Appendix C

Presentation Slides

WELCOME

Copper Biotic Ligand Model Workshop

May 13-14, 2015

Job of Facilitator & Note Takers

- Be helpful
- Get you through your agenda efficiently
- Capture your ideas
- Provide you with clear direction
- Promote understanding

Your Job as Participants

- Participate
- Make the most of your time together
- Listen as allies – be curious
- Be brief and and focused in your questions
- Provide clear answers to questions

Introductions

- Name
- Title and Organization
- Reason for Attending
- Do you….?

Prefer the Ocean or the Mountains?

Receiving Water?

Tributary?

Happy Hour

- **Happy Hour at Tap House Grill on Wednesday, May 13**
- **Address: 1506 6th Ave, Seattle, WA 98101**
  - 2 ½ blocks north of the EPA building on the same side of 6th Avenue.
  - We have reserved the dining area beyond the bar, across the room from the entrance at the bottom of the stairs.
  - http://www.taphousegrill.com/
- **Happy hour until 6:30**

The Biotic Ligand Model : Overview

Luis A. Cruz, Ph.D.
Ecological Risk Assessment Branch
Health and Ecological Criteria Division
Office of Science and Technology
Office of Water
US Environmental Protection Agency
and
Doug Endicott
Great Lakes Environmental Center

Copper

- Metals such as copper are naturally occurring.
- Copper has multiple uses: in paints, pipes, pesticides, fabricated metal products, leather production, electric equipment and others.
- Copper is both a micronutrient and a toxicant.
- Copper toxicity is proportional to the concentration of cupric ion (Cu^{2+} free ionic form) in water.
- Copper toxicity is dependent on its bioavailability due to local water chemistry
- Copper is responsible for many water impairments (303d listing).

Copper

- Copper bioavailability is affected by water chemistry (pH, organic matter, water hardness, alkalinity, cations and anions).
- Water chemistry parameters that affect bioavailability are variable: pH, DOC, hardness, etc., vary over time leading to variable toxicity at the same total copper concentration.

Metal Toxicity and Criteria

- EPA has addressed water chemistry dependency by adjusting metals criteria to local water hardness.
- Hardness equation is based on water where hardness typically covaries with pH and alkalinity.
- However, the hardness approach does not directly consider pH and DOC.
- Consequence: Hardness-based WQC do not reflect all the effects of water chemistry on copper bioavailability.
- When more refined site-specific limits were needed they have been derived using “Water Effects Ratio” procedure.

Copper BLM : History at EPA

- EPA Issued hardness-based copper criteria in 1984
- Historic EPA freshwater copper criteria (hardness based)

  1985 (EPA 440-5-84-031) and 1995 (EPA-B-96-001)

  - exp{m [*ln*(hardness)]+ b}
    - $m_{(acute)}$ = 0.9422 $b_{(acute)}$ = -1.700
    - $m_{(chronic)}$ = 0.8545 $b_{(chronic)}$ = -1.702
  - At hardness of 100 mg/L:

    CMC (acute, 1 hour) = 14 µg/L CCC (chronic, 4 days) = 9.3 µg/L

Copper BLM : History at EPA

- The Biotic Ligand Model (BLM) is based on conceptual modeling and experimental work that began in the early 1980's, with development continuing to the present day.
- In 1999, the BLM approach was presented to EPA's Science Advisory Board (SAB).
  - The SAB found that the BLM can “significantly improve predictions of the acute toxicity of certain metals across an expanded range of water chemistry parameters compared to the WER [Water-Effect Ratio]".

Copper BLM : History at EPA

- EPA refined the BLM and incorporated it into the 2003 Draft Update of Ambient Water Quality Criteria for Copper.
- The current BLM-based freshwater aquatic life criterion is EPA's Aquatic Life Ambient Freshwater Criteria – Copper 2007 Revision (EPA-822-R-07-001).
- EPA is currently updating this draft with a 2015 Freshwater Copper BLM Draft Criterion.

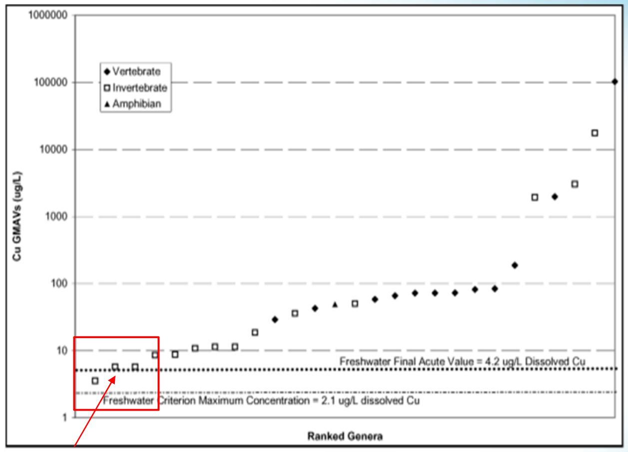
The Biotic Ligand Model

- The BLM is a predictive tool that can account for variations in metal toxicity using local water chemistry information.
- The BLM reflects the latest science on metals toxicity to aquatic organisms.

Ranked Freshwater GMAV – 2007 revision

Copper toxicity data represent 27 genera (15 species of invertebrates, 22 species of fish and 1 amphibian).

Data normalized to EPA moderately hard reconstituted water.



Using the 4 most sensitive genera, a least square regression is performed on the percentile ranks.
P = 100 R/(N+1)

Limitations/Challenges for BLM Application

- The BLM requires a number of input parameters; pH, DOC, Ca, Mg, Na, SO_4, K, Cl, alkalinity, temperature.
- States have limited resources for monitoring water chemistry on a statewide basis.
- Some BLM parameters (i.e., major ions, DOC) are not routinely collected while others (e.g., pH, hardness, temperature) are.
- Two of the BLM parameters (i.e. DOC, pH) are very influential to the resulting IWQC/FMB and should be collected on a routinely basis.

Limitations/Challenges for BLM Application

- The BLM output (IWQCs) shows the effect of variations in water chemistry over time and space on copper bioavailability at a site.
- The challenge is selecting a defensible IWQC that best protects the designated use(s) at a site.

The Biotic Ligand Model : Challenges and Solutions

Challenge 1: Completing a database for BLM use when a site has missing parameters.

- Solution: Estimate Missing Parameters

Challenge 2: Time variable water chemistry affects BLM results.

- Solution: The Fixed Monitoring Benchmark

Estimating Missing Parameters for the BLM

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Estimating Missing Parameters

Measure	Constant	Estimate
Temperature	Sulfide	Ca, Mg, Na, K, Cl, SO_4, Alkalinity
pH, DOC, dissolved Cu	Humic acid	
With sufficient resources all of the water chemistry parameters can be measured for reliable and site specific BLM application.		

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Estimating Missing Parameters

Estimate BLM parameters using national datasets and deriving Level III ecoregional estimates, with consideration of water body size (stream order).

Estimating Missing Parameters

- While it is preferable to collect data for the water quality parameters at the site, this may not always be practical or even possible.
- EPA recognizes that a practical method to estimate missing water quality parameters is needed.
- EPA has developed conservative (realistic but protective) estimates of the BLM water quality input parameters, based on existing data drawn from large National surface water quality datasets.

Estimating Missing Parameters : Ions

- Water quality data for conductivity and the BLM Geochemical Ions (GI) were retrieved from the USGS National Water Information System (NWIS).
- NWIS contains data from millions of sampling events at tens of thousands of individual sampling locations (stations) in the continental U.S.
- The data included 4,714,165 measurements from 959,946 samples, collected at 5,901 sites.
- Not all water quality parameters of relevance to the BLM were monitored at each location.

Estimating Missing Parameters : Ions

- Data used was collected from rivers and streams between 1984 and the present.
- A complete download of national water quality data at these sites from the NWIS was obtained.
- The number of sampling events at individual locations ranges widely, with a mean of 15 and a mode of one (i.e., many sites were only sampled once).
- Examination of the spatial distribution of numbers of sampling events per site reveals that the midwest and western states were sampled most intensively.
- Stream order of the sampling sites varied from 1 to 9.

Estimating Missing Parameters - GI

- IWQC predictions are positively correlated to the BLM water quality inputs.
  - IWQC predicted by the BLM increase with increasing values of each of the inputs.
- US EPA (2002) found that protective WQC for copper generally corresponded to ~ 2.5 percentile of the distribution of predicted BLM IWQCs.
- BLM IWQC predictions using the corresponding percentiles (i.e., 2.5%) of the water quality parameter distributions will be a conservative approximation of this WQC.

Estimating Missing Parameters - GI

- The concentrations of GI parameters tend to vary regionally.
  - Spatial variation of these factors is at least predictable.
- Default values of these inputs should be lower-bound estimates in order to produce conservatively protective (i.e., low) IWQC predictions.
- Values were selected from the lower "tail" of <u>measured</u> distributions of water quality data from national sources.

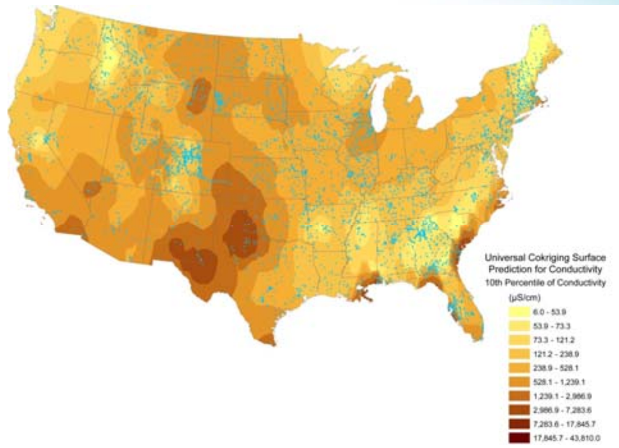
Estimating Missing Parameters - GI

- Conductivity is routinely monitored by state and federal agencies.
- Water quality data for conductivity were retrieved from the USGS NWIS.
- USEPA (2007): Conductivity is significantly correlated to ions in water.
- Correlation between conductivity and the BLM GIs was much stronger at the lower end of the concentration distributions.

Estimating Missing GI Parameters : Using Kriging

- We applied geostatistic methodologies that use spatial coordinates to predict BLM GI parameters.
- Statistically valid two-dimensional surface models for conductivity and for each of the BLM GI parameters were created using universal Kriging methods.
- Kriging is an interpolation which weights the surrounding measured values to derive a predicted value for an unmeasured location.
- The kriged prediction surface of 10th percentiles of conductivity is shown on the next slide.

BLM Parameter Estimates: Geochemical Ions

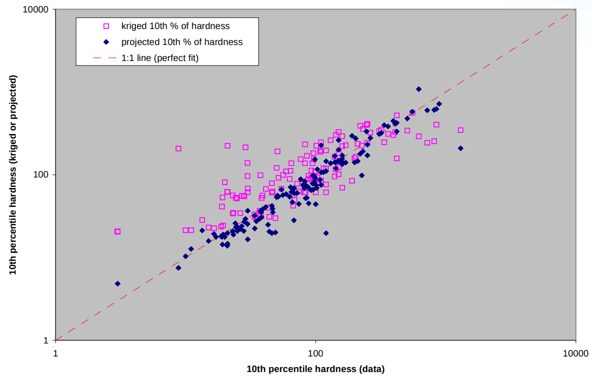


Kriged prediction for 10^{th} percentile of conductivity in the continental US

Estimating Missing GI Parameters : Co-Kriging

- Estimation of geochemical ions using co-Kriging
  - Kriging and regressions from conductivity.
- Co-kriging was used to predict BLM GI parameters by taking into account conductivity as a secondary variable.
- Universal co-kriging with conductivity was used to map the surface of 10^{th} percentile BLM GI concentrations.
- A comparison of universal Kriging and Co-Kriging for hardness is shown in the next slide.

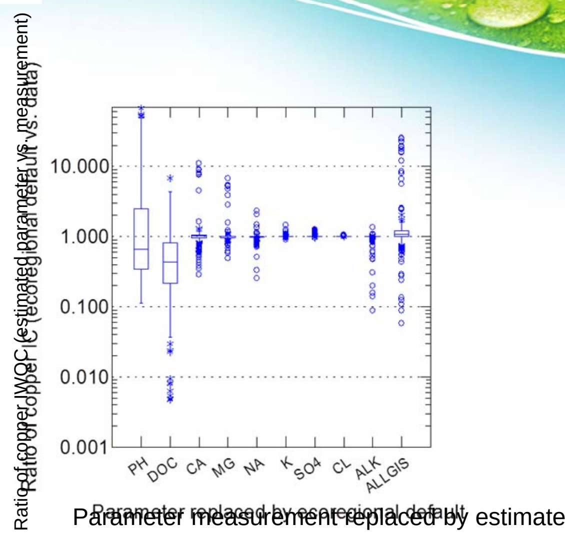
Comparison of the 10th percentile of hardness with estimates based on universal kriging of hardness data and kriging of conductivity to hardness via regression (co-kriging).



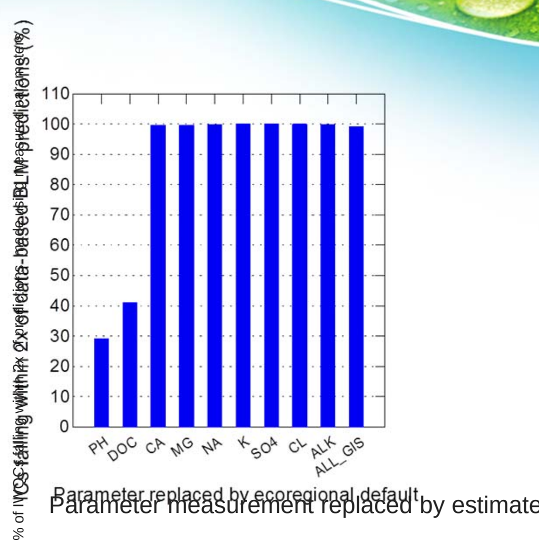
Co-Kriging (solid blue) $r^2 = 0.95$
Universal Kriging (open purple) $r^2 = 0.80$

Estimating Missing GI Parameters : Co-Kriging

- Co-kriging produced cross-validation errors that were superior in terms of the goodness-of-fit criteria to errors produced by universal kriging.
- Prediction surfaces for the other BLM GI's are generally similar to those for conductivity and hardness.
- Predictions of 10th percentile BLM water quality parameters were tabulated for each of the Level III ecoregions of the continental United States.



The box plots for IWQC errors ratios show that the errors in predictions made with estimated values of the GI parameters tend to be small. Not true for for pH and DOC.

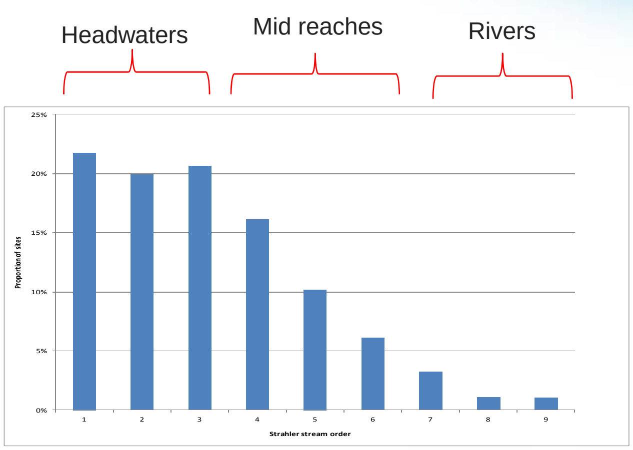


Bar graph displaying the percentage of IWQC predicted by the BLM using individual parameter estimates falling within a factor of 2 of predictions made using measured data for all parameters.

Estimating Missing Parameters: Consideration of Stream Order

- To account for surface water quality variability within ecoregions streams were classified by stream order (SO).
  - Strahler stream order was used to define stream size
- USGS NWIS data collected from rivers and streams between 1984 and 2009 was retrieved.
- Geographic information system (GIS) was used to determine the Strahler stream order of each NWIS surface water sampling location.
- Bar graph on next slide shows distribution of sites by stream order.

Distribution of Well-sampled NWIS sites by Stream Order

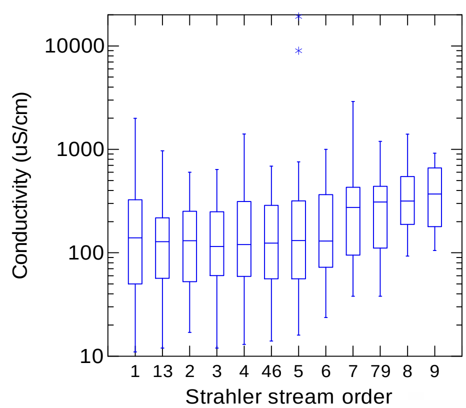


Stream order distribution in NWIS database sites. BLM GI estimates show a general increase with stream order.

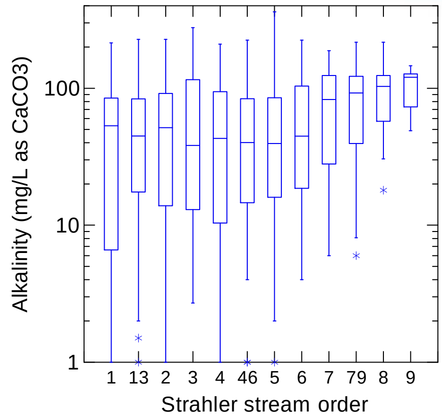
Estimating Missing Parameters: Stream Order

- BLM GI estimates were recalculated for individual stream orders or ranges (groups) of stream orders within each ecoregion.
- In general, BLM GI parameter estimates increased with SO.
- Based upon this trend, we grouped the estimates for each parameter by stream order: 1-3 (headwater streams), 4-6 (mid-reaches) and 7-9 (rivers).
- The next two slides show the trend in parameter estimates with stream order.

Box Plot of Estimated Ecoregional Conductivities as a Function of Stream Order (Classifications depicted as 13, 46, and 79 reflect groupings according to stream order: 1 through 3, 4 through 6, and 7 through 9)



Box Plot of Estimated Ecoregional Alkalinity Concentrations as a Function of Stream Order



Estimating Missing Parameters: DOC and pH

- DOC concentration data from two random statistical surveys of rivers and streams were combined:
  - National Rivers Streams Assessment (NRSA): 2113 sites.
  - Wadeable Streams Assessment: 1313 sites.
- These data were used to test the representativeness of EPA's organic carbon database at level III ecoregion.
  - EPA Organic Carbon Database data drawn from STORET and NWIS.
- GIS procedures were used to associate each site with the level III ecoregion corresponding to its location.

Estimating Missing Parameters: DOC and pH

- The statistical test used was the nonparametric Wilcoxon 2-sample test,
  - Null hypothesis: means of the two samples were equal.
  - Alternative hypothesis: mean DOC in the organic carbon database was significantly greater than in NRSA/WSA data.
- The test was applied to each of 83 level III ecoregions.
- Null hypothesis was rejected in majority of ecoregions, indicating significant and widespread bias in DOC concentrations in the organic carbon database.

Estimating Missing Parameters: DOC and pH

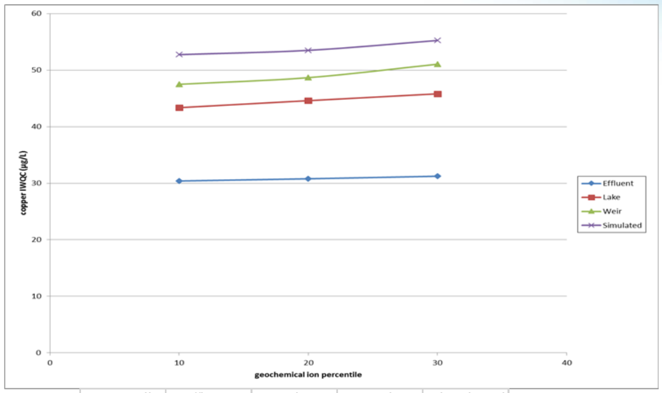
DOC

- Bias-compensated 10th percentile DOC estimates from all data for rivers and streams were tabulated at ecoregion level III.
  - However, the estimates tend to be overly conservative about 90% of the time.
  - Sometimes by a factor of 4 – 5.
- For best BLM calculations is recommended to measure DOC when possible.
  - If DOC measurements are not possible, EPA is considering recommending using 10th percentile estimates.

pH

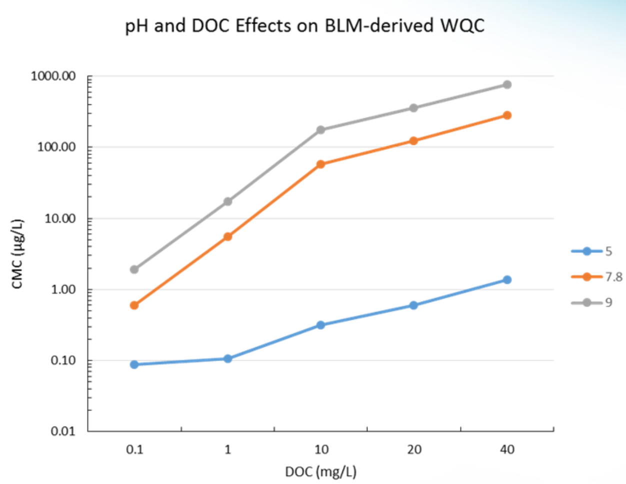
- There are no good estimates for pH.

GIs variability has little effect on IWQC at low percentiles



percentile	Effluent	Lake	Weir	Simulated
10	30.40	43.37	47.50	52.74
20	30.79	44.61	48.67	53.50
30	31.24	45.81	51.05	55.25

pH and DOC have a large effect on IWQC.



Estimating Missing Parameters: Recommendations

- Users do not need to measure all parameters at all sites.
- GI: EPA is considering recommending 10th percentile as default for GIs based upon both ecoregion and stream order, if GI data not available.
  - Provides for realistic but protective criteria.
- DOC: 10th percentile DOC estimates will provide protective criteria but not necessarily realistic.
  - Estimates are very conservative most of the time.
  - In absence of data EPA is considering recommending 10th percentile DOC estimates as defaults.
- For best BLM calculations EPA recommends measurement of site pH and DOC.

Status Update

- EPA is completing work on two technical documents
  - Derivation of a fixed monitoring benchmark (FMB)
  - Estimation of missing BLM water quality parameters
- Both documents have been externally peer reviewed.
- Copper aquatic toxicity data is being updated.
- Chronic BLM criteria are being derived.
  - SSD Regression based vs ACR based

data description	temp	Ca	Mg	Na	K	Alk	Cl	SO4	S	pH	DOC	Cu	CMC (ug/L)
IN0020656 Lake 10th	17.08	65.50	22.50	97.50	8.00	200.00	170.00	43.50	0.02	7.58	6.72	8.50	43.37
IN0020656 Lake 20th	17.08	69.00	23.00	110.00	8.00	200.00	190.00	45.00	0.02	7.58	6.72	8.50	44.61
IN0020656 Lake 30th	17.08	76.00	24.50	120.00	9.00	225.00	210.00	45.00	0.02	7.58	6.72	8.50	45.81
IN0020656 Simulated 10th	16.96	63.00	22.50	94.50	8.00	200.00	170.00	42.50	0.02	7.77	6.70	14.39	52.74
IN0020656 Simulated 20th	16.96	68.00	23.00	100.00	8.00	210.00	190.00	44.00	0.02	7.77	6.70	14.39	53.50
IN0020656 Simulated 30th	16.96	73.00	24.00	115.00	8.00	220.00	215.00	45.00	0.02	7.77	6.70	14.39	55.25
IN0020656 Weir 10th	17.04	59.50	22.00	89.50	8.00	200.00	170.00	42.50	0.02	7.69	6.67	8.26	47.50
IN0020656 Weir 20th	17.04	63.00	23.00	99.00	8.00	210.00	190.00	43.00	0.02	7.69	6.67	8.26	48.67
IN0020656 Weir 30th	17.04	72.00	24.00	120.00	9.00	220.00	215.00	45.50	0.02	7.69	6.67	8.26	51.05
IN0020656 Effluent 10th	17.21	88.50	25.50	125.00	9.00	225.00	235.00	38.50	0.02	7.24	6.53	23.20	30.40
IN0020656 Effluent 20th	17.21	90.00	27.00	130.00	10.00	240.00	250.00	45.00	0.02	7.24	6.53	23.20	30.79
IN0020656 Effluent 30th	17.21	93.00	27.50	135.00	10.00	255.00	250.00	46.50	0.02	7.24	6.53	23.20	31.24

Estimating Missing Parameters : Co-Kriging

Table 2. Model Selection and Cross Validation Statistics for Geostatistical Fitting of 10th Percentiles of BLM Geochemical Ion Parameters

Parameter	Geostatistical Model	Number of samples	Mean standardized error	Root Mean Square error	RMS Standardized error	Average Standard error
Conductivity	Universal kriging	4833	-0.01038	1361	1.081	1259
Calcium	Universal cokriging with conductivity	2590	0.0001694	26.81	1.186	22.02
Magnesium	Universal cokriging with conductivity	2578	-0.002258	15.92	1.16	13.58
Sodium	Universal cokriging with conductivity	2439	-0.002929	156.3	1.583	95.78
Potassium	Universal cokriging with conductivity	2379	-0.001184	3.488	1.429	2.381
Alkalinity	Universal cokriging with conductivity	1372	-0.001115	36.62	1.09	33.23
Chloride	Universal cokriging with conductivity	2792	0.001653	375.2	1.51	247
Sulfate	Universal cokriging with conductivity	2650	-0.0000225	114.5	1.29	87.04

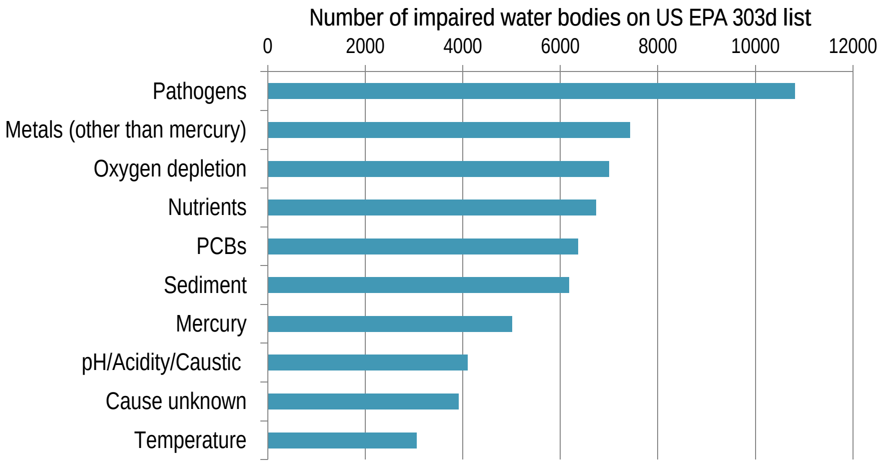
Overview of the Copper BLM

Robert Santore, Adam Ryan, Paul Paquin
HDR, Inc. Syracuse NY

Special Challenges for Metals Criteria

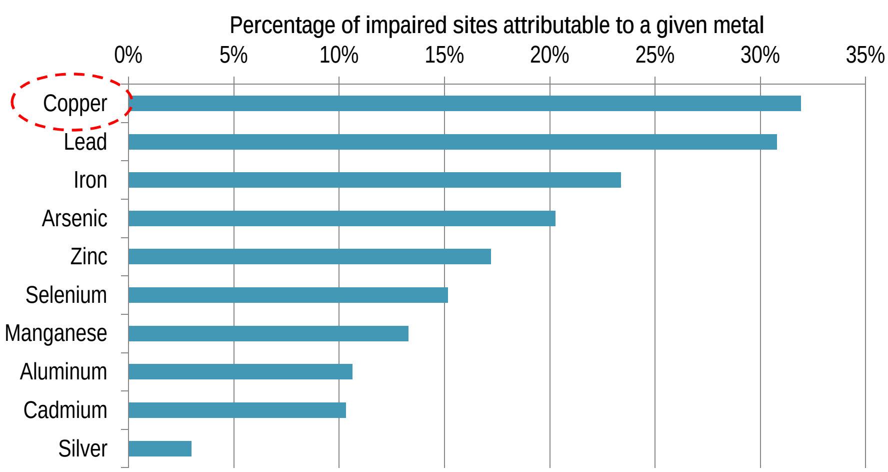
- Metals are naturally occurring and ubiquitous
  - o Natural sources contribute to loads at most sites
  - o Background concentrations can exceed criteria
  - o Metals are found in all water sources but may not be bioavailability
- Metals have complex chemistry
  - o Toxicity can vary widely from place to place due to local conditions (e.g., pH, ionic composition, presence of natural organic matter, etc).
- Metals regulations based on water quality criteria are typically very low

Top Ten Causes of Impairment for 303d Listed waters



Source water.epa.gov/lawsregs/lawsguidance/cwa/tmdl

Top Ten Metals (other than Hg) Responsible for Impairment



Source water.epa.gov/lawsregs/lawsguidance/cwa/tmdl

Metals criteria – US EPA

	Acute µg/L	Chronic µg/L	Dependent on
Aluminum	750	87	pH
Cadmium	2	0.25	hardness
Copper	13	9	hardness (prior to BLM)
Lead	65	2.5	hardness
Nickel	470	52	hardness
Silver	3.2		hardness
Zinc	120	120	hardness

Acute : "Criterion Maximum Concentration" or CMC
is the highest level for a 1-hour average exposure
Chronic: "Criterion Continuous Concentration" or CCC
is the highest level for a 4-day average exposure.
Hardness dependent metal criteria correspond to a hardness of 100 mg/L as CaCO3
Source: water.epa.gov/scitech/swquidance/standards/current/index.cfm

Many of the metals criteria are hardness dependent

Criterion = exp(A ln(H) + B)

- Attempt to account for bioavailability
- Applied to 7 metals:
  - Cd, Cu, Cr(III), Pb, Ni, Ag, Zn
  - *A* and *B* are regression parameters
  - H is hardness

Copper Criteria

Hardness mg/L CaCO3	Acute µg/L	Chronic µg/L
25	3.8	2.9
50	7.3	5.2
100	14.0	9.3
200	26.9	16.9
400	51.7	30.5

Average Dissolved Copper in Surface Waters

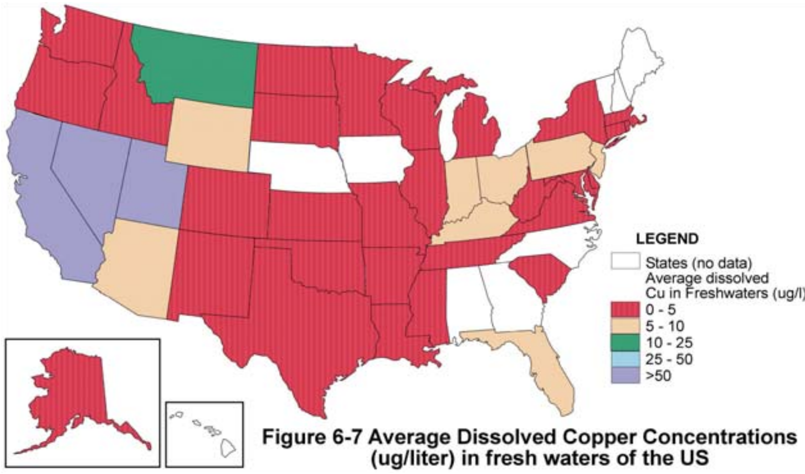
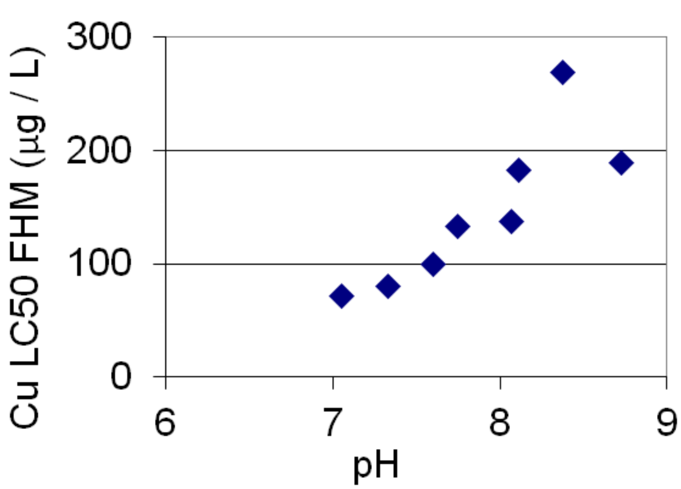


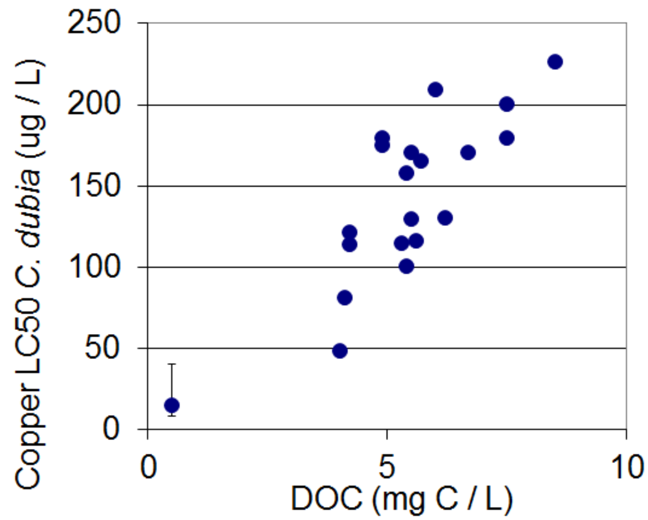
Figure 6-7 Average Dissolved Copper Concentrations (ug/liter) in fresh waters of the US

- From DIFFUSE SOURCES of ENVIRONMENTAL COPPER in the UNITED STATES. 2003. Copper Development Association, Inc., International Copper Association, Ltd. New York, New York

Traditional metals criteria do not account for **pH effects**



Traditional metals criteria do not account for **natural organic matter effects**



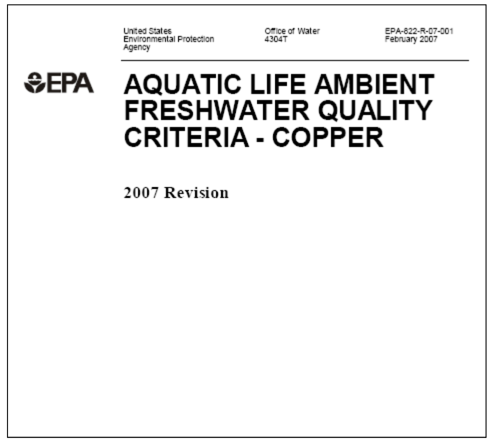
US EPA provides methods for deriving site-specific criteria

- In the early 1980's, members of the regulated community expressed concern that EPA's laboratory-derived water quality criteria might not accurately reflect site-specific conditions because of the effects of water chemistry . . . In response to these concerns, EPA created three procedures to derive site-specific criteria.

From: Tudor Davies, Director Office of Science and Technology. US EPA. 1994. Use of the Water-Effect Ratio in Water Quality Standards. EPA-823-B-94-001

US EPA adopts BLM for copper

"This criteria revision incorporated new data on the toxicity of copper and used the biotic ligand model (BLM), a metal bioavailability model, to update the freshwater criteria. With these scientific and technical revisions, the criteria will provide improved guidance on the concentrations of copper that will be protective of aquatic life"


United States Environmental Protection Agency

Office of Water 4304T

EPA-822-R-07-001 February 2007

EPA

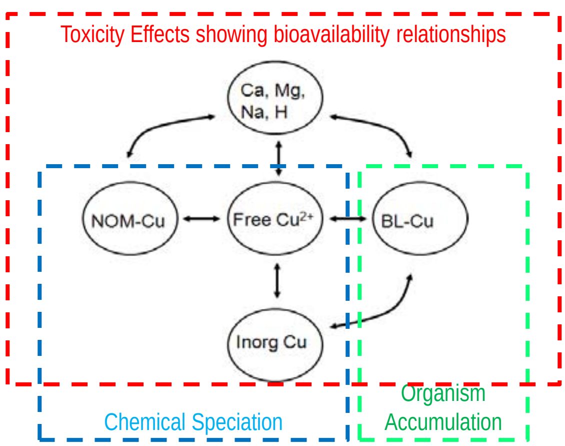
AQUATIC LIFE AMBIENT FRESHWATER QUALITY CRITERIA - COPPER

2007 Revision

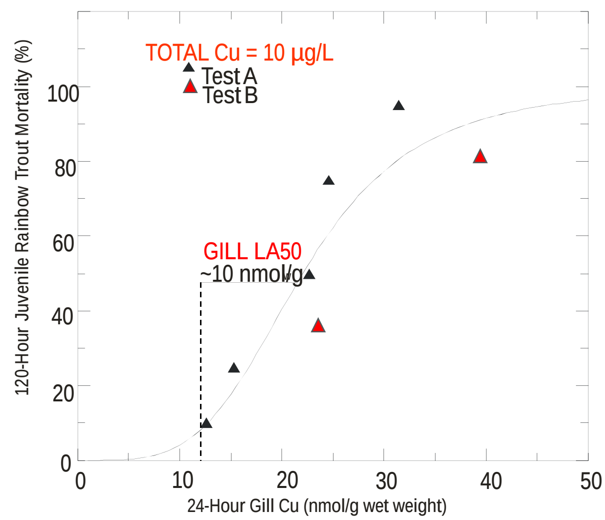
BLM conceptual model and data needs

Input Data

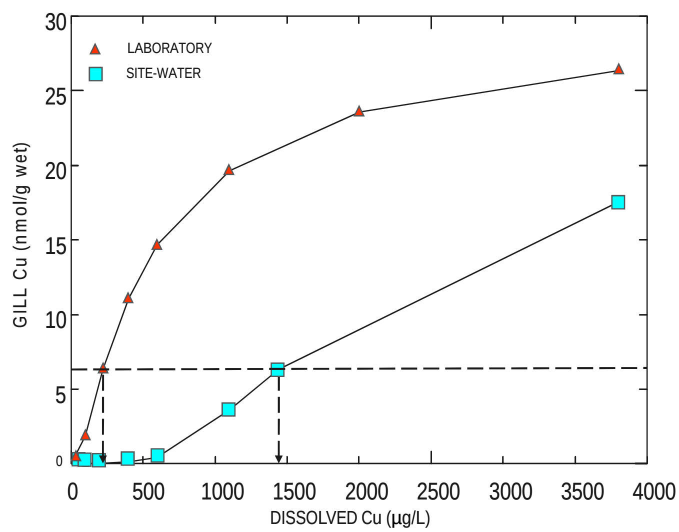
- pH
- DOC
- Major ions (Ca, Mg, Na, SO4, Cl, Alkalinity)
- Temperature



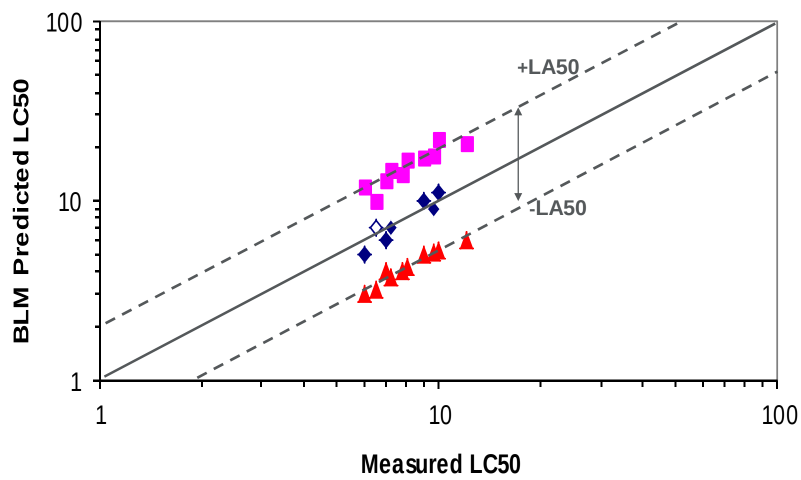
Gill-Cu is a predictor of Cu toxicity



BLM numerically simulates a titration at the biotic ligand



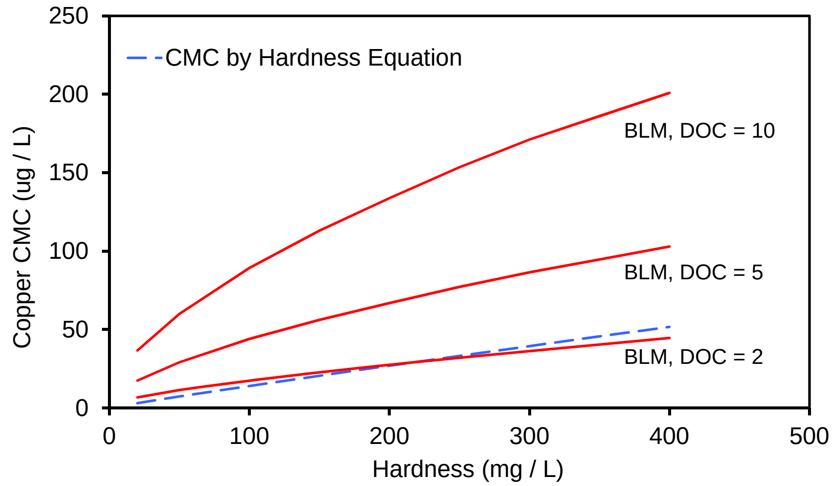
Application to Other Organisms: Interspecies calibration



BLM versus WER

	Advantages	Disadvantages
WER	• Comprehensive • Precedent in many states for deriving site-specific criteria	• Time consuming & expensive • Often performed with limited number of samples • Biological response - results may be variable & difficult to interpret • Testing requires clean metal techniques
BLM	• Requires only simple water chemistry • Expedient and cost effective • Large number of samples practical • Deterministic results are repeatable and understandable	• Focuses on major bioavailability factors but may not be comprehensive

Comparison of Criteria Approaches



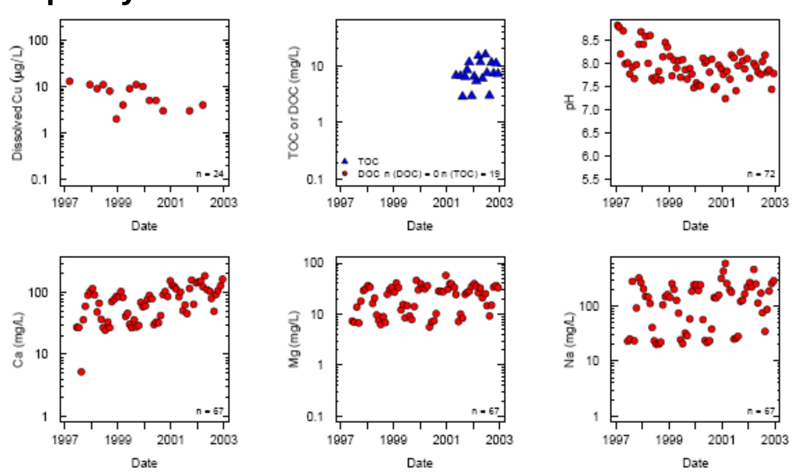
Anticipated BLM related activities, 2015+

- Fixed Monitoring Benchmark – deals with time-variability
- Simplified BLM inputs
  - Reduced parameters from 10 to 3
- Development of BLM-based chronic approaches for copper in US and Canada
- Marine WQC

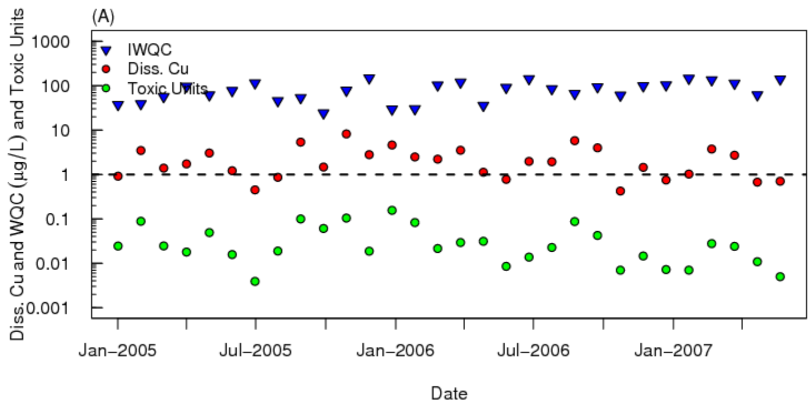
Using the BLM for IWQC and FMB

- Biotic Ligand Model (BLM) for copper
  - Released in 2007, uses water quality parameters to calculate freshwater copper acute and chronic criteria
- Time variable water quality
  - Parameters such as pH, DOC, hardness vary over time
  - Time variable WQC
- Fixed Monitoring Benchmark (FMB)
  - Probabilistic approach to consider time variable Cu and WQC

Water quality characteristics are variable



BLM calculated WQC are also variable

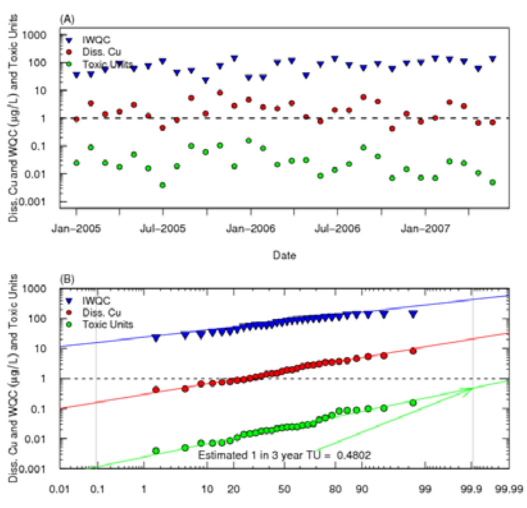


BLM calculated WQC are also variable

Model output is variable over time, and can be shown as a time-series,

or as a probability plot, which can be used to show exceedance frequency.

The WQC for a given point in time, is the instantaneous WQC or IWQC



Fixed Monitoring Benchmark (FMB)

- FMB is a probability-based method that incorporates time variability in BLM-predicted instantaneous water quality criteria (IWQC) and in-stream Cu concentrations.
- FMB can be used to evaluate compliance with time variable WQC.
- WQC will depend on characteristics of the receiving water independent of Cu concentrations
- FMB will depend on both the WQC and existing Cu concentrations (so in this sense it is different than a traditional WQC)
- The FMB is a value that will produce the same toxic unit distribution exceedence frequency as the time variable IWQC

Summary

- Metals such as copper present unique challenges for setting defensible water quality guidelines
  - Naturally occurring
  - Complex chemistry
  - Toxicity is strongly modified by environmental factors such as pH, competing ions, and the presence of organic matter
- Consideration of only total or dissolved metal will result in guidelines that are frequently overprotective, or underprotective (or both)
- These challenges can be addressed with bioavailability based approaches such as the BLM

BLM Demonstration

Robert Santore, Adam Ryan, Paul Paquin
HDR, Inc. Syracuse NY

BLM Website

Model and users guides can be downloaded from:

Water quality criteria version:
http://www.epa.gov/waterscience/criteria/copper/2007/index.htm

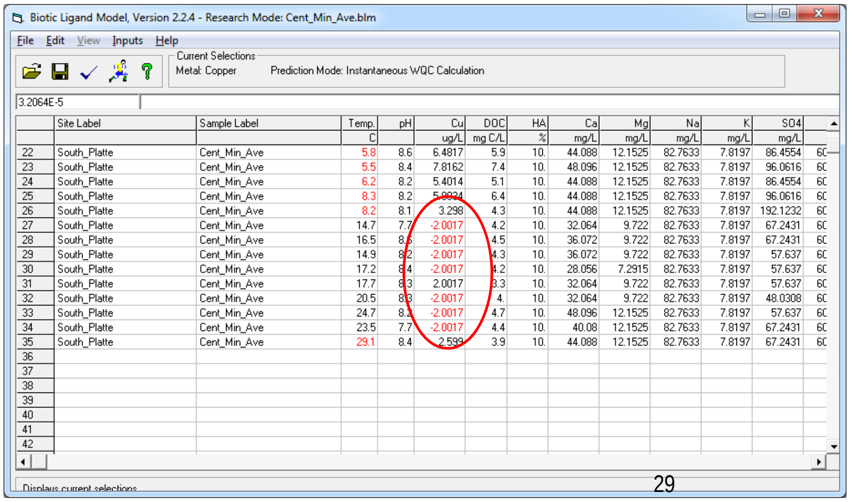
Summary

- FMB is a probability-based method that incorporates time variability in BLM-predicted instantaneous water quality criteria (IWQC) and in-stream Cu concentrations.
- FMB are automatically calculated in WQC simulations in BLM ver 2.2.4 and later

Biotic Ligand Model Input Files

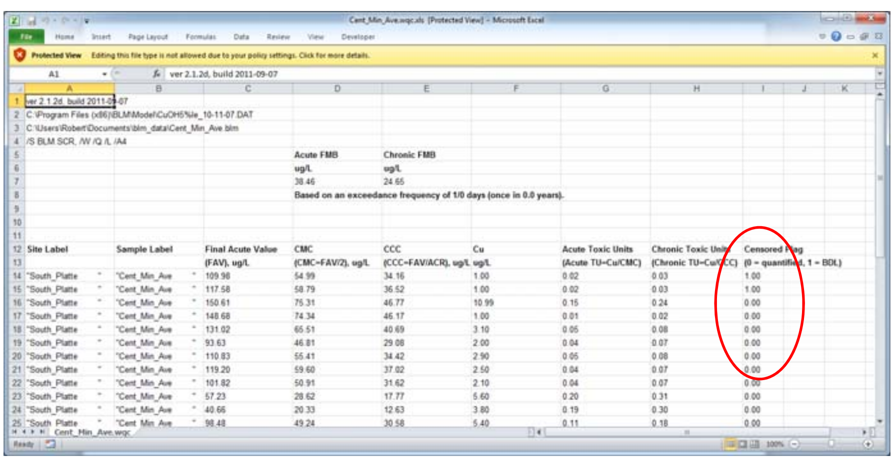
- Parameter File
  - Supplied with the software
  - Contains thermodynamic information
  - Specifies metal and organism
  - New windows software can use parameter files distributed with previous versions
- Input File
  - Created by the User
  - Contains water chemistry
  - New windows software can not use input files developed for previous versions

BLM ver 2.2.4 and later includes the ROBMLE procedure for BDL metal concentrations.
BDL values are specified as a negative Cu concentration.



	Site Label	Sample Label	Temp. C	pH	Cu ug/L	DOC mg C/L	HA %	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SO4 mg/L
22	South_Platte	Cent_Min_Ave	5.8	8.6	6.4817	5.9	10.	44.088	12.1525	82.7633	7.8197	86.4554
23	South_Platte	Cent_Min_Ave	5.5	8.4	7.8162	7.4	10.	48.096	12.1525	82.7633	7.8197	96.0616
24	South_Platte	Cent_Min_Ave	6.2	8.2	5.4014	5.1	10.	44.088	12.1525	82.7633	7.8197	86.4554
25	South_Platte	Cent_Min_Ave	8.3	8.2	5.0034	6.4	10.	44.088	12.1525	82.7633	7.8197	96.0616
26	South_Platte	Cent_Min_Ave	8.2	8.1	3.298	4.3	10.	44.088	12.1525	82.7633	7.8197	192.1232
27	South_Platte	Cent_Min_Ave	14.7	7.7	-2.0017	4.2	10.	32.064	9.722	82.7633	7.8197	67.2431
28	South_Platte	Cent_Min_Ave	16.5	8.5	-2.0017	4.5	10.	36.072	9.722	82.7633	7.8197	67.2431
29	South_Platte	Cent_Min_Ave	14.9	8.2	-2.0017	4.3	10.	36.072	9.722	82.7633	7.8197	57.637
30	South_Platte	Cent_Min_Ave	17.2	8.4	-2.0017	4.2	10.	28.056	7.2915	82.7633	7.8197	57.637
31	South_Platte	Cent_Min_Ave	17.7	8.3	2.0017	3.3	10.	32.064	9.722	82.7633	7.8197	57.637
32	South_Platte	Cent_Min_Ave	20.5	8.3	-2.0017	4.	10.	32.064	9.722	82.7633	7.8197	48.0308
33	South_Platte	Cent_Min_Ave	24.7	8.2	-2.0017	4.7	10.	48.096	12.1525	82.7633	7.8197	57.637
34	South_Platte	Cent_Min_Ave	23.5	7.7	-2.0017	4.4	10.	40.08	12.1525	82.7633	7.8197	67.2431
35	South_Platte	Cent_Min_Ave	29.1	8.4	2.599	3.9	10.	44.088	12.1525	82.7633	7.8197	67.2431
36												
37												
38												
39												
40												
41												
42												

Corresponding "Censored Flag" in WQC file will be set to 1.00 for BDL values



	A	B	C	D	E	F	G	H	I
1	ver 2.1.2d, build 2011-09-07								
2	C:\Program Files (x86)\BLM\Model\CuOH5%le_10-11-07.DAT								
3	C:\Users\Robert\Documents\blm_data\Cent_Min_Ave.blm								
4	/S BLM SCR, /W /Q /L /A4								
5				Acute FMB	Chronic FMB				
6				ug/L	ug/L				
7				38.46	24.65				
8				Based on an exceedance frequency of 1/0 days (once in 0.0 years).					
9									
10									
11									
12	Site Label	Sample Label	Final Acute Value	CMC	CCC	Cu	Acute Toxic Units	Chronic Toxic Units	Censored Flag
13			(FAV), ug/L	(CMC=FAV/2), ug/L	(CCC=FAV/ACR), ug/L	ug/L	(Acute TU=Cu/CMC)	(Chronic TU=Cu/CCC)	(0 = quantified, 1 = BDL)
14	"South_Platte "	"Cent_Min_Ave "	109.98	54.99	34.16	1.00	0.02	0.03	1.00
15	"South_Platte "	"Cent_Min_Ave "	117.58	58.79	36.52	1.00	0.02	0.03	1.00
16	"South_Platte "	"Cent_Min_Ave "	150.61	75.31	46.77	10.99	0.15	0.24	0.00
17	"South_Platte "	"Cent_Min_Ave "	148.68	74.34	46.17	1.00	0.01	0.02	0.00
18	"South_Platte "	"Cent_Min_Ave "	131.02	65.51	40.69	3.10	0.05	0.08	0.00
19	"South_Platte "	"Cent_Min_Ave "	93.63	46.81	29.08	2.00	0.04	0.07	0.00
20	"South_Platte "	"Cent_Min_Ave "	110.83	55.41	34.42	2.90	0.05	0.08	0.00
21	"South_Platte "	"Cent_Min_Ave "	119.20	59.60	37.02	2.50	0.04	0.07	0.00
22	"South_Platte "	"Cent_Min_Ave "	101.82	50.91	31.62	2.10	0.04	0.07	0.00
23	"South_Platte "	"Cent_Min_Ave "	57.23	28.62	17.77	5.60	0.20	0.31	0.00
24	"South_Platte "	"Cent_Min_Ave "	40.66	20.33	12.63	3.80	0.19	0.30	0.00
25	"South_Platte "	"Cent_Min_Ave "	98.48	49.24	30.58	5.40	0.11	0.18	0.00

Switch to software for demonstration

Questions?

For further information:

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HDR|HydroQual

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robert.santore@gmail.com

Copper and the Biotic Ligand Model in Alaska

Water Quality Standards

Alaska Dept. of Environmental Conservation

May 2015

Brock Tabor
Brock.tabor@alaska.gov
(907) 465-5185

Improving and Protecting Alaska's Water Quality

Alaska Copper Criteria

Freshwater: Hardness based (dissolved)
Marine: 4.8 µg/l (CCC)/3.1 µg/l (CMC) (dissolved)

For Both Freshwater and Saltwater Aquatic Life Criteria:

Chronic	4-Day Average
Acute	1-Hour Average

Alaska Regulatory Actions Related to Copper

Integrated Report 2012

- 4a: Three TMDLs for multiple metals (historic mine waste/stormwater)
- 4b: One (historic mine waste)
- 5: Four for multiple metals (historic mine waste/ARD)

WQ Standards

- One existing SSC, two in the works…

Permitting

- 23 individual with permit limits-we're just not that big of a state…yet

Alaska History with BLM

Southwest Alaska Salmon Habitat Partnership Salmon Science Workshop (2013)

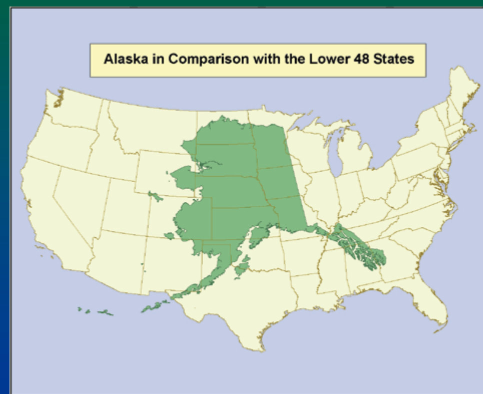
- Theme: Copper and Salmon- Are State and Federal Water Quality Standards Sufficiently Protective of Salmon in Southwest Alaska?
- Papers by NOAA, WSU, Stratus Consulting, ARCADIS

Alaska Potential For Adoption?

2015-2017 Triennial Review

State Position

- Most waters in Alaska have extremely limited monitoring data available.
- Lack of data limits the ability to apply the BLM as a meaningful statewide criteria for the foreseeable future.
- Alaska plans to assess options for using BLM in determining site specific criteria



Alaska BLM: Foregone conclusion?

While Alaska may not have adopted BLM, EPA has cited its use in numerous instances including *Bristol Bay Assessment* (2014)

"[s]tates such as Alaska may lag in adopting the latest criteria. In particular, the U.S. Environmental Protection Agency (USEPA) (2007) has published copper criteria based on the biotic ligand model (BLM), but Alaska still uses the hardness-based criteria for copper. We use the current USEPA copper criteria in this assessment *based on the assumption that, before permitting a copper mine in the Bristol Bay watershed, Alaska would adopt those criteria at the state level or would apply them on a site-specific basis to any discharge permits*." (USEPA, 2014. 8-3)

Main Questions

- Use of WER (lab) v. BLM (modeled)
- Data Restrictions- Can we think regionally?
- Specific things we should be aware of before we start collecting BLM data for SSC purposes?

Copper and the Biotic Ligand Model in Idaho

Idaho Department of Environmental Quality

May 2015

Jason Pappani
jason.pappani@deq.idaho.gov
(208) 373-0515

Idaho Copper Criteria

Aquatic Life: Hardness based (dissolved)

Chronic	**4-Day Average**
Acute	**Instantaneous or 1-Hour Average**

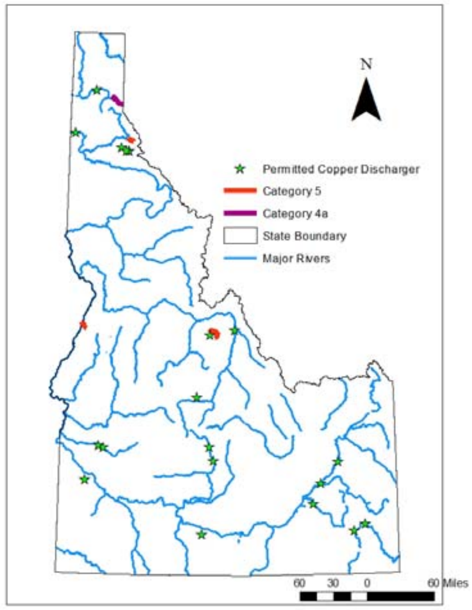
Copper in Idaho

2012 Integrated Report

- Category 5: 6 Assessment Units listed in 2012 IR, 20.5 miles
- Category 4a: One approved TMDL, 3 AUs, 12.4 miles (Clark Fork River)

Permits

- 20 individual with permit limits
- 10 WWTP, 8 mines, 2 fish hatcheries



Why Idaho is interested in BLM

May 2014: NOAA Biological Opinion:

found jeopardy and adverse modification of critical habitat due to several criteria, including acute and chronic Cu criteria

Reasonable and Prudent Alternative:

New criteria by May 2017, no less stringent than EPA's 2007 304(a) copper criteria (BLM model)

Idaho's pursuit of BLM

March 2015: Began internal rulemaking effort

Postponed due to existing workload, expected to resume this summer

Questions about BLM implementation in Idaho

What does the actual rule language look like? What about when model is updated?

What do we use as defaults when model inputs are missing?

How do we transition from hardness-based to BLM?

What do we use for IR?

Copper and the Biotic Ligand Model in Oregon

Water Quality Standards and Assessment

OR Dept. of Environmental Quality

State of Oregon Department of Environmental Quality

Andrea Matzke

matzke.andrea@deq.state.or.us

(503) 229-5384

Oregon Copper Summary

- FW Cu: Hardness-based criteria—total recoverable
- SW Cu: dissolved
- No SSC for metals

Statewide Copper Concentrations (ug/L):

Average: 2.4 Median: 1.9

Min: 0.02 Max: 64.3

CMC=18

CCC=12 (@ 100mg/L hardness)

Oregon Copper Summary

- **2010 Integrated Report (effective)**
  - Cat 5: 14
  - Cat 3 (insufficient data): 106
  - Cat 3B (potential concern): 26
  - Cat 2 (attaining): 11
- **TMDLs:** none
- **Permit limits:** ~21

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Jan. 2013 EPA Disapproval

- **Copper**
  - Hardness based criteria not consistently protective
  - NMFS: criteria would cause jeopardy to T&E species
- **EPA Remedies**
  1. Replace hardness criteria with BLM—account for temporal and spatial variability

     → Statewide defaults or regional criteria possible
  2. Revise hardness based criteria and re-submit with scientific rationale
  3. Re-submit disapproved criteria (1995 EPA rec's) with scientific rationale that shows protectiveness

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Anticipated Rulemaking Schedule

Oregon anticipates adopting the BLM in some manner

Statewide evaluation of model	June 2015
Advisory Committee meetings	Aug. 2015 – Jan. 2016
Public comment period and hearings	May 16 – June 29, 2016
Environmental Quality Commission meeting	Oct. 19, 2016
Submission to EPA for approval	November 2016
EPA action	March 2017 (estimated)

Challenges in Adopting the BLM

- Replacing hardness based criteria vs. use of BLM criteria (in context of EPA disapproval and NMFS jeopardy decision)
- insufficient data
- potential inability to use hardness-based criteria
  - Limited BLM datasets may lead to overly conservative BLM default values
    - ✓ permitting anti-backsliding concerns
    - ✓ determining spatial extent of BLM criteria
- Integrated Report—maintenance of BLM database and re-evaluation of BLM criteria every 2 yrs.

Copper and the Biotic Ligand Model in Washington

Water Quality Standards

Washington Department of Ecology

May 2015

Cheryl Niemi
cheryl.niemi@ecy.wa.gov
(360) 407-6440

Washington Copper Criteria

Freshwater: Hardness based (dissolved)
Marine: 4.8 µg/l (CCC)/3.1 µg/l (CMC) (dissolved)

For Both Freshwater and Saltwater Aquatic Life Criteria:

Chronic 4-Day Average
Acute 1-Hour Average

Washington Regulatory Actions Related to Copper

Category	Integrated Report 2008 Freshwater	Integrated Report Proposed Freshwater (with transition to NHD)
4a	0	0
4b	0	0
5	13	17

WQ Standards

- No aquatic life Cu actions since the 1997 total-to-dissolved conversion

Permitting

- 11 individual permits with effluent limits
- 1,100 Industrial stormwater general permittees (14 µg/L WWA, 32 µg/L EWA)
- 70 Boatyard general permittees (147 µg/L max., 50 µg/L ave.)

Washington History with BLM

Discussion during the last triennial review

Washington Potential For Adoption?

State Position:

- Planning to consider and likely adopt at next update of the aquatic life criteria for toxics.
- Date of update undetermined
- Stakeholders are enthusiastic about this criterion. Have expressed the desire to expand the approach to other metals and even assist with model development. (We refer them back to EPA on this request)

Washington BLM: Foregone conclusion?

Probably.

At this point the main concern is the process by which this criterion is put in place.

•Site-specific data requirements mean this will likely be phased in over time

•If phased in – how are the WQ standards structured to continue use of the hardness-based criterion and development and application of the BLM-based criterion without frequent rule-making for site-specific criteria?

•How to prioritize waterbodies for application of the BLM? Discharger requests, impaired waters and TMDLs, ESA, etc..?

•How about ESA consultation if the hardness-based criterion is retained in the standards and the BLM is phased in?

Copper and the BLM in Colorado

Presenting on behalf of Colorado
Lareina Guenzel
R8 EPA Water Quality Unit
303-312-6610
Guenzel.Lareina@epa.gov

Colorado BLM History

- 2004: first site-specific BLM/WER based criteria
  - Dischargers pursuing relaxed Cu WQBELs
  - CDPHE establishes minimum data requirements of 24 samples
- 2007: explored options to update the existing SSS
  - Generated several questions on temporal variability of IWQC
- 2008: development of the fixed monitoring benchmark (FMB)
- 2013: adopted first BLM-FMB based criteria
- 2014: reviewed two proposals
  - data aggregation and normality assumptions of the model
- 2015: Draft guidance for BLM-FMB based criteria

Copper in Colorado

- Legacy Mining Areas
  - Concentrations elevated; ranging from 10-20 µg/L
  - Only areas in the state with 303(d) listing and TMDLs
  - Not the areas where discharges are pursuing site-specific areas standards
- Metropolitan Areas
  - Hardness-based equations are attained in stream; chronic criteria typically range from 15-18 µg/L, ambient concentrations typically less than 10 µg/L with occasional spikes
  - Proposed BLM-base chronic criteria range from 20-43 µg/L

Future BLM work in Colorado?

- Continue to focus revisions on site-specific needs
- State-wide adoption constraints
  - Data
  - $$$
- Additional guidance needed
  - prepared a list of technical questions for EPA
- Finalize BLM-FMB guidance doucment

Cu BLM, IWQC, FMB…WTF

(What are the Tools For?)

Adam C. Ryan and Robert C. Santore

HDR

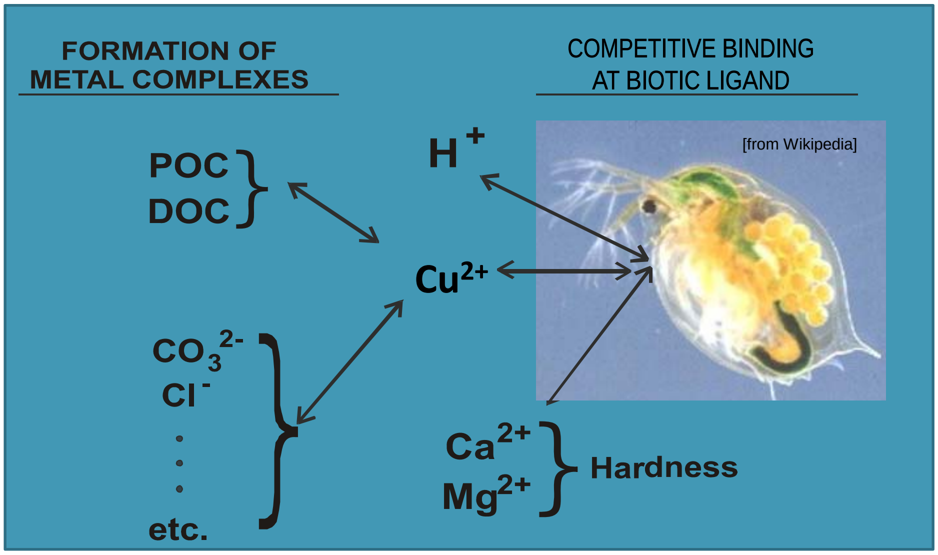
Description of BLM and IWQC

Time Variable IWQC

Description of FMB

Illustrative Examples

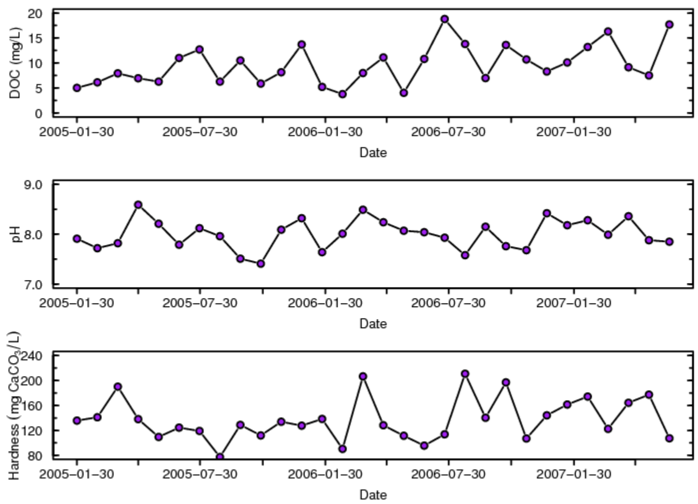
Generalized BLM Framework



BLM and Water Quality Criteria (WQC)

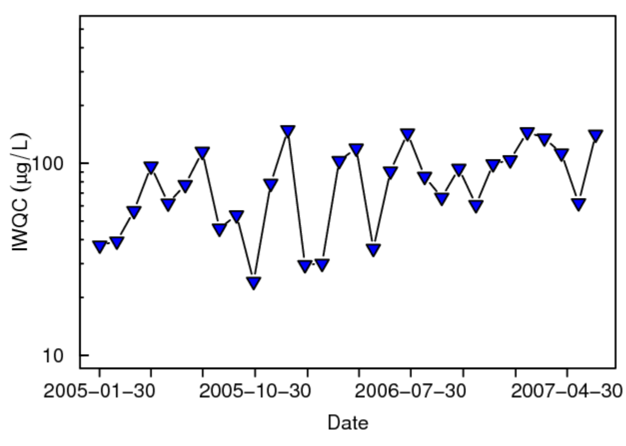
- In 2007, EPA published revised national recommended 304(a) freshwater criterion for copper
- Based on the BLM
  - Calculates IWQC that takes into account the bioavailability of the toxicant
- Recognizes that factors other than hardness (and typical covariates) influence bioavailability
- BLM is a site-specific tool

Time variable water chemistry



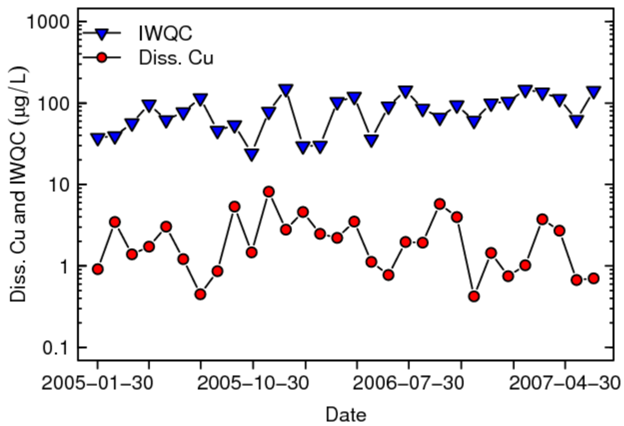
Influences the bioavailability of Cu, and this is accounted for with the BLM

Time variable water chemistry



Time variable WQC is not unique to the BLM; it is also apparent when the hardness equation is used

But dissolved Cu is also time variable



How can the BLM-predicted IWQC values be used to develop a fixed monitoring benchmark (FMB)?

Are there any IWQC exceedences?

- Calculation of TU, provides an idea of how Cu and IWQC are related
  - Indicates if there is or is not an exceedence

$$TU_i = \frac{Cu_i}{IWQC_i}$$

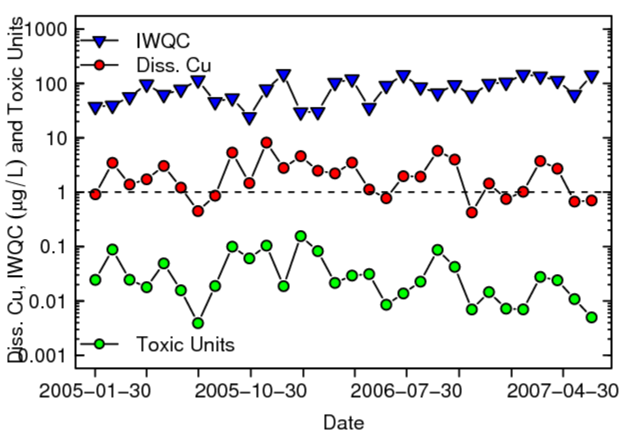
- This is a temporal pairing of Cu and IWQC values

Are there any IWQC exceedences?

- TU is an easy way to determine if Cu concentrations are higher or lower than the IWQC
  - TU > 1 → IWQC is exceeded
  - TU < 1 → IWQC not exceeded
- Commonly used to evaluate if an exposure concentration is higher than an effect concentration

• This is a temporal pairing of Cu and IWQC values

Leads to TU that are time-variable

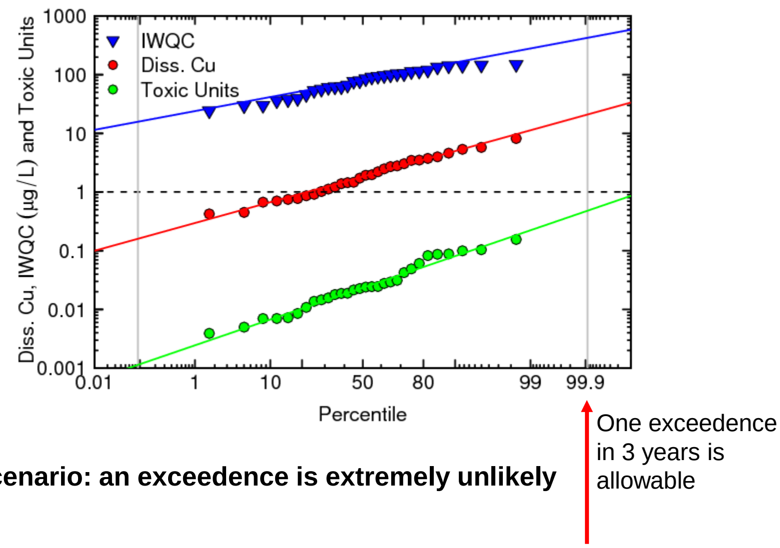


What is an acceptable exceedence frequency? The “Guidelines” state that 1 exceedence in 3 years is allowable.

Concept of FMB is straightforward

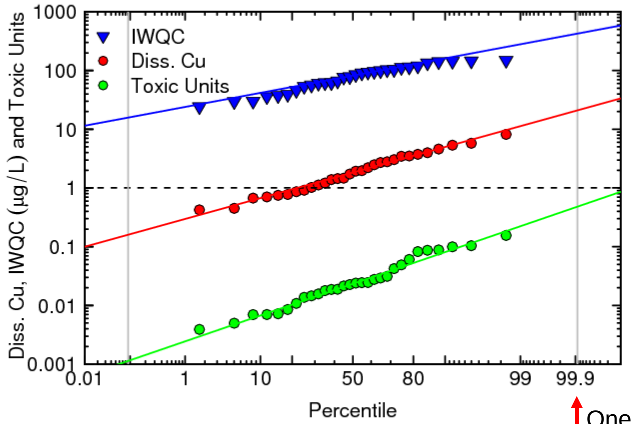
- FMB is benchmark that can be used to evaluate compliance with WQC
- To calculate an FMB:
  - o 1. Define TU distribution that is acceptable, given an allowable exceedence frequency (EF)
  - o 2. Define a dissolved Cu distribution that produces the allowable TU distribution
  - o 3. Calculate Cu concentration from the allowable Cu distribution that corresponds to the allowable EF
- It is helpful to look at probability plots

Make use of Cu and TU distributions



For this scenario: an exceedence is extremely unlikely

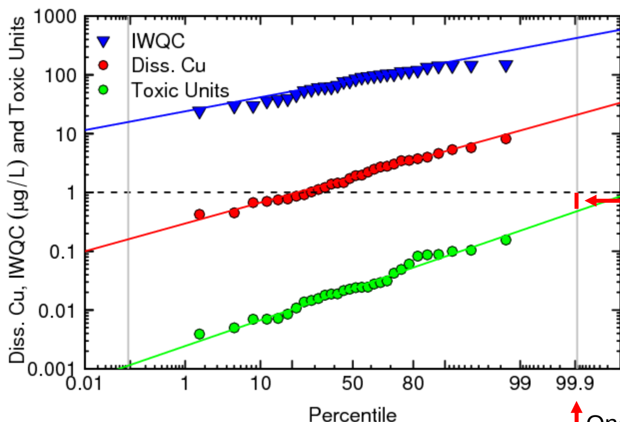
Make use of Cu and TU distributions



One exceedence in 3 years is allowable

Can make further use of this dataset to suggest a distribution of Cu values that meets the specified exceedence frequency

Make use of Cu and TU distributions

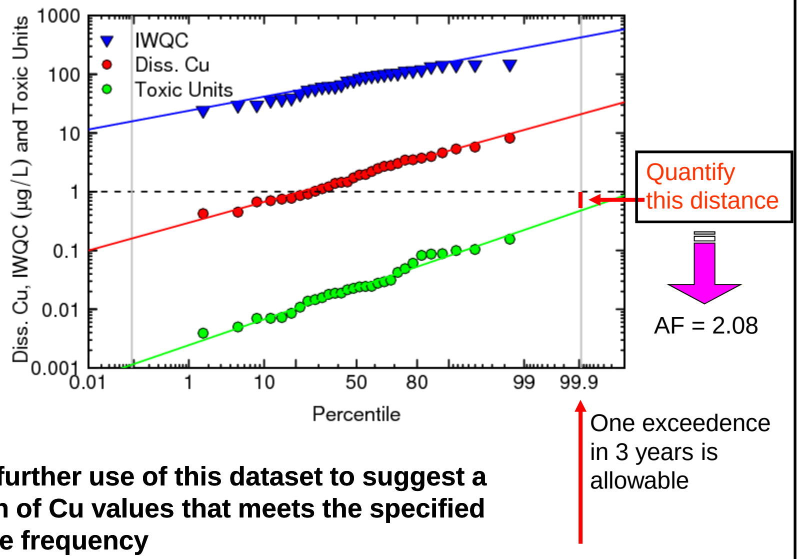


Quantify this distance

One exceedence in 3 years is allowable

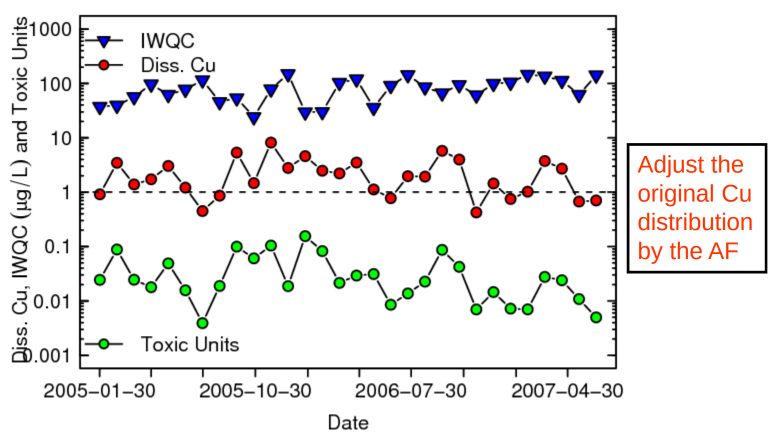
Can make further use of this dataset to suggest a distribution of Cu values that meets the specified exceedence frequency

Make use of Cu and TU distributions

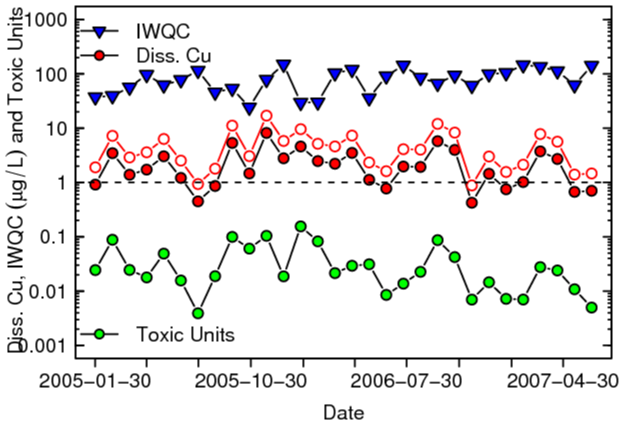


Can make further use of this dataset to suggest a distribution of Cu values that meets the specified exceedence frequency

Time series revisited; adjusted values

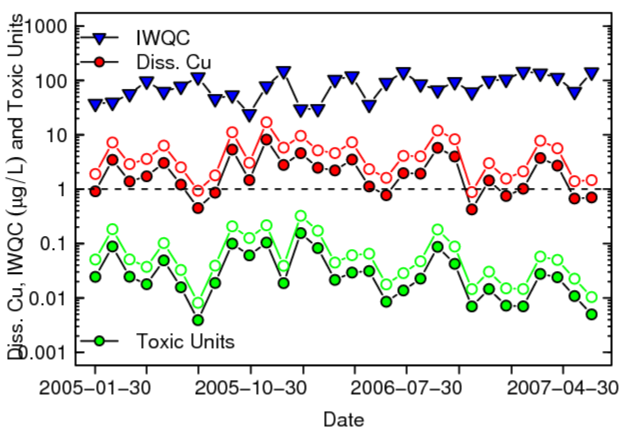


Time series revisited; adjusted values



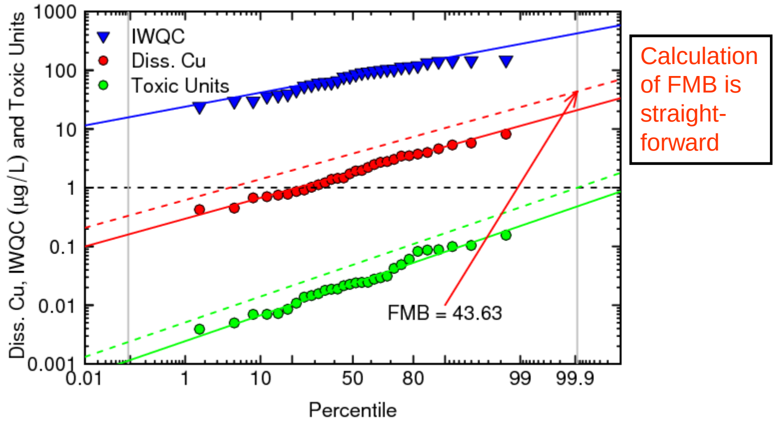
Adjust the original Cu distribution by the AF

Time series revisited; adjusted values



Results in adjusted TU distribution

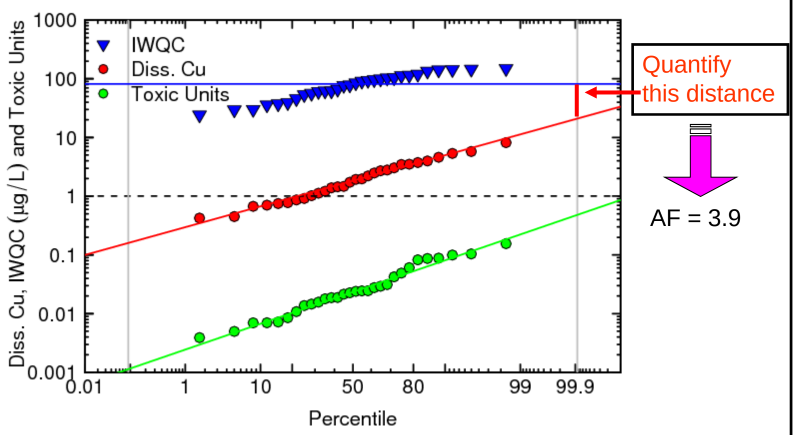
Calculation of the fixed monitoring benchmark (FMB)



$$FMB = 10^{[Z_{EF} * s_{\log 10(Cu)} + mean_{\log 10(Cu, allow)}]}$$

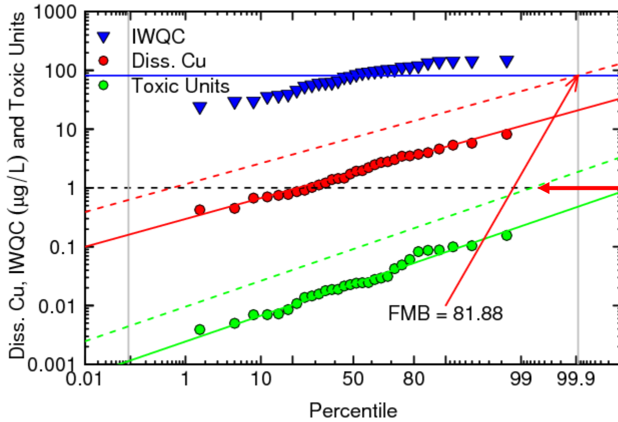
Need to have good estimates of mean and standard deviation

Can ask questions about alternative scenarios: median IWQC



We know that the FMB using this approach will be the median IWQC; determine the allowable Cu distribution, and examine TU

Can ask questions about alternative scenarios: median IWQC

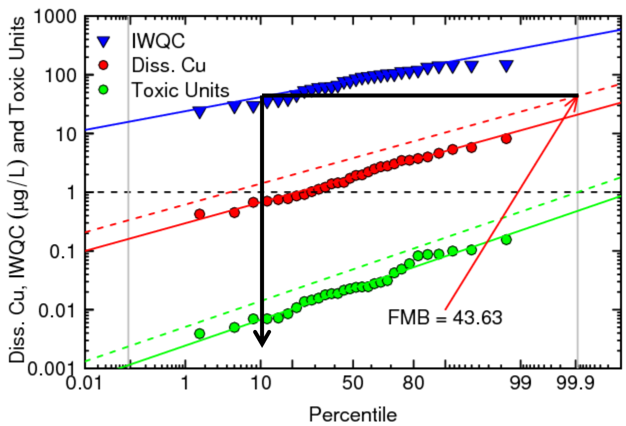


TU exceedence frequency is too high

EF ~ 10 in 3 years

In this case, median IWQC is not appropriate, because there are too many exceedences

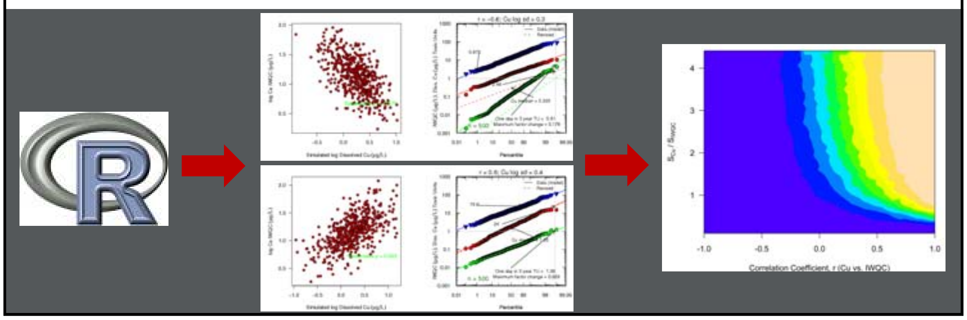
What was the appropriate IWQC percentile in this case?



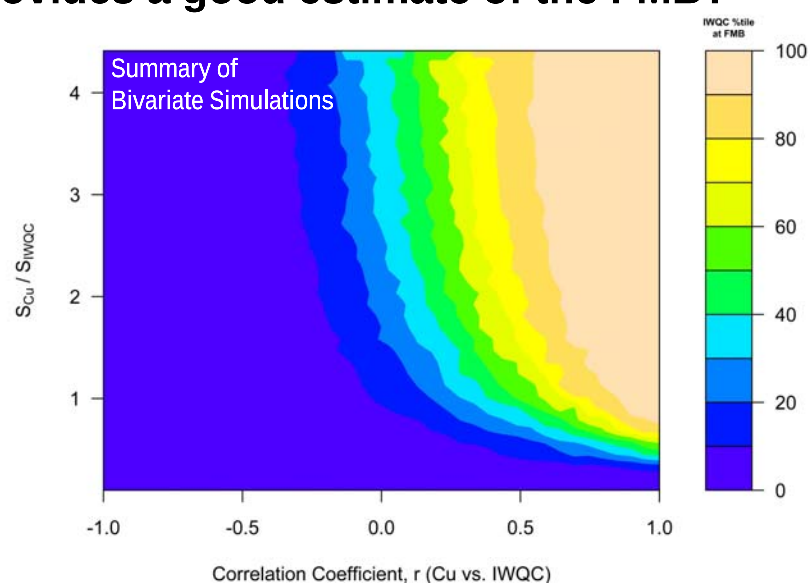
Calculated FMB is at roughly the **10th percentile** of IWQC

What percentile of the IWQC distribution provides a good estimate of the FMB?

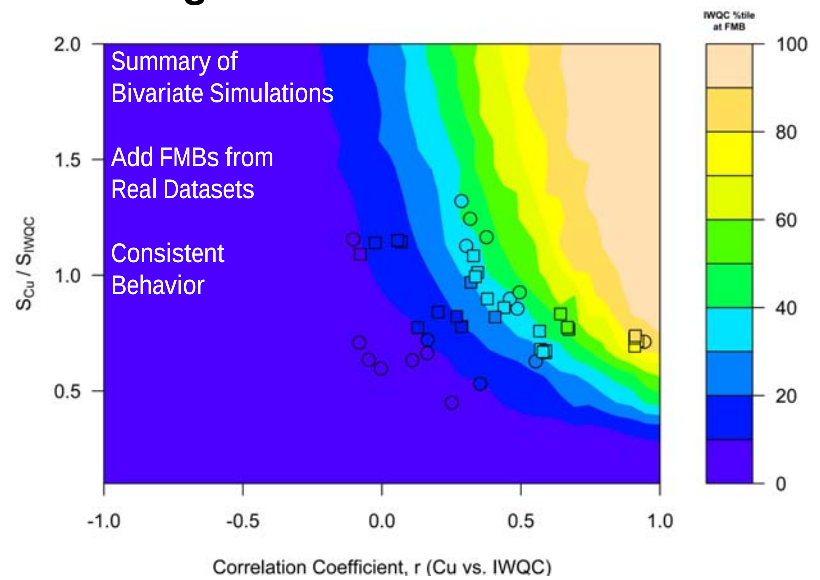
- After calculation of FMB for hundreds of datasets, it was clear that the FMB can correspond to any percentile of the IWQC distribution
- What is controlling this “behavior”?
- Preliminary analyses suggested that the variability of Cu and IWQC and their correlation were responsible
- Bivariate simulations confirmed that this was indeed the case



What percentile of the IWQC distribution provides a good estimate of the FMB?



What percentile of the IWQC distribution provides a good estimate of the FMB?



Can potentially make use of these results to identify an IWQC percentile for FMB

- Regional information could inform assumptions for sites that do not have Cu data
  - Use site-specific IWQC
  - From similar, related, or nearby locations use:
    - Standard deviation for Cu
    - Standard deviation for IWQC
    - Correlation coefficient for Cu and IWQC

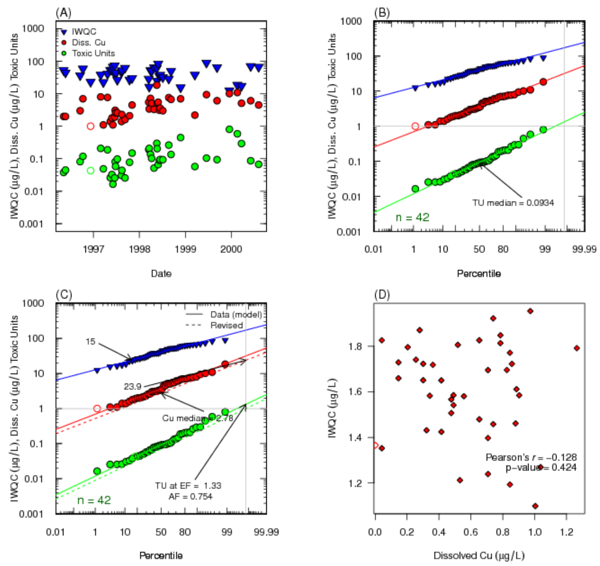
IWQC and FMB

- FMB can be at any percentile of IWQC
  - o FMB is site-specific
  - o Depends upon relative variability and correlation
  - o Direct correlation and high relative variability, FMB is at high percentile of IWQC
  - o Inverse correlation generally produces an FMB at low percentile of IWQC
  - o Weak correlation generally produces FMB at low percentile, but relative variability is important

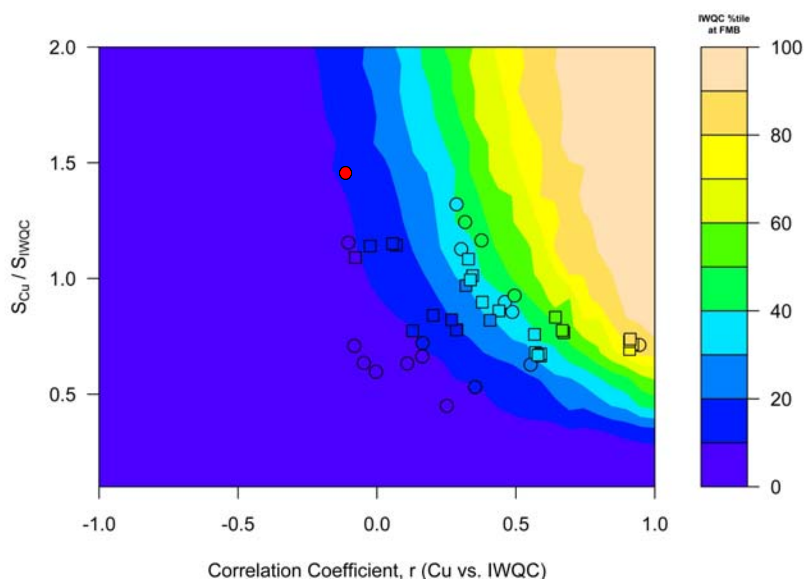
Illustrative Examples

- Variability and correlation
- Long period of record
- Trending data

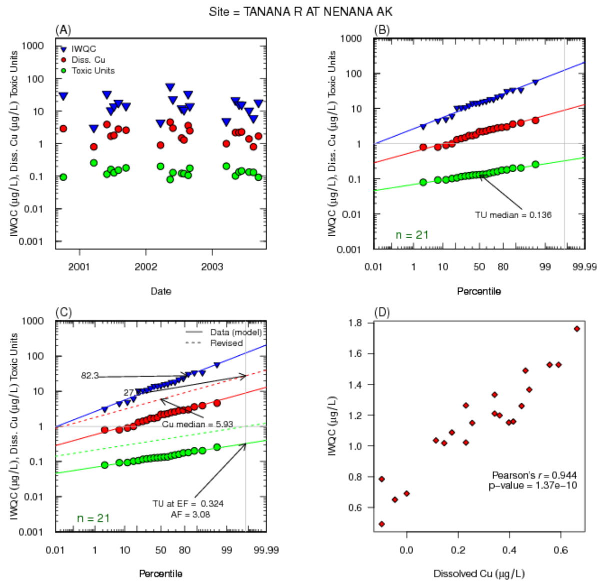
Weak indirect correlation, moderate s_{Cu}/s_{IWQC}



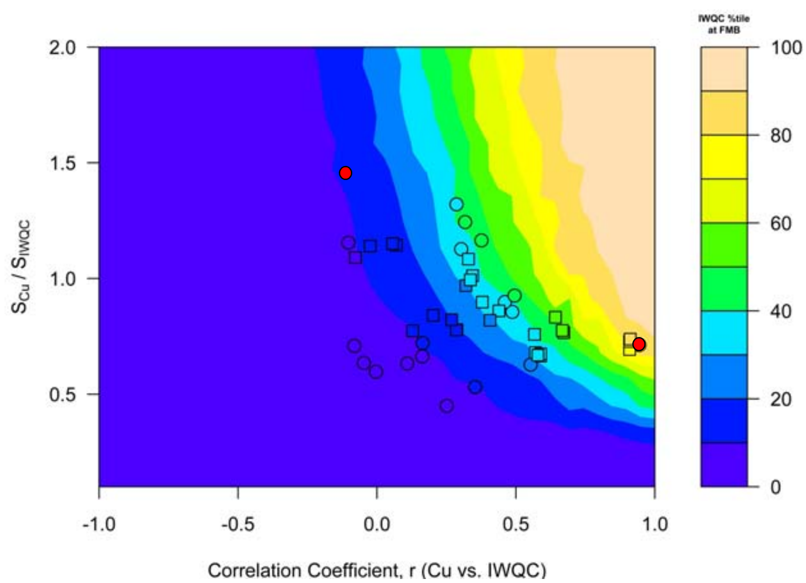
Weak indirect correlation, moderate s_{Cu}/s_{IWQC}



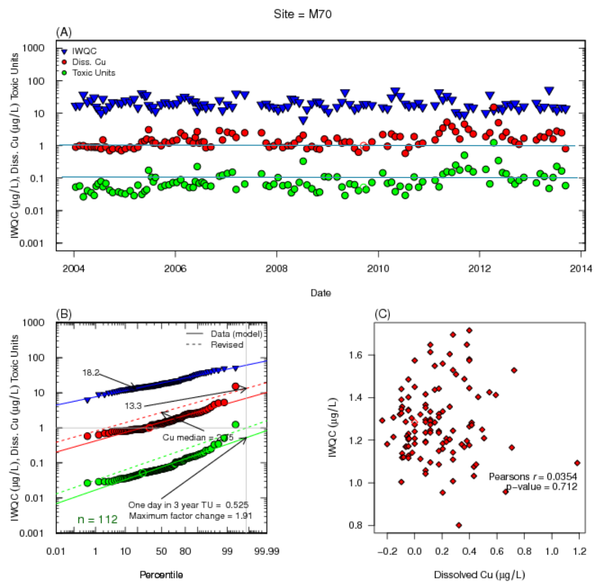
Strong direct correlation, low s_{Cu}/s_{IWQC}



Strong direct correlation, low s_{Cu}/s_{IWQC}



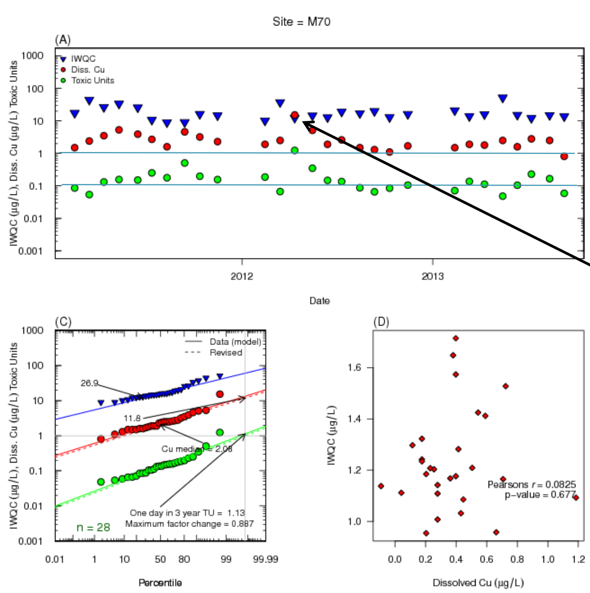
Long Period of Record



Suggests Trending Data…

Reviewing time-series is important

Long Period of Record



Use most recent data?

Highest data point still remains

Summary

- BLM is used to calculate site-specific WQC
- FMB is benchmark related to WQC
- FMB can occur at any percentile of IWQC distribution
  - Determined by relative variability of Cu and IWQC and their correlation
- Time-series plots should be prepared
  - Trends can affect distributional assumptions
  - Is more recent data more relevant, if a trend is present?

Thanks

USGS
science for a changing world

The accuracy and protectiveness of Biotic Ligand Model (BLM) toxicity predictions with copper

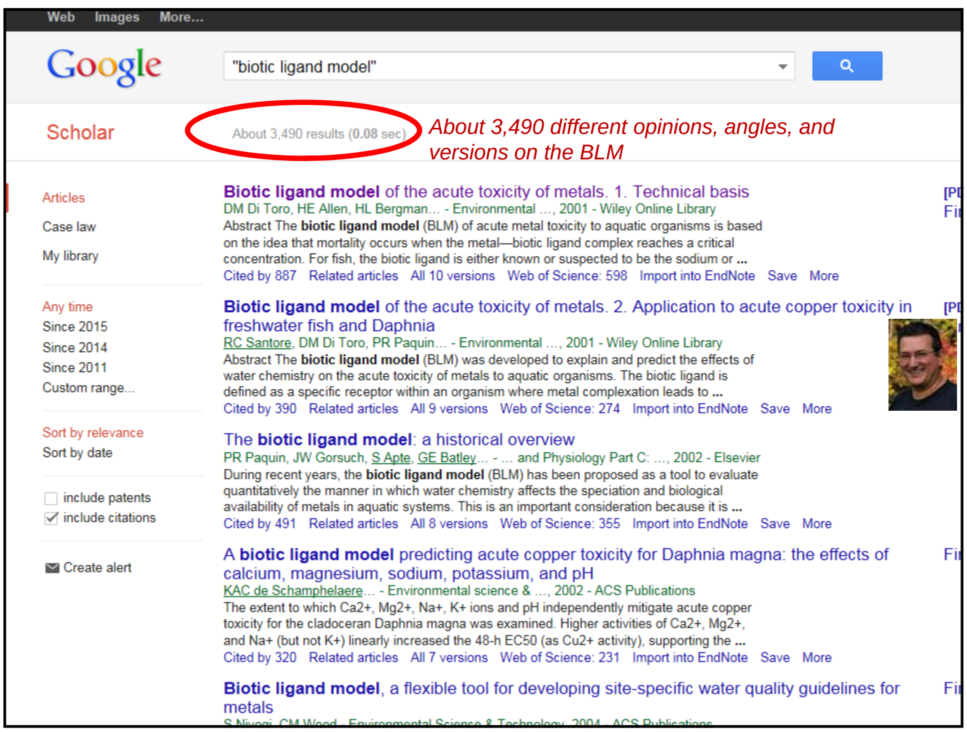
Christopher A. Mebane

U.S. Geological Survey, Boise, Idaho, USA

Workshop on Biotic Ligand Model application for copper
EPA Region 10, Seattle
May 13-14, 2015

U.S. Department of the Interior
U.S. Geological Survey

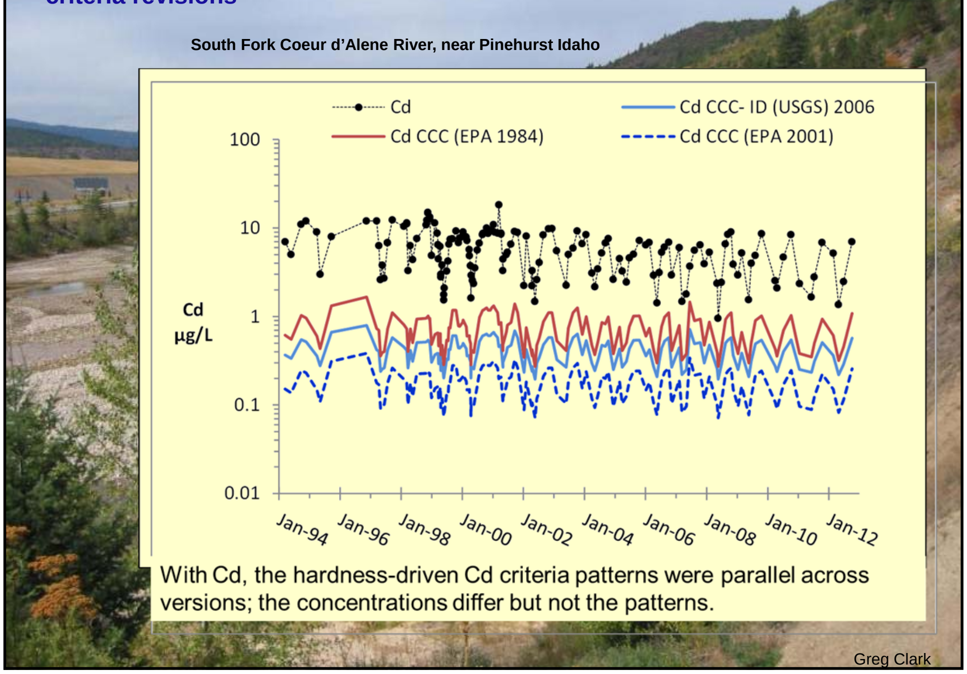
Analyses may be provisional and subject to revision



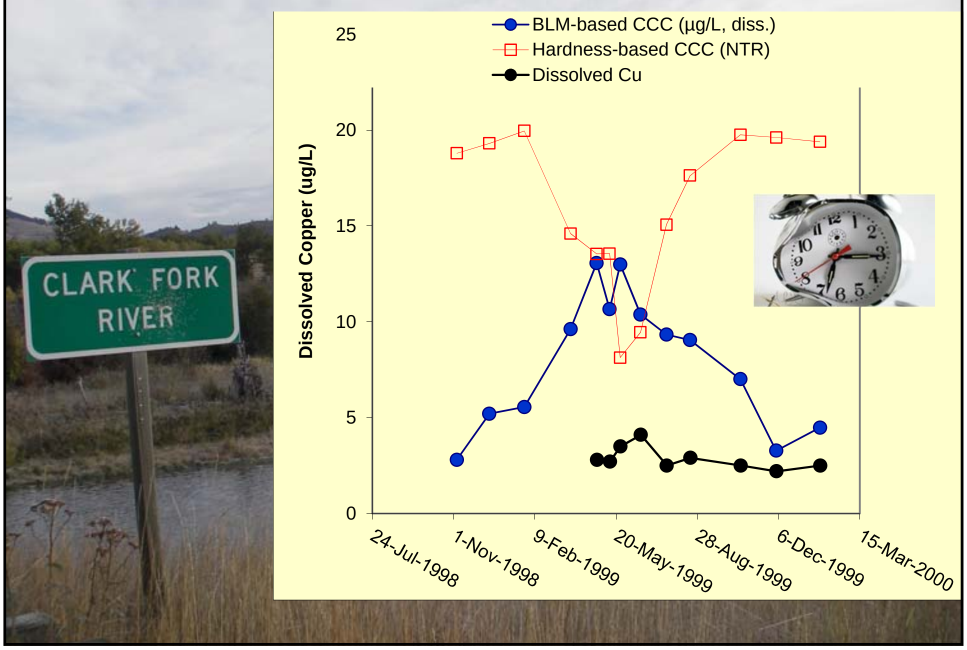
My topics

- **A tour of the BLM-Cu criteria in a watershed near you:**
  - ***How do Cu criteria concentrations result from the BLM- and hardness-based criteria compare in real world settings in the Pacific NW?***
- **Does it work?** ***Many untested assumptions in the 2007 criteria document.*** ***And what was so bad about the old hardness based criteria anyway?***
- **Performance evaluation: predictive accuracy and protectiveness** ***Predictive accuracy: how well do predicted toxic results compare to observed results?***
- ***Protectiveness of criteria: regardless of whether the model predictions are accurate, are the criteria concentrations protective?***
- ***Protective for sensitive functions or life stages of threatened or endangered species? (Thursday)***
-

What's the big deal with BLM-Cu criteria revisions? Contrast with Cd criteria revisions

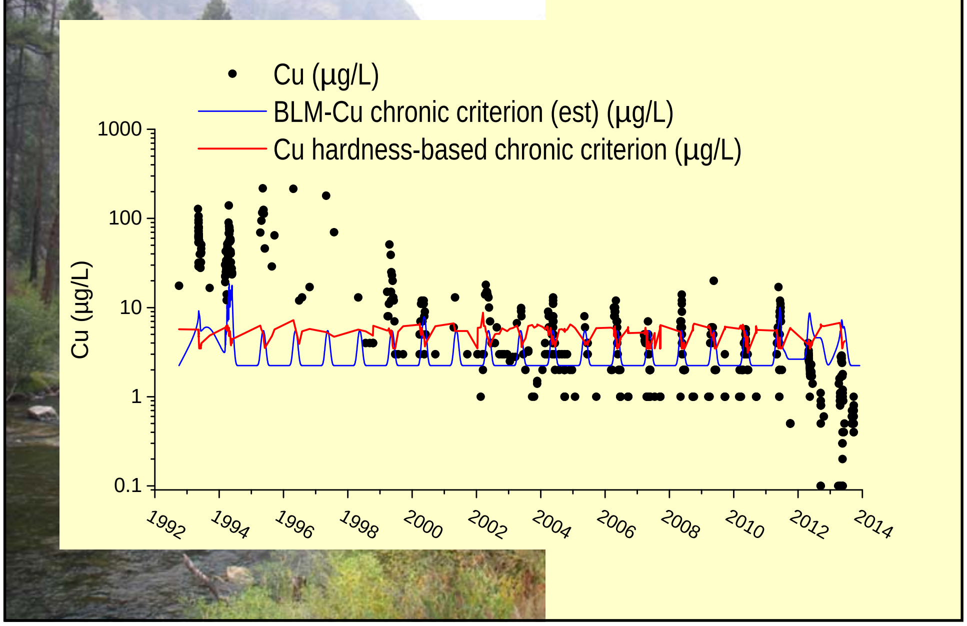


Not so with Copper.

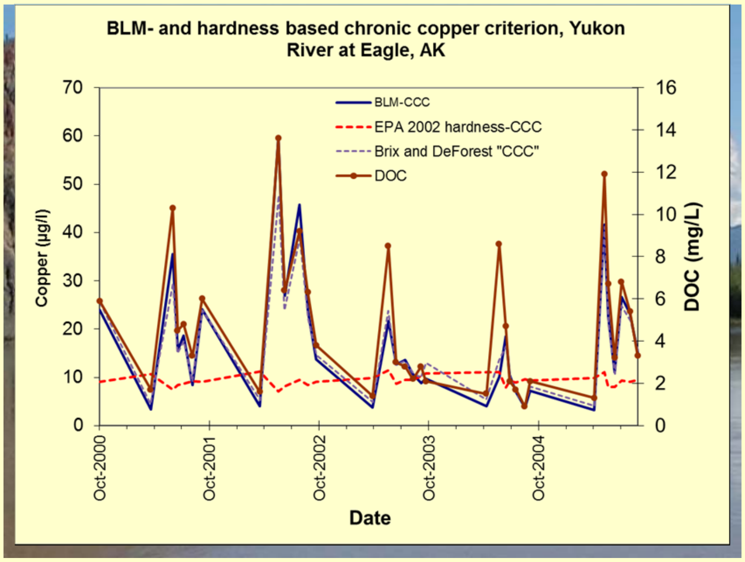


Hardness and BLM-criteria out of sync

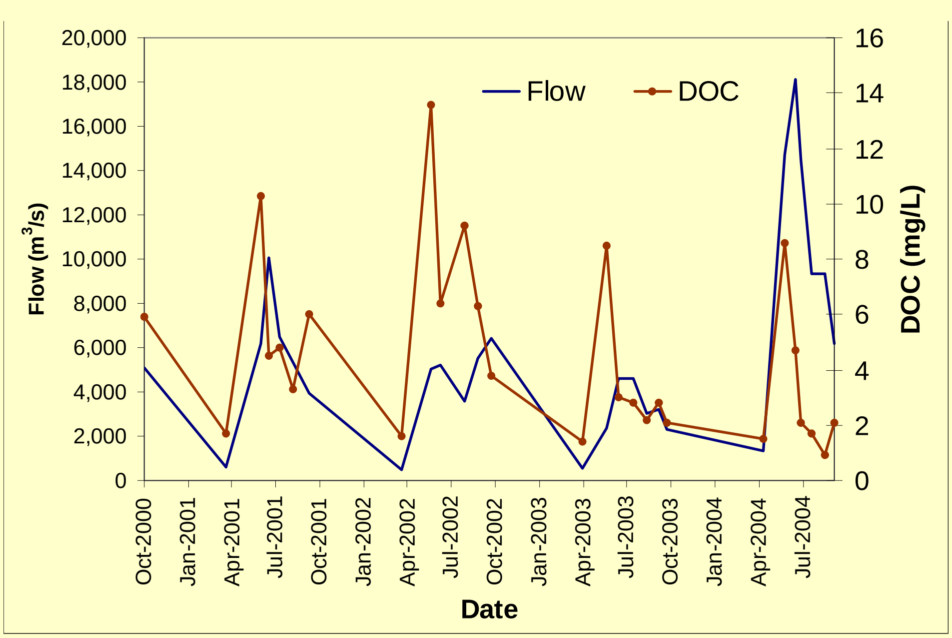
Panther Creek, near Salmon, Idaho



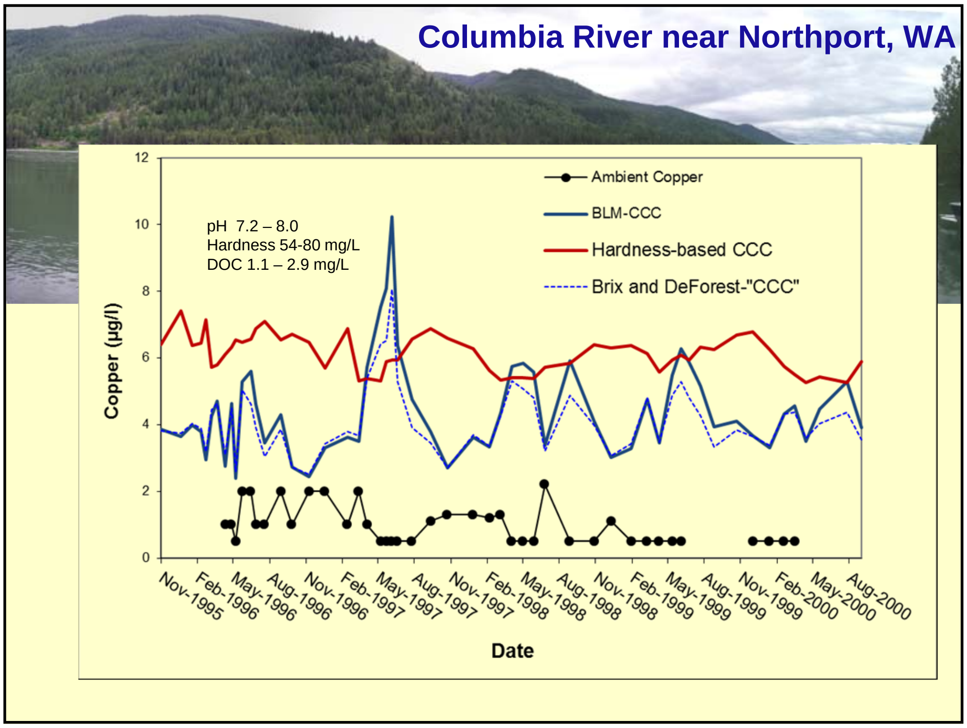
Yukon River at Eagle, Alaska



USGS Photo



USGS Photo


Columbia River near Northport, WA
pH 7.2 – 8.0
Hardness 54-80 mg/L
DOC 1.1 – 2.9 mg/L
Ambient Copper
BLM-CCC
Hardness-based CCC
Brix and DeForest-"CCC"
Copper (µg/l)
0
2
4
6
8
10
12
Nov-1995
Feb-1996
May-1996
Aug-1996
Nov-1996
Feb-1997
May-1997
Aug-1997
Nov-1997
Feb-1998
May-1998
Aug-1998
Nov-1998
Feb-1999
May-1999
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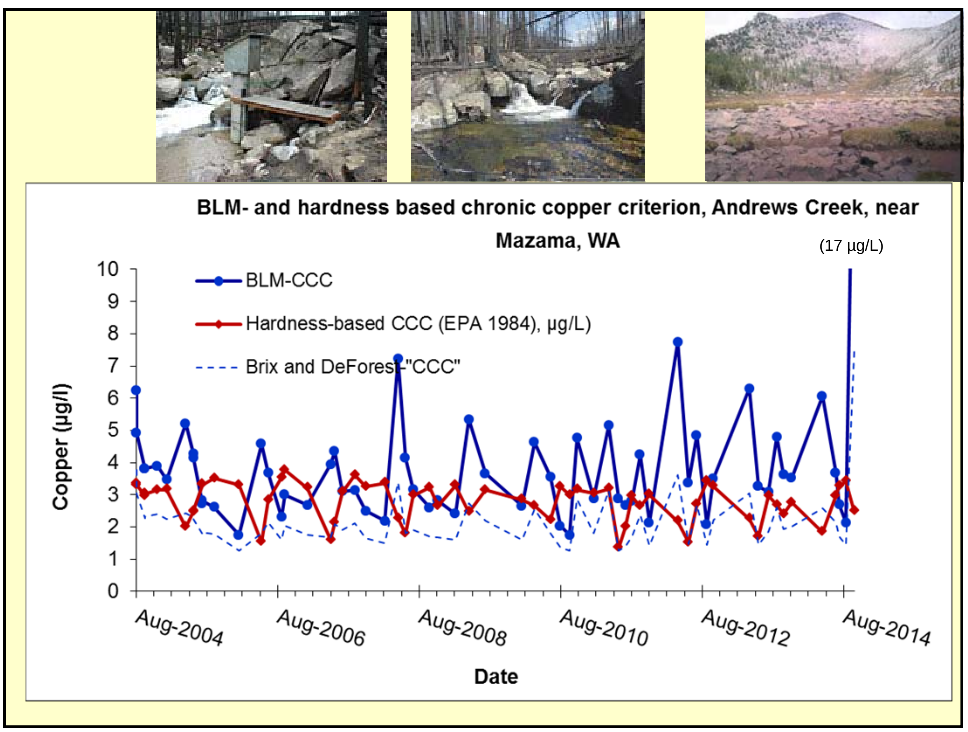
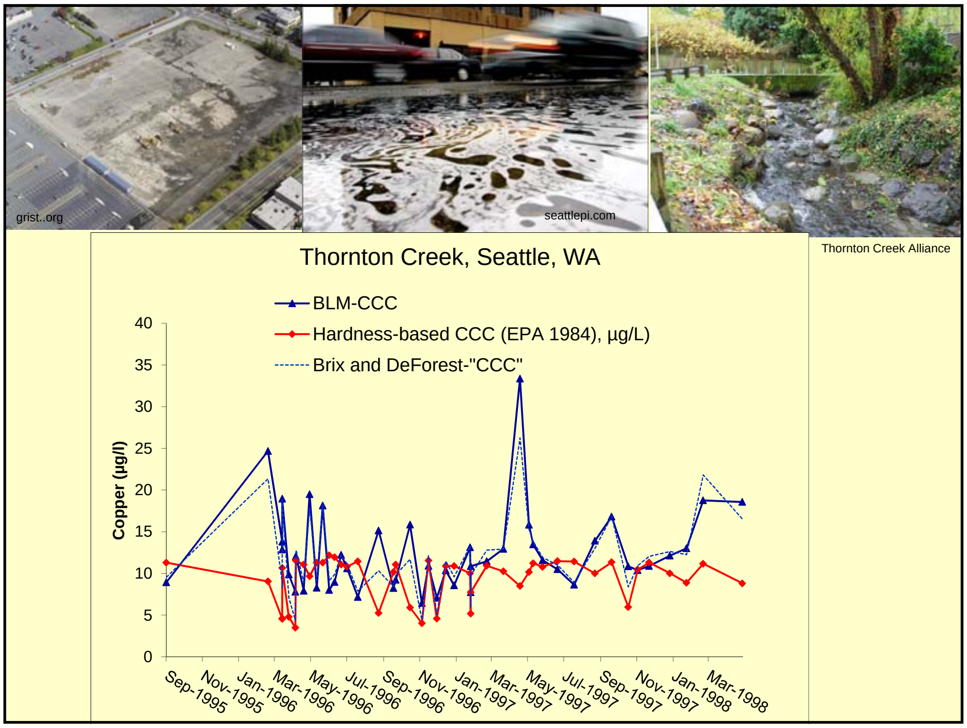
Nov-1999
Feb-2000
May-2000
Aug-2000
Date


BLM- and hardness based chronic copper criterion, Andrews Creek, near Mazama, WA
(17 µg/L)
BLM-CCC
Hardness-based CCC (EPA 1984), µg/L)
Brix and DeForest-"CCC"
Copper (µg/l)
0
1
2
3
4
5
6
7
8
9
10
Aug-2004
Aug-2006
Aug-2008
Aug-2010
Aug-2012
Aug-2014
Date


grist..org
seattlepi.com
Thornton Creek Alliance
Thornton Creek, Seattle, WA
BLM-CCC
Hardness-based CCC (EPA 1984), µg/L)
Brix and DeForest-"CCC"
Copper (µg/l)
0
5
10
15
20
25
30
35
40
Sep-1995
Nov-1995
Jan-1996
Mar-1996
May-1996
Jul-1996
Sep-1996
Nov-1996
Jan-1997
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Jul-1997
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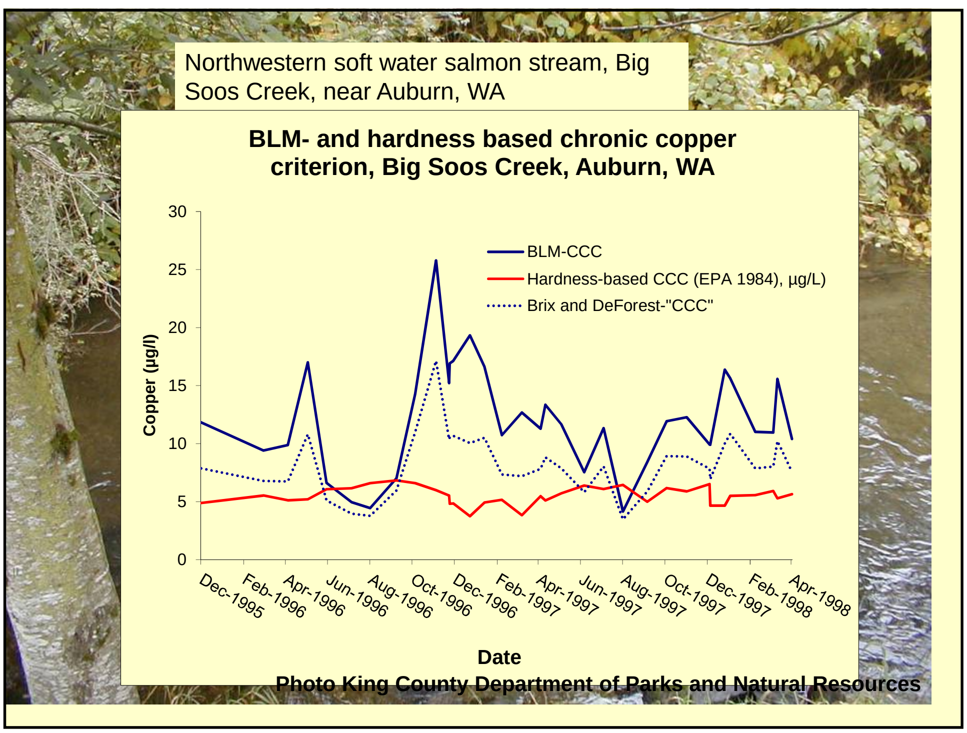
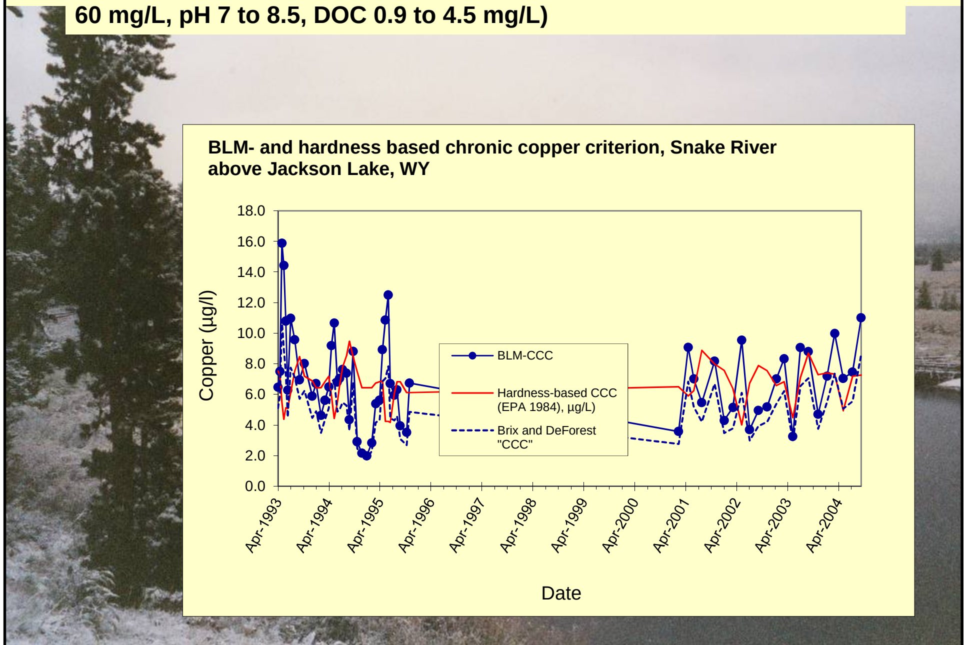
Nov-1997
Jan-1998
Mar-1998

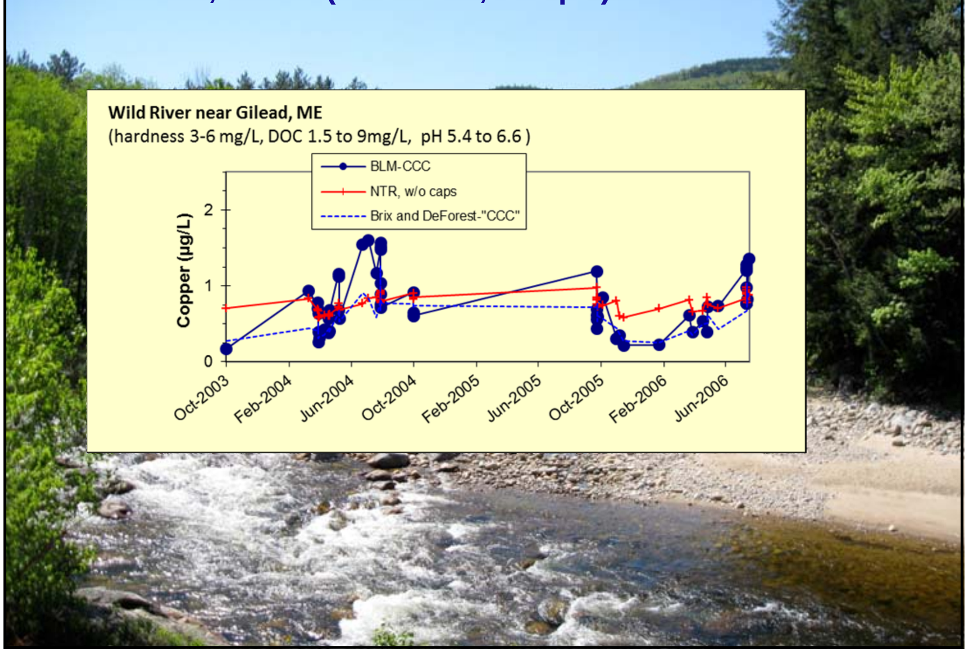

Northwestern soft water salmon stream, Big Soos Creek, near Auburn, WA
BLM- and hardness based chronic copper criterion, Big Soos Creek, Auburn, WA
BLM-CCC
Hardness-based CCC (EPA 1984), µg/L)
Brix and DeForest-"CCC"
Copper (µg/l)
0
5
10
15
20
25
30
Dec-1995
Feb-1996
Apr-1996
Jun-1996
Aug-1996
Oct-1996
Dec-1996
Feb-1997
Apr-1997
Jun-1997
Aug-1997
Oct-1997
Dec-1997
Feb-1998
Apr-1998
Date
Photo King County Department of Parks and Natural Resources

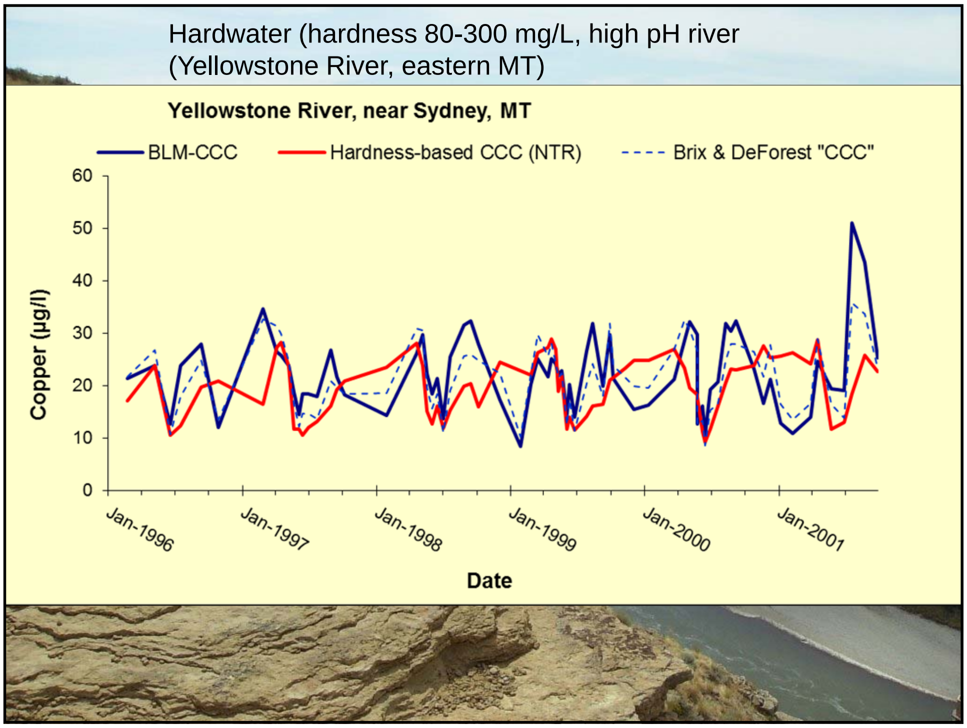
Snake River leaving Yellowstone National Park, Wyoming (hardness 25-60 mg/L, pH 7 to 8.5, DOC 0.9 to 4.5 mg/L)



wikipedia.org

Wild River, Maine (softwater, low pH)



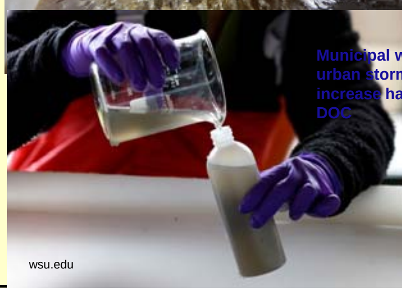


Hardwater (hardness 80-300 mg/L, high pH river
(Yellowstone River, eastern MT)
Yellowstone River, near Sydney, MT
BLM-CCC
Hardness-based CCC (NTR)
Brix & DeForest "CCC"
Copper (µg/l)
0
10
20
30
40
50
60
Jan-1996
Jan-1997
Jan-1998
Jan-1999
Jan-2000
Jan-2001
Date

Some dischargers may get more or less stringent criteria
Mining tends to increase hardness pH, but not DOC

wsu.edu

piquenewsmagazine.com



wsu.edu

Municipal wastewater or urban stormwater tends to increase hardness, pH, and DOC

City of Boulder

What to believe?

Spring-runoff is the critical, low-hardness period; Don't worry as much about copper during base flow because high hardness gives protection;

<u>Baseflows</u> when DOC is low are the most-critical period. Don't worry as much about copper during spring runoff when DOC is high

One of these guys must be wrong.

Some assumptions and questions about the BLM's performance and the criteria's protectiveness

1. **The BLM-criteria are intended to be protective of all freshwaters and their communities, but the performance of the BLM was initially validated with toxicity data from fathead minnows and daphnids.**

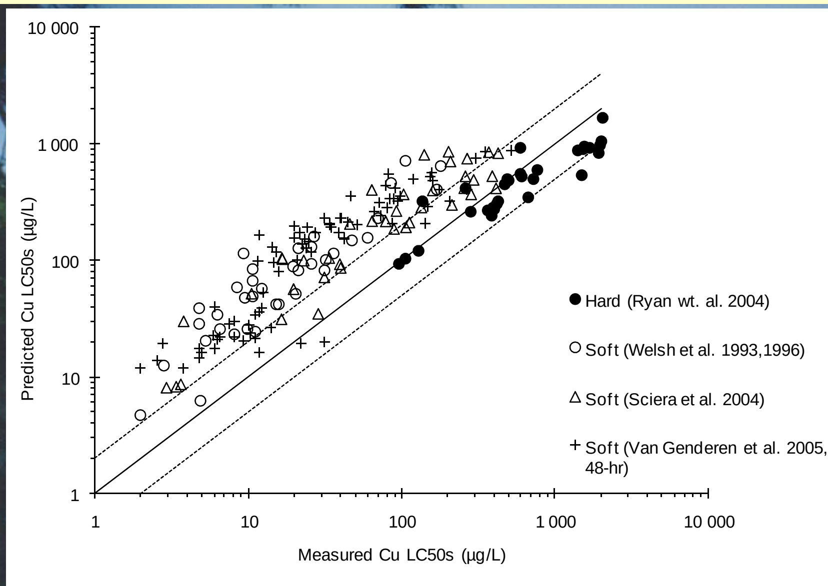
   Does the BLM reliably predict the toxicity or non-toxicity to other aquatic organisms?
2. **The original copper BLM was calibrated to toxicity tests series of contrived waters in which humic acid, major ions, and other factors were manipulated.**

   Does the copper BLM perform well in diverse natural waters, including natural water with very low hardness?

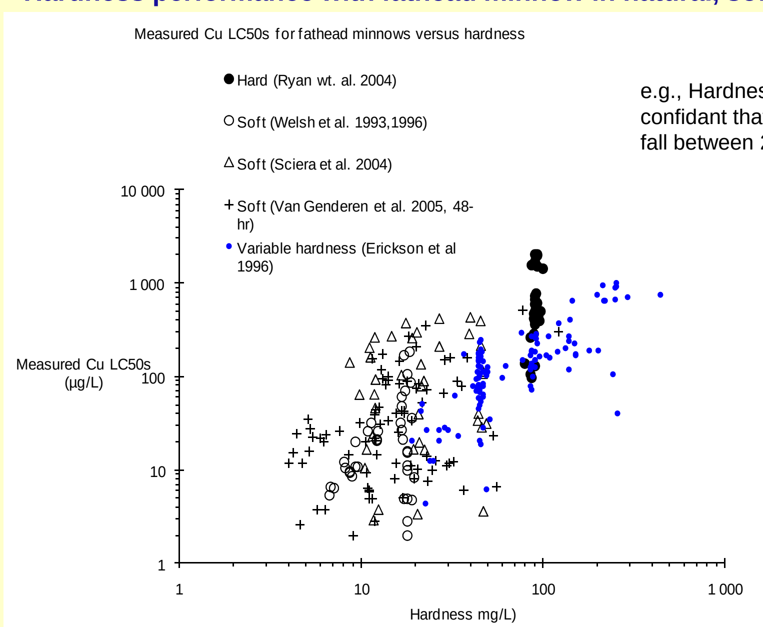
Assumptions and questions about the BLM's performance and the criteria's protectiveness

3. **The BLM was developed for predicting short-term, lethality from copper. Does the acute copper BLM- criteria also predict and protect against long-term, chronic effects of copper?**
4. **Sublethal effects related to chemosensation and related behaviors such as impaired olfaction, predator avoidance, and prey capture were not considered the development of the BLM-based criteria. Does the BLM reasonably predict and prevent against impairment of these types? *(Thursday)***
5. **Laboratory experiments with single-species have an inherent artificiality to them. Do the BLM-based criteria appear protective in more natural field settings or with experimental ecosystems?**

BLM performance with fathead minnow in natural, soft waters



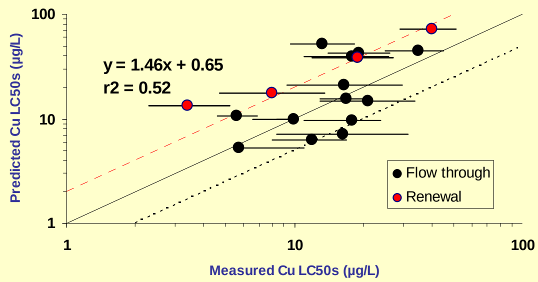
Hardness performance with fathead minnow in natural, soft waters



e.g., Hardness 20 mg/L, confidant that the LC50 will fall between 2 and 400 µg/L

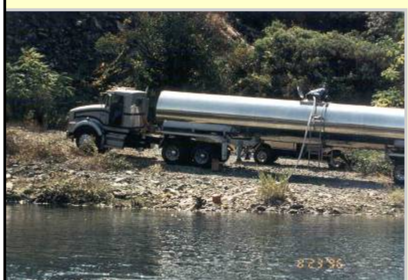
Rainbow trout flow-through and renewal tests using natural and lab waters, DOC <0.11 to 2.0 mg/L, pH 6-8.

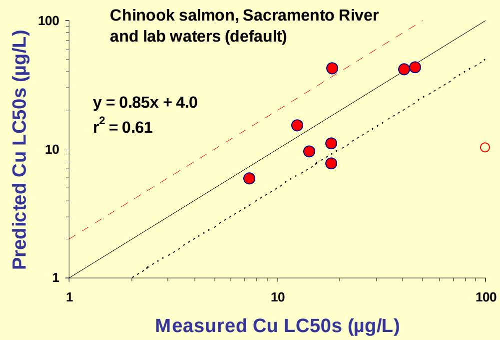
Welsh et al, unpublished (Hagler Bailley Consulting)



Chinook salmon flow-through tests

Welsh et al, unpublished (Hagler Bailley Consulting)

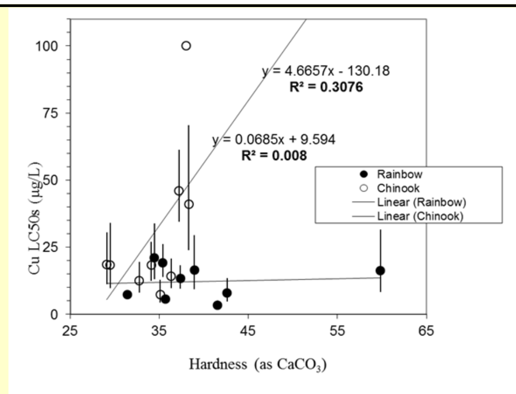


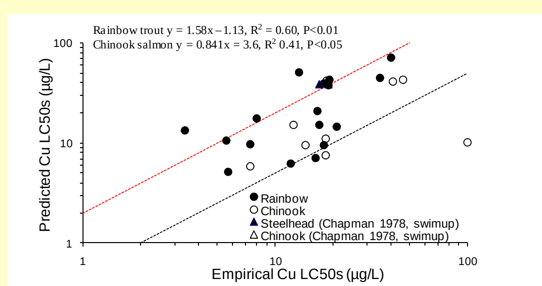


Josh Lipton

[Hardness vs. BLM, Chinook Salmon and Rainbow Trout]

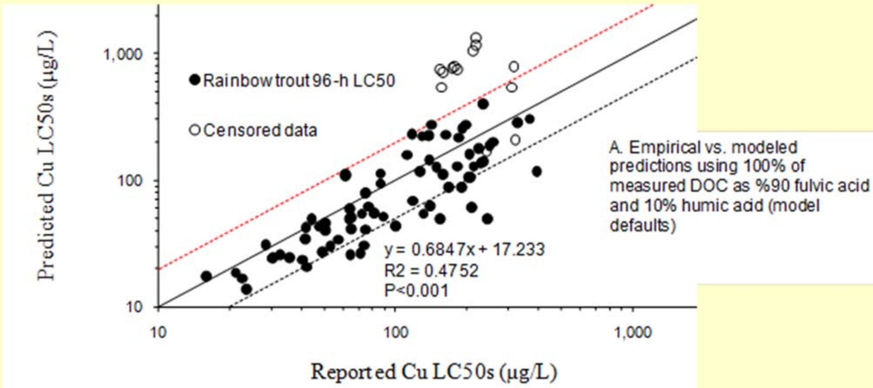
Welsh et al, unpublished (Hagler Bailley Consulting)





Josh Lipton

Rainbow trout, renewal exposures

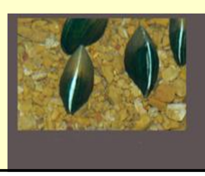


BLM Predicted vs. observed rainbow trout LC50s, in renewal tests using lab and site waters, hardwater, DOC from <1 to 11 mg/L, 3 of 4 seasonal rounds of testing (censoring (discarding) on set of tests for questionable DOC data).

ENSR. 1996. Development of site-specific water quality criteria for copper in the upper Clark Fork River: Phase III WER Program testing results. ENSR Consulting and Engineering, 0480-277, Fort Collins, Colo.

Fatmucket mussel, *Lampsilis siliquoidea*

Acute and chronic tests in waters with variable hardness and different DOC sources

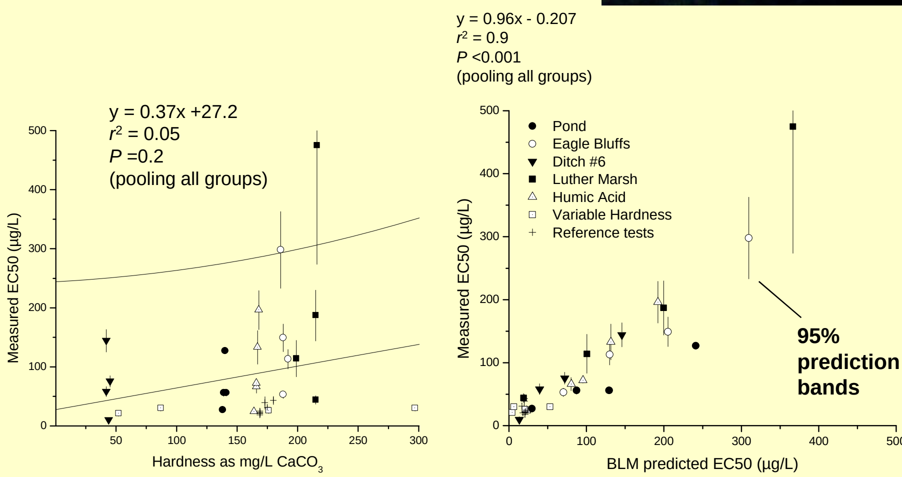


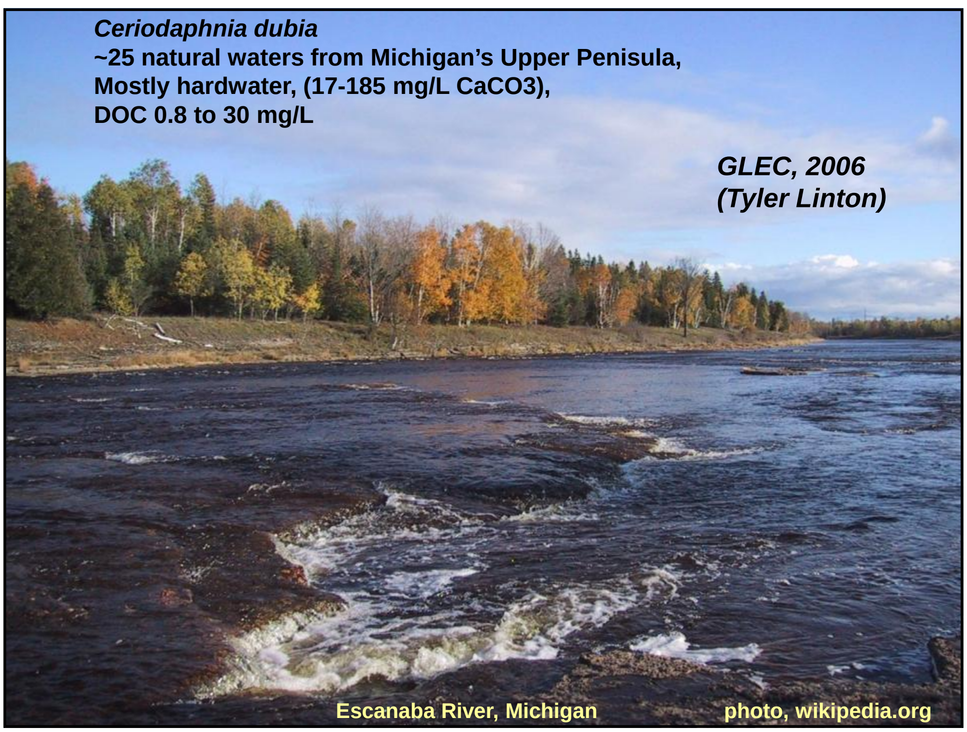
Wang et al. ET&C, 2009

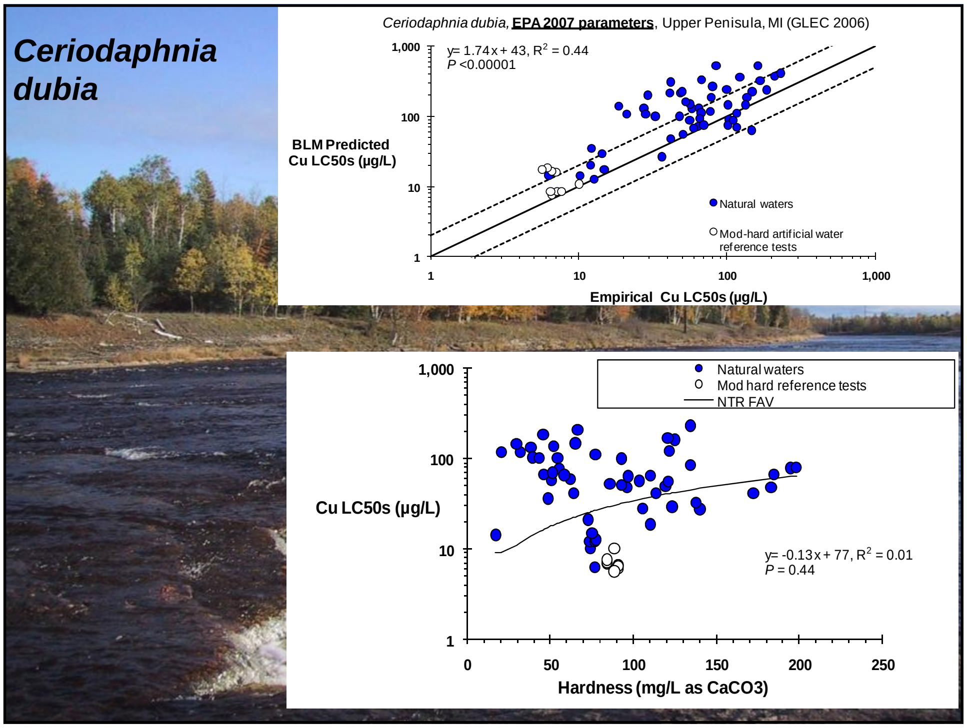
Photos by Doug Hardesty, USGS

Fatmucket mussel: hardness vs. BLM as predictor of toxicity

Wang et al. ET&C, 2009





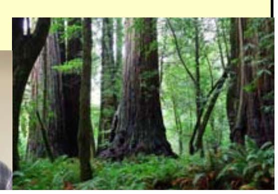


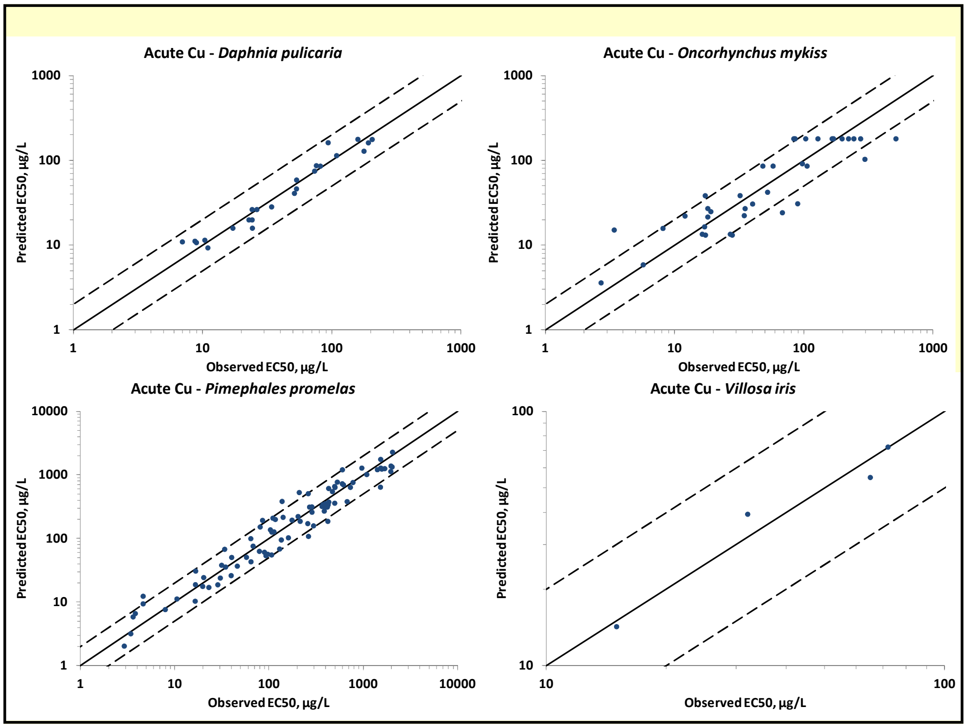
Comparisons of acute toxicity using a simplified BLM-like Linear Regression (MLR): a viable alternative?

- BLM provides mechanistic basis for predicting metal toxicity over wide range of water chemistries
  - <u>Perception</u> of being too complicated
- MLR represents an intermediate approach
  - Structure is similar to the familiar pH and temperature dependent ammonia criteria equations, produces a 3-parameter equation.
  - Relies on BLM to help identify the critical water chemistry parameters

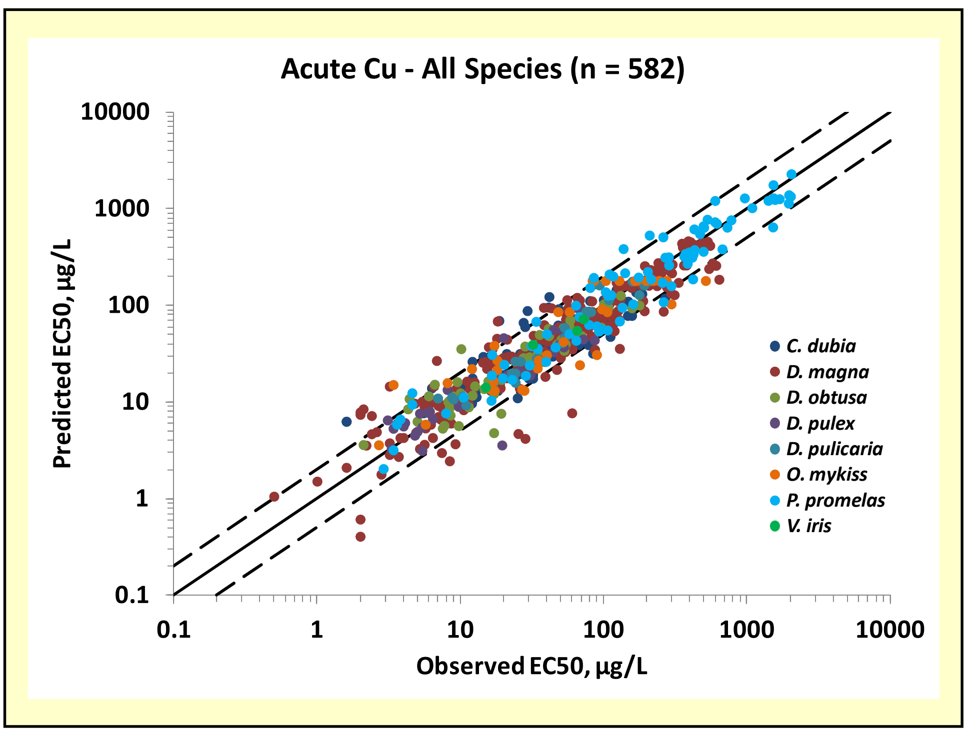
Brix

DeForest



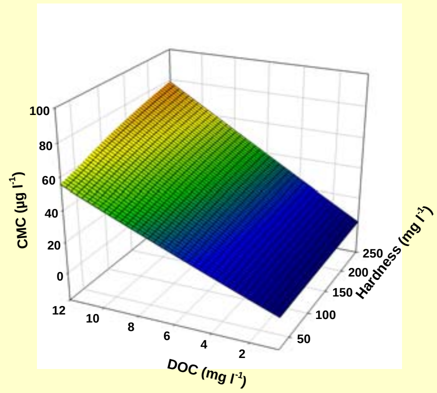


Acute Cu - *Daphnia pulicaria*
Predicted EC50, µg/L
Observed EC50, µg/L
Acute Cu - *Oncorhynchus mykiss*
Predicted EC50, µg/L
Observed EC50, µg/L
Acute Cu - *Pimephales promelas*
Predicted EC50, µg/L
Observed EC50, µg/L
Acute Cu - *Villosa iris*
Predicted EC50, µg/L
Observed EC50, µg/L

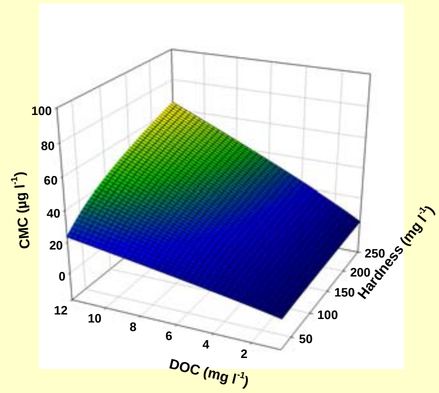


Acute Cu - All Species (n = 582)
Predicted EC50, µg/L
Observed EC50, µg/L
C. dubia
D. magna
D. obtusa
D. pulex
D. pulicaria
O. mykiss
P. promelas
V. iris

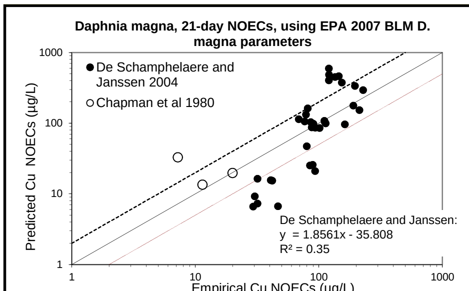
BLM



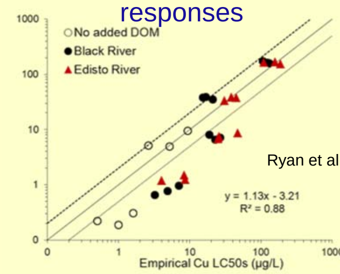
MLR

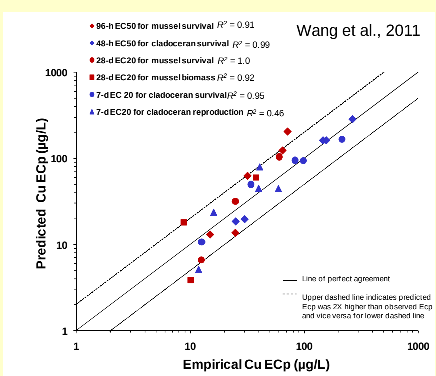


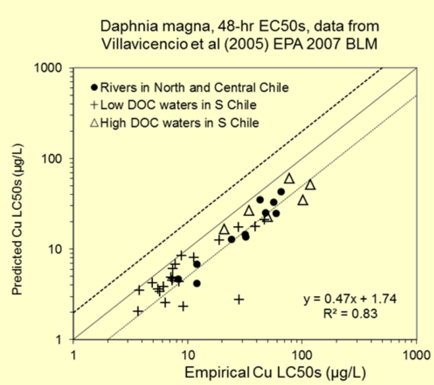
- **Performance generally similar**
- **BLM may over-respond to DOC**
- **MLR "tones down" the DOC response**
- **Strong performance of MLR warrants consideration in criteria**
- **Spreadsheet equation may have administrative rule advantages**



BLM: Chronic vs. acute responses





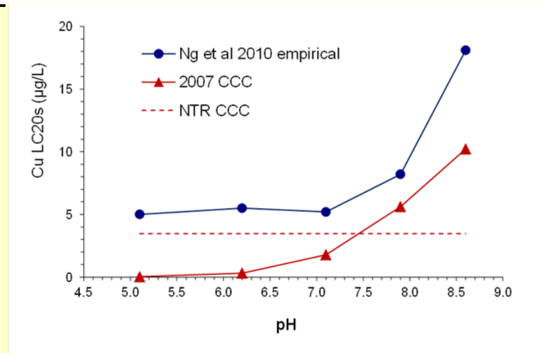


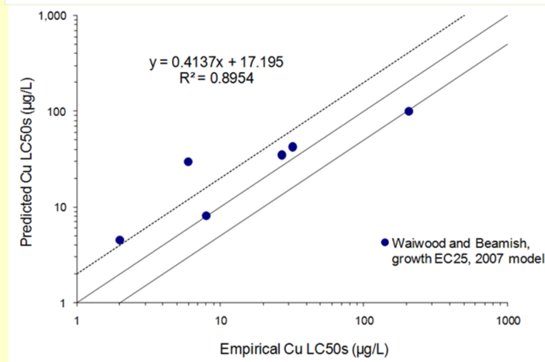
BLM performance with Rainbow Trout in <u>chronic</u> exposures

Ng, T.Y.-T., M.J. Chowdhury, and C.M. Wood. 2010. Can the biotic ligand model predict Cu toxicity across a range of pHs in softwater-acclimated rainbow trout? *Environmental Science and Technology*. 44(16): 6263–6268

Waiwood, K.G. and F.W.H. Beamish. 1978. The effect of copper, hardness and pH on the growth of rainbow trout, *Salmo gairdneri*. *Journal of Fish Biology*. 13(5): 591-598

(similar results with swimming performance)



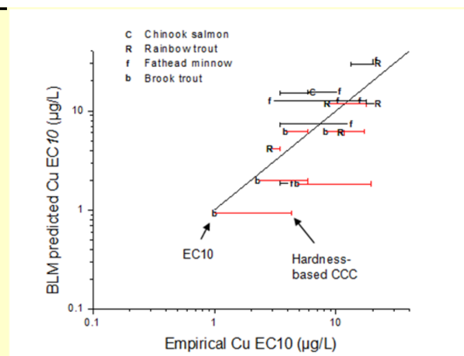


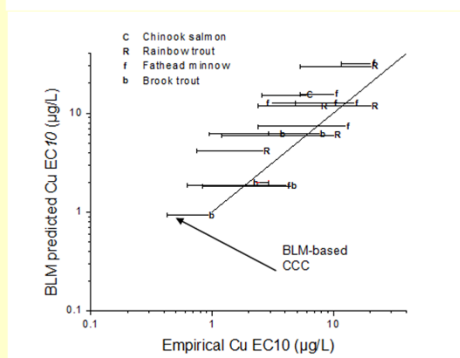
Protectiveness (or lack thereof) of hardness-based (top) or BLM-based Cu criteria (bottom) for <u>chronic EC10</u> values for:

- Chinook salmon
- Rainbow trout
- Brook trout and
- Fathead minnows

✓ BLM-based chronic criterion was protective

✓ Hardness-based chronic criterion was not always protective





Experimental control

We want to protect aquatic communities, not bugs in beakers. What about field and community-level testing?

Field studies

Doug Hardesty, USGS

USGS

Environmental relevance

Aquatic toxicology laboratory

1. Shayler Run, Ohio, USA

- **Stream experimentally dosed with copper, 1968-1972**
- **Integrated long-term field, streamside, and laboratory toxicity studies**
- **High calcium limestone geology**
- **DOC from natural and sewage sources**

Geckler and others, 1976. *Validity of laboratory tests for predicting copper toxicity in streams.* EPA 600/3-76-116

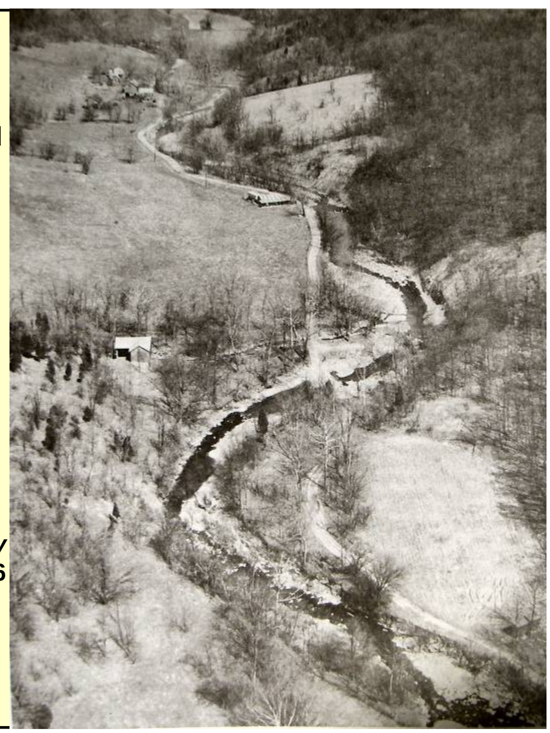
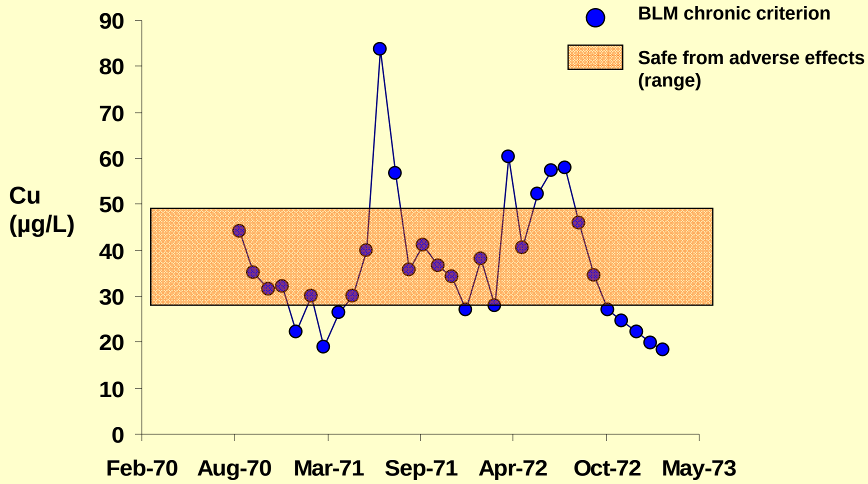


Photo from Geckler and others, 1976

BLM and field effects –Ohio Stream



- Threshold for adverse effects from
  - Full life cycle streamside toxicity tests with native fish
  - Fish behavioral changes in stream

Slow-water stream mesocosms, 18-month

Helene Roussel PhD work, INERIS (France)

- <u>Effects studied included:</u>
- Primary producers, leaf decomposition, fish
- Benthic macroinvertebrate community
  - No effects detected at 4 µg/L.
  - At 20 µg/L, total invert. abundance, taxa richness and community structure of zooplankton, macroinvertebrate and emerging insects were severely affected
  - 2007 BLM average CCC: 9.2 µg/L; 1985 CCC: 32 µg/L

2. Fast-water stream microcosms using benthic macroinvertebrate community

- 10-day exposures
- 5 µg/L Cu reduced overall Ephemeroptera (mayfly) density by 50%;
- BLM-CCC was about 6-7 µg/L, hardness CCC about 5 µg/L *(hardness 35 mg/L, DOC 2.5 to 3 mg/L)*

Environmental Science & Technology 2013 Article pubs.acs.org/est

Responses of Aquatic Insects to Cu and Zn in Stream Microcosms: Understanding Differences Between Single Species Tests and Field Responses

William H. Clements,*[†] Pete Cadmus,[†] and Stephen F. Brinkman[‡]

[†]Department of Fish, Wildlife and Conservation Biology, Colorado State University, Fort Collins, Colorado 80523, United States
[‡]Colorado Parks and Wildlife, 317 West Prospect Road, Fort Collins, Colorado 80526, United States

3. Progressive recovery of a copper contaminated stream as copper declined: Big Deer Creek, Idaho

ELEMENTA
Science of the Anthropocene

2013

Recovery of a mining-damaged stream ecosystem

Christopher A. Mebane[1*] • Robert J. Eakins[2] • Brian G. Fraser[2] • William J. Adams[3]

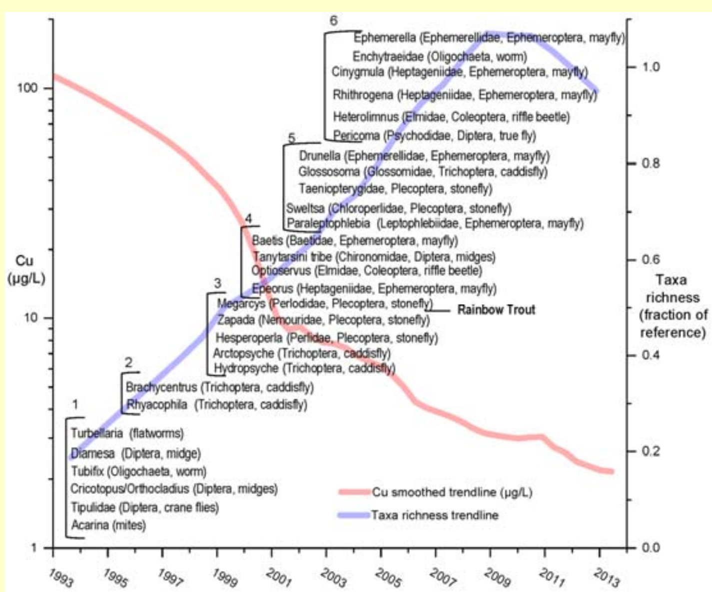
[1]Idaho Water Science Center, U.S. Geological Survey, Boise, Idaho, United States
[2]EcoMetrix Incorporated, Mississauga, Ontario, Canada
[3]Rio Tinto, Lake Point, Utah, United States
*cmebane@usgs.gov

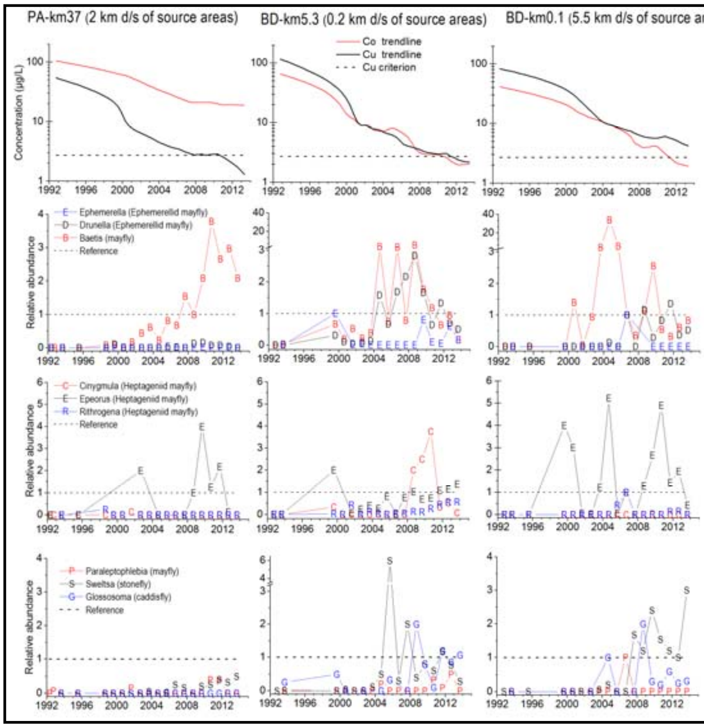
<u>Cu-contaminated tributary</u>

1992 4630 µg/L Cu	2012 56 µg/L Cu

3. Progressive recovery of a copper contaminated stream as copper declined (BLM-based Cu criterion ~ 3 µg/L during baseflow)

- By the time Cu dropped below about 5 µg/L, most detected;
- BLM-CCC was about 3 µg/L





3. Progressive recovery as copper declined

Some taxa remained uncommon even as Cu declined to near the CCC

What I've learned (so far)

- Many independent data sets with a diverse assortment of aquatic organisms and endpoints evaluated across a wide variety of natural and laboratory waters
- The BLM toxicity predictions were always at least correlated with empirical toxicity observations
- The 2007 criteria were mostly protective
  - Some ambiguity in protectiveness for community-level effects to primary producer and benthic invertebrate in results from field or model ecosystem studies
- The multiple linear regression (MLR) variation performed well and is a viable simplified alternative to the 2007-BLM version
- Following the traditional hardness-based criteria for copper could lead to misguided application of pollution controls and remedial efforts.
  - Calcium less important than DOC or pH in natural waters as a control on Cu toxicity

Environmental Solutions, Water Quality Standards and Assessment Section

Evaluating the Biotic Ligand Model for the development of new copper standards for Oregon

Copper Biotic Ligand Model Workshop
EPA, Region 10
May 13-14, 2015
Seattle

James McConaghie, WQ Specialist | Andrea Matzke, WQ Standards Specialist

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Topics

- Creation of a BLM database for Oregon
- Range and characteristics of Oregon data
- What are the most sensitive parameters?
- Where and how can we estimate missing parameters?
- Preliminary BLM results for Oregon

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Data Sources

- Existing Archived Databases
  - OR-DEQ LASAR database
  - USGS-NWIS parameters
- Current Field Monitoring
  - OR-DEQ Ambient Monitoring
  - OR-DEQ Toxics Sampling

Summary of Data Availability

Agency	Source	Time Period	# of Samples (n)	Complete Parameter Sets (n)	Incomplete Parameter Sets (n)
DEQ	Ambient Monitoring	Oct. 2013 – Present	14674	114	2041
DEQ	Toxics BLM	Jan. 2013 – Oct. 2014	2255	79	121
DEQ	LASAR	Jan. 2003 – Sept. 2013	13215	64	1452
USGS	NWIS	Jan. 2000 – Sept. 2014	125311	105	19230
			Totals:	362	22844

Sample dates: 2000-2014

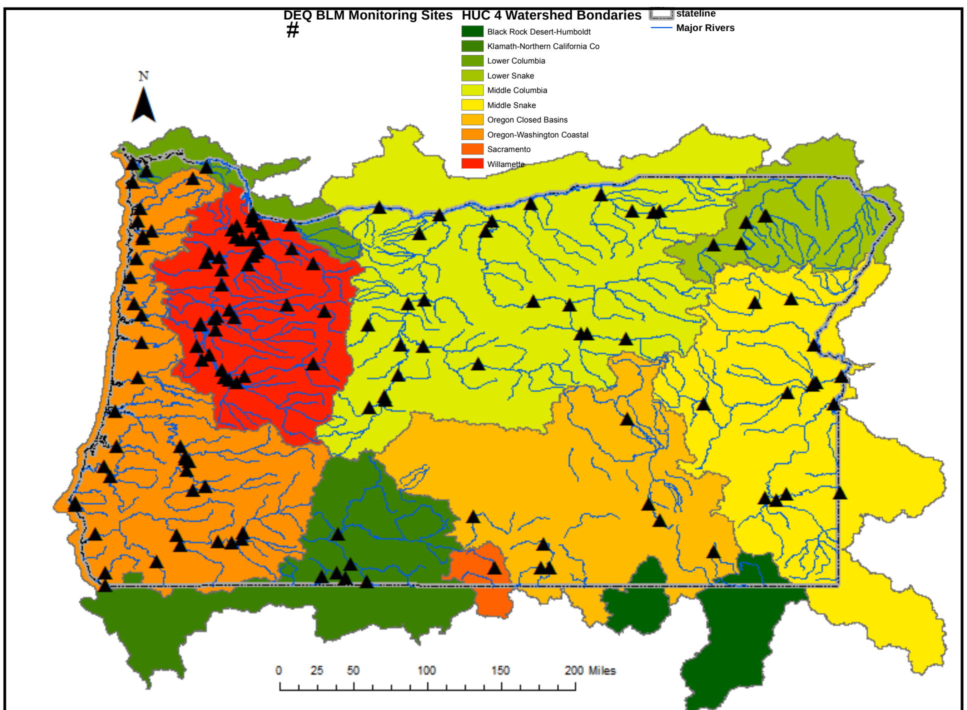
Preliminary Evaluation

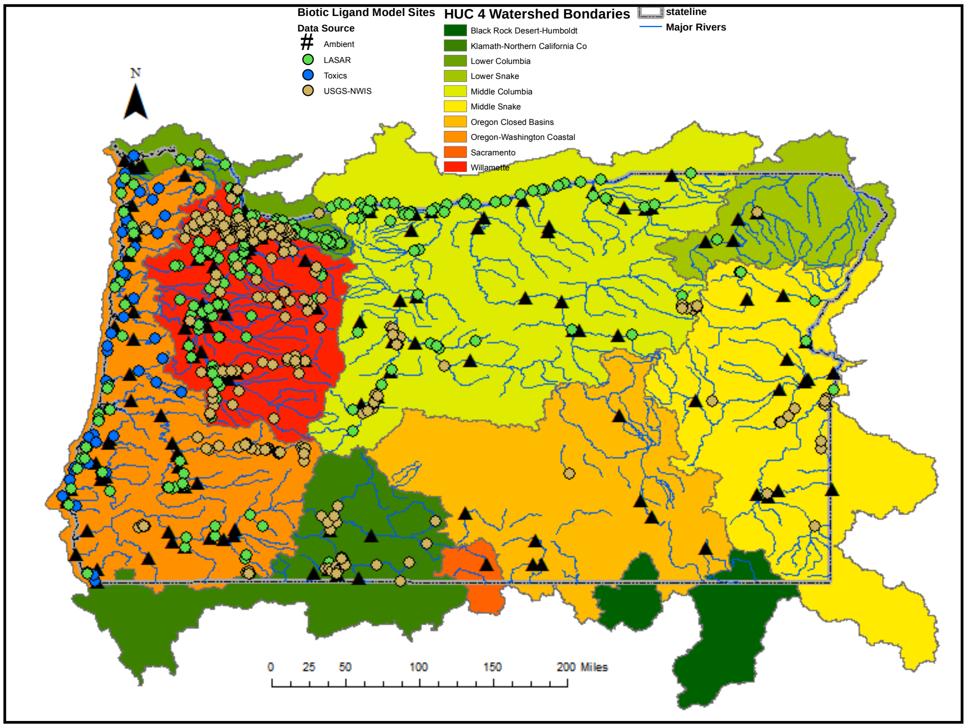
Complete by Estimating Values

Sites in the Oregon BLM Database

DEQ Ambient BLM	138
DEQ Other Ambient	26
DEQ Toxics	41
DEQ LASAR	413
USGS-NWIS	306
Total Sites	823

- Fresh water
- Surface Waters
- Streams/Rivers





Total vs. Dissolved Parameters

- BLM Model intended to use concentration of dissolved parameters
- Archived data is a mix of total and dissolved parameters
- Examined relationships between total and dissolved concentrations
- Guidelines for interchangeability of total vs. dissolved data

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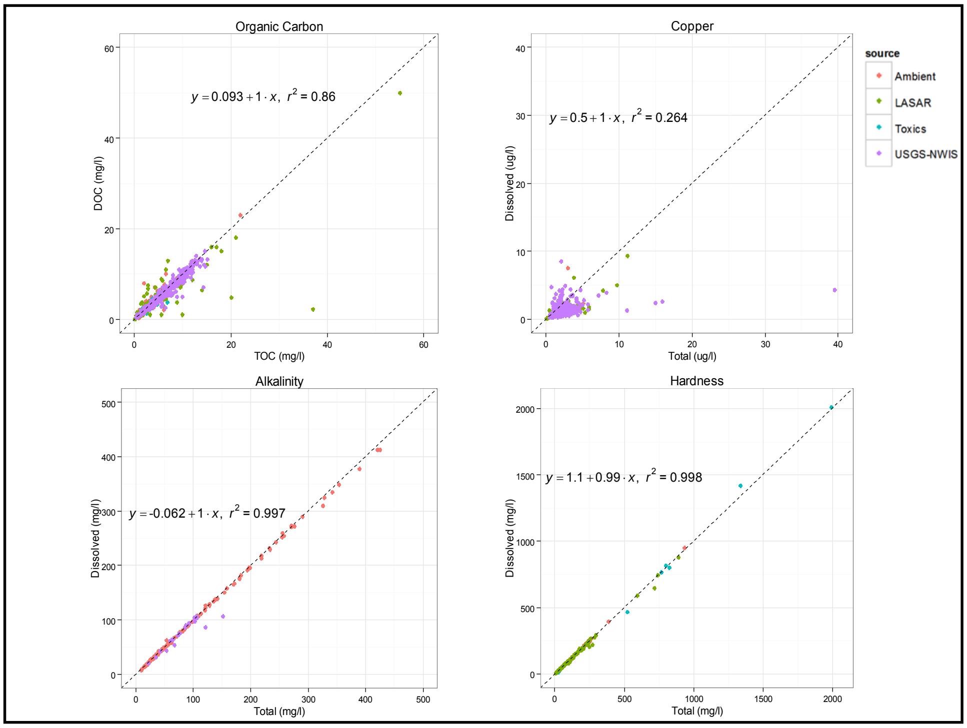
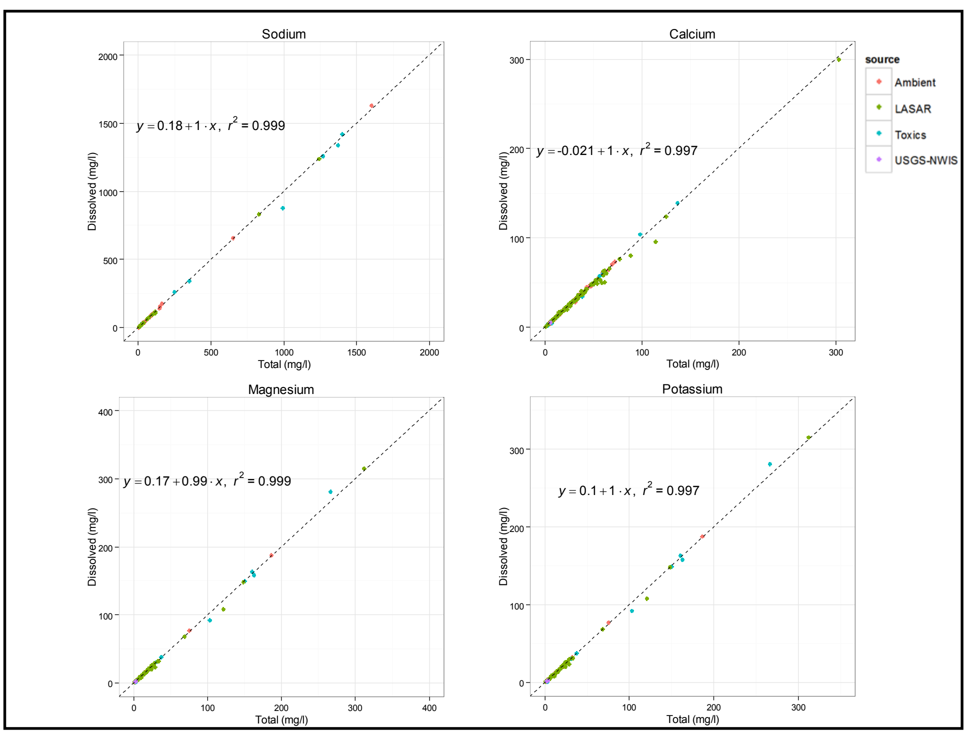

Organic Carbon
y = 0.093 + 1 · x, r² = 0.86
DOC (mg/l)
TOC (mg/l)
Copper
y = 0.5 + 1 · x, r² = 0.264
Dissolved (ug/l)
Total (ug/l)
source
Ambient
LASAR
Toxics
USGS-NWIS
Alkalinity
y = -0.062 + 1 · x, r² = 0.997
Dissolved (mg/l)
Total (mg/l)
Hardness
y = 1.1 + 0.99 · x, r² = 0.998
Dissolved (mg/l)
Total (mg/l)

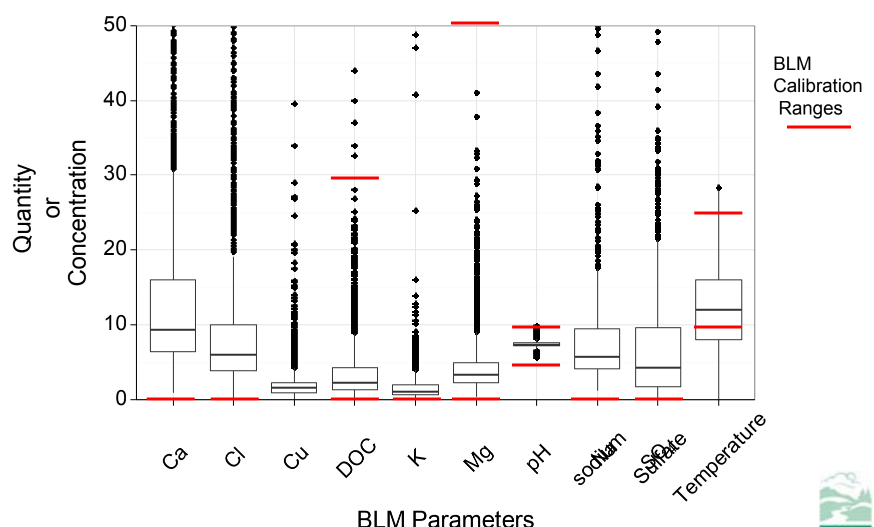

Sodium
y = 0.18 + 1 · x, r² = 0.999
Dissolved (mg/l)
Total (mg/l)
Calcium
y = -0.021 + 1 · x, r² = 0.997
Dissolved (mg/l)
Total (mg/l)
source
Ambient
LASAR
Toxics
USGS-NWIS
Magnesium
y = 0.17 + 0.99 · x, r² = 0.999
Dissolved (mg/l)
Total (mg/l)
Potassium
y = 0.1 + 1 · x, r² = 0.997
Dissolved (mg/l)
Total (mg/l)

Total vs. Dissolved Parameters

Conclusions:

- Total ≈ Dissolved for Geochemical Ions
  - Sodium
  - Calcium
  - Magnesium
  - Potassium
- Reasonably similar for TOC/DOC
- Copper, use Cu_T when Cu_D not available, but not equivalent.

Ranges of Chemical Data



Sensitivity Analysis

- Data limited by lack of sites with complete sets of BLM parameters (n = 362)
- Estimate values of missing parameters to increase size of database (n ≈ 22,000)
- What are the sensitive BLM parameters in an OR-specific dataset?

Sensitivity Analysis

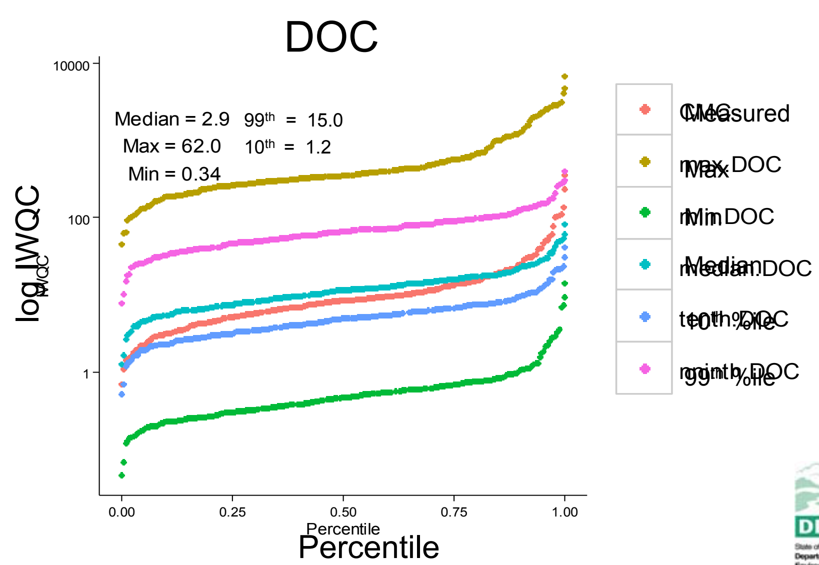
- Start with complete records of measured parameters (n=362)
- Calculate IWQC
- Replace measurements of 1 parameter piecewise with default values:
  - Max
  - Median
  - Min, etc.
- Maintain measured values for parameters not being tested
- Compare default IWQCs to measured IWQCs

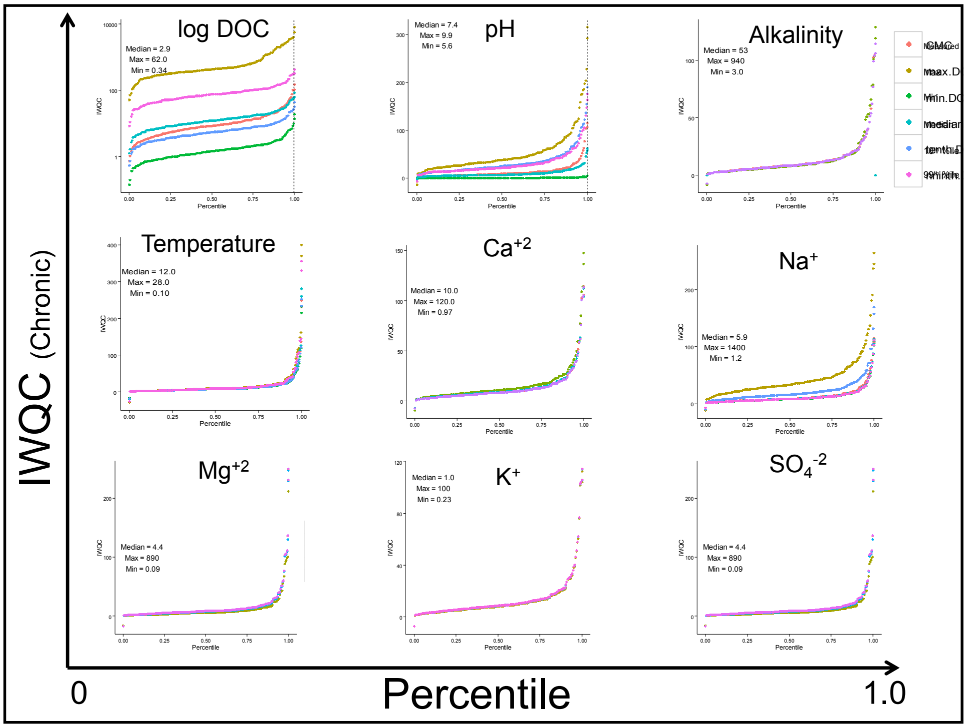
Sensitivity Analysis

Parameter Statistics

Analyte	N	Min.	10th Percentile	Median	99th Percentile	Max
Alkalinity	16760	3	25	52	180	420
DOC	2933	0.1	1.2	2.8	15	56
pH	17762	5.6	7.1	7.4	8.7	9.9
Temperature	18139	0.1	6	12	23	28
Ca	3229	1.2	4.9	10	53	140
K	698	0.1	0.47	1.2	11.09	130
Mg	3227	0.5	1.8	3.6	20	400
Na	732	1.2	2.71	5.8	127.6	1400
Cl	15161	0.18	3.2	6.4	45	2300
Sulfate	1200	0.09	0.779	4.4	81.13	890

Sensitivity Analysis—DOC Example





Most Sensitive Parameters

- DOC
  - Especially to values over model calibration range
  - 29.5 mg/L DOC calibration limit
- pH
- Na^+
  - Saline sites
    - Arid streams
    - Estuarine or tidally influenced surface water

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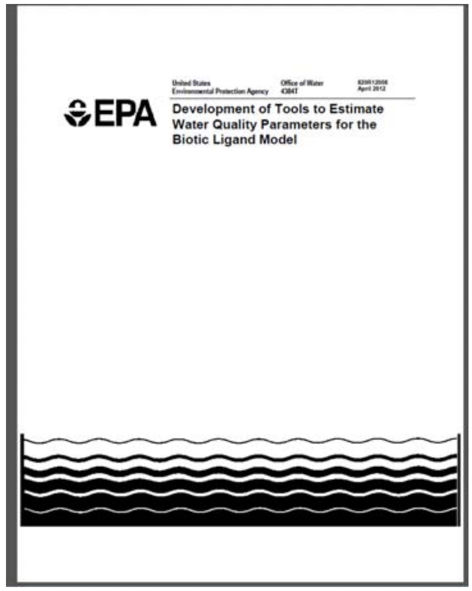
Data Conditioning

- Combine total and dissolved parameters
- Filtering Data:
  - Exclude extreme high/low DOC, pH
    - Effluent streams
    - Arid, alkaline locations
  - Exclude high Na^+ (high conductivity)
    - Freshwater definition is <1500 µmhos/cm
    - Tidally influenced sites
    - Effluent samples

Potential Size of Conditioned Database

Parameter	# of Samples	Required for:
pH	17762	Sensitive BLM parameter
DOC	5032	Sensitive BLM parameter
Conductivity	18443	For estimation of missing parameters
Copper	4284	FMB, TU, or compliance evaluation of BLM
Hardness	1179	Comparison of BLM with existing criteria and changes to listing or compliance

Estimation of Missing Parameters


United States Environmental Protection Agency
Office of Water 4304T
820R12008 April 2012

Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model

Estimation of Missing Parameters

- EPA 2012 Guidance Methods:
  - Regression on Conductivity
    - Empirical relationship between ion concentration and conductivity
    - Developed with data from CO, UT, WY
  - Use Eco-Regional Defaults
    - Unbiased mean of 10th Percentile Concentrations
- Evaluate these methods with an Oregon-specific dataset

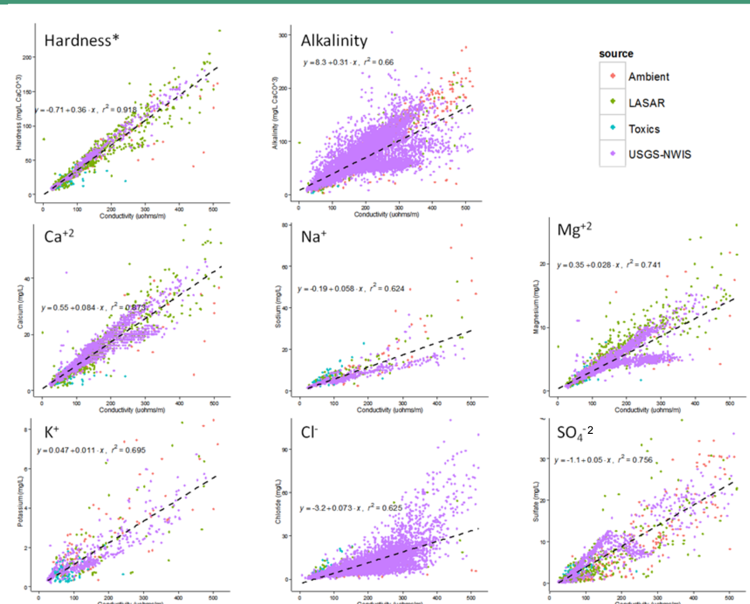
1. Estimating by Conductivity

Spearman Rank Correlations (ρ)

Parameter	Oregon Dataset	EPA 2012, Appendix C, Table2 (CO, UT, WY)
Alkalinity	0.89*	-0.600
Hardness	0.97*	N/A
Calcium	0.96*	0.867*
Potassium	0.83*	0.846*
Magnesium	0.95*	0.882*
Sodium	0.90*	0.921*
Chloride	0.89*	0.827*
Sulfate	0.89*	0.905*

* $p < 0.001$

1. Estimating by Conductivity



1. Goodness of Fit

	Goodness of Fit (Adj. R^2 of linear regression)			
Parameter	**Linear All Data**	**Linear 10th Percentile**	**Natural Log All Data**	**Natural Log 10th Percentile**
Alkalinity	0.65	0.31	0.77	0.29
Calcium	0.87	0.40	0.89	0.39
Hardness	0.92	0.25	0.92	0.26
Potassium	0.69	0.23	0.70	0.21
Magnesium	0.74	0.67	0.85	0.69
Sodium	0.62	0.28	0.82	0.30
Chloride	0.63	0.59	0.77	0.56
Sulfate	0.60	0.003	0.76	0.0005

* EPA goodness of fit evaluated as non-zero correlation coefficients with $p<0.001$

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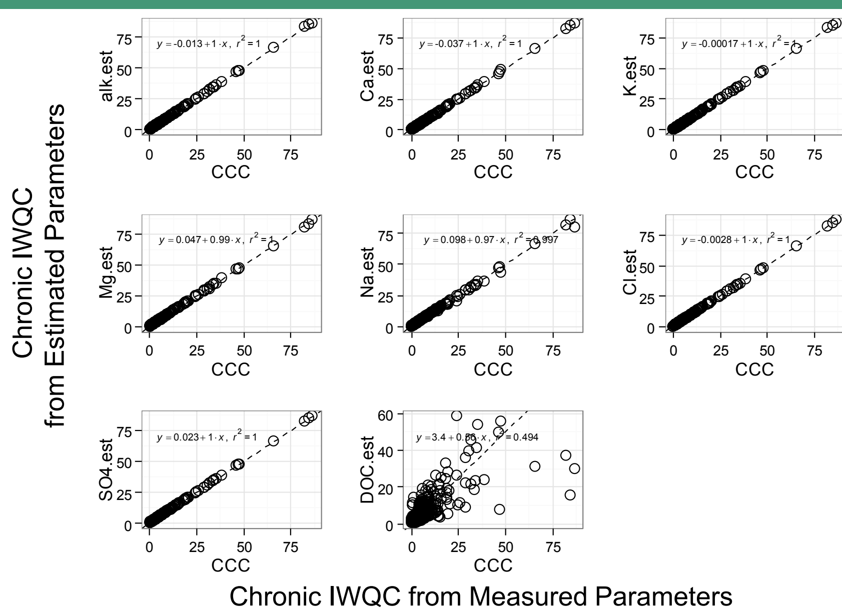
Estimation by Conductivity



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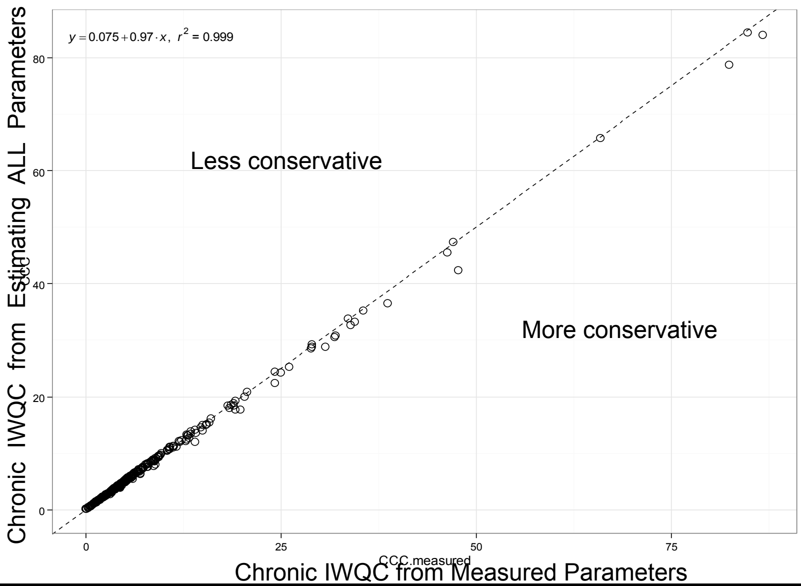
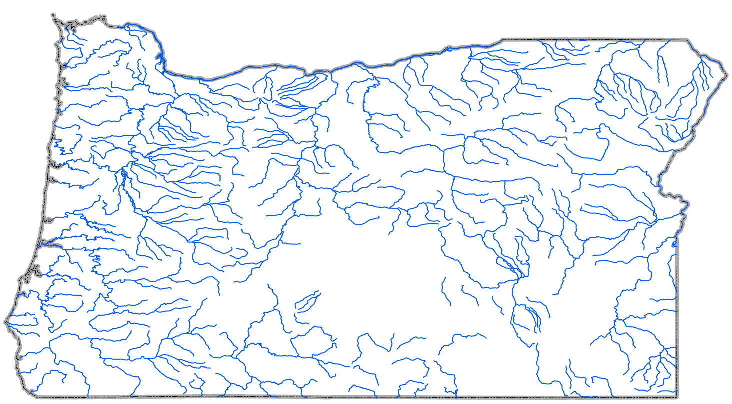
Estimation by Conductivity



2. Estimating using regional defaults

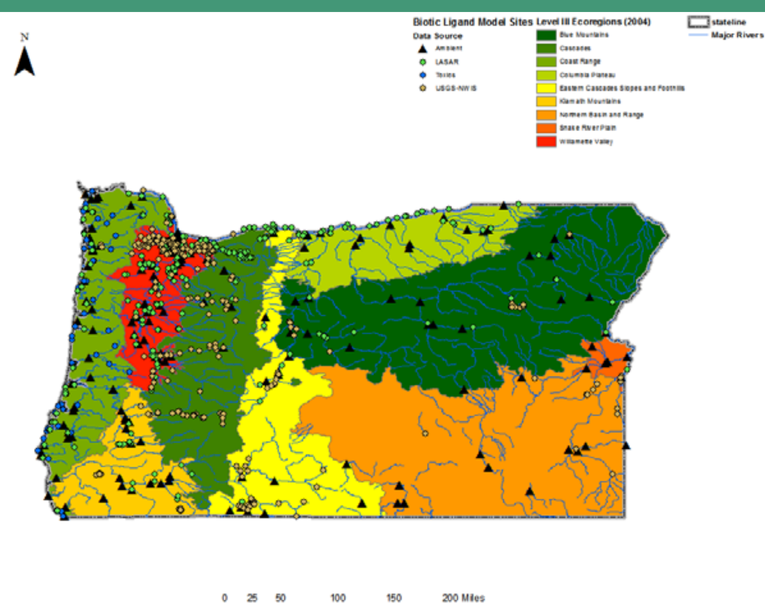
Where can we estimate parameters?

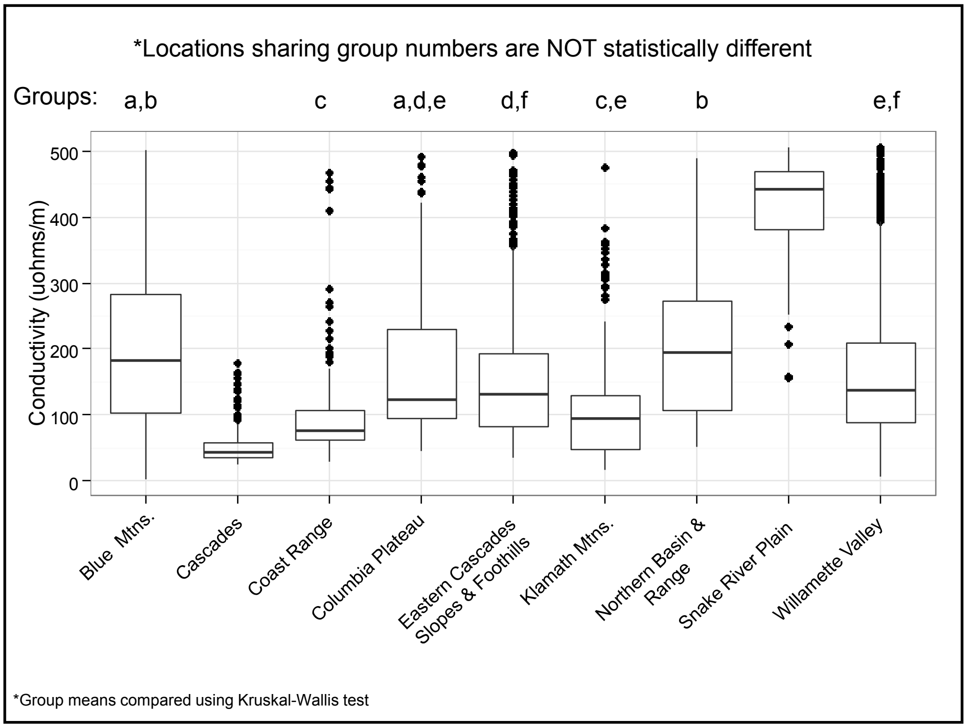


2. Site/Sample Characteristics

- Geographical
  - Level III Ecoregion
  - HUC 4 Watershed
- Seasonal
  - Dry = June – September
  - Wet = October – May
- Hydrology
  - Precipitation-driven = August – March
  - Snowmelt-driven = April – July

Level III Ecoregions

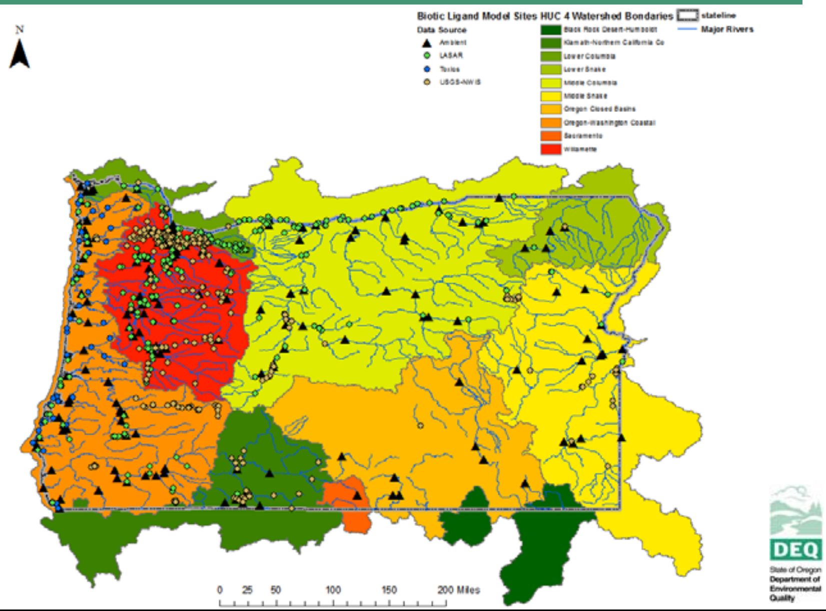


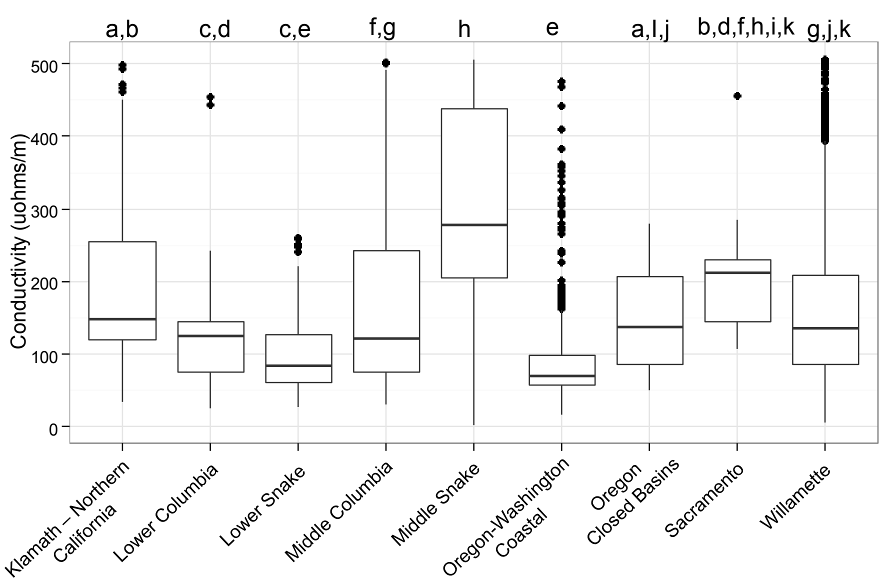


Level III Ecoregions

- Distribution of conductivity data not statistically different among L-III ecoregions
- Aggregating at this level does not result in significantly different default parameter estimates

HUC 4 Watersheds





*Group means compared using Kruskal-Wallis test

HUC 4 Watersheds

- Distribution of conductivity data not unique at level of HUC 4
  - Also not unique at HUC 6
- Aggregating at this level does not result in significantly different default parameter estimates

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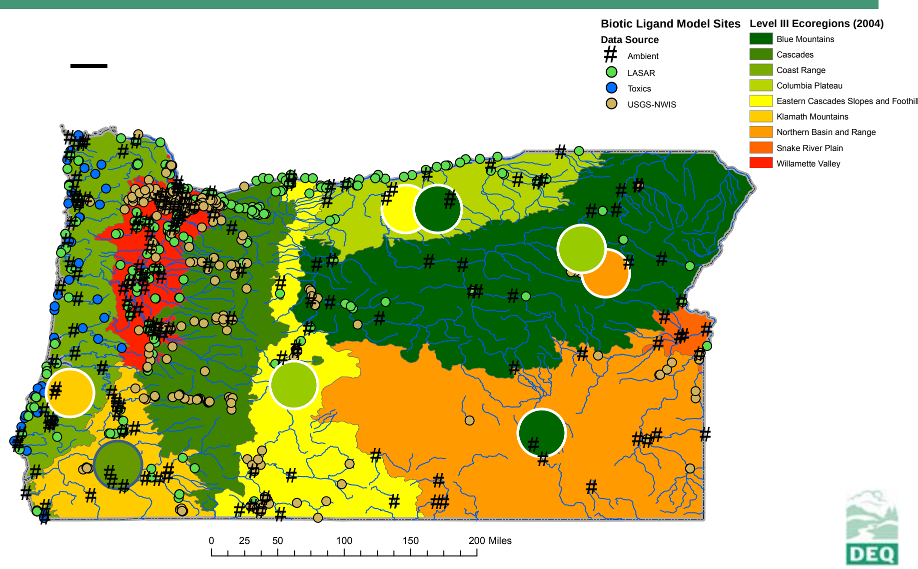
Similarity in Adjacent L-III Ecoregions



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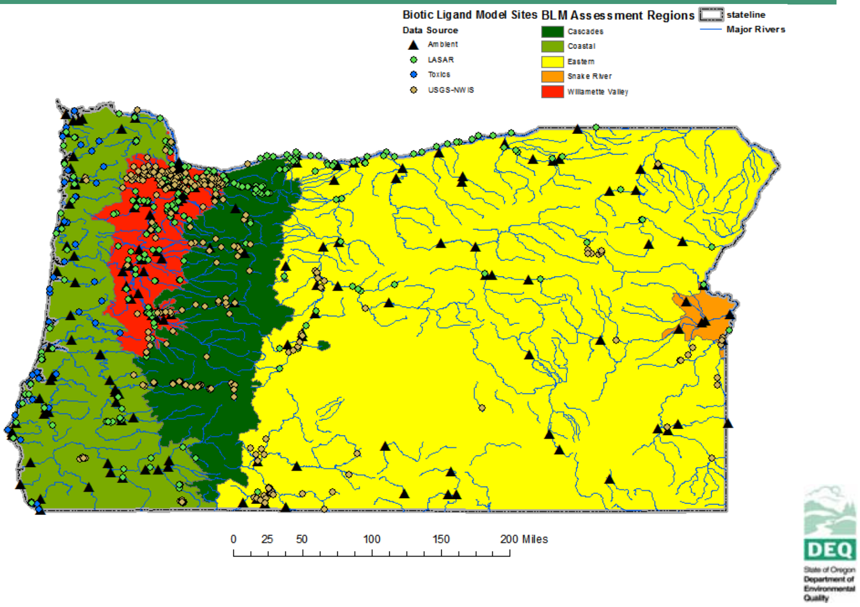
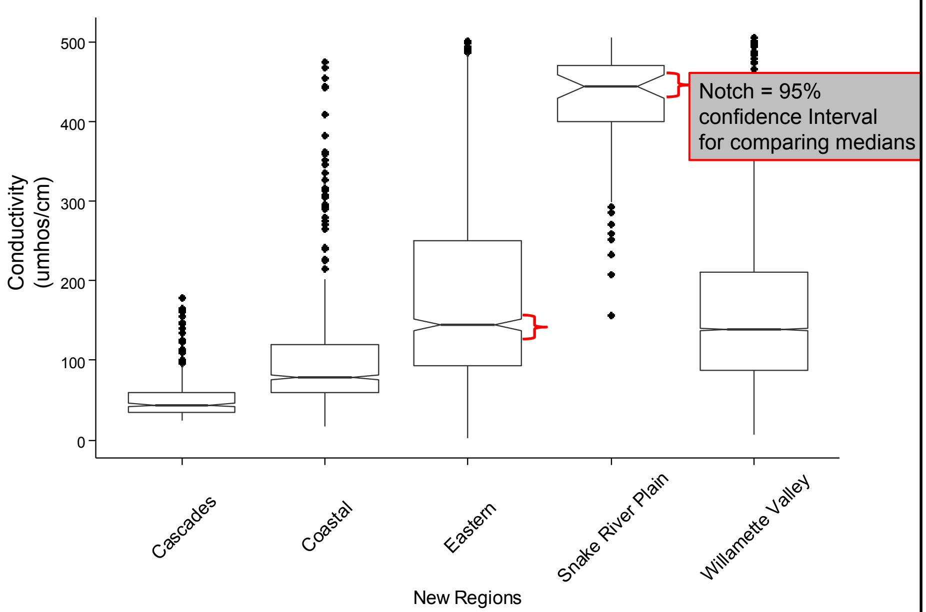
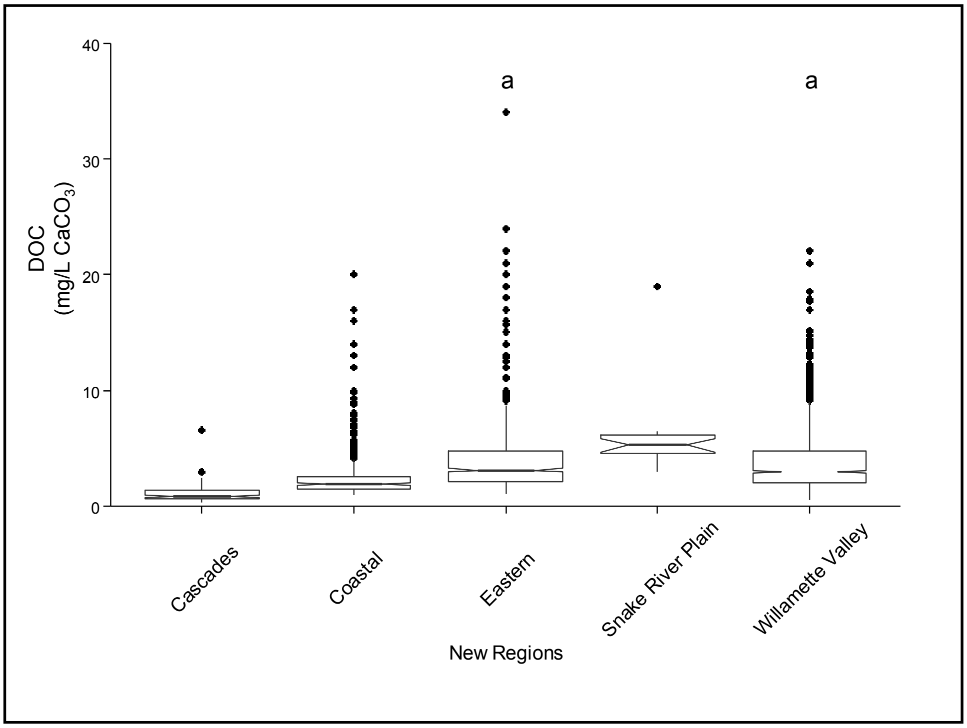
Potential OR Assessment Regions

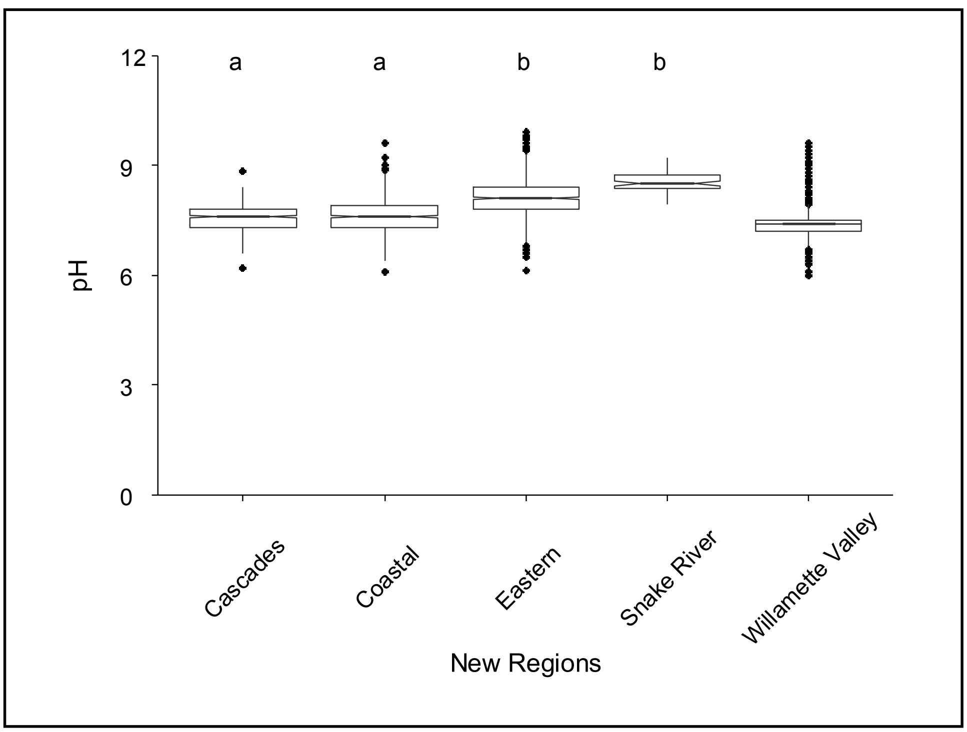




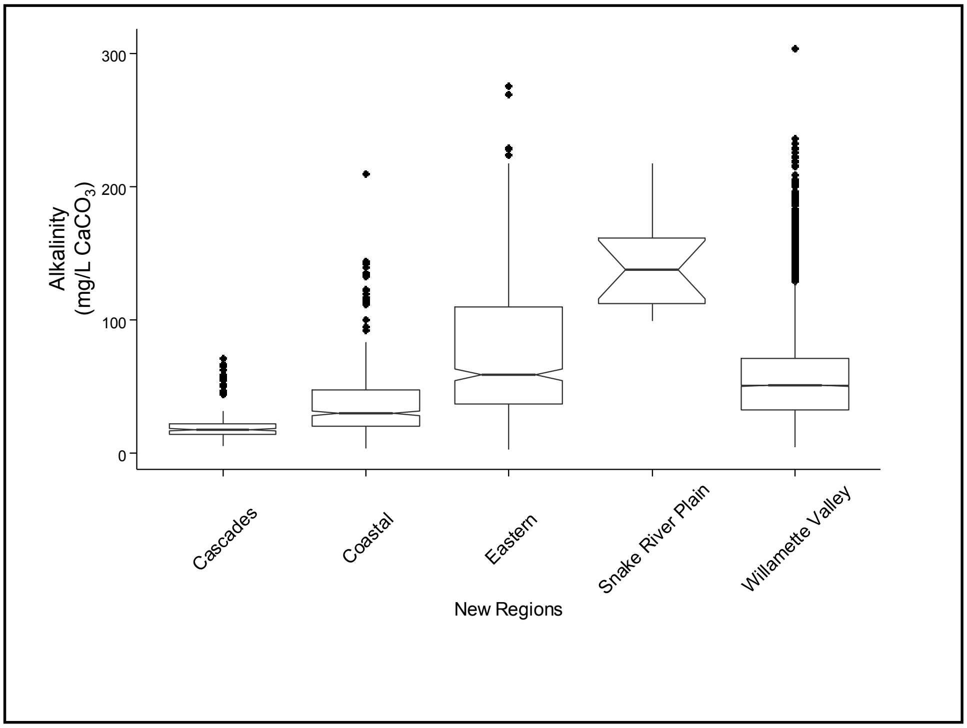
*All regions have significantly different sample means of conductivity according to a Kruskal-Wallis test

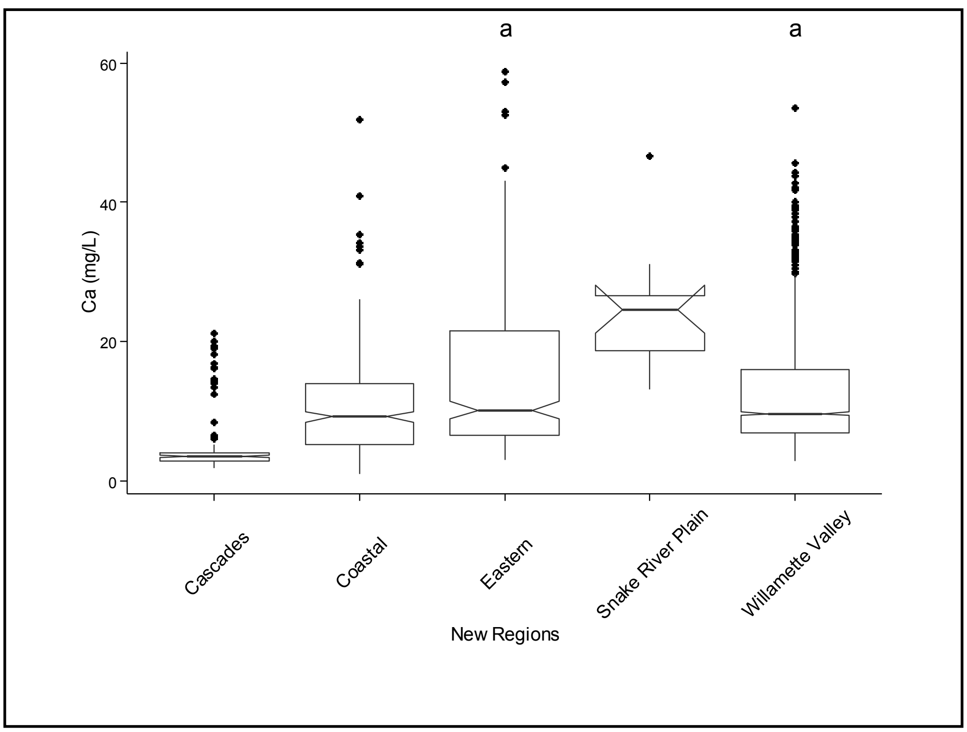


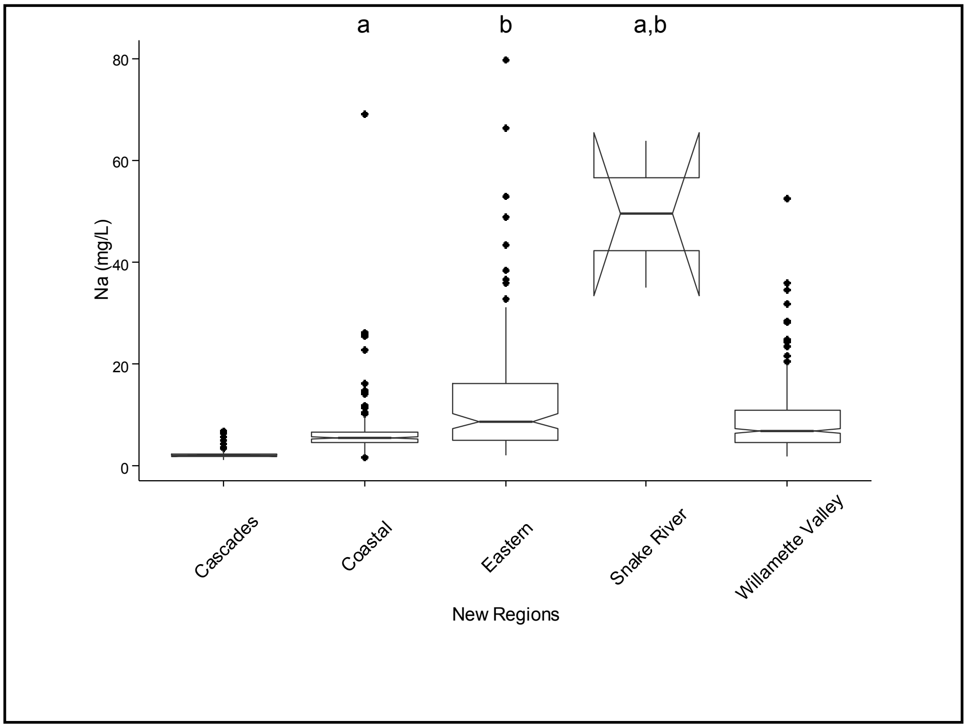
DOC
(mg/L CaCO3)
40
30
20
10
0
a
a
Cascades
Coastal
Eastern
Snake River Plain
Willamette Valley
New Regions



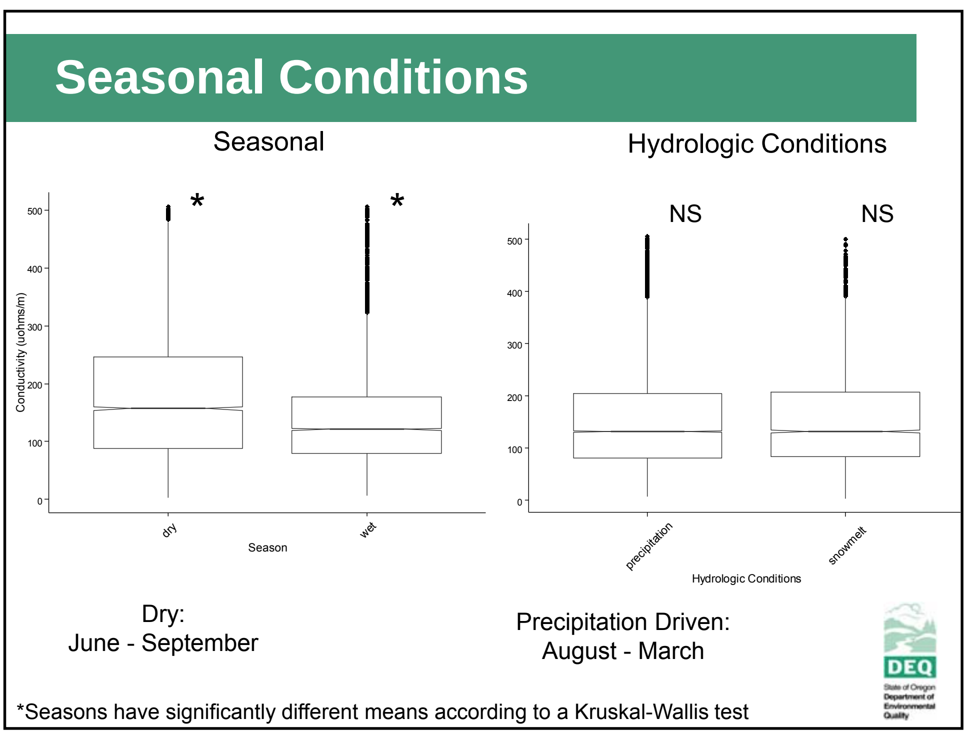
pH
12
9
6
3
0
a
a
b
b
Cascades
Coastal
Eastern
Snake River
Willamette Valley
New Regions


300
200
100
0
Alkalinity
(mg/L $CaCO_3$)
Cascades
Coastal
Eastern
Snake River Plain
Willamette Valley
New Regions


a
a
60
40
20
0
Ca (mg/L)
Cascades
Coastal
Eastern
Snake River Plain
Willamette Valley
New Regions



a
b
a,b
Na (mg/L)
0
20
40
60
80
Cascades
Coastal
Eastern
Snake River
Willamette Valley
New Regions



Seasonal Conditions
Seasonal
Hydrologic Conditions
*
*
NS
NS
Conductivity (uohms/m)
0
100
200
300
400
500
dry
wet
Season
precipitation
snowmelt
Hydrologic Conditions
Dry:
June - September
Precipitation Driven:
August - March
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*Seasons have significantly different means according to a Kruskal-Wallis test

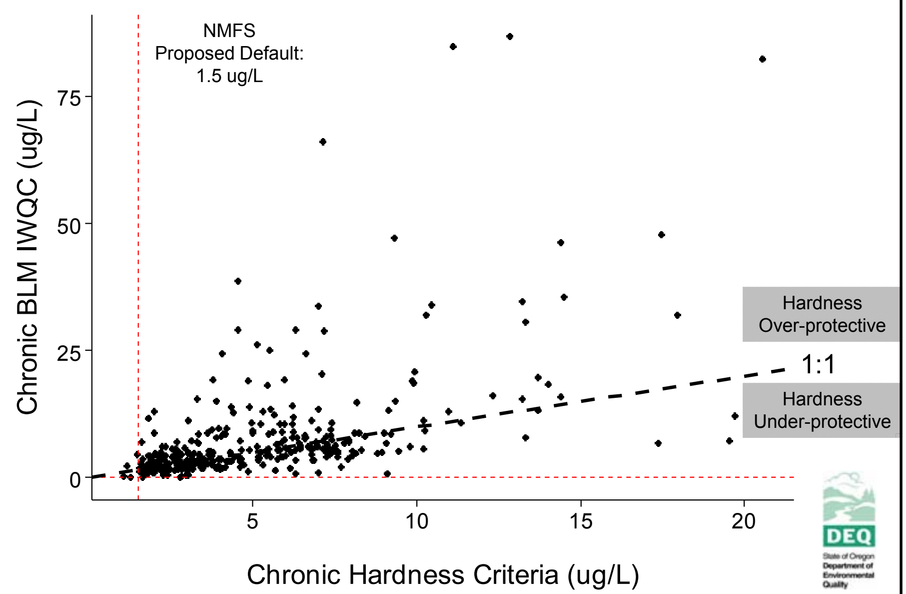
Potential BLM Assessment Regions

- Significant differences in distribution of samples within aggregated eco-regions
- Potential geographic units for default BLM parameters based on median, %ile, etc.
- Seasonal trends/distributions need further investigation
  - i.e. Kansas uses different BLM criteria in winter vs. summer

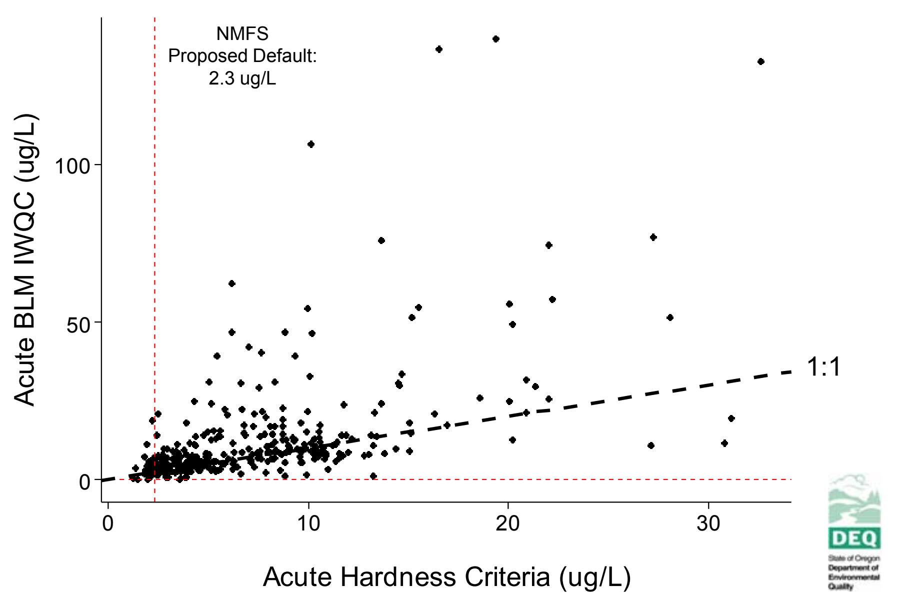
Preliminary BLM analysis

- Use measured parameter sets to evaluate:
  - BLM IWQC criteria
  - Compare IWQC vs. Hardness-based Criteria

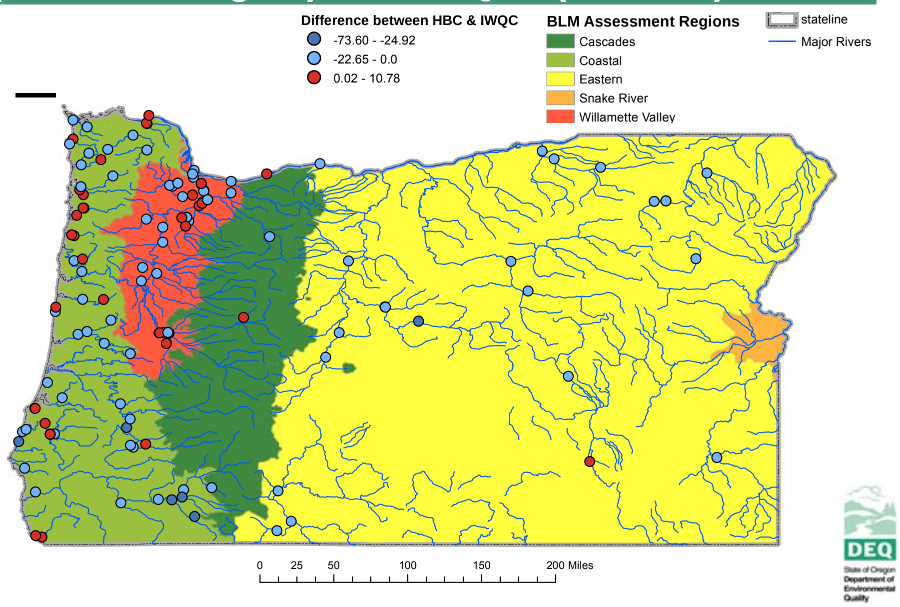
Chronic IWQC vs. Hardness Criteria



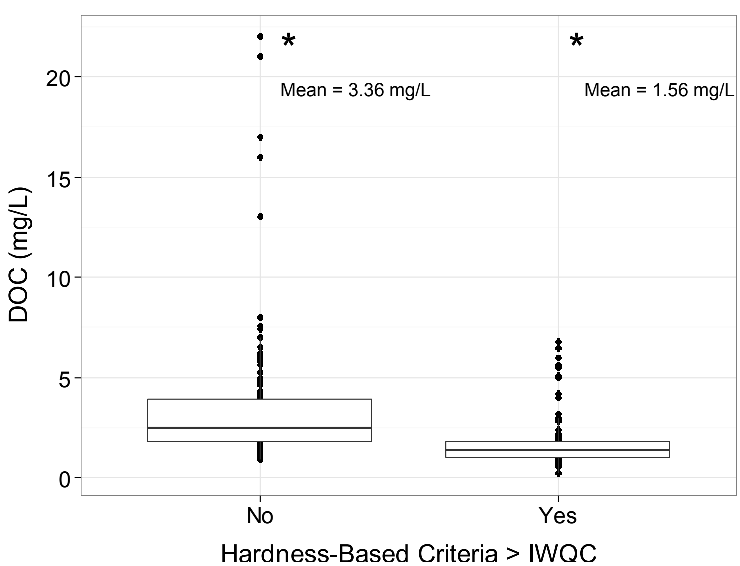
Acute IWQC vs. Hardness Criteria



Where are Hardness-Based Criteria > (i.e. less stringent) than IWQC? (red dots)

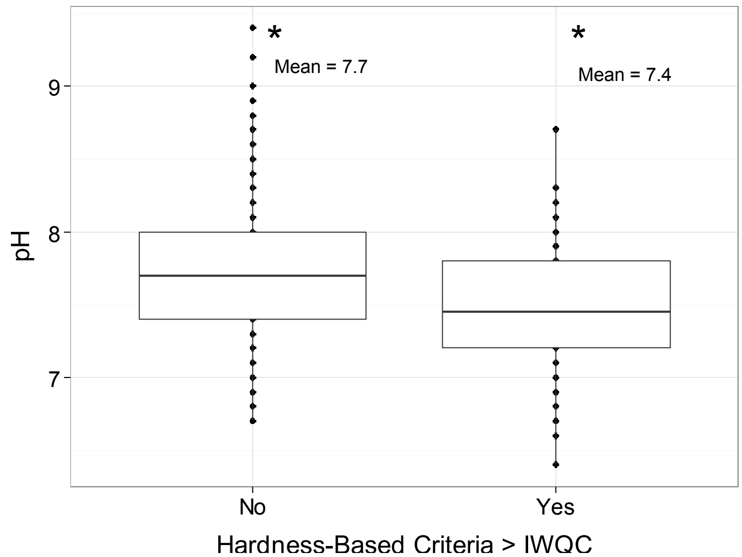


Where are Hardness-Based Criteria > (i.e. less stringent) than IWQC?



* Significantly different means according to Kruskal-Walis test

Where are Hardness-Based Criteria > (i.e. less stringent) than IWQC?



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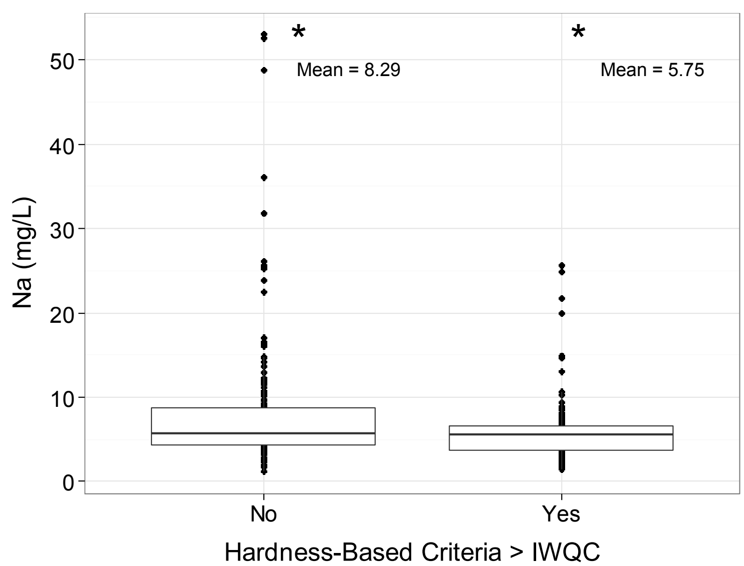
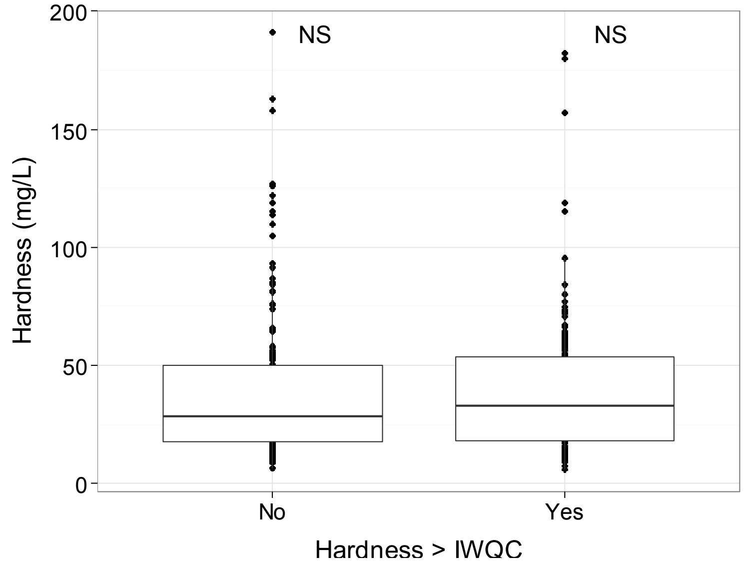
Where are Hardness-Based Criteria > (i.e. less stringent) than IWQC?



* Significantly different means according to Kruskal-Walis test

Where are Hardness-Based Criteria > (i.e. less stringent) than IWQC?



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Where are Hardness-Based Criteria > (i.e. less stringent) than IWQC?

Parameter	Mean Chronic HBC < IWQC	Mean Chronic HBC > IWQC	P-value (Kruskal-Walis)
Hardness	39.98	39.24	NS
DOC	3.36	1.56	<0.001
pH	7.7	7.4	<0.001
Alkalinity	44.82	37.32	NS
Sodium	8.29	5.75	<0.05
Calcium	9.73	9.94	NS
Potassium	1.51	0.99	NS
Magnesium	3.80	3.49	NS
Chloride	6.16	4.98	NS
Sulfate	4.92	6.02	NS

DEQ
State of Oregon Department of Environmental Quality

Conclusions to date

- Currently limited by data availability for a full evaluation of the BLM for developing criteria in Oregon
- Estimation of missing parameters essential
  - High potential to use either regression or georegional defaults
- Model sensitive to DOC, pH, Na in our dataset
  - IWQC are extremely high for saline sites, waste streams
  - Trim extreme values from the database
  - Only use records where these parameters are measured
- Restrict BLM to calibrated data ranges
- IWQC typically higher than Hardness-Based Criteria

DEQ
State of Oregon Department of Environmental Quality

How to apply BLM results in setting criteria?

- Select an estimation method for missing parameters
  - Is it justified to use parameters from nearby monitoring sites in certain circumstances, rather than using regression analyses to estimate?
- Derive site-specific criteria where BLM data is sufficient
  - Sample sufficiency and data representativeness?
  - Sites outside of BLM calibration range?
  - FMB or IWQC values?
  - Percentiles vs. median?
  - Compare results
- What is the geographic distribution of IWQC values, if any?
  - Possibility of using geographic default IWQC values where BLM data is insufficient
  - Use IWQC percentile or median values?

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Additional analyses planned

- Sensitivity analysis of IWQCs from estimated parameters
  - Georegional default values based on %ile, median
- Evaluate site-specific and georegional IWQCs
  - Statistical distributions
  - Geographic distributions

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Implementation of the BLM-FMB in Colorado

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South Platte River in Denver; photo by Jim Saunders

Outline

Colorado WQS Regulations

BLM Case Studies:

- Monument Creek, Plum Creek, Big Thompson River, South Platte River

Draft BLM-FMB Guidance

Outstanding Questions

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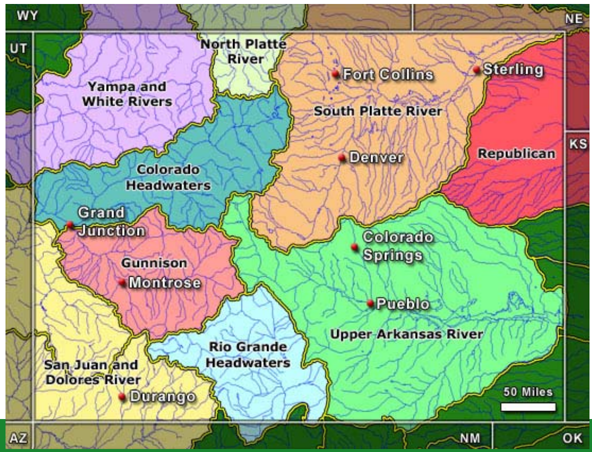
Colorado WQS Regulations

Regulation 31: THE BASIC STANDARDS AND METHODOLOGIES FOR SURFACE WATER

7 Basin Regulations and Tables: implement state-wide WQS on a segment by segment basis

32: Arkansas River Basin
33: Upper Colorado River & North Platte Basins
34: San Juan & Dolores Basins
35: Gunnison & Lower Dolores Basins
36: Rio Grande
37: Lower Colorado River
38: South Platte River



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Regulation 31: THE BASIC STANDARDS AND METHODOLOGIES FOR SURFACE WATER

31.7 (1) (b) (iii) Site-Specific-Criteria-Based Standards
For state surface waters where an indicator species procedure (water effects ratio), recalculation procedure, use attainability analysis or other site-specific analysis has been completed in accordance with section 31.16(2)(b), or in accordance with comparable procedures deemed acceptable by the Commission, the Commission may adopt site-specific standards as determined to be appropriate by the site-specific study results…..

31.16 TABLES
(1) …Water hardness is being used here as an indication of differences in the complexing capacity of natural waters and the corresponding variation of metal toxicity. Other factors such as organic and inorganic ligands, pH, and other factors affecting the complexing capacity of the waters may be considered in setting site-specific numeric standards in accordance with section 31.7. …

COLORADO https://www.colorado.gov/pacific/sites/default/files/Regulation-31.pdf

Regulation 31: THE BASIC STANDARDS AND METHODOLOGIES FOR SURFACE WATER

31.16(2)(b) Toxicity testing and Criteria Development Procedures

(i) The latest EPA Methods for Chemical Analysis of Water and Wastewater; ASTM, Standard Methods for Examination of Water, Wastewater;

(ii) Interim Guidance on Determination and Use of Water-Effect Ratio for Metals, EPA-823-B-94-001, U.S. Environmental Protection Agency, February, 1994.

(iii) Other approved EPA methods.

Example: Monument Creek

- First BLM-FMB based site-specific copper criterion adopted by Colorado's Commission in 2013
  - o ~5.8 miles of a 28 mile segment
- Study plan driven data collection (2004-2007, 2012-2013)
  - Baptist Rd (N=61)
  - North Gate (N=32)
  - Woodmen Rd (N=34)
- Water chemistry at most downstream site (Woodmen Rd.) suggested it was appropriate to retain the hardness-based criteria

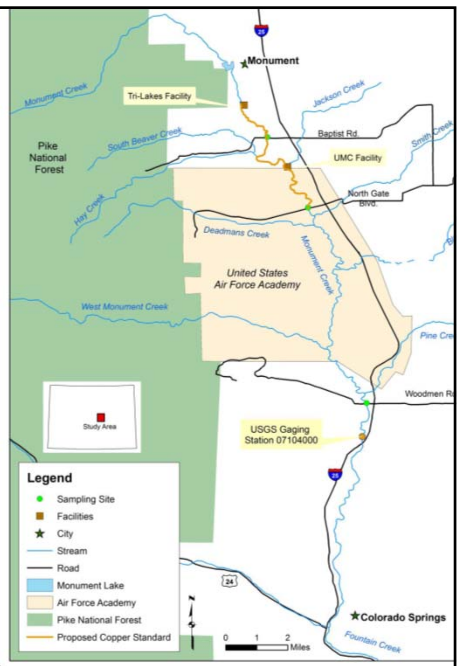

Figure from the rebuttal testimony OF GEI CONSULTANTS, INC. On behalf of TRI-LAKES WASTEWATER TREATMENT FACILITY.

Example: Monument Creek

Copper BLM-based Fixed Monitoring Benchmark (FMB)

FMBa = 28.4 µg/L

FMBc = 17.8 µg/L

For a sub-segment of Monument Creek from immediately above the Tri-Lakes Wastewater Treatment Facility to the North Gate Boulevard Bridge

REGION: 4 & 7 BASIN: FOUNTAIN CREEK Stream Segment Description	Desig	Classifications	NUMERIC STANDARDS PHYSICAL and BIOLOGICAL	INORGANIC mg/l		METALS ug/l			TEMPORARY MODIFICATIONS AND QUALIFIERS
4. All tributaries to Fountain Creek which are not within the boundaries of National Forest or Air Force Academy lands, including all wetlands, from a point immediately above the confluence with Monument Creek to the confluence with the Arkansas River, except for specific listings in segments 5 and 6.	UP	Aq Life Warm 2 Recreation E Water Supply Agriculture	T=TVS(WS-II) °C D.O. = 5.0 mg/l pH = 6.5-9.0 E.Coli=126/100ml Chla=150 mg/m^{2}[C]	NH_3(ac/ch)=TVS CL_2(ac)=0.019 CL_2(ch)=0.011 CN=0.005 S=0.002	B=0.75 NO_2=0.5 NO_3=10 Cl=250 SO_4=WS P=170 ug/l (tot)[C]	As(ac)=340 As(ch)=0.02-10(Trec)[A] Cd(ac/ch)=TVS CrIII(ac)=50(Trec) CrIII(ch)=TVS	CrVI(ac/ch)=TVS Cu(ac/ch)= TVS Fe(ch)=WS(dis) Fe(ch)=1000(Trec) Pb(ac/ch)= TVS Mn(ac/ch)=TVS Mn(ch)=WS(dis)	Hg(ch)=0.01(tot) Mo(ch)=160(Trec) Ni(ac/ch)= TVS Se(ac/ch)= TVS Ag(ac/ch)=TVS Zn(ac/ch)= TVS	
5. Marshland on Nash Property (60 acres at 13030 Old Pueblo Road, El Paso County) located in Section 28 T16S R65W; Jimmy Camp Creek from the irrigation diversion east of Old Pueblo Road to its confluence with Fountain Creek; unnamed tributary from the boundary of Fort Carson to the confluence with Fountain Creek; located in S1/2, SW1/4, Section 6 and N1/2. NW1/4, Section 7, T16S, R65W.		Aq Life Warm 1 Recreation N Agriculture	T=TVS(WS-II) °C D.O. = 5.0 mg/l pH = 6.5-9.0 E.Coli=630/100ml	NH_3(ac/ch)=TVS CL_2(ac)=0.019 CL_2(ch)=0.011 CN=0.005 S=0.002	B=0.75 NO_2=0.5 NO_3=100 P=170 ug/l (tot)	As(ac)=340 As(ch)=100(Trec) Cd(ac/ch)=TVS CrIII(ac/ch)=TVS CrIII(ch)=100(Trec) CrVI(ac/ch)=TVS Cu(ac/ch)=TVS	Fe(ch)=1000(Trec) Pb(ac/ch)=TVS Mn(ac/ch)=TVS Hg(ch)=0.01(tot) Mo(ch)=160(Trec)	Ni(ac/ch)=TVS Se(ac/ch)=TVS Ag(ac/ch)=TVS Zn(ac/ch)=TVS	
6. Mainstem of Monument Creek, from the boundary of National Forest lands to the confluence with Fountain Creek.		Aq Life Warm 2 Recreation E Water Supply Agriculture	T=TVS(WS-II) °C D.O. = 5.0 mg/l pH = 6.5-9.0 E.Coli=126/100ml Chla=150 mg/m^{2}[C]	NH_3(ac/ch)=TVS CL_2(ac)=0.019 CL_2(ch)=0.011 CN=0.005 S=0.002	B=0.75 NO_2=0.5 NO_3=10 Cl=250 SO_4=WS P=170 ug/l (tot)[C]	As(ac)=340 As(ch)=0.02-10(Trec)[A] Cd(ac/ch)=TVS CrIII(ac)=50(Trec) CrIII(ch)=TVS CrVI(ac/ch)=TVS Cu(ac/ch)=TVS	Fe(ch)=WS(dis) Fe(ch)=1000 (Trec) Pb(ac/ch)=TVS Mn(ac/ch)=TVS Mn(ch)=WS(dis) Hg(ch)=0.01(tot) Mo(ch)=160(Trec)	Ni(ac/ch)=TVS Se(ac/ch)=TVS Ag(ac/ch)=TVS Zn(ac/ch)=TVS	Copper BLM –based Fixed Monitoring Benchmark (FMB) Copper FMBa = 28.4µg/L Copper FMBc = 17.8µg/L for a subsegment of Monument Creek from immediately above the Tri-Lakes Wastewater Treatment Facility to the North Gate Boulevard Bridge.

Proposals using mined data sources

Increased N (>100)

Longer time frames – changing water quality

Missing parameters

Sample size differences

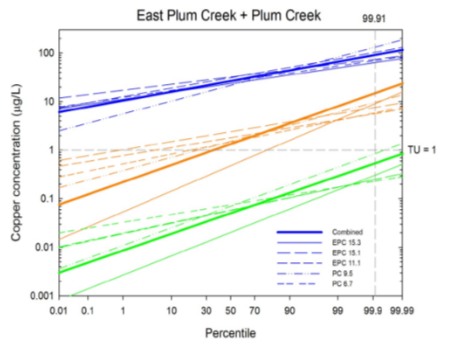

Figure 1. *Revised version of Figure 5 from Exhibit 1 of PCWRA PPHS, updated to visually differentiate distributions for each site, using only co-occurring data.* Probability distributions of acute instantaneous water quality criteria (IWQC; blue lines), instream copper concentrations (orange lines), and calculated toxic units (TU; green lines) for individual sites (solid and dashed thin lines) and combined data for East Plum Creek and Plum Creek (bold lines).

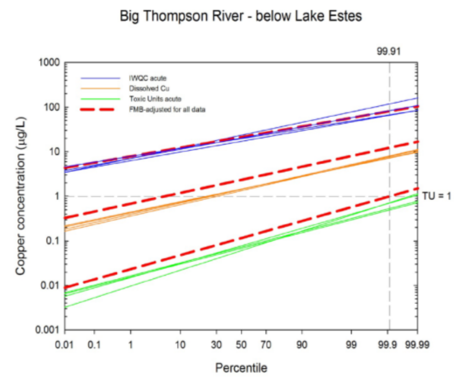

Figure 1: Probability distributions of acute instantaneous water quality criteria (IWQC), instream copper concentrations, and calculated toxic units (TU) for individual sites (solid lines) and FMB-adjusted combined data for Big Thompson River below Lake Estes (dashed red line).

Plum Creek

Location	N	Dates	FMBa	%ile IWQCa
EPC 15.3	126	07/08-08/14	20.1	60%
EPC 15.1	123	07/08-08/14	22.9	51%
EPC 11.1	25	09/13-08/14	20.2	17%
PC 9.5	25	09/13-08/14	11.7	10%
PC6.7	25	09/13-08/14	30.4	74%
Combined	324	07/08-08/14	34	--

UTSD - Big Thompson River

Location	N	Dates	FMBa	%ile IWQCa
M40	115	01/04-11/13	11.2	13.5%
M50	115	01/04-11/13	13.0	11.1
M60	115	01/04-11/13	16.9	27%
M70	112	01/04-09/13	14.1	17%
Combined	457	01/04-0913	12.7	--

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Figures from the rebuttal testimony of GEI CONSULTANTS, INC. on behalf of Plum Creek Water reclamation Authority and Upper Thompson Sanitation District

Implementation of BLM FMB Big Thompson River

Key concerns:

DATA: Spatio-temporal representativeness of sampling.
(Significant hydrological features, WWTPs & tributaries, etc.
Variability of annual water cycle), Strong Parameter Estimates.

MODEL: Accuracy of FMBs, Strength of Distributional Assumptions

GOAL: Develop strong basis for evaluating intersite variability of FMBs and develop site specific criteria that are protective of the entire segment and downstream uses.

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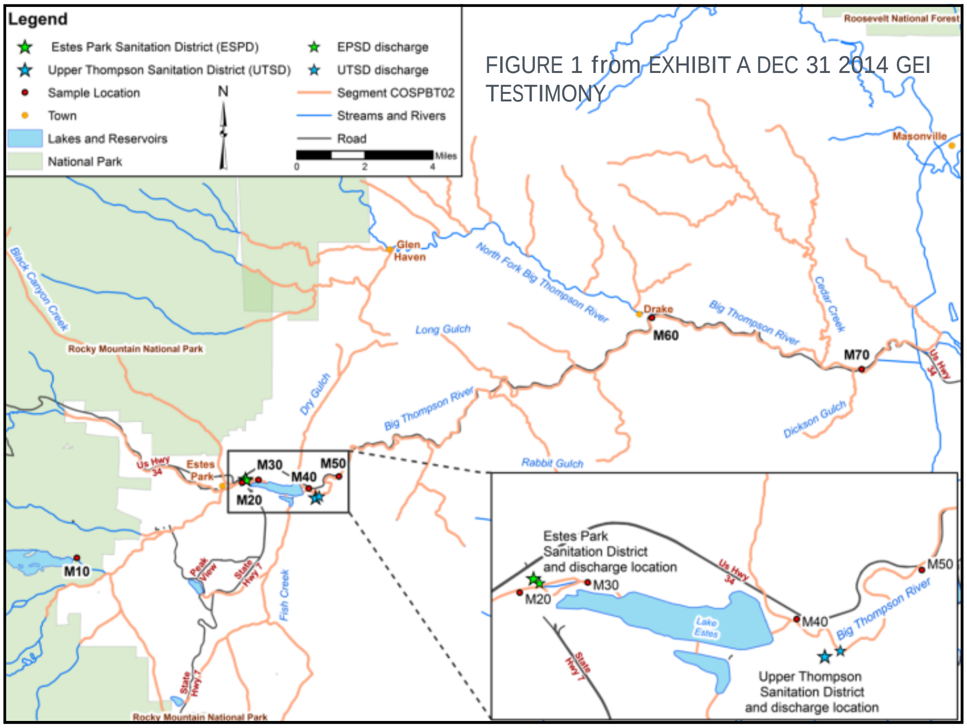


FIGURE 1 from EXHIBIT A DEC 31 2014 GEI TESTIMONY

Big Thompson Data

Sufficient length of time, (>2 years) and quantity of samples(>24 per site) to characterize the segment.

Representative sampling of the portion of segment below discharger which standard is to be applied (M50-M70)

Log-Normal Copper Distribution? No! But we'll come back to it.

15 values in the POR with pH>9…

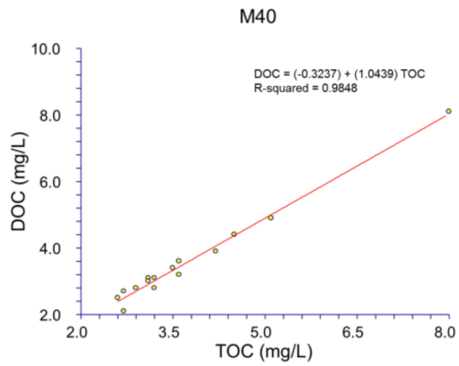
DATA Estimates

TOC to DOC Correlation:

-Strong relationship and rationale.

Missing alkalinity estimated from

hardness (R^2 =.908)



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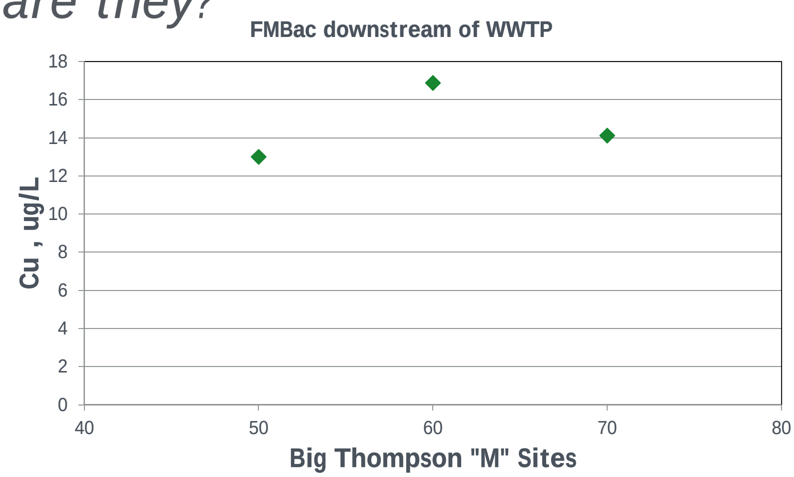
FMBs downstream-how different are they?



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Confidence Interval for a Percentile Assuming a Lognormal Distribution

Statistics for Censored Environmental Data using Minitab and R

Dennis. R. Helsel 2nd edition.

Hahn and Meeker (1991) g' statistic based on Noncentral t-distribution

Two sided confidence intervals around a percentile larger than the median.

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2-sided Confidence Interval for Percentile larger than Median

$$\exp\left[(\bar{y} + g'_{(\alpha/2),p,n} * s_y), (\bar{y} + g'_{(1-\alpha/2),p,n} * s_y)\right]$$

$\bar{y} = mean\ copper, \log transformed$

$g' = statistic\ based\ on\ noncentral\ t\ distribution$

$1 - \alpha = confidence\ coefficient$

$p = pth\ percentile; > 0.5$

$n = sample\ size$

$s_y = standard\ deviation\ of \log transformed\ copper$

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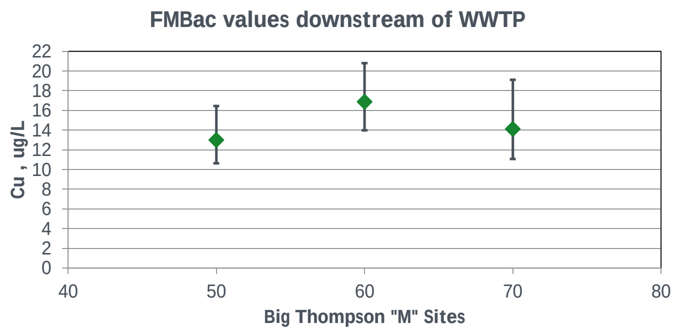
FMBac downstream -how different are these values?



Site	FMBac	Upper CI	Lower CI
50	13.00	16.91	10.09
60	16.88	21.87	13.83
70	14.12	18.25	11.27

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Non-Lognormality of Copper

From Hydroqual (2008) In the one case where neither the copper or TU distribution were well described by a lognormal distribution: “A goodness of fit statistic may be an appropriate diagnostic ”

Shapiro-Wilk test of log-transformed copper distribution at each site were significantly non normal.

M50 p = 1.13e-07

M60 p = 0.0006023

M70p == 1.666e-05

How strict to be? The FMB represents an extreme quantile therefore larger potential error.

BOTH BLM and CONFIDENCE INTERVAL METHODS ASSUME LOGNORMAL

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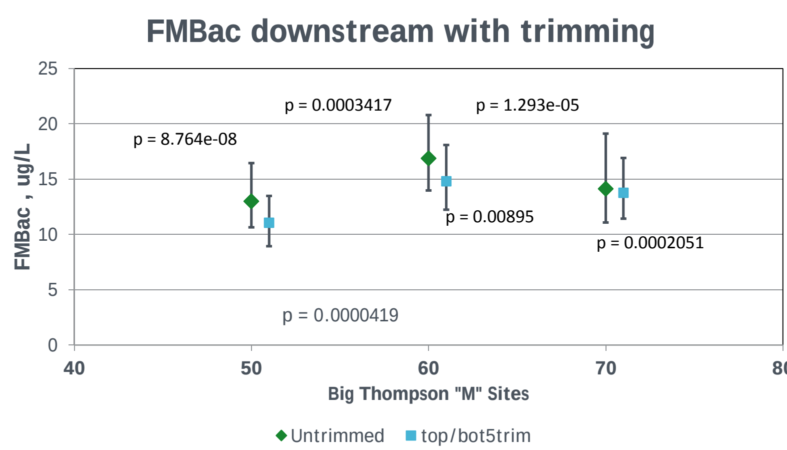

Trimmed Values			
Site	**FMBac**	**Upper CI**	**Lower CI**
M50	**11.06**	**13.48**	**8.94**
M60	**14.8**	**18.08**	**12.23**
M70	**13.77**	**16.91**	**11.42**

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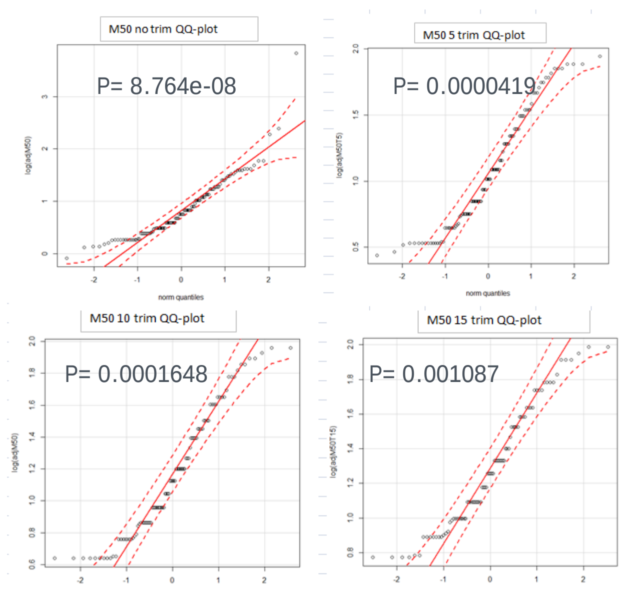

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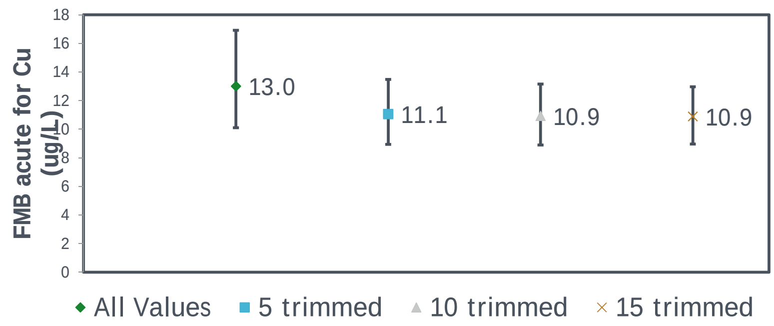
M50 FMB "Stabilization"



M50	No Trim	Up/Low 5 trimmed	Up/Low 10 trimmed	Up/Low 15 trimmed
FMBac	13	11.06	10.92	10.89
upper 95%CI	16.91	13.48	13.16	12.96
lower 95%CI	10.09	8.94	8.89	8.95
p-value	8.764e-08	0.0000419	0.0001648	0.001087

Aggregation of model inputs?

EPA(2012)-site specific nature of analysis

Effluent impacts downstream (DOC up, pH down. Non-conservative behavior)

Experience of aquatic life

Potentially more than 1in3 year exceedance at individual sites with FMBs that are more stringent

FMB was developed to characterize the temporal variability at a sampling location, not the spatial variability within a segment

CO BLM Guidance Development

First draft provided to the CO BLM workgroup 1/9/2015

Focuses on the development of site-specific standards based on the BLM-FMB

Addresses the following questions:

1) What are the minimum data requirements?
2) How should sampling sites be selected?
3) What preparations or requirements precede model operation?
4) How should model output be interpreted?

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CO BLM Guidance Development
1. Minimum Data Requirements

a. 24 useable* sampling events** to obtain data on all modeling parameters (including copper for FMB calculations)
   i. Sample size must be large enough to support estimation of an extreme quantile (99.91%)
   ii. Sample size also serves to provide adequate representation of seasonal variation and operational variability in water resource management

b. Sampling events should span at least two years

c. Data should be "representative" in the sense that there is adequate coverage of seasons and hydrologic conditions

*"Useable" simply means that a data set is sufficiently complete to include in model runs.
**Helsel (p.65) says: "MLE methods have not been found to work well for estimating the mean or variance of small (n<30; 50-70 for skewed populations) samples…, particularly for those assuming a lognormal distribution."

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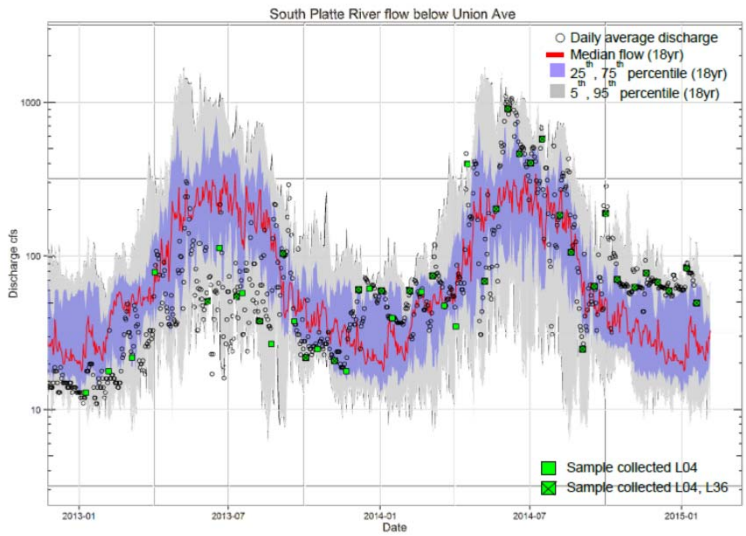

Figure 4. Comparison of flows measured by the US Geological Survey (USGS) at a gauge station (#06710247) located on the South Platte River below Union Ave. on the dates sampled by the Centennial Water and Sanitation District, against those measured over the last 18 years

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Figure from the prehearing testimony of GEI CONSULTANTS, INC.
On behalf of CENTENNIAL WATER AND SANITATION DISTRICT.

CO BLM Guidance Development

2. Recommendations for Sampling Sites

a. The number of sites will depend on site-specific conditions
   i. When only one site is sampled, the BLM-based copper standard may have limited applicability in the permit. Consideration should be given to the role of significant hydrologic features that would alter mass balance.
   ii. Multiple sites are desirable for understanding the role of important hydrologic features (e.g., tributaries) and assuring protectiveness
b. Since the focus of the guidance is on development of site-specific standards below permitted discharges, the primary interest is in sites downstream of the regulatory mixing zone.

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CO BLM Guidance Development
3. Processing Data

a. Sites are to be processed individually (i.e., no aggregation of data across sites)

b. pH values are to be capped at 9 (exceedances of the standard cannot be used to derive the IWQC)

c. Data handling issues – preliminary screening can be done with Check Inputs feature of BLM.

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CO BLM Guidance Development
3. Processing Data

Missing values (e.g., one parameter on a sampling date)

1. Exclude sampling event if copper, pH, DOC, or temperature are missing [there may be situations where interpolation between sites is defensible, on case-by-case basis]
2. For other missing constituents, substitute an estimate
   a. Interpolate between adjacent dates or adjacent sites on same date
   b. Rely on correlation (e.g., hardness and alkalinity often are highly correlated)
   c. Reconstitute Ca and Mg from hardness data

Missing parameter (all dates)

1. Do not attempt if Cu, pH, temperature, or DOC have not been measured
2. For other parameters, consider substitution with a geometric mean (or median) derived from comparable sites (as suggested in Implementation Guidance for Colorado). Alternatively, look for correlations as mentioned previously.

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CO BLM Guidance Development
3. Processing Data

Non-detects

1. Avoid multiple DLs if possible.
2. Exclude sampling event if DOC <DL
3. Copper median must exceed highest MDL

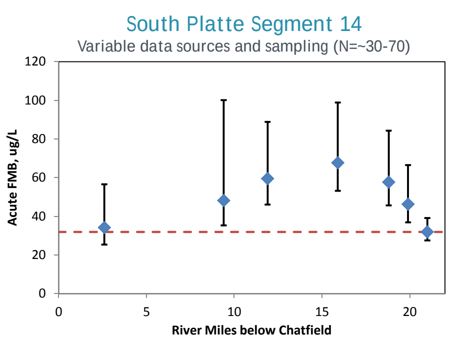
Copper data: test for lognormality

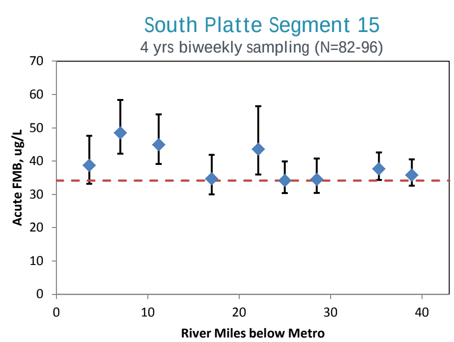
1. Testing informs processing at the next step
2. Statistical rejection of lognormality does not necessarily preclude modeling

CO BLM Guidance Development
4. Interpreting Model Output

Determine confidence limits for FMB_a at each site

i. The Division will prepare a table to facilitate the calculations
ii. Confidence intervals determine if FMBs can be aggregated





CO BLM Guidance Development

4. Interpreting Model Output

Revising FMBs when copper data are not lognormally distributed

i. Apply statistical procedure of "trimming" to reduce influence of extreme values
ii. Trim data incrementally until the FMB stabilizes
iii. Trimming is applied to the tails of the copper distribution, but involves removal of entire sampling events (ranked by copper concentration).
iv. Sites should be rejected if the FMB cannot be stabilized with at least 24 sampling events remaining in the data set.

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CO BLM Guidance Development

4. Interpreting Model Output

Calculate the FMB_c after revising the standard error

For multiple sites, plot FMBs in downstream sequence and base interpretation on the confidence intervals.

i. If the pattern is monotonic, increasing or decreasing
   1. Select the lowest FMB
   2. Aggregate adjacent low values if appropriate based on confidence interval
ii. If no pattern, aggregate FMB values based on the confidence intervals
iii. Aggregation of the FMBs means taking the average (arithmetic mean) of values that are indistinguishable based on the confidence intervals

Verify results!

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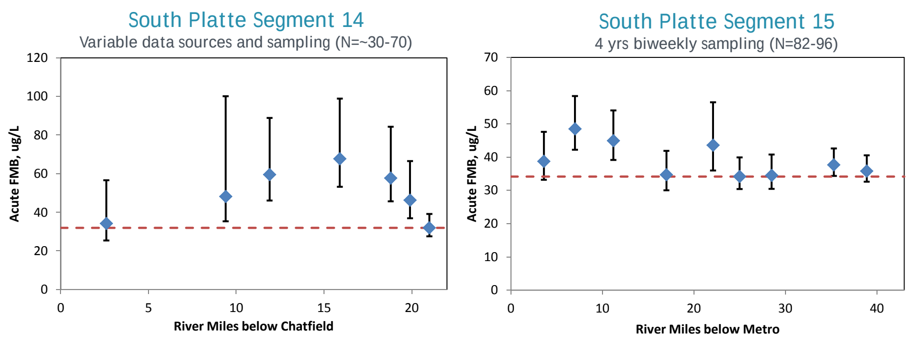
Example: South Platte River



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What happens after the initial standards are set?

What data are necessary to justify continuance of the standard at the next triennial review?

DOC? pH? Copper?

Is effluent quality enough, or are in stream data necessary?

Requesting the development of a longevity plan – what should be included?

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FMB as Percentile of IWQC

No consistency even within one stream

South Platte percentile range: 3.8–55.8%

Two sites with an FMB < 5th percentile

Site	Acute FMB	Percentile of IWQC
South Platte; L01	29.62	55.8%
South Platte; L04	33.87	18.1%
South Platte; S29	48.10	28.1%
South Platte; S14	59.47	34.7%
South Platte; N14	68.00	44.9%
South Platte; N38	57.69	34.1%
South Platte; N46	46.66	17.9%
South Platte; BD64	31.53	8.8%
South Platte; 64th	35.65	21.6%
South Platte; 88th	38.75	12.2%
South Platte; 104th	48.51	15.7%
South Platte; 124th	44.95	10.8%
South Platte; 160th	34.72	5.4%
South Platte; Rd 8	43.65	8.2%
South Platte; Ft Lupton	34.17	5.8%
South Platte; Rd 18	34.53	4.1%
South Platte; Rd 28	37.68	5.9%
South Platte; Rd 32.5	35.79	3.8%

COLORADO

Questions/Discussion

Jim Saunders, WQCD Standards Unit, jamesf.saunders@state.co.us
Patrick Bachmann, WQCD Standards Unit, patrick.bachmann@state.co.us
Blake Beyea, WQCD Standards Unit, blake.beyea@state.co.us
Sarah Johnson, WQCD Standards Unit Manager, sarah.johnson@state.co.us
Lareina Guenzel, R8 EPA Water Quality Unit, guenzel.lareina@epa.gov

COLORADO

Photo by Blake Beyea

Outstanding Questions
Lognormality

What is the sensitivity of the FMB calculation to deviations of TU and/or Cu from lognormality.

What options are available for data appear to deviate from lognormality to an unacceptable degree?

Are there any recommend methods (e.g., trimming, eliminating extreme and anomalous values) that might be used?

Outstanding Questions
Data Aggregation

Is it defensible to aggregate data from different sampling sites?

Is it appropriate to combine datasets that represent different time frames?

Is it appropriate to aggregate data that vary in their distribution of copper and/or IWQCs?

Outstanding Questions

Minimum Sample Size

Please explain the minimum sample size of 9 (p 4-4; BLM Manual 2.2.4) and 80% ND, especially given the importance of the median in calculations of the FMB (as shown in the CO Implementation Report)?

Is it possible that the minimum sample size for running the model is different from what is necessary for representativeness?

What are the advantage and disadvantages of a larger sample size? How does it influence the FMB?

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Outstanding Questions

Others

Is it possible to add the option to change the averaging period for chronic FMB? Colorado uses 30 day average instead of 4 days.

Please add the computation of confidence limits for each FMB to the model (and the output), to aid in comparison across FMBs.

COLORADO

Adoption and Implementation

COPPER BLM WORKSHOP

MAY 14, 2015

- Adoption and implementation of the Cu BLM are closely intertwined.
  - How you intend to implement the criteria in listing and permits affects what you should adopt, and vice versa.

Adoption Considerations

- Expression of the criteria in WQS
  - Narrative vs. numeric
- Default values
  - Include them in regulation? Guidance?
- Performance-based?
  - How does the public know what criteria apply?
- Regulatory clarity
  - Are the specifics in WQS or implementation?
- Incorporation by reference
  - How specific?

Expression of the Criteria in WQS

- Criteria should be expressed with enough specificity to allow implementing programs, EPA, and the public to understand what the desired condition of the water body is.
- This may not be sufficiently specific:
  - "Freshwater criteria calculated using the EPA Biotic Ligand Model"
- The more specific, the more likely it is to be performance based.

Performance-Based Approach

- One way to streamline adoption – and EPA approval of criteria.
- Relies on state adoption of a process rather than a specific outcome.
- When the process is sufficiently detailed, with safeguards to ensure predictable, repeatable outcomes, EPA approval of the process constitutes approval of the outcome as well.
- Relies on specific implementation procedures being adopted into regulation.
  - Sampling methodology, specifics on inputs, etc.
- Particularly useful for site-specific criteria.

Example Copper Criterion

- “Freshwater copper criteria shall be developed using EPA’s current Biotic Ligand Model (current criteria document : EPA 15 X-XXX-XX). When criteria are developed such criteria shall be made available on the state’s website. Data used to calculate criteria using the BLM shall be sufficient to characterize the short and long term variability of the water chemistry based on seasonal flow characteristics, as well as the variability of significant point and nonpoint source inputs. In the absence of sufficient ambient data for any of the parameters used as inputs to the BLM, default values corresponding to the 10^{th} percentile of the applicable ecoregional dataset for the relevant stream order for each missing parameter shall be used. Default values shall be found in EPA’s Missing Parameters document (EPA 15-G-4453-XX), hereby incorporated by reference.”

Copper BLM : Current Status at EPA

- The current EPA Freshwater Cu BLM is the 2007 model
- EPA is updating the Copper Freshwater Biotic Ligand Model
  - Adding new underlying toxicity data
  - Adding chronic data and sensitivity distribution to replace ACR
  - The latest BLM has the ability to calculate a fixed monitoring benchmark (FMB) value for acute and chronic criteria
  - Expect to release an updated draft Freshwater Cu BLM in 2015
- EPA is beginning development of BLM-based copper criteria for saltwater systems

Missing BLM Parameters Document

- To support states and others who want to use the copper BLM but do not have data for all of the BLM parameters, EPA has developed a draft Technical Support Document to provide default values for the Missing BLM Parameters
  - In the draft Missing Parameters document EPA is considering recommending use of the 10^{th} percentile values for ions and DOC if data are not available
  - Recommend measurement of site pH
- The "Missing Parameters" document is expected to be released in summer 2015

EPA Freshwater Copper BLM and Missing Parameter Documents: Status

Kathryn Gallagher, Ph.D.
Chief, Ecological Risk Assessment Branch
Health and Ecological Criteria Division
Office of Science and Technology
Office of Water
US Environmental Protection Agency

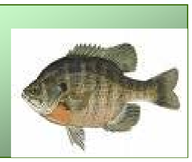
Reminder: Toxicity Data Underly the BLM

- EPA uses available toxicity data to develop a sensitivity distribution across a range of taxa to define expected responses in an aquatic ecosystem to a particular chemical
  - Acute and chronic data
- This same SD approach underlies the EPA copper Biotic Ligand Model
  - Defines the expected response to copper given water chemistry at a site

MINIMUM DATASET FOR FRESHWATER CRITERIA DERIVATION

SALMONID

SECOND FISH FAMILY



CHORDATA

PLANKTONIC CRUSTACEAN

BENTHIC CRUSTACEAN

INSECT

ROTIFERA, ANNELIDA, MOLLUSCA

OTHER INSECT OR MOLLUSCA

Copper BLM : Current Status at EPA

- EPA is updating the Biotic Ligand Model
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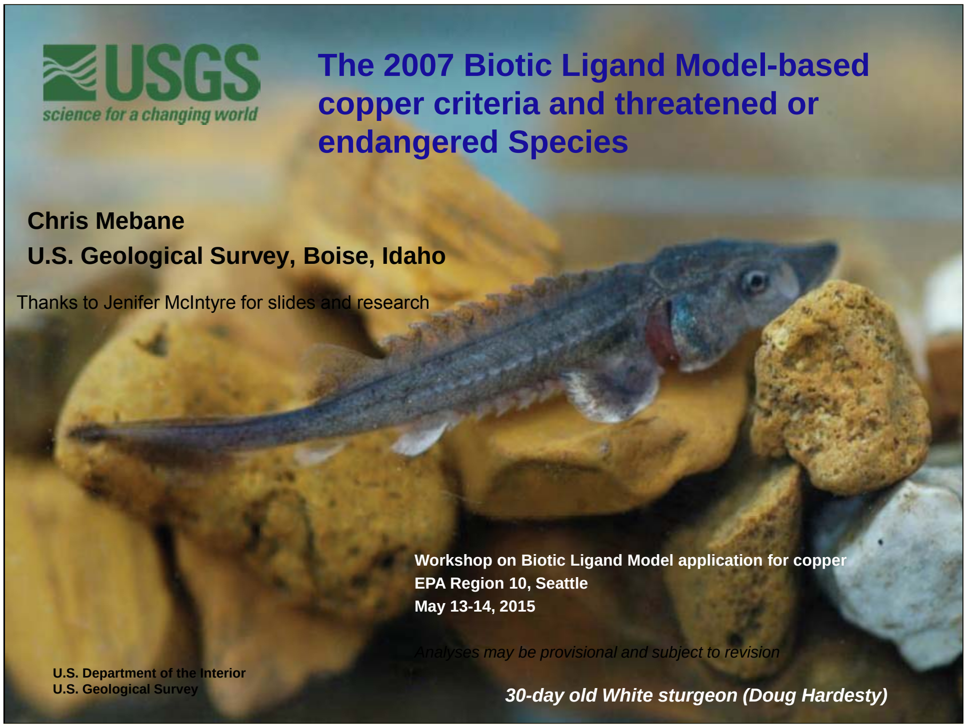
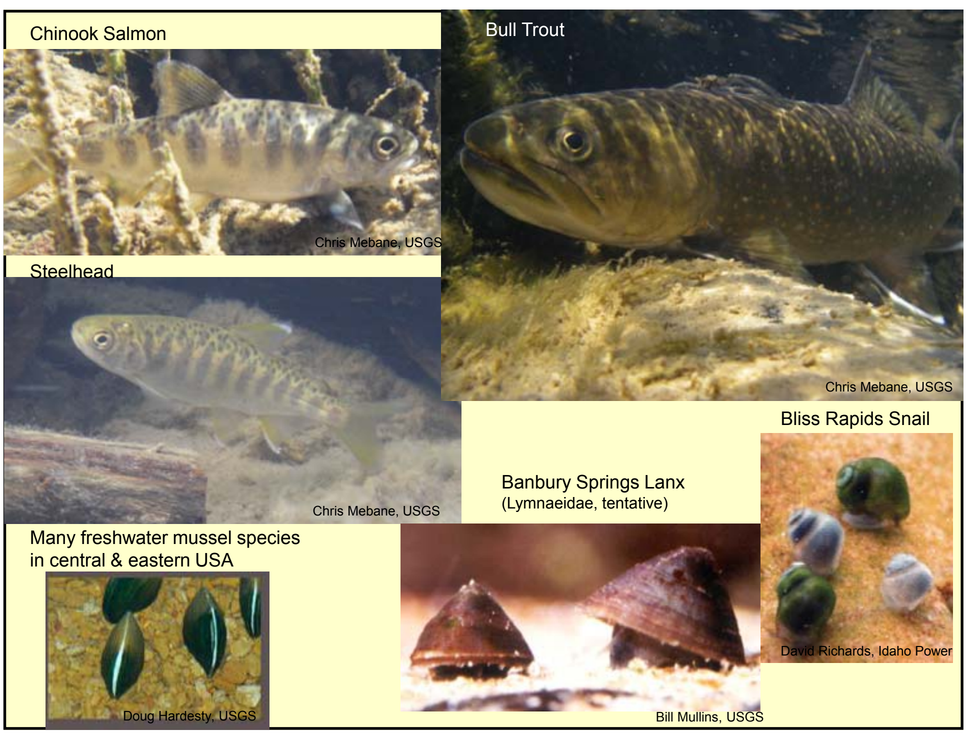
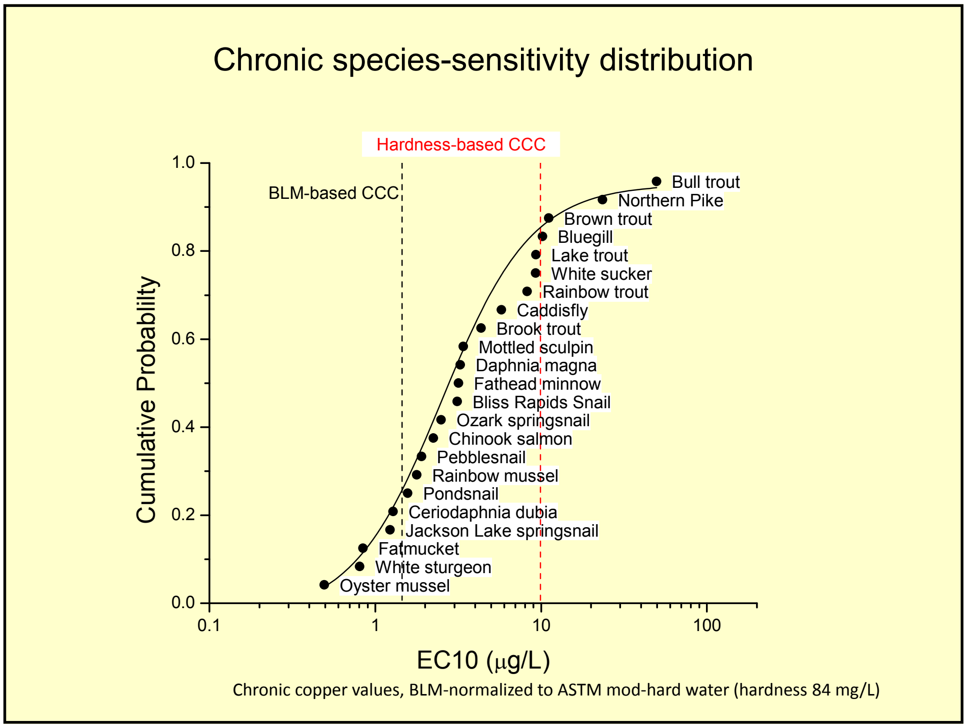

USGS
science for a changing world
The 2007 Biotic Ligand Model-based copper criteria and threatened or endangered Species
Chris Mebane
U.S. Geological Survey, Boise, Idaho
Thanks to Jenifer McIntyre for slides and research
Workshop on Biotic Ligand Model application for copper
EPA Region 10, Seattle
May 13-14, 2015
Analyses may be provisional and subject to revision
U.S. Department of the Interior
U.S. Geological Survey
30-day old White sturgeon (Doug Hardesty)


Chinook Salmon
Chris Mebane, USGS
Bull Trout
Chris Mebane, USGS
Steelhead
Chris Mebane, USGS
Bliss Rapids Snail
Banbury Springs Lanx
(Lymnaeidae, tentative)
David Richards, Idaho Power
Many freshwater mussel species
in central & eastern USA
Doug Hardesty, USGS
Bill Mullins, USGS



Chemoreception, Copper, and Criteria

- **Not directly considered in WQC development per Stephan et al.,(1985) can be invoked as "Other Data" to adjust a criteria downward to be protective if they are "biologically important."**
- **Olfactory function & electrophysiology critical in salmonids (probably ubiquitous)**
  - **Homing to natal streams, feeding, and avoiding predators**
- **Functions can be disrupted or destroyed by sub-lethal copper exposures**
- **Long the domain of ethology, recently "re-discovered" in ecotoxicology?**

Atlantic Salmon avoidance studies related to Miramichi River mining pollution, 1956- late 1960s

Water Research, Pergamon Press, 1967. Vol. 1, pp. 419–432. Printed in Great Britain.

EFFECTS OF COPPER–ZINC MINING POLLUTION ON A SPAWNING MIGRATION OF ATLANTIC SALMON

RICHARD L. SAUNDERS and JOHN B. SPRAGUE

Fisheries Research Board of Canada, Biological Station,
St. Andrews, New Brunswick, Canada

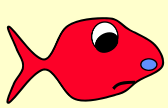
(*Received* 18 *April* 1967)

Abstract—Pollution from a base metal mine on a tributary of the Northwest Miramichi River caused many adult Atlantic salmon, which were on their normal upstream spawning migration, to return prematurely downstream through a counting fence on that river during summer and early autumn. These observations gave an opportunity to document avoidance reactions of salmon to pollution, which has seldom been done in the fishes' natural environment. Downstream returns of salmon rose from between 1 and 3 per cent during 6 years before pollution to between 10 and 22 per cent during 4 years of pollution. Early runs (June–July) of salmon to the headwaters were delayed and reduced in number. Chemical analyses of river water showed levels of Cu^{2+} and Zn^{2+} which varied with rates of river discharge. During some periods $Cu^{2+} + Zn^{2+}$ concentrations exceeded lethal levels for immature salmon, as established in another (laboratory) study. The threshold concentration for 50 per cent survival of fish under specified temperature conditions is designated as 1·0 toxic unit. Adult salmon in nature showed avoidance reactions at about 0·35–0·43 toxic unit of $Cu^{2+} + Zn^{2+}$. A level of 0·8 toxic unit may have blocked all upstream movement. Of the salmon returning downstream because of pollution, about 31 per cent reascended, 62 per cent were not seen again and 7 per cent were taken by angling and commercial fishing below the counting fence. Estimated losses from the stock available in the upper part of the river from 1960 to 1963 varied from 8 to 15 per cent of the total run. There is no evidence that successive year-classes of salmon are growing accustomed to the pollution.

Sub-Lethal Effects of Copper

Peripheral sensory system

Olfaction



Olfactory-mediated behaviors

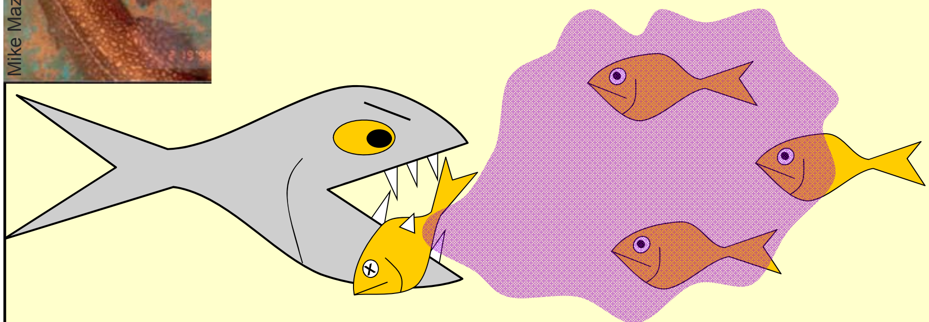
Defense | Feeding | Socializing | Migration | Reproduction

E.g. Alarm Response to Olfactory Cue

Copper Impacts Important Behaviors

Schreckstoff **= alarm cue in fish skin**

Released by mechanical damage



Alarm response = freezing

Schreckstoff - Schreck + stoff
Scary + stuff

(Aus dem Zoologischen Institut der Universität München).

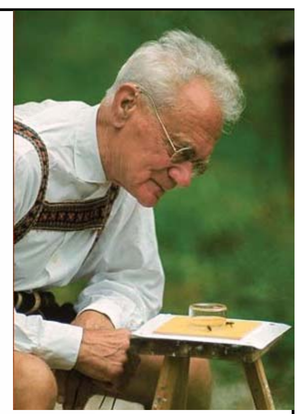
ÜBER EINEN SCHRECKSTOFF DER FISCHHAUT
UND SEINE BIOLOGISCHE BEDEUTUNG.

Von
K. v. Frisch.

Mit 17 Textabbildungen (19 Einzelbildern).

(Eingegangen am 29. Juni 1941.)

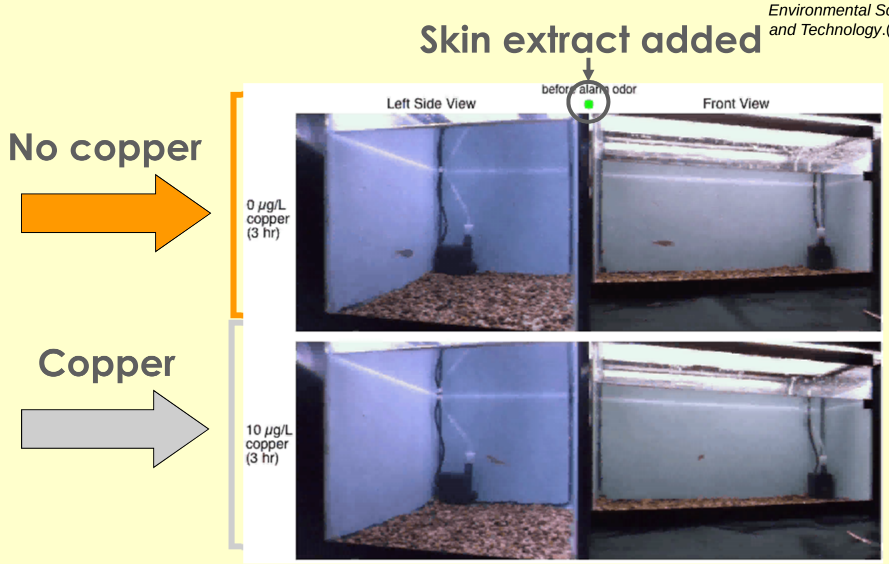
Inhalt.



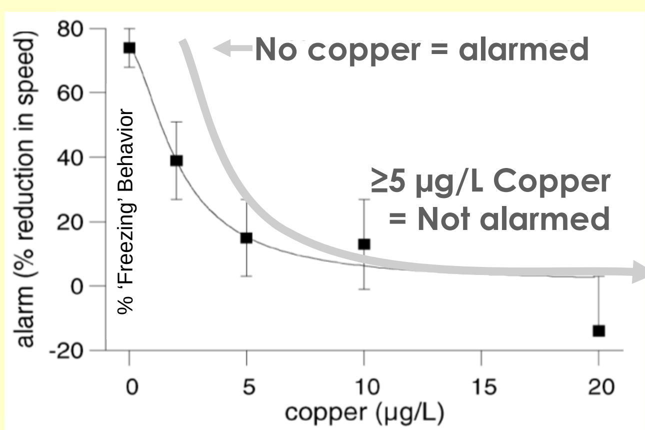
Karl von Frisch,
1882-1986,
1910 – First article of fish sensory abilities;
1938 – Discovered Shreckstoff (alarm substance in fish skin)
Nobel Prize, 1973

Copper Impacts Innate Alarm Behavior

Sandahl, J.F.,et al. (2007). A sensory system at the interface between urban stormwater runoff and salmon survival. *Environmental Science and Technology*.(2007)



Copper eliminates alarm behavior

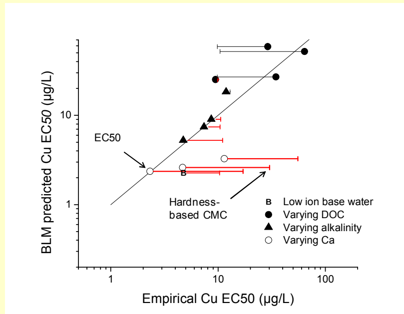


Sandahl et al. 2007. ES&T 41: 2998

Copper-exposed fish were not alarmed by '*Schreckstoff*' cue

BLM-based <u>acute</u> criterion protective?

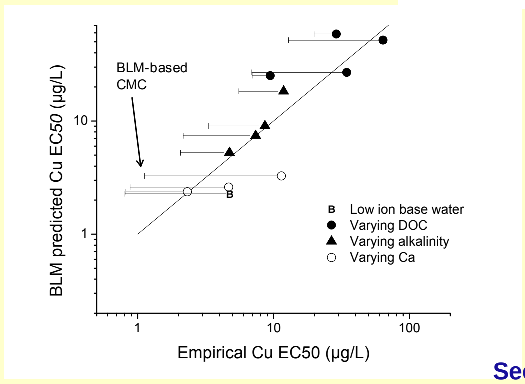
McIntyre, J.K., 2008. Chemosensory deprivation in juvenile coho salmon exposed to dissolved copper under varying water chemistry conditions. *Environmental Science and Technology*.



Varying DOC
y = 0.38x + 26
R^2 = 0.28

Varying Ca
y = 0.1031x + 1.9753
R^2 = 0.86

Varying alkalinity
y = 1.79x - 4.9
R^2 = 0.91



<u>Varying DOC</u>
y = 0.38x + 26
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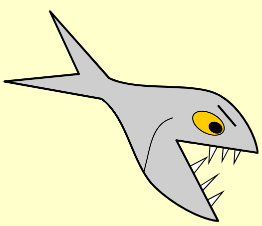
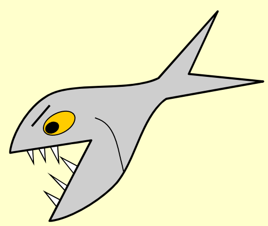
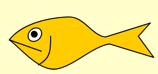
y = 0.1031x + 1.9753
R^2 = 0.86

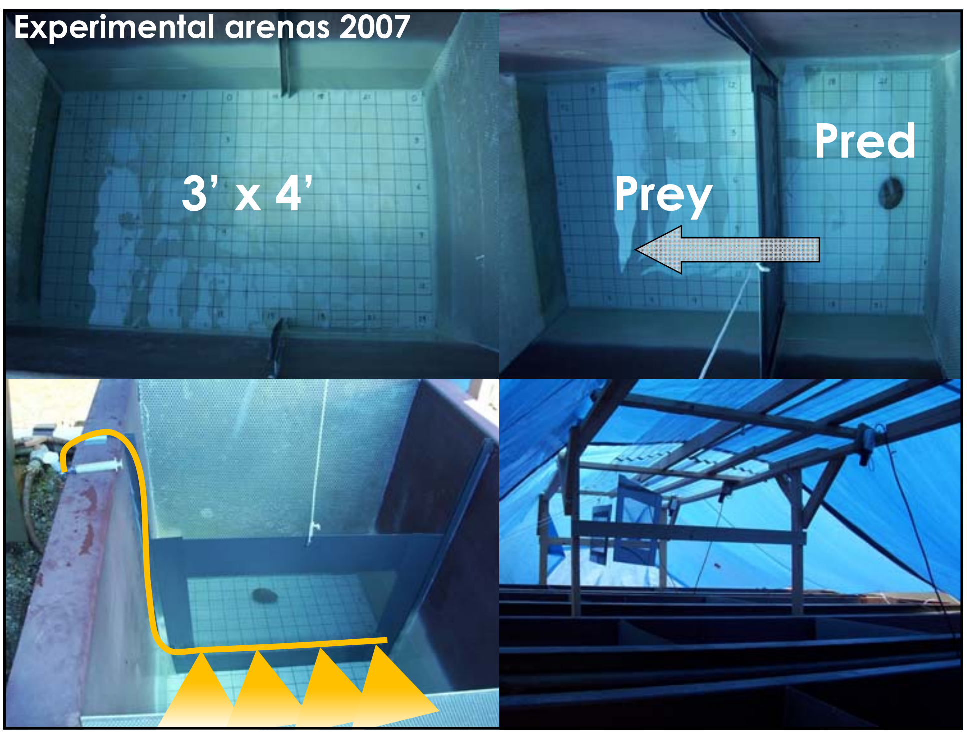
<u>Varying alkalinity</u>
y = 1.79x - 4.9
R^2 = 0.91

Seemed to be

Linking copper effects on behavior to survival

Jenifer McIntyre
PhD (2011)


Experimental arenas 2007
3' x 4'
Prey
Pred

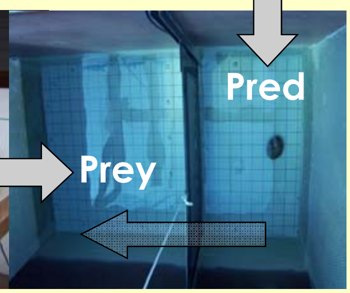
2007 Predation Experiment Protocol

Prey

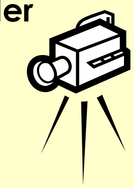
Wild age-0 coho

Predators

Wild BBC cutthroat



- Predators: overnight acclimation
- Prey copper exposure: 3h
- Prey: 30 min acclimation
- Olfactory cue
- Lift divider



2007 Predation Pilot Studies

<u>Spring 2007; Big Beef Creek</u>

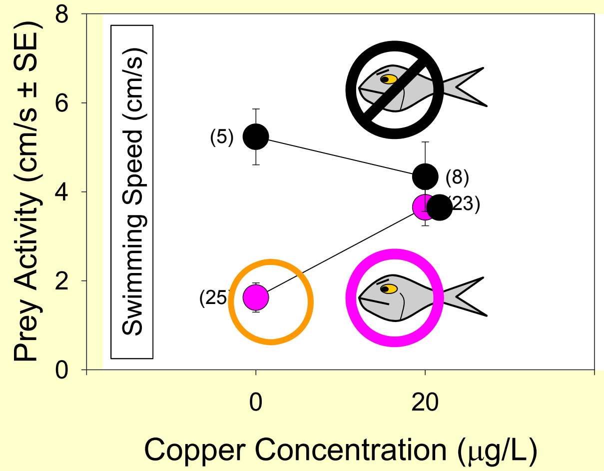
Effect of copper (20 µg/L):

1. Prey activity
2. Latency to capture

1

Prey Activity Downstream of Predator

(At end of acclimation = Compartments still divided)



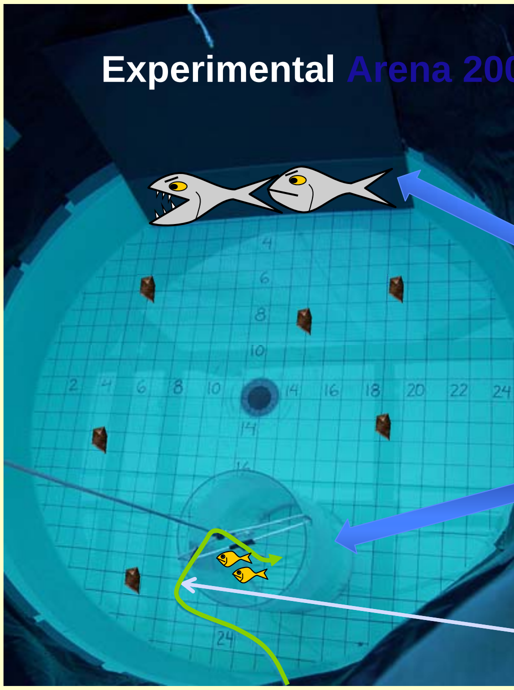
With an upstream predator, activity was reduced for control prey ($p \leq 0.003$)

Copper-exposed prey could not detect upstream predator ($p=0.3-0.8$)

2008 Predation Trials

- Test lower Cu concentrations (5,10 µg/L)
- Expose predators to copper

Experimental Arena 2008

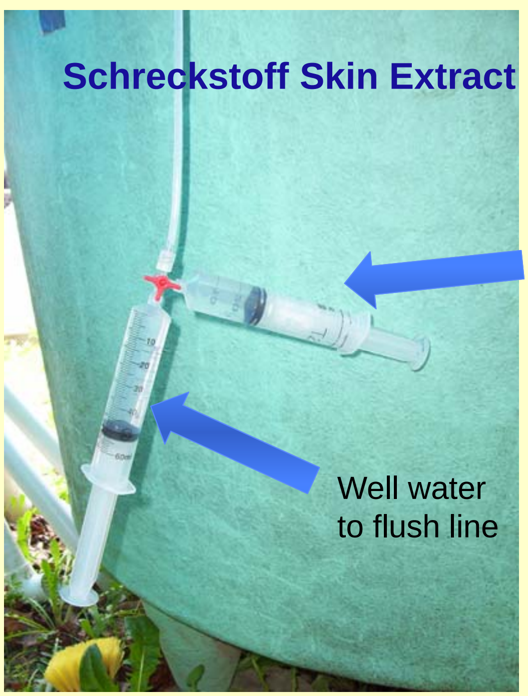


Predator chamber:
2 wild cutthroat (1h)

Prey chamber:
2 juvenile coho (15 min)

Skin extract tubing

Schreckstoff Skin Extract Injection



Skin extract at threshold concentration ($0.00002\ cm^2$ skin/L)

Well water to flush line

Predation Experiment Protocol

Lift prey chamber

1. Prey Activity

Add skin extract

Release predators

Prey acclimation (15 min)

Prey exposure (3h)

Predation

[Cu]: 0, 5, 10, 20 µg/L

Pred acclimation (1 hr)

2. Time to Attack, Capture

1 Prey Activity after Skin Extract

Control Prey

Video link (mov format)

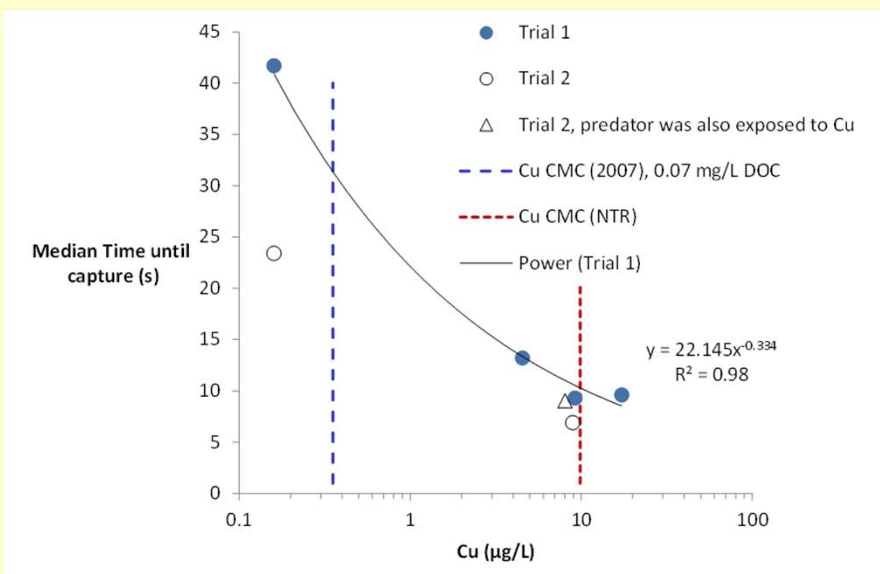
Copper Prey (10 µg/L)

2 When you move you lose

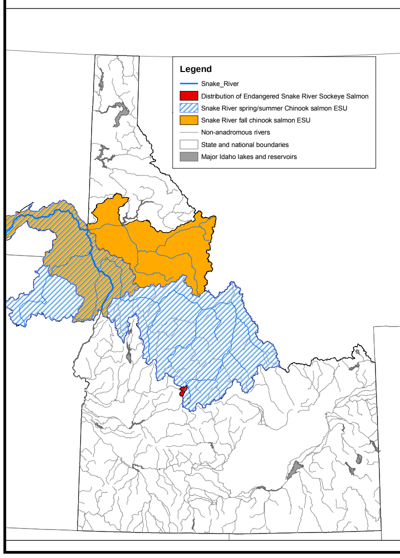
Video link (mov format)

Video link (mp4 format)

BLM-based <u>acute</u> criterion protective?



2014 NMFS Biological Opinion on Idaho Toxics Criteria



- **If surface waters were to actually contain the amount of chemical (copper) authorized by the Idaho criteria that EPA has proposed for approval, throughout the action area, then that would jeopardize the continued existence of the species or delay the recovery of listed salmon or steelhead (*paraphrasing*)**
  - **Essentially analyzed potential effects as if all waters were at criteria all of the time**
  - **Not consulting on ambient conditions: assessing criteria, not an environmental status assessment**

2.8.3.2. New Acute and Chronic Aquatic Life Criteria for Copper

" The EPA shall ensure, either through EPA promulgation of criteria or EPA approval of a state-promulgated criteria, that new acute and chronic criteria for copper are in effect in Idaho within 3 years of the date of this Opinion. The new criteria <u>shall be no less stringent</u> than the Clean Water Act section 304(a) 2007 national recommended aquatic life criteria (i.e. the BLM Model) for copper. The NMFS <u>does not anticipate</u> that additional consultation will be required if the 2007 national recommended aquatic life criteria for copper are adopted."

Commentary steps (address uncertainty, potential additive mixture toxicity)

- **Limit regulatory mixing zone to 25% of volume**
- **Whole effluent toxicity testing, specified mixing zone volumes**
- **Instream biomonitoring, specifics on interpretation**

An approach on implementation

1. Simple, conservative, default screening values by major river basin

↓ **Integrated list, RPTE for monitoring requirements. Could use straight up or have data collection triggers.**

2. Where warranted, Use MLR-based spreadsheet "criteria" values or BLM-criteria values to estimate critical conditions

↓ **Data needs? 6X per year 3/years**

3. Use critical condition concentrations in NPDES/IPDES in permit waste load allocations in the usual way

1.

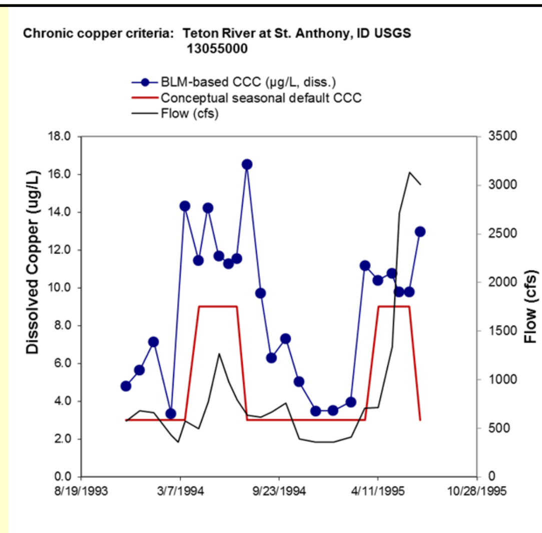
Appendix C: Evaluation of EPA's 2007 biotic ligand model (BLM) based copper criteria

Table 3. Ranges of chronic copper criterion concentrations estimated for critical late summer/fall baseflow conditions in subbasins within the range of anadromous salmonids in the Snake River basin, Idaho.

Subbasin	Common subbasin geologic characteristics	Critical late-summer Cu benchmark concentration (µg/L)	Based upon EPA's 2007 Cu chronic criterion (CCC) using data collected or estimated using:
Selway, Lochsa, MF Clearwater R	Granitic or intrusive rocks from Idaho Batholith or Precambrian metamorphic rocks	0.6	St Joe River at Red Ives, 9/14/2007; SF Coeur d'Alene R at Pinehurst, 9/10/2007; NFCDA Fig 25
SF Clearwater River	Idaho Batholith	1	SF Clearwater at Stites
MF and SF Salmon and tributaries	Idaho Batholith	1	Extrapolated using low conductivity measured in undisturbed streams in the Salmon R basin (Ott and Maret 2003), ~30 µs/cm, pH 6.9, using DOC of 1 mg/L and then estimating major ions with regression equations from streams in Coeur d'Alene R with similarly low conductivity
Upper Salmon R	Idaho Batholith and Challis volcanics	3	Snake River (Fig. 24); Johnson Creek at Yellow Pine, 10/10/2007
Upper Salmon R tributaries	Challis volcanics	3	Assumed similar to Panther Creek
Panther Creek	Challis volcanics and Idaho Batholith	3	Minimum BLM=CCC calculated for low-flow, low DOC conditions from a 1994 dataset (Maest *et al.* 1995)
Lemhi and Pahsimeroi Rivers	Tertiary sediments from ancient lake bottoms	6	Pahsimeroi at Ellis, 9/18/2007
Lower Salmon (downstream of SF Salmon)	Diverse	3	Salmon River at White Bird, 9/27/2007
Snake River	Diverse	6	Minimum BLM calculated for Snake River at mouth (Burbank, WA)

Data collected in 2007 were for a single data collection. It seemed reasonable to assume that late summer baseflow conditions were probably close the critical condition (i.e., annual minimum) CCC calculated using the BLM-based Cu criteria. However, because the BLM-based criteria is sensitive to pH and these mid-day collected samples probably represented close to the daily high for pH, pH was lowered by 0.6 units for those sites with high pH (>7.5) because

2.



3.

Cu “CMC” =EXP(-14.23+6.8067*LN(**pH**)+0.8947*LN(**DOC**)+0.4418*LN(**Hardness**))

"Just in case the ~~conference call~~ runs long."
consultation

Implementing the Cu BLM in the 303(d) listing program

JILL FULLAGAR AND MARTY JACOBSON

The impaired waters listing process

- Identify WQS updates and new data since last cycle
  - Incorporate WQS updates into listing methodology
  - Designated uses evaluation – evidence to support higher level of use/new existing uses
  - Numeric criteria
    - Compile monitoring data of known quality from all sources (since last cycle)
    - Compare pollutant concentrations or conditions on segment basis to criteria in effect and identify impaired waters
  - Narrative criteria
    - Translate narrative to numeric (where possible)
      - Use recommended values or criteria developed for comparable waterbodies
      - No situation where model needs to be run yet only simple calculations
    - Use qualitative index where available or needed

BLM– what data sources and tracking are necessary for listing process

- Defaults need to know how to find this information
- Parameterizations: Temperature, pH, DOC, Ca, Mg, Na, K, SO4, Cl, Alkalinity, S; Also Cu baseline
  - State agency data
  - USGS and other fed sources, universities, nonprofits, industry
  - Data in GIS based format and/or downloadable by site
- Data compilation and tracking system needed for reporting- must match reporting needs

Challenges

- Identifying what is in effect for different waterbodies around the state at any one time
  - Publicly accessible information
  - In regulation or outside of regulation?
  - Role of defaults
- Expectation to rerun the model based on available data during listing process or use default?
  - Data sufficiency of site-specific submissions
  - Knowledge of current criteria in effect and impact of parameter submissions during the listing process
    - Public submits parameters recalculation based on XX number or type of parameterizations
    - New list predicated on new data since last list need to track which models used, parameterizations, missing parameter estimates methods (if applicable), and outcomes (concentrations) in use

Discussion Questions

- What are the pros and cons of using a default (either subset parameterization or regionally calculated numbers) in listing?
- What are the pros and cons of using narrative to calculate a specific outcome during each listing cycle? Using FMB or IWQC?
- What are performance-based expectations in rule or guidance
- What information must be reportable to the system?
- How will the criteria, parameters, model version, (or outcomes of BLM) in effect be communicated ?
  - What are states' and tribes' thoughts on how they would compile and track this information

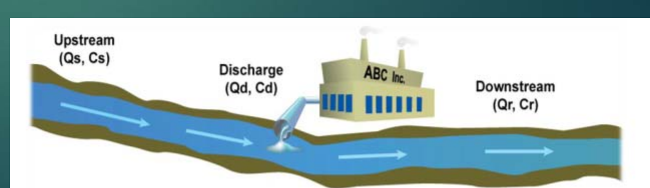
Implementing the Cu BLM in NPDES Permits

SUSAN POULSOM AND BRIAN NICKEL
US EPA REGION 10 NPDES PERMITS UNIT

Water Quality Based Effluent Limits (WQBELs) for Copper Using the BLM

Use same permitting process as for other toxic parameters

1. Identify the Applicable Water Quality Criteria (BLM)
   - Permit Writer Calculate using site specific characteristics?
2. Characterize the Effluent and Receiving Water
3. Determine the Need for WQBELs Reasonable Potential Analysis
   - Determine the expected receiving water concentration
   - Compare to applicable water quality criterion
4. If Reasonable Potential –
   - Calculate the Copper WQBELs



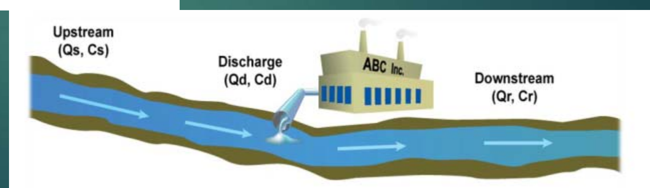
Reasonable Potential

Steady State Model
Simple Mass Balance Equation:

Qs = Critical stream flow (1Q10) for acute criterion
Qd = Critical effluent flow from discharge flow data
Qr = Sum of critical stream flow and critical effluent flow
Cs = Critical upstream pollutant concentration
Cd = Critical effluent pollutant concentration

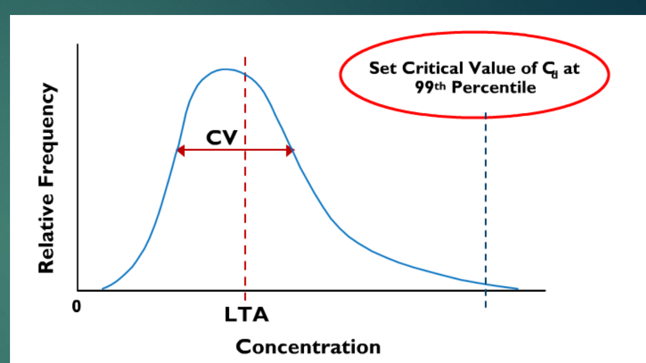
$$Cr = \frac{QsCs + QdCd}{Qr}$$

% Mixing Zone



Critical Effluent Pollutant Concentration

- EPA's Technical Support Document for Water Quality-Based Toxics Control "the TSD"
- Limited data set
- Variability of the data (CV)
- Lognormal distribution



Developing Chemical-specific WQBELs

Water Quality Criteria
Magnitude
Duration
Frequency

→

Effluent Limitations
Magnitude
Averaging Period

Permit writers calculate end of pipe WQBELs to ensure that water quality standards are attained in the receiving water.

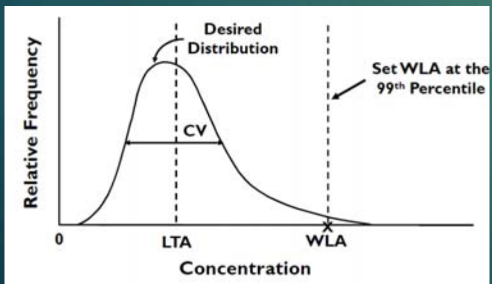
Developing Chemical-specific WQBELs

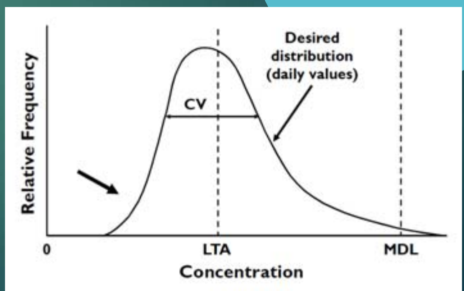
Determine Acute and Chronic Wasteload Allocations (WLAs)

Calculate Long-Term Average (LTA) for Each WLA

Select Lowest LTA

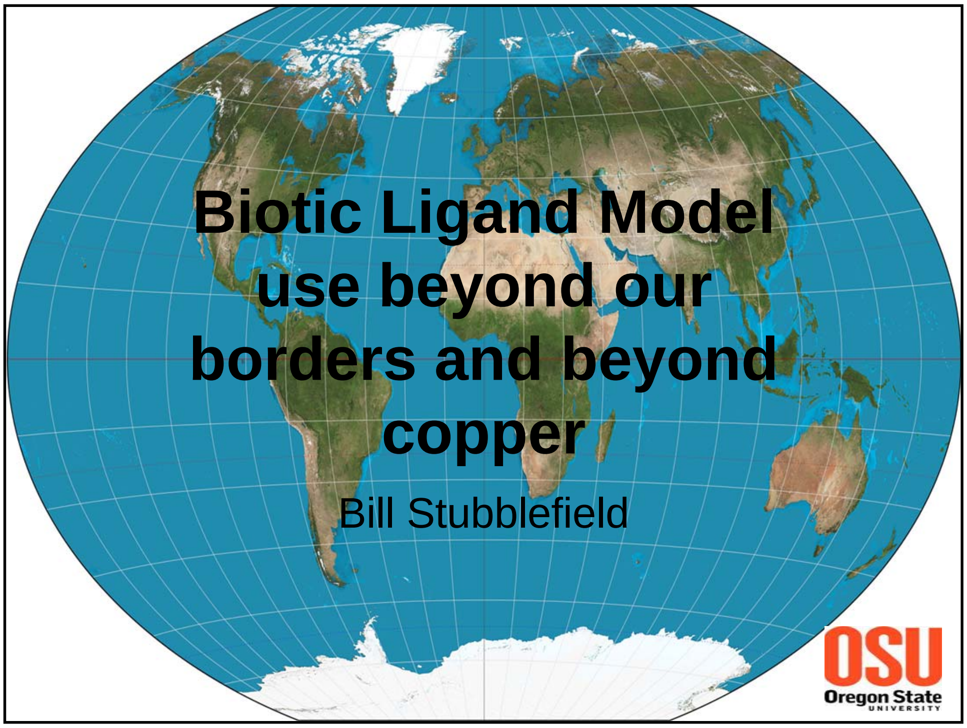
Calculate the Maximum Daily Average (MDL) and Average Monthly Limit (AML)





Permitting Considerations Using the BLM

- Limits will be expressed as total recoverable metal. Compliance monitoring will measure total recoverable. (40 CFR 122.45(c))
- Seasonal Limits
  - Variations in input parameters and critical flows
- Monitoring Requirements for Parameters in Reissued Permit
  - Sampling Events
- Influence of Discharge on Water Chemistry and BLM Criteria
- Anti-backsliding Provisions and Antidegration
- Downstream Protection (40 CFR 131.10(b) and 40 CFR 122.4(d))



Biotic Ligand Model use beyond our borders and beyond copper

Bill Stubblefield

Oregon State University

WHY SHOULD WE CARE ABOUT THE REST OF THE WORLD?

Why should we care?

- European approach is considered the "state-of-the-science" for developing water quality standards
  - US EPA approach is 30 yrs old
  - Little impetus in US to develop new data
  - Currently, Canada, Australia/New Zealand and many of the Asian countries all model their derivation approach after the European model

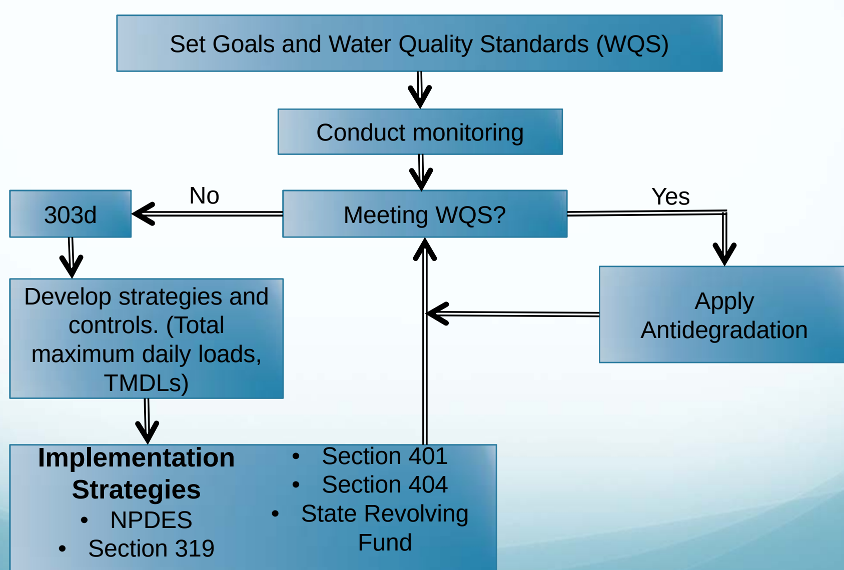
Why should we care?

- What is the driving force for data generation in EU?
  - REACH (TSCA Euro-style)
    - Requires the generation of toxicity data for all materials imported to or manufactured in Europe
    - Has lead to the development of bioavailability models
  - Water Framework Directive
    - Requires the evaluation of risk and derivation of Environmental Quality Standards (EQS)
    - New materials under evaluation now

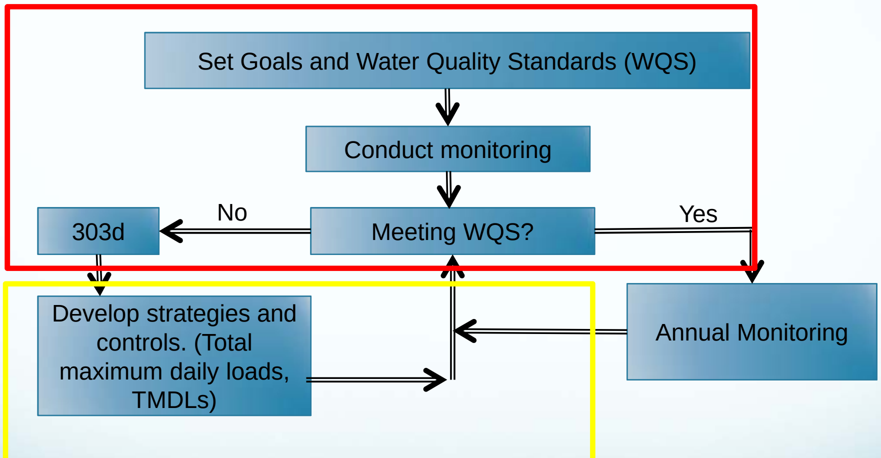
Topics

- US Clean Water Act (CWA) vs EU Water Framework Directive (WFD)
- Incorporation of bioavailability in Criteria/Standards
- Implementation strategies and others experiences
- Other metals?

Clean Water Act



Water Framework Directive



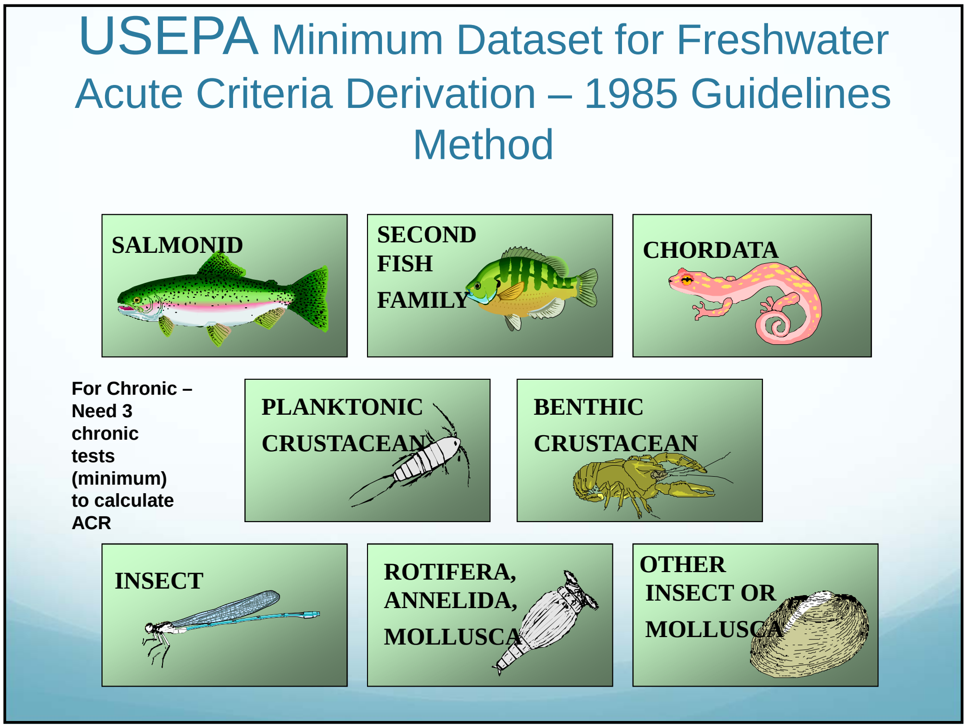
WFD is a “New” Regulation

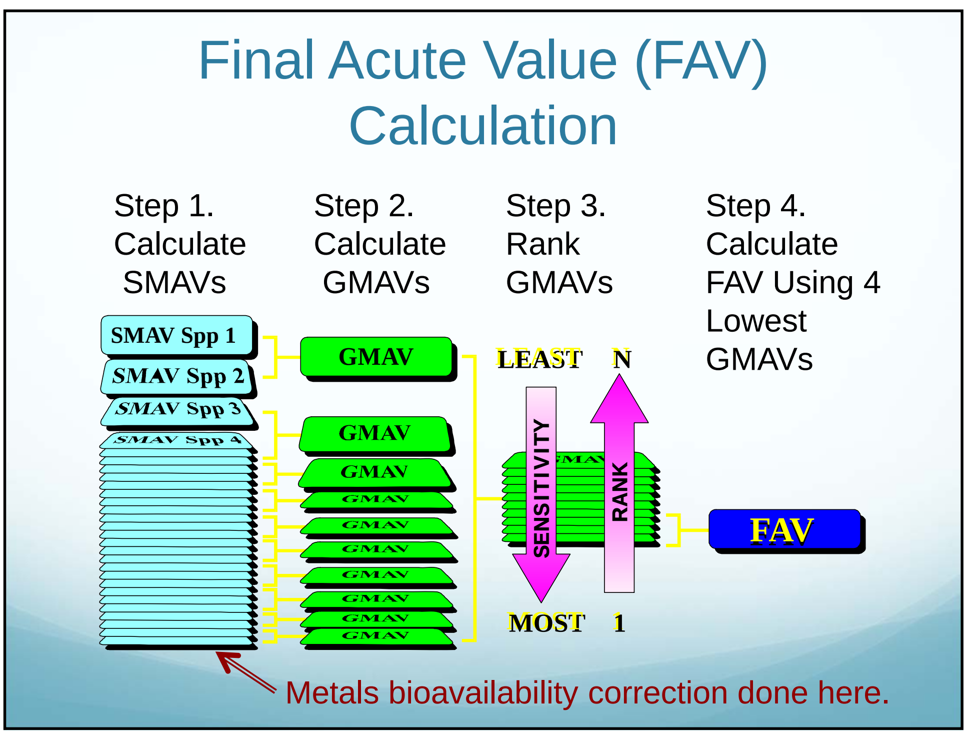
- 1995/1996: Fundamental rethink of Community water policy
  - The current water policy was fragmented
  - Need for a single piece of framework legislation to resolve these problems
- 2000: Adoption of the water framework directive (Directive 2000/60/EC)
- 2008: Priority substance directive or also called the “EQS & Mixing zone directive” (Directive 2008/105/EC)

Use of EQS

- Compliance assessment:
  - A comparison of the arithmetic mean of monitored concentration of a chemical, calculated from 12 monthly grab samples at one site, with an Annual Average EQS
  - If the EQS is exceeded then the water body will be classified as not achieving good status
- Permits to discharge are:
  - Set in such a way that the EQS would not be exceeded in any effluent receiving water (after due consideration of mixing zones)
  - Set differently by different authorities…..

HOW IS THE BLM USED IN DEVELOPING CRITERIA/STANDARDS


USEPA Minimum Dataset for Freshwater Acute Criteria Derivation – 1985 Guidelines Method
SALMONID
SECOND FISH FAMILY
CHORDATA
For Chronic – Need 3 chronic tests (minimum) to calculate ACR
PLANKTONIC CRUSTACEAN
BENTHIC CRUSTACEAN
INSECT
ROTIFERA, ANNELIDA, MOLLUSCA
OTHER INSECT OR MOLLUSCA

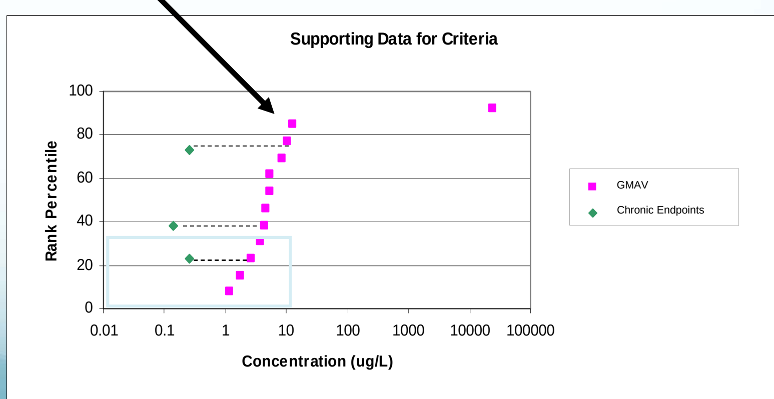

Final Acute Value (FAV) Calculation
Step 1. Calculate SMAVs
Step 2. Calculate GMAVs
Step 3. Rank GMAVs
Step 4. Calculate FAV Using 4 Lowest GMAVs
SMAV Spp 1
SMAV Spp 2
SMAV Spp 3
SMAV Spp 4
GMAV
LEAST
N
SENSITIVITY
RANK
MOST
1
FAV
Metals bioavailability correction done here.

Hardness based AWQC is a one-parameter BLM

- In deriving standard hardness based AWQC toxicity data are normalized to hardness of 50 mg/L as $CaCO_3$ based on the hardness:toxicity relationship prior to FAV/FCV calculation.

Aquatic Life AWQC Calculation

- Rank Genus Mean Acute Values (GMAV) and Calculate the Percentile of Each Rank (100 R/(N+1))



General EU framework for EQS derivation

1. Data compilation

2. Data selection
(reliability & relevance criteria)

3. Data aggregation

4. Reference Value & PNEC derivation

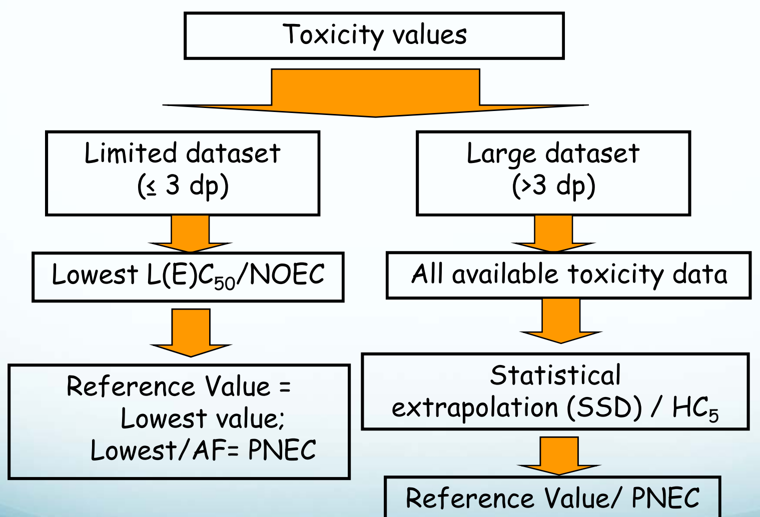
Test Species Requirements

US EPA	EU
the family Salmonidae in the Class Osteichthyes	Fish
A second family of fish in the Class Osteichthyes (preferably a commercially or recreationally important warm-water species)	Second family in the phylum Chordata
A third family in the phylum Chordata	
Planktonic crustacean	Crustacean
Insect	Insect
A family in a phylum other than Arthropoda or Chordata	A family in a phylum other than Arthropoda or Chordata
A family in any order of insect, or any phylum not already represented	A family in any order of insect of any phylum not already represented
Benthic crustacean	
	Algae
	Higher plant

Data requirements

- Only chronic standards are developed, therefore only chronic tests are considered.
  - Data requirements are "looser" than in the US.
- Data endpoints are EC10 (preferred) or NOEC
  - EC20 typically used by EPA

Reference Value/PNEC derivation



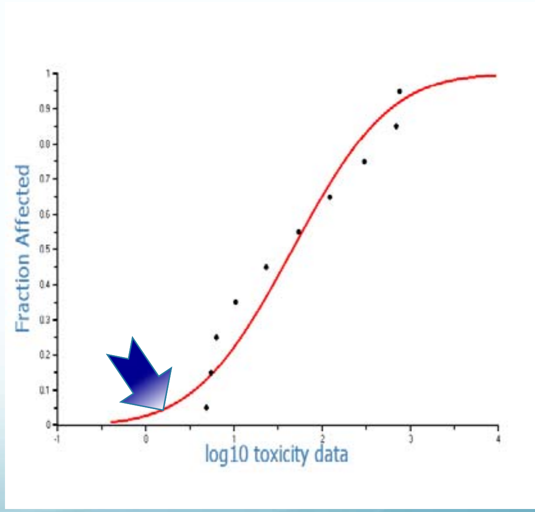
PNEC derivation - chronic exposure

1. Data poor substances
- Additional testing or
- Use of empirically derived assessment factors on the lowest acute/chronic value

Available data	Assessment factor
At least one short-term $L(E)C_{50}$ from each of three trophic levels of the base set (fish, Daphnia and algae)	1,000[a]
One long-term NOEC (either fish or Daphnia)	100[b]
Two long-term NOECs from species representing two trophic levels (fish and/or Daphnia and/or algae)	50[c]
Long-term NOECs from at least three species (normally fish, Daphnia and algae) representing three trophic levels	10[d]

2. Data rich substances: HC_5 calculation

- Chronic data (EC10) for all species available.
- Median HC_5 calculated using log normal distribution
- BLM corrects all data to common water quality conditions prior to HC_5 calculation



Calculated using ETX 2.0 (RIVM 2004

BIOAVAILABILITY

WHAT MAKES AN ACCEPTABLE BLM?

USEPA Guidance from the 1985 AWQC Guide

- "If the acute toxicity of the material to aquatic animals apparently has been shown to be **related to a water quality characteristic** such as hardness or particulate matter for freshwater animals or salinity or particulate matter for saltwater animals, a Final Acute Equation should be derived based on that water quality characteristic."
- "When enough data are available to show that acute toxicity to **two or more species** is similarly related to a water quality characteristic the relationship should be taken into account as described ……"
- "If useful slopes are not available for **at least one fish and one invertebrate** or if the available slopes are too dissimilar or if too few data are available to adequately define the relationship between acute toxicity and the water quality characteristic," return to home do not collect $200…….

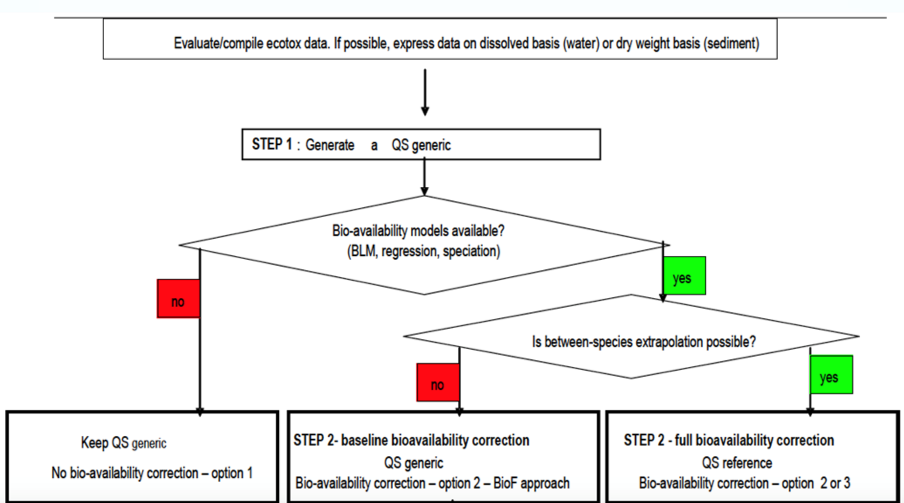
EU BLM requirements

- If models are available that involved bioavailability correction (BLM's), the **models may be species-specific** and, therefore, bioavailability correction is only possible if the BLM models have been developed and validated for **at least three higher taxonomic groups, including an algae, and invertebrate, and a fish species**.
  - This typically requires testing in natural waters and an evaluation of the predictive capability of the BLM.

EU BLM requirements

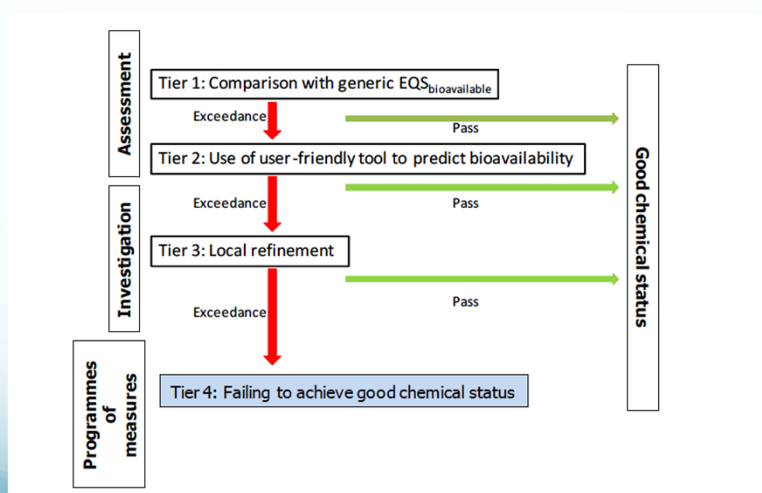
- Full BLM normalization of the entire NOEC dataset is justified and full bioavailable correction can be performed only if models are available and if additional quantitative evidence is available to **confirm the applicable at the of the three BLM's to at least three additional taxonomic groups** (at least at the level of class, but preferably at the level of phylum.
  - This requires "spotcheck" tests with additional species and comparison to predictions from the original BLM database.

Incorporation of bioavailability correction



COMPLIANCE

Tiered EQS compliance assessment under the WFD



Tier 1

- Compares “Generic” Standard to **dissolved** metal concentrations

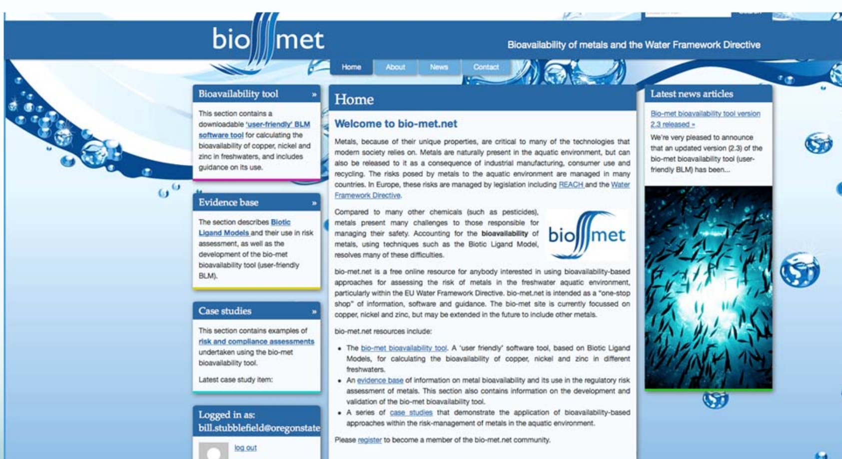
“Conventional” Bioavailability models (BLMs)

- Pros:
  - Quantitative
  - Mechanistically based, more robust and flexible than empirical approaches
- Cons:
  - Usually requires large amounts of data on environmental conditions (pH, DOC, Ca, Mg, Na, K, Cl, SO4, alkalinity, temperature)
  - Complicated and time consuming

Tier 2: BLM

- Starts with “User-friendly” modeling approach
  - Attempts to address the complexity and data requirement limitations of the “full” BLMs
  - Require data on a reduced suite of input parameters that have been found to predominantly influence bioavailability calculations after a sensitivity analysis – pH, DOC, Ca

BIOMET (http//bio-met.net)



Tier 3

- Not as specific as the first two tiers and is termed "local refinement".
- Provides an opportunity to consider local issues that might affect the assessment of risk due to metals, e.g. local background concentrations of metals, or a more robust assessment of local water chemistry conditions (including possible running the full BLM).

Tier 4

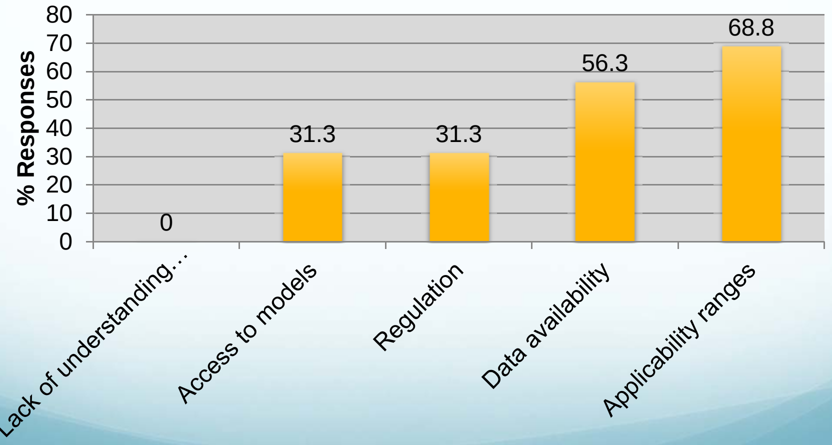
- At this tier the failure of a site to achieve the $EQS_{bioavailable}$ has been clearly determined.
- Consideration of a program of measures to mitigate the situation, within the appropriate cost/benefit framework, may be required.

EXPERIENCE/CONCERNS WITH THE IMPLEMENTATION OF THE BLM

Bio-Met experience

- A questionnaire was circulated to all registered users of the bio-met site (http://bio-met.net)

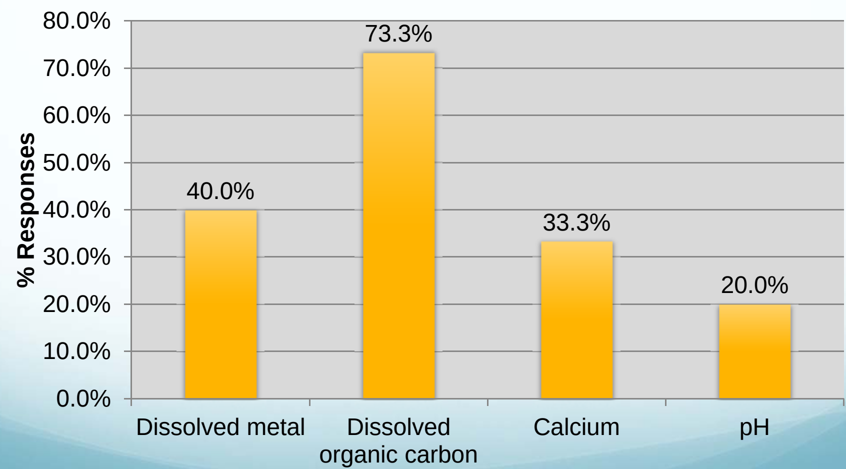
What issue is most limiting to the implementation of bioavailability for you?



Boundary limits for BioMet

Metal	pH	Ca (mg/L)	DOC (mg/L)
Zn	6-8.5	3-160	30
Ni	6-8.7	2-88	30
Cu	6-8.5	3.1-160	30

Does the availability of data for the supporting parameters limit the applicability of the bio-met tool?

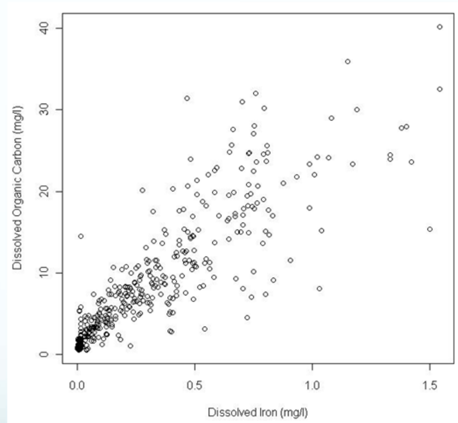


Conclusions and Recommendations

- DOC data availability was most commonly limiting (noted by almost 3/4 of respondents), although dissolved metal data was also considered to be a limiting factor by 40% of respondents.

Estimation of DOC from dissolved Fe

Relationship between dissolved iron and dissolved organic carbon (from 407 samples from England, Scotland and Wales)



DOC (mg l-1) = 20.79 . Fe (dissolved, mg l-1) + 2.32 $r^2 = 0.738$

log10(DOC, mg l-1) = 0.56 . log10(Fe, dissolved,mg l-1) + 1.24 $r^2 = 0.781$

Merrington G, Peters A, Brown B, Delbeke K, van Assche F, Sturdy L, Waeterschoot H, Batty J. 2008. The use of biotic ligand models in regulation: the development of simplified screening models and default water parameters. Paper presented at SETAC World Congress, Sydney, August 3-7th

Estimating major cations and anions from Ca

Integrated Environmental Assessment and Management — Volume 7, Number 3—pp. 437–444

437

Regulatory Consideration of Bioavailability for Metals: Simplification of Input Parameters for the Chronic Copper Biotic Ligand Model

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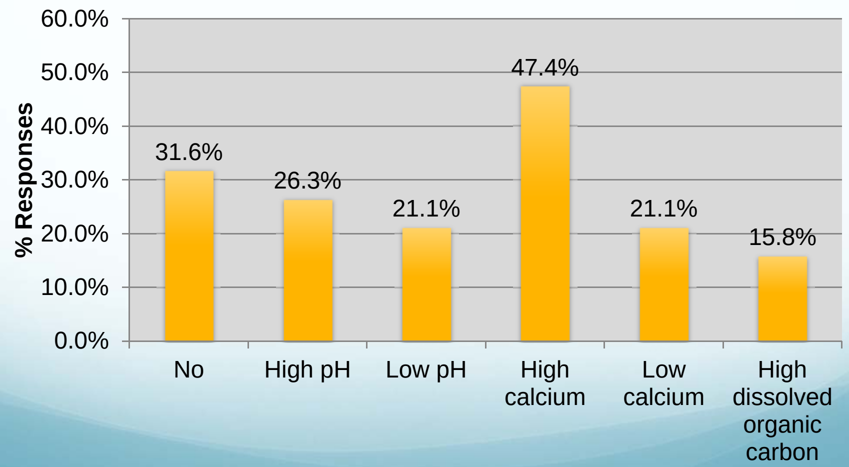
(Submitted 27 July 2010; Returned for Revision 19 October 2010; Accepted 5 November 2010)

ABSTRACT

The chronic Cu biotic ligand model (CuBLM) provides a means by which the bioavailability of Cu can be taken into account in assessing the potential chronic risks posed by Cu at specific freshwater locations. One of the barriers to the widespread regulatory application of the CuBLM is the perceived complexity of the approach when compared to the current systems that are in place in many regulatory organizations. The CuBLM requires 10 measured input parameters, although some of these have a relatively limited influence on the predicted no-effect concentration (PNEC) for Cu. Simplification of the input requirements of the CuBLM is proposed by estimating the concentrations of the major ions Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-, and alkalinity from Ca concentrations. A series of relationships between log10 (Ca, mg l^{-1}) and log10 (major ion, mg l^{-1}) was established from surface water monitoring data for Europe, and applied in the prediction of Cu PNEC values for some UK freshwater monitoring data. The use of default values for major ion concentrations was also considered, and both approaches were compared to the use of measured major ion concentrations. Both the use of fixed default major ion concentrations, and major ion concentrations estimated from Ca concentrations, provided Cu PNEC predictions which were in good agreement with the results of calculations using measured data. There is a slight loss of accuracy when using estimates of major ion concentrations compared to using measured concentration data, although to a lesser extent than when fixed default values are applied. The simplifications proposed provide a practical evidence-based methodology to facilitate the regulatory implementation of the CuBLM. Integr Environ Assess Manag 2011;7:437–444. © 2011 SETAC

Keywords: Copper Biotic ligand model Environmental regulation

Do water chemistries which are outside the application range of the models limit use of the bio-met tool? If so which waters?



Conclusions and Recommendations

- Approximately 1/3 of respondents did not consider the applicability ranges of the models to limit their use of Biomet.
- Unexpectedly, the most common conditions which prevented the application of Biomet was reported to be high Ca concentrations (this could be due to the upper limit of 88 mg l-1 Ca for Ni in particular) by almost half of respondents, with high pH noted as limiting by a quarter of respondents.
- Low pH and low Ca were both noted as being limiting by 1/5 of respondents, although low pH and low Ca were only identified together (i.e. soft, acid waters) in half of these cases.
- High DOC concentrations were considered to be limiting least frequently, and this factor was never identified alone.

Workshop on metal bioavailability under the Water Framework Directive: Policy, Science and Implementation of regulatory tools

June 2011

Conclusions from 2011 Workshop

- Bioavailability needs to be taken into account in the regulatory context of the WFD. The reason for this is that it clearly reflects the latest science and understanding
- The risk of not accounting for bioavailability is being both over-protective (i.e. taking measures where they are not needed because they have been wrongly identified as an issue), and under-protective (i.e. not taking measures where they are needed, but hadn't been identified)
- Using bioavailability approaches can help improve identification of real problems in sensitive waters, and in prioritizing sites or performing investigations
- The BLMs are relatively complex because, in part, these models reflect complex realities. Yet retaining some of the existing "old" approaches that are not representing the current science is not an option due to the potential for drawing spurious conclusions from their use
- Simplified models and tiered approaches seem to be promising tools to implement bioavailability correction in practice.

Conclusions from 2011 Workshop

- Monitoring and assessment conclusions:
  - There is a need to extend more widely the monitoring of dissolved concentrations of metals in the aquatic environment
  - Total concentrations may still be needed for other purposes (e.g. estimation of loads in permitting), but dissolved concentrations are needed for compliance checking of chemical status
  - Analytical issues need careful attention (filtering, etc) due to the requirement to ensure that the limits of detection are 10% of the EQSbioavailable
- There is a need to monitor at least the most important parameters that influence bioavailability: Ca, DOC and pH. These should be monitored at the same time as dissolved metal concentrations.
- In some circumstances it might be possible to use default values for Ca, DOC and pH. However, this will only be when sufficiently developed datasets are available to ensure the variability in the waterbody is well known

Use of tiered BLM approaches

- One of the main advantages of any tiered approach is that it is simple. In addition, there can be flexibility in implementation steps of tiered approaches.
- Any tiered approach needs to be based on simplified models that are protective enough so that we have high confidence we do not overlook problems.

Use of tiered BLM approaches

- The use of default values for Ca, DOC, pH in a tiered approach is possible if they are protective enough to account for variability, and this decision needs to be based on a thorough knowledge of variability at waterbody level.
- Clear documentation when using the tiered approach and tools on decision making is important, to enable someone to repeat the steps taken and come to the same conclusions.

Member States experience after implementation

- For Cu, using the bioavailability-based approaches there is quite a substantial reduction in the number of EQS exceedances.
- For Zn, there is some reduction in the number of EQS exceedances, but the reduction is less dramatic than for Cu.
- The location of the exceedances changes when accounting for bioavailability.
- There is a need to ensure “Best Practice” is promoted in sampling and analytical work.

Available BLMs

Metal	Acute BLM	Chronic BLM
Ag	X	X
Al	X	X
Cd	X	X
Co		X
Cu	X	X
Mn		X
Ni	X	X
Pb	X	X
Zn	X	X

ALUMINUM BLM