Simulation of Copper Release in Pipe Distribution System And Copper Rule Compliance

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Historically, groundwater has been the major water source for municipal use in Florida (1); however, the capacity of groundwater to meet future demands is inadequate, and alternate sources (brackish water, ocean water, and surface water) are needed. The different treatment techniques for these sources produce different finished-water qualities that can adversely impact distribution-system water quality when these waters are blended or are distributed as a sole source in distribution systems that have experienced only finished groundwater. This article discusses the effect of variable finished-water quality on distribution-system water quality. Such variations can cause regulatory violation of copper and lead action levels (2-8).

The current maximum contamination level (MCL) for copper is 1.30 mg/L at the 90 percentile of sampling sets collected from homes with copper plumbing after six hours of stagnation (9). Extensive research has been conducted on mechanisms of copper corrosion (2-7, 10-20). The primary controlling factors for copper corrosion are alkalinity and pH.

Dissolved copper speciation primarily consists of free Cu (I) and Cu (II), hydroxyl complexes, and carbonate complexes. The $CuCO_3^0$ complex accounts for 80 percent of total dissolved copper speciation. The remaining 10 to 20 percent consists of mostly hydroxyl species. Temperature affects copper release and generally increases particle and decreases dissolved copper release (2). Particulate copper can account for a significant fraction of total copper.

Although the specific effects of anions, cations, and physical parameters on copper corrosion have been studied, the confounding impacts of these factors are unknown and require extensive pilot-plant or system investigation. Accurate prediction of copper concentrations in full-scale distribution systems is best done using models which are statistically based on theoretical mechanisms and extensive field data.

Copper corrosion was investigated as affected by varying water quality using a large pilot facility over one year. The varying water quality was produced by blending finished groundwater, surface water, and desalinated water in 18 pilot distribution systems (PDSs) and copper loops over 1.5 years. The blends were changed quarterly.

The PDSs were made from PVC, lined cast iron (LCI), unlined cast iron (UCI), and galvanized steel (G) pipes taken from actual distribution systems. Models were developed using linear and non-linear statistical regression that correlated total copper concentration to water quality.

Parameter	Unit	Ground Water	RO Water	Surface Water
pH		7.6	8.3	8.3
Alkalinity	mg/L as $CaCO_3$	225	50	50
Cl-	mg/L	15	50	10
SO^{4}_{-2}	mg/L	10	30	180
TDS	mg/L	400	150	300
Conductivity	us/cm	560	340	470
Calcium	mg/L as $CaCO_3$	250	50	50
Silicate	mg/L as SiO_2	20	20	10

Table 2: Finished groundwater (G1), surface water (S1) and desalinization (RO) water quality

No.	I. D.	Source Water Unit Processes
1	G1	Gr

Table 1: Treatment systems and blending scenarios

Experiments and Methods

Pilot Unit Design

Varying water quality was produced from seven different finished waters, which were blends of finished waters produced from groundwater (G1, G2, G3, G4), surface water (S1, S2), and reverse osmosis (RO). Blended waters are shown in **Table 1**.

Post treatment for all finished waters included aeration, stabilization and disinfection. The G1 process consisted of only post treatment, which is typical for Florida groundwaters. Water was transported weekly from the Hillsborough River, stored in two 7,000-gallon tanks and treated by ferric sulfate coagulation, settling, cartridge filtration (CSF), ozone, and GAC filtration before post treatment. Some of the S1 process water was diverted to an NF membrane pilot unit for the S2 process.

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Variable	Unit	Range	Concentration	Linear Model Prediction-Cumg/L	Non-LinearModel Prediction-Cumg/L
Alkalinity	mg/Las $CaCO_3$	Maximum	225	1.74	1.54
		Minimum	50	1.15	0.70
pH		Maximum	8.30	0.96	1.05
		Minimum	7.60	1.56	1.28
Temperature	°C	Maximum	35		1.52
		Minimum	15		0.96
Sulfate	mg/L	Maximum	120		1.33
		Minimum	10		1.10
Silica	mg/L	Maximum	15.05		1.28
		Minimum	0.59		2.32

Table 3: Water-quality range and predicted 90th-percentile copper concentrations

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RO water was produced by high-pressure membrane filtration of groundwater and addition of sea salt to simulate the Tampa Bay Water (TBW) RO finished water. G4 was a nanofiltered blend (62 percent G1, 27 percent S, 11 percent RO), which was of interest to one of the member governments of TBW. G2 was softened water. G3 was a softened blend of partially treated waters and, like G4, was of interest to a TBW member government.

The PDSs receiving the blended waters were 100 feet long and made from pipe taken from MG distribution systems. Fourteen PDSs were made from PVC, lined cast iron (LCI), unlined cast iron (UCI), and galvanized steel (G) pipes. Four PDSs were made with a single material.

Lead and Copper Loops

PDS effluent was fed to 18 identical copper loops, which contained one each 50:50 tin: lead coupon. Thirty feet of 0.25-inch copper tubing was used in each loop. The samples for copper and lead monitoring were taken from the first 22 feet. All other fittings and materials were polymer materials, typically PVC. The coupon surface area was 3.38 square inches and was equivalent to 17 joint-ends or seven to eight fittings, given a 0.125-inch bead on the inside of each 0.5-inch diameter joint, which is a reasonable assumption for a home plumbing site required for compliance with the Lead and Copper Rule.

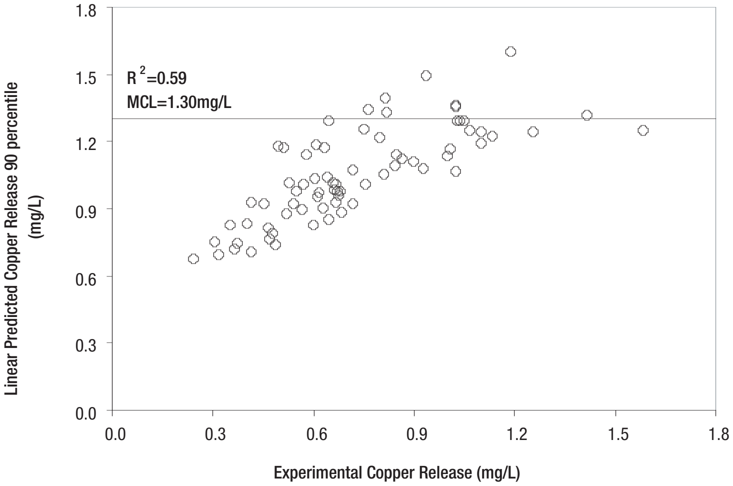

Figure 1: Actual versus predicted 90th-percentile copper concentrations using linear model

Samples were collected after a six-hour standing period once a week. Dissolved oxygen, pH, alkalinity, calcium, magnesium, silica, copper, and lead were monitored in and out of each loop.

Statistical Model Development

Water quality was changed every three months and 611 data points were collected over one year. The data was averaged by phase for each of the 18 loops and regressed to determine the influence of changing water quality on copper and lead concentration.

SigmaPlot™ software was used to develop linear and non-linear models at a 0.95 confidence interval (CI). The most insignificant water-quality parameter as determined by largest alpha value greater than 0.05 was discarded, and the regression was repeated until all parameters met a 0.95 CI. The same procedure was used for non-linear models. Dixon's Q test was used to decide the outlier pickup (21).

Results and Discussions

Statistical Model Development

The resultant linear and non-linear predictive models for 90th-percentile copper concentrations (copper violation) as a function of water quality are shown in equations (1) and (2). The units for the independent variable are: [Cu] total mg/L copper, mg/L alkalinity as $CaCO_3$, temperature as °C, mg/L sulfate, and mg/L silica as SiO_2. The range of the independent variables used to develop these models is shown in **Table 3**. Caution should be taken when applying these models outside the range of the independent variables shown in these models.

Linear Model

$$(1) \quad [Cu] = 7.48 + 0.0034 \text{ x Alkalinity} - 0.85 \text{ x pH}$$

Non-linear Model

$$(2) \quad [Cu] = 0.28 + \text{Temp}^{0.72} \text{ x Alkalinity}^{0.72} - \text{pH}^{2.86} \text{ x } (SO_4^{-2})^{0.10} \text{ x } SiO_2^{-0.72}$$

The linear and non-linear models both indicate that copper will increase as alkalinity increases and pH decreases. Temperature, sulfate, and silica were not significant in the linear model but were significant in the non-linear model. The non-linear model predicted copper concentration increases with increasing temperature and sulfate and decreasing silica. Increasing pH and silica were observed to decrease copper concentration for the conditions of this investigation.

As noted previously, these predictive equations should be used with caution outside the experimental range of the independent variables in equations (1) and (2). These variables undoubtedly affect dissolved copper concentration, but their effect on total copper is difficult to theoretically predict because of the effects of particulate copper. Hence, there was not much statistical difference between these two models.

The predicted copper release using the linear and non-linear models versus the actual copper released is shown in **Figures 1 and 2.** The coefficient of error (R2) for the linear and non-linear models was 0.59 and 0.57 respectively. While R2 is not high for these models, the independent variables shown to increase copper in the models have been shown to increase copper in the TBW MG copper samples and in other national works, and can be used by the MGs to proactively control copper release (2, 5, 7).

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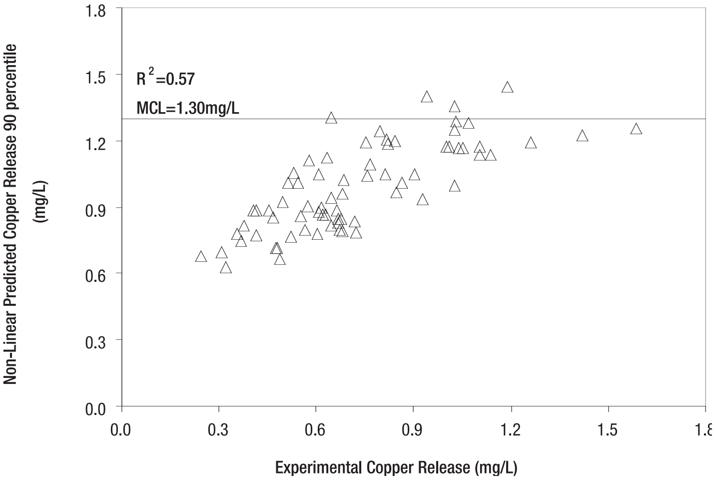

Figure 2: Actual versus predicted 90th-percentile copper concentrations using non-linear model

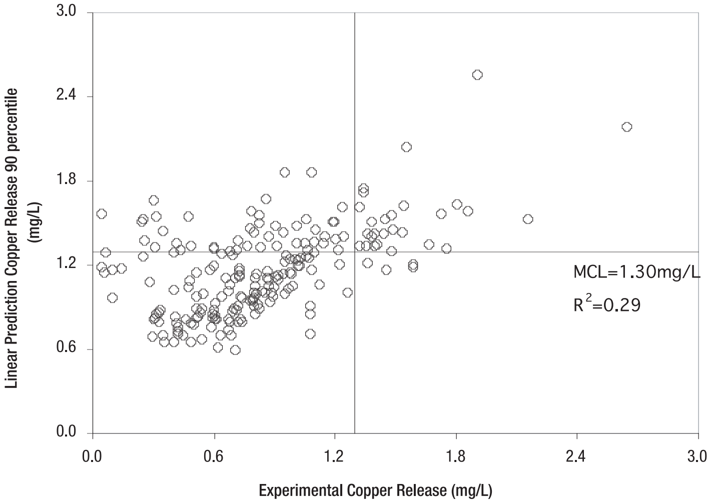

Figure 3: Verification plot of linear model

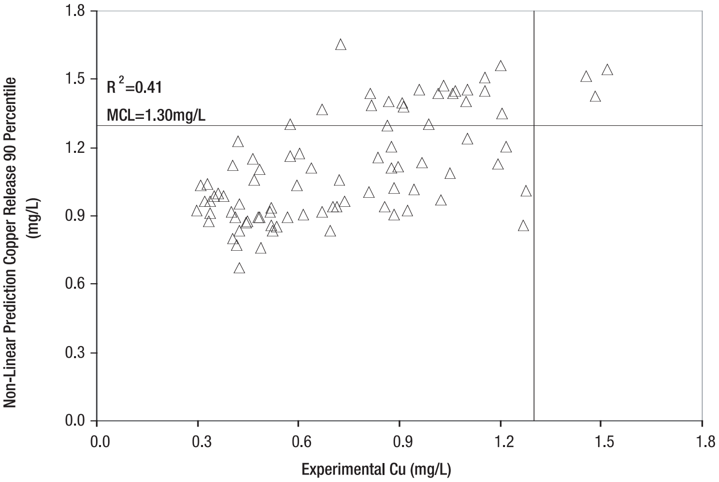

Figure 4: Verification plot of non-linear model

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Verification of Predictive Models

Model verification was done using data that was not used for model development. This data was collected over a six-month period following the one-year period of data collection. The predicted versus the actual copper concentrations during the verification phase are presented in **Figure 3 and 4** for linear and non-linear models, respectively.

The linear model error (predicted Cu minus actual Cu) was less than the error for the non-linear model. As shown in Figure 3, the linear model over-predicted actual copper concentrations in the lower range of the data set and under-predicted in the higher range. There was no such deviation for the predicted copper concentrations using the non-linear model. There was no statistical difference between the predicted and actual values for both models; consequently, both models were verified statistically.

Simulation of Copper Rule Compliance

The effect of blended water quality on copper concentration was assessed graphically for blends of G1, S1, and RO. The resulting ternary plots are shown in **Figure 5 and 6** using the linear and non-linear Cu models. These plots provide a desktop estimation of 90th-percentile copper concentrations for any combination of ground, surface, or RO finished water based on the water quality in **Table 2.** The Ternary plots can be read as follows:

1. Within the ternary plot region, the summation of three-source water ratio is 1.0, and any point represents a unique blend.
2. Assume a blend of 62 percent G1, 27 percent S1, and 11 percent RO.
3. Locate 0.62 on the G1 Ratio axis.
4. Draw a line parallel to the S1 axis that passes through the 0.62 G1 Ratio point. Note the parallel axis will always be the first axis that is clockwise to the axis containing the blend ratio point. Circular arrows have been inserted in Figure 5 to illustrate the location of the reference axis for drawing the parallel line. Hence, S1 is clockwise from G1 and is the parallel axis of reference for this line.
5. Locate 0.27 on the S1 Ratio axis.
6. Draw a parallel line to the RO Ratio axis that passes through the 0.27 S1 Ratio point. The intersection of these two lines defines the predicted 90th-percentile copper concentration for this blend using the linear model to be 1.51 mg/L, which violates the copper action level.
7. Locate 0.11 on the RO Ratio axis.
8. Draw a parallel to the G1 axis through the O.11 RO Ratio axis point (the intersection of this line passes through the 1.51 mg/L point found in Step 6 and confirms the graph was used correctly).

This procedure can be used to develop and predict singular water-quality parameters for any combination of blended water quality from three sources, given the models for prediction of water quality are available. The desktop technique can easily be used by engineering, scientific, operational, regulatory, and managerial personnel to manage water quality proactively.

Conclusions

- A method of managing distribution-system water quality proactively for controlling copper concentrations has been illustrated. This method can be used by the water community to predict the effect of blending three different finished waters on any water-quality parameter, given the models are available.
- Linear and non-linear models for predicting the 90th-percentile

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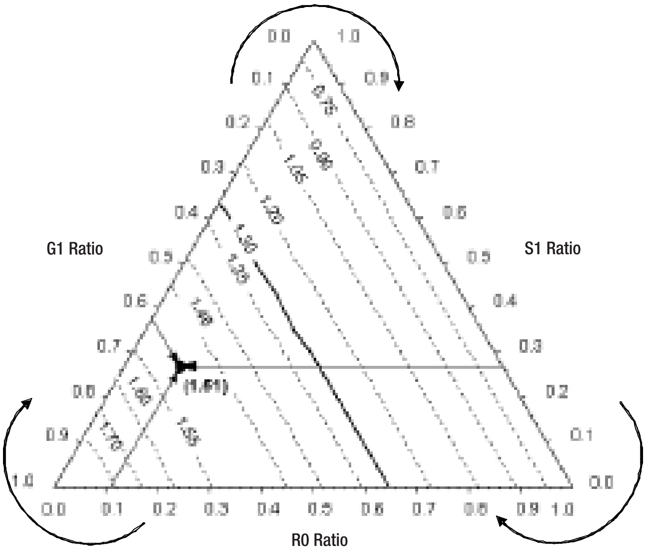
Figure 5: Ternary diagram showing predicted 90th-percentile copper concentration for blends of finished ground, surface and desalinated water using linear model//



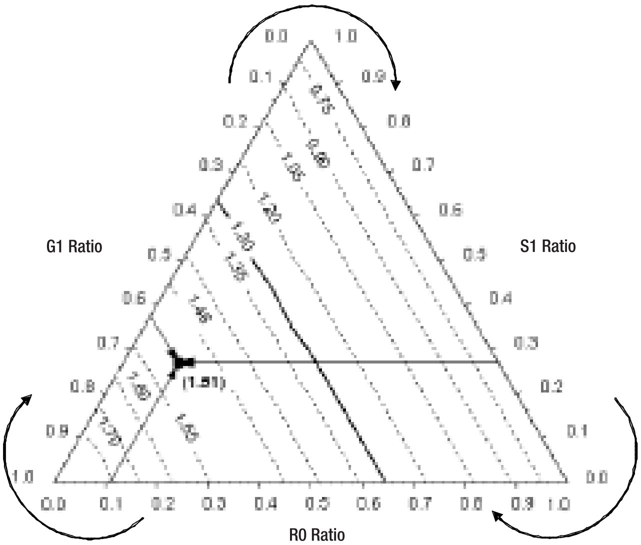


Figure 6: Ternary diagram showing predicted 90th-percentile copper concentration for blends of finished ground, surface and desalinated water using non-linear model

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copper concentrations were developed for varying water quality produced by blending finished groundwater, surface water, and RO water.

- Both linear and non-linear models revealed lower pH enhances copper release, higher alkalinity produces higher copper release.
- The non-linear model indicated high sulfate and temperature corresponds to higher copper release, while silica can inhibit the copper release.
- Sensitivity analysis indicated the copper action level would be violated for some blends. The predicted violation was due primarily to high alkalinity.

Acknowledgements

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