Controlling Lead and Copper Rule Water Quality Parameters

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The Lead and Copper Rule (LCR), enacted in 1991, was implemented to reduce exposure to lead and copper at consumers' taps. Water suppliers were required to initiate treatment that would reduce corrosion in the distribution system and thereby limit the release of lead and copper. The LCR required the supplier to initiate this treatment, called optimized corrosion control treatment (OCCT), and to monitor for certain water quality parameters (WQPs) to demonstrate that the OCCT was in place. The intent of this study was to determine how well WQPs can be controlled at actual water treatment plants and in distribution systems. In general, the data analyzed in this study demonstrated that utilities can successfully control these parameters within certain ranges, but variability does occur. The use of control charts for monitoring and responding to demonstrated variability of these WQPs is also presented. The value of control charts in observing trends and reacting to variations where appropriate is described.

In an effort to reduce consumers' exposure to lead and copper in drinking water, the US Environmental Protection Agency (USEPA) promulgated the Lead and Copper Rule (LCR) in 1991 (USEPA, 2008). It required all public water systems to monitor for lead and copper on a routine basis, ranging from once every six months to once every nine years. Action levels (ALs) were established at 0.015 mg/L for lead and 1.3 mg/L for copper. If more than 10% of the samples tested exceed an AL, the water system must increase monitoring, undertake additional corrosion control efforts, and develop and implement training and public education for customers.

The treatment strategy chosen by the water system must optimize corrosion control and minimize the release of lead and copper. The optimized corrosion control treatment (OCCT) strategy is chosen by the water system and is ultimately approved by the state primacy agency.

Corrosion control is a complex, long-term process, and it was recognized that monitoring was needed to make certain that the process was in place. The continued use of the OCCT by the water system is verified through the monitoring of water quality parameters that are approved by the state primacy agency. These water quality parameters—such as pH, alkalinity, or dissolved inorganic carbon (DIC)—are not themselves indicators of corrosion. They are a set of conditions that would be present if the OCCT is in place (USEPA, 2003, 1992). The work described in this article sought to determine how closely these parameters could be controlled in actual practice.

Some of the details of the LCR were modified in 2000 and 2007, but the basic regulatory framework outlined here remains. USEPA is scheduled to propose the Long-Term LCR (LTLCR) revisions in 2016, and the final LTLCR will likely be promulgated two years later.

CORROSION CONTROL STRATEGIES

OCCT strategies used. A recent survey of large utilities (Brown et al, 2013) found that OCCT strategies implemented by water utilities for compliance with this regulation are generally limited to one of two choices—control of pH and alkalinity or the addition of orthophosphate-based corrosion inhibitor chemicals such as zinc orthophosphate, phosphoric acid, and similar products. Either strategy can be used when free chlorine or chloramines are used as the residual disinfectant. One benefit of using orthophosphate is that the optimal pH range is about 7.2–7.8, thereby avoiding the need to adjust and maintain the pH in the distribution system at pH 9 or higher, although pH control is still required.

Another control practice is maintenance of high (> 1 mg/L) free chlorine residual throughout the distribution system (Brown et al, 2013). The high level of chlorine can contribute to lead control by promoting oxidizing conditions necessary for the formation of insoluble lead IV (lead in the +4 oxidation state, Pb(IV)). In the presence of an orthophosphate residual and a stable free chlorine residual, existing Pb(IV) scale can be maintained, but the orthophosphate can limit the development of new Pb(IV) scale (Lytle & Schock, 2005.)

Water quality parameters monitored. To confirm that OCCT is being maintained, utilities monitor water quality parameters (WQPs) that typically include pH, alkalinity, and orthophosphate residual. Which WQPs are monitored depends on the OCCT selected. Alkalinity, pH, and DIC are interrelated, so if two are known, the other can be determined, assuming no ionic strength

effects. Free chlorine residual could also be useful to monitor to demonstrate conditions conducive to the formation and maintenance of insoluble Pb(IV) scale in the absence of orthophosphate. Other constituents or parameters related to lead and copper corrosion or characterizing the conditions leading to corrosion could conceivably include conductivity, oxidation reduction potential, and other measures, but in practice, pH, alkalinity, and orthophosphate residual are much more commonly used. WQP limits established by the primacy agency have included maximum only, minimum only, or ranges of values (Brown et al, 2013). They are sometimes seasonally adjusted depending on the parameter, the state's philosophy on setting WQPs, and the anticipated water quality variability. WQPs are monitored to demonstrate that the chosen OCCT is in place. These parameters are not in themselves indicators of corrosion.

Table 1 summarizes the current federal regulatory scheme for WQP monitoring in the LCR, as well as some additional reporting of these parameters typically required by states or other primacy agencies. The table also lists some voluntary monitoring of the treatment process or in the distribution system as needed for evaluation of process control.

Sources of variability in WQPs and other drinking water characteristics. There are many factors that can affect the characteristics of water in the distribution system. Some of these factors influence water quality prior to the entry point, such as changes in source water, changes in water quality through treatment chemicals, variability in chemical feed pump accuracy, control loops and instrumentation, and other aspects of treatment and storage. Other factors cause changes after the entry point, such as microbiological, chemical, and physical interactions between the water and distribution system materials and associated scale and biofilm coating these materials. Most of the WQPs are affected by factors both before and after the entry point. Some of the potential factors that can produce variability in WQPs are described next.

Source water quality changes. Variations in source water quality can occur for a number of reasons, including weather events, fluctuations in river flow, changes in groundwater pumping patterns, wind- and/or temperature-induced mixing in a reservoir, or changes in watershed activities. These and other events can all affect the pH and alkalinity of the source water. For example, the raw water alkalinity for one of the sources at Utility F routinely varies from about 40 mg/L as calcium carbonate ($CaCO_3$) to 80 mg/L. Source waters also vary in their buffering capacity; those with limited buffering capacity could exhibit greater variability in pH over time as conditions change.

Another contributor to water quality variability is the use of different blends of source waters, particularly if these are fed into the distribution system at multiple entry points. This includes not only effects attributable to differences in source waters (e.g., multiple surface water and groundwater sources), but also variable contributions from these sources during different times of the year. These effects are compounded when seasonal variability of the different source waters is also factored in. In this situation, there are an infinite number of microblends of water that occur depending on the distance from each entry point, the variable flow rates from each entry point, the characteristics of the different sources, and the storage and pumping characteristics of the distribution system.

Analytical methods. WQPs such as pH and alkalinity are monitored through grab-sample or on-line instrumentation. Utilities use standard analytical methods for these analyses, but there is inherent variability in analytical techniques. For example, SM 2320 B, a titration method for analyzing alkalinity, states that a standard deviation of 5 mg/L and a bias of 9 mg/L can be expected in analyzing samples in the ranges reported by water utilities (*Standard Methods*, 2012). In actual use, on-line instrumentation can experience drift and report more variable data between system calibrations as a result of clogging in the feed lines, the instruments themselves, or power surges.

Variations caused by water treatment process. Treatment of source water using chemicals will obviously result in changes in WQPs such as pH and alkalinity. In some cases, utilities treat the water specifically to change these parameters, but in other situations the pH or alkalinity can be changed through the addition

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TABLE 1   Regulatory requirements for reporting WQP information and routine monitoring performed for process control

Information Dissemination	WQP	Lead and Copper

Federal LCR	Initial (for ≥1 year)
	  Tap samples every six months
	  Point of entry(ies) every two weeks
	Reduced
	  Annual or triennial
		Initial
		  Every six months
		Reduced
		  Annual or triennial < 3,300 population
		  Waiver available (nine years)

Routinely reported to state	Monthly reports include daily grab-sample or summary data, in some cases including WQP data. All process data are stored and are available to the state.	Compliance samples per sampling plan are used to calculate performance versus action level. All "LCR compliant" samples must be provided to the state.

Routinely monitored for process control	At WTP:
	  On-line instruments and/or grab samples each day or more frequently
	In the distribution system:
	  Grab samples in course of TCR or other sampling
		The revised LCR (2007) discourages collection of additional lead samples.

Source: USEPA, 2008

LCR—Lead and Copper Rule, TCR—Total Coliform Rule, WQP—water quality parameter, WTP—water treatment plant

of chemicals for other treatment objectives. For example, the addition of alum for coagulation can result in a change in water's pH and alkalinity. There is often variability in the feed rate of treatment chemicals in a water plant, particularly when water flow rate also fluctuates. Chemical feed pumps themselves have inherent variability, especially between calibration events. Process changes in response to system demands require process control systems to change chemical feed systems through process control feedback or feed-forward loops that can be a source of variability in the final feed concentration. In addition, equipment is prone to mechanical and electrical failure that can interrupt the chemical feed, causing fluctuations in the measured levels of constituents. The composition of the feed product can vary as a result of changes in manufacturing process or raw materials as well as vendor quality control. This type of process variability could affect the WQPs of interest here (pH, alkalinity, and phosphate dose) if these parameters are being adjusted by treatment.

Distribution systems impact on water quality. Once the treated water exits the water plant and enters the distribution system, many factors can result in variability in the monitored WQPs. Chemical and biochemical reactions will occur between the pipe and other parts of the distribution system infrastructure, including biomass and scale coating these materials, as well as other constituents in the water. The latter can include conflicting effects of multiple treatment chemicals added prior to the entry point. Some chemicals consume alkalinity and lower the pH; other treatment chemicals do the opposite. Similarly, there is a variety of analogous factors affecting orthophosphate residual. For example, excess aluminum residual from improper dosage and pH control for alum can result in precipitation of aluminum orthophosphate solids and consequent reduction of available orthophosphate residual.

Consequently, even when a water system has developed and implemented proper practices to monitor and control measured levels of different constituents and parameters in the water provided at entry points as well as within all parts of the distribution system, there is some amount of normal variation to be expected even under the best circumstances. The data analysis provided here illustrates this variability at a few typical water systems. Management data-monitoring tools that account for inherent variability are also proposed, thereby allowing the water system to identify the boundaries of inherent variability (acceptable performance) while also flagging values outside these boundaries (unacceptable performance).

EVALUATION OF UTILITY WQP DATA

As noted earlier, the current LCR is being revised. To support the revision, a study was undertaken to determine how well utilities have been able to meet the existing WQP requirements. Six water systems labeled A through F voluntarily provided data for evaluation as part of this effort. Characteristics of these water systems are summarized in Table 2. All of these systems serve populations of 1 million or more, and all but one uses surface water for their source. Each of the six varied in its choice of OCCT and the level of treatment needed to implement its chosen OCCT. Each of the utilities also had varying WQP monitoring requirements that were mandated by its primacy agency, all of which are listed in Table 2. In addition, each of the utilities adopted treatment goals based on these WQP requirements, as shown in Table 2.

One of these systems uses pH and alkalinity to control corrosion in the presence of free chlorine (therefore, some Pb(IV) could be present), two systems use pH and alkalinity with chloramines, one uses orthophosphate and free chlorine, and the other two systems use chloramines and orthophosphate. System

TABLE 2	Utility corrosion control strategies, WQP requirements, and treatment goals				
System	Corrosion Control Strategy and Treatment	Required WQP	Treatment Goal	Residual Disinfectant	Source
A	pH and alk. adjustment	Min. pH 9.0 in distribution system, min. alk. 37 mg/L	Min. pH 9.3, alk. 40 mg/L	Chloramines	Reservoir
B	pH and alk. adjustment	Min. pH 7.5, min. alk. 15 mg/L	pH 7.7–7.8, alk. > 15 mg/L	Chloramines	
Source 1, 2, 3	pH adjustment with sodium hydroxide				Reservoir
Source 3	Some alk. adjustment with lime				
C	pH and alk. adjustment, Pb(IV)			Free chlorine	
Source 1	pH adjustment with sodium hydroxide	Min. pH 8.0 at entry point	pH 8.6		River
Source 2	pH adjustment with lime No alk. adjustment	Min. pH 8.8 at entry point	pH 9.2		Groundwater
D	Phosphate addition pH adjustment with sodium hydroxide	Target pH at entry point 7.2–7.3, pH 6.8–8.2, PO_4 1–4 mg/L	7.2 pH, PO_4 2 mg/L	Free chlorine	Reservoir
E	Phosphate addition pH adjustment with lime or sodium hydroxide	Min. pH 7.2, dissolved PO_4 0.5–5.0 mg/L	pH ≥ 7.4 ≤ 8.0, dissolved PO_4 1.0–4.5 mg/L	Chloramines	River
F	Phosphate addition	PO_4 1.0–2.0 mg/L	pH 7.1 at entry point	Chloramines	
Source 1, 2, 3		pH 6.5–7.9	pH 6.9 distribution system $ZnPO_4$ 1.5 mg/L Zinc 0.12 mg/L		River

alk.—alkalinity, min.—minimum, Pb(IV)—lead in the +4 oxidation state, PO_4—phosphate, WQP—water quality parameter, $ZnPO_4$—zinc phosphate

B includes three sources referred to as sources 1, 2, and 3. However, because water from sources 1 and 2 are similar, only data from distribution system locations representative of water mostly originating at source 1, mostly originating at source 3, or possible blends of sources 1 and 3 are presented. System C includes distribution system samples representative of its two sources, plus an interface zone between the two.

All three WQP data were not collected from each system. All six provided pH data. System C did not provide alkalinity data because it is not a requirement to monitor this WQP at that utility. And only the three utilities (D, E, and F) that add phosphate reported phosphate residual data. When one considers the variability discussion that follows, it is important to note which parameters a specific utility was actually trying to control. All of the utilities controlled pH, three fed and controlled phosphate, and two controlled alkalinity. From these data, several assessments were developed:

• How variable were the monitored results of their WQPs?

• Was there an effect on this variability attributable to data-collection frequency?

• Was there an effect on this variability attributable to grab-sample versus continually recorded data?

• Was there an effect on this variability attributable to sample-collection location (distribution system versus tap samples)?

RESULTS

The data obtained from the six utilities included data collected by two methods. Some data were from grab samples and other data came from continuous on-line analyzers at entry points and distribution system monitoring points. These datasets include two to three years of data. The continuously recorded on-line data were typically recorded in 15-min increments.

The individual data from the six sites were analyzed to assess how well each utility was able to "control" its WQPs. Figures 1, 2, and 3 summarize the variability of individual pH, alkalinity, and orthophosphate residual data from these systems during two- to three-year periods. Samples were collected either from one or more distribution system entry points, distribution system locations representative of water primarily from one source, or distribution system locations representative of blends of two or more sources.
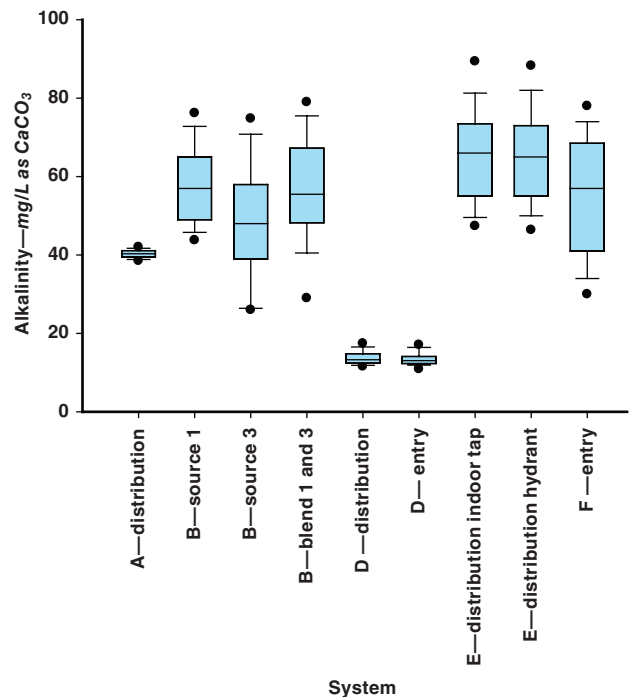

FIGURE 1   Range of pH data from six systems*
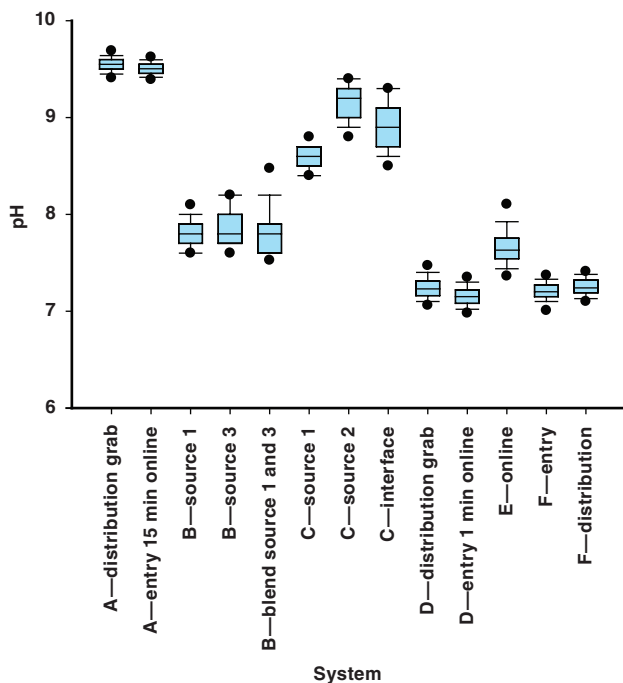
*Three years of data for all systems with the exception of two years for system F

These data are presented as box-and-whisker plots, with upper and lower boundaries of the blue box representing 75th and 25th quartiles, the line in the middle of the box representing the median (i.e., 50th percentile), the whiskers extended above and below the box representing 90th and 10th percentiles, and black circles representing fifth and 95th percentile values.


FIGURE 2   Range of alkalinity data from five systems*

CaCO₃—calcium carbonate

*Three years of data for all systems with the exception of two years for system F

These data are presented as box-and-whisker plots, with upper and lower boundaries of the blue box representing 75th and 25th quartiles, the line in the middle of the box representing the median (i.e., 50th percentile), the whiskers extended above and below the box representing 90th and 10th percentiles, and black circles representing fifth and 95th percentile values.

FIGURE 3   Range of orthophosphate residual data*

P—phosphorus

*Three years of data for systems D and E, two years of data for system F

These data are presented as box-and-whisker plots, with upper and lower boundaries of the blue box representing 75th and 25th quartiles, the line in the middle of the box representing the median (i.e., 50th percentile), the whiskers extended above and below the box representing 90th and 10th percentiles, and black circles representing fifth and 95th percentile values.
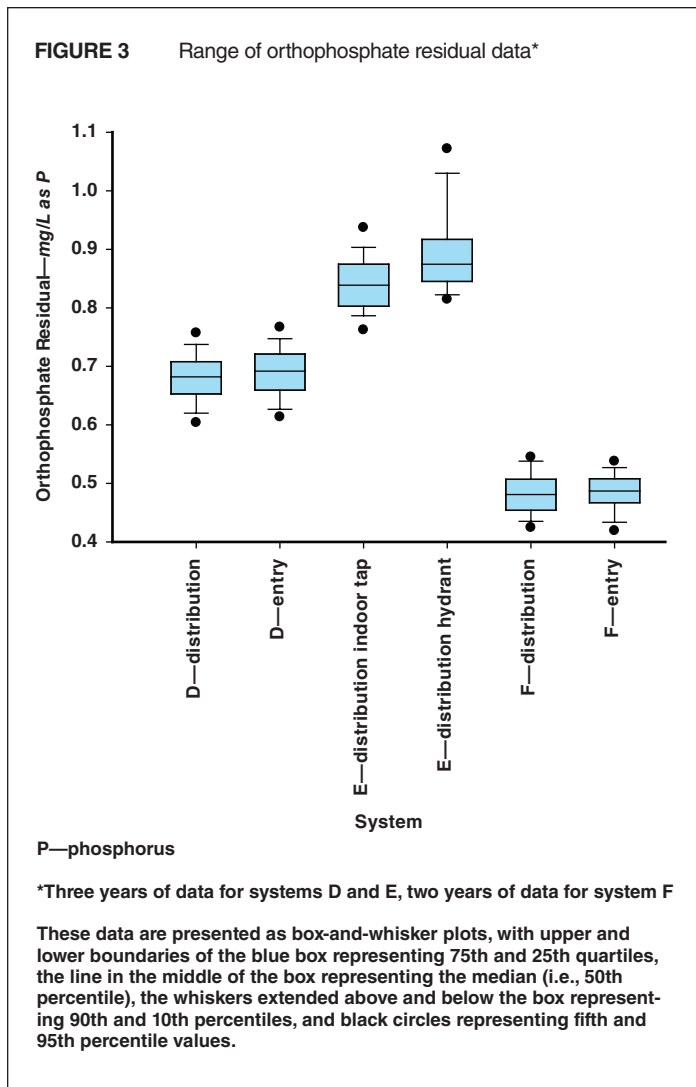
Figures 1, 2, and 3 display the data in whisker plots. Data from each system are shown, and data from all sampling locations for each of these utilities were combined for this analysis. Through the use of whisker plots, some important characteristics of the datasets can be observed. The median is shown, along with the extent of the variability as indicated by the 95th and fifth percentile values. These three figures demonstrate that for these three WQPs, the range of measured values varied by utility and by parameter. For example, as seen in Figure 2, alkalinity did not vary significantly over time in systems A and D but did vary in systems B, E, and F. Only systems A and B had alkalinity-control requirements, and both specified only a minimum alkalinity. Similar observations can be made for pH and phosphate residual, as shown in Figures 2 and 3. However, as described next, this variability is still within the utility's WQP requirements.

System A uses high pH and low alkalinity to control lead and copper corrosion. The pH for this system was shown in Figure 1 to occur within in a fairly narrow band, with about 97% of the results between the median (9.55) ± 0.15. Alkalinity also was recorded in a fairly narrow band, with a median value of about

40 mg/L as $CaCO_3$. Greater than 99% of the results were ± 3 mg/L as $CaCO_3$ from the median.

System B uses pH and alkalinity adjustment for its OCCT. It must maintain a minimum of 7.5 pH and 15 mg/L alkalinity. The two sources for system B used in these data analyses vary in some of their water quality data. The alkalinity for source 3 in Figure 2 is slightly lower than in source 1, and the blend is about the same as source 3. The pH for all three sets of locations is about 7.8 ± 0.4, but it can be seen in Figure 1 that the blended locations experience a wider variation than the locations receiving exclusively source 1 or 3.

The two sources for system C have about a 0.6 difference in the median pH, and the pH of the interface zone falls between the pH of the two sources. This variability is expected in that the two sources, as indicated in Table 2, have different treatment pH goals and pH adjustment methods.

Systems D, E, and F all use orthophosphate. Optimal pH for orthophosphate is about 7.2–7.8. The median pH values at systems D and F are about 7.2 and system E is at 7.6. Although all have median orthophosphate residuals exceeding 0.4 mg/L as phosphorus (1.2 mg/L as phosphate), System E is highest (~ 0.88 mg/L as phosphorus), system D is about 0.68 mg/L as phosphorus, and system F is about 0.48 mg/L as phosphorus. System E's treatment goal is 0.3–1.5 mg/L, system D's goal is 0.7 mg/L, and system F's goal is 0.3–07 mg/L, so the three systems' data are well within their operational goal ranges.

Tables 3, 4, and 5 show the same data in tabular form. In these tables, the medians of the datasets are shown for the three WQPs studied. Also shown are the percentages of sample points that are within set tolerance limits of these medians. For example, Table 3 shows that for system A, 105,211 data points were collected from on-line instruments for pH. The median of all of these data is pH 9.51. Further, 100% of the pH data from this location was within ± 0.5 pH units, and 83.9% of the data points were within 0.1 pH units.

DISCUSSION

pH. The pH of distributed water is an important metric in OCCT monitoring. However, unlike orthophosphate or alkalinity, the numerical value of pH is a log transform of the hydrogen ion concentration (H^+). Therefore, mean and standard deviation values actually should be computed after the pH is converted back to H^+ rather than on the pH values themselves. However, median and percentiles can be used directly. When ranking values as needed to determine percentile values, such as 50th (median), 90th, or 95th, it is appropriate to use either pH or H^+ (though the order will be inverted; i.e., x percentile H^+ will be equal to the negative log transform of the *100-x* percentile pH value; e.g., 10th percentile H^+ will equal 10^{-pH} for the 90th percentile pH value). In this analysis, median values were used for pH evaluation.

Table 3 summarizes the percentage of pH samples that fall within selected ranges of ± 0.1, 0.2, 0.5, 1, and 2 pH units of the median. More than 25% of the results from all locations at water system B, the interface and source 2 locations for system C, and the data presented for system E were more than ± 0.2 pH units from the median pH. The other water systems investigated were

TABLE 3 Number and percent of pH data within different tolerance limits of median from six systems

	System												
	A	A	B	B	B	C	C	C	D	D	E	F	F
	DS—on-line entry	DS—grab	DS—source 1	DS—source 3	DS—blend 1&3	DS—source 1	DS—source 2	DS—interface	Grab distribution	Grab entry	On-line	Distribution	Entry
Number of Samples													
Count	105,211	1,096	182	116	24	9,055	1,181	622	41,099	41,099	750	95	1,491
Median													
Median	9.51	9.55	7.80	7.80	7.80	8.60	9.20	8.90	7.23	7.23	7.63	7.20	7.24
Results Within Given Tolerance of Median—%													
± 0.1	83.9	81.2	46.7	44.8	41.7	81.9	41.4	33.0	60.4	60.4	47.3	73.7	70.4
± 0.2	99.1	98.6	67.0	64.7	54.2	89.4	70.1	42.6	89.9	89.9	74.0	94.7	96.0
± 0.5	100.0	99.9	98.4	98.3	91.7	99.8	96.3	94.4	99.5	99.5	93.1	100.0	100.0
± 1		100.0	100.0	100.0	100.0	99.9	100.0	100.0	100.0	100.0	96.8		
± 2											97.9		

DS—distribution system

All systems have a pH water-quality-parameter requirement (see Table 2).

TABLE 4 Number and percent of alkalinity data within different tolerance limits of median from five systems

	System										
	A*	B*	B*	B*	B*	B*	D	D	E	E	F
	Distribution	Source 1	Source 2	Source 3	Blend 1 & 2	Blend 1 & 3	Distribution	Entry	DS—hydrant	DS—tap	Entry
Number of Samples											
Count	1,094	35	19	23	12	24	799	36	35	35	309
Median Concentration—mg/L as CaCO$_3$											
Median	40	57	59	48	59	56	13	13	65	66	57
Results Within Given Tolerance of Median—%, mg/L as CaCO$_3$											
± 0.5	28.4	5.7	10.5	4.3	0.0	0.0	22.0	25.0	2.9	5.7	1.9
± 1	60.9	5.7	10.5	4.3	0.0	12.5	46.7	61.1	5.7	5.7	1.9
± 5	100.0	31.4	47.4	17.4	50.0	33.3	97.7	100.0	25.7	28.6	14.9
± 10		68.6	73.7	47.8	66.7	58.3	99.7		51.4	57.1	33.0
± 20		97.1	100.0	78.3	91.7	87.5	100.0		91.4	91.4	75.1

CaCO$_3$—calcium carbonate, DS—distribution system, WQP—water quality parameter

*Alkalinity is a required WQP; system has a minimum required.

able to demonstrate pH within ± 0.2 units of the median in more than 90% of samples. Overall, 90% of the data from all systems were within ± 0.5 pH units of the median. As noted earlier, some of the variability for systems B and C could be attributed to sample locations in the interface zones where the waters from different plants were mixed. These sources had different raw water quality and different pH treatment methods and goals.

Ranges displayed for pH data at system A, C (source 1), D, and F were fairly narrow. This may at least partially reflect the impact of evaluating more samples (see the "Count" row in Table 3). The narrow range may also reflect the system's operational target.

Table 2 contains the systems' requirements for pH value as a WQP—either as a range or as a minimum. All data from the six systems generally met these requirements. It should be noted, though, that the requirements for WQP values are typically set at the entry points. Much of the data in this study was collected from distribution-system sampling locations for which WQP requirements are not set. However, most of the data from the six utilities were well within the required ranges for WQPs, even though they were collected in the distribution systems.

The characteristics of the source and implementation of proper pH-adjustment practices prior to the entry points can also explain

some of the observed variability. The interface locations in system C reflect a wider range than locations identified as more representative of individual sources, as expected, because of different contributions from the two sources with different characteristics. In system B, the "blended" locations also have some wider pH variability than the locations representative of single sources. For the other system B locations, even though locations are identified as being solely from one source or another, it is possible that at some times of year there may be blending of the sources.

The chemical and feed system used at a particular utility may also explain some of the variability observed. For example, system C, source 1, uses sodium hydroxide to adjust pH but uses lime at source 2. It is possible that the wider range in pH readings from source 2 can be attributed to the different method of pH adjustment used. Also, source 2 water is softened and so the most important water quality target at that location is hardness, and pH is a secondary target.

Alkalinity. Table 4 and Figure 2 display alkalinity data similar to the way pH was shown in Table 3 and Figure 1. For Systems A and D, the alkalinity range shown in Table 4 and Figure 2 was narrower than for other systems. In these two systems > 98% of the data were within ± 5 mg/L as $CaCO_3$ of the median. This could be attributed to characteristics of the source water or to the larger number of samples used. Both of these two systems also adjust alkalinity as part of their OCCT strategy, while for other systems controlling alkalinity is not part of WQPs limits. It is possible that the data reflect good operational control and monitoring of their feed systems. For other systems, the median alkalinity was about 60 mg/L as $CaCO_3$ and at least 10-25% of the results were more than ± 20 mg/L as $CaCO_3$ from the median. Ninety percent of the data for each system were within 25 mg/L as $CaCO_3$ of the median. This variation is most likely attributed to variability in source waters during the year. For the systems that have WQP requirements for alkalinity, all data were within the prescribed ranges.

Orthophosphate. Table 5 and Figure 3 show the results for orthophosphate residual data for the three systems that add orthophosphate for corrosion control. As noted earlier, all have orthophosphate residuals above 0.4 mg/L as phosphorus (1.2 mg/L as phosphate). While the median values were different for these utilities, the variability was about the same—i.e., ~ 90% or more of the results were ± 0.1 mg/L as phosphorus from the median for a given water system. Because orthophosphate is present only when added for treatment, this narrow level of control is attributable to monitoring and control by operations staff at each water system.

Summary of pH, alkalinity, and orthophosphate. It is feasible that the degree of orthophosphate control mentioned earlier could be achievable by other water systems in addition to the three studied. However, because pH and alkalinity are affected by such a wide variety of conflicting factors, as described earlier, these parameters may vary over a wider range at systems with different sources, different combinations of sources throughout the year, and different seasonal water source characteristics. Therefore, although ± 0.5 for pH and ± 20 mg/L as $CaCO_3$ for alkalinity may have been achievable most of the time in the systems studied,

| TABLE 5	Number and percent of orthophosphate residual data within different tolerance limits of median for three systems					
	System					
	D	**D**	**E**	**E**	**F**	**F**
	Distribution	Entry	DS—hydrant	DS—tap	Distribution	Entry
	Number of Samples					
Count	41,104	1,093	35	35	95	321
	Median Residual—*mg/L as P*					
Median	0.68	0.69	0.87	0.84	0.48	0.49
	Results Within Given Tolerance of Median—*%, mg/L as P*					
± 0.1	96.4	96.1	85.7	94.3	98.9	99.1
± 0.2	99.9	99.8	97.1	100.0	100.0	99.7
± 0.5	100.0	100.0	100.0			100.0

DS—distribution system, P—phosphorus

it may not be appropriate to assume that other systems can meet these same limits if the source water varied in alkalinity levels.

Effect of data-collection frequency. Figure 4 depicts the cumulative distribution of on-line pH data recorded at 1-min intervals from one entry point location for one year (> 0.5 million data points). If 15-min intervals are used instead by ignoring all data except those recorded at 0, 15, 30, and 45 min after each hour, the number of data points is reduced by a factor of 15, but the median and data between the first and 99th percentile stay about the same. The median is about 7.15, and the 0.1th and 99.9th percentiles are about 6.75 and 7.62, respectively. Further reduc-

FIGURE 4   Continuously recorded pH data for one year at system D entry point
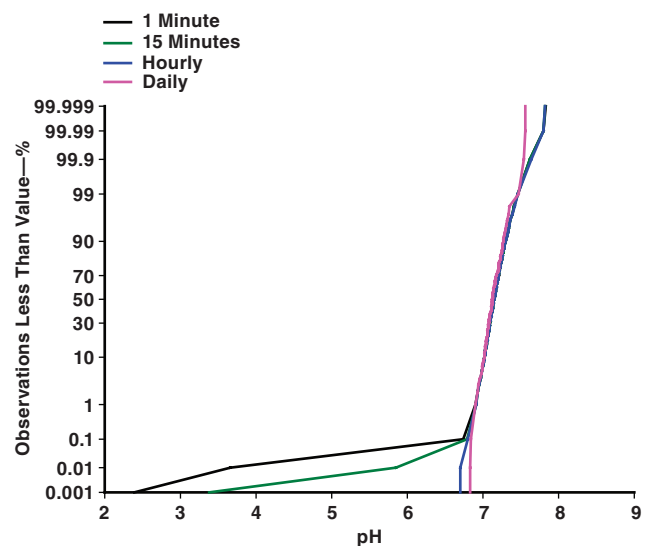
ing the frequency to hourly or daily samples provides nearly identical values for median and percentiles between 0.1 and 99.9%. Therefore, this analysis shows that the use of 15-min, 1-h, or daily data recording provides the same indication of central tendency and variability between 0.1th and 99.9th percentile as at 1 min and requires less data-storage capacity.

Monitoring pH or other parameters at greater frequencies can be useful for troubleshooting the system but only if the data are reviewed about as frequently as data are collected. For purposes of establishing the degree of variability of the data over time, such as to monitor WQP limits to see whether OCCT is being maintained, it may not be necessary to collect or record data as frequently as every 15 min or every minute.

Therefore, if the data are reviewed frequently or if alarms are used to bring operator attention to unusual values, more frequent monitoring can be useful to evaluate and troubleshoot a water system in real time as events are occurring. Although it must be recognized that some of the high or low data recorded on-line could be attributed to instrument error (see Figure 4), the data in this study indicate that when the goal is to characterize the performance and amount of variation of a water parameter, less frequent data recording may be sufficient to properly establish variability.

Grab-sample versus continually recorded data. When the daily grab-sample data for pH was compared with on-line data recorded at 1-min intervals, the results were nearly identical between the 0.1th and 99.99th percentiles. The median was 9.55, while 0.1th and 99.99th percentiles were 9.26 and 9.89, respectively. These results show that not only are less frequent data potentially as useful as more frequently recorded data for evaluating variation over time, but that grab samples and automatically recorded on-line data are potentially equally suitable for this purpose. Therefore, if the water system has automatic data-collection capability, it should not be necessary to also collect a separate set of grab samples for this purpose. Conversely, if a water system does not have automatically recorded data, it can successfully use grab-sample data for these purposes.

Distribution versus indoor tap samples. Figures 5, 6, and 7 compare median monthly grab-sample results from indoor tap locations with hydrant locations located near the tap. Data were collected monthly for each type at seven to 11 locations for three years. Figure 5 depicts pH, Figure 6 reports orthophosphate residual, and Figure 7 covers alkalinity. The results show that alkalinity data are about the same between the two groups, but that orthophosphate residual and pH values are both higher in the distribution system compared with the tap. Using Student's *t*-test, the difference in pH and orthophosphate residual between the tap and hydrant locations was statistically significant (p = .017 for pH and p = .0001 for orthophosphate) but that is not the case for alkalinity (p = .84).

The median pH in Figure 5 was about the same for both sampling locations—approximately 7.6—which is within the optimum range for systems using orthophosphate (~ 7.2 to 7.8 pH). However, about 10% of the pH tap location data was in the range between 7.2 and 7.4. The median orthophosphate residual in Figure 6 was about 0.87 mg/L as phosphorus at the hydrant, versus about 0.84 mg/L as phosphorus at the tap. About 30% of

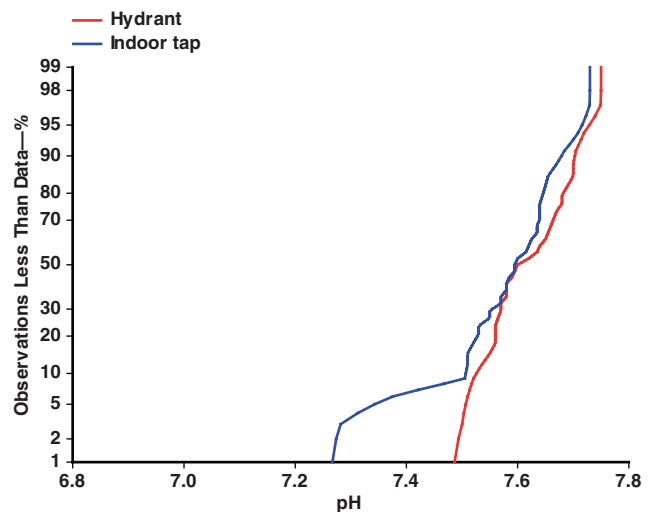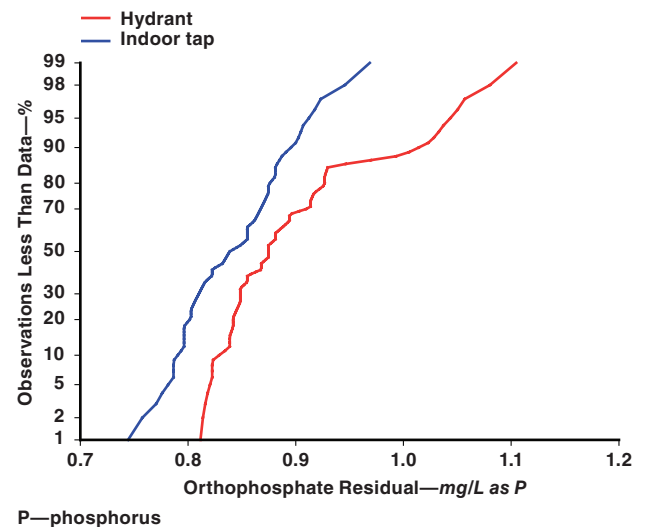FIGURE 5   Median monthly pH in system E distribution system from hydrants and indoor tap locations

FIGURE 6   Median monthly orthophosphate in system E distribution system from hydrants and indoor tap locations

P—phosphorus

the hydrant values were > 0.9 mg/L as phosphorus, but < 1% of the tap values were above this level. Although the pH and phosphate values were statistically different, all fell within an acceptable range for OCCT. The median alkalinity was about 65 mg/L as $CaCO_3$ at both sets of locations, with 80% of results between 50 and 80 mg/L as $CaCO_3$.

MANAGEMENT AND EVALUATION TOOLS

Use of control charts as a management monitoring tool. As discussed previously, regulatory limits for WQPs are often set as maximum, minimum, or ranges based on an evaluation by the

utility and state regulators of how best to monitor a specific OCCT. However, OCCT WQPs are not health parameters nor are they subject to health-based enforceable standards. Corrosion control is a long-term process for which months and years are required to achieve stability. The primary purpose of WQP monitoring is to allow the operator, as well as regulatory agencies, to determine whether the WQPs are being properly controlled to maintain OCCT conditions over a period of time. A limited number of values that are not within the target range for a parameter will not necessarily cause an OCCT to be upset. In fact, as discussed earlier, there is inherent variability in the parameters.

Control charts are statistical tools designed to accomplish monitoring and feedback on parameter variability within an acceptable range. The Shewhart control chart is a particularly appropriate tool (Grant, 1964). Shewhart control charts were developed primarily for managing manufacturing processes, and the stated objective is to separate out random variation, which is inevitable, and to allow the "diagnosis and correction of production troubles and to bring improvement to product quality" (Grant, 1964).

In the evaluation of drinking water treatment and distribution, control charts are designed to allow the plant operator to properly evaluate whether the WQPs are staying within an acceptable range, and if not, then the treatment and distribution system operation needs to be adjusted to bring the parameter back within goals. The charts are exactly aligned with the desired outcome of monitoring WQPs. Cantor et al (2012) described the use of control charts for reducing variability of WQPs. The approach in that project was to use what are referred to as individual data control charts. This can be a very useful approach. However, the use of individual data in control charts can result in the operator trying to control variability that is inherent to the process and, therefore, overreact by adjusting feeds too much (adapted from Grant, 1964).

An important first step is recognizing the inherent variability of each sampled parameter. Operators do not sample all of the water that is produced; rather, a subsample of water is collected. This subsample is analogous to manufacturing scenarios in which a subsample of product is tested. A control chart is more than plotting observed data or using statistical summaries. A plot of all observed data is sometimes erroneously referred to as a control chart, but these data do not account for inherent variability in the underlying process. In a worst-case situation, a failure to use appropriate techniques can be misleading and can lead to improper management of the treatment process. Figure 8 shows an example plot of all individual data points. Figure 8 illustrates the scatter associated with individual data, some of which is attributable to instrument, pump, or natural variability, as discussed previously.

The first step in creating a proper control chart is to define a subgroup (sometimes called "binning"—i.e., putting samples into "bins"). It takes about 25 subgroups to create a trend. Consequently, one factor to consider in defining subgroups is the availability of data to support at least this many subgroups. In the control chart examples that follow, weekly data have been used for a bin, with seven daily data points per bin.

FIGURE 7   Median monthly alkalinity in system E distribution system from hydrants and indoor tap locations
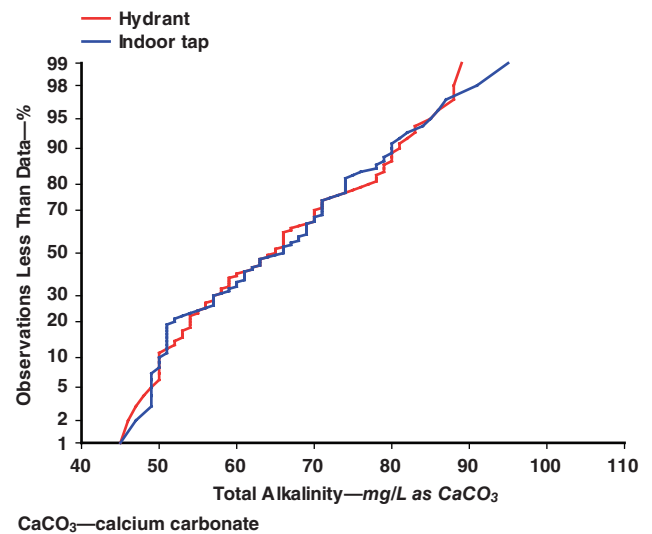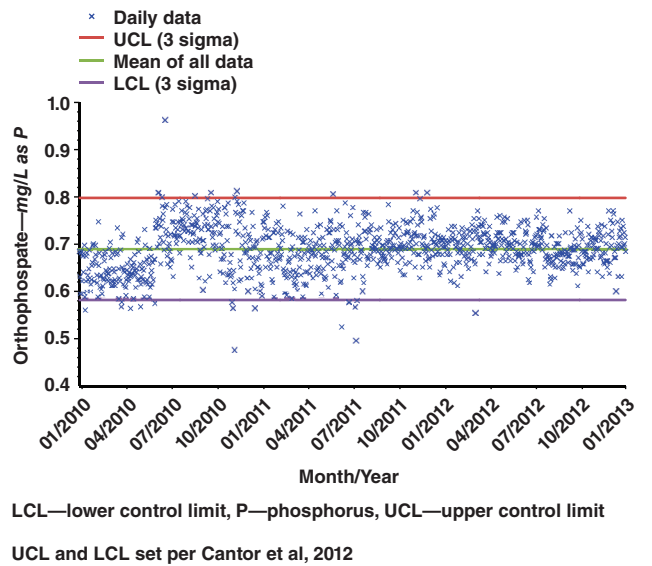
CaCO$_3$—calcium carbonate

FIGURE 8   Plot of orthophosphate daily data for system D

LCL—lower control limit, P—phosphorus, UCL—upper control limit

UCL and LCL set per Cantor et al, 2012

To prepare a control chart, data are needed for each subgroup. One approach uses the mean of each group, and then mean and standard deviation (SD) of the subgroup mean values are calculated. Typically, the upper control limit (UCL) and lower control limit (LCL) for the collection of subgroups are set equal to the mean of the group mean values ± 3.0 sigma values of the group mean values (Grant, 1964). Another approach uses the median and range of each subgroup, and then UCL and LCL are based on the median of the group median values and median of the

group ranges. UCL and LCL are calculated for group median values as described in Grant (1964).

The goal of this effort is to establish values representative of the boundaries of controllable variability (i.e., UCL and LCL) so that values outside these boundaries can be identified. The use of mean values, even the mean of group means, can create wide boundaries (UCL and LCL) when a single abnormally high or low value is present in the database.

To illustrate, in one of the systems studied here, the median pH of the group median values was 7.66 and the 99.9th and 0.1th percentile values for the group median values were 7.36 and 8.23, respectively. However, one group included a recorded pH value of $> 10^{38}$, resulting in a group mean of $> 10^{36}$ and a consequent mean of group means of $> 10^{34}$ and upper and lower percentile values of $+10^{35}$ and -10^{35}, respectively, for pH. If the $> 10^{38}$ value is excluded, the resulting median, 99.9th, and 0.1th percentiles of group medians remains the same, but the mean of group means reduces to 7.5 and UCL/LCL becomes 8.84/6.20. The control limit determinations using medians are less sensitive to a single abnormally high or low value than control limit determinations using mean and SD, and hence values not representative of inherent variability can be more readily identified using medians than mean and SD (Grant, 1964).

The median was used in this analysis instead of the mean as the indicator of data central tendency. The size of the control chart limits above and below the median was calculated at ± 3 sigma, as defined in the use of Shewhart control charts. Figure 9 shows a median control chart using a bin of one week for the same data as in Figure 8. Figure 9 illustrates much less variability than using the individual data in Figure 8. In Figure 8, the UCL and the LCL ranged from about 0.58 to 0.80, respectively. In Figure 9, the range is 0.65 to 0.75. The operator can easily view the trend data in Figure 9 and make adjustments.

For example, the operator would notice the low trend around January to May 2010 and a higher trend shortly after. By observing the control chart, the operator can make informed adjustments. From a control chart perspective, the orthophosphate was "not under control" from about January 2010 to the middle of 2012 but has been in control since. The term "not under control" is a control-chart term to alert the operator that improvements to the system can be made. The term should not be confused with a regulatory compliance issue.

Figure 10 shows a pH example that was not in process control. Control charts themselves are not appropriate for regulatory action. Control charts are constructed with tight bands referred to as sigma variations and are used for operator process control. The better operations become at reducing variability, the tighter the UCL and LCL bands will get.

CONCLUSIONS

Monitoring WQPs is an important part of OCCT for lead and copper control at drinking water utilities. This study analyzed historical WQP data collected at six utilities during two or three years in order to assess how variable the data were over time. WQPs in drinking water can be affected by a variety of factors. These include but are not limited to analytical issues, seasonal

FIGURE 9   Control chart of system D—orthophosphate one group per week

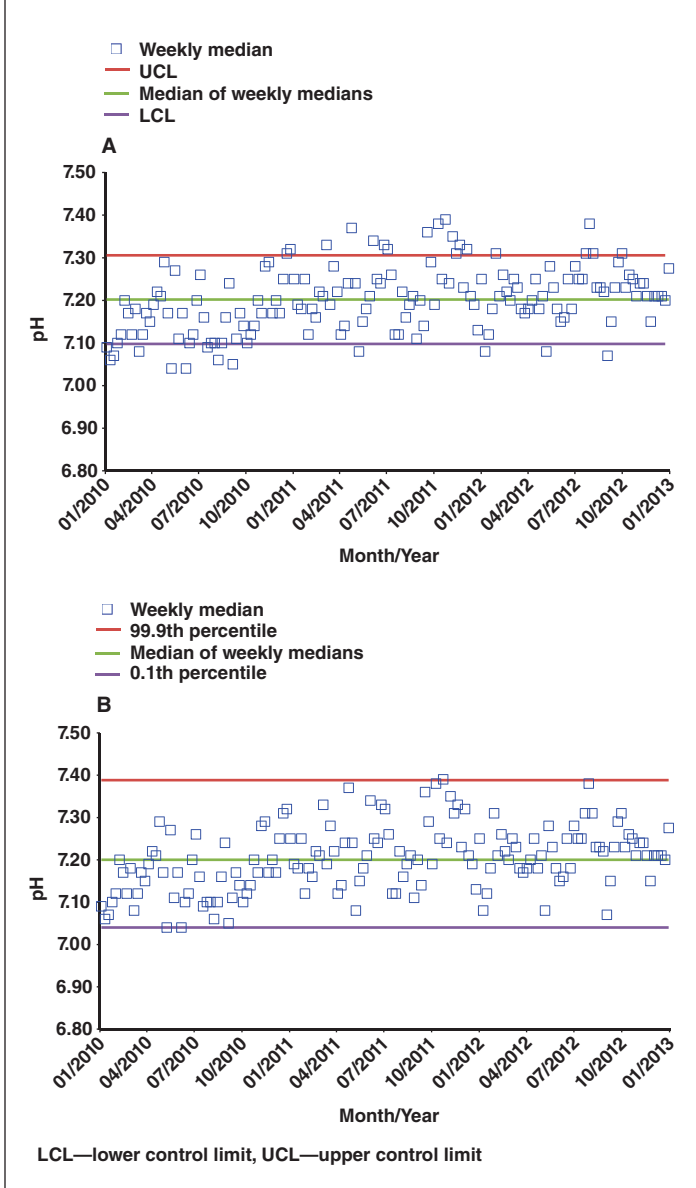LCL—lower control limit, P—phosphorus, UCL—upper control limit
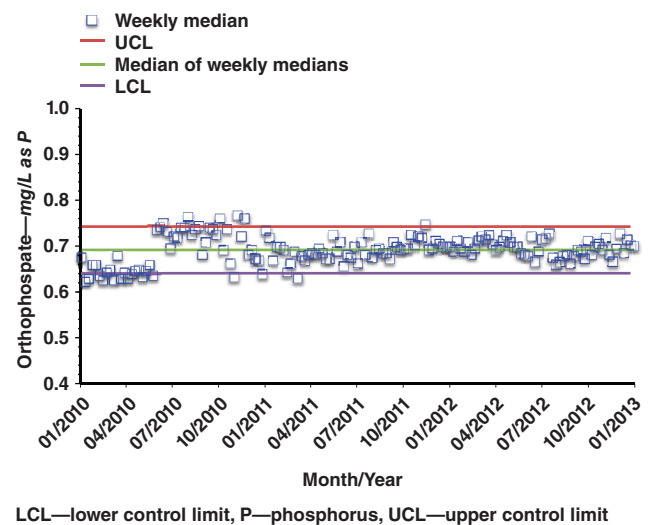
variations in water quality, variable contribution of water from sources with different characteristics from each other in different times of the year, and reactions prior to the entry point or in the distribution systems.

Overall, the results showed that some WQPs had little variability, while others demonstrated a wider range of values. More than 25% of the results from all locations at system B, the interface and source 2 locations for system C, and the data presented for system E were more than ± 0.2 pH units from the median pH. The other water systems investigated were able to demonstrate pH within ± 0.2 units of the median in more than 90% of the samples. Overall, 90% of the data from all systems were within ± 0.5 pH units of the median. The observed variability could be attributed to the impact of different sources, treatment techniques, and treatment goals.

Two systems, A and B, controlled alkalinity as part of their OCCT. System A had 100% of its data ± 5 mg/L as $CaCO_3$, whereas system B had about 90% of its data ± 20 mg/L as $CaCO_3$. This could be attributable to characteristics of the source water or to a larger number of samples used, or because alkalinity was adjusted during some periods at these plants. In these two systems, $> 98\%$ of the data were within ± 5 mg/L as $CaCO_3$ of the median. In the other four cases, the median was about 60 mg/L as $CaCO_3$ and at least 10–25% of the results were more than ± 20 mg/L as $CaCO_3$ from the median. Ninety percent of the data for each system were within 25 mg/L as $CaCO_3$ of the median.

Three systems that add orthophosphate for corrosion control were studied. Although the median values were different, the variability was about the same; i.e., ~ 90% or more of the results were ± 0.1 mg/L as phosphorus from the median for a given water system. Because orthophosphate is generally present only when

FIGURE 10 Control chart of system D using pH (A) weekly data subgroups and (B) one group per week (Sunday–Saturday)

LCL—lower control limit, UCL—upper control limit

data from 15 min or 1 min continuously recorded on-line data and still demonstrate the true variability of the conditions observed. This not only decreases data storage and makes analysis easier, but it may reduce the number of spurious data points.

Control charts using the median of groups based on data broken into subgroups—for example, daily data binned into a weekly subset—can be useful when evaluating water quality data like WQPs (as shown in the example control charts displayed in this article). The control-chart approach is an excellent tool to allow operators and regulators to assess trends and determine whether system adjustments are appropriate. However, the UCL and LCL used in making control charts should not be used for a regulatory action. A possible incorporation of a regulatory approach into a control chart would be to add boundaries at three SDs or at limits set by the primacy agency, with the latter being used for a compliance-monitoring purpose.

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PEER REVIEW

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added for treatment, this narrow band of control is attributable to monitoring and control by operations staff at each water system.

The use of frequently recorded on-line data is useful when results can be monitored in real time so that discrepancies can be identified and rectified, although continuous on-line data can include outlier data that need to be discounted. However, in instances like those described in this article, in which the goal is to evaluate data to demonstrate variability of performance over an interval of a month or more, it is suitable to extract hourly