

# EFFECT OF PRE-OZONATION ON REMOVAL OF ORGANIC MATTER DURING WATER TREATMENT PLANT OPERATIONS

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## ABSTRACT

Pre-ozonation altered removal of organic matter during bench or full-scale water treatment through two main effects. First, pre-ozonation directly removed organic matter by mineralization, volatilization and/or stripping reactions, improving removal in comparison to unozonated systems. On the other hand, pre-ozonation decreased the surface charge of floc formed after coagulation with hydrolyzable metal salts, hindering adsorptive removal of the anionic organic molecules by floc surfaces and/or inducing stabilized floc formation; changes that decrease removal in comparison to unozonated systems. The relative importance of the two effects determined whether pre-ozonation enhanced or hindered removal of organic matter. In most water treatment plants pre-ozonation is predicted to have an adverse effect on physical removal of organic matter at ozone doses above about 0.7 mg O<sub>3</sub>/mg TOC, while enhanced removal may occur if relatively high concentrations of volatile organic matter are present. In ancillary results, pre-ozonation hindered turbidity removal and increased the concentration of coagulant metal residuals in finished drinking water at low coagulant doses.

## KEYWORDS

Coagulation; Ozonation; Natural Organic Matter; TOC; THMFP; Sedimentation; Filtration.

## INTRODUCTION

Pre-ozonation of water sources containing natural organic matter (NOM) may alter TOC and particle removal processes, and increase the concentration of coagulant metal residuals in finished drinking water. Reactions of ozone with NOM, which decrease the MW and increase the acidity of the organic molecules, induce some of the aforementioned phenomena by altering coagulant-organic matter interactions. This section reviews previous reports of ozone-induced alterations to metal residual formation and TOC removal.

Ozone-induced increases to coagulant metal residual concentrations have been reported by a number of investigators (Van Breeman et al., 1979; Gervai et al., 1985; Jekel, 1986; Jekel and Heinzmann, 1989; Edwards and Benjamin, 1992a,b). These metal residuals may either be a soluble metal-organic complex or a stabilized colloid, and recent work (Edwards and Benjamin, 1992a,b) has identified the cause of metal residual formation. Under conditions typical of water treatment, most metal residuals formed after pre-ozonation are stabilized colloids (Figure 1). Increasing ozone doses decrease the surface charge of floc that forms at a given coagulant dose (due to sorption of more anionic organic charge to floc surfaces after

ozonation) producing stabilized flocs at certain coagulant doses. These findings confirmed a hypothesis of Jekel *et al.* (1986 and 1989) and are consistent with observations of Van Breeman *et al.* (1979). Soluble metal residuals are dominated by oxalate-metal complexes (oxalate is an ozonation by-product) that are significant only at high ozone doses (Edwards and Benjamin, 1991 and 1992a,b).

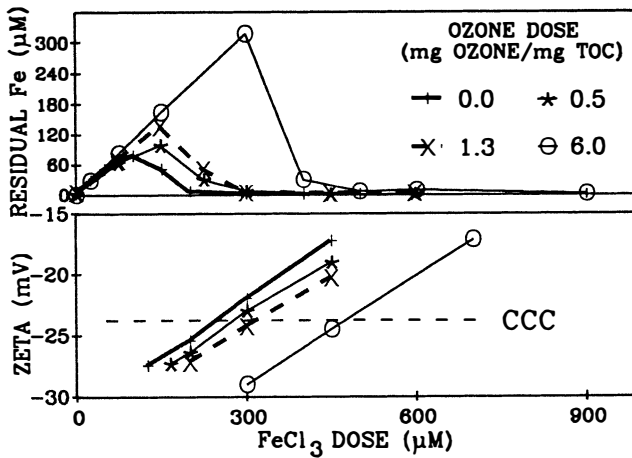


Fig. 1. Stabilized colloidal iron residuals forming after ozonation, coagulation, and filtration (above) arise from ozone-induced decreases to floc zeta potential (below). From Edwards and Benjamin (1992b).

Effects of ozone on TOC removal by metal oxides/hydroxides have been studied using two different approaches. In one study ozonated NOM was exposed to activated alumina (Chen *et al.*, 1987), in which case NOM sorption and removal increased with ozone dose. Other studies have examined removal of ozonated NOM via coagulation (Van Breeman, 1979; Reckhow and Singer, 1984; Jekel, 1986), and ozonation generally interfered with or had no effect on TOC removal. Recently, coagulation of ozonated NOM was investigated over a wide coagulant dose range (Edwards and Benjamin, 1992b) and ozonation improved, had no effect on, or hindered TOC removal depending upon coagulant dose (Figure 2). That work differentiated between components of TOC removal occurring through ozonation or coagulation, and combined TOC removal (Figure 2) is the sum of these two components. As before, the floc surface charge was decreased by ozonation at low or moderate coagulant doses (Figure 2), hindering removal of anionic organic molecules. At high coagulant doses surface charge was not a function of ozone dose, and in this coagulant dose range ozone had no or slightly positive effects on combined (overall) TOC removal.

While the recent experiments elucidated a fundamental basis for ozone-induced alterations to TOC removal and metal residual formation, applicability of the findings to full-scale systems and/or conventional operating conditions required confirmation. Thus, the goal of this work was to investigate effects of bench or full-scale ozonation on removal of organic matter during water treatment processes. Effects of ozone on metal residual formation or turbidity removal were examined as part of that evaluation.

## MATERIALS AND METHODS

The basic experimental protocol included pre-ozonation, coagulation, and sedimentation and/or filtration water treatment steps. Pre-ozonation was conducted at a 40 MGD water treatment plant (North Bay Regional (NBR) Water Treatment Plant Vacaville, CA) in the second week of June, 1991, at bench scale at the University of Washington, or via pipette transfer from standard ozone solutions as described in specific experiments. The air/liquid ratio ( $l_{\text{air}}/l_{\text{water}}$ ) was constant at 0.15 at full scale and 0.20 at bench scale, with ozone dose varied by manipulation of the gas phase ozone concentration. Two influent water sources are used at NBR (Table 1).

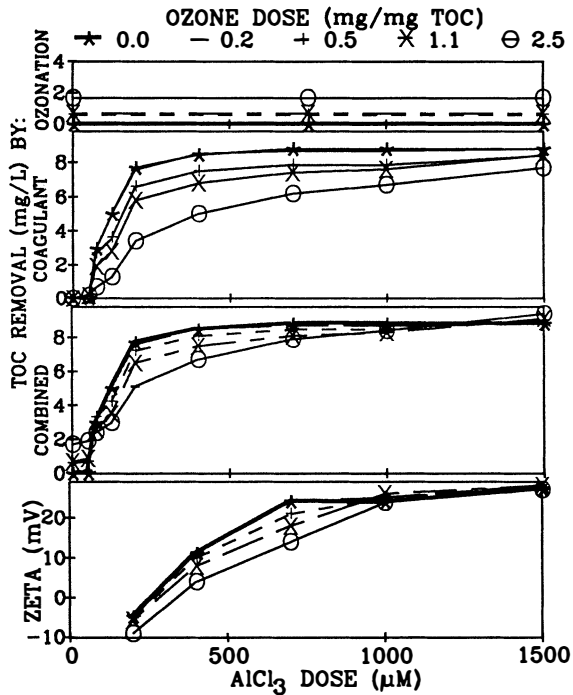


Fig. 2. TOC removed by ozonation, coagulation and filtration, and a combination of processes (upper) was influenced by flocculation zeta potential (below). From Edwards and Benjamin (1992b).

TABLE 1 Water Sources at the NBR Treatment Plant

Constituent	Water 1	Water 2
TOC (mg/L)	2.0-4.0	3.0-17.0
pH	8.0	7.7
Alkalinity (as $\text{CaCO}_3$ )	112	153
Hardness (as $\text{CaCO}_3$ )	114	168
Turbidity (ntu)	29.9	2.92
Color (Pt-Co Units)	60	10
Conductivity ( $\mu\text{mhos/cm}$ )	339	311
Bromide (mg/L)	< 0.2	0.34

Coagulant chemicals were prepared according to manufacturers' recommendation. Alum solutions at the plant were 20 g/L, ferric chloride was diluted to 20 g/L from a 42.5% solution (Imperial West Chemical), and poly-aluminum chloride (PACl) was used as shipped from the manufacturer (Westchlor FA 2000). Coagulation and flocculation were conducted in jar tests at the water treatment plant or at the University of Washington according to the following procedure. To start, six water samples were gang mixed at 300 rpm, and the pre-selected coagulant dose was injected into the center of the mixer. After 30 seconds at 300 rpm, flocculation speeds were maintained at 70 and 45 rpm for 5 and 10 minutes, respectively. In tests at the water treatment plant, solutions then settled quiescently for 30 minutes before sample collection from a tap located about 2.5 inches above the sludge blanket. The first 10 ml of sample were wasted, with the final sample analyzed for TOC, THMFP, soluble and particulate metals, and turbidity. In bench tests at the

University of Washington, coagulation was followed by a 2-foot (~600mm) deep bench scale rapid sand filter run at 5 gpm/sft (~12.5m/h), with effluent samples collected and analyzed for TOC and coagulant metal residuals.

TOC and THMFP were determined at the water treatment plant or at the University of Washington. THMFP measurements followed the method of Chang and Singer (1991) with the exception that a single (2.5 mg chlorine/mg TOC) chlorine dose was tested. Residual chlorine in samples ranged from 0.2 to 0.8 mg/L after the seven day incubation period. Iron and aluminum were analyzed with flame AA, and particle zeta potentials were determined with a zeta meter (Penkem System 3000).

## RESULTS AND DISCUSSION

Experimental results are organized into three sections. The first examines the direct removal of TOC or THMFP by pre-ozonation. Thereafter, coagulant doses were optimized for turbidity removal, and effects of pre-ozonation on turbidity removal are evaluated. A final section explores the impact of pre-ozonation on overall TOC removal during water treatment processes, including conventional treatment (coagulation/sedimentation) or direct filtration.

### Direct Removal of Organic Matter By Ozonation

Direct removal of organic matter by ozone was examined by bench and full-scale experimentation. Each water source at NBR was ozonated at bench scale using doses of 0.0, 0.5, 1.5, or 2.4 mg O<sub>3</sub>/L. After ozonation TOC and THMFP were determined and compared to their values before ozonation. For samples aerated without ozone (0.0 mg O<sub>3</sub>/L in Figure 3), the only possible mechanism of TOC and THMFP removal is stripping. In unozonated water 1, stripping removed about 25% of the TOC and 30% of the THMFP, while nearly no TOC or THMFP was removed from unozonated water 2. As ozone dose progressively increased to 2.4 mg/L, TOC and THMFP in each water increased slightly. These results are surprising because they indicate a link between TOC and THMFP removal, while ozone is generally believed to directly destroy THMFP without affecting TOC (Chang and Singer, 1991). Even more surprising is the fact that most removal occurred via stripping and not from reactions with ozone.

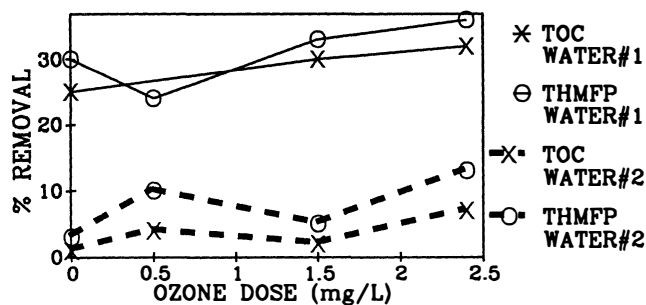


Fig. 3. Direct removal of TOC or THMFP by ozonation (ozone and aeration).

Recently, Chang and Singer (1991) reported TOC and THMFP concentrations at 6 full scale treatment plants before and after ozonation. Using that raw data and triplicate analysis of samples collected during full-scale operation in this work, THMFP and TOC removals by ozonation were calculated (Figure 4). Once again, there appears to be a significant relationship between TOC and THMFP removal. THMFP removals are less than 15% whenever TOC removals are insignificant (<3%), consistent with the conventional wisdom that ozone can destroy some THMFP directly without removing TOC. However, THMFP removals were highest (>15%) only when TOC removal was above 15%, suggesting THMFP removal is more closely linked to TOC removal than previously suspected. Other data is consistent with this

hypothesis. The average TOC removal in the Chang and Singer work (1991) reported above was 8% while THMFPP removals averaged 14%. Similarly, Veenstra et al. (1983) measured mean TOC removal by ozonation of 9% vs. a mean THMFPP removal of 15% over an 11 month study on a single water source.

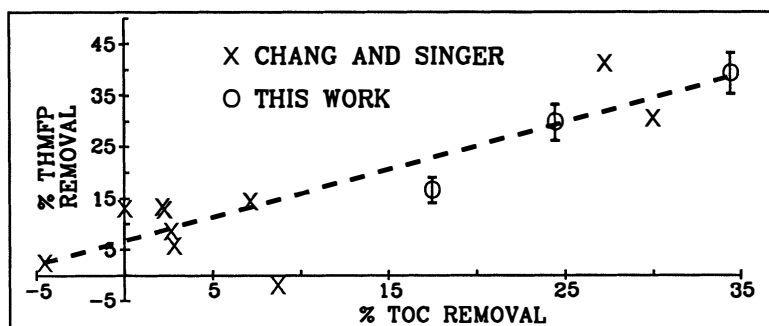


Fig. 4. Direct removal of TOC and THMFPP by ozonation at full-scale water treatment plants.

In sum, THMFPP removal during ozonation occurred as the result of direct NOM-ozone reactions and TOC removal. Removal of TOC during full-scale ozonation may be substantial (>15%), even though typical removals are less than 6%. While the mechanism of TOC removal at full-scale operation was not determined, results of bench tests coupled with the common observation that ozone does not significantly destroy TOC (by direct reactions) suggest stripping may be important.

#### Effect of Ozonation on Turbidity Removal

Coagulants were screened in jar tests at the water treatment plant to identify "optimal" coagulant doses for later experiments examining effects of ozone on turbidity and TOC removal. Impacts of ozone on turbidity removal are presented in this section, while effects of ozone on TOC removal are discussed in the section that follows.

The three coagulants tested had a broad optimal coagulant dose range for turbidity removal (Figure 5), though performance at lower coagulant doses deteriorated noticeably. On the basis of these results a low, moderate, and high coagulant dose was selected that spanned the range of effective turbidity removal. Thereafter, four water samples were produced at full-scale ozonation at doses of 0.0, 0.8, 1.6, or 2.5 mg O<sub>3</sub>/L, and each sample was coagulated with either alum, ferric chloride, or PACl at the "optimal" coagulant doses for each coagulant. Ozonation had no discernible impact on residual turbidity after settling, though a slightly adverse effect may have been observed above 1.6 mg O<sub>3</sub>/L (0.5 mg O<sub>3</sub>/mg TOC) for alum coagulation (Figure 5) consistent with operator experience at this plant. As a final point, pre-ozonation had no obvious effects on either floc particle size or settling velocities, nor did pre-ozonation alter metal residual concentrations after coagulation.

Pre-ozonation is often reported to alter floc particle settling, optimal coagulant doses, and the size of the floc particles produced during flocculation. Based on those reports experienced plant operators at NBR would typically increase alum doses by 15-30% when low or no ozone doses were applied, attempting to compensate for loss of the "coagulant-aid" (ozone). In these tests at least, ozone had no positive effects on turbidity removal via coagulation and sedimentation using alum alone. This is consistent with recent observations (Edwards and Benjamin, 1991; Reckhow, Edzwald, and Tobiason, 1991) and the fact that beneficial effects of ozone usually occur at doses lower than those applied at conventional (coagulation/sedimentation) treatment plants (Reckhow et al., 1986).

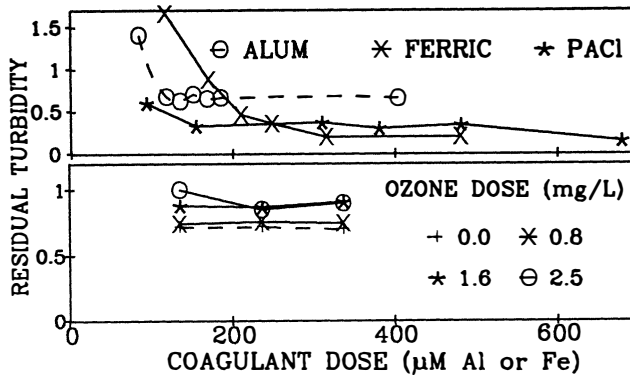


Fig. 5. Residual turbidity using various coagulants (above), and effect of ozone (below).

#### Effects of Ozone on TOC Removal During Water Treatment

The final section examines effects of ozone on TOC removal. Two different types of treatment were investigated, including conventional treatment and direct filtration.

**Conventional Treatment.** The experimental protocol in this section was identical to that in the earlier tests on turbidity removal. Four waters were collected after full-scale ozonation at doses of 0.0, 0.8, 1.6, or 2.5 mg/L, respectively. Thereafter, the samples were coagulated at low, moderate, and high coagulant doses for which turbidity removal was optimal before ozonation. After flocculation and settling, TOC removals that occurred via a combination of ozonation and coagulation were determined.

In the unozonated water alum and ferric chloride were nearly identical in TOC removal efficiency when plotted as a function of coagulant dose (Figure 6). Maximum TOC removal attained was about 60% (2.0 of 3.4 mg/L TOC initial), and only a 15% improvement in TOC removal was obtained by increasing coagulant dose from about 120 to 320 µM. In ozonated waters, TOC removal decreased as ozone dose increased above (0.5 mg O<sub>3</sub>/mg TOC), and adverse effects of ozone decreased with increasing coagulant dose. Similar results were observed with PACI.

Five months later, a sample was collected from the plant and shipped to the University of Washington. This sample was split into two sub-samples, one of which was ozonated at a dose of 2.5 mg/L (dosed from a standard ozone solution via the method of Reckhow) and the other was unozonated. Each sub-sample was then coagulated with the "low" coagulant dose used in the earlier tests and zeta potentials of the flocs were determined after pH adjustment to a constant value. TOC was then quantified after membrane filtration (0.45 µm). TOC after coagulation was 3.0 mg/L in the ozonated sample vs. 2.4 mg/L in the unozonated sample, a 15% decrease in TOC removal (3.7 mg/L initial TOC). The zeta potential of the flocs was also lowered by ozonation, +8 mV in the unozonated sample vs. -1 mV in the ozonated sample, suggesting that the more negative (less positive) floc surface charge was at least partly responsible for hindered removal of the anionic organic molecules from solution. This is consistent with arguments presented in the introduction and elsewhere (Edwards and Benjamin, 1992b).

**Direct Filtration.** Bench scale direct filtration experiments were conducted at the University of Washington after pre-ozonation from standard ozone solutions, ferric chloride coagulation, and flash mixing of a model water containing 3 mg/L NOM TOC, 0.5 mM NaHCO<sub>3</sub>, 5 mM NaCl at a pH of 7.5. The coagulant dose was selected to give a particle zeta potential of -12 mV in the unozonated sample, just beyond the critical level of zeta potential required for effective particle destabilization in this system (found to be about -14 mV in preliminary tests). Three influent samples were produced using ozone doses of 0.0, 0.3, or 0.6 mg O<sub>3</sub>/mg TOC producing flocs with zeta potentials of -12, -14, and -16 mV, respectively.

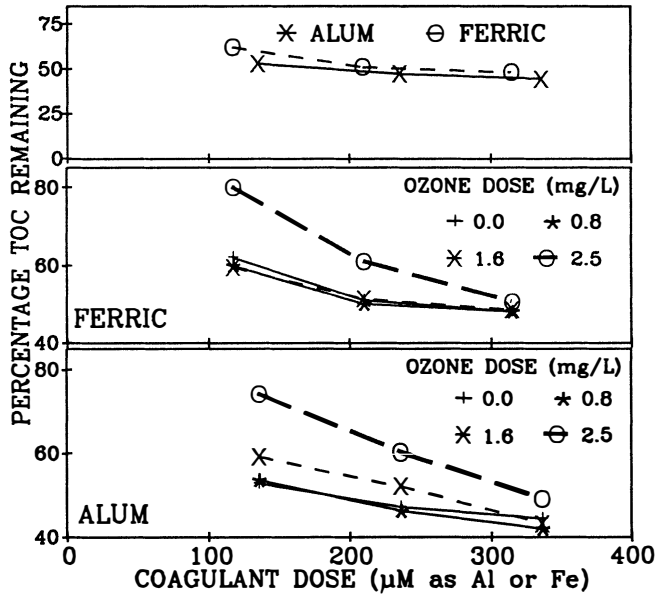


Fig. 6. TOC removal by coagulants (above), and effect of ozone on overall TOC removal (lower graphs).

Each influent was applied to filters at 5 gpm/sft, and the iron coagulant and TOC passing through the filter at each ozone dose were quantified. Nearly all the coagulant (and turbidity) was removed from the unozonated influent (Figure 7), while progressively more coagulant passed through the sand filter as ozone dose increased. At the highest dose (0.6 mg O<sub>3</sub>/mg TOC) about 75% of the iron coagulant added passed through the filter. Not surprisingly, given the results for coagulant metal, TOC removal decreased with increasing ozone dose, with only about 6% TOC removal at the highest ozone dose tested compared to 30% removal in the unozonated sample. At the highest ozone dose tested, even if some soluble TOC was sorbed to flocs or precipitated, the potential TOC removal was not realized due to poor particle removal by filtration.

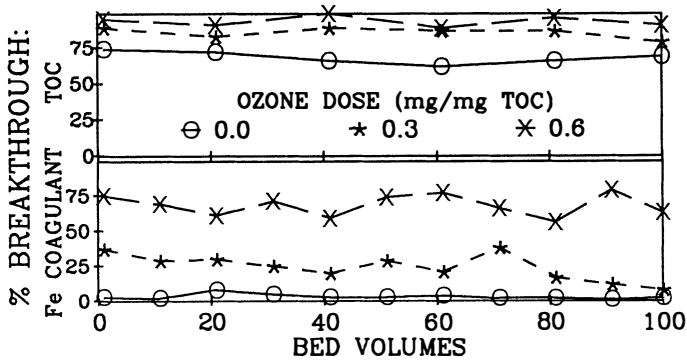


Fig. 7. Breakthrough of TOC (above) and iron coagulant (below) during direct filtration.

While this experiment was designed with obvious foresight to obtain significant results, it does make a point. That is, ozonation may increase the concentration of particulate metal residuals after ozonation, thereby decreasing the efficiency of TOC and particulate removal processes, especially if ferric chloride

coagulants are used at low coagulant doses. Similar phenomena reportedly occurred during pilot scale testing of pre-ozonation and direct filtration of Seattle water (Hilmoe, 1992).

**Synthesis.** The results of this and previous work into effects of pre-ozonation on TOC removal using aluminum coagulants are synthesized in Figure 8. Despite the wide range of experimental conditions employed, this presentation shows that there is a consistent pattern that unifies most results. The key parameter in the synthesis is the Al:TOC ratio, expressed as either mg Alum/mg TOC or M Al/M TOC. When this ratio is very low or very high, increasing ozone doses often improve TOC removal. Ozonation hinders TOC removal at moderate or conventional coagulant doses, and has nearly no effect at transitions between the described coagulant dose regimes. While it is anticipated that some systems will not fit this pattern, for instance, due to high concentrations of volatile or non-sorbable organic matter, effects of ozonation on each component of TOC removal outlined in this work and elsewhere (Edwards and Benjamin, 1992b) are predicted to apply independent of water source. As a final point, this discussion has focused exclusively on removal of TOC by physical processes. In many water treatment plants biological degradation of organic matter after ozonation would tend to improve overall TOC removal.

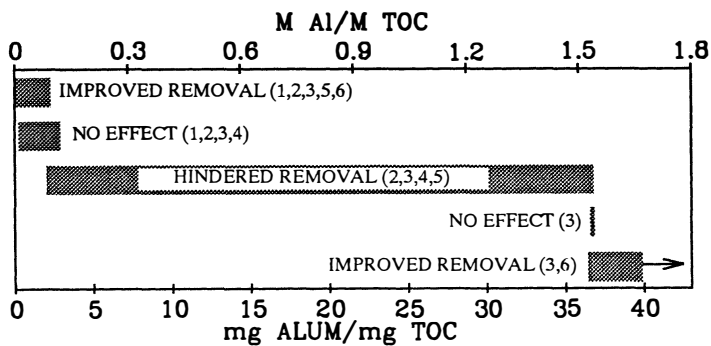


Fig. 8. Effects of ozonation on overall TOC removal at various alum doses (or equivalent doses as discussed in Edwards and Benjamin, 1992b). Referenced work: (1) van Breeman *et al.*, 1979; (2) Reckhow and Singer, 1984; (3) Edwards and Benjamin, 1992b; (4) Jekel, (1986); (5) This work; (6) Chen *et al.*, 1987.

## CONCLUSIONS

Pre-ozonation may remove organic matter directly from waters (TOC and THMFP) through a combination of stripping and direct reactions of ozone with organic matter. Examination of full-scale data illustrates that when THMFP removal by pre-ozonation alone is high, TOC removal is high as well. Stripping of organic matter played an important role in removal of TOC and THMFP in one water tested.

At full-scale ozonation and in well controlled sedimentation tests, pre-ozonation had no beneficial impacts on particle removal processes and may have had some adverse effects. TOC removal under the same conditions, however, was adversely affected by ozonation using PACl, ferric chloride, or alum coagulants. Floc formed in the presence of NOM was more negatively (less positively) charged after ozonation, decreasing removal of anionic organic molecules from solution. A similar change induced an adverse effect on direct filtration of a model water, as ozone increased concentrations of coagulant metal residuals and decreased TOC removal. Finally, previous experimental results regarding the effects of ozone on overall TOC removal during coagulation continue to follow a pattern described by Edwards and Benjamin (1992b) when examined as a function of normalized coagulant dose.



## ACKNOWLEDGMENTS

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