

The implementation of groundwater conservation measures has forced utilities with a historical reliance on groundwater sources to consider alternative sources to augment their supplies or to eliminate their groundwater dependence. Switching from traditional source water, however, can cause unacceptable changes in water quality that result from destabilization and the release of chemical and biological films from the interior surfaces of the existing distribution systems. Data from a two-year study were used to identify significant water quality parameters and to develop a predictive nonlinear model to estimate the corrosivity of blends based on water quality. The results of the statistical analysis indicate that alkalinity, chlorides, sulfates, sodium, and dissolved oxygen of the source water or blend of source waters have a significant effect on release of corrosion by-products in the form of red water. Temperature and hydraulic retention time were the significant physical and operational parameters identified.

Red Water Release in Drinking Water Distribution Systems

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Tampa Bay Water (TBW) is a regional water supplier in Florida that serves nearly two million consumers distributed over six member governments. TBW has historically relied on groundwater sources to meet its 250 mgd (946 ML/d) average daily demand. To reduce dependency on a single source and to protect the aquifer and the surrounding environment, the Southwest Florida Water Management District and TBW agreed to a series of groundwater withdrawal reductions. This plan required TBW to develop other sources of drinking water. As part of the first phase of the plan, a surface-water treatment plant and a desalination plant were constructed. To evaluate whether the introduction of new source waters, blends of source waters, or both could cause unacceptable changes in water quality in the existing distribution systems, the University of Central Florida (UCF) conducted a pilot-scale research study under the aegis of the AWWA Research Foundation (AwwaRF).

Water quality changes in drinking water distribution systems occur as a result of complex and often interrelated physicochemical and biological processes



A full report of this project, *Effects of Blending on Distribution System Water Quality (91065F)*, will be available in early 2006 as a downloadable PDF file from the AWWA Bookstore (1-800-926-7337) or from awwa.org/bookstore. Reports are free and currently available to AwwaRF subscribers by calling 303-347-6121 or from www.awwarf.org.

(Hedberg & Johansson, 1987). The mineral composition of the source water usually determines whether adverse conditions (conditions that will lead to corrosion and subsequent deterioration of quality) exist within the distribution systems (Pisigan & Singley, 1987). Biological conditions are also inextricably linked to the mineral contents of the source water (Carter et al, 2000; Fransolet et al, 1988). As a result, the effect of the chemical composition of the source water on the quality deterioration within the distribution system must be evaluated.

Historically, the main focus has been on the calcium carbonate (CaCO_3) solubility of the source water. Water slightly oversaturated with CaCO_3 will precipitate a

iron distribution systems is a function of a variety of water quality and flow characteristics. These parameters are usually interlinked by a complex relationship. For example, an increase in calcium hardness, pH, and alkalinity may be a mitigating factor in corrosion, whereas chlorides, dissolved oxygen, sulfates, and residual chlorine may increase the iron uptake in the distribution systems (Singley et al, 1985). Pisigan and Singley (1984) conducted a series of corrosion tests on metal specimens in jars and in pipe loops. They used the data obtained from these tests to develop a nonlinear model in which the corrosion rate was modeled as a function of different water quality parameters. Corrosion-rate increases were correlated to increases in chlorides, sul-

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calcite layer on the pipe surface. This precipitate would protect the surface from subsequent contact with the water, thereby reducing corrosion. Based on this principle, a number of corrosion indexes have been developed, including the Langelier index (LI). The LI is popular among drinking water utilities and professionals as an indicator of the stability of source water. A negative LI indicates undersaturated water as well as possible removal of the passivating layer of CaCO_3 formed on the pipe surface. The general practice, then, is to maintain a positive LI. This can be achieved by increasing alkalinity, calcium, temperature, or pH (Singley, 1981). Usually pH is increased by adding sodium hydroxide (NaOH). Blending water from different sources changes the water quality and characteristics in a complex way. Studies have shown that waters considered individually stable with respect to CaCO_3 precipitation may become unstable when blended (Trussell & Thomas, 1971).

Research has also shown, however, that CaCO_3 solubility is not the only water quality aspect that corrodes distribution systems (Pisigan & Singley, 1985). A number of additional corrosion indexes have been suggested to characterize corrosion potential that are not specifically related to CaCO_3 solubility. The Larson ratio implicates chlorides and sulfates as contributors of corrosion. It has been observed that an increase in alkalinity could overcome the adverse corrosive effects of chlorides and sulfates (Larson & Skold, 1957, 1958).

Unlined cast-iron and galvanized-iron pipes are the major source of iron in the distribution system and thus a major cause of red water problems. Corrosion in cast-

fates, alkalinity, and dissolved oxygen. Decreases in corrosion rates were correlated to increases in calcium, saturation index, and time.

It is necessary to make a distinction between red water problems in distribution systems and the actual corrosion rate of the pipe material. Iron pipes will corrode to varying degrees under any water quality. During a period of usage, the chemical precipitates and other corrosion by-products that form on the internal surface of the distribution system reach a steady state. Changes in the source water quality can lead to disruption of this equilibrium and a significant deterioration in water quality. The water quality deterioration in iron pipes is related to the destabilization of the surface films resulting either from hydraulic effects or changes in source water characteristics. Sander et al (1997) note that the detailed mechanisms for pipe corrosion coupled to different water compositions are not well understood. A number of water quality parameters have been implicated for causing iron release in the distribution systems. These parameters include pH, dissolved oxygen content, organics and nutrient content, chlorine dose and dissipation, chlorides, sulfates, microorganisms, calcium, and metals concentration. It would be difficult to incorporate all of these mechanisms into a unified theory of corrosion in distribution systems. It is feasible, however, to analyze the corrosion by-products or by-product indicators and identify which parameter is statistically and mechanistically significant. This analysis would help in evaluating blends based on water quality considerations for red water control.

MATERIALS AND METHODS

Pilot distribution system design. A pilot distribution system (PDS) was constructed at the TBW Cypress Creek well field, near Tampa, Fla., using pipes provided by the participating member governments. These pipes were transferred to the project site in a manner that would cause minimum disruption of the internal films and scales. The idea was to study the effect of the proposed changes on a PDS that could mimic the actual member government distribution system as closely as possible.

The PDS is composed of 18 different distribution lines. Lines 1–14 are hybrid lines made up of four different materials: polyvinyl chloride (PVC), unlined-iron, lined-iron, and galvanized-iron pipes. The average length of each hybrid line is 91 ft (27.7 m), of which 19 ft (5.8 m) is PVC, 19 ft (5.8 m) is lined iron, 13 ft (4 m) is unlined iron, and 40 ft (12.2 m) is galvanized-iron pipe, in that order. The PVC, lined-iron, and unlined-iron pipes are 6 in. (0.15 m) in diameter and the galvanized-iron pipe is 2 in. (0.05 m) in diameter. Line 15 is composed entirely of unlined-iron pipe. Similarly, lines 16, 17, and 18 are composed of lined-iron, PVC and galvanized-iron pipes, respectively.

Once on site, the pipes were assembled and allowed to equilibrate with TBW groundwater over a period of five months (Cullen, 2002). After equilibrium was established, different water blends were introduced into the PDS. The project was divided into six 3-month phases. Similar blends were used in alternate phases to evaluate the effect of seasonal conditions on the PDS and related water quality.

Pilot source waters. The pilot-plant facility was constructed so that different source waters with different chemical characteristics could easily be produced. Table 1 shows the different pilot processes and their mode of production. The finished water qualities from these pilot processes were set to match TBW's existing or proposed future sources of water. The different blends evaluated in this study, which were chosen by TBW to model anticipated operations, are

shown in Table 2. Table 3 enumerates the water qualities for the different source waters. All of the source waters were chloraminated and stabilized to maintain a positive LI.

Pilot distribution system operation. The PDS was operated initially (in phases 1–3) at a five-day hydraulic retention time (HRT) to simulate dead-end conditions. The HRT was changed to two days during phases 4 and 5 to permit chlorine residual maintenance. Different source waters and their blends were introduced into the PDS by

TABLE 1 Mode of production of simulated source waters*

Source Waters	Production Method
GW	Aeration of CC raw groundwater representing historical groundwater usage
SW	Ozonation and subsequent treatment with biological activated carbon of Hillsborough river surface water coagulated with ferric sulfate, settled and filtered. This simulates the TBW surface water treatment facility.
RO	Reverse osmosis membrane permeate of CC raw groundwater, with addition of ocean salt to simulate desalination. This simulates the TBW reverse osmosis desalination plant.
G2	Lime softening of raw CC groundwater
G3	Lime softening of GW, SW, and RO water blend
G4	Nanofiltration of GW, SW, and RO water blend
S2	Nanofiltration of Hillsborough river surface water coagulated with ferric sulfate, settled, and filtered

*All waters were stabilized to positive Langelier index and chloraminated.

CC—Cypress Creek, GW—groundwater, RO—reverse osmosis, SW—surface water, TBW—Tampa Bay Water

TABLE 2 Blends used for different PDS lines over the period of the study

PDS	Phase 1 and 3 Water Makeup—%	Phase 2 and 4 Water Makeup—%
1	100 GW	100 G2
2	100 G2	100 GW
3	100 SW	100 S2
4	100 G4	100 G3
5	100 RO	100 SW
6	55 GW, 45 SW	68 GW, 32 RO
7	68 GW, 32 RO	55 GW, 45 SW
8	23 GW, 45 SW, 32 RO	60 GW, 30 S2, 10 RO
9	60 GW, 30 SW, 10 RO	23 GW, 45 SW, 32 RO
10	50 G2, 50 SW	62 G2, 24 SW, 14 RO
11	61 G2, 24 SW, 14 RO	50 G2, 50 SW
12	100 G3	100 G4
13	100 S2	100 RO
14	23 GW, 45 SW, 32 RO	60 GW, 30 SW, 10 RO

G2—lime softening of raw Cypress Creek groundwater; G3—lime softening of GW, SW, and RO water blend; G4—nanofiltration of GW, SW, and RO water blend; GW—groundwater, PDS—pilot distribution system; RO—reverse osmosis; S2—nanofiltration of Hillsborough river surface water coagulated with ferric sulfate, settled, and filtered, SW—surface water

dosing pumps that feed individual influent standpipes for each line. The lines were flushed once a week during the five-day HRT period and once every two weeks for the two-day HRT period. The flush velocity was 1.0 f/s (0.3

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m/s) for at least three pipe volumes. Sampling for a number of water quality parameters was conducted once a week at the influent and effluent standpipes.

Water quality measurements. Samples were collected and analyzed in the field and at the UCF laboratory. Blind duplicates and spikes were used to determine the accuracy of measurements, and dynamic control charts were used to determine whether the results were acceptable.

STATISTICAL MODEL DEVELOPMENT

Red water releases in distribution systems result from a complex interrelation of physical, chemical, and biological effects. Empirical models offer a robust tool for predicting the effect of influent water quality on the changes within the distribution systems. To evaluate the effect of water quality

on red water release in the distribution system, a nonlinear regression model was developed. Analysis of variance (ANOVA) was used to identify the parameters that have significant effect as predictors of change in apparent color (measured in *cpu*). The change in apparent color, rather than total iron, was used as the dependent variable because investigators observed that the total iron was in particulate form and had a strong correlation to the apparent color. A high correlation between apparent color and total iron (Figure 1) indicates that apparent color is an appropriate surrogate measurement for total iron under the conditions of this study. Apparent color was more convenient to analyze on a regular basis on the site using a spectrophotometer.

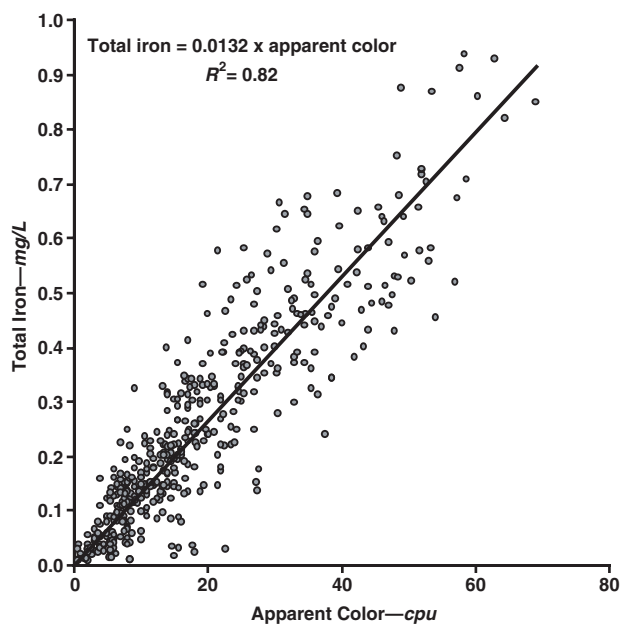
A balanced experimental design is necessary to avoid confounding effects among parameters. This can be achieved by evaluating different levels of chlorides, sulfates, alkalinity, and other water quality parameters in the source water for the PDS. Confounding in the database, however, complicated the resolution of the singular effect of each variable. Specific confounding effects of potential concern are noted between alkalinity and chlorides, alkalinity and sodium, alkalinity and sulfate, sodium and chlorides, and temperature and dissolved oxygen. These difficulties arise, for example, from the different characteristics of the sources (groundwater is high in alkalinity but low in chlorides), the requirement for electroneutrality (sodium is coupled with chlorides because sea salt is added to simulate desalination), and any seasonal effects (elevated temperatures are associated with low-dissolved-oxygen content). Any mitigation of corrosion-product release should also recognize the complexities and electroneutrality constraint associated with altering finished water chemistry.

TABLE 3 Average finished water quality values for simulated source waters

Source Water	GW	G2	G3	G4	SW	S2	RO
pH	7.9	8.0	8.1	8.2	8.2	8.3	8.3
Alkalinity— <i>mg/L as CaCO₃</i>	207	93	63	88	59	67	68
Calcium— <i>mg/L</i>	84	33	34	34	51	26	28
Magnesium— <i>mg/L</i>	8	8	6	3	5	1	2
Sodium— <i>mg/L</i>	18	13	38	28	50	45	52
Chlorides— <i>mg/L</i>	30	22	48	41	35	70	92
Sulfates— <i>mg/L</i>	37	26	76	5	159	12	5
UV ₂₅₄ — <i>cm⁻¹</i>	0.074	0.065	0.056	0.031	0.038	0.030	0.024
Total iron— <i>mg/L</i>	0.05	0.01	0.01	0.01	0.05	0.03	0.01
Turbidity— <i>ntu</i>	0.5	0.2	0.3	0.1	0.3	0.2	0.2
Dissolved oxygen— <i>mg/L</i>	7.5	7.8	8.6	8.4	9.7	8.2	8.2
Apparent color— <i>cpu</i>	5	2	1	0	1	1	0
Total chlorine— <i>mg/L as Cl₂</i>	4.7	4.8	4.6	4.6	4.4	5.0	4.8
Conductivity— <i>μS/cm</i>	514	292	426	312	589	356	410

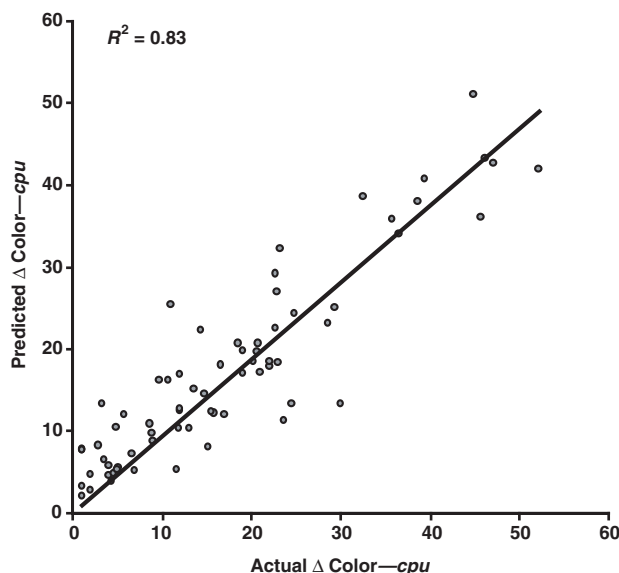
CaCO₃—calcium carbonate; Cl₂—chlorine; G2—lime softening of raw Cypress Creek groundwater; G3—lime softening of GW, SW, and RO water blend; G4—nanofiltration of GW, SW, and RO water blend; GW—groundwater; RO—reverse osmosis; S2—nanofiltration of Hillsborough river surface water coagulated with ferric sulfate, settled, and filtered; SW—surface water

FIGURE 1 Apparent color as a substitute for total iron measurement



Individual data pairs from phases 1–4

FIGURE 2 Model performance for average pilot distribution system response from phases 1–4



For the nonlinear modeling, water quality parameters analyzed during phases 1–4 of the study were used. Water quality for each area of the PDS was averaged over the respective phase, giving a total number of 70 data sets that were used in the modeling. Predictor water quality variables used were alkalinity, calcium, conductivity, pH, sulfate, chloride, sodium, silica, UV_{254} , dissolved oxygen,

sodium in mg/L, DO is the dissolved oxygen in mg/L, SiO_2 is the silica content in mg/L, UV is the UV_{254} in cm^{-1} , pH is the hydrogen ion activity in pH units, T is the temperature in degrees Celsius, and HRT_1 is the hydraulic retention time in days. The respective β_1 represent the least square estimate of the exponent of the i^{th} term in the model.

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temperature, and HRT. The dependent variable used was change in apparent color.

A full effects nonlinear model, involving all the predictor water quality variables, was selected as

$$\Delta C = \frac{10^{\beta_0} (DO)^{\beta_1} (Cond)^{\beta_2} \times (SO_4^{2-})^{\beta_3} (Cl^-)^{\beta_4} (Na)^{\beta_5} (T)^{\beta_6} (HRT)^{\beta_7}}{(Alk)^{\beta_8} (Ca^{2+})^{\beta_9} (SiO_2)^{\beta_{10}} (UV)^{\beta_{11}} (pH)^{\beta_{12}}} \quad (1)$$

in which ΔC is the difference in apparent color (cpu) between the feed and effluent from the PDS, Alk is the alkalinity in mg/L as $CaCO_3$, Ca^{2+} is the calcium in mg/L, $Cond$ is the conductivity in $\mu S/cm$, SO_4^{2-} is the sulfate in mg/L, Cl^- is the chlorides in mg/L, Na is

The F statistic (ANOVA) was used to determine whether dropping a term in the full model caused significant deterioration in model fit. The conventional process of eliminating nonsignificant variables could not be used because correlated parameters caused a confounding effect. Consequently, the investigators decided to evaluate all the combinations of the parameters to identify the best possible model. In all, 4,098 model combinations were evaluated, and the final model was selected based on the ANOVA.

RESULTS AND DISCUSSION

The empirical model selected is shown in Eq 2.

$$\Delta C = \frac{(Cl^-)^{0.485} (Na)^{0.561} (SO_4^{2-})^{0.118} (DO)^{0.967} (T)^{0.813} (HRT)^{0.836}}{10^{1.321} (Alk)^{0.912}} \quad (2)$$

TABLE 4 Variation in water quality parameters used in development of statistical model

Parameter	Minimum	Maximum	Average
Alkalinity—mg/L as CaCO ₃	51	210	106
Calcium—mg/L	23	88	50
Chlorides—mg/L	19	100	46
Sulfate—mg/L	4	232	60
Sodium—mg/L	12	65	35
Silica—mg/L	1	16	10
Dissolved oxygen—mg/L	6.9	12.2	8.3
UV ₂₅₄ —cm ⁻¹	0.0233	0.0688	0.0439
Conductivity—μS/cm	331	707	489
pH	7.8	8.4	8.1
Temperature—°C (°F)	16.8 (62.2)	27.0 (80.6)	23.5 (74.3)
Hydraulic retention time—days	2	5	

CaCO₃—calcium carbonate

The empirical model selected identifies alkalinity, chlorides, sulfates, sodium, dissolved oxygen, HRT, and temperature as the significant variables. Figure 2 shows the excellent correlation between the actual change in color and the one predicted by the model. The pseudo-*R*² is 0.83, which indicates that 83% of the variation in the data can be explained by the model. Contrary to con-

ducting a fifth independent phase of study. Phase 5 considered a wider range of alkalinity, chlorides, and sulfates than was available from phases 1–4 to support model development (Eq 2). The source waters were prepared by adding alkalinity in the form of sodium bicarbonate, chlorides from sea salt, and sulfates from calcium sulfate. The purpose of these additions was to simulate a par-

Alkalinity has a strong negative correlation to increase in color, but chlorides, sulfates, sodium, dissolved oxygen, temperature, and hydraulic retention time showed a positive correlation to increase in color. On the basis of the two-year pilot distribution system data, alkalinity greater than 80 mg/L as CaCO₃ seems to have a beneficial effect on reducing release of color.

ventional wisdom, calcium and pH were not identified as significant in the statistical model. The main reason for this omission is that all the waters were stabilized to achieve a positive LI. Stabilization of the source waters

resulted in a very narrow range of pH. The simulated source waters and the blends used in this study mimic either existing or planned changes in operation in the next few years. Thus a balanced design for determining the individual effects of the water quality parameters was incidental rather than planned. Table 4 gives the range of water quality parameters that were used in the nonlinear model development. The variation in the different water quality parameters during the two-year study encompasses a wider range than would be expected during blending of the different source waters. Application of the model, then, would not require extrapolation.

Model verification. The empirical model was verified by con-

TABLE 5 Analysis of variance table for verification of empirical model by independent data set from phase 5 of the study

Data Set	Degree of Freedom	Sum of Square Errors	Mean Square Error	F value
Phase 5	46	2250	48.9	=48.9/36.6
Phases 1–4	62	2270	36.6	1.34

ticular water quality rather than a specific process. An additional set of verification experiments was pursued using PDS lines 8–10, with blend changes every two weeks to adjust alkalinity within a range of 60 to 250 mg/L as CaCO₃. As Figure 3 shows, the performance of the model was consistent when verified on the independent data set from phase 5. To verify the hypothesis that the empirical model developed from phases 1–4 averaged PDS data (Eq 2) was applicable to independent data from phase 5, ANOVA was used (Table 5). The results indicate that there

is no significant difference between the performances of the model when it is used on an independent data set from phase 5.

MITIGATION

From the empirical model, the only water quality parameter that appears to be controllable with some success by chemical addition is alkalinity. The other parameters are inherent in the processes that produce the source waters. For instance, desalinated water will have an elevated chloride level that can be reduced only by modifying the desalination process. Surface water will have elevated sulfates that result from ferric sulfate coagulation. Temperature is based on seasonal

An empirical statistical model identified alkalinity, chlorides, sulfates, sodium, dissolved oxygen, temperature, and hydraulic retention time as being significant to change in apparent color in the hybrid pilot distribution system.

(and sometimes even diurnal) variations. HRT is governed by the dynamics of water demand. Figure 4 shows the response of the PDS to changes in alkalinity from phases 1–4 of the study. Alkalinity, however, shows an inverse relationship to the release of color. A clear line of demarcation can be seen at an alkalinity of 80 mg/L as CaCO₃; there is a drastic reduction in the release of color above an alkalinity of this level. With the exception of a few source waters (incidentally the ones high in sulfate and chloride; circled in Figure 4), waters with alkalinity greater than 80 mg/L as CaCO₃ tended to be less corrosive.

The empirical model developed from phases 1–4 as well as the verification data from PDS lines 1–6 and PDS lines 8–10 from phase 5 suggest that an increase in alkalinity is desirable to reduce the release of color. But chemical measures of alkalinity supplementation should be practiced with care. For instance, an increase in alkalinity resulting from the addition of sodium bicarbonate would also increase the sodium content of the water. On the basis of the empirical model, this corresponding increase in sodium may offset the intended benefit of increased alkalinity. Whenever feasible, alkalinity supplementation by blending with the high-alkalinity groundwater (>200 mg/L as CaCO₃) or the addition of lime plus carbon dioxide is recommended.

FIGURE 3 Verification of model by independent data from phase 5

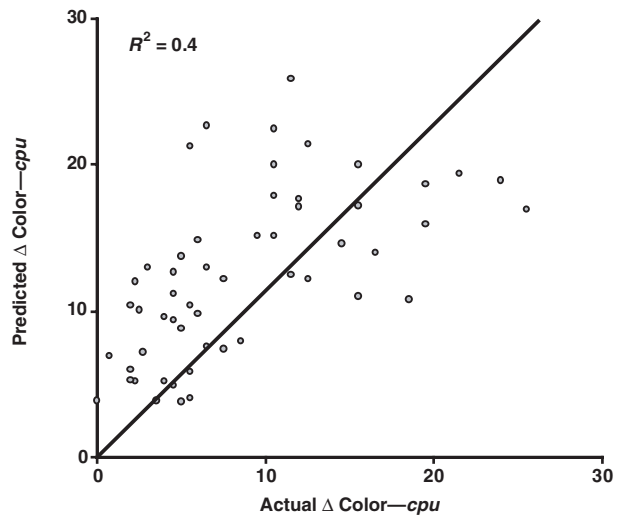
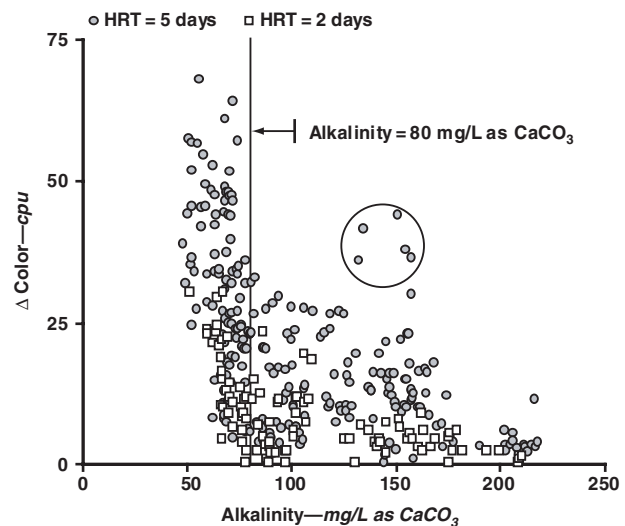


FIGURE 4 Dependence of color release on alkalinity of source water



CaCO₃—calcium carbonate, HRT—hydraulic retention time

Points enclosed within the circle identify waters with high sulfates (>100 mg/L) and chlorides (>40 mg/L)

CONCLUSIONS

Red water release in distribution systems, as measured by increase in apparent color, is caused by the release of corrosion products from unlined and galvanized-iron pipes.

An empirical statistical model identified alkalinity, chlorides, sulfates, sodium, dissolved oxygen, temperature, and HRT as being significant to change in apparent color in the hybrid PDS. Alkalinity has a strong negative correlation to increase in color, but chlorides, sulfates, sodium, dissolved oxygen, temperature, and HRT showed a positive correlation to increase in color.

Calcium and pH were not identified as significant variables during the statistical modeling, perhaps because all the waters were stabilized for CaCO₃ solubility.

The empirical model was verified with independent data from a subsequent set of experiments (phase 5).

Alkalinity is the only significant variable identified in this article that can be effectively controlled by chemical addition. On the basis of the two-year PDS data, alkalinity greater than 80 mg/L as CaCO₃ seems to have a beneficial effect on reducing release of color. Therefore, it is recommended that in addition to minimizing chlorides and sulfates (which may not always be possible because of production characteristics), alkalinity above 80 mg/L as CaCO₃ should be targeted.

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