

# Soil Aquifer Treatment (SAT) as a Natural and Sustainable Wastewater Reclamation/Reuse Technology: Fate of Wastewater Effluent Organic Matter (EfOM) and Trace Organic Compounds

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## Abstract

Through the use of innovative analytical tools, the removal/transformation of wastewater effluent organic matter (EfOM) have been tracked through soil aquifer treatment (SAT). While the total amount of EfOM is significantly reduced by SAT, there are trends of shorter term versus longer term removals of specific EfOM fractions. The preferential removal of non-humic components (e.g., proteins, polysaccharides) of EfOM occurs over shorter travel times/distances while humic components (i.e., humic substances) are removed over longer travel times/distances, with the removal of both by sustainable biodegradation. Dissolved organic nitrogen (DON), a surrogate for protein-like EfOM, is also effectively removed over shorter term SAT. There is some background humic-like natural organic matter (NOM), associated with the drinking water source within the watershed, that persists through SAT. While most effluent-derived trace organic compounds are removed to varying degrees as a function of travel time and redox conditions, a few persist even through longer term SAT.

**Key Words:** Soil Aquifer Treatment, Effluent Organic Matter, Organic Micropollutants

## Introduction

Soil aquifer treatment (SAT) represents a wastewater reclamation/reuse technology that can renovate wastewater effluent to drinking water levels, and hence can be an important component in an indirect potable reuse system. SAT has proven very effective in removing total nitrogen (TN) and viruses but is now receiving scrutiny in assessing its ability to remove organics, both bulk organic matter and trace organic compounds. The SAT technology (Figure 1) involves infiltration of secondary effluent through a recharge basin with subsequent extraction through recovery wells, and embodies both treatment, dominant in the vadose (unsaturated) zone, and storage within the saturated zone (aquifer). It is an advanced wastewater treatment process that is both natural and sustainable, and is dominated by biodegradation, initially aerobic and subsequently anoxic.

After conventional wastewater treatment, secondary effluent contains wastewater effluent organic matter (EfOM), consisting of natural organic matter (NOM) derived from the drinking water source(s) and dominated by humic substances, plus soluble microbial products (SMPs) derived from biological (secondary) wastewater treatment reflecting a microbial origin (Drewes and Fox 2001). In an indirect potable reuse system, the residual humic substances present in EfOM impart color and serve as a precursor to disinfection by-products (DBPs) while the nitrogen-rich SMPs present in EfOM represent a precursor to nitrogenous DBPs (N-DBPs) if extracted water is chlorinated upon recovery.

In addition to concerns about bulk EfOM, there are various effluent-derived trace organic compounds including endocrine disrupting compounds (EDCs), pharmaceutically actives compounds (PhACs), and personal care products (PCPs) that are present in secondary effluents. The presence of these organic micropollutants suggests their persistence through biological wastewater treatment processes (e.g., activated sludge) that embody short-term aerobic biodegradation.

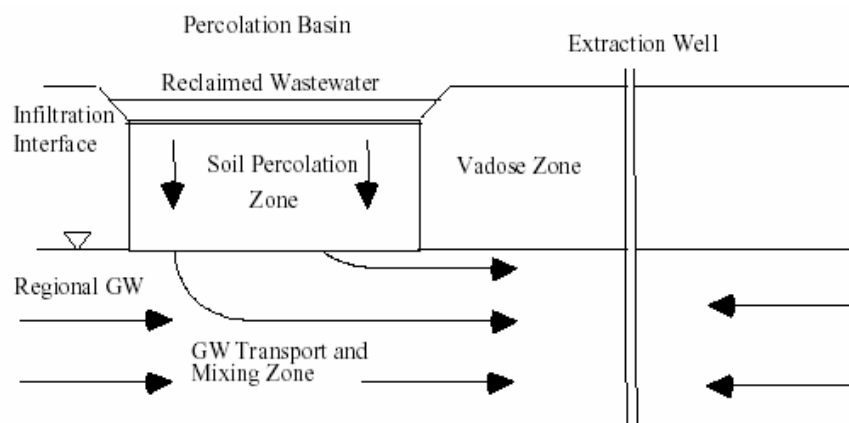


Figure 1. Schematic of Soil Aquifer Treatment (SAT) (AwwaRF, 2001).

This paper provides a detailed characterization of EfOM through a suite of analytical tools that describe transformation and/or removal by SAT. The fate of targeted effluent-derived trace organic compounds is also addressed. Samples have been selected for describing both shorter and longer term SAT and to contrast the effects of different redox conditions (aerobic (oxic) versus anoxic (denitrification)).

## Methods

### *Study Sites and Sampling Locations*

To characterize the amount and composition of EfOM through SAT, samples were collected from two operating SAT facilities situated in the USA: (i) the Northwest Water Reclamation Plant (Mesa WRP) in Mesa, Arizona; and (ii) the Sweetwater Underground Storage and Recovery Facility (Tucson WRP) in Tucson, Arizona. The Mesa WRP site has a dissolved oxygen concentration that remains below 1 mg/L throughout the infiltration zone below the first 1.5 meters, making almost the entire vadose zone of 15 meters thickness anoxic with only the first 1.5 meters aerobic; the plume of reclaimed water extends more than 2000 meters down gradient from the recharge site and is about 30 meters thick. A key attribute of the Tucson WRP is its deep vadose zone of 30 meters where high concentrations of EfOM and ammonia in the feed water (recharge basin) create a high oxygen demand; as the dissolved oxygen decreases with depth, and the ammonia is nitrified and denitrified, nitrate becomes the electron donor at a typical depth of about 1.5 meters.

A series of samples were taken from the Mesa WRP and included the effluent fed to the representative recharge basin, lysimeters beneath the recharge basins, and a series of monitoring wells situated along a transect following the hydraulic gradient of the aquifer (saturated zone). The sample designated as Mesa3eff represents the tertiary wastewater effluent (nitrified and partially denitrified followed by rapid sand filtration); the P5 and P15 samples corresponds to lysimeters lying beneath the recharge basin at depths of 1.5 and 5 meters, respectively; the NW-series wells correspond to samples immediately downgradient from the recharge basin; and the U-series wells correspond to samples further downgradient with greater travel distances and longer travel times. Table 1 summarizes pertinent information about these sampling points including (horizontal) travel distance downgradient (m), estimated travel time (months), and percent reclaimed water (based on sulfate levels as a tracer, with sulfate shown to be conservative for the Mesa WRP system). Also taken was a sample of a representative drinking water source within the watershed, the Val Vista drinking water (VVDW) taken from the Val Vista WTP treating a surface water source. The samples in the set taken from the Tucson WRP correspond to a monitoring well (MW5) penetrating the vadose (unsaturated) zone to a depth of 6 meters and a recovery well (WR 199) tapping into the underlying aquifer (saturated zone) beneath the recharge basin (RB1) fed by a non-nitrified effluent. The drinking water source is a low

NOM groundwater. Table 1 also summarizes the estimated travel distances, travel times (days), and percent reclaimed water for the Tucson WRP samples.

Table 1. Sampling Location Descriptions at Mesa WRP and Tucson WRP.

Sample	Travel Distance (meters)	Travel Time (months (Mesa) or days (Tucson))	Reclaimed Water (%)
<i>Mesa WRP</i>			
Basin	0	0	100
P5	1.5	2-3 days	100
P15	5	5-7 days	100
NW4	388	6-18	100
NW3	655	6-19	86
NW2	885	6-20	99
2U	1300	~24	95
6U	1620	12-96	75
10U	1950	12-96	61
26U	1950	12-96	71
44U	2700	12-96	39
<i>Tucson WRP</i>			
RB1	0	0	100
MW5	6	11	100
WR199	35	35	100

### Analytical Methods

The *amount* of EfOM was defined through dissolved organic carbon (DOC) measurements along with UV absorbance at 254 nm ( $UVA_{254}$ ). The *composition* of the EfOM in various SAT samples was characterized by: (i) specific UV absorbance ( $SUVA = UVA_{254}/DOC$ ); (ii) size exclusion chromatography with on-line DOC detection (SEC-DOC), describing the molecular weight (MW) distribution and classification of organic matter according to polysaccharides (PS), humic substances (HS), and low MW acids (LMA); (iii) fluorescence excitation-emission matrix (EEM), distinguishing humic-like organic matter from protein-like organic matter; and (vi) nitrogen (N) species used to calculate dissolved organic nitrogen (DON) as the difference between total nitrogen (TN) minus the sum of ammonia-nitrogen ( $NH_3-N$ ) and nitrate-nitrogen ( $NO_3^-N$ ). SUVA represents an index of the aromaticity or humic content of the EfOM. SEC-DOC chromatograms can be used to track transformation/removal patterns of PS, HS, and LWA components. EEM spectra, representing a 3-D plot of fluorescence intensity versus excitation and emission wavelengths, can be used to reveal removals of protein-like organic matter (corresponding to an EEM peak at lower excitation/emission wavelengths) and humic-like organic matter (corresponding to an EEM peak at higher excitation/emission wavelengths). Tracking nitrogen species through SAT serves two purposes: (i) an indication of redox zone transitions (e.g., aerobic to anoxic) that affect biodegradation pathways and (ii) a quantification of DON as a precursor for N-DBPs that exhibit a high cancer potency.

## Results and Discussion

### Bulk Effluent Organic Matter (EfOM)

Representative bulk EfOM parameters; DOC,  $UVA_{254}$ , SUVA, and DON; are summarized in Table 2 for samples taken from the Mesa WRP and Tucson WRP sites, respectively. At the Mesa WRP, long-term SAT is able to reduce the DOC to about 1.5 mg/L, accounting for dilution, which is similar to the drinking-water DOC in the watershed (~2.0 mg/L). The SUVA is less than 2 L/mg-m, consistent with an EfOM signature. The DOC after SAT at the Tucson WRP is about 1 mg/L, only slightly higher than the drinking-water DOC of ~0.5 mg/L. In contrast to the Mesa WRP results, the SUVA values after SAT at the Tucson WRP increase. An increase in SUVA reflects a preferential

removal (biodegradation) of non-humic over humic EfOM; this is consistent with the non-nitrified effluent at the Tucson WRP being less well treated than the nitrified/denitrified effluent at the Mesa WRP. The much lower DOC and DON values at MW5 demonstrate the significant removal achieved through the vadose zone. At the Mesa WRP, the tertiary-treated effluent contained about 2 mg/L of DON; shorter-term SAT reduced the DON to about 1 mg/L while longer-term SAT reduced the DON to a level approaching drinking water (0.2 mg/L). In contrast, at the Tucson WRP, a higher DON level was observed in the non-nitrified effluent, however, the DON was effectively reduced through the extensive vadose zone at this site.

Table 2. Representative Bulk DOC, UVA<sub>254</sub>, SUVA and DON for Mesa WRP and Tucson WRP Samples.

Sample	DOC (mg/L)	UVA <sub>254</sub> (cm <sup>-1</sup> )	SUVA (L/mg-m)	DON (mg/L)
<i>Mesa WRP</i>				
Mesa3eff*	6.10	0.099	1.62	2.1
NW4	1.47	0.024	1.63	1.8
NW3	1.76	0.022	1.25	1.7
NW2	1.52	0.022	1.45	1.1
10U	1.14	0.019	1.67	0.2
26U	0.75	0.011	1.46	n/a
44U	1.08	0.016	1.48	n/a
Drinking Water	~2.0	n/a	n/a	n/a
<i>Tucson WRP</i>				
RB1**	14.1	0.180	1.26	9.4
MW5	4.84	0.120	2.38	BDL
WR199	0.98	0.02	2.46	BDL
Drinking Water	~0.5	n/a	n/a	n/a

\*Nitrified/partially denitrified effluent sample which feeds the recharge basins at the Mesa WRP

\*\*Recharge basin sample derived from non-nitrified effluent

Two representative sets of SEC-DOC chromatograms are presented in Figure 2. Results for the Mesa WRP (left) reveal the almost complete elimination of the PS peak and partial removal of the HS peak, both attributable to (sustainable) biodegradation. A similar trend is seen for the Tucson WRP sample series (right). Overall, SEC-DOC chromatograms reveal transformation/removal patterns of PS, HS, and LWA components, with PS components readily removed in the upper vadose zone and HS components more slowly removed during travel through the vadose zone and aquifer under both first aerobic and then anoxic conditions; the apparent persistence of some LMA components likely reflects a by-product of HS components biodegradation.

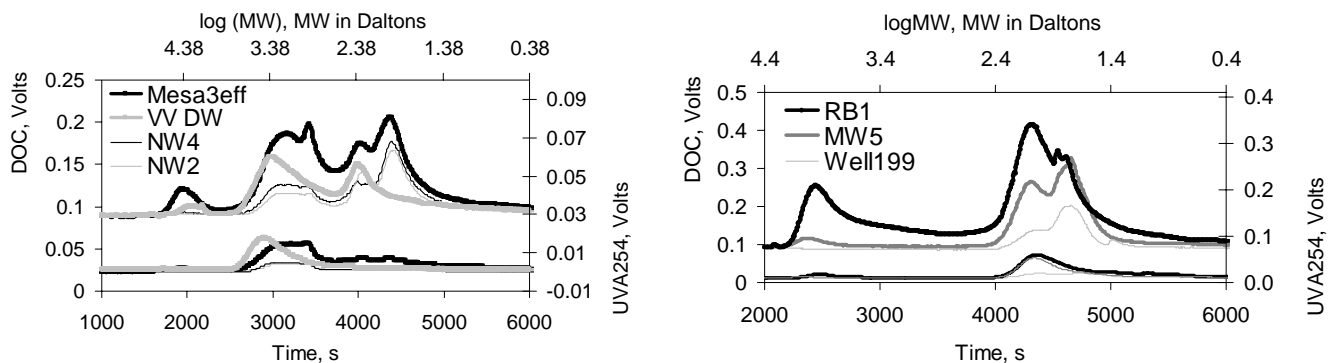


Figure 2. SEC-DOC Chromatograms for Mesa WRP (left) and Tucson (right) Samples.

As indicated earlier, an EEM spectrum shows fluorescence intensity (FI) as a function of excitation wavelength and emission wavelength. When EEM spectra are portrayed as a 2-dimensional plot, FI is represented by a series of iso-FI curves corresponding to the *topography* of FI versus excitation and emission wavelengths. Within this topography, a FI *peak* at higher values of excitation and emission wavelengths corresponds to humic-like organic matter while a FI *peak* at lower excitation and emission wavelengths corresponds to protein-like organic matter. Representative EEM spectra appear in Figure 3 for the Mesa WRP Mesa3eff (left) and the Tucson WRP RB1 (right).

One can compare corresponding EEM spectra before and after SAT to discern the removals of humic-like and/or protein-like organic matter. This comparison is facilitated by the use of *differential* spectra in which two spectra are subtracted; e.g., spectrum before SAT minus spectrum after SAT. Figure 5 shows differential EEM spectra where the P15 spectrum is subtracted from the Mesa3eff spectrum (top, left), revealing shorter-term SAT removals, and the NW4 spectrum is subtracted from the P15 spectrum (top, right), revealing longer-term SAT removals. Both humic-like and protein-like EfOM are removed over the shorter term while additional humic-like EfOM is removed over the longer term. More precisely, the significant diminishment of the lower excitation/emission wavelength peak over the shorter term corresponds to protein-like organic matter removed by (sustainable) biodegradation. Figure 4 also shows differential EEM spectra for the Tucson WRP samples: RB1 (recharge basin), MW5 (shallow monitoring well), and WR199A (deeper monitoring well). Again, one sees both humic-like and protein-like EfOM being removed in the upper vadose zone while only humic-like EfOM appears to be significantly removed in the lower vadose zone.

Significant removals of DOC were observed at both sites, ranging from greater than 50 % to almost 75 % after accounting for dilution with native groundwater. These DOC removals were accompanied by almost complete elimination of DON. Effective removal dominated by biodegradation was observed for polysaccharides and proteins with lesser but significant removals of humic substances under longer-term anoxic conditions.

### Trace Organic Compounds

Drewes and co-workers (Drewes, Heberer, Rauch, and Reddersen, 2003; Mansell, Drewes, and Rauch, 2004; Mansell, Drewes, and Rauch, 2004) have studied the fate of effluent-derived trace organic compounds through SAT including pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDCs), chlorinated flame retardants, and caffeine (a widely studied wastewater indicator).

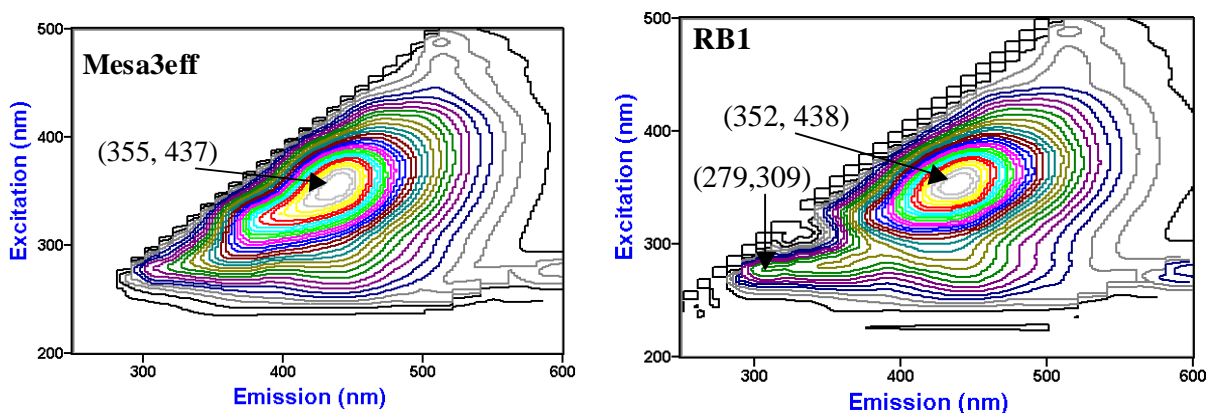


Figure 3. EEM of Mesa WRP Mesa3eff (left) and Tucson WRP RB1 (right).

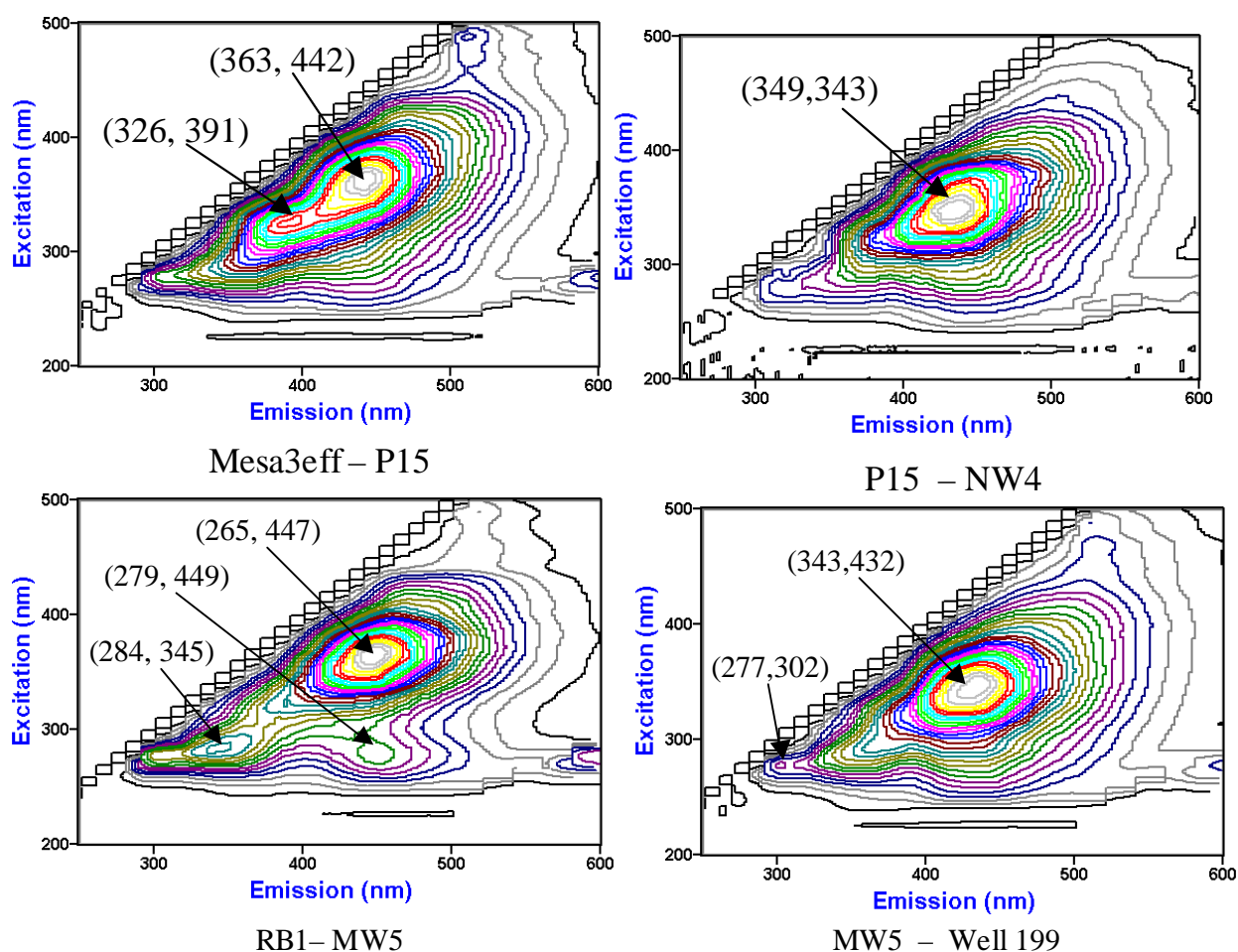


Figure 4. *Differential EEM of samples from the Mesa WRP (top) and Tucson WRP (bottom).*

Table 3 provides a summary of representative data describing the fate of selected PhACs including antiepileptics, analgesics/anti-inflammatories, lipid regulators, and X-ray contrast agents (Drewes, Heberer, Rauch, and Reddersen, 2003). In these studies, 15 compounds were measured in the Mesa WRP tertiary effluent and the Tucson WRP secondary effluent, with 4 and 9 compounds, respectively, found to be above detection limits. The lower number of detects for the Mesa WRP reflects more intensive wastewater treatment. Of the detected compounds, discounting one apparently anomalous value for ibuprofen, only two compounds (the antiepileptics carbamazepine and primidone) were detected after SAT. In addition, caffeine was also measured as well as adsorbable organic iodine (AOI), a surrogate for specific X-ray contrast agent compounds such as, for example, iopromide. Caffeine was not detected in any samples after SAT, suggesting that it is a poor wastewater indicator for SAT. In other related work on bank filtration and artificial recharge of a wastewater-impacted lake water (Grünheid, Amy and Jekel, 2005), AOI was shown to persist under aerobic conditions while being slowly biodegraded under anoxic conditions; however, iopromide was rapidly degraded under both aerobic (oxic) and anoxic conditions but only partially dehalogenated under anoxic conditions.

Table 4 provides a summary of representative data describing the fate of selected EDCs (Mansell and Drewes, 2004). Compared to the relatively more polar, and often ionized PhACs, many EDCs are hydrophobic neutrals as reflected by high octanol-water partition coefficient values. This suggests that removal can potentially be attributed to biodegradation and/or adsorption. The results show that EDCs are effectively removed over medium to longer term SAT with above detection levels only observed over shorter term SAT. It is noteworthy that these SAT sites have been operating for over a decade suggesting that biodegradation is more important as a removal mechanism than adsorption although biodegradation of adsorbed EDCs may occur.

Table 5 provides a summary of representative data describing the fate of two chlorinated flame retardants, TCEP (tris-(chloroethyl)-phosphate) and TCIPP (tris-(chloroisopropyl)-phosphate), through SAT. These results suggest that TCEP is biodegradable during long-term SAT but TCIPP is somewhat refractory, particularly when considering the long travel times at the Mesa WRP site. The lesser TCIPP removal at the Tucson WRP site may reflect shorter travel times and more aerobic (oxic) conditions.

Table 3. Removal of Selected Pharmaceutically Active Compounds (PhACs) through SAT at Mesa WRP and Tucson (WRP) (Drewes, Heberer, Rauch, and Reddersen, 2003).

Sample	Antiepileptics (ng/L)		Analgesics (ng/L)		Lipid Regulators (ng/L)	Wastewater Indicators (ng/L)	X-ray Contrast Agents
	Carbamazepine	Primidone	Ibuprofen	Naproxen	Gemfibrozil	Caffeine	AOI (ug/L)
<i>Mesa WRP</i>							
Mesa3eff	175	202	16	8.0	n.d.	n.d.	24.9
NW4	235	120	n.d.	n.d.	n.d.	n.d.	8.0
NW2	125	160	16	n.d.	n.d.	n.d.	8.9
2U	145	90	n.d.	n.d.	n.d.	n.d.	6.7
6U	85	100	n.d.	n.d.	n.d.	n.d.	12.5
<i>Tucson WRP</i>							
Tucson2eff	n.d.	110	3,380	6,280	1,235	15,700	16.7
WR199	610	155	n.d.	n.d.	n.d.	n.d.	20.5

n.d. = not detected

Table 4. Removal of Selected Endocrine Disrupting Compounds (EDCs) through SAT at Mesa WRP and Tucson WRP (Mansell and Drewes, 2004).

Sample	17-β Estradiol (ng/L)	Estriol (ng/L)	Testosterone (ng/L)
<i>Mesa WRP</i>			
Basin	4.2	4.9	3.0
P5	0.5	<0.6	<0.5
NW2	<0.4	<0.6	<0.5
NW4	<0.4	<0.6	<0.5
2U	<0.4	<0.6	<0.5
6U	<0.4	<0.6	<0.5
<i>Tucson WRP</i>			
RB1	7.2	21.3	11.5
MW5	1.8	<0.6	<0.5
WR199	<0.4	<0.6	<0.5

Biodegradation of trace organics at SAT sites occurs in association with DOC removal, under either aerobic or anoxic conditions, suggesting the possible role of cometabolism. Removal of hydrophobic EDCs (e.g., 17-β Estradiol) may be partially attributable to adsorption. The majority of effluent-derived trace organic compounds are degraded during SAT although a few persist. The health effects of such low (ng/L) levels are still being debated but it is noteworthy that I70 values (lifetime intake via drinking water based on 70 years and 2 L/day) are far less than daily therapeutic doses for almost all PhACs.

Table 5. Removal of Selected Chlorinated Flame Retardants through SAT at Mesa WRP and Tucson WRP.

Sample	TCEP (ng/L)	TCIPP (ng/L)
<i>Mesa WRP</i>		
Mesa3eff # 1	420	2,625
Mesa3eff # 2	310	1,085
NW4	<10	140
NW2	<10	470
2U	<10	420
6U # 1	<10	350
6U # 2	<10	150
<i>Tucson WRP</i>		
Tucson2eff	295	770
WR199	175	365

## Conclusions

Overall, significant removals of DOC were observed at both sites, ranging from greater than 50 % to almost 75 % after accounting for dilution with native groundwater, based on sulfate as a tracer. These DOC removals were accompanied by almost complete elimination of DON. Trends in SUVA, as an index of aromaticity, varied from similar to higher values in samples after SAT, with an increase reflecting a preferential removal of non-aromatic (non-humic) components. Effective removal dominated by biodegradation was observed for polysaccharides and proteins with lesser but significant removals of humic substances under longer-term anoxic conditions; these removal trends were supported by SEC-DOC and EEM results. SAT is effective in removing a majority of effluent-derived trace organic compounds although a few compounds persist at low (ng/L) levels of debatable health significance. SAT represents a sustainable advanced wastewater treatment process that can play an important role in a multi-barrier, indirect potable reuse system. Coupled with other studies documenting effective microbial and nitrogen removals (AwwaRF 2001), this study demonstrates effective removal of EfOM and organic micropollutants during SAT.

## Acknowledgement

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