

# MiniSipper: a New High-capacity, Long-duration, Automated *in situ* Water Sampler for Acid Mine Drainage Monitoring

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Special thanks to EPA partners  
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and Jean Wyatt



# Aquatic chemistry parameters under-sampled both spatially and temporally



Short duration (day)  
Hand sampling:  
(a few samples/yr)



Medium duration (days-weeks)  
24 one liter samples (~\$4000)  
Big, heavy, no over-winter



Long Duration (year)  
Submersible  
(52 samples, ~\$20,000)

- Field work is expensive! \$300-\$800/day (salary, vehicles, equip, per diem)
- Low cost, long-term, high-resolution monitoring is crucial for evaluating:
  - Details of major hydrologic loading events (snowmelt runoff, storms)
  - TMDLs (total maximum daily loads) and elemental budgets
  - Effects of remediation practices and land use changes



# Site Access Difficulties of Acid Mine Drainage Monitoring

Rocky Mountain, remote, high elevation, summer access usually 4WD

Winter Access (November to June) is very difficult:

- Laborious (skiing/snowshoeing) or expensive (snow machines)
- Avalanche danger, back-country safety and rescue training
- Deep snow and surface ice make sample collection difficult

Underground:

- Difficult and dangerous access (air quality, cave-in, flooding, etc)
- Requires Mine Safety Personnel to guide scientists
- Almost no underground temporal data



Dug out >8' of snow to access Penn adit



Sampling over 1 mile underground, Commodore Mine, Creede, CO



# A Tale of Two Colorado Mines

## Pennsylvania Mine (Keystone)

- Consideration for EPA Superfund
- ~11,000' elevation, snow (Nov-June)
- 303(d) listed for Zn, Cd, Pb, Cu, Mn
- Snowmelt dominated flow
- Impacts drinking water/recreation

## Standard Mine (Crested Butte)

- EPA Superfund site
- ~11,000' elevation, snow (Nov-June)
- 303(d) listed for Zn, Cd, Pb
- Snowmelt dominated flow
- Impacts drinking water/recreation



# Penn Mine

pH usually 3

Winter:

- Low flow-low cond

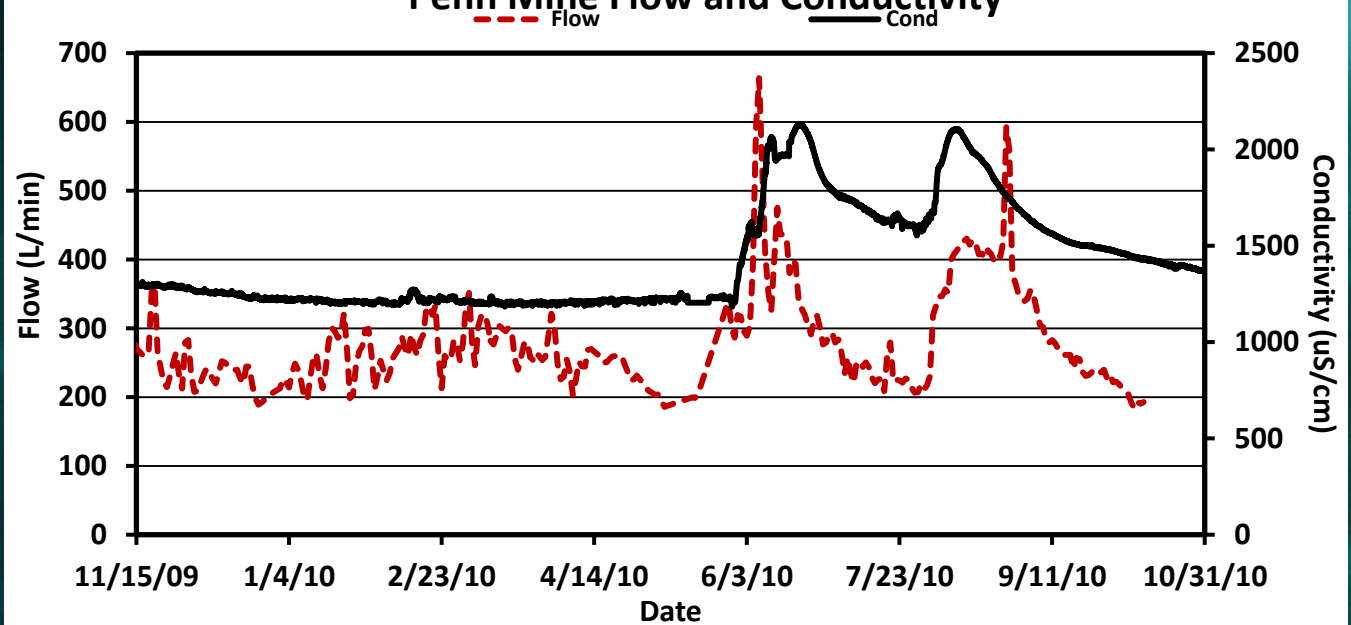
Runoff

- High flow-High cond

Summer Event

- High flow-High cond

## Penn Mine Flow and Conductivity



# Standard Mine

pH usually >6

Winter:

- Low flow-High cond

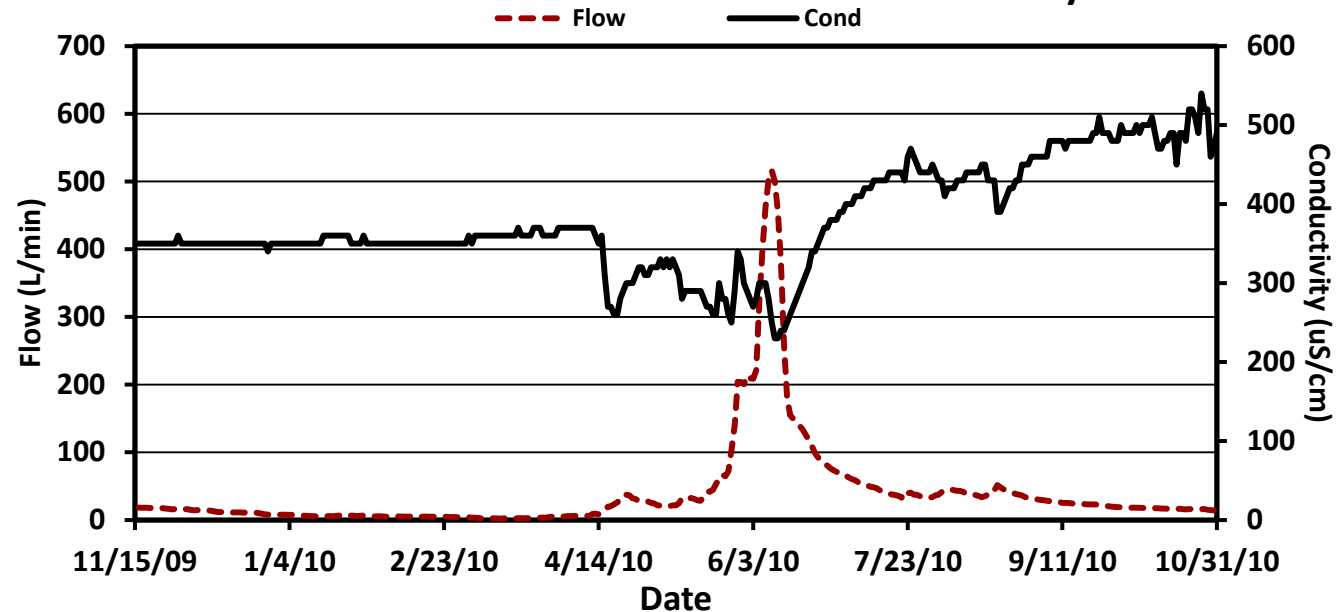
Runoff:

- High flow-Low cond

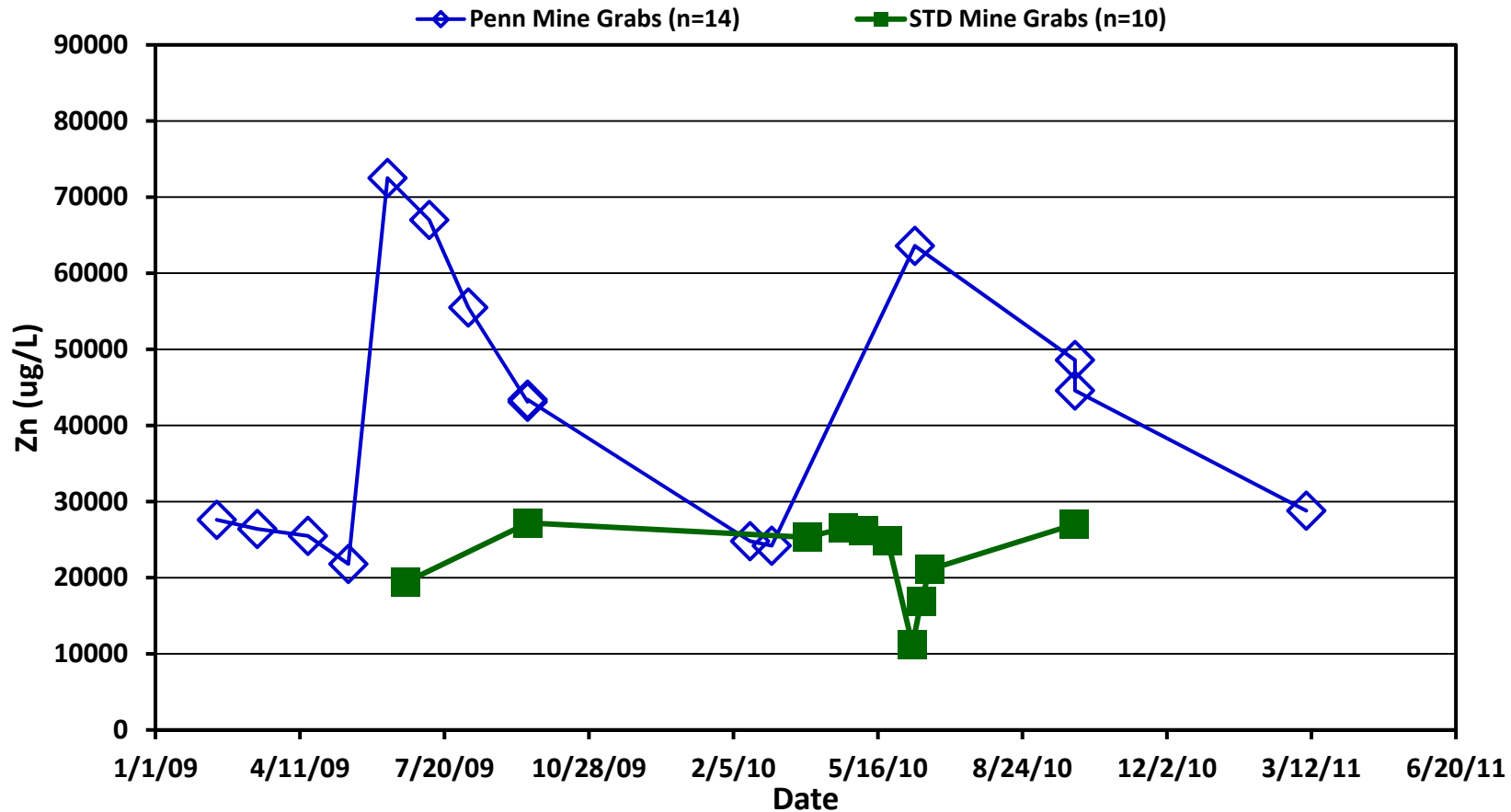
Fall:

- Low flow-High cond

## Standard Mine Flow and Conductivity

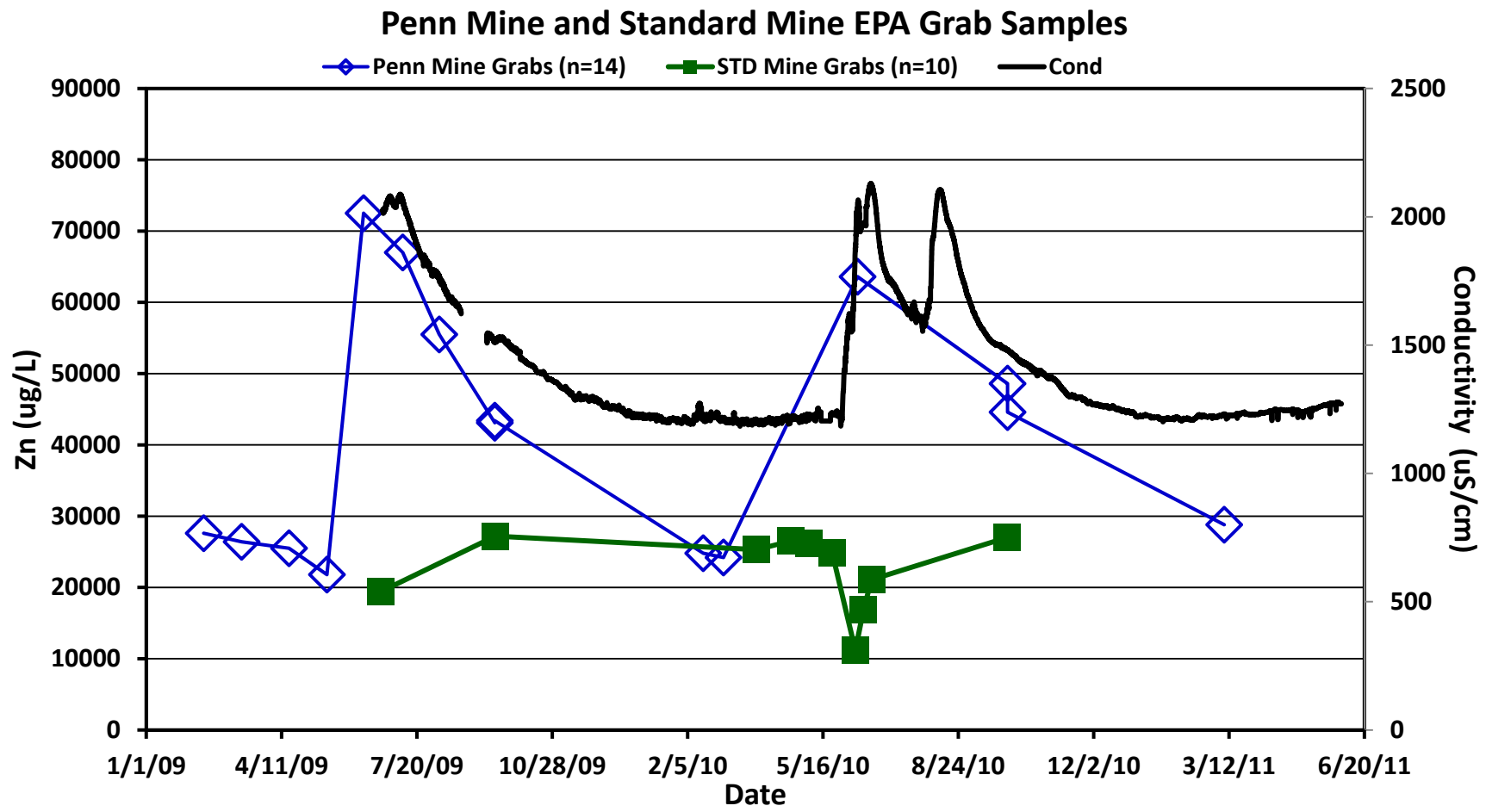


## Penn Mine and Standard Mine EPA Grab Samples



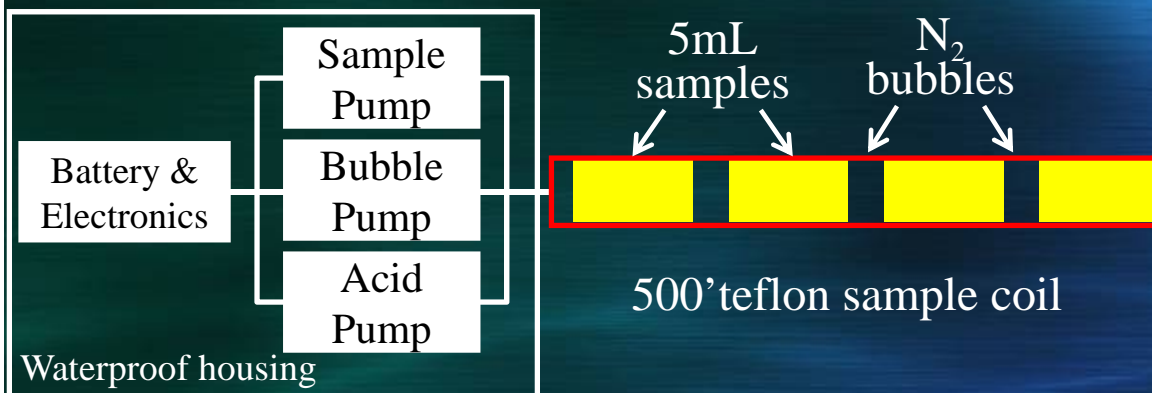
- Penn and Standard have similar winter Zn levels, ~25,000 ug/L
- Opposite annual signal
  - Winter: Penn has low Zn; Standard has high Zn
  - Runoff: Penn has high Zn; Standard has low Zn
- Grabs required skiing+snowmobiling in winter, 4WD in summer





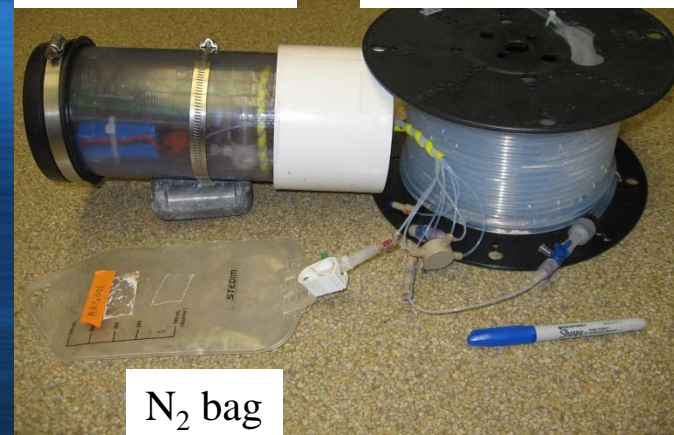
- Penn: Secondary conductivity peak in late summer
- Late summer event not observed before
- Event not sampled by regular grab sampling program
- Can we design low cost, high resolution, long duration water sampler?

## MiniSipper (mini segmented water sampler)



pump housing

500' sampler coil

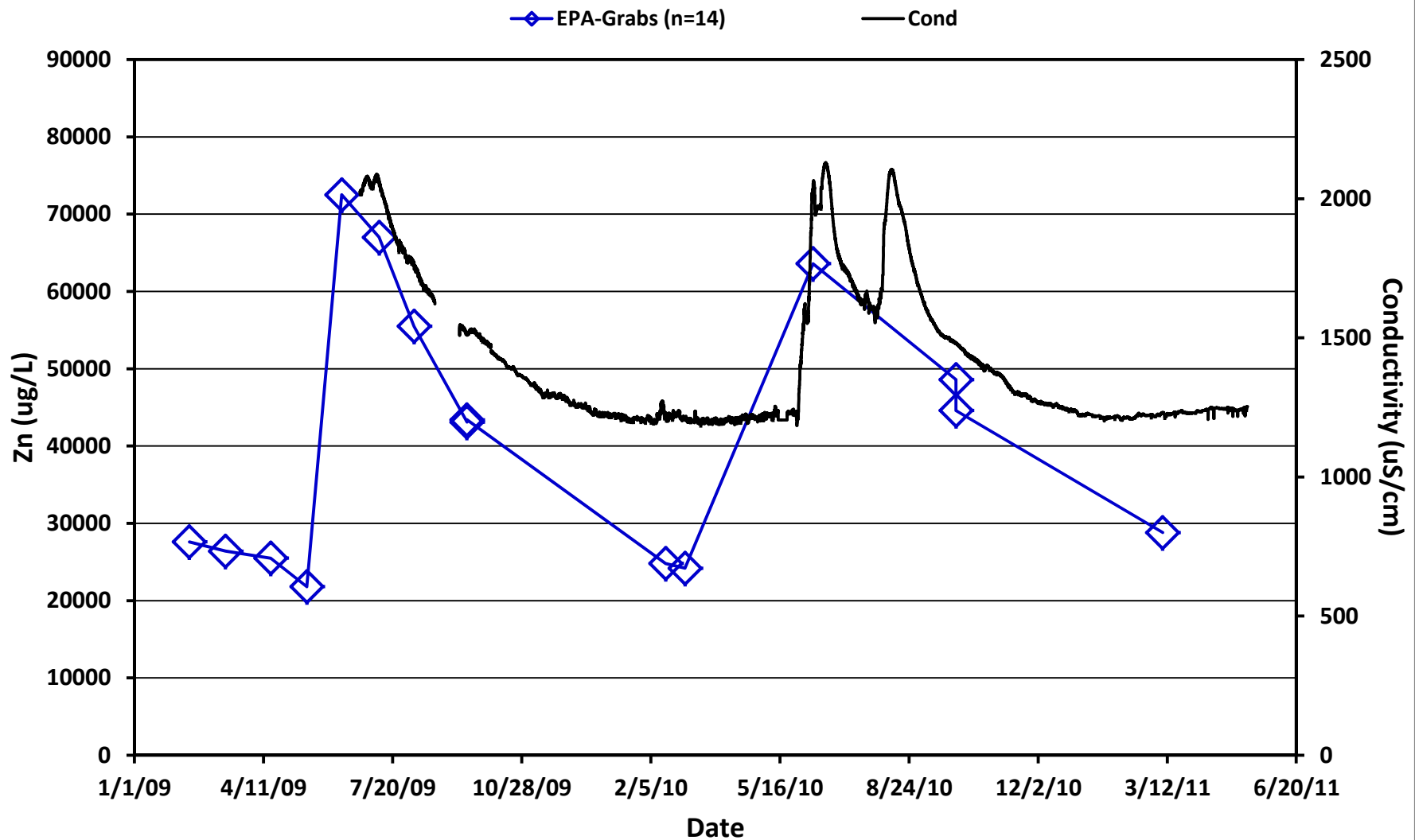


- **Small (20" x 6")**, submerged, self contained, easily concealed
- **Samples separated by inert gas bubble, <5% carryover**
- **Inexpensive (~\$2500)**, multiple sampling locations
- **Over winter capability (operates for > 8 months under ice)**
- **Online acidification and replicate samples possible**
- **Much lower field sampling costs (fewer site visits)**
- **~240 5mL samples (discrete or integrated)**
- **10 μm filtration, tracks the 0.45 μm dissolved fraction very closely**
- **Dual Sampling rate (low frequency in winter + high frequency during runoff)**
- **Transient Event Sampling (depth trigger)**
- **Samples analyzed by multi-element methods (ICP-MS, IC, etc)**
- **Submerged to <3' (can't go deep)**



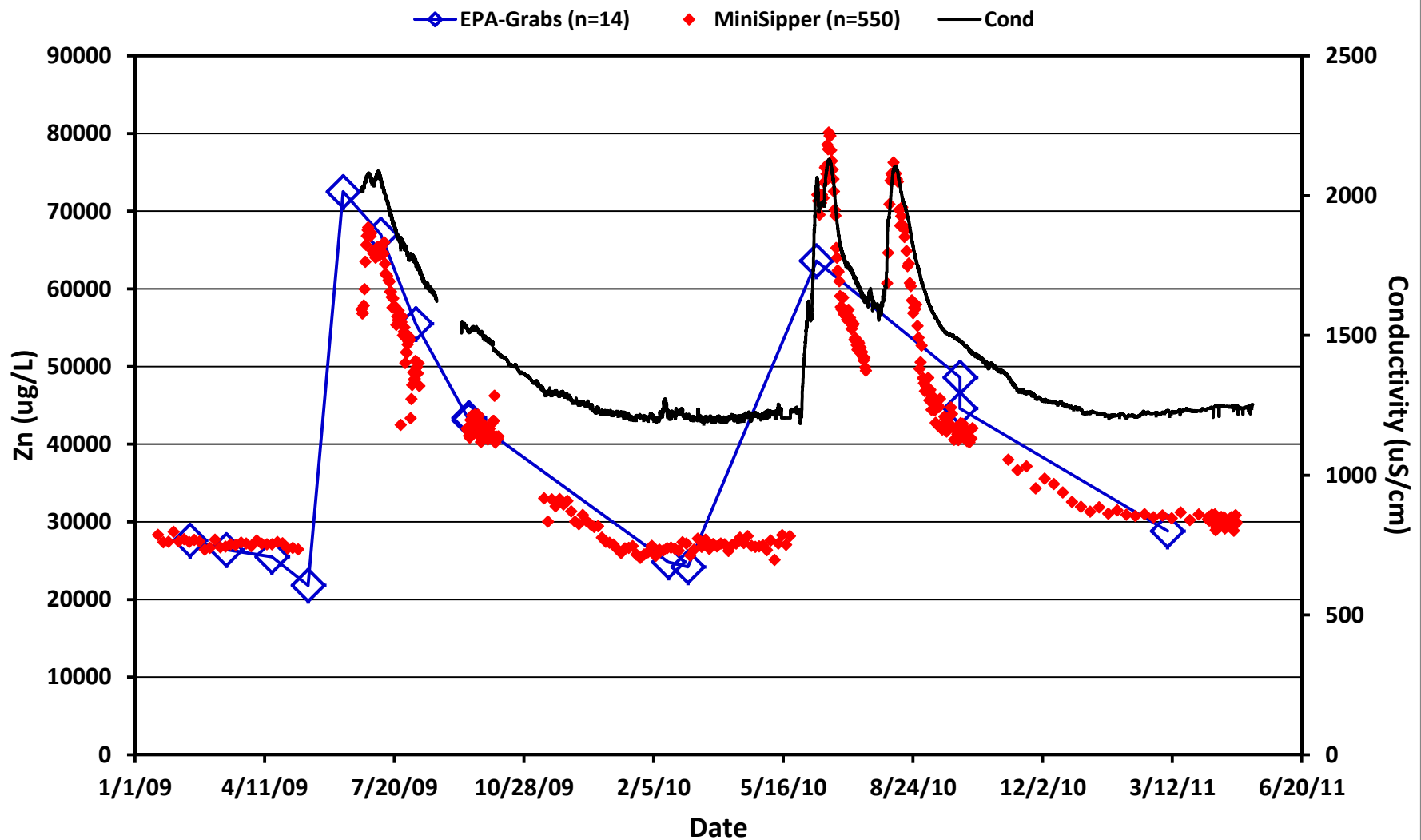


## Penn Mine EPA Grab Samples vs MiniSipper



- High resolution conductivity signal indicates major event in Sept 2010
- Late summer high conductivity event not sampled, not observed before
- Need a high resolution, long-term sampler to capture these major events.

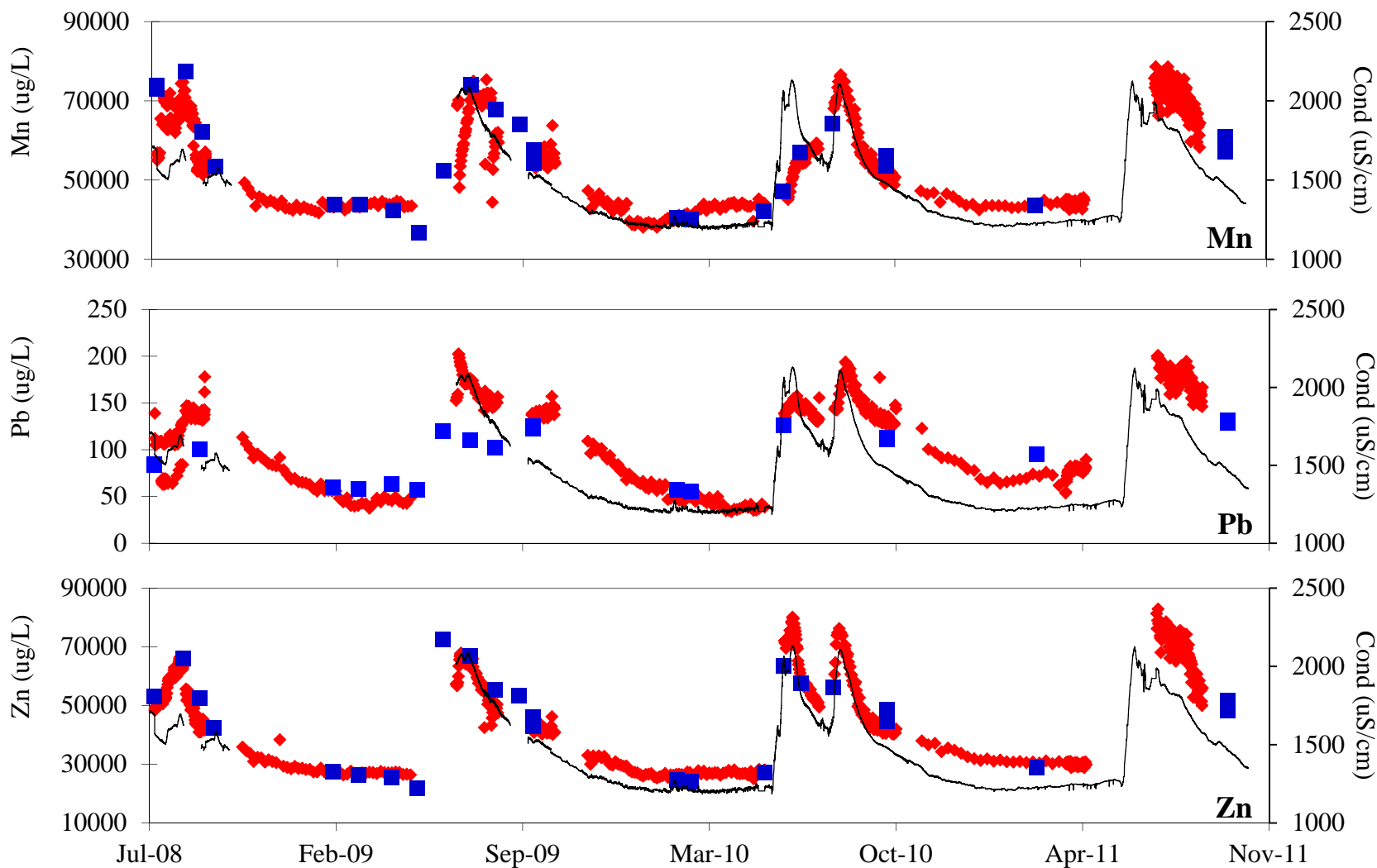
## Penn Mine EPA Grab Samples vs MiniSipper



- Excellent agreement between MiniSipper and EPA grab samples
- MiniSipper captured second runoff event in Sept 2010.



**Penn Mine MiniSipper (n=750)    Grab(n=25)    Cond**



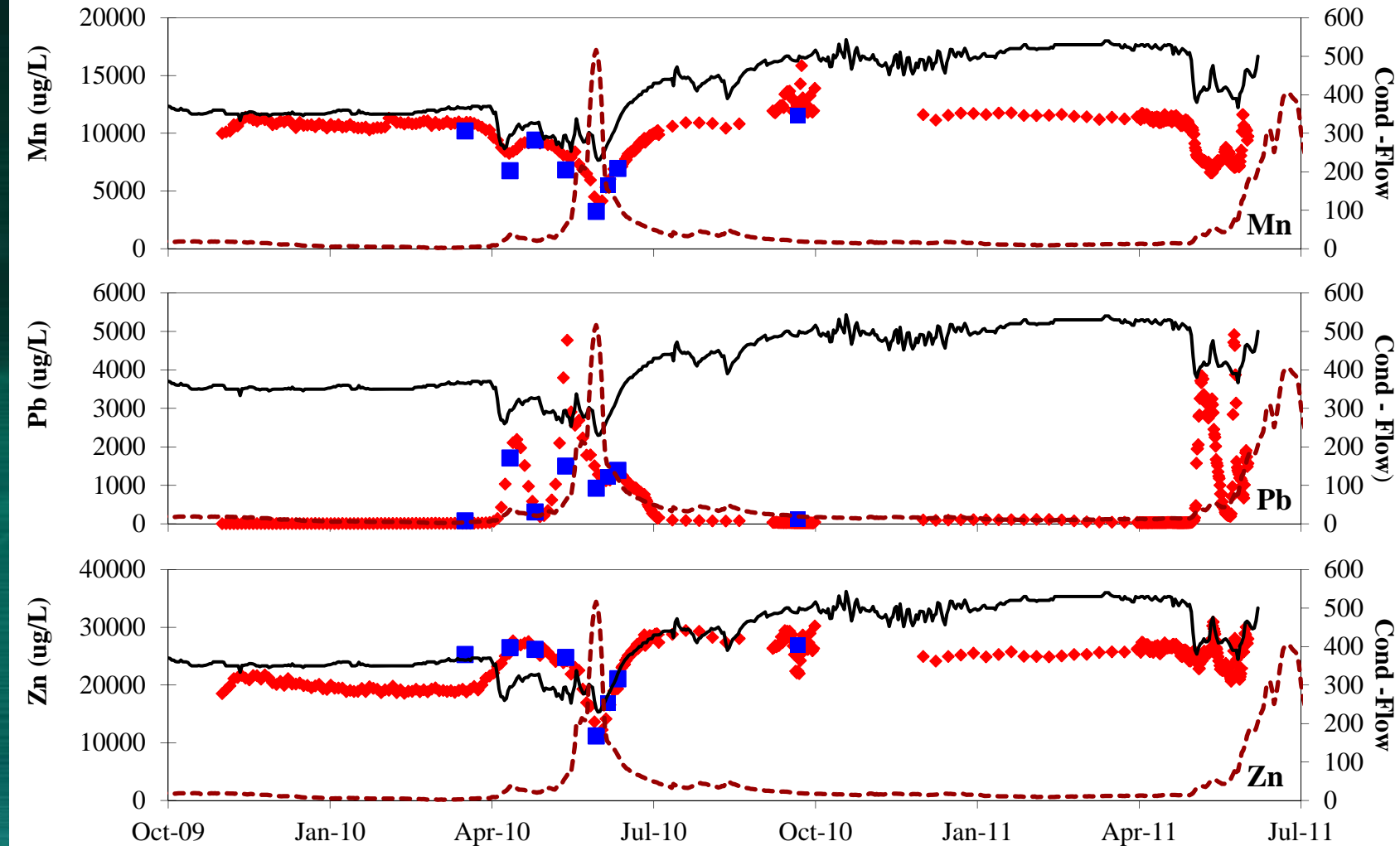
**Penn: All metals show the same pattern, excellent agreement with grabs**

- Winter: low flow, low cond, low metals
- Snowmelt Runoff: high flow, high cond, high metals
- Summer Rain effect: higher metals but not every year

**Standard mine MiniSipper (n=400)**

**Grab(n=8)**

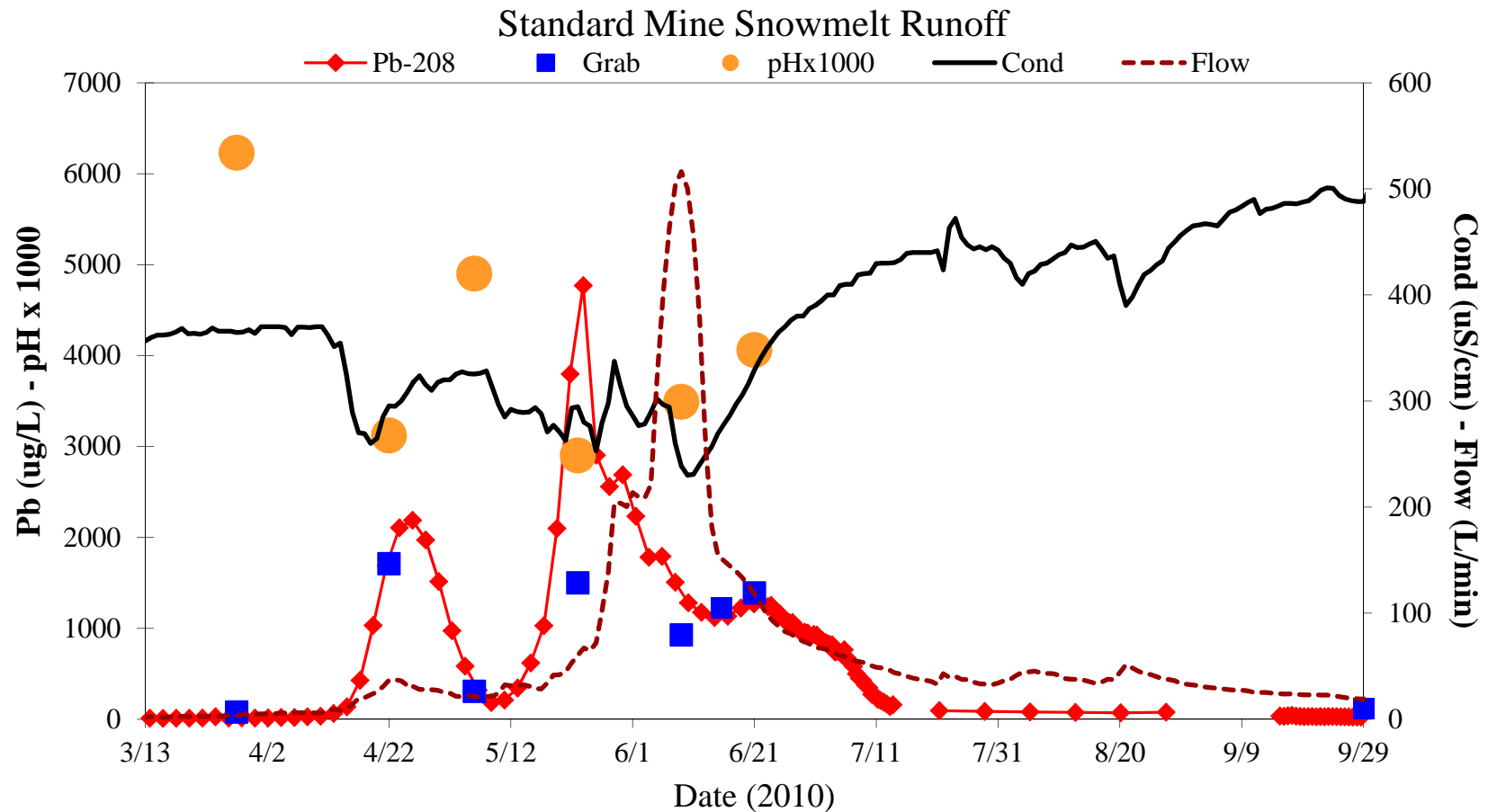
**Cond**



**Standard Mine: Different metal patterns, pH dependent**

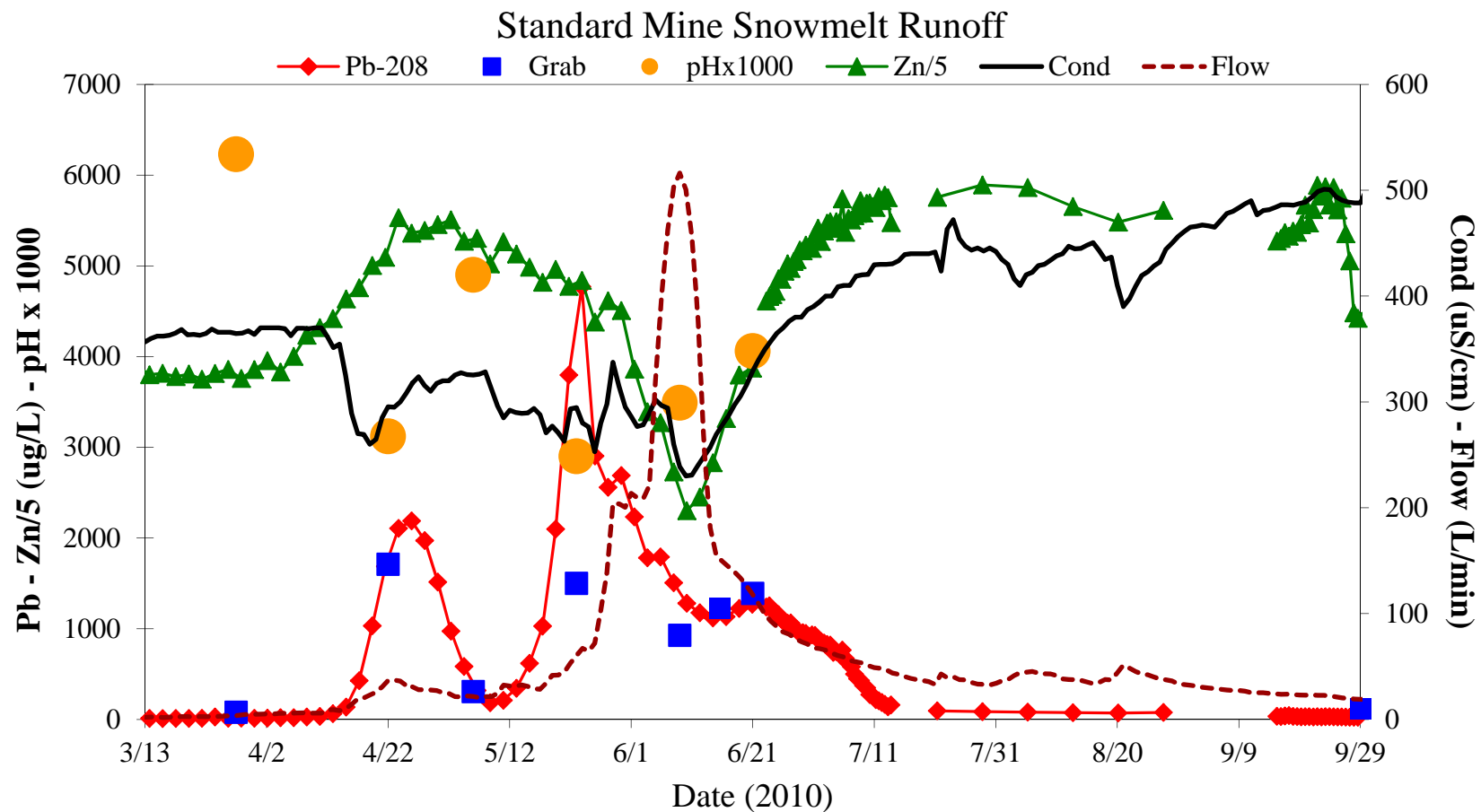
- Winter: very low flow; high pH; high cond; high Mn, Zn; low Pb
- Snowmelt Runoff: high flow; low Mn, Zn, and Pb
- Summer Rain effect: not observed





## Standard Mine: pH sensitive metals (Al, Cu, Pb)

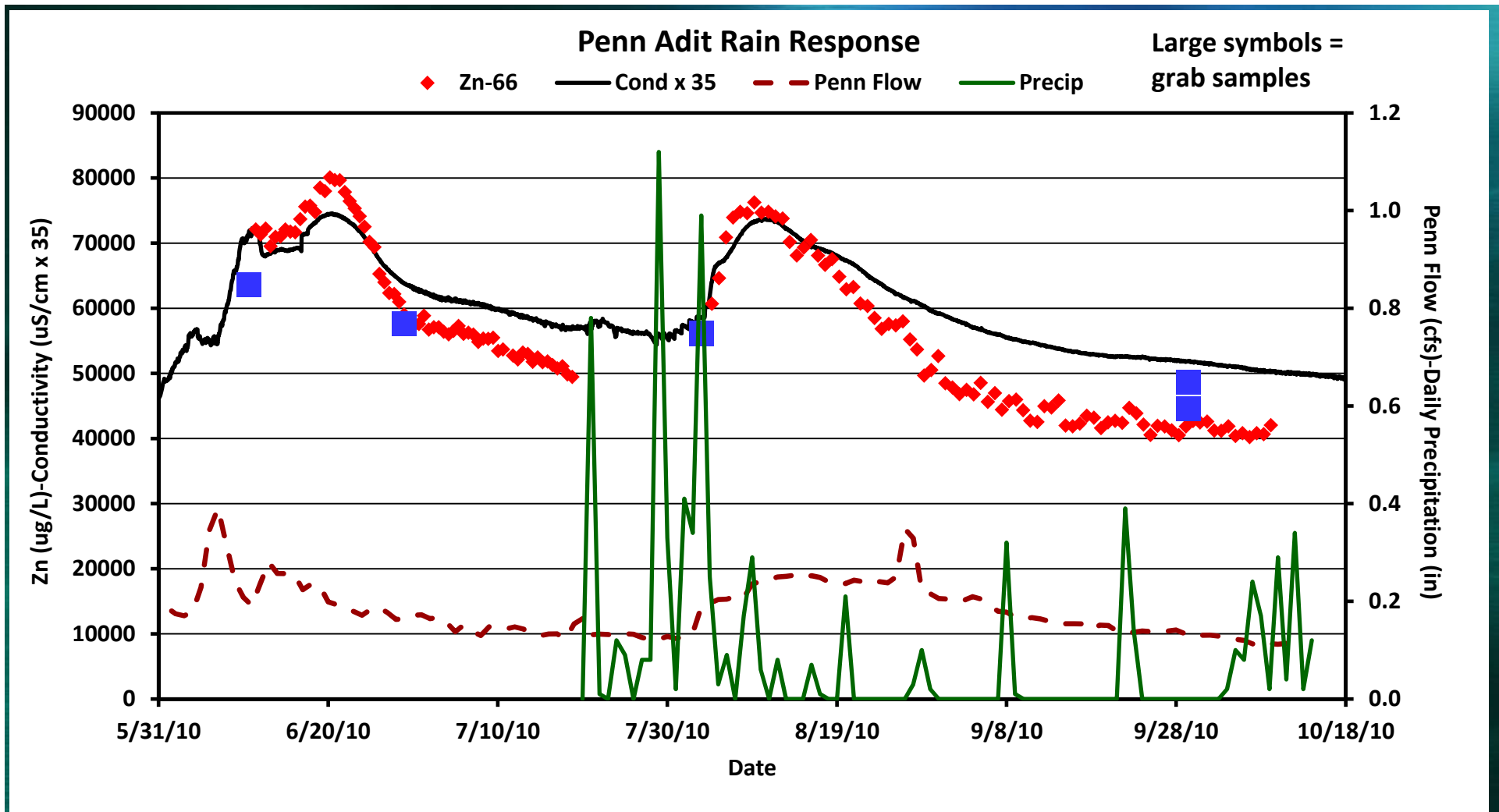
- Winter: lower flow; higher pH ( $\sim 6$ ), very low Al, Cu, Pb
- First Pulse (late April): pH  $\sim 3$ , spike in Al, Cu, Pb
- Late Spring snow+refreeze: decrease flow, increase pH, decrease Al, Cu, Pb
- Snowmelt Runoff: high flow, another high Pb spike then slow decrease
- Pattern repeated in 2011



## Standard Mine: Zn, Cd

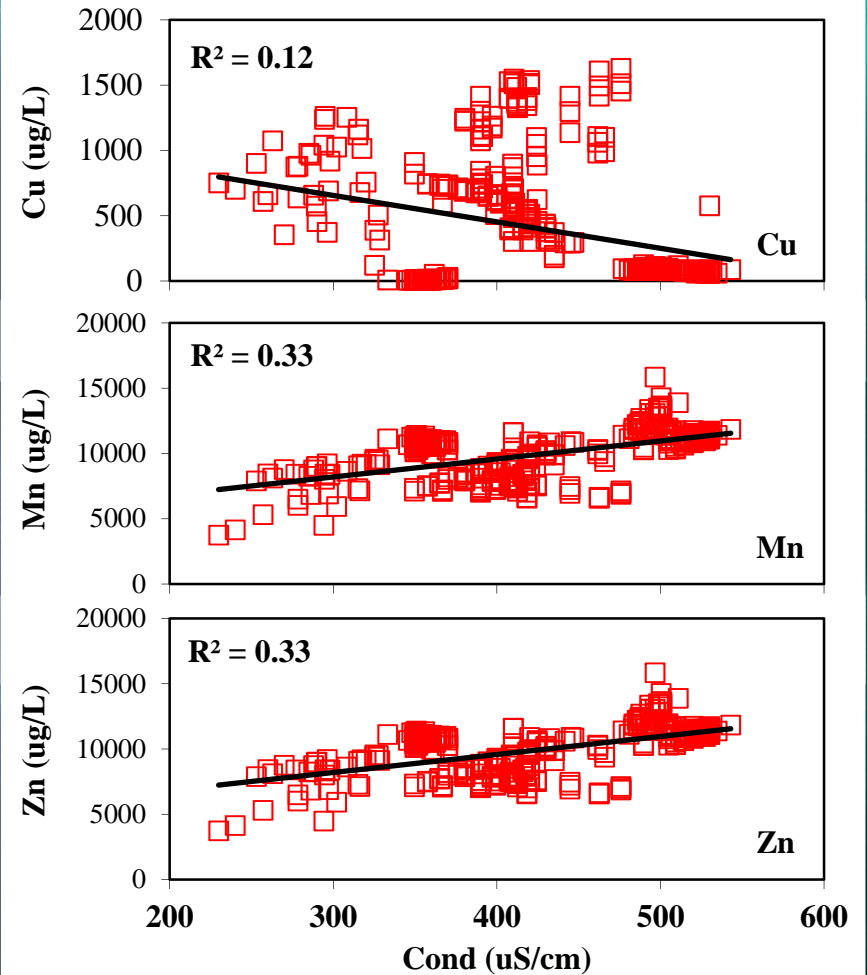
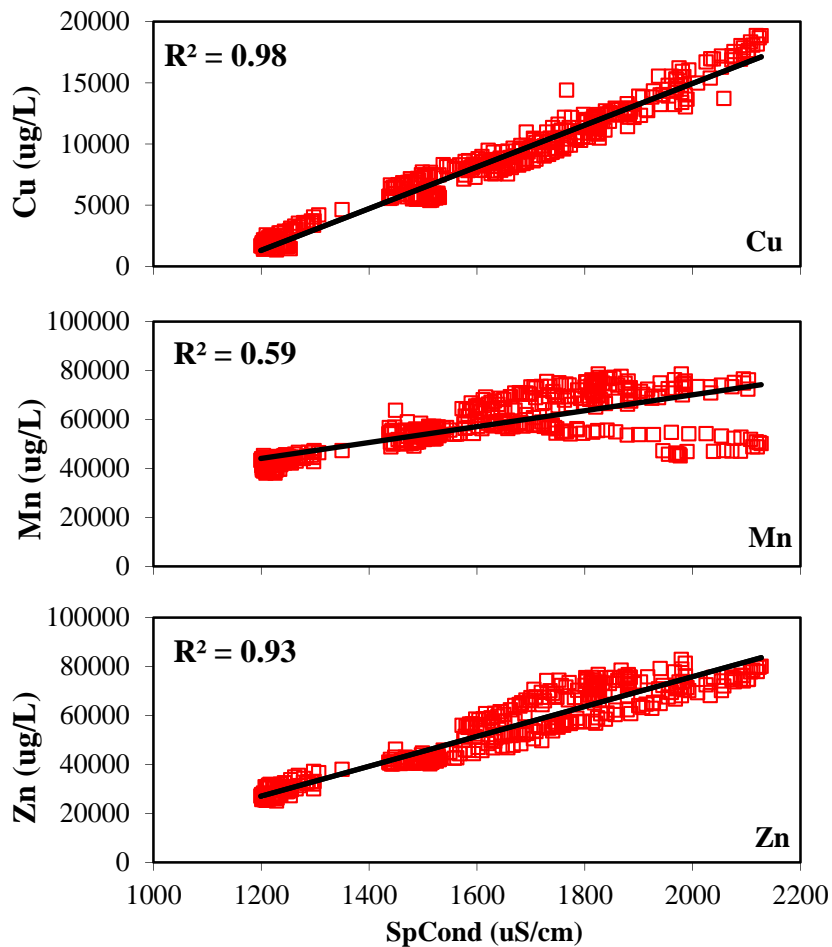
- Winter: low flow; high pH (~6), high Zn, Cd
- First Pulse (late April): pH~3, slow rise in Zn, Cd
- Late Spring snow+refreeze: decrease flow, increase pH, decrease Cd, Zn
- Snowmelt Runoff: high flow, dilution then gradual increase
- Pattern repeated in 2011





### Penn Mine Rain Response

1. Large rain events in late July 2010 increase flow and conductivity
2. Rain flux of Zn is comparable to snowmelt runoff Zn flux, fish kills?
3. Big summer storms with increases in Zn and cond not observed in '09 or '11
4. Have not observed big rain effects at Standard Mine



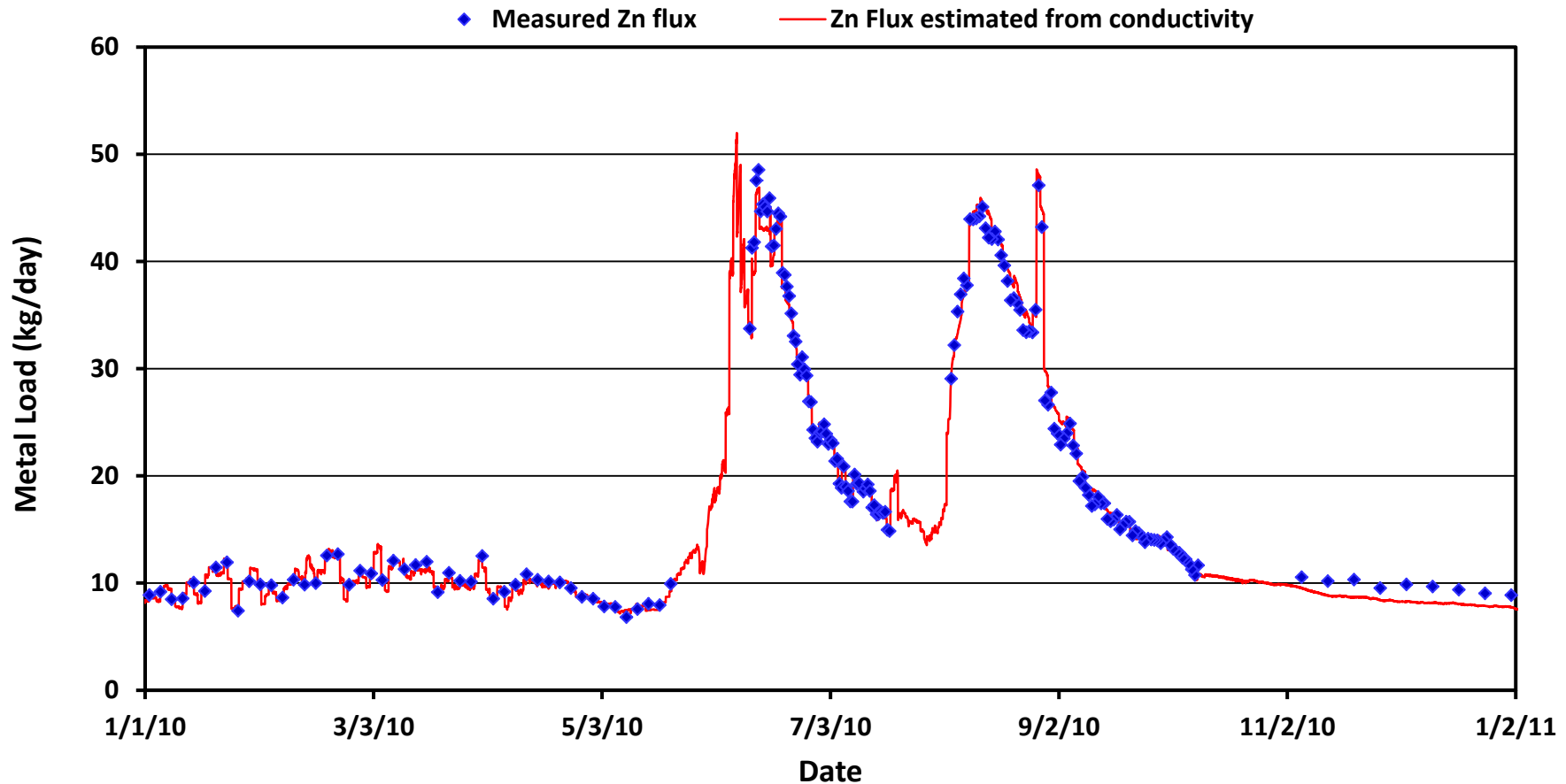
## Penn Mine

Most metals highly correlated with cond  
 Mn lower correlation  
 Conductivity as proxy for metal concs

## Standard Mine

Metals poorly correlated with cond  
 High pH doesn't release Al, Cu, Pb  
 Not a good choice for real time fluxes

## 2010 Penn Mine Zn Loading

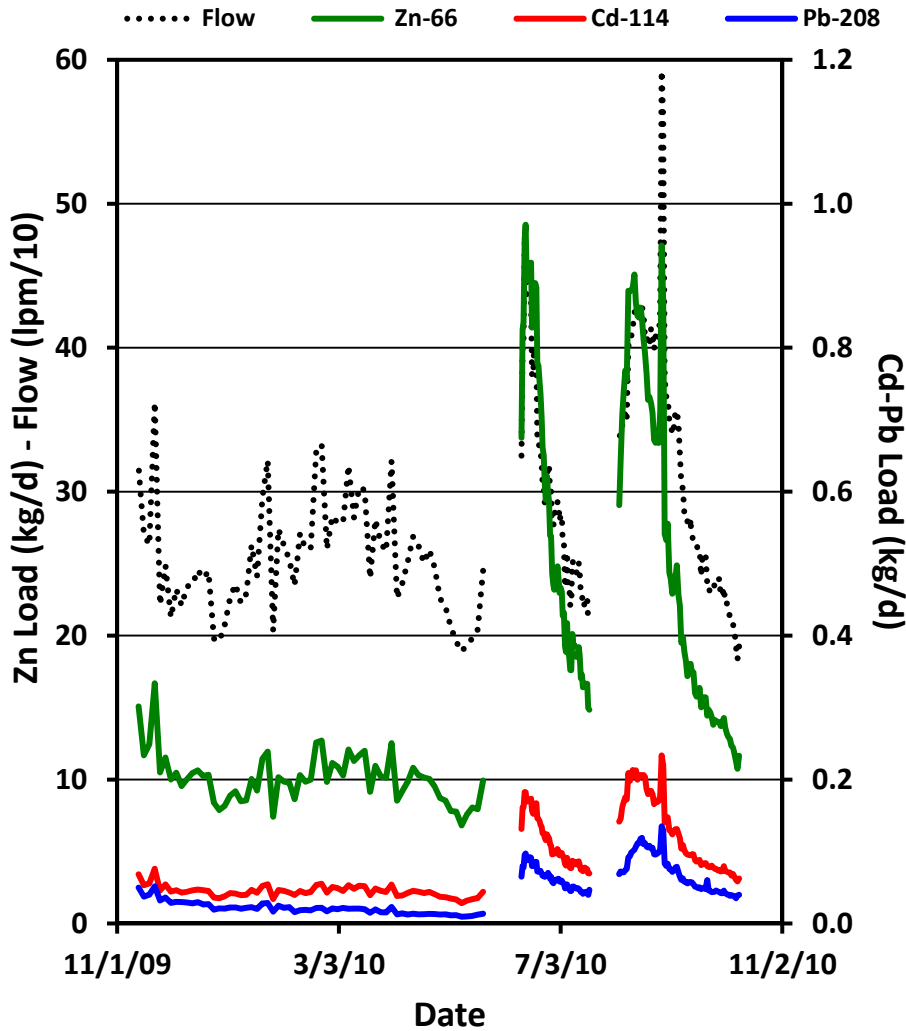


### Penn: Conductivity estimated metal loading

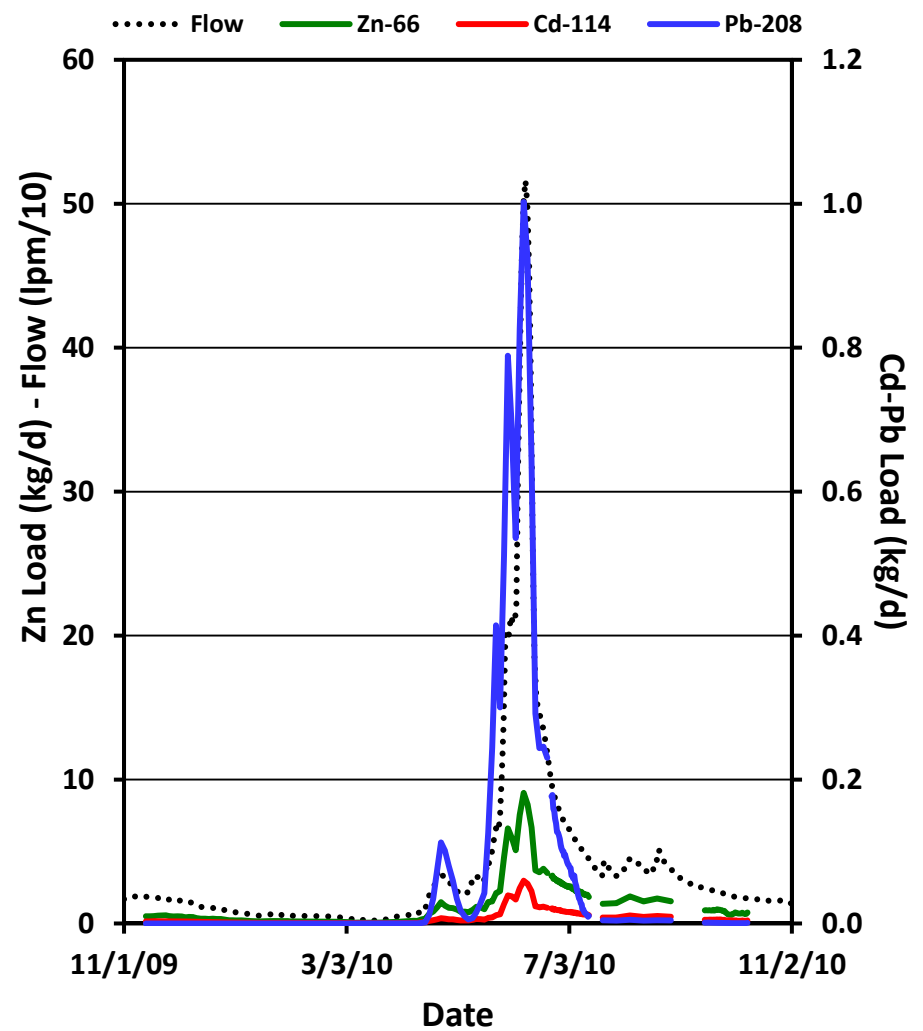
- High metal:conductivity correlations at Penn >> conductivity as proxy for metal
- High resolution conductivity and flow much easier and cheaper than metal monitoring
- Need a full year of MiniSipper samples to verify metal:conductivity correlations
- Data telemetry would allow real time metal flux estimates
- Doesn't work at Standard Mine (poor metal:conductivity correlations)



**Penn Mine Annual Metal Loading**



**Standard Mine Annual Metal Loading**



- Penn & STD: max loading in snowmelt
- STD: almost all loading during snowmelt
- Penn: storm loading ~ snowmelt loading
- All season data helps remediation design

Load (kg/yr)	Zn	Cd	Pb	Flow (L/min)
Penn	6500	30	16	250
Standard	500	3	23	40

# A Tale of Two Mines

## Pennsylvania Mine

- Higher metals during runoff events
- Lower metals during low flow
- Lower pH, usually pH 3, range 3-5
- High metal-conductivity correlations

## Standard Mine

- Lower metals during runoff events
- Higher Zn & Cd during low flow
- Higher pH, usually 5-7, range 3-7
- Al, Cu, and Pb track pH spikes
- Low metal-conductivity correlations



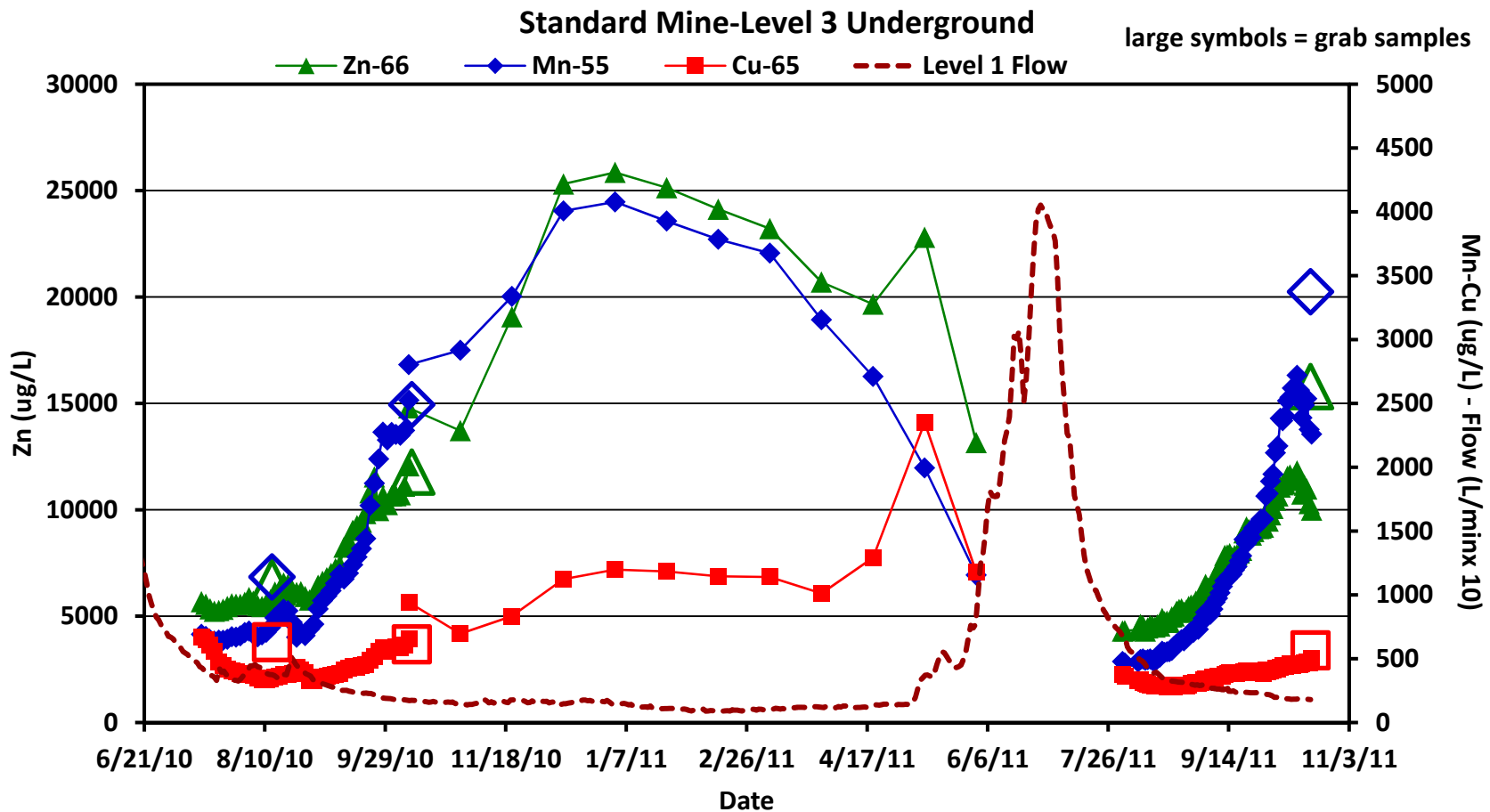




Level 3 becoming unstable and more dangerous to access

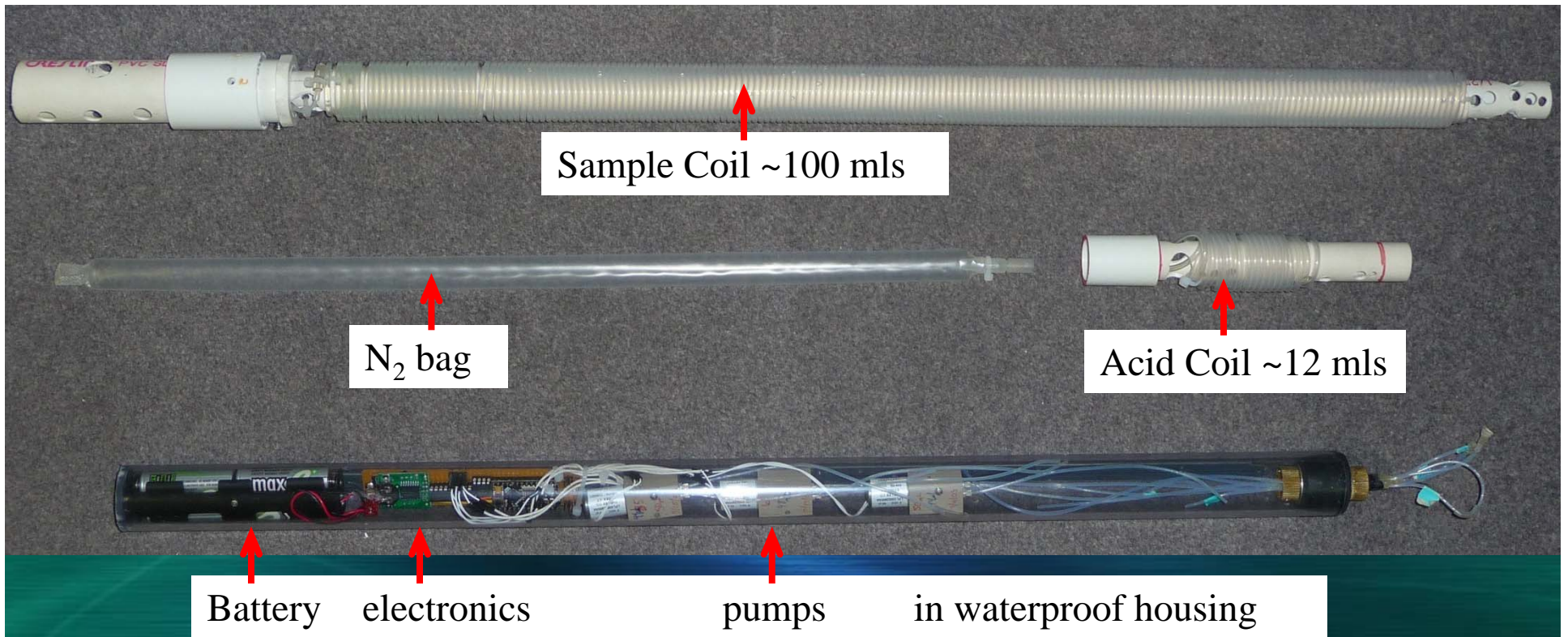
MiniSipper is ideal for underground work





## Standard Mine Level 3-Underground

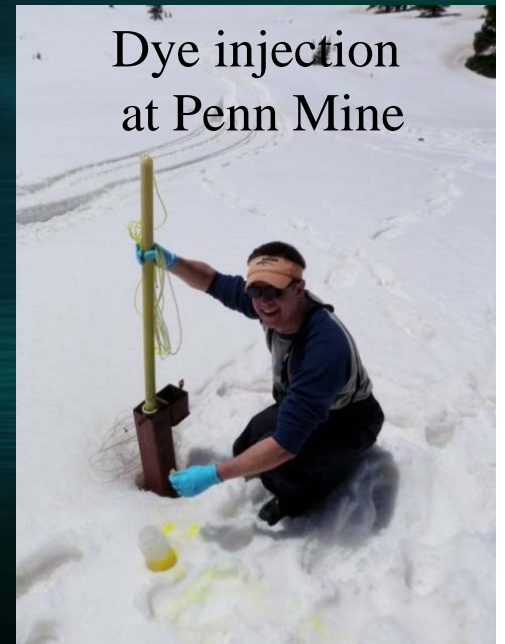
- 140 underground samples collected, deployed for 2012 snowmelt runoff
- MiniSipper problems in winter 2011 (coil backpressure, shutdown in June)
- Missed 2011 snowmelt runoff but there appears to be annual cycle
  - Snowmelt runoff leads to low metal concentrations in early summer
  - Metals increase during fall to max levels in winter



## Borehole Sipper

- ~6' long but fits down a 2" borehole
- Collects 30 three mL samples and can operate for > 1 yr
- Floats at ground water surface
- Currently in field for over-winter deployment
- Cost: \$2500
- Well monitoring, BCR monitoring, tracer studies

Dye injection  
at Penn Mine





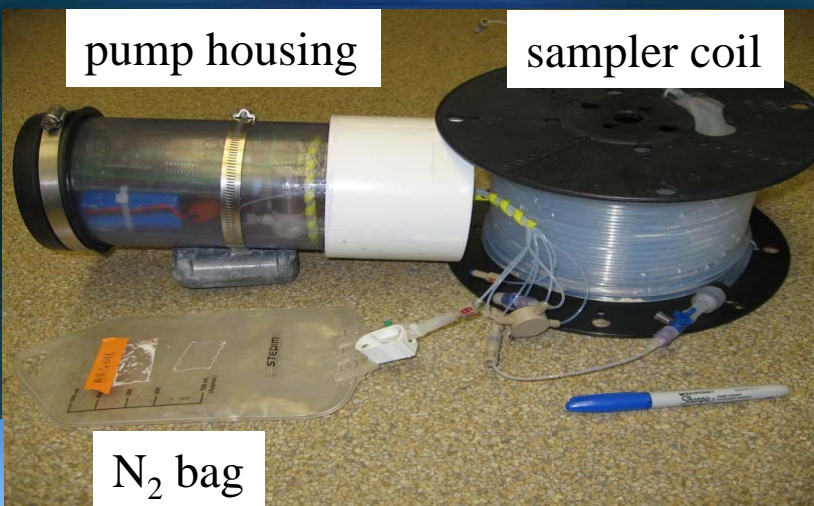
# MiniSipper Conclusions

- Provides low cost, high-resolution, long-duration sampling
- Excellent agreement with hand collected samples
- Difficult sampling (over-winter, underground, tracer, storm)
- Other applications (wildfires, other analytes, etc.)
- Improvements (event trigger, 0.45  $\mu\text{m}$ , reliability)
- Looking for partners and projects- USGS in kind analytical support

2" Borehole Sipper



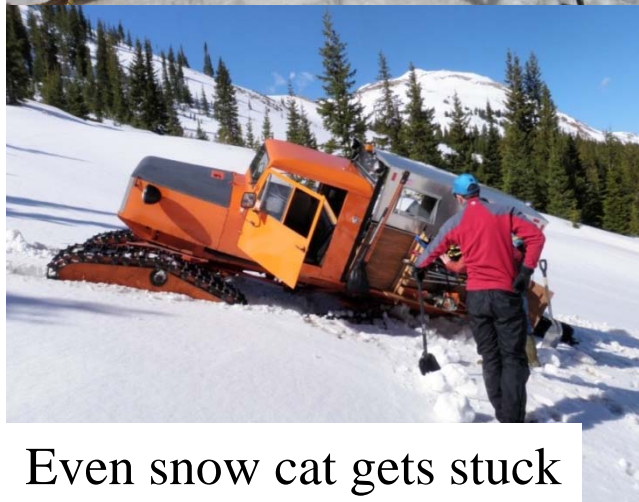
Stuck ATV



pump housing

sampler coil

N<sub>2</sub> bag



Even snow cat gets stuck

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Salt tracer injection  
1 mile underground