

OZONE DISINFECTION OF SECONDARY EFFLUENTS⁽¹⁾

By

Carl Nebel, Ronald D. Gottschling, Paul C. Unangst, H. J. O'Neill and
George V. Zintel⁽²⁾

Introduction

The current demand for water quality improvement has resulted in a search for new, improved and economically feasible treatment methods. As standards are raised and water re-use becomes more likely, tertiary treatment procedures become necessary. Recent investigations^{1,2} have indicated that secondary effluents disinfected with chlorine are toxic to aquatic life. A viable alternative to the use of chlorine is ozone for disinfection and concurrent tertiary treatment.

Ozone, O₃, is an unstable gas naturally occurring in the upper atmosphere. It is responsible for the characteristic sweet odor in the air immediately following an electrical storm. Because ozone is unstable it cannot be effectively stored or shipped and must be generated on-site. Commercial ozonators mimic nature by generating ozone by electrical discharge through air or oxygen. The process produces ozone as a mixture with either air or oxygen, and the exit gas from the ozonator typically contains 1 percent ozone from air feed or 1.7 percent ozone using oxygen feed. Higher concentrations are possible but less economically efficient. The ozonized gas can then be dispersed into the water to be treated either by various injection methods or by forcing the pressurized gas through a porous disperser at the bottom of a treatment tank. Various methods of ozone mass transfer have been recorded recently.³

A variety of laboratory studies^{4,5,6,7,8,9,10,11} initially demonstrated the effectiveness of ozone in secondary effluent disinfection and contaminant removal; however, the lack of uniformity in experimental techniques and methods has made comparison of data difficult. The goal of this work was to establish the degree of treatment possible with various ozone dosage levels. Additional information has been obtained in pilot scale studies in the cities of London, England,¹² Chicago, Illinois¹³ and Washington, D.C.,¹⁴ where water of potable quality has been produced by ozonation of a variety of effluents. As an extension of this work, a pilot study at the Louisville, Ky., Fort Southworth Sewage Treatment Plant was reported recently.¹⁵

Previous work has established that ozone treatment of sewage can be considered at several dosage levels: (1) as a treatment for primary sewage and storm water overflow (ozone dosages of 10 to 100 mg/l required), (2) as

(1) Presented in part by Mr. Carl Nebel at a meeting of the Environmental Group, February 26, 1975.

(2) Welsbach Ozone Systems Corporation, Philadelphia, Pennsylvania.

a tertiary treatment to convert secondary effluent to water of potable quality (ozone dosages greater than 50 mg/l required), and (3) as a replacement for chlorine for disinfection whereby a certain degree of tertiary treatment is concurrently observed (ozone dosages of 5 to 15 mg/l required). In this study we have attempted to elucidate more accurately the ozone dosages required for disinfection and to determine the effectiveness of removal of specific contaminants in the effluent which are removed simultaneously.

Experimental Methods

Secondary effluents obtained from sewage treatment plants in Millville, New Jersey (contact stabilization), Hatboro, Pennsylvania, (standard activated sludge), and Northeast Philadelphia, Pennsylvania, (pilot plant oxygen enriched activated sludge), were ozonized in a 6.5 in. (16.5 cm) I.D. Plexiglas ozone contact column of approximately 15 gal. (56.7 lit.) capacity (Figure 1). Ozone was generated from either air or oxygen feed with a Welsbach T-408 or T-816 ozonator. The column off-gases were passed through 2 per cent unbuffered potassium iodide solution for excess ozone analysis. Ozone analyses were performed via the iodine-standard thiosulfate titration procedure.¹⁶ Samples were removed from the column at specified times (i.e., ozone dosage levels) and were analyzed for contaminant concentrations. The bacteriological, suspended solids, and BOD analyses were performed by Dalare Associates, Inc., Philadelphia, Penna. COD analyses were determined by the dichromate method and dissolved oxygen via a modified Winkler procedure. Other contaminant analyses were performed on a Hach AC-DR colorimeter using standard procedures.

Disinfection By Ozonization

The potent germicidal properties of ozone have been attributed to its high oxidation potential, approximately twice that of chlorine in water. Both disinfectants destroy bacteria via chemical oxidation, possibly via inactivation of the essential enzymes of the cells. An important step in the action of disinfection is the penetration of the cellular membrane. In applying the criterion of free oxidant to ozone, it is assumed that the effectiveness of the bactericidal action is a function of the ozone remaining. This reasoning has been extended in the ozone literature^{13, 17} to the concept of "all or nothing" disinfection, implying that a certain threshold of ozone dosage must be reached before any disinfection takes place. Data developed within the scope of this work have shown that this effect is not valid, i.e., oxidation of pollutants takes place simultaneously with the destruction of microorganisms. Leiguarda's¹⁸ investigations support the finding that the bactericidal action of ozone proceeds in parallel with the oxidation of organic matter. It would be presumptuous to assume that a powerful oxidant such as ozone would selectively attack organic contaminants and not simultaneously destroy microorganisms that are also composed of organic compounds.

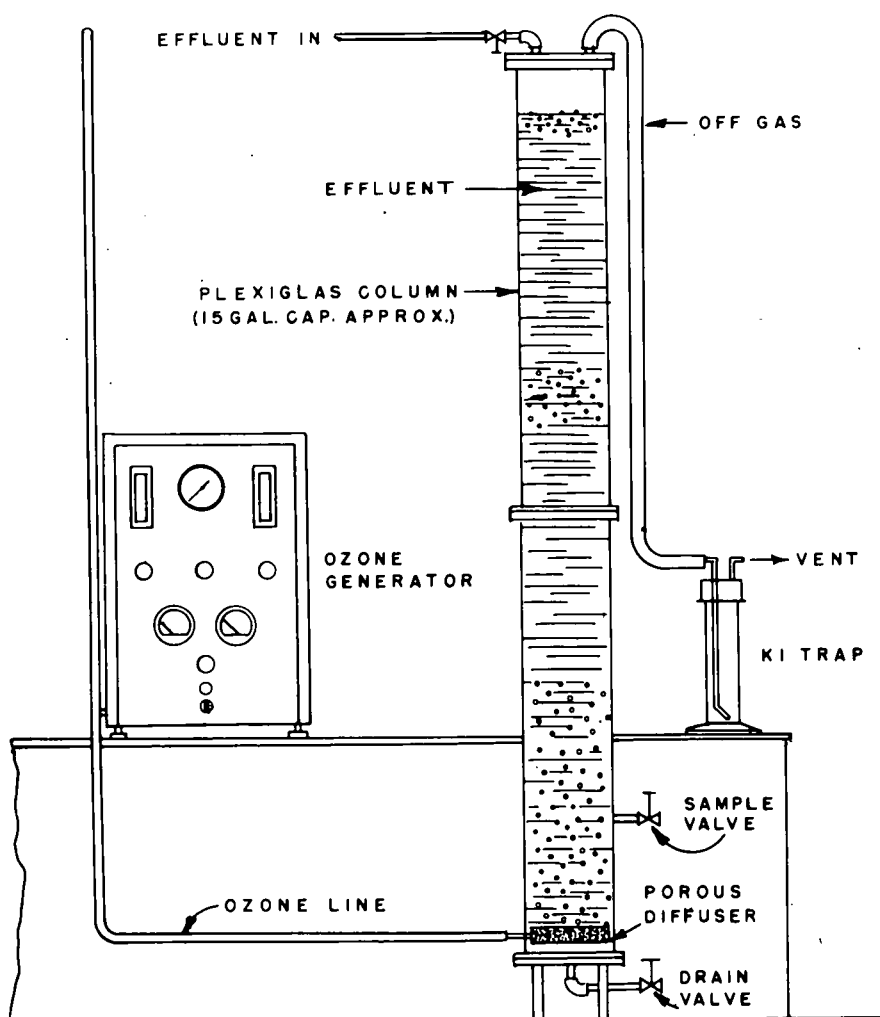
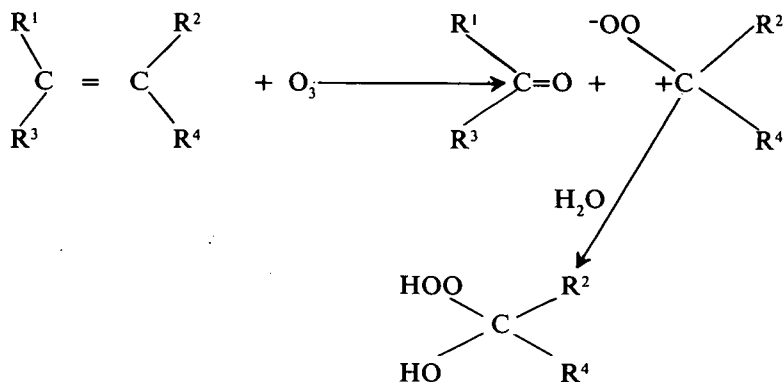


Figure 1. Ozonization apparatus

Leiguarda's findings imply that some particles produced by the ozonization of sewage are also effective in reducing the concentration of microorganisms. Modern organic ozone chemistry would predict that oxidized organic compounds containing carbon-carbon double bonds give rise to hydroperoxy alcohols by the following reaction route:



where R = alkyl, aryl, or hydrogen.

Indications exist that organic peroxides exert a stronger bactericidal action than hydrogen peroxide since they are more prone to decomposition.¹⁹ Thus the disinfection action of ozone can proceed by oxidation with ozone directly and by intermediate hydroperoxy compounds that can interact with the cellular cytoplasm. There is no indication in the literature of any microorganism resistant to the action of ozone.

The amount of ozone required to produce sterilization or any level of disinfection is dependent upon the exact nature of the effluent. The characteristics of a secondary effluent vary from one treatment plant to another and are also a function of time within a given plant. Figure 2 shows that destruction of total coliform in an ozonized effluent varies slightly from one treatment plant to another. Figure 3 indicates that the total coliform count is reduced at approximately the same rate as the fecal coliform count. The standard plate count, an indicator for a large number of microorganisms, was rapidly reduced from approximately one million to one hundred upon application of ten mg/l (ppm) of ozone in a typical example, Figure 4.

Although coliform standards among different regulatory agencies vary widely and are often ambiguous, requirements of 2.2 to 1000 M.P.N. per 100 ml are common. Most states require that secondary effluents be disinfected to a plate count of 200/100 ml of fecal coliform. Ozone dosages of five to ten mg/l are adequate for this level of disinfection with the particular effluents studied. The limited data available in the literature are in general agreement with our results,^{12,13,20} however, higher dosage levels may be required when significant amounts of ozone susceptible organic materials from industrial loading or other sources are present.^{15,21,22}

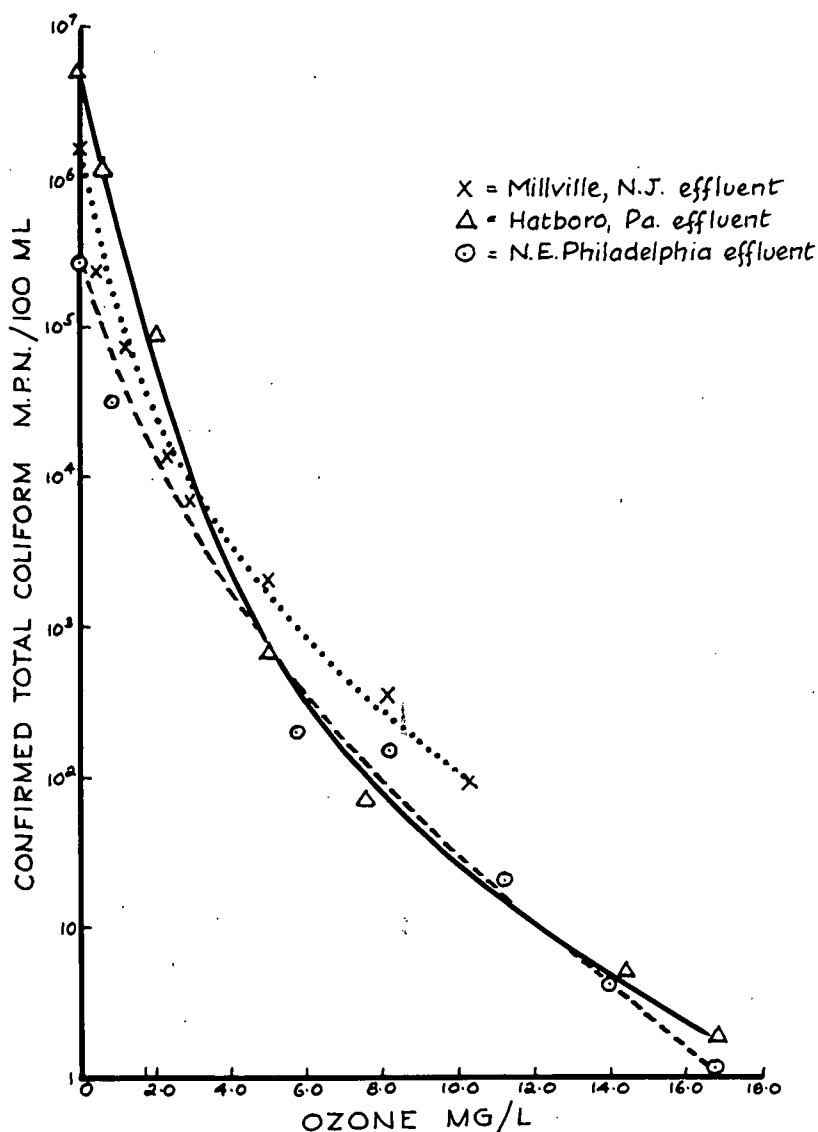


Figure 2. Total coliform reduction for different secondary effluents.

The rate of ozone disinfection has been shown to be 3125 times faster with ozone than with chlorine.²³ Secondary effluents have been disinfected within a 2.5 second contact time in a static mixer.²⁴ Hence it can be concluded that the rate of ozone disinfection is mass transfer controlled and not contact time controlled as is the case with chlorine.

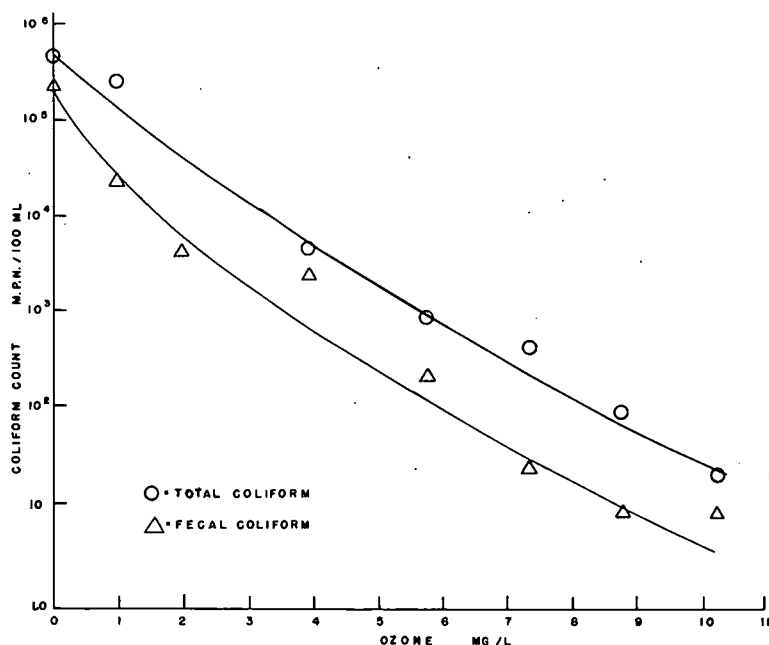


Figure 3. Total and fecal coliform reduction by ozonization.

Recent literature has shown that ozone is more effective than chlorine in removing virus from secondary effluents.^{15,25,26} Recent work has shown that approximately one ppm of ozone is required to remove polio virus from a secondary effluent.²⁷

Ozone Residual

Ozone is often considered as the choice of disinfectant because it is not harmful to the biota.² It is safe because no residual or harmful reaction products reach the receiving stream. Analysis of secondary effluents after treatment with up to 20 ppm of ozone do not show any true ozone residual. It appears that the rate of reaction of ozone in this concentration range (0-20 ppm) with carbonaceous materials is faster than the mass transfer step. Of course, true ozone residuals can be observed in secondary effluents when very high dosages (greater than 40 ppm) are applied.²⁸ In the high concentration ranges, the reaction is kinetically controlled rather than mass transfer controlled.

Without the presence of an ozone residual it is impossible to automatically pace ozone disinfection systems operating in the dosage range of 0-20 ppm. The present work has shown the existence of ozone reaction products which may be correlated with bacteria kill. In the previously shown ozone reaction scheme it was indicated that interaction of ozone with the carbon-carbon

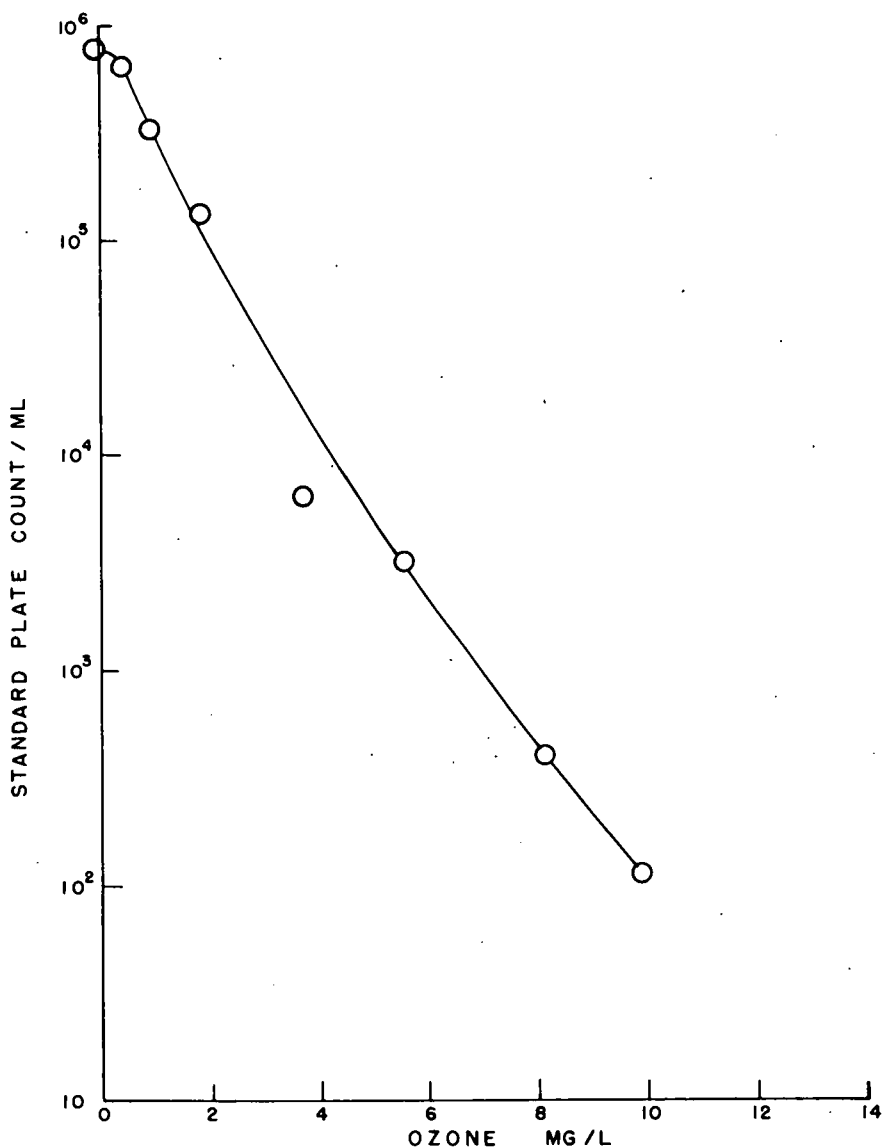


Figure 4. Standard plate count reduction by ozonization.

double bonds produces hydroperoxy alcohols. Compounds possessing carbon-carbon double bonds exist in all effluents after secondary biological treatment. The fact that peroxides are formed by the ozone reaction can be demonstrated by their free radical initiation of the polymerization of added styrene.

The exact nature of the peroxides formed by the ozone reaction depends on the structure of the molecule which contains the carbon-carbon double bond. Many of the different types of peroxides which can be formed include hydrogen peroxide, peracids, hydroperoxy alcohols and hydroperoxy ethers. Such peroxy compounds all react with potassium iodide to liberate iodine. The quantity of iodine generated can be readily determined by wet chemical, light absorption or amperometric techniques. Since it is impossible to identify which molecule in the secondary effluent has been attacked by ozone, it is impossible to determine the exact structure of the peroxide formed. It is convenient, therefore, to calculate the peroxide residual as a quasi ozone residual. Figure 5 shows that the quasi ozone residual increases as a function of the quantity of ozone absorbed by the secondary effluent. Increasing ozone residuals can also be correlated with decreasing total coliform counts. See Figure 6.

It is readily conceivable that peroxidic compounds might be harmful to the biota but toxicity studies show the contrary.^{2,38} Detailed studies of such compounds have shown that these peroxides are chemically very unstable and tend to decompose rapidly.^{29,30} They are also removed from the secondary effluent by oxidizing other molecules. The rate of removal to a given level depends on the initial concentration of these peroxides. See Figure 7.

Utilization of the above data shows that an ozone disinfection system can be automatically controlled by the analysis of the quasi ozone residual in a manner similar to the chlorine residual method.

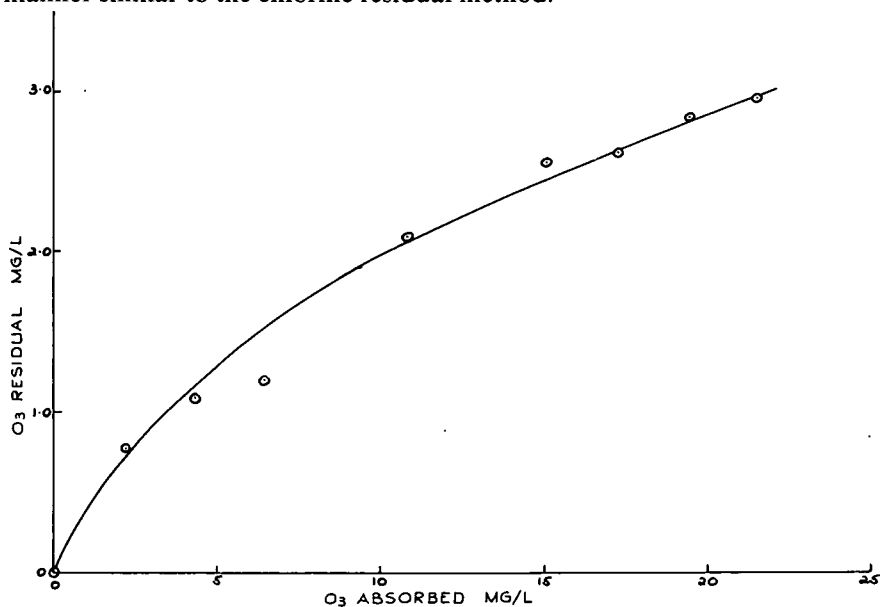


Figure 5. Increase of ozone residuals as a function of dosage levels, Millville secondary effluent.

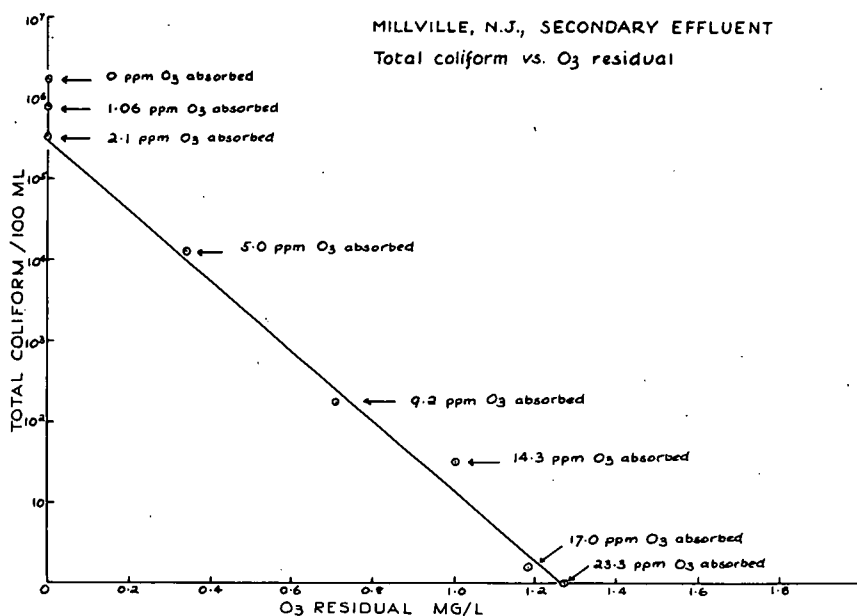


Figure 6. Total coliform as a function of ozone residual.

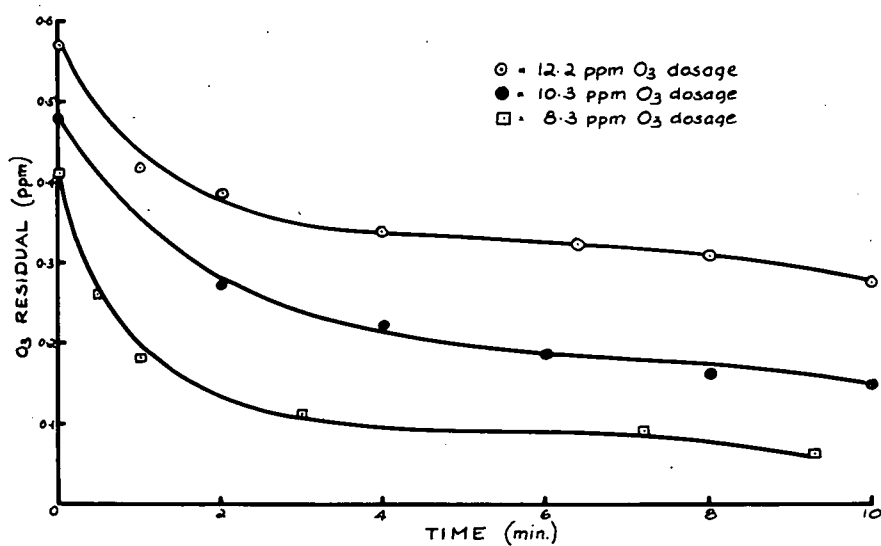


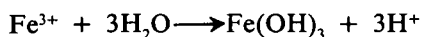
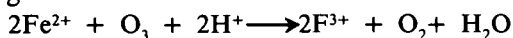
Figure 7. Rate of ozone residual decay.

Frothing Process and Contaminant Removal

Contaminant removal from secondary effluents proceeds by a two-fold process when ozone is properly applied. The classical method of pollution control with ozone is via chemical oxidation. With proper application, ozone can be used to produce a frothing operation that will also remove the pollutants by a physical flotation process. This process relies on the large volumes of inert gas introduced into the contact chamber with the ozone. (Recall that ozone is produced in one per cent weight concentration from air or 1.7 per cent from oxygen).

The utilization of this process does not require any additional ozone above that necessary for disinfection, but does require that the contact chamber be designed to remove the collapsed froth. Thus it can be envisioned that this secondary mode of pollution control would not require any additional capital or operating expense for ozone generating equipment.

Foulds, Wilson, and Clark³¹ have also observed frothing upon the ozonization of secondary effluents and theorize that a froth formed on the surface of the liquid in the ozone contact chamber may be stabilized by finely dispersed iron and manganese hydroxides formed by ozone oxidation of the naturally occurring metal ions in solution.³² These insoluble metallic hydroxide products act as coagulants for the organic material that is then floated to the surface of the liquid (rather than settling as would be the case in a clarifier) by the large volumes of gas flowing upward in the ozone contact chamber. Iron hydroxide is chemically produced with ozone by the following reactions:



In an effort to test the metal oxidation hypothesis, additional iron as ferrous ammonium sulfate was added to a secondary effluent, and the amount of froth formed on ozonization was measured. The results recorded in Table I clearly show that the addition of iron aids the process, yielding a greater amount of collapsed froth. In practice no additional iron salts need be added to the secondary effluent since there is an adequate concentration available as a natural background.^{33,34}

An alternate explanation may be envisioned where the frothing phenomenon is attributed to foaming induced by residual detergents present in secondary effluents. However, Ryckman^{5,6} has shown that ozone destroys the surfactant properties of anionic detergents by oxidative cleavage of the detergent molecule. The white detergent foam was replaced during ozonation by a thick, dark brown froth containing significant quantities of suspended solids that had been floated to the top of the contact chamber. This frothing was not observed in the absence of ozone when only air or oxygen was passed through the effluent. Only the white detergent foam was then

TABLE I
EFFECT OF ADDED $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ UPON
FROTH FORMATION

Amount of Iron Present	Weight of Collapsed Froth
Natural Background (0.29 ppm Fe)	11.6 g
Natural Background +5 ppm Fe added	21.8 g

observed, and no suspended solids flotation was evident.

The froth formed by this process is readily removed by a stationary skimmer installed in the top of the contact chamber. The stability of this gelatinous froth depends on the existence of moisture and large volumes of gas. When the froth flows into a skimming trough, the moisture and gas are no longer present and the froth collapses to a material that is analogous to secondary sludge. This process creates a super-clarifier that negates the use of sand filters or micro-straining apparatus. Studies have shown that ozone contact times in the range of ten minutes are adequate for the incorporation of the flotation process.

Visual Characteristics of Ozonated Effluent

Suspended Solids

The suspended solids not captured by the plant's secondary clarifier are readily removed from the ozone contact chamber by the flotation process previously described. Figure 8 shows that major portions of suspended solids can be separated by flotation and froth removal within the dosage levels of ozone required for disinfection. Field work with dynamic experiments has indicated that the suspended solids of an ozonized effluent are in the range of one to two ppm when the ozone contact chamber is properly designed.¹⁵

Turbidity

The turbidity of a secondary effluent is a composite of suspended solids and the dispersed colloidal matter. Removal of the suspended solids by flotation contributes to the turbidity decrease. Colloidal matter is material within a negatively charged spherical envelope. The negative charges of the sphere are neutralized by oxidation with ozone since this allotrope of oxygen often reacts as if it has a positive charge. Therefore, colloids are destroyed by a combination of charge neutralization and chemical oxidation. The complex nature of these reactions is composited in Figure 9, showing that ozone rapidly destroys the turbidity.

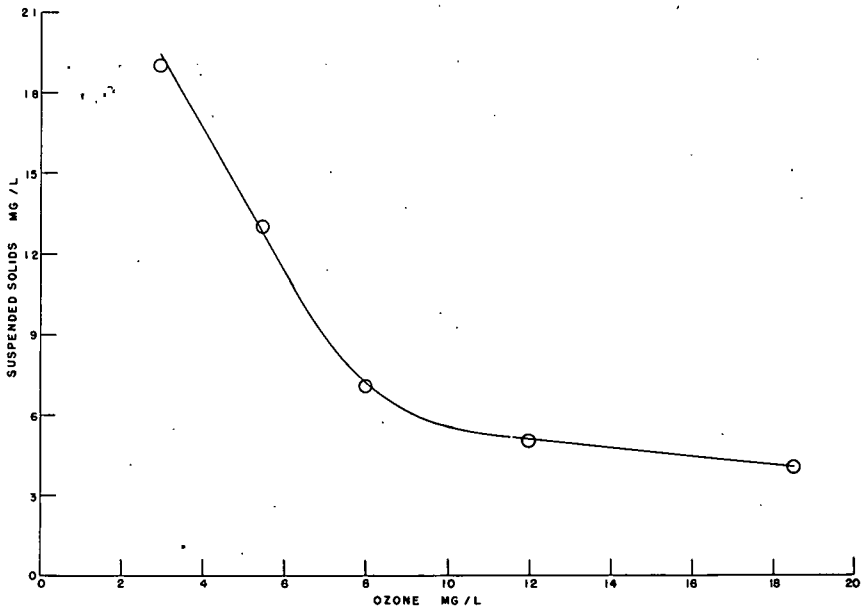


Figure 8. Suspended solids reduction by ozonization.

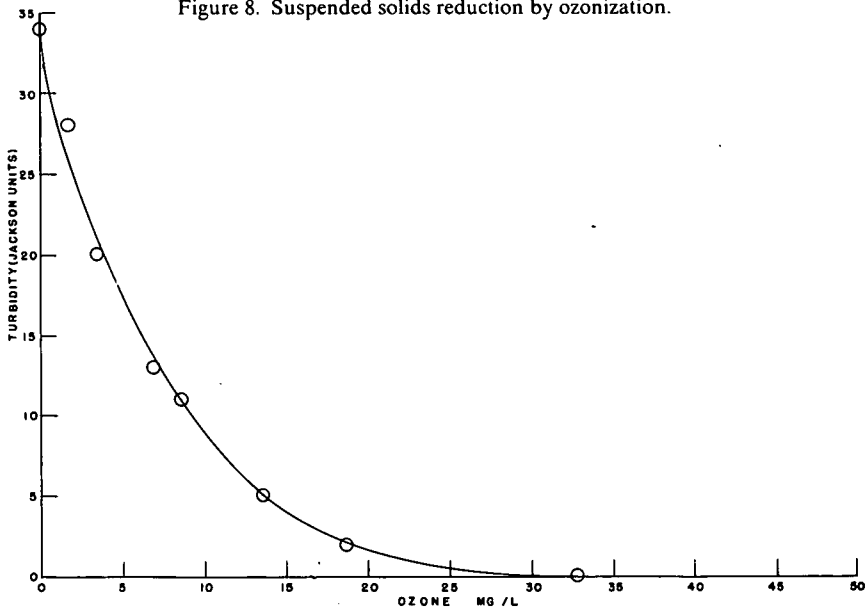


Figure 9. Turbidity reduction by ozonization.

Color

Color is most often caused by organic molecules having long chains of carbon-carbon double bonds that are conjugated with other functional groupings. Molecules of this type absorb light in the visible and ultraviolet region and reflect light in the visible spectrum. Breakage of the double bonds destroys such chromophoric groupings. Ozone is known as a double bond reagent, i.e. it is very effective in breaking double bonds. Large reductions in color are found when a secondary effluent is treated with ozone (Figure 10). Other workers^{12,13} have reported color reduction as high as 90 percent resulting from ozone treatment. Only small ozone dosages are required to remove substantial amounts of colored material. The combination of suspended solids, turbidity and color removal with ozone produces a secondary effluent that cannot be distinguished visually from potable water. Secondary pulp and paper mill effluents can also be decolorized with ozone,^{22,35} also effluents from synthetic dye operations.³⁶

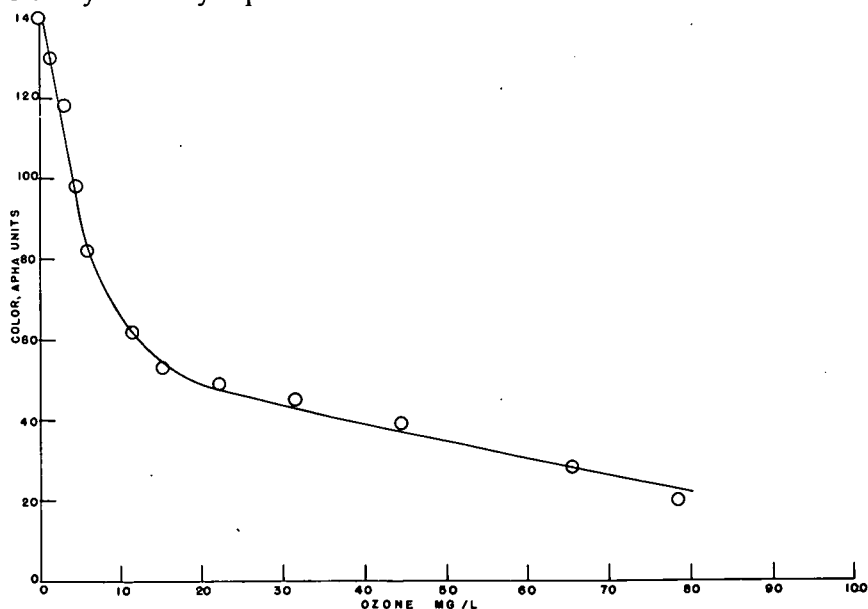


Figure 10. Color reduction by ozonization.

Removal of Carbonaceous Materials

Chemical Oxygen Demand

Reduction of COD levels of a secondary effluent via ozone oxidation and physical removal by frothing varied; however, an approximate correlation

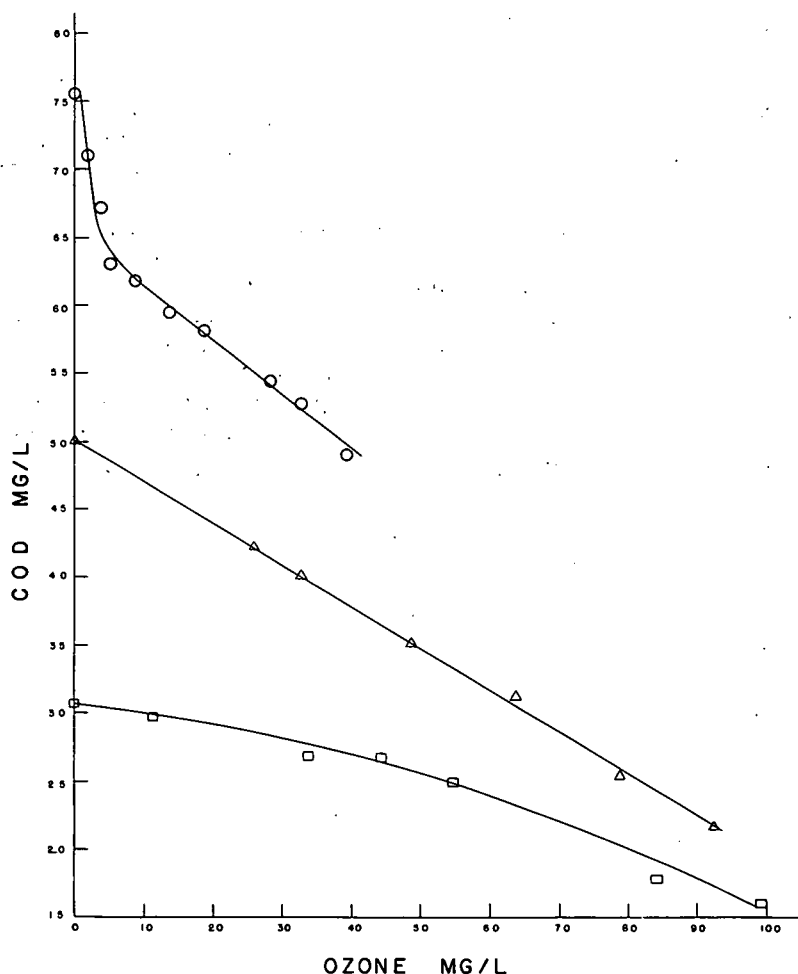


Figure 11. COD reduction of different secondary effluents.

could be made between the rate of reduction and the initial COD level of the effluent. Figure 11 depicts the decrease in COD upon ozonization of three samples of Millville, N.J., effluent collected at different times of the year. (Effluent collected during the winter had the highest initial COD, as might be predicted). The rate of COD lowering is generally proportional to the initial COD level. The higher COD effluents may contain a greater proportion of readily oxidizable organic materials, whose rates of reaction with ozone are often more rapid than those of the materials remaining after extensive secondary oxidation. These data show that it is virtually impossible to predict the exact amount of COD reduction to be expected from a given

ozone dosage level when grab sample techniques are employed; it depends on the inherent differences between various effluents, the nature of a given effluent, and the nature of its prior treatment. To obtain data that will allow COD predictions, a statistically significant number of experiments must be performed at various ozone dosage levels and effluent parameters.

Biological Oxygen Demand

The reduction of BOD_5 level of the ozonized effluent was less pronounced than the observed COD reductions. In some cases the soluble BOD_5 level of the ozonized effluent remained constant or actually increased slightly before being reduced (Figure 12). Initial increases in BOD_5 upon ozonization have been observed by previous workers.^{6,20} The COD decrease shows that oxidation is taking place in this secondary effluent. Non-biodegradable (refractory) organic compounds are made biodegradable by oxidation with ozone. Ozonation will introduce oxygenated functional groups into the refractory compounds, thus producing a site on the molecule where biodegradation can commence. The increase in the total amount of biodegradable compounds will, of course, exert an additional oxygen demand in the BOD_5 test. It should be noted that the refractory materials that are made biodegradable by ozonation are most often those materials that would have been otherwise toxic to the receiving stream.² The effect of mildly increasing BOD_5 values is generally observed in mixed industrial-municipal effluents and not in purely municipal effluents.¹⁵

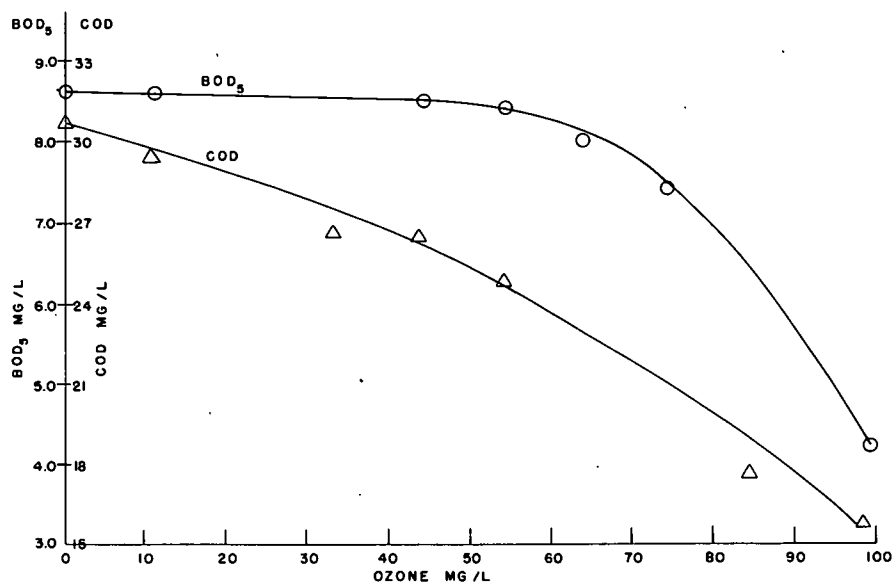


Figure 12. Concurrent COD and BOD_5 reduction by ozonation.

Oxidation of Nitrogenous Materials

Theoretically, all nitrogen-containing compounds should be oxidized by ozone to the nitrate (NO_3^-) anion. This prediction would be true if large enough dosages of ozone were applied. However, in ozone treatment, as in any other treatment process, practical limits are specified. The question then arises as to how much oxidation of nitrogenous materials can be expected if a practical limit (i.e., ozone dosage level) is specified.

Oxidation of Ammonia

Thermodynamic predictions indicate that ammonia should be readily oxidized to nitrate by ozone:



The literature^{8,10,11,12,13,20} records many inconclusive studies in this area. Laboratory results have shown only a mild reduction of ammonia despite high ozone dosage levels (Figure 13). These data indicate that the removal of ammonia from a secondary effluent is influenced by poor kinetics, utilizing ozone to oxidize carbonaceous materials rather than the ammonia. Although mild reduction of ammonia is seen, ozonolysis cannot be considered a nitrification process.

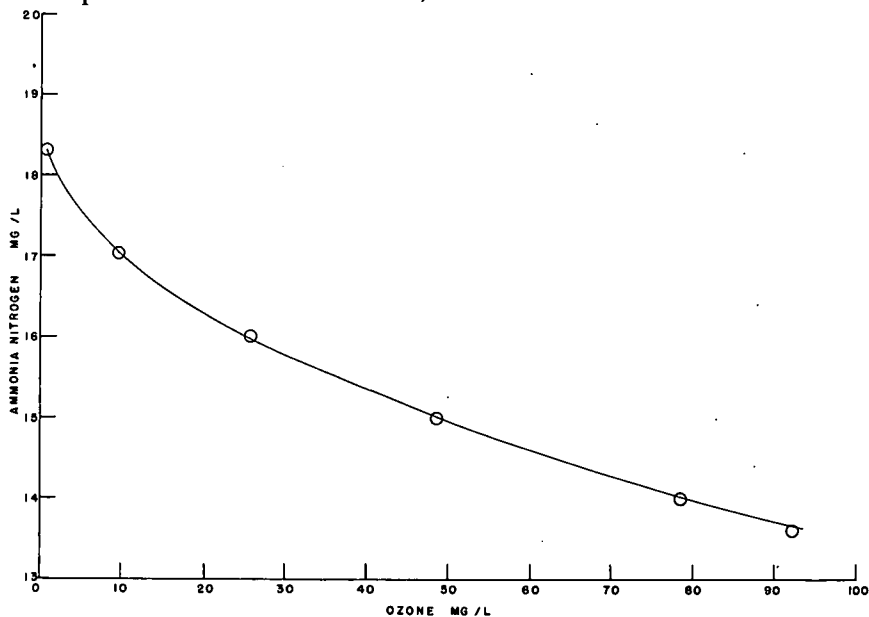


Figure 13. Ammonia nitrogen reduction by ozonization.

The efficiency of ozone disinfection is not greatly affected by the presence of ammonia, whereas the effectiveness of chlorine as a disinfectant is dependent on the amount of ammonia present. Ammonia is oxidized to the toxic chloramines by chlorine before the disinfection step occurs appreciably. Ozone disinfection can thus be considered as a process independent of the ammonia concentration.

Oxidation of Nitrite

Weingarden¹³ reported that small amounts of nitrite existing in secondary effluents are readily oxidized to nitrate by ozone. Since nitrite is so readily oxidized, it is not considered a severe pollutant in the small concentration in which it is normally found. Its ease of oxidation by ozone does not permit it to exert a BOD demand on the receiving stream. Figure 14 shows that nitrite was rapidly destroyed in the early stages of the laboratory ozone treatment. This oxidation is represented by the equation:

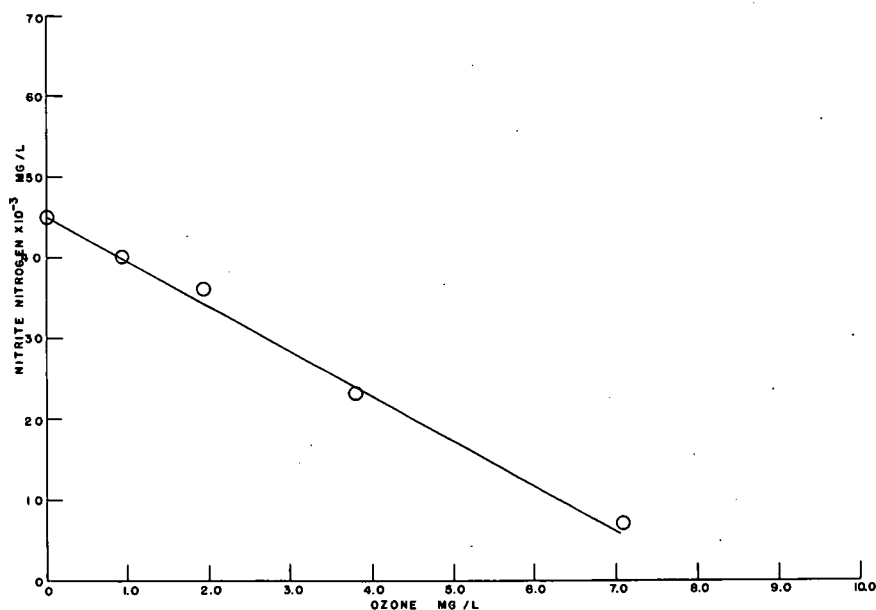
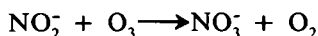


Figure 14. Nitrite nitrogen reduction by ozonization.

Increase in Nitrate Concentration

The oxidation of nitrogenous materials ultimately produces the nitrate anion. We have shown two processes that produce nitrate — the oxidation of nitrite and of ammonia. Certainly other paths of nitrate formation also influence the ozonolysis of secondary effluents. Figure 15 shows that only mild increases in nitrate concentration were experimentally observed despite the high levels of ozone applied.

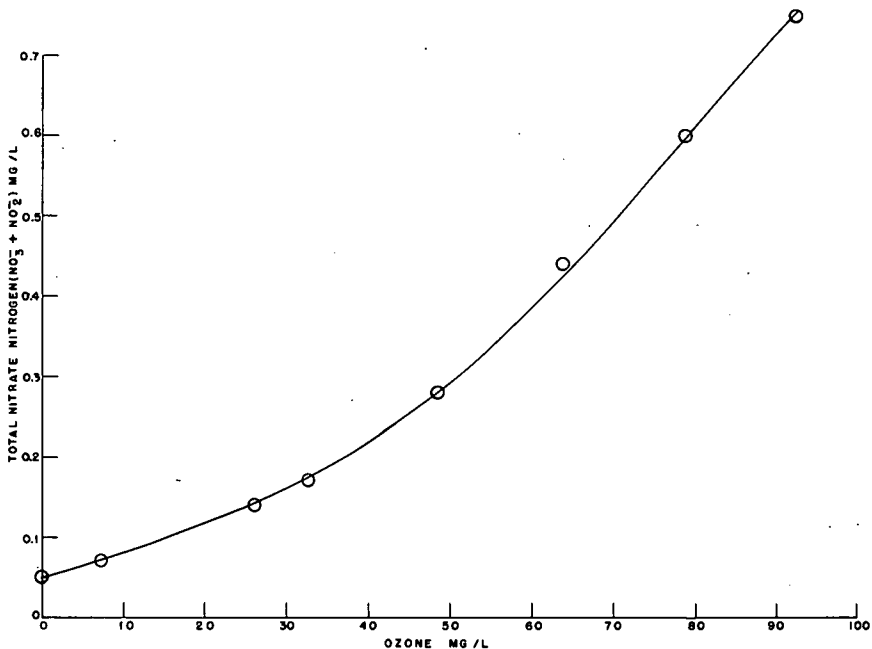


Figure 15. Total nitrate nitrogen increase by ozonization.

Effect of Ozonated Secondary Effluent on The Environment

Dissolved Oxygen Levels

Consideration of BOD_5 changes on ozonization must take into account the complete oxygen saturation of the effluent as an inherent part of the ozone treatment process. Table II depicts the amount of dissolved oxygen observed in the effluent as a function of the ozonized gas applied.

TABLE II
DISSOLVED OXYGEN CONTENT
OF OZONIZED EFFLUENT

Feed Gas	Ozone in Feed Gas (Wt. %)	Ozone Dosage to Effluent (mg/l)	Dissolved Oxygen in Effluent (mg/l)
Air	1.2	0	5.2
"	"	3.3	8.9
"	"	10.0	9.3
Oxygen	2.2	0	5.2
"	"	3.4	25.7
"	"	10.7	40.0

Note that use of oxygen feed gas at moderate ozone dosage levels results in a dissolved oxygen content of the effluent of 40 mg/l. Proper discharge of the ozonized effluent (containing the high D.O. level) below the surface of the final receiving stream will allow utilization of the available oxygen for the normal biological purification processes. In this manner the dissolved oxygen content of the receiving stream can be increased before the oxygen is lost to the atmosphere by equilibration. Because many discharge requirements are written with respect to a maximum BOD₅ content of the effluent, a credit can sometimes be obtained for the oxygen content of the discharged effluent above that of the receiving body of water. For example, an ozonized effluent having a BOD₅ of six mg/l and a D.O. level of 40 mg/l in effect has a negative BOD₅ of 34 mg/l. In all cases the need for a post aeration step is eliminated by the ozone disinfection step.

Phenol Removal

Phenol, C₆H₆O, is considered to be a stringent water pollutant. Annually, 1.5 billion pounds are produced domestically. This fundamental building block of the chemical industry finds uses in almost every manufacturing facility. Phenol is a water soluble material often used as a disinfectant, suggesting that it is toxic in nature and not very biodegradable. Shock loads of phenol have been known to kill the bacteria in an activated sludge process.

The severity of phenol pollution is felt in potable water. Since portions of the phenolic compounds are not completely biodegraded in the secondary process, they are expelled intact to the receiving stream. These materials are subsequently treated with chlorine in a potable water processing plant and are transformed into chlorophenols that are related to commercially produced insecticides and have been shown to taint the taste of fish. Chlorophe-

nols are more toxic and less biodegradable than the parent compound, phenol. Furthermore, chlorophenols have odor and taste thresholds approximately two orders of magnitude lower than phenol itself. Consequently most of the potable water in the large cities of our nation tastes and smells of "chlorine". Detailed analysis of these waters indicates that the taste and odor of chlorine does not come from chlorine itself but rather from products of chlorination, the chlorophenols.

The most practical way of eliminating this taste and odor problem is to eradicate its source, the phenolic materials in our effluents. Phenol has been removed from industrial effluents with ozone for over a decade.³⁷ An investigation of a purely municipal effluent has shown that trace amounts of naturally occurring phenol escape oxidation in an activated sludge system. Weingarden¹³ has shown that trace amounts of phenol are completely destroyed by ozone during the disinfection process. The ozone oxidation products of phenol are oxygenated materials that are nontoxic and biodegradable.³⁸ One of the first stable ozone oxidation products of phenol is the biodegradable *cis-cis* muconic acid. Large ozone dosages will oxidize this phenolic material to water and carbon dioxide.³⁹

A small amount of pure phenol was added to a secondary effluent sample before ozonization. Samples were taken as ozone addition continued and were immediately analyzed for residual phenol. Table III shows that phenol reduction is quite rapid at relatively low dosages of ozone. Although the lower limit of phenol detection was 0.05 ppm for the present study, Weingarden has shown that ozonization can remove phenol in the sub-ppm region.¹³

TABLE III
REDUCTION OF ADDED PHENOL BY OZONE

OZONE DOSAGE ppm	PHENOL CONCENTRATION ppm
0	0.73
1.2	0.56
3.4	0.05
6.8	<0.05
10.8	<0.05

pH Changes

A shift in the pH can be expected when ozone is employed as an oxidant for a secondary effluent. The formation of weak carboxylic acids from hydrocarbons would tend to reduce the pH. The carbon dioxide produced in the activated sludge process is removed by sweeping large volumes of air or oxygen through the sewage in the ozone contact chamber; this process tends

to increase the pH. These changes in pH are undoubtedly masked to a large extent by the large buffering capacity of domestic sewage.

Recently, workers at the Washington, D.C. Blue Plains treatment plant have reported¹⁴ that ozonolysis always shifts the pH towards neutrality, regardless of the nature of the secondary effluent to which ozone was applied. This observation was confirmed in a static experiment with large ozone dosages (Figure 16). Notice that large amounts of ozone must be applied before minor shifts in the pH occur.

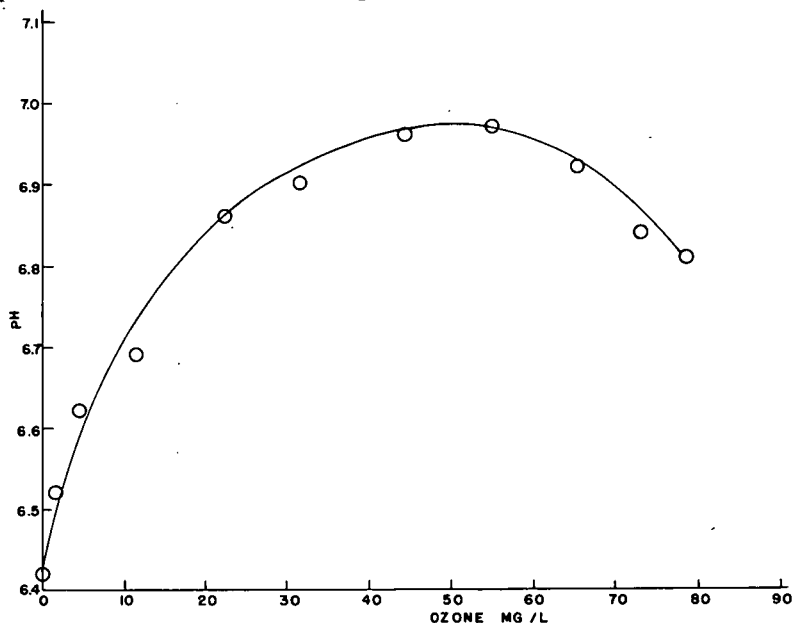


Figure 16. pH change by ozonization.

Cyanide Removal

Small amounts of cyanide are normally found in secondary effluents. These cyanide concentrations are usually not large enough to pose any health hazard to humans. Concentrations of cyanide are sub-ppm but it is nevertheless interesting to note that ozone will effectively destroy cyanide. Figure 17 shows that 6 ppm of ozone will destroy all the naturally occurring cyanide in a secondary effluent. The product of cyanide oxidation is cyanate anion (CNO^-). Cyanate is a nontoxic anion which is readily biodegradable and is also destroyed in the receiving stream by hydrolysis to ammonia and carbon dioxide. The use of ozone for cyanide oxidation has been practiced on a commercial basis for many years.⁴⁰ Thus, disinfection with ozone becomes important in municipal treatment plants where the possibility of cyanide influx from industry is prevalent.

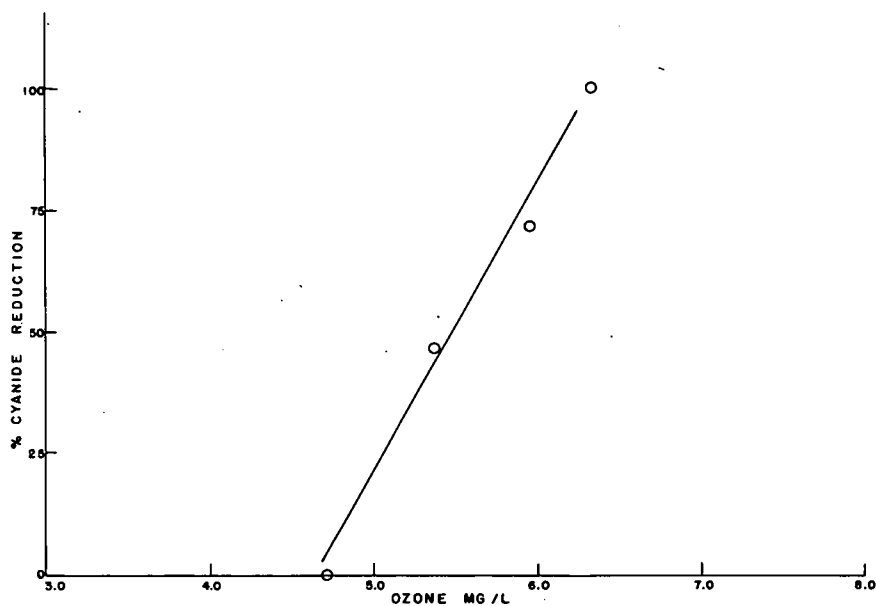


Figure 17. Cyanide reduction by ozonization.

Detergent Removal

Detergent foaming in treatment plant receiving streams was a severe problem prior to the introduction of biodegradable surfactants. The destruction of detergents by ozone oxidation is therefore well documented in the literature,^{5,10,12} since ozonolysis was considered as a solution to this problem.

Although problems associated with detergent foaming have been greatly reduced by the introduction of linear carbon chain detergents that are biodegradable, small amounts of detergents nevertheless can escape secondary treatment and cause problems. In addition, small fractions of the detergents may consist of branched-chains that are not amenable to biological oxidation. Detergent levels in the range of 1 to 4 mg/l are frequently seen in secondary effluents and are capable of generating foam.

Figure 18 illustrates the destruction of ABS and LAS detergents observed in laboratory ozonization of secondary effluent. While disinfection of a secondary effluent is being accomplished with ozone, substantial reductions in detergent levels are realized. In no case was any detergent foam observed in a secondary effluent that had been disinfected with ozone.

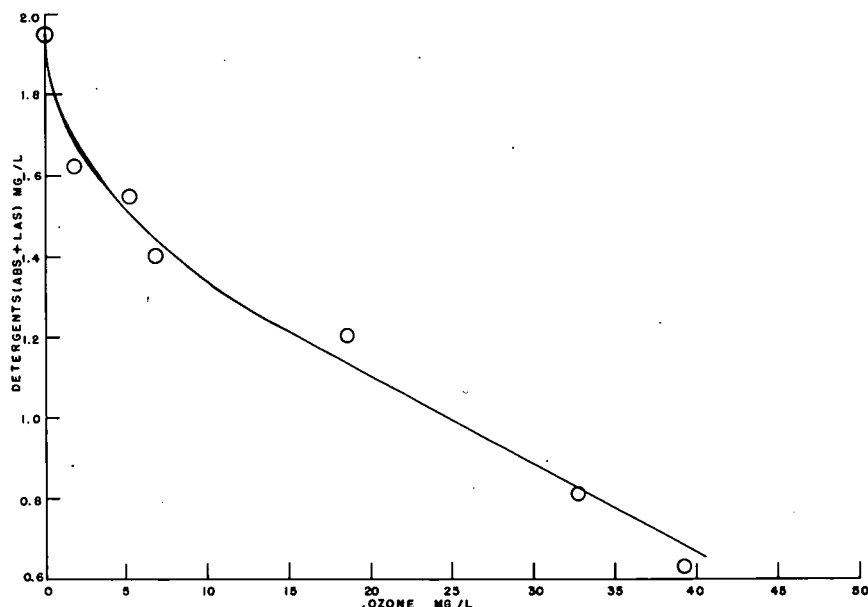


Figure 18. Detergent reduction by ozonization.

Pesticide Removal

The removal of toxic pesticides from surface waters remains an important ecological problem. It is obvious that a total ban on pesticides is not a practicable solution; we must therefore seek other solutions that will have a smaller impact on our way of life. Most pesticides are of the chlorinated hydrocarbon type whose composition makes them resistant to biological degradation; their removal from surface water must be accomplished either by physical or by chemical means.

Several workers have shown that ozone can be employed to reduce or eliminate organic pesticides.^{10,12} Ozone will react rapidly with most pesticides because these materials often contain carbon-carbon double bonds. Gardiner and Montgomery¹⁰ observed substantial lowering of pesticide concentrations when effluents containing chlorinated hydrocarbon pesticides were treated with ozone. In this study γ -BHC, Dieldrin, DDT and TDE were added to the sewage effluent. Dieldrin and γ -BHC were removed at approximately the same rate, about 50 per cent of each disappearing with the absorption of 20 ppm O_3 . A more rapid removal was observed with DDT and TDE.

Safety Considerations

Large-scale unit operations such as those under discussion should always be viewed in light of safety precautions. Ozone, being a very powerful oxidant, is also a toxic compound. When ozone is used for water pollution control it does not come in contact with man nor is it allowed to escape into the atmosphere; i.e., it is used under controlled conditions. Note that ozone is generated on-site and used immediately; there is no shipping, handling or storage of toxic materials. If all the ozone at a plant site treating 100 MGD of effluent with ten ppm ozone escaped at any one instant, only a few pounds of ozone would be released to the atmosphere; this certainly would not be sufficient to cause a fatality. The human nose can detect less than 0.01 to 0.02 ppm ozone in the atmosphere, and it is not possible to become insensitive to the odor of ozone. In the seventy years of large scale ozone usage for disinfection of potable water throughout the world, no known death has been attributed to ozone, yet fatalities are attributed to the use of chlorine almost monthly.

The human tolerance for ozone depends on ozone concentration and time of continuous exposure. The maximum allowable concentration of ozone in an enclosed area for continuous exposure is 0.1 ppm as determined by the American Council of Governmental Industrial Hygienists. The human tolerance for ozone is portrayed in Figure 19.⁴¹ Note that a deleterious condition can only exist when a combination of high ozone concentration and long exposure time occurs.

Conclusions

The above data have demonstrated that ozonization of secondary effluent is an effective method of disinfection, and effects a degree of tertiary treatment at no additional cost. Ozone dosages of five to ten mg/l can disinfect to a level below most legal requirements. Higher ozone dosages will probably be required if the effluent contains a significant amount of industrial loading that contains ozone oxidizable materials.

The concurrent decrease of COD and coliform levels with ozonization argues against the necessity of satisfying an "ozone demand" due to dissolved organics before any disinfection can occur. Indeed, since the disinfecting ability of ozone is ascribed to its high oxidation potential, it seems logical that disinfection and contaminant removal would occur simultaneously, although not all materials in solution will react at the same rate.

An added benefit of ozone disinfection is an ozone-induced frothing process capable of removing significant amounts of suspended and dissolved material via oxidation and physical separation by flotation. Exact reductions cannot always be predicted due to the variable nature of the effluent. Installation of suitable froth skimming devices in an ozone contact chamber would allow tertiary treatment as an adduct to disinfection.

Ozone should be given serious consideration as an alternate to chlorination for disinfection of secondary effluents, especially in view of the toxic nature of chlorinated effluents. In addition to coliform and other bacteria, ozone has also been shown to be effective against viruses.^{26,32} On-site generation of ozone avoids the storage of large quantities of hazardous gas. Small treatment plants could employ an air-feed ozone generator, while large requirements would be met by an oxygen-feed gas system.

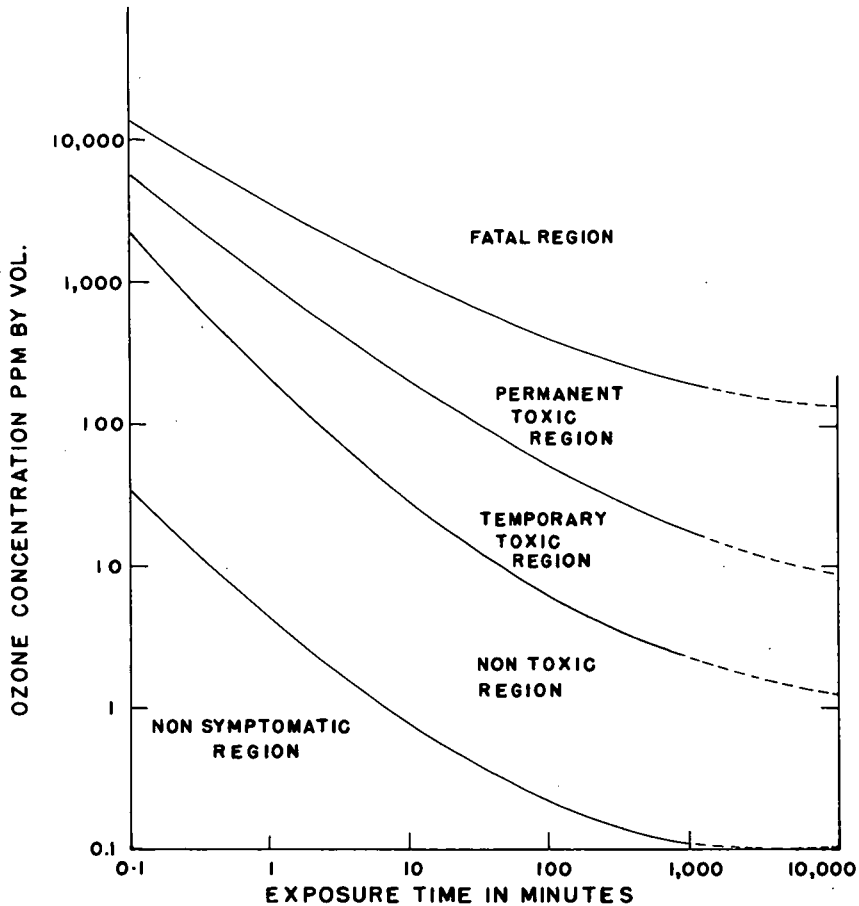


Figure 19. Human tolerance for ozone.

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