Predicting DXAA Formation During Chloramination

Mélanie Martin-Doole
M. Robin Collins
John Miyares and Sean Raymond
New England Water Treatment Technology Assistance Center (NEWTTAC)
University of New Hampshire

P. Greg Pope
Gerald E. Speitel Jr.
University of Texas at Austin

DXAAs

DCAA

DBAA

BCAA

Chloramine Disinfection

- More Stable and Less Reactive than Free Chlorine
- Detectable Residual Throughout Distribution System
- Penetrates Deeper into Biofilm Layer
- Much Less Disinfection By-Product (DBP) Formation than Chlorination
- DXAA Most Common DBPs, but Concentration Much Less than in Chlorination

Health Concerns

1. DCAA greater health concern than TCAA

2. Bromine containing Haloacetic acids (HAAs) such as DBAA and BCAA may be of higher carcinogenic risk than the chlorine containing HAAs

Regulatory Status

Regulated HAA:

1. Monochloroacetic acid
2. Dichloroacetic acid (DCAA)
3. Trichloroacetic acid
4. Monobromoacetic acid
5. Dibromoacetic acid (DBAA)

Unregulated HAA:

1. Tribromoacetic acid
2. Bromochloroacetic acid (BCAA)
3. Bromodichloroacetic acid
4. Dibromochloroacetic acid

Factors Influencing HAA Formation

- pH (DXAA increases as pH decreases)
- Cl_2/N Ratio (DXAA increases as Cl_2/N increases)
- Bromide Concentration (DXAA increases as Br^- increases; shift in speciation)
- Temperature (DXAA increases as Temperature increases)
- Chloramine residual concentration
- Mode of chloramine addition
- Precursor type and concentration

Objectives

1. Evaluate and rank factors influencing DXAA formation
2. Develop a data base on DXAA formation as a function of water characteristics and chloramination conditions
3. Develop regression models to predict DXAA formation
4. Full-scale system evaluation

Chloramination and Water Quality Variables-Batch I

Cl_2/N Ratio	pH	Temperature	Chloramine residual	Bromide Concentration
3/1	7	Ambient (70^oF)	2 mg/L	Ambient
5/1	9	85^oF	4 mg/L	Ambient + 0.5 mg/L

Experimental Design-Batch I

- <u>Fractional Factorial Design</u>
  - L16 Orthogonal Array (OA)
    - 16 Trials/Water
    - 16 DXAA Measurements/Water
    - Performed on 2 raw waters and 6 "Treated" waters
    - 128 total experiments
- <u>Statistics</u>
  - ANOVA: Percent contributions for ranking factors.

Water Sources Batch I

State	**New Jersey**	**Texas**
Town	**Brick**	**Austin**
Water Source	**Metedeconk River**	**Lake Austin**
Water Type	1. **Raw** 2. **Coagulated** 3. **Membrane Filtered** 4. **Biodegraded** 5. **Hydrophilic Fraction**	1. **Raw** 2. **Raw-Algal** 3. **Softened** 4. **Hydophilic Fraction**

Summary of Important Chloramination Factors-Batch I

pH	1
Br	2
Treatment/Source	3
Cl_2/N	4
Temperature	N.S.
Chloramine Residual	N.S.

Recommendation to Minimize DXAA Formation-Batch I

- Keep pH as high as possible
- Monitor bromide concentration
- Remove as much NOM as possible
- Cl_2/N ratio as low as possible

Recommendations for Additional Experiments

- Define Non-linear (>2 levels) effect of factors determined to be most important in Batch I
- Assess bromide influences normalized by DOC content (Br/DOC ratio)
- Expand study to include additional source waters (Geographic and NOM fingerprint diversity)

Chloramination and Water Quality Variables-Batch II

pH	Br/DOC (μg/mg)
7	<15
8	40
9	88

Cl_2/N ratio	Temperature	Chloramine residual
4/1	Ambient (70°F)	2 mg/L

Experimental Design-Batch II

- Fractional Factorial Designs
  - L4, L9, L32 OAs
    - 4, 9, or 32 Trials/Experiment
    - 4, 9, or 32 DXAA Measurements/Experiment
    - L4 Performed on 2 Treated Waters = 8 Exp.
    - L9 Performed on 3 Raw Waters = 27 Exp.
    - L32 Performed on 1 Raw Water = 32 Exp.
    - 67 total experiments
- Statistics
  - ANOVA: Percent contributions for ranking factors.

Water Sources Batch II

State	<u>New Jersey</u>	<u>Florida</u>	<u>Minnesota</u>	<u>South Carolina</u>
Town	Brick	Boca Raton	St-Paul	Charleston
Water Source	Metedeconk River	Biscayne Aquifer	Mississippi River	Surface impoundm.
Water Type	Raw	Raw Softened	Raw Softened	Raw

Summary of Important Chloramination Factors-Batch II

pH	**1**
Water Source	**2**
Br/DOC	**N.S.**

Modeling

Model Development:

1. Predictors (Independent Variables): Water characteristics and chloramination variables (pH, bromide concentration, UV, DOC, …)
2. Response (Dependent Variable): DXAA
3. LinearRegression Analyses: JMP IN (Cary, NC)

$$\mathbf{Y = a_1X_1 + a_2X_2 + \ldots + a_iX_i + b}$$

Ln DXAA Molar Yield =

Parameter	Coefficient
Intercept	-5.281
Cl_2/N Ratio, mg/mg	0.097
NH_2Cl Consumed, mg/L	0.082
NH_2Cl Residuals, mg/L	0.082
pH	-0.228
Bromide mg/L	0.484
SUVA, L/m-mg	0.361
UV, 1/cm	-1.782
Hydrophobic, mg/L	-0.220
Hydrophobic /DOC	1.928
Hydrophilic/DOC	3.451

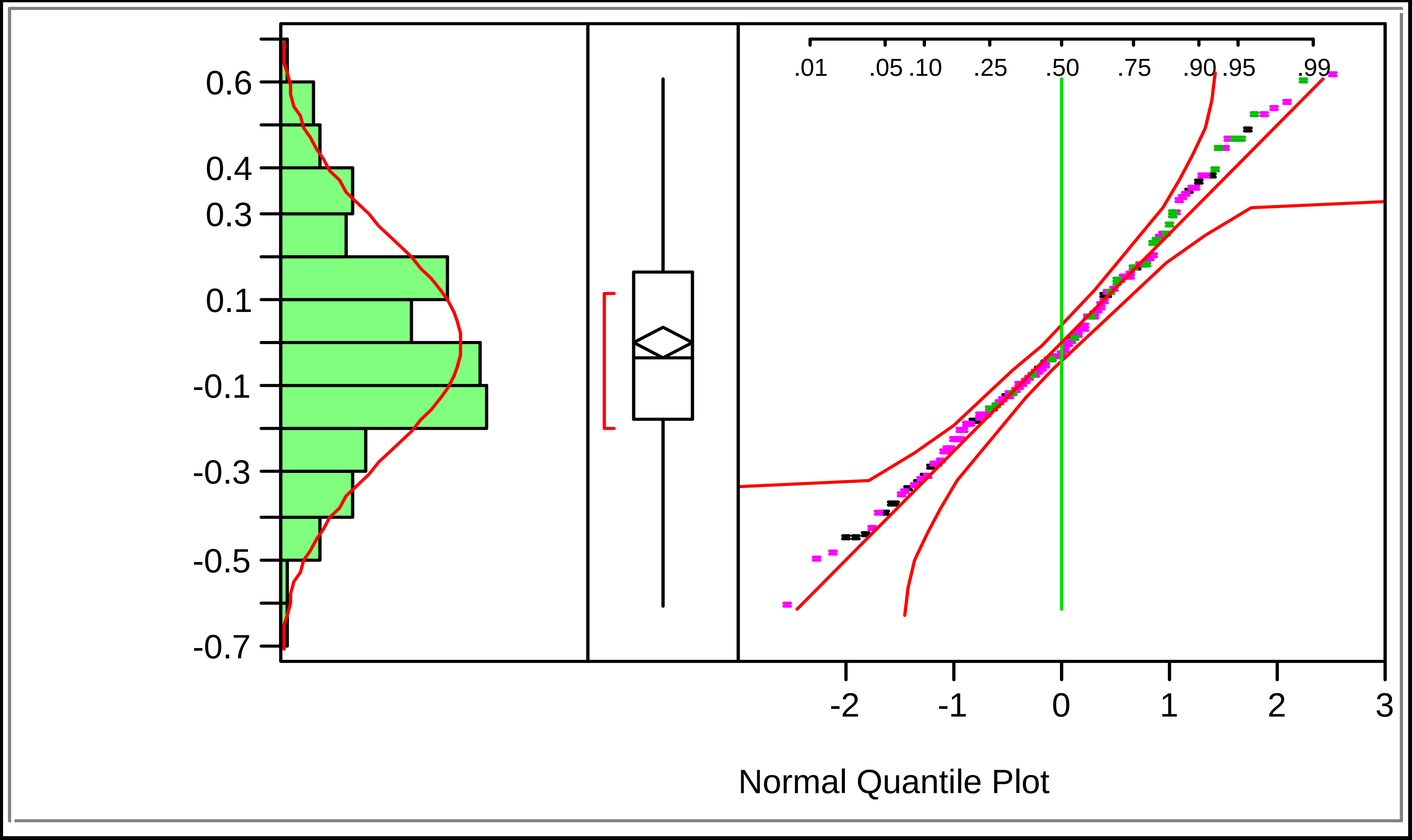
Ln DXAA Mass Yield =

Parameter	Coefficient
Intercept	-0.250
Cl_2/N Ratio, mg/mg	0.099
NH_2Cl Consumed, mg/L	0.064
NH_2Cl Residuals, mg/L	0.087
pH	-0.257
Bromide mg/L	0.734
SUVA, L/m-mg	0.388
UV, 1/cm	-2.117
Hydrophobic, mg/L	-0.234
Hydrophobic/DOC	1.967
Hydrophilic/DOC	3.763

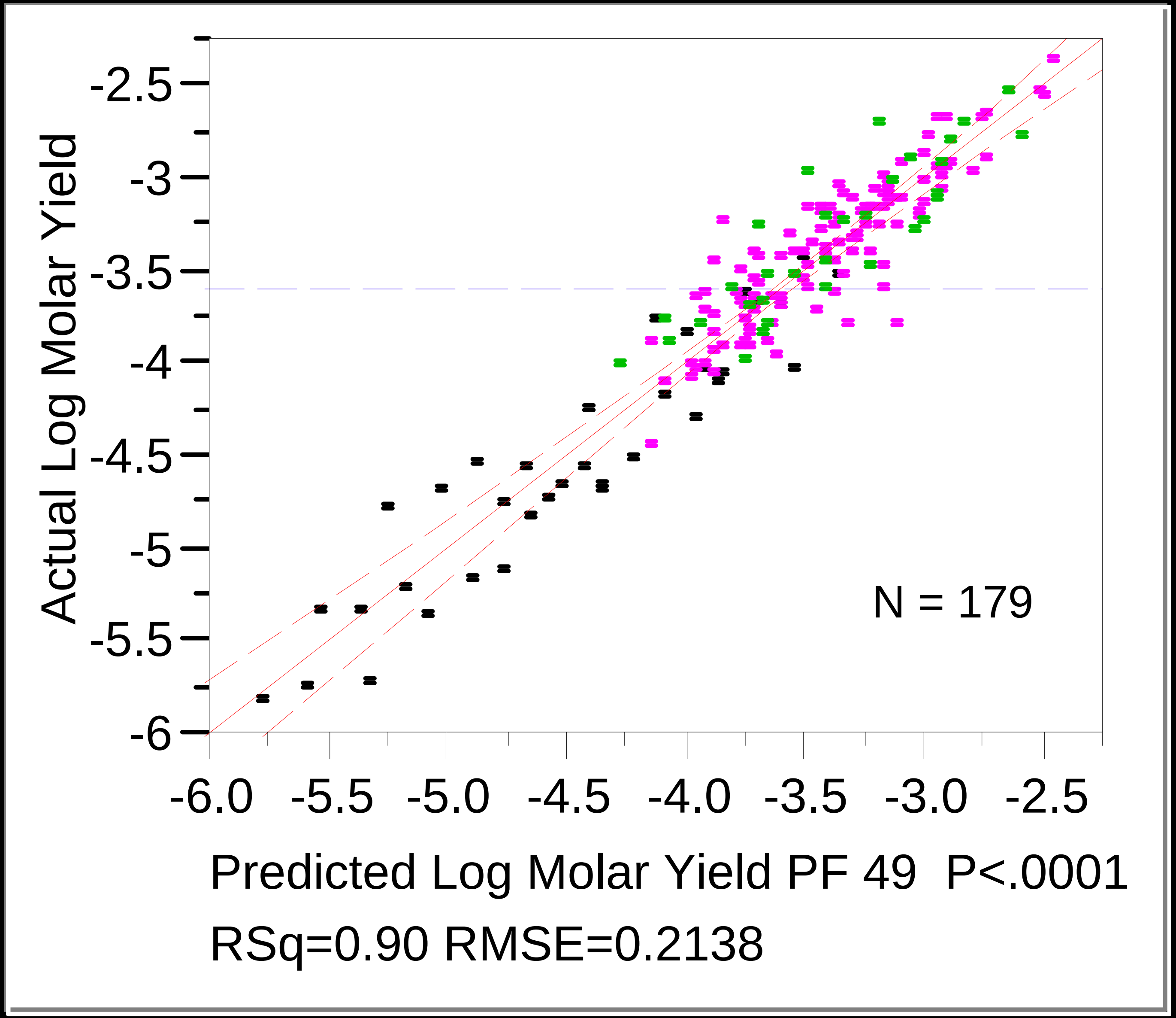
Ln DXAA Mass =

Parameter	Coefficient
Intercept	0.021
Cl_2/N Ratio, mg/mg	0.095
NH_2Cl Consumed, mg/L	0.075
NH_2Cl Residuals, mg/L	0.082
pH	-0.254
Bromide mg/L	0.735
SUVA, L/m-mg	0.310
UV, 1/cm	-1.805
Hydrophobic, mg/L	-0.283
Hydrophobic/DOC	1.947
Hydrophilic/DOC	3.328
Ln DOC	1.155

Normal Distribution
Ln DXAA Molar Yield



Actual by Predicted Plot



Models R^2

Model	Ln DXAA Molar Yield	Ln DXAA Mass Yield	Ln DXAA Mass
R^2	0.90	0.89	0.84

Highest Impact Model-Parameters

Impact	Log Molar Yield	Log Mass Yield	Mass
1	pH	pH	Log DOC
2	Hydrophobic	Hydrophobic	pH
3	Hydrophobic/DOC	Bromide concentration	Bromide concentration
4	Bromide Concentration	Hydrophobic/DOC	Hydrophobic
5	Hydrophilic/DOC	Hydrophilic/DOC	Hydrophobic/DOC
6	SUVA	SUVA	Hydrophilic/DOC

Full-Scale System Evaluation

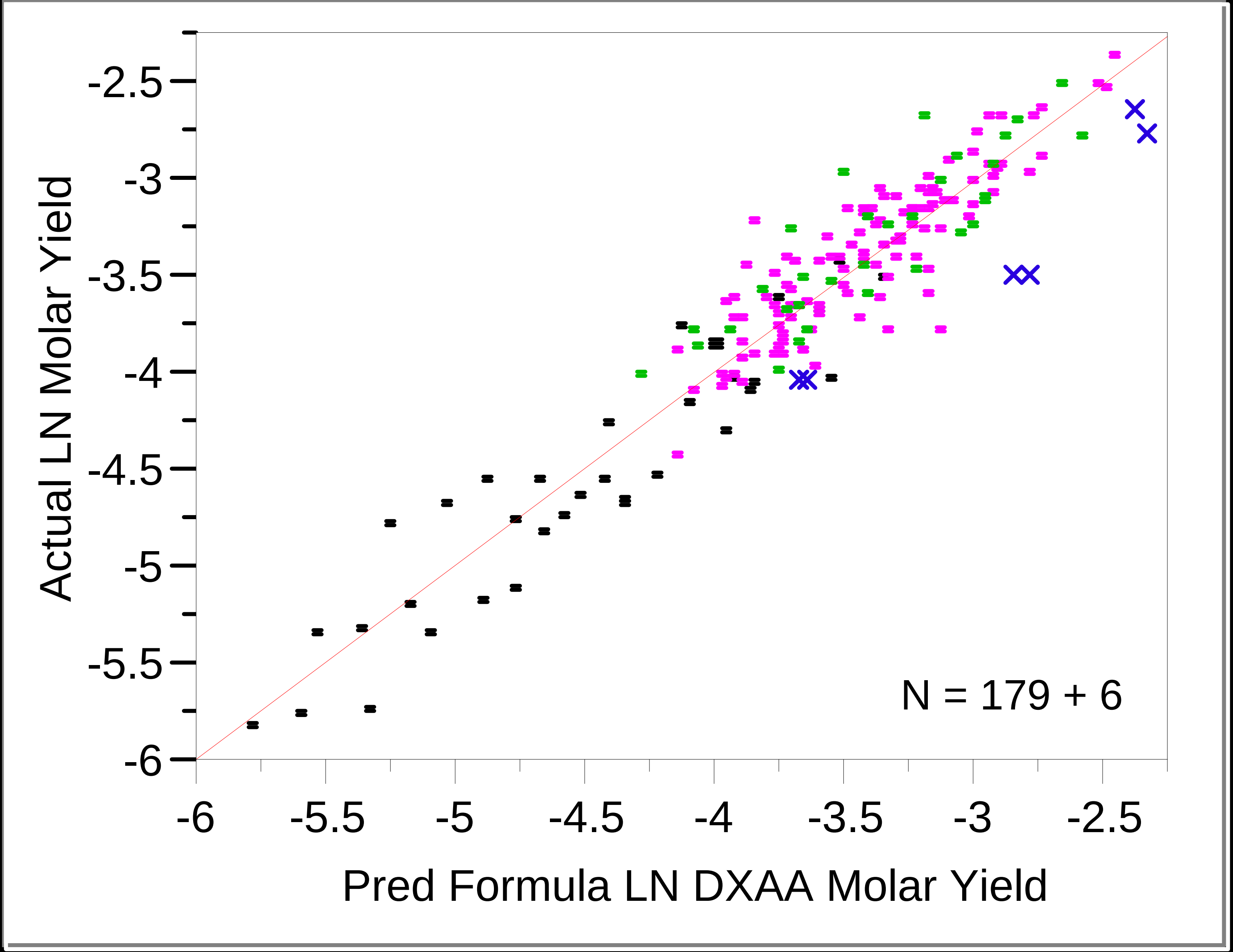
Utilities

1. Manatee, FL
2. Port-Orange, FL
3. Chalmette, LA

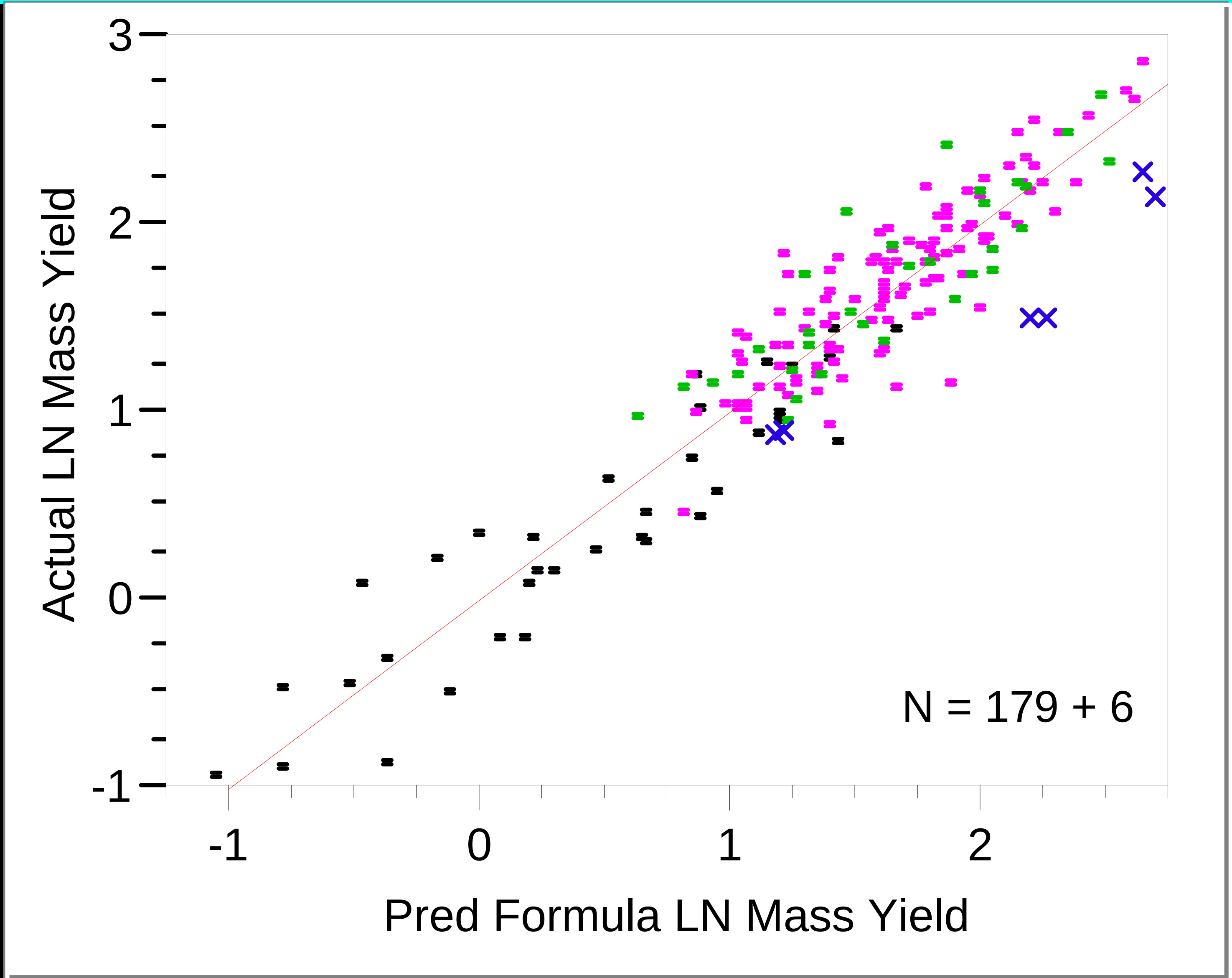
Distribution System Sampling

- 2 Sampling locations
- DXAA samples from distribution systems
- Water quality and chloramination variable from treated waters

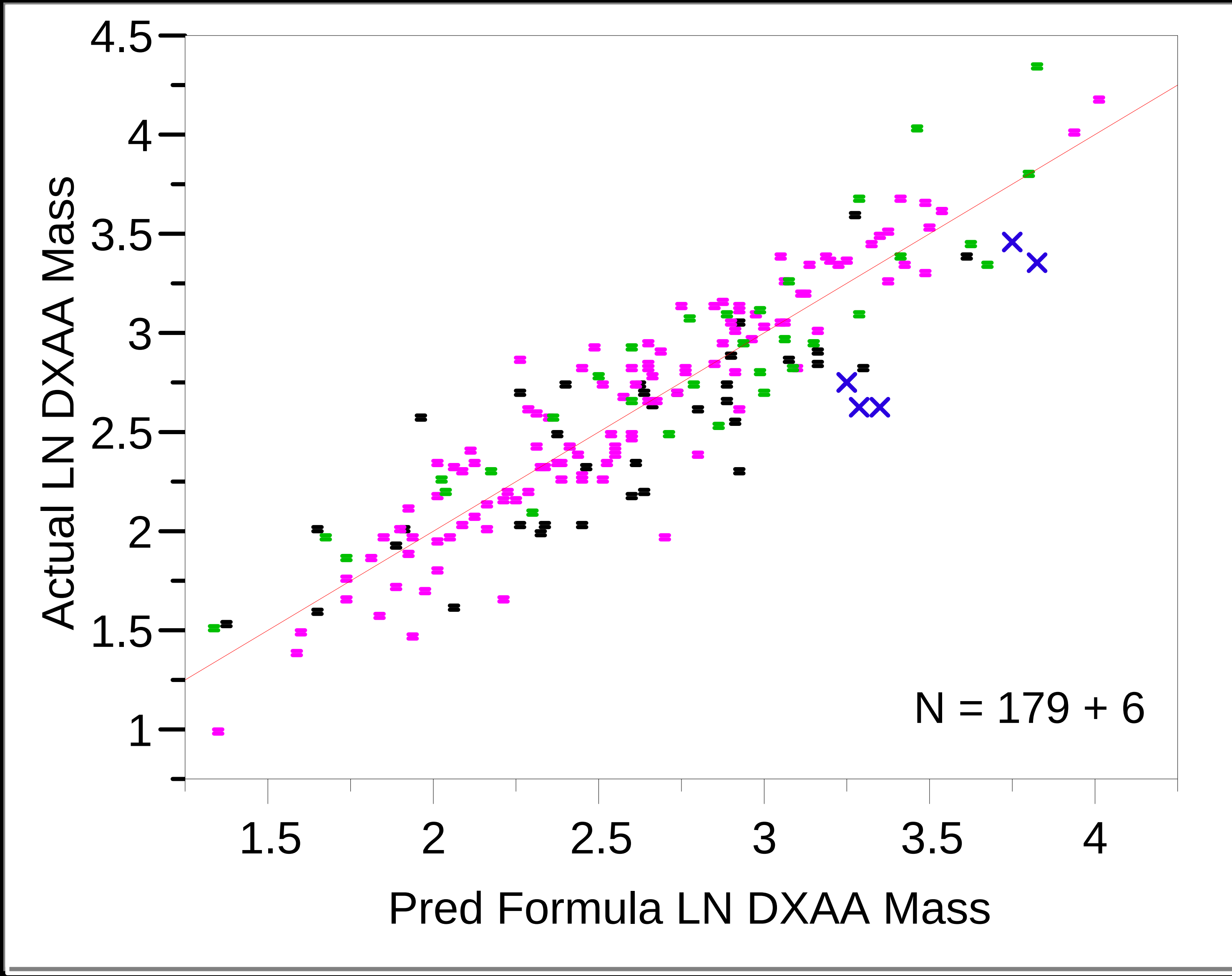
Ln DXAA Molar Yield Model Full-Scale System Evaluation



Ln DXAA Mass Yield Model Full-Scale System Evaluation



Ln DXAA Mass Model
Full-Scale System Evaluation



Summary and Conclusion

- **Important chloramination factor in Batch I and II:**
    - pH - As high as possible
    - NOM - Remove as much as possible
    - Bromide - Should be monitored.
- **Models are very similar; parameters, coefficients and signs are alike.**
- **Normal distribution of the residuals for all models**
    - **(Residuals = Actual – Predicted value)**
- **Ln DXAA Mass Model has one more model term:**

  Ln DOC

Summary and Conclusion

- **R^2 of Yield models (0.90 and 0.89) were higher than the Mass model due to DOC incorporated in the response as well as in the predictors.**
- **High impact terms:**
  1. pH or DOC
  2. Hydrophobic or pH
  3. Bromide
  4. Hydrophobic/DOC
  5. Hydrophilic/DOC
  6. SUVA
- **Full-scale system evaluation of the models was satisfactory.**

Recommendations

- Perform model calibration using a large number of water sources with varying water qualities
- Improved models by reducing the number of terms and predicting individual DXAA species.
- Explore more advanced NOM fractionation techniques to better define DOC reactivity

Acknowledgements

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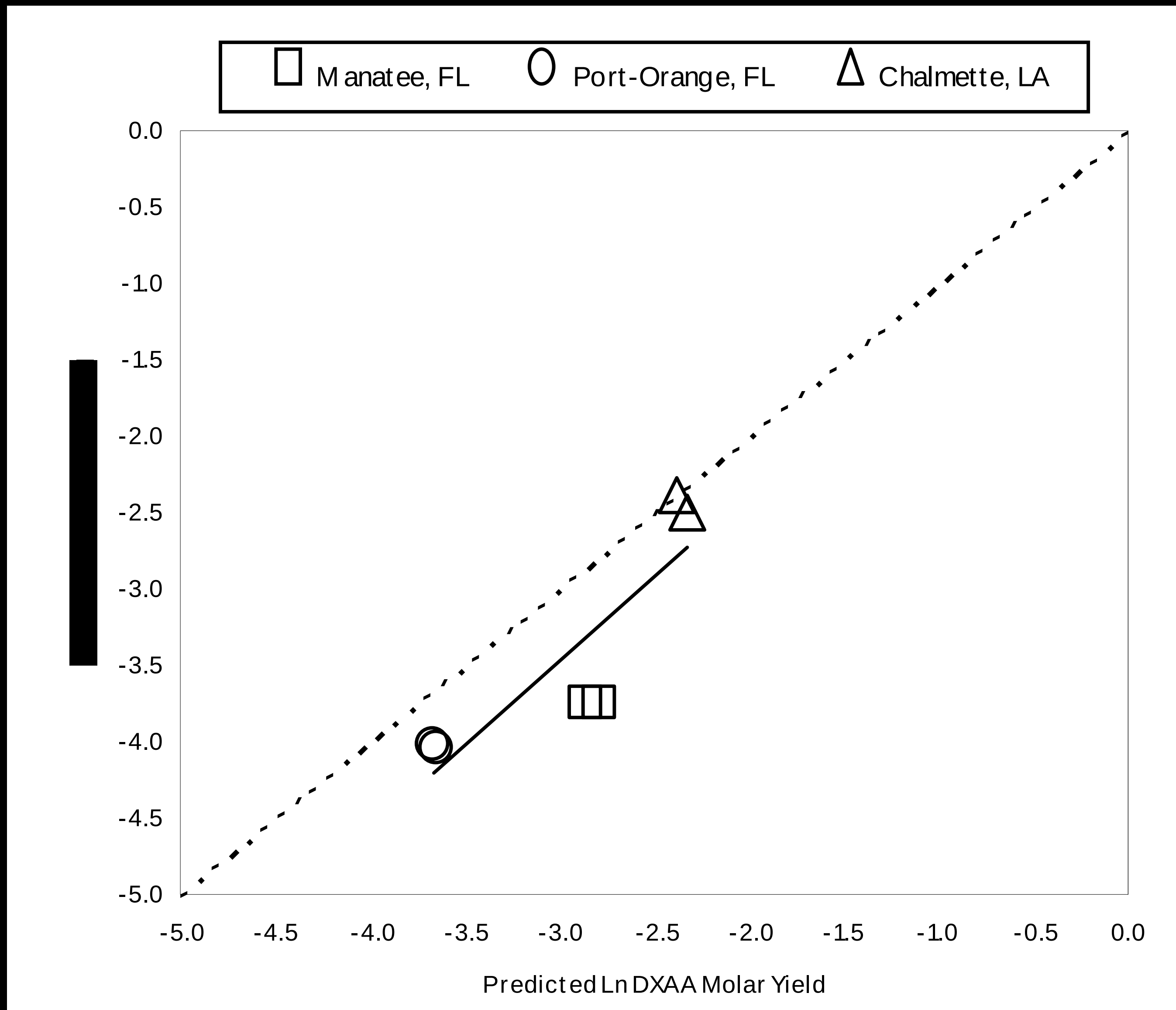
- John Miyares and Sean Raymond-Statistical Expertise

Any Questions ?

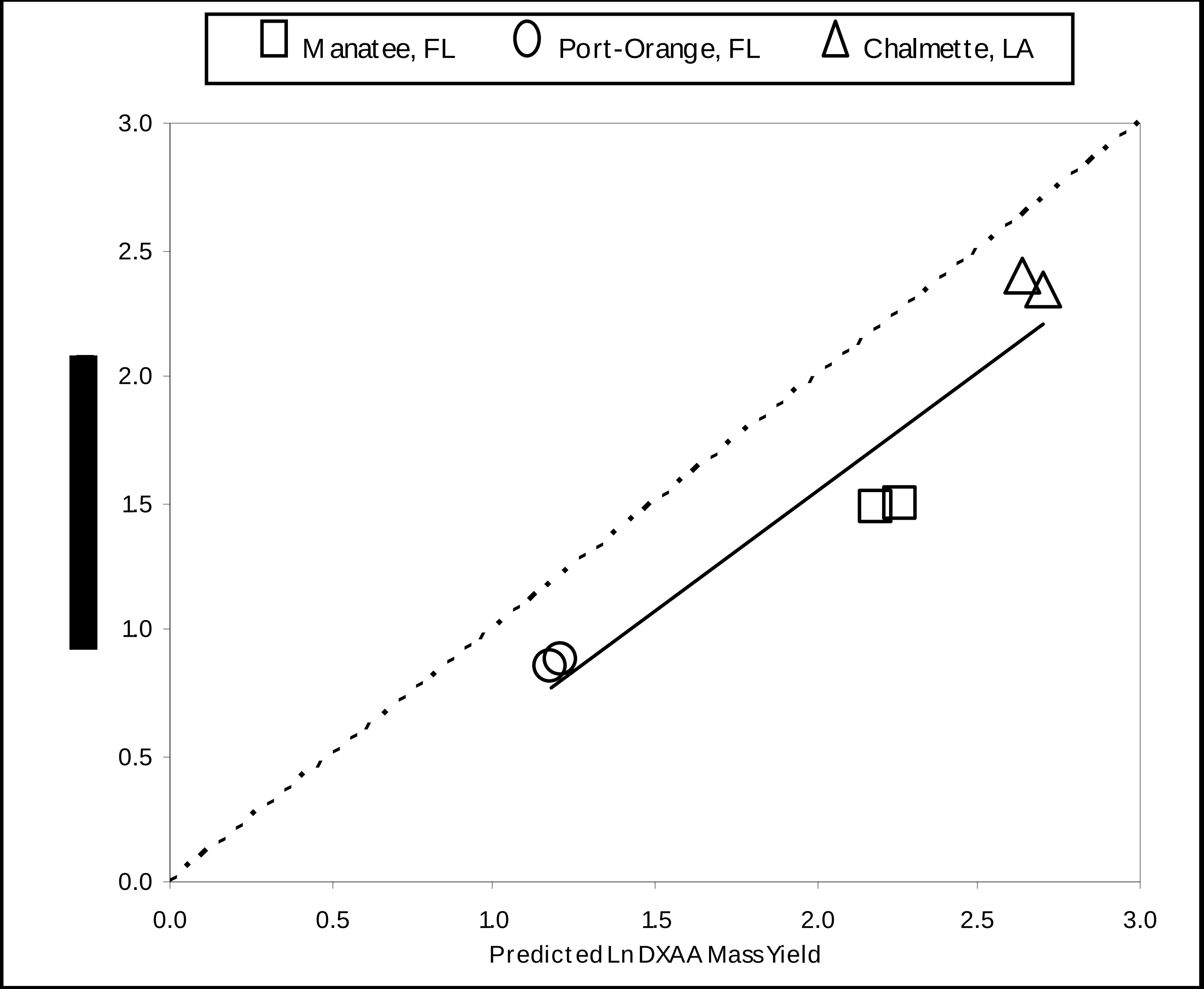
Recommendations

- Perform a model calibration using a large number of water sources with varying water qualities
- Improved models by reducing the number of terms
- Separate the transphilic carbon, hydrophilic acids plus neutrals, and hydrophilic bases, conduct chloramination study and characterization using elemental analysis, molecular weight measurements, and 13C Nuclear Magnetic Resonance (NMR) spectroscopy on each fraction.

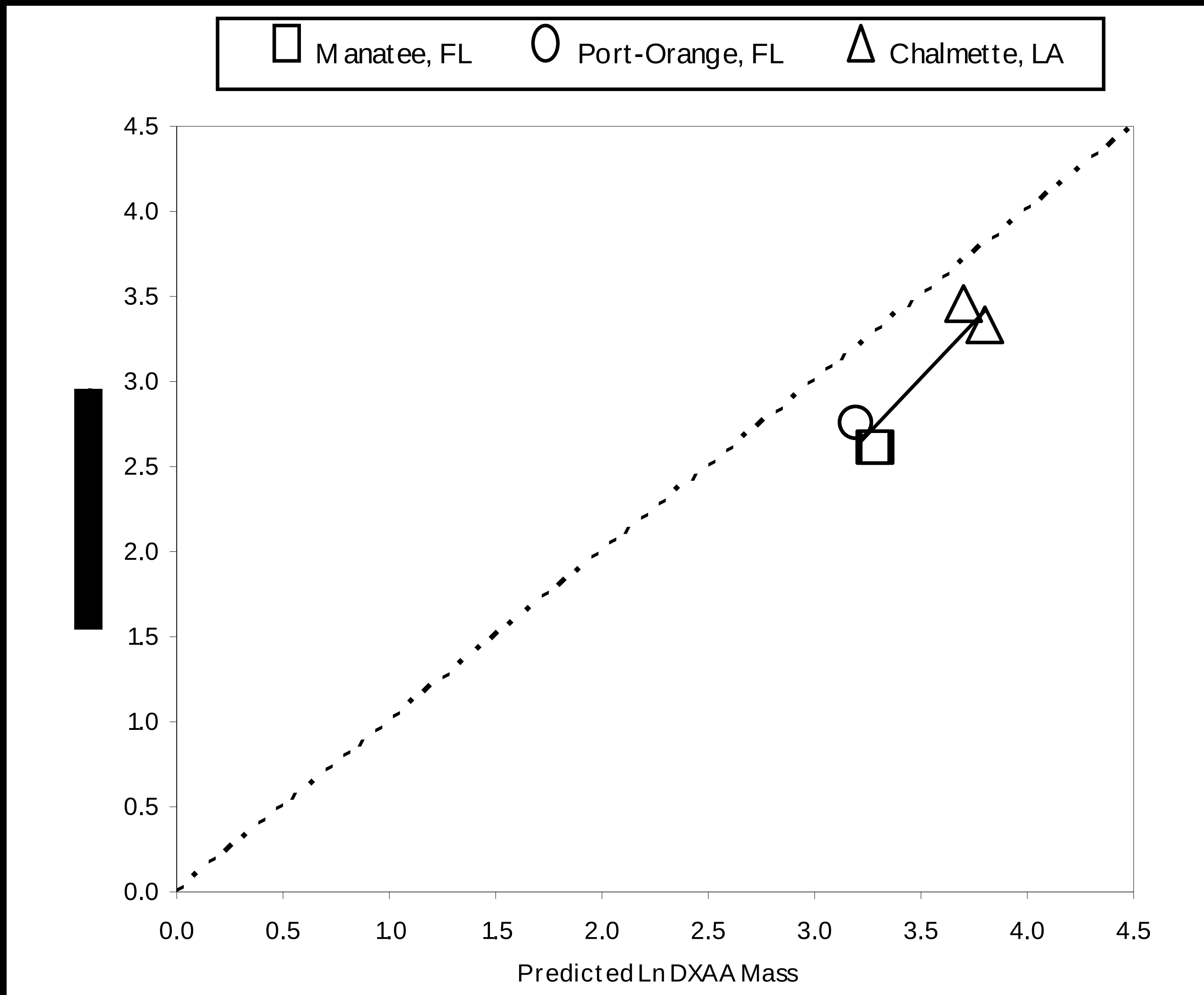
Ln DXAA Molar Yield Model
Full-Scale System Evaluation



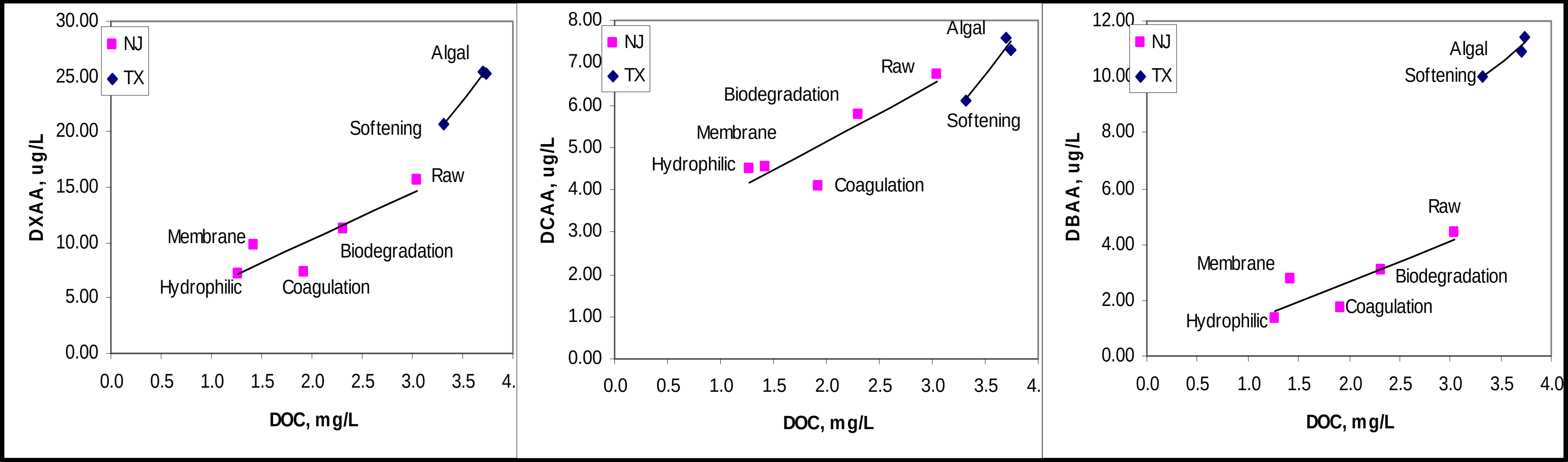
Ln DXAA Mass Yield Model
Full-Scale System Evaluation



Ln DXAA Mass Model
Full-Scale System Evaluation



Relationship between DOC and DXAA for Both Source and Treated Waters



Batch 1 Conclusions

- Most important factors: pH and Br^-
- Source water characteristics next in importance
- HAA concentration deceased as pH increased, and Cl_2:N decreased
- DXAA dominated
- Bromide shifted speciation and usually increased concentration
- Softening and coagulation resulted in less DXAA formation

Experimental Design

- Fractional Factorial Design
- L9 OA (Raw) and L4 OA (Treated)
  - 9 or 4 Trials/Experiment
  - 9 or 4 DXAA Measurements/Experiment
  - Main Factors
- Statistics
  - ANOVA
  - Modeling

Residuals Normal Quantile Plot (Residuals unit = Actual - Predicted)