In Situ Hydroxyapatite Permeable Reactive Barrier Performance at the Old Rifle, CO Uranium Processing Mill Site

SAND2018-13985C

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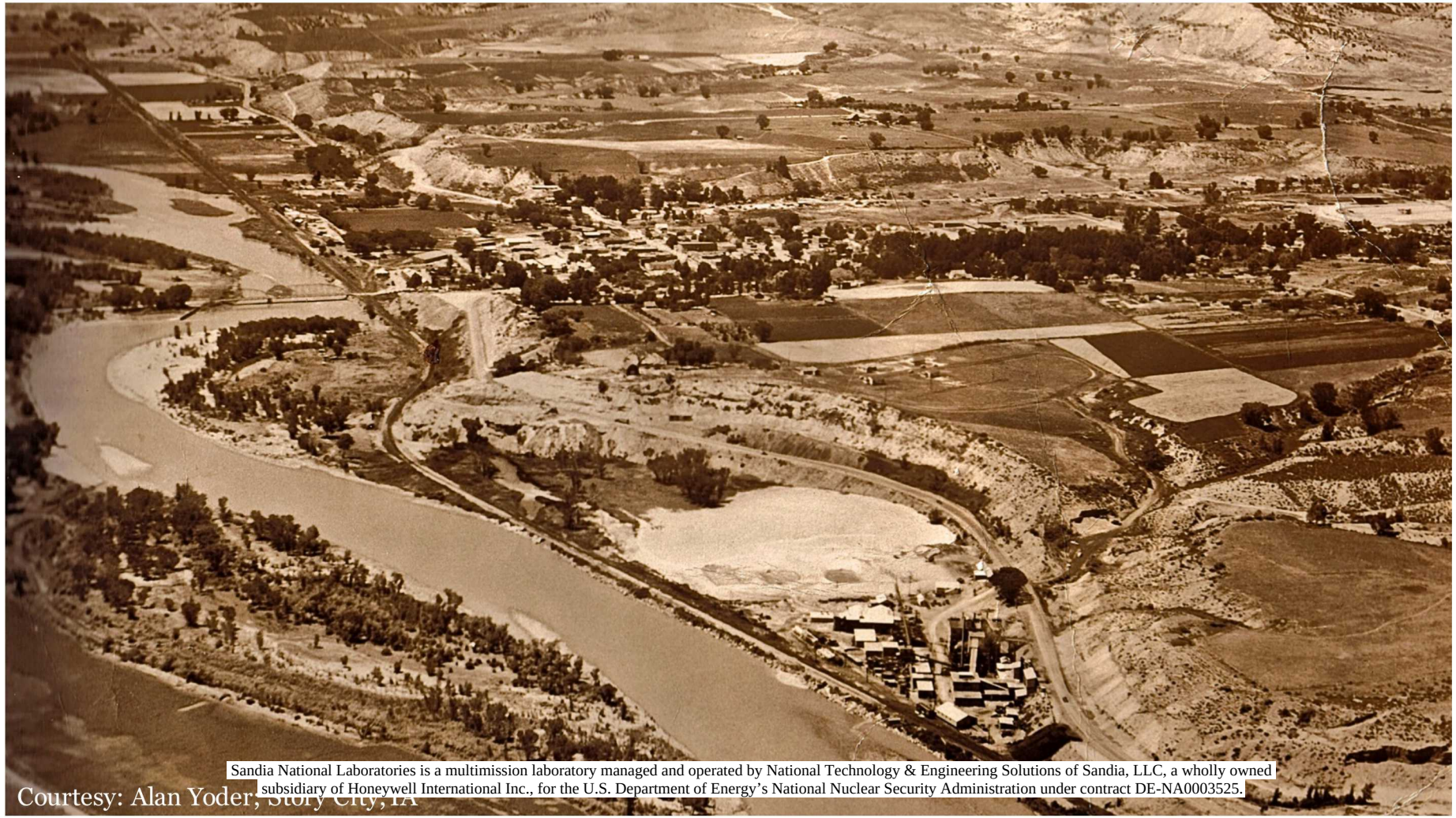

Courtesy: Alan Yoder, Story City, IA

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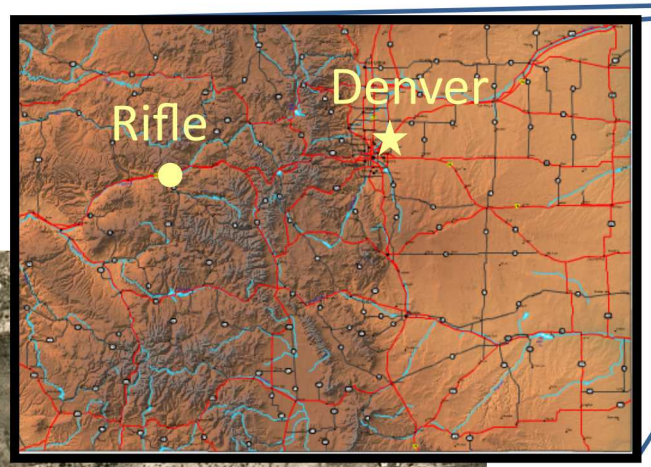
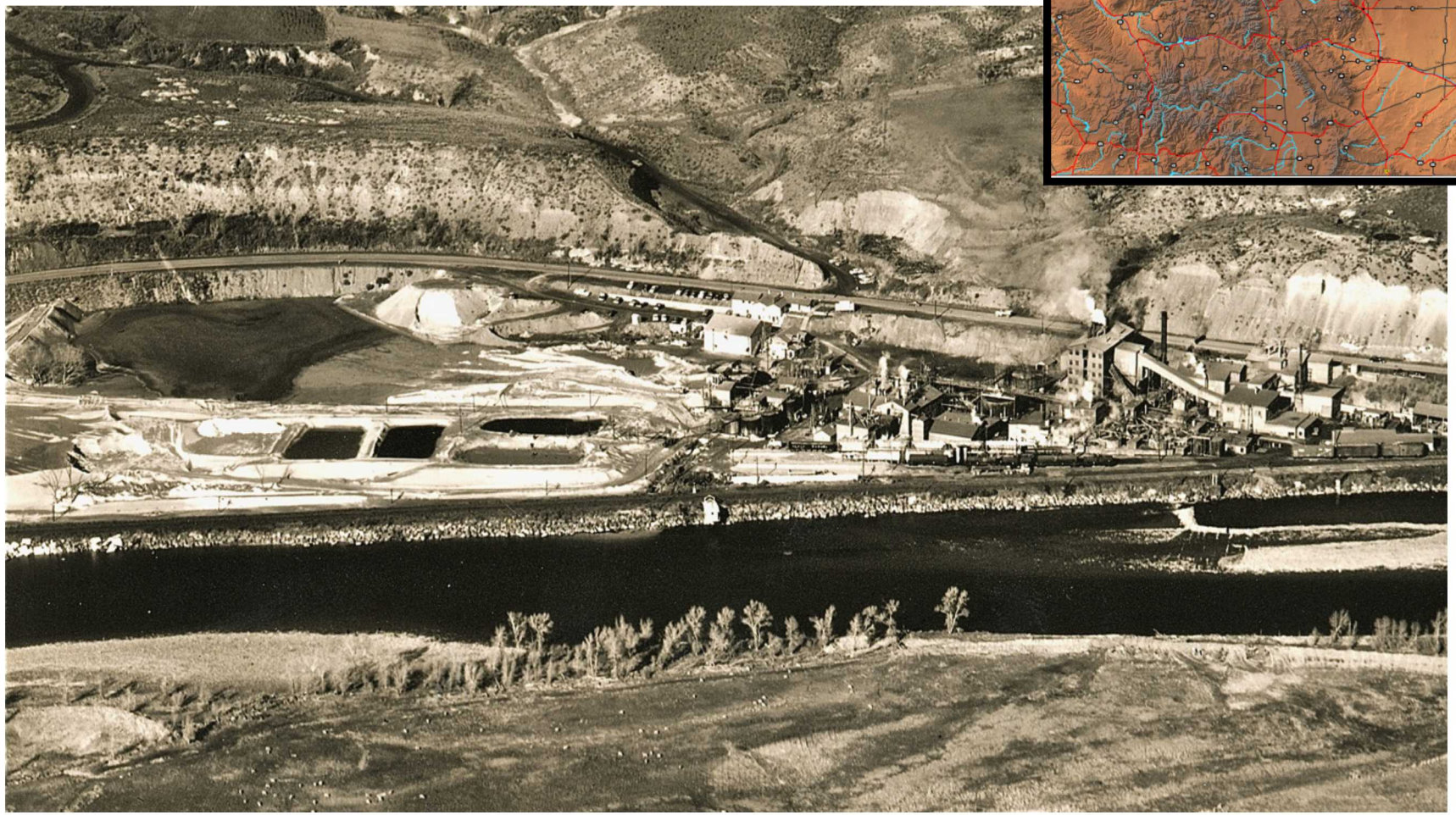
DOE's Old Rifle, CO former mill site

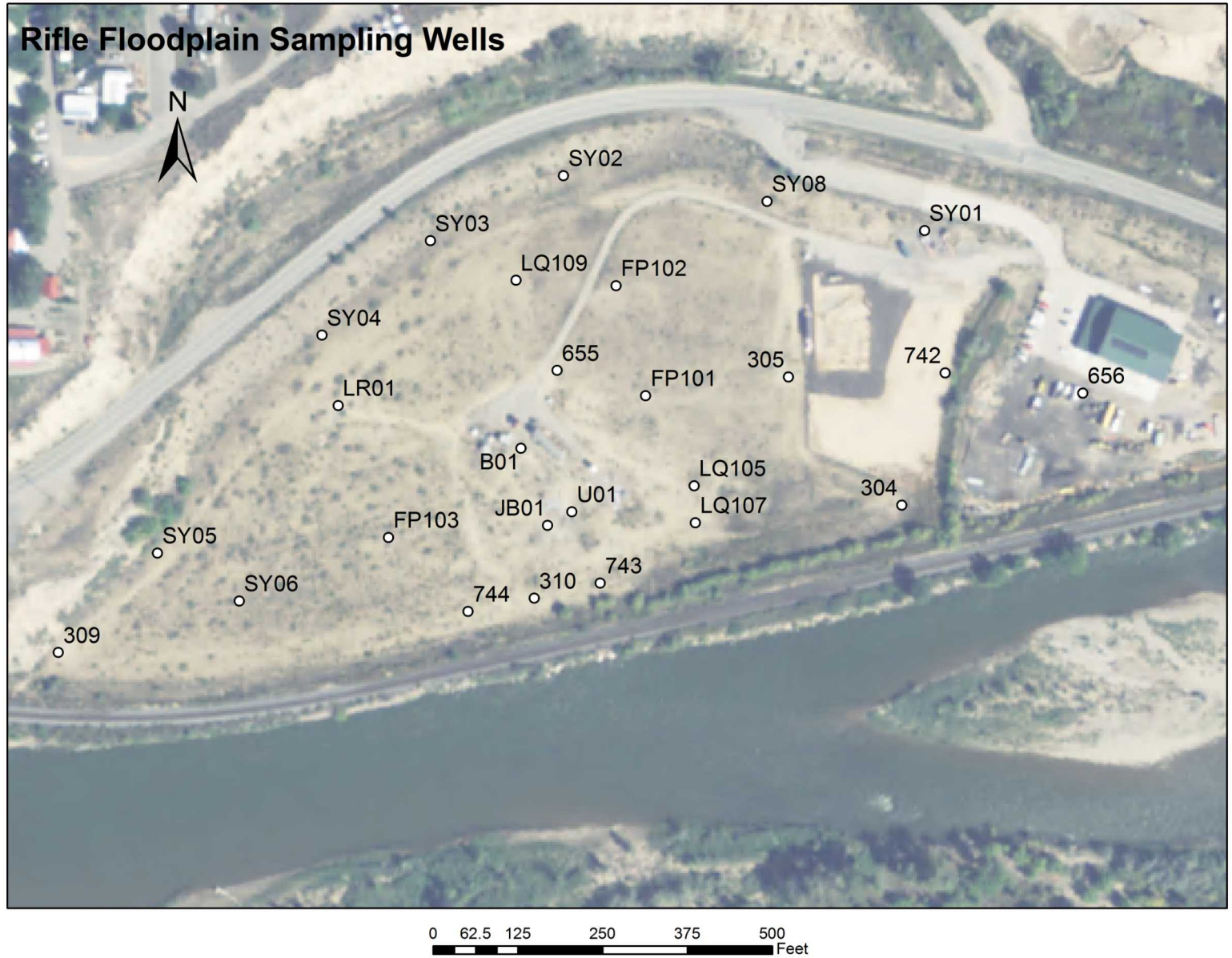


Rifle, CO: Mill site in ca. 1957



- Uranium/vanadium ore processing facility: 1924-58
- Tailings were consolidated & stabilized late 1950's & 60's
- Tailings removed; surface cover and closure in 1996

Old Rifle mill site legacy: Persistent uranium plume



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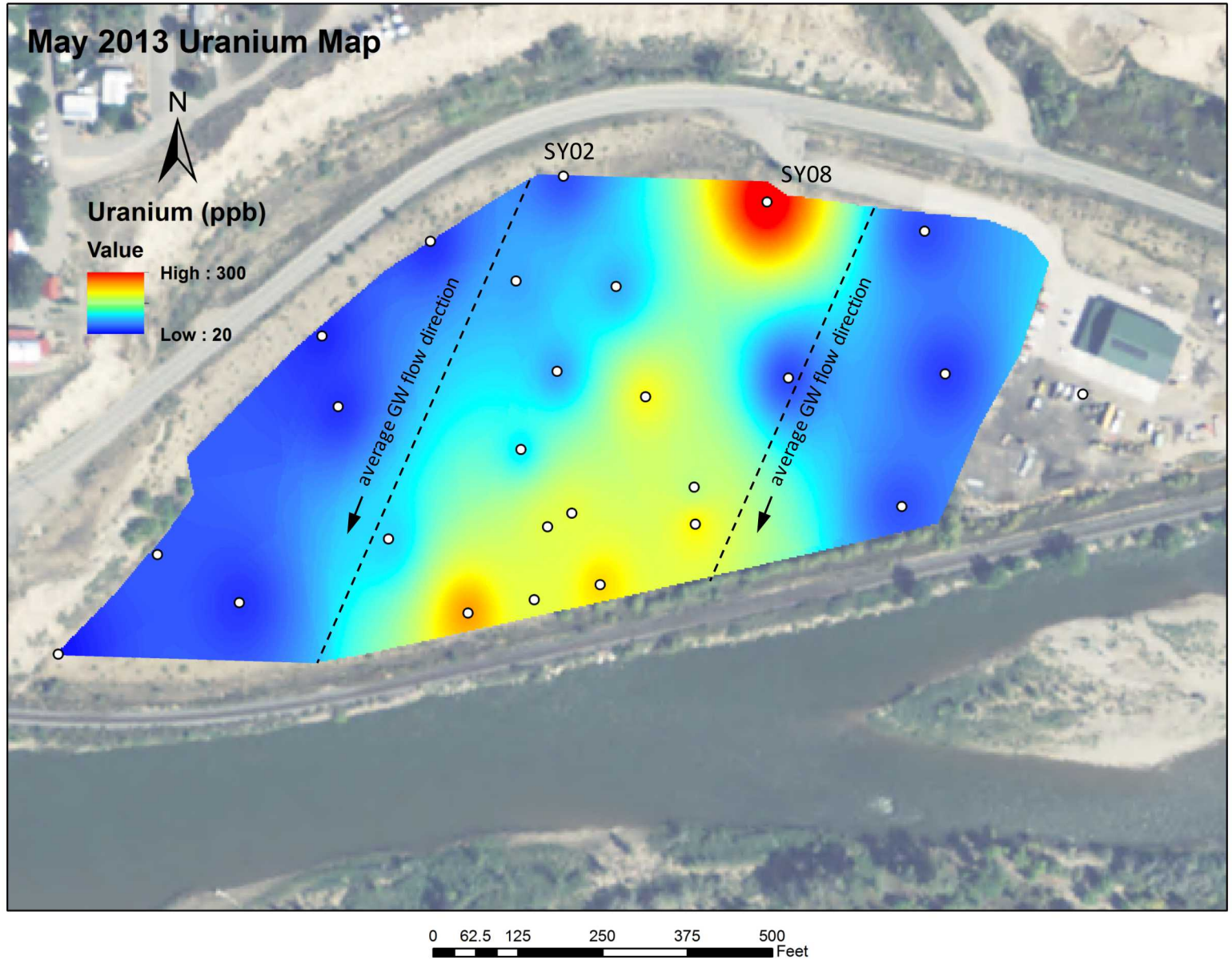

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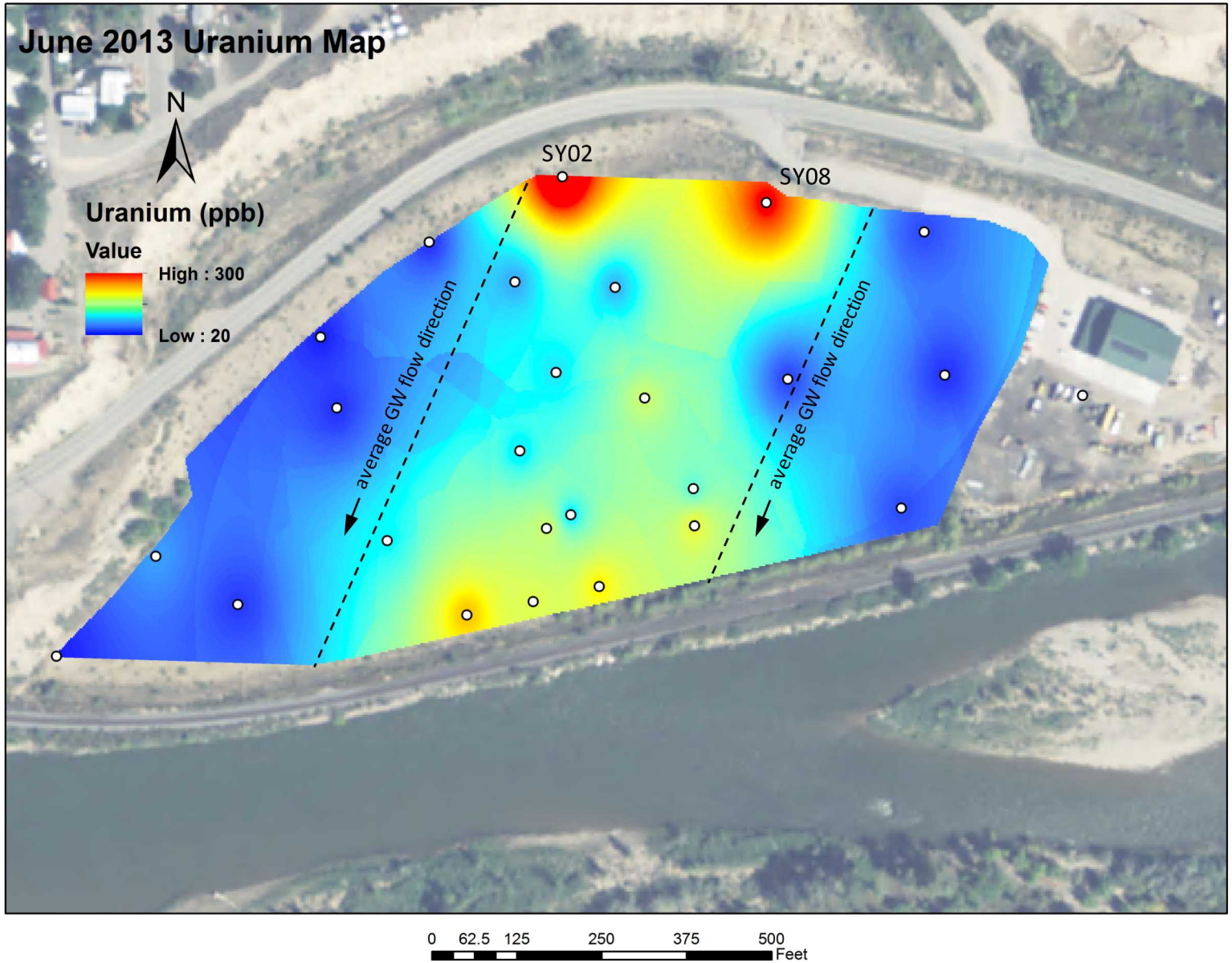
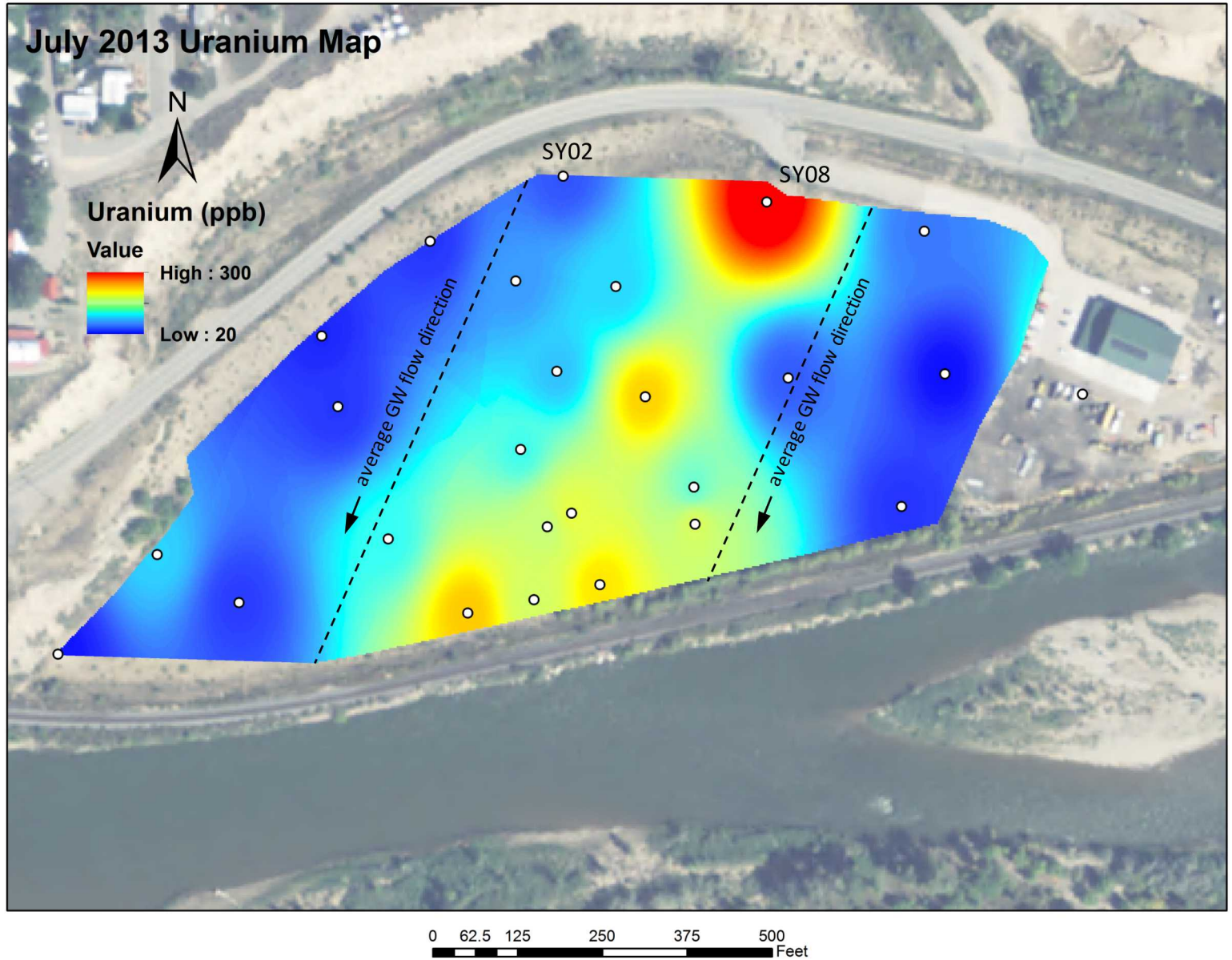
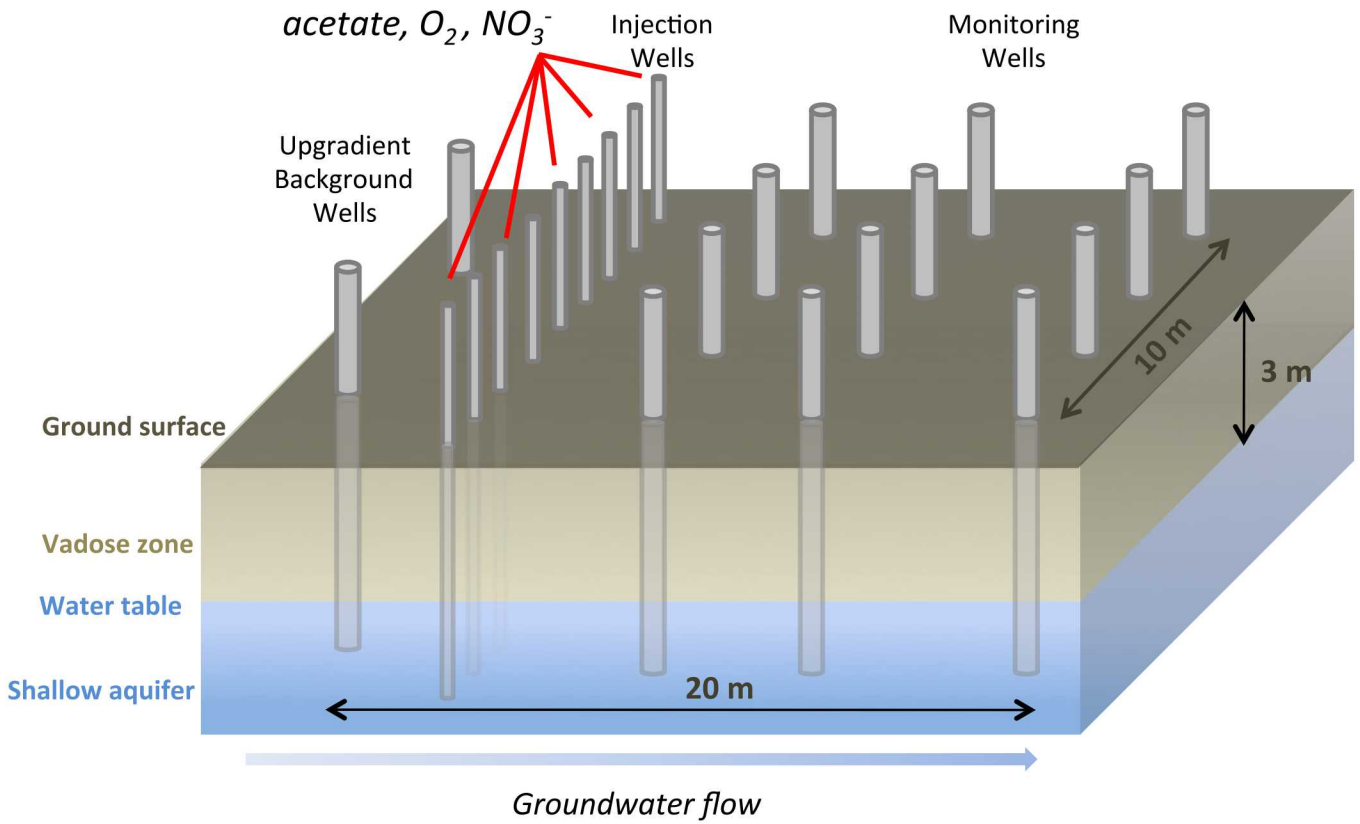
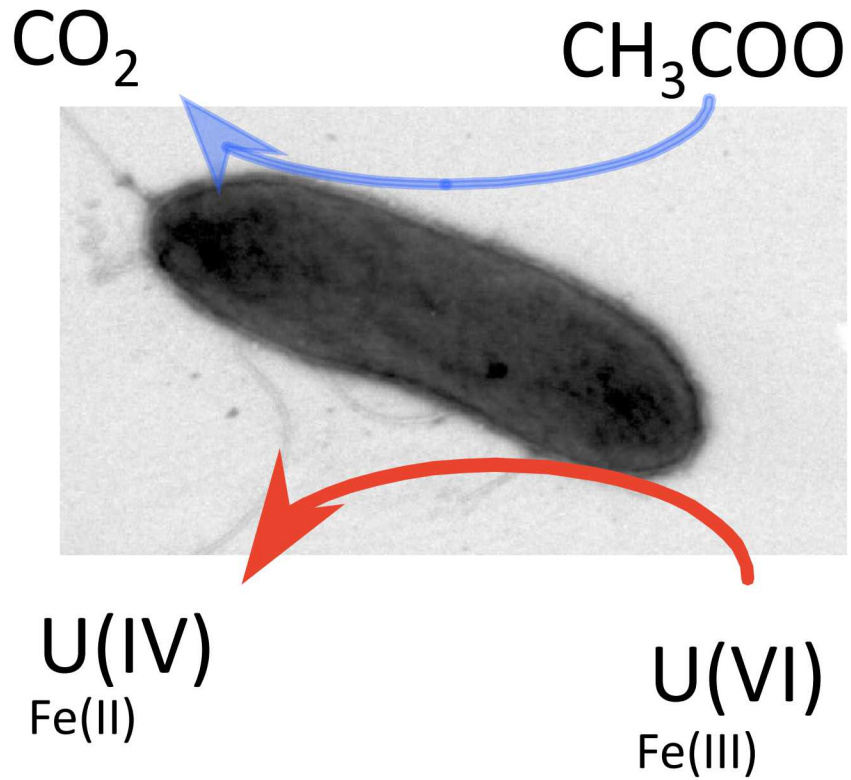


Old Rifle mill site legacy: Persistent uranium plume



Field testbed for uranium remediation

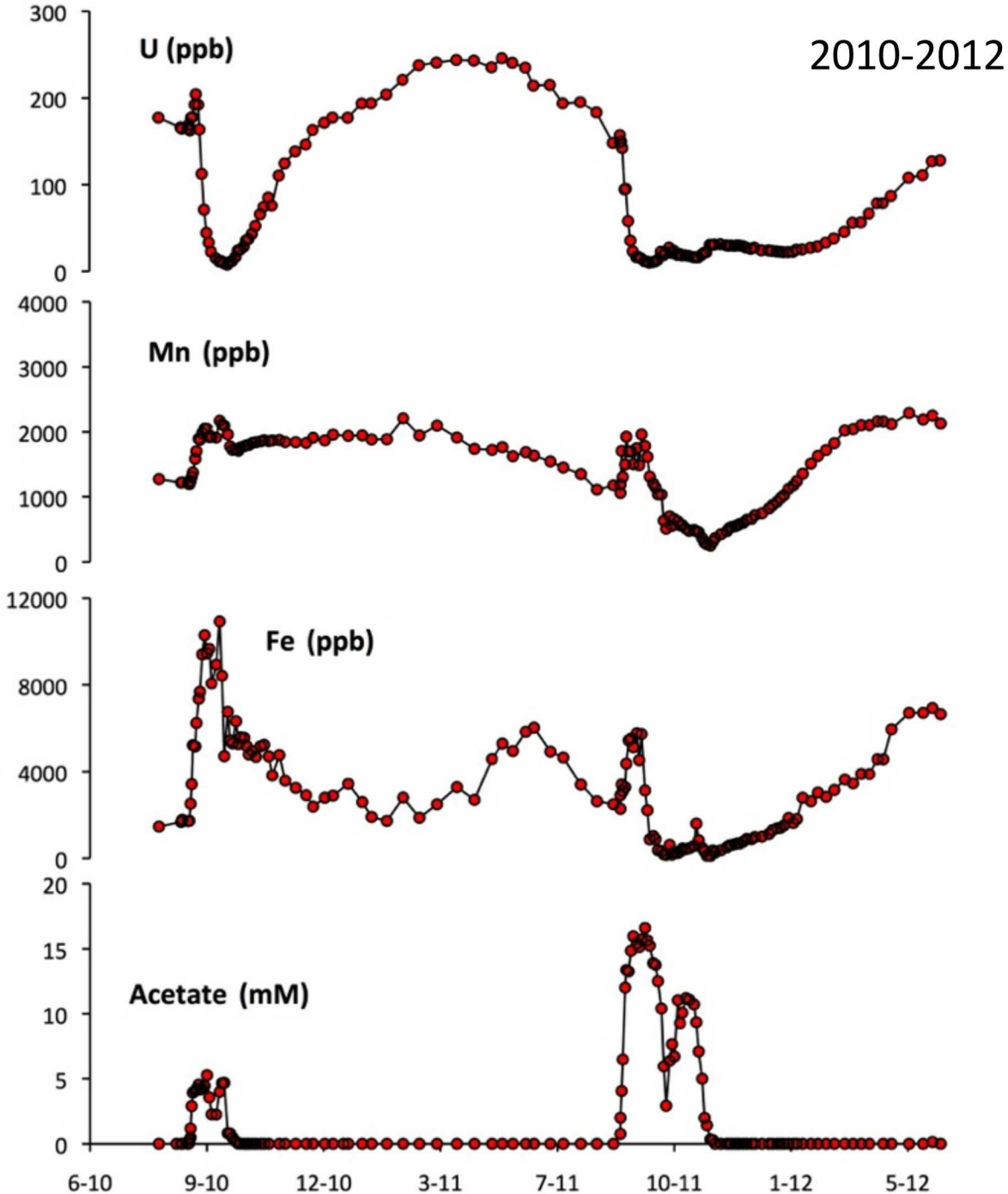




Six well fields installed from 2002-2010 to examine subsurface biogeochemistry and pathways relevant to uranium remediation

Reductive enzymatic immobilization of U through carbon (acetate) addition

Field testbed for uranium remediation studies

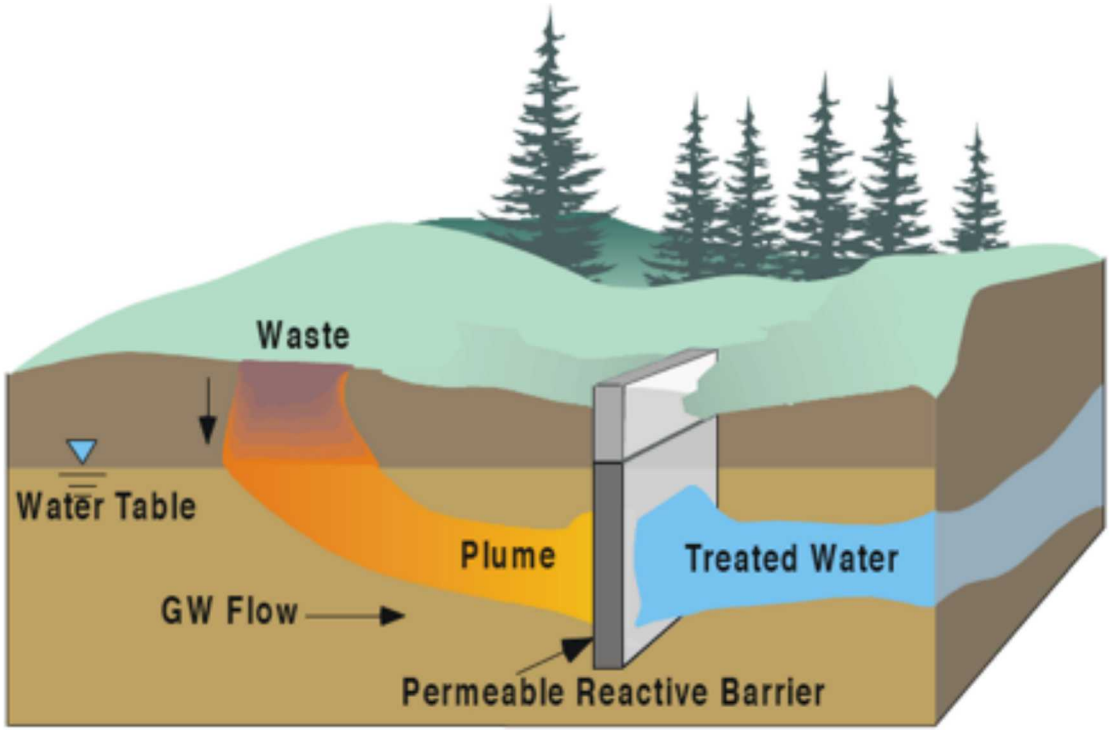


Key take away:

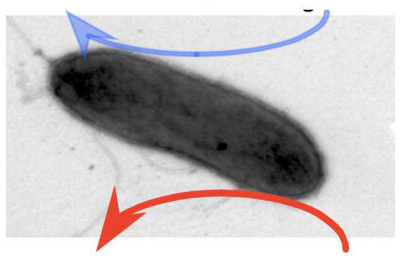
U removal through organic carbon addition can be effective *so long as the loading is sustained*

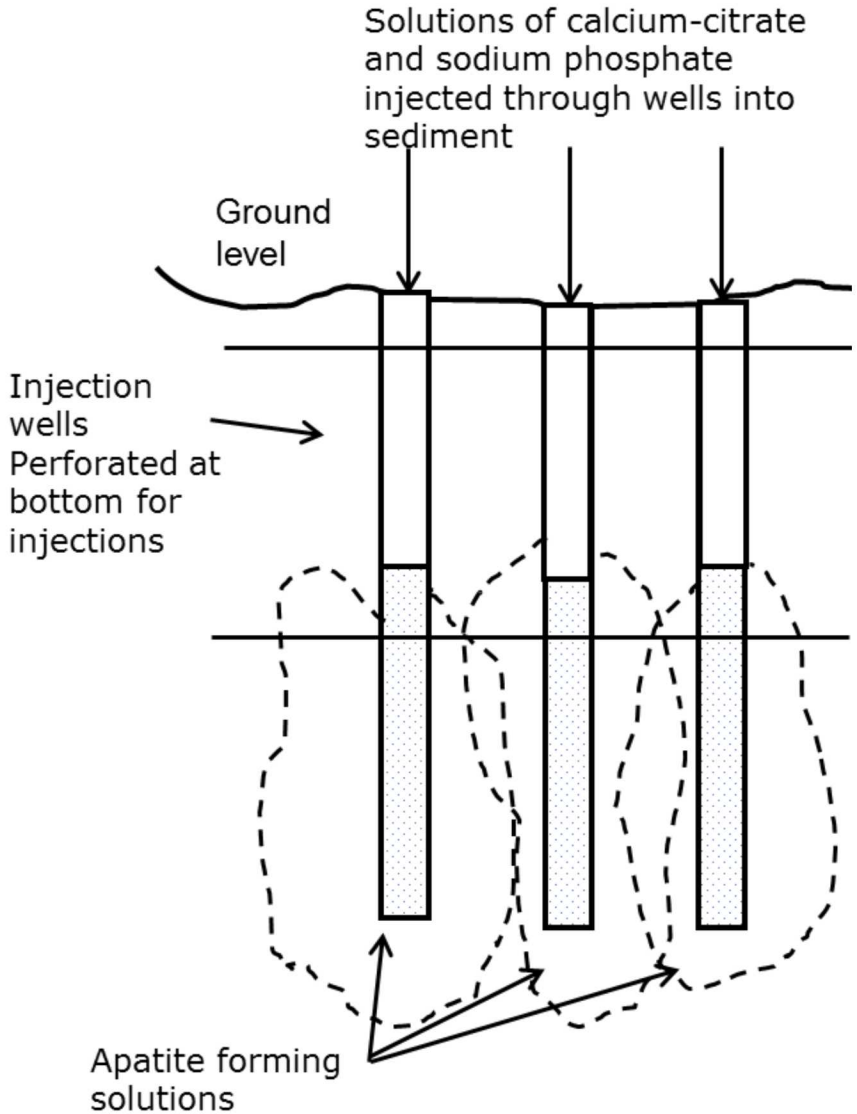
More effective alternatives?

Apatite-based “Chemically Induced” Permeable Reactive Barrier (PRB) Technology



Citrate degradation



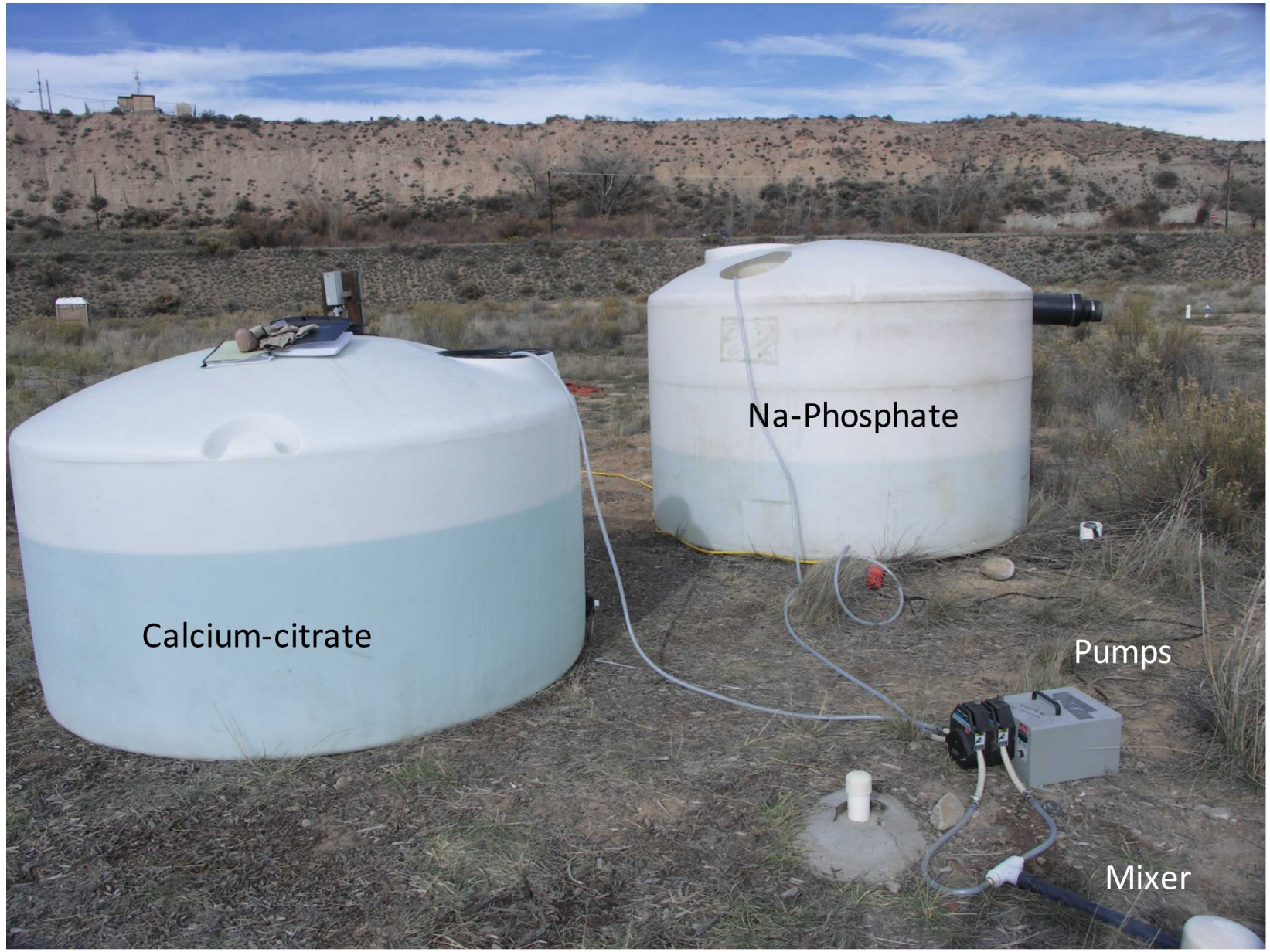


Slow release: calcium–$(citrate)_2$ + sodium phosphate → apatite

Hydroxyapatite as a PRB Material

- 3-dimensional lattice of calcium phosphate, $Ca_{10}(PO_4)_6(OH)_2$
- Very stable; extremely low solubility.
- Can sequester a wide variety of radionuclides, heavy metals and other contaminants through substitution into the structure or sorption onto the surface as metal phosphate compounds.
- Immobilization and sequestration of uranium as an oxidized (U^{6+}) form → less prone to (re)oxidative dissolution
- Can be formed in situ by solution injection in the subsurface…

Hydroxyapatite injection design



Hydroxyapatite injection parameters

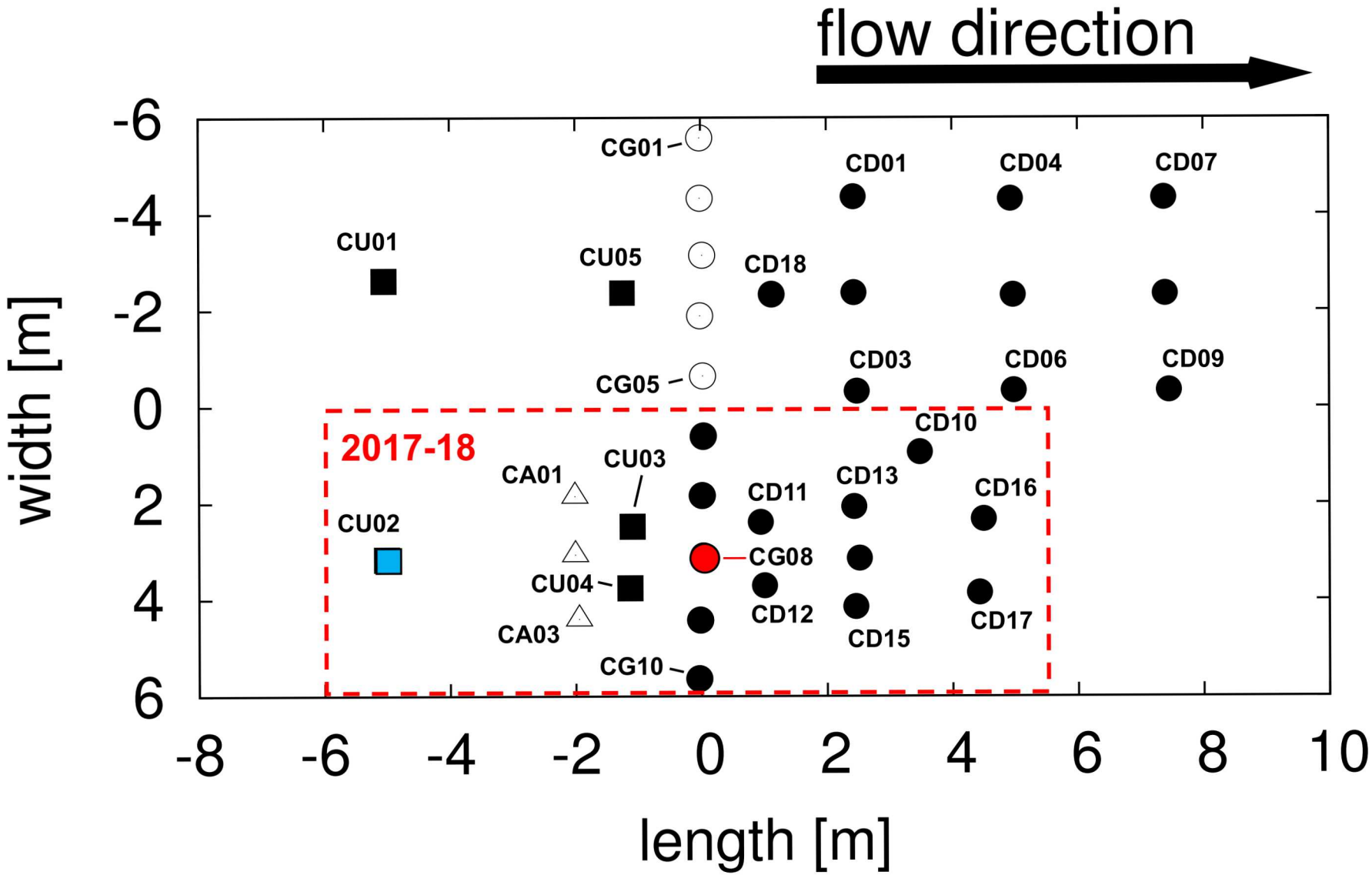
- Injection Formulation:

  Tank 1: Solution containing 40mM of Ca^{2+} (as $CaCl_2$), 100mM citrate (as Na-citrate) and 40mM Bromide (as NaBr)

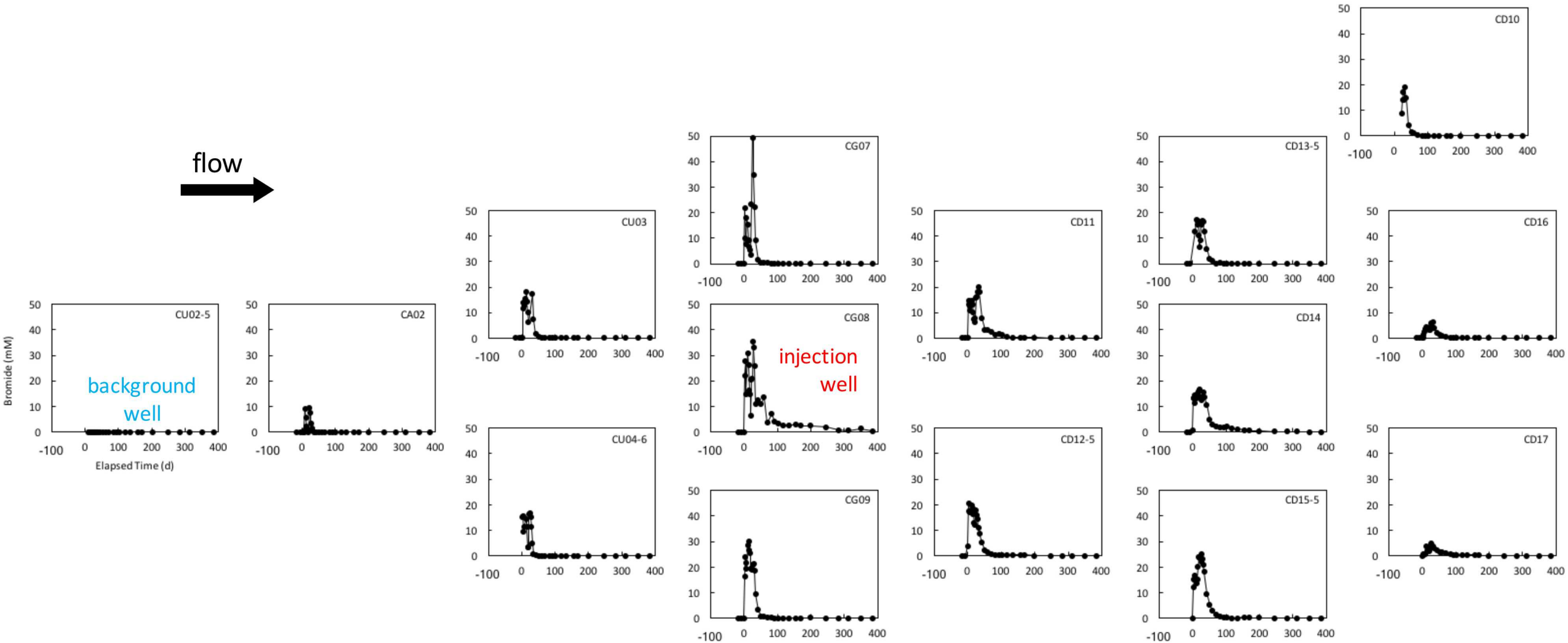
  Tank 2: Solution containing 40mM phosphate (as Na_3PO4)

- Injection of 18,000 L of solution total (~ 5 pore volumes)
- Three injections total: Nov. 14th, 21st, and Dec. 5th, 2017.
- Injection Rate Varied: ~4 to 16 liters per minute.
- Injections completed within 24 to 56 hours.

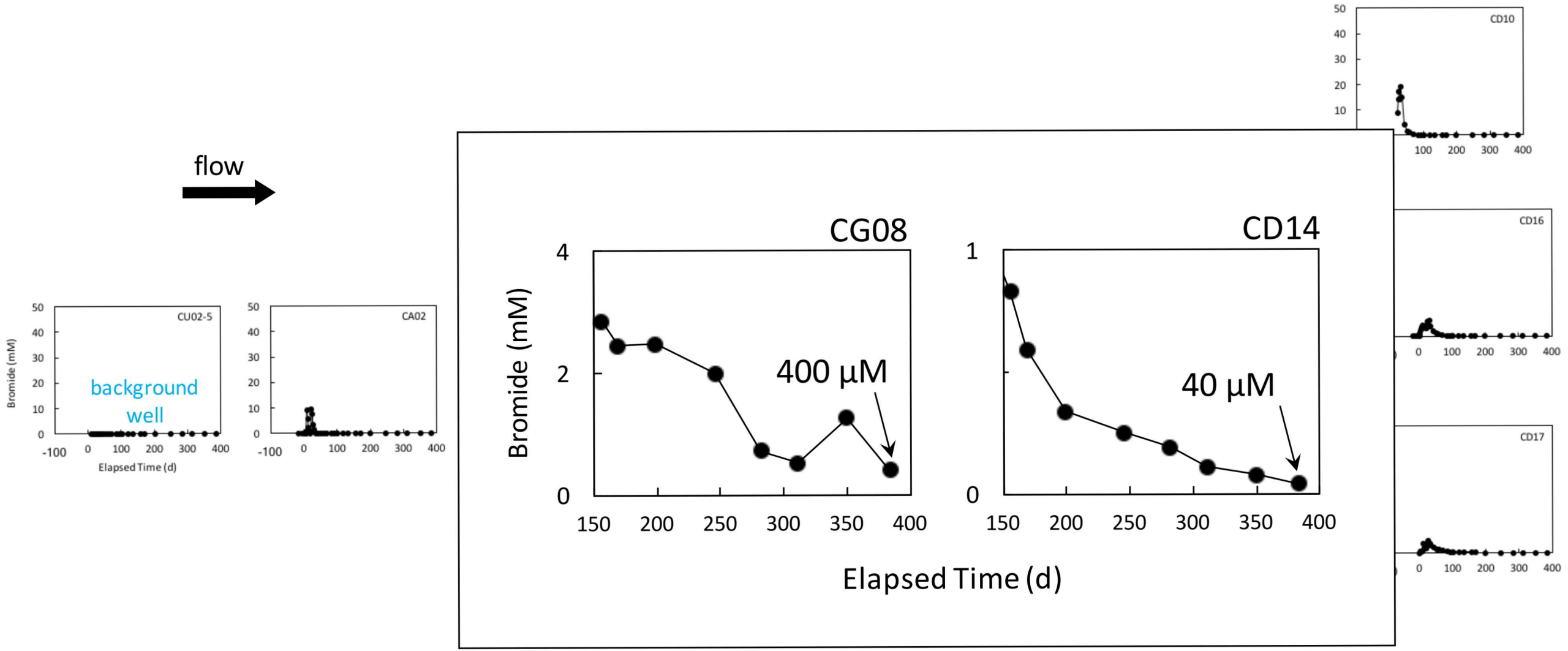
Plot C: Well field layout



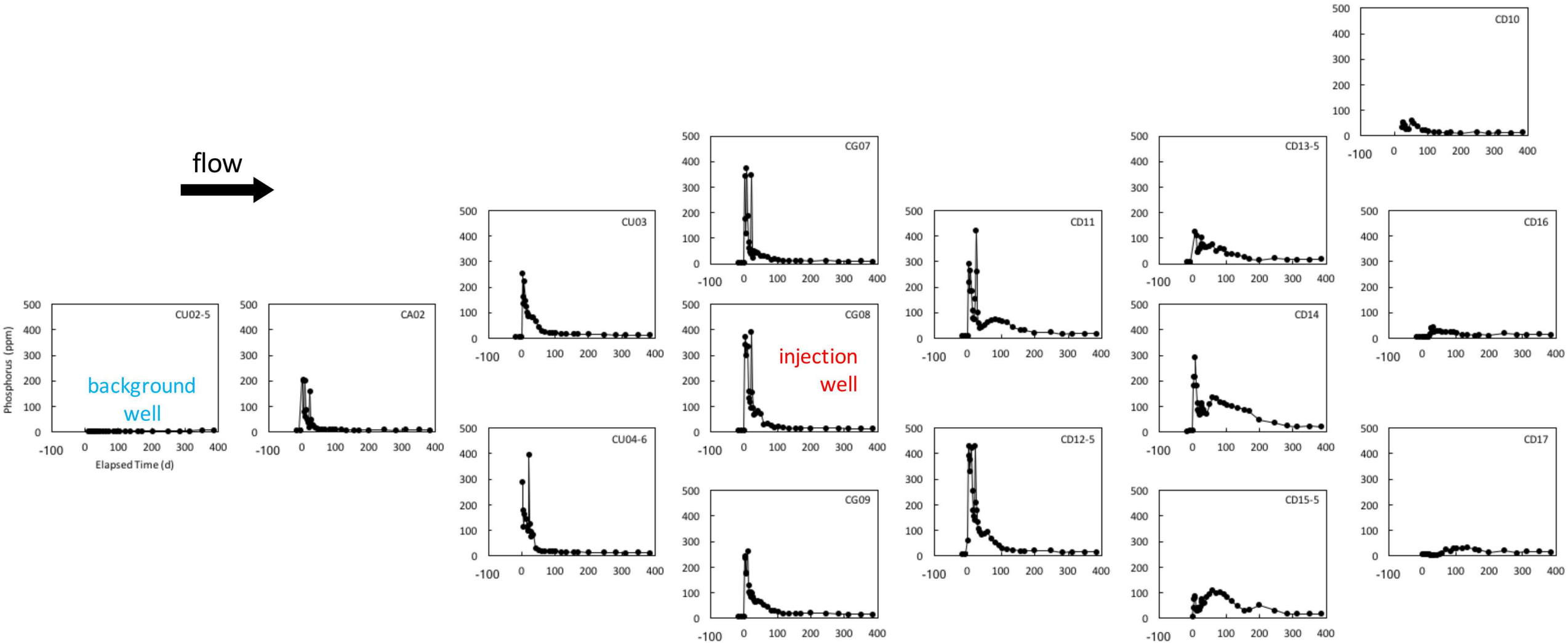
Bromide (mM)


flow
Bromide (mM)
Elapsed Time (d)
CU02-5
background well
CA02
CU03
CU04-6
CG07
CG08
injection well
CG09
CD11
CD12-5
CD13-5
CD14
CD15-5
CD10
CD16
CD17

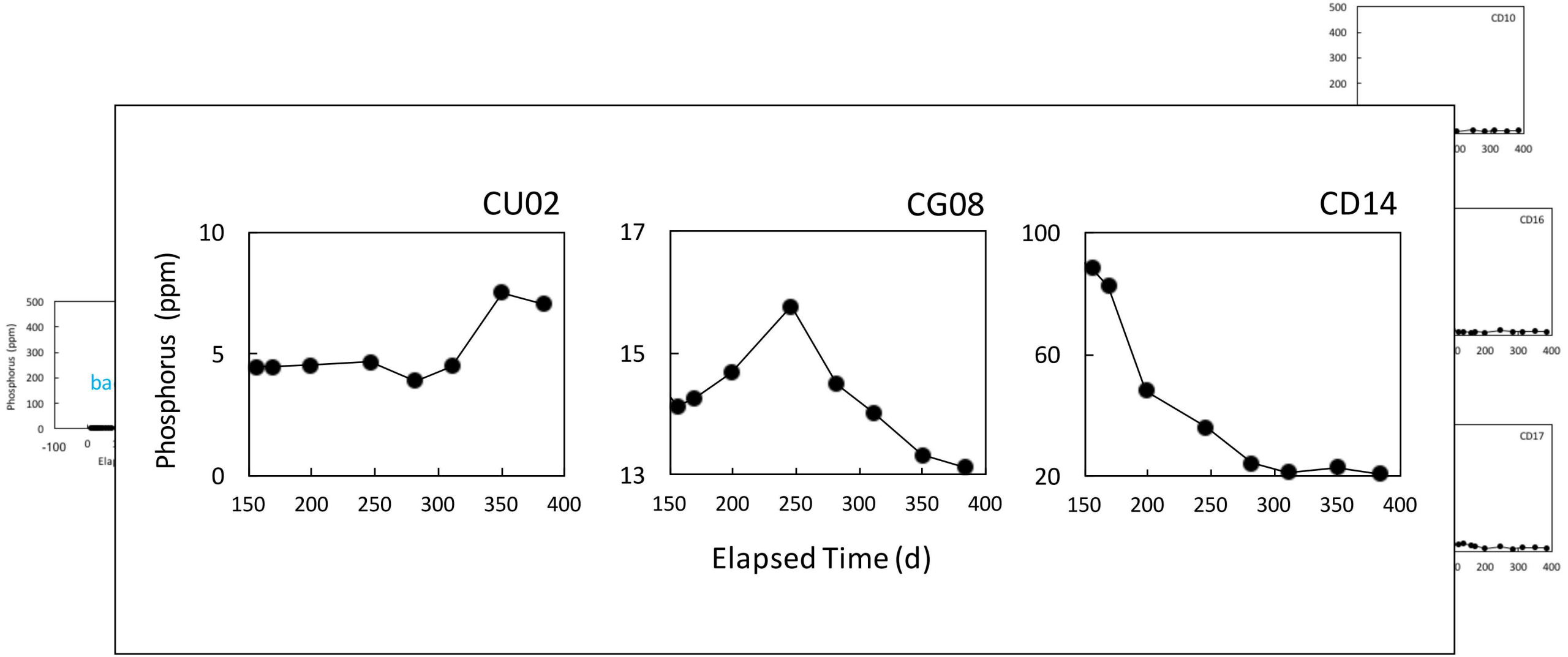
Bromide (mM)


flow
CU02-5
CA02
background well
Bromide (mM)
Elapsed Time (d)
CG08
CD14
400 µM
40 µM
CD10
CD16
CD17

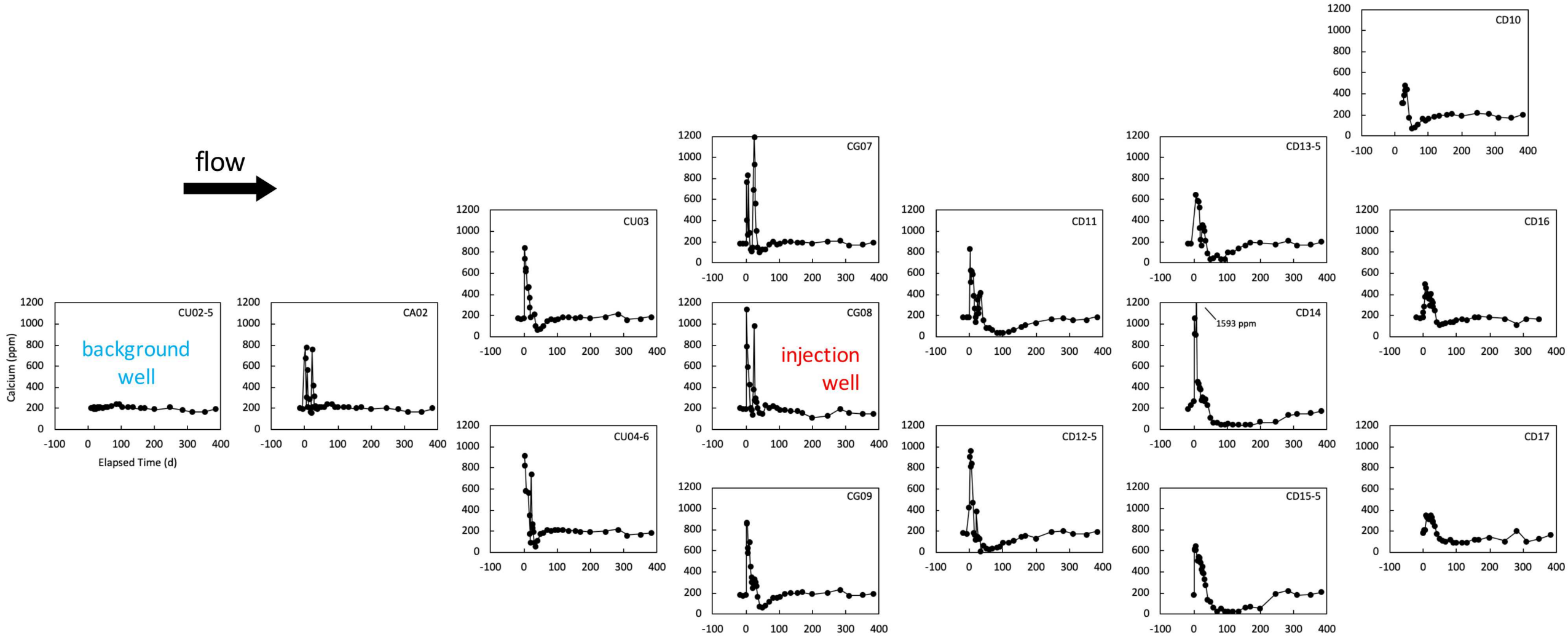
Phosphorus (ppm)



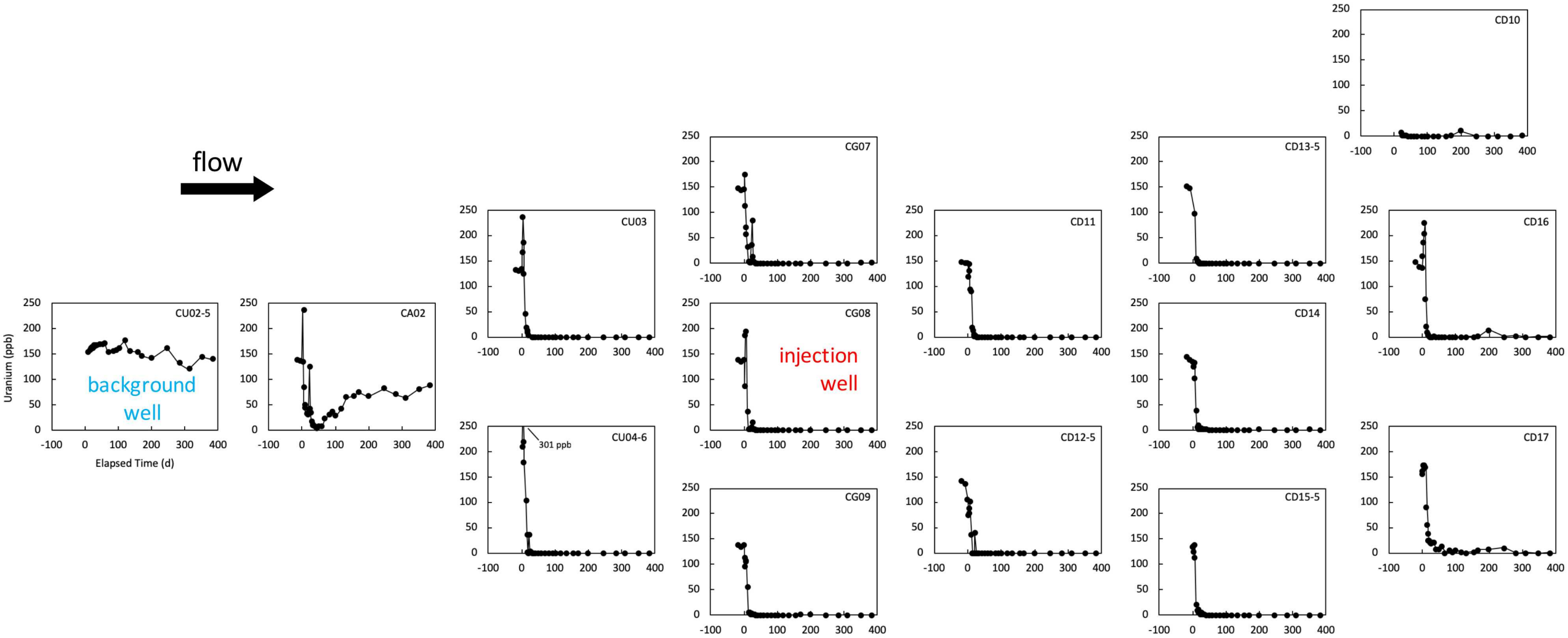
Phosphorus (ppm)



Calcium (ppm)

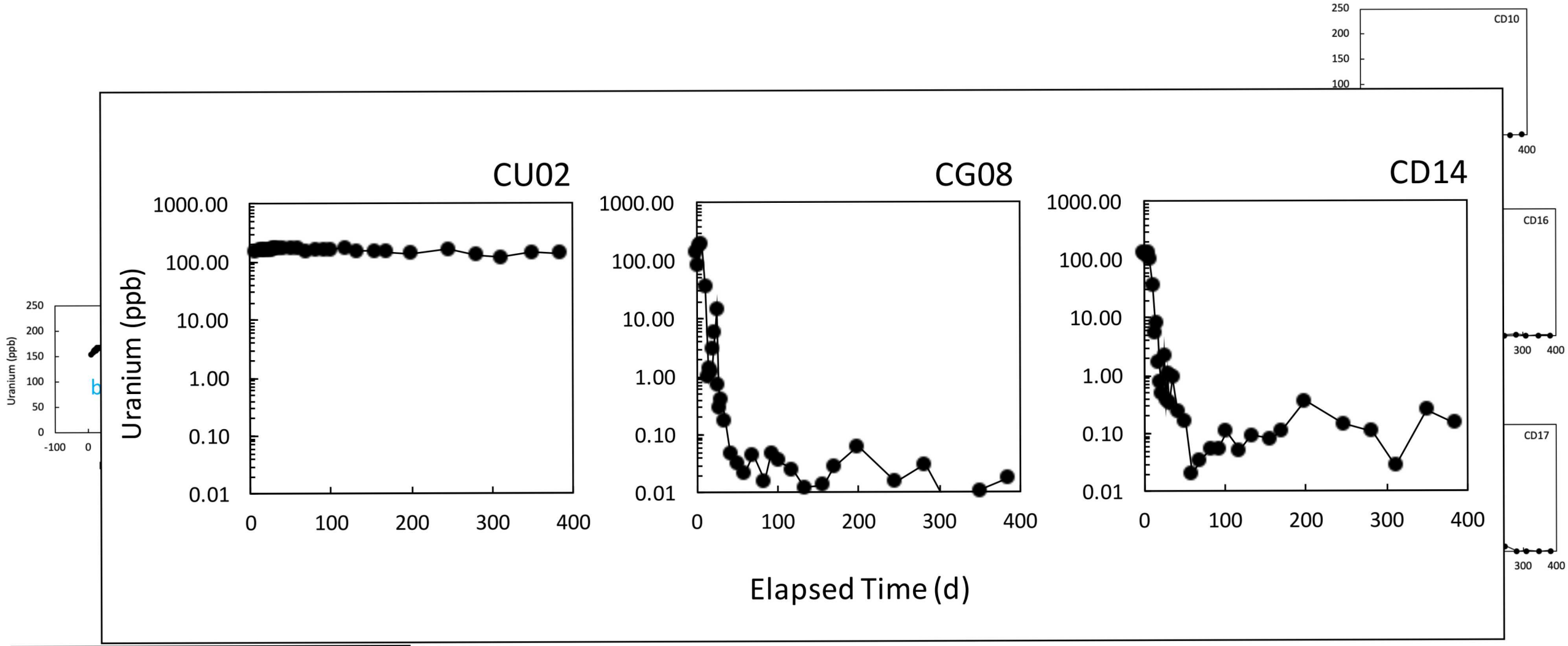

flow
Calcium (ppm)
Elapsed Time (d)
CU02-5
background well
CA02
CU03
CU04-6
CG07
CG08
injection well
CG09
CD11
CD12-5
CD13-5
CD14
1593 ppm
CD15-5
CD10
CD16
CD17

Uranium (ppb)



EPA MCL = 30 ppb
UMTRCA limit = 44 ppb

Uranium (ppb)



EPA MCL = 30 ppb
UMTRCA limit = 44 ppb

Next steps:

- Long-term monitoring to assess eventual U breakthrough
- Drilling / sediment recovery to assess removal pathway(s)
- Validation of the technology at other former U mill sites

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- Long-term
  eventual U
- Drilling / se
  assess rem
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Thank you.

Questions or comments?