



Removal and transformation of organic matter during soil-aquifer treatment*

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Abstract: This study investigated the removal and transformation of organic matter through laboratory-scale soil-aquifer treatment (SAT) soil columns over a 110-day period. Reductions in total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC), nonbiodegradable dissolved organic carbon (NBDOC) and absorbance of ultraviolet light at 254 nm (UV-254) averaged 71.46%, 68.05%, 99.31%, 33.27% and 38.96% across the soil columns, respectively. DOC/TOC ratios increased slightly with depth while BDOC/DOC ratios showed a converse trend. DOC exiting the soil-column system contained only a very small biodegradable fraction. SAT decreased the concentration of DOC present in feed water but increased its aromaticity, as indicated by specific ultraviolet light absorbance (SUVA), which increased by 50%–115% across the soil columns, indicating preferential removal of non-aromatic DOC during SAT. Overall, laboratory-scale SAT reduced trihalomethane formation potential (THMFP), although specific THMFP increased. THMFP reduction was dominated by removal in chloroform. All samples exhibited a common general relationship with respect to weight: chloroform>dichlorobromomethane>dibromochloromethane>bromofrom.

Key words: Soil-aquifer treatment (SAT), Organic matter, Dissolved organic matter, Trihalomethane formation potential, Biodegradable dissolved organic carbon (BDOC), Specific trihalomethane formation potential

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INTRODUCTION

Increasing population and higher standards of living have resulted in high demands for water. Wastewater reuse is becoming an alternative for solving the problem of the ever-increasing demand for water. Advanced treatment technologies are capable of treating wastewater even to potable standards (Viswanathan *et al.*, 1999) but have high capital and operation costs, require educated operators, which are not well suited for developing countries (Westerhoff and Pinney, 2000). To overcome this limitation, soil-aquifer treatment (SAT) systems are increasingly used for the treatment of wastewater. Factors in favor

of SAT systems are their economical attractiveness and low maintenance compared with the complex technology and high energy requirements of advanced wastewater treatments systems (Viswanathan *et al.*, 1999). SAT systems operate by the infiltration of treated wastewater through the vadose zone. Water quality benefits are obtained during percolation through vadose zone sediments and subsequent groundwater storage.

Organics are of concern in SAT systems using secondary or tertiary effluents, because they may pose health concerns (Drewes and Peter, 1999; Westerhoff and Pinney, 2000), and have the potential to generate harmful disinfection by-products, as a result of their reaction with chlorine (Drewes *et al.*, 2003; Yoon *et al.*, 2003).

This article will focus on removals of organic matter, transformations in dissolved organic carbon

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(DOC) structure and changes in reactivity of DOC with chlorine during SAT. In addition to DOC, water quality parameters forming the basis for evaluation of SAT performances included total organic carbon (TOC), absorbance of ultraviolet light at 254 nm (UV-254), biodegradable dissolved organic carbon (BDOC), nonbiodegradable dissolved organic carbon (NBDOC), and trihalomethane formation potential (THMFP).

MATERIALS AND METHODS

Description of laboratory systems

To study organics removal during SAT, an adapted soil-column system which simulated aquifer conditions in a series of three 55 cm-columns (diameter 10 cm) was used (Fig.1). The SAT columns were acrylic with top and bottom caps sealed with rubber gaskets. A screen was placed at the bottom of the column to support 2.5 cm of sand, 2.5 cm of gravel, plus 50 cm of soil. Each column was fitted with a sampling port at the bottom. A peristaltic pump recirculated water from the top of the first 55-cm-column (vertically mounted), which was equipped with a low volume constant head tank, back to the feed solution. The soil-column system operated under gravity flow conditions with approximately 2 cm of hydraulic head. Soils for the SAT columns were selected from the dry bed of the Songhuajiang River in Harbin. Soils were collected from below the root zones and particles larger than 5 mm were screened out. All soils (saturated hydraulic conductivity= 1.1×10^{-4} cm/s) were packed to field density at field moisture content. Infiltration rates average 0.5 ml/min, but decrease during flooding; these rates are restored during the drying period. Tertiary effluent of the Wenchang Wastewater Treatment Plant (WWTP), an effluent additionally treated by powered activated carbon (PAC) to eliminate organic carbon was used as influent for the laboratory-scale SAT. Table 1 summarizes the WWTP tertiary effluent water quality data collected from March 2005 to June 2006.

Prior to experiments the soil columns were biologically acclimated by infiltration of fresh feed water for a period of two months. Columns were operated in twenty-day cycles consisting of 10 d of flooding followed by 10 d of drying. During the wetting cycles, influents applied to the columns were changed

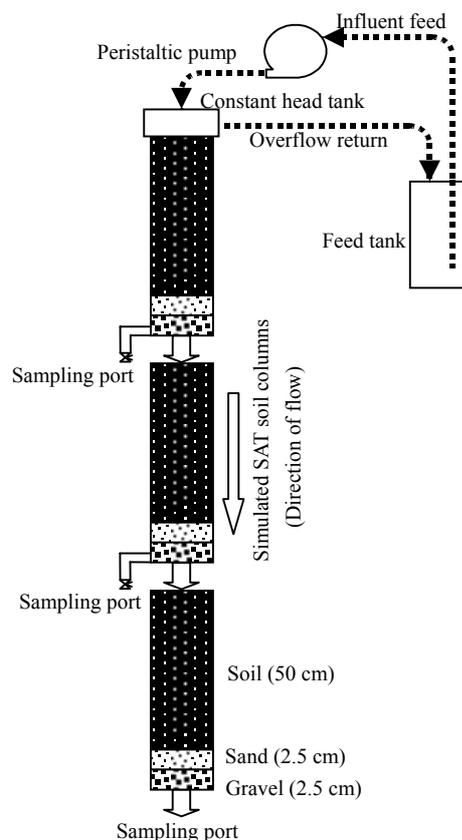


Fig.1 Scheme of the laboratory-scale soil-aquifer treatment system

Table 1 Water quality data for the WWTP tertiary effluent between March 2005 and June 2006 ($n=20$)

Parameter	Mean \pm SD
pH	7.6 \pm 0.1
COD (mg/L)	35 \pm 2.7
TOC (mg/L)	16.68 \pm 1.3
DOC (mg/L)	12.08 \pm 0.9
UV-254 (m^{-1})	13.7 \pm 0.7
Alkalinity (mg CaCO ₃ /L)	111.3 \pm 18.2
Total hardness (mg CaCO ₃ /L)	156.33 \pm 1.9
Nitrate (mg N/L)	3.2 \pm 1.7
Ammonia (mg N/L)	2.0 \pm 1.5
Total phosphorus (mg/L)	3.1 \pm 0.2
Chloride (mg N/L)	60.9 \pm 10.4
Sulfate (mg N/L)	39.9 \pm 11.1

every two days and effluents from the columns were sampled every two days. During the drying cycles wastewater application ceased, allowing time for re-establishing hydraulic permeabilities and for allowing oxygen diffusion into the subsurface (Westerhoff and Pinney, 2000).

Analytcs

All samples were filtered using 0.45 μm cellulose nitrate membrane filter and stored at 4 $^{\circ}\text{C}$ prior to analysis.

TOC and DOC were analyzed using a combustion technique with a Shimadzu TOC-5000 Total Organic Carbon Analyzer. Ultraviolet absorbance (UV) was measured with a Shimadzu UV-2550 UV/VIS spectrophotometer at 254 nm using a quartz cell with a 1 cm path length. The instrument was zeroed using ultra-pure water (Milli-Q) as a blank. Specific ultraviolet light absorbance (SUVA) was calculated as $(\text{UV-254}/\text{DOC}) \times 100$. SUVA is a measure of the contribution of aromatic structures to DOC (Leenheer and Croué, 2003). It also has been widely used as a surrogate of THM (Chow *et al.*, 2003).

The fraction of BDOC in DOC was assessed using BDOC reactors as described by Kwon *et al.* (2005). Briefly, 70 g of biologically acclimated sand, with an associated biofilm, was placed in a 500 ml flask, and a 250 ml sample was added. The reactor was loosely capped with tinfoil. The BDOC tests were performed with aeration of the sample, which was incubated at room temperature in the dark (Kwon *et al.*, 2005). BDOC was determined as the difference between the initial (day 0) and final (day 5) DOC values. NBDOC was that which remained after the 5-day incubation.

THMFP measurements were performed using a modified version of method 5710B described in (Chow *et al.*, 2003). Each sample, adjusted to about pH 7 with phosphate buffer, was chlorinated using concentrated HOCl solution, with a chlorine dosage level based on the inorganic and organic demand according to the following formula (Kwon *et al.*, 2005):

$$[\text{Cl}_2] = (3 \times [\text{DOC}]) + (7.5 \times [\text{NH}_4^+]).$$

The chlorinated samples were incubated at 25 $^{\circ}\text{C}$ for 7 d. Then, residual chlorine was quenched with 0.5 ml of 8% sodium thiosulfate solution after 7 d of incubation. The concentrations of chloroform (TCM), dichlorobromomethane (BDCM), dibromochloromethane (DBCM), and bromoform (TBM) were measured using a Hewlett Packard 5890 II gas chromatograph fitted with an auto injector, a capillary split-splitless inlet, and a Nickel⁶³ electron capture

detector. THMFP was calculated as the sum of the four THM species. All THM samples were analyzed in duplicate to compensate for the inherent variability of the analytical procedures. Samples with relative-percent differences of the duplicates that exceeded 30% were reanalyzed.

RESULTS

Organics removal

Removal of TOC was relatively rapid during percolation through laboratory-scale SAT soil columns. The TOC concentrations in the soil-column system influent and effluent are presented in Fig.2. In a period of 110 d of experimental run, the average influent and effluent TOC concentrations were 16.67 and 4.67 mg/L, respectively. TOC removal rates averaged 71.46%, corresponding to absolute TOC removals of (11.91 ± 1.68) mg/L in the soil-column system. Moreover, an effluent TOC concentration of less than 3.5 mg/L was not observed.

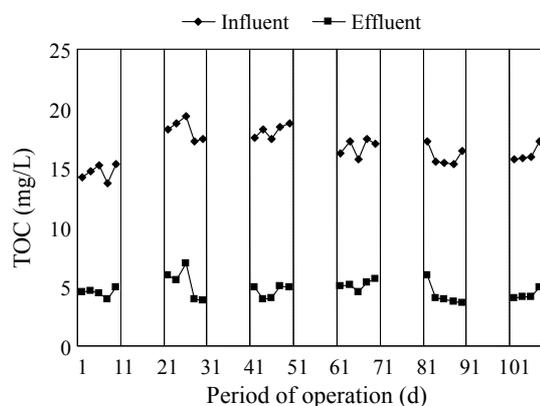


Fig.2 Influent and effluent TOC concentrations from laboratory-scale soil-aquifer treatment columns

Variations of the average removal efficiency for TOC, DOC, BDOC, NBDOC and UV-254 with depth are illustrated in Fig.3. The TOC removal rates averaged 51.85%, 65.35% and 71.46% as a consequence of 0.5 m-, 1.0 m- and 1.5 m-soil infiltration, respectively. It became obvious that the majority of TOC was eliminated during the initial infiltration and that the most significant TOC removal occurred in the top 0.5 m.

Trends in DOC paralleled TOC behavior with

the average removal rates of 47.63%, 62.42% and 68.05% across 0.5 m-, 1.0 m- and 1.5 m-soil column, respectively (Fig.3). As reported in previous studies, biodegradation is the primary DOC removal mechanism during SAT (Rauch-Williams and Drewes, 2004; 2006), which can be verified using SUVA data presented subsequently. Fox *et al.*(2005) suggested that soil-aquifer treatment could remove organic carbon without accumulation from adsorption that might eventually lead to breakthrough.

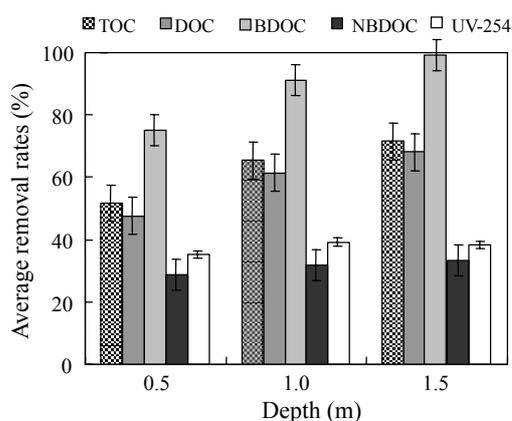


Fig.3 Removals of organics as function of depth (error bars indicate standard deviations. The numbers of measurements for TOC, DOC and UV-254 are all 30, and for both BDOC and NBDOC are 3, respectively)

BDOC experiments served as an independent assessment for the biological reactivity of DOC (Westerhoff and Pinney, 2000). In an attempt to investigate biodegradable portion of DOC as function of depth, BDOC tests were conducted. As shown in Fig.3, the BDOC reduction of 75.14% occurred in the first 0.5 m soil infiltration and BDOC in feed water was removed by 99.31% across the 1.5 m-soil columns. It can be seen in Fig.3 that BDOC was removed easily in comparison with TOC and DOC, suggesting preferential removal of biodegradable organic matter during SAT.

The removal in NBDOC was also observed during percolation through the soil columns, with average removal rates of 28.86%, 31.86 and 33.27% obtained at 0.5 m-, 1.0 m- and 1.5 m-depth, respectively (Fig.3). The reduction in NBDOC may result from sorption followed by decomposition. Quanrud *et al.*(2003) suggested that aerobic biodegradation is expected to be relatively unimportant in contribution

to removals of NBDOC and that anoxic biodegradation may be responsible for decreases in NBDOC during percolation. It is also possible that adsorption of organics to soil particles during transport has a modest overall effect on organic matter (Quanrud *et al.*, 2003).

The parameter of UV-254 was routinely measured as an indicator of aromatic content in all samples collected throughout the study. As shown in Fig.3, UV-254 removal was significant (35.17%) across the first 0.5 m-soil column. Nevertheless, only minor further UV-254 removal (3.79%) was observed during the subsequent percolation through the soil-column system.

As shown in Fig.4, influent, 0.5 m-, 1.0 m- and 1.5 m-effluent showed a slightly increasing trend in their DOC/TOC ratios, which increased by 11.9% from 83.13% to 93.01% across the soil columns, suggesting that colloidal organic matter was removed more efficiently than dissolved organic matter during SAT. In contrast to DOC/TOC ratios, BDOC/DOC ratios exhibited a tendency to decrease along with depth. It can be seen in Fig.4 that influent BDOC/DOC ratio was 59.33%, exhibiting high biological reactivity of DOC in feed water. In addition, it was also noticed that the BDOC/DOC ratio of 1.48% was significantly low for 1.5 m-effluent, corresponding to the BDOC concentration of 0.05 mg/L exiting the soil-column system. These data indicated that more than 99% of biologically degradable organic matter in feed water was removed during the initial 1.5 m of soil infiltration and that DOC exiting the soil-column system contained only a very small biodegradable fraction.

Transformations in DOC structure

DOC structure was assessed by SUVA. SAT decreased the concentration of DOC present in feed water but increased its aromaticity, as indicated by SUVA, which increased monotonically across the SAT columns over the course of the study (Fig.4). The influent SUVA ranged from 0.7 to 1.2 L/(m·mg), and SUVA values exiting the soil-column system were 0.6~1.4 L/(m·mg) higher than influent levels, representing a 50%~115% increase. Basu and Huck (2004) suggested that the parameter of SUVA incorporates the DOC value and that a higher degree of removal of readily degradable carbons will elevate the level of

SUVA since these non-aromatic components contribute little to the UV absorbance value.

Increased SUVA values across the soil columns may be attributed to preferential removal of non-aromatic compounds during soil infiltration. In addition, Westerhoff and Pinney (2000) suggested that release of high molecular weight soluble microbial by-products (SMPs) from the biomass and leaching of soil organic material may elevate the level of SUVA. Since biodegradation of lower molecular weight compounds leads to increased SUVA values, while sorption of larger molecular weight and more hydrophobic constituents has an opposite effect on SUVA (Westerhoff and Pinney, 2000), increased SUVA values observed in this study suggest the dominance of biodegradation of lower molecular weight compounds over adsorption of larger molecular weight and more hydrophobic constituents.

Reactivity of DOC with chlorine

The reactivity of DOC with chlorine was assessed in terms of THMFP several times in this study. Because formation potential is dependent on DOC

concentration, the reactivity of forming THMFP is also reported in terms of specific THMFP, that is, micrograms of THMFP formed per milligram of DOC precursor material in the water ($\mu\text{g THMFP}/\text{mg DOC}$) (Galapate *et al.*, 2001). The results of THMFP experiments are presented in Table 2. Of the four THM species in influent, TCM was the major THM chlorine product, constituting 78.18% of the total trihalomethanes (THMs) by weight, followed by BDCM and DBCM, accounting for 19.36% and 2.16% respectively. TBM was low enough to be ignored. In effluent exiting the soil-column system, TCM was greatest and TBM was lowest, accounting for 50.12% and 1.66%, respectively. BDCM and DBCM increased from 19.36% to 36.91% and from 2.16% to 11.31% across the soil columns, respectively. Similar distribution of THM was also found in 0.5 m- and 1.0 m-effluent (data not shown). It was noted that all samples exhibited a common general relationship with respect to weight: $\text{TCM} > \text{BDCM} > \text{DBCM} > \text{TBM}$.

Despite the decrease of 54.82% in overall THMFP, specific THMFP, or the reactivity of forming THMFP increased monotonically from 27.71 to 43.05 $\mu\text{g THMFP}/\text{mg DOC}$, indicating preferential removal

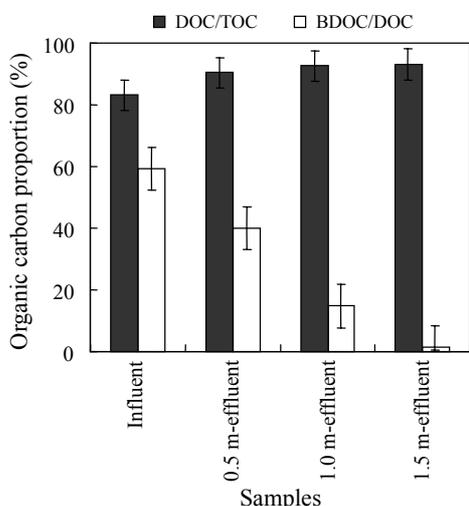


Fig.4 Fractions of DOC in TOC and fractions of BDOC in DOC for different-depth samples (error bars indicate standard deviations determined from triple measurements)

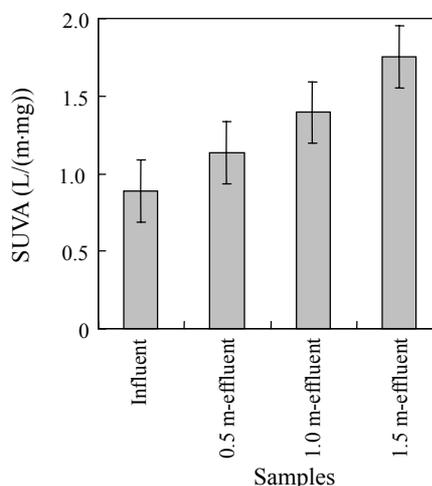


Fig.5 SUVA values for different-depth samples (error bars indicate standard deviations determined from 30 times measurements)

Table 2 Summary of THMFP experiments

Sample	Chlorine demand (mg Cl ₂ /L)	TCM ($\mu\text{g}/\text{L}$)	BDCM ($\mu\text{g}/\text{L}$)	DBCM ($\mu\text{g}/\text{L}$)	TBM ($\mu\text{g}/\text{L}$)	THMFP ($\mu\text{g}/\text{L}$)	Specific THMFP ($\mu\text{g THMFP}/\text{mg DOC}$)
Influent	114.78	262.94	65.11	7.28	1.01	336.342	27.71
0.5 m-effluent	20.24	113.64	66.23	16.26	3.12	199.250	30.37
1.0 m-effluent	14.27	95.06	62.50	16.17	2.89	176.620	37.35
1.5 m-effluent	11.18	76.18	56.09	17.18	2.52	151.970	43.05

of DOC with low THMFP yields across the soil columns. These sections do not overly contribute to THMFP but clearly contribute to the overall DOC value, therefore the removal of DOC with low THMFP yields results in a drop in DOC while a corresponding drop in THMFP is not observed, resulting in the higher specific THMFP values observed. As depicted in Table 2, BDCM was relatively constant at about 60 $\mu\text{g/L}$ in almost all samples while DBCM and TBM increased by more than 100% across the soil columns. It was also observed that THMFP reduction during initial infiltration was dominated by removal in TCM and that the majority of removal in TCM occurred in the first 0.5 m of soil infiltration. While the laboratory-scale SAT reduced THMFP on an absolute concentration basis, the DOC exiting the soil-column system had a greater propensity to form THMs during chlorine-based disinfection.

In addition, specific THMFP after SAT was low, about 43 $\mu\text{g THMFP/mg DOC}$ in this study, as compared to those from water containing solely natural organic matter (NOM), i.e. specific THMFP from rivers ranged from 47 to 190 $\mu\text{g THMFP/mg DOC}$, from groundwaters ranged from 25 to 83 $\mu\text{g THMFP/mg DOC}$, and from raw drinking waters ranged from 41 to 68 $\mu\text{g THMFP/mg DOC}$ (Rostad *et al.*, 2000). Leenheer *et al.* (2001) reported low THMFP yields for dissolved organic matter isolates from reclaimed water. They observed that a significant amount of the aromatic carbon in reclaimed water has sulfonic acid substituents and identified that these compound classes have lower chlorination yields than aromatic carbon in NOM.

CONCLUSION

Following percolation of tertiary effluent through laboratory-scale SAT columns over a 110-day period, bulk organics were effectively removed, demonstrated by the removal of TOC, DOC and BDOC. Moreover, a modest removal of biorefractory fraction was also observed in the soil-column system, in terms of NBDOC and UV-254 (removal rates of 33.27% and 38.96%, respectively). The most significant removal in organics in the soil-column system occurred in the initial 0.5 m of soil infiltration.

Influent, 0.5 m-, 1.0 m- and 1.5 m-effluent

showed a slightly increasing order in their DOC/TOC ratios while BDOC/DOC ratios decreased rapidly with depth. More than 99% of biologically degradable organic matter was removed during the initial 1.5 m of soil infiltration and DOC exiting the soil-column system contained only a very small biodegradable fraction.

SAT decreased the concentration of DOC present in feed water but increased its aromaticity, as indicated by SUVA, which increased by 50%~115% across the soil-column system, suggesting preferential removal of organics with low UV-254 absorbance during SAT.

Laboratory-scale SAT reduced the potential towards forming THMs during chlorine-based disinfection. However, specific THMFP increased from 27.71 to 43.05 $\mu\text{g THMFP/mg DOC}$, indicating potential preferential removal of DOC with low THMFP yields during SAT. THMFP reduction during initial infiltration was dominated by removal in TCM. All samples exhibited a common general relationship with respect to weight: TCM>BDCM>DBCMB>TBM.

Future research needs to address the transport and fate of pharmaceutically active compounds, endocrine-disrupting compounds, and other unregulated trace pollutants.

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