NATURAL RATE OF SELENIUM ATTENUATION AT SOUTHERN WEST VIRGINIA SURFACE MINES

West Virginia Mine Drainage Task Force
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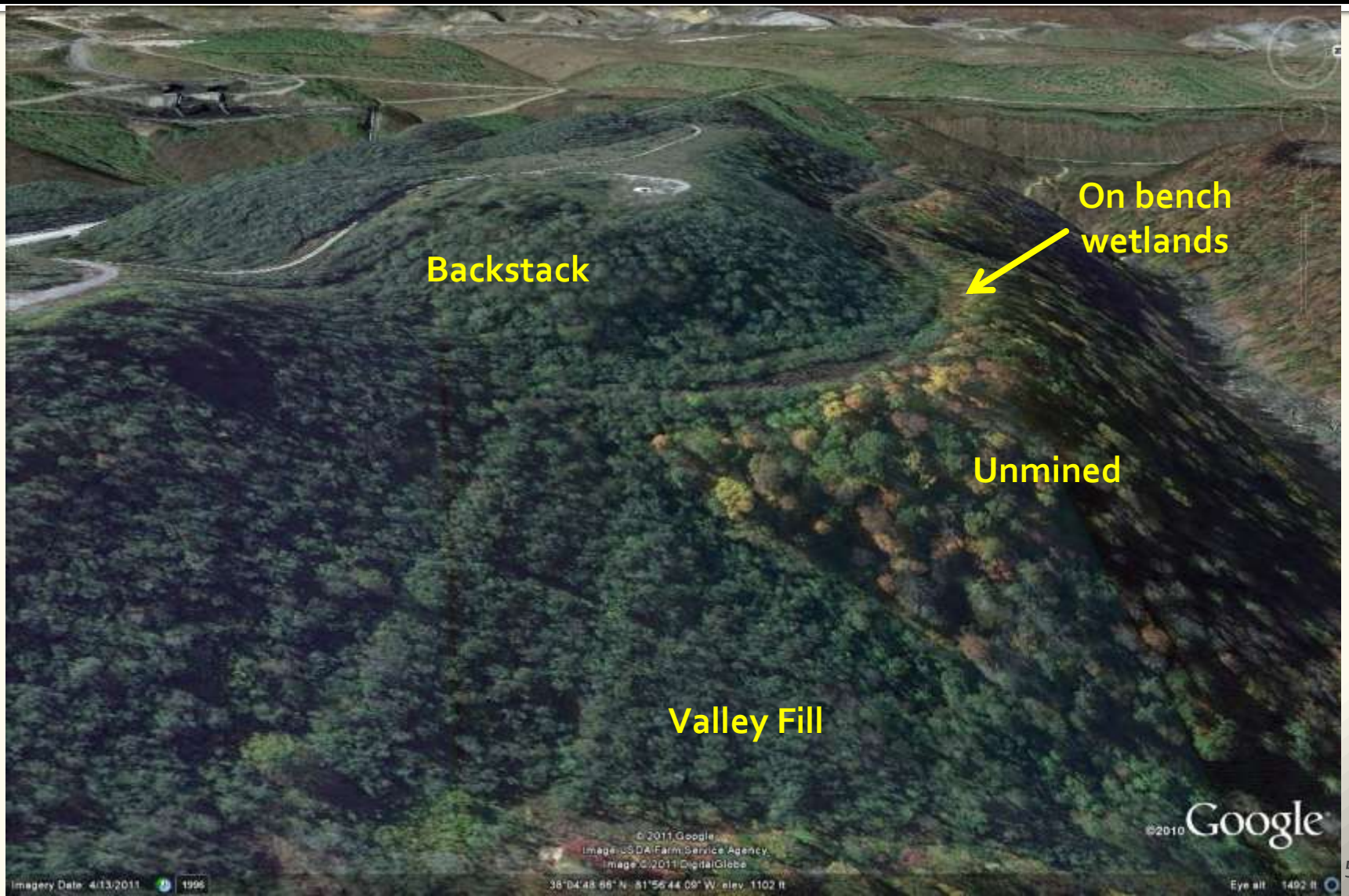
Allegheny Plateau-pre mining

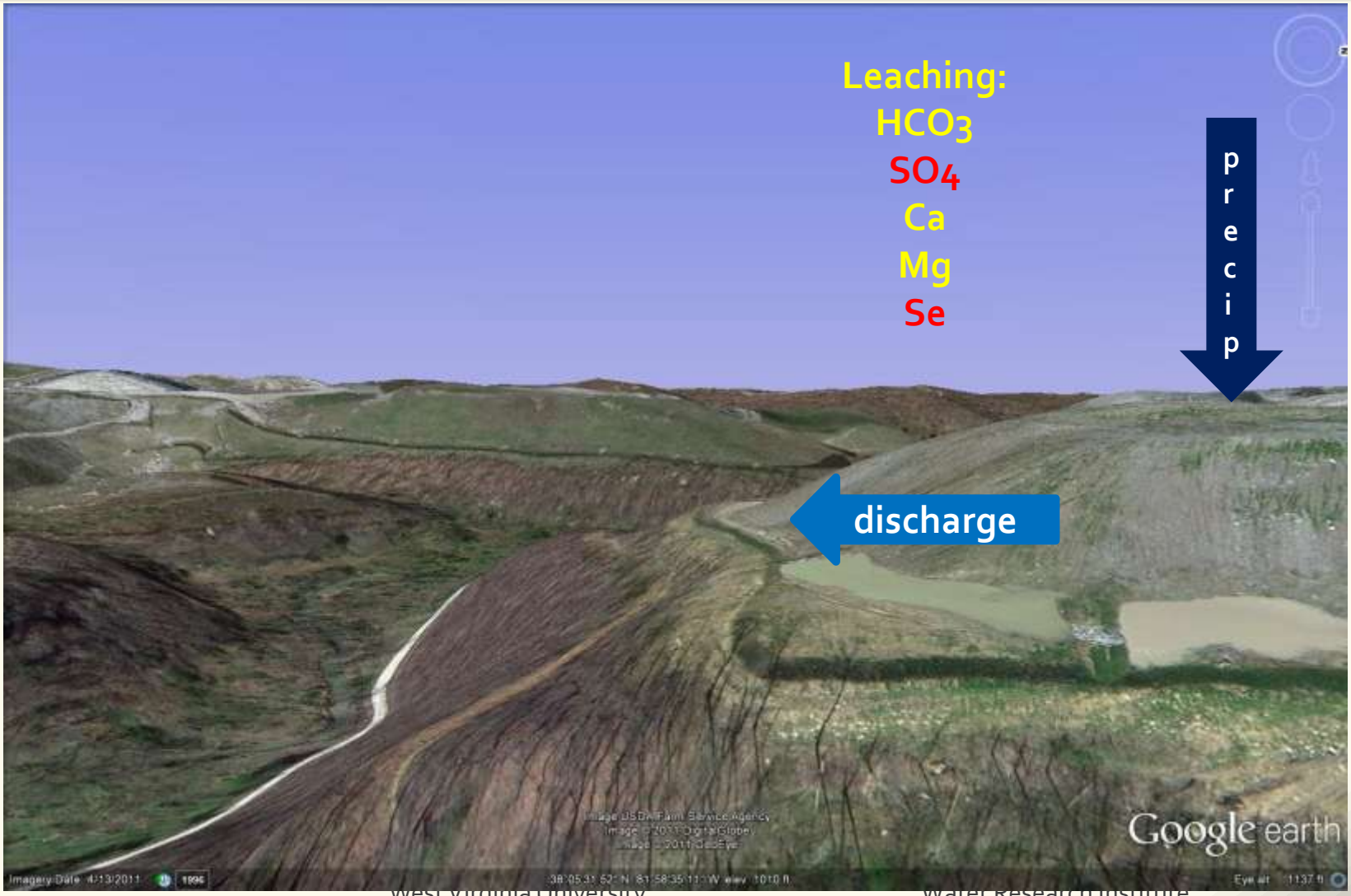
Typical mountaintop mine: Oldest mining (1985) in foreground

Stanley Fk-re established stream/valley fill

Mountaintop mining: Nomenclature



Southern WV mountaintop mining: Infiltration, leaching and discharge



The ratio of Sulfur to Selenium in coal overburden is at the low end of the crustal ratio

Coal overburden

Typical concentrations		mg/kg	S/Se
Se	1 mg/kg	1	
S_{low}	0.2%	2,000	2,000
S_{high}	1.0%	10,000	10,000

crustal concentrations*		mg/kg	S/Se
Se	50 µg/kg	0.05	
S	420,000 µg/kg	420	8,400

* http://www.webelements.com/periodicity/abundance_crust/

Potentially mobile selenium 25 to 35%

- Roy and Vesper: Sequential Extraction
  - 25 to 35%
- Pumure, Renton and Smart:
  - Sequential extraction: 36%
  - Sonication: 32%

In-situ Selenium Treatment

- Postulated selenium weathering process:

1. Selenide: Se^{-2} FeSe

   Rapidly oxidizes to:

2. Selenite: Se^{+4} SeO_3^{2-} Sorbs to FeOOH

   Slowly oxidizes to:

3. Selenate: Se^{+6} SeO_4^{2-} Highly Mobile !!

- The goal is to catch selenium at step #2

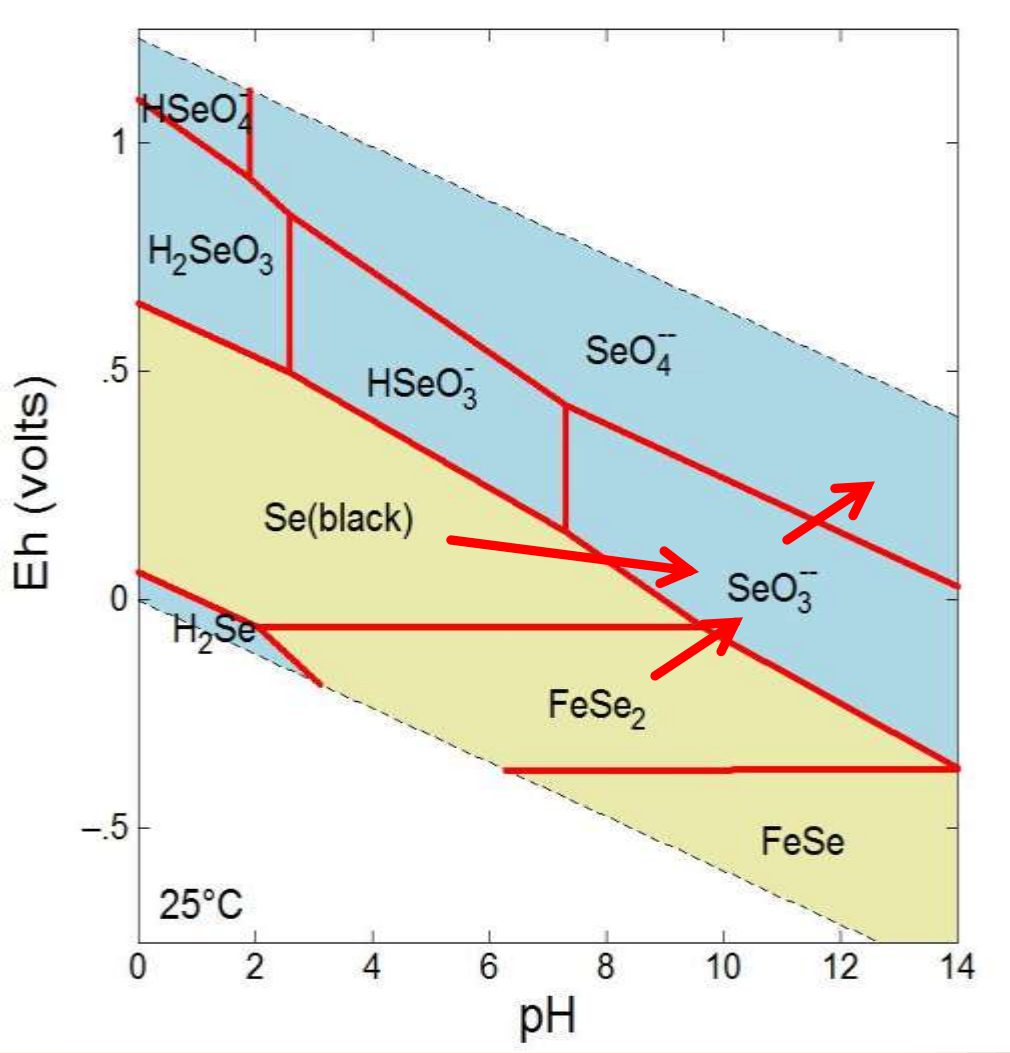
Selenium minerals in coal/sedimentary rock

Immobile fraction:
65 to 75%
(organically bound)

Most selenium occurs as organic mineral complexes. Likely remains immobile much like organic sulfur.

Mobile fraction:
25 to 35%
(inorganic)

Weathering causes elemental selenium and selenides to oxidize to the oxyanions selenite and selenate.

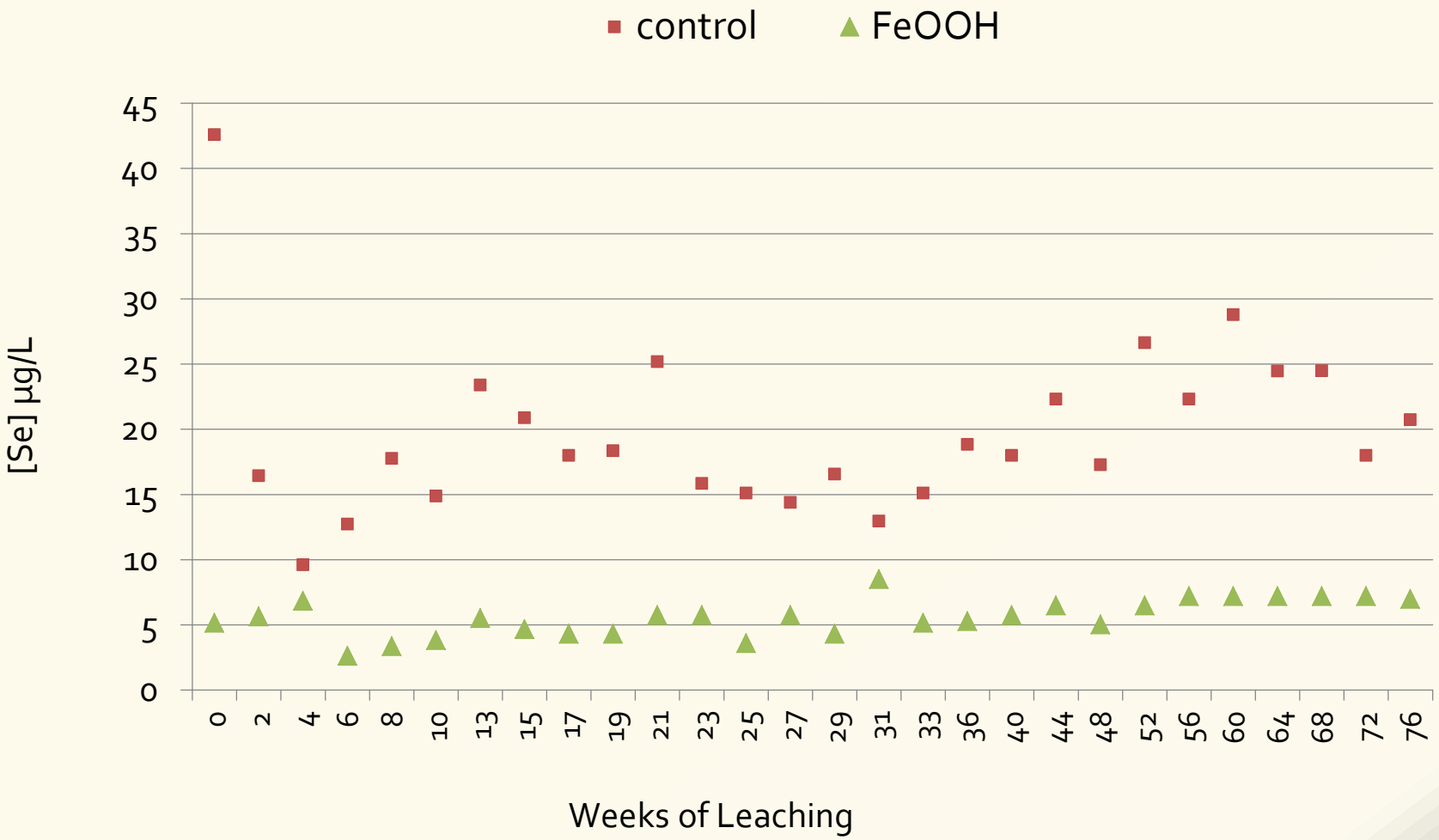


Selenium is released much more rapidly than sulfur and there is much less

- Sulfur release rates:
  - 0.006% /day-Coal iron sulfides to
  - 0.0007 %/day-Hydrothermal pyrite
  - 0.0061%/day –This experiment
- Selenium release rates:
  - 0.06 declining to 0.04%/day-This experiment
- Selenium is released about 10 times faster than sulfur
- Also, selenite is absorbed by ferrihydrite

About 75% of Se was absorbed by FeOOH*

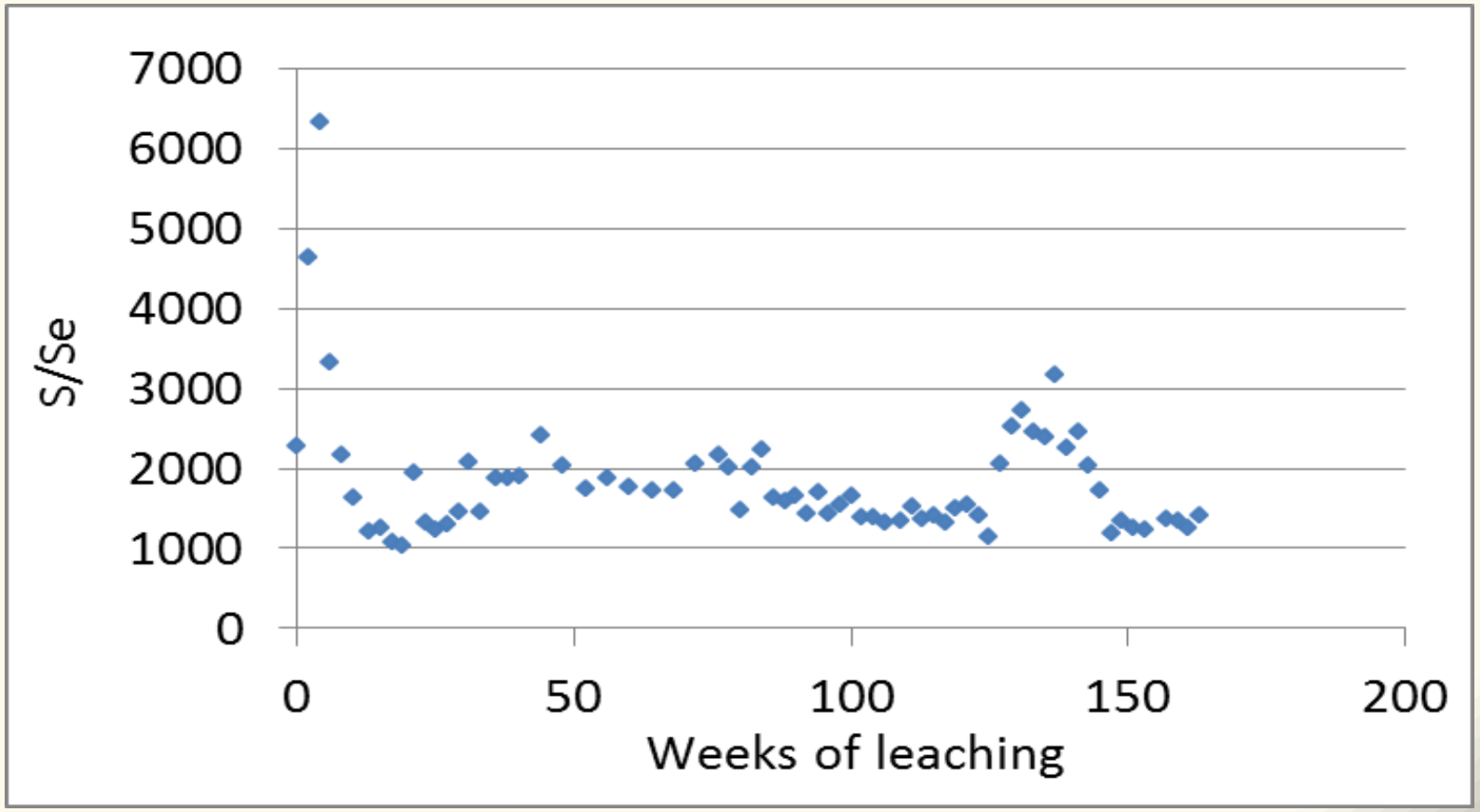
*Ziemkiewicz, O'Neal and Lovett . Mine Water Environ (2011) 30:141–150
DOI 10.1007/s10230-011-0154-4



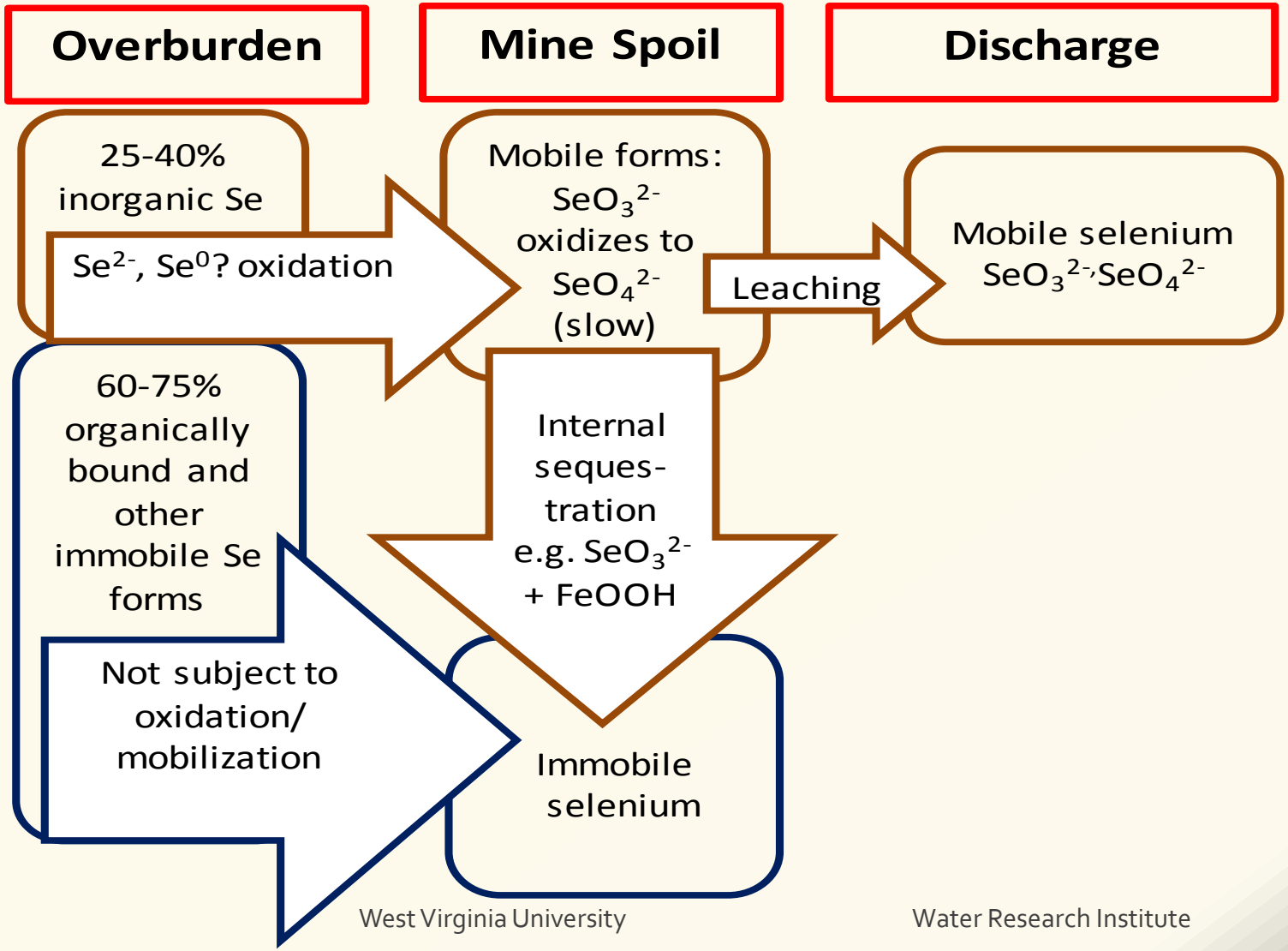
The ratio of sulfur to selenium is nearly constant suggesting a mineralogical link

Iron selenide replacement of pyrite? $Fe_xS(Se)$

average S/Se =1,833



Selenium weathering model



Selenium kinetics were studied at three scales

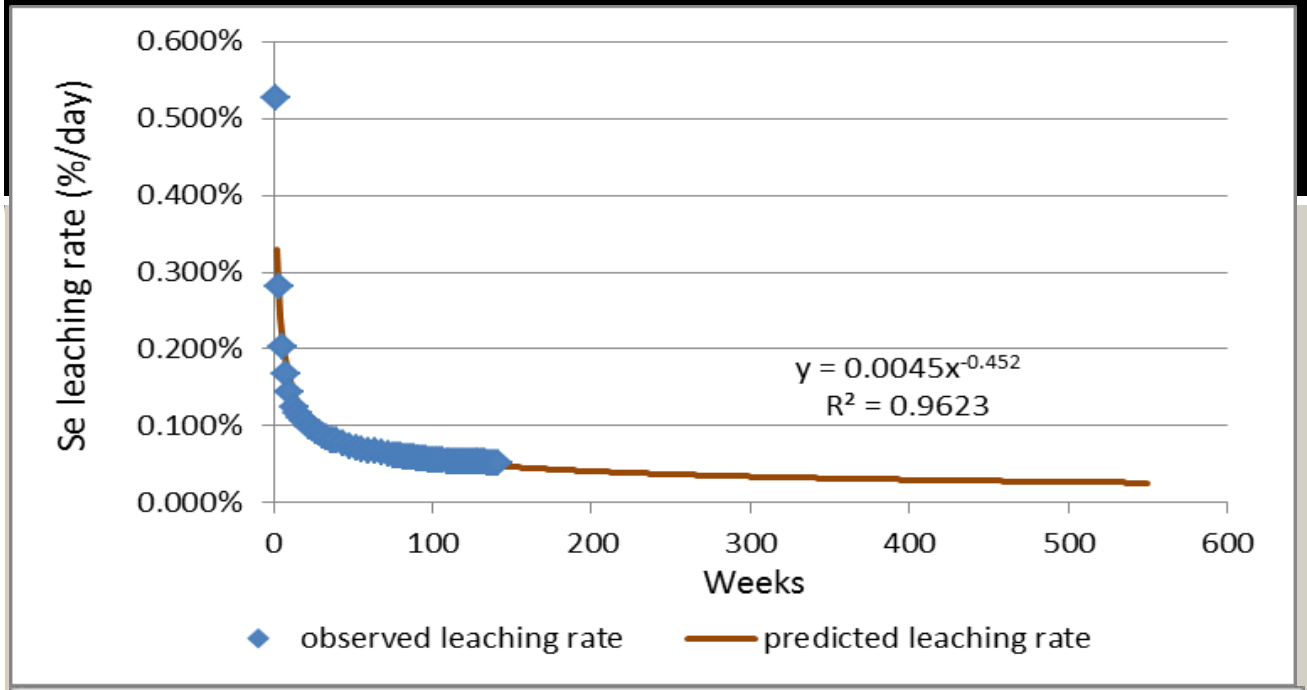
- Laboratory-145 weeks of weathering/leaching in humidity cells
- Field
  - Outlet study: 67 outlets sampled over an eight year period representing 25 years post initial mining-5,388 samples
  - Watershed study: Stream samples over two years representing 25 years post initial mining

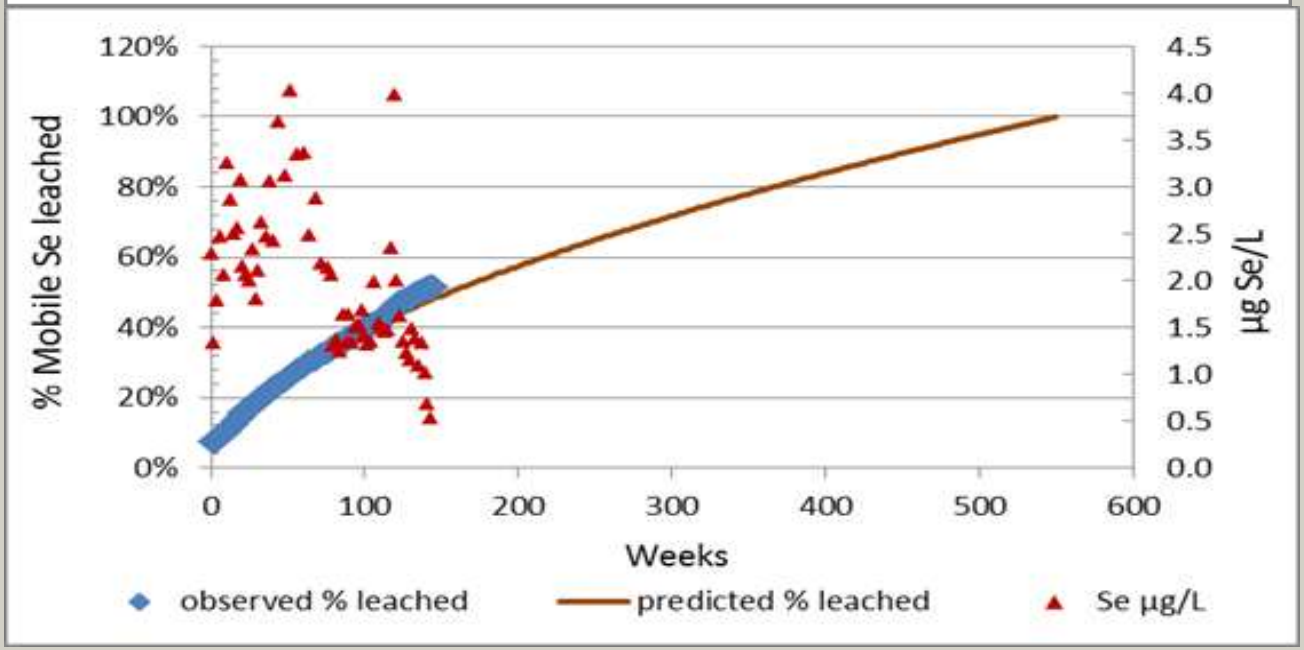
Laboratory study: Selenium leaching rates

The weathering/leaching of selenium is initially rapid, probably due to accumulated salts.

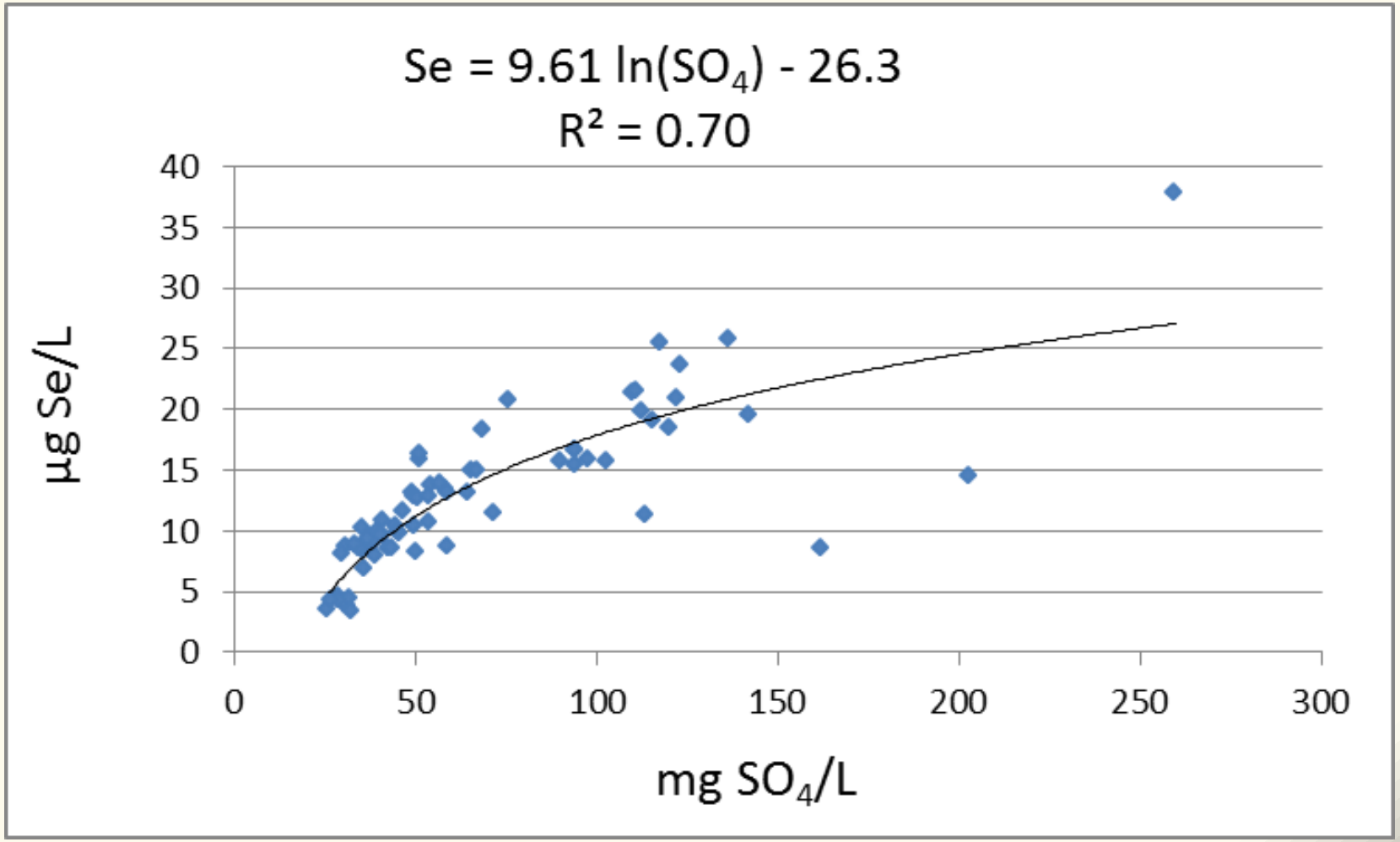
It then stabilizes to about 0.06% per day. Declining to about 0,04% per day after 150 weeks.

Selenium concentration initially increases rapidly to a peak at about 51 weeks, then declined over the next two years.

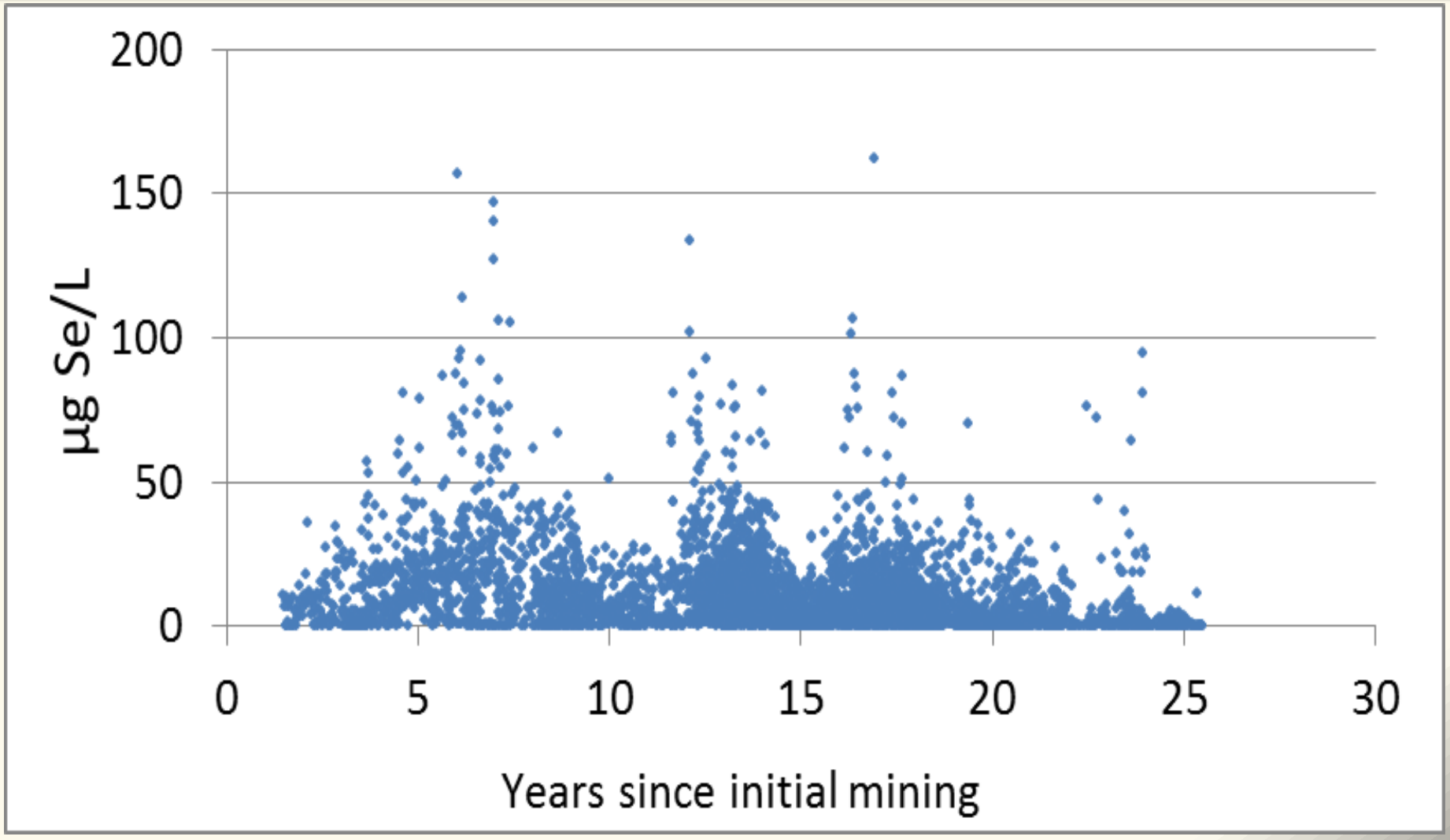




At least in the early stages of weathering, selenium concentration can be predicted by the sulfate concentration



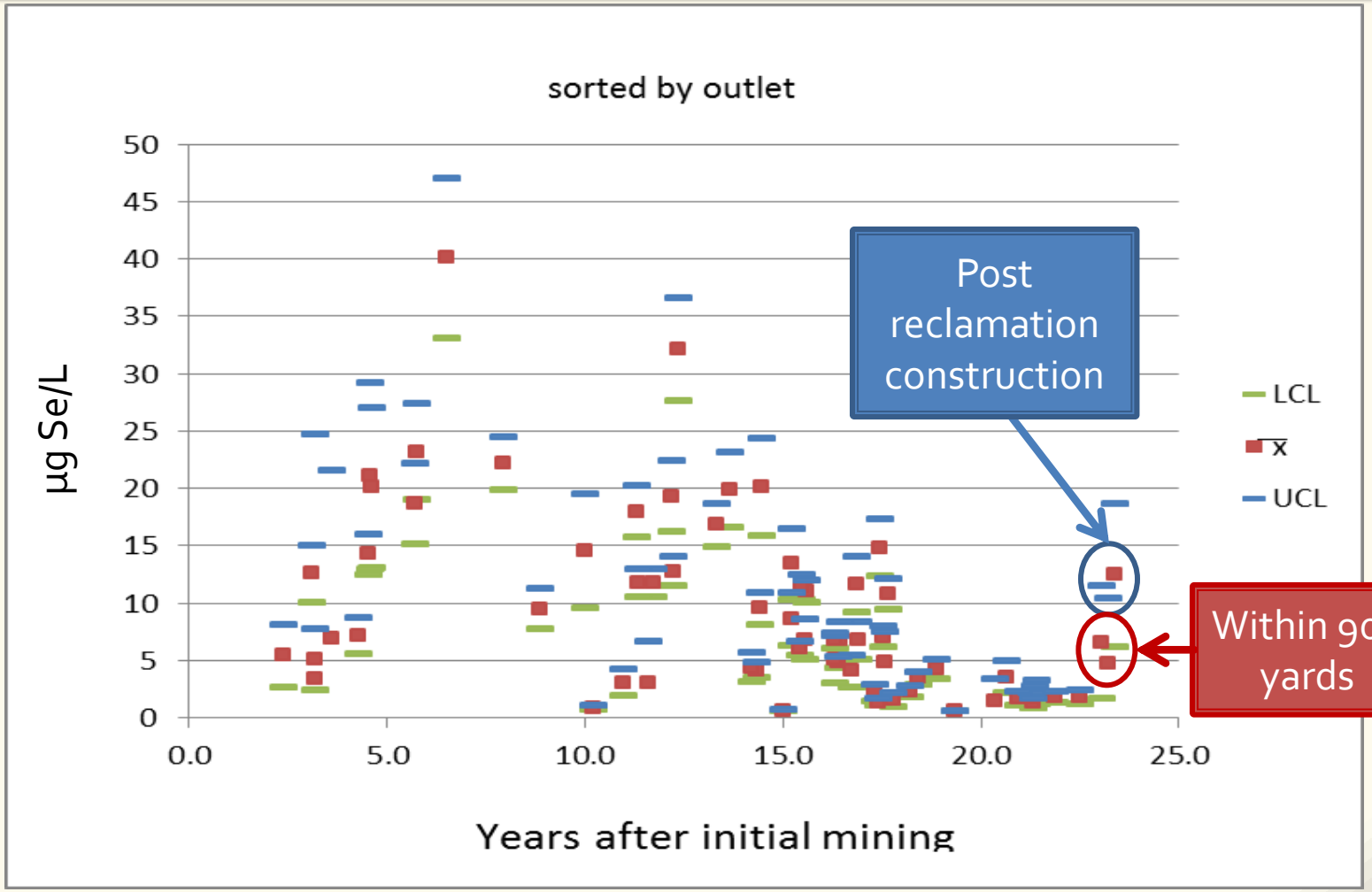
Outlet Study: 5,388 data points sorted by age



Organizing the 5,388 data points

- Individual outlets were sampled over a period of 1-8 years
- X axis always years between permit date and sampling date
- Y axis is the average selenium concentration sorted per:
  - One year age classes (25)
  - Average age of Mine Permit (67)

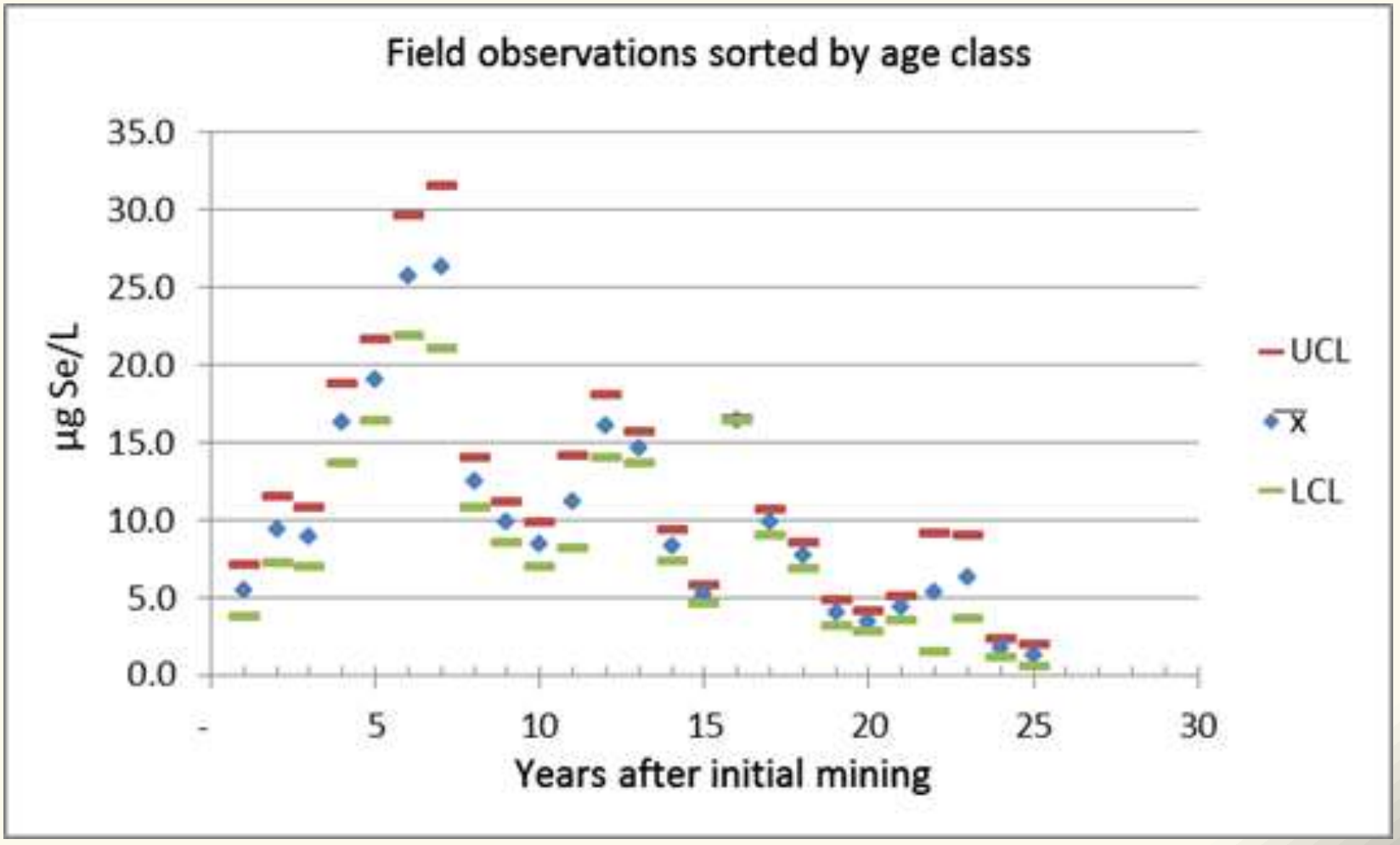
5,388 data points sorted by permit- 95% confidence intervals



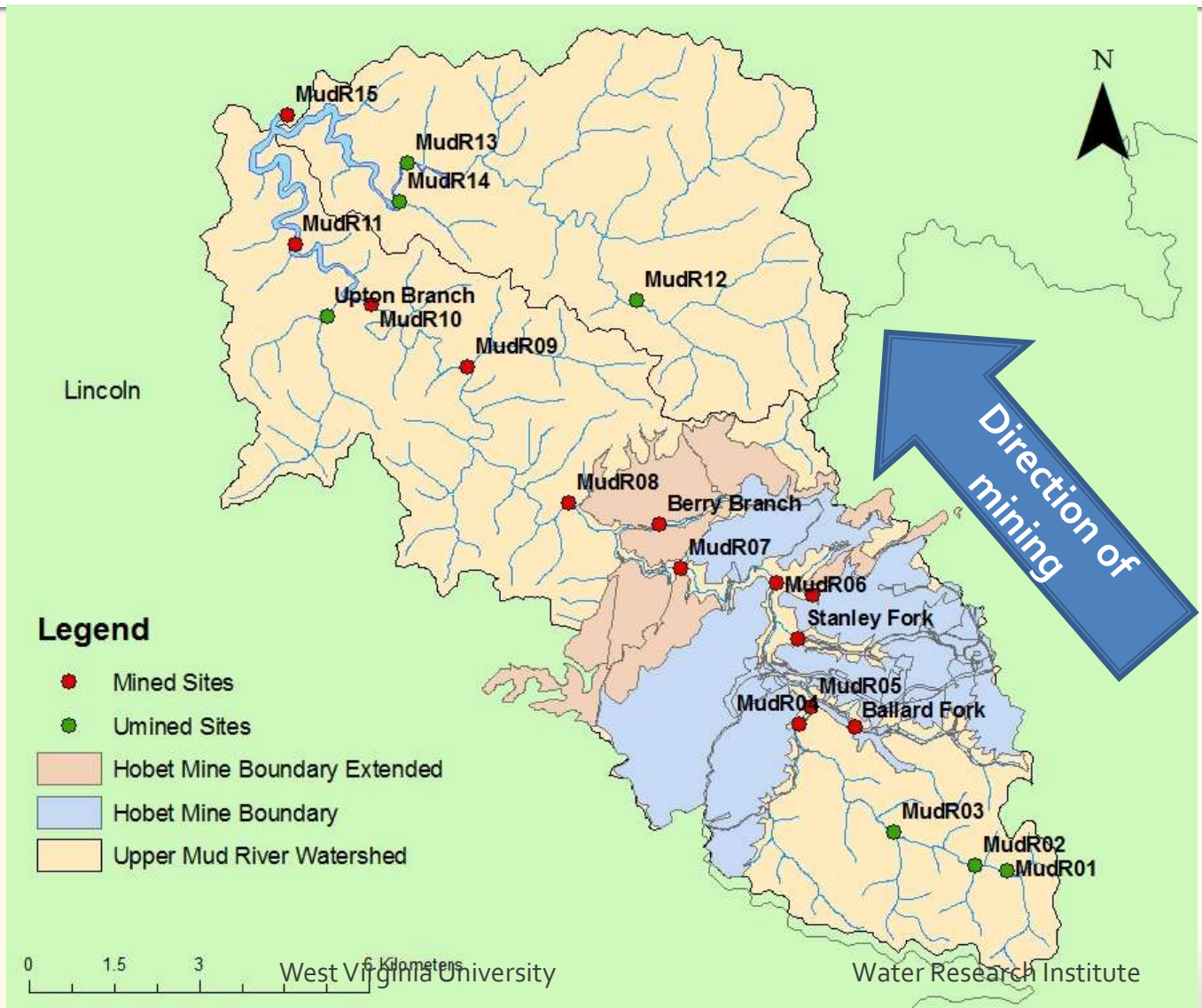
New construction can reset the clock: 1985 permit

New construction can reset the clock: 1985 permit

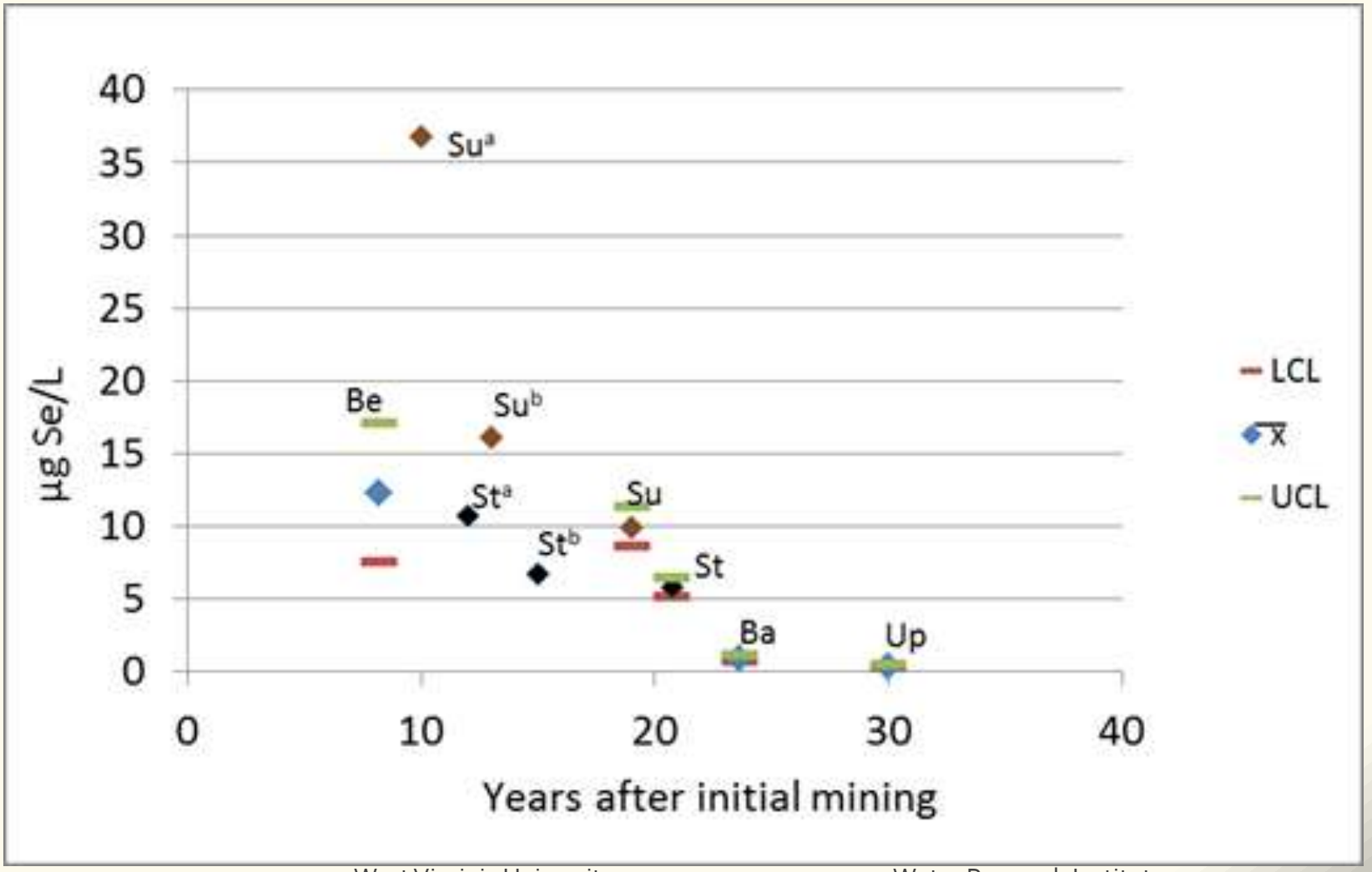
5,388 data points sorted by age class-95% confidence intervals



Field studies: Identifying the time-[Se] relationship at the stream level

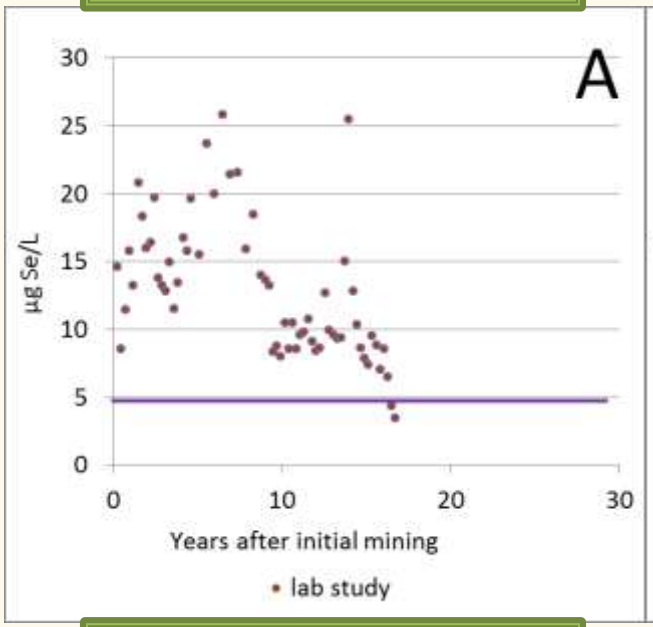


Watershed study

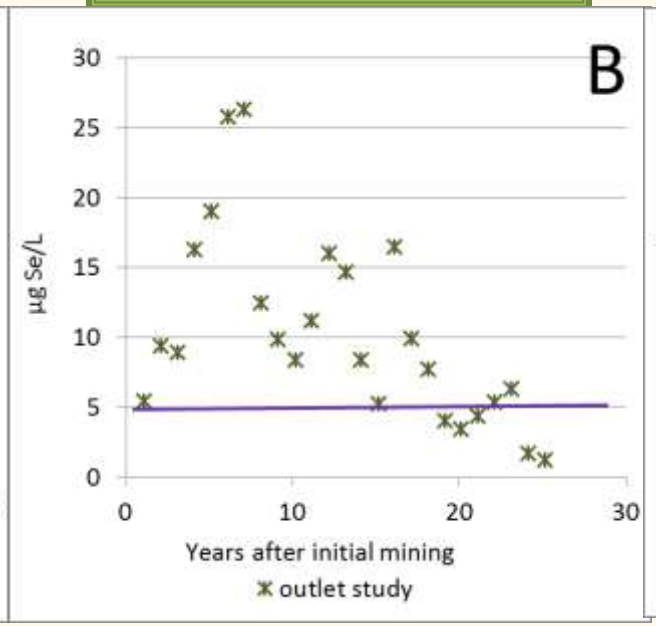


Laboratory and field studies yield similar attenuation curves

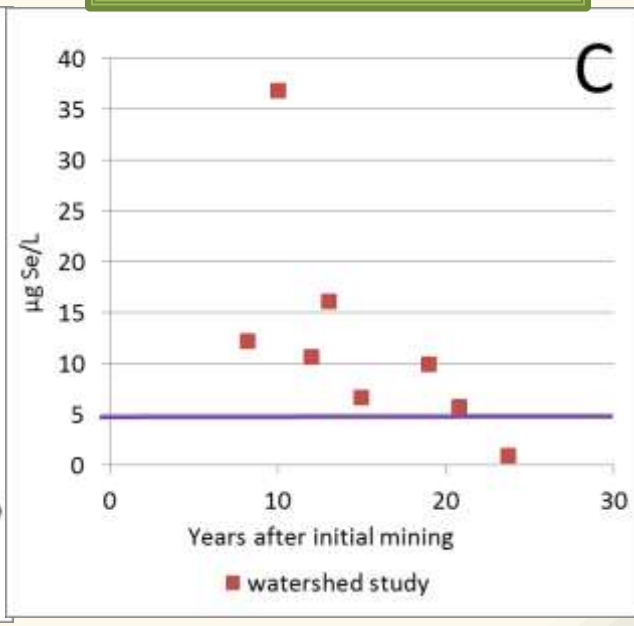
Lab study*



Outlet study



Watershed study



*Adjusted to estimate field concentrations

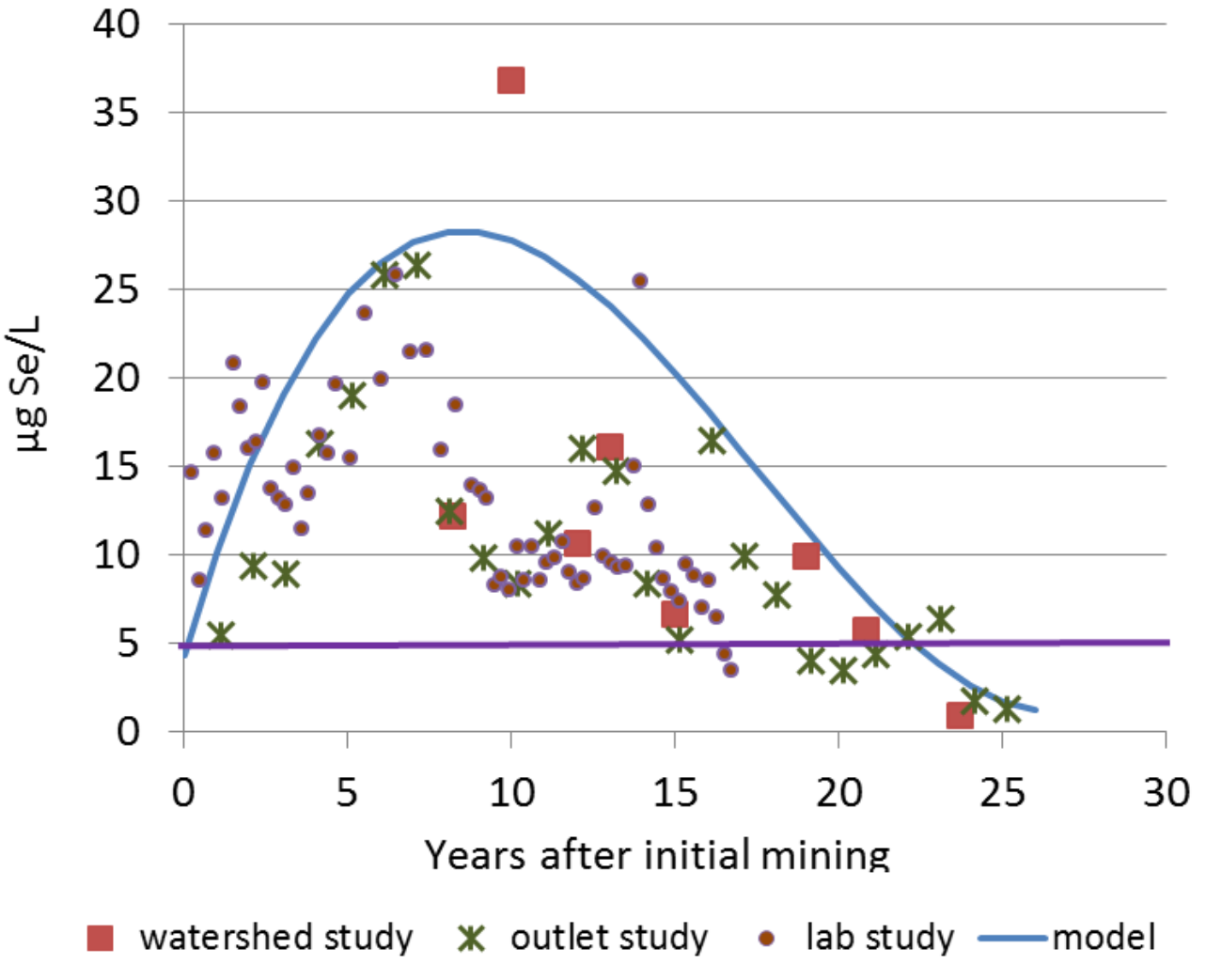
Descriptive Model

In the absence of FeOOH, the Se/time relationship will be described by:

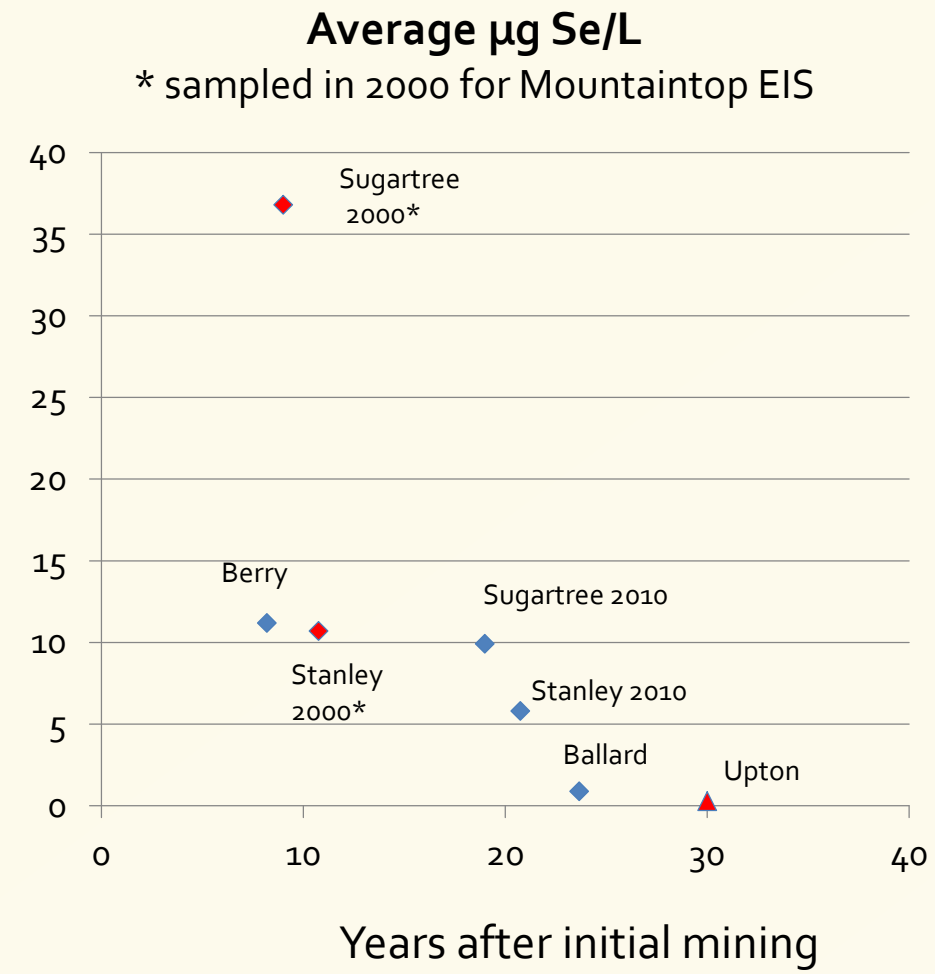
$$y=0.0093x^3+0.49x^2+6.30+4.31$$

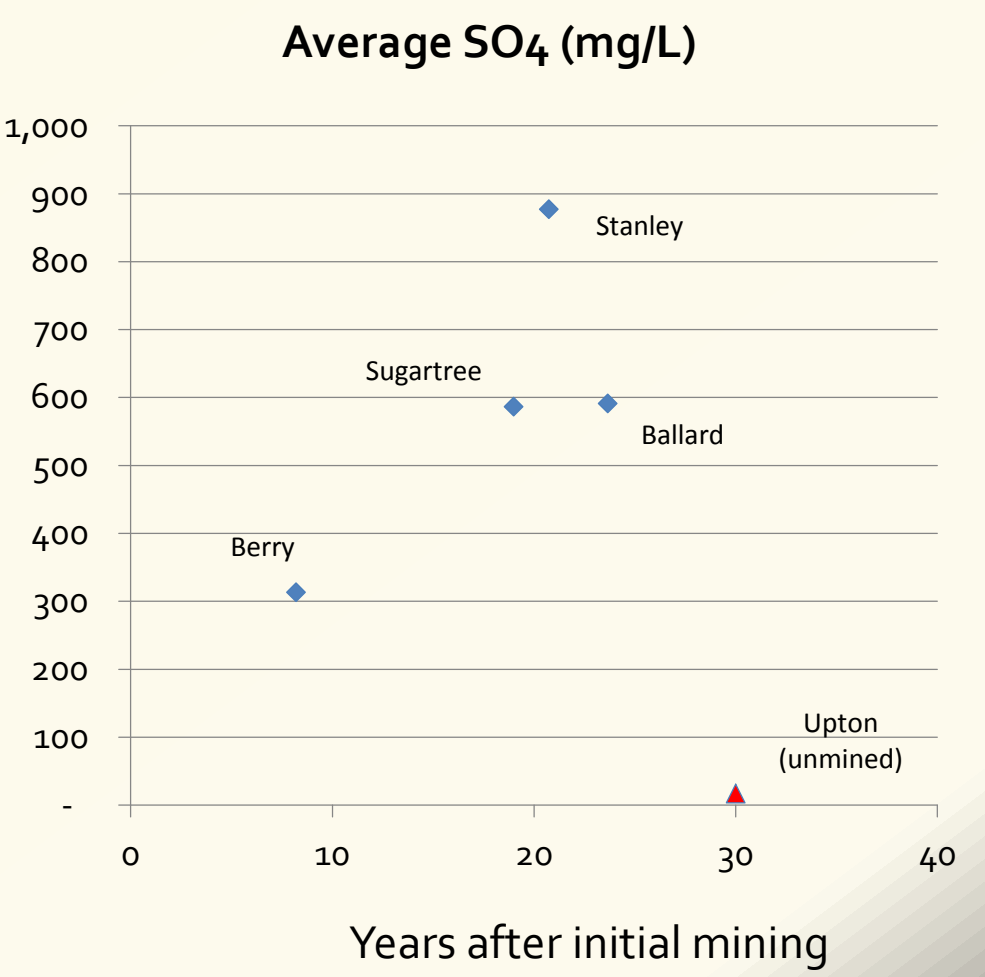
Postulated Ferrihydrite Sequestration

- Occurs at year seven in the lab and outlet studies.
- Coincides with the timing of maximum acidity generation
- (Meek, 1994)
- Saturation/exhaustion of ferrihydrite by year thirteen.
- Selenium then resumes according to the model
- The missing selenium appears to be permanently sequestered
- May be coincidental

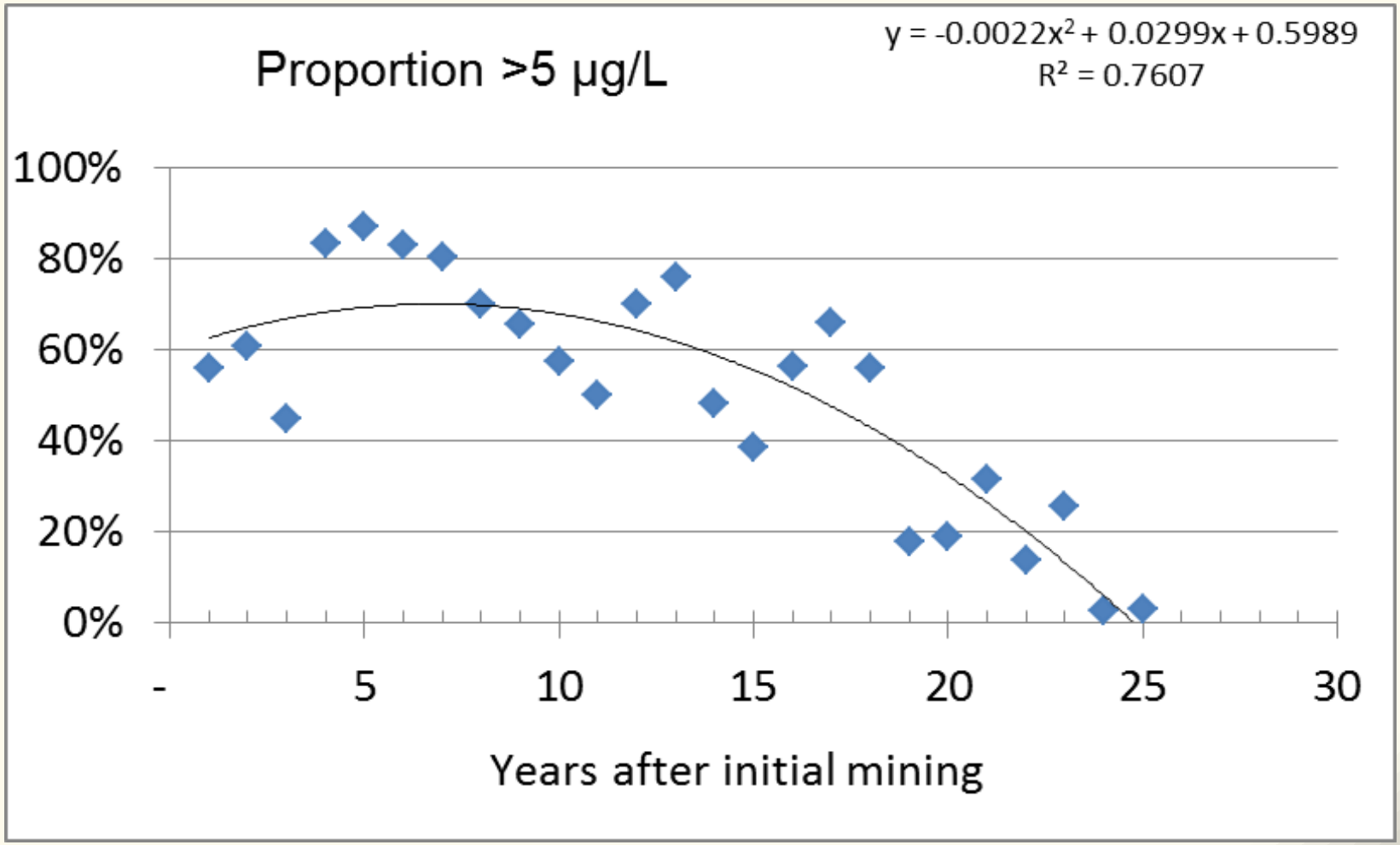


The rapid attenuation of Se is evident at the tributary scale. Not so with SO_4





97% of outlet samples were in compliance by year 25



Conclusions (previous studies):

- Between 25 and 35% of selenium in southern West Virginia coal mine spoil is potentially mobile
- Sulfur is between 2,000 and 10,000 more prevalent in unweathered spoil than selenium
- Selenium weathers and leaches out of spoil at about 10x the rate of sulfur

Conclusions (this study):

- Selenium discharges follow a pattern of rapid increase over the first seven years after mining followed by a decline over the next fifteen years to below 5 µg/L
- The same trends pertained at three scales:
  - Laboratory
  - Outlet
  - Watershed
- Laboratory (humidity cell)results can be scaled to predict field results
- A substantial portion of the original selenium is 'lost' probably due to ferrihydrite sequestration

Implications:

- Selenium discharges in excess of 5 µg/L appear to be predictable and transitory
- As a result, selenium should be conducive to a load based, site-specific, managed discharge approach that will maintain water column concentrations at levels that are protective of aquatic health
- Rehandling of spoil will reset the clock

Questions?

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