Calibration of a PHREEQC Based Geochemical Model to Predict Surface Water Discharge Compositions from an Operating Uranium Mill in the Athabasca Basin

John J. Mahoney, Ph.D.

Mahoney Geochemical Consulting, LLC
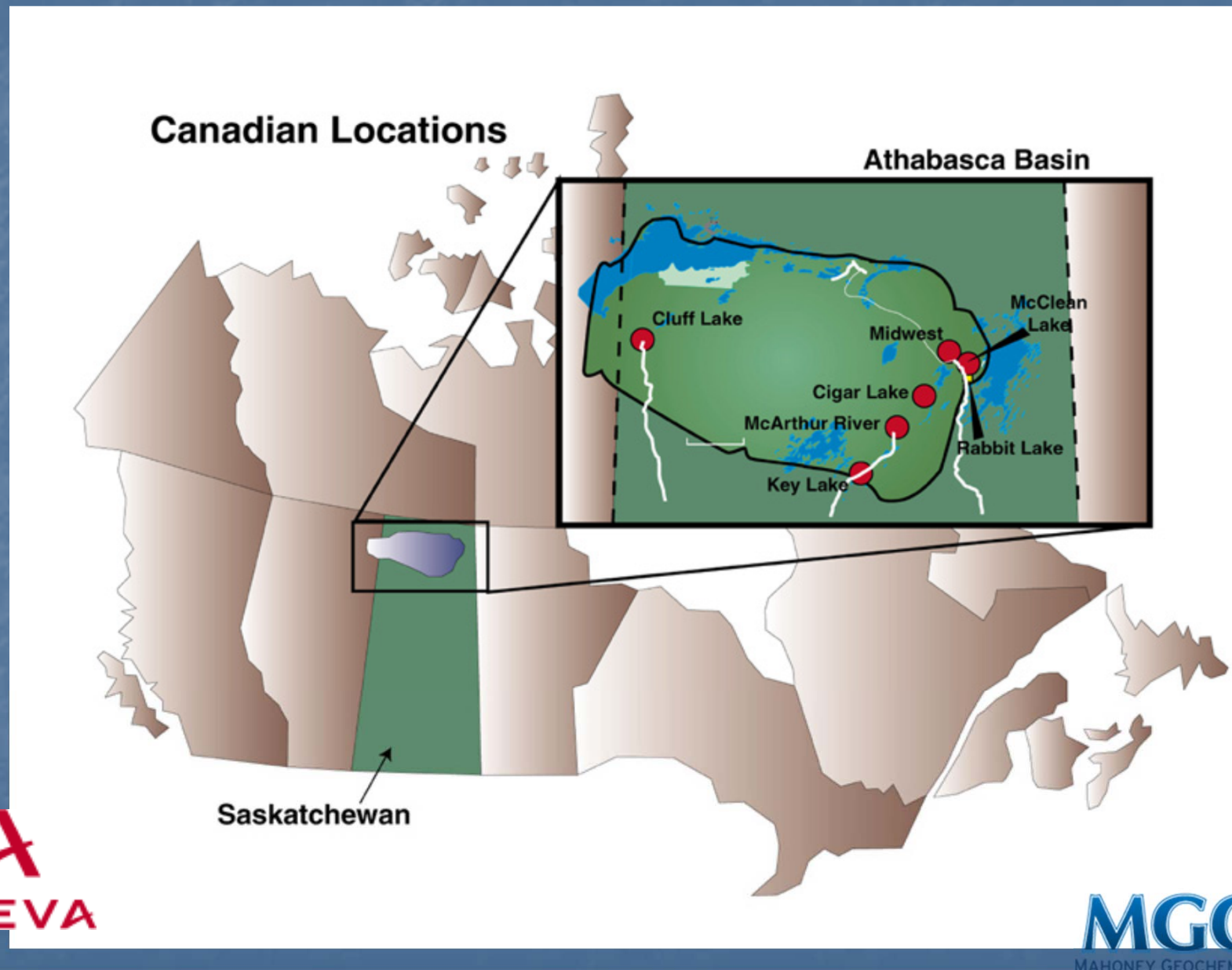
Ryan A. Frey

AREVA Resources Canada, Inc.

Objectives

- **Develop predictive model to estimate concentrations in the Sink Vulture Treated Effluent Management System (SVTEMS) for AREVA Resources Canada McClean Lake Mill**
  - **Sink Reservoir, Vulture and McClean Lakes**
  - **PHREEQC based calculations for geochemistry**
  - **Employ PHREEPLOT for data fittings**

- **Model designed to predict concentrations in response to changing conditions, including:**
  - **Different ores**
  - **Different processes**
  - **Different waters sources**
  - **Changing treatment conditions**

- **This is a batch mixing model**
  - **Think well mixed beakers**
  - **Each model represents one year**
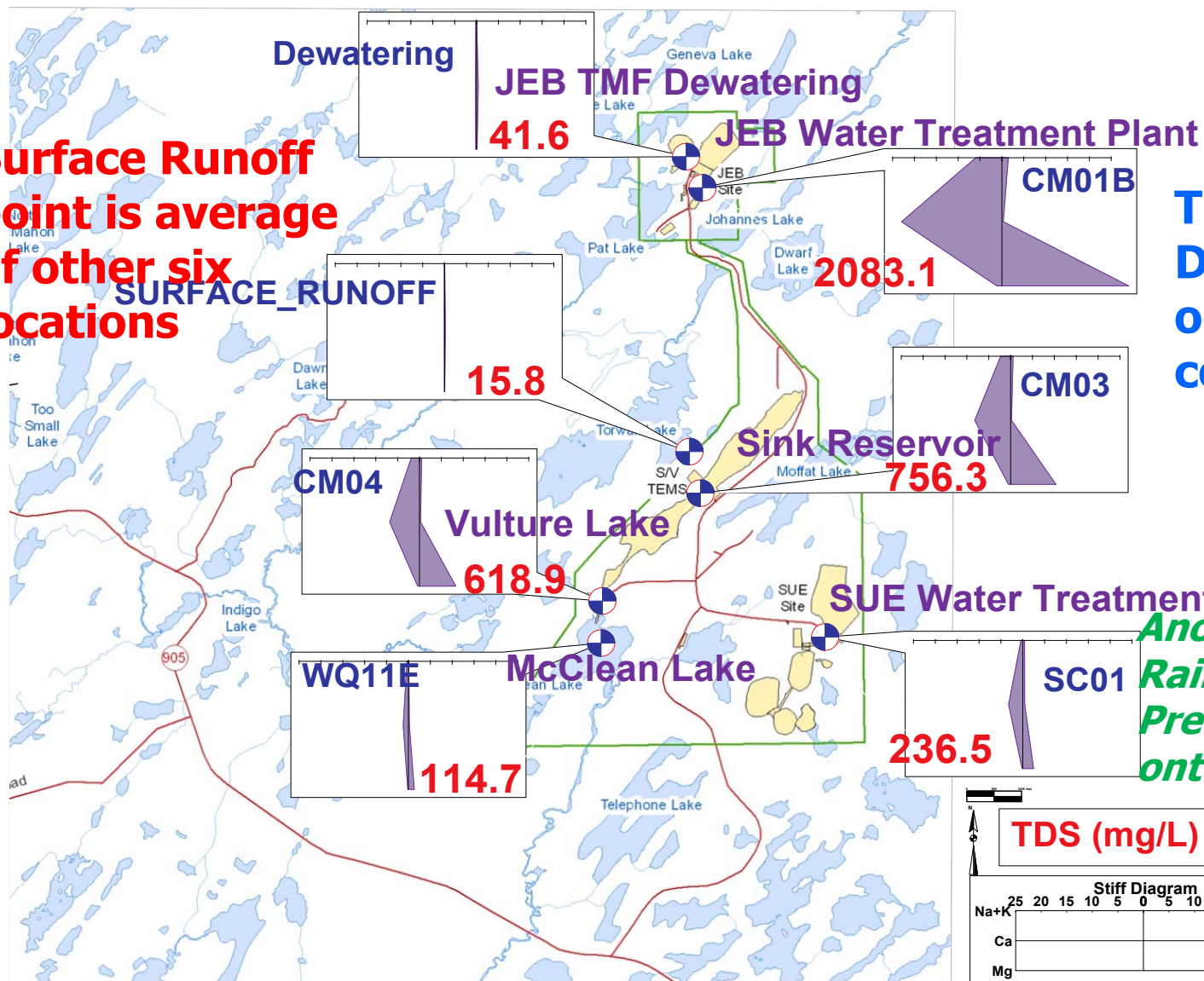 - **No year-to-year carry over in models**

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Location Map

McClean Lake Mill and JEB TMF

Dewatering
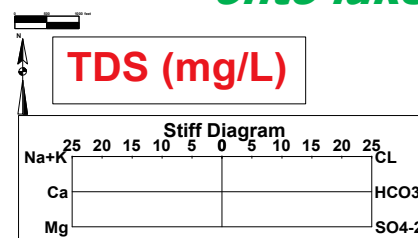
JEB TMF Dewatering

JEB Water Treatment Plant

41.6

Surface Runoff point is average of other six locations

CM01B

TDS and Stiff Diagrams based on average concentrations

2083.1

SURFACE_RUNOFF

15.8

CM03

Sink Reservoir

756.3

CM04

Vulture Lake

618.9

SUE Water Treatment

Another water source Rain or snow Precipitation directly onto lake surfaces

SC01

WQ11E

McClean Lake

114.7

236.5

TDS (mg/L)

Stiff Diagram

	25	20	15	10	5	0	5	10	15	20	25	
Na+K												CL
Ca												HCO3-
Mg												SO4-2

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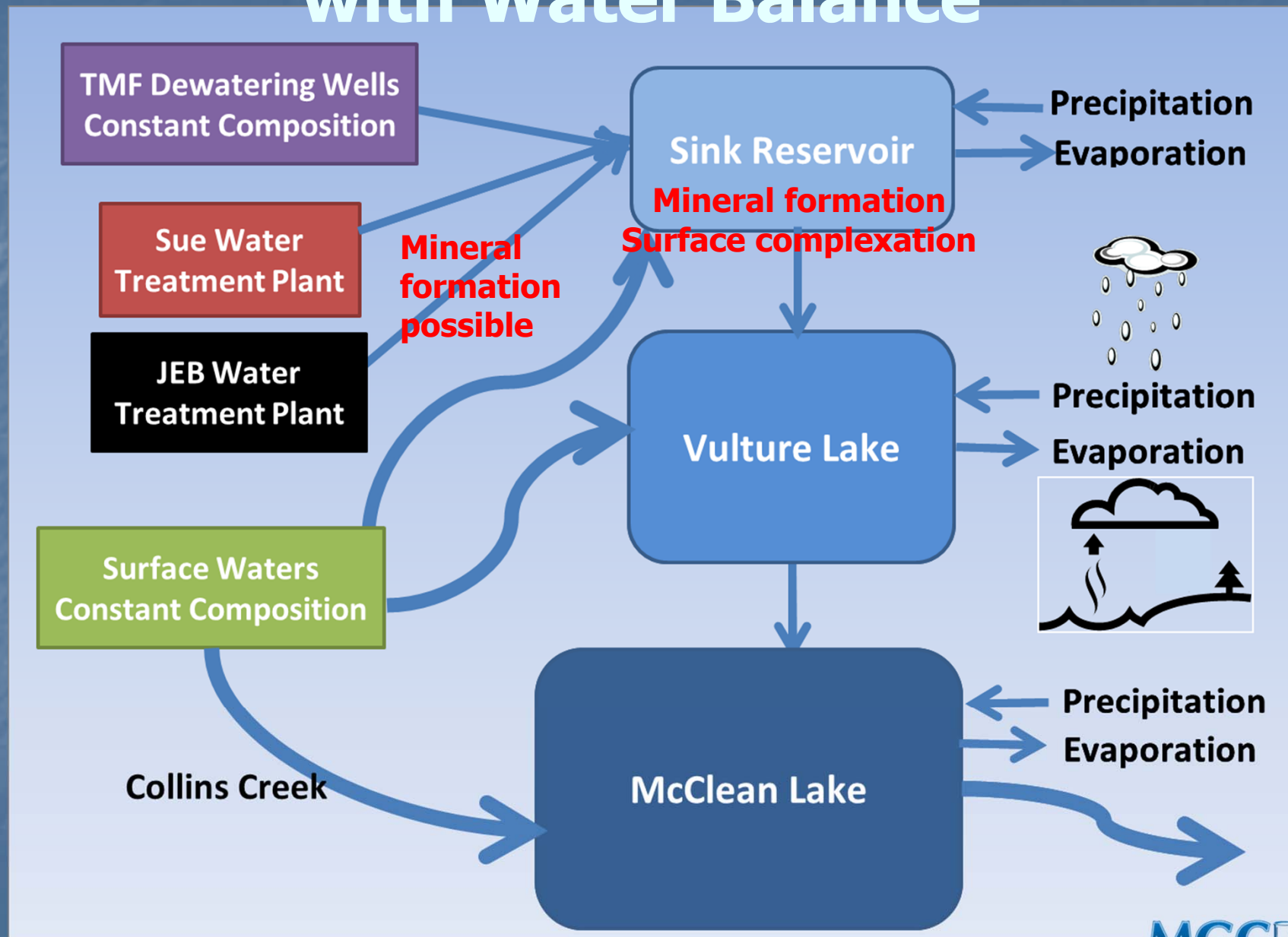
What is PHREEQC?

- **PHREEQE (1980) <u>pH</u> <u>R</u>edox <u>E</u>quilibrium <u>E</u>quations**
- **Performs aqueous geochemical modeling**
  - **Calculates activities of a component set**
  - **Calculates distribution of species in solution**
  - **Calculates mineral saturation indices**
  - **Mass transfer capabilities - mix, equilibrate, precipitate**

- **PHREEQC (1995, 1999, 2013) written in C language**
  - **Batch, Interactive and COM versions available**
  - **Public domain (USGS) ongoing support (David Parkhurst)**

- **PHREEQC Capabilities**
  - **Mixing of multiple solutions**
  - **Equilibration with gases/minerals**
  - **Surface complexation models**
  - **Ion exchange**
  - **Irreversible reactions/evaporation**
  - **Kinetics – Rate controlled processes**

≋USGS
science for a changing world

Description of Input and Examples for PHREEQC
Version 3—A Computer Program for Speciation,
Batch-Reaction, One-Dimensional Transport, and
Inverse Geochemical Calculations

Chapter 43 of
Section A, Groundwater
Book 6, Modeling Techniques

Techniques and Methods 6–A43

U.S. Department of the Interior
U.S. Geological Survey

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Conceptual Hydrogeochemical Model with Water Balance

Updated Thermo Database

- **WATEQ4F.DAT PHREEQC Version 2.0 HEAVILY REVISED**
- **Uranium**
  - OECD NEA (Guillaumont 2003) for uranyl complexes
  - Diffuse layer parameters for HFO uranyl surface complexation (Mahoney et al. 2009) for NEA database replaced Dzombak and Morel (D&M) values
  - Dong and Brooks (2006) - divalent uranyl carbonates
  - Removed $UO_2(HPO_4)_2^{-2}$ and $UO_2(H_2PO_4)_3^{-}$ per Grenthe et al. 1992

- **Arsenic**
  - Langmuir, Mahoney & Rowson (2006) for metal As complexes, and Scorodite
  - Marini and Accornero (2007) more metal As complexes, with 2010 corrections
  - Diffuse layer surface complexation constants from Gustafsson and Bhattacharya (2007) replaced D&M values

- **Molybdenum**
  - Surface reactions/values by Gustafsson (2003) replaced D&M values
  - NiMoO4 solid by Morishita and Navrotsky (2003)

- **Gibbsite Surface Complexes – Karamalidis and Dzombak (2010)**

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Overview

- **Use Water Balance from 2000 to 2011 to estimate proportions of different waters**
- **Water compositions from monitoring points**
- **Originally used EXCEL to:**
  - **Calculate mixing proportions for PHREEQC input**
  - **Calculate evaporation losses**
  - **Write majority of input file**
  - **Block and copy into PHREEQC**

Water Balance Calculations (m^3/year)												
	Direct Sources			Precipitation Rain/Snow			Calc groundwater, streams & runoff			Evaporation		
Year	Dewatering Wells	CM01B	SC01	Sink	Vulture	McClean	Sink	Vulture	McClean	Sink	Vulture	McClean
2000	2110337	1548498	1075486	89842	269525	822875	0	1773184	42029593	85750	257250	785400
2001	2328796	1476709	1303234	108731	326193	995887	0	1987207	40740609	85750	257250	785400
2002	1314516	1300817	263083	163146	489437	1494280	0	900954	64639280	85750	257250	785400
2003	1590610	1561785	59386	164959	494876	1510885	0	1300923	82451780	85750	257250	785400
2004	1619357	1559263	979574	84795	254384	776648	0	1541937	34705257	85750	257250	785400
2005	1460828	1635128	2537086	187499	562496	1717333	0	1823447	66190958	85750	257250	785400

Water Balance Converted to Mixing Proportions

units m³/year		Year	Solution #	2000	2001	2002
SINK INPUTS		D-Wells to Sink	200	2,110,337	2,328,796	1,314,516
	001	CM01B	102000001	1,548,498	1,476,709	1,300,817
		PRECIPITATION	100	89,842	108,731	163,146
	002	SC01	2000002	1,075,486	1,303,234	263,083
		Calc groundwater, streams & runoff	300	0	0	0
		EXTRA SOURCE NOT INCLUDED	400	0	0	0
	003	WATER IN SINK AT START OF YEAR	2000003	395000	395000	395000
VOLUME Sum use for mixing proportions				5,219,163	5,612,470	3,436,562
Calc input to Sink FROM WATER BALANCE				4,738,413	5,131,720	2,955,812
Evaporation LOSS			Sink	85,750	85,750	85,750
		CHECK CALCULATION		5,133,413	5,526,720	3,350,812
MIXING CALCULATION		D-Wells to Sink		0.404	0.415	0.383
		CM01B		0.297	0.263	
		PRECIPITATION		0.017	0.019	
		SC01		0.206	0.232	
		Calc groundwater, streams & runoff	300	0.000	0.000	
		EXTRA SOURCE NOT INCLUDED		0.000	0.000	
		SINK WATER PREVIOUS YEAR		0.076	0.070	
		SUM		1.000	1.000	
EVAPORATION CALCULATION		FRACTION EVAP LOSS		0.0164	0.0153	0.0250
		Reactant Amount for evaporation		-0.913	-0.849	-1.386
		MIXING PROPORTION FOR volume correction		1.016	1.015	1.025

Can easily expand and add additional years
Extra water (blank at this time) available to modify model

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Preparation of PHREEQC Model

- **We are writing a program using the PHREEQC syntax**
  - **SOLUTION_SPREAD**
  - **PRINT**
  - **SELECTED_OUTPUT**
  - **USER_PUNCH**
- **Followed by mixing and reaction sections for each year**
  - **Each year is about 200 lines**
  - **Total File ~2800 lines**
- **Color coded section in EXCEL to simplify revisions**
- **Now using IPHREEQC.COM**

PHREEQC INPUT FILE FOLLOWS

Fix JWTP Waters Equilibrate holding ponds settling mineral ppt and surface complexation

		# GREEN	# GREEN	# GREEN
# YEAR		2000	2001	2002
USE SOLUTION		2000001	2001001	2002001
REACTION		#	#	#
END		#	#	#
USE SOLUTION		2000001	2001001	2002001
EQUILIBRIUM_PHASES		2000001	2001001	2002001
CO2(g)		-3.1562 10	-2.8016 10	-2.9798 10
O2(g) -0.7 10		#	#	#
#Gibbsite 0 0		# JWTP EQ_PHA	# JWTP EQ_P	# JWTP EQ_PI
Gypsum 0 0				#
Barite 0 0				#
CaMoO4				0.3 0
CuMoO4				#
FeMoO4				#
#Ferrihydrite				#
#PbMoO4				#
# Boehmite				#
Carnotite 0 0				#
SURFACE				2002001
Hfo_wOH 1e-				#
# Hfo_sOH Fe				#
# above lines				10102002
SAVE SOLUTION				#
END				10102002
USE SOLUTION				#
REACTION				#
END				#
				1002002
MIX				0.38251
				10102002 0.3
				0.04747
				2002002 0.07
				0
				0
				2002003 0.11
SAVE SOLUTION				1002002
END		#	#	#
USE SOLUTION		1002000	1002001	1002002
REACTION 1 Evaporation of water		#	#	#
H2O 1		#	#	#
		-0.91277	-0.8488	-1.38624
		#		#
SAVE SOLUTION		1012000	1012001	1012002
END		#	#	#

```
Microsoft Visual Basic for Applications - runphreeqc refit site densities to As forward model.xlsm - [Modul

File  Edit  View  Insert  Format  Debug  Run  Tools  Add-Ins  Window  Help

Ln 10, Col 32

(General)                              RunPhreeqc

Sub RunPhreeqc()
    On Error GoTo ErrHandler:
    ChDir ActiveWorkbook.Path
    Set Phreeqc = CreateObject("IPhreeqcCOM.Object")
    Db = "phreeqcmaster2014.dat"
    Phreeqc.LoadDatabase (Db)

    'Format input from sheet1
    Dim Istring As String
    Worksheets("Sheet1").Activate
    FirstRow = ActiveSheet.UsedRange.Row
    FirstColumn = ActiveSheet.UsedRange.Column
    For r = FirstRow To (FirstRow + ActiveSheet.UsedRange.Rows.Count)
        For c = FirstColumn To (FirstColumn + ActiveSheet.UsedRange.Columns.Count)
            Istring = Istring & CStr(Cells(r, c)) & vbTab
        Next c
        Istring = Istring & vbNewLine
    Next r

    'Run and save selected output to sheet2
    Phreeqc.RunString (Istring)
    arr = Phreeqc.GetSelectedOutputArray()
    Worksheets("OUTPUT").Activate
    Range(Cells(1, 1), Cells(Phreeqc.RowCount, Phreeqc.ColumnCount)) = arr
    MsgBox "Phreeqc ran successfully."
    Exit Sub

ErrHandler:
    MsgBox "Phreeqc errors: " & Phreeqc.GetErrorString()
End Sub
```

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Ockham's

Shaving away unnecessary assumptions
Since 1285

- "*Pluralitas non est ponenda sine neccesitate*"
    - **Pluralities should not be posited without necessity**
    - **One should not increase, beyond what is necessary, the number of entities required to explain anything**

- **Using generally accepted geochemical principles with only slight adjustments**
    - **Dominantly mixing processes**
    - **Equilibration with atmospheric gases and simple minerals**
    - **Adjusted one solubility product constant (Powellite)**
    - **Lower surface site density values - about 1/2**

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Conservative Species

- **Na, K, Mg, Cl - Most conserved**
  - Good matches between observed and modeled values
  - Mixing based upon water balance – only process

- **Minimal attenuation - Sulfate, Ca**
  - Gypsum ($CaSO_4:2H_2O$) precipitation if oversaturated
  - Only three samples from JWTP oversaturated

- **Aluminum appears to be conserved**
  - Most samples
  - Early models looked at gibbsite [$Al(OH)_3$] or boehmite (AlOOH) precipitation
  - Produced poorer fits downstream
  - Maybe sulfate inhibits Al precipitation?

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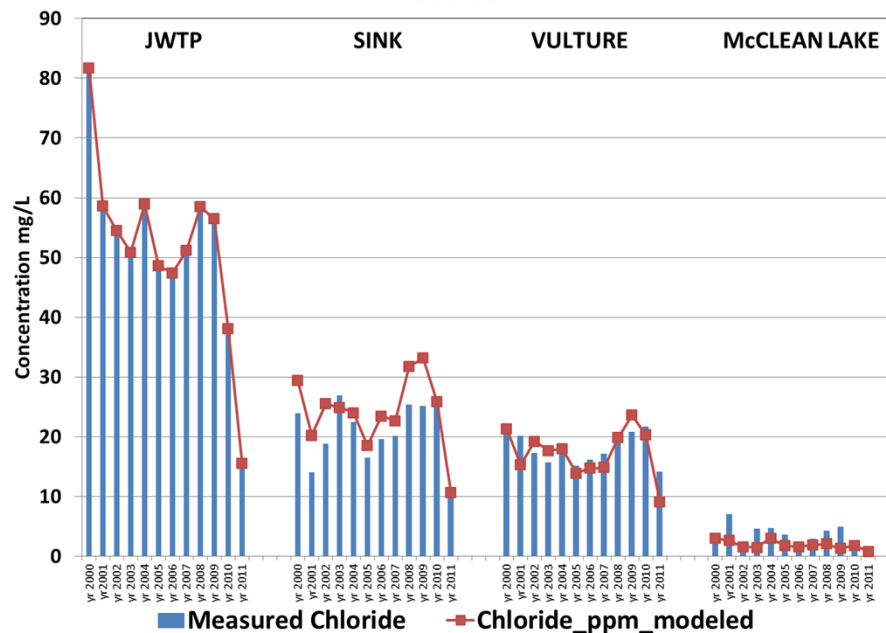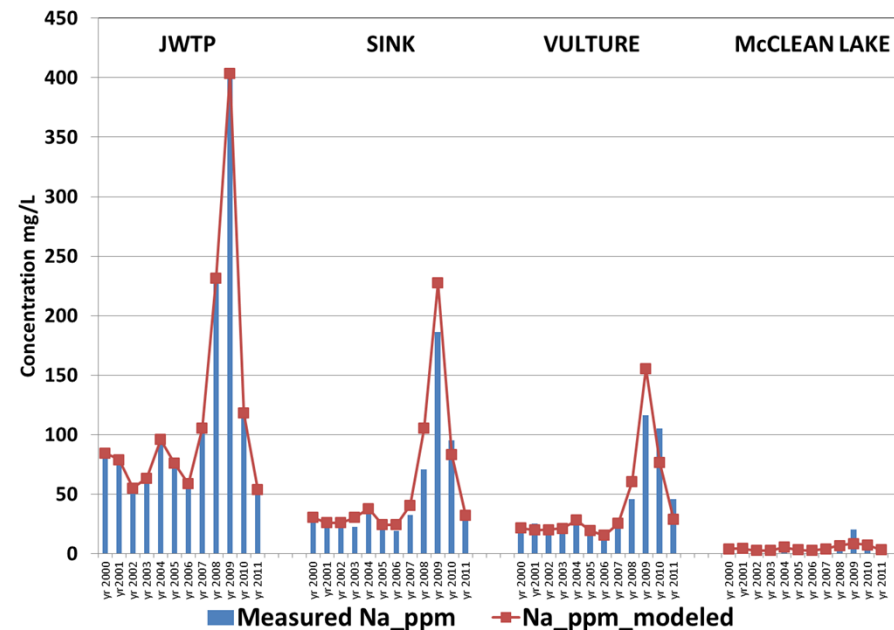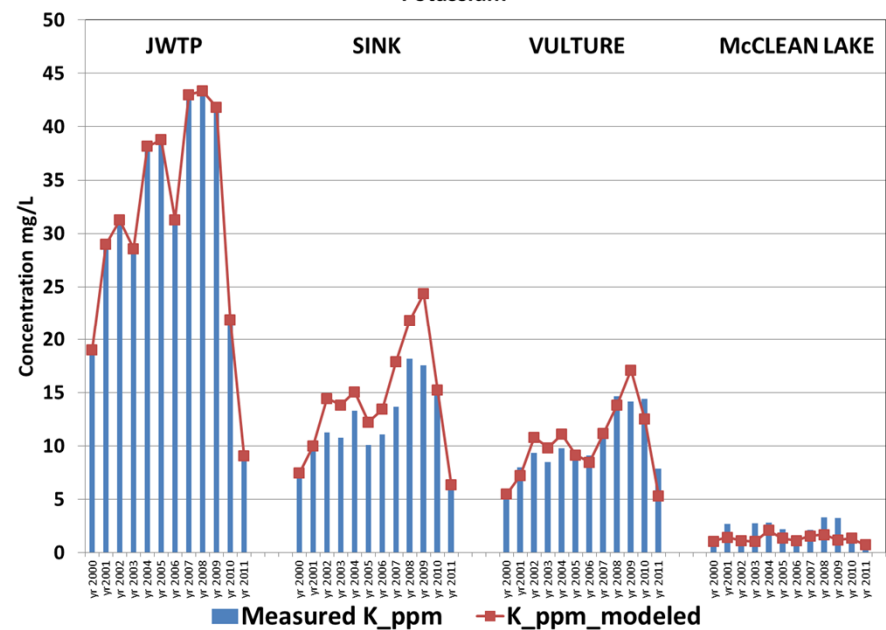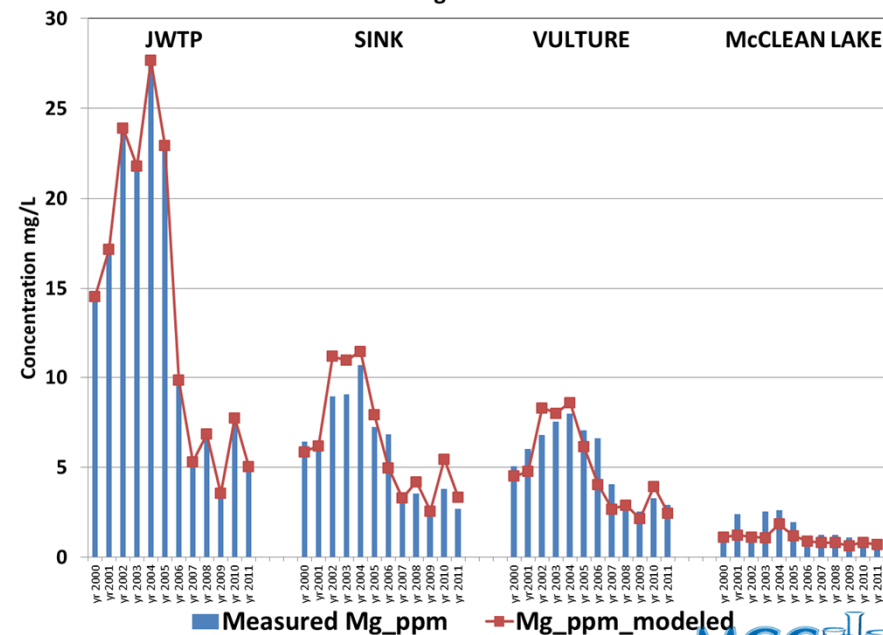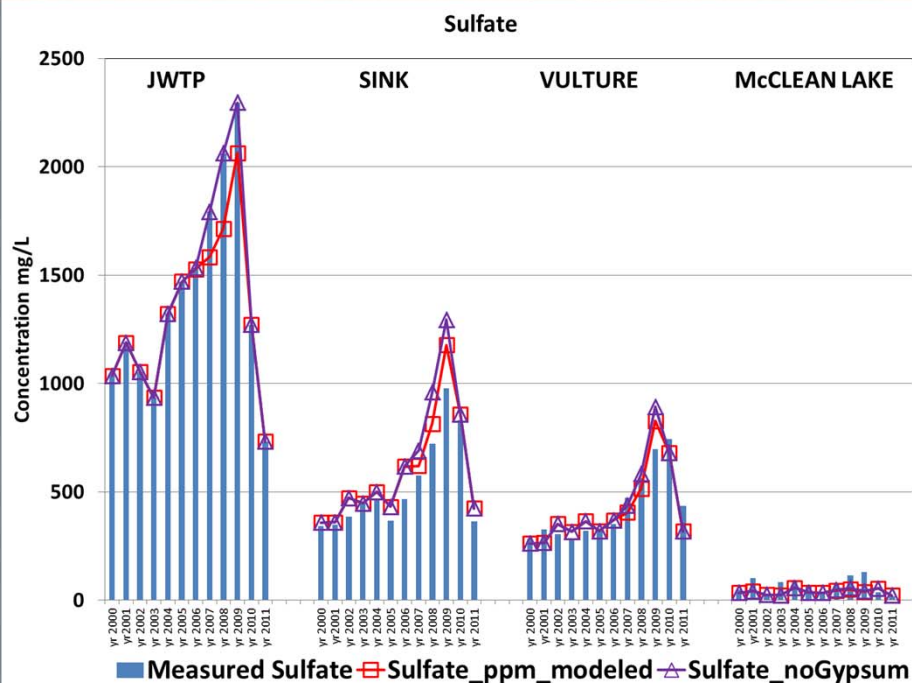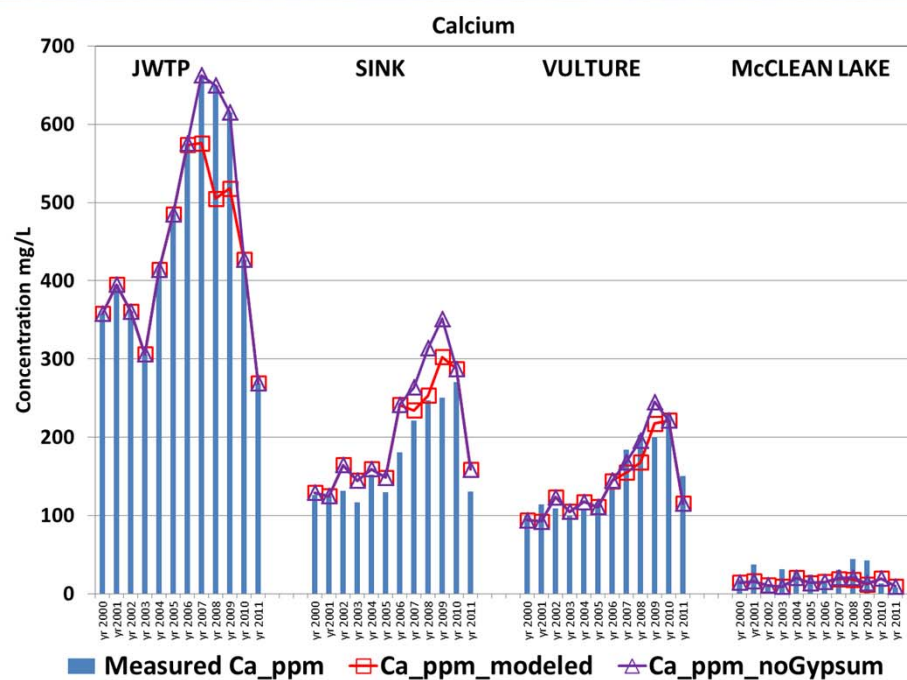
Calcium and Sulfate

Gypsum Precipitation in Three Waters

Aluminum
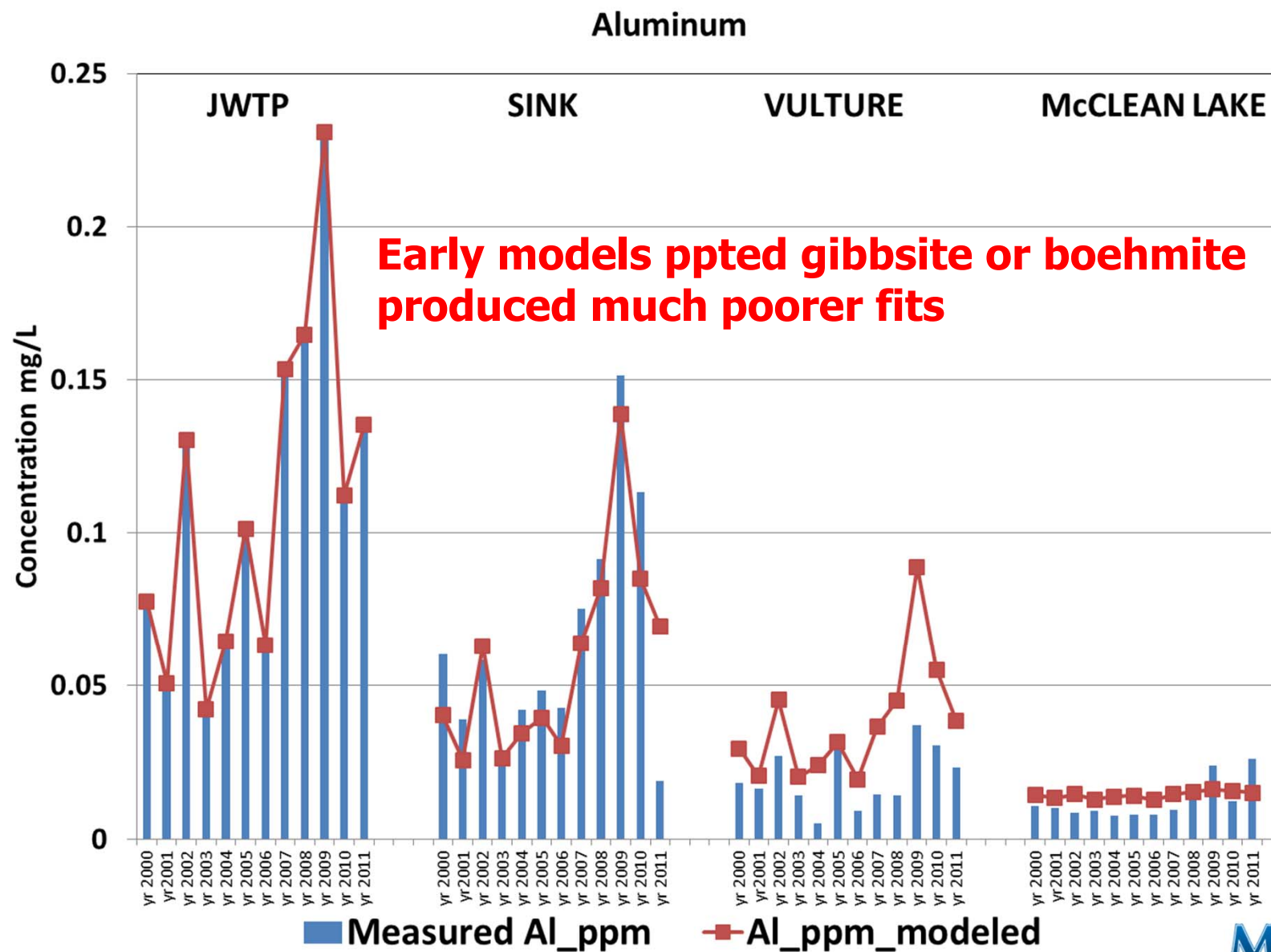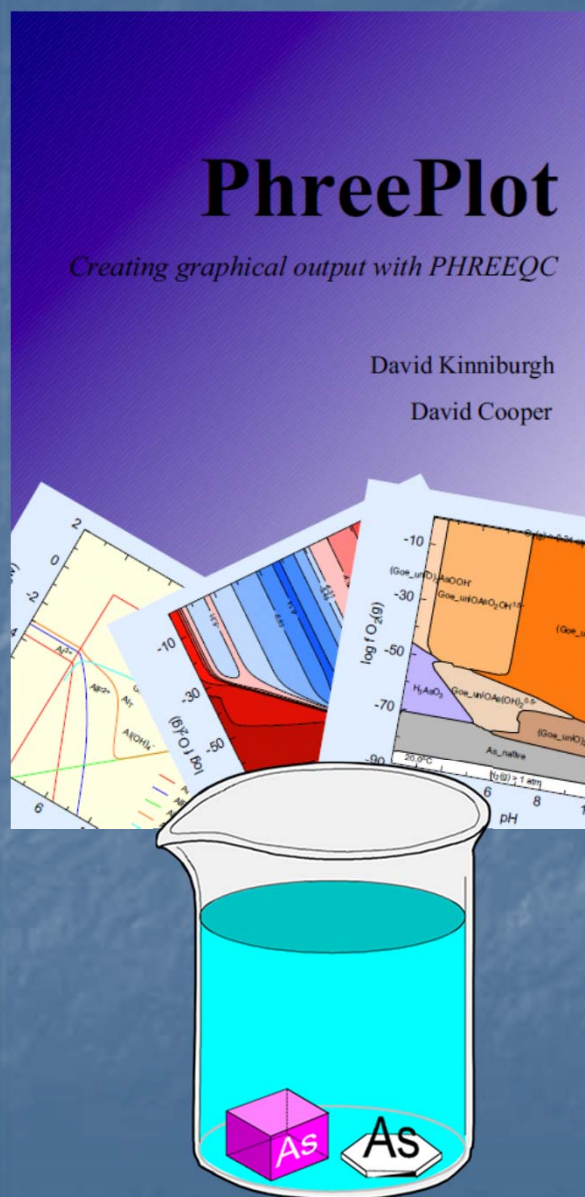
Reliability of Water Balance and Analyses

- **Agreement between modeled and observed concentrations for conserved species demonstrate that the conceptual model, water balance, analyses and the calculations using PHREEQC are correct**

- **Allows insights into reactive trace metals and other species such as ammonia**

Optimization with PhreePlot

- **PHREEQC with data fitting functions**
    - Iterative process between observations and modeled concentrations
    - Calculates Weighted Residual Sum of Squares
    - Minimizes (W)RSS
    - Rigorously fitted parameters

- **Used to model As and U surface complexation on Ferrihydrite (HFO)**
    - Sorption onto a surface
    - Hydrous Ferric Oxide (HFO)
    - HFO comes from dissolved iron in discharges

- **Originally adjusted HFO concentrations – JWTP, then Sink Reservoir**
    - Applied to estimate HFO sites_per_mole value based upon HFO precipitation

- **Fit molybdenum solubility product**

Surface Complexation Reactions

Provides alternative method to remove compounds from solution

Often occurs at concentrations less than the solubility limit

Anions decrease sorption on HFO with increasing pH

(from Stumm, 1992), See also Langmuir, 1997)

(from Stumm, 1992)
See also Langmuir, 1997
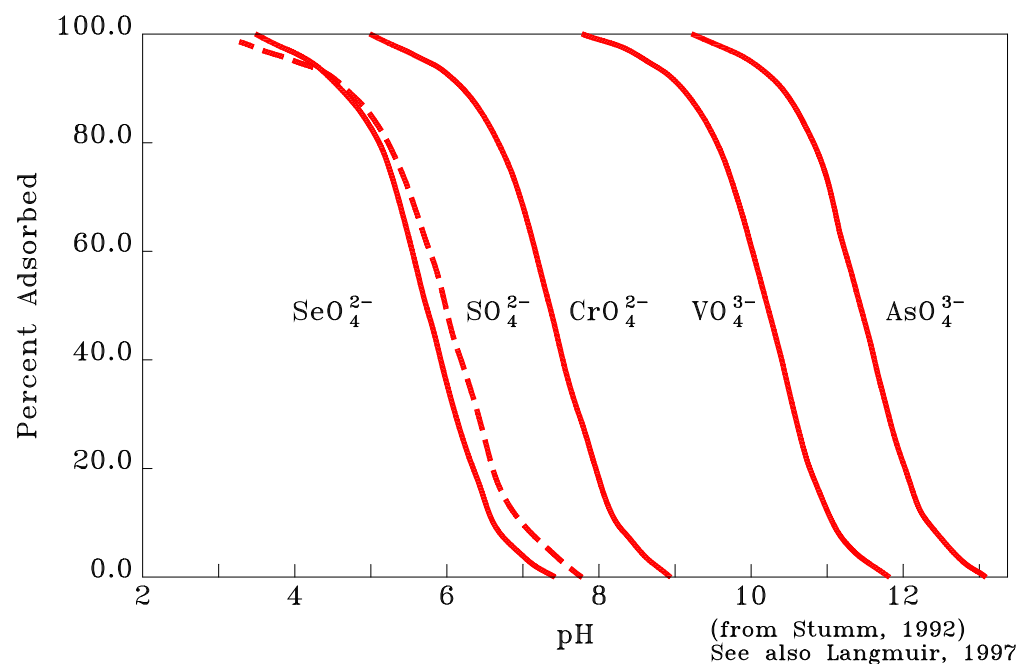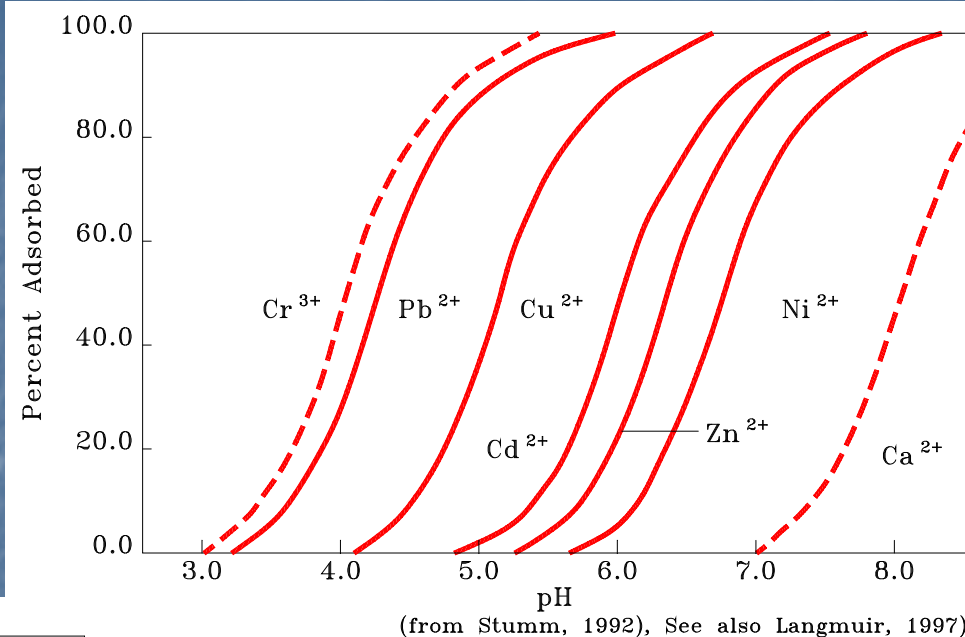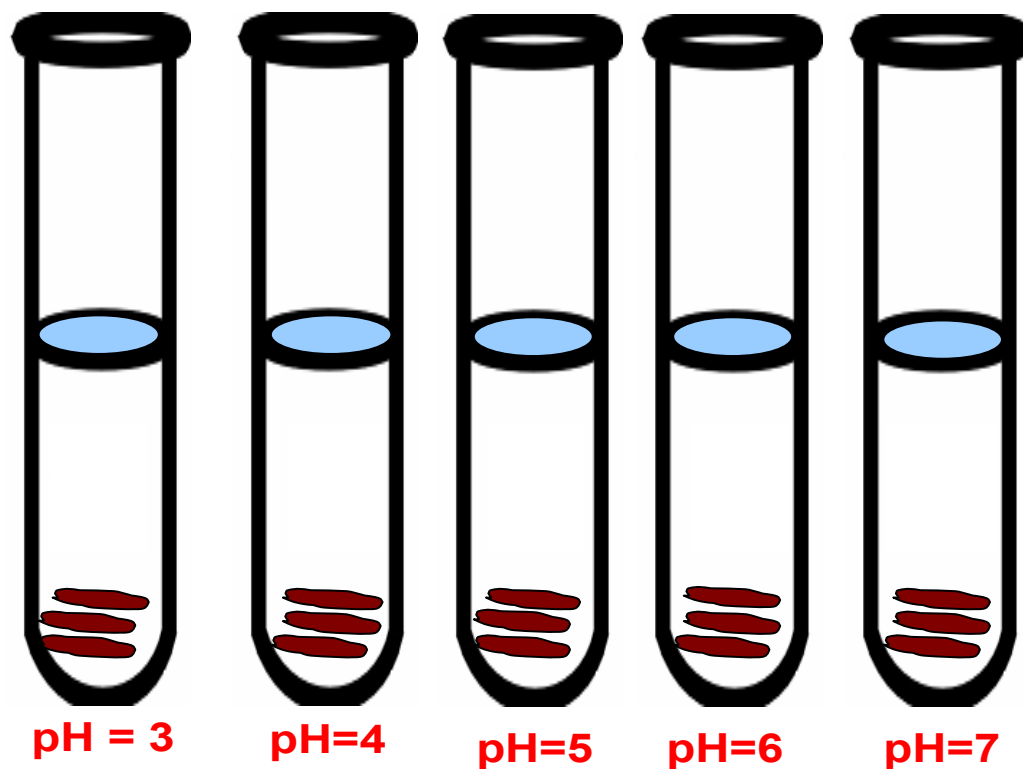
Cations increase sorption on HFO with increasing pH

Because of complexation with carbonate uranium increases then decreases

Uranium Adsorption Experiments

Initial Composition U(VI) = 2,380 µg/L, in 0.1NaNO$_3$

1g/L Ferrihydrite

pH = 3   pH=4   pH=5   pH=6   pH=7
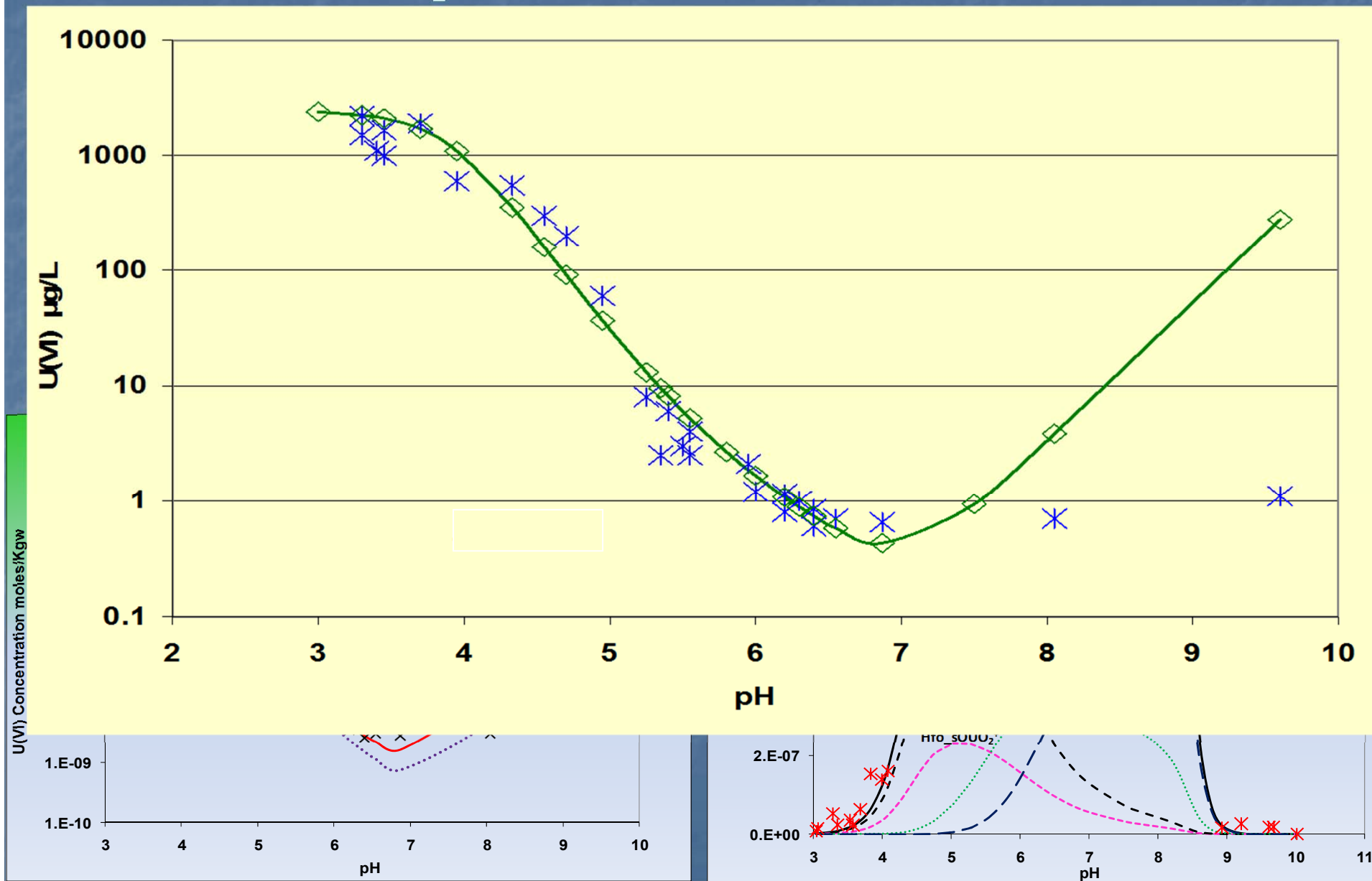
2,380 µg/L = 1.0×10^{-5} m U

No Carbonate Present

Refit of Uranium Surface Complexation Reactions

Surface Complexation Reactions for NEA database

$Hfo\_sOH + UO_2^{+2} = Hfo\_sOUO_2^+ + H^+$
    log_k 3.792   D&M = 5.2

$Hfo\_wOH + UO_2^{+2} = Hfo\_wOUO_2^+ + H^+$
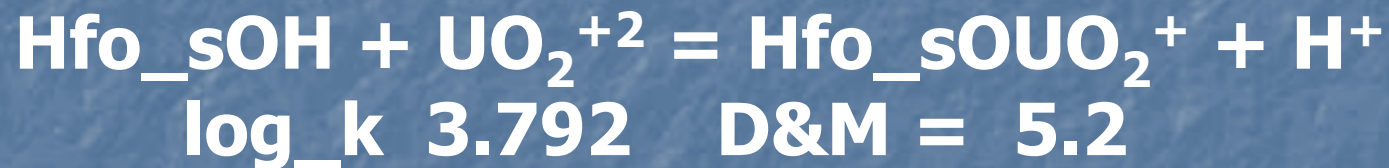
Need to estimate surface site concentrations of Hfo_wOH and Hfo_sOH

$Hfo\_wOH + UO_2^{+2} + 2CO_3^{-2} = Hfo\_wOUO_2(CO_3)_2^{-3} + H^+$
    log_k   15.28   D&M not included
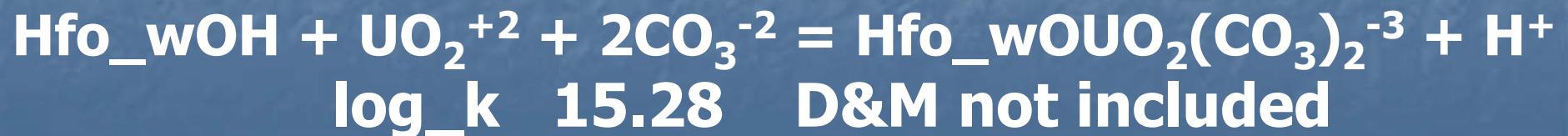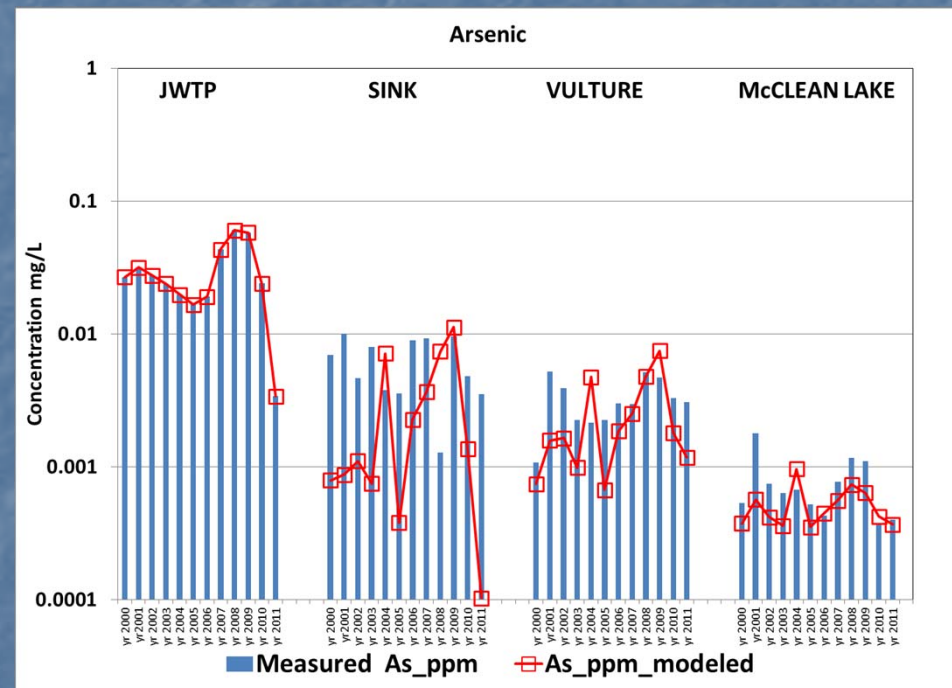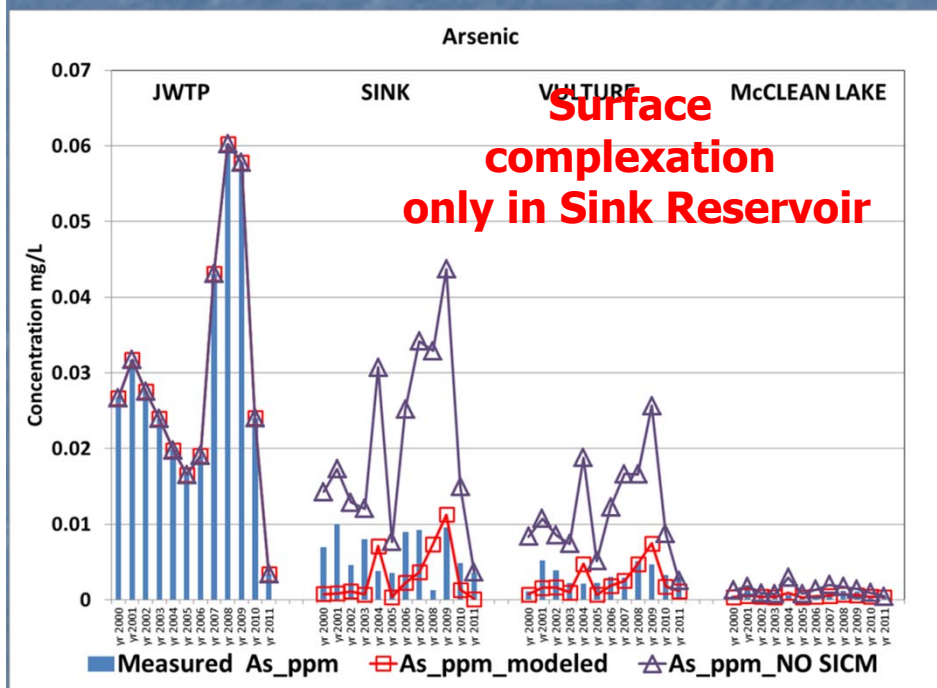
Arsenic With and Without Surface Complexation

Linear Concentration Scale   Log Concentration Scale

Surface complexation only in Sink Reservoir

Final fit from PHREEPLOT
Uses 0.09 for first six points, and
0.129 for last six points for site density function

Uranium
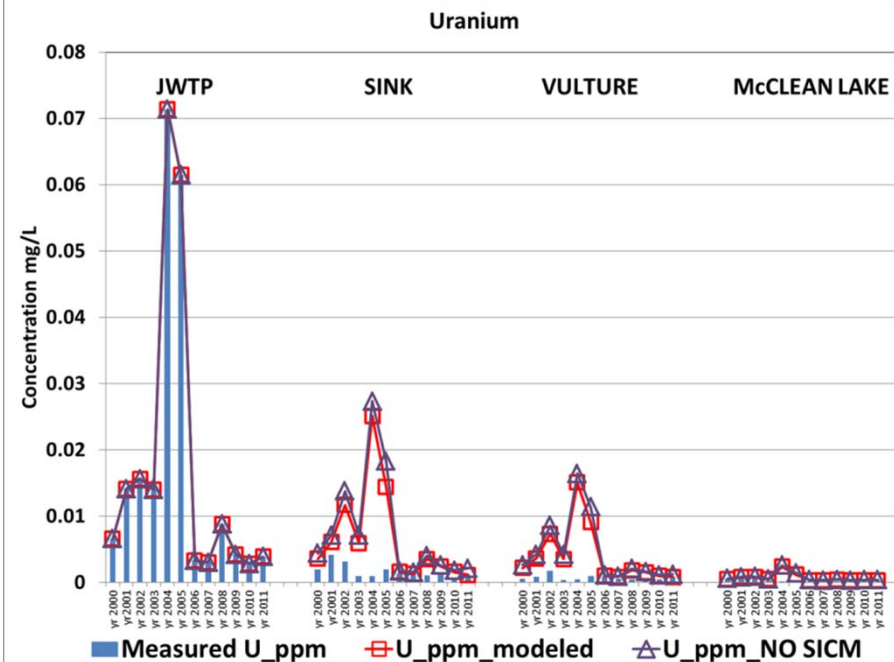
Linear Concentration Scale **Log Concentration Scale**
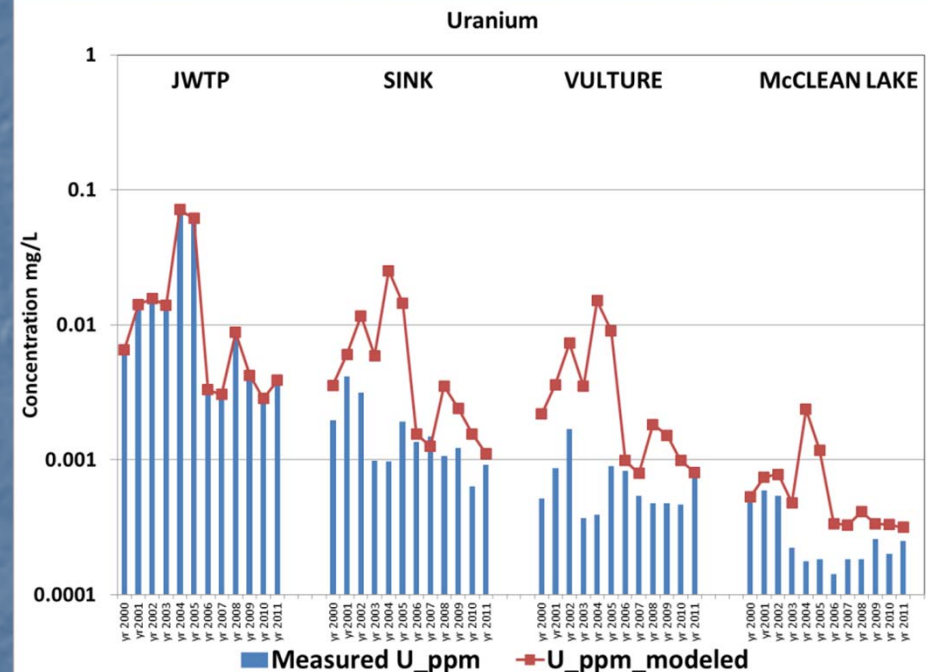
**Deliberately selected lower site concentration to match As
More conservative setup for Uranium
i.e., produces higher modelled values**

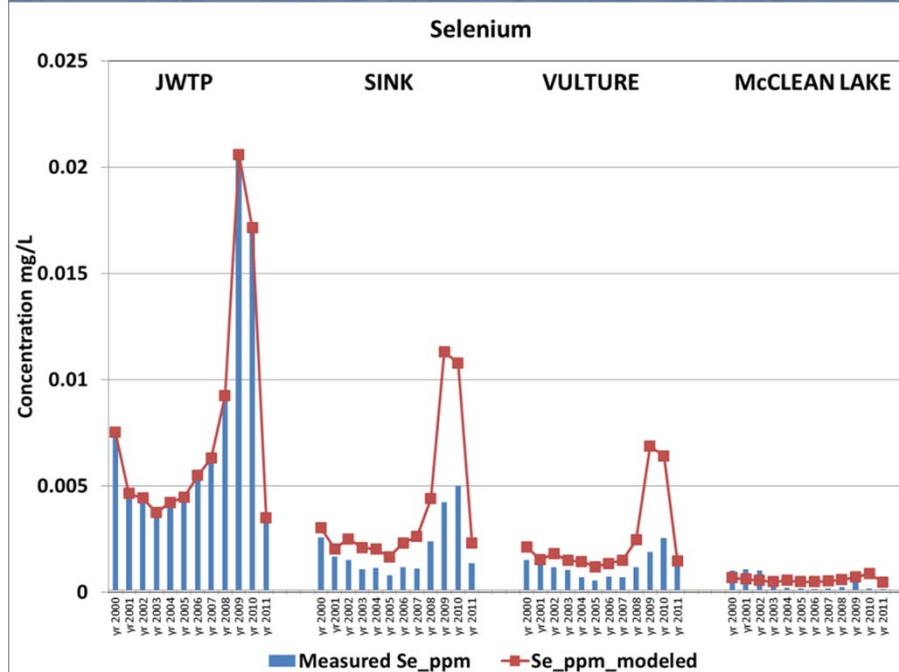Molybdenum Precipitation - Powellite
K_{sp} = -7.95 and -7.67 (PhreePlot Fitted)
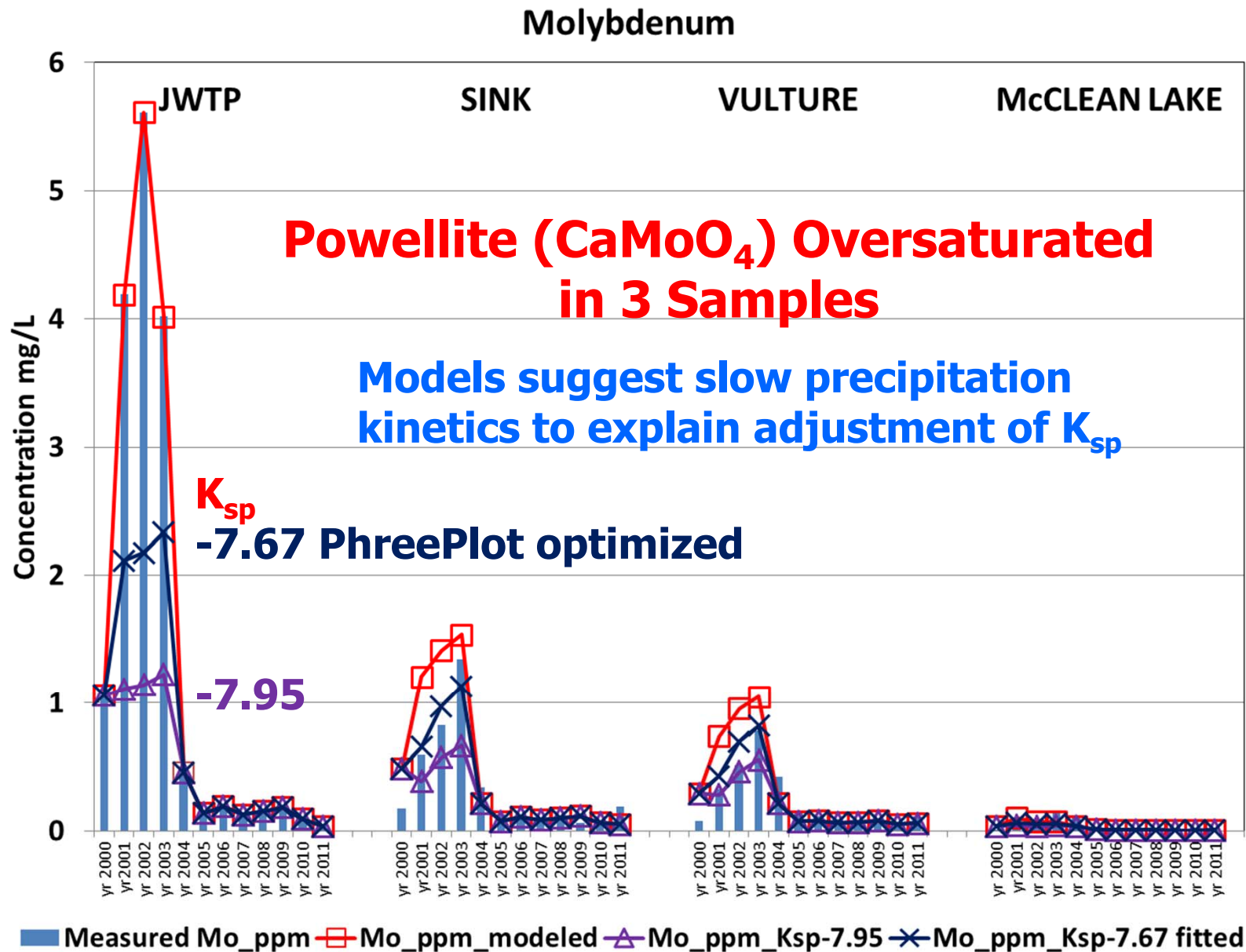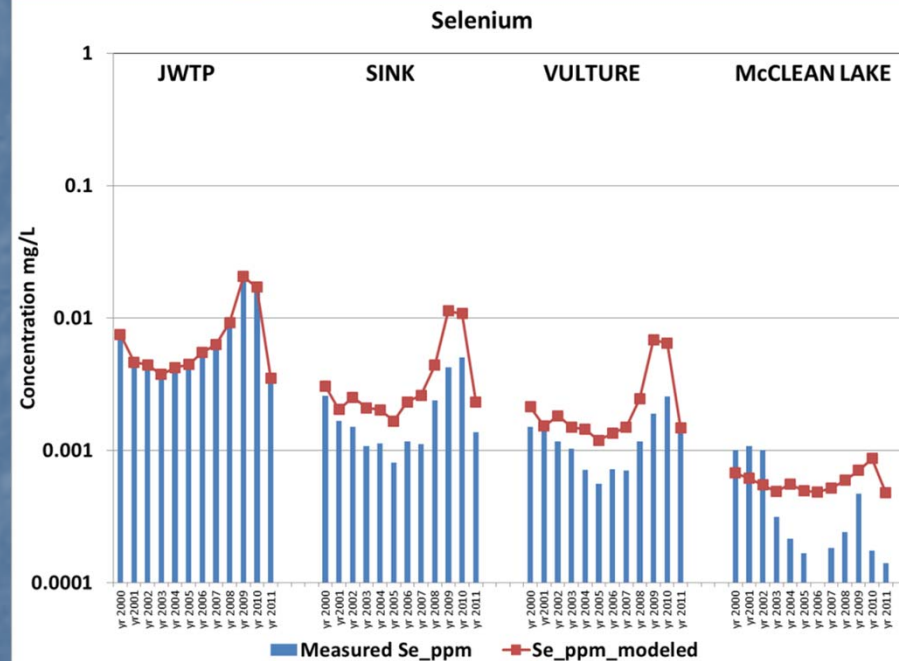
Selenium

Linear Concentration Scale   Log Concentration Scale

Continuing Work

- **Evaluate Seasonal and Redox Effects**
  - **Three samples per year**
  - **Evaluate seasonal effects**
  - **Better handle on redox processes**
  - **Iron related processes**

- **pH and better estimate of $CO_2(g)$ PP**

- **Iron needs additional work**
  - **Poor observed/modeled matches in Sink Reservoir, but**
  - **Good matches in Vulture and McClean Lakes**

- **Possible role of humic substances**
  - **Redox control**
 - **Sorbent phase**

Conclusions

- **Good predictions for conservative species:**
  - **Cl, Mg, K, Na, - Ca, Sulfate, - (Al)**
  - **Reliability of water balance and analyses**
  - **Mainly mixing of waters and dilution**
  - **No reason to change water balance/mixing proportions**

- **Better than order of magnitude fits for trace metals**
  - **Often within a factor of ± 2.0, but most within 25% RPD**
  - **Some elements agree down to ppb levels**

- **Surface complexation attenuates As and U**

- **Precipitation of powellite ($CaMoO_4$) explains Mo concentrations**

- **Conservative assumptions used in model setup**
  - **Not all possible attenuation processes included**
  - **Slight overestimates for uranium, selenium, ammonia**

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Questions?

Ammonia is Consumed
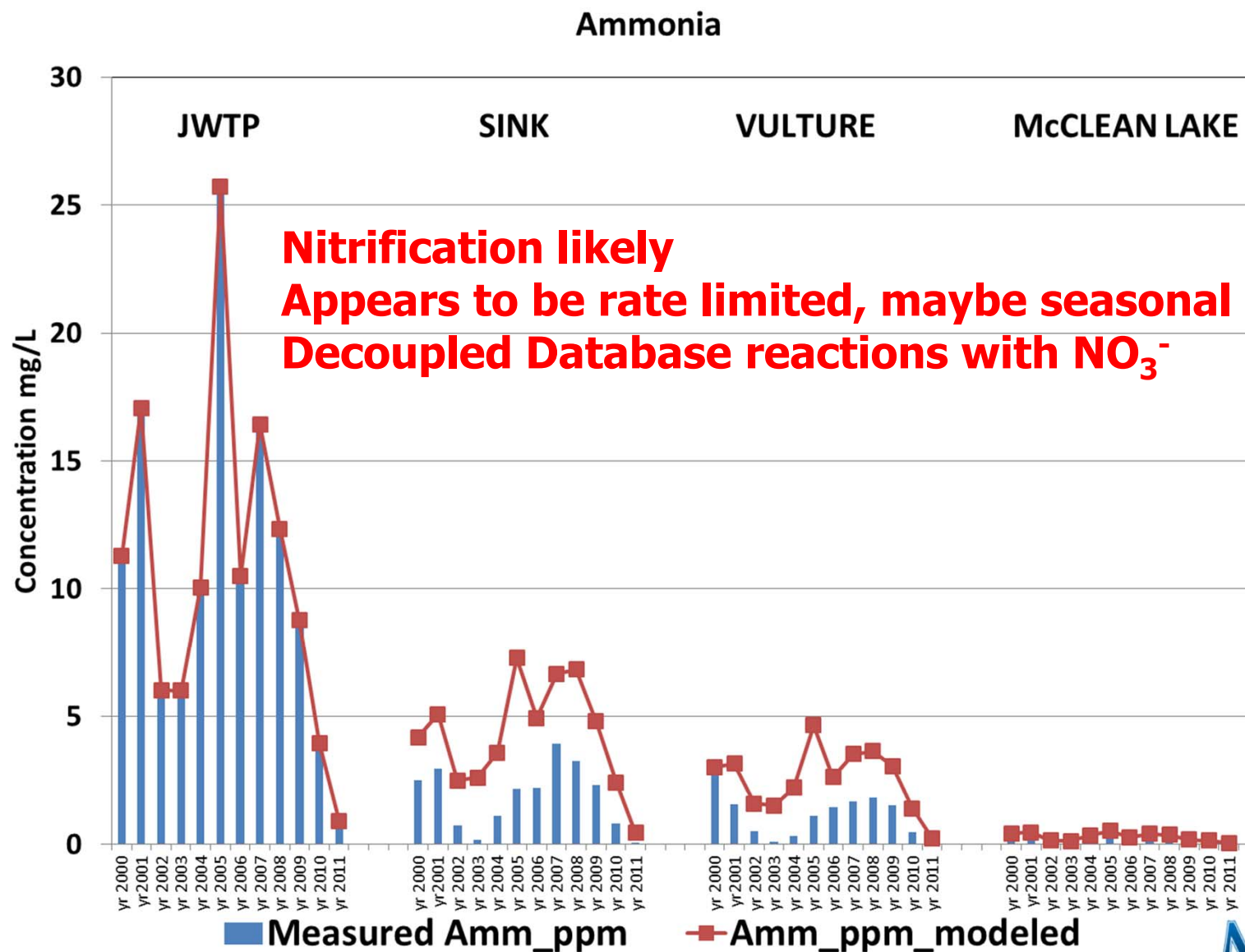
SURFACE SITE CALCULATIONS

SURFACE 4 # user defined surface site concentration
Hfo_wOH <Hfo_CONC> 600 0.045
Hfo_SOH <strong>

Alternative method EQ_P and Surface keywords linked

EQUILIBRIUM_PHASES 3
O2(g) -0.7 10 # oxygen at atmospheric pressure
CO2(g) -3.5 10 # carbon dioxide at atmospheric pressure

SURFACE 3
Hfo_wOH Ferrihydrite equilibrium_phase <sitedens> 53400
Hfo_sOH Ferrihydrite equilibrium_phase <strong>

Uses PHREEPLOT to adjust <sitedens> to optimize fit between measured and modeled arsenic concentration in Sink, Vulture and McClean Lakes

PHREEPLOT will also calculate <strong> site concentration in agreement with the <sitedens> value and original D&M assumptions

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IPhreeqcCOM Module

- **Original Version of Model**
  - EXCEL File Setup
  - model is copied into PHREEQCi
  - Water compositions pre-loaded
  - Supporting keywords pre-loaded
  - Output file and selected output file
- **Now IphreeqcCOM**
  - Component Object Module
  - Can run as module in VBA macro in EXCEL
  - Whole process is run within EXCEL
  - Water balance, mixing calculations, PHREEQC syntax,
  - Run macro
  - Reads PHREEQC input file
  - Write selected output to sheet
  - Facilitates preparation of graphics
  - Improves tracking of models