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Citation	Water Science & Technology: Water Supply (2015), 15(1): 101-106
Issue Date	2015-02
URL	<a href="http://hdl.handle.net/2433/200271">http://hdl.handle.net/2433/200271</a>
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Type	Journal Article
Textversion	author

# Effect of Preozonation on the Wastewater Reclamation by the Combination of Ozonation and Soil Aquifer Treatment

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## Abstract

A series of column experiments and risk evaluation revealed that preozonation was found to be a better option to enhance the performance of soil aquifer treatment (SAT) than ozonation after SAT for controlling a wide range of dissolved organic carbon (DOC), trace organic contaminants and disinfection byproducts. Our results are a good example to show that upgrading pretreatments can be more effective than adding extra treatments after SAT, and it is important to optimize a water reclamation system as a whole system.

## Keywords

Soil aquifer treatment; ozonation; trace organic compounds; disinfection byproducts

## INTRODUCTION

Many parts of the world are facing serious water shortage because of the uneven distribution of water resources and the concentration of the population in large cities. Also, extreme weather conditions caused by global climate change may further complicate the situation (e.g., Arnell, 1999). Water reclamation has become an important option to make up for the limited access to water sources. In extremely dry areas of the world, wastewater reclamation has been employed even for direct potable use in the past several decades (e.g., Asano et al., 2007).

Soil aquifer treatment (SAT) is a common way for water reclamation. This technique is different from other engineered treatment technologies (e.g., reverse osmosis (RO)) for its use of natural environment (Dillon et al., 2010). SAT, however, is not a popular option in highly populated areas because of the limitation in land space (i.e., short HRT) and the complex geological structure in the subsurface environment. Under this situation, it is ideal to fully utilize the advantage of SAT as a part of water reclamation systems along with wastewater treatment and drinking water treatment. That is, an effective combination of SAT and other treatment processes should be sought to design reclamation systems to overcome the limitations of SAT in urban areas.

Ozonation and other oxidation technologies are promising options to improve the performance of water reclamation systems with SAT in various ways. Preoxidation treatment is expected to enhance the biodegradability of organic compounds. Hübner et al. (2012) found that the combination of ozonation and artificial groundwater recharge of a lake water receiving wastewater effluent was better than artificial groundwater recharge alone for DOC reduction. Also, postoxidation could be more effective for the oxidation of trace organic compounds because it is performed under a lower DOC concentration than preoxidation (i.e., with a higher availability of oxidants). However, to the best of our knowledge, no systematic comparison between these two processes (i.e., preoxidation + SAT and SAT + postoxidation) has been made. In this study, to maximize the potential of SAT, we evaluated the effect of preozonation on the removal of organic compounds (i.e., DOC and other trace organic compounds including major disinfection byproducts). Also, postozonation experiments were performed for comparison.

## MATERIALS AND METHODS

## Reagents

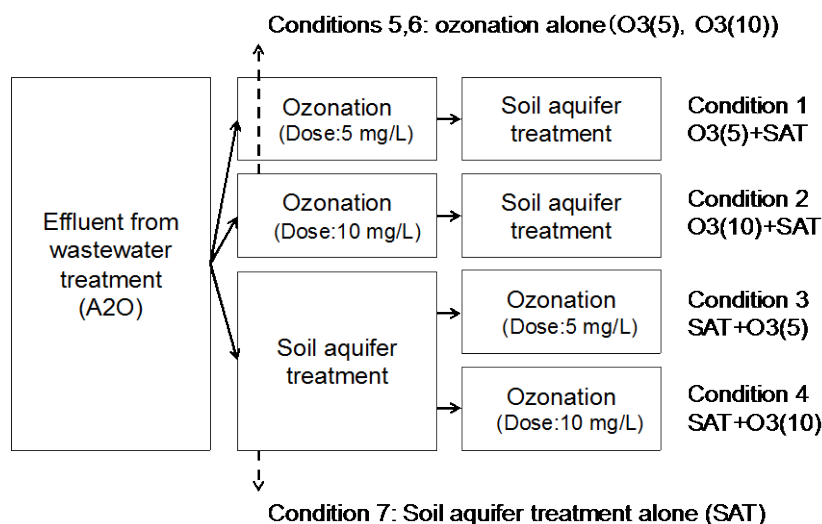
All the chemicals used in this study were purchased from Wako (Japan), and of special grade or the highest grade available unless otherwise noted. They were used without further purification. For chlorination, sodium hypochlorite (Chemical grade, Wako) was used. For the analysis of pharmaceutical and personal care products (PPCPs) with an LC-MS/MS system, formic acid and acetonitrile (LC/MS grade, Wako) were used for the preparation of mobile phase. Carbamazepine (CBZ, biochemical grade, Wako), clarithromycin (CAM, biochemical grade, Wako), sulpiride (SLP, biochemical grade, Wako), DEET (>98%, TCI (Japan)), and crotamiton (CRT, >97%, Sigma-Aldrich (USA)) were purchased as the standard compounds of PPCPs. All the aqueous solutions were prepared with ultra pure water produced with a Millipore Academic-A10 system.

## Feed water

An effluent from an actual wastewater treatment with anaerobic-anoxic-aerobic process (A<sub>2</sub>O) in Kyoto City (Japan) was used as the feed water for this study. This effluent was filtered with a cellulose membrane (5A, Advantec (Japan)) and store in a refrigerator before use.

## Experimental matrix and target indices

Treatment performances under seven different conditions were compared in this study (Figure 1): ozonation alone, SAT alone, and the combination of ozonation and SAT with different orders and ozone doses (5 or 10 mg/L). DOC and chlorine demand were monitored as the general water quality indices. EDTA and 1,4-dioxane, and the five PPCPs mentioned above were measured as the representative trace organic compounds. In addition, bromate ion concentration and the formation potentials of four major trihalomethanes (THMs) and nine major haloacetic acids (HAAs) were evaluated as the major disinfection byproducts (DBPs). Ozonation conditions are denoted as “O3(5)” for ozonation at an ozone dose of 5 mg/L, and “O3(10)” for 10 mg/L.



**Figure 1.** Experimental Matrix.

## Soil aquifer treatment (SAT)

Three laboratory-scale sand columns were operated under an aerobic condition. The columns (150 cm height, 15 cm i.d.) consisted of the bottom layer (10 cm of gravel layer) and the sand layer (110 cm). The sand was collected in the Shiga area, Japan, and used without sieving. The water head was maintained at 20 cm below the top of the sand layer (i.e., the top 20 cm was operated under unsaturated conditions). The columns were fed with different test solutions at a flow rate of 0.8 mL/min: A<sub>2</sub>O water or ozonated A<sub>2</sub>O water. The HRT and temperature were controlled at

approximately 7 days and 20 °C, respectively. The three columns were operated for two to three months for acclimatization before routine monitoring of effluent quality was started in the first week of August 2012.

### **Preozonation and postozonation**

Ozonation was performed in semibatch mode. Ozone gas produced from ultrapure oxygen by an ozone generator (AZH-3S, Hamamatsu Vegetable(Japan)) was continuously fed to the A<sub>2</sub>O water in the glass ozone contactor (volume, 3.3 L) through a bubble diffuser at the bottom.

### **Analytical methods**

DOC was determined with a TOC analyzer (TOC-L, Shimadzu(Japan)) in nonpurgeable-organic-carbon (NPOC) mode. Chlorine demand was determined based on the chlorine consumption in 24 hours. EDTA was measured by an HPLC method after derivatization (Kemmi et al., 2007). 1,4-dioxane concentration was measured by GC/MS after solid-phase extraction (Nishimura et al., 2010). PPCPs were measured by LC-MS/MS after solid-phase extraction (Yonetani et al., 2012). Bromate ion concentration was determined by an ion-chromatography with a postcolumn-derivatization method (JWWA, 2011). For the formation potentials of THMs and HAAs, samples were chlorinated for 24 hours. HAA concentrations were determined by GC/MS after derivatization to the corresponding methyl esters (USEPA, 2003). THM concentrations were measured by GC/MS analysis using the same column as in HAA analysis following liquid-liquid extraction with pentane (APHA et al., 2005).

## **RESULTS AND DISCUSSION**

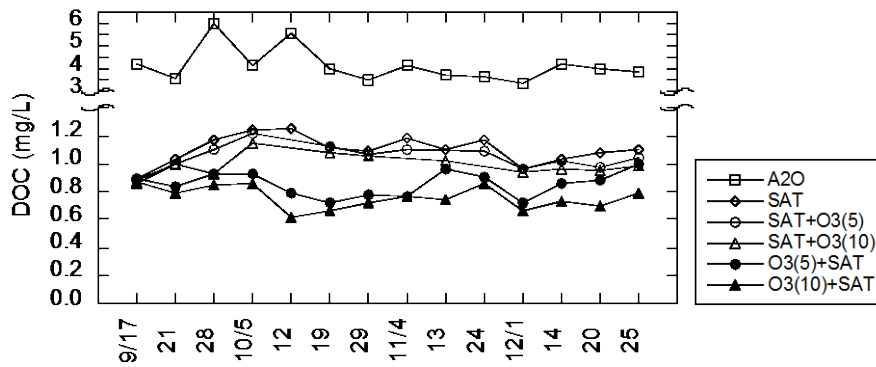
### **DOC profiles**

The DOC profiles after acclimatization are shown Figure 2. As expected, preozonation itself did not change DOC. When preozonation was applied, however, regardless the ozone dose, the DOC levels after SAT were lower than that of SAT alone (average DOC removals: 80.4% for O<sub>3</sub>(5)+SAT, 82.4% for O<sub>3</sub>(10), and 74.3% for SAT alone). This was probably because the biodegradability of dissolved organic matter (DOM) in the A<sub>2</sub>O water was enhanced by ozonation (Treguer, et al., 2010; Sallanko, J. and Välsänen, T., 2013). Postozonation decreased DOC levels to some extent, but was less effective than the combination of preozonation and SAT. Relatively high ozone doses to low DOC levels appeared to result in partial mineralization of DOM through radical reactions (i.e., self-decomposition of ozone) (e.g., von Gunten, 2003).

### **Chlorine demand**

SAT alone reduced chlorine demand by 85.9%, and was much more effective than ozonation alone for the reduction of chlorine demand. Postozonation did not decrease chlorine demand. On the other hand, the combination of preozonation and SAT achieved slightly lower chlorine demand (approximately 90% reduction for both ozone doses) than SAT alone.

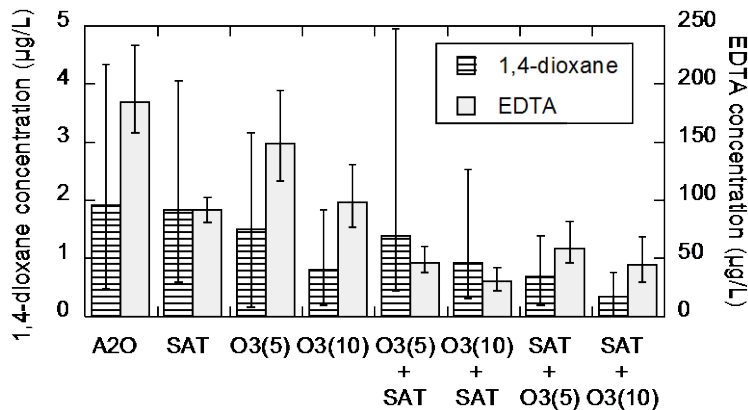
The above results on DOC and chlorine demand suggest that the combination of preozonation and SAT be effective for the removal organic compounds and the reduction of the reactivity of DOM to oxidizing and halogenating reagents in general. However, for recalcitrant compounds (e.g., 1,4-dioxane), the combination of SAT and postozonation may be better as a lower DOC during ozonation would enhance the availability of hydroxyl radicals to target compounds. This point will be further discussed in the next subsection.



**Figure 2.** Comparison of Time-DOC profiles after acclimatization.

### Trace organic compounds

The combination of SAT and postozonation was the most effective option for the removal of 1,4-dioxane among the options tested contrary to the results on DOC (Figure 3). The removal was very limited when SAT alone was applied. Also, no clear difference was observed between ozonation and the combination of preozonation and SAT. Thus, 1,4-dioxane was mainly removed during ozonation, and the efficiency of ozonation was improved by higher availability of hydroxyl radicals with the reduced background DOC level after SAT.



**Figure 3.** Comparison of 1,4-dioxane (n = 8) and EDTA (n = 7) removals.

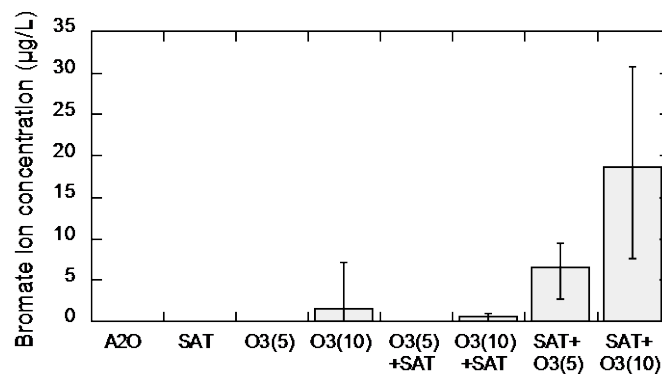
For EDTA, the combination of preozonation and SAT was better than other treatment conditions. Similarly to the DOC profiles, the enhanced biodegradability of DOM by preozonation improved the removal under this condition.

PPCPs were almost completely removed during ozonation regardless the order of treatment. Thus, it can be said that ozonation is a good way to backup SAT for controlling this class of chemicals. However, one should keep in mind that ozonation does not completely mineralize these compounds. The health effects and fate of these transformation products need to be addressed in the future research. It is also of note that CBZ concentration increased after SAT. This could be due to deconjugation reactions (Vieno et al., 2007).

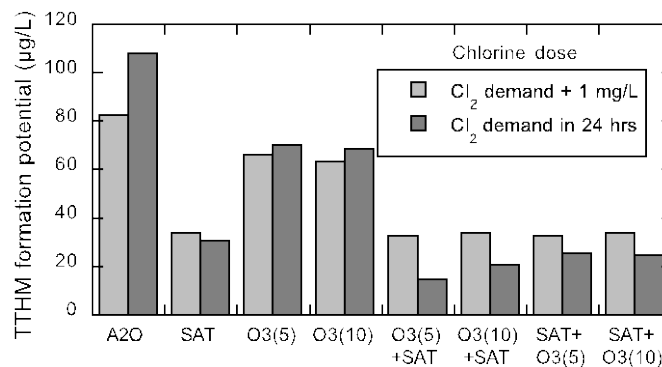
### Disinfection byproducts

Bromate ion was below the detection limit (< 0.5 µg/L) for SAT, O3(5), O3(5)+SAT (Figure 4). Ozone appeared to be consumed rapidly by the reaction with DOM under these conditions. Bromate

ion was detected under other conditions. In particular, higher bromate ion concentrations than the WHO guideline value (10 µg/L) were found for the SAT + O3(10) condition. Obviously, this is due to higher availability of molecular ozone and hydroxyl radicals for oxidation of bromide ion. It should be noted that bromate ion would be a major constraint when applying postozonation to remove trace organic compounds resistant to biological treatment.



**Figure 4.** Comparison of bromate ion concentration (n = 8).



**Figure 5.** Comparison of THMFPs (n = 6 for chlorine dose = chlorine demand for 24 hrs, and n = 2 for chlorine dose = chlorine demand for 24 hrs + 1 mg/L).

Similar THMFPs were observed for SAT alone, preozonation + SAT, and SAT + postozonation. The combination of preozonation + SAT with the lower chlorine dose (= chlorine demand for 24 hours) was slightly better for the reduction of THMFPs than the postozonation option (Figure 5). The bromine incorporation ratio was higher for the preozonation option. These results may reflect the fact that DOM after the treatment by preozonation + SAT is less reactive to chlorine than DOMs in other conditions. A similar trend was found for HAAFPs (data not shown).

### Risk evaluation

Based on the results obtained in this study, we attempted to compare the total risks for the options tested. For this purpose, the results (the maximum concentrations for the target compounds or indices, hereinafter denoted as  $C$ ) were classified into three categories: the safe zone, for  $C$  lower than 10% of the standards or guideline values (STD); the monitoring zone, those for  $10\% \text{ of STD} \leq C \leq \text{STD}$ ; danger zone, those above STD. Then, for data points in the safe zone and the monitoring zone, 0 point and  $C/\text{STD}$  point were assigned, respectively. A treatment option with items in danger zone was excluded from the evaluation. Table 1 summarizes the result of the evaluation. In total, the combination of preozonation and SAT at an ozone dose of 5 mg/L was the best option among those tested in this study. One may argue that lower risks were obtained for the preozonation options because of high concentration of bromate ion resulting from high ozone doses as drinking

water treatment, and the postozonation options could be better if the ozone dose was optimized. However, our evaluation excluding bromate ion also indicated that preozonation options are better than postozonation options. Thus, even with the optimized ozone dose, preozonation would be a more appropriate treatment option.

The above results imply the importance of upgrading a water reclamation system as a total system. That is, upgrading pretreatment may be more effective than upgrading the following drinking water treatment process. Also, it should be emphasized that relatively high ozone doses were used in this study, and only the combination of ozonation and SAT was discussed. For more detailed and realistic optimization including cost, considerations on lower ozone dose and other treatment steps (e.g., coagulation and activated carbon treatment) would be necessary.

**Table 1.** Summary of risk evaluation (Values shown in the table are C/STD. The standard value for HAA5 is the one regulated by USEPA (2006). Other standard and guideline values are those in Japan. The evaluation on 1,4-dioxane and PPCPs are not listed as all the evaluations were in the safe zone.)

	A2O	SAT	O3(5)	O3(10)	O3(5)+SAT	O3(10)+SAT	SAT+O3(5)	SAT+O3(10)
TCM	>STD	0.22	0.53	0.61	0.20	0.21	0.24	0.24
BDCM	0.61	0.39	>STD	0.97	0.41	0.45	0.36	0.45
DBC	0.00	0.10	0.15	0.16	0.00	0.00	0.00	0.00
TBM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
T-THMs	0.89	0.36	0.83	0.72	0.35	0.38	0.33	0.37
DCA	0.93	0.26	0.59	0.69	0.19	0.20	0.27	0.25
TCA	0.23	0.00	0.14	0.13	0.00	0.00	0.00	0.00
HAA5	>STD	0.34	0.90	0.95	0.31	0.27	0.32	0.30
EDTA	0.47	0.21	0.39	0.26	0.12	0.00	0.16	0.14
BrO <sub>3</sub> <sup>-</sup>	0.00	0.00	0.00	0.71	0.00	0.11	0.95	>STD
Total	>STD	1.88	>STD	5.20	1.58	1.62	2.63	>STD

## CONCLUSIONS

The combination of preozonation and SAT was compared with the combination of SAT and postozonation for controlling DOC, chlorine demand, PPCPs, and disinfection byproducts for water reclamation. Better reductions of DOC and EDTA were observed with the preozonation option. On the other hand, for the removal of 1,4-dioxane, the postozonation option was better. The PPCPs monitored were almost completely oxidized in both preozonation and postozonation. The comparison of total risks for the options tested indicated that the combination of preozonation and SAT was the best option for the target compounds and indices monitored in this study.

## ACKNOWLEDGEMENTS

This study was supported by JST, CREST. We also appreciate Kyoto City Waterworks Bureau for providing the feed water and technical supports for this project.

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