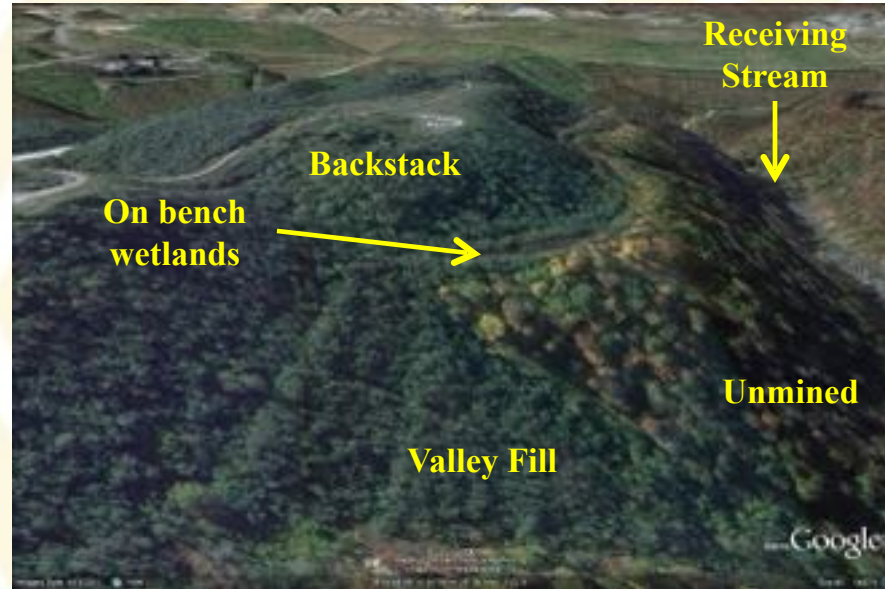


Long-term trends in selenium attenuation at a Central Appalachian surface mine

Paul Ziemkiewicz, Water Research Inst., WVU
Barry Doss, Doss Engineering Inc.



Allegheny Plateau-pre mining



Old, contour/auger
mining



Hobet: a typical mountaintop mine: Oldest mining (1985) in foreground



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



2012 STUDY

1. Humidity Cells
2. Outlet Study
3. Stream Study



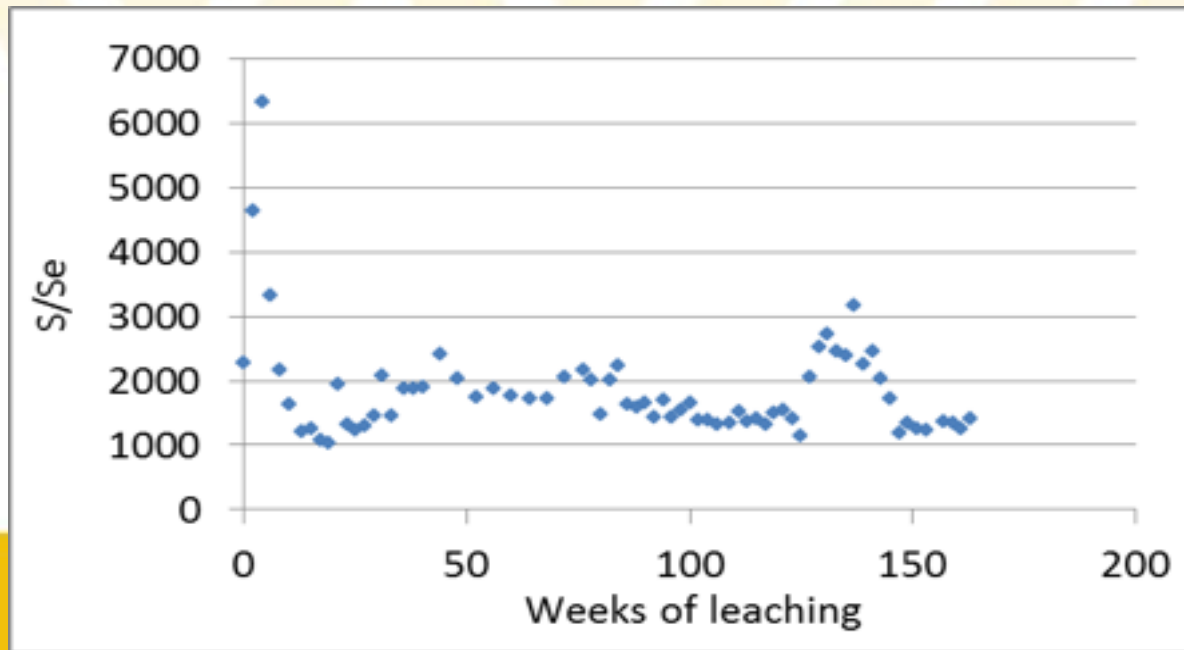
The ratio of sulfur to selenium release is nearly constant suggesting a mineralogical link

Iron selenide, replaces pyrite?



average S/Se = 1,833

	15 VA	16 VIA	17 VIIA	18 VIIIA
	7 N Nitrogen 14.007 7.0	8 O Oxygen 15.999 8.0	9 F Fluorine 18.998 9.0	10 Ne Neon 20.180 10.0
	15 P Phosphorus 30.974 15.0	16 S Sulfur 32.06 16.0	17 Cl Chlorine 35.45 17.0	18 Ar Argon 39.948 18.0
	33 As Arsenic 74.922 33.0	34 Se Selenium 78.96 34.0	35 Br Bromine 79.904 35.0	36 Kr Krypton 83.798 36.0
	51 Sb Antimony 121.757 51.0	52 Te Tellurium 127.6 52.0	53 I Iodine 126.905 53.0	54 Xe Xenon 131.29 54.0



Most of the selenium is probably in organic shale: where the pyrites are



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



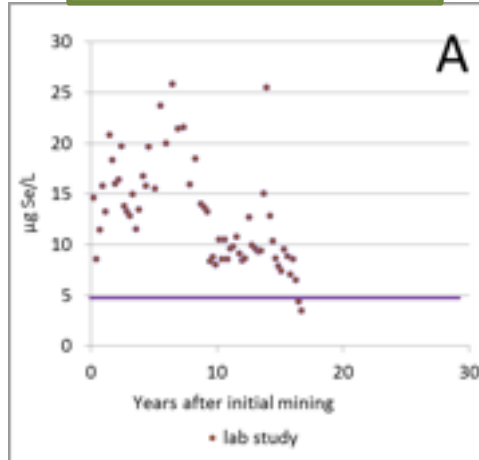
Organizing the 5,388 data points

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

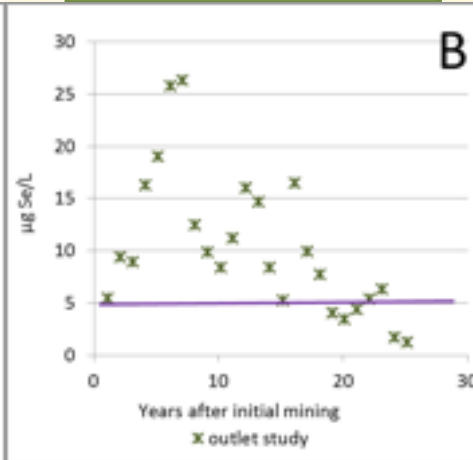


Laboratory and field studies yield similar attenuation curves

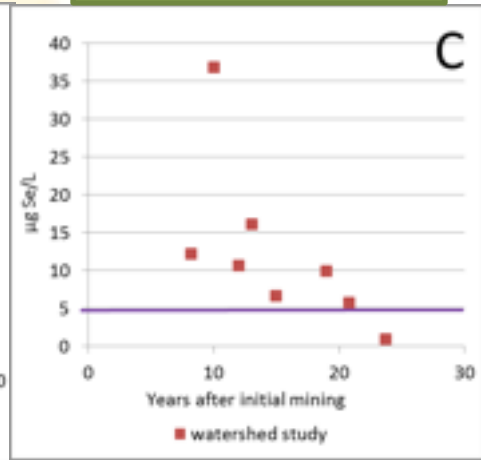
Lab study*



Outlet study



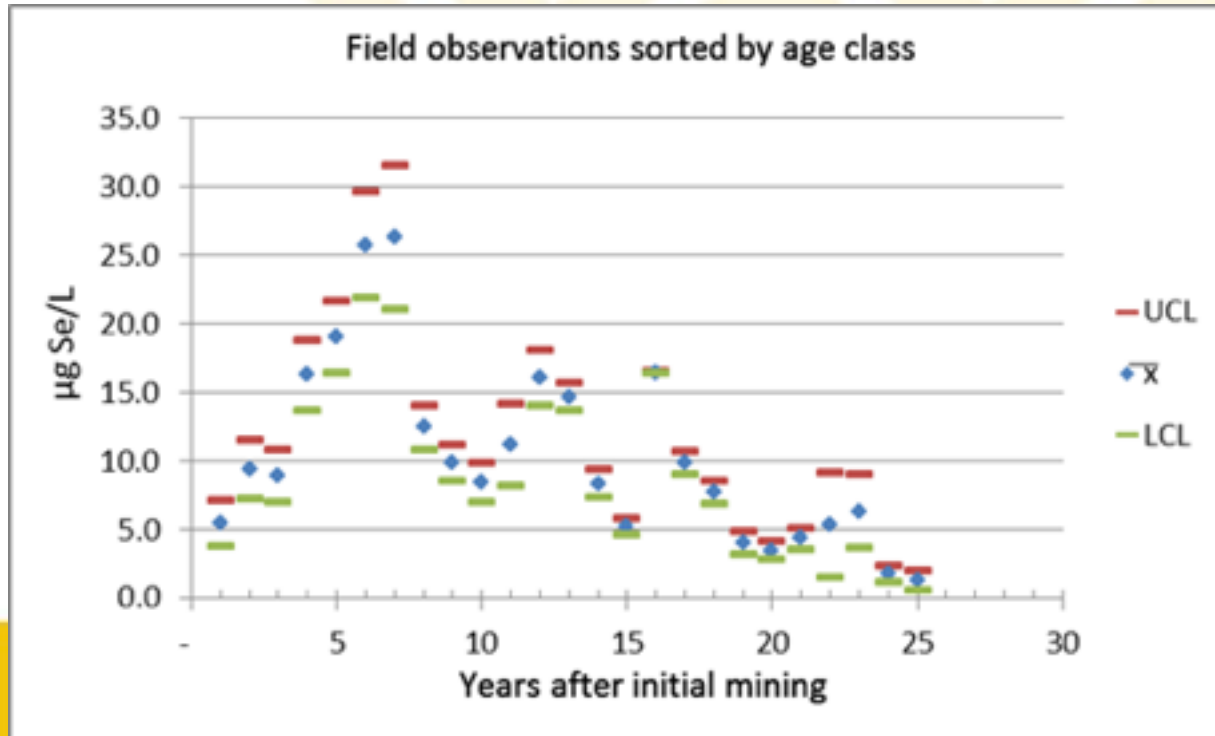
Watershed study



*Adjusted to estimate field concentrations



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



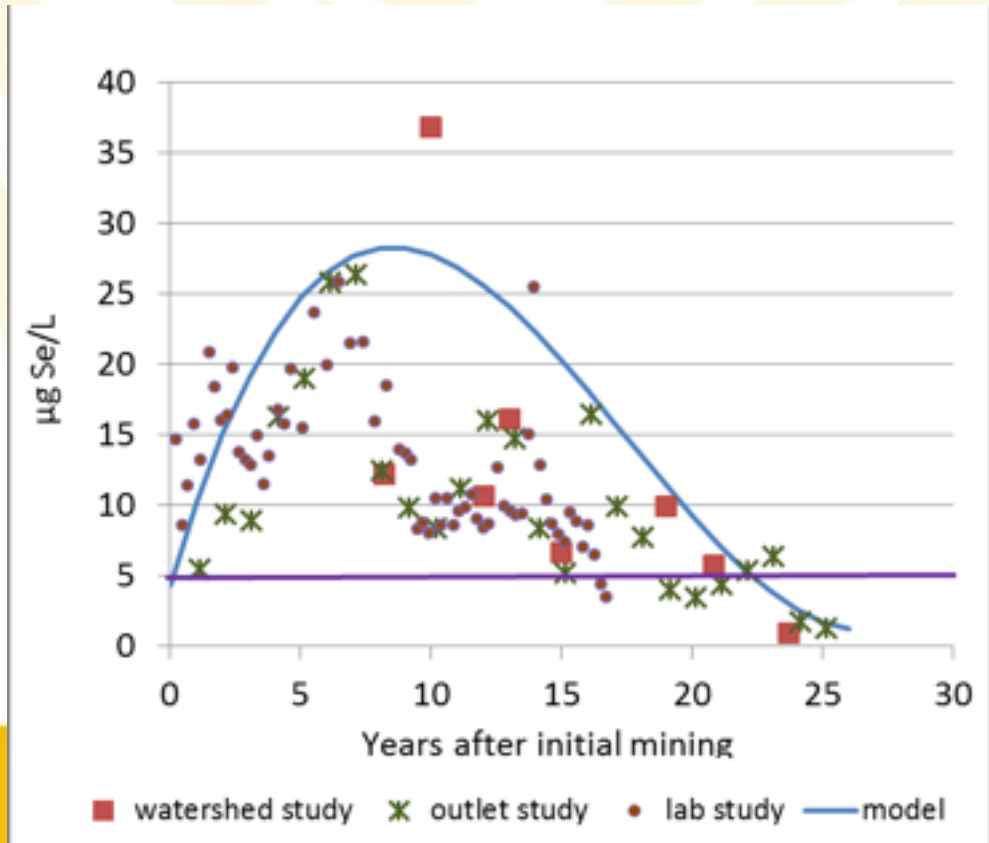
Descriptive Model

Postulated Ferrihydrite Sequestration

- Occurs at year seven in all three studies.
- Coincides with 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

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

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



Conclusions (2012 study):

- Selenium increase rapidly over the first seven years after mining followed by a decline over the next fifteen years to below 5 $\mu\text{g/L}$
- The same trends pertained at three scales:
 - Laboratory
 - Outlet
 - Watershed



Conclusions (2012 study)

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

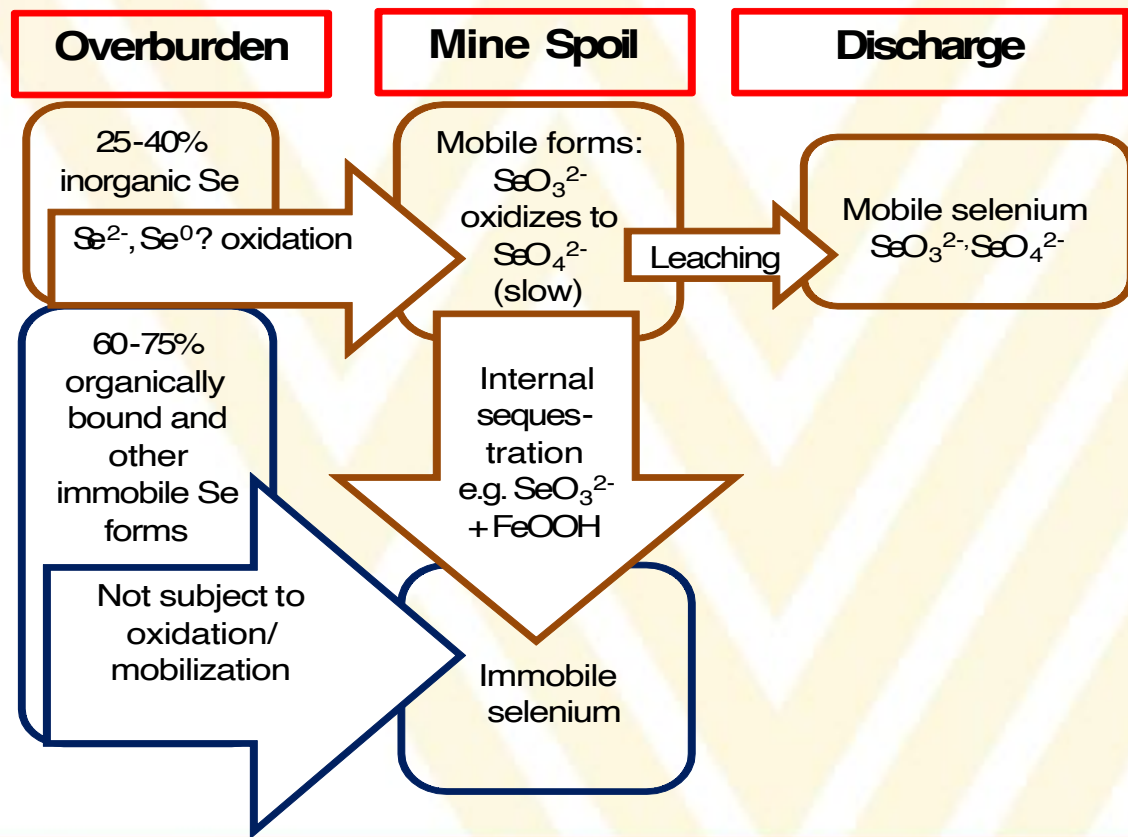


Conclusions (2012 study)

- Laboratory results can be scaled to predict field results
- A substantial portion of the original selenium is 'lost' probably due to ferrihydrite sequestration
- Any spoil disturbance resets the clock

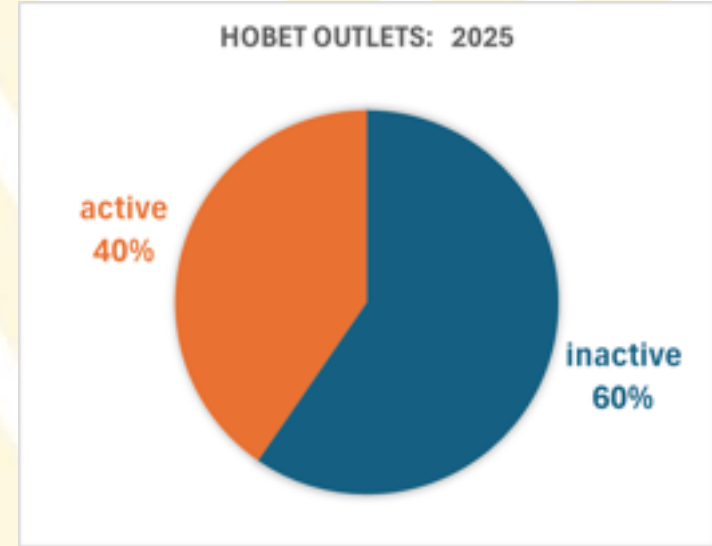


SELENIUM WEATHERING MODEL



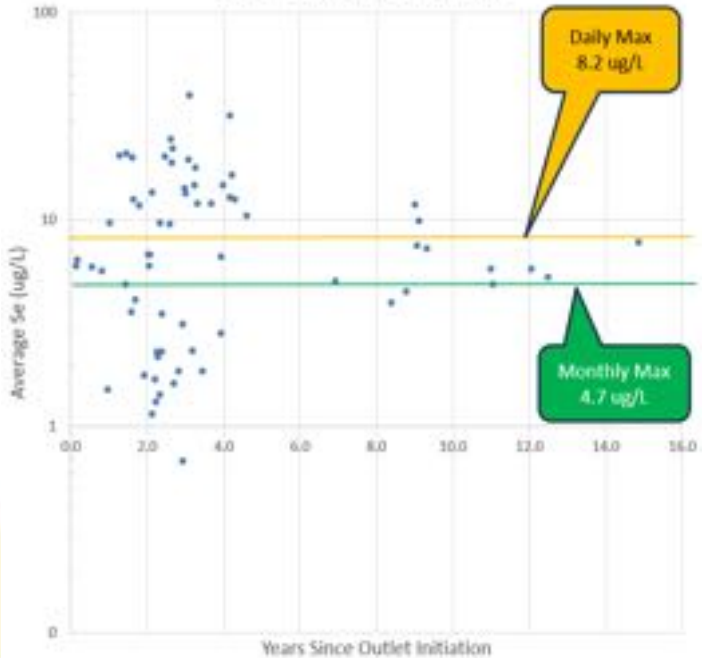
Current study at Hobet:

- 198 total outlets
- 80 active outlets: currently monitored
- 118 inactive outlets: compliant, dried up, reconfigured
- Sampled over 20 years
- Metric: Average Se per outlet **since outlet initiation**

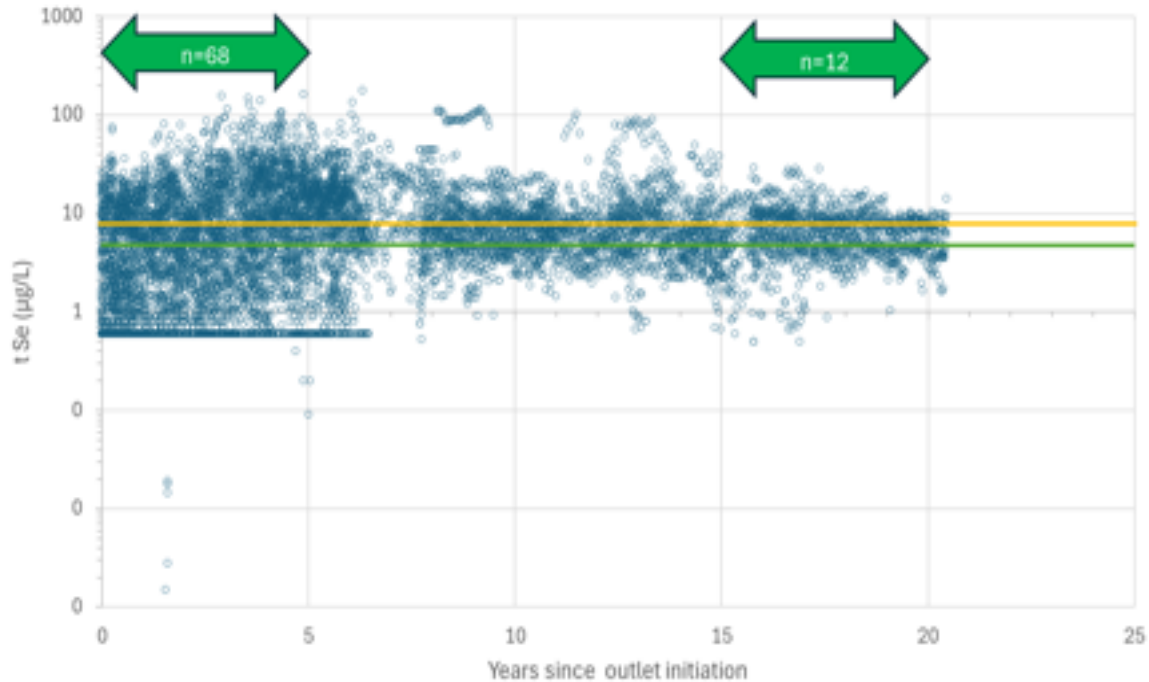


82.4% of outlets are compliant after 20 years

Hobet active NPDES permits

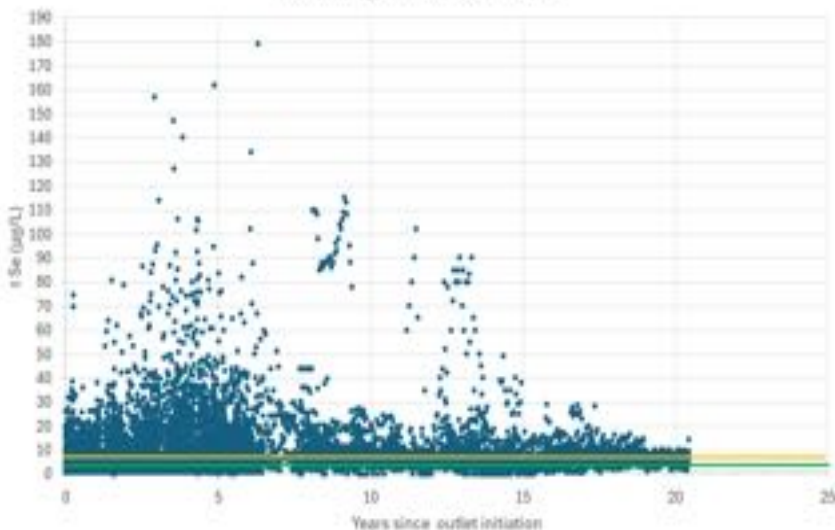


82.4% of original outlets are $< 5 \mu\text{g Se/L}$: $n=9,434$

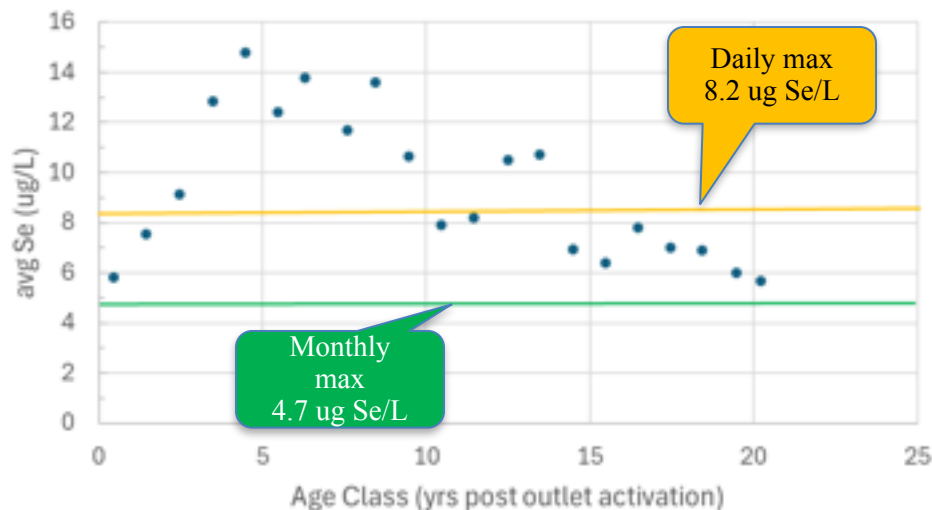


Se vs. years post outlet initiation

Remaining 80 outlets; n=9,434



Avg Se (ug/L)

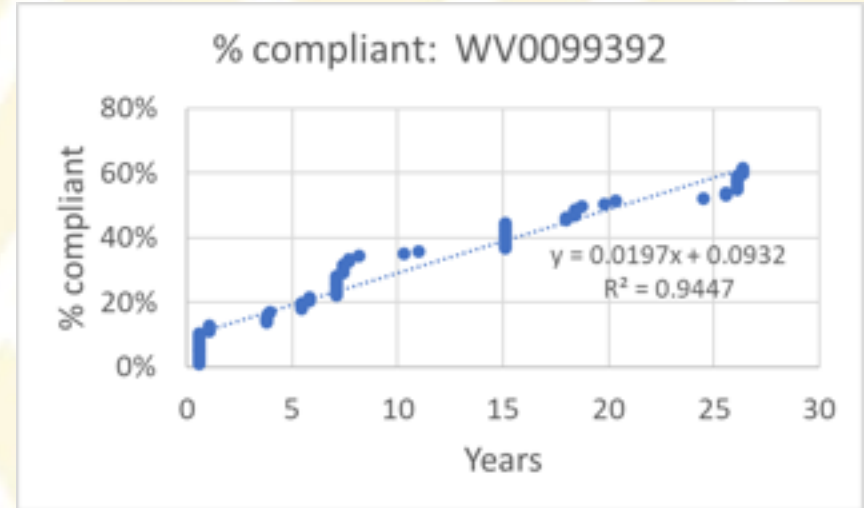
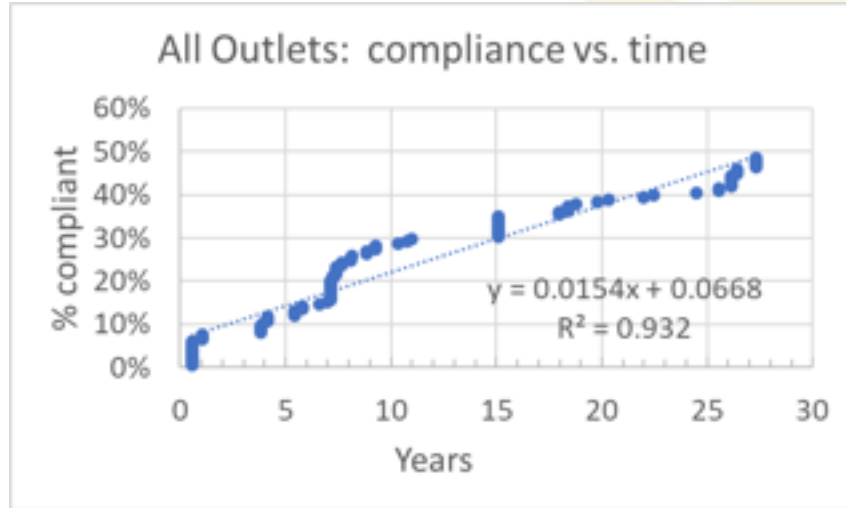


All Hobet outlets

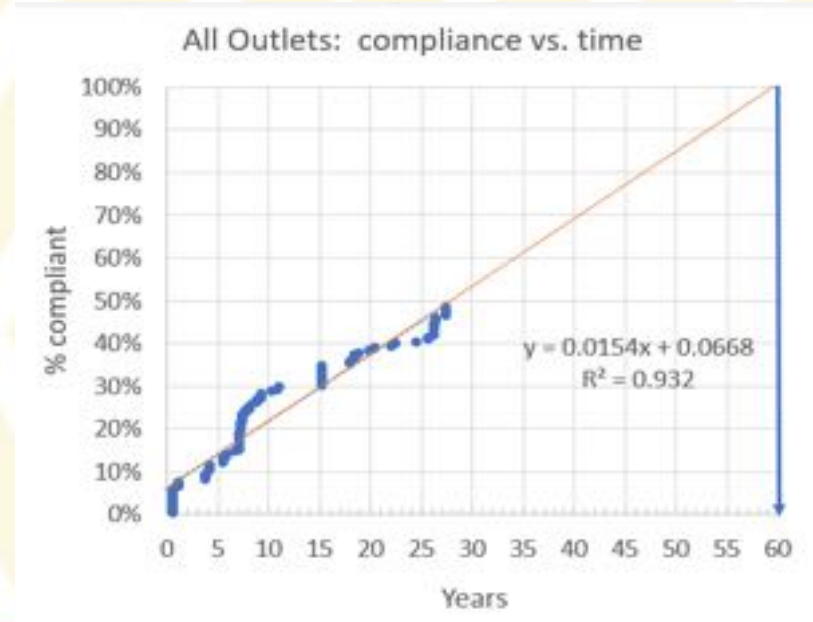
permit	# outlets	avg outlet age yrs	# in compliance	% in compliance
WV0099392	117	11.1	72	62%
WV1016776	44	18.6	12	27%
WV1017225	7	8.9	4	57%
WV1021028	13	7.2	2	15%
WV1020889	17	5.9	6	35%
	198	10.3	96	48%



About half of the outlets fall below $5 \mu\text{g Se/L}$ within 30 years



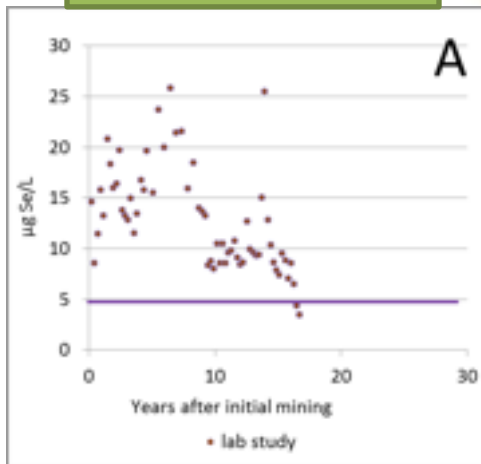
All outlets should fall below
5 $\mu\text{g Se/L}$ within 45-60 years



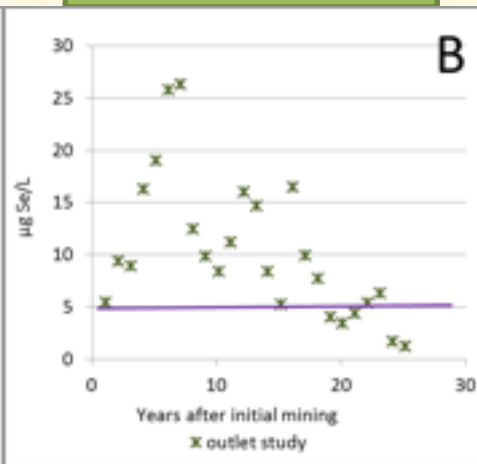
Rapid selenium attenuation explains why the three curves below look similar:

Se is not cumulative in CAPP mining

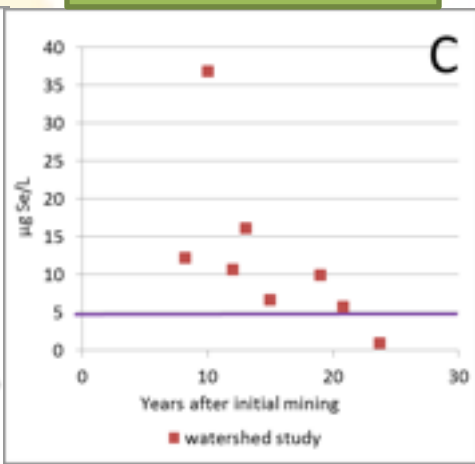
Lab study*



Outlet study



Watershed study



*Adjusted to estimate field concentrations



QUESTIONS?

Paul Ziemkiewicz, PhD, Director
West Virginia Water Research Institute
West Virginia University
pziemkie@mail.wvu.edu

