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Technical Report No. 251
October 1980

CHLORINE DIOXIDE FOR WASTEWATER DISINFECTION: A FEASIBILITY EVALUATION

by

Paul V. Roberts, E. Marco Aieta, James D. Berg, and Bruce M. Chow

Supported by

Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Grant R-805426

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U.S. Environmental Protection Agency
Cincinnati, Ohio 45268
Research Grant R-805426

Project Officer
Mark C. Meckes

ABSTRACT

Chlorine dioxide was compared with chlorine for the disinfection of wastewater in laboratory experiments. Disinfection with chlorine dioxide was also demonstrated at a full-scale wastewater treatment plant. Criteria for comparison included coliform kill, inactivation of poliovirus and other indicators, and formation of halogenated organic byproducts.

Laboratory experiments were conducted using a 4-liter batch reactor characterized by intense mixing. The experiments were conducted according to a full factorial design, with mass dose of disinfectant (3 levels) and contact time (3 levels) as independent variables. The fractional survival of coliform bacteria was correlated with the product of disinfectant residual times contact time.

In general, chlorine dioxide accomplished a given fractional kill of total coliforms with a smaller product (residual × time) than chlorine. For a given contact time, the residual required to achieve a given fractional kill of coliforms was 2 to 70 times smaller for chlorine dioxide than for chlorine. The disinfectant demand is greater for chlorine dioxide than for chlorine in a conventional activated sludge effluent, but less than for chlorine in a nitrified, filtered effluent, when residuals are expressed on a mass concentration basis and conditions are chosen to result in equal disinfection performance. Considering both required residual and demand, the required doses of the disinfectants were estimated to satisfy three assumed coliform disinfection levels with two types of effluents: conventional activated sludge and filtered, nitrified activated sludge. The required mass doses of the disinfectants were approximately equal for treating conventional activated-sludge effluent--approximately 2 mg/l to satisfy a standard of 1000 total coliforms/100 ml, 2.5 mg/l to satisfy a 200 coliforms per 100 ml standard, and 8 mg/l to satisfy a standard of 2.2 coliforms per 100 ml. The required dose of chlorine was approximately 2 to 10 times greater than that of chlorine dioxide for treating filtered, nitrified effluent, depending on the coliform standard. The results of studies conducted at a full-scale plant generally agreed within a factor of two with the predictions from laboratory studies, when compared on the basis of the product (residual × time) required to accomplish a given fractional kill.

For the case likely to be most typical in practice--the disinfection of conventional secondary effluent to meet a total coliform standard of 1000 per 100 ml--disinfection with chlorine is estimated to cost 0.3 to 1.7 cents per m^3 (1.1 to 6.4 cents per 1000 gallons), depending on plant size, compared with 1.5 to 3.5 cents per m^3 (5.8 to 13.4 cents per 1000 gallons) for disinfection with chlorine dioxide (1979 price levels).

Chlorine dioxide was found to be more effective for inactivating Poliovirus I and natural populations of coliphage in both non-nitrified and filtered, nitrified wastewater effluents. Chlorine dioxide treatment formed no measurable amounts of trihalomethane byproducts, whereas chlorine treatment formed 0.5 to 5 μMol per liter of trihlomethanes, chiefly chloroform, in experiments using wastewater effluents. The measured amount of total organic halogen (TOX) formed by chlorine dioxide disinfection was so small as to be on the margin of statistical significance; chlorination formed at least 10 to 20 times more undesirable halogenated byproducts measured as TOX than did chlorine dioxide treatment. These advantages of chlorine dioxide should be considered, along with the cost-effectiveness comparison based on coliform kill, to reach decisions as to when and where to employ chlorine dioxide as a disinfectant in wastewater treatment.

This report was submitted in fulfillment of Grant No. R-805426 by Stanford University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 5, 1977 to June 5, 1980, and work was completed as of June 5, 1980.

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ACKNOWLEDGMENTS

The active assistance of the staff of the Dublin-San Ramon Services District, particularly Robert Swanson, Plant Superintendent, was essential in carrying out the full-scale field tests of chlorine dioxide. The Rio Linda Chemical Co. made available chlorine dioxide generating facilities for the full-scale demonstration.

The staff of the Palo Alto Regional Water Quality Control Plant and the San Jose-Santa Clara Water Pollution Control Plant provided samples for the laboratory studies. The Fischer-Porter Company generously loaned an amperometric titrator. Dr. Gary Stevenson gave useful advice on residual measurement techniques.

Gary D. Hopkins assisted in the full-scale demonstration experiments and determined total organic halogen concentrations. Annie M. Godfrey, Christoph Munz, Paul Dandliker, John Gonzales, Laurie Lapat, Mette Hom, Niambi Loud, and Christian Drozier performed many of the microbiological and chemical analyses.

We are grateful to Professor Robert Cooper, School of Public Health, University of California, Berkeley, and Professor Carleton Schwerdt, Department of Medical Microbiology, Stanford University, for the virus assays performed in their laboratories.

SECTION 1

INTRODUCTION

BACKGROUND

Disinfection of wastewaters has long been practiced in areas where the use of the receiving waters for public water supply, contact recreation, and/or shellfish habitat is to be protected. Many wastewater-effluent discharge permits allow a maximum geometric mean of 1000 total coliforms per 100 ml, or 200 fecal coliforms per 100 ml, in a 30-day period. The State of California permits only 2.2 total coliforms per 100 ml if an effluent is to be used for groundwater recharge.

Chlorine has been the favored disinfectant in both water and wastewater treatment by virtue of its bactericidal effectiveness, low cost, convenience, and relatively long-lived residual. However, chlorination as normally practiced in water treatment recently has been found to result in the formation of trihalomethanes and other chlorinated organics that are undesirable from the viewpoint of public health and water pollution control in general. Although the formation of chlorinated organics during disinfection of wastewater by chlorine previously has not been investigated thoroughly, there is reason to believe that such hazardous byproducts are formed. In view of the residual organic contamination of even highly treated wastewater effluents and the resulting high doses of chlorine needed to provide a chlorine residual in wastewaters, it can be expected that undesired, chlorinated organic byproducts will be formed to a greater extent during wastewater chlorination than has been reported for water chlorination.

Thus there is a need to find a substitute for chlorine as a disinfectant in wastewater treatment that fulfills the following criteria:

1. Cost effectiveness as measured by the relationship of the total cost (amortization plus operating costs) to the effectiveness as a bactericide under the conditions encountered in practice.
2. Absence of participation in side reactions that yield undesirable byproducts, particularly chlorinated organic compounds.
3. Safety and convenience of use and ease of installation in existing wastewater treatment plants.
4. No residual toxicity to aquatic organisms in receiving waters.

Of the possible substitutes for chlorine, ozone has attracted the most attention. Ozone is a powerful disinfectant but is more expensive than chlorine and does not provide a stable residual.

Chlorine dioxide (ClO_2), although more expensive than chlorine, may offer an attractive alternative because it:

1. Is a powerful disinfectant over a broad pH range,
2. Provides a residual that is easily measurable for purposes of control,
3. Does not react with ammonia to form chloramines,
4. Does not enter into reactions with organic material to form some classes of chlorinated organic compounds considered hazardous to health (e.g., trihalomethane compounds), and
5. Does not react to form chlorinated phenols to the extent that chlorine does.

The second factor mentioned above gives chlorine dioxide an inherent advantage over ozone from the viewpoint of process control. All the other factors are advantages compared with chlorine. Factor (3), the absence of reactivity with ammonia, constitutes an especially important advantage for chlorine dioxide over chlorine in wastewater disinfection, if a free chlorine residual is required; the chlorine demand to reach the breakpoint may exceed 100 mg Cl_2 per liter.

OBJECTIVES

The purpose of this project is to evaluate chlorine dioxide as an alternative to conventional chlorination for the disinfection of wastewater.

The specific objectives are:

1. To assemble and evaluate the available information concerning the chemistry of chlorine dioxide generation and of its behavior in aqueous solution, the technology and costs of manufacture, its effectiveness as a disinfectant, and the possible side effects of its use.
2. To establish the dose-effectiveness relationship for chlorine dioxide as a disinfectant of wastewater after secondary treatment and after various stages of advanced treatment, using as a criterion the survival of coliform bacteria.
3. To compare the effectiveness of chlorine dioxide with that of chlorine as a disinfectant.
4. To develop a concept for a continuous reactor system to fulfill coliform requirements corresponding to standard secondary treatment, and advanced treatment for the purpose of wastewater reclamation and reuse.
5. To prepare a preliminary design for treatment plants of 1-, 5-, 10-, 50-, and 100-mgd capacity and to estimate the costs of construction and operation.

6. To obtain preliminary evidence as to whether the formation of chlorinated organic byproducts during wastewater disinfection conforms to the results from studies of water disinfection.

SECTION 2

CONCLUSIONS

The use of chlorine dioxide as a disinfectant in wastewater treatment is technically feasible. This was demonstrated in short-term, continuous operation at a full-scale wastewater treatment plant, which served to confirm laboratory results.

Results of chlorine dioxide disinfection can be conveniently correlated using the logarithm of the surviving fraction of organisms as the dependent variable and the logarithm of the product of the disinfectant residual times the contact time as the independent variable. The form of the correlations so obtained for chlorine dioxide is similar to that for disinfection with chlorine. Compared with chlorine, however, a given degree of disinfection was achieved with a smaller value of the product (residual × time) when chlorine dioxide was used. Based on this general finding, it is concluded that, in a technical sense, chlorine dioxide is superior to chlorine for the disinfection of wastewater.

The chlorine dioxide disinfection process can be controlled conveniently and with adequate precision by adjusting the dose to provide a desired residual. Proven residual measurement techniques, such as automated amperometric titration, are suitable for measuring the chlorine dioxide residual for control purposes.

To satisfy a given coliform standard at a given contact time, the required chlorine dioxide residual is only one-third to one-tenth the corresponding chlorine residual (mass concentration basis). The ratio of required doses (mass ClO_2:mass Cl_2) ranges from approximately 0.05 to 1.0. Hence, in general less chlorine dioxide than chlorine must be used to satisfy the coliform standards usually applied in wastewater disinfection.

The unit cost of chlorine dioxide is approximately twenty times that of chlorine. This difference is attributed almost entirely to the high cost of the sodium chlorite raw material.

The cost of disinfection with chlorine dioxide to achieve a given coliform standard is greater than or equal to that with chlorine in all cases evaluated; the higher unit cost of chlorine dioxide generally more than offsets its lower dose requirement. For the most typical case--disinfection of conventional activated-sludge effluent to satisfy a total coliform standard of 1000 per 100 ml--chlorine dioxide is two to five times more expensive than chlorine.

Chlorine dioxide forms no significant amounts of undesirable chlorinated organic byproducts under the conditions of wastewater disinfection. No measurable amounts of trihalomethane compounds (THMs) were formed when secondary effluents were dosed with 20 mg/l or 40 mg/l ClO_2. Total organic halogen (TOX) was formed to a small (but statistically significant) extent in one of four experiments with ClO_2. Chlorine at equal mass doses formed copious amounts of THMs (0.5 to 5 µMol per liter) under the same conditions. The average TOX formation from chlorine was 10 to 20 times that from chlorine dioxide at the same mass dose of disinfectant.

SECTION 3

RECOMMENDATIONS

The evaluation of chlorine dioxide as an alternative to chlorine for the disinfection of wastewater has resulted in a decision-maker's dilemma. On the one hand, chlorine dioxide is found to be superior to chlorine according to technical criteria. On the other hand, chlorine dioxide is not cost-effective when the customary performance criterion (total coliform standard) is applied.

Two important classes of questions remain: Are the unquantified benefits of chlorine dioxide compared with chlorine--namely, negligible formation of potentially hazardous chlorinated organic byproducts and superior virus inactivation--worth the additional cost? Can the unit cost of chlorine dioxide be reduced to a level at which chlorine dioxide would be economically attractive in the customary sense, even without considering its additional, unquantified advantages? Both types of questions deserve further study.

The chemical composition of disinfection byproducts and endproducts of all disinfectants should be studied systematically. There is an urgent need for better understanding of the halogenated organic byproducts of wastewater chlorination.

The apparent advantage of chlorine dioxide with regard to virus inactivation needs to be documented more convincingly. Comparison of the kill of coliforms with that of other indicators, using alternative disinfectants, is worthy of further investigation. Also of potential significance is the deviation of disinfection data from the simple first-order model usually assumed to apply. The causes underlying these deviations should be studied with a view toward re-evaluating the adequacy of the total coliform count as an indicator of disinfection performance.

Development of processes to produce chlorine dioxide more cheaply at treatment plant sites should be encouraged by supporting demonstration of candidate concepts.

SECTION 4

MATERIALS AND METHODS

WASTEWATER CHARACTERIZATION

pH

The pH was determined using a pH meter (Corning Model 610A), with a precision of ± 0.05 pH unit. The pH meter was standardized using a pH-buffered standard at a pH near the value expected in the sample.

Alkalinity

Alkalinity was determined by potentiometric titration to pH 4.3.

COD

COD was determined using the low-level COD procedure outlined in Standard Methods, Section 508 (1). A potassium acid phthalate standard was run with each set of determinations to assure accuracy. Samples were stored as for the ammonia nitrogen test.

Non-Filterable Residue

Non-filterable residue dried at 103-105°C was determined by the procedure outlined in Standard Methods (1), Section 208A, using Gooch crucibles. Samples were tested on the day of the experiment where possible. If storage was required, the storage procedure used was the same as for the ammonia nitrogen test.

Ammonia Nitrogen

Two methods were used to determine ammonia nitrogen. From October 1977 to January 1979 a specific ion probe made by Orion Co. was used. The procedure was as follows:

1. A standard curve (semi-log) was prepared at the beginning of each set of tests and every two hours afterwards using 100-, 10-, and 1-mg/l ammonium chloride standards. The standardization procedure was the same as for measuring ammonia in samples as well. The meter was zeroed using the 10-mg/l standard.

2. Readings were made as follows: (a) 100-ml samples were prepared; (b) 1 ml of 10N NaOH was added and the sample was stirred continuously until a stable meter reading was attained, which took approximately 15 min.

All samples were allowed to temperature equalize for at least 1/2 hr before the NaOH was added.

After January 1979 samples became too numerous, and a change was made to the distillation followed by acidimetric titration procedure described in Standard Methods (1), Sections 418A and B. In addition, total Kjeldahl nitrogen was measured by the method listed under "Nitrogen (Organic)" in Section 421 in Standard Methods (1). An ammonium chloride standard and a glycine standard were used during each set of determinations to assure accuracy. Samples were acidified to below pH 2 using H_2SO_4 and refrigerated at 4°C. Samples were analyzed within two weeks.

TOC

TOC analysis was done using a Dohrmann Envirotech DC-52 Organic Carbon Analyzer with an Oceanographic International Ampule Crushing Unit adapted to it. Sample preparation was as follows, using 10-ml glass ampules:

1. 1 ml of saturated potassium persulfate was added to each ampule.
2. Sample water was added (0.5 to 1.5 ml for secondary effluent).
3. Distilled water was added to fill the ampules to no more than 10 ml total volume.
4. 0.2 ml of 10% phosphoric acid solution was added.
5. The ampules were purged for 7-9 min using pure oxygen cleaned by passing the O_2 over a 475°C cupric oxide catalyst.
6. The ampules were sealed and autoclaved for 4 hrs.
7. The special crushing unit was used to open the ampule and purge the ampule with a helium carrier gas which passed into a flame-ionization detector.

Note that the initial purging in step 5 to remove inorganic carbon also removed volatile organics. Therefore the TOC value is actually a non-purgeable TOC. A calibration curve was made by running sucrose standards in the same manner as the samples. Reagent blanks were also run in this manner.

Samples awaiting sealing in ampules were stored in teflon sealed hypovials with aluminum seals. These samples were also acidified to pH 2 using HCl and stored at 4°C.

The detection limit of the TOC procedure is 0.1 mg/l C. The precision is approximately ± 5% at TOC concentrations greater than 1 mg/l C.

MICROBIOLOGICAL ANALYSES

Bacteria

Samples for microbiological analysis were collected in sterile bottles containing sodium thiosulfate to neutralize any residual oxidant and were analyzed immediately. Three field experiments were run at the Dublin-San Ramon Wastewater Treatment Plant. During these experiments, samples were collected, stored on ice, and analyzed after return to the lab, approximately one hr after the completion of a 6-hr set of replicate runs. A set of samples that had been disinfected by chlorine and chlorine dioxide, as well as an untreated influent sample, were analyzed immediately for total coliform bacteria at the field site and compared with the iced and transported samples. There were no significant differences between the analyses conducted in the field and in the laboratory-analyzed samples. Therefore, it is assumed that the microbiological integrity of the samples was maintained during the course of a long experiment.

Most probable number (MPN) and membrane filter (MF) methods of bacterial enumeration were done according to Standard Methods (1). MPN media used were lactose broth as a presumptive medium and brilliant green bile broth for confirmation of total coliforms and EC medium for confirmation of fecal coliforms. Gelman GN-6 0.45-micron filters were used for the MF tests with M-Endo Agar for total coliforms using the single-step direct technique and M-FC medium for fecal coliforms. KF streptococcal agar was used to assay for the fecal streptococcus group.

MF tests and MPN presumptive tests were incubated at 35°C ± 0.5°C for 24 ± 2 hrs. Confirmed MPN tests and fecal streptococcus tests were incubated at 35°C ± 0.5°C for 48 ± 3 hrs. Fecal coliform analyses, either by MPN or MF method, utilized an incubation period of 24 ± 2 hrs and a temperature of 44.5°C ± 0.2°C in a circulating water bath.

Viruses

Two bacterial virus methods were evaluated to find a suitable *in situ* model for virus inactivation by ClO_2. One method, that of Kott (2), also has been used in earlier studies (3). The method uses *Escherichia coli* B as the host. Samples were enriched overnight in nutrient broth at 35°C and plated for observation of plaques as a positive test. The procedure employs MPN tables; low numbers of coliphage, < 2 plaque-forming units/100 ml, are detectable. The procedure is time-consuming, however. A second method, the Reverse Phage Titer Rise Reaction (RPTRR), as developed by Atlantic Research (1978) (4), was also used. The RPTRR method uses *E. coli* C as the host bacteria, and yields results in 4 to 6 hrs. The host *E. coli* C is thought to be susceptible to a broader range of coliphage than is *E. coli* B.

The animal virus used in the study was Poliovirus I LSC strain that had been grown in Buffalo Green Monkey Kidney cells (BGM). The virus were harvested from the cells by freezing, thawing, and centrifugation to a titer of approximately 10^9 plaque-forming units per milliliter (PFU/ml). The virus were recovered after experimentation using a standard plaque assay. The animal

virus assays were performed in the laboratories of either Dr. Robert Cooper, Sanitary Engineering Research Laboratory, University of California at Berkeley, or Dr. Carleton Schwerdt, Department of Medical Microbiology, Stanford University.

DISINFECTANT CHEMISTRY

Chlorine Dioxide Generation

Chlorine dioxide was generated according to the method described in Standard Methods (1), Section 411A, diagrammed in Fig. 1, except that the acid and sodium chlorite concentrations were doubled to obtain higher chlorine dioxide concentrations in the stock solution. The concentration so obtained was 1000 to 1500 mg/l as ClO_2. Spectrophotometric analysis at 360 nm was used to verify that the chlorine species in solution was indeed chlorine dioxide.

Chlorine Generation

Aqueous chlorine stock solutions were made by bubbling 99.99% chlorine gas through chilled water. The solutions so prepared contained chlorine at a concentration of 2000 to 4000 mg/l as Cl.

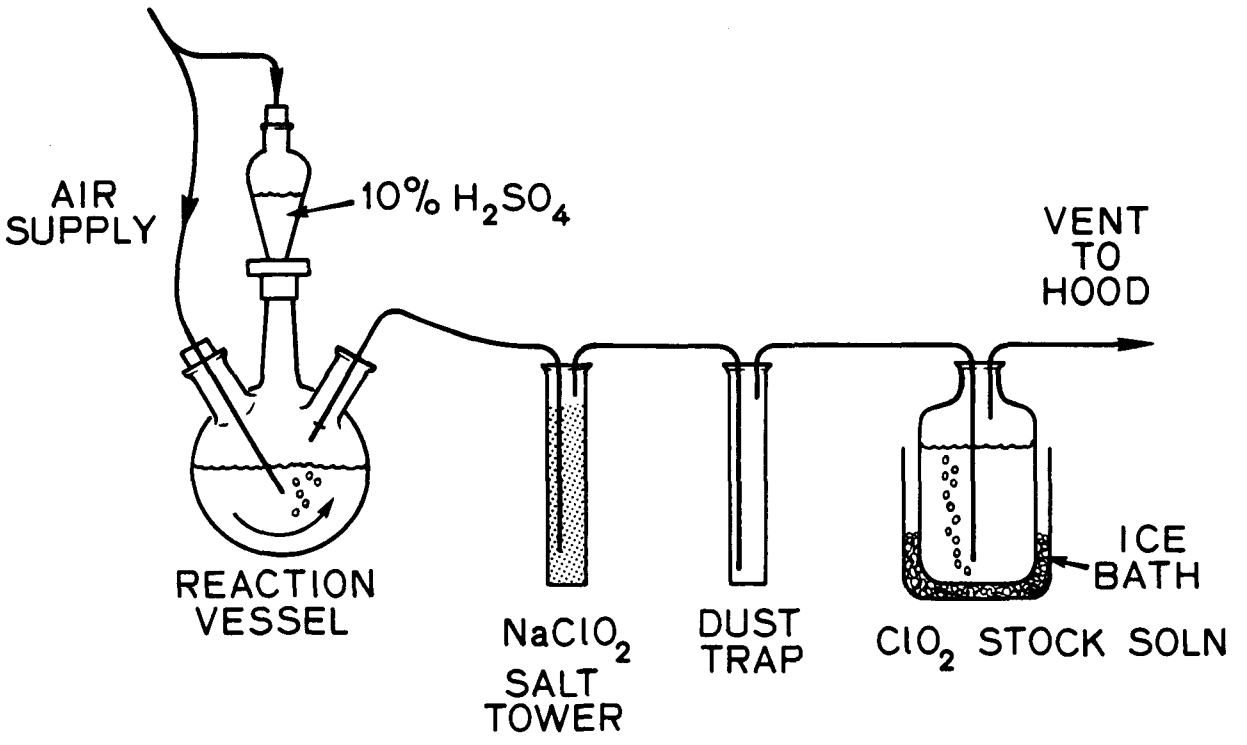


Figure 1. Chlorine dioxide generator using acid activation of a sodium chlorite solution.

Standardizing of Disinfectant Stock Solutions

Disinfectant stock solutions were standardized on the day of each experiment by the iodometric method described in Standard Methods (1), Sections 409A and 411A. Standard sodium thiosulfate titrant at 0.01N was used, standardized by the dichromate method. Blank titrations were omitted because it was found that blank contributions were negligible.

Residual Measurement for Routine Analyses

Both chlorine and chlorine dioxide residuals were measured by amperometric titration (1). The amperometric titrating unit used was a prototype model made by Fischer and Porter, similar in function to the Fischer and Porter Model 17T1010 amperometric titrator. The back-titration procedure was used for both disinfectants. It consists of the following steps:

1. A known volume of 0.00564N phenylarsine oxide solution was added to a 250-ml beaker in excess of the expected chlorine or chlorine dioxide residual.
2. 2 ml of the appropriate pH buffer was added. A pH-4 buffer (acetate) was used for chlorine analysis and a pH-7 buffer (phosphate) was used for chlorine dioxide analysis.
3. A 1-ml aliquot of 5% weight-per-volume potassium iodide solution was added.
4. A known volume of sample was carefully poured into the beaker, approximately 150-175 ml.
5. The titrator was turned to the "Total" position and the above solution was titrated with 0.00564N iodine solution to an amperometric endpoint. For this particular amperometric titrator, the endpoint was denoted by sudden needle deflection.

Residual was calculated by the following formulas:

$$\text{mg/l Cl} = [\text{PAO} - (I_2 - \text{blank}) \times \text{CF}] \frac{0.00564\text{N} \times 35453 \text{ mg Cl/equiv}}{\text{vol sample (ml)}}$$

$$\text{mg/l } ClO_2 = [\text{PAO} - (I_2 - \text{blank}) \times \text{CF}] \frac{0.00564\text{N} \times 67500 \text{ mg Cl/equiv}}{\text{vol sample (ml)}}$$

where PAO = volume of 0.00564N phenylarsine oxide used in ml

I_2 = volume of 0.00564N I_2 titrant used in ml

blank = volume of I_2 found for blank (see below)

CF = correction factor for I_2 titrant (see below).

The correction factor was found as follows:

1. A beaker was prepared with 2 ml of the phenylarsine oxide solution, the appropriate pH buffer, and potassium iodide solution.
2. 150 ml of deionized water was added.
3. The sample was titrated as in Step 5 above. This procedure was repeated for each pH.

$$CF = \frac{\text{vol phenylarsine oxide}}{\text{volume } I_2 \text{ titrant}}$$

The blank was found by the same procedure as for the correction factor except that the appropriate amounts of undisinfected sample water were added:

$$\text{Blank} = I_2 \text{ volume} - I_2 \text{ volume from CF determination}$$

A blank was determined for each pH and for each different sample volume used.

HALOGENATED ORGANICS ANALYSES

Trihalomethane (THM) Analysis

THM analysis was accomplished by liquid-liquid extraction to concentrate the organics, and subsequent gas-liquid chromatographic analysis according to the procedure of Henderson et al. (5). Liquid-liquid extraction consisted of the following steps:

1. 1 ml of specially cleaned pentane [purchased as Basic Alumina (Activity 1) grade] was injected into each of the sealed 60-ml hypovials containing the samples (displaced water was discarded).
2. A prescribed amount of 1,2-dibromoethane internal standard was injected so that its concentration in the hypovial was near that expected for THMs (between 10 and 30 μg/l).
3. The samples were agitated at 250 to 400 rpm for about 30 min on a gyrorotatory agitator.
4. A 5-μl aliquot from the pentane phase was injected into the gas-liquid chromatograph.

The gas-liquid chromatograph was equipped with a linearized electron-capture detector (Ni^{63} beta source) with a 20-pg detection limit. The column was made up of 10% squalane on 80/100-mesh Chromosorb W. Column temperature was held constant at 75°C while the detector temperature was held at 275°C. Carrier gas and makeup gas were argon/methane mixtures. Column gas flow was 60 ml/min; makeup gas flow was 40 ml/min making a total 100 ml/min gas flow. Concentrations were determined by integrating the peak area and comparing with the peak area of the internal standard. Unknowns were identified by matching their retention times to those of known standards.

The following definition of total THM (TTHM) is used:

$$[TTHM] = 3[CHCl_3] + 3[CHBrCl_2] + 3[CHBr_2Cl] + 3[CHBr_3]$$

with results presented in µmol per liter as halogen atoms. The standard deviation of this procedure is given in Table 1.

TABLE 1. ESTIMATED STANDARD DEVIATION OF THM ANALYSIS

Sample	TTHM µmol/l-x
1	0.351
2	0.330
3	0.301
4	0.288
5	0.307
6	0.310
7	0.311
8	0.316
9	0.337
10	0.241
Average	0.309
Std. Dev.*	0.03

TTHM produced = (TTHM of sample) - (TTHM of unchlorinated sample)

*

$$s_{TTHM\ produced} = \sqrt{s^2_{TTHM\ sample} + s^2_{TTHM\ unchlor.\ sample}} \approx \sqrt{2s^2}$$

$$= \sqrt{2 \times 0.03^2} = 0.04\ \mu mol/l$$

TOX Analysis

TOX analysis was performed on a prototype instrument made available by Dohrmann Envirotech. The procedure is diagrammed in Fig. 2 and is detailed as follows:

1. Organics recovery was achieved by two activated-carbon filters connected in series. Each filter contained 40 milligrams of powdered activated carbon. Secondary effluent samples filtered were 25 milliliters in volume.
2. The carbon filters were washed with a potassium nitrate solution containing 5000 milligram per liter as nitrate to remove inorganic halide. Initially, a four-milliliter aliquot of this solution was used for each set of filters. Subsequently, the volume of nitrate used was reduced to 2 milliliters.
3. The carbon was extruded from the filters and placed into a quartz boat. Under a CO_2 atmosphere the boat was introduced

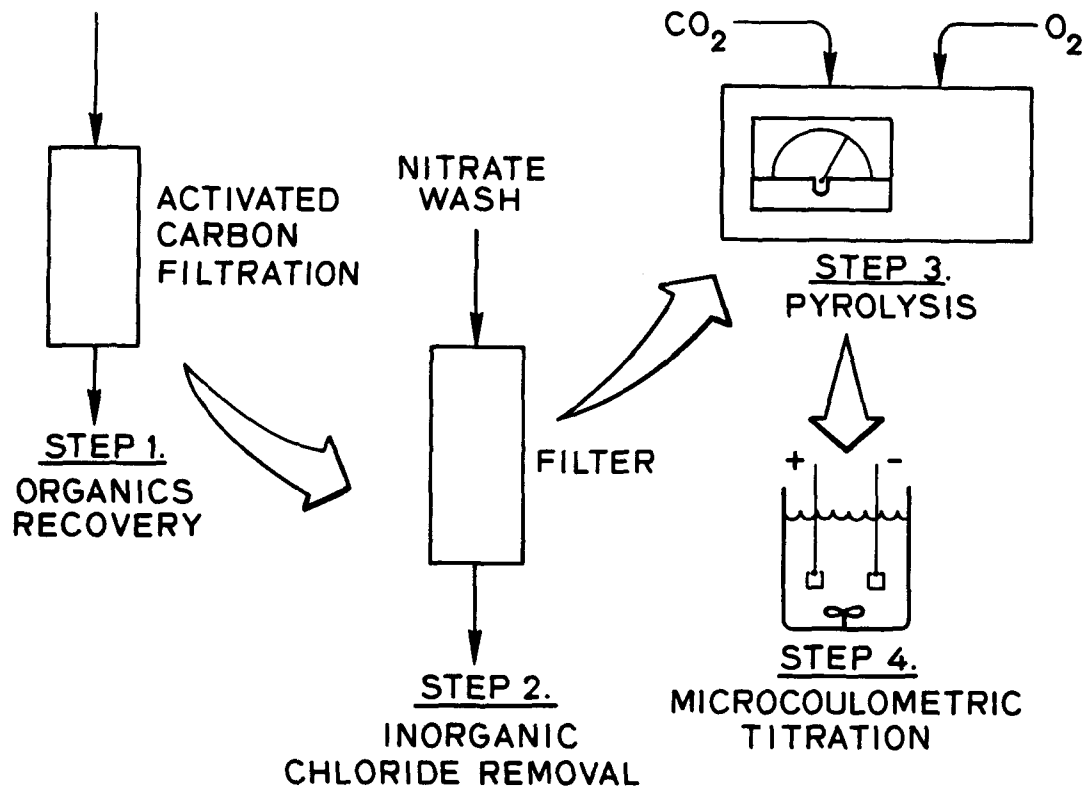


Figure 2. Diagram of TOX analysis.

into a 200°C zone to vaporize the volatile organics. Next, the boat was pushed into the 800°C zone. The CO_2 atmosphere allowed more complete recovery of bromides. Finally the atmosphere was changed to a CO_2/O_2 mixture for completing the combustion.

4. A microcoulometric titration unit served as the detector to measure the amount of chloride and bromide released in the pyrolysis process. In the microcoulometric titration method, silver ion was titrated in a 70% acetic acid electrolyte solution.

Generally, 25-ml samples were filtered. Higher volumes often resulted in clogging due to particulates.

The precision of the TOX method was investigated by determining TOX in ten replicate samples of secondary effluent (Table 2). The average TOX was 4.25 µMol/l-X; the standard deviation of the individual measurements was 0.69 µMol/l-X, or 16 percent of the mean. The calculation of the amount of TOX formed during disinfection entails subtracting the TOX concentration in the unchlorinated sample from that in the chlorinated sample; both quantities incorporate a blank correction (Table 3). The variance of estimated quantity of TOX formed by chlorination is given as:

TABLE 2. PRECISION OF TOX MEASUREMENT

Sample	TOX in µmol/l-X
1	5.92
2	4.76
3	3.85
4	3.89
5	4.16
6	4.27
7	3.85
8	4.43
9	3.87
10	3.45
Average	4.25
Std. Dev.	0.69

TABLE 3. BLANK CORRECTION FOR TOX CALCULATION

Sample	TOX in µMol/l-X
1	1.55
2	1.54
3	1.46
Average	1.52
Std. Dev.	0.05

$$s_{\text{TOX formed}} = \sqrt{s^2_{\text{TOX sample}} + s^2_{\text{TOX unchlor. sample}} + 4s^2_{\text{TOX blank}}}$$

In the case of our measurements, the standard deviation was taken to be 0.69 µMol/l-X for both the treated and untreated samples (Table 2), whereas that of the blank was 0.05 µMol/l-X (Table 3). Hence, the standard error of estimating the amount of TOX formed was calculated as:

$$s_{\text{TOX formed}} = \sqrt{2 \times 0.69^2 + 4 \times 0.05^2} = 0.98 \text{ µmol/l-X}$$

This value was used in judging whether observed amounts of TOX formed should be considered statistically significant.

SECTION 5

CHLORINE AND CHLORINE DIOXIDE CHEMISTRY AND GENERATION

MEASUREMENTS OF CHLORINE DIOXIDE AND CHLORINE SPECIES

Several methods are available for the measurement of chlorine residuals in wastewater. These methods have been extensively developed over many years and the strengths and weaknesses of each are reasonably well understood. Many of these same methods are also applicable to the measurement of chlorine dioxide residuals, with some modifications. Two methods for residual measurement of chlorine dioxide were chosen for investigation in this study: (1) Diethyl-p-phenylene diamine, ferrous ammonium sulfate (DPD-FAS) Titrimetric Method, and (2) Amperometric Method.

Comparison of Residual Measurement Methods

In attempting to measure residual chlorine dioxide by the DPD-FAS technique (6,7,8), some difficulties were encountered. The residual as measured by DPD was consistently higher than the chlorine dioxide dose. The stock solution was standardized immediately before use by the iodometric method, and the dose calculated on this basis. The discrepancy between the DPD-FAS and the iodometric methods was observed not only in wastewater, but also in deionized water, distilled water and tap water. This discrepancy was not seen when chlorine was the oxidant of interest.

In the iodometric method, chlorine dioxide is reduced to chloride (Cl^-). However, several researchers (8,9,10) have reported that the pH used in the iodometric analysis (pH ~ 1.8) is not low enough to assure complete reduction of the chlorine dioxide to Cl^- (see Fig. 3). If, indeed, this is the case, the iodometric results would give a low value for the concentration of chlorine dioxide in the stock solution. The DPD method, which is performed at pH 6.2 to 6.4, is assumed to measure the reduction of chlorine dioxide to chlorite, and would therefore indicate a higher value of chlorine dioxide than that given by the iodometric analysis. It was hypothesized that the iodometric analysis was not measuring all the chlorine dioxide and hence the discrepancy between the two methods.

$$ClO_2 + e^- \longrightarrow ClO_2^- \qquad pH\ 7$$

$$ClO_2 + 5e^- \longrightarrow Cl^- + 2\,O^{--} \qquad pH < 2$$

Figure 3. Reduction of chlorine dioxide as a function of pH.

To test this hypothesis, two experiments were performed. In the first experiment, the iodometric analysis was performed at various pH values ranging from 2.0 to 0.8. No difference in titration value was found. In the second experiment, the iodometric analysis performed at pH 1.8 was compared to the amperometric analysis at pH 7. The amperometric method is analogous to the iodometric method with these exceptions:

1. In the amperometric analysis the endpoint is detected by observing the change in current flow in the sample while adding a strong reducing agent as titrant.
2. In the amperometric analysis, phenylarsine oxide (PAO) is the titrant instead of sodium thiosulfate as used in the iodometric method.
3. In the amperometric analysis the determination is performed at pH 7. At this pH only one electron transfer is possible for chlorine dioxide.

Since at pH 7, chlorine dioxide is reduced only to chlorite, a higher concentration of chlorine dioxide as measured by the amperometric analysis would indicate that chlorine dioxide was not being fully reduced to chloride as assumed in the iodometric method. The analyses were run in distilled water. The results appear in Table 4, and a statistical analysis appears in Table 5.

TABLE 4. COMPARISON OF AMPEROMETRIC AND IODOMETRIC METHODS FOR DETERMINING CONCENTRATION OF ClO_2

Trial	Iodometric*	Amperometric*
1	563.7	547.2
2	563.7	554.8
3	566.4	571.9
4	561.0	560.5
5	560.3	558.6
Mean	563.0	558.6
Std.Dev.	2.18	8.06
s^2	4.77	64.98

*mg/l as ClO_2.

TABLE 5. COMPARISON OF AMPEROMETRIC AND IODOMETRIC METHODS BY ANALYSIS OF VARIANCE

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Between Methods	1	48.8	48.8	1.12*
Error	8	348.7	43.6	
TOTAL	9	397.5		

*Not significant ($p < 0.05$).

As seen in Table 5, the difference between the values obtained by the two methods is not significant. It can be inferred from these data that the iodometric method accurately measures the concentration of chlorine dioxide in stock solutions. The inconsistency must then be in the assumed reactions of the DPD-FAS method. It is hypothesized (although untested at this time) that the chlorite from the reduction of chlorine dioxide reacts with the DPD reagent to a slight extent. Due to the continuing problems with the DPD-FAS method, further investigations into utilizing the amperometric method for measurement of residual chlorine dioxide were made.

Amperometric Back-Titration

The amperometric titration measures iodine (I_2) released into solution when iodide is oxidized by any powerful oxidant such as chlorine dioxide or chlorine. If this released I_2 comes into contact with organic constituents in the sample (as in the case of wastewater), the I_2 will react with the organics. To prevent this, a back-titration procedure is recommended, in which the liberated I_2 is immediately reacted with phenylarsine oxide (PAO), which has been added to the sample prior to the addition of iodide (as KI). The PAO is added in excess and the unreacted PAO is back-titrated with an I_2 solution of known concentration. The concentration of chlorine dioxide (or chlorine) is then determined by difference. To evaluate the need for this back-titration procedure, chlorine dioxide residual measurements were made in Palo Alto secondary effluent, comparing the amperometric method with and without back-titration.

The results of this experiment are reported in Table 6. The experiment entailed dosing 2 liters of Palo Alto secondary effluent to 4.50 mg/l with pure chlorine dioxide. The sample was then contacted for 2 minutes. After

TABLE 6. AMPEROMETRIC TITRATION EVALUATION*

	Secondary Filtered		Secondary Unfiltered	
Sample	Forward Titration	Back Titration	Forward Titration	Back Titration
1	1.90	2.12	1.62	1.88
2	1.86	2.31	1.62	1.97
3	1.90	2.13	1.52	2.07
4	1.84	2.22	1.52	1.88
5	1.81	2.22	1.52	1.88
6	1.73	2.12	1.39	1.88
7	1.67	2.12	1.39	1.88
8	1.91	2.12	1.27	1.79
Mean	1.80	2.17	1.49	1.90
Std.Dev., s	±0.083	±0.067	±0.109	±0.077
s^2	0.0069	0.0045	0.0119	0.0060

*Results are given as mg/l ClO_2 at 2-minute contact time; dose = 4.50 mg/l ClO_2. Titrations were performed at pH 7.

the contact period, sufficient KI and pH 7 buffer were added to the sample to react with all the chlorine dioxide present. In the case of the I_2 back-titration, sufficient PAO was added to swamp the released I_2. Eight replicates were run at approximately one-minute intervals. The experiment was repeated for filtered Palo Alto secondary effluent. The values reported have been corrected for blank titrations. In the case of the forward titration, no correction was necessary, but for the I_2 back-titration more I_2 solution was required in the blank than was indicated by the amount of PAO added. (The I_2 solution was standardized immediately prior to use.) Although not shown in Table 6, the blank titrations (done in triplicate) showed the same variation as the forward or backward titration. The standard deviations shown in Table 6 are not statistically different from one another as measured by the F-test.

An analysis of variance (ANOVA) comparing the forward titration with the I_2 back-titration showed that there is a significant difference between the values measured by the two titrations (Table 7). Based on the ANOVA results, the amperometric back-titration method was chosen for the measurement of chlorine dioxide residuals in wastewater.

TABLE 7. ANALYSES OF VARIANCE FOR AMPEROMETRIC TITRATION

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
ANOVA for Filtered Secondary Effluent:				
Between forward and back-titrations	1	0.54023	0.54023	82.79*
Error	14	0.09135	0.006525	
TOTAL	15	0.63158		
ANOVA for Unfiltered Secondary Effluent:				
Between forward and back-titrations	1	0.67651	0.67651	66.35*
Error	14	0.14274	0.01020	
TOTAL	15	0.81924		

*$P < 0.001$ that F is exceeded.

Chlorite Interference

To investigate the possible interference of chlorite in the determination of chlorine dioxide by the amperometric method, a solution of sodium chlorite was added to a sample containing chlorine dioxide in distilled water. Since the sodium chlorite used was only ~ 95% pure, glycine (aminoacetic acid) was added to the sample to react any chlorine or bromine compounds present which would give an apparent positive result from the chlorite (7). The results of this experiment (Table 8) showed no significant difference caused by the presence of chlorite.

TABLE 8. THE EFFECT OF CHLORITE ON THE DETERMINATION OF CHLORINE DIOXIDE BY AMPEROMETRIC TITRATION

Sample	ClO_2	ClO_2 + 4.33 mg/l ClO_2^- + Glycine*
1	5.47	5.55
2	5.55	5.51
3	5.72	5.55
4	5.61	5.61
5	5.59	5.61
Mean	5.59	5.57

*Two ml of 100 g/l solution of glycine added to 200 ml of sample.

The amperometric back-titration method for measurement of chlorine residuals in wastewater is a widely used and well-accepted method (11). Since this method was found acceptable for chlorine dioxide residual measurements, it was also chosen for the measurement of chlorine residuals. The analyses for chlorine residuals (as Total Available Chlorine) are performed at pH 4 to ensure quantitative response from all forms of combined chlorine (11). Results from our laboratory indicate that at pH 4 there is no need for a blank correction. The reaction of PAO with I_2 must be somewhat slower at pH 7 than at pH 4, so that some of the added I_2 titrant would be available for reaction with other sample constituents; hence the need for blank correction in determining chlorine dioxide residuals at pH 7.

MEASUREMENT OF CHLORINE DIOXIDE GENERATOR PRODUCT COMPOSITION

Chlorine dioxide for use in wastewater disinfection is generated by either a chlorine-sodium chlorite reaction or by a mineral acid-sodium chlorite reaction. Impurities of the reactants and incomplete reaction necessitate a methodology to identify all possible chlorine species. The possible chlorine species in the final products are:

1. Chlorine - Cl_2, HOCl
2. Chlorine Dioxide - ClO_2
3. Chlorite - ClO_2^-
4. Chlorate - ClO_3^-
5. Chloride - Cl^-

Analysis of Chlorine Species

The analytical methodology developed for this study to identify reactor product composition is essentially an iterative process in which successive measurements include one more chlorine species than the previous measurement. The method is as follows:

1. Measurement of chlorine dioxide: Chlorine dioxide absorbs ultraviolet radiation in the 240-440 nm wavelength. A wavelength of 360 nm was chosen for chlorine dioxide determinations because this corresponds to the peak of the absorbance curve; also, there is no interference from other chlorine species at this wavelength.

A calibration curve was prepared by appropriate dilutions of a standardized stock solution to yield concentrations in the 5 mg/l to 60 mg/l range. The response of ClO_2 is linear in this concentration range and an equation can be derived relating concentration to absorbance. A typical concentration equation with correlation coefficient r^2 is given below:

$$\text{mg/l } ClO_2 = 58.26 \times (\text{absorbance}) - 0.255$$

$$r^2 = 0.998$$

The calibration equation will depend on the instrument and path length used and should be checked often.

A sample of reaction product was diluted so that the concentration of ClO_2 to be analyzed was in the linear range (5-60 mg/l). The instrument was set to zero absorbance with a blank of the dilution water just prior to sample analysis. The concentration of ClO_2 in the diluted solution was calculated using the calibration equation and the appropriate dilution factor was applied. This was "Reading A."

2. Measurement of chlorine dioxide and chlorine: Chlorine dioxide and chlorine were measured by forward amperometric titration at pH 7. An appropriate sample size was chosen so that no more than 5 ml of phenylarsine oxide were used in the titration. To approximately 200 ml of distilled water, were added 2 ml pH 7 buffer, the sample, and 2 ml of 5% KI solution, in that order. This mixture was titrated with 0.00564N PAO and the resulting volume (ml) of PAO solution was recorded as "Reading B."

3. Measurement of chlorine dioxide, chlorine, and chlorite: Chlorine dioxide, chlorine, and chlorite were measured by iodometric titration at pH 2. To 50 ml of distilled water were added 5 ml of concentrated acetic acid, 5 ml of sample and approximately 1 g of KI. This mixture was allowed to react in the dark for 5 min and was then titrated to a starch endpoint with 0.1N (standardized) sodium thiosulfate. This was "Reading C."

4. Measurement of chlorine dioxide, chlorine, chlorite, and chlorate: This procedure was essentially as in Step 3 of this enumeration, with the following exceptions. To a 50-ml erlenmeyer flask was added 5 ml concentrated hydrochloric acid and 0.5 g KI. To this mixture was added 5 ml of sample. The mixture was sealed and allowed to react in the dark in a closed flask for 10 min. A blank was also carried through the procedure since KI is oxidized by oxygen in this low pH environment (pH < 0.1). After 10 min, the mixture was diluted to ~ 50 ml and titrated with 0.1N sodium thiosulfate. This reading minus the blank value was "Reading D."

5. Measurement of chloride: This procedure was essentially the Mercuric Nitrate Method (408B) as given in Standard Methods (1) with the following exception: when measuring the chloride concentration in a reaction mixture containing high levels of chlorine dioxide, the sample was diluted to yield a final chlorine dioxide concentration of about 10 mg/l. To 100 ml of this solution was added 4.0 ml of indicator-acidifier reagent instead of 1.0 ml as given in (1). The sample was then titrated as specified. This reading minus the blank value was "Reading E."

All calculations, with the exception of the chlorine dioxide/spectrophotometric measurement and the chloride measurement were based on the equivalents of reducing titrant required to react with the equivalents of oxidants present. The equivalent weight of a compound was defined as that weight of the compound which contains one gram atom of available electrons, i.e., equivalent weight equals molecular weight divided by number of electrons transferred. For chlorine dioxide, the equivalent weight is pH-dependent, because at pH 7 chlorine dioxide is reduced to chlorite, while at pH $<$ 2 chlorine dioxide reduces to chloride. Chlorite and chlorate also exhibit an equivalent weight pH-dependency. A listing of the equivalent weights used in the calculations is shown in Table 9.

Evaluation of Chlorine Dioxide Reactor Yields and Reactor Stoichiometry

Acid Activation of Sodium Chlorite--

When chlorine dioxide is generated from sodium chlorite by acid activation, chlorine dioxide is not the only end product. The final composition is dependent on several variables, among which are: sodium chlorite concentration; purity of sodium chlorite used; acid concentration and pH of reaction mixture; reaction time; and temperature of reaction.

Several stoichiometries have been reported in the literature for acid activation of a chlorite solution (12). The two stoichiometries which are most widely accepted are (shown as sulfuric acid activations):

$$4NaClO_2 + 2H_2SO_4 = 2Na_2SO_4 + 2ClO_2 + HCl + HClO_3 + H_2O \quad (1)$$

and

$$10NaClO_2 + 5H_2SO_4 = 8ClO_2 + 5Na_2SO_4 + 2HCl + 4H_2O \quad (2)$$

The first reaction is catalyzed by the chloride ion, which is also a product of the reaction. Not only has it been reported that the reaction is accelerated by the product, chloride ion, but also that the stoichiometry is altered to that of the second reaction (12). Although chlorine has been reported among the reaction products of chlorine dioxide generation, most evidence appears to be against the formation of significant amounts of chlorine (12).

TABLE 9. EQUIVALENT WEIGHTS FOR CALCULATING CONCENTRATIONS ON A MASS BASIS

pH	Species*	Molecular Weight (mg/mole)	Electrons Transferred	Equivalent Weight (mg/eq)
7	ClO_2	67,450	1	67,450
2, 0.1	ClO_2	67,450	5	13,490
7, 2, 0.1	Cl_2	70,900	2	35,450
2, 0.1	ClO_2^-	67,450	4	16,863
0.1	ClO_3^-	83,450	6	13,908

*Species Calculations:

Chlorine dioxide: $mg/l\ ClO_2 = 58.26\ (\text{absorbance}) - 0.255 = A$

$$\text{Chlorine:}\quad mg/l\ Cl_2 = \frac{35{,}450\ mg}{eq}\left(\frac{B(ml) \times normality(eq/l)}{sample(ml)} - \frac{mg/l\ ClO_2}{67{,}450\ mg/eq}\right)$$

$$\text{Chlorite:}\quad mg/l\ ClO_2^- = \frac{16{,}863\ mg}{eq}\left(\frac{C(ml) \times normality(eq/l)}{sample(ml)} - \frac{mg/l\ Cl_2}{35{,}450\ mg/eq} - \frac{mg/l\ ClO_2}{13{,}490\ mg/eq}\right)$$

$$\text{Chlorate:}\quad mg/l\ ClO_3^- = \frac{13{,}908\ mg}{eq}\left(\frac{D(ml) \times normality(eq/l)}{sample(ml)} - \frac{mg/l\ ClO_2^-}{16{,}863\ mg/eq} - \frac{mg/l\ Cl_2}{35{,}450\ mg/eq} - \frac{mg/l\ ClO_2}{13{,}490\ mg/eq}\right)$$

$$\text{Chloride:}\quad mg/l\ Cl^- = \frac{35{,}450\ mg/eq \times E(ml) \times normality(eq/l)}{sample(ml)}$$

where A, B, C, D, E denote the respective Readings A, B, C, D, E, as defined in the text.

Reaction Stoichiometry in Laboratory Generation--

To determine reaction stoichiometries, a mass balance on chlorine around a reactor must be made using the analytical technique previously described. Prior to examining a commercial reactor, a laboratory reaction mixture was prepared, a mass balance performed, and a reaction stoichiometry determined. There are significant differences between laboratory reaction conditions and those typically found in full-scale commercial reactors. Therefore, the stoichiometries observed would not necessarily be the same. In the laboratory, the concentration of sodium chlorite in the reaction vessel was 0.083M, while in commercial reactors the concentration is typically 2.0M. Concentration not only affects the time until the reaction is complete but may affect

the stoichiometry as well. In commercial reactors the concentrated reaction mixture is allowed to react for approximately 5 to 25 min and is then diluted (within the reactor) before being fed to the process stream.

The initial and final compositions of the laboratory reaction mixture are shown in Table 10. Under these conditions the laboratory reaction was complete within 3 hrs; no change in composition was found after this time. The recovered mass of chlorine represents 104% of the initial mass of chlorine; considering experimental error, this value is not significantly different from the expected value of 100%.

If the initial composition of the reaction mixture is equated to the final composition, the following equation results:

$$\begin{aligned} 0.083\ ClO_2^- + 0.0004\ ClO_3^- + 0.0177\ Cl^- \\ = 0.0037\ ClO_2^- + 0.0206\ ClO_3^- + 0.0424\ Cl^- \\ + 0.0380\ ClO_2 + 0.0007\ Cl_2 \end{aligned} \quad (3)$$

TABLE 10. COMPOSITION OF REACTANTS AND PRODUCTS IN LABORATORY GENERATION OF CHLORINE DIOXIDE BY SULFURIC ACID ACTIVATION OF SODIUM CHLORITE

Species	Chlorine Atoms Moles per liter
Reactants	
ClO_2	0.0
ClO_2^-	0.083
ClO_3^-	0.0004
Cl_2	0.0
Cl^-	0.0177
Total	0.1011
Final Composition (pH 1.75)	
ClO_2	0.038
ClO_2^-	0.0037
ClO_3^-	0.0206
Cl_2*	0.0004
HOCl*	0.0005
Cl^-	0.0424
Total	0.1056

*Calculated assuming equilibrium is attained in chlorine hydrolysis, $K_H = 3 \times 10^{-4}$.

Collecting terms and relating all species to a reaction involving four moles of chlorite, analogous to Reaction 1, yields:

$$4\ ClO_2^- = 1.92\ ClO_2 + 1.02\ ClO_3^- + 1.25\ Cl^- + 0.04\ Cl_2 \qquad (4)$$

This stoichiometry is essentially that of Reaction 1.

Reaction Stoichiometry in Full-Scale, Continuous Generation--

A reaction mixture from a continuous, full-size generator (commercially available from Rio-Linda Chemical Company) was analyzed. This reactor utilized the sulfuric acid activation of sodium chlorite. The reactor consists of a section of PVC pipe, 100 mm in diameter and 660 mm long, packed with turbulence-inducing packing. Its nominal capacity is approximately 2 kg/h ClO_2 (Fig. 4). The composition of reactants (calculated from the flow rate and composition of reactant streams) and products (obtained from determination of reactor product composition) are shown in Table 11. The sample was taken four hrs before the analyses were performed, and it is not known to what extent the reaction may have proceeded during transportation. Therefore, the values reported in Table 11 should be taken as equilibrated values for the reaction mixture at the time of analysis.

The recovered mass of chlorine atoms represents 104% of the initial mass; this is not significantly different from 100%. The stoichiometry related to a reaction involving four moles of ClO_2^- is:

$$4\ ClO_2^- = 2.63\ ClO_2 + 0.53\ ClO_3^- + 1.01\ Cl^- + 0.05\ Cl_2 \qquad (5)$$

which can be compared to the result from the laboratory reaction (Eq. 4), or, on the basis of ten moles of ClO_2^- reacting:

$$10\ ClO_2^- = 6.58\ ClO_2 + 1.32\ ClO_3^- + 2.52\ Cl^- + 0.12\ HOCl \qquad (6)$$

Comparing Eqs. 5 and 6 with Eqs. 1 and 2, it appears that the reactor stoichiometry falls between stoichiometries 1 and 2. This may indicate that the overall reaction in an acid-chlorite generator is a combination of Reactions 1 and 2. In addition, from Table 11, it can be seen that only 78% of the added chlorite is participating in the reaction at all, and of that 78%, 66% is converted to chlorine dioxide. This gives an overall yield of 51%, i.e., 51% of added chlorite is converted to chorine dioxide, 10% is converted to chlorate, 22% is unreacted chlorite, and the remainder is accounted for as chloride and a trace of chlorine. Under the most favorable conditions, the maximum yield of chlorine dioxide found from the sulfuric acid activation of sodium chlorite was in the 50-55% range.

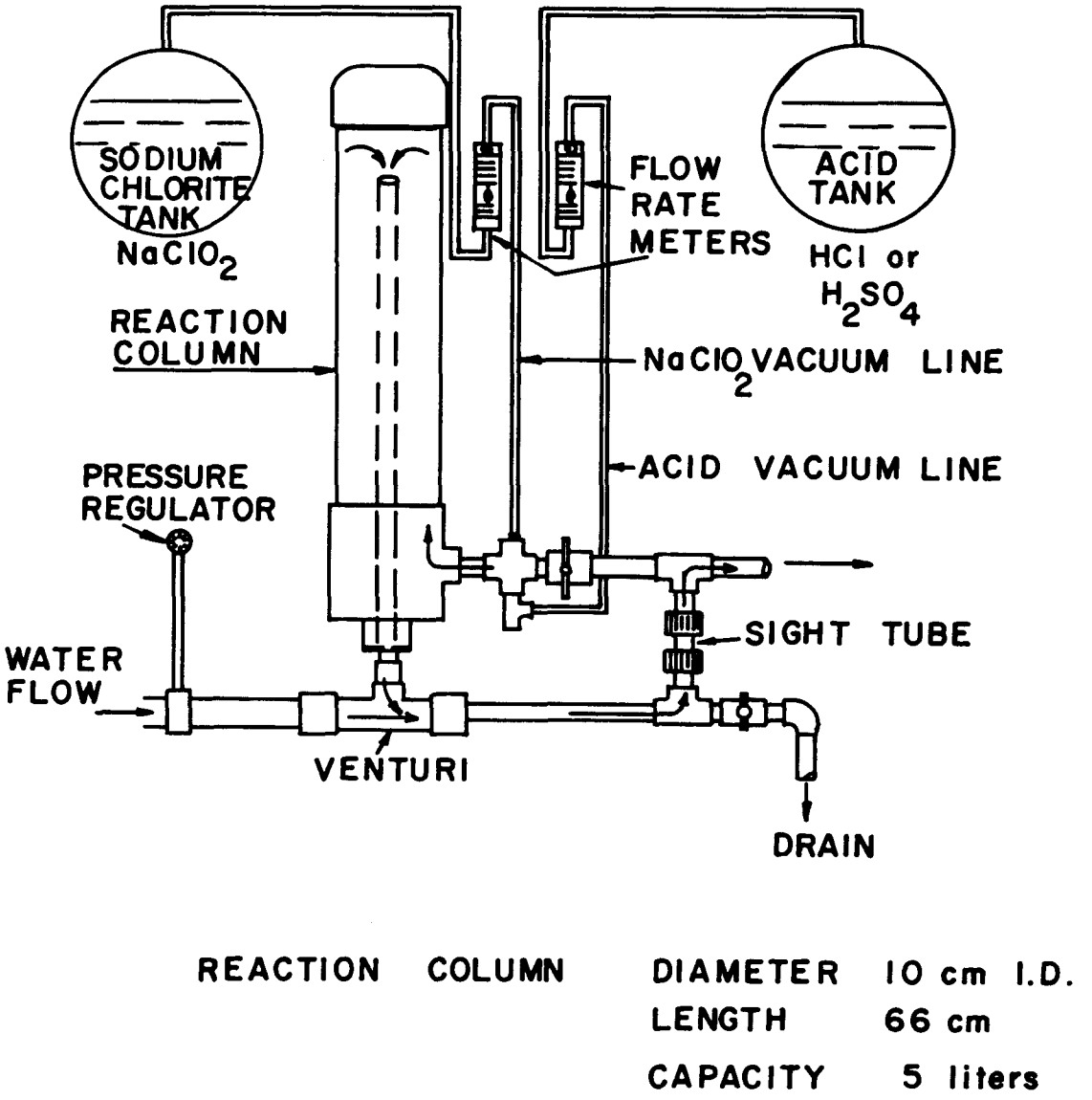


Figure 4. Chlorine dioxide generator, acid-chlorite process.

Since it had been reported (12) that the chloride ion catalyzes the reaction and alters the stoichiometry to the more favorable Reaction 2, the commercial reactor under study was converted to hydrochloric acid activation from sulfuric acid activation. To evaluate this generation process, a mass balance on chlorine atoms was again performed around the commercial reactor. The results of this mass balance are reported in Table 12.

The recovered mass of chlorine represents 99.7% of the initial mass. If the stoichiometry of this mixture is determined and related to an equation involving 10 moles of chlorite, the following stoichiometry is found:

$$10\ ClO_2^- = 8.04\ ClO_2 + 0.28\ ClO_3^- + 1.58\ Cl^- \qquad (7)$$

TABLE 11. COMPOSITION OF REACTANTS AND PRODUCTS FROM CHLORINE DIOXIDE GENERATION IN A CONTINUOUS, FULL-SIZED ACID-CHLORITE REACTOR USING H_2SO_4

Species	Chlorine Atoms Moles per liter
Reactants	
ClO_2	0.0
ClO_2^-	0.0214
ClO_3^-	0.0003
Cl_2	0.0
Cl^-	0.0021
Total	0.0238
Final Composition (pH 2.1)	
ClO_2	0.0109
ClO_2^-	0.0048
ClO_3^-	0.0025
Cl_2*	< 0.0001
HOCl*	0.0002
Cl^-	0.0063
Total	0.0247

*Calculated assuming equilibrium is attained in chlorine hydrolysis, $K_H = 3 \times 10^{-4}$.

Reaction 7 very closely approximates Eq. 2, the stoichiometry reported by Gordon et al. (12) as optimum for acid activation of sodium chlorite.

From Table 12 it can be seen that 97% of the chlorite has reacted, compared to only 77% previously reported for activation of sodium chlorite by sulfuric acid. Of the feed chlorite 78.2% is converted to chlorine dioxide. The average conversion of feed sodium chlorite observed in three field experiments (Table 13) was 78.5%. In view of the agreement between laboratory and field data, it is reasonable to expect consistent reactor yields of 78% conversion of sodium chlorite to chlorine dioxide by acid activation with hydrochloric acid. The complete stoichiometry expected from hydrochloric acid activation of sodium chlorite is as follows:

$$5NaClO_2 + 5HCl = 4ClO_2 + 5NaCl + HCl + 2H_2O \quad (8)$$

TABLE 12. COMPOSITION OF REACTANTS AND PRODUCTS FROM CHLORINE DIOXIDE GENERATION IN A CONTINUOUS, FULL-SIZED ACID-CHLORITE REACTOR USING HCl

Species	Chlorine Atoms Moles per liter
Reactants	
ClO_2	0.0
ClO_2^-	0.0110
ClO_3^-	0.0000
Cl_2	0.0000
Cl^-	0.0260
Total	0.0370
Final Composition (pH 2.2)	
ClO_2	0.0086
ClO_2^-	0.0003
ClO_3^-	0.0003
Cl_2 and HOCl	< 0.0001
Cl^-	0.0277
Total	0.0369

TABLE 13. YIELD OF CHLORINE DIOXIDE FROM ACID ACTIVATION IN FIELD EXPERIMENTS

Date	ClO_2^- - Feed (mg/l)	ClO_2-Output (mg/l)	% yield
1-16-79	2111.4	1573.4	74.5
2-5-79	2072.3	1581.0	76.3
2-13-79	1454.3	1231.0	84.6
Average conversion			78.5

Chlorine-Chlorite Generation of Chlorine Dioxide--

An alternative generation method for chlorine dioxide utilizes the reaction of sodium chlorite with chlorine. A mass balance on chlorine around a reactor using this reaction was attempted but time limitations of the analytical procedure precluded a meaningful mass balance. The simplified stoichiometry for this reaction is:

$$2NaClO_2 + Cl_2 = 2ClO_2 + 2NaCl \quad (9)$$

From Reaction 9, theoretically 100% of the sodium chlorite can be reacted to chlorine dioxide. An excess of chlorine above the stoichiometric requirement as predicted by Reaction 9 has been found to increase yields of chlorine dioxide substantially and ensures complete conversion of sodium chlorite. The excess chlorine (predominately as HOCl) presented the analytical problem mentioned above. Hypochlorite ion reacts with chlorine dioxide over time to produce chlorate ion according to Reaction 10:

$$2ClO_2 + OCl^- + H_2O = 2ClO_3^- + Cl^- + 2H^+ \quad (10)$$

While this reaction is not instantaneous, it is sufficiently rapid to cause significant decreases in the chlorine dioxide concentration between sampling time and analysis for mass balance. Therefore, samples were analyzed immediately for chlorine dioxide to determine yields of chlorine dioxide, and chlorite measurements were made within 6 hours to estimate extent of reaction.

Chlorine dioxide yields were found to vary from 93 to 98% based on feed chlorite. Chlorite conversion amounted to 97% of that fed to the reactor. Chlorine feed was approximately 4% above the stoichiometric requirement based on chlorite.

Chlorine Dioxide from Sodium Chlorate--

Chlorine dioxide may also be generated directly from chlorate (13), rather than passing through the intermediate step of reducing the chlorate to chlorite. Generation of chlorine dioxide directly from chlorate is practiced widely in the pulp and paper industry, but not in water treatment. Problems of reactor instability reportedly are encountered. There is an economic incentive for developing a generation process based on chlorate for use in water and wastewater treatment. The chemical costs are considerably lower than in processes based on chlorite.

SECTION 6

MODELS OF DISINFECTION KINETICS

FIRST-ORDER KINETICS

To compare the relative disinfection capabilities of chlorine and chlorine dioxide, an empirical model relating degree of bacteria inactivation to the contact time and residual concentration was used in this study. The model was first applied to disinfection to approximate kinetics that deviated greatly from the often assumed first-order disinfection kinetics referred to as "Chick's law."

In 1908, Harriette Chick published her "Investigation of the Laws of Disinfection" (14). She examined the destruction of several bacterial organisms in buffered distilled water by phenol and other compounds. It is interesting to note that in only one experiment, the destruction of unicellular anthrax spores by phenol, did she observe the rate expression which carries her name. That expression is the familiar first-order kinetic rate expression:

$$\frac{dN}{dt} = - kN \tag{11}$$

or in integrated form:

$$\frac{N}{N(0)} = e^{-kt} \tag{12}$$

where N = number of surviving organisms at time = t;

N(0) = number of organisms at time = 0;

k = rate constant.

DECREASING RATE AND LAG TIME

In the majority of experiments, however, Chick observed that the rate constant k did not remain constant and in fact decreased over the course of an experiment. This type of relationship is generally what is observed in wastewater disinfection: namely, a decreasing rate of bacterial inactivation as the disinfection process proceeds (15). In wastewater disinfection, however, the disinfection process begins after some finite time interval, the lag

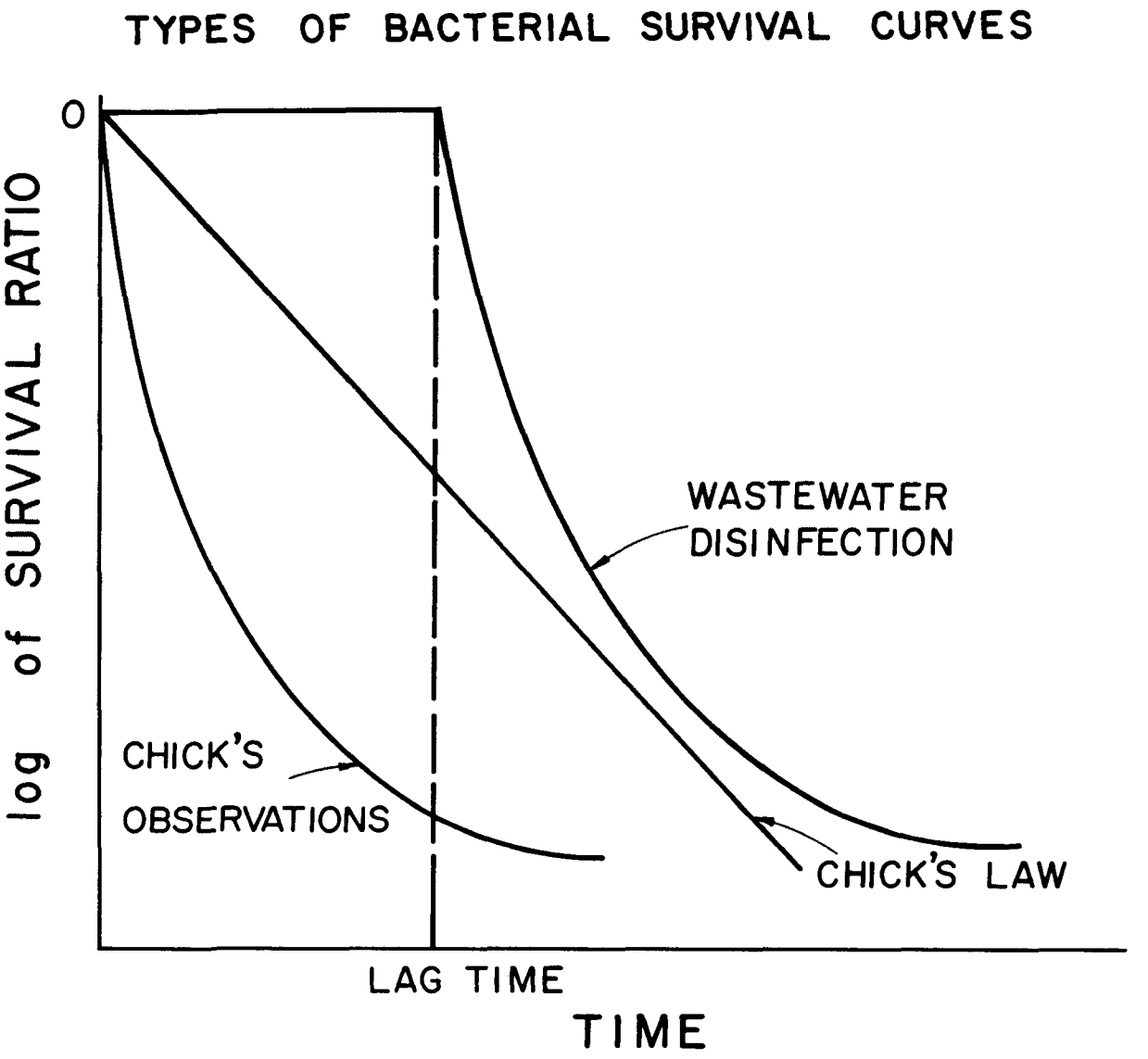


Figure 5. Types of bacterial survival curves.

time. (Chick also observed a lag time with some pure cultures in clean systems.) These relationships are shown in Fig. 5.

Several hypotheses have been formulated to explain both the lag time and the decreasing rate of disinfection:

1. The lag time is indicative of the diffusion to and transport across the cell membrane and the reaction time for inactivation within the cell (16).
2. The organisms are not isolated but are associated in groups, so that the internal organisms are protected by those on the periphery of the agglomeration. The lag time is then related to the size of the aggregation and is indicative of the time to reach the inner-most organism (17).
3. The decreasing rate is due to a decrease in the germicidal properties of the disinfecting agent, i.e. residual (18).
4. The bacterial population has an ab origine distribution of susceptibilities to the disinfecting agent so that the observed decreasing rate is the sum of several first-order rate constants (19).
5. The decreasing rate is the result of the bio-chemical disinfection reaction inducing an increased resistance in the population of organisms, i.e. induced heterogeneity (20).

Chick postulated several mechanisms of bacterial destruction to account for the decreasing rate of inactivation (14), and attempted to test them. She found that the rate of inactivation she observed was related to the age of the pure culture used and the seed material from which the culture was grown.

RETARDANT REACTION APPROACH

In the 1930s, Fair and Thomas (21) observed the same type of kinetic behavior in studies of biochemical oxygen demand, (BOD). Fair applied an empirical model, called the "retardant" formula, to his observations of decreasing rate of reaction. As applied to the BOD reaction, this rate expression is:

$$-\frac{dL}{dt} = \frac{k}{1 + at} L \tag{13}$$

and in integrated form is:

$$L_t = L_o(1 + at)^{-k/a} \tag{14}$$

where L = BOD;

L_o = ultimate BOD;

L_t = BOD at time t;

k = velocity constant;

a = coefficient of retardation; and

t = time.

An intuitive rationalization of this expression for BOD is based on the relative rates of oxidation by bacteria of the organics present in a test sample. The least stable compounds are oxidized at a high rate early in the test. As these compounds are depleted, the rate of reaction becomes a function of the more stable organics and the overall rate of reaction slows. This same relationship was also applied by Fair and Geyer (22) to the removal of BOD through a trickling filter.

Phelps (23) reported on the self-purification of streams and rivers as regards bacterial numbers. It was found that the bacteria disappear according to a decreasing rate of inactivation and that Fair's retardant formula (21) is applicable to this situation also.

In 1957, at a Ciba Foundation Conference (24), a discussion between Jonas Salk, the discoverer of polio vaccine, and Sven Gard, a Swedish researcher, centered on the kinetics of chemical virus inactivation. There was more than just an academic interest in this area since children in the U.S.A. were being vaccinated with formaldehyde-inactivated polymyelitis virus. Salk contended that the inactivation proceeded according to first-order kinetics (Chick's law), while Gard presented evidence that the rate of inactivation deviated from first order in that the rate was decreasing over time. Gard then applied a model identical to Fair's retardant formula (although Gard did not call it that, nor did he reference it) to his data and showed excellent agreement between his experimental data and this model. In Gard's formaldehyde-virus system, he observed that both an increase in formaldehyde and an increase in reaction time had the same effect on inactivation. He reasoned that concentration (R) and time (t) should be interchangeable and should appear in the reaction equation together as a factor "Rt," This is equivalent to the statement that for a given level of inactivation Rt = constant . Gard merely stated this conclusion with no explanation or evidence to support it.

This relationship between concentration and time had been discussed by both Chick (14) and Watson (25). Watson formulated as a general relationship that $R^n t$ = constant . He interpreted this relationship as a chemical reaction between one molecule of one substance with n molecules of a second substance, or analogous to a chemical process:

$$[R]^n[t] = K \tag{15}$$

with $[t]$ as an artificial concentration. In kinetic terms, n depicts the empirical reaction order with respect to disinfection concentration. Fair et al. (26) reported some experiments on the effect of concentration on bacterial inactivation and found n to vary from 0.8 to 1.4 for free chlorine and n to equal 1.3 for chloramines. The value of n is probably temperature-

dependent and organism-specific. Incorporating this concept into the retardant formula, Gard's model (taking $n = 1$) as a rate equation for inactivation is:

$$-\frac{dN}{dt} = \frac{k}{1 + a(Rt)} N \tag{16}$$

or in integrated form

$$N(t) = N(0)\ (1 + a(Rt))^{-k/a} \tag{17}$$

where N = number concentration of target organism;

$N(t)$ = concentration at time t;

$N(0)$ = initial concentration;

k/a = velocity coefficient;

R = concentration of chemical species held constant over time;

a = coefficient of retardation; and

t = time.

It is important to note that in the integration of the above rate reaction, the concentration (R) is assumed to be constant during the entire time interval of integration.

Selleck et al. (27) have applied Gard's model to the disinfection process in primary effluent. They have, however, made some modifications and relaxed the assumptions required for integration of Gard's rate equation.

Typically in wastewater disinfection, there is a lag time, t', during which no disinfection or bacterial inactivation takes place. This is true for constant concentration of chemical disinfectant. If, however, the disinfectant concentration R is allowed to vary, then a minimum product $(Rt)'$ must be exceeded before inactivation takes place. Selleck et al. (27) have taken the basic rate expression as:

$$\frac{dN}{dt} = -kN \tag{18}$$

where

$$k = 0 \quad \text{for} \quad (Rt) < (Rt)' \tag{19}$$

$$k = k' \quad \text{for} \quad (Rt) = (Rt)' \tag{20}$$

and

$$k = \frac{k'}{a(Rt)} \quad \text{for} \quad (Rt) > (Rt)' \tag{21}$$

Equations 20 and 21 above are equivalent to the statement that $(Rt)' = a^{-1}$. Integrating the rate expression for the general case and applying the boundary condition that at $Rt = (Rt)'$; $N(t) = N(0)$ yields:

$$N(t) = N(0)\left[\frac{(Rt)}{(Rt)'}\right]^{-k'/a} \tag{22}$$

$$N(t) = N(0) \quad \text{for} \quad (Rt) < (Rt)' \tag{23}$$

where all variables are defined as before.

An implicit assumption made in the integration of the above rate expression is that the concentration (R) remains constant. In the case of wastewater disinfection with either chlorine or chlorine dioxide, the concentration (R) decreases with time. Selleck et al. (27) use a mathematical extrapolation to estimate the active residual concentration of chlorine after the immediate demand of the wastewater has been satisfied and assume the bactericidal properties of the residual to remain constant.

In this study, the modified retardant formula has been used to describe the disinfection process in several wastewaters of varying quality. In order to incorporate into the model some means of adjusting for the difference in quality among wastewaters and hence the oxidant demand, the residual oxidant is measured at the actual exposure time of the bacteria. This allows the more general application of the model and renders more meaningful the comparisons between wastewaters of different levels of treatment. In addition, measurement of residual at the end of the organism exposure time yields a lower limit on (Rt) for the measured level of inactivation. The model used in this study is given by Equations 24 and 25:

$$N(t) = N(0)\left[\frac{(Rt)}{b}\right]^{k} \quad \text{for } Rt > b \tag{24}$$

$$N(t) = N(0) \quad \text{for} \quad Rt < b \tag{25}$$

where N(0) = initial total coliform bacteria;

N(t) = total coliform bacteria at time = t;

R = residual oxidant in mg/l as measured at time t;

b = lag time coefficient (Rt)' in mg-min/l;

k $= -k'/a$ = velocity coefficient; and

t = time in minutes.

In all of the above rate expressions, the assumption has been made that the disinfectant concentration is not a function of time. This is not the case, but without this simplification, an expression for the residual as a function of time is required and to date no satisfactory, generally valid formulation exists.

It must be emphasized that the model presented for use in this study has no rational, mechanistic basis in describing disinfection by chemical agents. Nonetheless, it does approximate empirically the behavior of the real system and as such provides a useful design tool.

SECTION 7

DISINFECTION EXPERIMENTS WITH CONVENTIONAL COLIFORM INDICATORS

EXPERIMENTAL DESIGN

For evaluation of chlorine dioxide as a wastewater disinfectant, experiments were performed in wastewaters from three treatment plants in the San Francisco Bay Area. Identical experiments were run in parallel with chlorine as the disinfecting agent in order that the relative efficiency of chlorine dioxide could be determined. The wastewaters used were from the Palo Alto Water Pollution Control Plant (Palo Alto), the Dublin-San Ramon Services District Wastewater Treatment Plant (Dublin), and the San Jose-Santa Clara Wastewater Treatment Plant (San Jose).

Treatment Plant Descriptions

Palo Alto--

The Palo Alto Water Pollution Control Plant is a non-nitrifying activated-sludge plant with a capacity of 1.5 m^3/s (35 mgd). Samples for disinfection experiments and water-quality characterizations were of secondary effluent before chlorination. Two sets of disinfection experiments were run on Palo Alto wastewater. The first set (Palo Alto - 1978) were experiments in which either chlorine or chlorine dioxide were dosed to the secondary effluent as received from the treatment plant. For both chlorine and chlorine dioxide, eight separate experiments were performed on five different days over a two-week period in July of 1978. On three days, two experiments were run on the same wastewater. The second set (Palo Alto - 1979) were experiments in which one disinfectant, either chlorine or chlorine dioxide, was dosed to two samples of Palo Alto wastewater, one of which had been filtered. The filter utilized was a laboratory-scale multimedia filter. The filter is shown in Fig. 6. The filtration rate was 20 liters/hr. The filter was backwashed immediately before each use and ripened by allowing 20 liters of wastewater sample to pass to waste before collection of 20 liters for experimentation. The filter was then rinsed with tap water, drained to the top of the anthracite layer, and allowed to stand until it was needed for the next experiment. The empty-bed volume is ~ 1.5 liters. These experiments were run on six days over a three-week period in August 1979. Three experiments were run for chlorine and four for chlorine dioxide, comparing their performance between filtered and non-filtered secondary effluent.

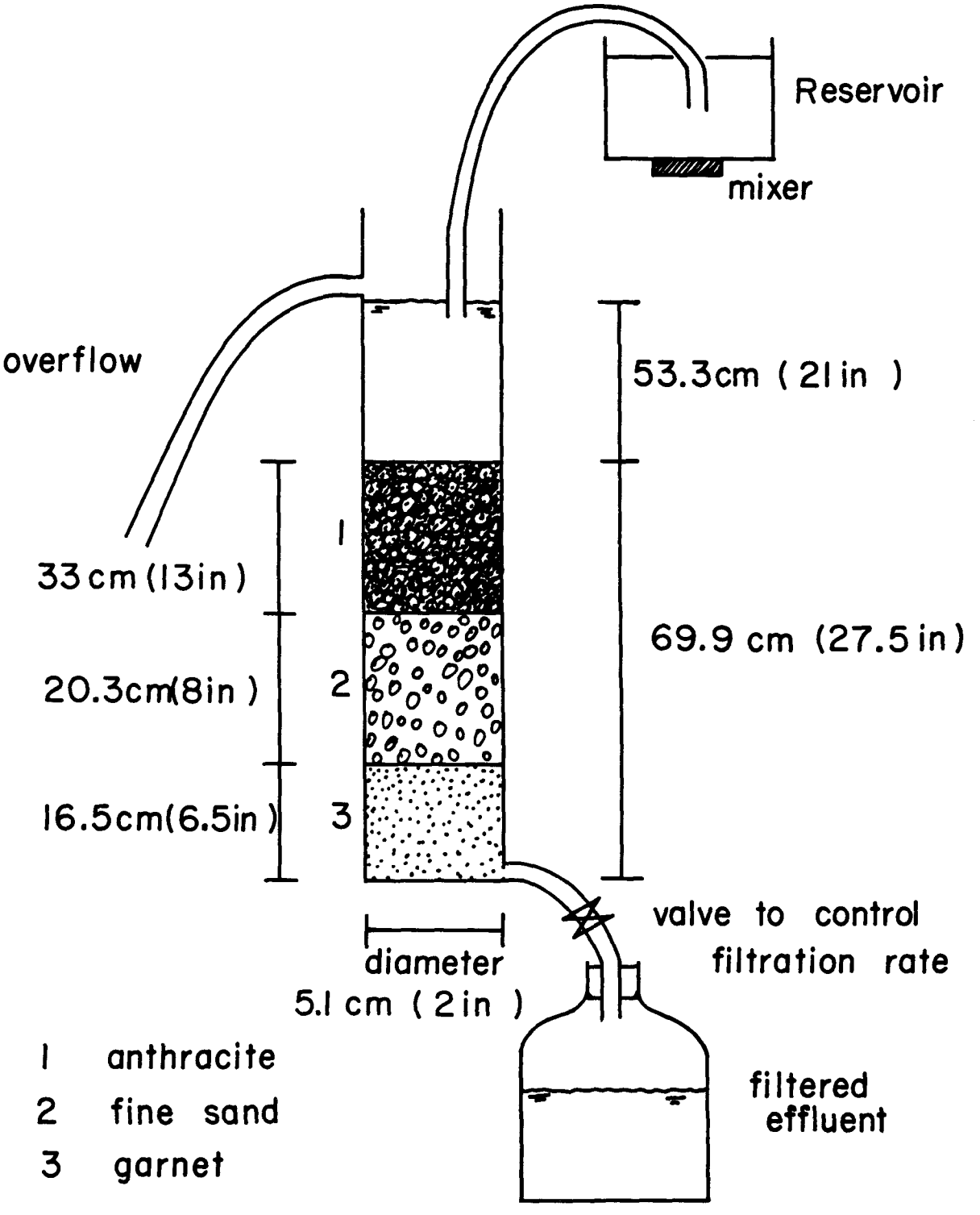


Figure 6. Multimedia filtration column.

Dublin--

The Dublin-San Ramon Wastewater Treatment Plant is a combined-process activated-sludge/nitrification plant. The effluent from the secondary clarifier is filtered through a dual-media anthracite-sand filter. The capacity of the plant is 0.22 m^3/s (5 mgd). Samples for laboratory disinfection experiments and water-quality characterizations were taken after filtration and before chlorination. These laboratory experiments were run on three days in January and February 1979.

Experiments were also conducted at full-scale at the Dublin Plant. Plant flows were controlled manually, as were either the chlorine feed rate or the chlorine dioxide feed rate. For experiments with chlorine dioxide as the disinfectant, the chlorine feed was turned off and chlorine dioxide feed solution was introduced into the rapid mixing chamber through the same header system used for normal aqueous chlorine feed. This assured that both disinfectants would be subjected to the identical conditions of mixing with the wastewater. Experiments using chlorine dioxide were performed on the same days as experiments with chlorine, allowing sufficient equilibration time between experiments. Chlorine dioxide was generated in a commercially available continuous packed reactor, utilizing the HCl-acid activation technique (2 kg/hr maximum capacity). For doses higher than 2.5 mg/l chlorine dioxide, 2 generators were used in parallel and plant flow was diverted to a holding pond as required. Samples for bacterial analysis and residual analysis were taken at the entrance to the contact tank, the mid-point of the contact tank and at the overflow weir. These points had been chosen to provide reasonable contact time for the doses used. These experiments were run on five days from January through April 1979.

San Jose--

The San Jose-Santa Clara Wastewater Treatment Plant is a 7.0 m^3/s (160 mgd) plant with separate activated sludge and nitrification processes followed by multimedia filtration. Samples were taken of secondary effluent, nitrified effluent, and filtered effluent for laboratory disinfection experiments and water-quality characterizations. Each sample point was sampled once each week (not on the same day nor at the same time) and the experiment was repeated three times for each sample point in June and July of 1979.

Process Sequence and Wastewater Characteristics

The flow diagrams for these three treatment plants and the points from which samples were taken for laboratory disinfection experiments are shown in Fig. 7. Average wastewater characteristics for each plant at each sample point are shown in Table 14. The values given are the means of all experiments at the particular sample point ± the standard deviation of the parameters over the period in which experiments were performed.

Design of Experiments

Laboratory experiments were performed in a randomized complete block design. Each experiment consisted of dosing wastewater samples with chlorine or chlorine dioxide at three concentrations, usually 2, 5, and 10 mg/l. Samples were taken at 5, 15, and 30-min intervals for both total coliform

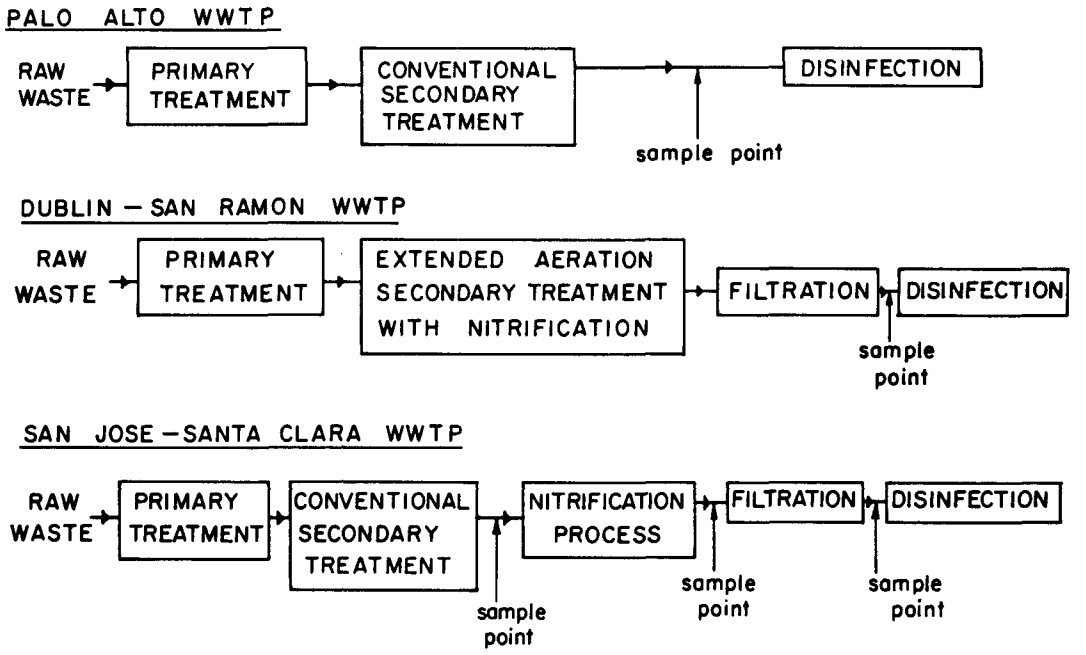


Figure 7. Wastewater treatment plant flow schemes.

analysis and residual analysis. Samples for bacterial analysis were also taken at time 0. All of the six runs within an experiment (two disinfectants each at three doses) were done in a randomized order. From three to eight experiments were performed at each sample point (Palo Alto, Dublin, and three points at San Jose). Wastewater for experiments was collected immediately before an experiment was conducted. The basic dose-time matrix for an experiment is shown in Fig. 8. In some cases, more than one replicate experiment could be conducted on one wastewater sample on one day. However, most replicate experiments were conducted on separate days, each with fresh wastewater samples. Therefore, the wastewater characteristics would not be identical for all replicates of an experiment. The data from these experiments were used to evaluate the constants of the disinfection model discussed above. In some instances, the number of dose levels was augmented to include an additional experiment at a dose of 1 mg/l, and the contact times were augmented with samples at 1 and 60 min. This was done to provide an adequate range of data for use in the model.

The Palo Alto - 1979 experiments were designed to compare one disinfectant between filtered and unfiltered wastewater. The question of concern in these experiments was the effect of the filtration process on disinfection kinetics.

Laboratory-Scale Reactor Design

The reactor for all laboratory experiments was a specially modified four-liter aspirator bottle. The modifications include: four indentations similar to those of a trypsinizing flask; oxidant injector and sample ports located in

TABLE 14. CHARACTERIZATION OF WASTEWATER EFFLUENTS USED IN DISINFECTION EXPERIMENTS

Wastewater	SS* mg/l	COD* mg/l	Alkalinity* mg/l as $CaCO_3$	pH (Range)	NH_3N* mg/l as N	Total Coliforms* log of #/100 ml
Palo Alto Secondary - 1978	17.4 ± 8.6	32.7 ± 6.2	234.5 ± 10.1	6.7 to 7.4	30.4 ± 2.7	6.21 ± 0.48
Palo Alto Secondary - 1979						
Chlorine, unfiltered	13.8 ± 6.5	47.6 ± 2.7	89.8 ± 6.3	6.8 to 7.3	24.1 ± 1.9	4.97 ± 0.21
Chlorine, filtered	4.4 ± 0.5	37.0 ± 4.2	90.3 ± 7.0	7.0 to 7.4	23.9 ± 1.7	4.86 ± 0.35
Chlorine Dioxide, unfiltered	13.8 ± 3.7	52.6 ± 2.9	112.8 ± 15.8	6.7 to 7.2	29.3 ± 7.0	5.38 ± 0.27
Chlorine Dioxide, filtered	3.3 ± 1.2	45.9 ± 6.0	114.3 ± 13.6	7.0 to 7.1	29.0 ± 7.3	5.27 ± 0.62
Dublin Filtered - nitrified						
Laboratory experiments	3.0 ± 3.7	33.4 ± 1.2	115.6 ± 38.8	6.9 to 7.1	0.4 ± 0.6	4.41 ± 0.47
Field Experiments	3.6 ± 2.6	23.3 ± 6.3	161.2 ± 57.6	6.8 to 7.3	0.2 ± 0.4	4.36 ± 0.39
San Jose						
Secondary	42.5 ± 35.3	68.2 ± 37.5	216.3 ± 117.5	7.0 to 7.4	16.3 ± 7.4	6.51 ± 0.23
Nitrified	18.3†	41.5 ± 4.6	146.3 ± 79.7	6.9 to 7.3	0.8 ± 0.8	4.76 ± 0.39
Filtered	3.9 ± 5.4	38.2 ± 6.9	184.7 ± 84.1	7.0 to 7.2	0.6 ± 0.9	4.81 ± 0.98

*Mean ± standard deviation.

†One value only.

		CHLORINE DOSE mg/l			CHLORINE DIOXIDE DOSE mg/l		
		2	5	10	2	5	10
CONTACT TIME	5 MIN						
	15 MIN						
	30 MIN						

Figure 8. Experimental dose-time matrix for chlorine-chlorine dioxide comparison.

the most active mixing zone of the reactor, and all glass or teflon connections. The reactor was maintained at 184 kPa (12 psig) and both disinfectant injection and sample delivery were pressure driven. Stirring was provided by a 60-mm (2-1/2") magnetic stir bar (cylindrical) with rotational speed of approximately 600 rpm. The reactor was maintained at 24°C for all experiments.

To evaluate the dispersion efficiency of added chemicals within this batch reactor, a dye-tracer study was performed. The dye-tracer study involved dosing three liters of deionized water with a methylene blue stock solution of 500 mg/l. Sufficient dye was added to make a final concentration of 5 mg/l in the reactor. These conditions mimicked those in which actual disinfection experiments were performed. Samples were taken at 2, 5, 10, 20, 40, 60, and 120 sec and analyzed spectrophotometrically for methylene blue. The results of this experiment indicate that the half-time of response is less than 5 seconds. This reactor is shown in Fig. 9.

Characterization of the Dublin (Full-Scale) Disinfectant Contact Tank

Since the residence time varies with the flow rate in a fixed-volume reactor, the contact time in the disinfectant contact tank can be determined for any flow if the contact time is known for a known flow rate. The contact times are related by

$$t_1 Q_1 = t_2 Q_2 \tag{26}$$

where t_i = contact time at flow = Q_i .

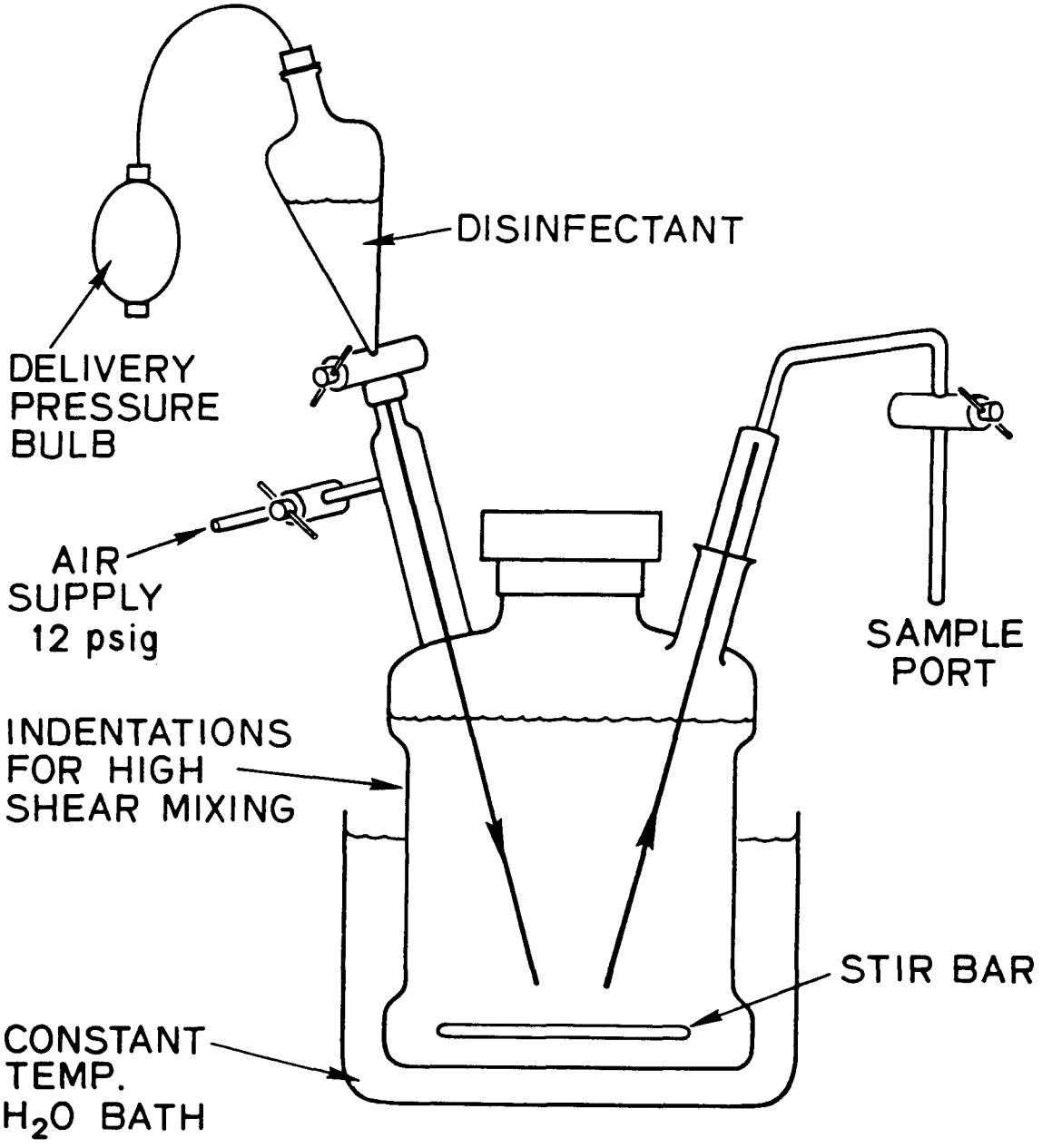


Figure 9. A rapid-mix, rapid-sampling 4-liter batch reactor. 12 psig = 184 kPa absolute pressure.

A tracer study was performed in the Dublin chlorine contact tank at a constant flow rate of 0.14 m^3/s (3.25 mgd). Sufficient rhodamine-WT dye was injected through the chlorine injection system to yield a concentration of 100 μg/l based on dilution in the entire volume of the contact tank. The chlorine feed was turned off for 15 min before injection and 10 min after injection to avoid destruction of the rhodamine-WT tracer by high concentrations of chlorine. Figure 10 shows the physical layout of the chlorine contact system. Figure 11 shows the concentration of dye as a function of time at the three

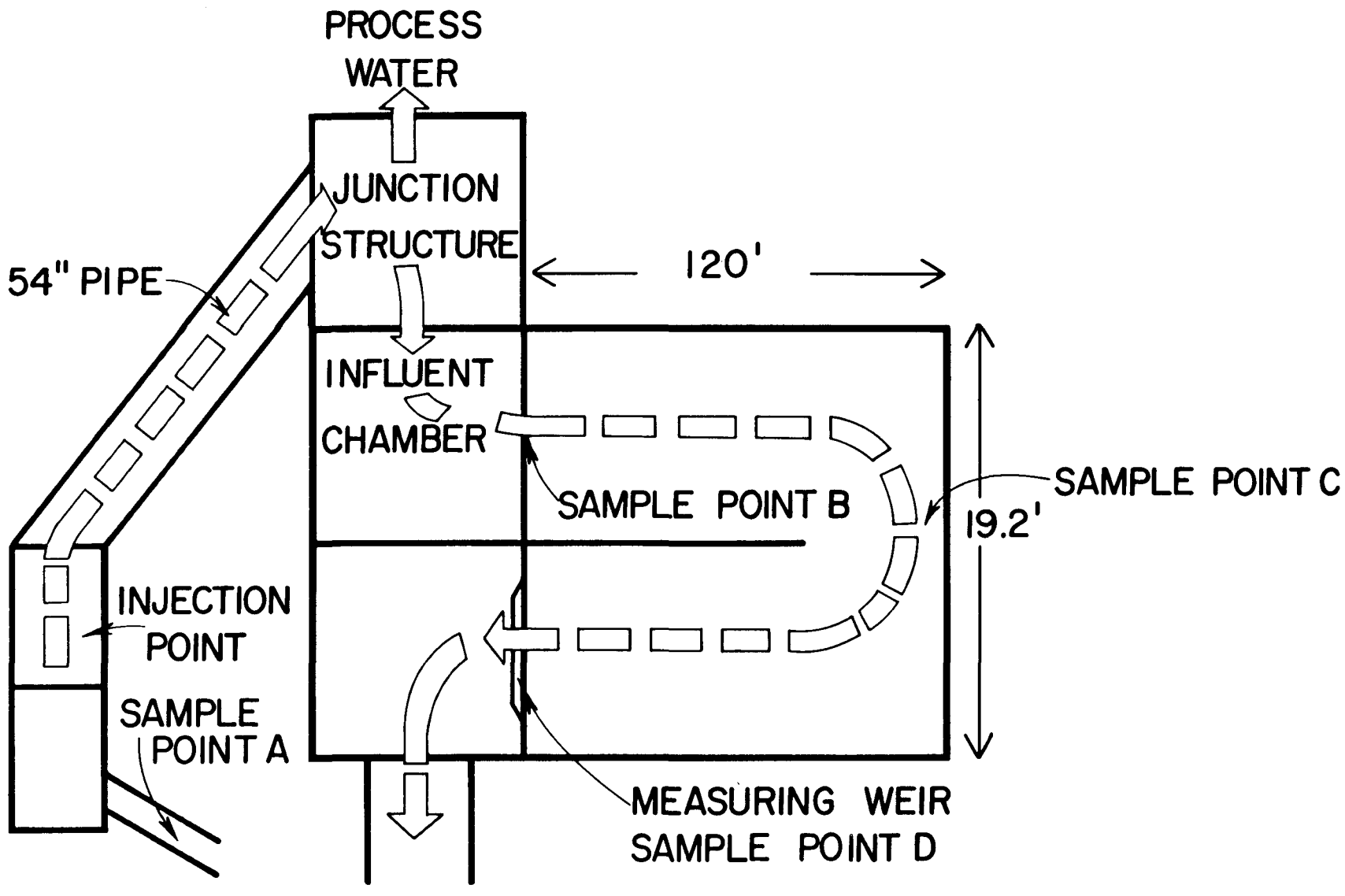


Figure 10. Disinfection contact tank at the Dublin-San Ramon wastewater treatment plant.

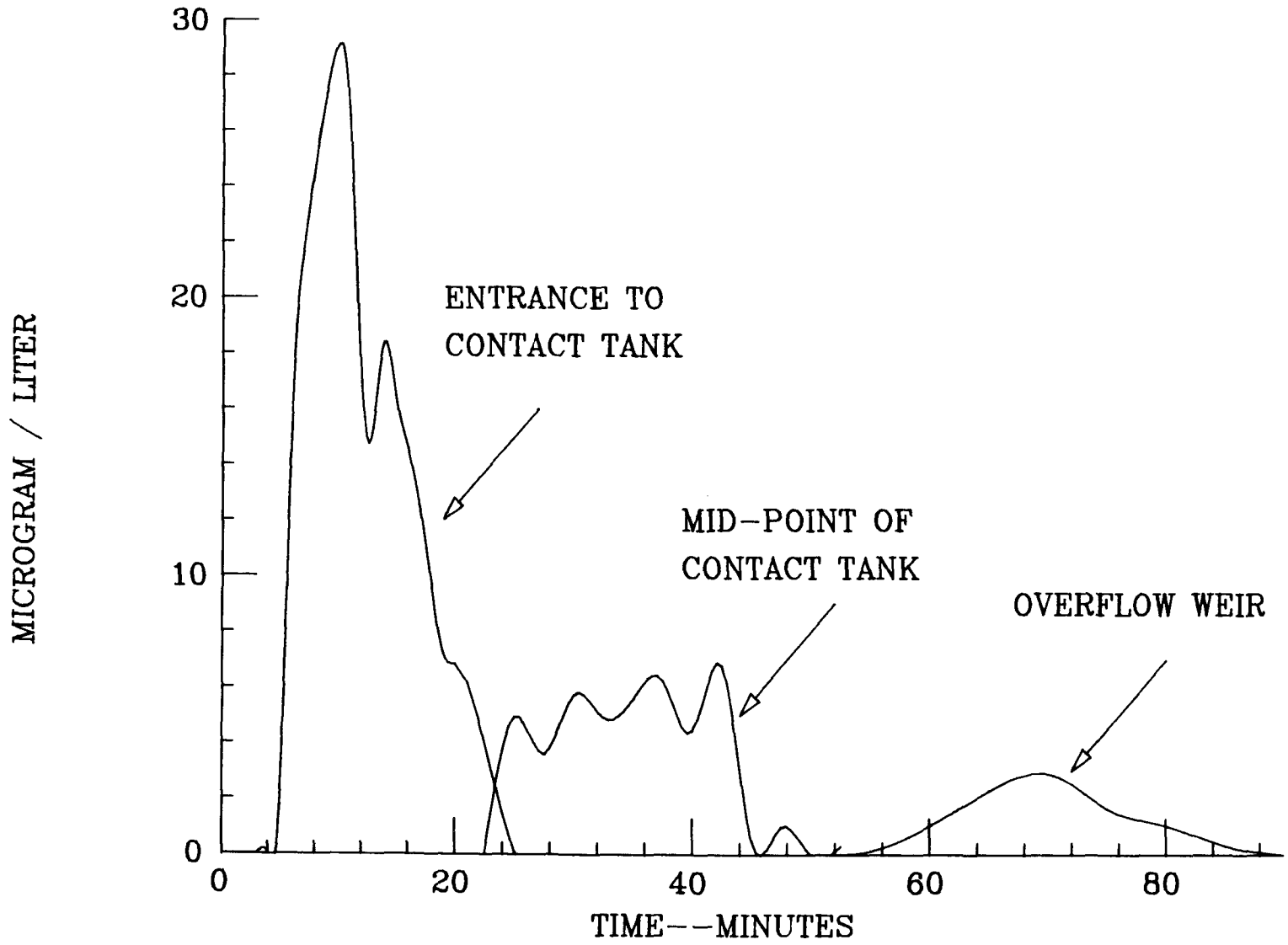


Figure 11. Results of tracer study of disinfectant contact tank.

sample points, inlet to contact tank, midpoint of contact tank, and overflow weir. The areas under the three curves (i.e., the mass of dye) are not equal. In fact, the mass of dye as calculated under the first peak is about 80% of the mass injected. This initial loss of 20% of dye is due to the removal of water between the injection point and the first sample point for use as process water throughout the plant. The continued decrease of dye mass through the remainder of the contact tank is believed to be caused by photodecomposition and destruction of the dye by chlorine remaining in the contact tank. Mean residence times were determined for the influent to the tank, the midpoint, and the overflow weir. They are 12.3 min, 34.6 min, and 70.1 min, respectively.

In addition to determining the average contact time of the contact tank, the dye study also provided a measure of the hydraulic efficiency of the contact tank. Figure 12 shows the concentration of dye versus time for the overflow weir sample point. The initial appearance of tracer (t_{in}) indicates the minimum contact time of the tank. In this case, t_{in} is approximately 52 min. An exact determination cannot be made due to loss of dye as previously mentioned. The theoretical contact time for this tank at the constant flow at which the dye study was performed is 78.9 min, while the average contact time calculated from Fig. 12 is 70.1 min. The ratio of average contact time to theoretical contact time is a measure of dead space or inactive space within the tank. For the Dublin-San Ramon contactor this ratio equals 0.89. (In the absence of any inactive space the ratio would equal 1.0.)

Another measure of hydraulic efficiency that is widely used in chemical engineering is the reactor dispersion number "d". The value of "d" approaches 0 for ideal-plug flow and infinity for complete mix. (For a complete discussion of the reactor dispersion number, see Levenspiel (28).) The reactor dispersion number for this contact tank is 0.0045. A study performed by the California Department of Health in which dye studies were performed on 15 chlorine contact tanks reports the range of values for dispersion number as 0.005-0.36 and the range of values for the ratio average to theoretical detention times as 0.63-1.05 (29).

In summary, the Dublin-San Ramon disinfectant contact tank closely approximates a plug-flow reactor with very little dead space, and as such is an example of a well-designed disinfectant contactor.

STATISTICAL ANALYSIS OF EXPERIMENTAL RESULTS

The raw data from the experiments described above are given in Appendix A. The data from the Palo Alto - 1978 experiments were chosen for a statistical analysis intended to investigate the sources of experimental error, the relationships of dose and contact time with bacterial survival, the variation between replicate experiments on the same wastewater (i.e., two experiments on one day performed on different aliquots of the same wastewater sample), the variation between experiments on wastewater from one source but sampled on different days, and finally the difference in bacterial response as a function of disinfecting agent, i.e., chlorine or chlorine dioxide.

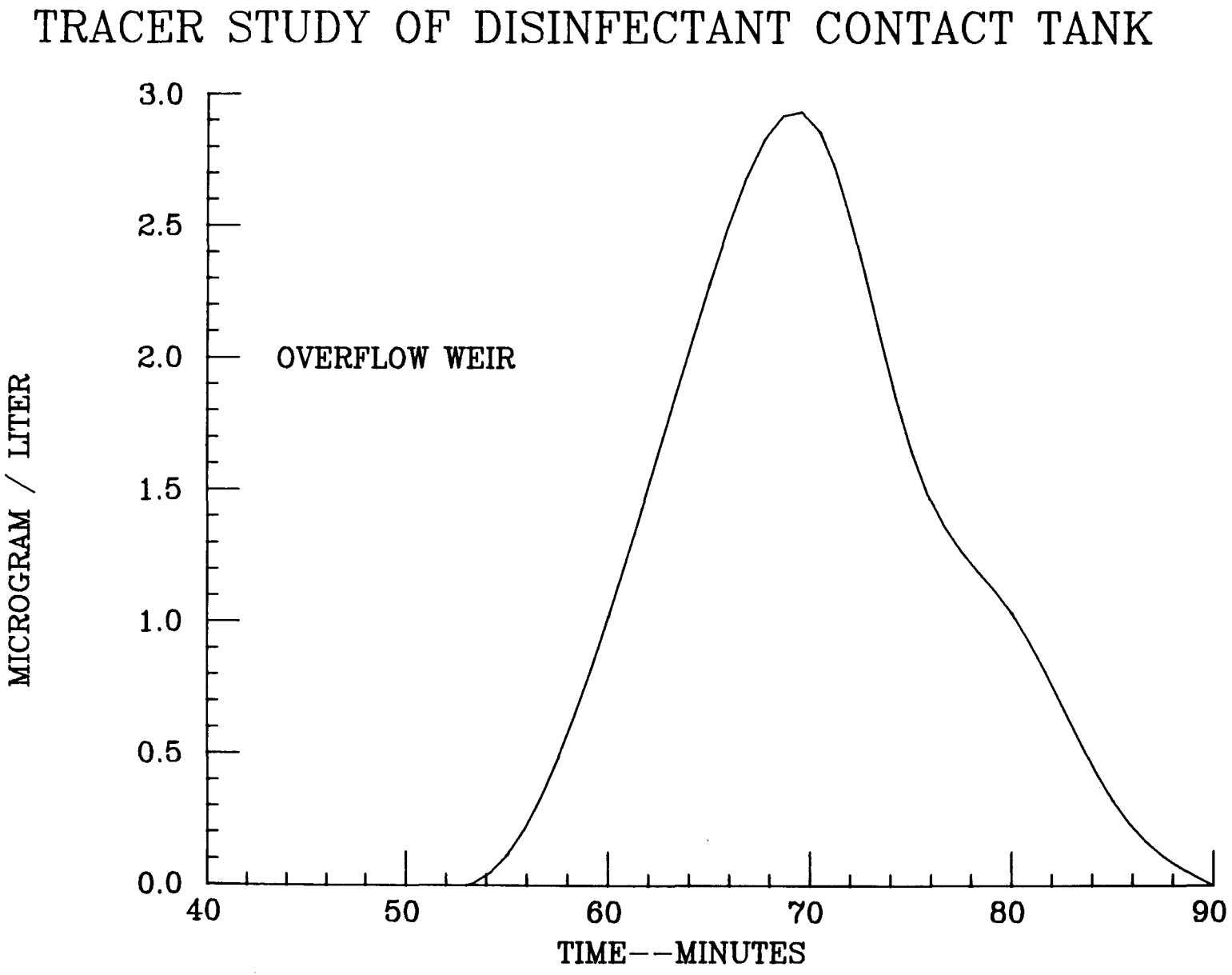


Figure 12. Dye tracer concentration measured at overflow weir.

TABLE 15. MEAN LOG_{10} SURVIVING TOTAL COLIFORMS IN 1978 BATCH EXPERIMENTS WITH PALO ALTO EFFLUENT*

	Contact Time, min.	Mean Value† of $\log_{10}$ (N/100 ml) Experiment Number 1	2	3	4	5	6	7	8
Disinfectant: ClO_2									
2 mg/l Dose	0#	5.90	6.12	6.27	6.73	6.79	6.50	6.48	5.84
	5	5.52	4.52	4.42	5.01	5.02	5.14	5.11	5.12
	15	5.13	4.41	4.31	4.96	5.21	5.20	5.23	4.73
	30	4.39	4.33	3.81	4.87	5.01	5.02	5.25	5.03
5 mg/l Dose	0#	5.48	6.15	6.26	6.83	6.76	6.52	6.67	5.55
	5	3.73	<2.0	3.04	3.64	3.85	3.24	3.66	3.40
	15	3.14	2.00	1.70	2.49	2.98	3.57	2.52	2.76
	30	3.27	1.86	1.27	3.02	3.27	3.37	3.08	3.45
10 mg/l Dose	0#	5.74	6.25	6.18	6.83	6.70	6.73	6.93	5.84
	5	2.02	0.87	1.71	2.52	2.00	2.28	2.28	1.72
	15	1.74	0.54	0.32	2.11	1.58	1.45	1.19	0.95
	30	0.44	<0.34	0.34	0.32	0.32	1.13	0.90	0.39
Disinfectant: Cl_2									
2 mg/l Dose	0#	5.88	6.18	6.09	6.58	6.81	6.63	6.62	5.76
	5	4.89	5.52	5.82	6.32	6.14	6.29	6.34	5.46
	15	4.48	4.48	4.86	5.46	4.61	5.58	5.48	4.59
	30	<4.34	3.30	3.53	4.47	3.85	4.83	4.77	3.98
5 mg/l Dose	0#	5.58	6.23	6.23	6.79	6.83	6.67	6.63	5.91
	5	3.92	3.94	3.88	4.19	4.26	4.53	4.08	3.99
	15	3.16	2.19	2.80	3.48	3.50	4.52	3.80	3.34
	30	2.60	1.69	1.80	3.05	3.21	2.86	3.05	2.63
10 mg/l Dose	0#	5.96	6.30	5.96	6.70	6.84	6.67	6.60	5.59
	5	2.86	2.25	2.31	3.77	2.64	3.16	3.24	2.84
	15	1.85	1.16	1.62	1.32	2.04	1.97	1.97	1.70
	30	0.71	0.58	0.74	1.42	0.30	0.92	1.24	0.43

*The raw data from which the mean values were calculated are given in Appendix A, Tables A-1 and A-2.

†Mean value of 8 replicates.

#N(0), prior to disinfection

Statistical Analysis

Preliminary statistical analyses were done on the data from Palo Alto - 1978 shown in Tables A-1 and A-2 (Appendix A). To investigate any bias in the data due to the order of experiments or sampling technique, the data from time

Experimental Results -- Palo Alto 1978

All samples for bacterial analysis were analyzed by the membrane-filter technique for total coliform bacteria (1). Generally, four dilutions of each sample were analyzed in order to obtain an incubated sample plate with a significant number of colonies to count, but a sufficiently small number so that the colonies do not overlap (usually 20-80 colonies are adequate). It is possible to have from one to four measurements of coliform bacteria for each sample. The mean values of the logarithms of the numbers of bacteria for each sample (Palo Alto 1978) are given in Table 15.

Statistical Analysis

Preliminary statistical analyses were done on the data from Palo Alto - 1978 shown in Tables A-1 and A-2 (Appendix A). To investigate any bias in the data due to the order of experiments or sampling technique, the data from time 0 were subjected to an analysis of variance (ANOVA). The grouping variables used were wastewater, disinfectant, and disinfectant dose. In setting up the ANOVA in this way, the difference between coliform density at time 0 with respect to wastewater could be tested for all experiments. The results of this ANOVA are shown in Table 16.

The only effect that is significant is that of wastewater, indicating that the variance in bacterial numbers at time 0 for each experiment is due only to the difference inherent in the wastewater used for that particular experiment. No significant correlation was found between measured wastewater parameters (total filterable residue, COD, alkalinity, pH, ammonia-nitrogen) and bacterial counts.

The next step in the statistical analysis was to investigate any differences between experiments performed on the same wastewater sample, that is the reproducibility of experiments. Again, analysis of variance was used with grouping variables of wastewater, experiment, disinfectant, disinfectant dose, and contact time. The ANOVA is reported in Table 17. The dependent variable was $\log_{10}[N(t)]$. As seen in this ANOVA, all variables <u>except</u> experiment had a significant effect on the number of surviving bacteria. (These effects will be examined in subsequent ANOVAs.) This implies that the duplicate experiments run on the same wastewater are not significantly different from each other. For this reason, the experiments were no longer grouped according to wastewater, so that variations seen between experiments in subsequent statistical analyses are due to variations in the wastewater. In other words, the wastewater variable is redundant in that the experiments differ only due to the effects of wastewater composition.

The statistical analyses shown in Tables 16 and 17 have been calculated using the logarithms of bacterial numbers from each sample (Appendix A) as the dependent variable. In order to compare the bactericidal efficiency of chlorine and chlorine dioxide and to examine the relationships of disinfectant doses and contact times to bactericidal efficiency, a survival ratio for each experiment was calculated and the logarithms of these survival ratios were substituted as the dependent variable.

TABLE 15. MEAN LOG_{10} SURVIVING TOTAL COLIFORMS IN 1978 BATCH EXPERIMENTS WITH PALO ALTO EFFLUENT*

	Contact Time, min.	Mean Value† of log_{10} (N/100 ml) Experiment Number 1	2	3	4	5	6	7	8
Disinfectant: ClO_2									
2 mg/l Dose	0#	5.90	6.12	6.27	6.73	6.79	6.50	6.48	5.84
	5	5.52	4.52	4.42	5.01	5.02	5.14	5.11	5.12
	15	5.13	4.41	4.31	4.96	5.21	5.20	5.23	4.73
	30	4.39	4.33	3.81	4.87	5.01	5.02	5.25	5.03
5 mg/l Dose	0#	5.48	6.15	6.26	6.83	6.76	6.52	6.67	5.55
	5	3.73	<2.0	3.04	3.64	3.85	3.24	3.66	3.40
	15	3.14	2.00	1.70	2.49	2.98	3.57	2.52	2.76
	30	3.27	1.86	1.27	3.02	3.27	3.37	3.08	3.45
10 mg/l Dose	0#	5.74	6.25	6.18	6.83	6.70	6.73	6.93	5.84
	5	2.02	0.87	1.71	2.52	2.00	2.28	2.28	1.72
	15	1.74	0.54	0.32	2.11	1.58	1.45	1.19	0.95
	30	0.44	<0.34	0.34	0.32	0.32	1.13	0.90	0.39
Disinfectant: Cl_2									
2 mg/l Dose	0#	5.88	6.18	6.09	6.58	6.81	6.63	6.62	5.76
	5	4.89	5.52	5.82	6.32	6.14	6.29	6.34	5.46
	15	4.48	4.48	4.86	5.46	4.61	5.58	5.48	4.59
	30	<4.34	3.30	3.53	4.47	3.85	4.83	4.77	3.98
5 mg/l Dose	0#	5.58	6.23	6.23	6.79	6.83	6.67	6.63	5.91
	5	3.92	3.94	3.88	4.19	4.26	4.53	4.08	3.99
	15	3.16	2.19	2.80	3.48	3.50	4.52	3.80	3.34
	30	2.60	1.69	1.80	3.05	3.21	2.86	3.05	2.63
10 mg/l Dose	0#	5.96	6.30	5.96	6.70	6.84	6.67	6.60	5.59
	5	2.86	2.25	2.31	3.77	2.64	3.16	3.24	2.84
	15	1.85	1.16	1.62	1.32	2.04	1.97	1.97	1.70
	30	0.71	0.58	0.74	1.42	0.30	0.92	1.24	0.43

*The raw data from which the mean values were calculated are given in Appendix A, Tables A-1 and A-2.

†Mean value of results from one to four dilutions.

#N(0), prior to disinfection

TABLE 16. ANOVA FOR BACTERIAL ANALYSIS BEFORE DISINFECTION USING $LOG_{10}[N(0)]$ AS DEPENDENT VALUE

Source of Variance	Degrees of Freedom	Sum of Squares	F-Value	Probability F Exceeded
Wastewater (X_1)	4	13.2259	80.64	0.0001
Disinfectant (X_2)	1	0.0002	0.00	0.9516
Dose (X_3)	2	0.1625	1.98	0.1483
Interactions				
(X_1) × (X_2)	4	0.4077	0.25	0.9092
(X_1) × (X_3)	8	0.4897	1.49	0.1831
(X_2) × (X_3)	2	0.1686	2.06	0.1384
(X_1) × (X_2) × (X_3)	8	0.2568	0.78	0.6197
Error	51	2.0911		

N(0) = number of bacteria before disinfection.

TABLE 17. ANOVA FOR EXAMINING EXPERIMENTAL REPRODUCIBILITY

Source of Variance	Degrees of Freedom	Sum of Squares	F-Value	Probability F Exceeded
Time (X_1)	2	48.247	217.20	0.0001
Level (X_2)	2	781.544	3518.42	0.0001
Disinfectant (X_3)	1	7.569	68.15	0.0001
Waste (X_4)	4	40.366	90.86	0.0001
Experiment (X_5)	3	0.553	1.66	0.1735
Interactions*				
(X_1) × (X_2)	4	9.229	20.77	0.0001
(X_1) × (X_3)	2	17.296	77.86	0.0001
(X_1) × (X_4)	8	2.607	2.93	0.0035
(X_1) × (X_5)	6	2.038	3.06	0.0063
(X_2) × (X_3)	2	3.102	13.97	0.0001
(X_2) × (X_4)	8	2.896	3.26	0.0013
(X_2) × (X_5)	6	1.774	2.66	0.0154
(X_3) × (X_4)	4	4.430	9.97	0.0001
(X_3) × (X_5)	3	1.5064	4.52	0.0042
Error	355	39.428		

*Interactions of order higher than 2 are included in the error term.

The survival ratio was defined as:

$$\text{Survival ratio} \equiv N(t)/N(0) \tag{27}$$

where N(t) = number of bacteria measured at time t,

N(0) = number of bacteria measured at time 0.

The logarithm of survival ratio is then

$$\log[N(t)/N(0)] = \log[N(t)] - \log[N(0)] \ . \qquad (28)$$

Log[N(t)] was calculated as the arithmetric mean of the logarithms of bacterial numbers from each sample (see Table 15) for each time t. The log[N(0)] was similarly calculated at time 0. This calculation yields the geometric mean of the replicate analyses for bacterial numbers.

Experiment, disinfectant, disinfectant dose, and time were used as independent variables. The resulting ANOVA is shown in Table 18. This ANOVA reveals that all of the main effects--disinfectant, disinfectant dose, contact time, and experiment--were highly significant, as evidenced by the fact that $P(F > F_{calc}) = 0.0001$ in all cases.

With respect to the comparison between chlorine dioxide and chlorine, the ANOVA (Table 18) implied that there was a significant difference between the two disinfectants. The implications of this significant difference are discussed below. The significant effects of contact time and dose were expected: The survival ratio declined with increasing disinfectant dose and contact time for both disinfectants. The significant difference between experiments is believed to be attributable to variations in properties of the wastewater.

Several of the second-order interactions were found to be significant (Table 18), notably those between the disinfectant variable on the one hand and the disinfectant dose, the contact time, and experiment on the other hand. Clearly, the difference between disinfectants with respect to coliform inactivation was not the same at all doses, at all contact times, and in all wastewater samples. Also, the interaction between disinfectant dose and contact time was found to be significant, indicating that the effect of dose on coliform inactivation by a given disinfectant depended significantly on the contact time and vice versa. None of the third-order interactions was found to be significant.

The meaning of the significant effects can be interpreted by comparing the means of log[survival ratio] for chlorine dioxide with those for chlorine for various combinations of dose and contact time (Table 19). The values in Table 19 represent means of the eight experiments. The mean values in Table 19 show the observed differences between chlorine and chlorine dioxide and between dose levels and contact times for a given disinfectant, corresponding to the ANOVA main effects in Table 18. From Table 19, the difference between disinfectant doses is obvious, as is the difference between contact times. The significant difference between disinfectants seen in the ANOVA of Table 18 is modified by the ANOVA interactions. The relationship of the difference between disinfectants to the values of dose and contact time can be better understood with the help of Figs. 13, 14, and 15.

TABLE 18. ANOVA FOR COMPARING CHLORINE AND CHLORINE DIOXIDE AS BACTERICIDES IN PALO ALTO EFFLUENT

Source of Variance	Degrees of Freedom	Sum of Squares	F-Value	Probability F Exceeded
Disinfectant (X_1)	1	4.858	38.36	0.0001
Dose (X_2)	2	279.297	1102.76	0.0001
Experiment (X_3)	7	21.869	24.67	0.0001
Contact Time (X_4)	2	37.341	147.43	0.0001
Interactions*				
(X_1) × (X_2)	2	1.339	5.29	0.0104
(X_1) × (X_3)	7	2.109	2.38	0.0445
(X_1) × (X_4)	2	6.423	25.36	0.0001
(X_2) × (X_3)	14	2.463	1.39	0.2146
(X_2) × (X_4)	4	3.403	6.72	0.0005
(X_3) × (X_4)	14	1.253	0.71	0.7515
(X_1) × (X_2) × (X_3)	14	0.904	0.51	0.9096
(X_1) × (X_3) × (X_4)	14	1.788	1.01	0.4691
(X_2) × (X_3) × (X_4)	28	3.134	0.88	0.6277
Error	32	4.052		

*Fourth-order interaction neglected.

TABLE 19. MEAN LOG[SURVIVAL RATIO] OF TOTAL COLIFORMS: COMPARISON OF DISINFECTANTS AT DIFFERENT COMBINATIONS OF DOSE AND CONTACT TIME

Contact Time	Mean* of log[Survival Ratio] = log[N(t)/N(0)]					
	Chlorine Dose mg/l			Chlorine Dioxide Dose mg/l		
	2	5	10	2	5	10
5 minutes	-0.49	-2.23	-3.44	-1.34	-3.01	-4.40
15 minutes	-1.38	-2.98	-4.62	-1.43	-3.69	-5.09
30 minutes	-2.18	-3.72	-5.53	-1.61	-3.50	-5.81

*Calculated means of eight experiment replicates.

Chlorine and chlorine dioxide are compared by dose at 30-min contact times in Fig. 13. These values are means over eight experiments. The values in parentheses are the means of the residual over the eight experiments. Chlorine gives a lower log[survival ratio] at the 2- and 5-mg/l doses, while chlorine dioxide gives a lower log[survival ratio] at 10-mg/l dose. This illustrates the disinfectant dose interaction mentioned above. The reason for

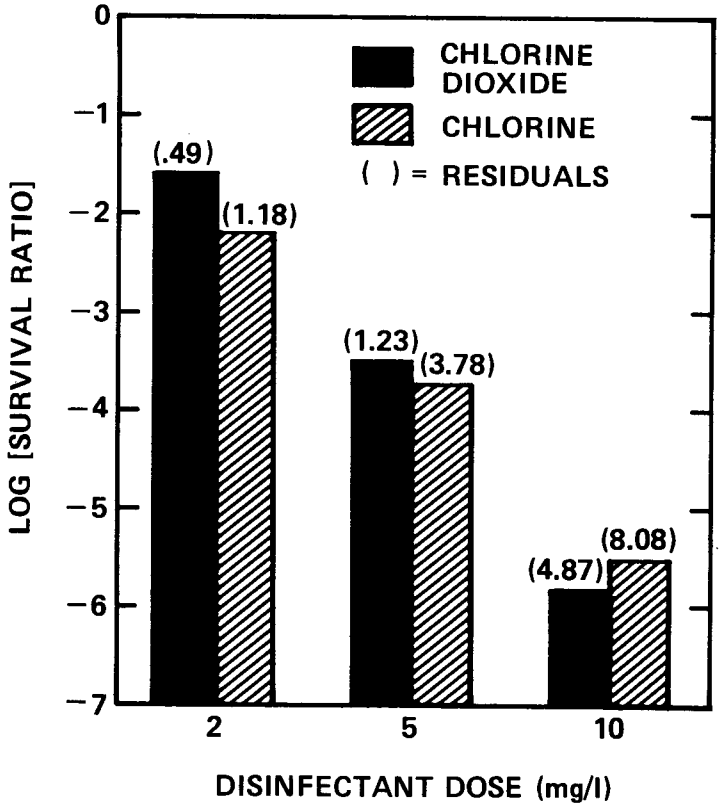


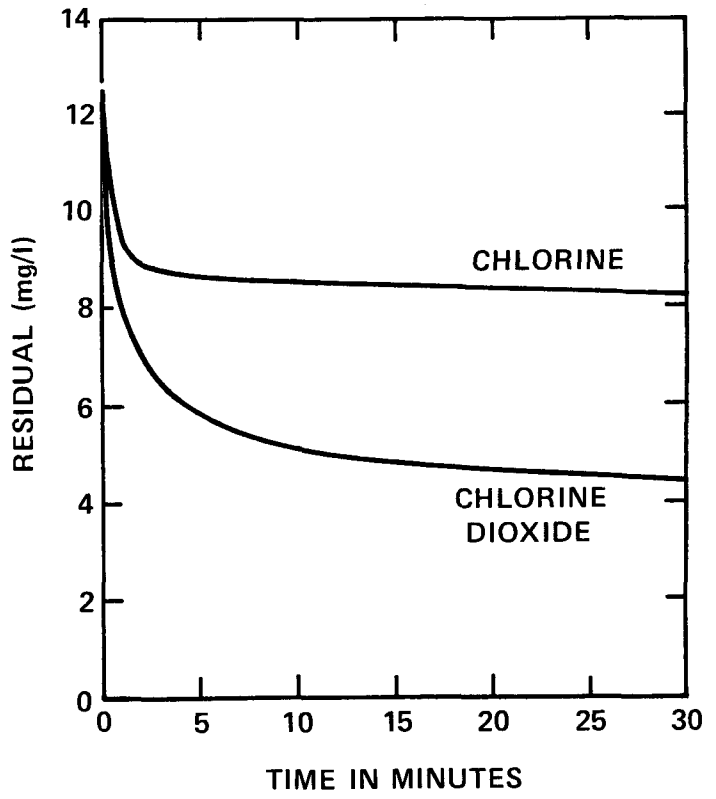
Figure 13. Comparison of chlorine and chlorine dioxide bactericidal effectiveness at 30-min contact time.

this dose-dependent disinfectant difference can be found in the die-away curves of chlorine and chlorine dioxide. Figure 14 shows typical chlorine and chlorine dioxide die-away curves in secondary effluent. The initial oxidant demand reduces the disinfectant concentration significantly. Hence, the rate of disinfection will be slowed.

When disinfectants are compared with respect to contact times, the disinfectant-contact time interaction can be evaluated. In Fig. 15 chlorine and chlorine dioxide are compared by contact time at 10-mg/l dose. This figure indicates a different time-dependent mode of action for chlorine versus chlorine dioxide. Chlorine dioxide effects a major portion of bacteria inactivation at shorter times, while chlorine requires longer contact times to achieve the same degree of disinfection.

Summary

The conclusions concerning the comparative bactericidal action of chlorine and chlorine dioxide derived from the statistical analysis of the data on Palo Alto effluent are as follows:



INITIAL DOSE OF 12.5 mg/l FOR BOTH
CHLORINE AND CHLORINE DIOXIDE

Figure 14. Chlorine and chlorine dioxide die-away in Palo Alto secondary effluent.

1. Both chlorine and chlorine dioxide give decreased survival ratios when dose or contact time is increased.
2. Although some variations exist, chlorine and chlorine dioxide give essentially the same survival ratios when compared on a mass dose basis at 30-minute contact time.
3. Chlorine dioxide is a more rapid disinfecting agent, effecting greater bacterial inactivation than chlorine at the shorter contact times.
4. Comparing chlorine and chlorine dioxide on a residual basis, chlorine dioxide effects the same survival ratio as chlorine but with a much lower residual concentration.

THE EFFECT OF PROCESS SEQUENCE ON BACTERIAL NUMBERS

The experiments with San Jose effluents provided data for evaluation of process sequence effects on disinfection kinetics. Additionally, analysis of the bacterial concentrations at each sample point permitted evaluation of process sequence effects in removal of bacteria before disinfection. Intuitively,

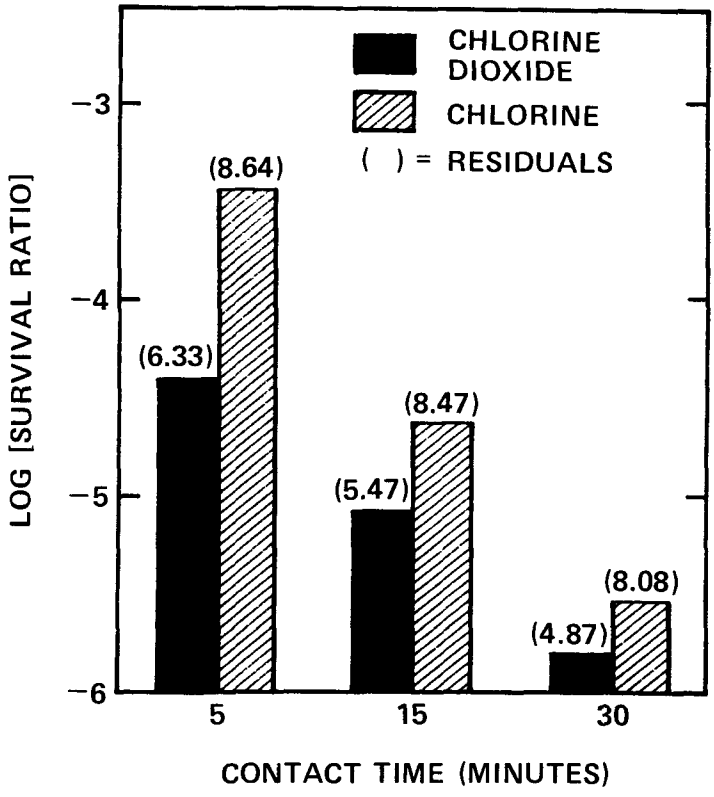


Figure 15. Comparison of chlorine and chlorine dioxide bactericidal effectiveness at 10-mg/l dose. Values of residual concentration are given in mg/l.

decreases in bacterial numbers would be expected to result from additional treatment, due to physical processes that remove or select for particulates. For example, the clarification step of activated-sludge treatment selects for those microorganisms that aggregate into particulates with a density greater than that of water. Therefore, any bacteria (including total coliform) that exhibit aggregation or "clumping" would be expected to be removed in the process.

The logarithms of the initial bacteria counts from each of the sample points at San Jose were compared. Summary statistics are shown in Table 20 and an ANOVA is shown in Table 21.

TABLE 20. INITIAL TOTAL COLIFORMS IN UNDISINFECTED EFFLUENTS FROM THE SAN JOSE WASTEWATER TREATMENT PLANT

Statistic	Sample Point		
	Secondary Effluent	Nitrified Effluent	Filtered Effluent
Mean, $\log_{10}[N(0)]$	6.51	4.76	4.81
Variance	0.0548	0.1501	0.9516
Standard Deviation	0.2342	0.3875	0.9755
Number of Samples	18	18	18

TABLE 21. ANOVA OF SAN JOSE INITIAL BACTERIA NUMBERS

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Treatment Level	2	35.5562	17.7781	43.35
Error	51	20.8183	0.4082	
Total	53	56.3745		

As shown by the F-value [$P(F > 43.35) < 0.001$] of the ANOVA in Table 21, there is a highly significant difference in initial bacteria numbers among the treatment levels. To identify statistically which means are different from others, critical sums of squares were computed and comparisons were made (*a posteriori* test) on the means of Table 20. These tests showed a statistically significant difference between bacterial numbers in the secondary effluent and nitrified or filtered effluent. No difference was found between nitrified effluent and filtered effluent. This result was surprising. While removal of bacteria through the nitrification process might be due to the final clarification step or predation, it was expected that greater reductions would occur in filtration than were observed. If the physical processes of particulate removal are analyzed and filter efficiency is computed as a function of particulate size (30), a minimum efficiency of removal is found for particulates on the order of 1 μm. An individual coliform bacteria cell is in the size range of 1-5 μm (31). It can be inferred from this analysis that the bacteria in the nitrified effluent exist as singlets or small aggregates.

A similar analysis for the Palo Alto - 1979 experiments is shown in Tables 22 and 23. As shown, there is no significant difference [$P(F > 0.6588) = 0.429$] between the initial bacteria numbers of secondary effluent and lab-filtered secondary effluent. It can be inferred from these data that the bacteria in secondary effluent are also mono-dispersed or nearly so.

At most wastewater treatment plants (all in this study), it is common practice to use chlorinated finished water as process water throughout the treatment process. For example, both the Dublin and San Jose plants use water from the chlorine contact tank (8-10 mg/l total chlorine residual) to backwash

TABLE 22. LOGS OF INITIAL BACTERIAL NUMBERS AT THE PALO ALTO WASTEWATER TREATMENT PLANT

Statistic	Secondary Effluent, Unfiltered	Secondary Effluent, Lab-Filtered
Mean	4.97	4.86
Variance	0.1199	0.0423
Standard Deviation	0.3462	0.2056
Number of Samples	9	9

TABLE 23. ANOVA OF PALO ALTO INITIAL BACTERIAL NUMBERS

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Treatment Level	1	0.0601	0.0601	0.6588
Error	16	1.4593	0.0912	
Total	17	1.5194		

the filters. This backwash water is settled and blended with the influent to the primary sedimentation basin. Dublin also uses a small fraction of the chlorinated water (12-14 mg/l total chlorine residual) from the chlorine rapid-mix tank for foam control in the activated-sludge process. The dose and form of chlorine that is applied to the wastewater in processes other than disinfection is difficult, if not impossible, to determine. Additionally, the possible effects of low doses of chlorine species on the morphology of the coliform bacteria group and the potential consequences for disinfection kinetics are largely matters of conjecture. One area of concern in comparing chlorine and chlorine dioxide as disinfectants in real wastewaters is the question of induced resistance. If a bacterial population has an induced resistance to chlorination due to low-level exposure (such as cited above), the bacteria may appear relatively more sensitive to chlorine dioxide than to chlorine, a bias which may disappear after long-term use of chlorine dioxide.

COMPARISONS AMONG WASTEWATERS

The data (Appendix A) from the experiments described above were used to determine the coefficients of the model used in this study. The coefficients were determined by linear regression of log(residual-time product) on log survival ratio. This regression yields:

$$\log[N(t)/N(0)] = \log b' + k \log(RT) \tag{29}$$

$$= k \log[RT \cdot (b')^{1/k}] \tag{29'}$$

or

$$N(t)/N(0) = [RT \cdot (b')^{1/k}]^k \tag{30}$$

where

$$b' = b^{-k}$$

so that

$$N(t)/N(0) = [\frac{RT}{b}]^k \tag{31}$$

An analysis of the standardized residuals from the regressions of each experiment showed in all cases except chlorine dioxide disinfection of Palo Alto wastewater - 1979, the simple regression model

$$y = \beta_o + \beta_1 x + \varepsilon \tag{32}$$

was adequate in describing the relationship between survival ratio and residual-time product (i.e., the standardized regression residuals were normally distributed). For the chlorine dioxide disinfection of Palo Alto wastewater - 1979, the doses and sample times provided low enough residual-time products, so that bacterial samples were taken before any inactivation had occurred. To remove these points from the linear regression, a 95% confidence interval around $N(t)/N(0) = 1.0$ was estimated using the variance of the membrane-filter technique, as calculated from replicates of zero-time bacterial numbers. Any survival ratios which fell into this interval were excluded from the regression, and analysis of the resulting standardized regression residuals showed conformity to the regression model.

The coefficients of the disinfection model determined by linear regression are shown in Table 24. Log-log plots of the model predictions and data points for each experiment are shown in Appendix B.

The San Jose treatment plant had brought their separate nitrification process and the filtration process on line only six months prior to our laboratory disinfection studies. Complete nitrification of the wastestream was not always achieved during the sample period, so that low levels of ammonia were measured in both the nitrified effluent and the filtered effluent. The model coefficients reported in Table 24 for chlorine disinfection of San Jose nitrified and filtered effluents are from linear regressions with all data from these sample points. If the experiments are segregated according to the chlorine:ammonia ratios, then the experiments in which free chlorine is the predominant disinfecting agent can be separated from those experiments in which disinfection is due to combined chlorine. Extensive research has been reported in the literature on the reactions of chlorine with ammonia, the breakpoint phenomenon (11). For complete oxidation of ammonia to nitrogen gas, the following stoichiometry follows:

TABLE 24. VALUES OF FITTING CONSTANTS FOR CHLORINE AND CHLORINE DIOXIDE IN THE DISINFECTION MODEL

Experimental Description	Chlorine Dioxide						Chlorine					
	b†	95% CI* for b	k†	95% CI for k	r#	n**	b	95% CI for b	k	95% CI for k	r	n**
Palo Alto - 1978	1.56	0.99 to 2.47	-2.90	-2.49 to -3.30	0.86	72	5.17	2.72 to 7.62	-3.15	-2.82 to -3.47	0.92	72
Palo Alto - 1979 Unfiltered	0.67	0.32 to 1.41	-2.30	-1.78 to -2.83	0.86	29	2.21	0.61 to 5.82	-2.22	-1.67 to -2.76	0.83	31
Palo Alto - 1979 Lab Filtered	0.004	0.002 to 0.010	-1.21	-1.03 to -1.40	0.89	44	0.84	0.38 to 1.83	-2.10	-1.65 to -2.54	0.86	32
Palo Alto Unfiltered 78 & 79 Comb.	1.29	0.88 to 1.91	-2.75	-2.42 to -3.07	0.86	101	3.95	2.62 to 5.95	-2.79	-2.50 to -3.07	0.88	103
Dublin-San Ramon Lab	0.14	0.07 to 0.28	-1.84	-1.15 to -2.51	0.78	22	0.65	0.37 to 0.86	-1.62	-1.31 to -1.92	0.91	26
Dublin-San Ramon Field	0.57	0.37 to 0.87	-2.20	-1.86 to -2.54	0.84	69	1.67	0.56 to 4.93	-1.79	-1.32 to -2.27	0.93	12
San Jose Secondary	0.89	0.33 to 2.43	-2.18	-1.41 to -2.95	0.78	21	4.06	1.50 to 10.98	-2.82	-2.14 to -3.51	0.86	26
San Jose Nitrified	0.78	0.18 to 3.30	-2.06	-1.23 to -2.88	0.75	19	2.70	0.83 to 8.81	-2.58	-1.67 to -3.48	0.79	24
San Jose Filtered	0.003	0.001 to 0.01	-1.13	-0.74 to -1.51	0.81	18	0.59	0.13 to 2.75	-2.12	-1.16 to -3.07	0.69	21

*CI = confidence interval.

†For definitions of b and k , see Eqs. 24 and 25.

#r = correlation coefficient for log-log transformation of raw data.

**n = number of observations.

$$2NH_3 + 3HOCl \rightleftarrows N_2 + 3H_3O^+ + 3Cl^- \quad (33)$$

The theoretical weight ratio of Cl:N is 7.5 for completion of this reaction. However, the stoichiometry is a simplification of a complex series of reactions, all of which show some pH dependency (11,32). Weight ratios of Cl:N up to 10:1 are required in some situations to achieve breakpoint, depending on the pH of the reaction and the aqueous system involved. For our purposes, a Cl:N ratio of less than 6.25 was chosen as indicative of combined chlorine residual, while a Cl:N ratio of 12.0 was interpreted as indicating predominately free chlorine.

The chlorine to ammonia nitrogen ratios for the San Jose nitrified and filtered experiments are shown in Table 25. Based on these data, the following decisions were made to classify the San Jose effluent samples into the "free residual" or combined residual categories. In nitrified effluent, Experiment 1 at all chlorine doses and Experiment 2 at 2 mg/l dose were considered to have a combined chlorine residual; the rest with the exception of Experiment 2 at 5 mg/l dose were considered to have free chlorine residuals. Experiment 2 at 5 mg/l dose was excluded from the analysis altogether because of the uncertainty of residual composition near breakpoint. In filtered effluent, all Experiment 1 doses were considered as below breakpoint, the remaining experiments were used as beyond breakpoint. Linear regressions of these subgroups yielded model coefficients which are compared in Table 26 with the model coefficients of all experiments within the wastewater of interest. These relationships are shown graphically in Figs. 16 and 17 for nitrified and filtered San Jose wastewater, respectively.

The nitrified and filtered experiments in which the Cl:N ratios indicate disinfection with combined chlorine are compared with disinfection by chlorine in secondary effluent (Cl:N ratios << 6.0, i.e. combined chlorine) in Fig. 18. The three curves are essentially identical. To simplify further discussion, "secondary effluent" will be used in referring to disinfection by combined chlorine whether in partially nitrified or in conventional secondary effluent, and will be represented by the curve from the secondary effluent experiments.

TABLE 25. CHLORINE TO AMMONIA NITROGEN RATIOS FOR SAN JOSE EXPERIMENTS

Experiment	NH_3-N mg/l	Chlorine:Ammonia-N Dose 2 mg/l	5 mg/l	10 mg/l
Nitrified Effluent				
1	1.7	1.18	2.94	5.88
2	0.7	2.86	7.14	14.29
3	< 0.04	50	125	250
Filtered Effluent				
1	1.6	1.25	3.13	6.25
2	0.12	16.67	41.67	83.33
3	< 0.04	50	125	250

TABLE 26. COMPARISON OF MODEL COEFFICIENTS, SEGREGATING DISINFECTION WITH FREE VS COMBINED CHLORINE

Experiment	b*	k*	r†	n
San Jose Nitrified				
All data	2.70	-2.58	0.79	22
Combined residual data	6.74	-3.17	0.91	11
Free residual data	1.33	-2.40	0.87	11
San Jose Filtered				
All data	0.59	-2.12	0.69	21
Combined residual data	5.24	-3.25	0.80	6
Free residual data	0.44	-2.16	0.77	15

*For definitions of b and k , see Eq. 24.

†r = correlation coefficient.

"Nitrified effluent" and "filtered effluent" will be understood to imply disinfection by free chlorine and will be represented by the free chlorine curves in Figs. 16 and 17.

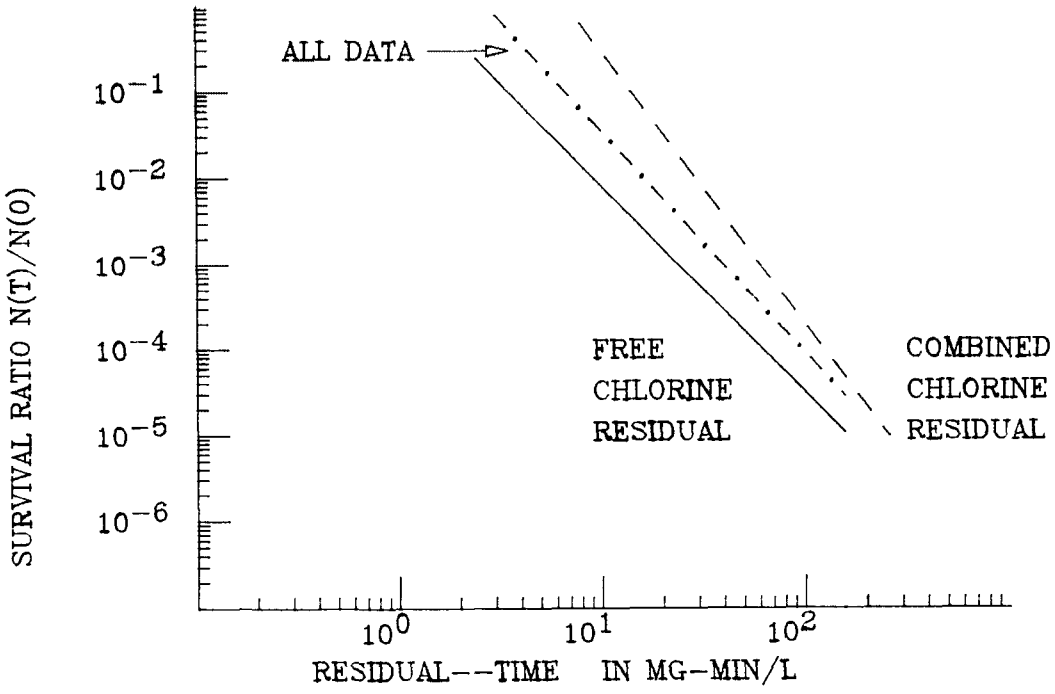


Figure 16. Coliform interaction by free and combined chlorine in San Jose nitrified effluent.

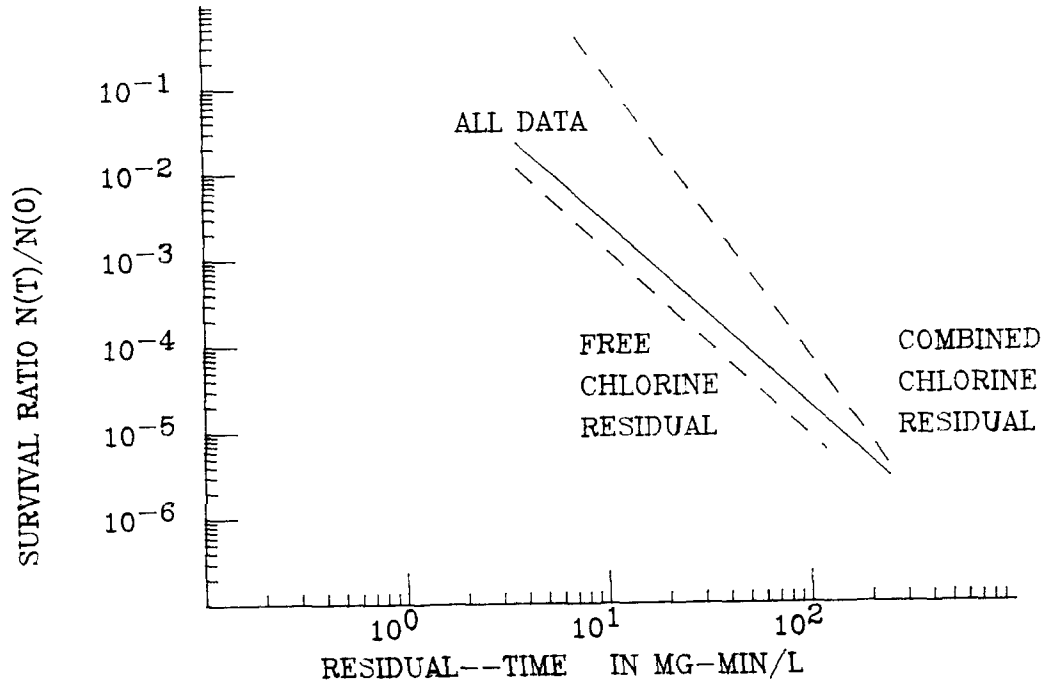


Figure 17. Coliform inactivation by free and combined chlorine in San Jose filtered effluent.

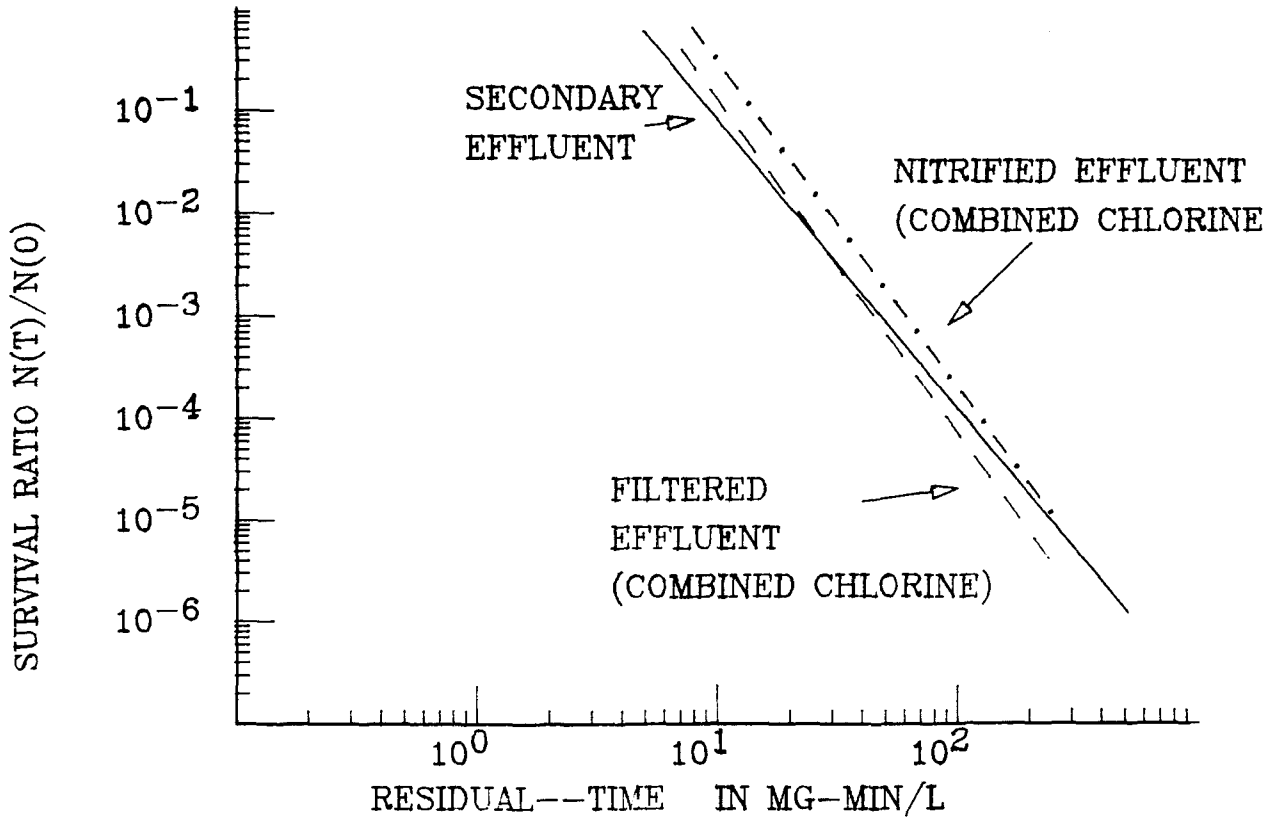


Figure 18. Coliform inactivation by combined chlorine in San Jose wastewater at three sampling points.

EFFECTS OF TREATMENT LEVEL ON THE DISINFECTION PROCESS

Disinfection with Chlorine

The San Jose experiments provide comparisons of disinfection efficiency* in wastewater effluents of progressively increasing quality. As discussed above, a significant difference was found in the initial bacterial concentration between secondary and nitrified wastewater at San Jose. This finding, coupled with the observation that combined chlorine disinfection in partially nitrified wastewater and in partially nitrified, filtered wastewater was nearly identical to disinfection in secondary effluent, suggests that disinfection kinetics are not affected by variations in initial bacterial concentration of the magnitude encountered in this study.

Figure 19 compares the disinfection process by chlorine at three treatment levels in San Jose wastewater, after adjustment of the data base by deleting combined chlorine residual data points in the "nitrified" and "filtered" categories. Hence the "nitrified" and "filtered" categories correspond to a free chlorine residual, whereas the "secondary" category corresponds to a combined chlorine residual. Superior disinfection efficiency is observed when the wastewater has been nitrified compared to conventional secondary effluent. This increased efficiency is believed to be due to the superior germicidal properties of free chlorine in nitrified effluent (11). A further increase in disinfection efficiency is found in comparing the nitrified and filtered effluents. A decrease in the "non-target organism" chlorine demand (that demand not associated with bacterial inactivation) might account for the increased efficiency in filtered effluent vs nitrified effluent. The one-hour chlorine demands, however, were found to be equivalent or slightly higher in the filtered effluent. The one-hour demands for chlorine in filtered and nitrified effluents are shown in Table 27.

The Palo Alto - 1979 experiments also indicate an increase in disinfection efficiency due to filtration, shown in Fig. 20. Hence, the increase in disinfection efficiency of chlorine achieved by prior filtration is not dependent on the form of chlorine responsible for the bacterial inactivation and cannot be explained by the removal of bacteria associated with solids, since no difference was found in initial bacterial concentration between nitrified and filtered effluents in San Jose wastewater, or between Palo Alto secondary and Palo Alto filtered secondary. Moreover, the increased efficiency is not a result of decreased chlorine demand, since comparison of one-hour demands in both San Jose and Palo Alto wastewaters (see Table 27) indicate that the filtered wastewater demand is equal to--if not greater than--the non-filtered demand.

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*Disinfection efficiency is defined in relation to the residual-time product required to achieve a given level of bacterial inactivation as measured by the survival ratio $N(t)/N(0)$. An increase in disinfection efficiency corresponds to a decrease in residual-time product required to achieve the same survival ratio.

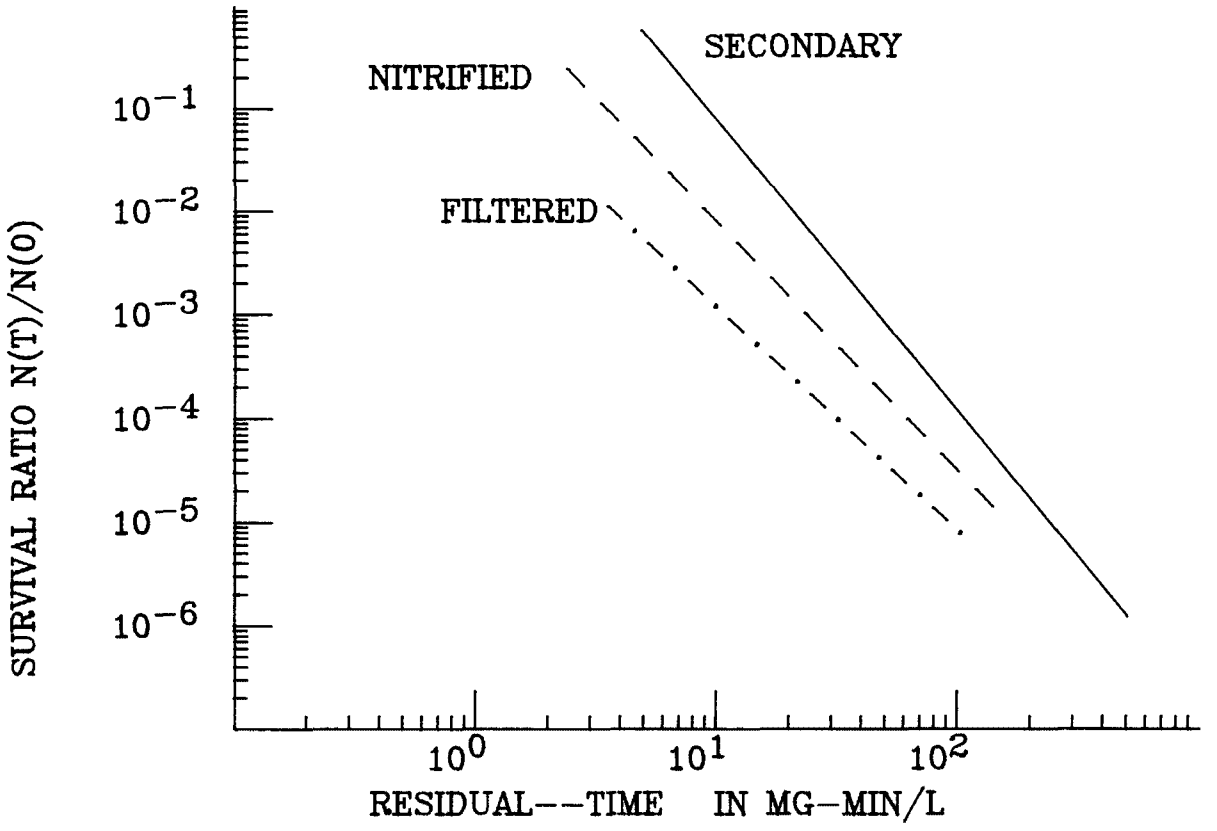


Figure 19. Coliform inactivation by chlorine in San Jose wastewater at various levels of treatment after segregating data base according to the form of chlorine residual.

TABLE 27. ONE-HOUR CHLORINE DEMAND

Wastewater and Treatment Level	Demand,* mg/l		
	Doses		
	2 mg/l	5 mg/l	10 mg/l
San Jose, Nitrified	1.71	4.36	6.52
San Jose, Filtered	1.73	4.28	6.92
Palo Alto - 79, Unfiltered Secondary	1.01	1.72	3.12
Palo Alto - 79, Filtered Secondary	1.38	2.32	4.05

*The one-hour demands are calculated in the manner of Feben and Tarus (33) from residual measurements made over the course of the experiments. This method involves calculation of the demand at time t as dose minus residual. A regression analysis of log(chlorine demand) on log(time) yields an equation for demand of the form:

$$D = D_{one\text{-}hour}\ t^{\alpha}$$

where D = chlorine (or chlorine dioxide) demand; $D_{one\text{-}hour}$ = one-hour demand, mg/l; t = time, hours; and α = a coefficient.

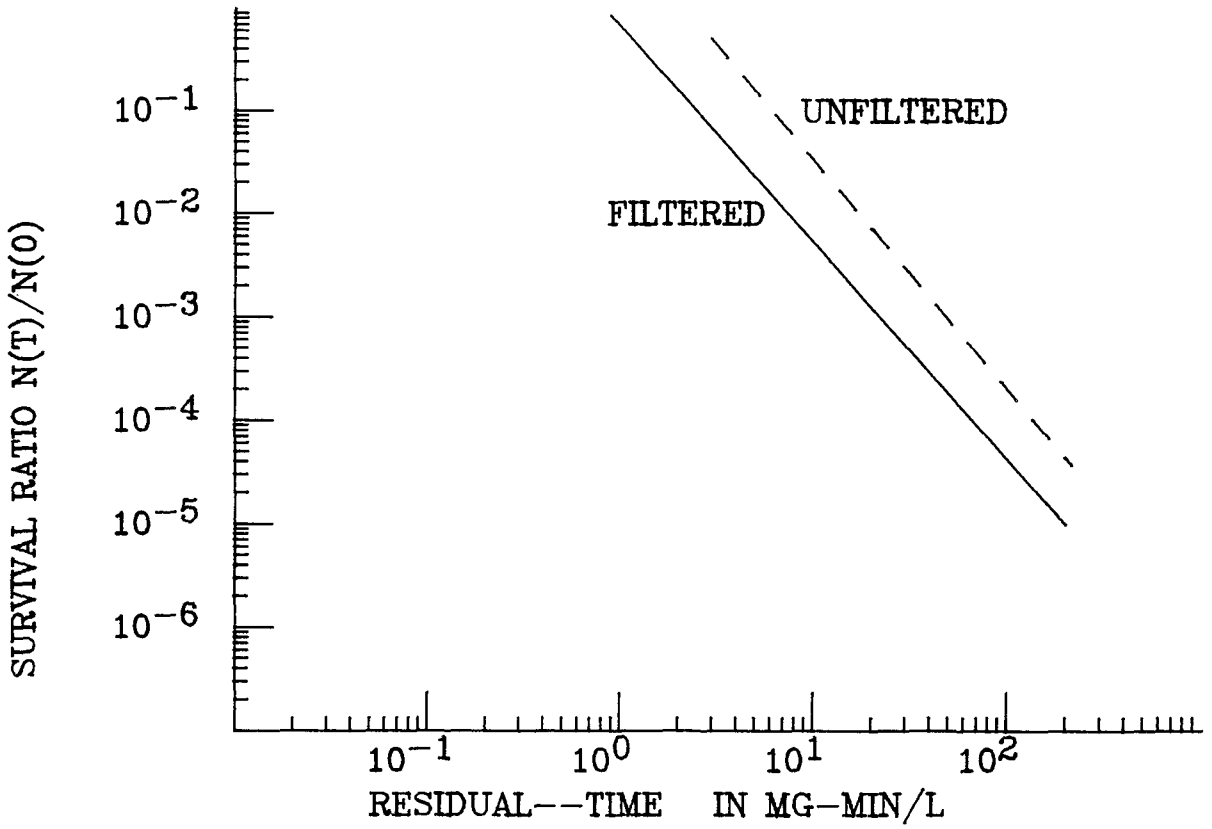


Figure 20. Coliform inactivation by chlorine in filtered and unfiltered secondary effluent, Palo Alto.

Disinfection with Chlorine Dioxide

The results of the San Jose experiments with chlorine dioxide as disinfectant are shown in Fig. 21. In contrast to the corresponding experiments with chlorine as disinfectant, no increase in disinfection efficiency is seen when wastewater quality changes from that of secondary effluent to that of nitrified effluent. This is expected, because the form of the disinfecting agent, chlorine dioxide, is not affected by NH_3-N concentration (34). This observation further supports the conclusion that variations in initial bacterial concentration of the order of magnitude observed in this study (Table 20) do not affect the disinfection process, in view of the fact that the coliform concentrations in the undisinfected nitrified effluent were nearly one hundred times lower than in non-nitrified effluent.

The similarity of disinfection in nitrified and secondary effluent by chlorine dioxide (Fig. 21) is in good agreement with the results obtained with chlorine when the experiments with chlorine in nitrified effluent are segregated by Cl:NH_3-N ratios. When the species of chlorine is unchanged, no difference in disinfection efficiency is seen between secondary and nitrified effluents (Fig. 18).

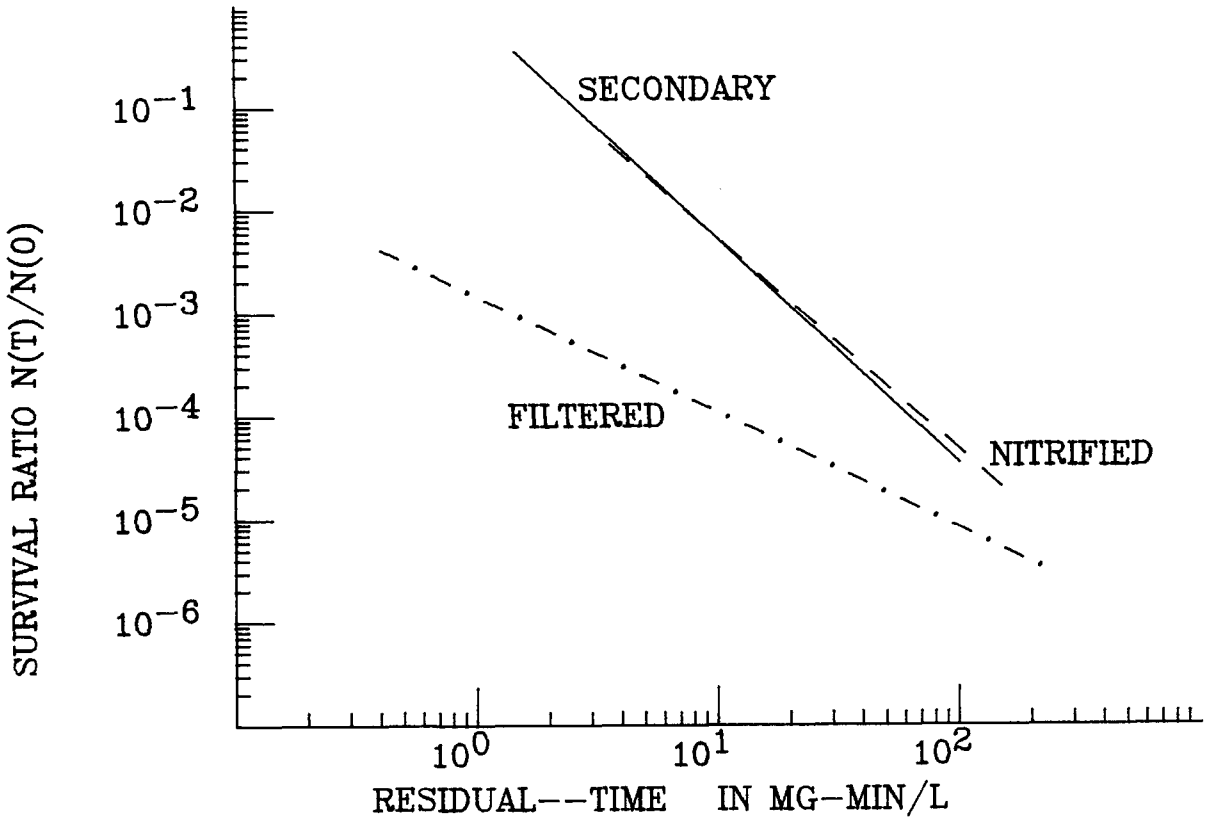


Figure 21. Coliform inactivation by chlorine dioxide in San Jose wastewater effluents.

The San Jose experiments with chlorine dioxide as disinfectant show an increase in disinfection efficiency in filtered wastewater as compared with either secondary or nitrified effluent, similar to that seen for chlorine disinfection but of greater magnitude. This increase in efficiency is again seen in the Palo Alto - 79 experiments, shown in Fig. 22, between unfiltered and filtered secondary effluent, similar to that previously shown (Fig. 20) for chlorine disinfection in Palo Alto wastewater. However, the increase in efficiency for chlorine dioxide is again of greater magnitude than that for chlorine.

The one-hour chlorine dioxide demands are shown in Table 28. Judging from the data in Table 28, the increase in disinfection efficiency using chlorine dioxide seen between unfiltered and filtered wastewater cannot be attributed to a decrease in demand.

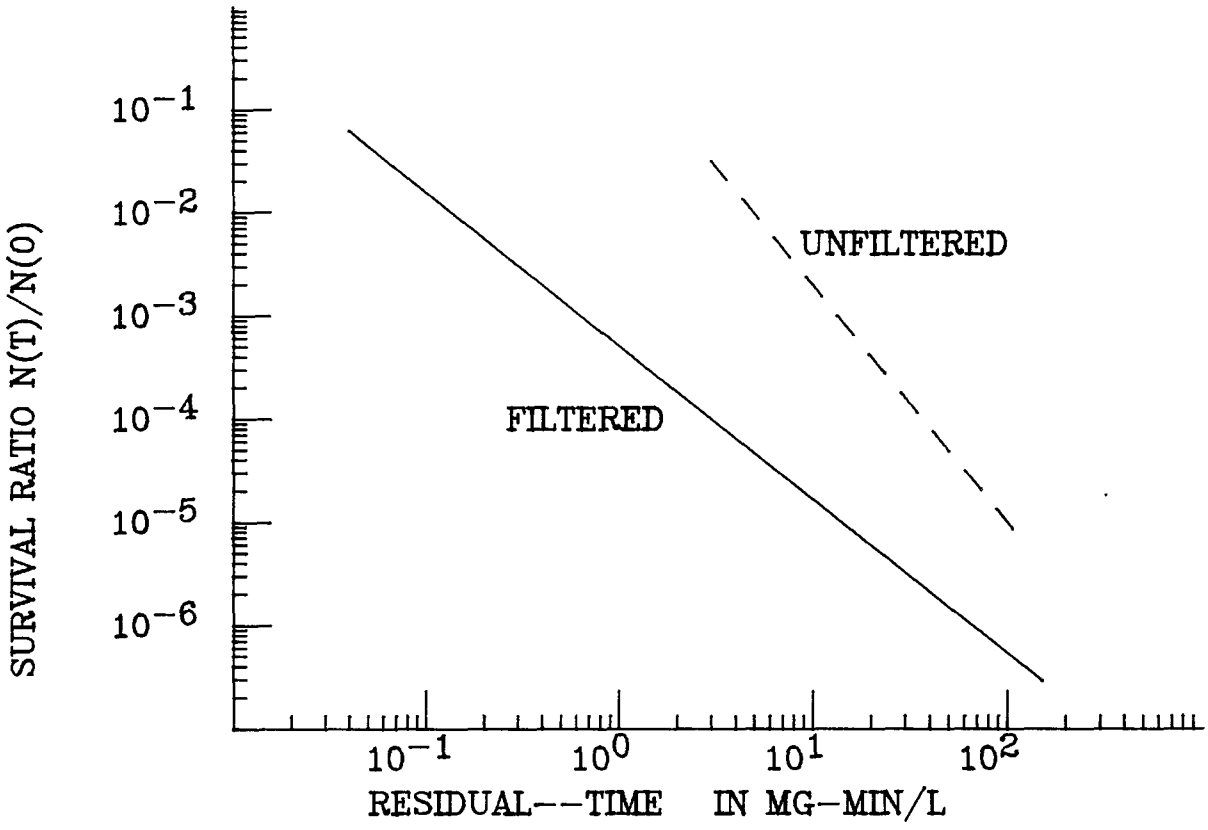


Figure 22. Coliform inactivation by chlorine dioxide in filtered and unfiltered secondary effluent, Palo Alto.

TABLE 28. ONE-HOUR CHLORINE DIOXIDE DEMAND

Wastewater and Treatment Level	Demand,* mg/l Doses 2 mg/l	5 mg/l	10 mg/l
San Jose, Nitrified	1.45	3.56	4.86
San Jose, Filtered	1.80	3.85	4.19
Palo Alto - 79, Unfiltered Secondary	1.99	4.46	7.46
Palo Alto - 79, Filtered Secondary	1.94	4.57	6.79

*Demand in mg/l calculated as described in Table 27.

COMPARISON OF DISINFECTION WITH CHLORINE AND CHLORINE DIOXIDE

Secondary Effluent

Chlorine and chlorine dioxide disinfection are compared in Palo Alto secondary effluent (1978 experiments) in Fig. 23. Chlorine dioxide is a more efficient bactericide than chlorine when compared on the basis of residual-time product required for a given survival ratio. This is true for the full range of Rt products (or equivalently survival ratios) of the experiments.

Because of the nature of the log-log representation, however, it is difficult to visualize how the chlorine dioxide advantage varies with changes in survival ratio. For illustrative purposes, a ratio of chlorine dioxide residual to chlorine residual (calculated assuming one-hour contact time) will be presented at two levels of inactivation, survival ratio of 10^{-1} and survival ratio of 10^{-5}. A value of required residual ratio (RR) less than unity indicates superiority for chlorine dioxide compared to chlorine. For example, in the case of Palo Alto secondary effluent (Fig. 23) at a survival ratio of 10^{-1}, the residuals required are 0.06 and 0.18 mg/l for chlorine dioxide and chlorine, respectively, yielding a ClO_2: Cl_2 residual ratio of 0.33. At a survival ratio of 10^{-5}, the residuals are 1.38 and 3.33, respectively, yielding a residual ratio of 0.41. The implication is that at lower residual-time

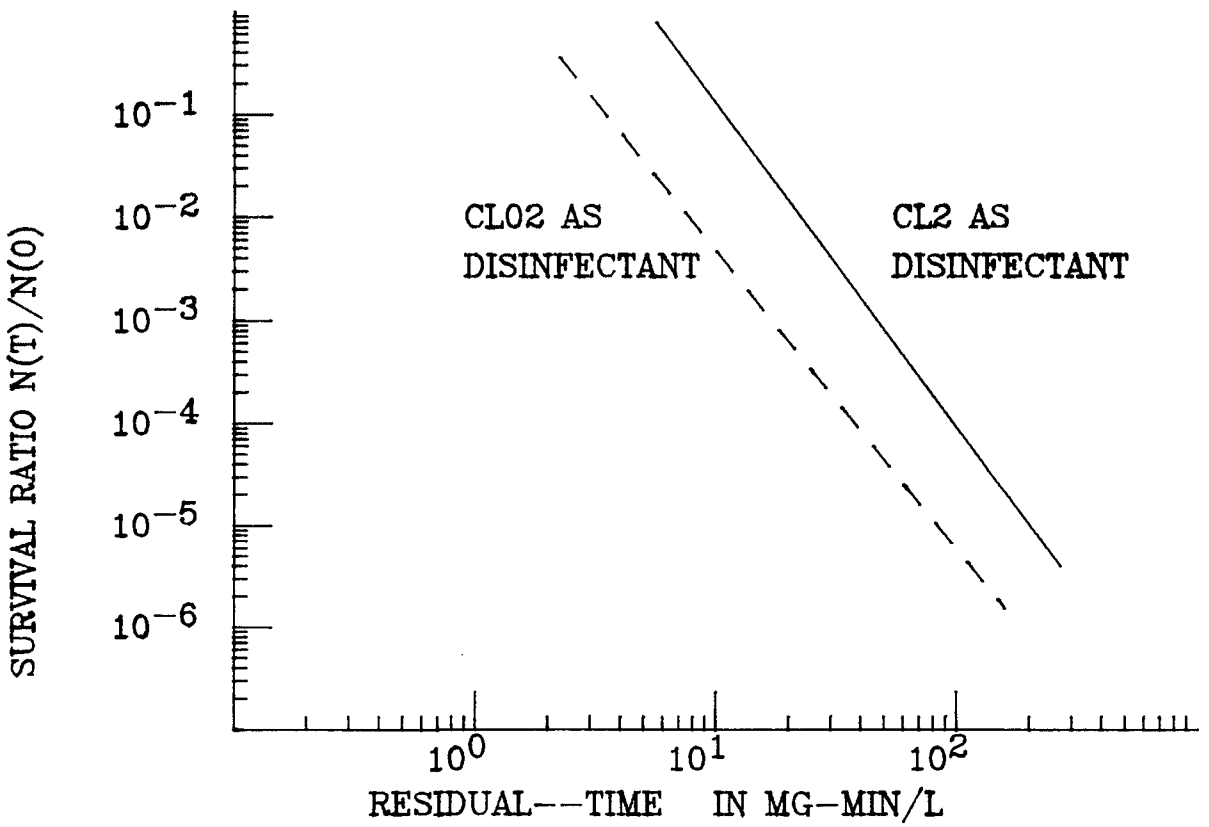


Figure 23. Coliform inactivation by chlorine dioxide in 1978 laboratory experiments with unfiltered secondary effluent from Palo Alto.

products, chlorine dioxide has a greater advantage in disinfection efficiency over chlorine than at higher residual-time products. This convention will be used for the comparison of chlorine dioxide and chlorine disinfection presented below. The residual ratios at survival ratios of 10^{-1} and 10^{-5} will be referred to as RR_1 and RR_2, respectively.

Disinfection in Palo Alto unfiltered secondary effluent (1979 experiments) is compared in Fig. 24, with $RR_1 = 0.29$ and $RR_2 = 0.25$. Chlorine dioxide is again shown to be a more efficient bactericide over the entire range of Rt products studied and the advantage remains relatively constant.

Figure 25 shows comparison of chlorine and chlorine dioxide disinfection of filtered Palo Alto secondary effluent (1979 experiments). The RR_1 and RR_2 in this case are 0.01 and 0.26, respectively. The large advantage realized for chlorine dioxide due to filtration is apparent in this comparison. This advantage, however, decreases with increasing Rt product to the advantage seen in unfiltered Palo Alto secondary effluent.

The results of disinfection experiments with chlorine and chlorine dioxide in San Jose secondary effluent are compared in Fig. 26. In this case, RR_1 and RR_2 are 0.28 and 0.73, respectively, which indicates a decrease in chlorine dioxide advantage with increasing Rt product.

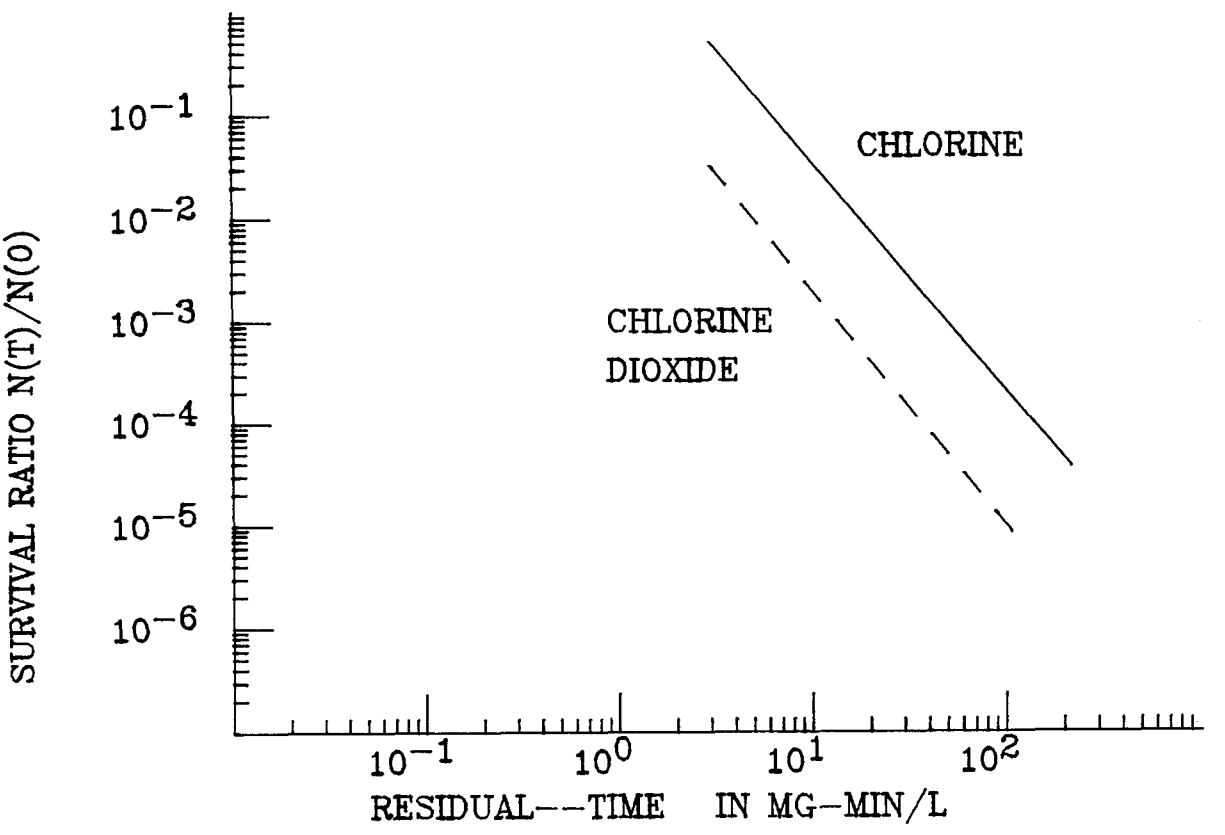


Figure 24. Coliform inactivation by chlorine and chlorine dioxide in 1979 experiments with unfiltered secondary effluent from Palo Alto.

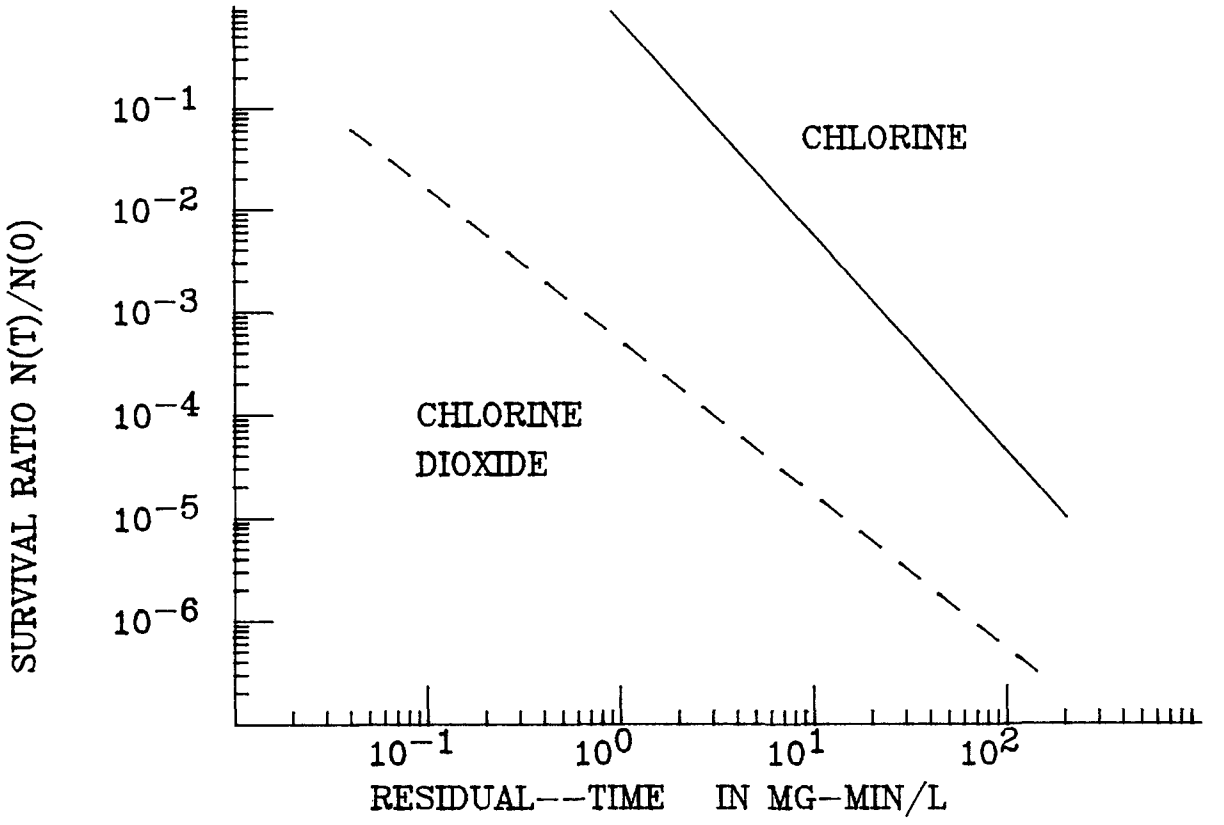


Figure 25. Coliform inactivation by chlorine and chlorine dioxide in 1979 experiments with filtered secondary effluent from Palo Alto.

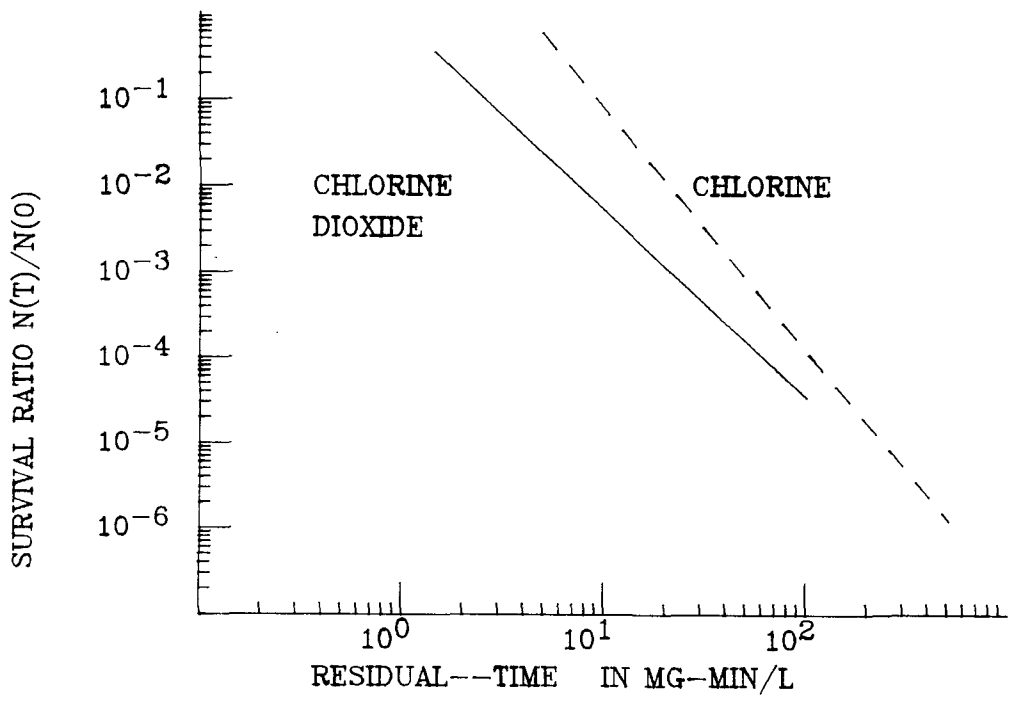


Figure 26. Coliform inactivation by chlorine and chlorine dioxide in San Jose secondary effluent.

In general, chlorine dioxide is a more efficient bactericide in secondary effluent than chlorine when comparison is made on a residual or residual-time product basis at a given level of inactivation. The advantage for chlorine dioxide is greatest in filtered secondary effluent and at lower Rt values or correspondingly higher survival ratios.

Nitrified Effluent

A comparison of bacterial inactivation in San Jose nitrified effluent is shown in Fig. 27. The advantage of chlorine dioxide over chlorine seen in secondary effluent has disappeared due to the increase in efficiency of the free chlorine residual in the nitrified effluent. RR_1 and RR_2 are 0.69 and 1.29, respectively for these experiments.

Nitrified-Filtered Effluent

The results of experiments with San Jose filtered effluent are compared in Fig. 28, with corresponding RR_1 and RR_2 of 0.02 and 0.88, respectively. The tremendous advantage of chlorine dioxide disinfection seen due to filtration at low values of Rt decreases with increasing Rt product. This result is consistent with the results of experiments in Palo Alto filtered (secondary) wastewater as discussed above.

The correlations based on Dublin lab experiments are shown in Fig. 29. In this case, however, the RR_1 and RR_2 of 0.18 and 0.09 indicate that the chlorine dioxide advantage remains relatively constant over the full range of Rt products considered. The Dublin field experiments confirm this observation as seen in Fig. 30. The RR_1 and RR_2 for field experiments are 0.27 and 0.10, respectively.

In general, chlorine dioxide is a more efficient bactericide than chlorine in filtered, nitrified wastewater. The advantage found for chlorine dioxide is due to filtration and not nitrification. The advantage for chlorine dioxide decreases at lower survival ratios in San Jose nitrified-filtered effluent, while remaining relatively constant in Dublin nitrified-filtered effluent.

Summary

The results obtained in this work indicate that chlorine dioxide is a generally superior disinfectant when compared to chlorine on the basis of residual × time product required to achieve a given total coliform survival ratio. This conclusion is in agreement with previously reported laboratory investigations (34-39) and field studies (40-43).

PREDICTING FULL-SCALE PERFORMANCE FROM LABORATORY EXPERIMENTS

A comparison of the laboratory and field (full-scale) experiments in Dublin wastewater are shown in Figs. 31 and 32 for chlorine dioxide and chlorine, respectively. In both cases, the regression equations from the laboratory experiments slightly underestimate the survival observed at the

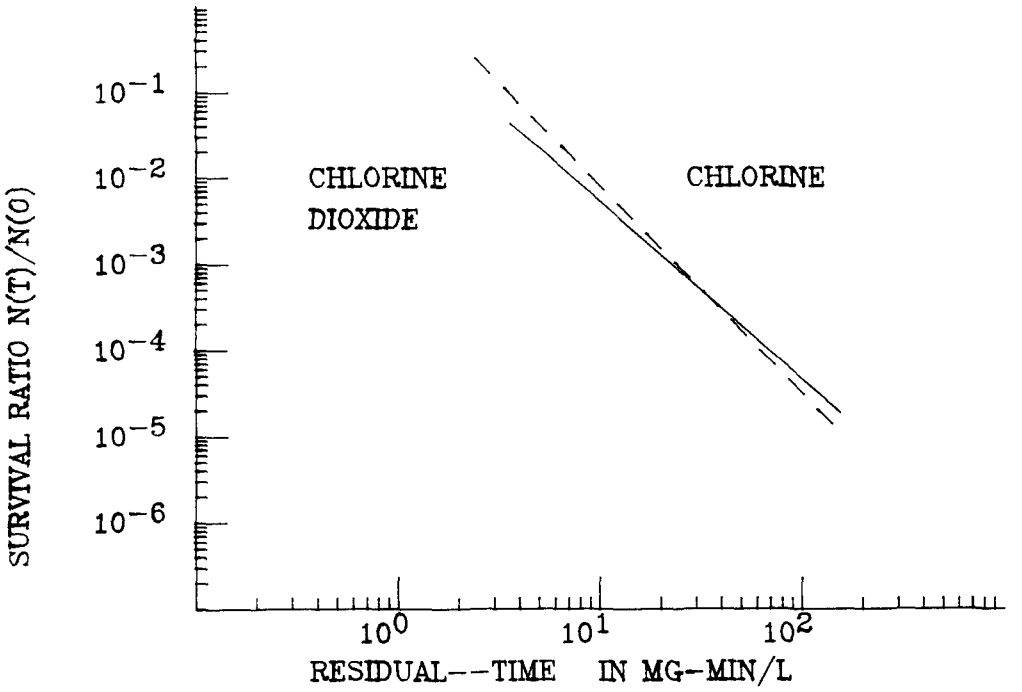


Figure 27. Coliform inactivation by chlorine and chlorine dioxide in San Jose nitrified effluent.

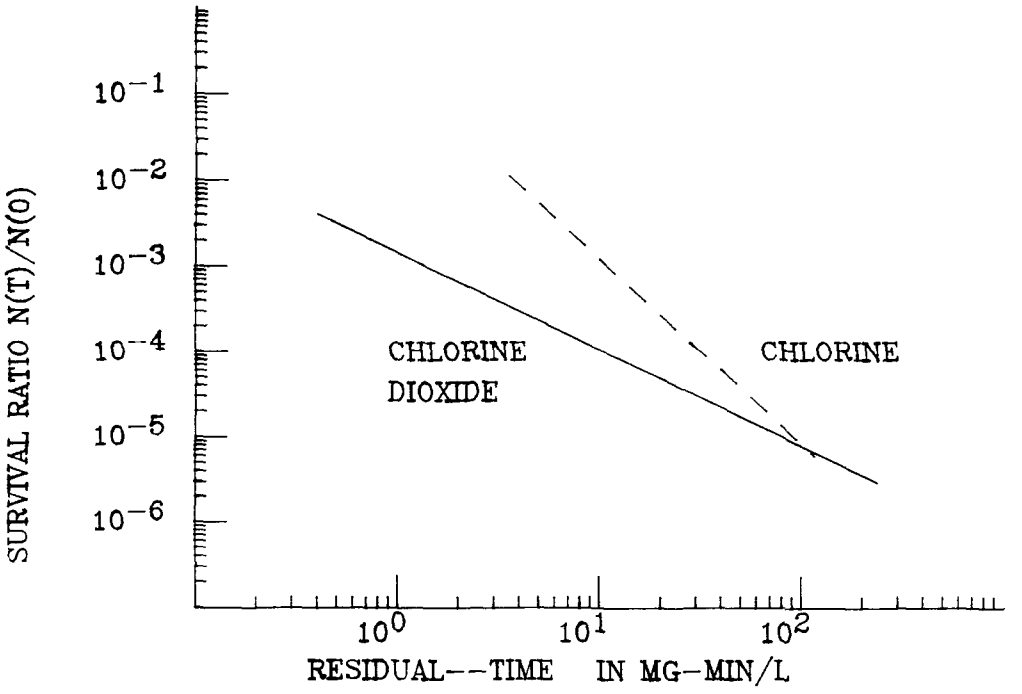


Figure 28. Coliform inactivation by chlorine and chlorine dioxide in San Jose filtered effluent.

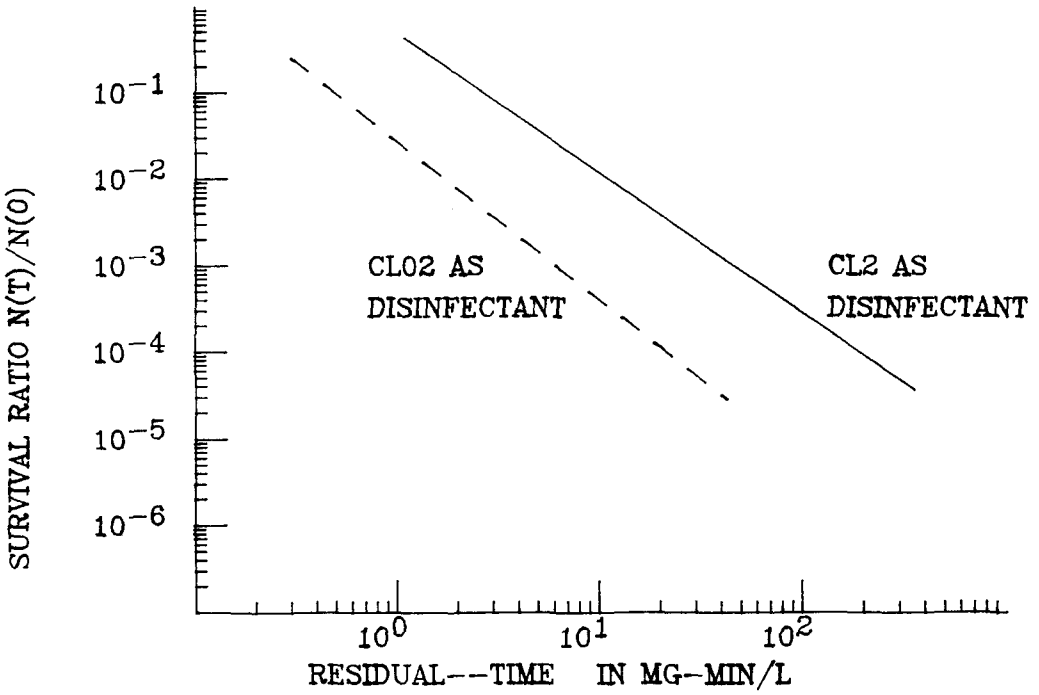


Figure 29. Coliform inactivation by chlorine and chlorine dioxide in laboratory experiments with Dublin effluent.

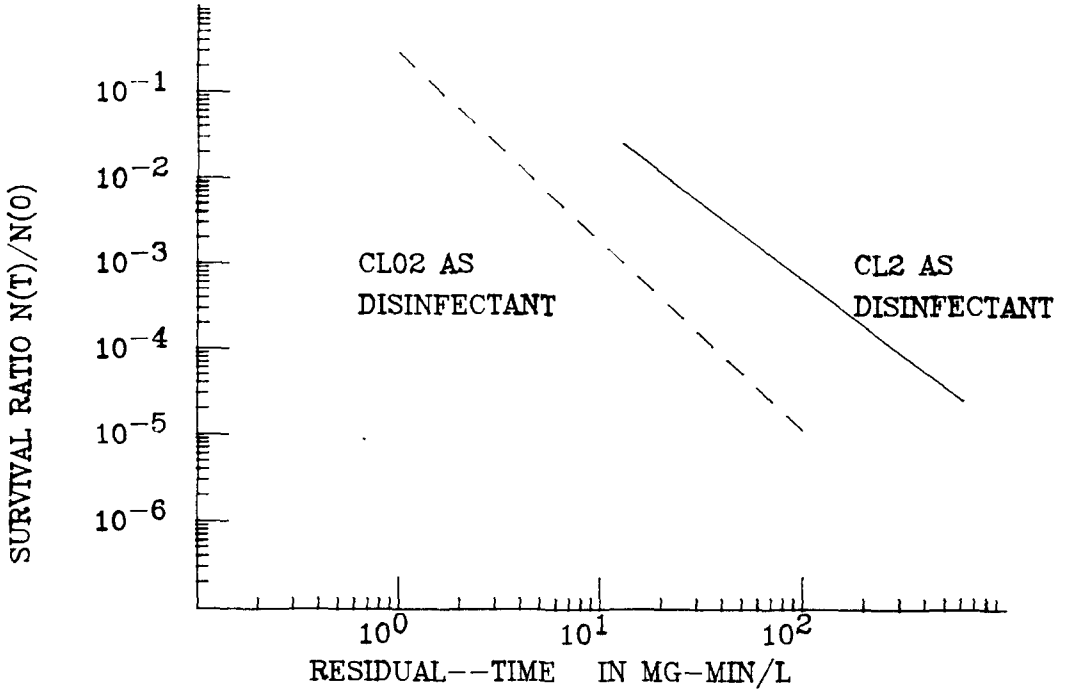


Figure 30. Coliform inactivation by chlorine and chlorine dioxide in field experiments with Dublin effluent.

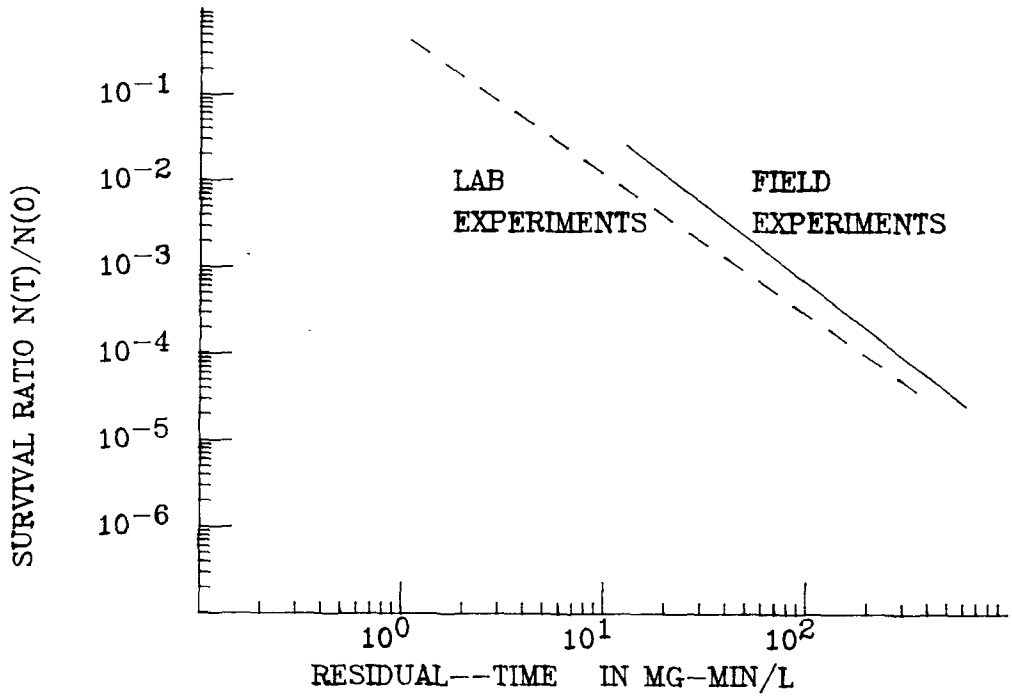


Figure 31. Coliform inactivation by chlorine in laboratory and field experiments with Dublin effluent.

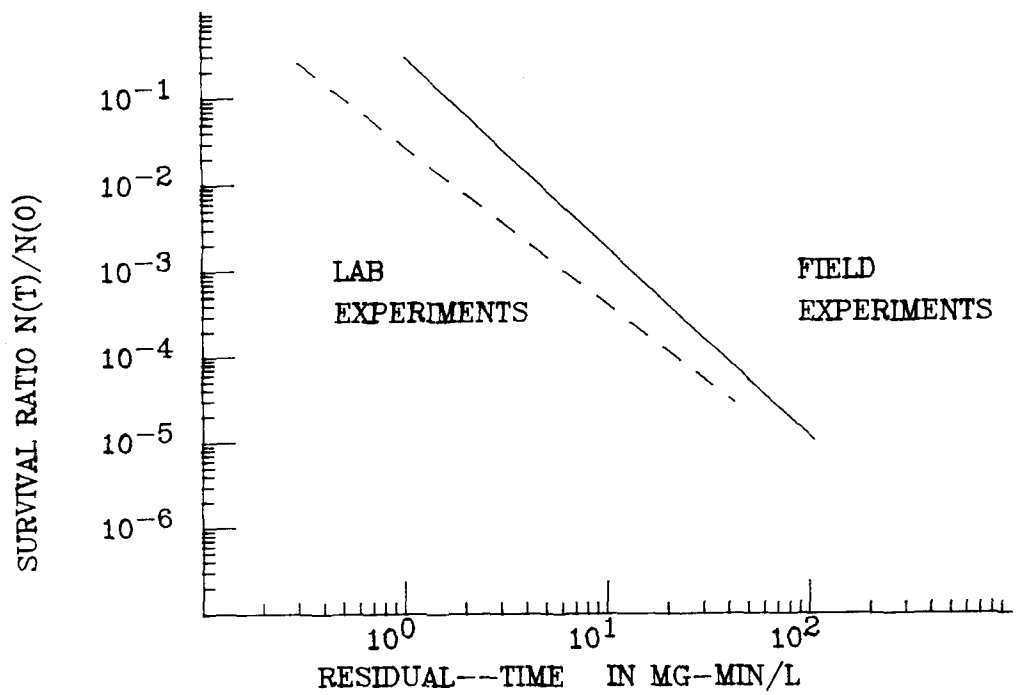


Figure 32. Coliform inactivation by chlorine dioxide in laboratory and field experiments with Dublin effluent.

full-scale treatment plant. The regression lines, however, are not statistically different from each other for either chlorine dioxide or chlorine. The agreement is actually quite good when factors such as temperature, contact time, and chemical mixing are considered. In field experiments, it is extremely difficult to reproduce the ideal mixing, constant temperature, and controlled oxidant generation chemistry found in the laboratory experiments. From Figs. 31 and 32 it can be concluded that laboratory bench-scale experiments of the type described in this report would be a valuable design aid in predicting the residual and/or contact time required to achieve an effluent bacterial standard. Bacterial response to disinfectants is sufficiently varied in different wastewaters and within the same treatment plant at different levels of treatment that no universal disinfection equation could be expected to yield accurate predictive results. The coefficients of the model used to describe the experimental results in this study are highly dependent on wastewater quality and treatment history of the wastewater under consideration, as well as on the choice of disinfectant.

SECTION 8

VIRUS INACTIVATION

In view of the controversy over the validity of the coliform group as adequate indicators of disinfection using chlorine (44-49) or chlorine dioxide (50,51), additional indicators should be compared in evaluating a disinfectant. The use of animal viruses is suggested, since several authors have shown that viruses, such as the widely studied poliovirus, are typically more resistant to disinfectants than are enteric bacteria (52,53). Poliovirus, while not of epidemiological significance in the United States, may serve as an indicator for viruses, such as the Hepatitis virus, that can be disseminated via the water route. Katzenelson and Kedmi (54), however, noted that poliovirus may not be a suitable indicator since the virus could not be detected consistently in urban sewage. For that reason, and also for ease of recovery and analysis, other groups such as Kott et al. (55) and Atlantic Research Corp. (4) have proposed observing coliphages in wastewater disinfection studies. These bacterial viruses are generally present in number concentrations approaching those of the coliforms, and their structure more closely approximates that of pathogenic viruses than do coliform bacteria. The use of viruses to monitor water quality in receiving waters has also been suggested, since human enteric viruses have been observed in water that were determined to be safe by bacteriological standards (56-58).

Analogous protective mechanisms offered by particulates to bacteria apply toward the protection of viruses against inactivation. Virions may be protected against chlorine by aggregation (59-61), adsorption onto particulates (62), or occlusion within organic solids (63). Also, the physical and chemical conditions that permit viral aggregation may not only protect against inactivation, but may also allow partially inactivated virions to reassociate and to cooperatively infect host cells (64). The same protective mechanisms apply for disinfection with chlorine dioxide (65) and may be even more important, because chlorine dioxide can react very quickly and be consumed in competing reactions with other sources of demand in the wastewater.

RESULTS

Palo Alto (Non-Nitrified) Effluent

Selected experiments were conducted to assess the viricidal effectiveness of chlorine dioxide as compared with chlorine. *In situ* coliphage and an inoculum of Poliovirus I (10^6 PFU/100 ml) in Palo Alto secondary effluent were dosed with 5 mg/l chlorine dioxide and chlorine. Samples were taken at 2-,

5-, and 10-minute contact times and analyzed for coliphage (Kott Method), Poliovirus (standard plaque assay), and for fecal coliforms (MF method). The results are shown in Fig. 33. In both trials, chlorine dioxide was a much more effective viricide than was chlorine, although the coliform survivals would indicate that both disinfectants were performing equally well.

Also, the log reductions of the coliphage and poliovirus by each of the disinfectants were similar, a response that had been observed in preliminary experiments not reported. Chlorine dioxide inactivation of both phage and virus was more rapid and of a much greater magnitude than was inactivation of these indicators by an equivalent dose of chlorine. Since the test procedure for poliovirus is much more expensive and time-consuming than the recovery procedure for coliphage, the coliphage was chosen as an indicator of virus response to both disinfectants. Therefore, in situ phage, which may be a more realistic indicator of native populations of other pathogens, was used as opposed to using inocula of laboratory-grown strains of virus.

The results of the phage analyses that were run parallel with the total coliform analysis are shown in Figs. 34 and 35. Once again, the total coliform bacteria respond similarly to the stress of a given disinfectant dose (Fig. 34), whereas all three doses of chlorine dioxide (2, 5, and 10 mg/l) are much more effective at inactivating the coliphage than even the highest dose (10 mg/l) of chlorine (Fig. 35). The curve for the 10 mg/l dose of chlorine dioxide represents the detection limits of the Kott assay for coliphage. Therefore this curve is an upper limit for the survival ratio and should be interpreted not as equivalent to, but rather as less than or equal to the survival at 5 mg/l chlorine dioxide dose. This suggests that accepted indicator organisms (total coliform bacteria) yield conservative performance data for the viricidal effectiveness of chlorine dioxide in secondary effluent.

Another set of experiments was conducted to assess the biocidal effectiveness of each disinfectant at very short contact times, since the results of Fig. 35 indicate that ClO_2 reacts rapidly, within less than 5 min, to inactivate phage. These experiments were run at 5-mg/l doses of chlorine dioxide or chlorine and sampled at 15, 45, 90, and 120 seconds. The results (Fig. 36) again indicate that chlorine dioxide is a more effective viricide than a bactericide, and that chlorine dioxide performs better in secondary effluent than chlorine within a short contact time (< 120 seconds).

Comparison of Virus Inactivation in Palo Alto and Dublin Effluents

Additional experiments were conducted to compare several indicator organisms with the conventional total coliform group in different wastewaters. Two effluents, a non-nitrified (Palo Alto) and a nitrified, sand-filtered (Dublin) secondary effluent were compared in laboratory studies. The nitrified, sand-filtered effluent was used in bench-scale and full-scale studies, whereas the non-nitrified effluent was used only in bench-scale studies. Wastewater characteristics for the Palo Alto and Dublin effluents are shown in Table 14 and Fig. 37. Microbiological analyses consisted of: total coliforms by MF method, coliphage (Φ_B) by the Kott method, coliphage (Φ_C) by the RPTRR method, and inoculated Poliovirus 1 ($N_o = 10^6$ PFU/100 ml) by the standard plaque assay.

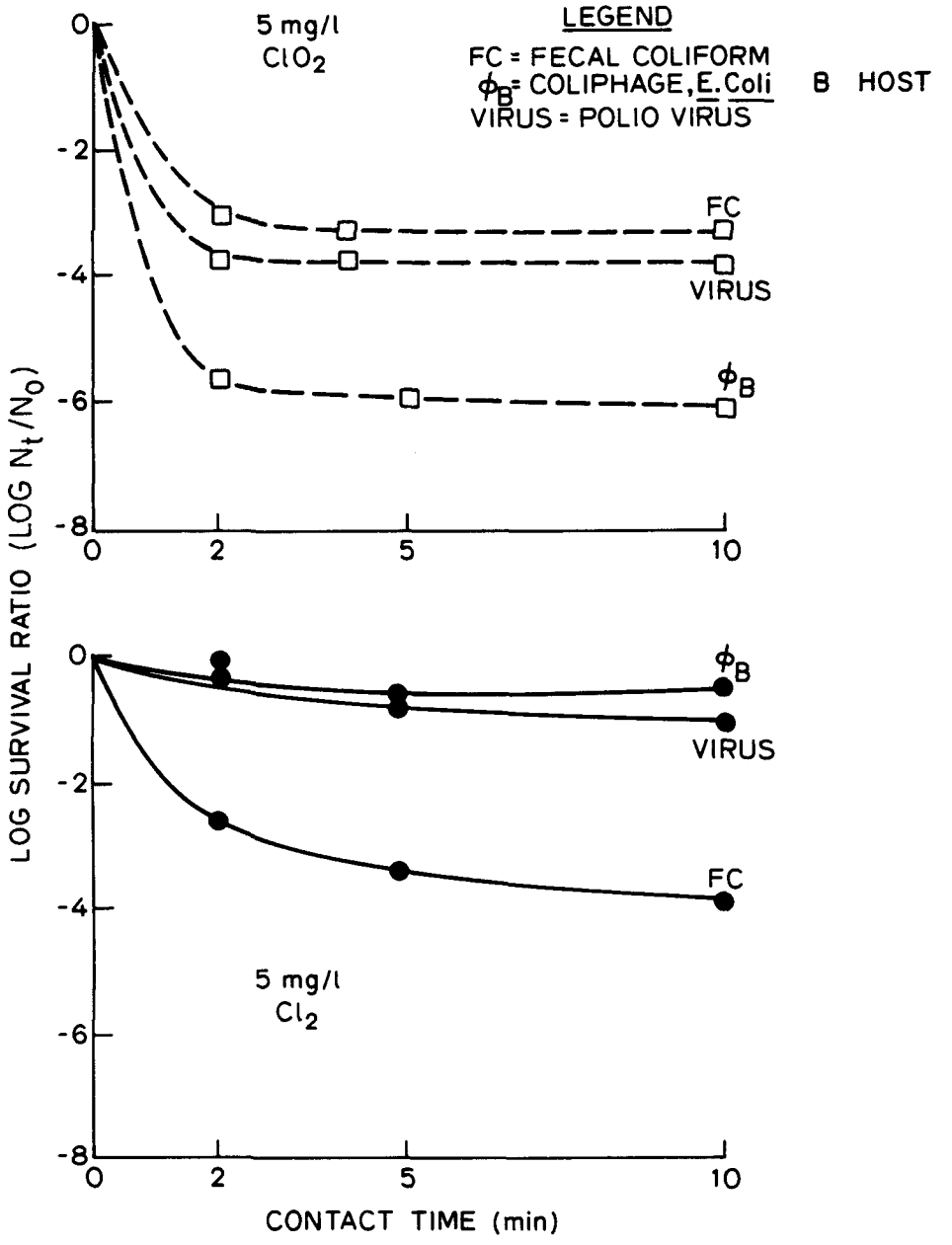


Figure 33. Comparison of in situ coliphage and an inoculum of Poliovirus I in non-nitrified secondary effluent. Above, treatment with 5 mg/l chlorine dioxide; below, treatment with 5 mg/l chlorine.

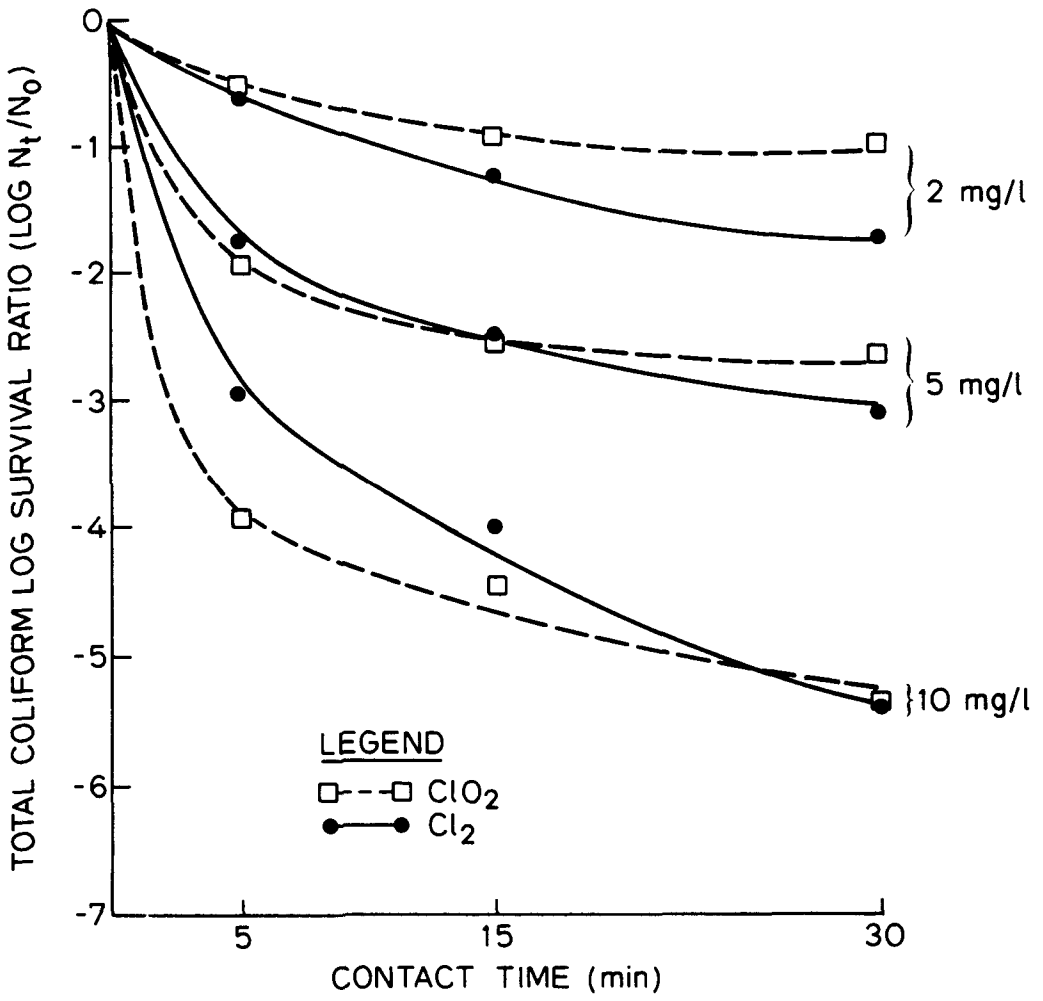


Figure 34. Total coliform survival in non-nitrified secondary effluent, comparing chlorine dioxide and chlorine at three doses and three contact times.

The nitrified sand-filtered effluent (Dublin) was markedly different from the non-nitrified secondary effluent (Palo Alto). Typical characteristics for each wastewater are summarized in Fig. 37. The results from bench-scale experiments (Fig. 37) indicate that chlorine dioxide and chlorine perform equally well at a 2-mg/l dose in the non-nitrified effluent, yet chlorine dioxide is more than twice as effective as chlorine in the nitrified, sand-filtered effluent as measured by total coliform survival. Disinfection as modeled by inactivation of inoculated Poliovirus 1 is much greater for chlorine dioxide than chlorine at the 2-mg/l dose. Similar results were shown earlier (Fig. 33) for a 5-mg/l dose in the non-nitrified effluent. Therefore, the total coliform group serves as an adequate, and possibly conservative, indicator of virus inactivation for chlorine dioxide in both effluents but may not be an adequate indicator when chlorine is used as a disinfectant.

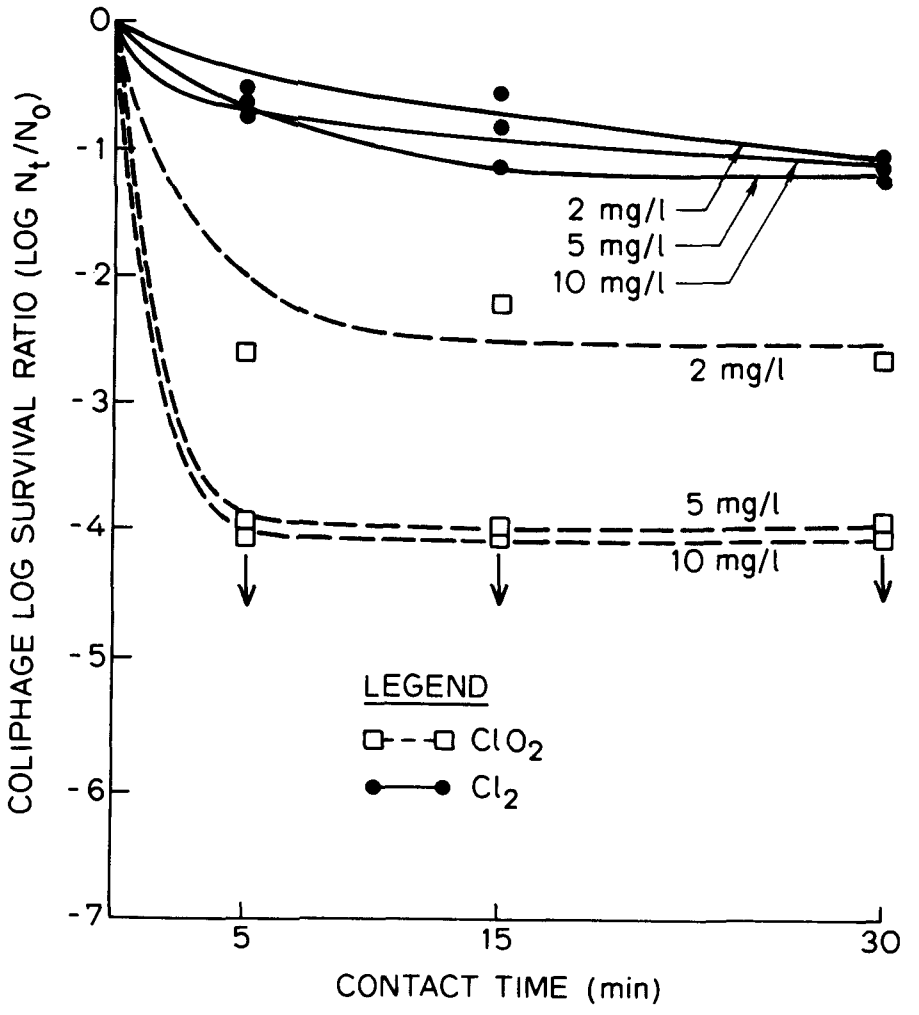


Figure 35. In situ coliphage (E. coli B host) survival in non-nitrified secondary effluent, comparing chlorine dioxide and chlorine at three doses and three contact times.

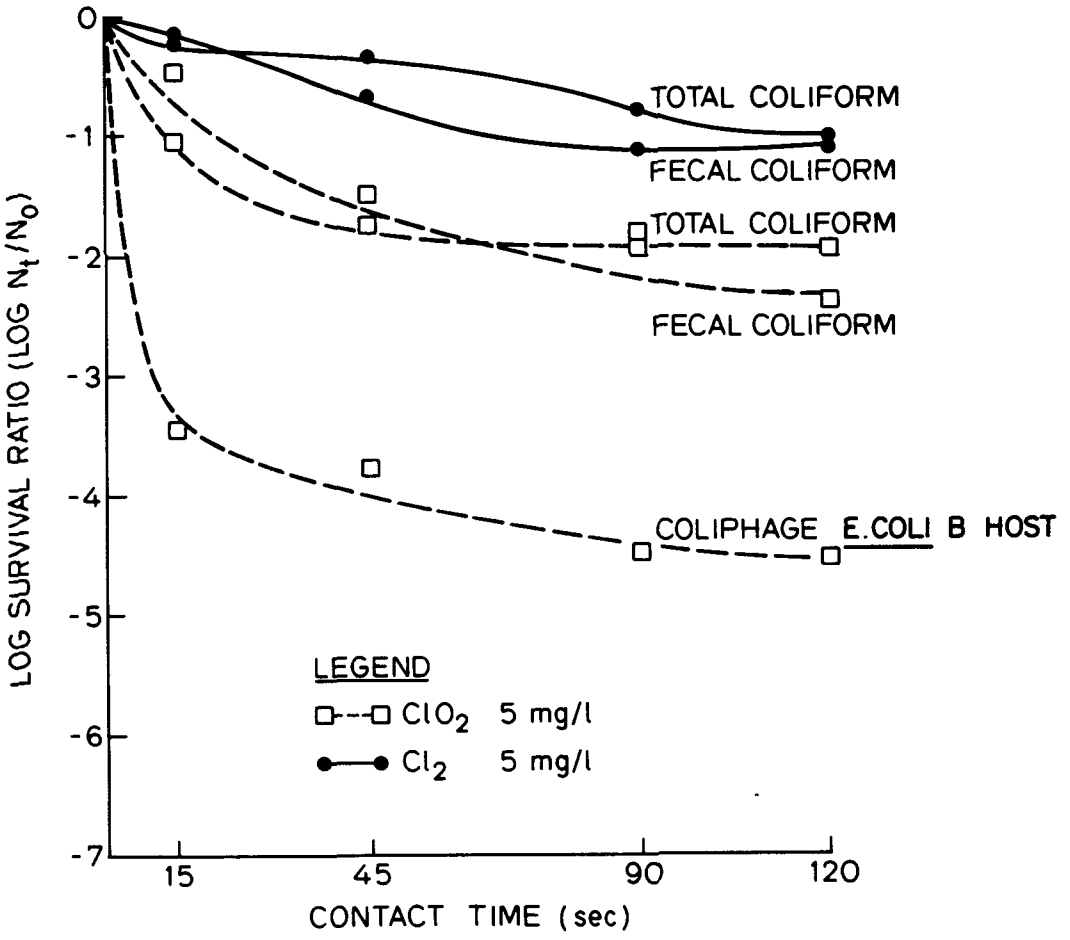
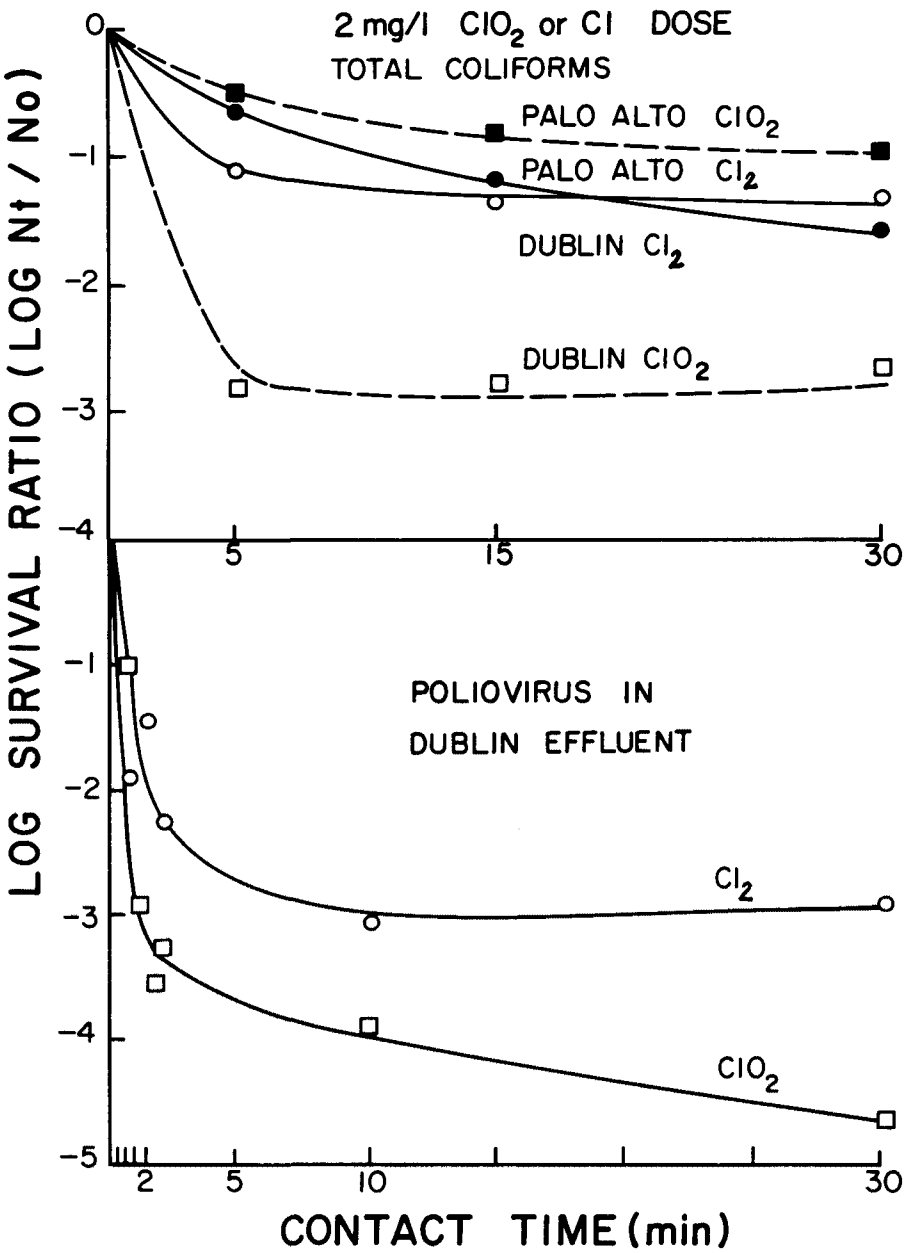


Figure 36. Responses of several *in situ* organisms to chlorine dioxide and chlorine at very short contact times in non-nitrified secondary effluent.



TYPICAL CHARACTERISTICS					
	NH_3-N mg/l	COD mg/l	Suspended Solids, mg/l	COLIFORMS No. / 100ml	30min DEMAND, 5 mg/l ClO_2 Dose
Palo Alto	35.5	33	17	10^6	4.0
Dublin	$<$ 1.0	27	6	10^5	4.6

Figure 37. Total coliform and Poliovirus I survival in non-nitrified activated-sludge effluent (Palo Alto) and in nitrified, filtered effluent (Dublin).

SECTION 9

RECOVERY FOLLOWING DISINFECTION

The need to disinfect wastewater has been questioned (66,67) for a number of reasons. Firstly, the environmental hazards posed by disinfection (e.g. carcinogenic byproducts) have been suggested to outweigh the benefits (e.g., public health protection). Secondly, there is little epidemiological evidence that non-consumptive contact with receiving waters that have been contaminated with fecal material can cause human disease. Although subclinical infections from recreational contact are possible (68), they are difficult to associate with contaminated water sources. Thirdly, there is evidence that more regrowth of bacteria can occur following chlorination than if the effluent were discharged without disinfection (69-81).

The conditions can exist in receiving waters for coliforms to persist for long periods of time (82-84). It is also possible for pathogenic strains of coliforms, such as Klebsiella species, to proliferate (85) and maintain their virulence (86-88). Several factors affect the survival of bacteria and viruses in receiving waters, including temperature, light, and predators. The disinfection process may reduce the controlling biological factors such as predation and competition, and allow wastewater flora to recover and grow in the receiving environment.

EXPERIMENTAL

A set of experiments was designed to test for aftergrowth of bacteria following disinfection. Three replicate experiments were run, each lasting five days. In each experiment, evidence of bacterial growth was sought in three reactor vessels: a secondary effluent control (no treatment), chlorine-dioxide-treated secondary effluent, and chlorine-treated secondary effluent. Each of the latter two were dosed at 5 mg/l. All reactors were diluted 1:4 with lake water after 30 min to simulate receiving water dilution. All reactors were exposed to the same conditions of temperature and light. Parallel samples were taken for total coliforms, fecal streptococcus, seeded poliovirus, and coliphage.

RESULTS

The results (Figure 38) indicate a slight decline in coliforms in the control. A slight increase (approximately one log unit) was observed in both chlorine-dioxide- and chlorine-treated samples, although for chlorine dioxide

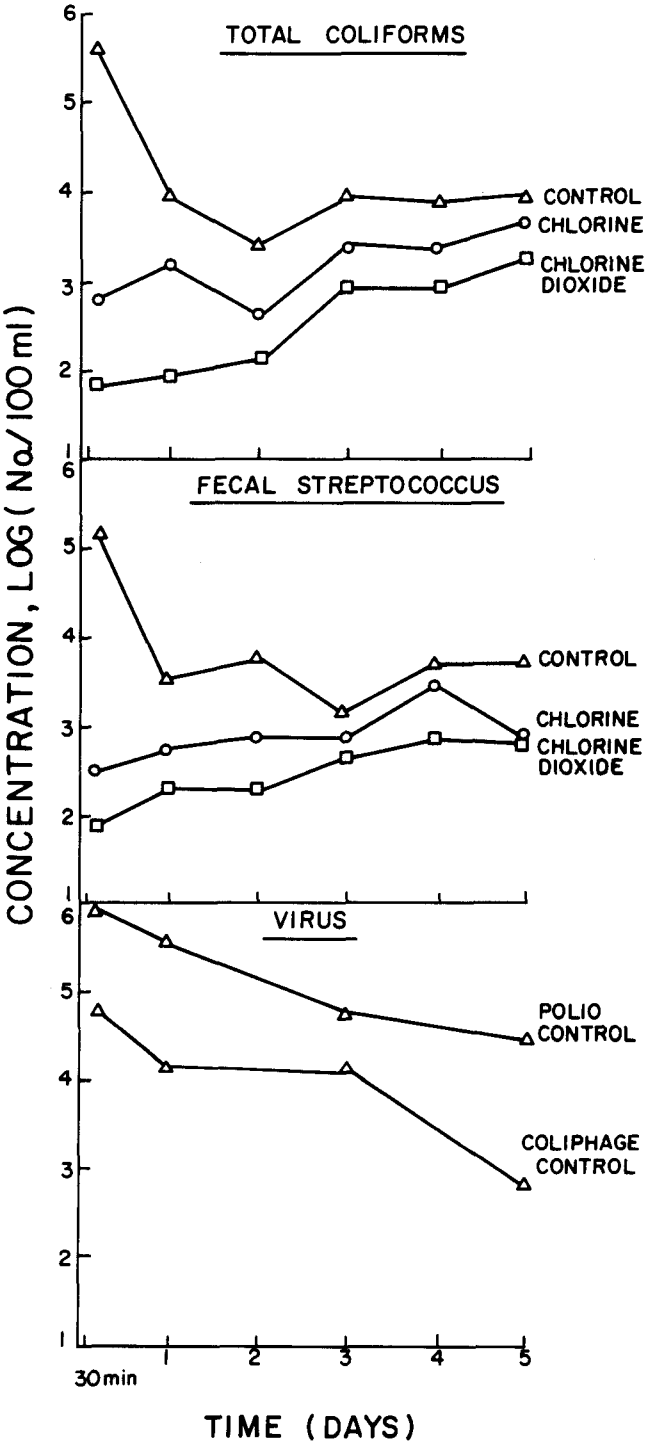


Figure 38. Five-day recovery following disinfection.

the initial kill (30 min contact) was greater, and the number of coliforms remaining was more suppressed than for chlorine. However, the rate of regrowth of coliforms after chlorine dioxide treatment was equal to or greater than that following chlorine treatment. The untreated fecal streptococcus samples showed a marked decline after 24 hrs that remained relatively stable, while both disinfected samples showed a slight but perhaps insignificant recovery.

The Poliovirus I and coliphage concentrations declined steadily in the untreated control samples. The log values for the 30-min treated samples of polio and coliphage were 1.99 and 1.3, respectively, and remained at or below these detection limits for the duration of the experiment. Therefore, only the control values for the phage and virus are shown, since meaningful data could not be obtained in disinfected samples. The inactivation rate (approximately 0.5 log/24 hr) of Polio I at these temperatures (22-24°C) is slightly lower than has been reported for thermal inactivation and lysis by bacterial enzymes in a surface water (89). The inactivation rate for coliphage, the animal virus model, parallels the polio inactivation rate (approximately 0.5 log/24 hr). The mechanisms of inactivation may or may not differ, however, since the phage is capable of reproduction under these conditions whereas the poliovirus is not. The fact that the phage did not increase may mean that the host coliforms were not growing actively enough to allow reproduction, and hence a measurable increase, in the phage population.

The general trends observed in the recovery experiments agree with previously reported results (66-71). Namely, a reduction in fecal indicator bacterial levels, and presumably the levels of enteric pathogens, occurs within about 24 hrs after discharge of an untreated wastewater into a receiving water; conversely, an aftergrowth of indicator bacteria occurs following disinfection by chlorine. This same recovery pattern is observed for an effluent disinfected with chlorine dioxide. The specific rates of inactivation or recovery may depend on such experimental variables as temperature, dilution ratio (wastewater:receiving water), concentration of predators in receiving water, and water chemistry. These observations confirm the concerns of previous workers (65-67) that the need to disinfect effluents discharged into a receiving water with which humans will not experience immediate, direct contact, should be re-examined with epidemiologically designed experiments similar to that of Cabelli et al. (104). This conclusion is subject to uncertainty as to whether enteric pathogens generally exhibit behavior similar to the indicators studied here with respect to: inactivation during disinfection; *in situ* inactivation in receiving waters; and recovery following disinfection.

SECTION 10

HALOGENATED ORGANICS PRODUCED DURING DISINFECTION

CHLORINE DIOXIDE VERSUS CHLORINE

Introduction

The concern over halogenated byproducts of chlorine disinfection has stimulated a search for alternative disinfectants, among which is chlorine dioxide. In this section chlorine dioxide is compared with chlorine alone on an equal mass-dose basis with regard to the amount of halogenated organics formed in wastewaters. Halogenated organics are quantified as total trihalomethanes (THMs) and as total organic halogen (TOX). Comparisons between the two disinfectants were carried out in bench-scale studies and in full-scale field studies.

Within normal pH ranges encountered in water and wastewater treatment, chlorine dioxide reduces to chlorite when it reacts with organics (12,13,90). Chlorine dioxide does not oxidize bromide ion as does chlorine (91).

Chlorine dioxide apparently does not form trihalomethanes (91,92), but it can produce halogenated organics in some cases. Compounds with carbon-carbon double bonds are one group of compounds which can be halogenated. Work with aqueous solutions of cyclohexane and methyl oleate has produced chlorinated products (13). Chlorine dioxide can also react with phenol to produce chloroquinones, chlorohydroquinones, and chlorophenols (13,91). When chlorine dioxide is used in excess with respect to the organic reactants, such as cyclohexane and phenol, non-chlorinated organic acids are formed rather than chlorinated products (13,91).

Studies dealing with the nature of humic compounds suggests that phenol derivatives and benzene carboxylic acids are major subunits (93). Therefore, considering the chlorinated products resulting from chlorine dioxide reaction with phenol, one can expect to find some halogenated organics resulting from reactions in water containing humic substances. Manka et al. (94) have shown that humics are present in treated wastewater effluents. Phenols themselves have been found in domestic secondary effluent at 0.1 to 1.0 mg/l concentrations (95).

Experimental

The experiments presented in this section examine the production of halogenated organics in wastewater by chlorine or by chlorine dioxide. Two types

of wastewaters were used in these experiments: secondary effluent from an activated-sludge process at the Palo Alto Wastewater Treatment Plant and effluent from the Dublin-San Ramon Wastewater Treatment Plant which had received extended-aeration, activated-sludge treatment (achieving full nitrification) and multimedia filtration. The characteristics of the wastewater effluents are summarized in Table 29. Each experiment represents a wastewater sample taken on a different day.

The experiments were primarily bench-scale experiments; however, some full-scale field experiments were conducted to supplement the findings from the bench-scale experiments. In the bench-scale experiments wastewater effluents from both Palo Alto and Dublin-San Ramon were used. As shown in Fig. 39, three or four liters of wastewater was dosed with either chlorine or chlorine dioxide. The doses for both disinfectants were 40 mg/l and 20 mg/l measured as ClO_2 for chlorine dioxide and as Cl for chlorine. The dosed effluents were mixed and then transferred into individual 0.5- and 1-liter glass-stoppered reactor bottles within five minutes after dosing. The reactor bottles were filled completely to exclude headspace. These reactor bottles were also covered with aluminum foil to prevent light from influencing the reactions. The secondary effluent in these bottles was allowed to react for 1 to 24 hrs or longer at 25°C. At the completion of the respective reaction periods, each reactor bottle was opened, and samples for THM and TOX analyses were transferred immediately to 60-milliliter hypovials. Excess sodium thiosulfate previously introduced into these hypovials quenched any disinfectant residual. The remaining water from the reactor bottle was analyzed for disinfectant residuals. TOX analysis was by the Dohrmann method (Section 4).

The field experiments were run at the disinfection facilities of the Dublin-San Ramon Wastewater Treatment Plant. The influent to the contact tank was nitrified, filtered activated-sludge effluent. A diagram of the contactor is shown in Fig. 10. Wastewater characteristics in the chlorine contactor are summarized in Table 30. At steady state, THM and TOX samples were taken upstream from the disinfectant injection point (Point A in Fig. 10) and also at the end of the contactor just upstream of the outfall (Point D in Fig. 10). Sodium thiosulfate was used to quench disinfectant residuals. Disinfectant

TABLE 29. TYPICAL CHARACTERISTICS OF WASTEWATER EFFLUENTS USED TO MEASURE FORMATION OF HALOGENATED ORGANICS

Parameter	Ranges	
	Palo Alto (Non-Nitrified)	Dublin-San Ramon (Nitrified)
COD, mg/l	20-55	20-35
NH_3-N, mg/l-N	20-35	< 0.04-0.2
Total Kjeldahl N, mg/l-N	26-42	< 0.8-1.1
Alkalinity, mg/l $CaCO_3$	190-250	100-300
pH	6.9-7.3	6.9-7.7
Suspended Solids, mg/l	10-50	0-13

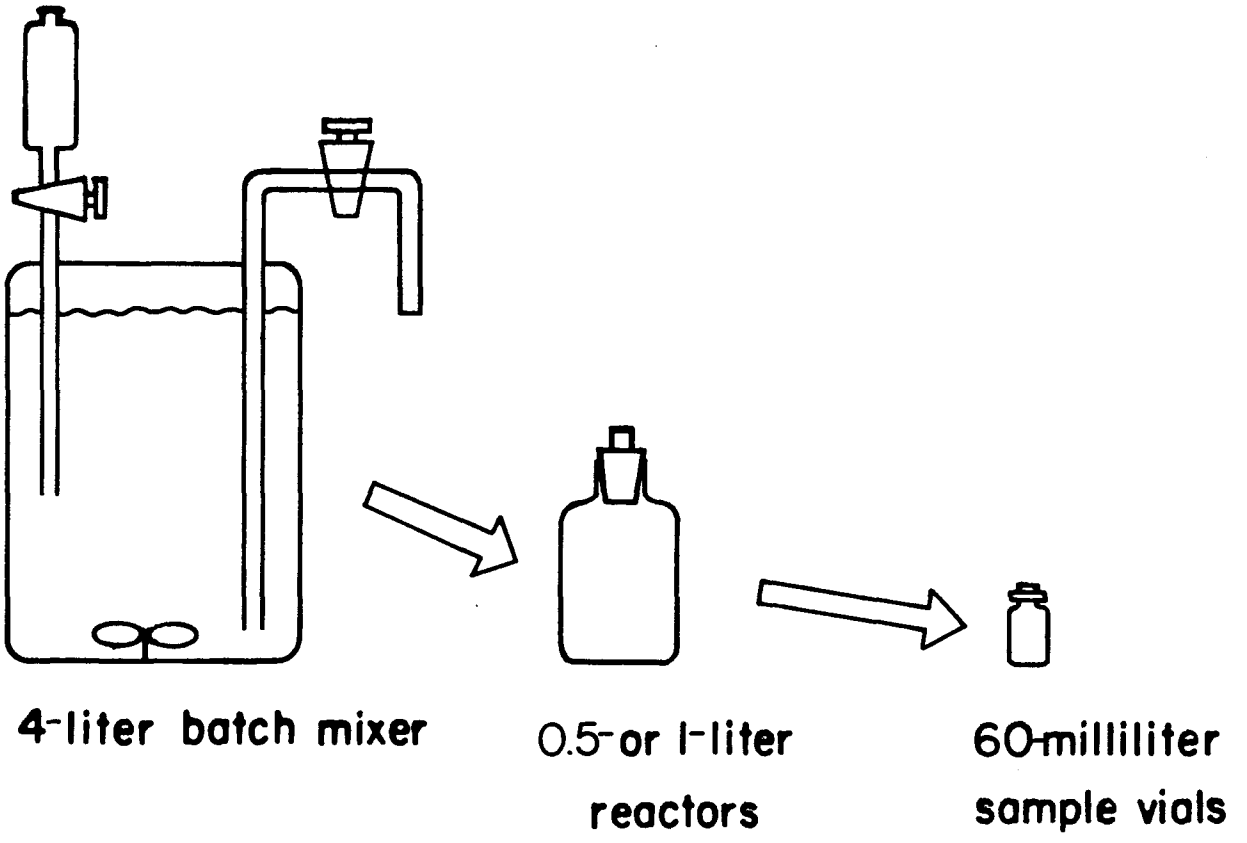


Figure 39. Procedure for the bench-scale determinations of halogenated organics formation.

TABLE 30. WASTEWATER CHARACTERISTICS IN THM AND TOX FIELD EXPERIMENTS AT THE DUBLIN-SAN RAMON CHLORINE CONTACTOR

Parameter	Range in Contactor Influent
COD, mg/l	23-33
NH_3-N, mg/l-N	< 0.06
Total Kjeldahl-N, mg/l-N	0.9-2.0
Alkalinity, mg/l $CaCO_3$	105-296
pH	7.0-7.4
Suspended Solids, mg/l	1-7

doses were chosen to achieve a desired bacterial kill; hence, the two disinfectants could not be compared on an equal mass basis in the field experiments. For the two later field experiments, only chlorine dioxide was used. TOX analysis was by the Jekel method (Section 4).

Results

The bench-scale experiments showed that chlorine produced THMs and TOX in both wastewaters tested. Experimental conditions and the amounts of THM and TOX formed during 24-hr contact are summarized in Table 31. Typical results for the THM and TOX formation by chlorine and chlorine dioxide in Palo Alto

TABLE 31. THM AND TOX FORMATION BY CHLORINE AND CHLORINE DIOXIDE IN BENCH-SCALE EXPERIMENTS

Wastewater	Exp. No.*	Chlorine Dose, mg/l Cl	Chlorine Dioxide Dose, mg/l ClO_2	Average 24-hr Production TOX µmol/l-X	Average 24-hr Production THM µmol/l-X	Average 24-hr Residual Cl_2 mg/l-Cl	Average 24-hr Residual ClO_2 mg/l-ClO_2
Non-Nitrified (Palo Alto)	1	20	none	6.0	0.53	6.1	NA
		none	20	0.0	-0.03	NA	0.5
	3	20	none	--	0.22	6.0	NA
		none	20	--	-0.06	NA	8.0
		40	none	--	0.91	9.1	NA
		none	40	--	-0.02	NA	8.0
	4	20	none	10.0	0.18	6.5	NA
		none	20	3.0	0.02	NA	3.4
		40	none	--	0.85	16.2	NA
		none	40	1.6	0.00	NA	3.4
	8	20	none	7.4†	0.43†	6.8†	NA
		none	20	1.7	0.00	NA	--
		40	none	8.1	1.31	15.1	NA
		none	40	-0.8#	0.10#	NA	10.4#
	12	20	none	7.1	0.45	9.3	NA
		none	20	0.9	-0.01	NA	5.2
		40	none	7.1	0.98	18.5	NA
		none	40	-0.7	0.01	NA	3.8
Nitrified (Dublin-San Ramon)	6	20	none	22.4	3.97	6.6	NA
		none	20	0.5	0.01	NA	8.4
		40	none	26.2	4.87	19.0	NA
		none	40	1.4	0.03	NA	24.5
	7	20	none	19.3	3.75	7.5	NA
		none	20	-0.2	0.02	NA	11.2

NA = not applicable

*All pertinent experiments are shown; missing experiment numbers refer to experiments conducted with other objectives.

†23 hrs.

#25 hrs.

wastewater are shown in Fig. 40 as a function of contact time up to 24 hrs. The data in Figure 40 illustrate the lack of production of THMs by chlorine dioxide and a small apparent TOX production by chlorine dioxide. However, other bench-scale experiments in the Palo Alto wastewater show no TOX production by chlorine dioxide at 24-hr contact time. THM and TOX production in one of the two bench-scale experiments which used the Dublin-San Ramon wastewater is shown in Fig. 41. As with the Palo Alto wastewater, chlorine dioxide caused no production of THMs, but caused a slight TOX production as shown in Fig. 41 for the 40-mg/l chlorine dioxide dose.

Results of the field experiments, in which THM and TOX formation were measured during approximately one-hr retention in the Dublin-San Ramon contact tank, are summarized in Table 32. These experiments were conducted at disinfectant doses having approximately equal disinfection effectiveness (survival ratio); the dose of chlorine dioxide is nearly ten times less than that of chlorine. Under these conditions, chlorine dioxide clearly formed no significant amounts of either THM or TOX, whereas chlorine increased the values of both parameters substantially.

Chlorine dioxide in some cases produced small amounts of TOX in batch experiments at doses of 20 and 40 mg/l. Of the 10 values given in Table 31, one value (Experiment 4, 20 mg/l dose) showed TOX production by chlorine dioxide greater than two standard deviations (page 15) for the Dohrmann TOX procedure, i.e., TOX > 1.96 μmol/l. The mean values and standard deviations of TOX and THM production in the bench-scale experiments are shown in Table 33. Apparent negative TOX production values are less than two standard deviations and are therefore statistically indistinguishable from zero production.

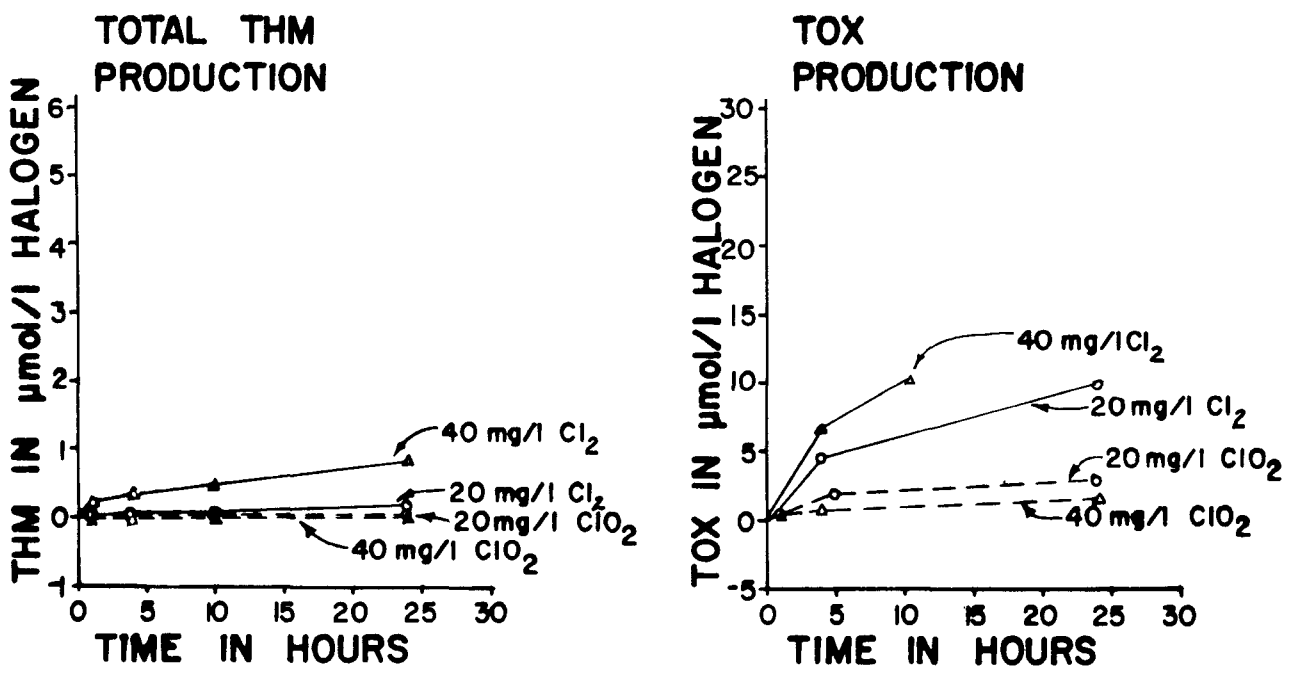


Figure 40. TOX and THM production in non-nitrified effluent (Experiment 4--Palo Alto wastewater).

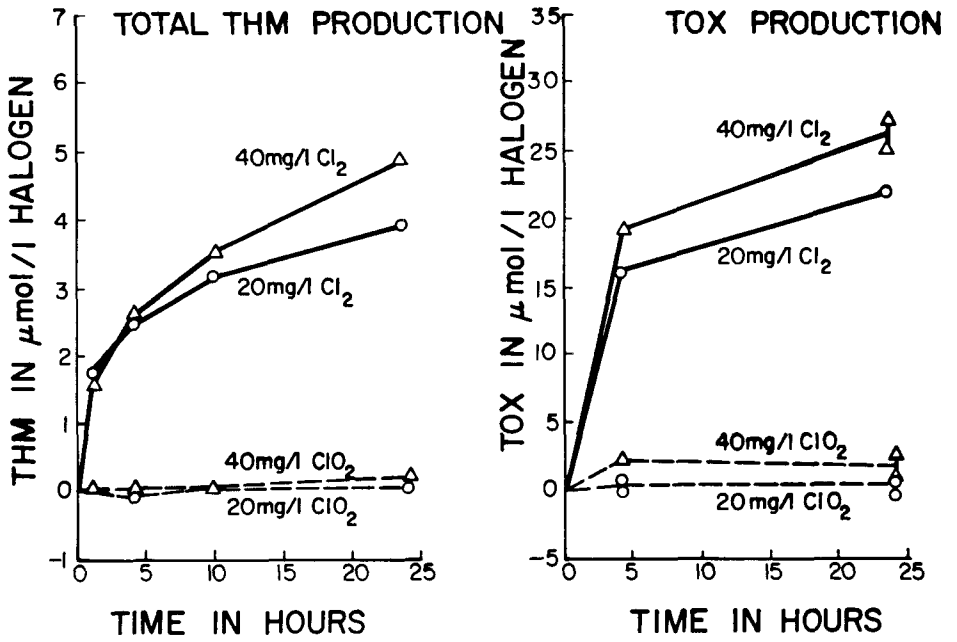


Figure 41. TOX and THM production in filtered, nitrified effluent (Experiment 6--Dublin-San Ramon wastewater).

TABLE 32. SUMMARY OF THM AND TOX FIELD EXPERIMENTS

Field Exper. Date	Chlorine Dose mg/l-Cl	Chlorine Dioxide Dose mg/l-ClO_2	Contact Time Minutes	Average Production at Point D		Average Residual at Point D	
				TOX μmol	THM μmol/l-X	mg/l-Cl	mg/l-ClO_2
2-6-79	18.7	none	55	10.2	1.02	12.8	NA*
	none	3.1	55	-0.5	-0.04	NA	0.6
2-15-79	19.6	none	49	8.1	0.94	1.0	NA
	none	2.3	46	0.4	0.04	NA	0.1

*NA = not applicable.

Except for the 20 mg/l chlorine dioxide dose in Experiment 4, the other instances of significant TOX production mentioned are near to the two standard deviation limit. Nonetheless, it cannot be excluded from possibility that chlorine dioxide can form halogenated organics in wastewater. More experiments with greater precision in TOX analysis will be required to make a firm conclusion as to whether chlorine dioxide does produce halogenated organics in wastewater. More important, however, is the fact that chlorine dioxide produced markedly less halogenated organics, if indeed any, compared to chlorine in the two types of wastewaters tested.

The means and standard deviations of THM production shown in Table 33 support previous findings (91,92) that chlorine dioxide does not form THMs. Of all of the bench-scale experiments (Table 31), only the 40 mg/l chlorine dioxide dose in Experiment 8 showed a THM production exceeding two standard deviations for THM production, i.e., THM > 0.08 μmol/l-X (Table 1). This THM production value is the only instance exceeding two standard deviations among many other results to the contrary. Also, this value exceeds the two standard deviation limit by only a slight margin. Therefore, it is safe to conclude that chlorine dioxide did not produce THMs in the wastewaters tested. The apparent negative THM production values in a few experiments are within two standard deviations of zero production and are therefore statistically indistinguishable from zero.

TABLE 33. MEAN VALUES AND STANDARD DEVIATIONS OF 24-HOUR HALOGENATED ORGANIC BYPRODUCT FORMATION WITH CHLORINE DIOXIDE AND CHLORINE

			Increase* During 24-Hr Contact μMol/l-X					
			TTHM			TOX		
Effluent	Mass Dose mg/l	Disinfectant	Mean	Std.Dev.	n†	Mean	Std.Dev.	n†
Palo Alto	20	Chlorine Dioxide	0.005	0.02	4	1.3	1.3	4
	20	Chlorine	0.39	0.15	4	7.6	1.7	4
	40	Chlorine Dioxide	0.05	0.06	2	-1.2	0.6	2
	40	Chlorine	1.15	0.23	2	7.6	0.7	2
Dublin	20	Chlorine Dioxide	0.015	0.007	2	0.15	0.5	2
	20	Chlorine	3.9	0.14	2	20.8	2.2	2
	40	Chlorine Dioxide	0.03	-	1	1.4	-	1
	40	Chlorine	4.9	-	1	26.2	-	1

*Increase calculated as concentration measured after 24 hours less concentration measured before.

†n = number of replicates.

Halogenated Organics Yield Versus Disinfectant Dose

The TOX produced in both the Palo Alto and the Dublin-San Ramon wastewaters by chlorine is on the order of one percent of the chlorine dose. This result is the same as that found by Jolley (96) in his work with secondary effluent. However, the total chlorine residuals had decreased to half of the initial chlorine dose or less after 24 hrs in nearly all of the bench-scale experiments (Figs. 42 and 43). This result suggests that 99% of the chlorine demand is in the form of redox-type reactions, whereas only 1% of the chlorine demand is in the form of halogenation reactions.

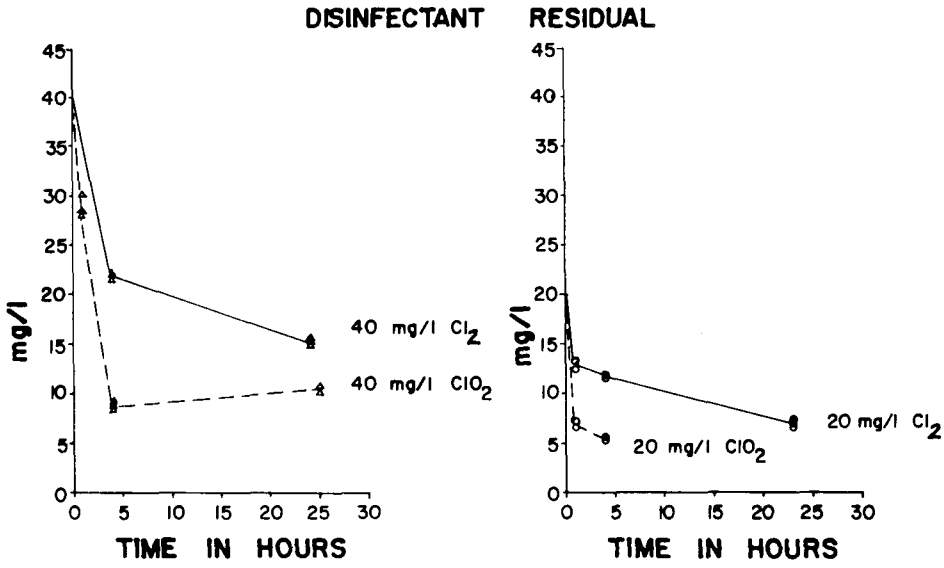


Figure 42. Disinfectant residuals in Experiment 8 (Palo Alto wastewater).

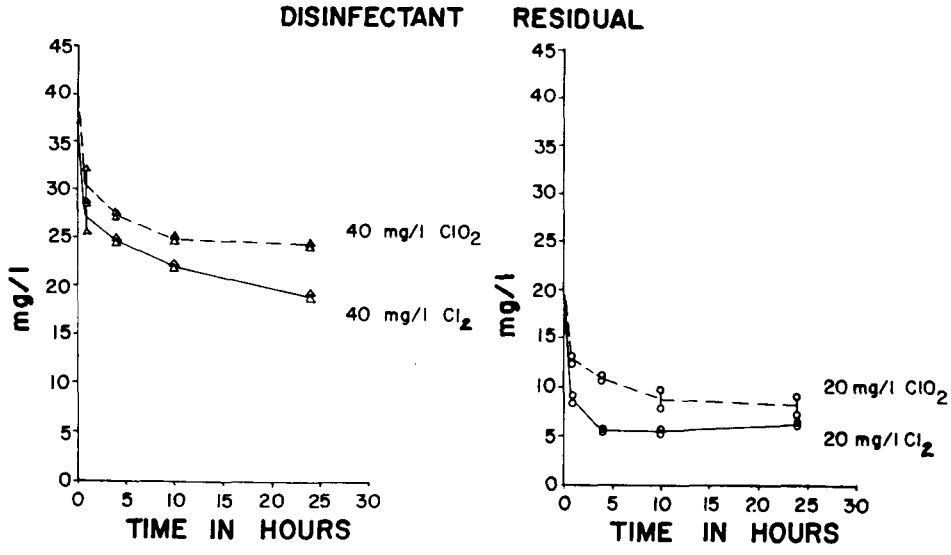


Figure 43. Disinfectant residuals in Experiment 6 (Dublin-San Ramon wastewater).

Since TOX production by chlorine dioxide is not well documented by the experiments conducted, it is not appropriate at this time to estimate how much of the initial chlorine dioxide demand is in the form of halogenation products. However, it is worthwhile to point out that chlorine dioxide residuals also decreased to half (or less in some cases) of the value of the initial chlorine dioxide doses (Figs. 42 and 43). This result indicates that chlorine dioxide does enter into redox reactions with the substances in wastewater, consistent with the findings of Noack and Doerr (97).

Figures 40 and 41 show that higher chlorine doses result in higher THM productions in both wastewaters. In contrast, from Table 31 (Experiments 8 and 12), it can be seen that in the Palo Alto wastewater, there is no significant difference in TOX production between the two chlorine doses used (20 and 40 mg/l). The single experiment (Experiment 6) using Dublin-San Ramon wastewater and two chlorine doses does show a significantly different TOX production between the two chlorine doses. The difference in THM production in the Palo Alto wastewater experiments is too small to be detected by TOX analysis. Therefore, the dose effect on halogenated organics production in the Palo Alto wastewater is very small, indicating that the 20-mg/l chlorine dose is sufficient to nearly exhaust the amount of precursors of halogenated organics available to it. In order to observe a less ambiguous dose effect, lower chlorine doses should be used for the Palo Alto wastewater.

The Relationship Between TOX and THM Production

The results summarized in Tables 31 and 32 show the 24-hr TOX production to be between five and fifty times greater than THM production in the Palo Alto wastewater and approximately five times greater than THM production in the Dublin-San Ramon wastewater. These results are consistent with the fact that TOX represents a broader spectrum of halogenated organics than does THM.

The Behavior of Disinfectant Residuals

At a given chlorine dioxide dose, the chlorine dioxide residuals were lower than the chlorine residuals in the Palo Alto wastewater (Fig. 42). In contrast, the chlorine dioxide residuals were higher than the chlorine residuals in the Dublin-San Ramon wastewater (Fig. 43). Of course, the results of comparing the residuals of different disinfectants depends on the units chosen to express the residual concentration. In this work, a mass basis generally was used, because of the direct relation to disinfectant dose and hence to cost. A better comparison of disinfectant behavior is on an electron-equivalent basis for disinfectant demand as shown in Table 34. From Table 34 it is clear that the disinfectant demand for chlorine is greater than for chlorine dioxide in both wastewaters; that is, more electron-equivalents of chlorine than of chlorine dioxide are used up in both wastewaters. This is relevant to questions of reactions between oxidants and organics, because the number of electron equivalents of oxidant that is reduced is a measure of the extent to which redox reactions have occurred.

TABLE 34. DISINFECTANT DEMAND

		24-hr Demand in meq/l*			
		20 mg/l Dose†		40 mg/l Dose#	
Wastewater	Experiment	Cl_2	ClO_2	Cl_2	ClO_2
Palo Alto	1	0.39	0.29	-	-
	3	0.39	0.18	0.59	0.52
	4	0.38	0.25	0.67	0.54
	8	0.37	-	0.70	0.44
	12	0.30	0.22	0.61	0.54
Dublin-San Ramon	6	0.38	0.17	0.59	0.23
	7	0.35	0.13	-	-

*Assumes chlorine dioxide undergoes a single electron transfer, i.e., it is reduced to chlorite ion.

†20 mg/l-Cl = 0.56 meq/l; 20 mg/l-ClO_2 = 0.30 meq/l.

#40 mg/l-Cl = 1.13 meq/l; 40 mg/l-ClO_2 = 0.59 meq/l.

MIXTURES OF CHLORINE DIOXIDE AND CHLORINE

Introduction

One of the methods used to produce chlorine dioxide is the chlorine/chlorite process. Using excess chlorine could lead to a product that is a mixture of chlorine and chlorine dioxide. Miltner (98) has shown that a mixture of chlorine dioxide and chlorine would produce less THMs than would chlorine alone in the same concentration as for the chlorine used in the mixture.

Experimental Design

The experiments using mixtures of chlorine and chlorine dioxide were bench-scale experiments. The mixtures of chlorine and chlorine dioxide were based on the mass ratios of chlorine dioxide (as ClO_2) to chlorine (as Cl). These mass ratios were 1:5, 1:1, and 5:1; experiments with 100% Cl_2 and 100% ClO_2 were run for comparison. The chlorine dose was kept constant at 5 mg/l-Cl. Dublin-San Ramon wastewater was added directly to the 0.5- and 1-liter glass-stoppered reactor bottles identical to those used for the experiments presented under "Chlorine Dioxide Versus Chlorine." The chlorine and chlorine dioxide doses were added with mixing, and the reactor bottles were closed and allowed to react at 25°C for one hour. This short reaction time was chosen because it approximated the detention time observed in the chlorine contact basin at the Dublin-San Ramon facility. After the one-hour reaction period, samples were taken in the same manner as for the bench-scale experiments described earlier. TOX analysis was by the Dohrmann method.

Results

Results of two experiments using mixtures of chlorine and chlorine dioxide are shown in Figs. 44 and 45 and are summarized in Table 35. In general, both experiments show a decrease in THM production as the proportion of chlorine dioxide increases (Fig. 44). The same phenomenon is seen for TOX in Fig. 45. Because of analytical difficulties, the TOX data for Experiment 2 were unreliable; therefore, TOX production values are not shown for that experiment. The decrease in THM and TOX production appears to require equal mass doses of chlorine dioxide and chlorine before these decreases become significant.

Figure 44 shows an initial increase in THM production from the point with no chlorine dioxide to the point where the chlorine dioxide to chlorine ratio is 1:5. Although the increase is greater than two standard deviations for THM analysis, the general behavior of the rest of the data in Figs. 44 and 45 suggest that this increase is probably due to an operator error in sampling or in performing the THM analysis.

If the mechanism of THM decrease is by chlorine dioxide reacting with precursors of halogenated organics to prevent THM production, as Miltner proposed (98), the decrease in TOX production would indicate that this interaction with precursors may prevent halogenation altogether and not just prevent THM production. However, there still remains a possible reaction between chlorine and chlorite as proposed by Noack and Doerr (97) and also a possible direct reaction between chlorine and chlorine dioxide noted by Miltner (98).

Better understanding of the properties and reactions of mixtures of chlorine and chlorine dioxide is necessary. Experiments need to be conducted using longer reaction times. Non-nitrified as well as nitrified wastewaters need to be studied. Finally, more investigations into the precise nature of possible interactions between chlorine and chlorine dioxide in terms of the species formed and their disinfection capabilities are required.

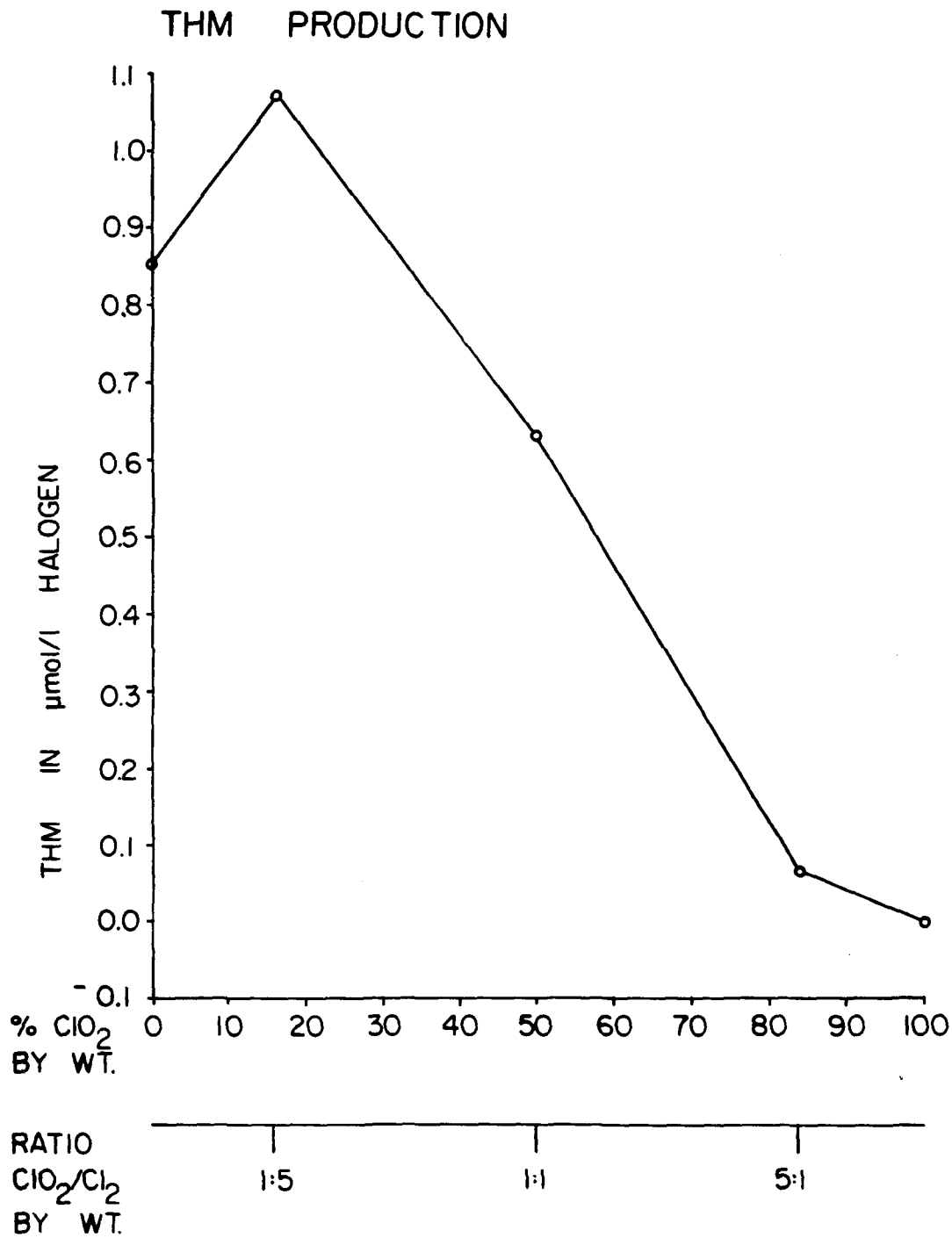


Figure 44. THM production resulting from various mixtures of chlorine and chlorine dioxide in Experiment 2 (Dublin-San Ramon wastewater).

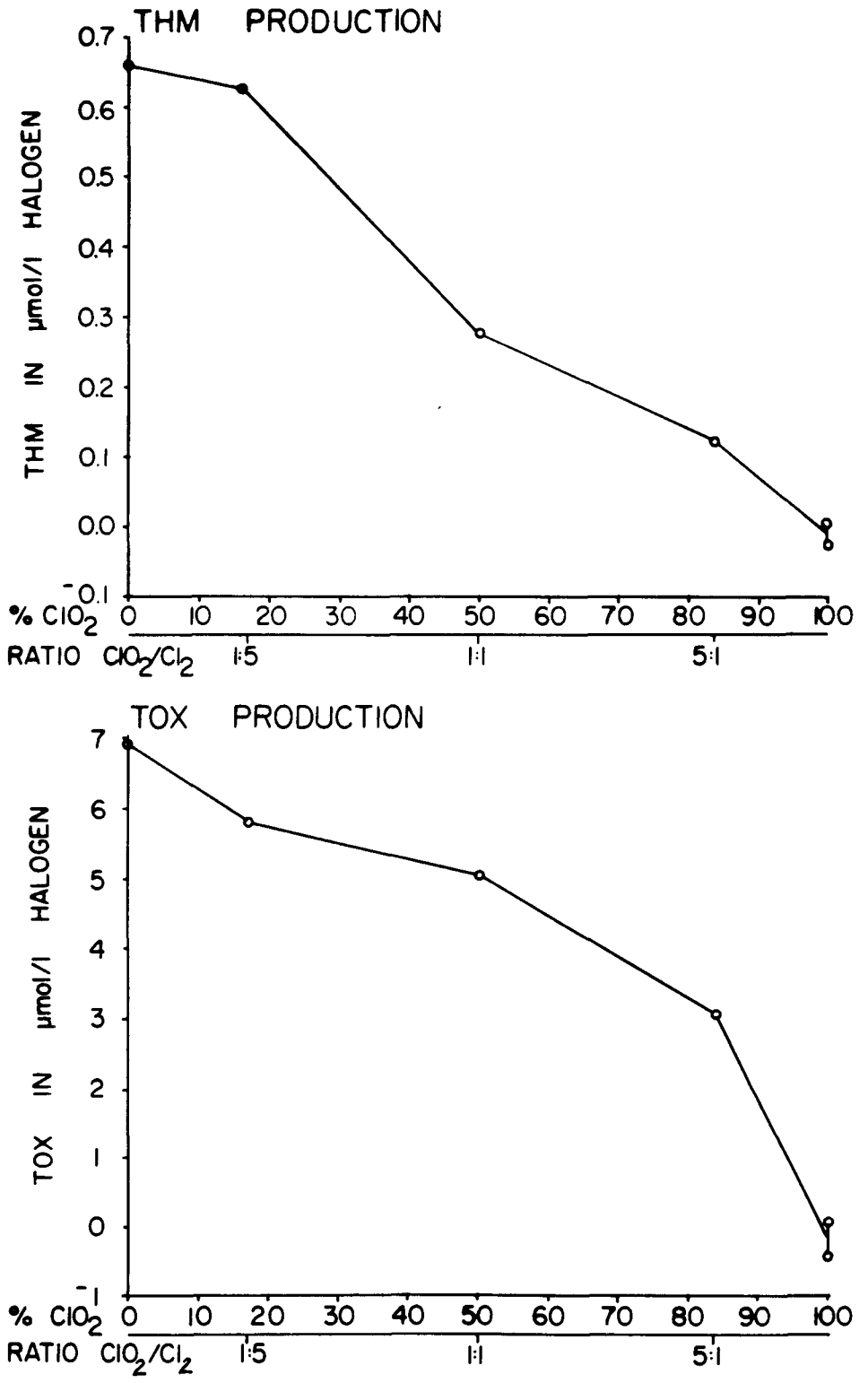


Figure 45. TOX and THM production resulting from various mixtures of chlorine and chlorine dioxide in Experiment 5 (Dublin-San Ramon wastewater).

SECTION 11

COST COMPARISON BETWEEN CHLORINE DIOXIDE AND CHLORINE FOR WASTEWATER DISINFECTION

BASIS OF COMPARISON

An economic comparison is presented between disinfection of wastewater with chlorine dioxide and with chlorine. In the analysis five treatment plant sizes, 0.044, 0.22, 0.44, 2.2, and 4.4 m^3/s (1, 5, 10, 50, and 100 mgd), are considered. A nominal contact time of 1 hour is assumed for the disinfection process. Chemical costs are compared between chlorine and chlorine dioxide generated from the chlorine-chlorite process.

Three levels of disinfection are compared, corresponding to 2.2/100 ml, 200/100 ml, and 1000/100 ml total coliforms. The latter case (1000/100 ml total coliforms was included in the analysis at the request of the EPA Project Officer [M. C. Meckes], who felt that it more nearly corresponds to the effluent standard imposed for secondary effluent in states such as Ohio. The 1000/100 ml total coliform standard is approximately equivalent to a 200/100 ml fecal coliform standard if the ratio of total to fecal coliforms is approximately 5:1 as found by Hunt and Springer (99). The 1000/100 ml total coliform standard also is that reportedly recommended by ORSANCO, and widely emulated in the U.S. (100).

Two levels of prior treatment are considered: conventional activated-sludge treatment as typified by the Palo Alto 1978 laboratory experiments, and nitrified-filtered activated-sludge treatment as practiced at the Dublin-San Ramon treatment plant. It is believed that the conventional activated-sludge effluent represents the majority of biologically treated wastewater effluents in the U.S.A., whereas the nitrified, filtered effluent corresponds to a higher degree of treatment, such as might be practiced for water reclamation.

All costs, except chemical costs, have been updated to third-quarter 1979 costs by use of the Environmental Protection Agency Sewage Treatment Cost Index (101,102). The EPA-STP index for third quarter (September) 1979 was 337.8. Chemical costs are based on competitive supplier bids, f.o.b. docks, January 1980 (103,104). For simplicity, the comparisons will be referred to as cases A through F, summarized in Table 36.

TABLE 36. CASES FOR EVALUATION OF THE RELATIVE COSTS OF DISINFECTION WITH CHLORINE AND CHLORINE DIOXIDE

Type of Effluent to Be Disinfected	Case	Disinfection Standard as Total Coliform Count (N/100 ml)
Conventional Activated Sludge	A	2.2
	B	200
	C	1000
Filtered, Nitrified Activated Sludge	D	2.2
	E	200
	F	1000

CAPITAL COSTS

Capital costs were estimated from generalized correlations (101,102). These estimates were adjusted for inflation as described above. Capital costs are amortized over 20 years at 11 percent.

Contact Basins

The common current practice in designing disinfectant contact basins is to provide a serpentine routing of flow following mixing of the disinfectant and wastewater. For the purposes of this report, costs are estimated for basins which generally provide a flow routing length to channel width ratio between 20:1 and 25:1. The Dublin disinfectant mixing and contact facility is typical of the design considered in this analysis (see Fig. 10).

Chlorine Feed and Storage Facilities

The feed used most widely in wastewater treatment plants is chlorine gas. The required equipment and storage facilities are well known; commercial equipment is readily available.

Feed facility costs include distribution panels, cylinder chocks, installation, manufacturers' preparation of shop drawings, installation check and startup, and contractor's overhead and profit. Chlorinator costs include one standby chlorinator and chlorine evapotators on systems having a capacity greater than 4,000 lbs per day. Also included are miscellaneous piping and valves, which typically amount to 5-10% of the installed chlorination equipment costs.

Storage facility costs include housing, hoist equipment, ventilation equipment and safety monitors.

Chlorine Dioxide Generation and Feed Systems

For the purpose of this analysis, it is assumed that chlorine dioxide is generated by the chlorine-chlorite process. The stoichiometry measured for this process in a full-scale plant has been reported in Section 5. In theory, 1.34 lbs of pure sodium chlorite and 0.5 lbs of chlorine react to give one pound of chlorine dioxide. However, sodium chlorite is normally purchased with a purity of 80%. Therefore, assuming 100% conversion of $NaClO_2$, and 100% yield of ClO_2 based on $NaClO_2$ reacted with 4% excess chlorine feed (Section 5), 1.68 lbs of 80% sodium chlorite and 0.70 lbs of chlorine are required per pound of chlorine dioxide generated. This basis is somewhat more optimistic than generally assumed, but is justified according to the results in Section 5 of this report.

Generation and feed systems costs are based on the costs for a sodium chlorite mixing and metering system, a chlorine dioxide generator, and the appropriately sized chlorine feed system. The sodium chlorite system consists of a polyethylene day tank, a mixer for the day tank, and a dual head metering pump. The chlorine dioxide generator is a PVC tube filled with porcelain Raschig Rings or other transport-enhancing media, and is sized for a detention time of 20 min.

Disinfectant Feed Capacity--

The sizing of generating, feed, and storage facilities is based on the required disinfectant feed capacity in kg or pounds per day. (A detailed example of this procedure appears in Appendix C.)

In determining the feed capacity required, the procedure is as follows:

1. Determine the initial bacterial concentration in the waste stream to be disinfected (Table 14).
2. Calculate the required survival ratio, N(t)/N(0), from the disinfection standard N(t) and initial bacterial concentration, N(0).
3. Calculate the required residual-time product using Eqs. 24 and 25 and the model fitting constants from Table 24.
4. Calculate the required residual, based on the provided contact time, namely one hour.
5. Calculate the disinfectant dosage needed to provide the required residual disinfectant concentration

A summary of the results from steps 1-5 from above for Cases A-F is given in Table 37. The quantities of disinfectant required per day shown in Table 38 were calculated from the required dosages given in column 5b of Table 37.

OPERATION AND MAINTENANCE COSTS--EXCLUDING CHEMICAL COSTS

Operation and maintenance (O&M) costs include electrical power, maintenance material, and labor costs (101,102).

TABLE 37. SUMMARY OF ESTIMATES OF REQUIRED DISINFECTANT DOSAGES USED IN COST EVALUATION CASES

	(1)	(2)	(3)		(4)		(5a)		(5b)	
	Initial Bacterial Concentration	Survival Ratio	Residual-Time Product (mg-min/l)		Residual Required at 1-hr Contact Time (mg/l)		1-hr Disinfectant Demand (mg/l)		Required Disinfectant Dose (mg/l)	
Case*	$\log\left(\frac{\text{total coliform}}{100\text{ ml}}\right)$	$\log(N(t)/N(0))$	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
A	6.21	-5.87	376.58	164.45	6.28	2.74	1.61	5.18	7.89	7.92
B	6.21	-3.91	90.11	34.79	1.50	0.58	0.95	2.32	2.45	2.90
C	6.21	-3.21	54.01	19.95	0.90	0.33	0.80	1.84	1.70	2.17
D	4.41	-4.07	210.73	22.74	3.51	0.38	7.64	5.14	11.15	5.52
E	4.41	-2.11	13.02	1.96	0.22	0.03	2.39	0.57	2.61	0.60
F	4.41	-1.41	4.82	0.82	0.08	0.01	2.52	0.13	2.60	0.14

*See text for explanation of cases, procedure, and calculations.

TABLE 38. AMOUNTS OF DISINFECTANTS REQUIRED TO ACHIEVE TOTAL COLIFORM STANDARDS

	Disinfectant Usage, pounds* per day				
	Treatment Plant Size - mgd†				
	1	5	10	50	100
Case A					
Cl_2	66	329	658	3290	6580
ClO_2	66	330	661	3303	6605
Case B					
Cl_2	20	102	204	1022	2043
ClO_2	24	121	242	1209	2419
Case C					
Cl_2	18	90	180	900	1800
ClO_2	14	70	140	700	1400
Case D					
Cl_2	93	465	930	4650	9300
ClO_2	46	230	460	2302	4604
Case E					
Cl_2	22	110	220	1100	2200
ClO_2	5	25	50	250	500
Case F					
Cl_2	22	110	220	1100	2200
ClO_2	1.2	6	12	60	120

*1 pound = 0.4536 kg.

†1 mgd = 0.0438 m^3/s.

Electrical requirements include power for the gaseous chlorination system, the sodium chlorite metering and mixing systems, and building heating, lighting, and ventilation.

Maintenance material requirements are based on experience with gaseous chlorine systems and liquid metering systems. Costs for chemicals required for residual monitoring are included.

Labor requirements consist of labor for the gaseous chlorination systems, plus the labor required to mix the sodium chlorite solution, to adjust its feed rate, and to maintain the mixing and metering equipment.

CHEMICAL COSTS

All chemical costs are f.o.b. works. It is assumed that the 50- and 100-mgd plants will be able to take advantage of the lower chemical costs

associated with larger quantity purchases. Chemical unit costs are shown in Table 39.

TABLE 39. UNIT COSTS OF CHEMICALS REQUIRED IN WASTEWATER DISINFECTION

Chemical	Unit Cost, $ per pound*
Chlorine - one ton cylinders	0.155
Chlorine - rail cars	0.075
Sodium chlorite (80%), less than 250,000 pounds annually	2.67
Sodium chlorite (80%), more than 250,000 pounds annually	1.98

*Prices are f.o.b. works; 1 pound = 0.4536 kg.
Source: References (103,104).

The price given for sodium chlorite (Table 39) and used in this evaluation is based on manufacturers' quotations for a solution of 25% sodium chlorite content. The equivalent price is $4.36/kg or $5.88/kg ($1.98 per pound or $2.67 per pound) of sodium chlorite content, depending on the quantity purchased. The price of dry sodium chlorite is considerably lower: $2.67/kg ($1.21 per pound) of sodium chlorite if purchased in drum quantities at January 1980 prices (105). The higher price quoted by manufacturers who supply sodium chlorite to the water industry has been chosen to be conservative. However, it should be recognized that sodium chlorite possibly could be purchased for approximately 45 to 60% of the values given in Table 39.

COST SUMMARIES

The cost of wastewater disinfection are summarized in Tables 40 through 45, for Cases A-F, respectively. Disinfection with chlorine dioxide is at least as expensive as, and generally more expensive than, disinfection with chlorine under the assumptions embodied in the cases compared here. The relative cost factor for disinfection with chlorine dioxide compared to chlorine ranges from a high of 15 to one (Case A, 4.4 m^3/s [100 mgd] plant) to a low of 1.0 to one (Case F, 0.044 m^3/s [1-mgd] and 0.22 m^3/s [5-mgd] plants). The predominant factor influencing the higher cost of chlorine dioxide disinfection is the cost of the sodium chlorite.

Case C (conventional activated-sludge effluent, 1000/100 ml total coliform standard) is believed to represent most nearly among the cases studied the typical situation of disinfecting secondary effluent in the U.S. In Case C, the cost of disinfection with chlorine dioxide ranges from 2 times as expensive (at 0.044 m^3/s [1 mgd]) to 5 times as expensive (at 4.4 m^3/s [100 mgd]) compared to the cost of disinfection with chlorine.

TABLE 40. DISINFECTION COST SUMMARY FOR CASE A

	Annual Cost, Thousand $ per Year									
	Treatment Plant Size, mgd									
	1		5		10		50		100	
Cost Item	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
Contact Basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and Feed Equipment	1.7	6.1	4.0	10.0	6.3	12.7	18.0	25.9	29.7	35.5
O & M Cost	7.4	9.9	10.5	18.9	13.2	22.5	17.1	55.0	18.9	81.0
Chemical Cost										
Cl_2	3.7	2.6	18.6	13.0	37.2	26.0	90.1	63.3	180.1	126.6
$NaClO_2$	-	108.1	-	540.3	-	1082.2	-	4010.3	-	8019.4
Total Cost										
$1000/yr	27.5	141.4	69.1	618.2	111.5	1198.2	297.5	4326.8	541.7	8575.5
(¢/1000 gal)	(7.5)	(38.7)	(3.8)	(33.9)	(3.1)	(32.8)	(1.6)	(23.7)	(1.5)	(23.5)

TABLE 41. DISINFECTION COST SUMMARY FOR CASE B

	Annual Cost, Thousand $ per Year									
	Treatment Plant Size, mgd									
	1		5		10		50		100	
Cost Item	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
Contact Basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and Feed Equipment	1.6	4.5	2.0	7.1	3.0	8.7	8.1	16.6	14.1	21.1
O & M Cost	6.1	7.8	7.9	12.2	9.0	17.1	14.8	30.0	16.1	43.0
Chemical Cost										
Cl_2	1.1	0.9	5.8	4.7	11.5	9.4	28.0	23.1	55.9	46.2
$NaClO_2$	-	39.3	-	198.1	-	396.2	-	1467.9	-	2937.0
Total Cost										
$1000/yr	23.5	67.2	51.7	258.1	81.3	486.2	223.2	1709.9	399.1	3360.3
(¢/1000 gal)	(6.4)	(18.4)	(2.8)	(14.1)	(2.2)	(13.3)	(1.2)	(9.4)	(1.1)	(9.2)

TABLE 42. DISINFECTION COST SUMMARY FOR CASE C

	Annual Cost, Thousand $ per Year									
	Treatment Plant Size, mgd									
	1		5		10		50		100	
Cost Item	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
Contact Basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and Feed Equipment	1.8	3.7	3.5	6.4	4.6	9.4	10.8	20.5	17.7	27.3
O & M Cost	6.0	7.1	7.9	10.0	8.6	12.2	15.5	25.0	23.0	33.0
Chemical Cost										
Cl_2	1.0	0.6	5.1	2.8	10.2	5.5	24.8	13.5	49.6	27.0
$NaClO_2$	-	22.9	-	114.6	-	229.2	-	849.9	-	1699.8
Total Cost										
$1000/yr	23.5	49.0	52.5	169.8	78.2	311.1	223.4	1081.2	403.3	2100.1
(¢/1000 gal)	(6.4)	(13.4)	(2.9)	(9.3)	(2.1)	(8.5)	(1.2)	(5.9)	(1.1)	(5.8)

TABLE 43. DISINFECTION COST SUMMARY FOR CASE D

	Annual Cost, Thousand $ per Year									
	Treatment Plant Size, mgd									
	1		5		10		50		100	
Cost Item	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
Contact Basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and Feed Equipment	1.80	5.5	5.0	8.7	7.8	10.9	21.9	20.5	36.0	28.6
O & M Cost	7.8	9.0	11.2	16.5	15.8	20.8	17.9	45.0	19.8	68.0
Chemical Cost										
Cl_2	5.3	1.8	26.3	9.1	52.6	19.3	127.3	44.1	254.6	88.2
$NaClO_2$	-	75.3	-	376.6	-	753.1	-	2794.9	-	5589.9
Total Cost										
$1000/yr	29.6	106.3	78.5	446.9	131.0	857.9	339.4	3076.8	623.4	6087.7
(¢/1000 gal)	(8.1)	(29.1)	(4.3)	(24.5)	(3.6)	(23.5)	(1.9)	(16.9)	(1.7)	(16.7)

TABLE 44. DISINFECTION COST SUMMARY FOR CASE E

	Annual Cost, Thousand $ per Year									
	Treatment Plant Size, mgd									
	1		5		10		50		100	
Cost Item	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
Contact Basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and Feed Equipment	1.7	2.6	4.1	4.5	6.6	5.5	20.0	9.3	30.5	11.1
O & M Cost	7.5	7.4	10.8	7.8	13.6	9.0	17.3	16.6	19.1	21.8
Chemical Cost										
Cl_2	1.2	0.2	6.2	1.0	12.4	2.0	62.2	4.8	124.5	9.6
$NaClO_2$	-	8.2	-	40.9	-	81.9	-	303.5	-	607.1
Total Cost										
$1000/yr	25.1	33.1	57.1	90.2	86.4	153.2	271.4	506.5	487.1	962.6
(¢/1000 gal)	(6.9)	(9.1)	(3.1)	(4.9)	(2.4)	(4.2)	(1.5)	(2.8)	(1.3)	(2.6)

TABLE 45. DISINFECTION COST SUMMARY FOR CASE F

	Annual Cost, Thousand $ per Year									
	Treatment Plant Size, mgd									
	1		5		10		50		100	
Cost Item	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
Contact Basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and Feed Equipment	2.2	1.4	3.82	2.6	5.1	3.5	11.9	6.1	21.8	7.8
O & M Cost	6.2	6.0	8.0	6.8	9.1	7.1	16.3	9.5	26.2	12.0
Chemical Cost										
Cl_2	1.2	0.1	6.2	0.2	12.4	0.5	30.3	1.2	60.6	2.3
$NaClO_2$	-	2.0	-	9.8	-	19.6	-	72.8	-	145.7
Total Cost										
$1000/yr	24.3	24.2	54.0	55.4	81.4	85.5	230.8	261.9	421.6	480.8
(¢/1000 gal)	(6.7)	(6.6)	(3.0)	(3.0)	(2.2)	(2.3)	(1.3)	(1.4)	(1.2)	(1.3)

The costs summarized in Tables 40 through 45 include the cost of contact facilities. The economies of scale in contact basin construction are an important reason why the unit cost of disinfection decreases with increasing plant size. In our cost analysis, we have not differentiated between contact basin designs for chlorine dioxide and chlorine. Rather, we have expressed the differences between disinfectants as differences in required dose. Hence, the capital costs of contact basins are identical for the two disinfectants for all cases and plant sizes.

For large plants, chemical usage will be sufficiently large to permit purchasing at lower unit costs. This cost advantage is greater for chlorine than for chlorine dioxide on a percentage basis. Hence, the results of this analysis show greater cost advantages for chlorine at large plants (50 and 100 mgd) than at smaller ones.

Freight costs have not been included in these cost comparisons. Were freight costs to be considered, the cost advantage of chlorine might be lessened in some cases (e.g., Cases E and F) in view of the lesser quantities of chemicals that must be transportd when chlorine dioxide is used (Table 38).

DISCUSSION

When the costs of disinfection of municipal wastewater effluents using chlorine dioxide and chlorine are compared as above (using a coliform standard as the disinfection criterion and assuming presently available technology and current market prices), chlorine dioxide generally is not cost-effective in the usual sense. However, several factors should be considered to put this conclusion into proper perspective. These are: (1) the potential for reducing the costs of chlorine dioxide generation, and (2) the intangible advantages of chlorine dioxide that are not taken into account in the "cost-to-kill-coliforms" comparison.

Potential for Cost Reduction

The possibility of reducing the unit cost of chlorine dioxide hinges largely on the potential for reducing the unit cost of the sodium chlorite reactant, or for developing a process suitable for generating chlorine dioxide from chlorate at the wastewater treatment plant site. Investigation of these possibilities was beyond the scope of this work, and hence we can only speculate as to the probability of success in these directions.

Sodium chlorite is produced commercially from the reduction of chlorine dioxide (produced from chlorate) by hydrogen peroxide in sodium hydroxide solutions (105). With the increase of interest in chlorine dioxide for water and wastewater disinfection, an economic incentive exists for increasing the efficiency of the current commercial production techniques for sodium chlorate or for developing a new technology for sodium chlorite production from chlorate. It is conceivable that an expansion of the market for sodium chlorite in water and wastewater treatment could result in a relative decrease in the unit cost. This could occur as a result of economics of scale in production

and marketing, as well as by virtue of increased competition. Presently, one supplier dominates the market.

There is a strong motivation for developing a feasible process to generate chlorine dioxide from chlorate at the wastewater treatment site. Based on raw material costs, the unit cost of chlorine dioxide could be reduced by approximately half if chlorate rather than chlorite were used. Processes based on chlorate are widely used in the pulp and paper industry where large quantities of chlorine dioxide are required. However, there are reputed to be substantial problems of smaller-scale reactor instability, resulting occasionally in minor explosions. From the perspective of the required operator training, such a generation facility probably would not be feasible in the context of wastewater treatment. Hence, the wide-spread use of chlorate-based generation technology would require further process development, the evaluation of which is beyond the scope of our work.

There is no appreciable potential for improving the yield of chlorine dioxide from chlorite. In the simple, commercially available reactor studied in this work, the chlorine dioxide yield closely approximated that corresponding to accepted reaction stoichiometry.

Intangible Advantages of Chlorine Dioxide over Chlorine

The additional advantages of chlorine dioxide compared to chlorine that were not considered quantitatively in the cost analysis in this section are negligible amounts of halogenated byproducts and superior virus inactivation. These advantages of chlorine dioxide compared to chlorine have been demonstrated experimentally in this work. The superiority of chlorine dioxide with respect to virus inactivation can be concluded only tentatively from the results of this work; a program of experimental verification is necessary. The advantage of chlorine dioxide over chlorine with respect to formation of halogenated byproducts is unequivocal. It should weigh heavily in the ultimate decision as to whether to employ chlorine dioxide as an alternative to chlorine, in view of the concern over halogenated and other hazardous pollutants in the nation's water supplies.

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APPENDIX A

COLIFORM INACTIVATION DATA

Table A-1. Log[Surviving Bacteria] in Eight Replicate Experiments Using Chlorine Dioxide as Disinfectant

Table A-2. Log[Surviving Bacteria] in Eight Replicate Experiments Using Chlorine as Disinfectant

Table A-3. Full-Scale Experiments Conducted at Dublin-San Ramon Treatment Facility on Nitrified, Filtered Secondary Effluent Using Chlorine Dioxide and Chlorine

Table A-4. Results of Laboratory Experiments with Dublin Filtered Nitrified Activated-Sludge Effluent

Table A-5. Results of Laboratory Experiments with Unfiltered and Filtered Palo Alto Secondary Effluent Using Chlorine Dioxide

Table A-6. Results of Laboratory Experiments with Unfiltered and Filtered Palo Alto Secondary Effluent Using Chlorine

Table A-7. Results of Experiments with San Jose Secondary Effluent

Table A-8. Results of Experiments with San Jose Nitrified Effluent

Table A-9. Results of Experiments with San Jose Filtered, Nitrified Effluent

TABLE A-1. LOG[SURVIVING BACTERIA] IN EIGHT REPLICATE EXPERIMENTS USING CHLORINE DIOXIDE AS DISINFECTANT

DOSE:	2 mg/l								5 mg/l								10 mg/l							
CONTACT TIME / EXPERIMENT:	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
0 MIN	5.91	6.05	6.09	6.73	6.79	6.41	6.48	5.85	5.83	6.02	6.26	6.83	6.76	6.52	6.67	5.77	5.87	6.12	6.15	6.83	6.70	6.73	6.93	5.93
	5.90	6.18	6.45			6.67		5.91	5.60	6.28						5.88	5.60	6.38	6.20					5.75
								5.90	5.00							5.00								
								5.70																
5 MIN	5.08	4.41	4.34	5.00	4.99	5.21	5.08	5.03	3.99	2.00	2.78	3.76	3.45	3.41	3.98	3.20	1.90	1.30	1.78	2.62	2.15	2.26	2.45	1.60
	5.95	4.36	4.50	4.97	4.99	5.02	4.94	5.04	3.91		3.30	3.90	3.75	3.30	4.08	3.30	1.95	1.00	1.78	2.46	2.15	2.56	2.43	2.08
		4.30		5.08	5.11	5.34	5.41	5.30				3.60	4.15	3.00	3.30	3.70	2.18	0.30	1.56		1.70	2.32	1.95	1.65
		5.00		5.00	5.00	5.00	5.00					3.30	4.04		3.30		2.04					1.98		1.53
15 MIN	5.26	4.38	4.38	5.06	5.25	5.17	5.20	4.93	3.23	2.00	1.70	2.38	2.89	3.03	2.28	2.68	1.98	0.60	0.30	2.11	1.40	1.60	1.18	0.70
	5.00	4.38	4.26	4.95	5.44	5.00	5.09	4.61	3.20			2.27	3.15	3.82	2.28	3.04	1.75	0.48	0.34		1.68	1.56	1.30	1.00
		4.48	4.30	4.78	5.15	5.48	5.38	4.60	3.00			2.30	2.90	3.72	3.00	2.30	1.49				1.66	1.20	1.08	1.15
				5.04	5.00	5.15	5.26	4.78				3.00		3.70		3.00								
30 MIN	4.00	4.20	3.60	4.78	4.81	5.09	5.15	4.91	3.33	1.78	1.20	2.89	3.15	3.12	2.99	3.46	0.31	0.34	0.34	0.34	0.34	1.11	0.90	0.48
	4.78	4.32	3.04	4.81	4.90	4.92	5.05	5.08	3.37	1.90	1.30	3.06	3.15	3.15	3.24	3.56	0.60			0.30	0.30	1.15		
		4.48	4.30	4.90	5.26	5.08	5.45	4.11	3.11	1.90	1.30	3.11	3.50	3.83	3.00	3.32	0.40							
			4.30	5.00	5.08	5.00	5.36																	

TABLE A-2. LOG[SURVIVING BACTERIA] IN EIGHT REPLICATE EXPERIMENTS USING CHLORINE AS DISINFECTANT

DOSE:	2 mg/l								5 mg/l								10 mg/l							
EXPERIMENT:	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
CONTACT TIME: 0 MIN	5.85	6.09	6.00	6.43	6.81	6.63	6.62	5.89	5.78	6.14	6.10	6.79	6.83	6.67	6.63	5.83	5.92	6.30	6.08	6.70	6.84	6.67	6.60	5.73
	5.90	6.28	6.18	6.74				5.90	5.66	6.32	6.36					6.30	6.00		5.84					5.75
								5.78	5.30							5.60								5.30
								5.48																
5 MIN	4.78	5.75	5.95	6.16	6.13	6.30	6.34	5.37	4.09	3.83	3.96	4.15	4.15	4.53	3.90	3.86	2.91	2.51	2.34	3.77	2.81	3.24	3.24	3.00
	5.00	5.30	5.70	6.48	6.15	6.28		5.40	4.08	3.90	4.08	4.06	4.15		4.26	4.06	2.81	2.26	2.40		2.69	3.08		2.67
								5.60	3.60	4.08	3.78	4.41	4.30			4.08		2.16	2.42		2.42			
										3.95	3.70	4.14	4.49			3.95		2.07	2.09					
15 MIN	4.48	4.70	4.92	5.34	4.72	5.45	5.41	4.60	2.84	2.28	2.36	2.78	3.49	4.26	3.85	3.01	2.27	1.00	1.74	1.34	2.04	2.24	2.22	2.04
		4.62	4.79	5.25	4.46	5.62	5.55	4.58	3.15	2.00	3.23	3.34	3.70	4.79	3.75	3.40	1.81	1.41	1.76	1.30		1.91	1.79	1.66
		4.30	4.90	5.72	4.78	5.68			3.48	3.30		3.48	3.30			3.34	1.76	1.20	1.50			1.75	1.91	1.41
		4.30	4.84	5.53	4.48							4.30				3.60	1.57	1.04	1.48					
30 MIN	4.34	3.30	3.30	4.70	4.00	4.78	4.41	4.00	2.71	1.88	1.76	2.91	3.23	2.86	3.30	2.34	1.04	0.60	1.15	1.53	0.30	0.95	1.23	0.48
			3.30	4.58	3.70	4.70	4.80	3.95	2.48	1.90	1.30	2.87	3.21	2.89	3.11	2.73	0.60	0.60	0.34	1.30		0.70	1.26	0.34
			4.00	4.60		5.00	4.78	4.00		1.30	2.15	3.38	3.20	2.84	3.00	2.86	0.48	0.54						0.48
				4.00		4.85	5.08				2.00					2.60								

TABLE A-3. FULL-SCALE EXPERIMENTS CONDUCTED AT DUBLIN-SAN RAMON TREATMENT FACILITY ON NITRIFIED, FILTERED SECONDARY EFFLUENT USING CHLORINE DIOXIDE AND CHLORINE

Date	Disinfectant	Dose mg/l	Replicate No.	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	8	24	48
1/16/79	ClO_2	4.76	1	4.28	<0.30	<0.30	<0.30
			2	4.38	0.78	<0.30	0.30
			3	4.30	<0.30	0.30	<0.30
			4	4.30	<0.30	0.30	<0.30
			5	4.45	<0.30	<0.30	0.30
			6	4.48	<0.30	0.30	0.30
2/6/79	ClO_2	3.12	1	3.82	0.30	<0.30	0.30
			2	3.90	<0.30	0.30	<0.30
			3	3.79	0.30	0.30	0.30
			4	3.87	0.30	0.30	0.30
			5	4.04	<0.30	0.30	0.30
			6	4.93	0.30	<0.30	<0.30
2/13/79	ClO_2	2.25	1	4.70	2.41	2.41	2.28
			2	4.75	2.72	2.27	2.22
			3	4.99	2.33	2.36	2.39
2/13/79	Cl_2	4.60	1	4.84	2.70	2.45	2.24
			2	4.69	2.72	2.40	2.36
			3	4.59	2.51	2.61	2.34
2/13/79	Cl_2	19.60		4.83	2.08	1.04	0.30

TABLE A-4. RESULTS OF LABORATORY EXPERIMENTS WITH DUBLIN FILTERED NITRIFIED, ACTIVATED-SLUDGE EFFLUENT

Disinfectant	Dose mg/l	Replicate No.*	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	5	15	30
ClO_2	2	1	3.74	<0.30	<0.30	<0.30
		2	4.08	4.01	4.20	4.18
		3	5.18	4.38	4.43	4.13
	5	1	3.78	<0.30	<0.30	1.30
		2	4.20	2.37	2.39	2.35
		3	4.90	2.06	2.09	2.26
	10	1	3.93	<0.30	0.95	<0.30
		2	4.08	0.30	<0.30	<0.30
		3	4.99	0.88	0.98	0.34
Cl_2	2	1	6.07	3.30	3.65	3.30
		2	4.24	3.84	3.87	3.68
		3	4.98	3.85	3.64	3.74
	5	1	3.93	-†	2.23	1.60
		2	4.54	2.69	2.76	2.26
		3	4.95	2.08	1.90	2.62
	10	1	3.88	1.65	1.38	1.10
		2	4.43	2.02	0.30	<0.30
		3	4.86	1.37	0.26	0.79

*Dates of replicate experiments: 1, 1/9/79; 2, 2/16/79; 3, 2/22/79.

†- signifies sample lost.

TABLE A-5. RESULTS OF LABORATORY EXPERIMENTS WITH UNFILTERED AND FILTERED PALO ALTO SECONDARY EFFLUENT USING CHLORINE DIOXIDE

Type of Effluent	Dose mg/l	Replicate No.*	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	1	5	15	30	60
Unfiltered	2	1	5.80	4.35	4.32	4.82	4.04	-†
		2	5.06	4.40	4.30	4.13	3.86	-
		3	5.02	4.50	4.36	4.43	4.22	-
		4	5.55	4.80	4.88	4.82	4.60	-
	5	1	5.84	-	<2.0	<2.0	<2.0	<2.0
		2	5.24	-	4.62	2.56	2.52	2.5
		3	5.29	-	3.14	2.46	1.84	1.08
		4	5.72	-	3.34	2.52	2.35	2.84
	10	1	5.24	-	1.00	<0.4	<0.4	-
		2	5.26	-	1.84	1.30	<0.4	-
		3	5.26	-	1.59	0.59	<0.4	-
		4	5.31	-	2.54	<0.4	<0.4	-
Filtered	2	1	5.82	3.04	3.35	3.09	3.00	-
		2	5.00	3.48	3.28	3.46	3.22	-
		3	4.82	3.09	2.74	2.86	2.74	-
		4	5.07	3.98	3.19	3.50	2.65	-
	5	1	6.22	-	<1.0	<1.0	1.0	<1.0
		2	5.01	-	0.78	0.60	<0.3	<0.3
		3	4.72	-	0.30	<0.4	0.3	0.6
		4	5.31	-	1.64	0.98	0.79	0.98
	10	1	6.68	-	<1.0	<1.0	<1.0	-
		2	4.58	-	1.00	<0.4	<0.4	-
		3	4.86	-	<0.4	<0.4	<0.4	-
		4	5.15	-	<0.4	<0.4	<0.4	-

*Dates of experiments: 1, 8/8/79; 2, 8/14/79; 3, 8/17/79; 4, 8/21/79.

†- signifies that experiment was not conducted.

TABLE A-6. RESULTS OF LABORATORY EXPERIMENTS WITH UNFILTERED AND FILTERED PALO ALTO SECONDARY EFFLUENT USING CHLORINE

Type of Effluent	Dose mg/l	Replicate No.*	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	1	5	15	30	60
Unfiltered	2	1	4.69	4.80	4.39	3.04	3.12	-†
		2	4.92	4.48	4.67	3.52	3.30	-
		3	4.95	5.10	4.48	2.04	2.95	-
	5	1	4.82	-	3.19	1.17	0.39	0.30
		2	4.78	-	2.95	1.00	1.00	1.00
		3	5.04	-	3.34	1.40	1.44	1.26
	10	1	4.96	-	0.79	<0.3	<0.3	-
		2	5.23	-	1.03	<0.3	0.80	-
		3	5.38	-	2.72	1.46	2.20	-
Filtered	2	1	5.78	4.64	4.23	2.69	1.30	-
		2	4.50	5.09	4.40	3.23	1.47	-
		3	4.65	4.57	4.42	3.50	2.70	-
	5	1	4.81	-	1.53	0.67	<0.3	<0.3
		2	4.74	-	1.86	1.06	0.24	0.15
		3	4.77	-	1.64	1.38	1.22	0.30
	10	1	4.66	-	0.39	0.70	<0.3	-
		2	4.89	-	0.83	<0.3	0.15	-
		3	4.89	-	1.47	0.66	0.26	-

*Dates of duplicate experiments: 1, 8/23/79; 2, 8/24/79; 3, 8/22/79.

†- signifies that experiment was not conducted.

TABLE A-7. RESULTS OF EXPERIMENTS WITH SAN JOSE SECONDARY EFFLUENT

Disinfectant	Dose mg/l	Replicate No.*	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	5	15	30
ClO_2	2	1	6.08	5.11	4.70	4.30
		2	6.81	3.10	6.60	6.30
		3	6.67	5.71	5.62	5.40
	5	1	6.40	3.64	3.40	3.52
		2	6.63	4.57	4.21	3.77
		3	6.58	4.56	3.76	3.43
	10	1	6.16	1.48	-†	-
		2	6.75	2.60	1.32	1.48
		3	6.49	2.59	2.76	-
Cl_2	2	1	6.30	5.80	-	4.00
		2	6.76	6.51	5.71	5.55
		3	6.45	6.42	5.43	4.45
	5	1	6.27	5.70	3.23	3.84
		2	6.94	4.62	2.52	2.41
		3	6.30	5.06	2.28	1.78
	10	1	6.29	3.18	1.70	-
		2	6.69	2.49	2.10	2.30
		3	6.54	2.15	1.54	1.40

*Dates of experiments: 1, 6/28/79; 2, 7/10/79; 3, 7/17/79.

†- signifies that sample was lost.

TABLE A-8. RESULTS OF EXPERIMENTS WITH SAN JOSE NITRIFIED EFFLUENT

Disinfectant	Dose mg/l	Replicate No.*	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	5	15	30
ClO_2	2	1	4.98	3.88	3.85	3.84
		2	4.98	3.55	3.41	3.47
		3	4.25	3.04	3.78	2.78
	5	1	4.96	2.08	1.50	1.48
		2	4.66	1.04	1.38	1.95
		3	4.53	1.11	0.30	0.30
	10	1	5.34	1.30	0.30	-†
		2	4.73	0.85	0.30	0.30
		3	4.21	0.84	0.30	<0.3
Cl_2	2	1	4.78	4.76	3.77	3.77
		2	4.72	4.43	4.19	3.35
		3	4.35	3.60	3.15	3.04
	5	1	5.67	3.38	2.00	-
		2	4.72	1.78	-	0.30
		3	4.40	2.04	-	2.11
	10	1	4.87	1.78	0.30	0.30
		2	5.26	0.84	<0.3	<0.3
		3	4.30	0.90	0.64	0.75

*Dates of experiments: 1, 7/7/79; 2, 7/12/79; 3, 7/19/79.

†- signifies that sample was lost.

TABLE A-9. RESULTS OF EXPERIMENTS WITH SAN JOSE FILTERED, NITRIFIED EFFLUENT

Disinfectant	Dose mg/l	Replicate No.*	Average Log Surviving Total Coliforms $\log_{10}$[N/100ml] Contact Time, min 0	5	15	30
ClO_2	2	1	2.79	-†	1.30	-
		2	5.46	4.12	2.95	3.18
		3	4.73	-	-	2.00
	5	1	4.90	0.48	<0.3	<0.30
		2	5.38	1.11	0.85	0.75
		3	4.72	<0.3	<0.3	<0.3
	10	1	4.81	<0.3	<0.3	0.30
		2	5.71	0.45	0.30	<0.3
		3	4.59	<0.3	<0.3	<0.3
Cl_2	2	1	4.75	4.4	3.59	2.41
		2	4.91	4.26	3.18	1.74
		3	4.76	2.30	2.00	-
	5	1	1.90	0.30	0.30	0.3
		2	5.84	2.53	0.84	0.45
		3	4.86	1.11	0.95	0.84
	10	1	4.89	0.20	0.30	<0.3
		2	5.84	1.94	1.51	1.21
		3	4.78	0.69	0.65	0.52

*Dates of experiments: 1, 7/2/79; 2, 7/13/79; 3, 7/20/79.

†- signifies that sample was lost.

APPENDIX B

LOG-LOG PLOTS OF MODEL PREDICTIONS AND DATA POINTS FOR ALL EXPERIMENTS

Figure B-1. Inactivation of coliform bacteria by chlorine dioxide in Palo Alto wastewater - 1978.

Figure B-2. Inactivation of coliform bacteria by chlorine in Palo Alto wastewater - 1978.

Figure B-3. Inactivation of coliform bacteria by chlorine dioxide in Palo Alto wastewater - 1979.

Figure B-4. Inactivation of coliform bacteria by chlorine in Palo Alto wastewater - 1979.

Figure B-5. Inactivation of coliform bacteria by chlorine dioxide in filtered Palo Alto wastewater.

Figure B-6. Inactivation of coliform bacteria by chlorine in filtered Palo Alto wastewater.

Figure B-7. Inactivation of coliform bacteria by chlorine dioxide in Palo Alto wastewater - 1978 and 1979.

Figure B-8. Inactivation of coliform bacteria by chlorine in Palo Alto wastewater - 1978 and 1979.

Figure B-9. Inactivation of coliform bacteria by chlorine dioxide in Dublin lab experiments.

Figure B-10. Inactivation of coliform bacteria by chlorine in Dublin lab experiments.

Figure B-11. Inactivation of coliform bacteria by chlorine dioxide in Dublin field experiments.

Figure B-12. Inactivation of coliform bacteria by chlorine in Dublin field experiments.

Figure B-13. Inactivation of coliform bacteria by chlorine in San Jose secondary effluent.

Figure B-14. Inactivation of coliform bacteria by chlorine dioxide in San Jose filtered effluent.

Figure B-15. Inactivation of coliform bacteria by chlorine dioxide in San Jose nitrified effluent.

Figure B-16. Inactivation of coliform bacteria by chlorine dioxide in San Jose secondary effluent.

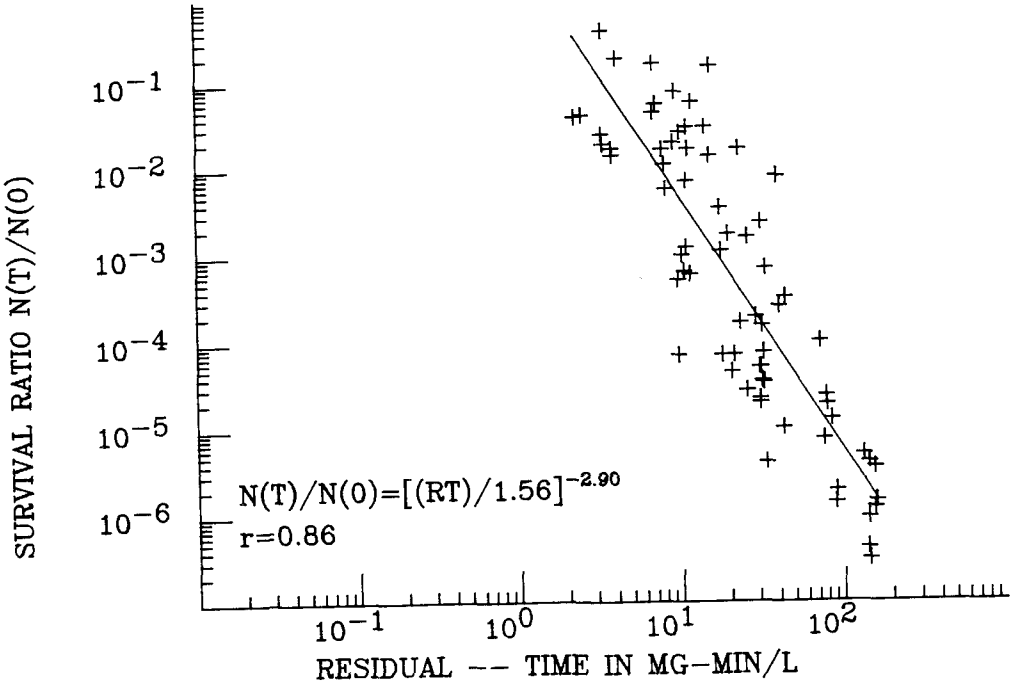

Figure B-1. Inactivation of coliform bacteria by chlorine dioxide in Palo Alto wastewater - 1978.

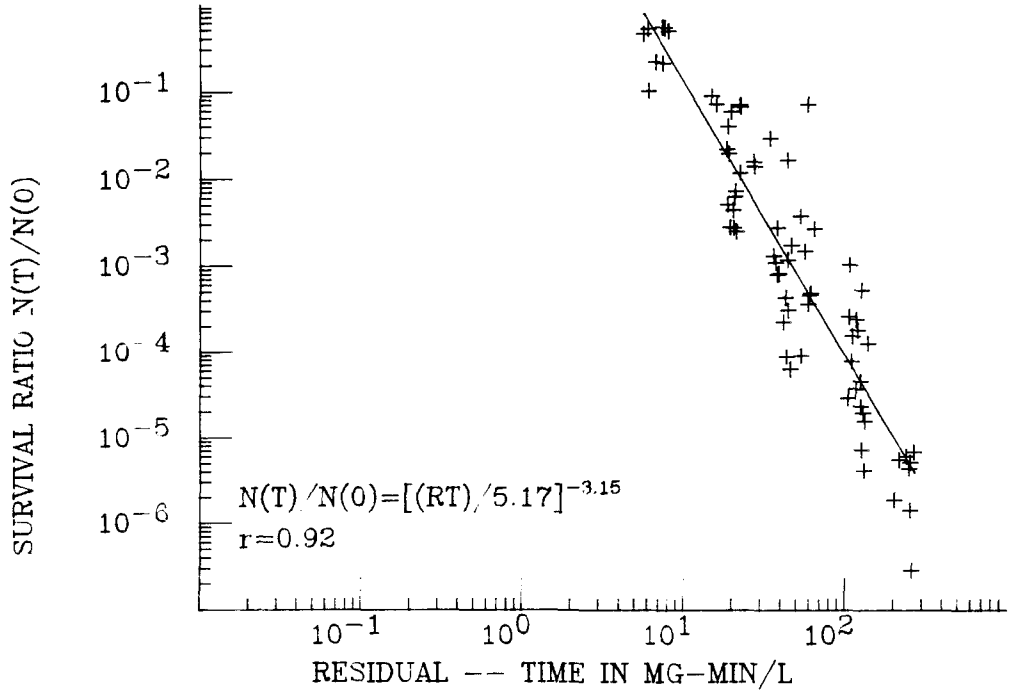

Figure B-2. Inactivation of coliform bacteria by chlorine in Palo Alto wastewater - 1978.

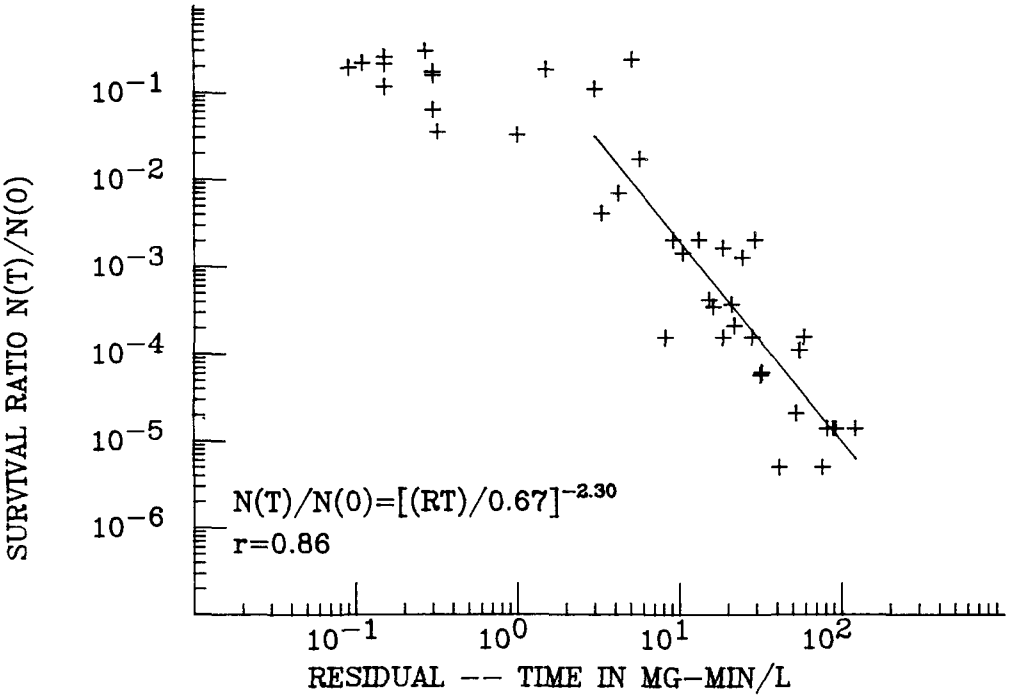

Figure B-3. Inactivation of coliform bacteria by chlorine dioxide in Palo Alto wastewater - 1979.

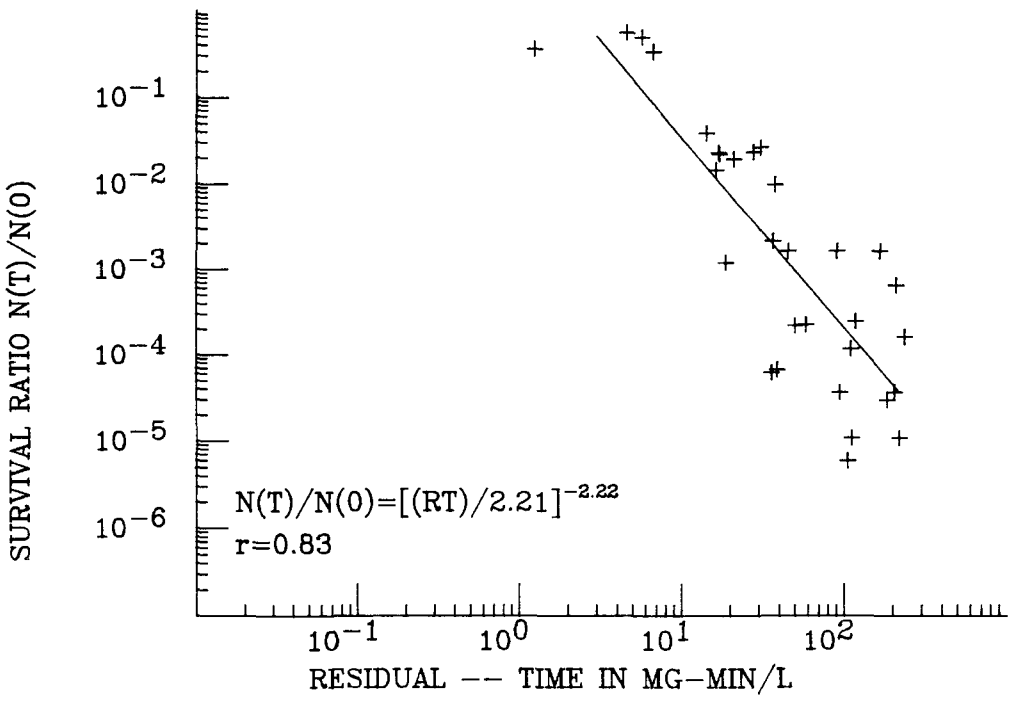

Figure B-4. Inactivation of coliform bacteria by chlorine in Palo Alto wastewater - 1979.

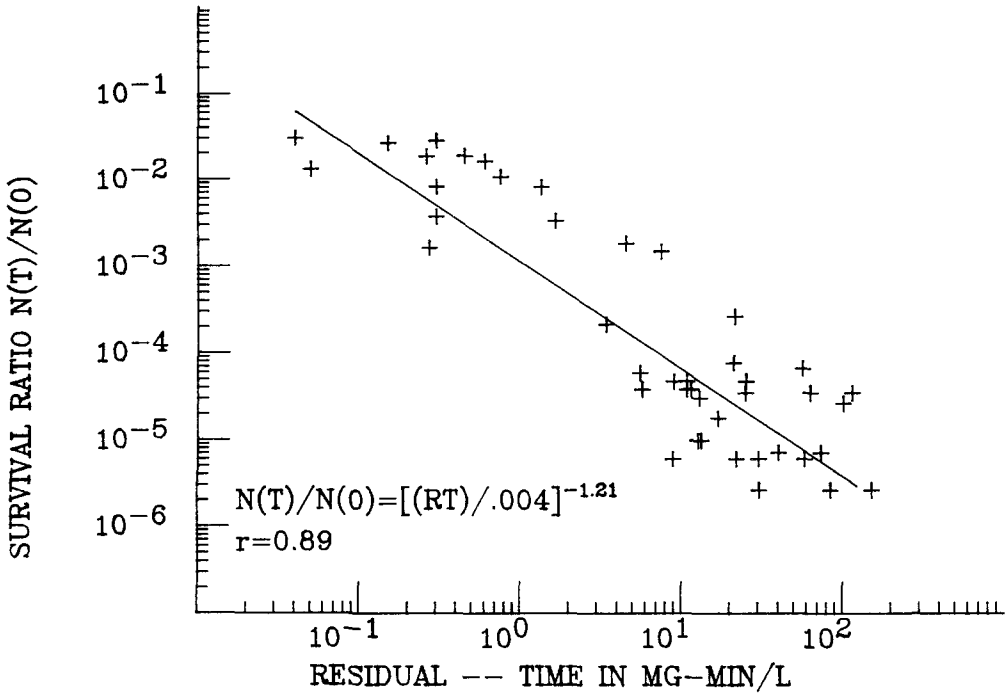

Figure B-5. Inactivation of coliform bacteria by chlorine dioxide in filtered Palo Alto wastewater.

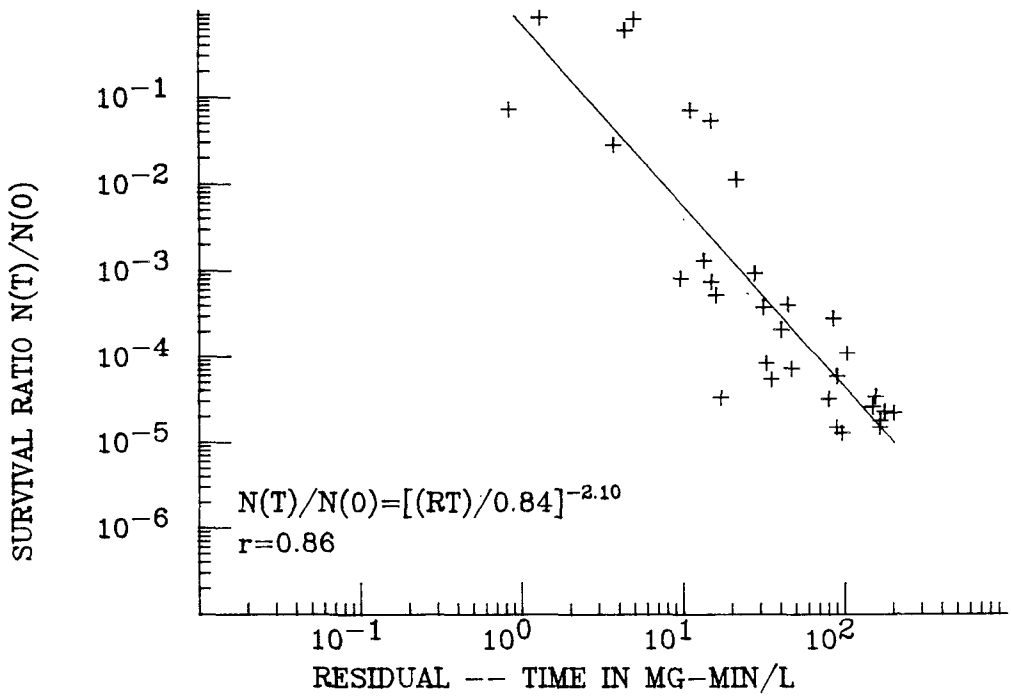

Figure B-6. Inactivation of coliform bacteria by chlorine in filtered Palo Alto wastewater.

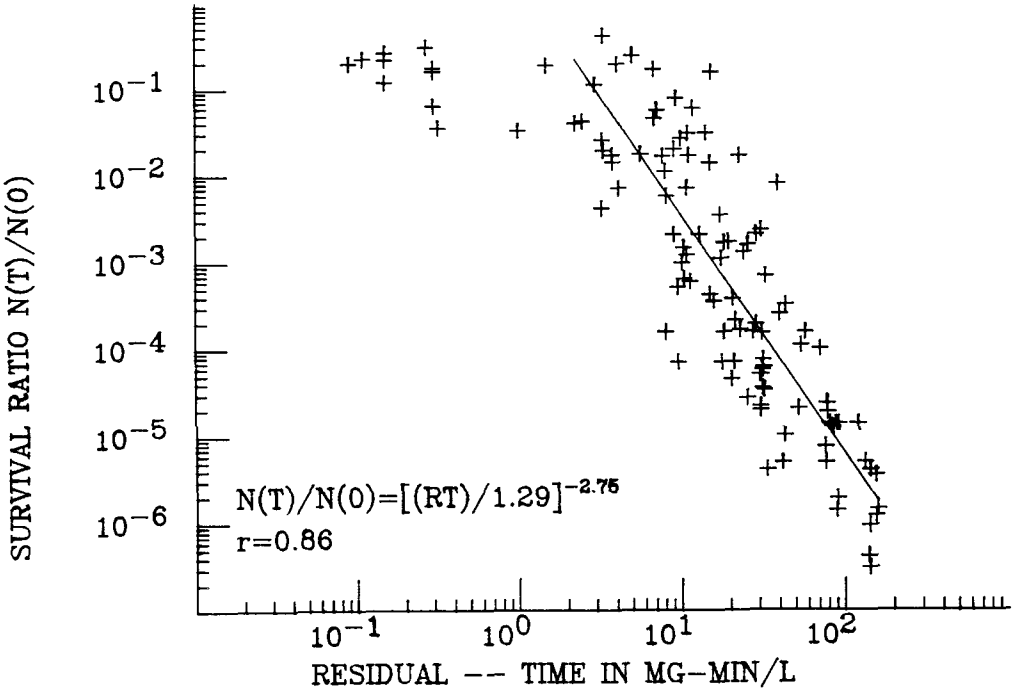

Figure B-7. Inactivation of coliform bacteria by chlorine dioxide in Palo Alto wastewater - 1978 and 1979.

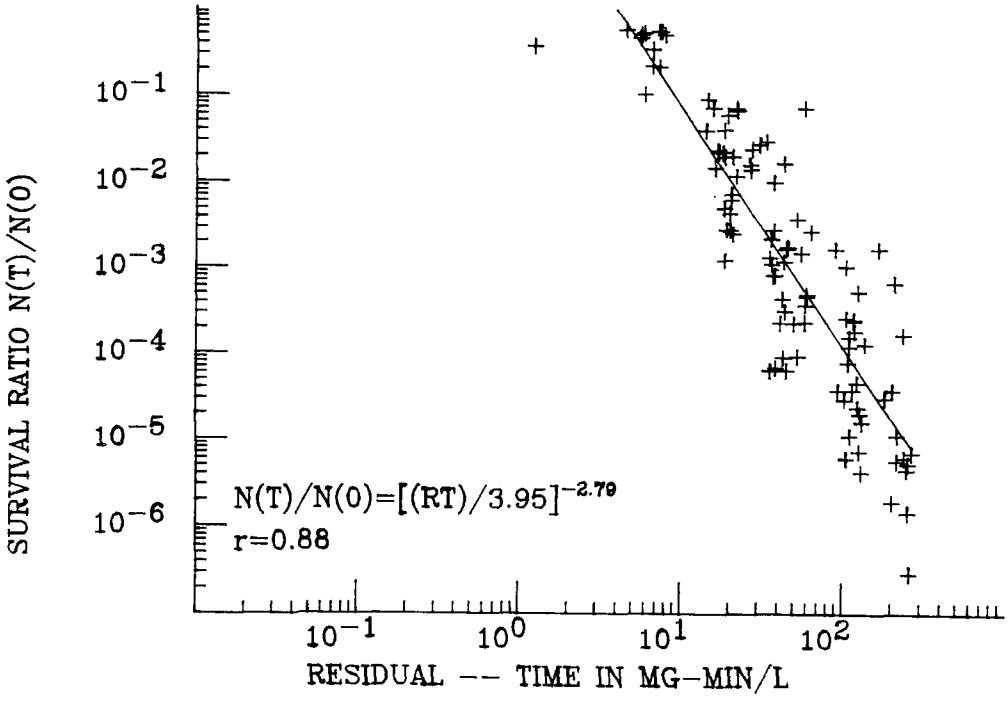

Figure B-8. Inactivation of coliform bacteria by chlorine in Palo Alto wastewater - 1978 and 1979.

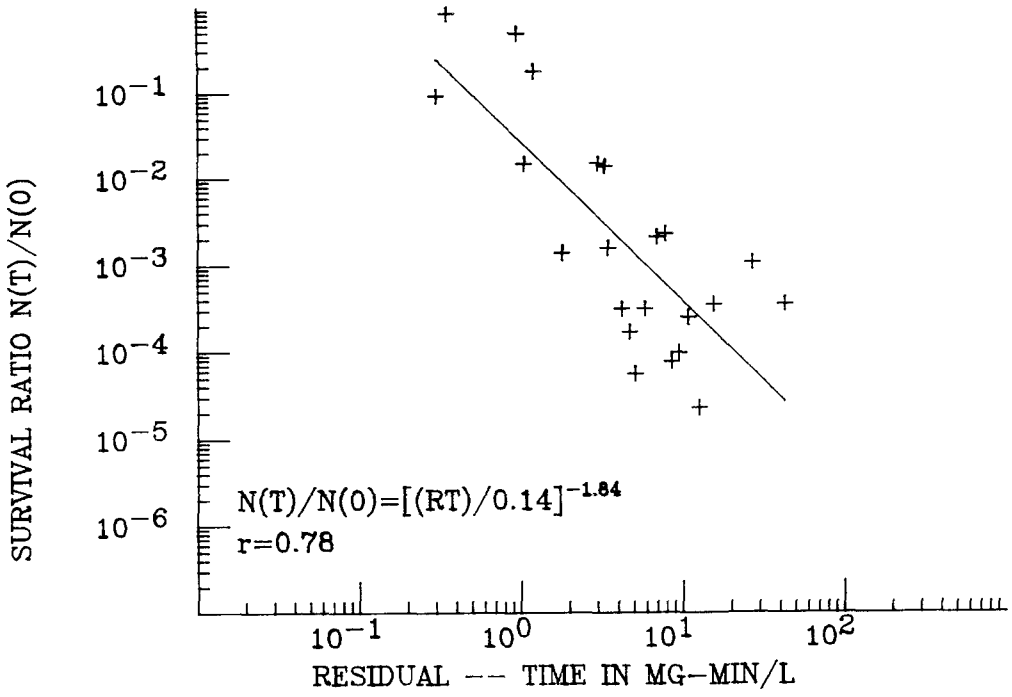

Figure B-9. Inactivation of coliform bacteria by chlorine dioxide in Dublin lab experiments.

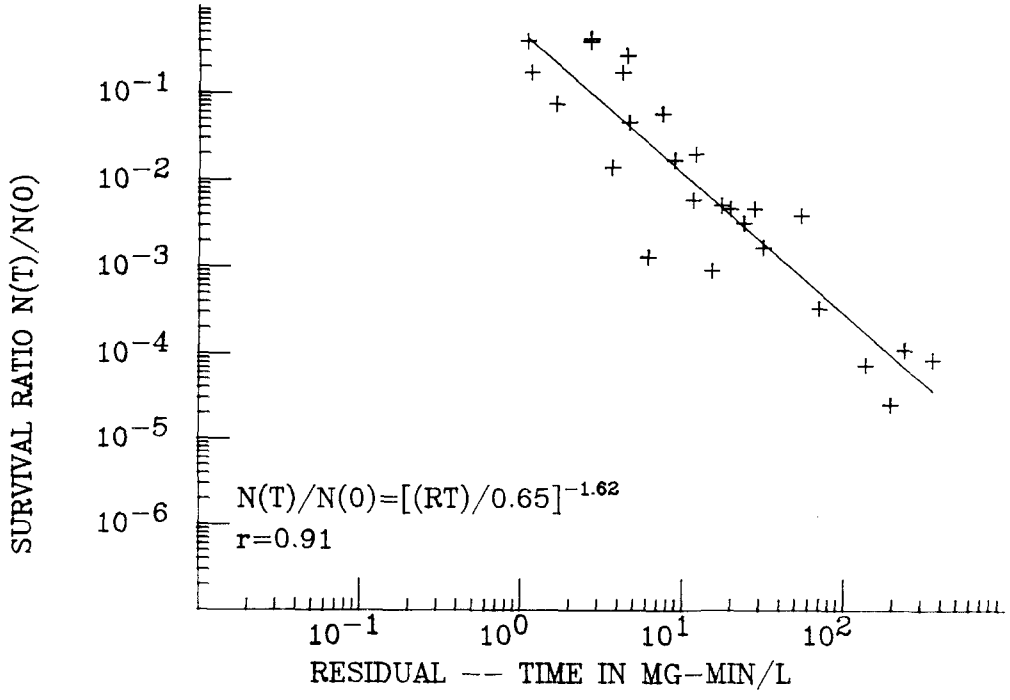

Figure B-10. Inactivation of coliform bacteria by chlorine in Dublin lab experiments.

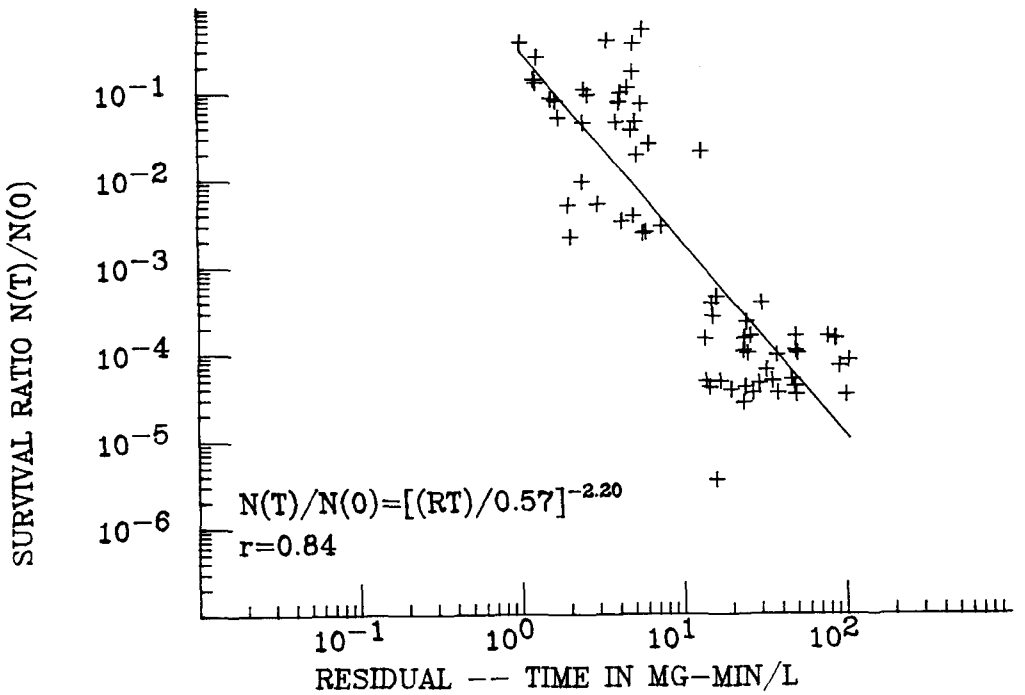

Figure B-11. Inactivation of coliform bacteria by chlorine dioxide in Dublin field experiments.

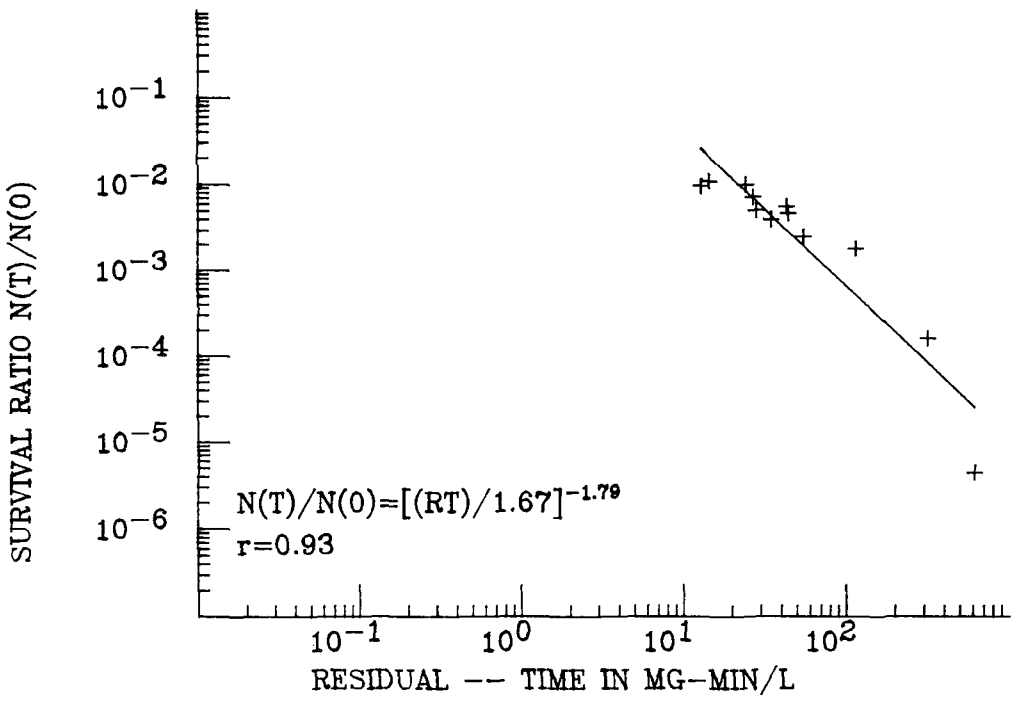

Figure B-12. Inactivation of coliform bacteria by chlorine in Dublin field experiments.

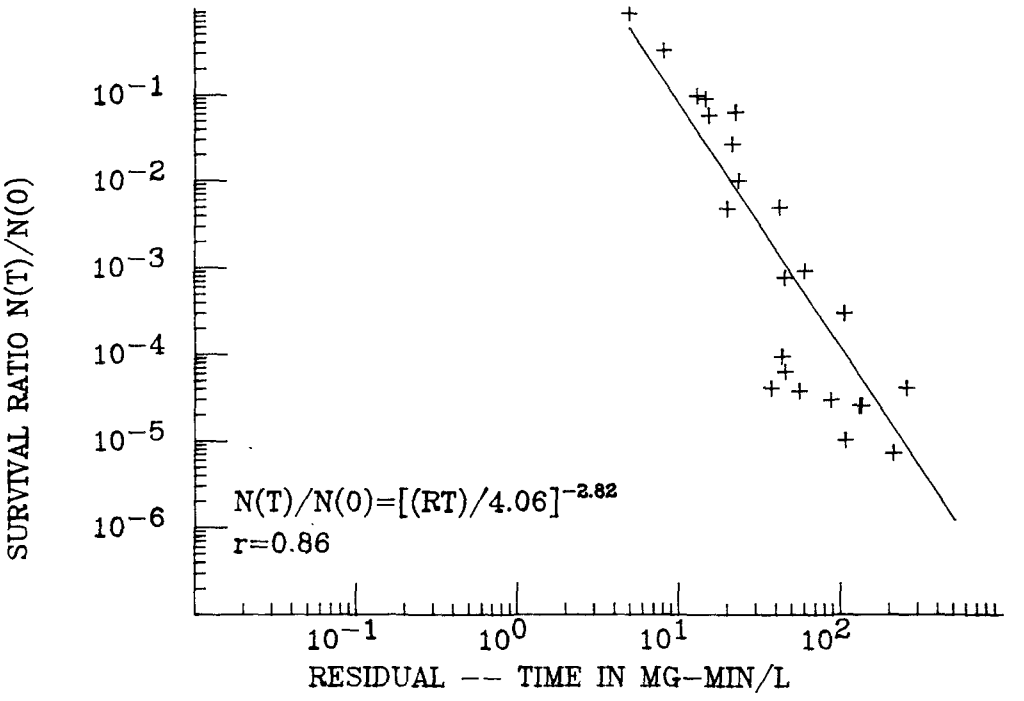

Figure B-13. Inactivation of coliform bacteria by chlorine in San Jose secondary effluent.

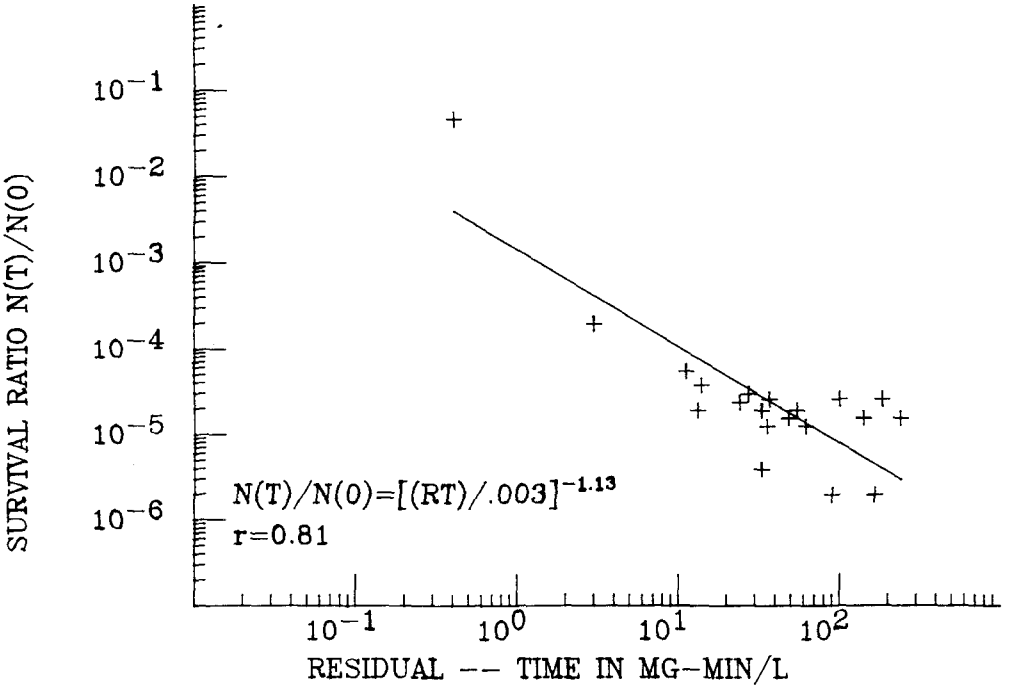

Figure B-14. Inactivation of coliform bacteria by chlorine dioxide in San Jose filtered effluent.

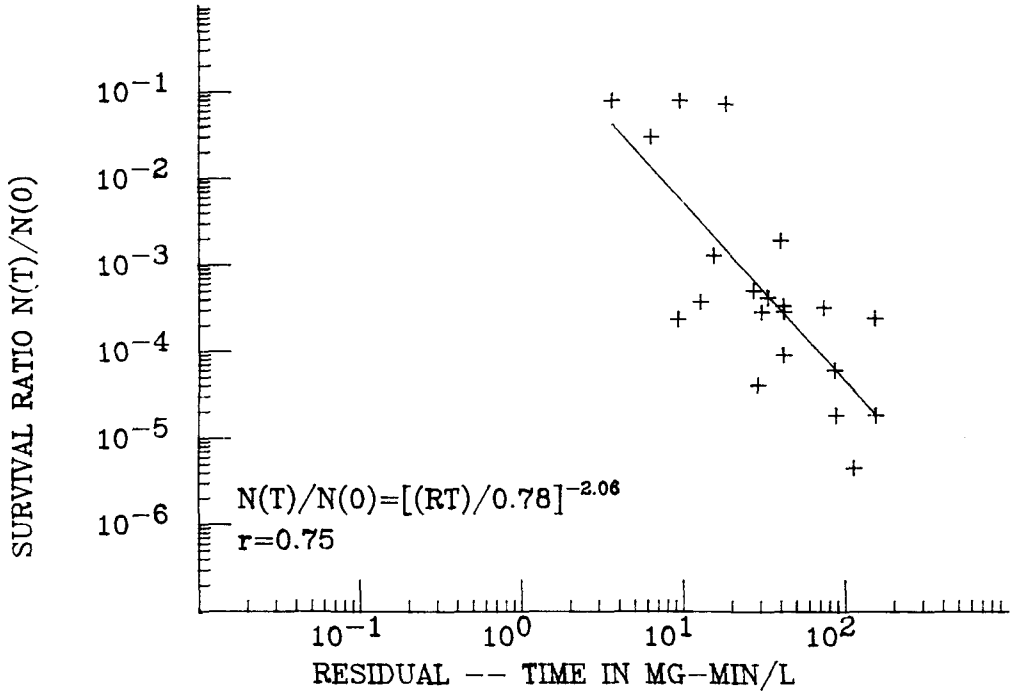

Figure B-15. Inactivation of coliform bacteria by chlorine dioxide in San Jose nitrified effluent.

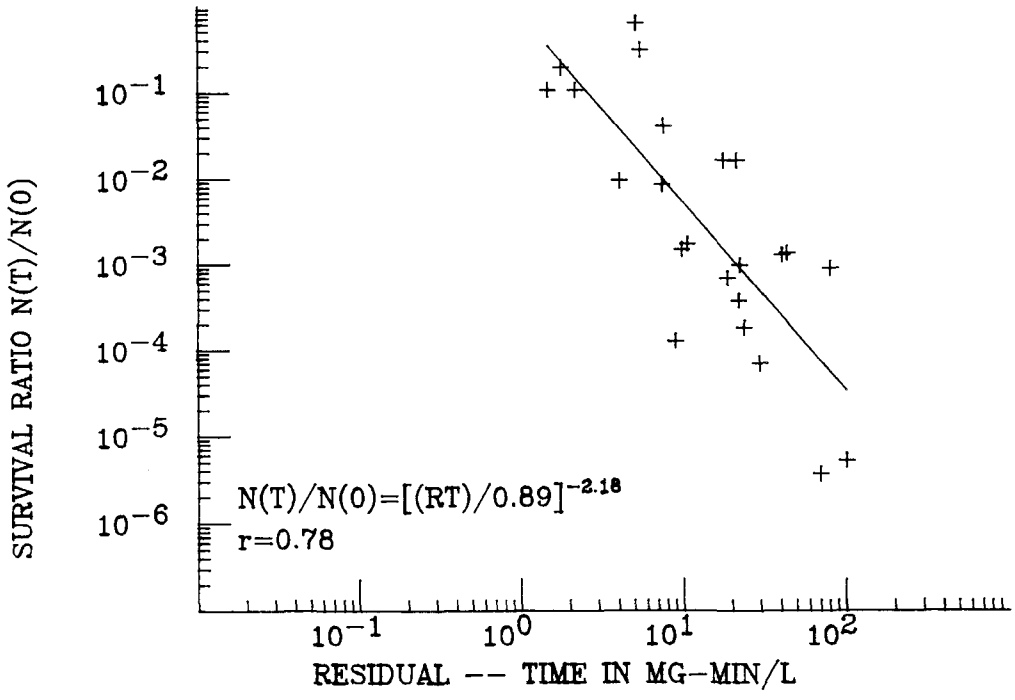

Figure B-16. Inactivation of coliform bacteria by chlorine dioxide in San Jose secondary effluent.

APPENDIX C

A DETAILED EXAMPLE OF THE CALCULATIONS TO DETERMINE THE REQUIRED DISINFECTANT FEED CAPACITY--POUNDS PER DAY

These example calculations are for the disinfection by chlorine dioxide of a conventional activated-sludge treatment effluent with a 1000/100 ml total coliform standard at the treatment plant outfall. This corresponds to Case C discribed in the main body of this report, Table 36.

1. Determine the initial bacterial concentration in the waste stream to be disinfected.

   For conventional activated-sludge treatment, the value read from Table 14 is 1.62×10^6 total coliforms/100 ml.

2. Calculate the required survival ratio, N(t)/N(0), from the initial bacterial concentration, N(0). For Case C, the disinfection standard is 1000 total coliforms/100 ml. The survival ratio is then:

$$\frac{1000 \text{ total coliforms/100 ml}}{1.62 \times 10^6 \text{ total coliforms/100 ml}} = 6.17 \times 10^{-4}$$

3. Calculate the required residual time product using Eqs. 24 and 25 and the model-fitting constants from Table 24.

$$N(t) = N(0)\left[\frac{(Rt)}{b}\right]^k$$

$$N(t) = N(0) \quad \text{for} \quad Rt < b$$

where N(0) = initial total coliform bacteria;

N(t) = total coliform bacteria at time t;

R = residual oxidant in mg/l as measured at time t;

b = lag time coefficient (Rt)' in mg·min/l;

k =-k'/a = velocity coefficient; and

t = time in minutes.

The model fitting constants for Case C, disinfection with chlorine dioxide are:

$$b = 1.56$$

$$k = -2.90$$

The required residual-time product is then:

$$N(t)/N(0) = \left[\frac{Rt}{b}\right]^k$$

Solving for Rt:

$$Rt = [N(t)/N(0)]^{1/k} \cdot b$$

$$Rt = [6.17 \times 10^{-4}]^{-1/2.90} \cdot 1.56$$

$$Rt = 19.95 \text{ mg } ClO_2 \cdot \text{min/l}$$

4. Calculate the required residual, based on the provided contact time, namely one hour. The required residual is then:

$$\frac{Rt}{60 \text{ min}} = \frac{19.95 \text{ mg } ClO_2 \cdot \text{min/l}}{60 \text{ min}}$$

$$R = 0.33 \text{ mg } ClO_2/l$$

5. Calculate the disinfectant dosage needed to provide the required residual disinfectant concentration.

In order to be able to calculate the disinfectant dosage, an empirical relationship relating disinfectant dose to residual has been developed using the observed values of oxidant demand (see Table 27 and Reference 33). The dose required is then given by the sum of the required residual to achieve the disinfection standard plus the one-hour oxidant demand. The one-hour demand, however, is also a function of dose, as it must be since demand equals dose minus residual. A linear regression of log[1-hour oxidant demand] on log[dose] yields the equation:

$$D_{1\text{-hour}} = \beta(\text{Dose})^{\alpha}$$

where $D_{1\text{-hour}}$ = one-hour oxidant demand-mg/l,

β,α = constants, dependent on the oxidant and the wastewater,

Dose = oxidant dose-mg/l.

The equation to be solved is:

$$\text{Dose} = \text{Residual required} + \beta(\text{Dose})^{\alpha}$$

The values of β and α and the regression correlation coefficients for Palo Alto and Dublin Wastewaters are shown in Table C-1.

TABLE C-1. CONSTANTS FOR ONE-HOUR DISINFECTANT DEMAND EQUATION AS A FUNCTION OF DOSE

Case	ClO_2			Cl_2		
Type of Effluent)	β	α	r^*	β	α	r^*
A, B, and C (conventional activated sludge)	0.99	0.80	0.97	0.63	0.46	0.81
D, E, and F (filtered, nitrified activated sludge)	0.94	0.995	0.99	1.11	0.80	0.98

*r = correlation coefficient

For Case C, the required dose is:

$$\text{Dose} = 0.33 + 0.99(\text{DOSE})^{0.80}$$

$$\text{Dose} = 2.17 \text{ mg/l } ClO_2$$

The required feed capacity in pounds per day is given by:

$$2.17[\text{g/m}^3] \times 1/454[\text{lb/g}] \times 1/264.2[\text{m}^3/\text{gal}] \times 10^6[\text{million gal/gal}]$$

$$= 18.1 \text{ [pounds } ClO_2 \text{ per day]/[mgd wastewater treated]}$$

The corresponding values are entered in the row designated "Case C, Cl_2" in Table 38.