Effect of preozonation on wastewater reclamation by the combination of ozonation and soil aquifer treatment
S. Echigo, M. Nakatsuji, Y. Takabe and S. Itoh

ABSTRACT
A series of column experiments and risk evaluation showed that preozonation was a better option to enhance the performance of soil aquifer treatment (SAT) than ozonation after SAT with respect to dissolved organic carbon, trace organic contaminants, and disinfection byproducts. This is a good example to show that upgrading pretreatments can be more effective than adding extra treatments after SAT, and that it is important to optimize a water reclamation system as a whole system.

Key words | disinfection byproducts, ozonation, soil aquifer treatment, trace organic compounds

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 form of water reclamation. This technique is different from other engineered treatment technologies (e.g. reverse osmosis) for its use of the natural environment (Dillon et al. 2010). SAT, however, is not a popular option in highly populated areas because of the limitation on land space (i.e. short hydraulic retention time (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 a reclamation system 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 in SAT. 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 dissolved organic carbon (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 control 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 a liquid chromatography-tandem mass spectrometry (LC-MS/MS) system, formic acid and acetonitrile (LC/MS grade, Wako) were used for the preparation of mobile phases. 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 ultrapure water produced with a Millipore Academic-A10 system.

**Feed water**

An effluent from an actual wastewater treatment with anaerobic–anoxic–aerobic process (A2O) in Kyoto City (Japan) was used as the feed water for this study. The effluent was collected at the outlet of the A2O process (i.e. before chlorine disinfection). This effluent was filtered with a cellulose membrane (5A, Advantec (Japan)) and stored 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 potential of four major trihalomethanes (THMs) and nine major haloacetic acids (HAAs) were evaluated as the major disinfection byproducts.

**Soil aquifer treatment**

Three laboratory-scale sand columns were operated under aerobic conditions. 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: A2O water or ozonated A2O 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 A2O water in the glass ozone contactor (volume, 3.3 L) through a bubble diffuser at the bottom.

**Analytical methods**

DOC was determined with a total organic carbon (TOC) analyzer (TOC-L, Shimadzu (Japan)) in nonpurgeable-organic-carbon mode. Chlorine demand was determined based on the chlorine consumption in 24 h. EDTA was measured by a high-performance liquid chromatography (HPLC) method after derivatization (Kemmei et al. 2011). 1,4-dioxane concentration was measured by gas chromatography-mass spectrometry (GC/MS) after solid-phase extraction (Nishimura et al. 2010). PPCPs were measured by LC-MS/MS after solid-phase extraction (Yonetani et al. 2010).
et al. 2012). Bromate ion concentration was determined by ion-chromatography with a postcolumn-derivatization method (JWWA 2011). For the formation potential of THMs and HAAs, samples were chlorinated for 24 h. HAA concentrations were determined by GC/MS after derivatization to the corresponding methyl esters (USEPA 2003). THM concentrations were measured by GC/MS after 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, the DOC levels after SAT were lower than that of SAT alone (average DOC removals: 80.4% for O3(5) + SAT, 82.4% for O3(10), and 74.3% for SAT alone) regardless of the ozone dose. This was probably because the biodegradability of dissolved organic matter (DOM) in the A2O water was enhanced by ozonation (Treguer et al. 2010; Sallanko & Väisänen 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 chain 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 (Figure 3). Postozonation did not decrease chlorine demand. Conversely, 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 is effective for the removal of 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 for the decomposition of target compounds. This point will be further discussed in the next subsection.

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 of DOC (Figure 4). The removal was very limited when SAT was applied alone. Also, no clear difference was observed between ozonation and the combination of preozonation and SAT. Thus, 1,4-dioxane was mainly oxidized during ozonation, probably through the reaction with hydroxyl radical (OH) as 1,4-dioxane is a saturated compound. Although the decomposition mechanism of 1,4-dioxane during ozonation or ozone-based advanced
oxidation processes (AOPs) is not fully understood, a reaction pathway starting from hydrogen abstraction is expected (Merayo et al. 2014; Stefan & Bolton 1998). The efficiency of ozonation was improved for the post-ozonation conditions with higher availability of hydroxyl radicals because of the reduced background DOC level after SAT.

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.

Most PPCPs were almost completely removed during ozonation regardless of the order of treatment (Figure 5). The removal percentages were more than 91% except for DEET (0–83%) under the treatment conditions with ozonation. It can be said that ozonation is a good way to back up 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 future research. It is also of note that CBZ concentration increased after SAT from 28 to 74 ng/L. This could be because of 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 6). 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.

Similar THM formation potential (THMFP) was observed for SAT alone, preozonation + SAT, and SAT + postozonation. The combination of preozonation + SAT with the lower chlorine dose (= chlorine demand for 24 h) was slightly better for the reduction of THMFP than the postozonation option (Figure 7). 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 HAA formation potential (HAAFP) (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% of STD ≤ C ≤ STD; the danger zone, those above STD. Then, for data points in the safe zone and the monitoring zone, 0 point and C/STD point were assigned, respectively. Treatment options with an item in the danger zone were excluded from the evaluation. Table 1 summarizes the results 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 lower bromate ion concentration, and that the postozonation options could be better if the ozone dose were optimized. However, our evaluation excluding bromate ion also indicated that preozonation options are still better than postozonation options. Thus, even with the optimized ozone dose, preozonation would be the 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.

**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 options. Conversely, for the removal of 1,4-dioxane, the

![Figure 7](https://iwaponline.com/ws/article-pdf/15/1/101/414400/ws015010101.pdf)
postozonation option was better. Most 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.

REFERENCES


Arnell, N. W. 1999 Climate change and global water resources. Global Environ. Change. 9, S31–S49.


USEPA 2003 Method 552.3: Determination of haloacetic acids and dalapon in drinking water by liquid–liquid microextraction, derivatization, and gas chromatography with electron capture detection.


First received 8 April 2014; accepted in revised form 18 August 2014. Available online 28 August 2014