COPPER SPECIATION IN WASTEWATER-IMPACTED SURFACE WATERS

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ACWA's Water Quality Committee Workshop

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Clean Water Services

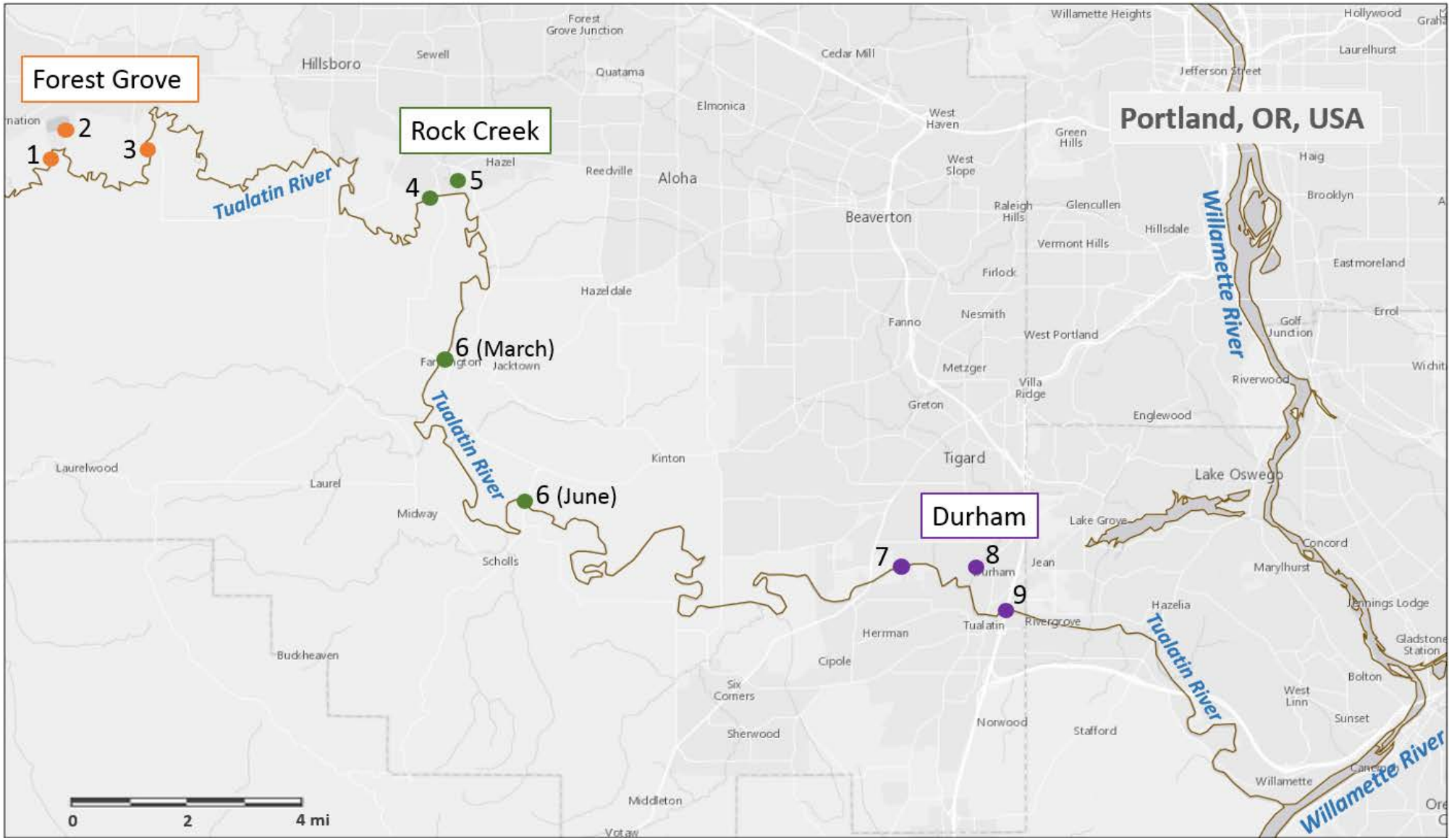
NOM, EfOM, and the BLM

- The BLM is based off of natural organic matter (NOM)
- Effluent organic matter (EfOM) is chemically different from NOM
- EfOM may bind copper differently than NOM
- Mixing NOM and EfOM may alter the copper binding in a water body

TUALATIN RIVER SAMPLING

Wet Season
(March, 2016)

Dry Season
(June, 2016)



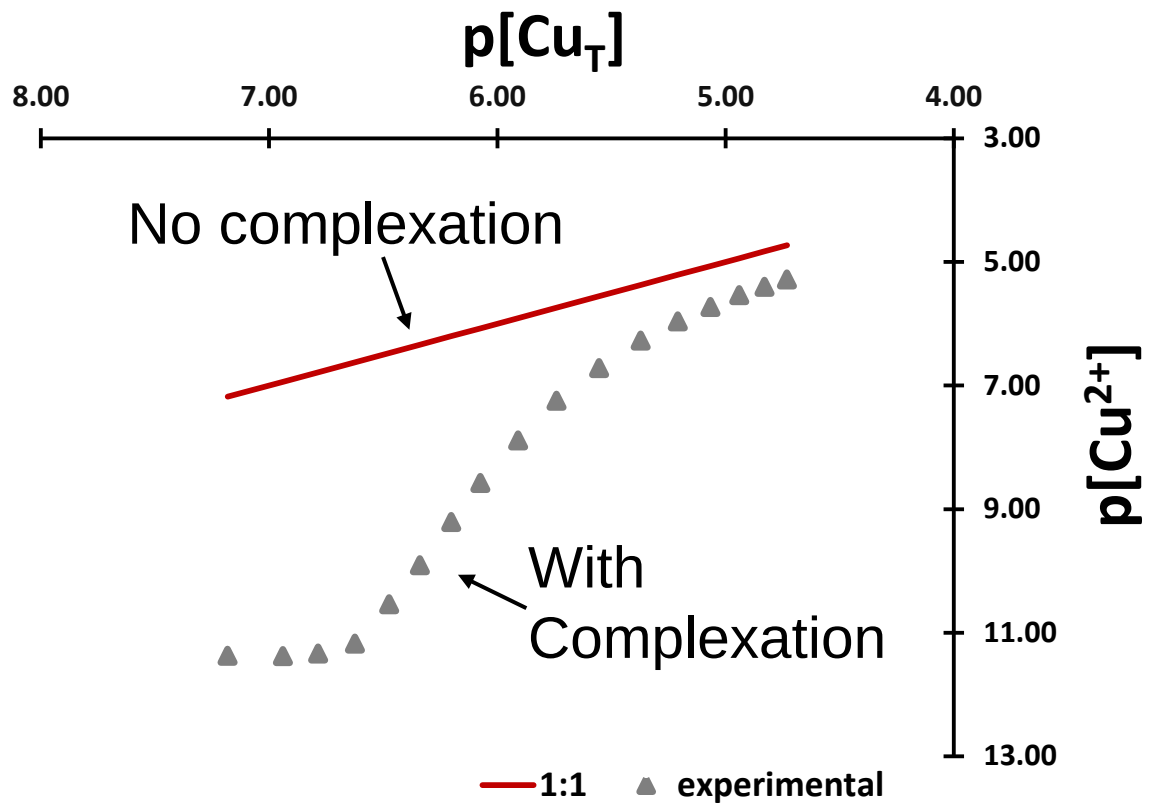
CUPRIC ION-SELECTIVE ELECTRODE (CuISE) METHODS

CuISE:

- Daily calibration with ethylenediamine[4]
- Minimum 5 min equilibration time
- ±0.1 mV/min

Controlled Variables:

- Temperature (25°C)
- pH (6.00±0.05)
- Ionic Strength (0.025 M as $NaNO_3$)
- Head space (ultra-pure N_2 gas)



Example titration – Rock Creek AWWTF

2-LIGAND MODEL

"Weaker Ligand"

L_1

$$Cu^{2+} + L_1^{-1} \leftrightarrow CuL_1^{+1}$$

$$K_{CuL_1} = \frac{[CuL_1^{+1}]}{\{Cu^{2+}\}[L_1^{-1}]}$$

"Stronger Ligand"

L_2

$$Cu^{2+} + L_2^{-1} \leftrightarrow CuL_2^{+1}$$

$$K_{CuL_2} = \frac{[CuL_2^{+1}]}{\{Cu^{2+}\}[L_2^{-1}]}$$

FITTING TITRATION DATA TO A BINDING MODEL

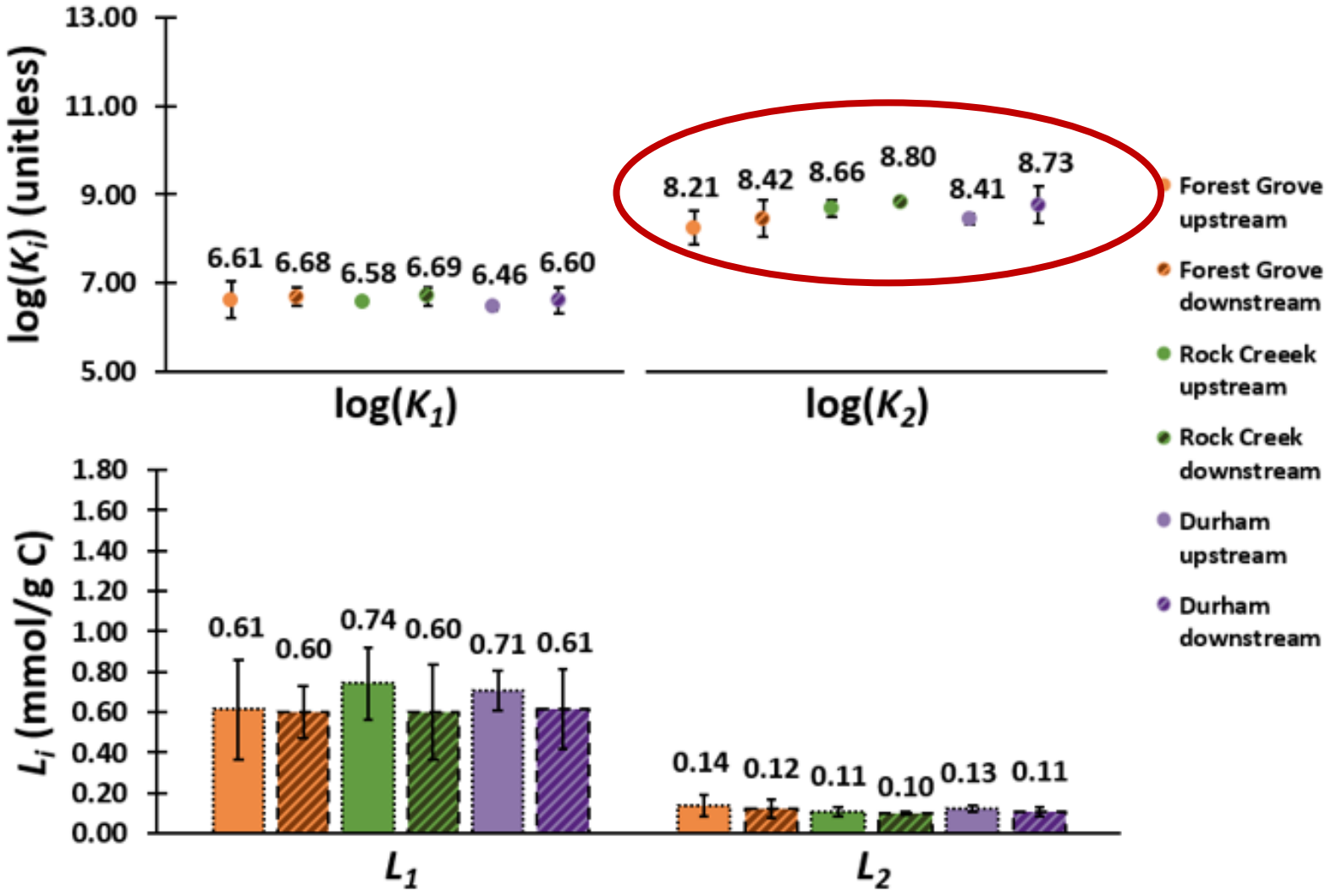
- Used a 2-ligand model for Cu-DOM complexation

$$[CuL_T] = \frac{[L_{1,T}]K_{CuL_1}\{Cu^{2+}\}}{1 + K_{CuL_1}\{Cu^{2+}\}} + \frac{[L_{2,T}]K_{CuL_2}\{Cu^{2+}\}}{1 + K_{CuL_2}\{Cu^{2+}\}}$$

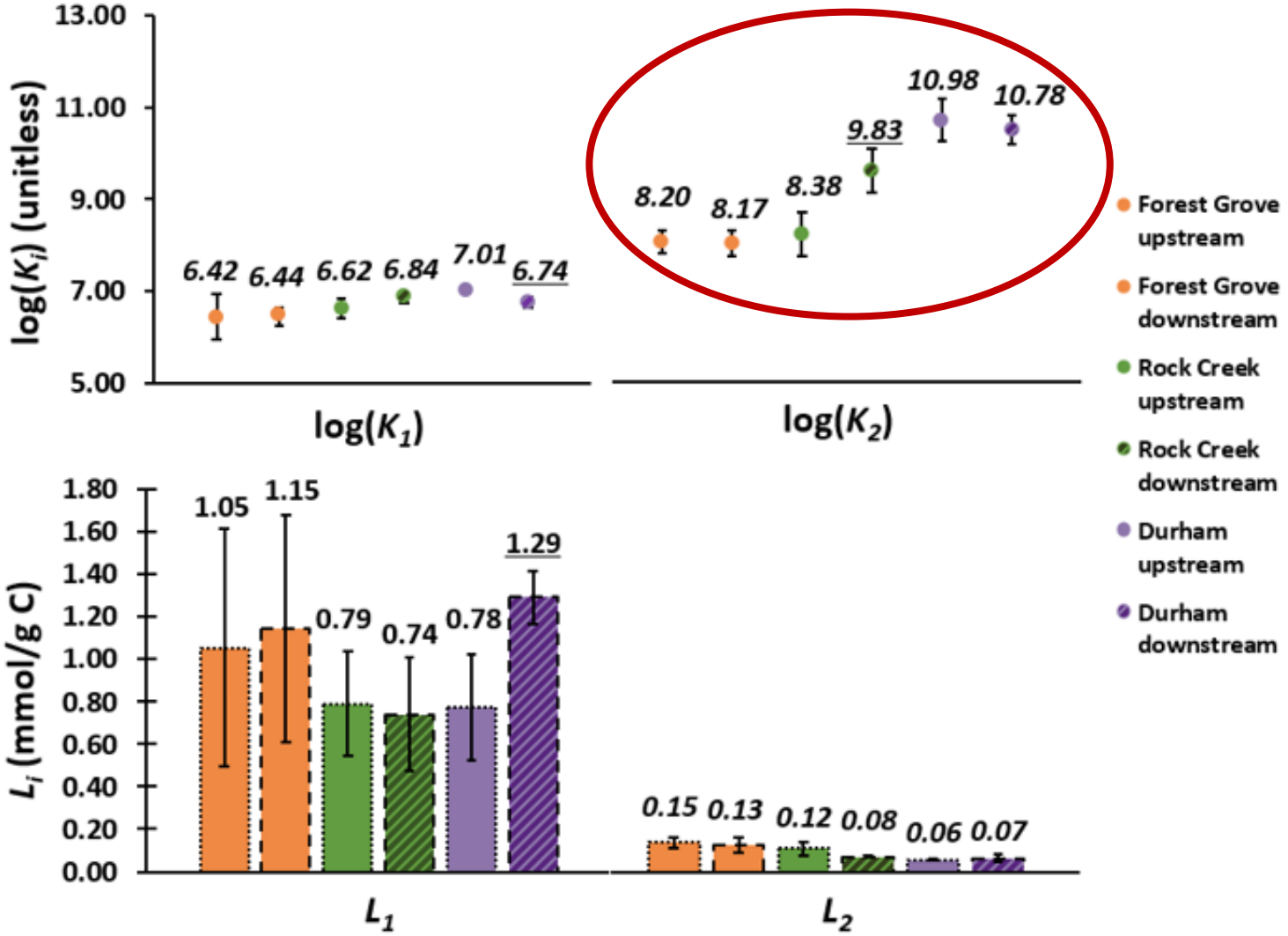
  - ***K*** values represent conditional stability constants for copper-DOM complexation
  - ***L*** values represent the densities (mmol ligand/ g DOC) of copper binding ligands

- Experimental results were best fit with this model to estimate two *K* values (K_{CuL_1}, K_{CuL_2}) and two L values ($L_{1,T}$, $L_{2,T}$)

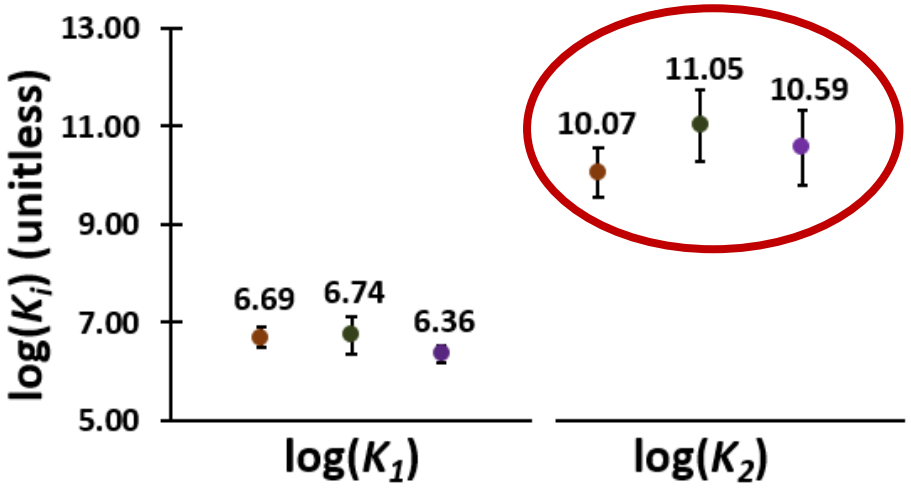
RIVER WATER WET SEASON – K_{CuL_1}, K_{CuL_2}, $L_{1,T}$, $L_{2,T}$

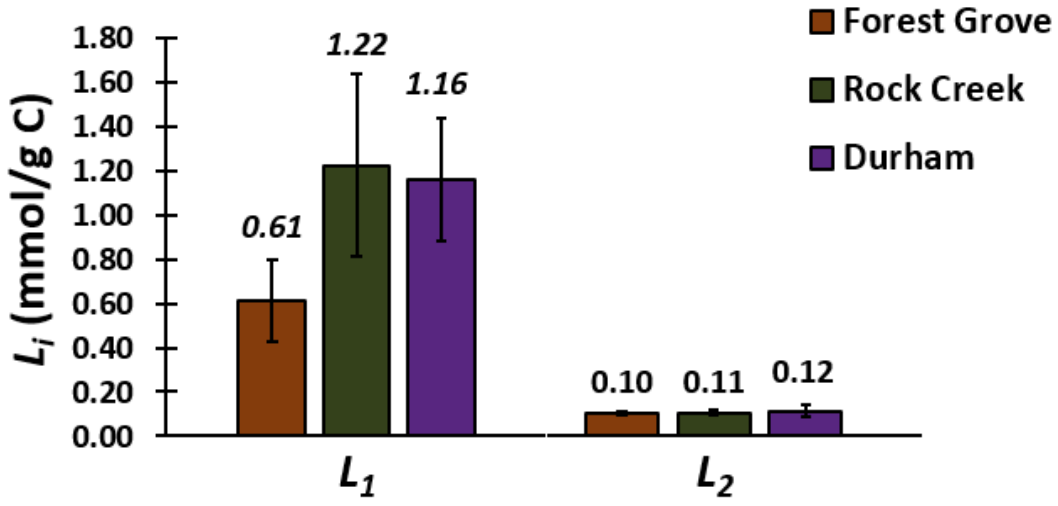


RIVER WATER DRY SEASON – K_{CuL_1}, K_{CuL_2}, $L_{1,T}$, $L_{2,T}$

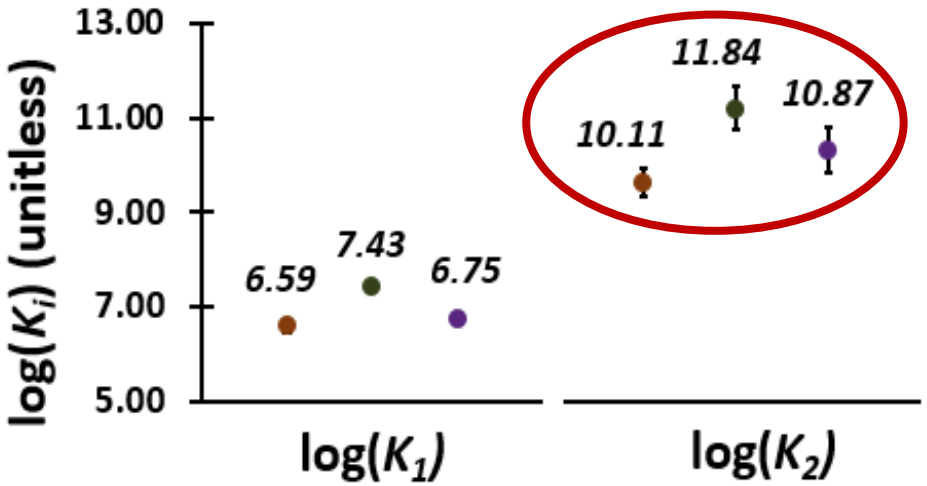


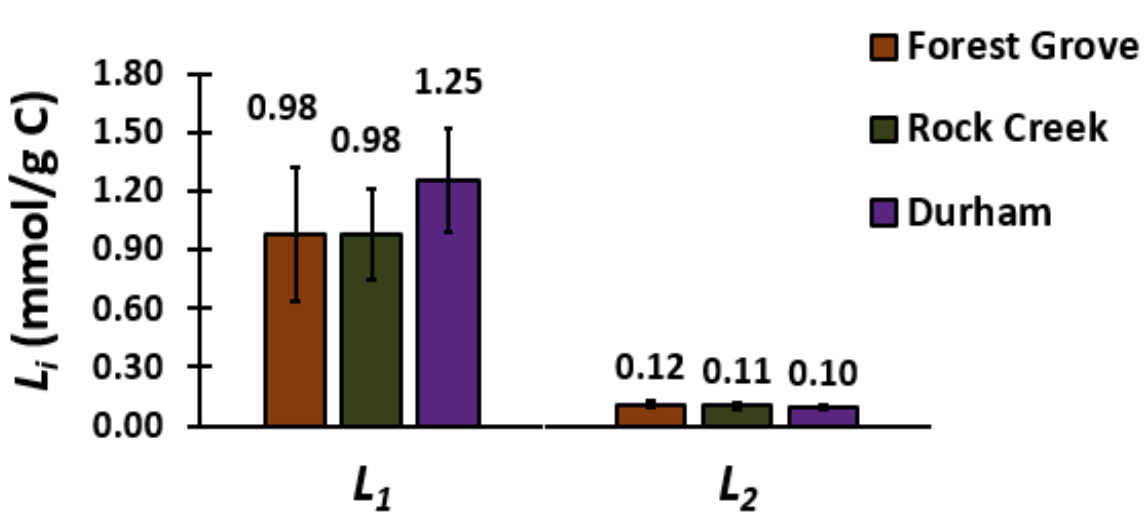
WWTFs ONLY – K_{CuL_1}, K_{CuL_2}, $L_{1,T}$, $L_{2,T}$





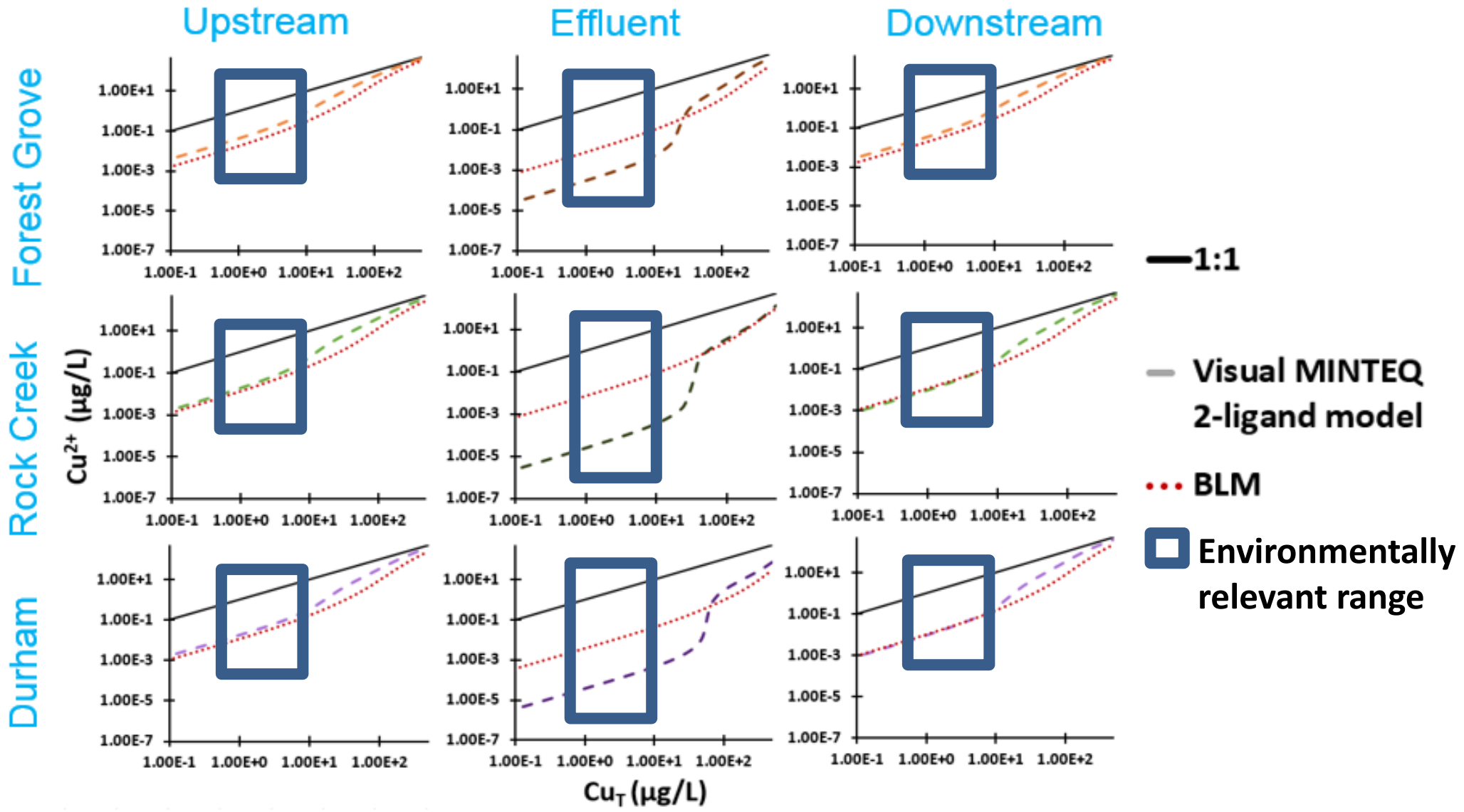
Wet Season



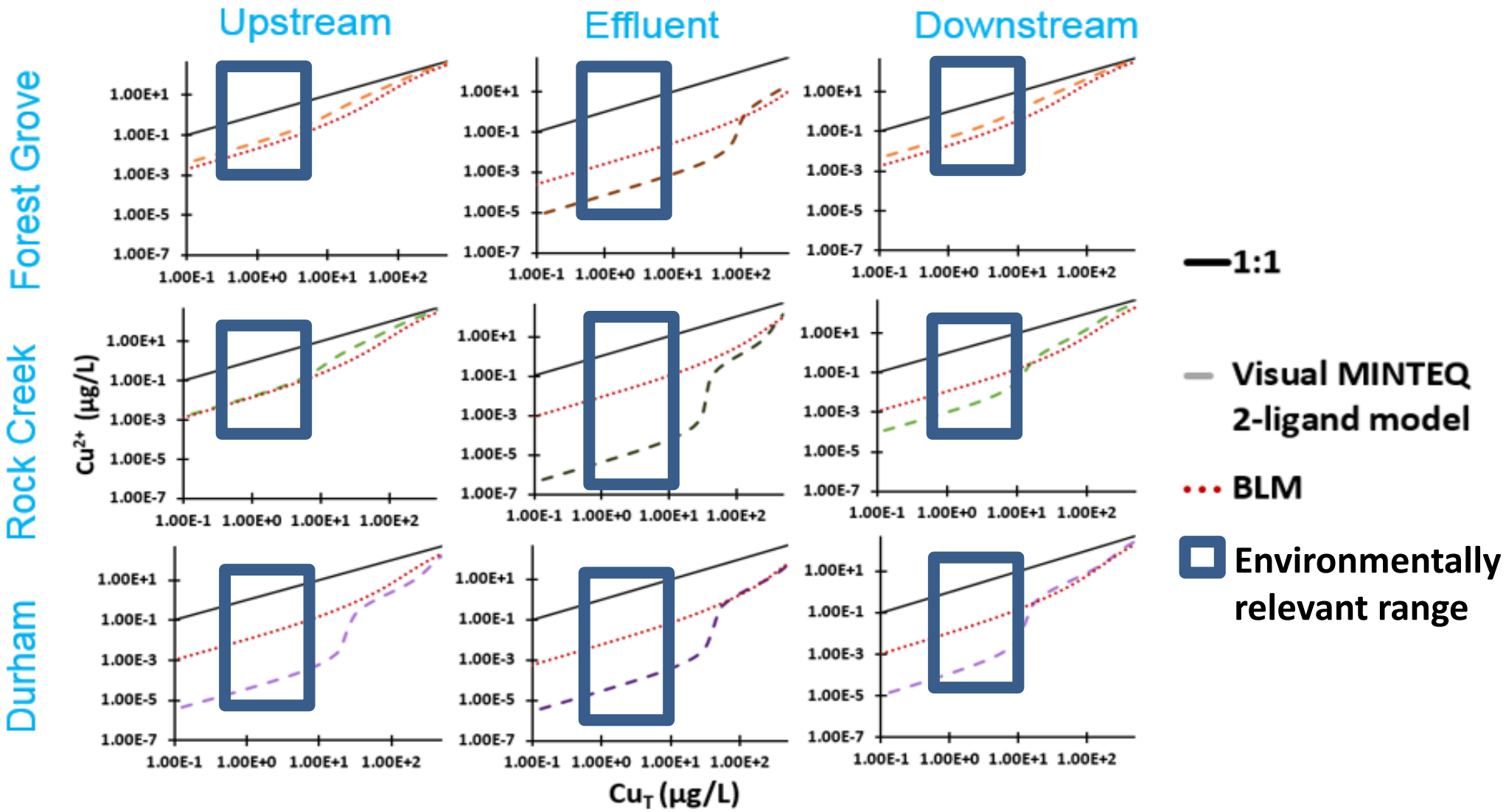


Dry Season

BLM VS EXPERIMENTAL RESULTS – WET SEASON



BLM VS EXPERIMENTAL RESULTS – DRY SEASON



CONCLUSIONS

- The current model predicts complexation with natural organic matter (NOM) adequately
- Effluent organic matter (EfOM) complexes copper more strongly than NOM
  - This is consistent across WWTFs
- The current BLM does not account for this increased binding capacity of EfOM

FUTURE DIRECTIONS

- A mass-balance approach coupled with the BLM may be able to predict copper speciation in mixtures of natural waters and wastewater effluents
- Developing an autotitrator for CuISE analyses
- Testing more dilution ratios
- Looking to test water samples from other utilities in the near future

DISCUSSION

Questions?

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FITTING TITRATION DATA TO A BINDING MODEL