Influence of adsorption on the transport of inorganic contaminants: conceptual and quantitative models

USGS Toxic Substances Hydrology Program
National Point Source Research Meeting

January 26-29, 2009

San Diego, CA

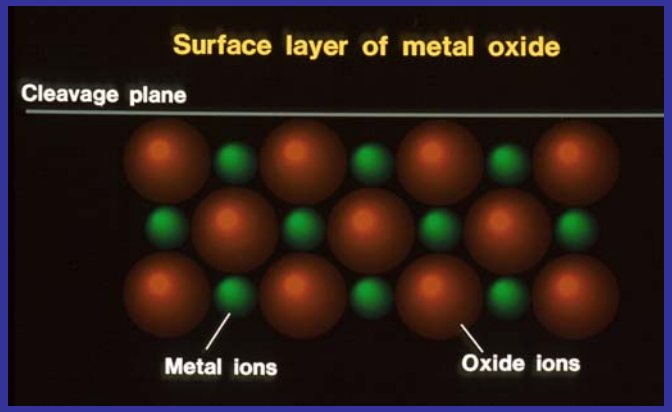
USGS
science for a changing world

Outline

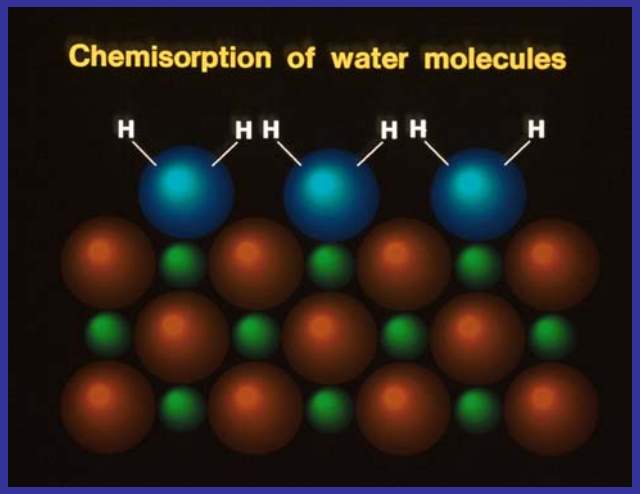
- Background
- Adsorption and chemical speciation
- Quantitative modeling of the influence of variable chemistry
- Critical issues and future research

Why mineral surfaces drive adsorption

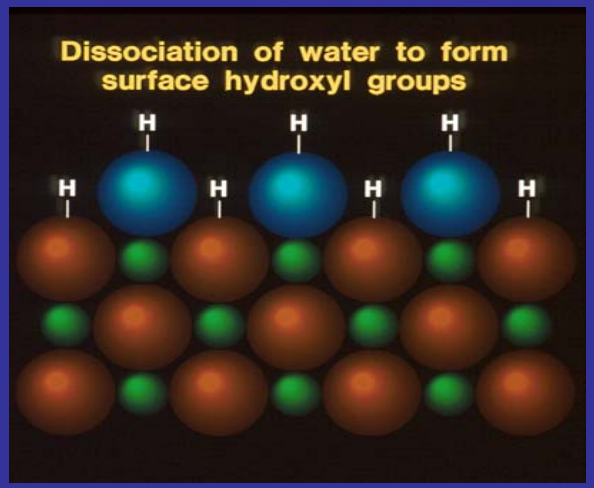
Coordination of ions interrupted at surface



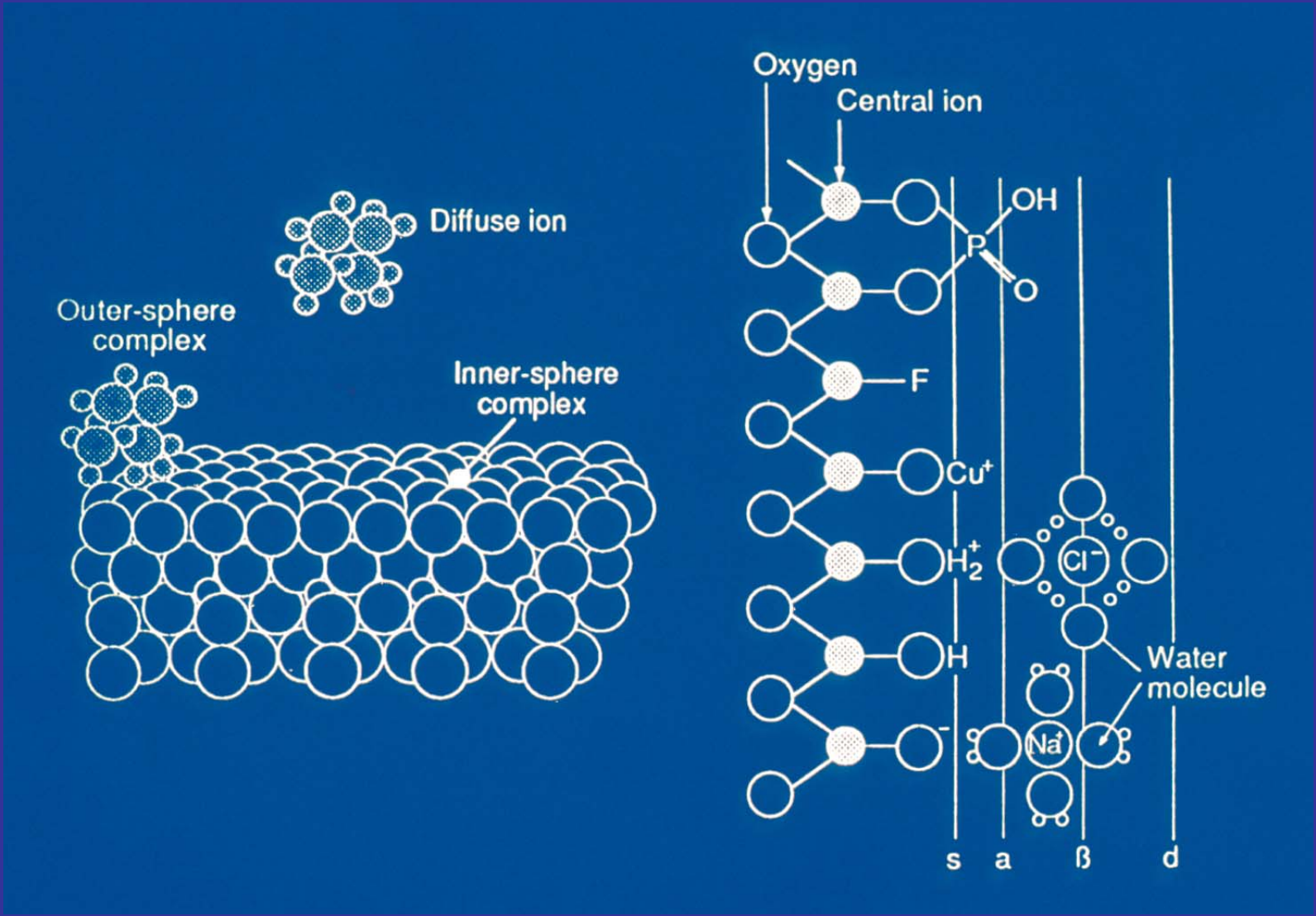
Adsorption of water



The hydrated oxide surface

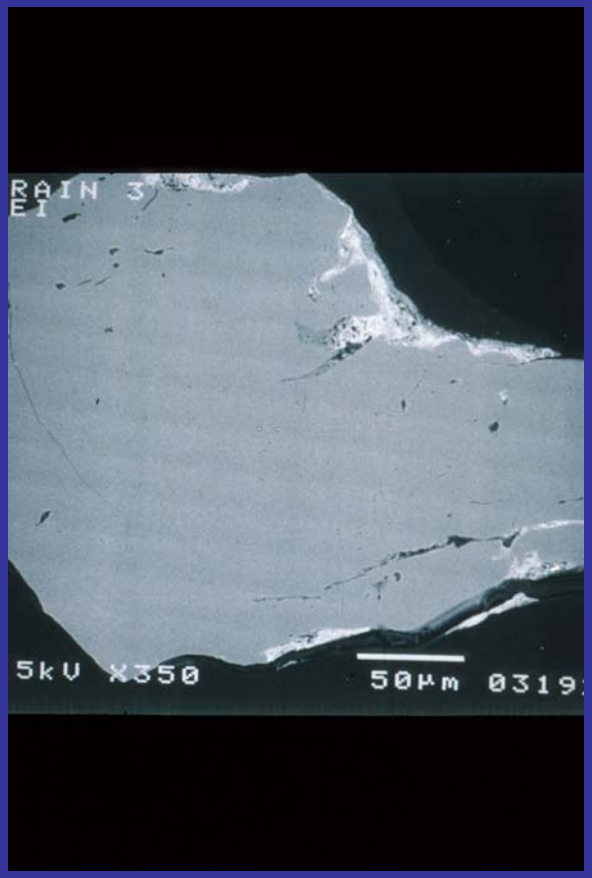


Solutes bind to surface sites



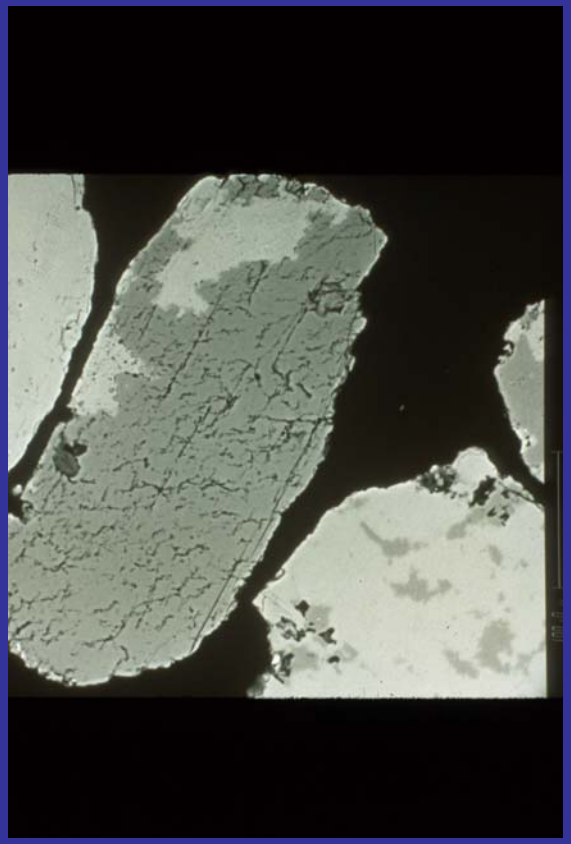
Cape Cod aquifer sediments

Cape Cod aquifer sediments



>90% quartz

Coston et al. (1995)

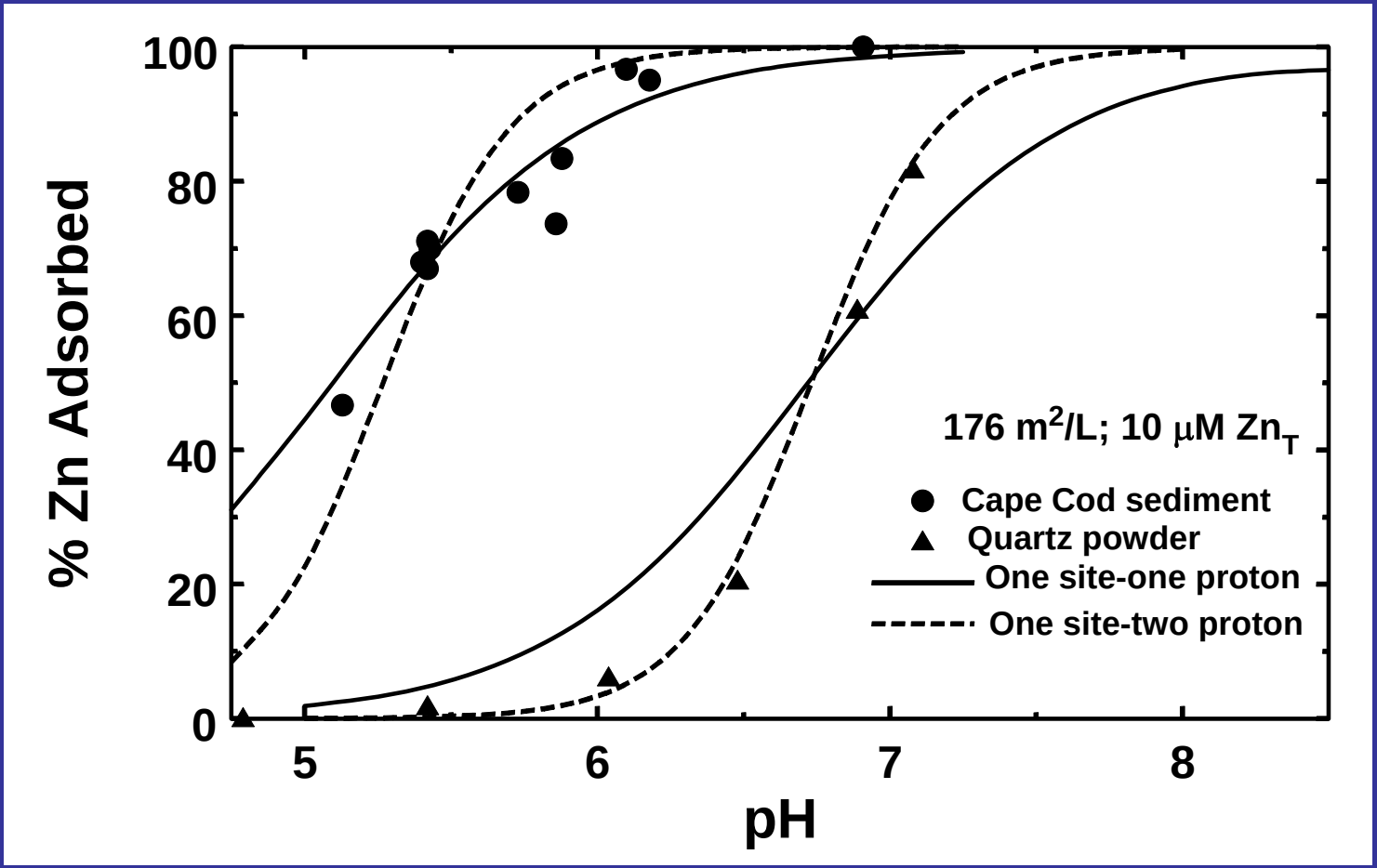


~5% feldspars

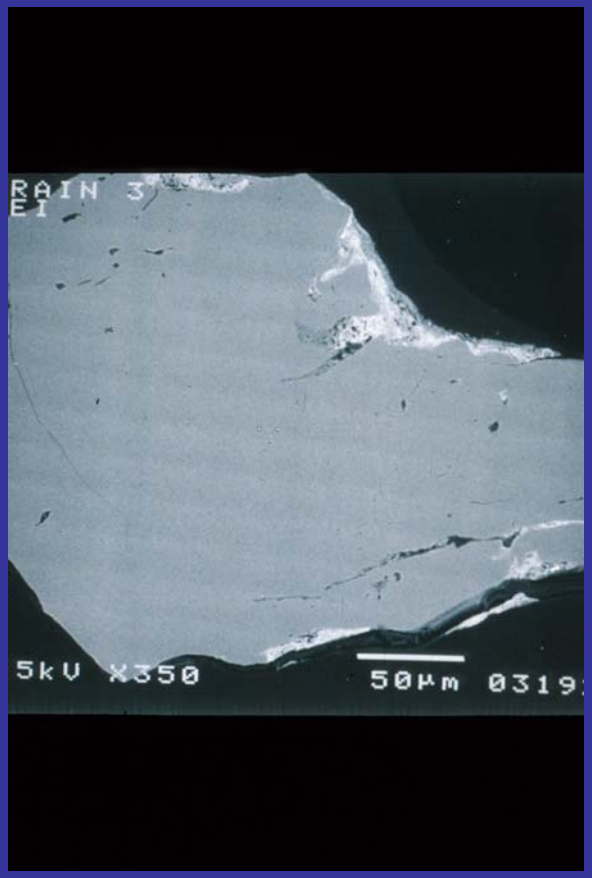
Wood et al. (1990)

Zinc adsorption on quartz and sediments

- Adsorption of metal ions like zinc vary with pH



Cape Cod aquifer sediments



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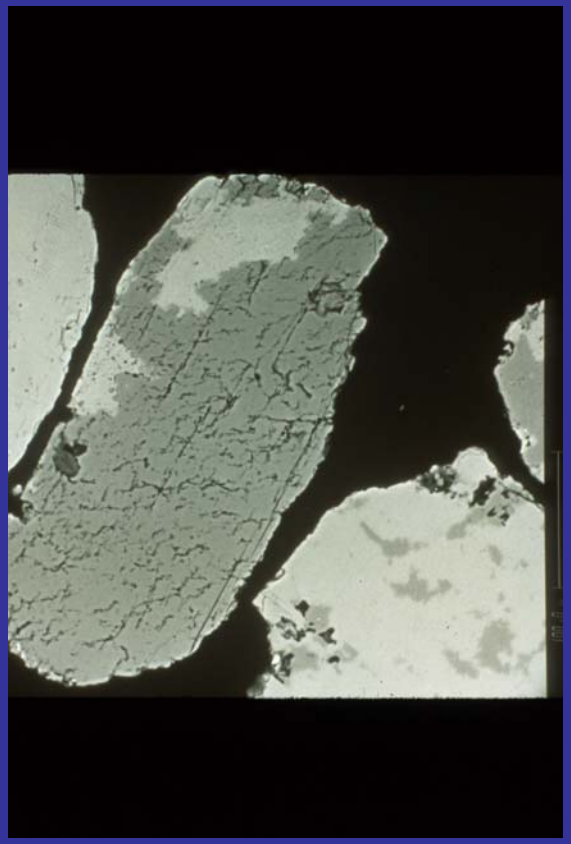

~5% feldspars

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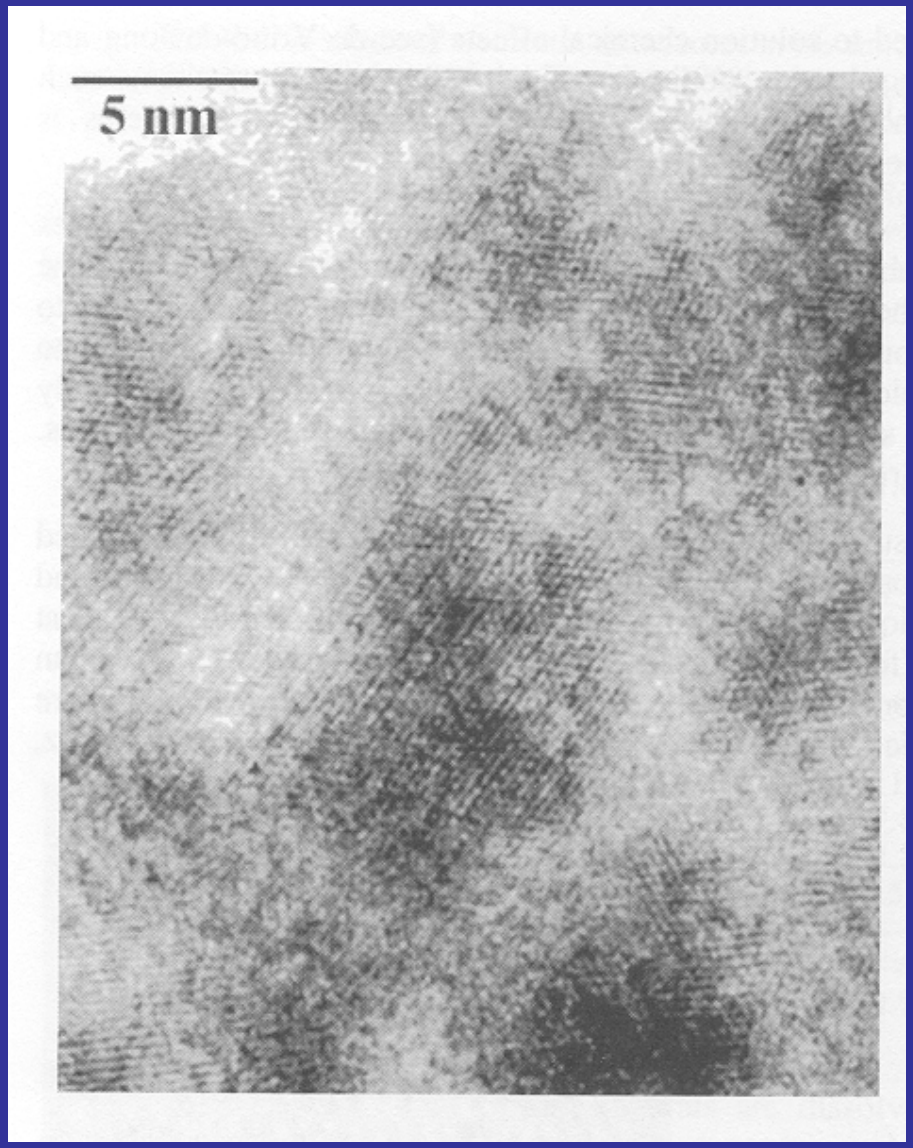
TEM image



Coating on quartz grain

Goethite, 5-10 nm

Major components: Al, Si, Fe

Banfield and Hamers (1997)

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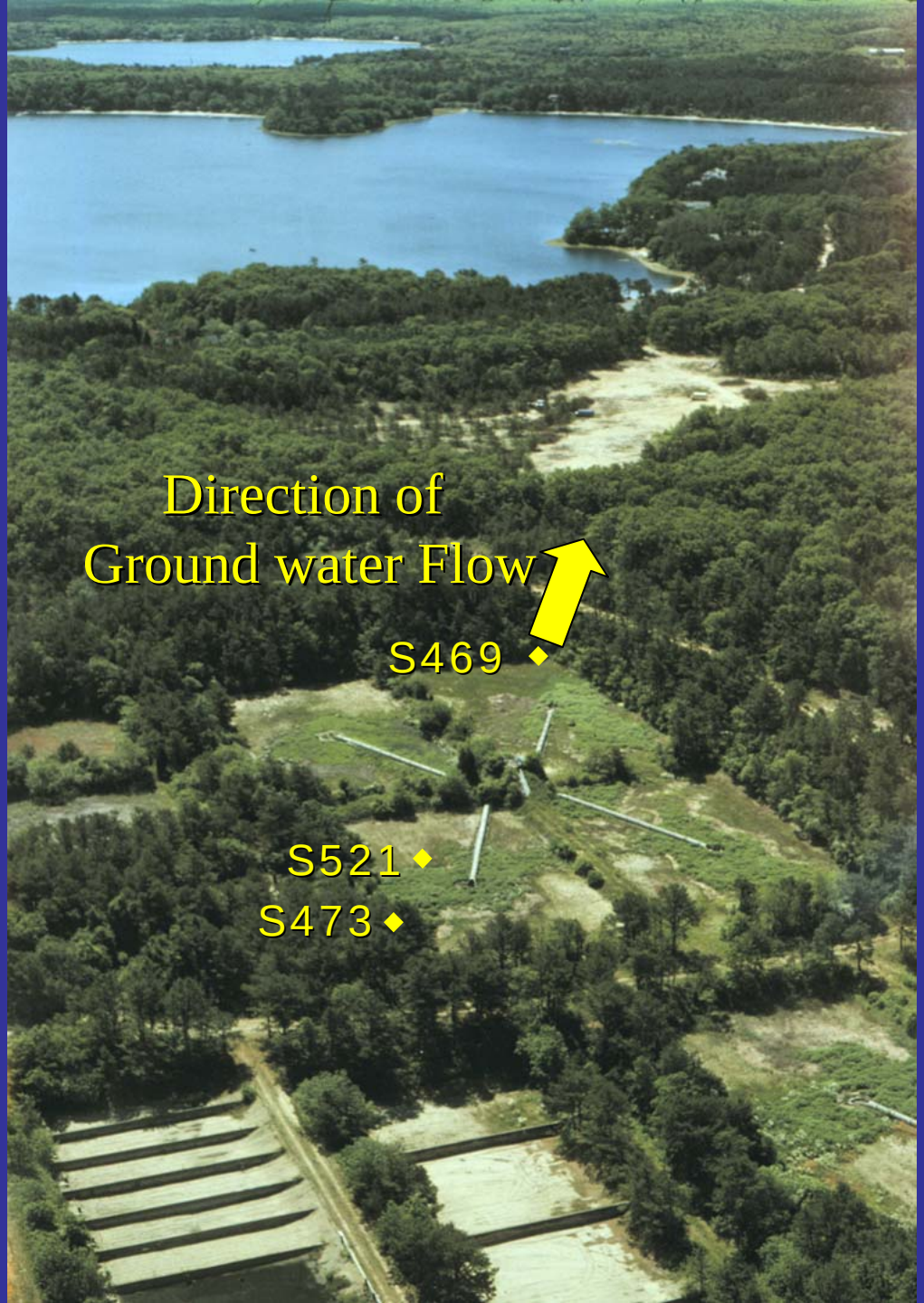
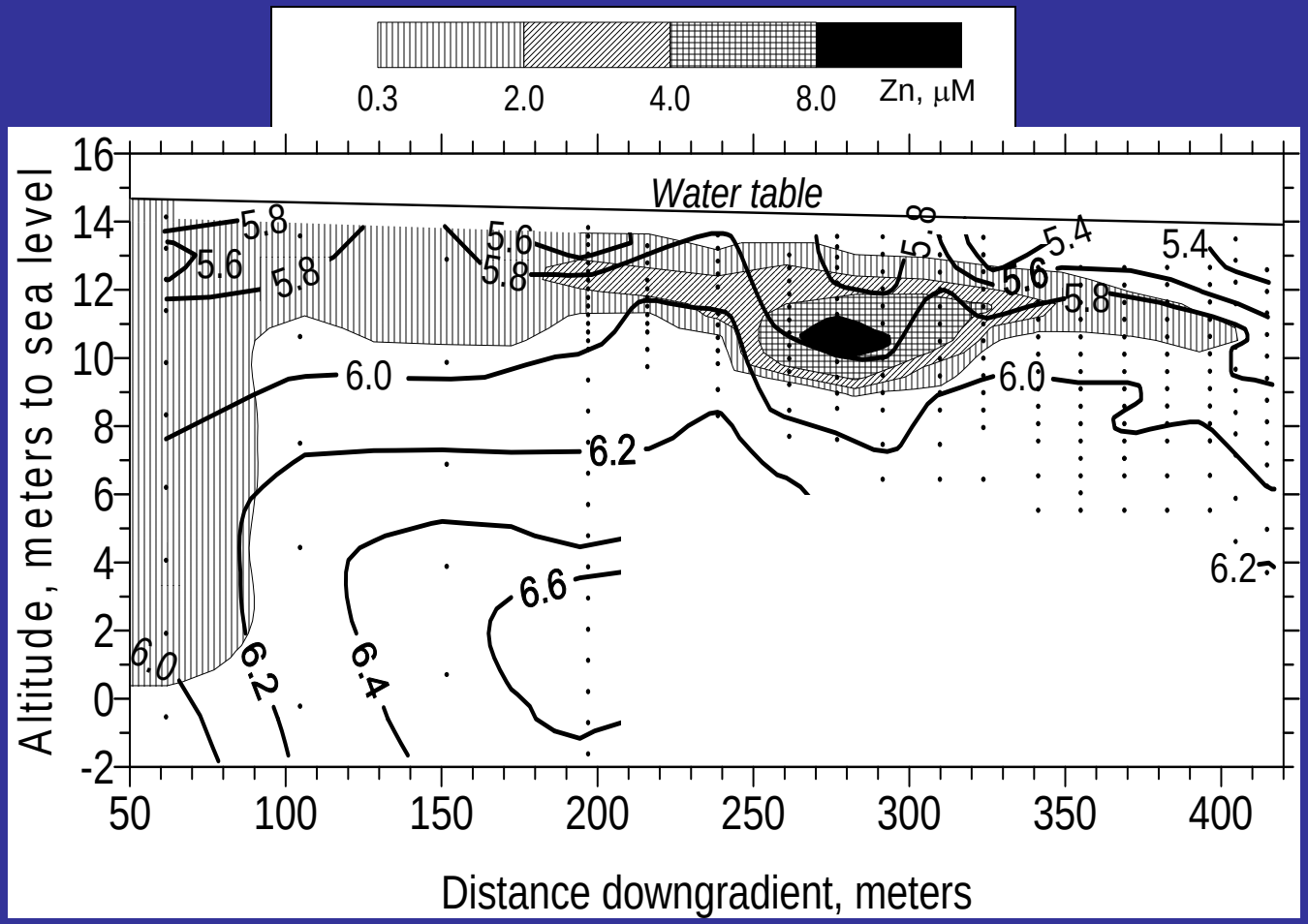
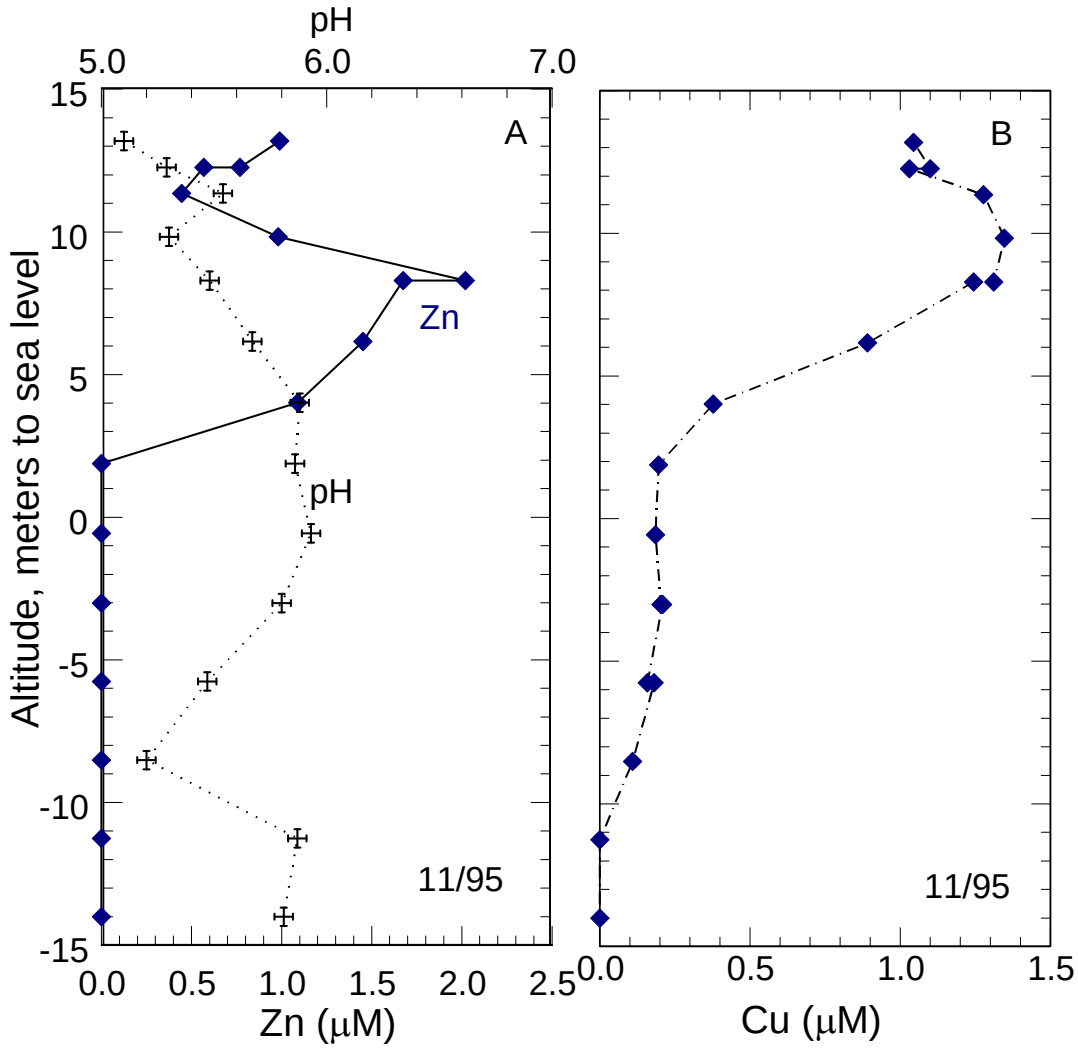
Effect of speciation on transport

Strongly sorbed solutes		Weakly sorbed solutes
M_1^{z+}	$\xleftrightarrow{\text{Complexation}}$	$M_1L_1, M_1L_2, \ldots M_1L_x$
M_2^{z+}	$\xleftrightarrow{\text{Redox}}$	M_2^{z-1+}

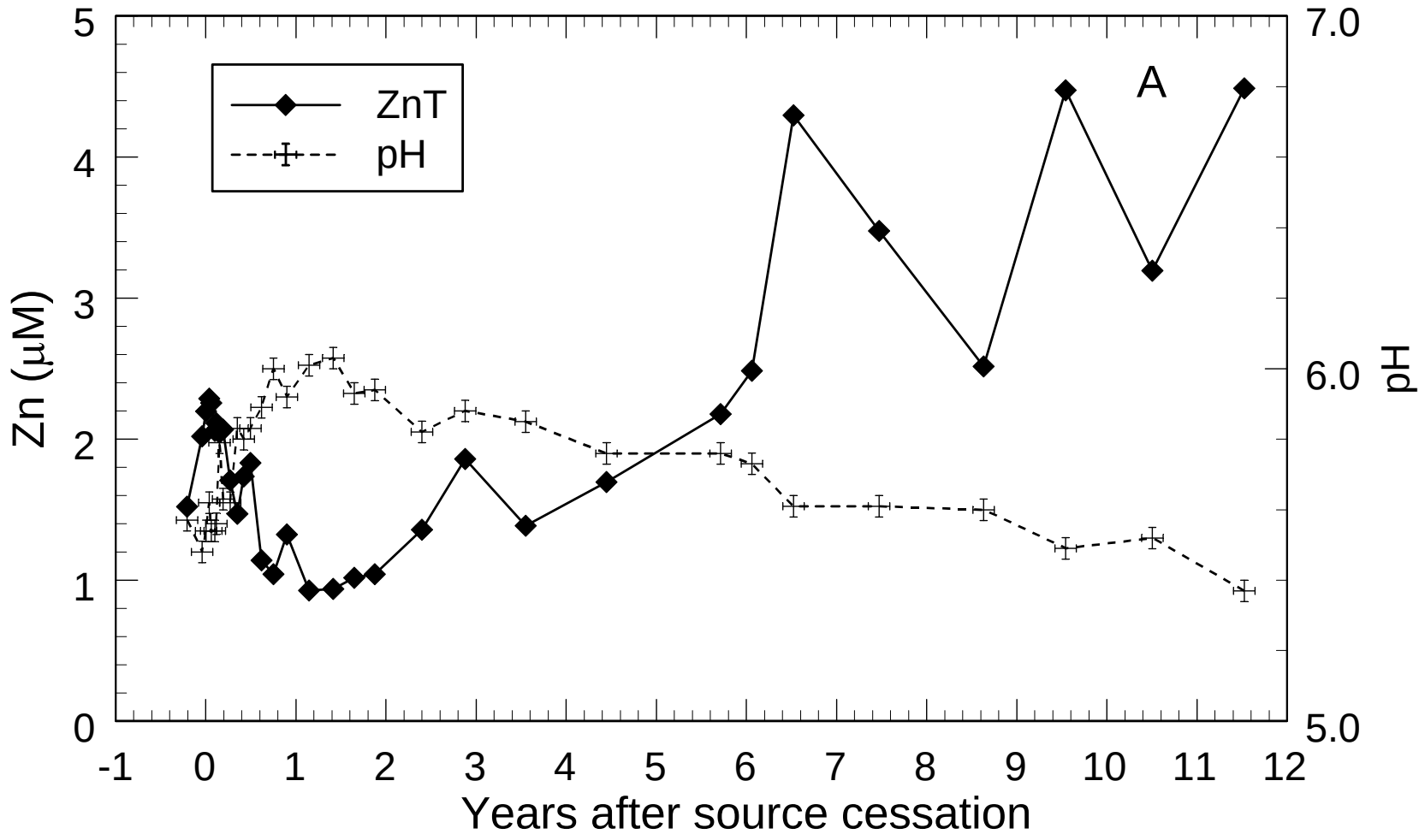

Direction of
Ground water Flow
S469
S521
S473


0.3
2.0
4.0
8.0
Zn, μM
Water table
Altitude, meters to sea level
Distance downgradient, meters
16
14
12
10
8
6
4
2
0
-2
50
100
150
200
250
300
350
400
5.8
5.6
5.8
5.6
5.8
5.8
5.4
5.4
5.6
5.8
6.0
6.0
6.2
6.2
6.6
6.0
6.2
6.4

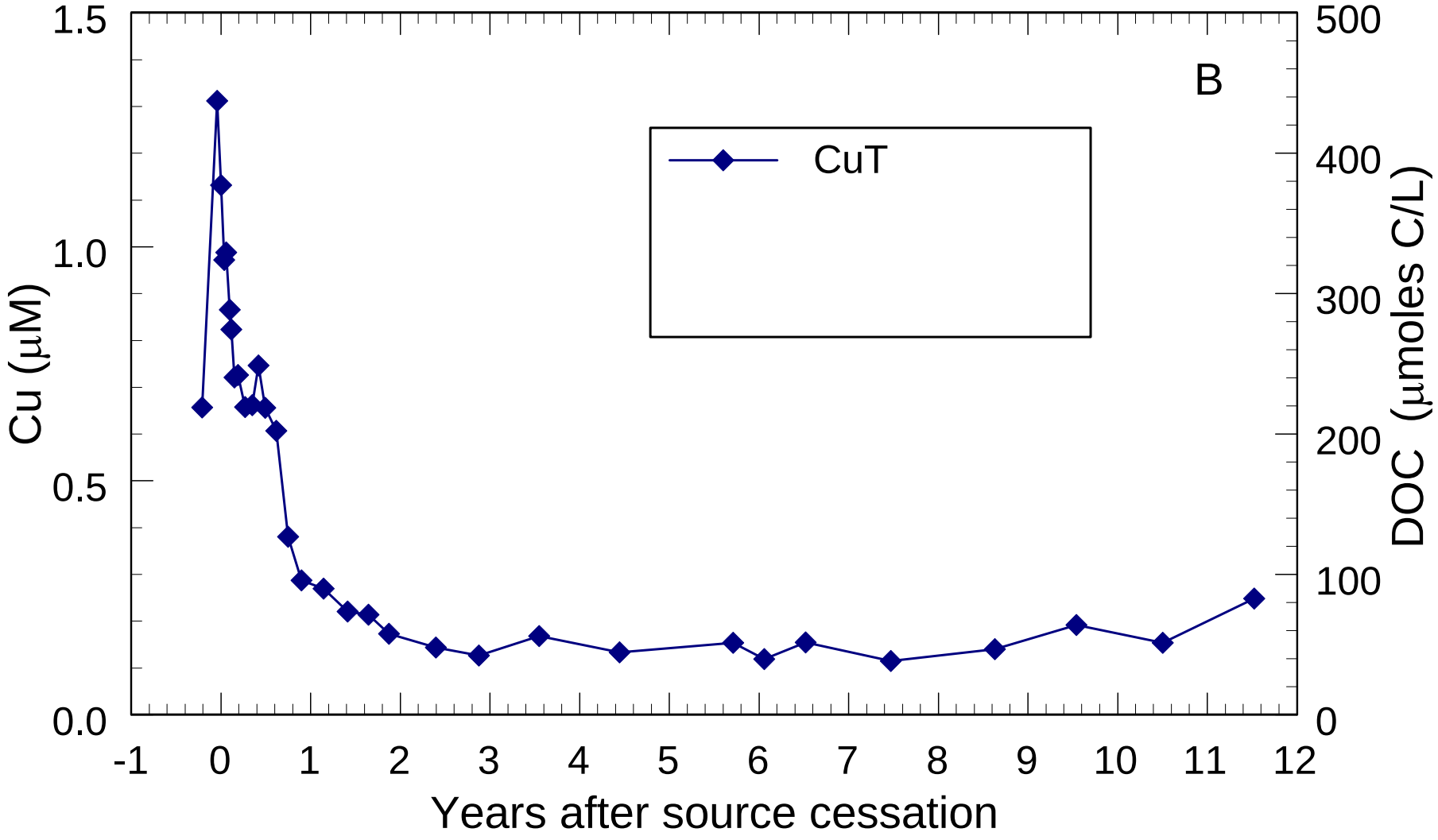
Copper and zinc prior to source cessation



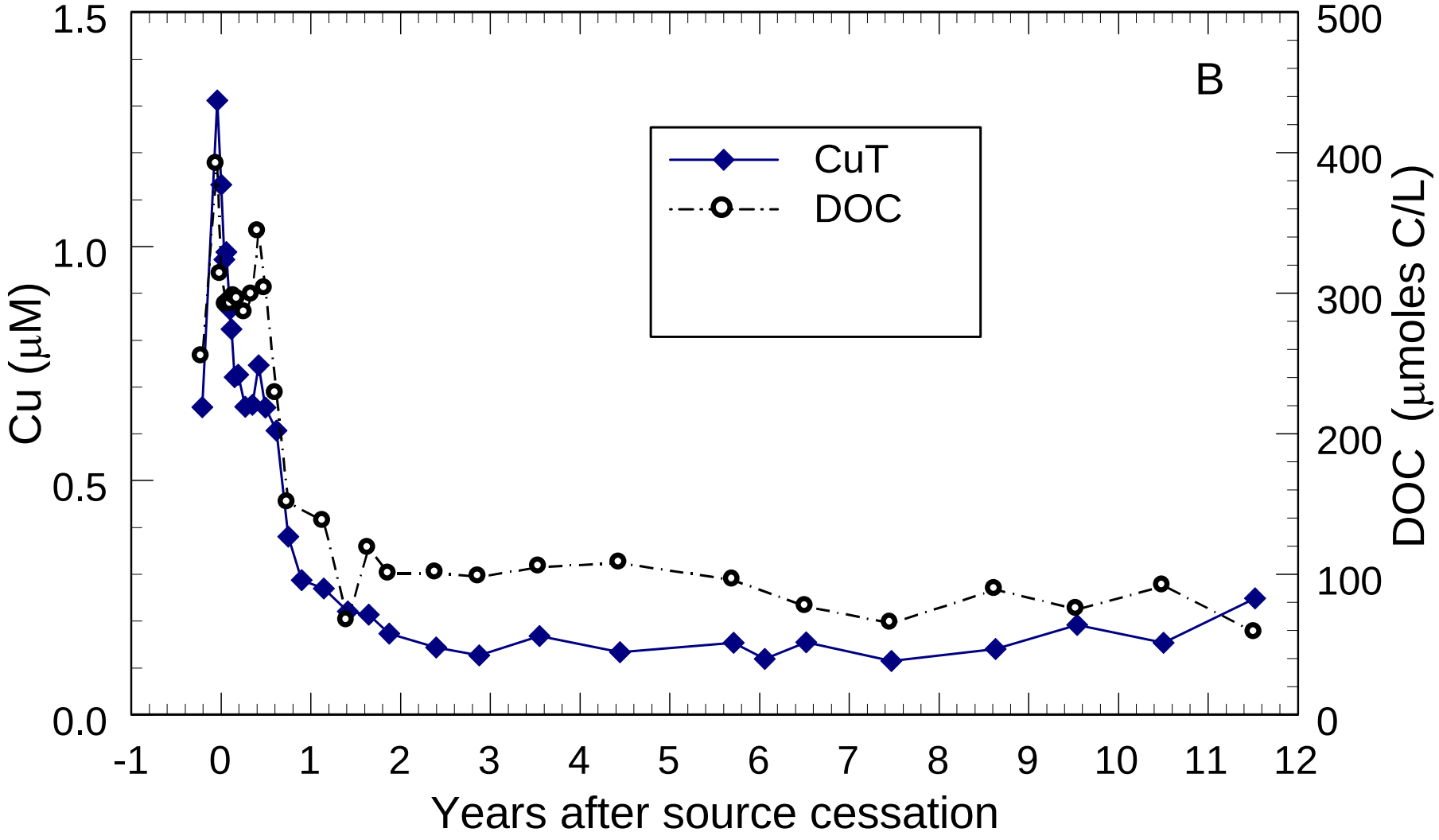
Fate of zinc post cessation



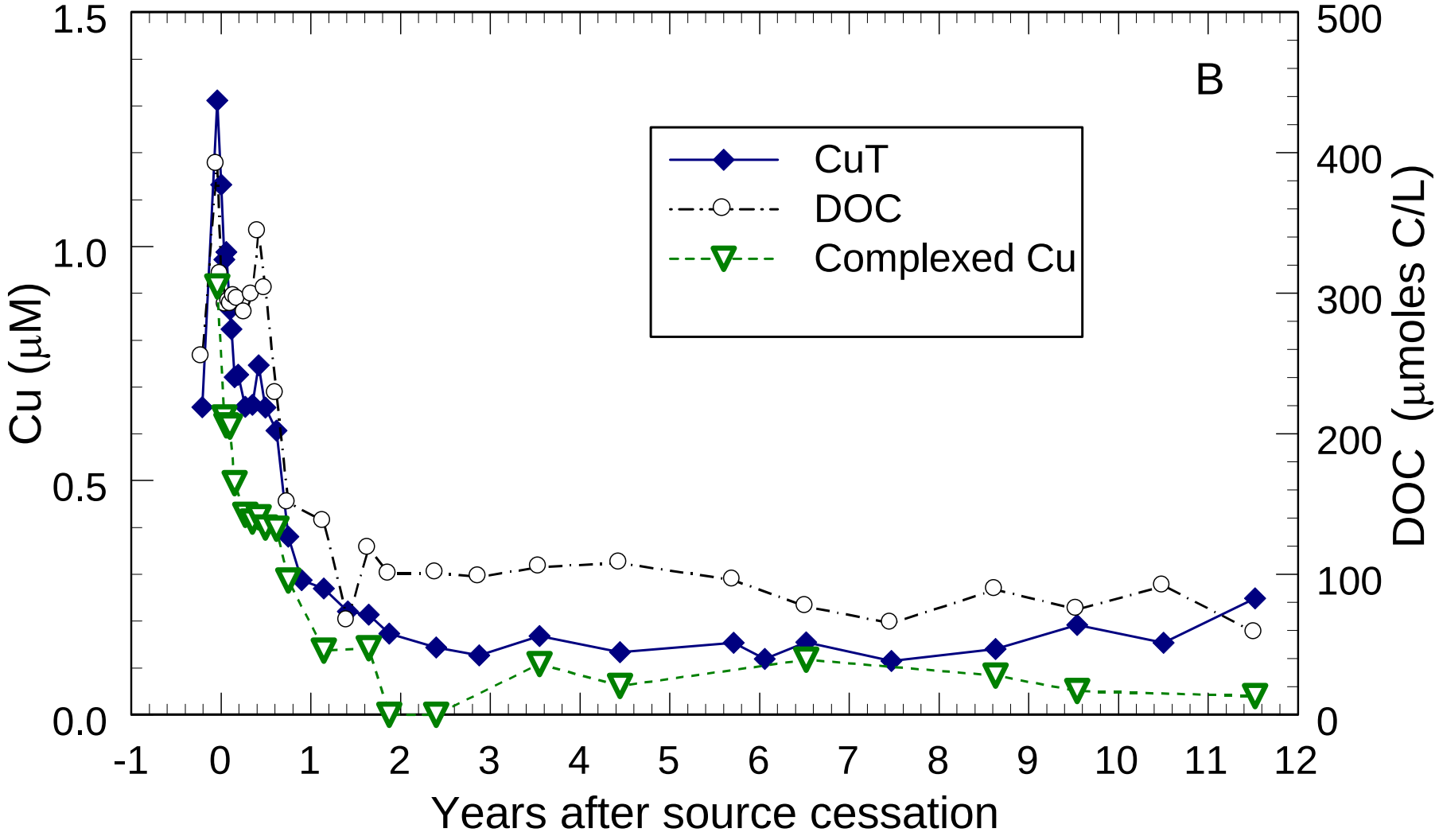
Fate of copper post cessation



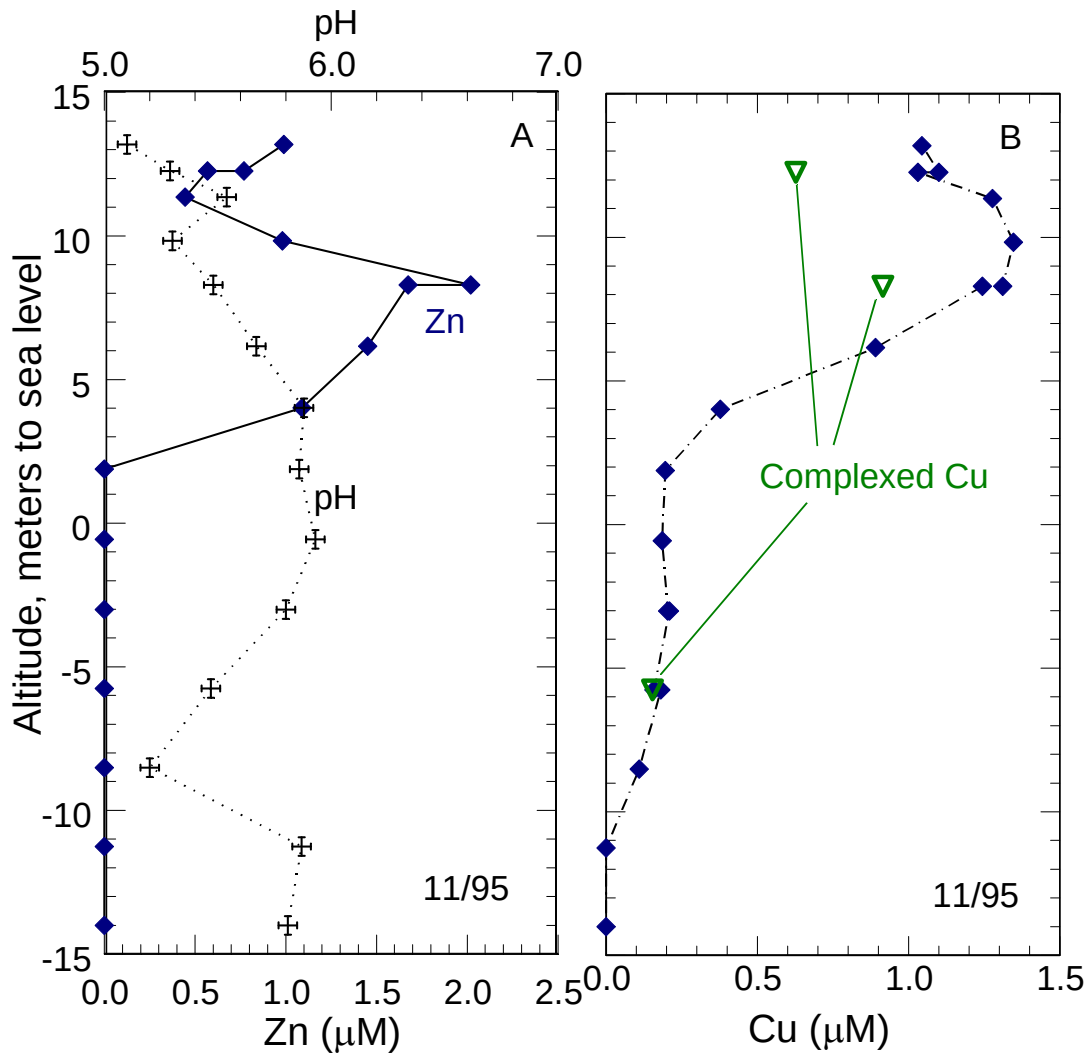
Dissolved organic carbon



Complexed copper



Copper and zinc prior to source cessation



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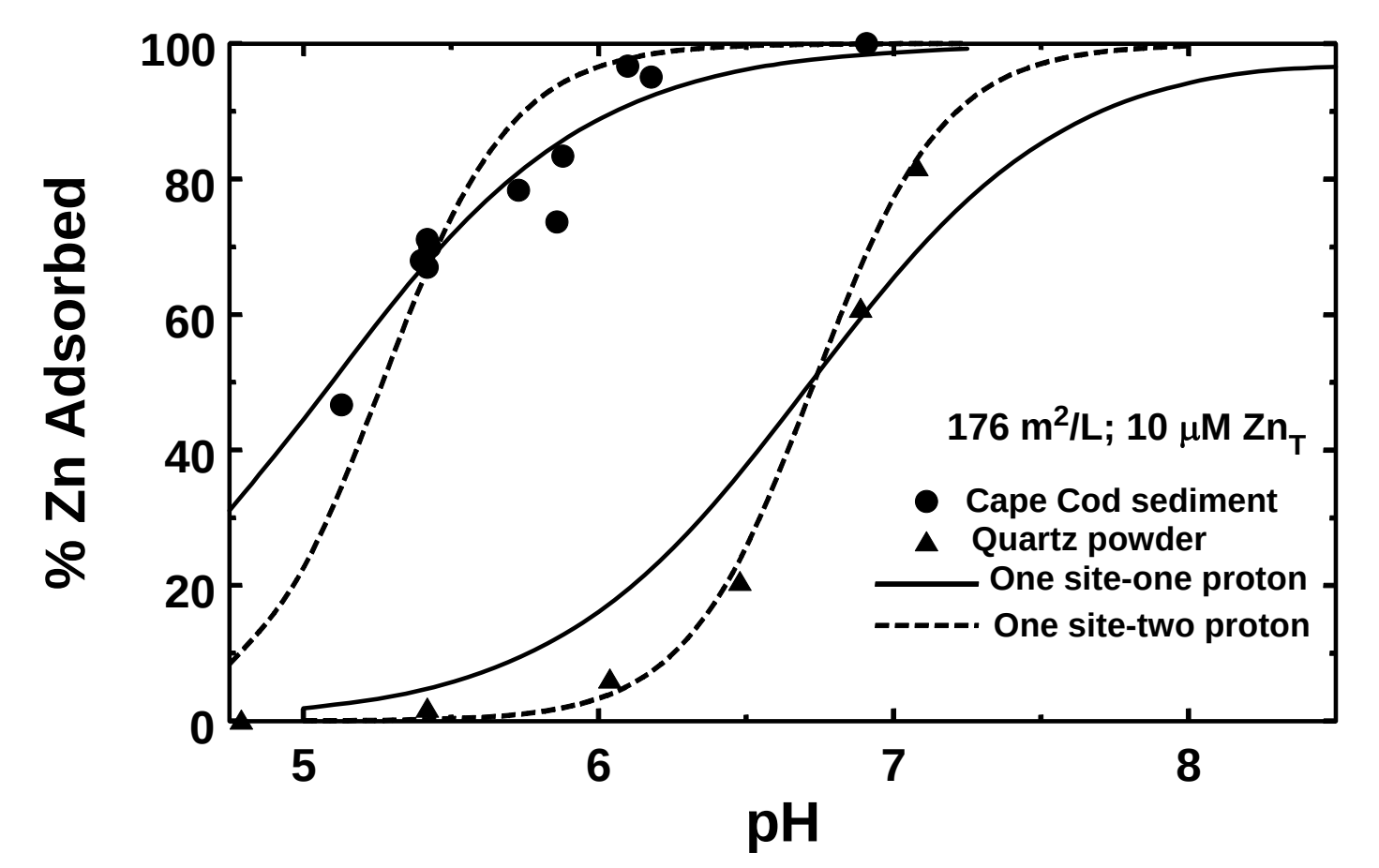
Zinc adsorption on quartz and sediments



Modeling Zn adsorption

Surface-complexation modeling approach

One-site SCM

$Zn^{2+} + >SOH = >SOZn^{+} + H^{+}$

Parameters:

>SOHT, logK

Two-site SCM

$Zn^{2+} + >S_sOH = >S_sOZn^{+} + H^{+}$

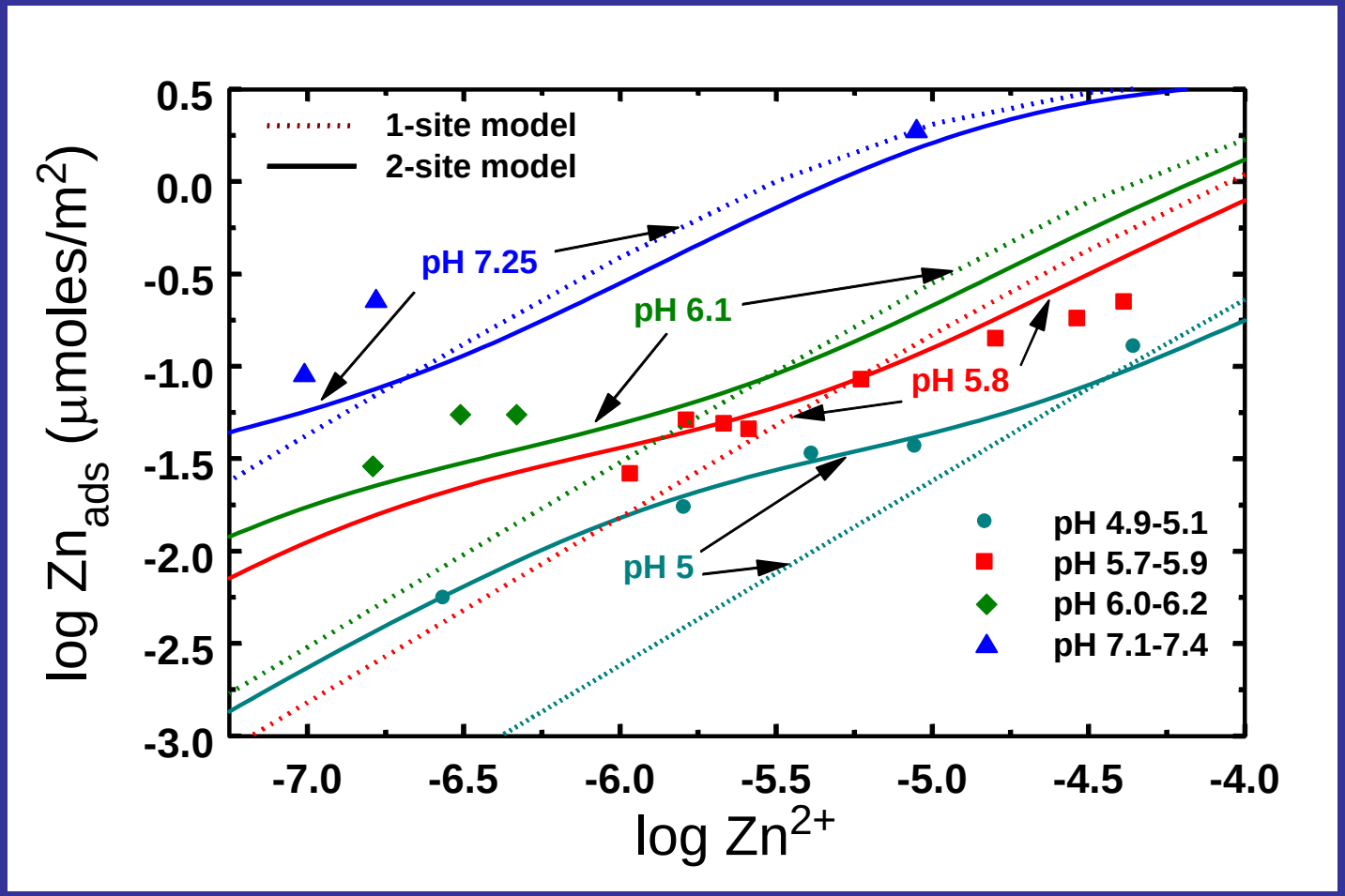
$Zn^{2+} + >S_wOH = >S_wOZn^{+} + H^{+}$

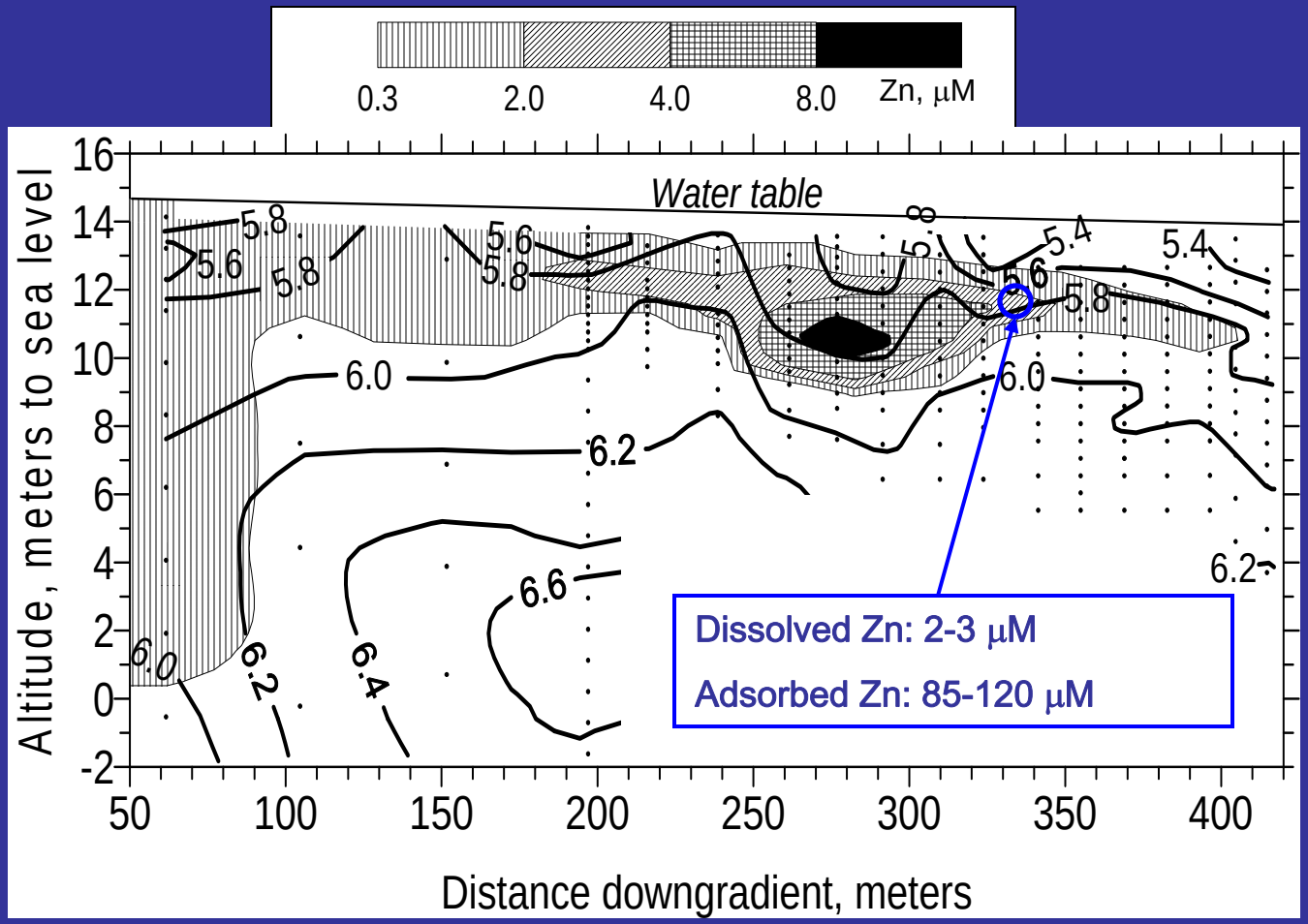
Parameters:

$>S_sOHT$, $>S_wOHT$

$logK_s$, $logK_w$

Zinc adsorption on Cape Cod sediments




0.3
2.0
4.0
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Zn, μM
Water table
Altitude, meters to sea level
Distance downgradient, meters
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5.8
5.6
5.8
5.8
5.6
5.4
5.4
5.8
6.0
6.0
6.2
6.2
6.6
6.0
6.2
6.4
Dissolved Zn: 2-3 μM
Adsorbed Zn: 85-120 μM

Tracer test design

- **Natural gradient (0.4 m/d)**
- **Inject pulse of groundwater with KBr (2 mM) and pH 4.5 (CO_2)**
- **Injected groundwater had no Zn**

Model calibration: surface ionization and major cation adsorption or ion exchange reactions

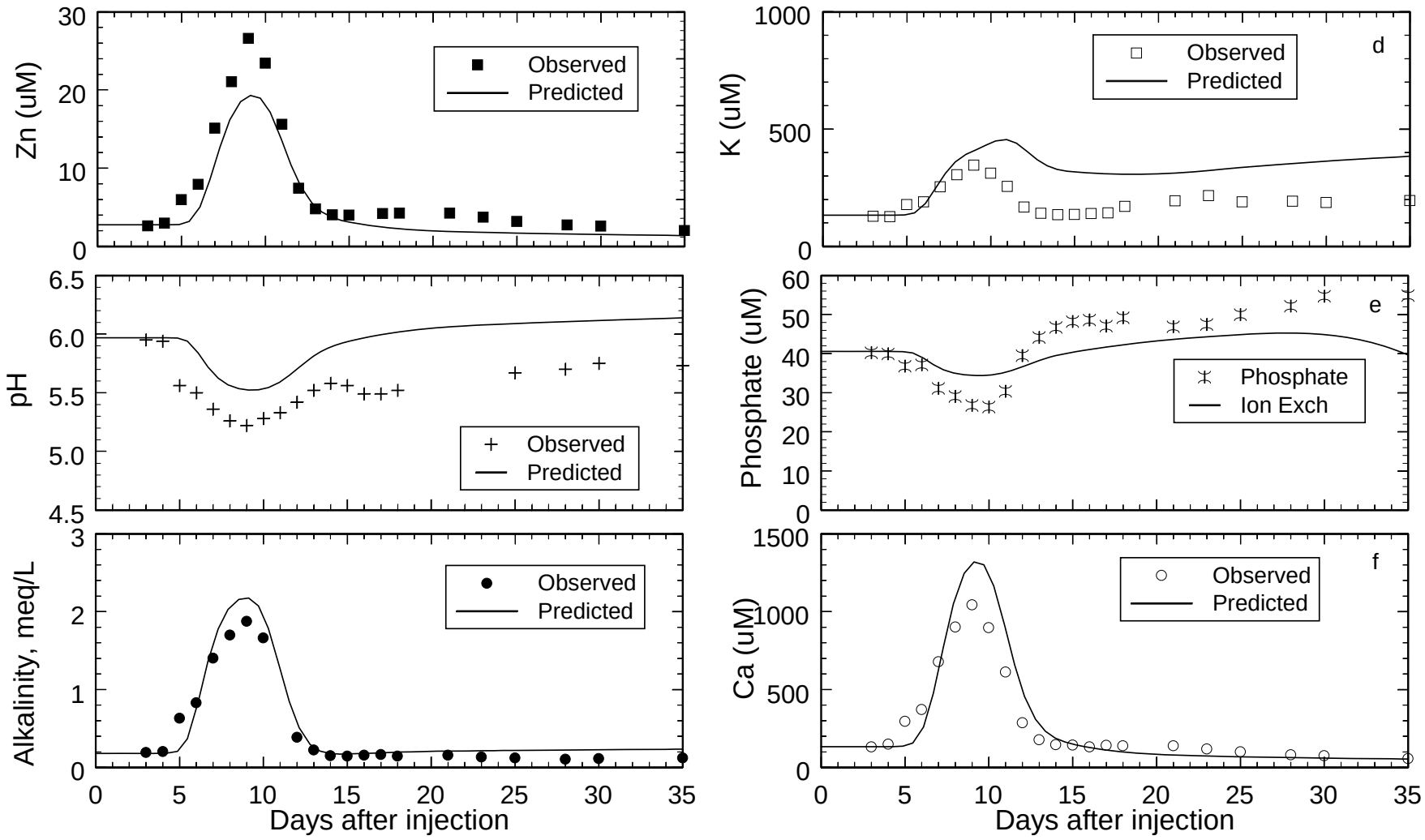
Reaction	logK
$>S_sOH + H = >S_sOH_2$	3.99
$>S_wOH + H = >S_wOH_2$	3.99
$Na + XH = H + XNa$	-4.65
$K + XH = XK + H$	-3.63
$Mg + 2XH = X_2Mg + 2H$	-6.72
$Ca + 2XH = X_2Ca + 2H$	-6.72

XHTOT = 0.5 meq/100 g → 20 meq/L

>SOHTOT = 3.84 μmoles/m² → 5 mM

Non-electrostatic model

Breakthrough 4.6 meters downgradient



Other applications

- Ligand-enhanced metal-ion mobility: **Kent et al. (2008)**
- Lead and nickel tracer tests at Cape Cod: **Gillian Fairchild's poster**
- Uranium at DOE UMTRA sites: **Curtis et al. (2006)**
- Cr(VI) reactive barrier: **(Uli) Mayer et al. (2001)**

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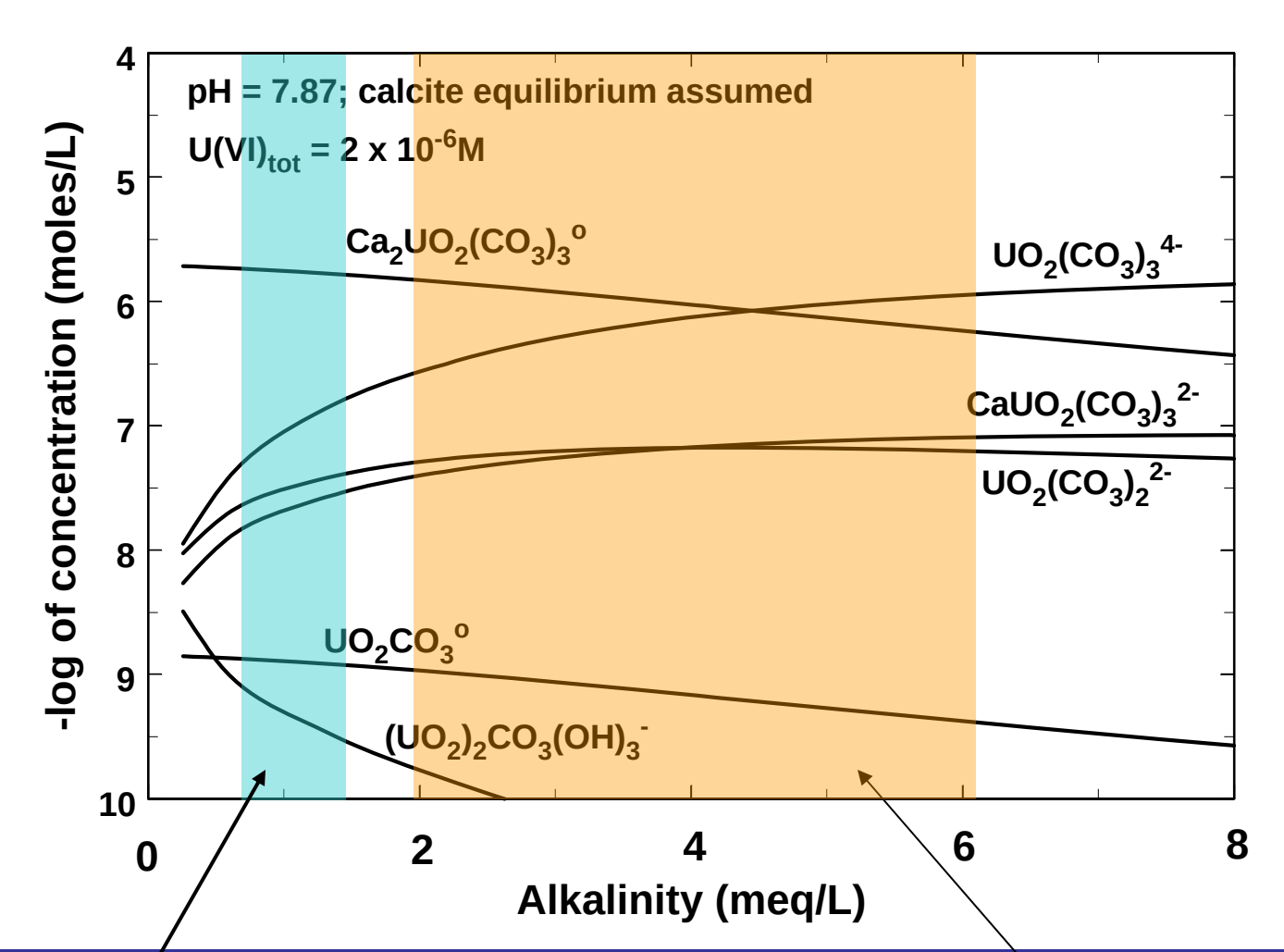
Hanford, Washington

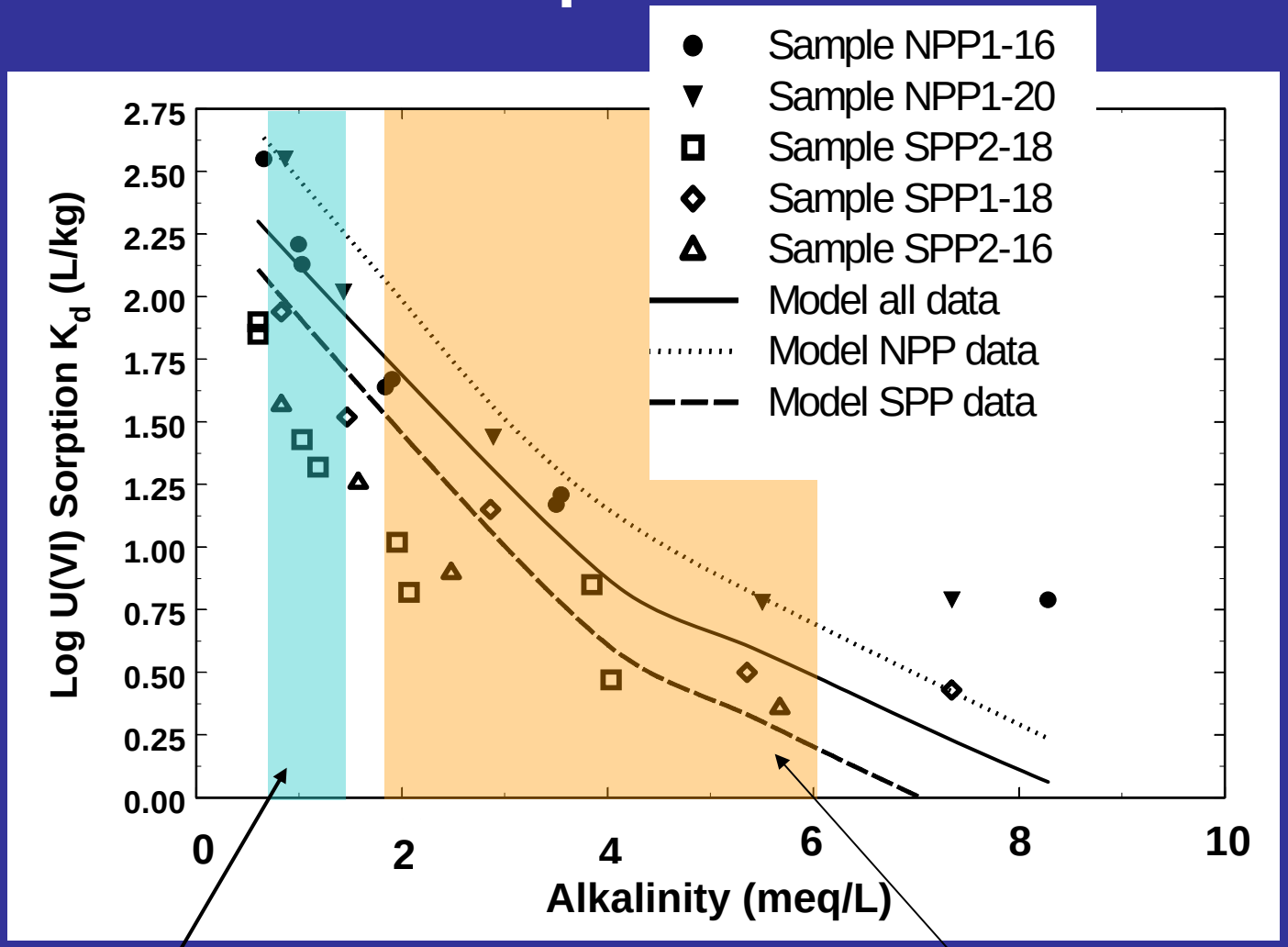
Dissolved U(VI) speciation



Columbia River

300 Area Groundwater

Surface Complexation Model



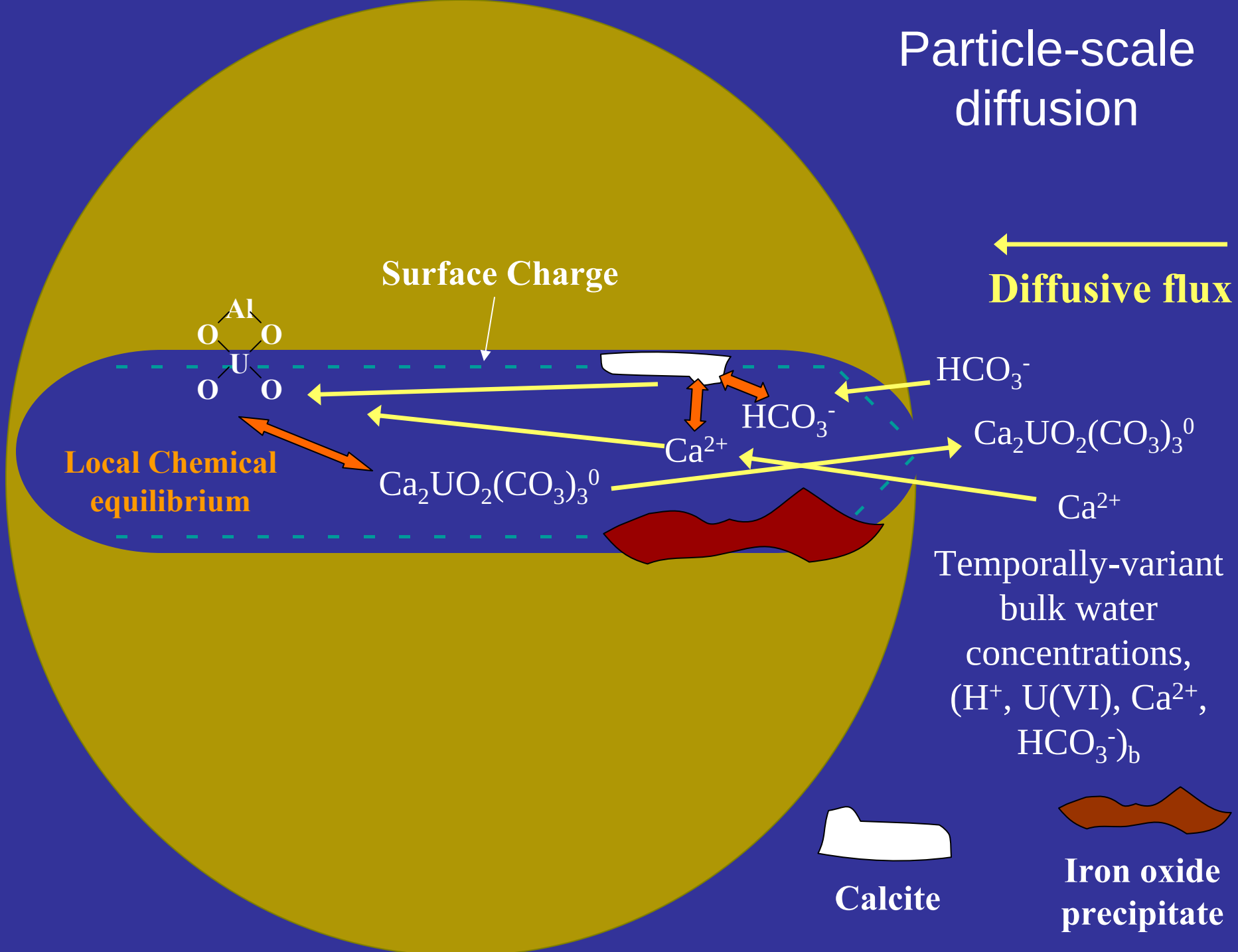
Columbia River

300 Area Groundwater

$$>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^+$$

$$>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^+$$

Particle-scale diffusion



Adsorption coupled to other reactions

- Abiotic arsenic(III) oxidation
- Microbial arsenic and iron oxidation, reduction, precipitation, dissolution: Poster by Kent and others
- Tractable approach to modeling

Further information

Curtis et al. (2006) Water Resour. Res. 42(4), art. No. W04404.

Friedly et al. (2002) Environ. Sci. Technol. 36, 355.

Bond et al. (2008) Chapt. 14 in Develop. Earth & Environ. Sci. (M. O. Barnett and D. B. Kent, eds), p. 375.

Davis and Kent (1990) Mineral. Water Interf. Geochem. (M. F. Hochella and A. F. White, eds.) Rev. Mineral. Series, p. 177.

Davis et al. (1998) Environ. Sci. Technol. 32, 2820.

Davis et al. (2000) Water Resour. Res. 36, 119.

Kent et al. (2000) Water Resour. Res. 36, 3411.

Kent et al. (2007) Water Resour. Res. 43(7) art. No. W07440.

Kent et al. (2008) J. Environ. Qual. 153, 44.

Mayer et al. (2001) Water Resour. Res 37, 3091.