Effect of operating conditions in soil aquifer treatment on the removals of pharmaceuticals and personal care products

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ABSTRACT

Soil aquifer treatment (SAT) is an alternative advanced treatment for wastewater reclamation, and it has the potential to control micropollutants including pharmaceuticals and personal care products (PPCPs). However, the relationship of operating conditions in SAT and removals of micropollutants was not clear. In this study, the effects of operating conditions on the removals of PPCPs were evaluated by using lab-scale columns and plant pilot-scale reactors under different operating conditions. Firstly, weathered granite soil (WGS), standard sand (SAND) and Toyoura standard sand (TS) have different soil characteristics such as total organic carbon (TOC) and cation exchange capacity (CEC). In the columns with these packing materials, the removals of carboxylic analgesics and antilipdemics were effective regardless packing materials. The removals of antibiotics were more effective in WGS than in TS and SAND, indicating high TOC and CEC enhance the sorption in SAT. Secondly, with the extension of hydraulic retention time (HRT), the removals of sulfamethoxazole, acetaminophen, crotamiton, and antipyrine were improved in WGS columns, and adaptable biodegradation for moderately removable PPCPs was formed. Thirdly, the removal efficiencies of sulfamethoxazole and crotamiton were higher in the WGS column under vadose condition than in the WGS column under saturated condition, because of aerobic condition in WGS column under vadose condition. Though long HRT and vadose condition had positive influence on the removals of several PPCPs such as sulfamethoxazole, WGS column with an HRT of 7 days under saturated condition removed most PPCPs.

KEYWORDS

PPCPs; SAT; Packing materials; Hydraulic retention time; Saturated condition

1.# INTRODUCTION

Micropollutants including pharmaceuticals and personal care products (PPCPs) are ubiquitous (from ng/L to low µg/L) in the effluents from wastewater treatment plants (WWTPs) (Boyd et al., 2003; Ellis, 2006; Focazio et al., 2008; Kim et al., 2009; Lin et al., 2009; Okuda et al., 2009; Ort et al., 2010; Stuer-Lauridsen et al., 2000; Yonetani et al., 2012), and they may pose risks to both human and ecosystems (Nakada et al., 2010). Thus, an additional process after the treatments in WWTPs is required on the improvement of water quality (Suárez et al., 2008), and soil aquifer treatment (SAT) is an option for this purpose. Though SAT has benefits such as low operating cost and stable performance (Gerba et al., 1991; Idelovitch and Michail, 1984), not all micropollutants are degraded completely in SAT (Hernández et al., 2012). Degradation of micropollutants including EDCs and PPCPs in soil were affected by environmental conditions such as temperature, pH, moisture content, organic carbon, the presence of specific microorganisms, and DO conditions (Aga, 2007; Colucci et al., 2001; Monteiro and Boxall, 2009). Schaffer et al. (2015) demonstrated that the

hydrophobicity of compounds and the solid organic matter in SAT column enhanced the sorption of neutral and anionic compounds. However, our understanding on the relationship between these operating conditions and the properties of micropollutants is still poor, and the roles of SAT as an additional process to wastewater treatment remain unclear.

This study addresses these unanswered questions by monitoring the removals of various PPCPs in SAT. PPCPs are an ideal group of compounds for this purpose because of their variety of chemical properties (Suárez et al., 2008), giving insight into the removal mechanism in SAT. The removals of PPCPs in SAT were assessed in both field- and laboratory-scale studies: Drewes et al. (2001) mentioned that six to ten years of saturated anoxic flow led to 60% removal of X-ray contrast media in a field-scale groundwater recharge. In another experiment, the removal efficiency of sulfamethoxazole in a bank filtration system was 95%, but only 53% in an artificial recharge system (Grünheid et al., 2005). Xu et al. (2009) observed that the removal of six PPCPs varied in four agricultural soils. These studies indicated that the operating conditions influenced the removals of PPCPs in SAT, but the number of target compounds is limited.

Though previous studies revealed the removal characters of several PPCPs in SAT, no study systematically evaluated the relationship between the removals of PPCPs and operating conditions with respect to the properties of PPCPs. In this study, the effects of operating conditions (packing materials, hydraulic retention time (HRT), and saturated conditions) on the removals of PPCPs were evaluated in the SAT columns under setting operating conditions. Furthermore, the cooperation between SAT and conventional activated sludge (CAS) treatment was discussed with respect to the removals of micropollutants.

2.# MATERIALS AND METHODS

In this study, the experiments were divided into three parts: the effects of 1) packing materials, 2) HRT and 3) vadose condition on the removals of PPCPs in SAT. Firstly, columns packed with weathered granite soil (WGS), standard sand (SAND) and Toyoura standard sand (TS) were operated to evaluate the effects of packing materials on the removals of PPCPs. Secondly, two series of experiments were conducted to evaluate the effect of HRT. In the first set, WGS with HRTs of typical SAT operation (i.e., 7, 30 and 180 days); in the second set, shorter HRTs (i.e., 4 hours, 8 hours, 1 day and 7 days) were used to understand the removals of PPCPs in SAT with short-term HRT. The experiments were divided into two parts of time-scales: WGS columns with HRTs of 7, 30, and 180 days were evaluated to understand the influences of the long-term HRTs (day-scale) in SAT as well as WGS columns with HRTs of 7 days, 1 day, 8 hours and 4 hours for the short-term HRTs (hour-scale). Thirdly, WGS columns under vadose and saturated conditions were operated to evaluate the effect of vadose condition on the removals of PPCPs in SAT.

2.1.# Reagents

In this study, 42 PPCPs were selected according to the frequency of their detection in the effluents of WWTPs (Okuda et al., 2009; Yonetani et al., 2012) (Table 1). DEET was the abbreviation of *N, N*-Diethyl-meta-toluamide. CAM and SDIME were dissolved into acetone (Okuda et al., 2009). CPFX, LVFX, NRFX, and ERFX were dissolved into a water/acetonitrile solution, and all the other PPCPs were dissolved into acetonitrile to prepare the stock solutions. For the analysis of PPCPs with a LC-MS/MS system, formic acid, methanol, and acetonitrile (LC-MS grade) were used for the preparation of mobile phase.

CAF and CTC were purchased from Cosmo Bio Co., Ltd; IPP and LVFX were purchased from Tokyo Chemical Industry Co., Ltd; ATP, LCM, ATL, AZM, CPF, DTZ, ERF, FNP, FSM, GFB, MFA, OTC, SMT, TC, IBP, SMETH, and TRM were purchased from Funakoshi Co., Ltd, and all other compounds were purchased from Wako Pure Chemical Co., Ltd. All the aqueous solutions were prepared with ultra-pure water produced with Millipore Academic-A10 system (hereinafter call MQW).

2.2.# Feed water

An effluent from an actual WWTP using anaerobic–anoxic/oxic (A_2O) process (hereinafter called A_2O water) in Kyoto City (Japan) was used as the feed water for the experiments. Water quality of feed water was shown in [Table 3](#).

2.3.# SAT columns setting

In this study, WGS, SAND and TS were used as the packing materials for SAT columns. WGS is a typical soil in the west of Japan, and TS is a typical sand in Japan (van Wijhe, 2002). The characteristics of these packing materials (WGS, SAND and TS) were shown in [Table 2](#). WGS has higher cation exchange capacity (CEC) and total organic carbon (TOC) than SAND and TS.

In order to evaluate the influence of operating conditions of SAT on the removals of PPCPs, SAT columns under different conditions were operated. Two large lab-scale acrylic columns ([TS-7](#) and [Sand-7](#); i.d., 15 cm; H, 150 cm), two medium lab-scale acrylic column ([WGS-7](#) and [WGS-1](#); i.d., 8 cm; H, 100 cm), two small lab-scale acrylic columns ([WGS-4H](#) and [WGS-8H](#); i.d., 5 cm; H, 40 cm), and three pilot plant-scale stainless steel reactors ([WGS-30](#), [WGS-180](#), and [WGS-Sat](#); L, 1.5 m; W, 1.5 m; H, 3.0 m) were used. The operating conditions of columns are summarized in [Table 4](#). The concentration of dissolved organic carbon (DOC) ranged from 0.806 (WGS-180) to 2.551 ng/L (WGS-4H), and pH of SAT effluents was at a steady range from 6.26 to 7.11. These values did not show clear difference between samples, and these indicated that the performances of SAT columns were stable in long-term operation. Feed water for large lab-scale acrylic columns was fed by peristaltic pumps (7554-80, Thermo Fisher Scientific), and feed water for medium and small lab-scale acrylic column was fed by peristaltic pumps (SJ1220, ATTA). The operation of the large lab-scale acrylic columns, medium lab-scale acrylic columns, and small lab-scale acrylic columns started in January 2012, April 2013, and July 2014, respectively.

Feed water for pilot plant-scale stainless steel reactors was pumped into reactors by centrifugal pumps. The soil pilot-plant scale reactors consisted of the bottom layer (gravel level) and the soil layer. For the vadose condition, the water head was maintained at 20 cm below the top of the WGS/SAND layer. For the saturated condition, the water head was maintained at 20 cm above the top of the WGS layer. Sand pilot plant-scale reactor started in October 2011; and WGS pilot plant-scale reactors started in April 2012. The schematic of pilot plant-scale reactors is shown in [Figure 1](#).

2.4.# Analytical methods

200 mL of water samples for LC-MS/MS measurement was filtered by glass fiber membrane filters (ADVANTEC GF-75, 90 mm). All filtrates were concentrated with solid-phase extraction (SPE). The SPE cartridge (Oasis HLB cartridges (Waters), 250 mg bed) was conditioned with 5 mL of methanol and 5 mL of MQW at pH 3 (adjusted with hydrochloric acid). Samples were pumped through the cartridge at a flow rate of 10 mL/min for 20 minutes. After drying the SPE cartridges with nitrogen gas, the retained compounds were eluted with 5

mL of methanol. The eluted solution was evaporated to dryness under a gentle stream of nitrogen gas (Okuda et al., 2009; Yonetani et al., 2012). The residues of the A₂O water and SAT effluent samples were re-dissolved in 2 mL and 1 mL of 0.1% formic acid-acetonitrile (90/10, v/v), respectively. The solution was analyzed by LC-MS/MS. In this study, prominence 20A (Shimadzu system) interfaced to 4000 QTRAP (AB SCIEX) with a C-18 column (Kinetex, 2.1 mm, 2.6 µm) and a VP-ODS column (Shimadzu, 4.6 mm, 4.6 µm) was used for negative mode analysis and positive mode analysis, respectively. In the LC-MS/MS measurement, multiple-reaction monitoring (MRM) mode was chosen for the quantification of target compounds. Operating conditions of LC-MS/MS were optimized by using MQW with the addition of standard compounds. LC-MS/MS conditions, MRM parameters, and LC gradient for the separation of target compounds were shown in **Tables S1-S7 (supplement information)**.

The recoveries of the target compounds were determined by fortifying standard compounds into A₂O water or SAT effluent. The fortified sample and the blank (i.e. A₂O water without fortification) were concentrated as described above. These samples were prepared in duplicate, and the average recovery rate of each target compound in A₂O water and SAT effluent was shown in **Figure S1 (Supplementary information)**. The standard curve was checked before each measurement of PPCPs, and the recovery experiment was checked about every two months. The method of standard addition was used for calculating the recoveries of PPCPs referring to the works of Okuda et al. (2009).

3.# RESULTS AND DISCUSSION

3.1.# Occurrence of PPCPs in the A₂O water

The concentrations of PPCPs in A₂O water were summarized in **Figure 3**. The total concentration of target PPCPs in A₂O water was more than 5000 ng/L. Okuda et al. (2008) reported that total concentration of 66 PPCPs in the WWTPs effluents was up to approximately 10000 ng/L. Yang et al. (2011) reported that total concentration of 19 PPCPs in the effluent after membrane treatment was up to approximately 2000 ng/L. Referring to the works of Tootchi (2010), the concentration of PPCP above 20 ng/L was considered as a high concentration in the water treatment. Antibiotics and analgesics were the major PPCPs in A₂O water (**Figure 3**). This result confirmed that CAS treatment cannot remove PPCPs completely.

For antibiotics, CAM, AZM, LVFX, and CPFX were observed at relatively high concentrations (769, 175, 28, and 23 ng/L, respectively), while ERFX was not detected in the A₂O water. These were in agreement with other studies on the occurrences of antibiotics in wastewater effluents (Narumiya et al., 2009; Yasojima et al., 2006). For analgesics, CRT was the most abundant in A₂O water (806 ng/L on average). In previous studies, CRT was also detected at relatively high concentration (1240 ng/L and 921 ng/L, respectively) in the effluents of several WWTPs (Nakada et al., 2006; Narumiya et al., 2009). In addition, KTP, DCF, MFA, ACEAM and NPX were also dominant in A₂O water (639, 80, 75, 17, and 34 ng/L respectively), which were in agreement with the works of Tixier et al. (2003). In this study, IBP was not detected in the A₂O water. Kobayashi et al. (2006) and Narumiya et al. (2009) mentioned that IBP was detected at a relatively high concentration in wastewater influents, but not detected in wastewater effluents. This could be attributed to biodegradation in treatment (Kraigher et al., 2008; Nakada et al., 2006; Radjenović et al., 2009).

For other groups of selected PPCPs, BZF, SLP, TEP, DEET, CAF, DSP and FSM were observed at high concentrations (193, 397, 108, 455, 94, 237, and 203 ng/L, respectively). These PPCPs were also detected at relatively high concentration in the effluents of other WWTPs (Kim et al., 2012; Kimura et al., 2007; Lin et al., 2009).

The selected PPCPs have a wide range of physical-chemical properties and complex chemical structures (In [Table 1](#), their K_{oc} values (i.e., soil organic carbon-water partition coefficient) range from 0.69 to 61000, and their pK_a values range from 1.4 to 9.5.), and were widely detected in A_2O water. Thus, PPCPs were appropriate as the indicators of micropollutants in SAT. In addition, because the concentrations of PPCPs fluctuated in A_2O water and SAT effluents during the monitoring period, the monthly average values ($n=11$) were used to calculate the removal efficiencies of SAT in the following parts (Karnjanapiboonwong et al., 2011). Considering the concentration of PPCPs in A_2O water in [Figure 3](#) (>10 ng/L) and the frequencies of detection (GFB, ATP, LCM, and IPP), 29 PPCPs were chosen as target compounds to evaluate the removal characters of PPCPs in SAT under different operating conditions.

3.2.# Effects of packing materials on the removals of PPCPs

Their removal efficiencies in SAT were divided into four levels: 1) highly efficient ($>90\%$), 2) efficient (80-90%), 3) moderate (50-80%) and 4) poor ($<50\%$) (Matamoros et al., 2008b; Reif et al., 2011; Reungoat et al., 2011). The removals of PPCPs in SAT were mainly attributed to the sorption and biodegradation (Hoppe-Jones et al., 2012). Removal efficiencies of selected PPCPs (max, average, and min values) in SAT columns of 7 days packed with weathered granite soil (WGS-7), SAND (Sand-7) and Toyoura sand (TS-7) were shown in [Figure 4](#).

Among antibiotics, effective removals (above 90%) were observed for CAM, LCM, and AZM in WGS-7 and Sand-7. In TS-7, the removal efficiencies of CAM, LCM and AZM were 71.1%, 52.5% and 92.7%, respectively, which were less efficient than those in WGS-7 and Sand-7. Polar (2007) mentioned that macrolides (i.e., CAM, LCM and AZM) were readily adsorbed in bank filtration. In addition, Schlüsener and Bester (2006) studied the persistence of macrolides, and the half lives of macrolides were longer than 20 days. Thus, abiotic process mainly contributed to their effective removals in SAT columns with HRT of 7 days. The pK_a values of CAM, LCM, and AZM ranged from 7.60 to 8.99 (above the pH in SAT columns (i.e., approximately 6.0)), and significant ionic interaction was expected to be significant for their removals in SAT (Göbel et al., 2005; Sibley and Pedersen, 2007). Cation exchange is an important ionic interaction, and contributed to the sorption of antibiotics in soil (Figuerola et al., 2004; Sassman and Lee, 2005). WGS and SAND have higher CEC values (15.6 and 2.39 meq/100mg, respectively) than TS (0.192 meq/100mg). Gao and Pedersen (2005) mentioned that CEC had positive influence on the sorption of sulfonamide antimicrobial agent to clay minerals. Thus, the effective removals of CAM, LCM, and AZM were attributed to the CEC of WGS and SAND.

LVFX, one of fluoroquinolones, was removed by 97.7%, 85.3%, and 61.7% in WGS-7, Sand-7, and TS-7, respectively, and their high removals in soil were also reported in other works (Drillia et al., 2005; Picó and Andreu, 2007; Tolls, 2001). Their effective removals were attributed to abiotic degradation in SAT because their resistance on biodegradation was expected in solid matrices such as soil and sand (Golet et al., 2003; Picó and Andreu, 2007; Uslu et al., 2008). The K_{oc} value of LVFX (44143 mL/g) is high as well as other fluoroquinolones (CPFX, ERFX and NRFX, their K_{oc} values range from 15800-61000 mL/g),

and K_{oc} can enhance the immobility of compounds in soil, and compounds with K_{oc} values of more than 5000 mL/g were expected to be immobile in soil (Khan and Anjaneyulu, 2005). Thus, the effective removals of LVFX in columns were attributed to the sorption because of its high K_{oc} . Among columns with different packing materials, WGS-7 and Sand-7 removed LVFX more effectively than TS-7. The TOC values of WGS, TS and SAND were 0.0159%, 0.0144% and 0.0094%, respectively. Soil organic matter (SOM) enhanced the sorption of micropollutants in soil (Bot and Benites, 2005), and this explained the improvement of removals of LVFX in WGS-7 column compared with TS-7. Furthermore, for the characteristics related to sorption, not only organic content of soil influenced the sorption of micropollutants in soil (Yu et al., 2009), but also surface characters of soil such as specific surface area strongly enhanced the sorption (Bailey and White, 1970; Tolls, 2001). In this study, WGS and SAND have much higher values of specific area (5.95 and 2.40 m²/g) than TS (0.812 m²/g). This can explain the difference of removal efficiencies of LVFX between Sand-7 and TS-7. Furthermore, TOC and specific area of soil enhanced the sorption of antibiotics having high K_{oc} . Overall, WGS showed better performance on the sorption of antibiotics, and this is attributed to high TOC, CEC, and specific area of WGS. From the perspective of practical use, WGS was suitable for SAT packing materials to remove antibiotics in wastewater effluents.

Among the analgesics and antilipidemics PPCPs, the removal efficiencies of DCF, KTP, NPX, MFA, BZF, CFB, and GFB (carboxylic PPCPs) were in the range of 81.8% and 99.6% (in WGS-7); 80.6% and 99.0% (in Sand-7); 84.9% and 98.7% (in TS-7). Their removals in SAT are all high regardless packing materials. In addition, the removal efficiencies of FSM, another carboxylic PPCP, were 94.4%, 98.8%, and 99.6% in WGS-7, Sand-7, and TS-7, respectively. The removal efficiencies of DEET were 70.3%, 55.3%, and 54.2% in WGS-7, Sand-7, and TS-7, respectively. In previous studies, these compounds were biodegradable in treatments including soil and activated sludge treatments (Drewes et al., 2006; Fang et al., 2012; Onesios et al., 2009; Tiehm et al., 2011). Thus, biodegradable PPCPs were similarly removed efficiently regardless packing materials (WGS, SAND and TS). For amide PPCPs (Nakada et al., 2007) (ATP, IPP, CRT, PRM, and CBM), their removals were poor regardless packing materials (less than 50%) except the removal of ATP in Sand-7 (57.2%). Furthermore, the concentration of CBM increased in SAT columns with different packing materials (78.8%, 114.0% and 52.5% in WGS-7, Sand-7 and TS-7, respectively). For persistent PPCPs, their removals were still poor in SAT columns with different packing materials. Kasprzyk-Hordern et al. (2009) also reported that CRT and CBM were removed only slightly in soil infiltration. For persistent PPCPs, their poor removals, more specifically, negative removals would be discussed in the following part. Similar biodegradation among columns with different packing materials could be attributed to the similar microbial metabolic patterns among the top layers of SAT because of the continuous usage of wastewater effluent (Takabe et al., 2014). In order to evaluate the removal mechanism of SAT, control experiment by using sterilization will be required in our future study. Packing materials had little influence on the biodegradation in SAT, and the effect of HRT on biodegradation would be discussed in the following part.

In summary, WGS possessing high TOC, CEC and specific surface showed strong sorption for the removals of antibiotics, but packing materials had little influence on the biodegradation of SAT.

3.3.# The effect of HRT on PPCP removals in SAT

In this section, the removal efficiencies of target PPCPs in SAT columns of 7, 30 and 180 days packed with weathered granite soil (WGS-7, WGS-30 and WGS-180) were shown in [Figure 5](#). The removals of LVFX were efficient in WGS columns regardless HRT (above 90%). In addition, the removals of CAM, LCM, AZM, TRC, and TRM were also highly efficient (above 90%). Rapid sorption of compounds was also observed in other works ([Allaire et al., 2006](#); [Song and Guo, 2014](#)). Thus, HRT had little influence on the sorption process in SAT. For SMETH, another antibiotic agent, its removal efficiencies were low in WGS columns with an HRT of 7 days. SMETH possesses sulfonamide group, and the persistence of sulfonamide compounds was observed in soil ([Accinelli et al., 2007](#); [Boxall et al., 2002](#); [Yang et al., 2009](#)). However, the removal of SMETH was enhanced by extending HRT (81.5% in WGS-180). [Gimbel et al. \(2006\)](#) demonstrated that long HRT enhanced the removal of SMETH in slow sand filters. Furthermore, [Stoob et al. \(2006\)](#) reported that the concentration of spiked SMETH decreased with extending contact time in soil. These indicated that the effective removals of SMETH in WGS columns were attributed to the sufficient HRT.

For carboxylic PPCPs (DCF, KTP, NPX, MFA, BZF, CFB, GFB, and FSM), their removals in WGS columns were efficient with HRTs of 7, 30, and 180 days, respectively (above 80%). The removals of NPX were more efficient in SAT with an HRT of 7 days or longer (81.8%, 83.8% and 87.5% in WGS-7, WGS-30, and WGS-180, respectively). For biodegradable PPCPs except NPX, their removals were high in WGS-7. [Abel \(2014\)](#) mentioned that SAT with several days (5 days) removed pharmaceutically active compounds (PhACs) effectively. [Ternes et al. \(2007\)](#) reported that IBP and BZF were readily removed at above 90% in SAT with an HRT of 1 day. During the long-term operation, effective removals of carboxylic PPCPs occurred in the WGS column with an HRT of 7 days, and extending HRT had little influence on improvement of their removals. However, in short-term operation, several hours were not sufficient for the removals of carboxylic PPCPs, and their removals efficiencies increased with extending HRT. For example, removal efficiencies of KTP were 47.1%, 62.0%, 80.4%, and 99.6% in WGS-4H, WGS-8H, WGS-1, and WGS-7, respectively. In WGS-8H, the removal efficiencies of most carboxylic PPCPs (DCF, KTP, NPX, MFA, BZF, GFB, and FSM) achieved the moderate level (>50%), and the pK_a values of these PPCPs ranged from 3.8 (FSM) to 4.5 (GFB) as well as that their K_{oc} values ranged from 204 (BZF) to 880 (MFA). CFB showed poorer removal than these carboxylic PPCPs. [Yuan et al. \(2005\)](#) mentioned that the value of pK_a reflects the proton releasing ability of a compound, and the biodegradability of phenols was positively correlated with pK_a . Relatively poor removal of CFB (36.3%) in WGS-8H could be attributed to that CFB is harder to penetrate cells and arrive at the enzyme active with lower pK_a (3.18), and HRT in SAT enhanced the removals of CFB more clearly than the removals of other carboxylic PPCPs. In addition, the removal of TEP was improved with extending HRT (from 67.3% to 82.4% in WGS), and the removal efficiencies of BP ranged from 61.5% to 94.7% with extending HRT. [Zhang et al. \(2011\)](#) demonstrated that biodegradations of estrogen in soil columns were enhanced by extending HRT. [Drewes et al. \(2006\)](#) mentioned that a longer HRT in SAT eliminated organic pollutants more effectively. For the biological communities in SAT columns with a long HRT, [Idelovitch and Michail \(1984\)](#) mentioned that adaptable biodegradation of organic substances required a long period of time for the development and acclimatization of the microbial population, and the growth of the adaptable biological communities was expected in SAT by extending HRT ([Gielen et al., 2011](#); [Lin et al., 2010](#)). These indicated that the biodegradation of moderately removable PPCPs can be improved by sufficient HRT (longer than 7 days).

For amide PPCPs such as ATP, IPP, CRT, and PRM, their removals were poor in WGS-7 column (20.0%, 42.2%, 31.9%, and 9.3%, respectively), and the clear improvements on their removals were not observed by extending HRT (28.7%, 40.4%, 49.2%, and 14.6% in WGS-180, respectively). These indicated that extending HRT cannot improve the removals of amide PPCPs in SAT. All SAT columns showed negative removal on CBM. Matamoros et al. (2008a) observed that CBM was persistent in subsurface flow. Gibson et al. (2010) also illustrated that CBM was resistant to degradation in soil. Furthermore, Yonetani et al. (2016) mentioned that CBM was formed by deconjugation of its metabolites (i.e., hydroxylated CBM). Maeng et al. (2011) found that the concentration of CBM increased in sand column with feeding non-chlorinated tap water. In addition, the increases of CBM were reported in wastewater treatments (Clara et al., 2005; Kreuzinger et al., 2004; Vieno et al., 2007). Thus, the negative removal on CBM in SAT could be attributed to degradation of its metabolites.

Long HRT improved the removals of PPCPs in SAT, which was in agreement with other works (Drewes et al., 2001; Grünheid et al., 2005; Matamoros et al., 2008b), but the extension of HRT requires unrealistically large space for treatment. In Figure S2 (supplementary information) Error! Reference source not found., the removal efficiencies of different categories were summarized by calculating the total concentration of each category in the influent and effluent from each column. Antibiotics were removed effectively in WGS columns even with a short HRT. The removals of analgesics, antilipdemics and others were improved by extending HRT, but the removal efficiencies of all selected categories reached above 60% in the WGS column with an HRT of 7 days. These indicated that HRT of 7 days could be sufficient for the effective removals of most PPCPs.

In summary, short HRT was sufficient for the sorption of most antibiotics except SMETH, and the effective removal of SMETH required long SAT in SAT. The removals of amide PPCPs (ATP, IPP, PRM, and CBM) were poor regardless HRT, and the removals of moderately removable PPCPs (ACEAM, TEP, and BP) were improved by extending HRT. Overall, several hours were not suitable for the effective removals of carboxylic PPCPs, and an HRT of 7 days can be sufficient for their removals.

3.4.# The effect of saturated conditions on PPCPs removals in SAT

In actual SAT operation, the aerobic and anaerobic conditions were considered as key operating conditions for biodegradation (Kim et al., 2004). The effects of saturated and vadose conditions on PPCP removals were evaluated by using SAT columns packed with weathered granite soil under saturated and vadose conditions with HRT of 30 days (WGS-Sat and WGS-30) (Figure 7).

For LVFX, CAM, LCM, AZM, TRC and TRM, their removals were high (above 80%) in WGS columns under both vadose and saturated conditions. According to the results, for the removals of antibiotics by sorption and ionic interaction, they did not vary under vadose or saturated conditions.

For highly biodegradable PPCPs (DCF, KTP, NPX, MFA, BZF, CFB, GFB, and FSM), their removals were effective regardless saturated and vadose conditions. Conkle et al. (2012) mentioned that the half-lives of GFB and IBP in wetland under anaerobic condition were longer than under aerobic condition. Jim et al. (2006) reported that PPCPs such as ACEAM, DCF, IBP, GFB, NPX and KTP were effectively biodegraded under aerobic conditions. Lin and Gan (2011) also reported that NPX, TRM, DCF, IBP, and SMETH were susceptible to biodegradation under aerobic condition. These indicated that aerobic condition enhanced the

biodegradation of most highly biodegradable PPCPs in SAT. However, in this study, SAT under saturated condition showed similar removal efficiencies of profens and antilipdemics as SAT under vadose condition. The concentration of dissolved oxygen (DO) in the feed water was 3.36 mg/L on average (Takabe et al., 2014), so aerobic condition was maintained in the top level of the saturated column. The biodegradation of highly biodegradable PPCPs could be effectively removed in the top of saturated column because of relatively high DO in feed water. For amide PPCPs (ATP, IPP, CRT, PRM, and CBM), their removals were consistently poor (less than 50%) under saturated and vadose conditions. These indicated that vadose condition had little influence on the resistance of amide PPCPs in SAT.

Though most selected PPCPs were similar on their removals in WGS columns under saturated and vadose conditions, the removal efficiencies of SMETH were 46.4% and 72.7% in WGS-Sat and WGS-30, respectively. The vadose condition was helpful to make the air trapped in soil and increase the oxygen concentration in the soil to support the aerobic biodegradation of SMETH. Monteiro and Boxall (2009) mentioned that aerobic bacteria contributed to the removals of SMETH in soil. Similarly, Liu et al. (2010) and Baumgarten et al. (2011) reported that aerobic bacteria could degrade SMETH easily under vadose condition. Compared with profens and antilipdemics, the removal of SMETH arrived at the effective level in WGS-180 column, and this indicated that the biodegradation of SMETH need long-term contact time. In SAT under vadose condition, sufficient DO concentration was expected in deeper levels. Thus, continuous aerobic condition was expected in the SAT column under vadose condition to support the long-term biodegradation of SMETH.

Highly biodegradable PPCPs such as profens and antilipdemics were removed effectively regardless of vadose conditions, but the removals of SMETH and CRT were improved under vadose condition. From the perspective of practical use, saturated condition has been sufficient for the removals of PPCPs in SAT, and sufficient DO in A₂O water support the biodegradation of most biodegradable PPCPs in SAT. Cooperation of SAT and CAS treatment (A₂O process) was practical for wastewater reclamation to remove micropollutants.

Comparing SAT with studied soil treatments (Table 5), WGS-7 showed effective removals on antibiotics as well as other treatments. For BZF, CFB, and FSM (halogenated carboxylic acids), SAT achieved higher removal efficiencies than other treatments. However, the negative removal of CBM was observed as well as the work of Drewes et al. (2002). These indicated that additional advanced treatment was necessary to improve the control of micropollutants during wastewater reclamation.

4.# CONCLUSIONS

Packing materials had little influence on the characteristics of biodegradation in SAT, but WGS possessing high values of TOC, CEC and specific area was suitable to remove antibiotics by sorption.

Removal efficiencies of biodegradable PPCPs (i.e., carboxylic PPCPs) were improved by extending HRT. However, for most PPCPs except SMETH, ATP, CRT and ACEAM, their removals were sufficiently high in the WGS column with an HRT of 7 days.

Wastewater effluent after A₂O process provided sufficient DO for biodegradation of most selected PPCPs, but the removals of SMETH and CRT were more effective under vadose

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condition than saturated condition. Thus, cooperation of SAT and CAS treatment (A_2O process) was practical for wastewater reclamation to control micropollutants.

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Table 1 List of the target PPCPs.

Compounds	K_{oc}	pK_a	COOH	Use/category	Abbr.
Ampicillin	6.423	2.5, 7.3	+	Antibiotic	AMP
Azithromycin	3100	8.74	-	Antibiotic	AZM
Chlortetracycline	6.575	1.4		Antibiotic	CTC
Ciprofloxacin	61000	6.09	+	Antibiotic	CPFX
Clarithromycin	150	8.99	-	Antibiotic	CAM
Enrofloxacin	15800	5, 8-9	+	Antibiotic	NRFX
Erythromycin	570	8.88		Antibiotic	ERY
Levofloxacin	44143	6.24, 8.74	+	Antibiotic	LVFX
Lincomycin	69	7.6	-	Antibiotic	LCM
Norfloxacin		6.34, 8.75	+	Antibiotic	NRFX
Oxytetracycline	4.319	9.5	-	Antibiotic	OTC
Sulfadimethoxine	285.2	6.91		Antibiotic	SDIME
Sulfamethazine	208	7.59		Antibiotic	SMT
Sulfamethoxazole	72	1.6, 5.7		Antibiotic	SMETH
Tetracycline	0.69	3.3	-	Antibiotic	TC
Triclosan	19952	7.9		Antibiotic	TRC
Trimethoprim	75	7.12	-	Antibiotic	TRM
Acetaminophen	41	9.6	+	Analgesic	ACEAM
Antipyrine	11.65	4.15		Analgesic	ATP
Aspirin	100		+	Analgesic	ASP
Crotamiton	244	10.45		Analgesic	CRT
Diclofenac	245	4.5	+	Analgesic	DCF
Fenoprofen	233.8	4.15	+	Analgesic	FNP
Ibuprofen	3400	9.38	+	Analgesic	IBP
Isopropylantipyrine	84.96	4.91		Analgesic	IPP
Ketoprofen	229	4.20	+	Analgesic	KTP
Mefenamic acid	880.1	4.20	+	Analgesic	MFA
Naproxen	330	4.45	+	Analgesic	NPX
Atenolol	4.081	3.83		Antiarrhythmic	ATL
Disopyramide	288	3.18		Antiarrhythmic	DSP
Bezafibrate	204	3.61	+	Antilipidemic	BZF
Clofibric acid	43.7	3.18	+	Antilipidemic	CFB
Gemfibrozil	430	4.5	+	Antilipidemic	GFB
DEET	300			Rejectant	DEET
Benzophenone	517			Ultraviolet absorber	BP
Caffeine	741			Cardiac	CAF
Carbamazepine	510	13.9		Antipilepsy	CBM
Primidone	23.84	11.5		Antipilepsy	PRM
Sulpiride	13.85	9.12		Peptic ulcer	SLP
Theophylline	517			Cardiac	TEP
Diltiazem	197.8	8.06		Blood-vessel dilator	DTZ
Furosemide	302	3.8,7.5	+	Blood-vessel dilator	FSM

Table 2 Soil characteristics of WGS, sand and Toyoura standard sand.

	WGS	Sand	Toyoura standard sand

Ignition loss (%)	2.74	1.36	0.376
Water content (%)	1.1	0.567	0.0654
pH	6.53	6.64	6.87
CEC (meq/100mg)	15.6	2.39	0.192
TOC (%)	0.0159	0.0094	0.0144
Porosity	0.40	0.44	0.43
Particle size distribution (0.05 mm-, %)	>99	>99	100
Specific surface (m ² /g)	5.95	2.40	0.812

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Table 3 Water quality of A₂O water.

pH	DO(mg/L)	DOC(mg/L)	UV₂₅₄(cm⁻¹)
6.43 (6.37-6.50)	1.47(1.13-1.75)	3.68(3.31-4.19)	0.082(0.070-0.128)

DTP-P (mg/L)	DTN-N(mg/L)	NH₄⁺-N(mg/L)	NO₂⁻-N(mg/L)
0.400 (0.280-0.805)	4.43(3.87-4.89)	<0.02(<0.02-0.56)	0.046(0.014-0.080)

NO₃⁻-N(mg/L)	Organic-N(mg/L)		
3.41(3.26-3.46)	0.92(0.53-0.97)		

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Table 4 Operating conditions of the columns.

Fr αp qv#	Vf ddn#	Sdf nlqj #p dndvdv#	KUV#	Vdvxudlv q# f r qglvr q#	Hiiαhqv#GRF# tp j 2Q#	Hiiαhqv#K#
TS-7	Lab	Toyoura standard sand	7 days	Unsaturated	1.659±0.219 (n=17)	6.77±0.43 (n=29)
Sand-7	Lab	Standard sand	7 days	Unsaturated	1.020±0.138 (n=18)	6.80±0.42 (n=29)
WGS-7	Lab	Weathered granite soil	7 days	Unsaturated	1.082±0.099 (n=8)	6.98±0.19 (n=8)
WGS-30	Pilot plant	Weathered granite soil	30 days	Unsaturated	0.819±0.110 (n=11)	6.50±0.40 (n=11)
WGS-180	Pilot plant	Weathered granite soil	180 days	Unsaturated	0.806±0.128 (n=11)	6.26±0.48 (n=11)
WGS-Sat	Pilot plant	Weathered granite soil	30 days	Saturated	1.050±0.306 (n=11)	6.54±0.35 (n=11)
WGS-1	Lab	Weathered granite soil	1 days	Unsaturated	2.055±0.103 (n=7)	7.01±0.11 (n=7)
WGS-4H	Lab	Weathered granite soil	4 hours	Unsaturated	2.551±0.289 (n=7)	7.11±0.22 (n=7)
WGS-8H	Lab	Weathered granite soil	8 hours	Unsaturated	2.483±0.408 (n=7)	7.07±0.06 (n=7)

Table 5 Comparison of removal efficiencies of target PPCPs between this study and previous studies.

Compounds	Removal efficiencies in WGS-7 (%)	Removals in studied systems (%)	systems studied
AZM	98.77	>90(Berglund et al., 2014)	Surface-flow constructed wetlands(Berglund et al., 2014)
CAM	99.76	>88(Ternes et al., 2007)	Subsurface flow(Ternes et al., 2007)
LVFX	97.71	-	-
LCM	90.09	78(Chen et al., 2015)	Integrated constructed wetland(Chen et al., 2015)
SMETH	61.80	82(Ternes et al., 2007), 95(Grünheid et al., 2005)	Subsurface flow(Grünheid et al., 2005; Ternes et al., 2007)
TRC	96.11	67.9(Waltman et al., 2006)	Constructed wetland(Waltman et al., 2006)
TRM	99.29	>92(Ternes et al., 2007)	Subsurface flow(Ternes et al., 2007)
ACEAM	29.72	86 (Teerlink et al., 2012) 96(Maeng et al., 2011)	Laboratory experiment for onsite wastewater soil treatment (Teerlink et al., 2012) Managed aquifer recharge (Maeng et al., 2011)
ATP	19.99	-	-
CRT	31.89	22(Shinohara et al., 2006)	Soil column(Shinohara et al., 2006)

DCF	94.08	96(Massmann et al., 2006), (>87, >98)(Drewes et al., 2002), 71.0(Hua et al., 2003)	Constructed wetland(Massmann et al., 2006), Subsurface flow(Drewes et al., 2002), lab column(Hua et al., 2003)
IPP	42.22	-	-
KTP	99.55	97(Matamoros et al., 2008b)	Constructed wetland(Matamoros et al., 2008b)
MFA	95.21	45-46(Shinohara et al., 2006)	Soil column(Shinohara et al., 2006)
NPX	81.75	92(Matamoros et al., 2008b) >99(Drewes et al., 2002)	Constructed wetland(Matamoros et al., 2008b) Subsurface flow(Drewes et al., 2002)
ATL	93.15	>93(Ternes et al., 2007)	Subsurface flow(Ternes et al., 2007)
DSP	97.9	-	-
BZF	98.75	>80(Ternes et al., 2007)	Subsurface flow(Ternes et al., 2007)
CFB	82.1	36, 32 (Matamoros et al., 2008b), 48.3(Hua et al., 2003), >79(Ternes et al., 2007)	Constructed wetland(Matamoros et al., 2008b), Lab columns(Hua et al., 2003), Subsurface flow(Ternes et al., 2007)
GFB	95.08	>99(Drewes et al., 2002)	Subsurface flow(Drewes et al., 2002)
DEET	70.3	48(Teerlink et al., 2012) >60 (Yoon et al., 2013)	Laboratory experiment for onsite wastewater soil treatment (Teerlink et al., 2012) Aquifer recharge and recovery (Yoon et al., 2013)
BP	61.45	-	-
CAF	87.19	>88(Ternes et al., 2007)	Subsurface flow(Ternes et al., 2007)
CBM	-78.76	5(Matamoros et al., 2008a)	Subsurface flow(Matamoros et al., 2008a)
PRM	9.25	<-5(Drewes et al., 2002)	Subsurface flow(Drewes et al., 2002)
SLP	98.47	-	-
TEP	67.26	-	-
DTZ	98.9	~96(Wu et al., 2010)	Soil amended with biosolids(Wu et al., 2010)
FSM	94.41	71(Matamoros et al., 2009)	Constructed wetland(Matamoros et al., 2009)

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