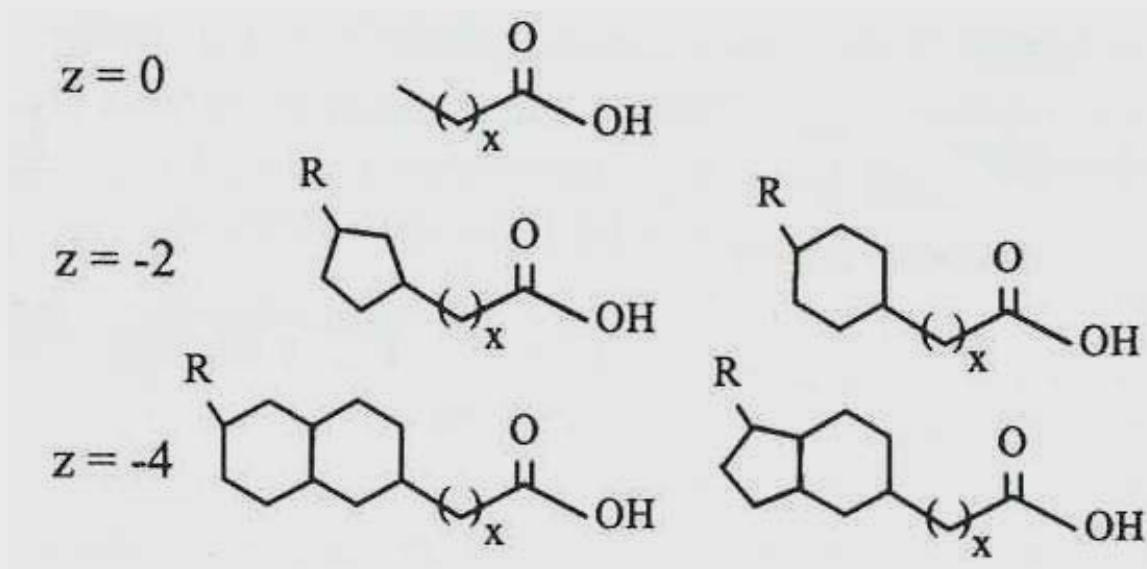


**Sorption of an oil sands naphthenic acid mixture to soils – implication for transport in groundwater and aquatic toxicity**

**Arash Janfada, John V. Headley, K.M. Peru, and S.L. Barbour**

# Background - naphthenic acids:

- OSTW naphthenic acids
  - complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids
  - consist of >200 individual compounds.



$n$  → represents the carbon number

$Z$  → the number of hydrogens lost due to addition of rings

## Naphthenic acids (NAs) are:

- Naturally occurring organic compounds found in most petroleum sources
- Occurring at 1 – 5 mg/L in adjacent (ground and surface) waters in the Alberta oil sands region. (Holowenko et al. 2002)
- Solubilized from bitumen during processing
- Present in tailings pond water at a concentration ranging between 40 - 120 mg/L (Holowenko et al. 2001)

## Naphthenic acids (NAs) are:

- Major contributors to acute toxicity of oil sands tailings water
- Acutely toxic to aquatic organisms. Toxic to mammals and other microorganisms (USEPA)
- Individual NAs have unique toxicities
- Not well established which of the many NA species in the mixtures have the greatest toxicity; low molecular weight species are likely candidates

## Importance of transport studies:

- Biodegradation of contaminants in soils is controlled by mass transfer processes (Griebe et al. 2000).
- Understanding transport – leads to remediation, control, and protection of human water supplies
- Currently, few studies done on the transport properties of OSTW naphthenic acids

# Factors governing sorption

- Sorption of non-polar and ionizable compounds such as naphthenic acid are governed by several parameters (Delle Site 2001; Schramm 2003; Fetter 1999)
  - Degree of water solubility
  - Equilibrium constant ( $k_a$ ) and pKa of the adsorbate
  - pH of the system
  - Mineralogy of sorbent
  - Organic carbon content of sorbent
- These parameters vary considerably in the field both spatially and temporally (Hackbarth 1981; Bachu and Underschultz 1993)

## Factors governing sorption (cont.)

- pKa of naphthenic acids varies in the range of 4.71 - 5.1 (Harve et al 2003) others give btw. 5-6 (Headley 2002).
- ionizable organic acidic considered 100% deprotonated when the pH is 2 above the pKa (Delle Site 2001)
- Mechanisms of adsorption complex since depending on the pH, naphthenic acids can exist both in neutral and ionized forms
- partitioning to the organic fraction ( $f_{oc}$ ) and as adsorption to mineral surfaces can occur (Delle Site 2001; Fendel 1988).

## Factors governing sorption (cont.)

- Surface-solute sorption mechanisms are of three types
  - a) Physical
  - b) Chemical
  - c) Electrostatic
- The degree to which each acts being governed by the aforementioned parameters (Delle Site 2001).
- Surface activity, cation/anion exchange capacities of soils also change with pH of solution (Hyun and Lee 2004; Delle Site 2001).



## Scope of the study

- Picked a relevant set of conditions under which adsorption behavior of NAs was analyzed.
- “Representative of field conditions” – illusive term since field conditions are variable.

**Examples in the oil sands region...**

# Scope of the study

- McMurray and Grandrapids aquifer/aquitard systems tend to be complex with interwoven beds of sands, shale, and silt (Bachu and Underschultz 1993).
- Salinity of aquifers varies both spatially and temporally in the area and by orders of magnitude higher than that used in this study (Hackbarth 1977; Bachu and Underschultz 1993).
- Bicarbonate has remediating characteristics for naphthenic acids but varies in concentration spatially and temporally (Gervais 2004; Compton and Brown 1994).

# Objectives of the study

1. Develop an analytical method for NAs in OSTW Mixtures:
  2. Apply to illustrative case of soils, groundwater and NA source using
    - Soils from the Athabasca oil sands region
    - NAs extracted from the Mildred Lake Mine Tailings water
    - Elevated salinity
  3. Conduct a preliminary evaluation of impact of following on NA adsorption
    - Elevated salinity
    - Selected species sorption
- Study not focused on:
    - Partitioning mechanisms (ex. Hydrophilic/hydrophobic)
    - Recommendation of adsorption isotherms in oil sands.

# Materials

- Soil 1 was a mixture of peat and mineral soil that was produced during soil salvage operations.
- Soil 2 was a sandy clay to clay loam mineral mixed with a small amount of peat.
- A 3190mg/L stock solution of the naphthenic acids was obtained by liquid-liquid extraction of 200L of OSTPW.

Properties	Soil No. 1	Soil No. 2
Organic carbon (%)	2.7	1.6
Organic matter (%)	4.7	2.8
Inorganic carbon (%)	0.26	0.23
Na <sup>+</sup> (µg/g)	107	64
Ca <sup>2+</sup> (µg/g)	177	98
Mg <sup>2+</sup> (µg/g)	37	16
K <sup>+</sup> (µg/g)	4	3
CEC (mequiv./100g)	19.4	16.2
pH	7.7	7.7
SAR	1.9	1.6
Moisture (%)	2.3	1.9

# Procedures

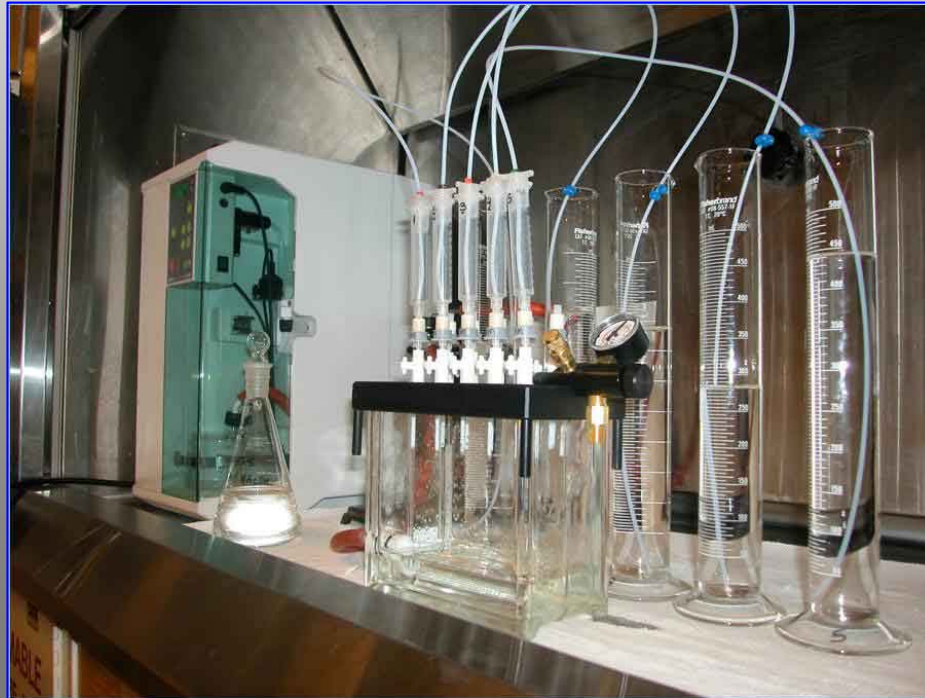
- The adsorption data was obtained using a modified ASTM batch partitioning method.
- SGW was prepared according to Donahue (1994) as summarized in Table 2. with Sodium Azide added as a microbial inhibitor.

Composition	Concentration (mg/L)
CaSO <sub>4</sub> (BDH Chemicals, Poole, UK)	1013
MgSO <sub>4</sub> (BDH Chemicals, Toronto, ON)	938
NaN <sub>3</sub> (BDH Chemicals, Toronto, ON)	525

- The pH of all solutions was fixed at  $8.0 \pm 0.4$ , and all pH
- Regression analysis was used to determine the confidence intervals of the  $K_d$  values (Caulcutt and Boddy 1983).

# Procedures

- The concentration/characterization of all solutions was analyzed using a triple quadrupole mass spectrometer with an electrospray (ES) interface operating in the negative-ion mode.(Headley and Peru 2002).
- Both SGW and DI water solutions were subjected to a solid phase extraction procedure to remove matrix interference before any analysis was conducted.

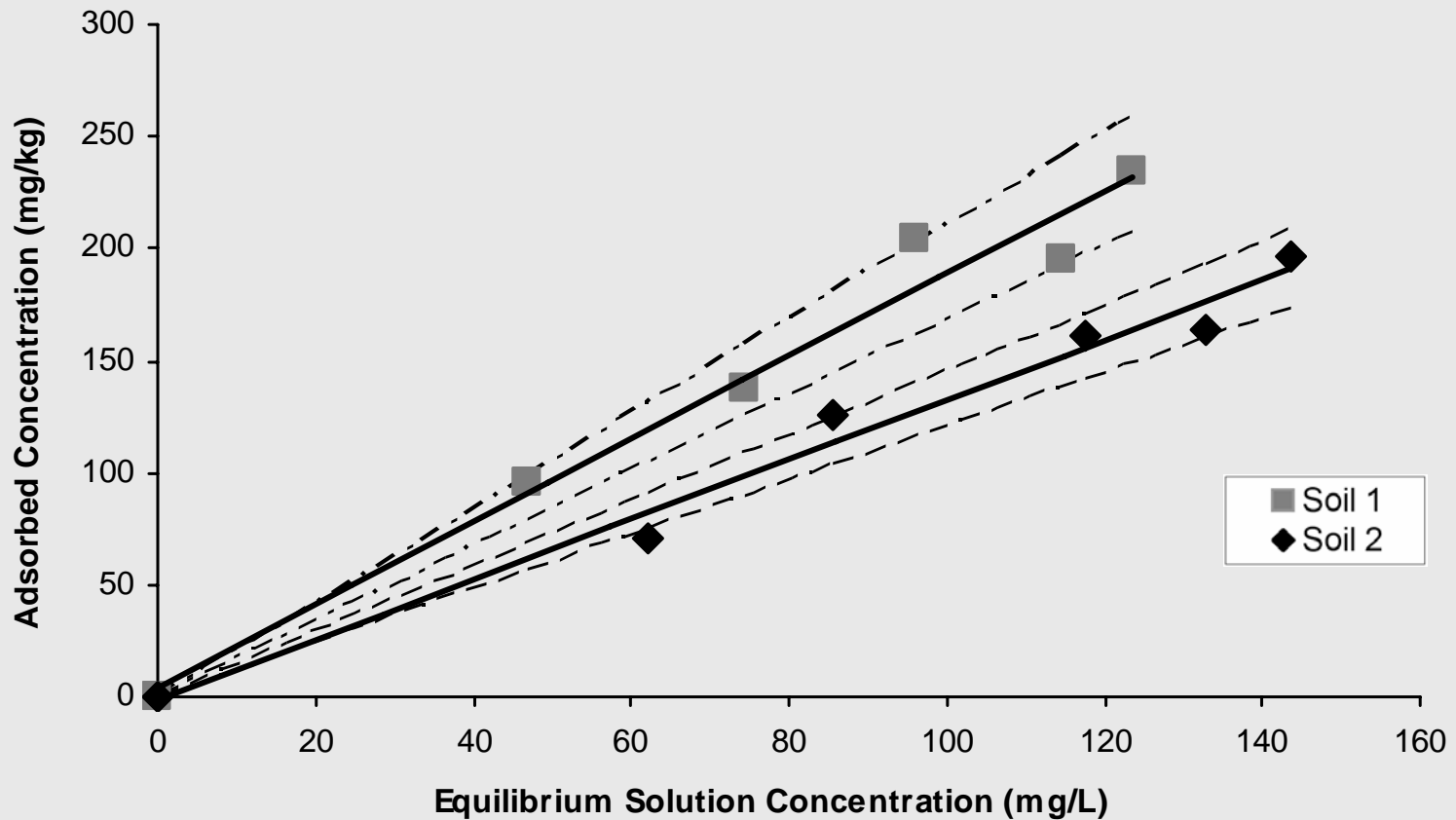


## Results: DI water

- Preliminary study of kinetics of the adsorption were conducted and it was concluded that after 48 hour adequate equilibrium conditions had been reached.
- The adsorption coefficients for the mixture of naphthenic acids in DI water were determined to be  $1.9 \pm 0.2$  (ml/g) and  $1.3 \pm 0.15$  (ml/g) for soils 1 and 2 respectively.

Recall – primary difference between the two soils being a near 2-fold difference in OC/OM content of soil 1.

## Sorption isotherms for NAs on soils 1 and 2 with DI water

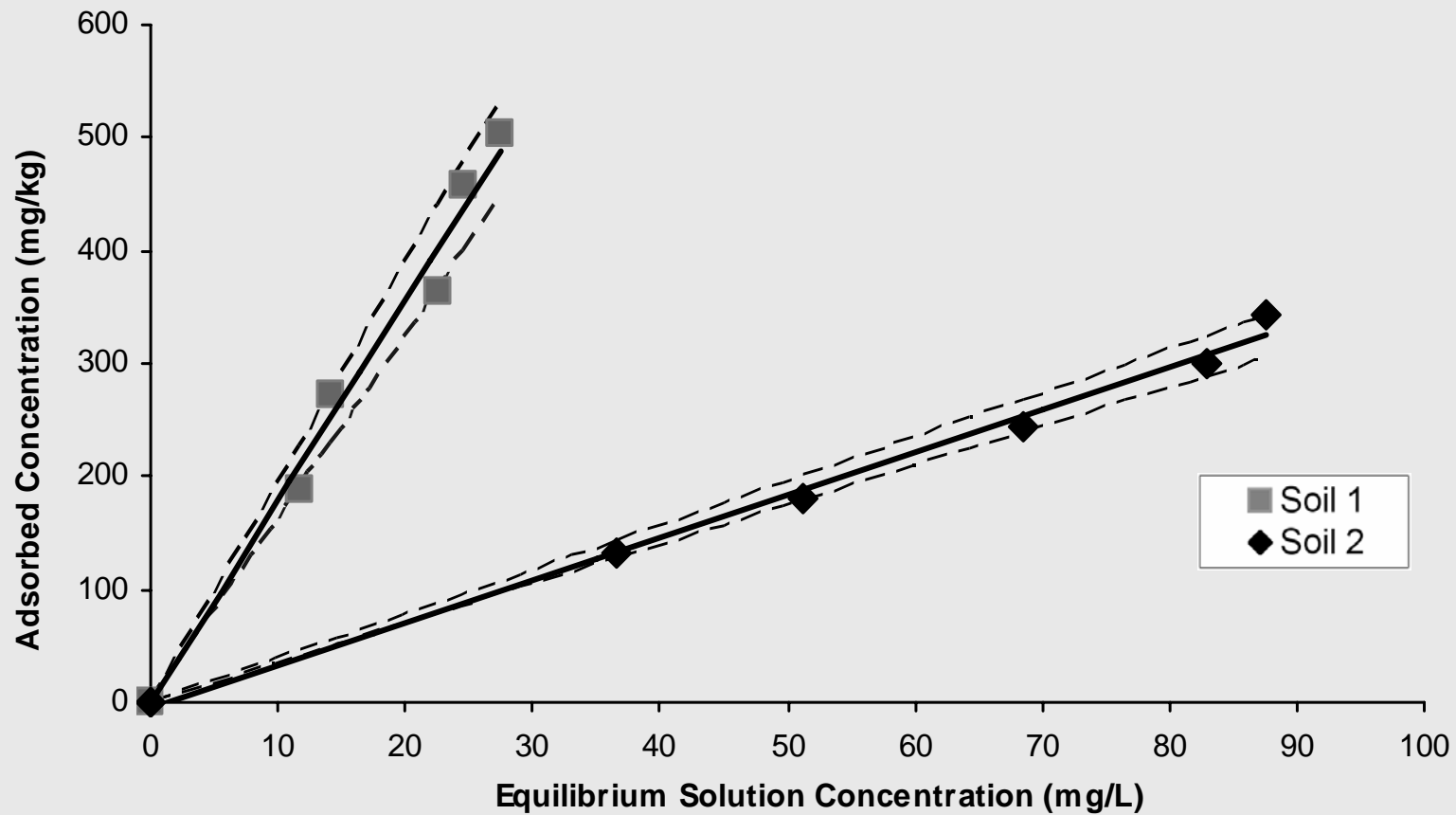




## Results: SGW

- In the presence of SGW,  $K_d$  on soil 1 increased from  $1.9 \pm 0.2$  (ml/g) to  $17.8 \pm 1.5$  (ml/g).
- This is an order of magnitude higher than in the DI water solution.

## Sorption isotherms for NAs on soils 1 and 2 with SGW water



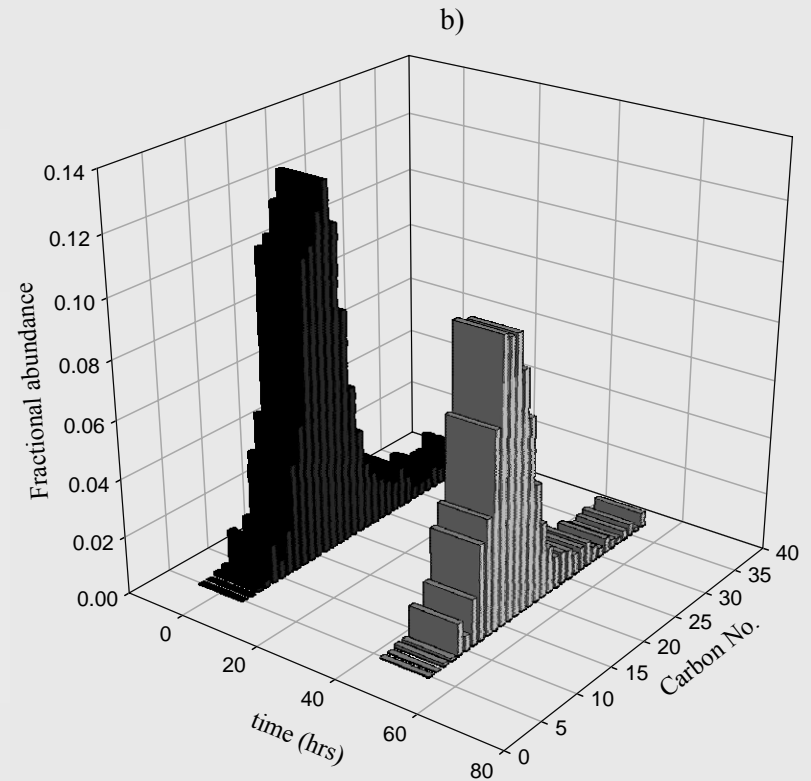
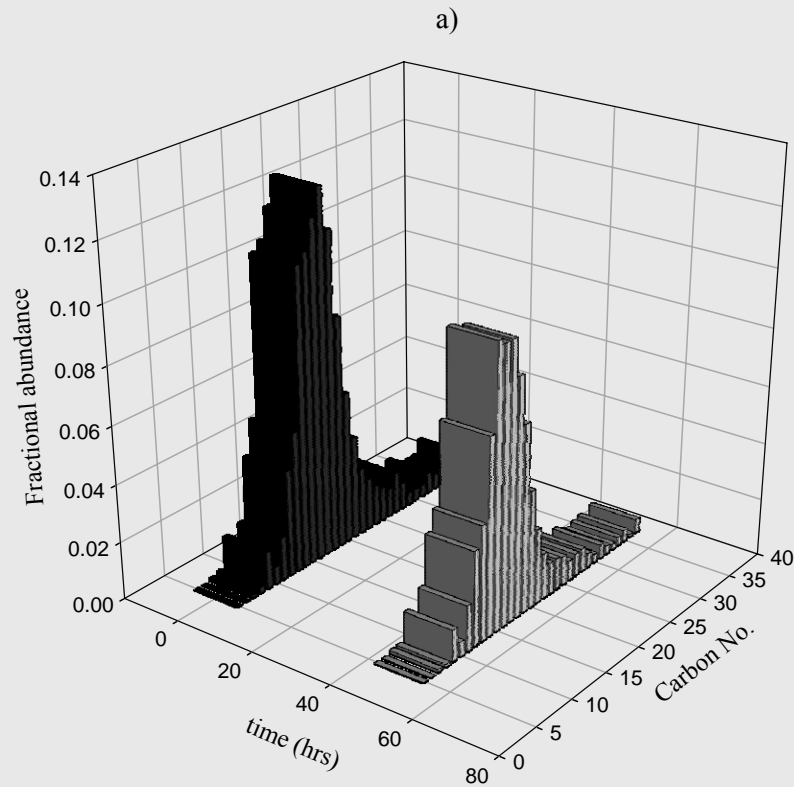
## Results (cont.)

- In both cases the  $K_d$  value for the two soils are significantly different likely resulting from soil 1 having nearly double the OM and  $f_{oc}$  than soil 2 (Fetter 1999; Pignatello 2000).
- Salting out is the likely mechanism at play in SGW solution
- The presence of inorganic salts can enhance the adsorption capacity hydrophobic ionizable organic compounds (Ping and SenGupta 2004; Martins, Jean M.; Mermoud 1998; Horng 2000).

## Evidence for selective sorption

- The relative abundance of each of the naphthenic acids was then plotted according to -Z family, against time and varying carbon numbers between n=5 and n=37; a different plot was produced for each -Z family. (St. John 1998; Holowenko 2001).
- naphthenic acids in carbon No. range ~13 -17 seemed to sorb preferentially; evidenced by their change in fractional abundance
- the fractional abundance of compounds with nearby carbon numbers remains relatively constant.

# Relative abundance for Z=-2 family of acids at t=0 and t=48hrs – DI water

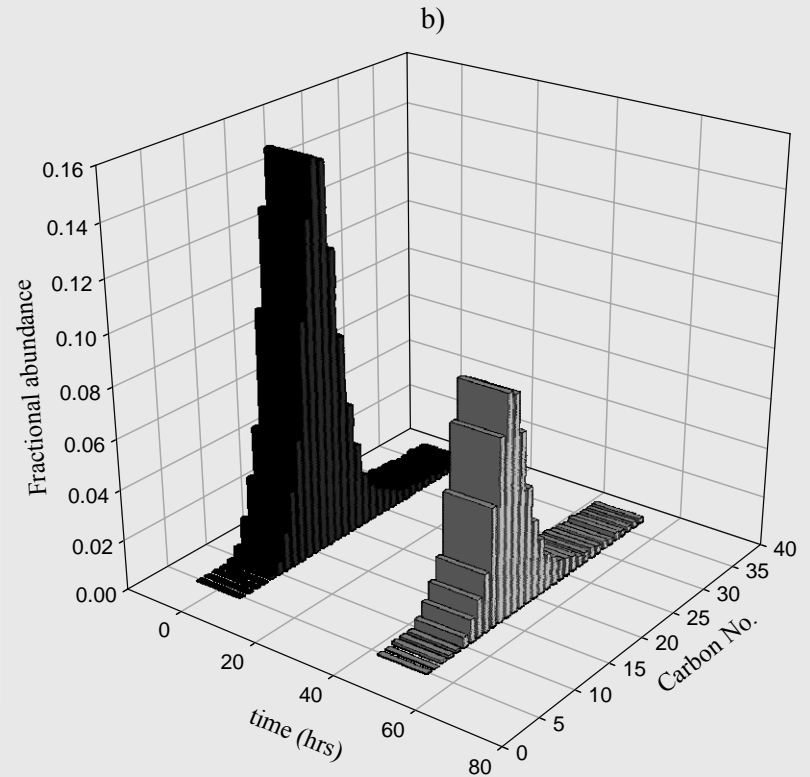
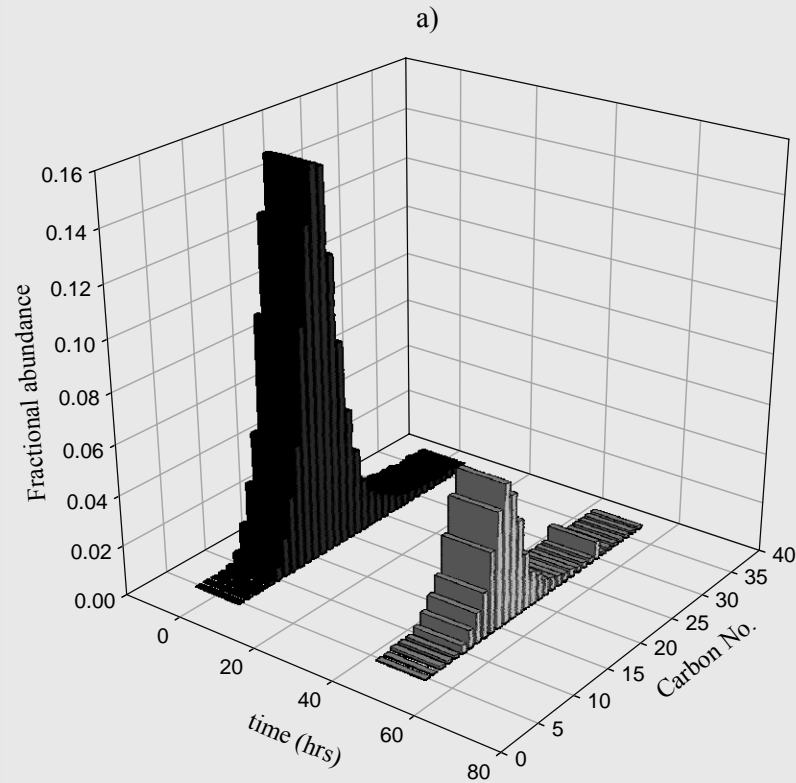


- a) Z=-2 family change in fractional abundance of individual species with time, soil 1 in DI water
- b) Z=-2 family change in fractional abundance of individual species with time, soil 2 in DI water

## Evidence for selective sorption

- Two sample t-test was applied to the transformed data for each Z family comparing t=0 and t=48 samples
- With samples in SGW solutions it was found – for all Z families
  - Carbon No. 5 to 14 ***did not*** adsorbed significantly
  - Carbon No. 15 to 24 adsorbed significantly
  - Carbon No. 25 to 37 adsorbed significantly

# Relative abundance for Z=-2 family of acids at t=0 and t=48hrs - SGW

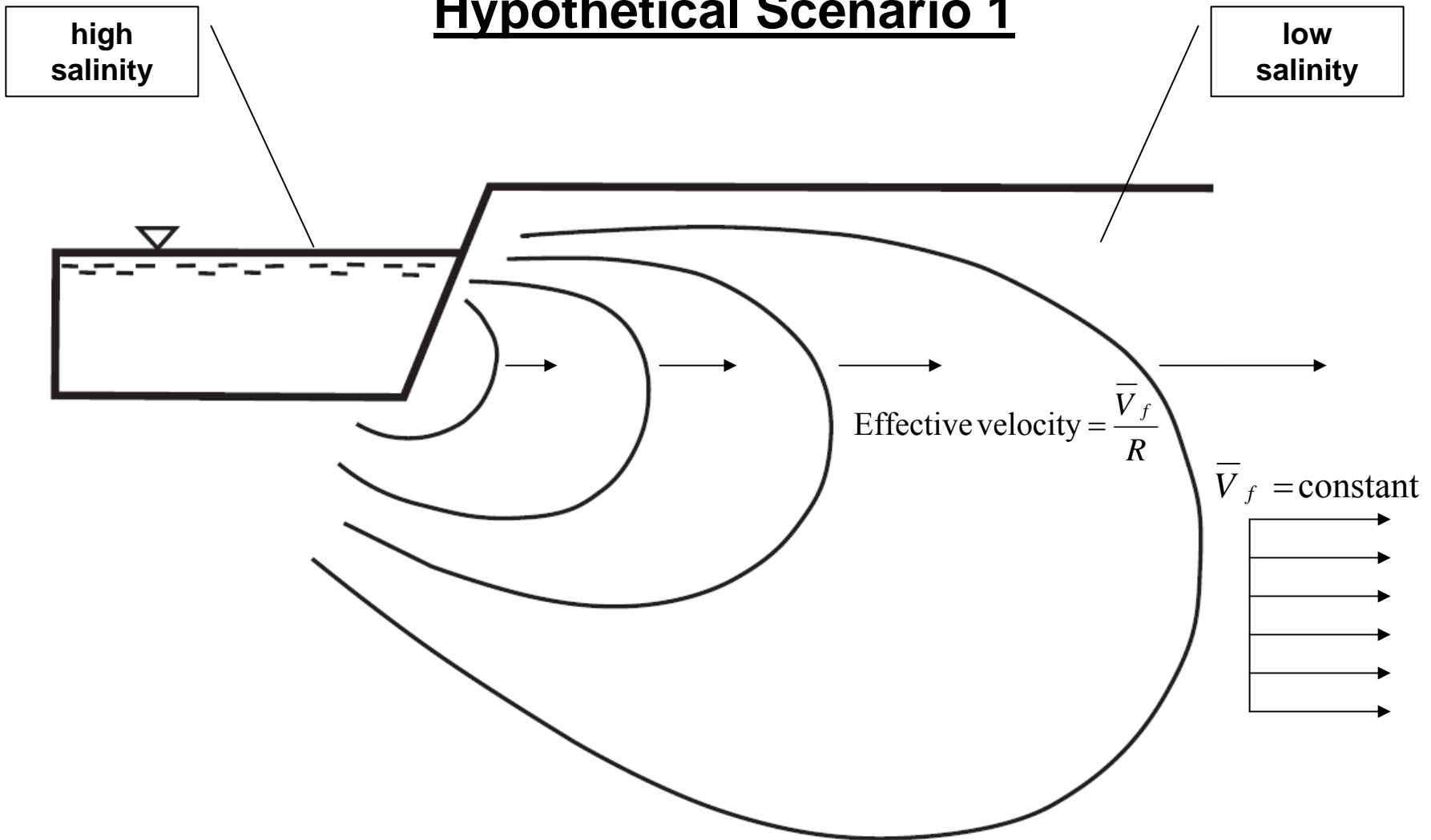


- a) Z=-2 family change in fractional abundance of individual species with time, soil 1 in SGW
- b) Z=-2 family change in fractional abundance of individual species with time, soil 2 in SGW

**Implications and practical  
relevance ...**

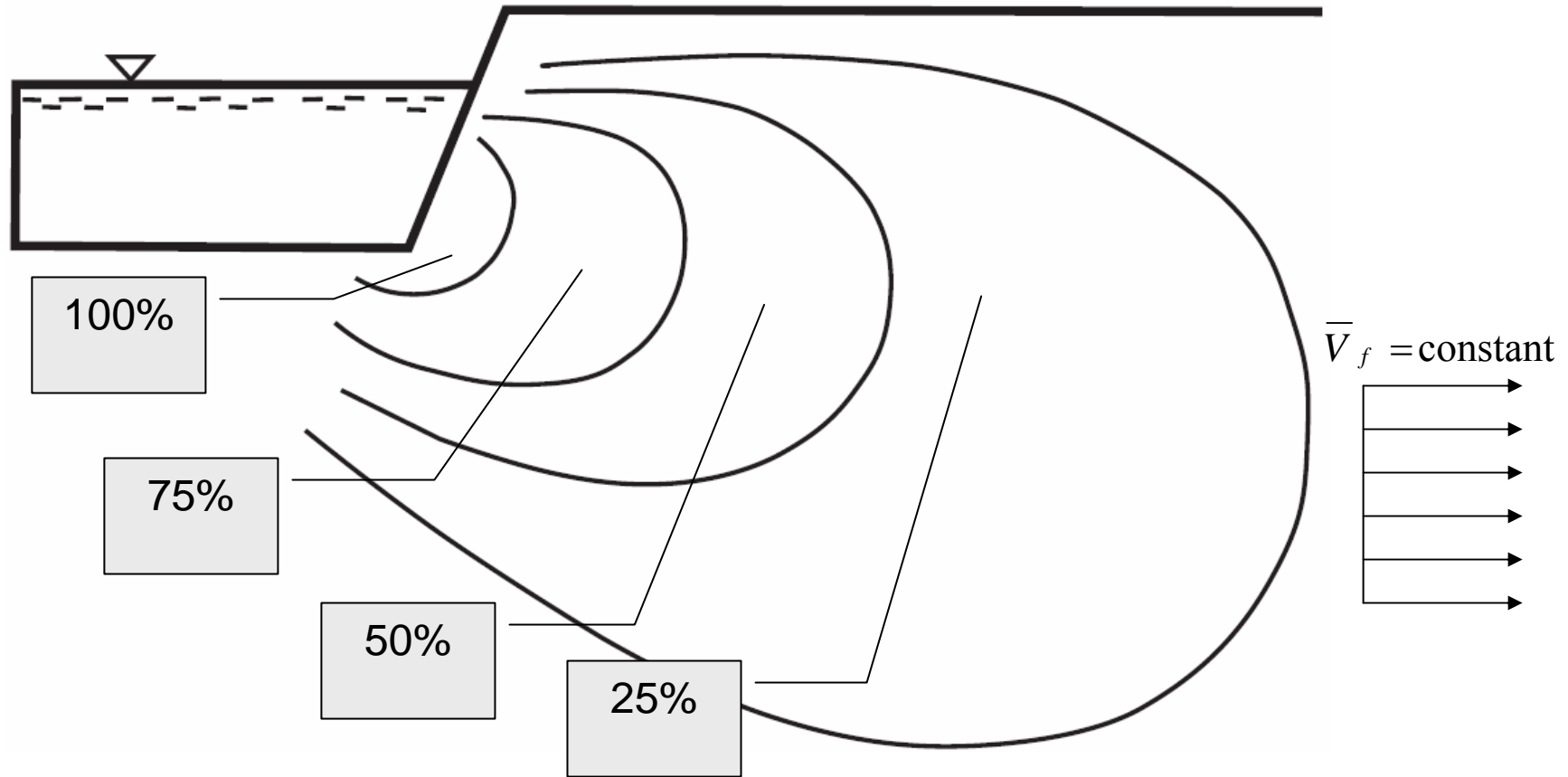


# Hypothetical Scenario 1



- As the plume becomes more dilute,  $K_d$  decrease,  $R$ , decrease and effective velocity increases to ground water velocity.
- May look like an increase in longitudinal dispersivity but is more complex

## Hypothetical Scenario 2



- As plume advances, higher sorption affinity NAs partition out leaving more mobile fraction.
- Mobile fraction likely to be lower molecular weight NAs – Toxicity concerns; bioavailability.

# Conclusions

- OSTW Naphthenic acids exhibit increase sorption under conditions of high salinity
- The lower molecular weight naphthenic acids experience no significant sorption under saline conditions where naphthenic acids of carbon number 15 to 37 do sorb significantly.

**Questions or  
comments?**