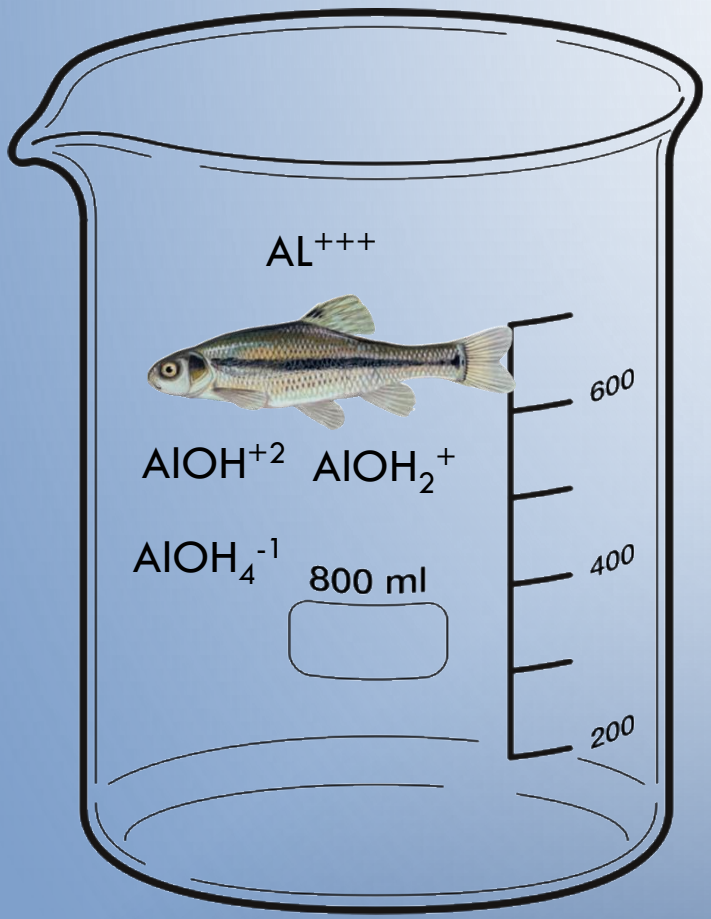
MEASURING BIOAVAILABLE ALUMINUM IN NATURAL WATER SAMPLES



William Adams[1], Patricio Rodriguez[2], William Stubblefield[3], Allison Cardwell[3] and Eirik Nordheim[4]

1- Red Cap Consulting, Lake Point, UT
2- Phr Consulting, Santiago, Chile
3-Oregon State University, Corvallis, OR
4- European Aluminium, Brussels, Belgium

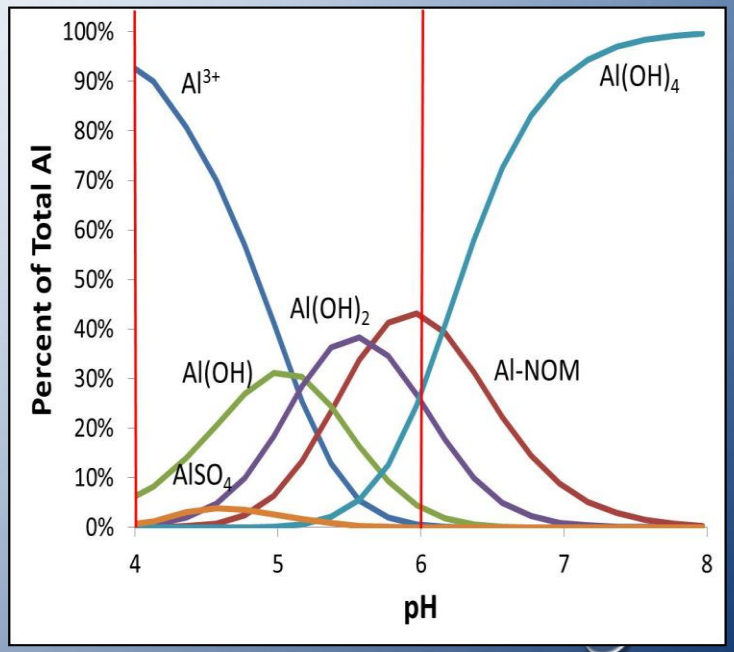
Adamsw10546@gmail.com
801-558-0222

WHAT'S THE ISSUE?

- Natural waters contain suspended solids high in Al
- Effluent permits require measurement of total recoverable aluminum
- Non-compliance can result due to TSS

What we want to measure is the free / labile Al:

Al^{+++}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_4^{-1}$



Example: Al Speciation diagram as a function of pH

USEPA Water Quality Criteria for Aluminum

EPA Water Quality Criteria for Aluminum		
	1988 µg/L	2018
Acute	750	1 - 4,800
Chronic	**87**	0.63 - 3,200

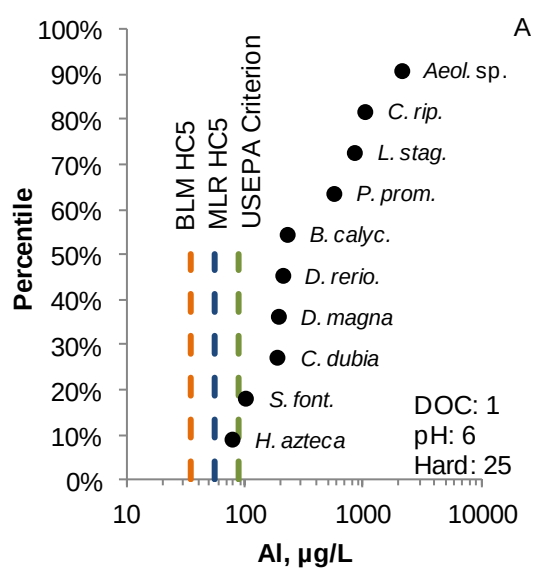
USEPA 2018 Water Quality Criteria are now based on a Multiple Linear Regression Model

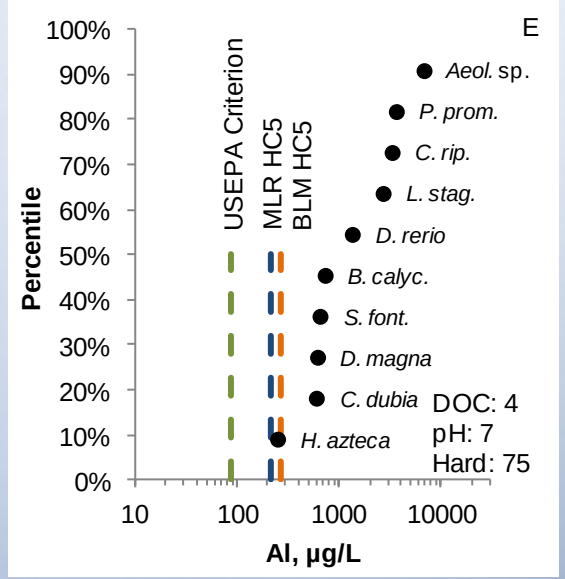
DeForest et al 2018. Environmental Toxicology and Chemistry—37 (1): 80–90
See special section in January issue of ETC on aluminum

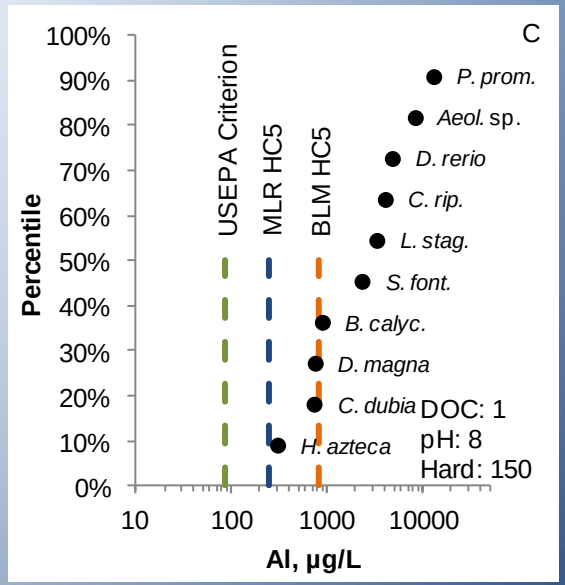
USEPA Water Quality Criteria for Aluminum

- Multiple Linear Regression Model (MLR)
- MLR model runs on an excel spreadsheet and requires only three input parameters
- Predicts toxicity as a function of pH, hardness (Ca:Mg) and dissolved organic carbon
- Model is used to estimate a site-specific water quality standard
- Biotic Ligand Model (BLM) has also been developed.
  - A mechanistic approach – binding to a key receptor

Species Sensitivity Distributions for Aluminum Influenced by Water Chemistry



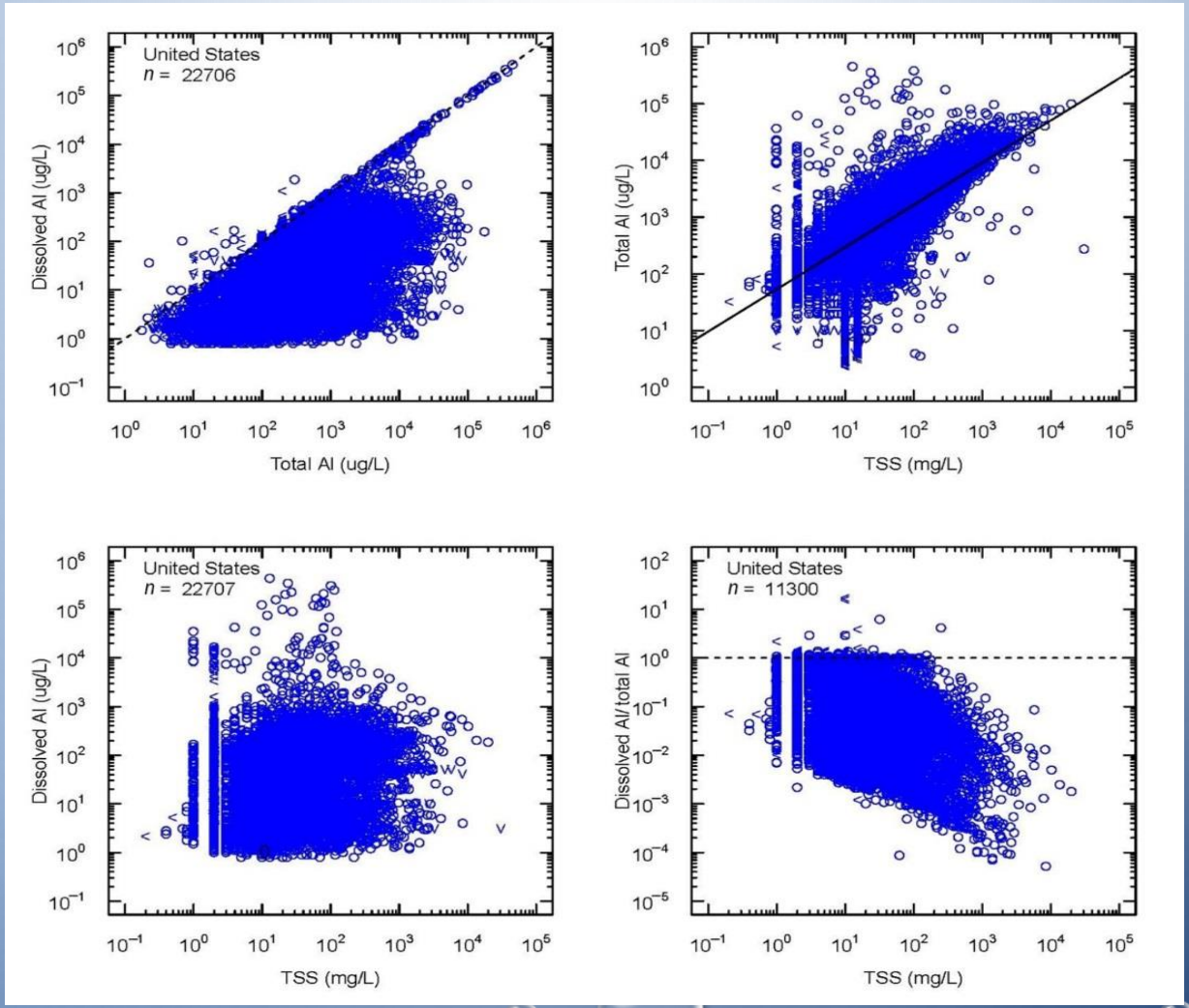




Sensitivity distributions for aluminum based on genus mean EC20s for different water chemistries – corrected for bioavailability using BLM and MLR models.

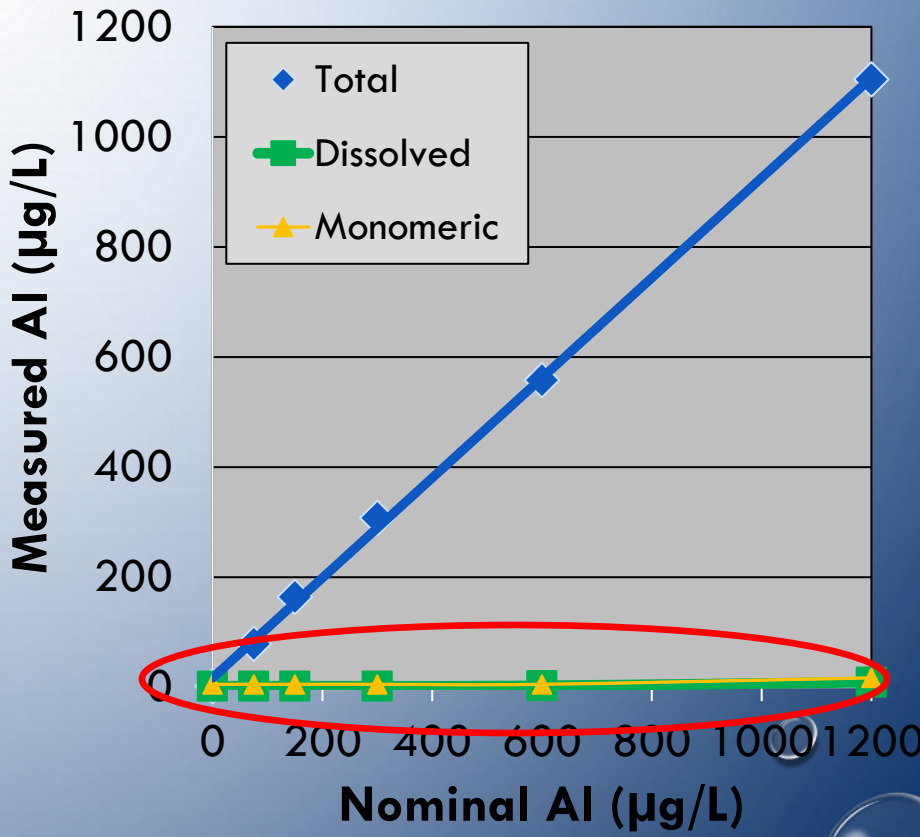
Santore et al. 2018. Biotic Ligand Model ET&C 37: 80-90
DeForest et al. 2018. Multiple Linear Model ET&C 37:70-79

Al in Natural Water Samples as a Function of TSS



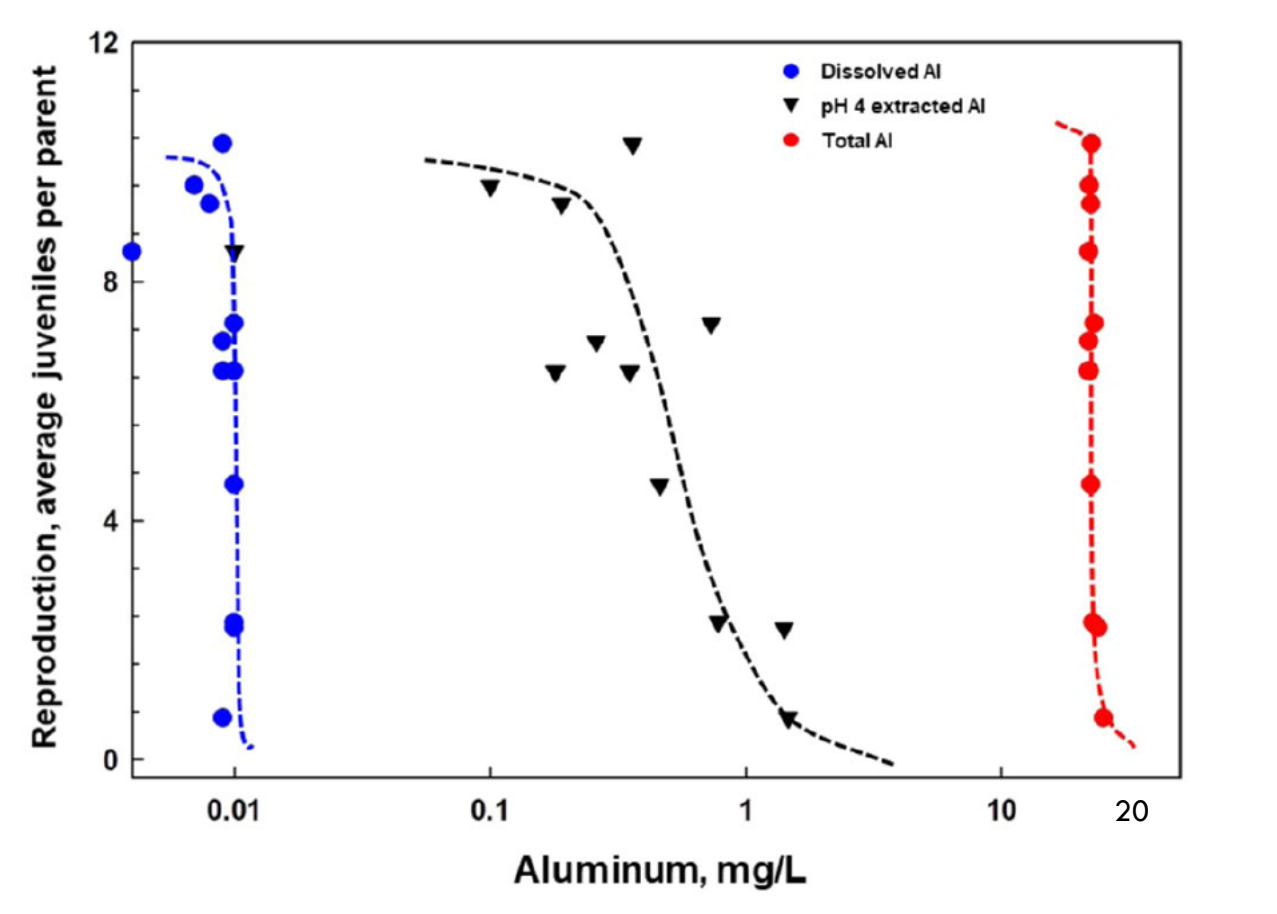
RESULTS

- Total Al correlates well with nominal exposure concentrations
- Dissolved and monomeric Al are low across all test concentrations
  - due to precipitation



Example: Fathead minnow Early-Life Stage Test pH 6

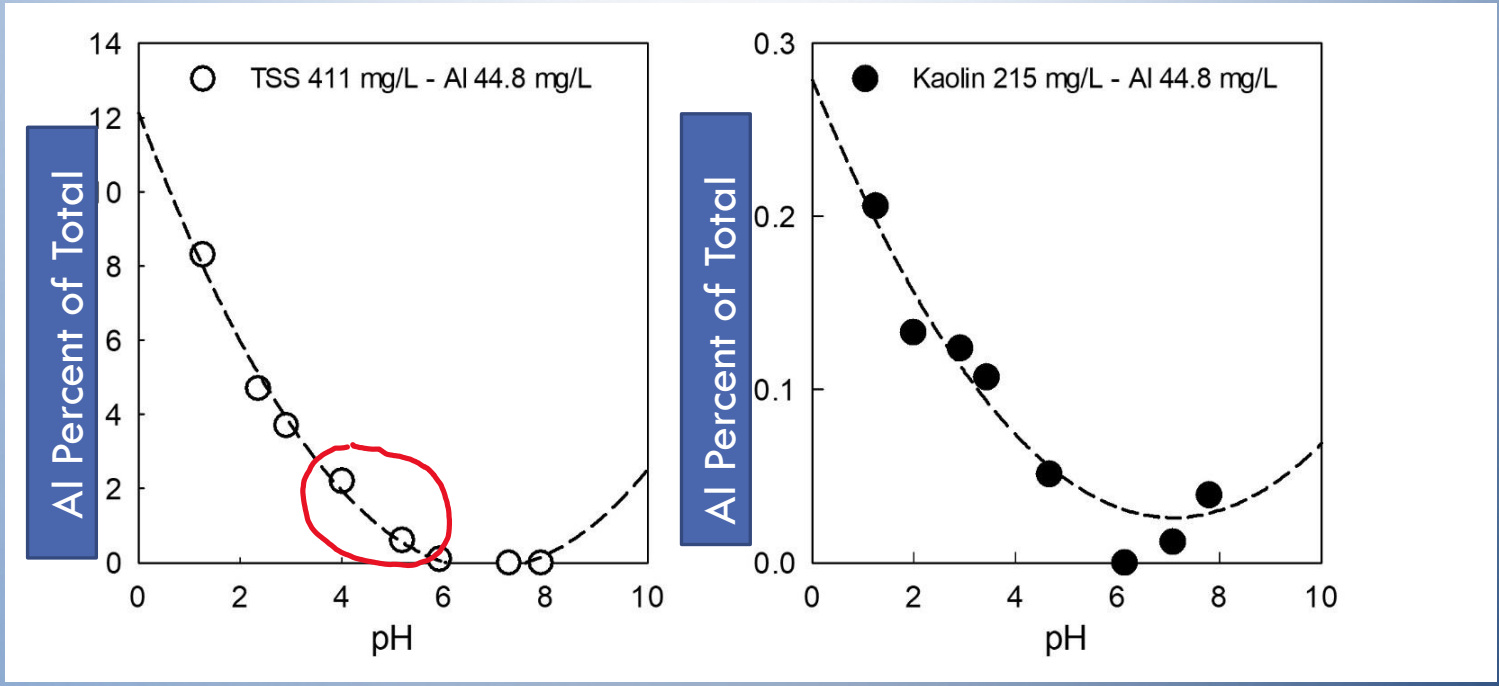
Toxicity of Al in Natural Water Samples With TSS



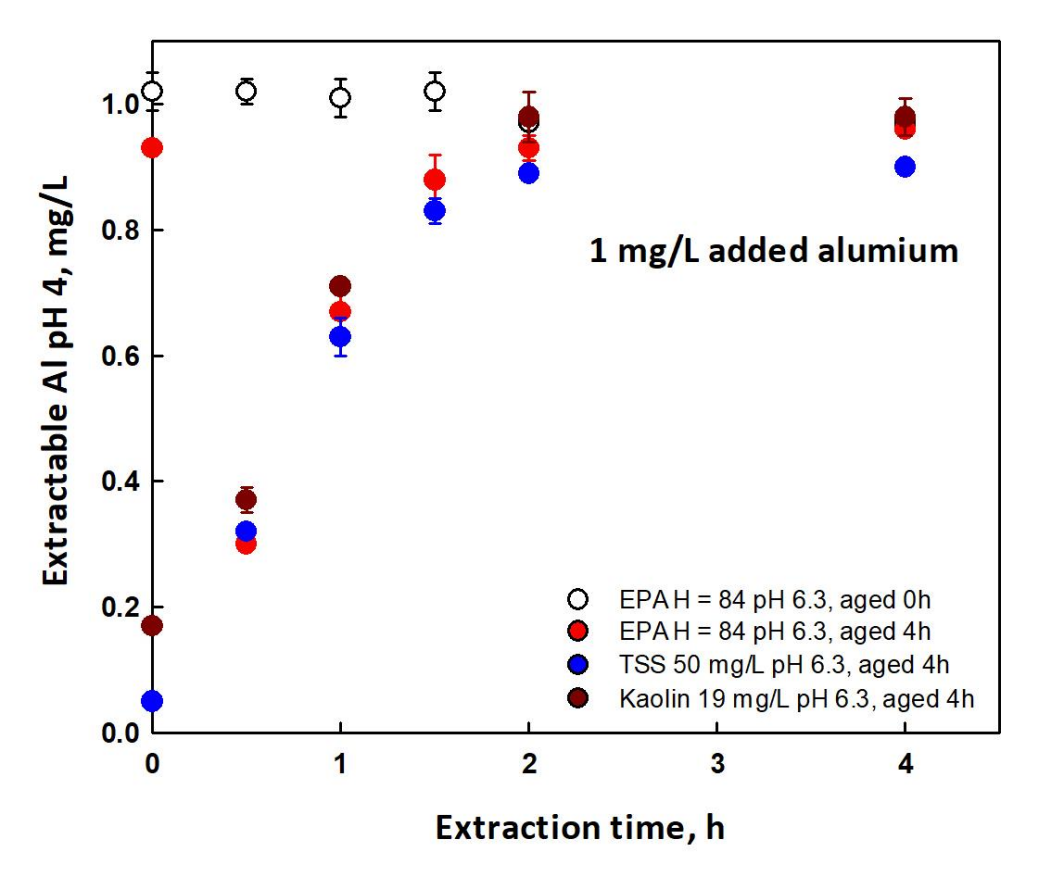
- TSS = 200 mg/L
- Total Al = 22 mg/L
- Toxicity at 0.1-1 mg/L

Al Dissolution as a Function of pH from Waters High in TSS

- Total Al in both Figures was 45 mg/L
- 1 Hour Incubation



- Al Recovery - Water Samples With 5 mg Al/L from TSS
- 1 mg/L added as dissolved Al - Aged 0 and 4 Hours
- Extracted at pH 4 …… Method measures only the added Al



Al in Natural Water Samples as a Function of TSS

Al concentrations in water samples as measured by various methods and degree of pH of extraction procedure.

River	Measured Concentration (µg/L Al)					TSS
	Total Recoverable	Total	Acid-Soluble	pH 4 extracted	Dissolved	
	pH <1.0	pH <2.0	pH 1.65-1.85	pH 4.0	NA[1]	
	Average	Average	Average	Average	Average	
Zollner Creek	6700	3134	775	146	8.5	136
Luckiamute River	3970	2428	725	38.1	34.9	89.2
Ohio River	3165	2724	410	71	0.9	140
Bear River	2370	966	309	43.9	1.4	290
N. Santiam River	1690	882	396	30	20.5	36.6

1 Sample is filtered and then pH adjusted to <2.0.

SUMMARY

- Al toxicity correlates with total metal….. And pH4 extraction
- Laboratory toxicity test waters do not contain TSS.
- Total Al and pH4 Al give the same analytical result in waters with no TSS.
- A method is needed to measure Al in natural waters without dissolving the suspended solids; i.e., pH 4 extraction.
- A balance has to be struck in the degree of aggressiveness of the extraction procedure.
- EPA Office of Water and several States have acknowledged the need for the method.

NEXT STEPS

- Development of an ASTM standard method
  - Draft document prepared – first vote taken
- Interlaboratory comparison in progress

THE DILEMMA…

Bear River, Utah, USA