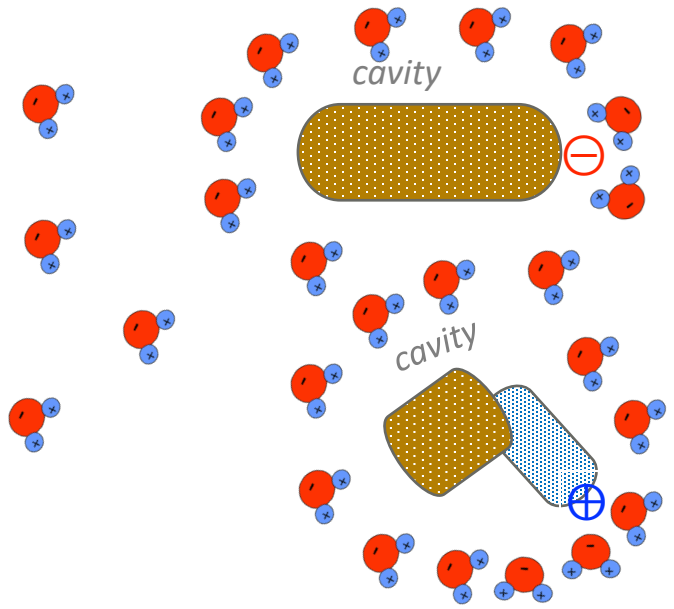
Si-tetrahedron

no defects, all charges balanced

= no surface charge

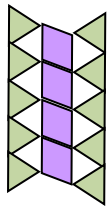
Mineral



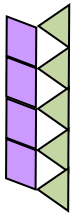


Anionic and cationic PFAS, solvated via cavity formation

pyrophyllite, talc

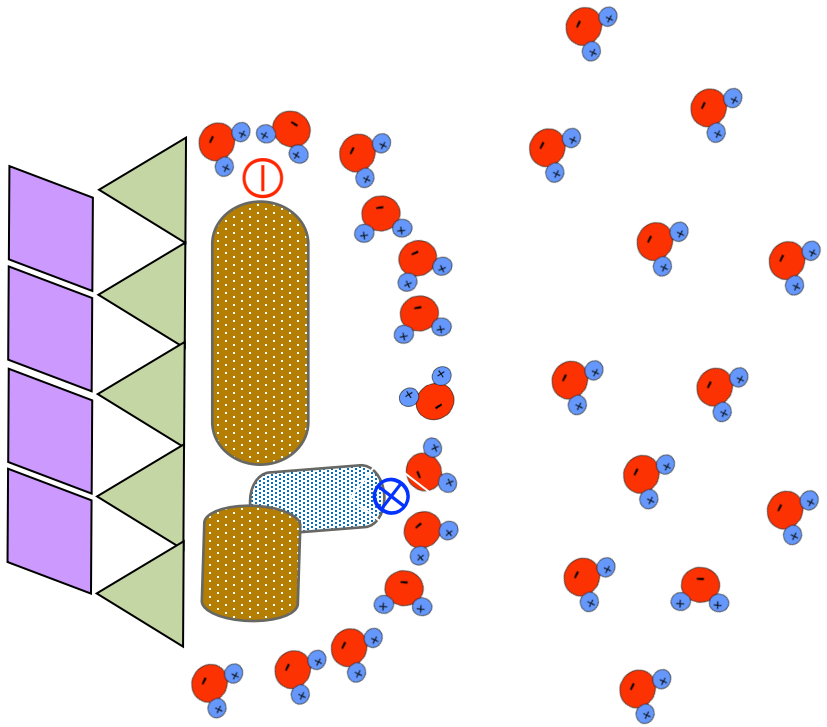


kaolinite



Surfaces without charge: PFAS surface associated

„hydrophobic“ Mineral surface, lacking any surface charge



Following second law of thermodynamics, entropy (= disorder among water molecules) is maximised by arranging hydrophobic PFAS parts in contact with hydrophobic mineral surface

- involves nonpolar/hydrophopbic region of amphiphilic organic molecule
- works only in system with **polar solvent = water!**
- no chemical bonding involved!

Summarizing (OM)

PFAS may associate with the solid environmental matrix in various ways

The organic phase is endowed with multiple functionalities OC, enabling it to interact with both charged and uncharged parts of PFAS

Particularly noteworthy here is the very high negative charge (quantifiable as Cation Exchange Capacity, CEC) of well decomposed OM, facilitating electrostatic bonding of cationic PFAS and cation bridging with anionic PFAS

Less decomposed OM will have hydrophobic functionalities that permit partitioning of hydrophobic parts of PFAS through hydrophobic exclusion

Summarizing (Mineral matter)

Adsorption needs room, and the abundance of spaces for adsorption processes is quantified through the parameter BET-N_2 Surface Area (**SA**) = area of mineral surfaces measured through adsorption of Nitrogen gas [m^2 g^{-1} soil]

PFAS with anionic functionalities will respond to the availability of positive charges, this capacity is quantified through the metric **Fe_o** = oxalate extractable iron [% weight, dry soil]

Negatively charged mineral surfaces can host anionic PFAS through the mechanisms of **cation bridging**, the efficacy of this mechanism depends on the abundance and valence of electrolytes in the aqueous phase

Note of caution

Consideration of the multitude of potential modes of interaction between multifunctional PFAS and complex environmental matrices drives home the insight that

→ Even minor variations in source zone structure (mineralogically, organic matter chemistry and solvent properties) will modify the fate and transport of a complex AFFF mix

→ PFAS behavior can not be generalized across source zones

Controls on PFAS fate and transport: a practical guide for site assessments

4. Mining open access data for fast assessments

Tom Wanzek
Jennifer Field
Markus Kleber

Oregon State University

SERDP
DOD • EPA • DOE

Reminder

The retention and release of PFAS from Source Zones results from the interplay between three major system components:

1. PFAS Compound(s),
2. Environmental Matrix, and
3. Aqueous phase (solvent)

Interactions between system components can be assessed based on information about component properties

What information is needed ?

→ which opportunities for PFAS attachment does a given environmental matrix offer?

As per our research results, this involves issues such as:

- Is there a prominent OM component? What is its depth distribution? What is its likely chemical makeup?
- How big is the available mineral surface area?
- What kind of surface charge is associated with the mineral phase (negative, positive, neutral?)
- How intense is that charge, quantitatively speaking [$mmol_c\ g^{-1}$] ?

Not to forget:

It is also necessary to estimate the state of the soil solution = the aqueous solvent in our system.

This includes information on :

- pH of the soil solution (and its variation across adjacent land areas)
- Type and ideally, concentration of background electrolytes (Ca^{++} or Al^{+++})
- Redox state (positively charged Fe-oxides will dissolve in reducing environments)
- Size and architecture of the available pore space (determining flow rates and residence times of pore waters)
- Groundwater recharge rate/hydraulic gradients

Challenge: Large physical diversity of source zones

679 military sites across US with known or suspected PFAS contamination or discharge (EWG, 2022)

Variation among site properties to be expected

Fortunately, the **USDA NRCS** provides publicly and immediately accessible soil data for the contiguous United States

USDA/NRCS WebSoilSurvey

This is the direct link to the national soil data source:

https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx

The California Soil Resource LAB, UC Davis, provides several apps/interfaces that are much more user friendly than the above, such as the **SoilWeb** app (developed together with NRCS):

https://casoilresource.lawr.ucdavis.edu/soilweb-apps/

Useful reference materials

Soilweb uses numerous terms and expressions that may not be familiar (for instance, what is an "isotic*" mineralogy?) It will be convenient to have the official reference documents at hand :

Schoeneberger, P.J., D.A. Wysocki, E.C. Benham, and Soil Survey Staff. 2012. **Field book for describing and sampling soils, Version 3.0.** Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE. Free pdf at:

https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_052523.pdf

Keys to Soil Taxonomy, Twelfth Edition (2014). Free pdf at:

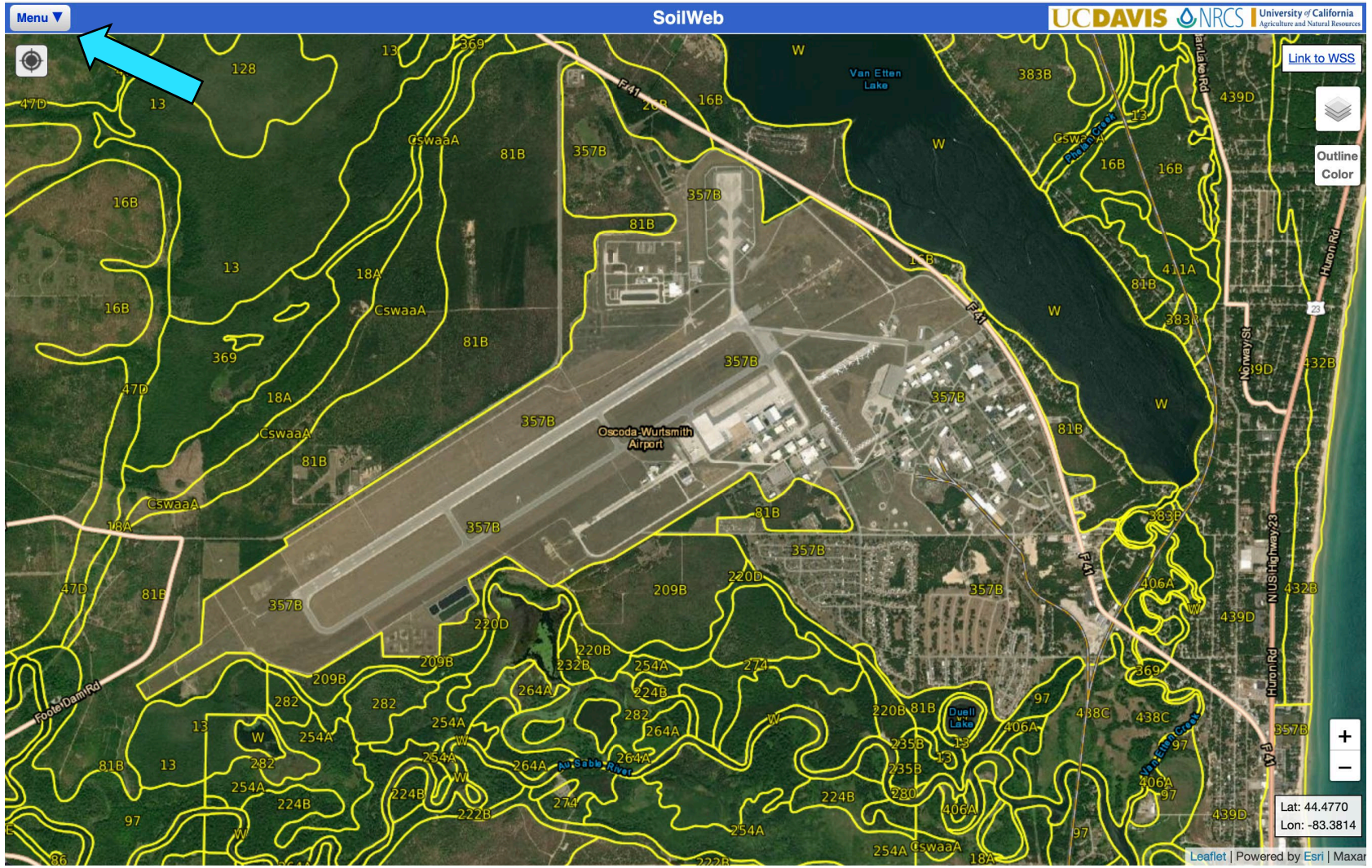
https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/class/taxonomy/?cid=nrcs142p2_053580

"isotic" means the matrix has a component of **short range order minerals – these have abundant Fe-OH and Al-OH groups and can hence develop **positive charge** – significant to the retention of anionic PFAS*

Working with SoilWeb

Google “soilweb” and open the app. The screen will show a soil map (very likeley of the Sacramento, CA area) and a welcome message.

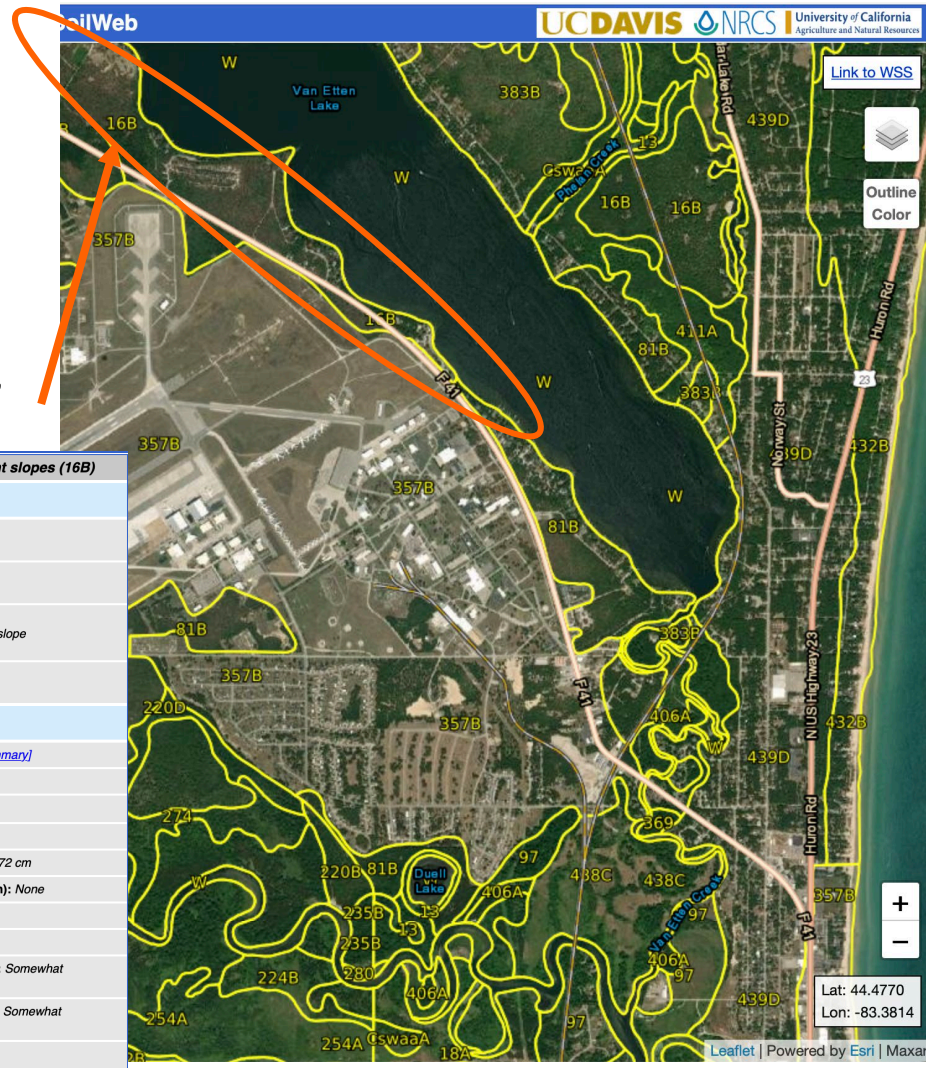
Navigate to the location of interest, either by zooming out and scrolling across the map or by typing coordinates into the Menu “zoom to location” function.



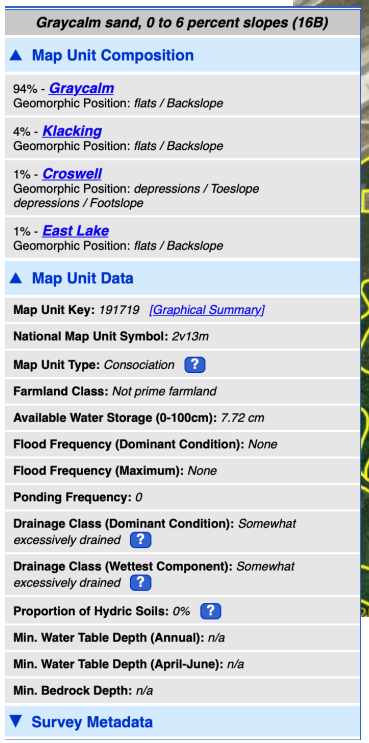
Working with SoilWeb

For demonstration purposes, lets assume we want to assess whether the soil between the Wurtsmith airfield and Van Etten Lake might have some ability to retard PFAS transfer = act as a buffer zone.

Note this map unit is labeled as “16B”

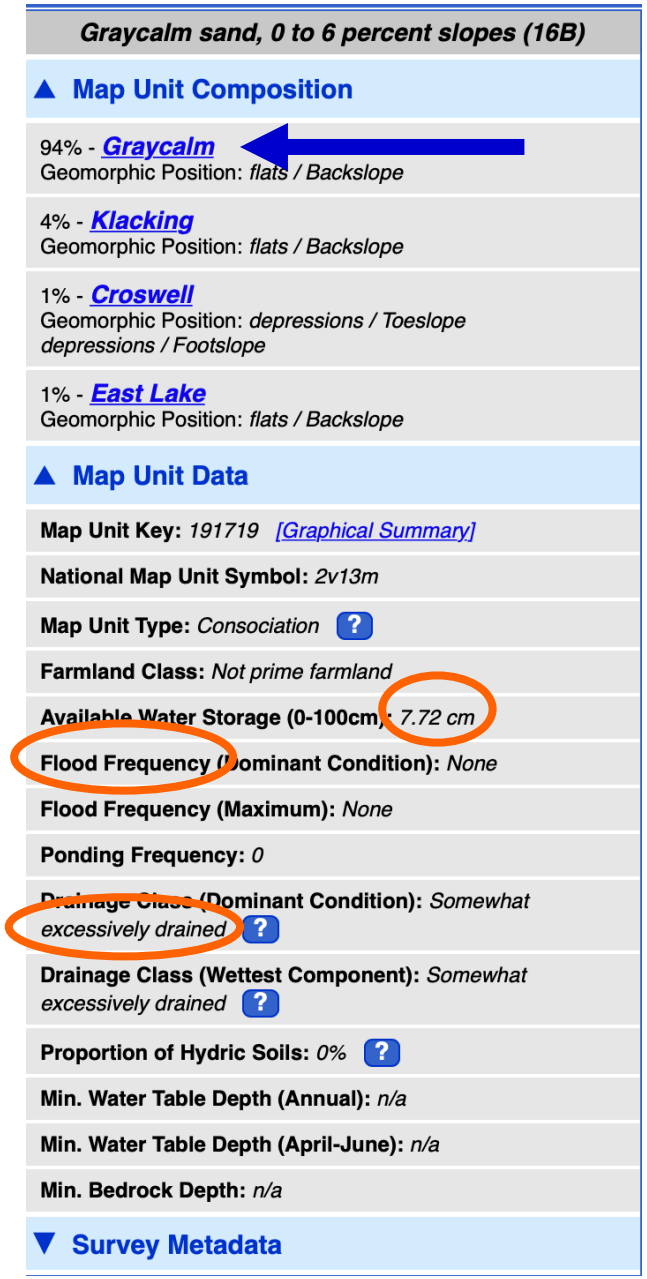


To gather information on the properties of map unit 16B, place cursor inside the map unit and click once.



A table will appear that provides
a) some general site properties and
b) very detailed data on the soils within the map unit, accessible by clicking on the soil names (such as “Graycalm”)

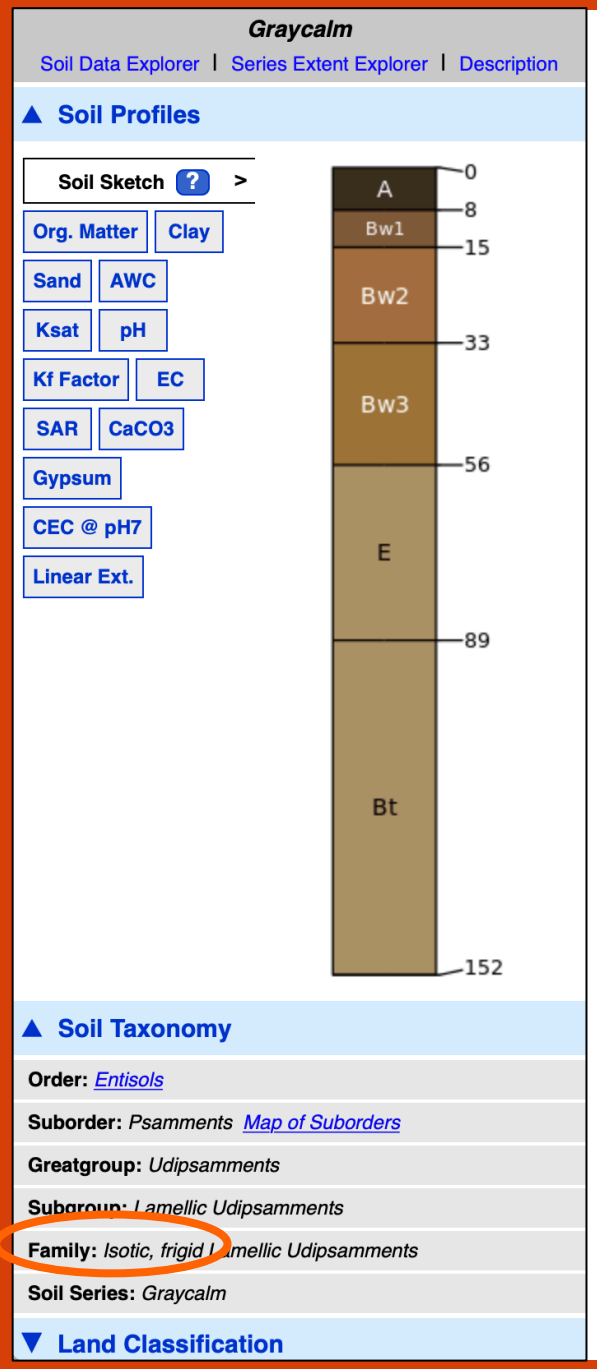
Working with SoilWeb



The vast majority (94%) of the soils in this mapping unit are the **Graycalm** soil series. Clicking on the name label leads to data repositories. More about that soon.

This part gives mostly hydrological and hydraulic information. For instance, it tells us that the soils can only hold **7.72 cm** [= 77 liters of water per m^2 and down to one meter depth] against gravity, and that they are "**excessively drained**" = have very high porosity. We also learn that the soil is **not prone to flooding**. Question marks open up tabs with definitions.

Lets now click on the **Graycalm** soil series to find out more about the dominant soil in this mapping unit.



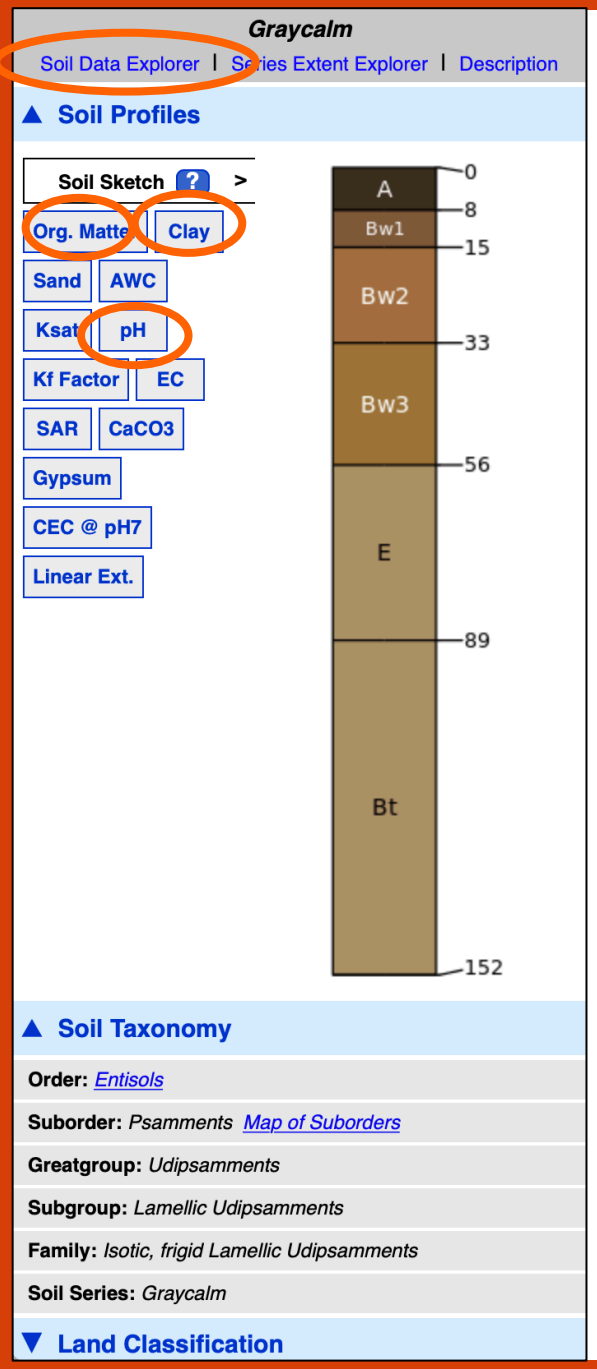
Working with SoilWeb

This function gives us a visual of the horizons into which the soil is differentiated, including a host of parameters that are relevant for PFAS retention including their depth functions.

It also identifies the taxonomic type of the soil, including the dominant mineralogy, which in this case is **isotic**.

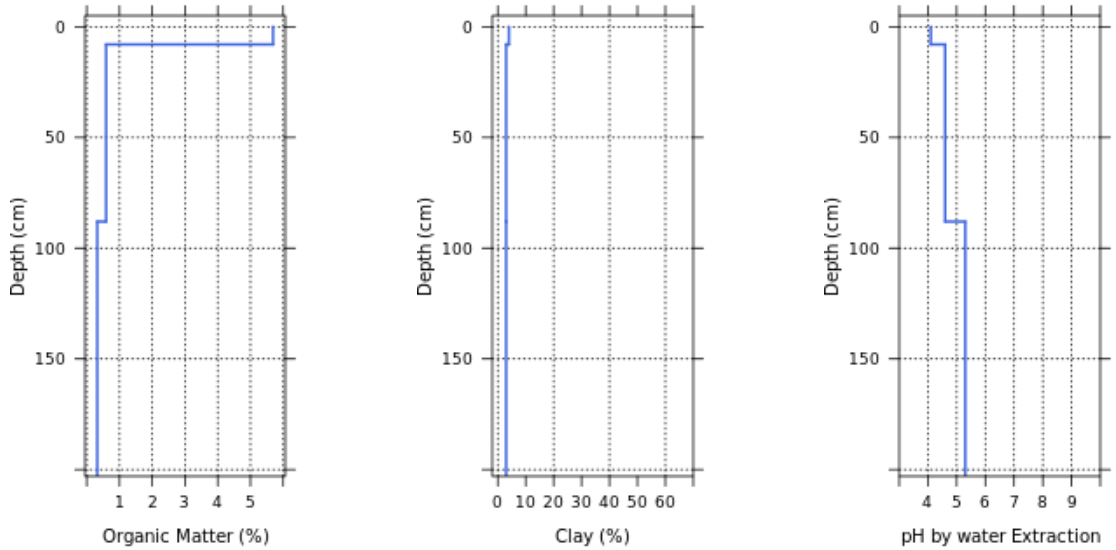
To look up the definition of isotic, refer to the ”Keys to Soil Taxonomy”, and to learn the meaning of horizon designators such as “E” or “Bt”, consult the ”Field book for describing and sampling soils”

Lets now go through some of the data and discuss their meaning for PFAS retention



Working with SoilWeb

The tabs to the left will open graphs that plot a depth function of the respective parameter, such as the three representations of OM, Clay and pH shown here:



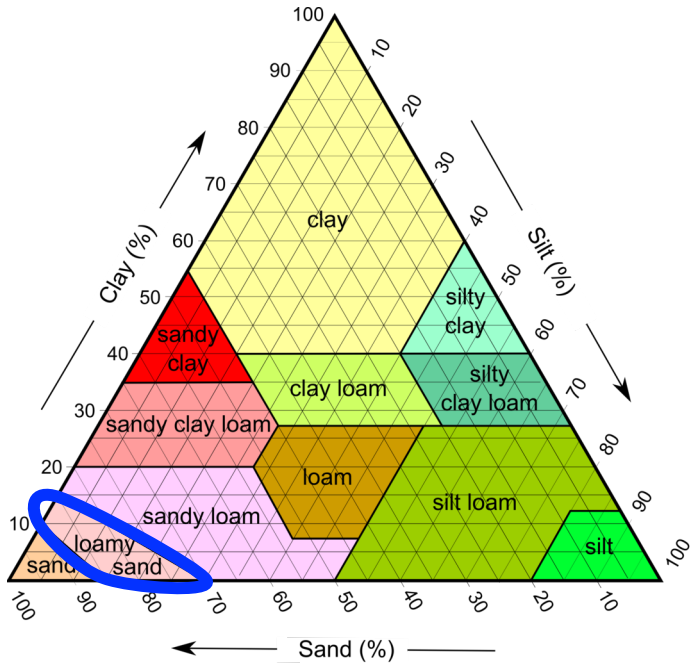
However, a more substantial function is available in the form of the **soil data explorer**

Soil data explorer

Clicking on the soil data explorer button opens a stack of file cards that look like this:

Soil data explorer

The **OSD** tab has the official soil series description, including horizon depths, texture (such as **loamy sand***), and other details (if present) such as the content of "acid-**oxalate extractable** Al plus 0.5 **Fe****" (look for this in the verbal description of the Bw horizon)



*Knowing that texture is a loamy sand translates into a sand (2000 μm – 50 μm) content of at least 70% and a clay (< 2 μm) content of no more than 15%, the rest being silt (50 μm – 2 μm) sized particles = this is a very coarse textured, permeable matrix

**Remember that we found the oxalate extractable Fe to be a predictor for the mass of PFAS retained by our soil columns

Soil data explorer

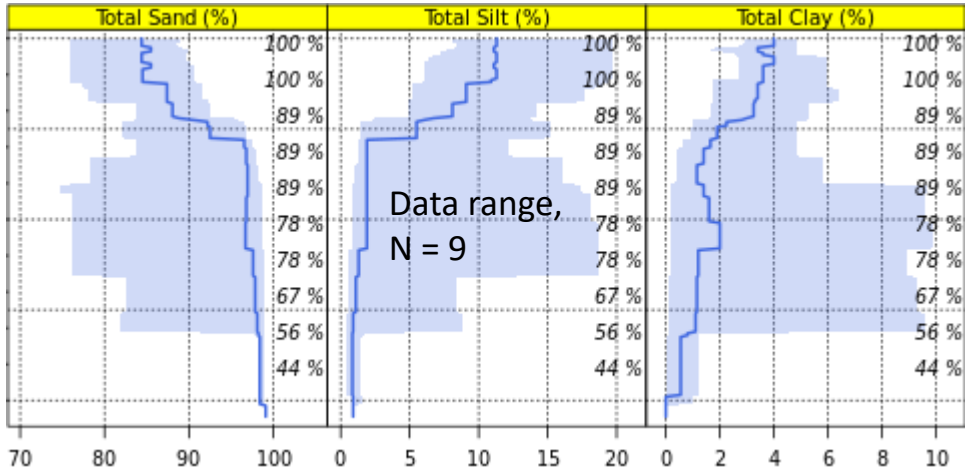
The **Lab Data** tab shows the composition of the soil aggregated over all the representatives of this specific soil type for which data are available (in the case of the Graycalm, that is N = 9), thus giving us an idea of the range within which soil properties vary.

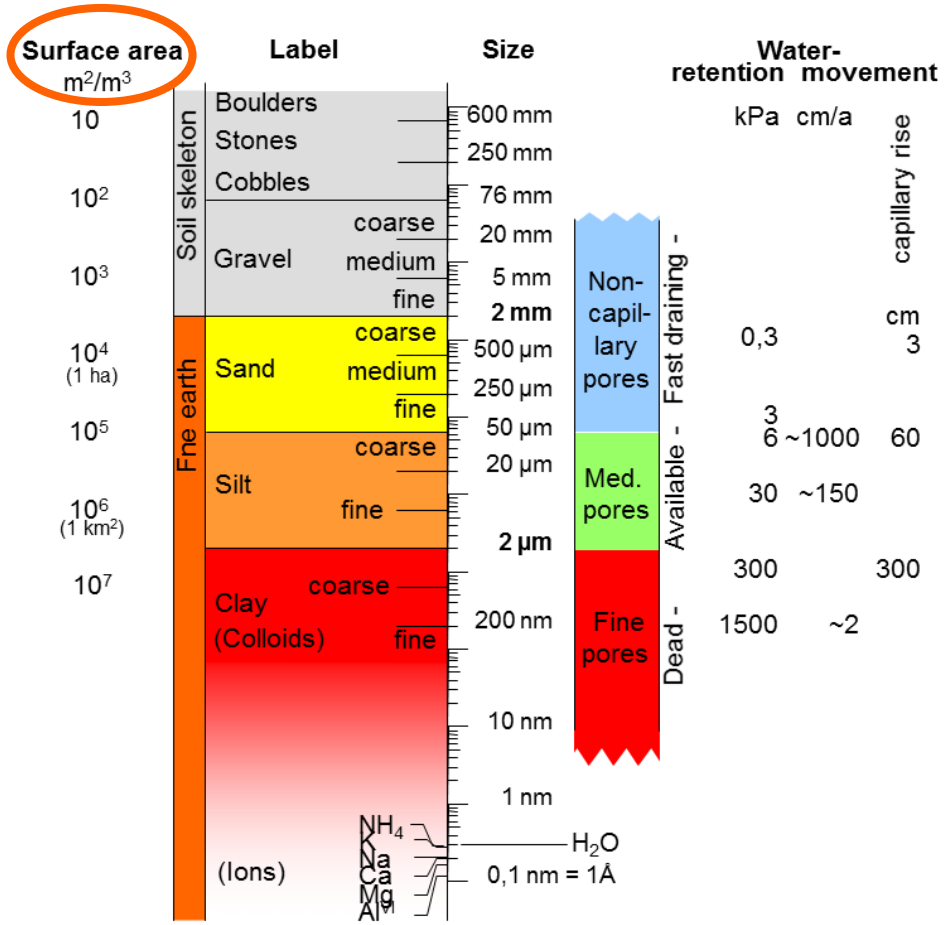
There is a lot of information here and we will discuss some of the information for its relevance to PFAS retention on the next slides

Lab Data tab - texture

Remember that we found **surface area** to be a predictor for the mass of PFAS retained by our soil columns. Note how, in the figure to the right, particle size classes correspond to surface area categories

Now look at the detailed particle size data provided by the Lab Data tab:

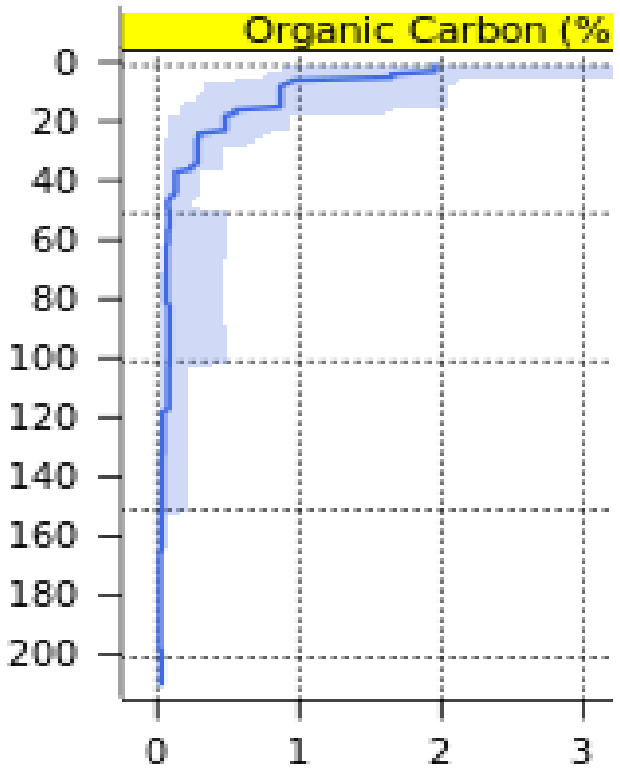




There is almost no clay and silt in our soil = very little surface area to work with for PFAS retention

Lab Data tab – Organic matter

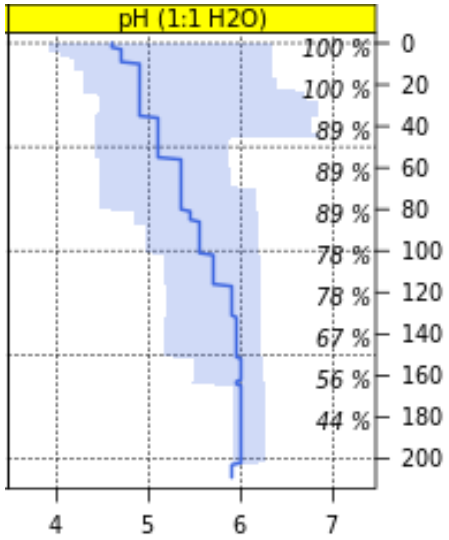
The mass proportion of organic matter (% Organic carbon) was also among the predictors for PFAS retention. The Lab Data tab tells us how much OC is in the soil and how its depth distribution looks like



The data for our Graycalm soil series are not very encouraging: below about 20 cm of depth, OC concentration becomes negligible and can be ruled out as a significant contributor to PFAS retention

Lab Data tab – pH

We recall that PFAS have ionizable functional groups that are behind the mechanism of electrostatic attraction to oppositely charged surfaces. The majority of COO^- and SO_3^- groups are so keen on getting rid of their proton (= have pKa values in the pH 1-3 range) that at the pH of our Graycalm soil, they will be fully dissociated.

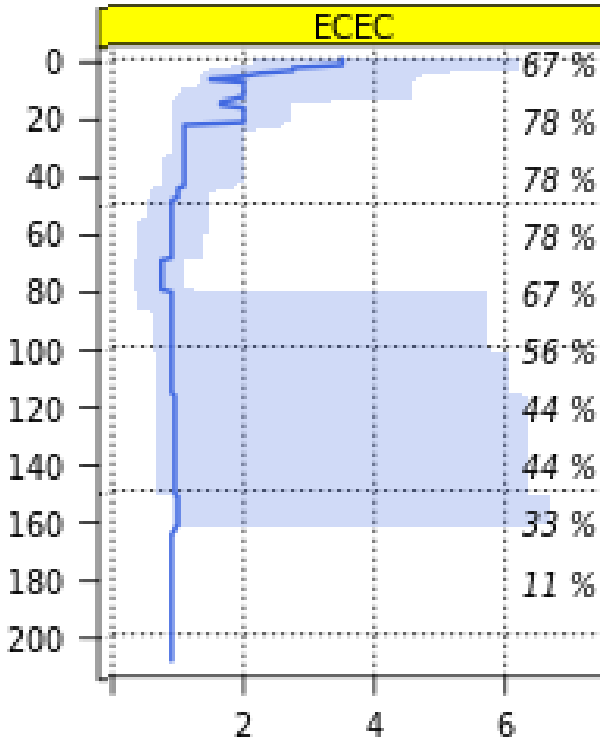


As the pH in our Graycalm soil stays above 4 and below 6 throughout (although there is some variability, compare light blue variability range), we find that anionic functionality of PFAS will be unaffected and all secondary and tertiary amine groups in PFAS will be protonated.

We also remember that certain minerals, especially Fe- and Al oxides, can develop positive charge at pH values below their point of zero charge (pH 8-9). We did learn from the **OSD tab** that we have such mineral phases in our system ("isotic" mineralogy and noticeable Al_o + Fe_o in the Bw horizon) ➔ some **PFAS anions** will get stuck at those mineral surfaces!

Lab Data tab – ECEC

The cation exchange capacity (CEC) reveals the extent to which environmental matrices are negatively charged. Because that charge varies with pH for some (not all) minerals and for organic matter, there is a distinction made between potential CEC (measured at neutral pH) and **effective CEC** (= ECEC), measured at the ambient pH of the soil. Low pH saturates and so reduces negative charge, hence, in acidic soils, the ECEC value is lower than the CEC value. For our purpose of understanding PFAS behavior, we want to go with the ECEC value.



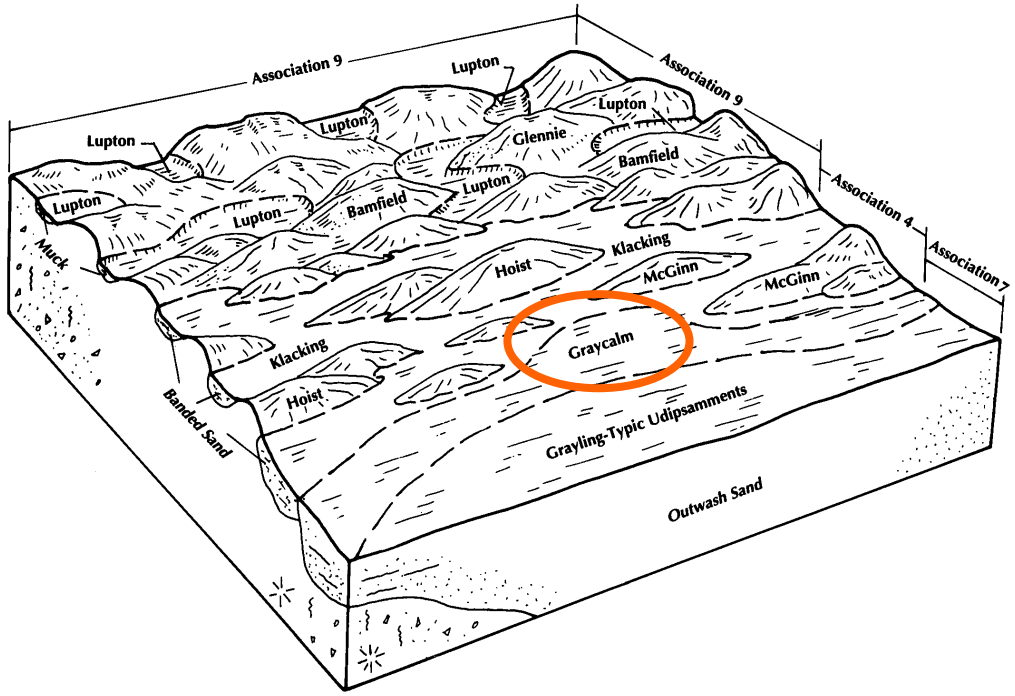
The CEC data for the Graycalm soil are less than spectacular. We find the amount of negative charge on our mineral surfaces is at or less than 1 $cmol_c\ kg^{-1}$.

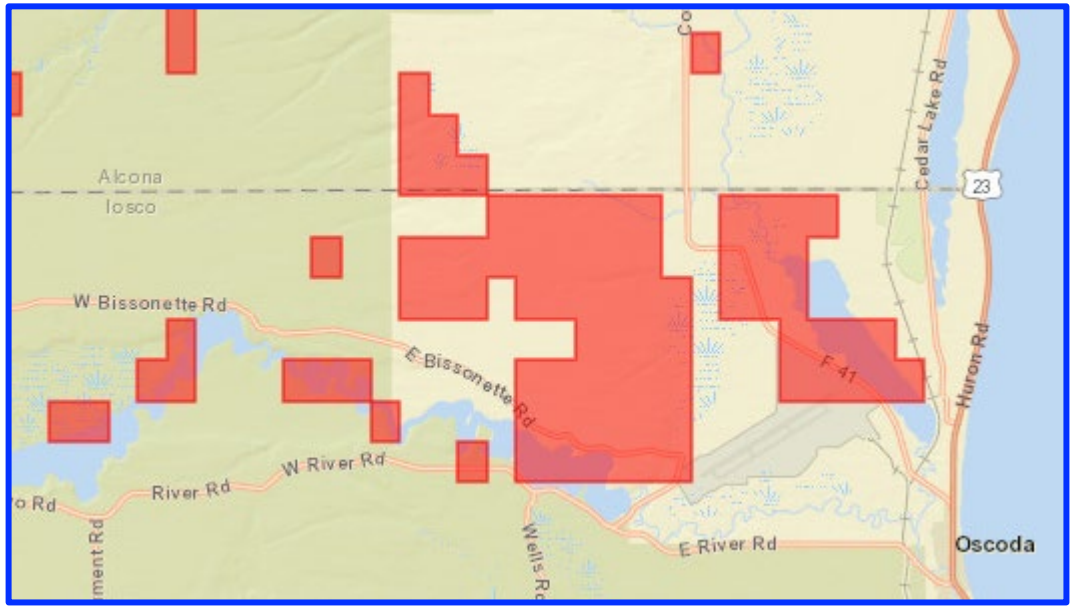
This has important implications for our assessment of PFAS bonding: Because mineral surfaces are pretty much un-charged (with the exception of a bit of Fe-oxide in the Bw horizon), attachment of PFAS to these surfaces will largely happen through hydrophobic exclusion, a mechanism that is highly dependent on the size of the fluorinated sidechain (and reversible when the soil ever dries out)

Other tabs of interest in Data Explorer

The **Water Balance Tab** offers an annual water budget. In the case of the Graycalm, indicating that the soil tends to evaporate just a tiny bit (5 liters = 1.2 gallon per m^2 and year) more water than it receives through the water year

The **Block Diagrams Tab** offers 3D cartoons of landscape positions in which the soil is preferentially found





The **Extent Tab** gives the approximate geographic distribution (red squares) of the soil

Summary

The mechanisms governing the fate and transport of PFAS are quite well known

There are freely accessible, publicly funded and scientifically rigorous sources of information regarding the properties of environmental matrices in source zones

Retrieval and application of information from USDA/NRCS repositories does require some familiarization and practice

But: There isn’t really a good reason to not utilize this reservoir of data when it comes to protecting groundwater quality and public health