Tastes and Odors Associated With Chlorine Dioxide

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Andrea M Dietrich
Virginia Polytechnic Institute and State University

Tastes and Odors Associated With Chlorine Dioxide

Andrea M. Dietrich, Margaret P. Orr, Daniel L. Gallagher, and Robert C. Hoehn

A survey was conducted to determine practices and problems associated with the use of chlorine dioxide (ClO_2) by US water utilities. The survey acquired data concerning raw- and finished-water quality as well as treatment processes. A specific emphasis of the survey was to investigate the association of adverse odors (particularly those resembling kerosene and cat urine) with ClO_2 application. The results indicate that ClO_2 is primarily applied to reduce the formation of trihalomethanes. Offensive odors associated with the application of ClO_2 were not correlated with raw- or finished-water quality. Odors were more intense and more diverse when ClO_2 was used, and increased numbers of complaints about odors were associated with the presence of new carpets in customers' homes.

Chlorine dioxide (ClO_2) is a powerful oxidant applied in treatment plants for control of odors, disinfection, oxidation of soluble metals, and minimization of trihalomethane (THM) formation.[1–3] Although ClO_2 has historically been applied for taste-and-odor control in water treatment,[2,4] in recent years adverse odors in distribution systems have been associated with this oxidant. The reported odors were sporadic, occurred randomly throughout the distribution system, and were most commonly described as chlorinous, kerosenelike and cat-urine-like. Previous investigations conducted by the authors demonstrated that in many cases these odors were produced from the gas-phase reaction of ClO_2 (present in the tap water at customers' homes) with organic chemicals in household air, particularly those emitted from new carpets.[5]

Many US water utilities apply ClO_2 to aid in the control of THMs. Although most of the ClO_2 is consumed during treatment, its by-products—chlorite (ClO_2^-) and chlorate (ClO_3^-) ions—appear in the distribution system. In the future, these utilities will be required to meet additional US Environmental Protection Agency (USEPA) standards for residual oxidants. A regulatory standard of <1.0 mg/L for total oxychloride residuals in drinking water is being considered.[6–8] The standard would be based on possible adverse health effects associated with the consumption of ClO_2, ClO_2^-, and ClO_3^-. Oxychlorine compounds are known to cause oxidative stress, hemolytic anemia, and inflammation of nasal passages in mammals.[9,10] Although monitoring of these oxidants is required by some states, no maximum contaminant levels (MCLs) exist; thus only limited data are available on actual concentrations of these species in drinking water.

This survey was initiated to collect information concerning the use of ClO_2 in water treatment plants. One focus of the survey was to investigate the causes of adverse odors encountered when ClO_2 is in use. The purpose of the survey was fivefold: (1) compile current data on water quality, water treatment practices, and ClO_2 generation at plants using ClO_2, (2) collect data on the types of tastes and odors that occur in systems served by these plants, (3) investigate correlations between specific tastes and odors and water quality characteristics, (4) determine whether the use of chlorine and chloramines as final disinfectants is related to the presence of tastes and odors, and (5) determine whether the occurrence of tastes and odors is caused by the application of ClO_2 for water treatment.

Methods and materials

Design of the survey. The survey was sent to 37 water utilities in the United States that use ClO_2 in their treatment process, including utilities within the American Water Works Service Company. The survey consisted of 18 questions in 4 general sections: source description, treatment provided, ClO_2 use, and history of taste-and-odor problems. The survey methodology followed Dill-

TABLE 1
Classes of tastes and odors

Class	Individual Descriptors Listed in the Survey
Cat urine	Cat urine
Disinfection	Antiseptic, bleach, chlorinous, Clorox, medicinal, phenolic, Purex, swimming pool
Hydrocarbon	Diesel fuel, gasoline, hydrocarbon, kerosene, lighter fluid, natural gas, organic solvent, plastic, plastic pipe, rubber, varnish
Musty	Earthy, moldy, potato, potato bin, varnish, wet paper, woody
Pleasant	Floral, fragrant, sweet
Rotten	Decayed vegetation, fishy, marshy, pig pen, septic, sewage, swampy
Vegetation	Cucumber, grassy, haylike

A full report of this project (no. 90589) is available from the AWWA Research Foundation, 6666 W. Quincy Ave., Denver, CO 80235.

man's total design method,[11] which consisted of sending the initial survey with a letter of explanation and then following up with additional letters of reminder or another survey, as necessary.

The source description section acquired water quality and water treatment data concerning the type of raw-water source, population served, and raw-water-quality characteristics. Requested raw-water-quality data included the annual average values and ranges for color, total organic carbon (TOC), iron, manganese, turbidity, pH, nitrogen species, odor threshold, total dissolved solids (TDS), chloride, bromide, coliforms, and types of algae.

The section entitled treatment provided was designed to acquire data concerning the type of pretreatment (coagulants and oxidants), clarification, filtration, and application of activated carbon. Requested data concerning the finished-water quality included the annual average and range of values for color, TOC, iron, manganese, turbidity, pH, nitrogen species, odor threshold, dissolved solids, chloride, free chlorine, combined chlorine, chlorine dioxide, and chlorite ion.

The section on the use of chlorine dioxide was included to determine purposes for applying ClO_2, months of application, type of generation equipment, monitoring technique, and general operating conditions such as composition of the feed stock, ClO_2 generator efficiency, application point, and target dosage.

The final section of the survey acquired specific data on tastes and odors at the treatment plant and in the distribution system in the presence and absence of ClO_2. Thirty-nine specific tastes and odors (Table 1) were provided, and respondents rated the specific taste or odor from "never occurring" (value = 1) to "frequently occurring" (value = 5) on an integer scale. Utility personnel were asked to rate tastes and odors when ClO_2 was being applied and when it was not. Data concerning frequency of customer complaints, types of complaints, location of complainant in the distribution system, and presence of new carpets or remodeling in complaining customers' homes were also collected.

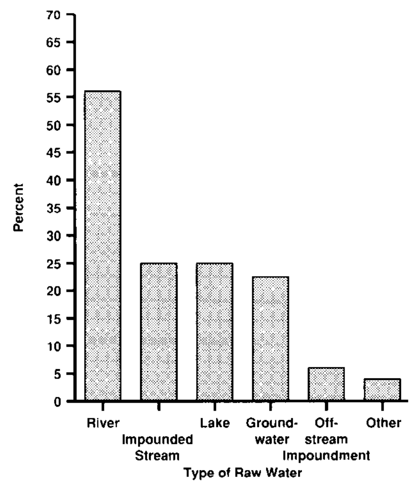

Figure 1. Distribution of raw water sources *(32 utilities responding; percentages do not sum to 100 because many utilities indicated that they use more than one type of raw-water source)*

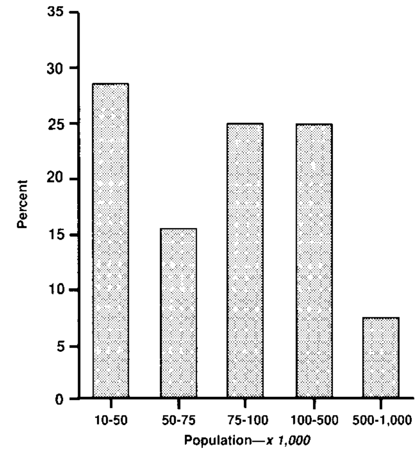

Figure 2. Distribution of populations served by utilities *(32 utilities responding)*

TABLE 2

Annual average raw-water-quality data as reported by water utilities

Characteristic	N*	Mean	SD†	Minimum	Maximum
Color units—*number*	17	41.65	45.46	2.5	200.0
TOC—*mg/L*	7	7.65	7.84	2.0	25.0
Fe—*mg/L*	24	1.26	2.81	0.019	13.0
Mn—*mg/L*	21	0.13	0.13	0.004	0.45
Turbidity—*ntu*	29	20.11	27.82	0.44	138.0
pH	29	7.4	0.7	5.7	8.2
Ammonia-N—*mg/L*	8	0.25	0.17	0.02	0.49
Odor—*TON*	14	5.07	6.13	1.00	24.0
TDS—*mg/L*	16	248.9	159.1	26.0	558.0
Bromide—*mg/L*	5	0.24	0.35	0.0	0.86
Chloride—*mg/L*	22	43.23	41.57	4.9	200.0
Coliforms—*number/100 mL*	25	3,942	8,315	1	37,300
Total Kjeldahl nitrogen (TKN)—*mg/L*	4	1.09	1.18	0.23	2.80

**N*—number of respondents to question
†SD—value of one standard deviation

Analysis of the survey. Questions in the survey were designed to gather descriptive information (e.g., type of coagulant, population served) and to investigate correlations (e.g., relation of tastes and odors to water quality). The descriptive data accumulated in the survey were analyzed to generate means, standard deviations, minima, maxima, and bar charts.

The survey data were also used to investigate the associations of tastes and odors with the application of ClO_2. First, taste-and-odor ratings were tested for correlation with characteristics of raw- and finished-water quality. Second, taste-and-odor ratings were correlated with ClO_2 dose. Third, chlorinous, cat-urine, and kerosene tastes and odors were tested for correlation with the point of ClO_2 application. Fourth, comparisons were made between the final disinfectants (chlorine and chloramine) to determine whether differences in kerosene, cat-urine, and chlorinous tastes and odors were related to the type of final disinfectant. Fifth, comparisons were made between the individual tastes and odors reported when ClO_2 was in use and when it was not in use. Sixth, the association of tastes and odors to one another was determined by cluster analysis.

Statistical methods. Statistical analyses were conducted by the Statistical Analysis System (SAS, release 5.18) on a mainframe computer at the Virginia Polytechnic Institute and State University Computing Center.* In all cases, the chosen level of significance was 95 percent (alpha = 0.05). Standard SAS procedures were employed to generate means, maxima, minima, graphs, correlations, chi-square analyses, the Wilcoxon test results, and cluster analyses.

Each survey consisted of 396 potential responses. Some respondents either did not answer all questions or answered "not applicable." These blank or "not applicable" responses were not included in the analysis. Many questions requested that respondents check all that apply; thus, the responses to several questions total more than 100 percent.

Statistical correlations procedures were used for evaluating relationships between tastes and odors and other parameters. The 39 individual taste-and-odor descriptors in the survey were grouped into seven classes by the authors (Table 1). All correlations were conducted on the basis of these classes of tastes and odors, not the individual responses themselves, to increase the potential number of responses in a given category. Pearson's correlation coefficient (r) was used to determine associa-

*3090, IBM, Armonk, N.Y.

TABLE 3
Annual average finished-water-quality data as reported by water utilities

Characteristic	N*	Mean	SD†	Minimum	Maximum
Color units—*number*	19	2.02	1.82	0.0	5.0
TOC—*mg/L*	7	3.88	2.21	1.0	8.0
Fe—*mg/L*	28	0.05	0.06	0.01	0.30
Mn—*mg/L*	27	0.03	0.01	0.0	0.09
Turbidity—*ntu*	30	0.32	0.21	0.1	1.0
pH	30	7.8	0.6	6.8	9.0
Ammonia-N—*mg/L*	7	0.34	0.36	0.06	1.0
Odor—*TON*	18	1.76	1.59	0.0	0.38
TDS—*mg/L*	21	273.1	203.5	48.0	1,000
Free chlorine—*mg/L*	29	1.25	0.87	0.0	2.9
Combined chlorine—*mg/L*	21	1.29	0.87	0.0	3.0
Chlorine dioxide—*mg/L*	20	0.17	0.32	0.0	1.0
Chlorite—*mg/L*	12	0.32	0.28	.001	0.8

*N—number of respondents to question
†SD—value of one standard deviation

TABLE 4
*Location of chlorine dioxide control point**

Control Point	Number of Utilities	Percentage of Utilities
Flash mixer	4	15.4
Floc basin	3	11.5
Presedimentation	2	7.7
Clarifier water	5	19.2
Before filtration	2	7.7
Filtered effluent	2	7.7
Clearwell	2	7.7
Effluent	3	11.5
Distribution system	1	3.8

*Twenty-six utilities responded; two of the 26 did not use a control point for ClO_2.

tions between the classes of tastes and odors, which were rated from "never observed" to "frequently observed," and water quality characteristics such as color or turbidity. This statistic measures the extent to which an increase in the water quality parameter predicts an increase in the taste-and-odor rating.

The chi-square (χ^2) statistic was used to determine whether the reported frequencies of kerosene, cat-urine, or chlorinous odors were different when chlorine or chloramines were used as the final disinfectant. The chi-square statistic is based on a contingency table that compares the observed frequencies and expected frequencies of odor intensity ratings for the two final disinfectants. The chi-square statistic indicates the probability that the differences in frequencies are due to random chance.

Cluster analysis was performed on the 39 individual taste-and-odor descriptors, both when ClO_2 was in use and when it was not in use, to identify associations between certain odors or tastes; association was determined from the intensity responses (i.e., the 1–5 rating) in the survey. For example, if a utility responded that the water frequently smelled like Clorox, the analysis determined whether the water also frequently smelled like a swimming pool or bleach, which were associated odors. The analysis divided the tastes or odors into nonoverlapping clusters. The procedure began with all variables in one cluster; variation within a cluster was determined by a correlation matrix. When the variation between elements in the cluster was high, the cluster was divided into two clusters. For ease of analysis, the data were plotted as flow charts in order to depict the way the 39 taste-and-odor descriptors were separated into clusters. The alpha value for this test was 0.05.

To determine whether the presence of ClO_2 enhanced tastes and odors, the Wilcoxon paired-sample test was used to compare responses concerning each taste and odor when ClO_2 was in use and when it was not in use. This statistic indicates when the responses are significantly different and when the responses are not different as a result of chance. The test itself is a nonparametric test that is applicable when it cannot be assumed that the differences between pairs of responses are from a normal population. Because the distribution of the differences between pairs was unknown, the Wilcoxon test was selected rather than the Student's *t*-test.

Results and discussion

Thirty-seven surveys were sent to utilities in 18 states, and 35 (95 percent) were returned. Three of the 35 were not completed because ClO_2 was no longer in use at the utility. Respondents spent, on average, 1.82 h filling out the survey, with a range of 0.25–5.5 h.

The survey was sent to water utilities that used ClO_2 but not to a control group that did not apply ClO_2. Therefore, some bias may be inherent in all the results. This bias was minimized by asking the utilities to describe their taste-and-odor events both when ClO_2 was being used and when it was not being used. Thus, for questions related to tastes and odors, utilities served as their own controls.

The survey encompassed a variety of water treatment facilities in terms of raw-water sources, volumes treated, and raw-water quality. Some of the raw-water quality characteristics varied among the utilities by orders of magnitude (e.g., color ranged from 2.5 to 200). On the other hand, the finished-water quality did not vary as greatly, especially among those characteristics for which MCLs are established.

The results that are tabulated here reflect the effect of ClO_2 usage at the utilities that participated in the survey. Inclusion of fewer or more utilities may have yielded slightly different conclusions.

Source. Raw-water sources, in order of frequency, included rivers, lakes, impounded streams, and groundwater; many utilities obtained water from more than one source (Figure 1). Populations served varied from 10,000 to 1,000,000 customers (Figure 2). The annual averages of the raw-water quality characteristics were fairly typical (Table 2). Twenty species of algae were identified in raw-water supplies, including *Anabaena, Ankistrodesmus, Aphanizomenon, Asterionella, Ceratium, Chlamydomonas, Cyclotella, Dinobryon, Fragilaria, Gomphosphaeria, Hydrodictyon, Melosira, Nostoc, Oscillatoria, Scenedesmus, Stephanodiscus, Synedra, Synura, Tribonema*, and *Volvox*.

Treatment and finished-water quality. During treatment, most facilities applied alum or polymer (or both)as the coagulant (Figure 3). Chlorine (81.3 percent) and ClO_2 (87.5 percent) were the oxidants applied most frequently during pretreatment. Four utilities applied ClO_2 after either sedimentation or filtration. Clarification was achieved by conventional flocculation followed by settling at 71.0 percent of the installations; the remaining utilities used sludge-blanket clarifiers. Filtration was most commonly accomplished with either rapid sand (31.3 percent) or dual-media (anthracite and sand) (31.3 percent) filters; 21.6 percent of the utilities surveyed used trimedia filters of anthracite, sand, and garnet. Activated carbon was employed by 15.6 percent of the utilities surveyed.

None of the finished-water characteristics were atypical for drinking waters (Table 3). For instance, the ranges for the annual average pH was 6.8–9.8 and for TOC it was 1.0–8.0 mg/L. The ranges for the annual average oxidant concentrations in finished water were 0.0–2.9 mg/L free chlorine, 0.0–1.0 mg/L ClO_2, and 0.0–0.8 mg/L ClO_2^-.

Chlorine dioxide use. The main purpose for adding ClO_2 was to provide preoxidation and predisinfection while at the same time avoiding THM formation (Figure 4). Utilities also reported adding

ClO_2 either as a preoxidant for iron or manganese control or for taste-and-odor control (Figure 4). Although some utilities only applied ClO_2 in the summer months, many applied it throughout the year (Figure 5). Generators used by the utilities came from a variety of manufacturers; one utility fabricated its own generator. Some ClO_2 generators were installed as early as 1960, but 90 percent had been installed since 1980.

The facts that most of the utilities used ClO_2 for THM precursor control and had installed their generators after 1980 indicate that the utilities were working to comply with the USEPA's 1979 mandate for the reduction of THMs (0.10 mg/L). Eleven utilities applied ClO_2 every month of the year, which may indicate that some utilities need to apply ClO_2 year-round to control THM levels in finished water.

Several analytical methods were used to monitor for oxidant concentrations, and some utilities reported using more than one method. The N,N-diethyl-*p*-phenylenediamine (DPD) method[12] was used by 56.7 percent of the utilities to monitor ClO_2 and ClO_2^-, and the amperometric titration method[12] was used by 46.7 percent to monitor these oxidants. Four utilities (13.3 percent) reported using a chlorophenol red method, whereas only one utility monitored ClO_2^- and ClO_3^- by ion chromatography. The DPD and amperometric titration methods are subject to interferences from other oxidants during analysis of an individual oxidant in drinking water;[13–15] furthermore, these methods are severely limited for determination of submilligram-per-litre levels of ClO_2 or ClO_2^-.[13] Chlorate ion is not measured by the DPD method; low concentrations are difficult to measure with accuracy by amperometric titration.[13,16] Because analyses of low levels of ClO_2 and its by-products by some methods are questionable, values reported below several tenths of a milligram per litre must be interpreted with caution. New methods are under development that may be more accurate and possess lower detection limits.[7,17–20]

At 32 water treatment plants, ClO_2 was most often applied at the intake (40.6 percent) and the flash mixer (46.9 percent). The target dose of ClO_2 ranged from a low of 0.6 mg/L to a high of 6.0 mg/L. The mean applied concentration was 1.24 mg/L with a standard deviation of 1.18 mg/L. The applied concentration of ClO_2 reported here is similar to the previously reported range of 1–5 mg/L.[21]

The control point for ClO_2 (the point in the treatment process at which ClO_2 was monitored to control the dosage) varied from plant to plant, with no site being predominant. Specific responses regarding the location of the control point are given in Table 4. Different oxidants were measured at the control point, with some utilities monitoring more than one oxi-

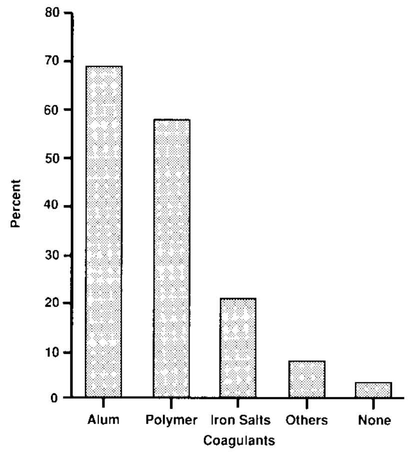

Figure 3. Distribution of primary and secondary reasons for applying chlorine dioxide *(32 utilities responding)*

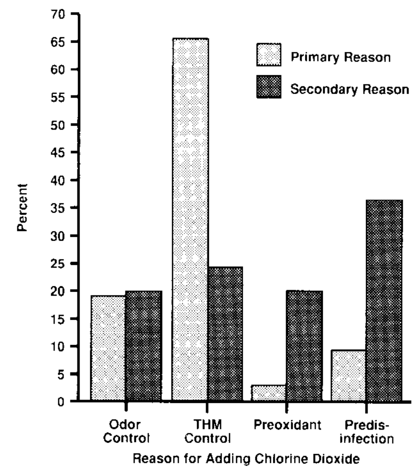

Figure 4. Distribution of primary and secondary reasons for applying chlorine dioxide *(32 utilities responding)*

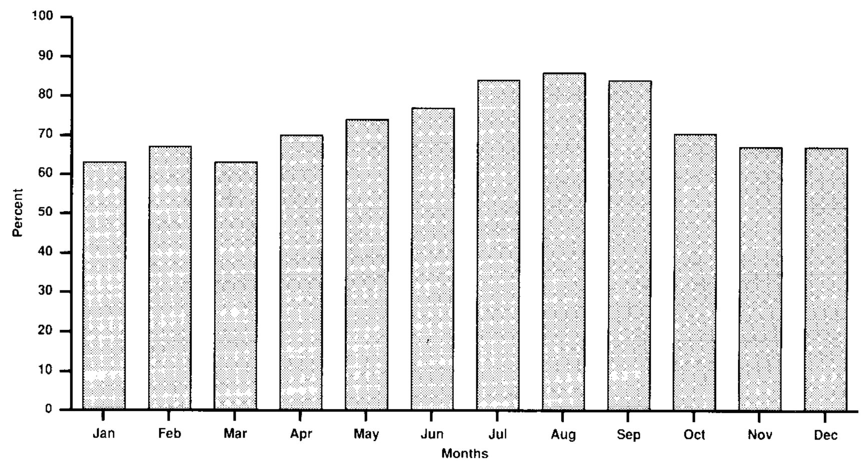

Figure 5. Month during which utilities apply chlorine dioxide *(30 utilities responding)*

TABLE 5

Clusters of odors formed when chlorine dioxide was applied

Cluster Number	Odor Descriptors
1	Decayed vegetation, earthy, grassy, haylike, marshy, moldy, septic, sewage, swampy, woody
2	Organic solvent, phenolic, plastic, plastic pipe, rubber, varnish
3	Floral, fragrant, pig pen, wet paper
4	Antiseptic, cucumber, fishy, medicinal, potato, potato bin, sweet
5	Bleach, chlorinous, Clorox, Purex, swimming pool
6	Diesel fuel, gasoline, kerosene, natural gas
7	Cat urine, hydrocarbon, lighter fluid

TABLE 6

Clusters of tastes formed when chlorine dioxide was applied

Cluster Number	Taste Descriptors
1	Bleach, Clorox, diesel fuel, gasoline, kerosene, lighter fluid, natural gas, organic solvent, phenolic, plastic, plastic pipe, Purex, rubber, swimming pool, varnish
2	Cucumber, fishy, haylike, potato, potato bin, septic, sweet
3	Antiseptic, floral, fragrant, hydrocarbon, pig pen, wet paper
4	Decayed vegetation, earthy, marshy, moldy, sewage, swampy, woody
5	Cat urine, chlorinous, grassy, medicinal

TABLE 7
Clusters of tastes formed when chlorine dioxide was not in use

Cluster Number	Taste Descriptors
1	Antiseptic, cat urine, cucumber, decayed vegetation, diesel fuel, fishy, floral, fragrant gasoline, haylike, hydrocarbon, kerosene, lighter fluid, marshy, natural gas, organic solvent, phenolic, pig pen, plastic, plastic pipe, potato, potato bin, Purex, rubber, septic, sewage, swampy, sweet, swimming pool, varnish, wet paper, woody
2	Bleach, chlorinous, Clorox, earthy, grassy, medicinal, moldy

dant. For 26 responding utilities, 73.1 percent measured ClO_2, 42.3 percent measured ClO_2^-, and only 15.4 percent measured ClO_3^-.

During the generation process, aqueous sodium chlorite was fed by 88.2 percent of the utilities. ClO_2 was generated in every instance by reaction of the aqueous ClO_2^- with either chlorine gas or hypochlorous acid. Generation by reaction between ClO_2^- and strong acid was never used. The generator efficiency was reported to be 88.8 percent with a standard deviation of 13.1 percent. Forty-two percent determined efficiency weekly, and another 26.3 percent of the responding utilities determined it more frequently. The remaining utilities determined the efficiency either monthly, yearly, or only at the time of installation.

The efficient generation of ClO_2 requires a delicate balance between chlorine, ClO_2^-, and hydrogen ion concentrations.[21,22] That only 20 percent of the responding utilities evaluated their generator efficiency daily (and most determined it less often) implies that many utilities may not know the true efficiency of their generators. In addition, the generators could be producing excess by-products such as ClO_3^-, and because ClO_3^- is infrequently analyzed by most utilities, its concentration is not widely known. Also, the literature contains little concerning the impact of generator efficiency on ClO_2^- and ClO_3^- residuals.

If an MCL of <1 mg/L for total residual ClO_2^- related oxidants is promulgated, methods may be required for economically reducing the concentrations of ClO_2 and its by-products. Potential technologies that have been considered for reducing ClO_2 and ClO_2^- levels include treatment with sulfur dioxide,[18] reduced sulfur compounds such as sulfite,[18] reduced iron compounds,[23] powdered activated carbon (PAC),[24] and granular activated carbon (GAC).[25,26] All but reduced iron and PAC, however, have proved to be ineffective for plant-scale applications.[27–29] Identification of the potential sources of ClO_3^- in systems that apply ClO_2 and techniques for effectively reducing ClO_3^-) levels in the distribution system are issues that have yet to be resolved.

Tastes and odors. Odors reported during times of ClO_2 addition were usually observed in both the air and water. The mean number of customer complaints reported when ClO_2 was being applied was 5.3 per week, whereas a mean of only 3.0 complaints per week was registered when ClO_2 was not being applied. Customer complaints from random locations throughout the distribution system were reported by 73.3 percent of the utilities. The complaints were usually received throughout the day rather than during a specific period according to 90.0 percent of the utilities. Thus, taste-and-odor problems occurred throughout the region served by a utility and were not confined to a particular neighborhood or service line. Tastes and odors were most commonly detected in the kitchen or the bathroom and occasionally in the laundry room. Threshold odor number was the method used to quantitate the tastes and odors by 75.9 percent of the utilities; no utilities used the flavor profile analysis method.

Utility personnel were asked whether they noted an increase in complaints when the ClO_2 dosage at the plant exceeded a certain level. Ten of 29 responding to this question said "yes." Some indicated the level to be as high as 3 mg ClO_2/L, whereas others said it was as low as 0.1 mg ClO_2/L. The average level was 1.5 mg ClO_2/L with a high variability (±1.0 mg/L standard deviation). The majority responding to this question (19 of 29), however, said that complaints were not related to dosage; thus, other factors must have been important in causing complaints.

When asked if an association was noted between complaints and the presence of new carpets, 17 of 28 utilities (60.7 percent) responded "yes." On average, 46 percent of the complaints investigated at these utilities were from customers who had recently installed carpets, but in some instances, all the complaining customers had new carpeting. Personnel at several utilities stated that they never thought to inquire whether the customer had new carpets.

Customers who had recently redecorated or painted their homes complained slightly less often than those that had recently installed new carpet. Of the total number of complainants at a single utility, the mean percentage who had recently redecorated was 40.6 percent, with a range from 5 to 100 percent. Thus, the survey corroborates earlier evidence that tastes and odors associated with ClO_2 use are related to the presence of new carpeting or remodeling in the home.[5] There was a 100 percent association between odors and the presence of new carpeting for certain utilities that had been sufficiently informed to inquire about carpeting.

None of the seven classes of tastes and odors (Table 1) were correlated with any raw- or finished-water quality characteristic, and none correlated with the target dosage of ClO_2. The point of ClO_2 application was not correlated with cat-urine, chlorinous, or kerosene tastes and odors. This lack of correlation was not unexpected because previous evidence had suggested that air quality in the home was related to the odor problem.

Chi-square tests. Chi-square tests were performed to determine whether the choice of final disinfectant applied by the utility was related to the formation of cat-urine-like, chlorinous, and kerosene-like tastes and odors. Only four utilities applied chloramines for distribution system disinfection, and the statistical analysis indicated that the frequency of kerosenelike, cat-urine-like, and chlorinous complaints was no greater in these systems than in those that applied free chlorine as the final disinfectant. The inability of the statistical test to detect a relationship between the choice of residual disinfectant and the rating of the odor complaints no doubt was influenced by the small number of responding utilities that applied chloramines.

This result is in contrast to the experience of individual water utilities that reported decreases in the kerosenelike and cat-urine-like odors when ammonia was applied to chlorinated finished water that had also been treated with ClO_2. Ammoniation of chlorinated water forms chloramines, thus potentially removing the pathway for ClO_2 regeneration by the reaction of ClO_2^- and chlorine.[5] More studies need to be conducted to substantiate this potential amelioration technique.

Cluster analysis. Clusters were established to determine whether certain odors or tastes were commonly associated with one another. The association in cluster analysis is based on a similar rating of the intensity for the individual tastes and odors.

Odors reported at times when ClO_2 was in use formed seven clusters (Table 5). Because the clustering routine begins with all 39 odors in one cluster, the separation of clusters (i.e., how the odors are related) throughout the process is of interest. Figure 6 is a flow chart that illustrates the manner in which the 39 odor descriptors were separated into seven clusters. Five clusters of tastes were formed when ClO_2 was applied (Table 6).

Odors reported at times when ClO_2 was not in use formed only one cluster (i.e., all odors were in one group), and the tastes were separated into only two groups (Table 7). The lack of clusters when ClO_2 was not applied indicates that the intensities of tastes and odors were given similar rankings, and no single taste or odor dominated. This interpretation supports previous reports that demonstrated that the taste-and-odor problems are associated primarily with the application of ClO_2.[5,30]

The formation of a cluster indicates that the odors were reported at the same level by many of the utilities; for instance, most utilities indicated that their water never smelled floral, fragrant, pig-pen-like, or wet-paper-like. Cat urine was considered a "stand alone" odor by the authors, but clusters generated by similar ratings in the survey grouped this odor with hydrocarbon and lighter fluid odors. These data support the association of hydrocarbon-type smells (diesel fuel, gasoline, kerosene, and natural gas) and cat-urine odors, which are often reported by customers experiencing odors in their home resulting from ClO_2 use.[5] The petroleum smells were also found to be statistically associated with one another (Table 5, cluster 6).

The associations among odors reported when ClO_2 was in use are of particular interest. As can be seen in Figure 6, the 39 odor descriptors initially segregated into two large clusters, one containing descriptors that could be categorized as "natural" (e.g., cucumber, earthy, grassy) and one containing descriptors that could be categorized as "chemical" (e.g., chlorinous, diesel fuel, varnish). The cluster of "natural" descriptors was segregated into only two additional clusters, one of which contained mostly terms describing woodlands, meadows, and swamps, and the other containing terms more related to medicines and vegetables.

The "chemical" cluster was further subdivided into two clusters, one containing primarily chlorinous, plastic, and petroleum-related odors, the other containing a variety of diverse descriptors ranging from disagreeable odors such as cat urine and pig pen to hydrocarbonlike and even pleasant odors such as floral. Further differentiation occurred as the statistical segregation of odors according to intensity continued, and the final result was five smaller clusters, each containing descriptors that, for the most part, were somewhat similar. An exception was the cat-urine descriptor, which, instead of standing alone as the authors had originally anticipated (Table 1), was included in a cluster containing the hydrocarbon and lighter fluid descriptors. It was surprising that those two appeared with the cat-urine descriptor rather than in the other petroleum-related cluster which contained diesel fuel, gasoline, kerosene, and natural gas.

The final product of the cluster analysis was seven clusters (Table 5 and Figure 6), many of which resembled the seven classes originally generated by the authors to perform correlations of the tastes and odors with water quality data (Table 1). For example, the class in Table 1 entitled "disinfection," which contained the descriptors antiseptic, bleach, chlorinous, Clorox, medicinal, phenolic, Purex, swimming pool, was similar to cluster 5 in Table 5 which contained the descriptors bleach, chlorinous, Clorox, Purex, swimming pool. Although the agreement between the seven classes in Table 1 and the seven clusters in Figure 6 is not perfect, clearly the judgments made by the authors when grouping the taste-and-odor descriptors resemble those that resulted from statistical interpretation of the data by cluster analysis.

Cluster analysis provides no information on the physical relationships of the descriptors. For example, this statistical methodology does not associate the descriptors chlorinous and Clorox as having similar meanings. Instead, cluster analysis assesses the intensities assigned to the responses and then groups the descriptors accordingly. Thus, the respondents tended to find (or rate) the descriptors within each cluster at nearly the same intensity. When physically dissimilar odors were grouped together, it simply meant that the descriptors had nearly the same level of response or lack thereof. For instance, cluster 3 in Table 5 contains the unlike odor descriptors of floral, fragrant, pig pen, and wet paper because most respondents stated that their water never smelled like any of these. When ClO_2 was applied, many different clusters were formed and most of these have a meaningful physical interpretation. Because only one odor cluster was formed when ClO_2 was not applied, the use of ClO_2 must have caused a wide variety of odors at different intensities, not just hydrocarbon or cat urine, to become more apparent.

Wilcoxon test. Twenty-one utilities provided data for tastes and odors both when ClO_2 was in use and when it was not in use. The Wilcoxon paired-sample test was used to compare the intensity ratings of individual tastes or odors in the presence and absence of ClO_2 application. No significant differences in tastes were observed as a result of the application of ClO_2 according to this statistical test, but significant differences were observed for odors. Six odors were more intense when ClO_2 was in use: cat urine, diesel fuel, gasoline, kerosene, natural gas, and organic solvent.

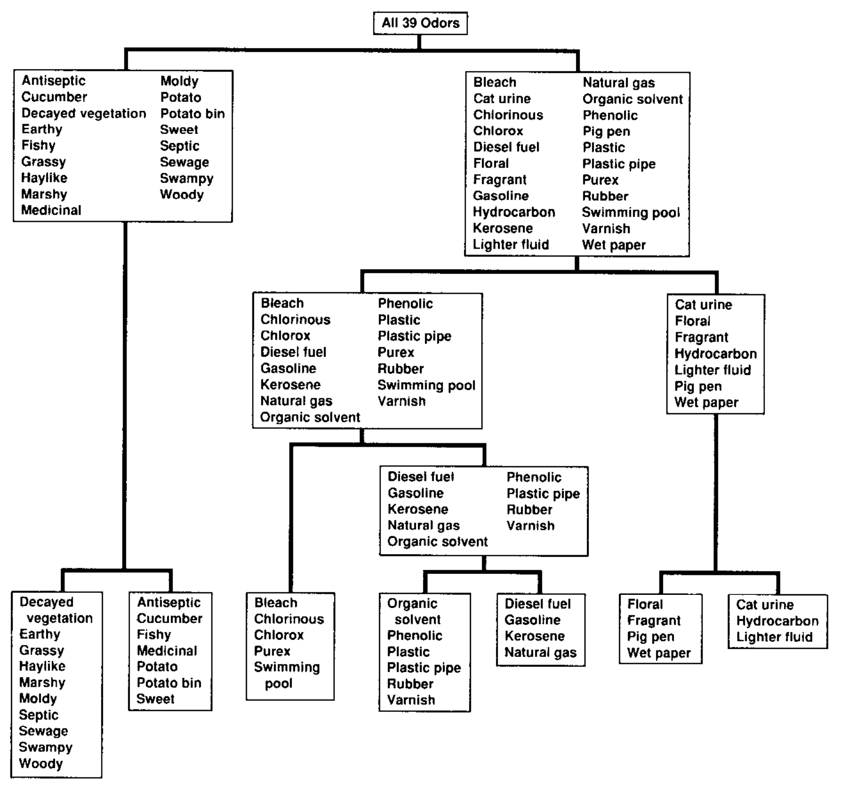

Figure 6. Cluster analysis for 39 individual odor descriptors when chlorine dioxide was in use

As previously discussed, cluster analysis showed that all odor descriptors were rated at about the same intensity at times when ClO_2 was not in use, and only one cluster was generated. In contrast, seven clusters were produced by analysis of odor descriptor intensities reported during periods when ClO_2 was being applied. For example, Figure 6 shows that odors described as diesel fuel, gasoline, kerosene, and natural gas appeared in one cluster (which means that they were at about the same intensity), whereas odors described as cat urine, hydrocarbon, and lighter fluid appeared in another cluster.

Although cluster analysis can illustrate groupings of odor descriptors according to intensity, it does not directly compare intensities when ClO_2 is being applied and when it is not. The Wilcoxon analysis makes that distinction, however, and it showed that odors were indeed intensified during periods when ClO_2 was being applied. Thus, these two statistical analyses confirm that the diesel fuel, gasoline, kerosene, natural gas, cat urine, hydrocarbon, and lighter fluid odors are related to one another and are intensified when ClO_2 is applied to treat drinking water.

Summary

An exceptionally good response to the survey was obtained. The survey results summarize the reasons for—and operations associated with—ClO_2 use by US water utilities. Important findings associated with ClO_2 application are (1) ClO_2 was primarily applied to reduce precursors of THM; (2) many utilities used ClO_2 throughout the year; (3) ClO_2 was frequently applied with chlorine in conventional water treatment plants (coagulation, filtration, sedimentation); (4) intensity of tastes and odors did not correlate with raw- or finished-water quality characteristics; (5) odors associated with ClO_2 were more of a problem than tastes, although an increase in both taste and odor complaints was associated with application of this oxidant; (6) cat-urine and kerosene odors, which are commonly reported when ClO_2 is applied, were demonstrated by cluster analysis to be statistically correlated; (7) the reported intensities and types of odors increased when ClO_2 was applied; and (8) taste-and-odors complaints were associated with the presence of new carpeting or remodeling in complainants' homes.

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About the authors: *For the past four years, Andrea M. Dietrich has been an assistant professor in the Environmental Engineering and Environmental Sciences Division of the Civil Engineering Dept., Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, VA 24061-0105. She is a graduate of Boston College, Chestnut Hill, Mass. (BS), Drexel University, Philadelphia, Pa. (MS), and the University of North Carolina at Chapel Hill (PhD). A member of AWWA, ACS, and the Environmental Mutagen Society, Dietrich is active in AWWA's Virginia Section and is currently chairperson for the student activities committee. Margaret P. Orr is an engineer with The Dow Chemical Co., 1078 Building, Midland, MI 48667. Daniel L. Gallagher is an assistant professor and Robert C. Hoehn is professor in the Charles E. Via Jr. Dept. of Civil Engineering at Virginia Tech.*