

# THE IMPACT OF PRETREATMENT WITH OZONE, CHLORINE DIOXIDE AND POTASSIUM PERMANGANATE ON THM FORMATION - LABORATORY CASE STUDIES

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## ABSTRACT

This paper discusses the impact of surface water pretreatment with ozone, chlorine dioxide and potassium permanganate on THM formation through two laboratory case studies; one relates to the treatment of eutrophic lowland reservoir water in the UK, and the other concerns the treatment of a surface water in China and a simulated low alkalinity, high humic water. The value of pre-oxidants for diminishing ultimate THM formation is determined by their ability to: destroy THM precursor material, improve the removal of precursor material by subsequent treatment processes, and reduce the chlorine-demand of the treated water prior to final chlorination. These effects have been considered using various laboratory experimental protocols applied to raw water samples and model waters. From this study it can be concluded that for raw waters with a high chlorine demand ( $> 3 \text{ mg Cl/l}$ ) and high THMFP (eg.  $> 300 \mu\text{g/l}$ ), the beneficial impact of replacing pre-chlorination by pretreatment with ozone or chlorine dioxide, at practical concentrations (viz.  $< 2 \text{ mg O}_3/\text{l}$  and  $< 1 \text{ mg ClO}_2/\text{l}$ ), on total THM formation is likely to be substantial, mainly as a result of the reduction in chlorine demand. Pretreatment with potassium permanganate at practical concentrations (viz.  $< 2 \text{ mg KMnO}_4/\text{l}$ ) is unlikely to achieve an adequate reduction in THM formation. The relative performances of the alternative pre-oxidants is considered to be related, in part, to their respective oxidation strengths.

**Key Words:** trihalomethane formation, chloroform, ozone, chlorine dioxide, potassium permanganate, surface water, chlorine demand, laboratory studies, drinking water treatment.

## RÉSUMÉ

Cet article discute l'influence du pré-traitement des eaux de surface par ozone, bioxyde de chlore, et permanganate de potassium sur la formation des THMs à l'aide de deux études au laboratoire; la première étude concerne le traitement des eaux de réservoir eutrophiques en GB, et la deuxième est relative au traitement d'une eau de surface en Chine et une eau synthétisée de faible alcalinité et importante concentration humique. La valeur de pré-oxydants pour réduire la formation ultime de THMs est déterminée par leur capacité à: détruire les précurseurs de THMs, améliorer l'élimination des précurseurs par des traitements postérieurs à la pré-oxydation, et réduire la demande en chlore des eaux traitées avant la chloration finale. Ces effets ont été pris en considération en utilisant différents protocoles expérimentaux au

laboratoire appliqués à des eaux brutes et à eaux modèles. La capacité de détruire les précurseurs de THMs peut être liée partiellement à leur potentiel d'oxydation et dans des conditions basiques (viz. les eaux de réservoir) le potentiel relatif à l'électrode standard pour ozone est nettement plus élevé que celui de permanganate. Les résultats de cette étude ont ainsi montré que la réduction en pourcentage maximal de THMFP total pour les eaux de réservoir était approximativement 12-15% avec l'ozone ( $[O_3] \geq 20 \mu M$ ) comparativement à 5-8% pour le permanganate ( $[MnO_4^-] \geq 6 \mu M$ ). A la suite du traitement à l'ozone et au permanganate des eaux de réservoir, la réduction de THMFP total n'a pas augmenté significativement avec le dosage d'oxydant sur la gamme normale (viz. 1 à 5 mg  $O_3/l$ , et  $< 2$  mg/l  $KMnO_4$ ), ce qui indique que seulement une concentration relativement faible d'oxydant ( $\leq 1$  mg/l) est nécessaire pour arriver à des réductions maximales de THMFP total. Néanmoins, avec des eaux modèles de haute altitude, il y avait une tendance à l'augmentation de la réduction de THMFP avec le dosage de permanganate, phénomène identique à celui observé par d'autres chercheurs (e.g. Singer *et al.*, 1980), ce qui confirme la suggestion que l'impact de l'oxydation au permanganate dépend de la nature des eaux brutes. Pour les deux oxydants ozone, et permanganate, la réduction de THMFP total est associée avec une plus grande réduction de potentiel de formation de chloroforme que celui de bromoforme.

En ce qui concerne l'amélioration de l'élimination des précurseurs par les procédés consécutifs conventionnels, la pré-ozonation n'a que peu ou pas d'effet sur les eaux de basse altitude eutrophiques. Les tests au laboratoire n'ont pas montré d'amélioration significative en élimination de COD avec pré-ozonation, et les études sur usine-pilote ont confirmé des effets négligeables sur COD et turbidité avec des dosages de pré-ozonation jusqu'à 0,16 mg  $O_3/mg$  COD. Par contre, la pré-oxydation au permanganate semble conduire à une amélioration faible ( $< 10\%$ ), mais mesurable en élimination de COD pour des dosages de 1 à 2 mg/l  $KMnO_4$ . L'étude comparative de pré-oxydation des eaux de basse altitude avec ozone, bioxyde de chlore, et permanganate a montré que tous les trois oxydants sont capables de réduire la demande en chlore des eaux. Parmi ces trois oxydants, le permanganate est le moins efficace pour la satisfaction de la demande en chlore et il est estimé que la demande en chlore satisfaite était approximativement 0,07 mg Cl/l par  $\mu mol$   $MnO_4^-$ . Dans le cas du bioxyde de chlore, la demande en chlore satisfaite était approximativement une fonction linéaire du dosage de  $ClO_2$  sur la gamme de 0,1 à 0,53 mg  $ClO_2/l$ , conduisant à une valeur pour la demande en chlore satisfaite de 0,22 mg Cl/l per  $\mu mol$   $ClO_2$ . La valeur correspondante pour l'ozone était 0,37 mg Cl/l per  $\mu mol$   $O_3$ , bien que la demande en chlore satisfaite fut constante sur une large gamme de dosages d'ozone appliqués (0,25 à 5 mg/l) et la valeur était calculée sur la base du plus faible dosage d'ozone.

De cette étude, il peut être conclu que pour les eaux brutes avec une grande demande en chlore ( $> 3$  mg Cl/l) et important THMFP (e.g.  $> 300 \mu g/l$ ), l'impact positif du remplacement de la pré-chloration par un pré-traitement à l'ozone ou au bioxyde de chlore, à concentrations pratiques (viz.  $< 2$  mg  $O_3/l$  et  $< 1$  mg  $ClO_2/l$ ), sur la formation totale de THMs est probablement significatif, principalement à cause de la réduction de la demande en chlore. Il est improbable que le pré-traitement au permanganate à concentrations pratiques (viz.  $< 2$  mg  $KMnO_4/l$ ) puisse accomplir une réduction suffisante de la formation de THMs. La performance relative des différents pré-oxydants est partiellement liée à leur potentiels d'oxydation relatifs.

**Mots-clefs:** formation de trihalométhane, chloroforme, ozone, bioxyde de chlore, permanganate de potassium, eaux de surface, demande en chlore, études au laboratoire, traitement d'eaux potables.

## INTRODUCTION

The effective reduction in concentrations of trihalomethane (THM) compounds and other chlorinated disinfection by-products in drinking water is still of considerable interest to water utilities throughout the world. This interest has been strengthened by the setting of new guideline values for these compounds by the WHO (WHO, 1993). In the UK, water utilities must comply with a standard that limits the maximum total THM concentration to  $100 \mu g/l$ , calculated as a rolling 3 month average (Great Britain, 1989). Recent annual surveys (Great Britain, 1990, 1991, 1992) of drinking water quality in England and Wales have indicated a significant increase in the number of supply zones (supply zone population  $\leq 50,000$ ) where the THM standard has been exceeded. Of particular concern are surface water sources which contain substantial

quantities of THM-precursor material. This includes lowland rivers receiving organic matter derived from land runoff and sewage effluents, reservoir impoundments with significant algal development, and upland waters rich in humic substances.

In all these cases pretreatment by oxidation is receiving much attention as a means of reducing ultimate THM formation, as well as achieving other water treatment benefits (eg. algae inactivation, disinfection, colour removal, metal ion oxidation). Ultimate THM formation may be diminished by a combination of individual effects: destruction of THM precursors, improving precursor removal by subsequent treatment processes, and lowering the chlorine-demand of the final water. Three alternative chemicals to chlorine are widely considered as potential pre-oxidants since they themselves do not directly form chlorinated by-products. These are ozone, chlorine dioxide and potassium permanganate. Whilst ozone is of particular importance in Europe currently, where it is being widely installed at lowland surface water treatment plants, it is expensive compared to the use of chlorine dioxide or potassium permanganate.

This paper discusses the impact of surface water pretreatment with ozone, chlorine dioxide and potassium permanganate on THM formation through two laboratory case studies; one relates to the treatment of a eutrophic lowland reservoir water in the UK, and the other concerns the treatment of a surface water in China and a simulated low alkalinity, high humic water.

### CASE 1: EUTROPHIC LOWLAND RESERVOIR WATER

The impoundment of lowland river waters typically enriched with organic matter, is a common raw water source for drinking water supply in southern England. In such cases, pre-chlorination is often practised as the first stage of the treatment process in order to control biological growths and increase the removal of algae and zooplankton in the subsequent clarification and filtration processes. Thus, a breakpoint chlorine dose is applied initially to provide a free-chlorine residual through the subsequent treatment stages. This, in combination with final chlorine disinfection often leads to the production of substantial concentrations of trihalomethane compounds ( $> 100\mu\text{g/l}$ ). In order to evaluate the comparative benefits of alternative pre-oxidants in reducing THM formation, a laboratory study has been undertaken using raw water samples from a particular source. Table 1 provides a summary of the raw water quality during the period of sampling and experimentation; the values are those determined from the samples obtained for use in the laboratory experiments.

Table 1: Variability of raw water quality for the period of sampling and experimentation.

Parameter	Values*
Temperature ( $^{\circ}\text{C}$ )	6 to 19.5
pH	7.3 to 8.5
Colour (Hazen)	6.1 to 15.2
Hardness (as $\text{CaCO}_3$ )( $\text{mg l}^{-1}$ )	248 to 325
Alkalinity (as $\text{CaCO}_3$ )( $\text{mg l}^{-1}$ )	120 to 180
TOC** ( $\text{mg l}^{-1}$ )	3.9 to 7.1
Ammonia (as N)( $\text{mg l}^{-1}$ )	0.01 to 0.18
Chlorophyll 'a' ( $\mu\text{g l}^{-1}$ )	2.1 to 94.2

\*Corresponding to sampling days; \*\*Strictly DOC (dissolved organic carbon)

### PRE-OXIDATION WITH OZONE

An initial series of experiments was undertaken to investigate the ability of ozone to destroy THM-precursors and to study the combined impact of pre-ozonation and conventional treatment (coagulation-sedimentation-filtration) on THM formation potential (THMFP).

## 1. Experimental Procedure

Samples were collected from the surface water reservoir site in 25 litre polyethylene jerricans, brought to the laboratory and stored in the dark at 4°C. Ozonation of waters was carried out in a recirculating bubble column contactor (3.4 litres) coupled to an ozone generator, and the application of a specified ozone dose was achieved by ozonation for a fixed time period, previously calibrated. The ozone dose transferred was determined by the difference between applied ozone and measured off-gas ozone. Conventional treatment (coagulation-sedimentation-filtration) was simulated using a six-beaker Jar-test apparatus followed by filtration. In the Jar-test experiments ferric sulphate was used as the coagulant at a constant pH of 8; this pH value is typical for many operational plants. To maintain a constant pH sodium hydroxide solution was added. For the Jar-tests the mixing speed was 100 rpm for 2 min, followed by flocculation at 15 rpm for 20 min and quiescent settling for 2h. Filtration of the supernatant water was carried out using glass microfibre filter paper (porous size 1.2 µm). Trihalomethane formation potential (THMFP) was determined by adding a chlorine dose (NaOCl) sufficient to provide a free chlorine residual after 7 days at 20°C. Total and individual THM compounds were determined by a standard method (Standing Committee of Analysts, 1981) based on extraction into pentane followed by gas chromatography with electron capture detection.

## 2. Results

### 2.1 Destruction of THM-Precursors

The total THMFP for the raw water samples in this study was in the range, 210 to 380 µg/l. The chloroform (CHCl<sub>3</sub>) component of this was in the range, 110 to 250 µg/l, and this indicates that there was a substantial formation of brominated THM compounds (>30%) arising from bromide in the raw water. The beneficial impact of ozone on THMFP can be seen in Figure 1. The results indicate that over the usual range of ozone doses (0 to 1 mg O<sub>3</sub>/mg DOC) there is a modest reduction in THMFP (≤ 15%), with the extent of the reduction increasing rapidly with ozone dose in the range of 0 to 0.2 mg O<sub>3</sub>/mg DOC, and much more gradually at ozone doses above 0.2 mg O<sub>3</sub>/mg DOC. In view of the relative scatter of the results, it could be concluded that the reduction in THMFP is insensitive to ozone dose in the range of 0.2 to 1.1 mg O<sub>3</sub>/mg DOC. The results for chloroform (Figure 2) were very similar to total THMFP with a fairly consistent reduction in CHCl<sub>3</sub>-FP of approximately 15% for the ozone dose range, 0.2 to 1.1 mg O<sub>3</sub>/mg DOC. The anomalously higher reduction (21%) in CHCl<sub>3</sub>-FP at the ozone dose of 0.47 mg O<sub>3</sub>/mg DOC was not repeated in a subsequent test (16%), although repeatability was observed at the other ozone doses. The effect of ozone dose on brominated - THMFP appeared to be more complicated as shown in Figure 3. The results indicate a peak reduction in Br - THMFP of 10% at an ozone dose in the range, 0.2 to 0.3 mg O<sub>3</sub>/mg DOC, and in the range, 0.6 to 1.1 mg O<sub>3</sub>/mg DOC. At ozone doses in the range, 0.3 to 0.5 mg O<sub>3</sub>/mg DOC, there appeared to be substantially less reduction in Br - THMFP. This pattern of behaviour was exactly repeated with a subsequent sample.

### 2.2 Pre-Ozonation and Treatment

The effect of pre-ozonation and treatment (coagulation - sedimentation - filtration) on total THMFP can be seen in Figure 4. The treatment was carried out with different ferric sulphate coagulant doses in the range, 0 to 8 mg/l, as Fe. The general pattern of results concerning the variation of THMFP reduction with ozone dose appeared to remain the same with or without the treatment stage, whilst the overall reduction in THMFP systematically increased with coagulant dose. These results indicate that the pre-ozonation had no significantly beneficial effect on the treatment stage and this was confirmed by the results of the removal of DOC with ozone and treatment; in particular, the systematic reduction in DOC with coagulant dose. For a typical coagulant dose of 3.5 mg/l as Fe, the overall removal of DOC was approximately 10% (with or without ozone) in the laboratory experiments which is somewhat lower than usually found on pilot - or full-scale studies (10-25%). The corresponding results for the variation of CHCl<sub>3</sub>-FP and Br-THMFP (Figure 5) showed that the pattern and magnitude of the results are consistent with the previous observation that pre-ozonation does not significantly improve the treatment stage. It was speculated that an increasing removal of DOC with coagulant dose might lead to a proportionally greater formation of brominated - THM

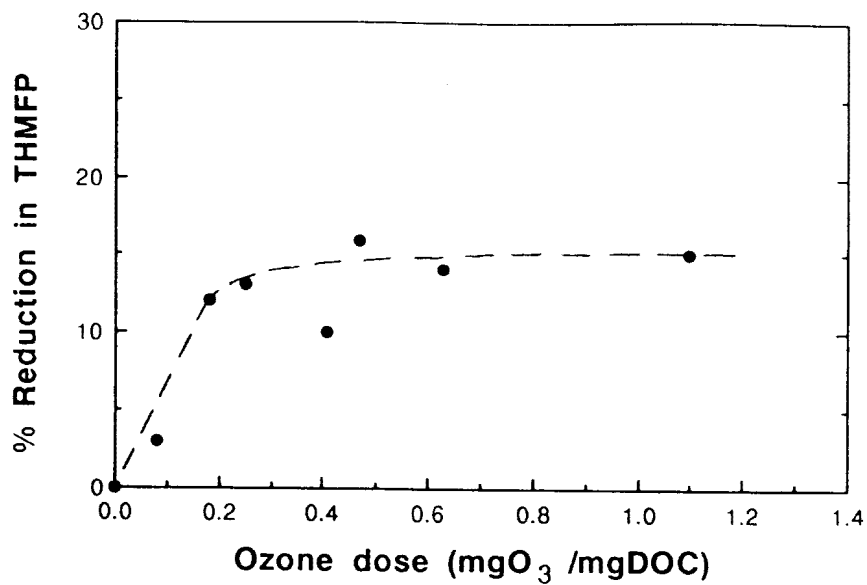


Figure 1: Effect of ozone dose on total THMFP  
 (1 mg/l O<sub>3</sub> = 0.2 mg O<sub>3</sub> / mg DOC)

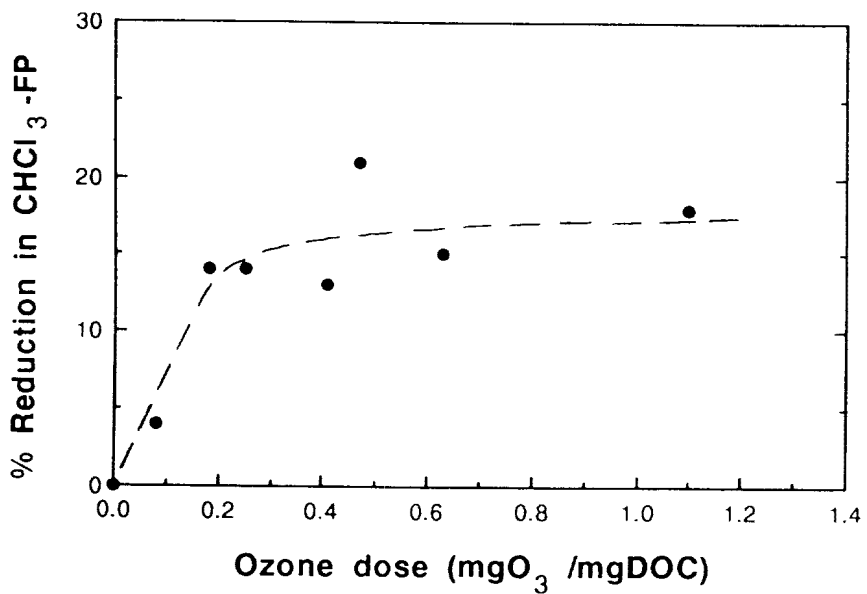


Figure 2: Effect of ozone dose on CHCl<sub>3</sub>-FP

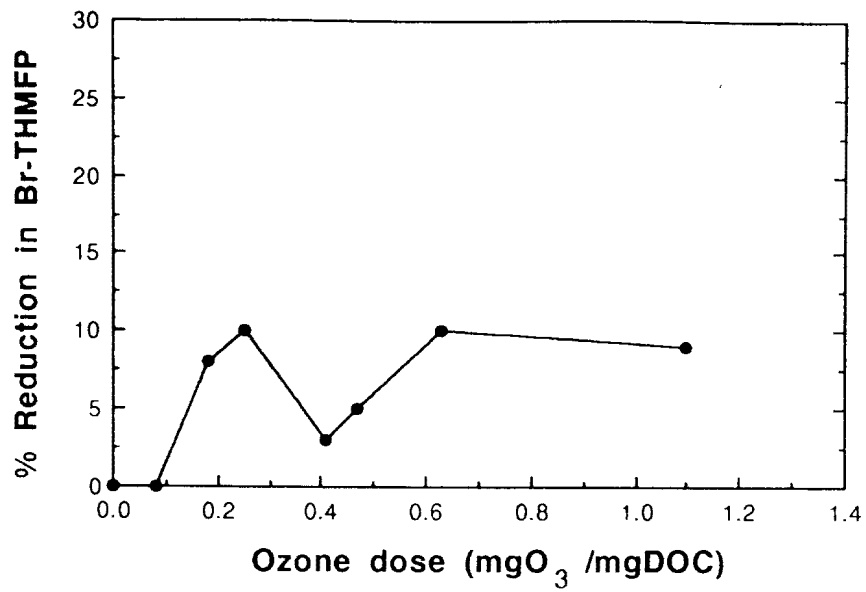


Figure 3: Effect of ozone dose on Br-THMFP

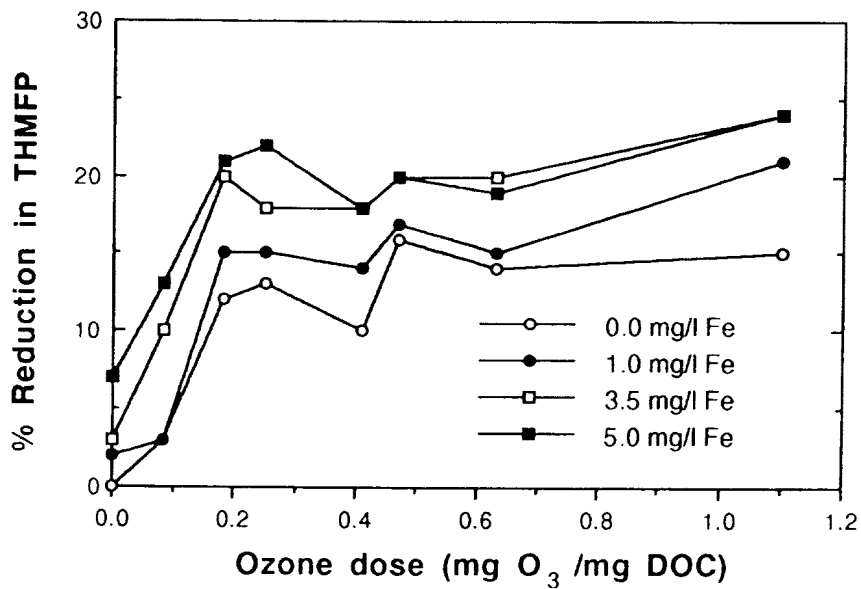


Figure 4: Effect of ozone and treatment on total THMFP

compounds, due to an increasing Br-/DOC ratio, and therefore a lower percentage reduction in Br - THMFP. The results in Figure 5, whilst showing a clear, systematic reduction in Br - THMFP with coagulant dose, are not substantially different and this may be a reflection of the speculated effect. Interestingly, the existence of the peak reduction in Br-THMFP corresponding to the ozone dose range of 0.2 to 0.3 mg O<sub>3</sub>/mg DOC, and a minimum reduction at an ozone dose range of 0.3 to 0.5 mg O<sub>3</sub>/mg DOC, were repeated at all coagulant doses.

## PRE-OXIDATION WITH POTASSIUM PERMANGANATE

A second series of experiments was undertaken to investigate the ability of potassium permanganate to destroy THM-precursors and to study the combined impact of pre-oxidation (with KMnO<sub>4</sub>) and conventional treatment (coagulation - sedimentation - filtration) on THM formation potential (THMFP).

### 1. Experimental Procedure

Stock solutions of potassium permanganate were standardized by titration with sodium thiosulphate (Standard Methods, 1985) immediately prior to use. Pre-oxidation was carried out at room temperature ( $20 \pm 2^\circ\text{C}$ ) using the six-beaker (1 litre beakers) Jar-test apparatus. The reaction time was 1h. Some of the water samples were subjected to coagulation with the addition of 3 mg/l of aluminium sulphate (as Al) immediately after ( $< 5$  min) the potassium permanganate dose. The samples were mixed at 300 rpm for 2 min, followed by slow mixing at 35 rpm for 20 min, and settled for 1h before filtration with glass microfibre filter paper (porous  $1.2\mu\text{m}$ ). Those samples which were not subjected to coagulation and filtration were stirred continuously (at 35rpm) for the remainder of the 1h reaction period. Excess potassium permanganate was reduced by titration with sodium sulphite and the water samples stored at room temperature ( $20 \pm 2^\circ\text{C}$ ) prior to chlorination. Chlorination tests were conducted in 300ml BOD bottles. Appropriate dilutions of the stock chlorine solution were added to the treated and control samples. After mixing ( $\sim 10\text{s}$ ) each sample was siphoned into the 300ml bottles, capped and sealed with no head space, and stored in the dark at room temperature ( $20 \pm 2^\circ\text{C}$ , for instantaneous THM) and at  $25 \pm 2^\circ\text{C}$  (for THMFP). Instantaneous THM was studied in two ways, one performed at various chlorine doses and a reaction time of 1h, and the other performed at specific chlorine doses for different reaction times. Prior to the analysis of instantaneous THM, residual chlorine was removed by the addition of sodium sulphite. THMFP was determined at pH7 and at a chlorine dose of 20 mg/l in order to provide a sufficient chlorine residual for seven days. Total and individual THM compounds were determined by the standard method (Standing Committee of Analysts, 1981).

### 2. Results

#### 2.1 Destruction of THM-Precursors

The total THMFP for the raw water in this series of experiments was in the region of  $500\mu\text{g/l}$ . The chloroform component of this was approximately half, with the remainder consisting of the brominated THMs (principally monobromodichloromethane). The impact of permanganate on THMFP is shown in Figure 6. It can be seen that for the range of permanganate doses used ( $\leq 2\text{ mg/l}$ ; or  $\leq 0.38\text{ mg KMnO}_4/\text{mg DOC}$ ) some destruction of THM precursors has occurred, although the extent of this is not substantial ( $< 10\%$  reduction in total THMFP). Since only two permanganate doses were used in the tests it is not clear whether, and at which dose, a maximum in reduction occurs. However, the observation that the reduction is greater at a dose of  $0.19\text{ mg KMnO}_4/\text{mg DOC}$  compared to  $0.38$  was repeated on samples co-treated with coagulation (see Figure 6 and next section). A very similar result was obtained for chloroform formation potential. No detectable change in the brominated-THMFP occurred with or without permanganate dosing.

#### 2.2 Pre-Oxidation and Treatment

The effect of pre-oxidation with KMnO<sub>4</sub> and treatment (coagulation - sedimentation - filtration) on total

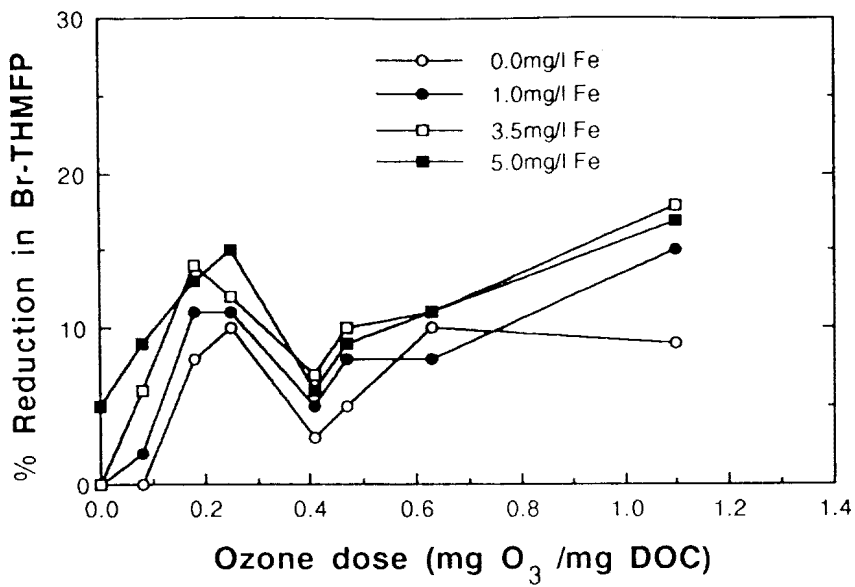


Figure 5: Effect of ozone and treatment on Br-THMFP

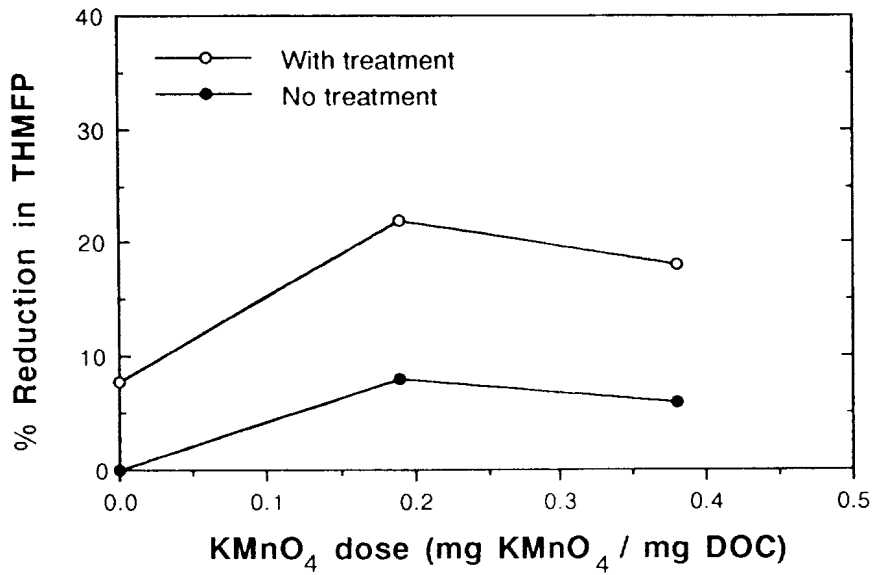


Figure 6: Effect of potassium permanganate on total THMFP for lowland surface water  
(1 mg/l KMnO<sub>4</sub>=0.19 mg KMnO<sub>4</sub> / mgDOC)



THMFP can be seen in Figure 6. The pattern of results concerning the variation of THMFP reduction with  $\text{KMnO}_4$  dose appeared to remain the same with or without the treatment stage, although the overall reduction in THMFP increased with treatment. The results indicate that the pre-oxidation with  $\text{KMnO}_4$  appeared to have little, or no, beneficial effect on the treatment stage.

## COMPARATIVE PRE-OXIDATION WITH $\text{O}_3$ , $\text{ClO}_2$ AND $\text{KMnO}_4$

This study involved a laboratory experimental protocol developed to measure THM formation as a consequence of both pre- and post- disinfection stages where ozone, chlorine dioxide and potassium permanganate were evaluated as alternative pre-disinfectants in direct comparison with pre-chlorination: chlorine was applied at the post-disinfection stage. Further details of this work can be found elsewhere (Graham *et al.*, 1989; Graham *et al.*, 1992). The objectives of this study were as follows:

- To determine the degree of chlorine demand satisfied when applying  $\text{O}_3$ ,  $\text{ClO}_2$  and  $\text{KMnO}_4$  as pre-oxidants.
- To determine the THM formation characteristics when applying chlorine (breakpoint and sub-breakpoint),  $\text{O}_3$ ,  $\text{ClO}_2$  and  $\text{KMnO}_4$  as pre-oxidants.

### 1. Experimental Protocol

A summary of the experimental protocol is shown in Figure 7. One litre samples of raw water were maintained at ambient pH conditions in amber glass bottles in a temperature-controlled water bath at a temperature approximately equivalent to the in situ water temperature at the time of sampling. Chlorine,  $\text{ClO}_2$ , or  $\text{KMnO}_4$  was added at a specified dose to the sample solutions. Chlorine was added in the form of sodium hypochlorite and chlorine dioxide was prepared by the acidification of chlorite. Ozonation of waters was carried out in a recirculating bubble column contactor as described previously. Samples of ozonated raw water were subsequently transferred into one litre amber glass bottles and treated like other samples after their respective pre-oxidation. Doses of free chlorine, sufficient to achieve a free-chlorine residual of 0.1 to 0.2 after a 4-h pre-disinfection period, were applied to raw water samples (termed 'breakpoint' chlorination). Alternatively, for comparison, a lower chlorine dose (termed 'sub-breakpoint' chlorination) was applied which was insufficient to achieve a free chlorine residual after the 4-h contact period. The pre-disinfectant doses of  $\text{KMnO}_4$  (0.6 mg/l),  $\text{ClO}_2$  (maximum 0.5 mg/l as weight  $\text{ClO}_2$ ) and  $\text{O}_3$  (maximum 5 mg/l) were selected as representing a realistic range for potable water treatment. Coagulation - sedimentation - filtration was undertaken on one of duplicate samples, for each pre-oxidant, 2.5h after addition of the pre-oxidant. A conventional Jar-test apparatus was used and the procedure was similar to that described in the previous study. The coagulant, ferric sulphate, was applied at a dose equivalent to that typically used at the treatment works where the sample was taken. Coagulation was carried out at ambient pH. Four hours after the initial disinfection, all samples were post-chlorinated to achieve free-chlorine residuals of approximately 0.5 mg/l after a 30-min contact period. Following determination of the residual which was achieved at this stage, one of the treated samples received the addition of ammonium sulphate to convert the free chlorine to combined chlorine, and all samples were allowed to stand for a period of 4 days.

### 2. Results

#### 2.1 Chlorine Demand

The chlorine demand satisfied by each pre-oxidant was determined via the experimental protocol by subtracting the chlorine dose required to achieve a 0.5 mg/l free chlorine residual after 30 min (see Figure 7, Time = 4.5h), for the pre-oxidant treated water, from the total chlorine dose applied to the duplicate sample receiving the breakpoint pre-chlorination. A summary of the results can be seen in Table 2. The total chlorine demand of the raw water varied between 2.5 and 5.0 mg/l and the variation was believed to be strongly associated with the water TOC, chlorophyll 'a' concentration and temperature. The results in Table 2 indicate that at the pre-oxidant doses used, and considered realistic,  $\text{KMnO}_4$  satisfied less than 10%

of the chlorine demand and only 50% or less of the chlorine demand was satisfied by ClO<sub>2</sub> and O<sub>3</sub>. In the case of chlorine dioxide, further tests were carried out with samples subjected to various doses of ClO<sub>2</sub> (0.1 to 0.53 mg/l) and by applying linear regression to the results, 66% of the variation in chlorine demand satisfied could be explained by the following relationship: [CLDS] = 0.18 + 2.39 [ClO<sub>2</sub>], where [CLDS] is the chlorine demand satisfied (mg/l) and [ClO<sub>2</sub>] is the applied ClO<sub>2</sub> dose (mg/l). With ozone as the pre-oxidant, samples were subjected to a range of applied ozone doses in the range of 0.25 to 5 mg/l. A constant amount of chlorine demand was satisfied, within the limits of experimental accuracy, irrespective of the applied ozone dose.

Table 2. Reduction of chlorine demand by individual pre-oxidants

Pre-oxidants	Chlorine demand satisfied by Pre-oxidant*			
	mg/l Cl		% of total Cl demand	
	range	mean	range	mean
KMnO <sub>4</sub> (0.6 mg/l)	0.2 to 0.3	0.25	3.8 to 9.1	6.5
ClO <sub>2</sub> (0.5 mg/l)	1.0 to 2.5	1.6	38.9 to 55.6	45.7
O <sub>3</sub> (3 mg/l)	1.5 to 2.5	1.9	40.4 to 55.6	50.5

\*Protocol without coagulation/filtration

## 2.2 THM Formation

For all samples THM compounds were not formed in the period following the application of pre-oxidants other than chlorine. In contrast, for breakpoint pre-chlorination, approximately 50% or more of the total THMs which are present after 4 days are formed in the pre-disinfection period. The total THM concentrations in samples comprised individual concentrations of chloroform, bromodichloromethane and dibromochloromethane, indicating the presence of bromide in the raw waters. However, no measurable quantities of bromoform were found in samples. The impact of the different pre-oxidants on THM formation is summarised in Table 3. Under the conditions of the experimental protocol, the ultimate (4-day) total

Table 3. Impact of pre-oxidant on THM formation

Oxidant/ Disinfectant Combination	Mean 4-day total THM (µg/l)		
	without coagulation/filtration		
	without (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	with (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	
Cl/Cl	101.4	74.2	76.9
KMnO <sub>4</sub> /Cl	129.5	80.0	na
ClO <sub>2</sub> /Cl	54.7	38.5	50.1
O <sub>3</sub> /Cl	40.8	24.8	34.5

na - not available

THM concentrations based on pre- and post- chlorination were found to have a mean of 101.4 µg/l without conventional treatment (coagulation-sedimentation-filtration), and 76.9 µg/l with treatment. In the case of pre-oxidation with KMnO<sub>4</sub> (at a dose of 0.6 mg/l) there appeared to be no reduction in ultimate total THM formation as a consequence of this treatment, instead the results in Table 3 suggest an increase in THM

formation. However, since the number of samples treated with  $\text{KMnO}_4$  were fewer than for the other oxidants, the mean THM value for the  $\text{KMnO}_4$  treated samples may not be as representative as the mean values for the other oxidants. In contrast, pre-treatment with  $\text{ClO}_2$  and  $\text{O}_3$  caused a substantial reduction in THM formation (Table 3). The effect of different  $\text{ClO}_2$  doses (0.1 to 0.5 mg/l) on THM formation was studied and for each water sample THM levels were consistently reduced as the  $\text{ClO}_2$  dose increased. Thus, the mean value for the ultimate (4-day) total THMs produced was 30% lower at a  $\text{ClO}_2$  dose of 0.53 mg/l (53.7  $\mu\text{g/l}$  total THM) than at a  $\text{ClO}_2$  dose of 0.27 mg/l (76.3  $\mu\text{g/l}$  total THM). The effect of different ozone doses (0.25 to 5.0 mg/l) on THM formation was also investigated and, within the limits of experimental accuracy, the ultimate total THM value did not vary as the pre-ozone dose was varied. This is consistent with the earlier observation that the chlorine demand satisfied was independent of the pre-ozone dose.

## CASE 2: IMPACT OF $\text{KMnO}_4$ ON OTHER SURFACE WATERS

In this study, two kinds of surface waters having quite different quality characteristics were evaluated in order to compare the impact of  $\text{KMnO}_4$  on the formation of THM. Firstly, samples of the River Songhua in the Peoples Republic of China were tested at the Harbin University of Architecture and Civil Engineering (P.R. China). A limited analysis of the quality of the samples of the River Songhua during the testing period was as follows:  $\text{COD}_{\text{Mn}}$  9-15 mg/l; pH 7.0 - 7.3; and turbidity 80-250 NTU. The second type of water was a model water prepared by dissolving specific amounts of organic extract into high purity water (< 18 M  $\Omega$  cm). The organic extract was previously separated from an upland, acidic and highly coloured surface water source by a reverse osmosis procedure (Brandao, 1990). The characteristics of the model upland water is shown in Table 4, and it has been shown previously that the quality of the model water is very similar to the original source (Lambert, 1992).

Table 4. Characteristics of Model Upland Water

Total solids, 105°C (mg/l)	109.1
Total alkalinity (mg $\text{CaCO}_3/\text{l}$ )	8.0
Hardness (EDTA) (mg $\text{CaCO}_3/\text{l}$ )	33.95
Dissolved carbon (mg C/l)	10.08
Non-purgeable dissolved organic carbon (mg C/l)	7.87
UV-Absorbance, 254 nm (Abs/m)	36.1
Vis-Absorbance, 420 nm (Abs/m)	2.85
Specific UV-Absorbance ( $\text{m}^{-1}/\text{mg C.l}^{-1}$ )	4.11
pH	7.0
$E_4/E_6$	9.29

### 1. Experimental procedure

The experimental procedure used in these tests was identical to that described earlier (Case 1, Pre-oxidation with Potassium Permanganate). Standard permanganate stock solutions were prepared from analytical grade reagents (either Tianjing Chemical Co., P.R. China or BDH Chemicals Ltd, U.K.) and calibrated using sodium oxalate (Standard Methods, 1985).

### 2. Results

#### 2.1 River Songhua Water

Figure 8 shows the instantaneous total trihalomethanes formed after Songhua river water was treated with different amounts of potassium permanganate for 1h, followed by chlorination for 1h. Generally, the total

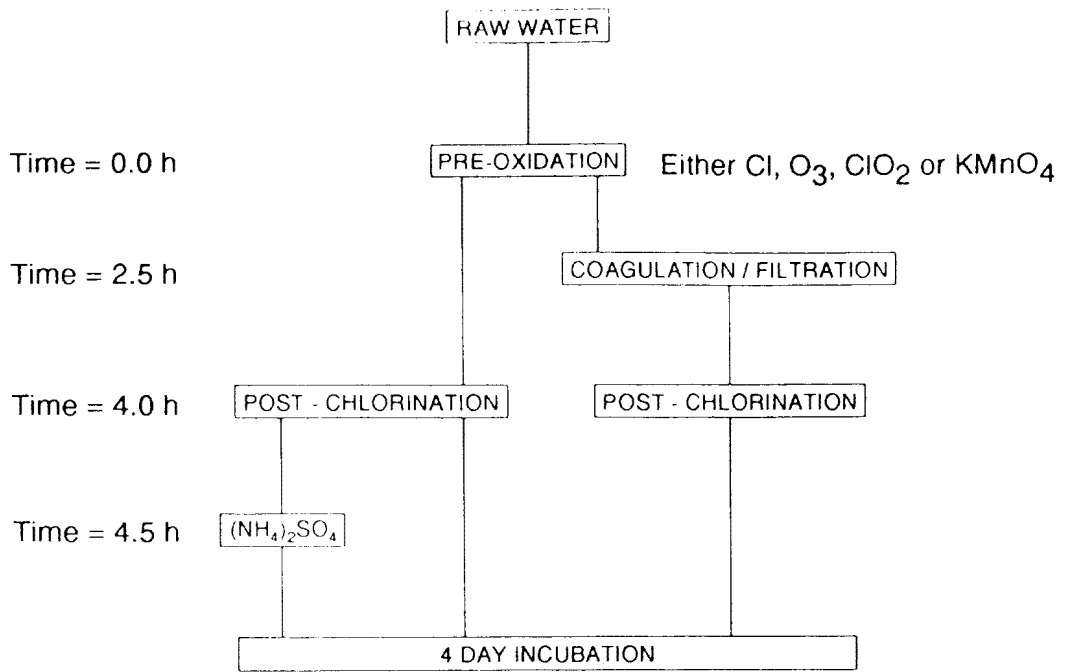


Figure 7: Experimental protocol

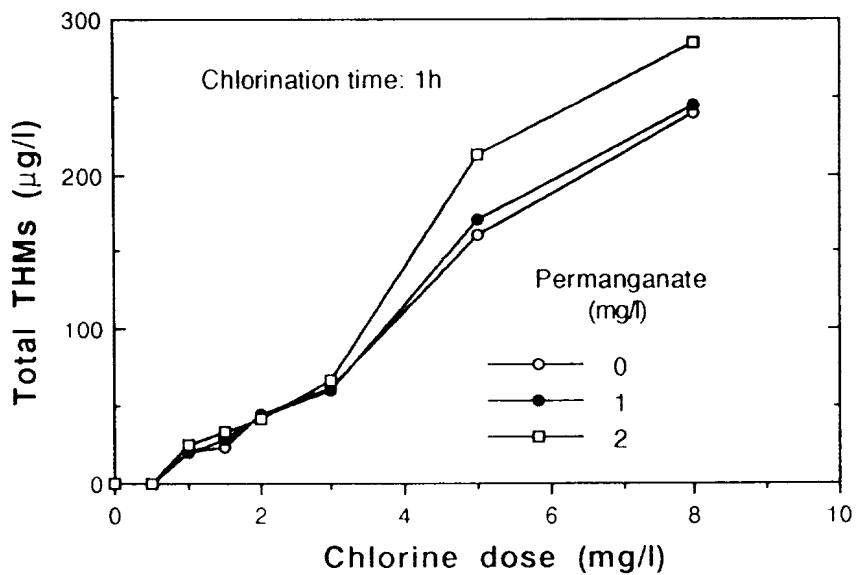


Figure 8: Effect of potassium permanganate on the formation of instantaneous THMs during the chlorination of River Songhua water

THM production increased with increasing chlorine dosages in all the water samples. When the chlorine dosages were less than 3 mg/l, the production of total THM was the same with and without potassium permanganate pre-oxidation. For chlorine dosages above 3 mg/l, a higher production of THMs was observed in the samples pre-oxidised by potassium permanganate, although 1 mg/l of potassium permanganate caused only a very limited increase in the production of total THMs. The variation of chloroform and the brominated THMs with chlorine dosage were very similar to the total THMs.

## 2.2 Model Humic Water

Figure 9 shows the effect of potassium permanganate pre-oxidation on total THM production for the low hardness, low alkalinity model humic water. It can be seen that potassium permanganate pre-oxidation had a similar impact on the formation of total THMs as in the case of the Songhua river water. However, in this case the total THM increase was substantial at a potassium permanganate dosage of 1 mg/l (for chlorine dosages > 2 mg/l), but not much additional increase in total THMs was observed at the higher dose of 2 mg/l. Again, the variation of chloroform and brominated - THMs with  $\text{KMnO}_4$  dose was very similar to the total THMs. It is believed that the observed increase in instantaneous THM formation with permanganate pre-oxidation for the River Songhua and model humic water is the consequence of the destruction of some of the THM-precursor material leading to a net increase in the concentration ratio of chlorine to remaining THM-precursor material.

The impact of permanganate on THMFP for the model humic water is shown in Figure 10. For this water the total THMFP was approximately 680  $\mu\text{g/l}$ , of which 650  $\mu\text{g/l}$  corresponded to chloroform. It can be seen that for the range of permanganate doses used ( $\leq 2$  mg/l;  $\leq 0.25$  mg  $\text{KMnO}_4/\text{mg DOC}$ ) considerable destruction of THM precursors occurred, with a trend of increasing reduction in THMFP with permanganate dose. This trend was different to that previously found with the eutrophic lowland reservoir water (Figure 6).

## DISCUSSION

The value of pre-oxidants for diminishing ultimate THM formation is determined by their ability to: destroy THM precursor material, improve the removal of precursor material by subsequent treatment processes, and reduce the chlorine-demand of the treated water prior to final chlorination. The ability to destroy THM precursor material may be related in part to their oxidation strength and in basic conditions (viz. lowland water samples) the standard electrode potential for ozone is substantially higher than for permanganate. Thus, the results in this study have shown that the maximum percentage reduction in total THMFP for lowland water samples was approximately 12-15% for ozone ( $[\text{O}_3] \geq 20\mu\text{M}$ ) compared to approximately 5-8% for permanganate ( $[\text{MnO}_4^-] \geq 6\mu\text{M}$ ). For ozone and permanganate treatment of lowland waters the reduction in total THMFP did not significantly increase with oxidant dose over the usual range of oxidant doses (viz. 1 to 5 mg  $\text{O}_3/\text{l}$ , and  $< 2$  mg/l  $\text{KMnO}_4$ ) indicating that only a relatively small oxidant concentration ( $\leq 1$  mg/l) is required to achieve the maximum reduction in total THMFP. However, with the model upland water there was a clear trend of increasing THMFP reduction with permanganate dose, as observed by others (eg. Singer *et al.*, 1980), suggesting that the impact of permanganate oxidation depends on the nature of the raw water. For both ozone and permanganate the reduction in total THMFP is associated with a greater reduction in chloroform-FP than brominated - THMFP. Generally, this is to be expected since although the pre-oxidation undoubtedly destroys some THM precursor material, it also converts some of the background  $\text{Br}^-$  into reactive HOBr. Since both effects are dependent on the pre-oxidation dose, and the subsequent HOBr reactions are not limited solely to those resulting in THM formation, the influence of applied ozone dose, for example, on brominated THMFP is complex (see Figure 3).

In terms of improving the removal of precursor material by subsequent conventional treatment processes, pre-ozonation has little or no effect on eutrophic lowland waters. The laboratory tests showed no significant improvement in DOC removal with pre-ozonation, and pilot-plant studies have confirmed no measurable effect on DOC and turbidity for pre-ozone doses up to 0.16 mg  $\text{O}_3/\text{mg DOC}$ . In contrast, permanganate

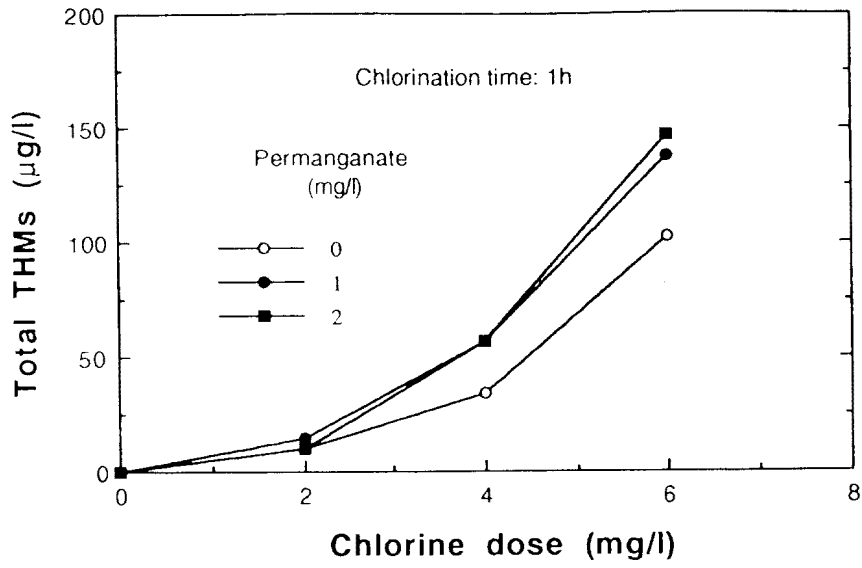


Figure 9: Effect of potassium permanganate on the formation of total THMs during the chlorination of model upland water

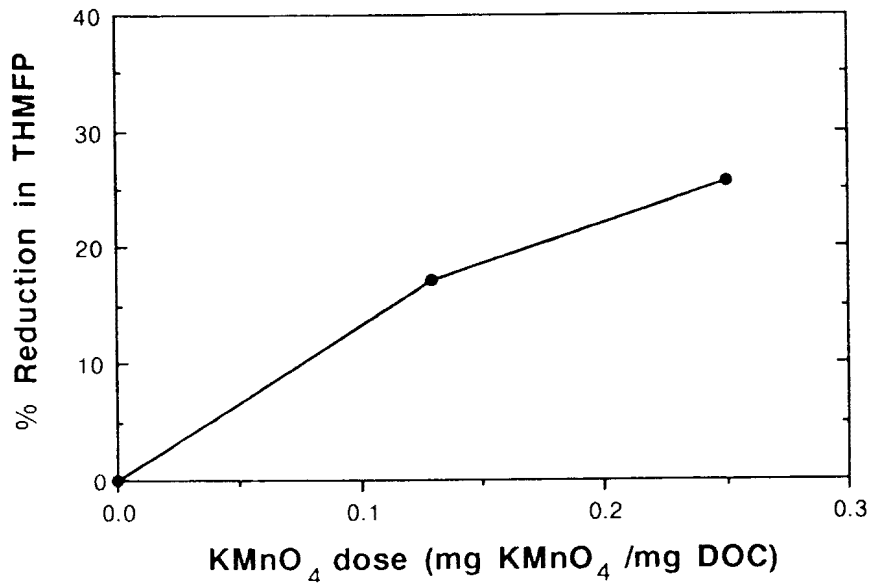


Figure 10: Effect of potassium permanganate on total THMFP for model upland water (1 mg/l  $KMnO_4$  = 0.13 mg  $KMnO_4$  / mg DOC)

pre-oxidation appears to lead to a small (< 10%), but measurable, improvement in DOC removal at doses of 1 to 2mg/L  $\text{KMnO}_4$ . This is believed to be due to the adsorption of organic substances on to particulate  $\text{MnO}_2$ , which are subsequently removed by coagulation and filtration (Colthurst and Singer, 1982).

The comparative study of lowland water pre-oxidation with ozone, chlorine dioxide and permanganate has shown that all three oxidants can reduce the chlorine demand of the water. Of the three oxidants, permanganate was the least able to satisfy chlorine demand and it was estimated that the chlorine demand satisfied was approximately 0.07 mgCl/l per  $\mu\text{mol MnO}_4^-$ . This value compares quite well with the value of 0.03 reported by Singer *et al* (1980). For chlorine dioxide, the chlorine demand satisfied was related approximately linearly to the  $\text{ClO}_2$  dose in the range of 0.1 to 0.53 mg  $\text{ClO}_2$ /l, giving a value for the chlorine demand satisfied as 0.22 mgCl/l per  $\mu\text{mol ClO}_2$ . The corresponding value for ozone was 0.37 mg Cl/l per  $\mu\text{mol O}_3$ , although the chlorine demand satisfied was constant over a wide range of applied ozone doses (0.25 to 5 mg/l) and the value was calculated on the basis of the lowest ozone dose. Although these values are estimates they may reflect the oxidation strength of the two chemicals under the conditions studied;  $E = 1.24$  V for  $\text{O}_3$ , and  $E = 0.95$  V for  $\text{ClO}_2$  (cf.  $E = 0.58$  V for  $\text{MnO}_4^-$ ).

From this study it can be concluded that for raw waters with a high chlorine demand (> 3 mg Cl/l) and high THMFP (eg. > 300  $\mu\text{g/l}$ ), the beneficial impact of replacing pre-chlorination by pretreatment with ozone or chlorine dioxide, at practical concentrations (viz. < 2 mg  $\text{O}_3$ /l and < 1 mg  $\text{ClO}_2$ /l), on total THM formation is likely to be substantial, mainly as a result of the reduction in chlorine demand. Pretreatment with potassium permanganate at practical concentrations (viz. < 2 mg  $\text{KMnO}_4$ /l) is unlikely to achieve an adequate reduction in THM formation. The relative performances of the alternative pre-oxidants is considered to be related, in part, to their respective oxidation strengths.

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