# Demo — Adsorption and transport of elements in the GWB

Instructions are provided for calculating a speciation diagram using **React** and tracing a model of mass transport using **X1t**. A complete list of input files for the remaining examples follows. Double-click on a .rea, .x1t, or .x2t file to run that example. The .tdat and .sdat files are special thermodynamic or surface reaction datasets loaded in some of the examples. The As\_reduction\_scatter.gss contains scatter data which can be overlain on the results of the Arsenate\_reduction.rea example in **Gtplot**.

Examp	les	Files needed
1	Speciation diagram	Spec.rea*
2	Surface Complexation	Complexation.rea
3	Microbial Arsenate	Arsenate_reduction.rea
	reduction	thermo+Lactate.tdat
		As_reduction_scatter.gss
4	Mass transport	Pulse.x1t*
		Dispersion.x2t
5	Dual Porosity	DualPorosity.x1t
		DualPorosity.x2t
6	Sorption	Sorbing.x1t
		Pb-Kd.sdat
		Pb-Freundlich.sdat
		Sorbing.x2t
7	Surface Complexation	3metals.x1t
		3Metals.x2t
8	Biodegradation	Benzene.x1t
		thermo+benzene.tdat
		Benzene_Kd.sdat
		Benzene.x2t
9	Dissolution and Precipitat	tion
	*Instructions provided be	low

## <u>Speciation diagram — Uranium speciation</u>

**React** is a flexible program that models equilibrium states and geochemical processes in systems that contain an aqueous fluid. Like **SpecE8**, **React** can calculate the equilibrium distribution of aqueous species in a fluid, a fluid's saturation state with respect to minerals, and the fugacities of gases dissolved in a fluid.

The program can also trace the evolution of a system as it undergoes reversible or irreversible reaction in an open or closed system, either at a given temperature or polythermally. **React** can integrate kinetic rate laws and simulate the fractionation of stable isotopes in a reacting system.

As an example, you can use it to see how the speciation of uranium changes with pH. Doubleclick on file "Spec.rea" and when **React** opens, look at the **Basis** pane

React : Spec.rea - C:\Users\bfarrell\Desktop\Soil Physics			×
Eile Edit Run Config View Help Simple uranium			
Basis Reactants Medium Command Res solution			
constraints on initial system			^
H2O 1.0 ▼ free kg ▼		solvent	
U++++ ₽ 1.0 ▼ log ug/kg ℃	•		
Na+ 🛱 0.2 🔻 molal 🔻			
H+ ₽ 2.0 ▼ pH ▼			
temperature 25.0 V C V			
+ advanced			
add delete			
☐ time start 0.0 ▼ day ▼ end 1.0 ▼ day ▼			
<			,
Ready		NUM	

The pane shows the concentration of the dissolved uranium component in the fluid and the initial pH. In this simple example we've turned off the requirement for maintaining charge balance.

### Move to the **Reactants** pane.

React : Spec.rea - C:\Users\bfarrell\Desktop\Soil Physics	_	×
<u>Eile E</u> dit Run Config <u>V</u> iew <u>H</u> elp		
Basis Reactants Medium Command Results		
reactants and kinetic reactions Target value for pH		
- Slide pH to 12.0 PH		_
reactants times 1.0		 

The input causes **React** to scan over a range of pH values, starting with the value of 2.0 and ending at 12. If the slide command was not already set, you would do so by clicking **add**  $\rightarrow$  **Sliding**  $\rightarrow$  **pH** and setting the target value.

On the **Config**  $\rightarrow$  **Iteration**... dialog

ξ Iteration			×
			]
epsilon	5.0e-11	•	
itmax	400	itmax0	999
nswap	30	nswap0	200 💌
timax	3.0	simax	3.0
Pitzer -	<b></b>		
precon	Precipit	ation	
relax	not allo	wed <sup>la</sup>	0.1
- options	$\overline{}$		
Kd	precipitati	on 🗌 sorb	oate
ОК	Apply	Cancel	Reset

we see the precipitation option has been deselected. This setting will prevent supersaturated minerals from forming in our simulation (since we assume a fixed solution composition). Click **OK** 

On **Config**  $\rightarrow$  **Output...** set a suffix "\_Spec".

Output	aset dxprint 0.1	: 
arrange	numerically      o alphabetic	ally
include	aqueous species     surface complexes     mineral saturation states     gas fugacities     stagnant zone	basis composition     original basis composition     elemental composition     reactions loaded
✓ plot data format title	eset dxplot 0.005	•
suffix [	_Spec	
	OK Apply	Cancel Reset

Click **OK**, then on the main window select **Run**  $\rightarrow$  **Go** (or touch ctrl+g). **React** will move to the **Results** pane and trace the simulation.

ξ React : Spe	c.rea - C:\Users\	bfarrell\Desktop	Soil Physics				—		×	
<u>F</u> ile <u>E</u> dit Ru	ın Config <u>V</u> i	ew <u>H</u> elp								
Basis	Reactants	Medium	Command	Results						
Step 99, 1 supersa	Xi = .99 Aturated ph	(10 iterati ase, Uranir	ions) nite						^	
Warning Step 100, 1 supersa	Warning, Node 0 has a charge imbalance of 0.1886 faradays Step 100, Xi = 1 (10 iterations) 1 supersaturated phase. Uraninite									
Warning Successful	g, Node 0 h L completio	as a charge n of reacti	e imbalance ion path.	of	0.1856	faradays	1		~	
	t								>	
Run	View Results	Plot Results	>							

Click on the **Plot Results** button to launch **Gtplot**.





Your diagram should look like this:



## Mass transport — Migration of a non-reacting contaminant

Let's construct a model of how a contaminant might migrate in flowing groundwater, neglecting for the moment the possibility of chemical reaction.

In our model, inorganic Pb contamination passes into an aquifer. After 2 years, the source is removed and the aquifer is flushed with ambient water.

A1t - C:\U	Jsers\bfarrell						_		×
<u>F</u> ile <u>E</u> dit R	Run Config <u>V</u> ie	ew <u>H</u> elp							
Initial	Intervals	Fluids	Flow	Reactants	Clean wate	dium	Command	Resu	lts
- constraints	s on initial system –					: <b>r</b>			^
		H2O		+ 1	.0 •	free kg 🔻	solvent		
		Na+ 🛱		+ 1	.0.0	mmolal 🔻			
		Pb++ 🛱		+ 1	.0e-12 r	mmolal 🔻			
		d- 🛱		+	•	mmolal 🔻	charge b	alance	
	te	mperature		+ 2	5.0 🔻 (	c <b>-</b>			
				+ ad	lvanced				
add	copy delete								~
<									>
Ready								NUM	

Double-click on file "Pulse.x1t" and look at the Initial pane in X1t

We've specified here that the aquifer be filled initially with clean water.

### Moving to the Intervals pane

→ X1t - C:\Users\bfarrell					_	
<u>File E</u> dit Run Config <u>V</u> iew <u>H</u> elp						
Initial Intervals Fluids	Flow	Reactants	Domain	Medium	Command	Results
inlet intervals						
start at 0.0	▼ yr ▼	left contar	minated	right same	as left 🔹	
elution • at 2.0	▼ yr ▼	left flush	•	right same	as left 🔹	
end <b>v</b> at 10.0	<b>т</b> уг <del>−</del>	The first in	nterval runs	from 0 to 2	2 years. The	
add delete		second	interval run	s from 2 to	10 years.	
<						>
Ready						NUM

we've set start and end times for two reaction intervals, the imbibition and elution legs of the simulation. We've additionally designated two fluids, "contaminated" and "flush", to flow into the left side of the domain during the imbibition (start) and elution intervals, respectively.

The Fluids pane contains the two boundary fluids



By expanding the "+" signs, we can view the "contaminated" fluid, which will be introduced in the imbibition leg

<mark>→</mark> X1 <u>F</u> ile <u></u>	t - C:\Users <u>E</u> dit Run	∖bfarrell Config	<u>V</u> iew	<u>H</u> elp									_		×
Ini	itial	Interval	s 🤇	Fluids	ightarrow	Flow	Reactan	its	Domai	n	Medium	Со	mmand	Resul	ts
inle	et fluids —				-										_^
-	contamin	ated	•												
l r	- constraint	s on fluid -						_		_					-
				H2O				1.0		•	free kg 🔻		solvent		
				Na+	t			10.0	)	•	mmolal 🔻				
				Pb++	¢			0.1	$\wedge$	•	mmolal 🔻				
				Cl-	Ħ				Water	СС	ontains		charge bala	ance	
			te	emperature				ĺ	20 mg	kg	<sup>-1</sup> Pb <sup>2+</sup>				
							+	advar	nced						
Į	add	сору	delete												
	flush		•												
	- constraint	s on fluid -													- 1
				H2O				1.0		•	free kg 🔻		solvent		
				Na+	₽			10.0	)	•	mmolal 🔻				
				Pb++	t			1.0e	-12	•	mmolal 🔻				
				Cl-	t				–⁄ – – Clean r	ins	se water		charge bala	ance	
			te	emperature				25.0	)	•	с 🕶				
							+	advar	nced	_					
	add	сору	delete												
a	dd cop	v dele	ete												_
															~~~
Ready			_		_			_		_				NUM	>

as well as the "flush" fluid: clean rinse water that will flow in during elution.

Initial I	ntervals	Fluids	Flow	Reactants	Domain	Medium	Command	Result
medium properties	5							
diffusion coefficie	nt	+ 1.0e-06	▼ cm2/s ▼					
porosity		+ 0.3	· < ,	a = 30%				
inert volume		+ 0.0	▼ cm3 ▼					
thermal conductiv	vity	+ 0.004	▼ cal/cm/s/	c <b>-</b>				
neat capacity	cpw (fluid)	+ 1.0	▼ cal/g/C 、	-				
ср	r (minerals)	+ 0.2	▼ cal/g/C ▼	-				
internal heat sour	rce te	mperature: mini	mum	▼ °C maxim	um	▼ °C		
		+ 0.0	▼ cal/cm3/s	• •				
mass transport								
longitudinal disper	rsivity	+ 1.0	• m • <	$\alpha_L = 1 \text{ m}$				
permeability: log k	x (darcy) = (	(A x porosity (vo	lume fraction)) + I	в				
A (porosity)		+ 15.0	•					
B (intercept)		+ -5.0	▼ darcy ▼					

On the **Medium** pane you can see the values set for porosity and dispersivity

Check the domain size and gridding by moving to the **Domain** pane

ł	🕨 X1t - C	\Users	\bfarrell							_		$\times$
E	le <u>E</u> dit	Run	Config	<u>V</u> iew	<u>H</u> elp							
	Initial		Interval	s	Fluids	Flow	Reactants	Domain	Medium	Command	Resu	lts
	Linear		•									
	height (	z) 1	.0	•	cm 🔻							
	wid	th (y)	1.0		▼ cm ▼	nodes (N	x) 400	→ → <	Domain is into 400 i blocks, 1	s divided nodal km long		
						length (x	) 1000.0	▼ m ▼				
						🔾 delta x	+ 10.0	▼ cm ▼				

→ X1t - C:\Users\bfarrell <u>F</u> ile <u>E</u> dit Run Config <u>V</u> iew	v <u>H</u> elp				_		×
Initial Intervals	Fluids Flow	Reactants	Domain	Medium	Command	Result	s
flow field: O set by interval	• set for all intervals						
+ all intervals: discharge = 3	30 m3/m2/yr						
boundaries: left normal ▼	right normal ▼	$q_x = 30 \text{ m}^3 \text{ m}^{-2} \text{ y}$ $(v_x = q_x/n = 100)$	yr <sup>−1</sup> m yr <sup>−1</sup> )				> <b>`</b>
Ready				1		NUM	

We set the rate at which fluid passes into the domain by moving to the **Flow** pane

A positive specific discharge indicates that fluid will flow from left to right. The simulation spans 10 years, so given the porosity and discharge values we've set, the fluid in the aquifer will be displaced once over the course of the simulation.

Before launching the run, go to **Config → Output...** and enter "\_pulse" in the suffix field

Output				×
print dataset dxprint 0	.1	spacing	<ul> <li>linear</li> </ul>	
arrange		ly	exact	$\bigcirc$ approx
include 🖂 aqueous spec	ies	basis cor	nposition	
surface comp	exes	🔳 original b	asis compo	sition
mineral satura	ation states	elementa	al compositio	on
gas fugacities		reaction:	s loaded	
stagnant zon	2			
✓ plot dataset dxplot      ✓     format      ● binary      t     title	ext	spacing	<ul><li>● linear</li><li>● exact</li></ul>	O log O approx
suffix _pulse				
ОК	Apply	Ca	ancel	Reset

The suffix will be appended to the names of your output datasets, so you can go back to examine the results without rerunning the model. Click **OK**.

Trigger the calculation by selecting  $Run \rightarrow Go$ . X1t will move to the **Results** pane, trace the simulation, and when it's done, offer to extend the run



Click No.

Now, look at the bottom of the Results pane

→ X1t - C:\Us	ers\bfarrell							_		×
<u>F</u> ile <u>E</u> dit Ru	ın Config <u>V</u> ie	w <u>H</u> elp								
Initial	Intervals	Fluids	FI	ow Read	tants	Domain	Medium	Command	Results	$\supset$
Step 751,	Xi = 0.993	61 (Co :	= 0.5	56)						^
Step 752,	Xi = 0.995	(Co =	= 0.5	56)						
Step 753,	Xi = 0.996	39 (Co:	= 0.5	56)						
Step 754,	Xi = 0.997	78 (Co:	= 0.5	56)						
Step 755,	Xi = 0.9993	17 (Co•	= 0.5	56)						
Step 756,	Xi = 1	(Co =	= 0.33	33)						
Successful	l completion	n of react:	ion s:	imulation.						
Simulation	n required	5.1 second:	s of (	computing t	ime (1	.9 seconds	s clock tim	ne):		
3.7 sec	conds solvi	ng chemica	l read	ction equat	ions,					
0.8 sec	conds solvi	ng transpo	rt equ	uations,						
0.6 sec	conds perfo	rming othe:	r tasl	ks.						
Simulation	n ran using	4 threads	on 4	computing	cores					
	CPU ti	ne Clock	time	Utilizati	on					
Parallel	4.7	s :	1.3 s	353.5	8					
Serial	0.4	s (	).6 s	69.2	4					
Total	5.1	s :	1.9 s	261.4	8					~
<									3	
Follow Out	out									
Run	View Results	Plot Results								
Ready									NUM	

and click on the **Plot Results** button to launch **Xtplot**.

Configure the plot as indicated below



Your diagram should look like this:



Now, let's animate the plot. On the **XY Plot** dialog, go to the **Y Axis** pane and uncheck the "Auto-scale" option

Axis Y Axis	Position	Time Lev	/el		
Variable type Consider	Component	s in fluid			<b>*</b>
Cl- H2O Na+ Pb++					First Previous Next Last Select all
Auto-scale	Revers	e axis 005	<u>*</u>	mmol/k	kg V
Auto-scale Mitrimum Maximum	Revers	e axis 005 .1		mmol/k as Pb+	⟨g ∨ + ∨

In this way, you hold steady the *y*-axis range over the animation. Then, on the main window, choose **Edit**  $\rightarrow$  **Animate...** 

Animate				×				
Animate from:	0 day 73.05 day 146.1 day 219.2 day 292.2 year 1	to:	year 9 year 9.2 year 9.4 year 9.6 year 9.8 year 10	<b>^</b>				
Step:	🗌 Loop continuo	usly	🗌 Full scre	en				
Animation spee	Animation speed: Delay (ms):							
Slower	Slower Faster							
Save animation	on to image files							
Image size:	Image size: width 800 height 600 pixels							
Image format:	Image format: PNG (.png)							
Image directory: Browse C:\Users\bfarrell								
	Run	Cance		Reset				

and click on the **Run** button. How does the shape of the pulse change as it traverses the aquifer from left to right?

### Mass transport — Effects of dispersion (continued from previous exercise)

How does dispersion affect contaminant migration? Let's find out.

Go to the **Medium** pane and change the entry for dispersivity from "1 m" to "10 m"

→ X1t - C:\Us	ers\bfarrell						_		×
<u>F</u> ile <u>E</u> dit Ru	n Config <u>V</u>	(iew <u>H</u> elp							
Initial	Intervals	Fluids	Flow	Reactants	Domain (	Medium	Command	Results	
medium prope	erties								î
diffusion coef	fficient	+ 1.0e-06	▼ cm2/s ▼						
porosity		+ 0.3	•						
inert volume		+ 0.0	▼ cm3 ▼						
thermal cond	uctivity	+ 0.004	▼ cal/cm/s/0	•					
heat capacity	cpw (fluid)	+ 1.0	▼ cal/g/C ▼						
	cpr (minerals)	+ 0.2	▼ cal/g/C ▼						
internal heat	source t	emperature: minim	num	▼ °C maxim	um	<b>•</b> •C			
		+ 0.0	▼ cal/cm3/s	•					
mass transpo	rt								-
longitudinal d	ispersivity	+ 10.0	<b>*</b> m <b>?</b>						
permeability:	log ky (darcy) =	(A x porosity (volu	me fraction)) + B						-
A (porosity)		+ 15.0	<b>•</b>						
B (intercept)		+ -5.0	▼ darcy ▼						
add d	elete								ł
<								>	- Y
eady								NUM	

On **Config → Output...** set a new suffix "\_disp"

suffix _disp	)			
	ОК	Apply	Cancel	Reset

Click **OK**, then on the main window select **Run**  $\rightarrow$  **Go**. When **X1t** finishes, launch **Xtplot** to render the results. Compared to the first model, how have the results changed?

You can compare side-by-side instances of **Xtplot**. Double-click on "X1t\_plot\_pulse.xtp" to render your earlier results. If you feel ambitious, you can build up a composite diagram in MS PowerPoint to show both results in one diagram.