

# Water quality transformations during soil aquifer treatment at the Mesa Northwest Water Reclamation Plant, USA

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**Abstract** Water quality transformations during soil aquifer treatment at the Mesa Northwest Water Reclamation Plant (NWWRP) were evaluated by sampling a network of groundwater monitoring wells located within the reclaimed water plume. The Mesa Northwest Water Reclamation Plant has used soil aquifer treatment (SAT) since it began operation in 1990 and the recovery of reclaimed water from the impacted groundwater has been minimal. Groundwater samples obtained represent travel times from several days to greater than five years. Samples were analyzed for a wide range of organic and inorganic constituents. Sulfate was used as a tracer to estimate travel times and define reclaimed water plume movement. Dissolved organic carbon concentrations were reduced to approximately 1 mg/L after 12 to 24 months of soil aquifer treatment with an applied DOC concentration from the NWWRP of 5 to 7 mg/L. The specific ultraviolet absorbance (SUVA) increased during initial soil aquifer treatment on a time-scale of days and then decreased as longer term soil aquifer treatment removed UV absorbing compounds. The trihalomethane formation potential (THMFP) was a function of the dissolved organic carbon concentration and ranged from 50 to 65  $\mu\text{gTHMFP}/\text{mgDOC}$ . Analysis of trace organics revealed that the majority of trace organics were removed as DOC was removed with the exception of organic iodine. The majority of nitrogen was applied as nitrate-nitrogen and the reclaimed water plume had lower nitrate-nitrogen concentrations as compared to the background groundwater. The average dissolved organic carbon concentrations in the reclaimed water plume were less than 50% of the drinking water dissolved organic concentrations from which the reclaimed water originated.

**Keywords** Soil aquifer treatment; dissolved organic carbon; groundwater; travel time

## Introduction

Soil aquifer treatment has been studied primarily through the use of column studies, vadose zone sampling, and sampling of the mound directly below a recharge basin (Bouwer *et al.*, 1980, 1984, Kopchynski *et al.*, 1996, Ho *et al.*, 1992, Wilson *et al.*, 1995, Drewes and Jekel, 1998). These studies have documented significant reductions in dissolved organic carbon (DOC) and other contaminants during soil-aquifer treatment in the vadose zone with time-scales on the order of days. Bouwer *et al.* (1980) and Wilson *et al.* (1995) both reported dissolved organic carbon concentrations of less than 2 mg/l from samples in the mound below recharge basins when reclaimed water with DOC concentrations greater than 20 mg/L was applied. Both these studies had vadose zones greater than 20 m and the efficient removal was attributed to the extensive vadose zone. During column studies, DOC concentrations of 5 to 6 mg/L were reported after flow through 2-m soil columns and the results were independent of applied effluent quality (Kopchynski *et al.* 1996). Long-term transformations during saturated flow have not been the focus of many studies since tools to distinguish reclaimed water from native groundwater have not been readily available. Consequently, most information that is available suggests that the majority of removal occurs in the vadose zone and subsequent transformations in the saturated zone are not important. This hypothesis has been translated into regulations that require minimum vadose zone depths

and do not provide credit for transformations in the saturated zone (National Research Council, 1998). This study focuses on a field site located in Mesa, Arizona, USA where the majority of flow that occurs during soil aquifer treatment is under anoxic saturated conditions.

The city of Mesa (AZ) Northwest Water Reclamation Plant (NWWRP) has recharged reclaimed water since 1990 at an approximate rate of  $0.14 \text{ m}^3/\text{s}$ . The Mesa (AZ) Northwest Water Reclamation Plant is a nitrifying-denitrifying activated sludge treatment system followed by filtration. The reclaimed water is applied to four recharge basins occupying an area of 12 hectares. Fine clay lenses result in low infiltration rates (6–12 cm/d) and therefore, the hydraulic resistance of a clogging layer is less than the resistance of the soil. The majority of flow occurs under saturated conditions as a consequence of the local hydrogeological conditions. The nitrifying-denitrifying system provides a consistent effluent for application to the recharge basins with DOC concentrations of 5–7 mg/L and total nitrogen concentrations less than 10 mg-N/L.

### Materials and methods

The majority of recharged water at the NWWRP has not been recovered and a plume of reclaimed water extends greater than 2,000 metres downgradient from the recharge site. The plume is primarily contained in an upper alluvial unit approximately 30 m thick. Over twenty down gradient groundwater monitoring wells within the upper alluvial unit have been sampled to characterize water quality changes in the reclaimed water plume (Table 1). In addition, thirty-six shallow monitoring wells were installed directly below the recharge ponds at depth of 1.6 m to 9 m and two sets of multiple-depth sampling wells (OW-1 and OW-2) were sampled downgradient of the basin. The vadose zone below the ponds is typically less than 1.6 m deep and saturated samples were taken from well points 1.6 m below the basin surface. The multi-depth sampling wells include two screened intervals within the upper alluvial unit and two screened intervals in the middle alluvial unit. Inorganic data in the form of cations and anions was available from downgradient monitoring wells monitored by the City of Mesa and the United States Environmental Protection Agency since 1990 prior to operation of the NWWRP. Arizona State University took samples beginning in 1996, on a monthly or quarterly basis from the downgradient monitoring wells and samples were analyzed for a wide variety of constituents. In addition, sampling of multiple-depth wells (OW-1 and OW-2) began in 1998 along with sampling of well points located directly below the recharge basins.

Samples obtained by Arizona State University were analyzed for pH, temperature, conductivity and dissolved oxygen in the field. In the laboratory, anions were analyzed by ion chromatography and cations were analyzed by atomic absorption spectrophotometry. Dissolved organic carbon was additionally characterized by UV absorbance, fluorescence and trihalomethane formation potential. In addition, selected samples were analyzed for trace organic compounds at Stanford University including ethyldiamine tetraacetic acid (EDTA), alkylphenol ethoxycarboxylates (APECs), and naphthalene dicarboxylic acid (NDC) by gas chromatography/mass spectrometry. Samples were also analyzed for adsorbable organic halide (AOX) species at the Technical University of Berlin as described by Drewes and Jekel (1998). Dissolved organic carbon (DOC), UV absorbance and trihalomethane potential are used to assess changes in the bulk organics including natural organic matter and soluble microbial products. Fluorescence, AOX species and trace organic compound measurements were used to characterize anthropogenic compounds and disinfection by-products.

**Table 1** Estimation of percent reclaimed water based on sulfate concentrations

Well ID	Distance. From Recharge basin (m) <sup>1</sup>	Percent Reclaimed Water <sup>2</sup>	Sulfate(W) (mg/L)	Sulfate(B) (mg/L) <sup>3</sup>	Water Table Depth Above Perforated Interval (m) <sup>4</sup>
NW1	1090	82	142	62	4
NW2	973	94	154	62	4
NW3	722	81	141	62	Insufficient Data
NW4	426	94	154	62	3
MRW-1	288	44	110	70	Insufficient Data
OW-1 <sup>6</sup>	288	Varies with depth		62	
OW-2 <sup>6</sup>	219	Varies with depth		62	
2U	1000	74	134	62	7
37U	1200	85	145	62	-9
36U	1300	57	118	62	-11
6U	1400	80	140	62	3
9U	1425	64	125	62	7
53U	1450	79	139	62	-9
32U	1600	81	141	62	-10
30U	1600	65	126	62	-7
43U	1825	32	93	62	-5
WMW-4	1875	26	87	62	-12
1U	2025	39	100	62	6
10U	2150	55	121	74	0
26U	2150	55	128	90	-11
44U	2475	18	80	62	-7
3U	2900	14	100	90	3
39U	2950	ID <sup>5</sup>	118	ID	-12
25U	3625	ID	86	ID	-7
40U	4250	ID	120	ID	-7

<sup>1</sup>Distance was estimated from mid-point of recharge basins prior to changes in basin location

<sup>2</sup>Calculated using an average reclaimed water sulfate concentration of 160 mg/L

<sup>3</sup>Background concentrations assumed to be same as NW-4 unless historical data for wells was available

<sup>4</sup>Based on most recent water depth measurement

<sup>5</sup>ID = Insufficient data

<sup>6</sup>Multiple depth samplers with screened intervals of 17–24 m, 30–37 m, 44–51 m and 61–68 m bgs

## Results

### Reclaimed water plume definition

Sulfate concentrations in reclaimed water are more than 100% greater than the native groundwater allowing for sulfate concentrations to be used to estimate the percent reclaimed water in groundwater samples. Historical sulfate data was available for the majority of wells from the time recharge was initiated in 1990. Wells directly downgradient had a marked increase in sulfate concentrations six months after operation of the infiltration basins began and these wells became dominated by reclaimed water after 18 months of operation (Table 1). Since the wells are sampled over a 30 m screened interval, the observed breakthrough curves (Figure 1) for sulfate represented reclaimed water flowing over the top of the aquifer with a six-month travel time while water reaching the bottom of the screened interval had travel times of 18 months or greater. Therefore, samples from these wells represent a range of travel times from six months to 18 months. As the distance from the recharge basins increases, the velocity of reclaimed water at the edge of the plume decreases. Steadily decreasing sulfate concentrations are observed at wells 1600 to 3000 m downgradient as the reclaimed water plume continues to increase in size. The majority of wells at downgradient distances of 1600 m or less are dominated by reclaimed water (Table 1). Multi-depth sampling at wells less than 350 m downgradient demonstrate that the upper alluvial unit is dominated by reclaimed water while the middle alluvial unit has

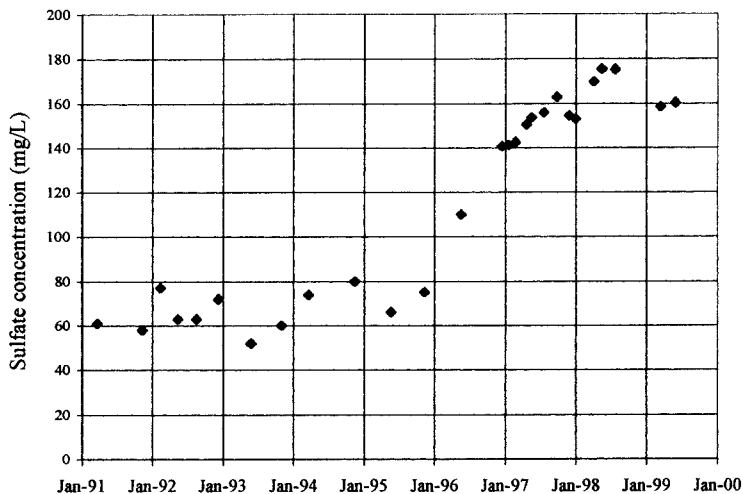
not been significantly impacted by reclaimed water. The only recovery well is screened through the middle alluvial unit and therefore recovery of reclaimed water has been negligible in comparison to the quantity of reclaimed water recharged.

#### Dissolved oxygen

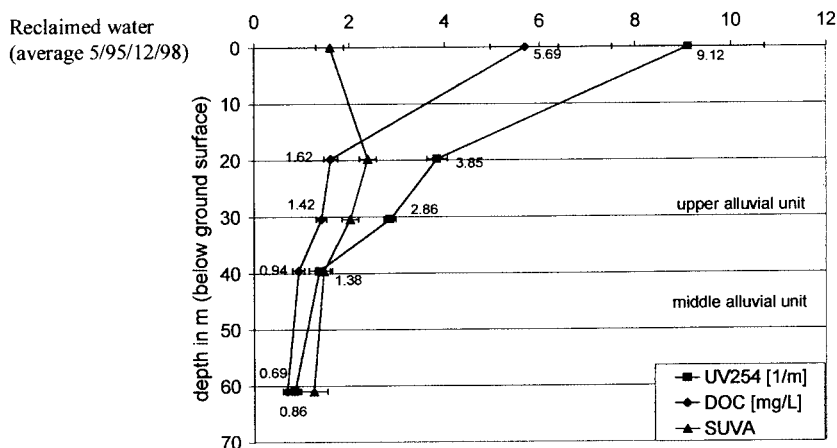
Dissolved oxygen measurements of samples from the upper alluvial unit demonstrate that the reclaimed water plume is anoxic. Even when dissolved oxygen levels in the pond are greater than 250% of saturation as a consequence of algae, dissolved oxygen concentrations at depths greater than 1.6 m below the pond are less than 1 mg/L. During multi-depth sampling in the upper and middle alluvial units, the oxygen concentration tends to increase with depth in the middle alluvial unit as the influence of reclaimed water decreases.

#### Dissolved organic carbon

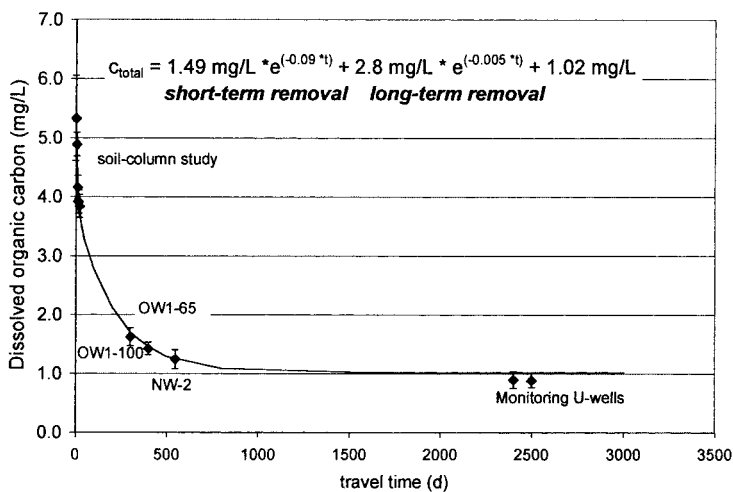
Dissolved organic carbon (DOC) concentrations in the effluent range from 5–7 mg/L and were found to directly correlate with DOC concentrations in drinking water (Drewes & Fox (2000)). The water supply varies between surface water and groundwater resulting in large variations in the DOC of the drinking water supply. The average DOC of the drinking water supply is 2.2 mg/L while the average DOC concentration in groundwater wells that are dominated by reclaimed water is less than 2.0 mg/L. Figure 2 demonstrates how DOC varies with depth at a point less than 300 m downgradient. The DOC concentrations at the top (~ 20 m) and the bottom of the upper alluvial unit (~ 30 m) are 1.62 mg/L and 1.42 mg/L respectively. The vertical variations in concentration may be explained by the water in the top of the upper alluvial unit having a shorter travel time as compared to water at the bottom of the upper alluvial unit. The top of the middle alluvial unit (~ 40 m) represents a mixture of native groundwater and reclaimed water while native groundwater dominates at greater depths. While changes in the upper alluvial unit do occur as a function of depth, changes in DOC concentrations as a function of downgradient distance or travel time are also observed. Immediately below the recharge basins, DOC concentrations of 3 mg/L are consistently observed at depths of 1.5 m to 4.5 m. As horizontal flow occurs downgradient to monitoring wells located 300 to 500 m downgradient, DOC concentrations decrease to 1.6 to 1.2 mg/L and at distances greater than 1000m DOC concentrations in the reclaimed water plume do not vary significantly and vary from 0.8 to 1.1 mg/L. Background ground-



**Figure 1** Breakthrough of sulfate in well NW-4. Note that NW-4 served as a background well until 1995 when a change in location of the recharge basins resulted in rapid breakthrough of sulfate



**Figure 2** DOC and UVA variations as a function of depth at multi-depth sampling well cluster OW-1. The upper alluvial unit (< 30 m) is dominated by reclaimed water and the top of the middle alluvial unit (~ 40 m) is influenced by reclaimed water



**Figure 3** DOC concentrations as a function of predicted travel time using an exponential decay model to describe biodegradation as a function of long-term and short-term SAT

water DOC concentrations average less than 0.5 mg/L. Figure 3 presents a model to estimate DOC concentration as a function of travel time within the reclaimed water plume assuming an easily biodegradable fraction that is removed over short-term SAT and a less biodegradable fraction that is removed over long-term SAT. The model is calibrated using soil columns with saturated flow to determine short-term removal rates. Since the fraction of DOC removed during long-term SAT is very small, minor variations in DOC concentrations results in large changes of travel time.

#### Specific UVA

Changes in the bulk characteristics of the carbon were characterized by calculating the specific UVA (SUVA = UV absorbance/DOC). The SUVA represents the relative aromaticity of the bulk of organics. Previous research has indicated that as organics are initially removed during SAT, the SUVA increases representing preferential removal of non-

aromatic compounds (Fox *et al.*, 1997). The effect of increasing SUVA during short-term SAT occurs as the effluent SUVA of  $1.7 \text{ (m-mg/L)}^{-1}$  increases to greater than  $2.5 \text{ (m-mg/L)}^{-1}$  directly below the recharge basins. This effect during short-term SAT was observed to a greater extent in previous studies with lower quality effluents (Fox *et al.*, 1997) as compared to the NWWRP. As downgradient distance and associated travel time increases, the SUVA tends to decrease to values less than  $1.5 \text{ (m-mg/L)}^{-1}$ . This trend represents long-term transformations of bulk organic carbon where aromatic compounds are either preferentially removed or converted to non-aromatic products. A similar trend is observed as depth increases in the multi-depth sampling wells located in the upper alluvial unit (Figure 2).

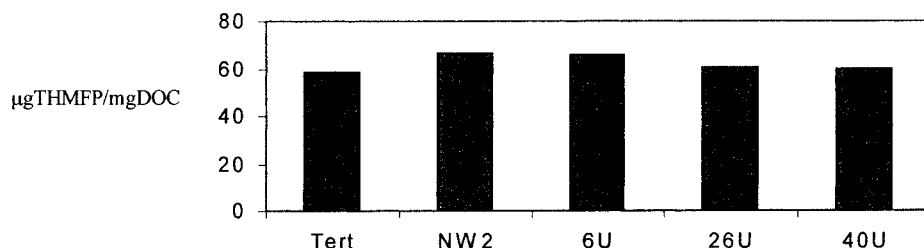
#### Trihalomethane formation potential (THMFP)

The THMFP of tertiary effluent, background groundwater and samples from the reclaimed water plume demonstrate no distinct trend as a function of DOC concentration. Average THMFP/DOC values range from 50 to  $65 \mu\text{g/mg}$  and do not appear to be a function of transformations of the bulk dissolved organic carbon (Figure 4). This result implies that the reactivity of the bulk organics with chlorine does not change although there are distinct changes in SUVA. The reactivity of natural organic matter has often been better correlated with SUVA as compared to DOC and therefore this result is inconsistent with results for natural organic matter in surface waters. This result is consistent with previous research on SAT where THMFP correlated with DOC and not SUVA (AWWARF Final Report, 1998). The bulk of organics in reclaimed water are composed of both soluble microbial products and natural organic matter which combined with SAT removal mechanisms might explain the observed correlation between DOC and THMFP.

#### Trace organics

Measurements of trace organic compounds were performed including EDTA, alkylphenol ethoxycarboxylates (APECS), naphthalene dicarboxylic acid and adsorbable organic halogens. The concentrations of APECS and naphthalene dicarboxylic acid consistently decreased to below detection levels as downgradient distance increased (Figure 5). EDTA concentrations decreased with increasing distance until a persistent background concentration was observed in the reclaimed water plume.

Adsorbable organic halides represent a combination of disinfection by-products and anthropogenic compounds. Adsorbable organic halide concentrations increased after chlorination at the NWWRP as expected. Adsorbable organic chlorine and adsorbable organic bromine concentrations decrease with increasing distance downgradient to levels consistent with background groundwater while organic iodine persisted. Organic iodine appeared to be the most persistent trace compound and was identified in the majority of samples tested. This is consistent with work performed at the Technical University of Berlin where the source of the persistent organic iodine has been identified as a pharmaceutical compound



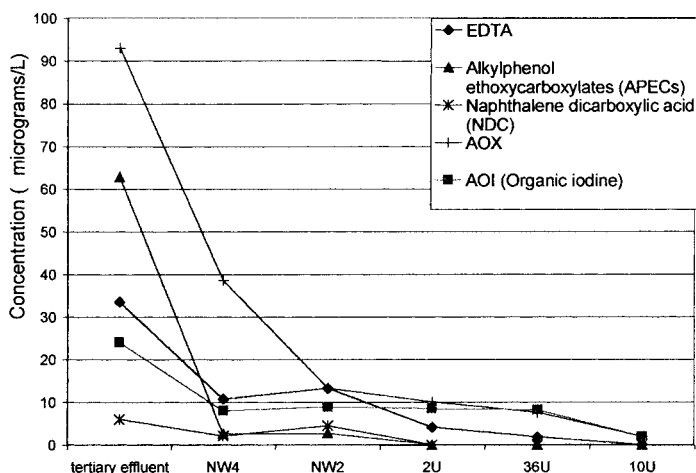
**Figure 4** THMFP/DOC ( $\mu\text{g/mg}$ ) as a function of downgradient distance including tertiary effluent and a background well (40U)

used for X-ray analysis (Drewes & Jekel, 1998). The compound has been observed to be persistent under aerobic and anoxic conditions and is only transformed under anaerobic conditions. Since conditions are primarily anoxic in this reclaimed water plume, the organic iodine is not transformed. The decrease in organic iodine concentration observed in well 10U (Figure 5) is probably a consequence of dilution since 10U is located on the edge of the reclaimed water plume and is approximately 55 percent reclaimed water (Table 1).

Fluorescence intensities at several wavelength pairs were found to correlate with DOC concentrations at DOC concentrations above 2 mg/L. Fluorescence is believed to be an indicator of anthropogenic compounds and soluble microbial products since fluorescence intensities in surface water and background groundwater samples at the tested wavelength pairs were negligible. In groundwater samples influenced by reclaimed water, fluorescence intensities correlated with UV absorbance. As UV absorbance decreased with distance downgradient, fluorescence intensities tended to decrease with the exception of the wavelength pair 290 nm (excitation)/340 nm (emission). This wavelength pair might represent a recalcitrant compound that persists during long-term SAT similar to organic iodine. The observed correlation of UV absorbance with fluorescence is expected since aromatic structures are often responsible for fluorescence.

#### Nitrogen species

Total nitrogen concentrations in the reclaimed water averaged less than 10 mg-N/L and the major nitrogen species in the reclaimed water is nitrate-nitrogen. Nitrate concentrations decrease during SAT as evidenced by a 20 to 50% decrease in total nitrogen concentrations when reclaimed water is infiltrated and moves towards wells adjacent to the recharge basins. Nitrate concentrations tend to increase as downgradient distance increases. This could be the result of historically lower nitrogen removal efficiencies during early years of treatment plant operation resulting in higher tertiary effluent nitrogen concentrations from 1990 to 1993 as compared to 1994 until the present. Background nitrate concentrations are also higher than concentrations within the reclaimed water plume as a consequence of previous agricultural activities. Anoxic conditions are evident directly below the basin and in the groundwater plume indicating that appropriate redox potentials for denitrification exist



**Figure 5** Trace organic compounds are removed as a function of downgradient distance with the exception of organic iodine that persists in the reclaimed water plume. Wells NW-4 to 36U represent a range of downgradient distances from 400 m to 1,300 m. Well 10U is located on the edge of the plume and the decrease in organic iodine might represent dilution with native groundwater.

and aerobic reactions are negligible. However, the levels of biodegradable organic carbon are low and should not support significant heterotrophic denitrification.

### Summary and conclusion

In conclusion, DOC concentrations in groundwater samples from the Mesa NWWRP recharge site are lower than the average DOC concentrations in the drinking water supply. The majority of removal occurs under saturated anoxic conditions and the removal of DOC may be characterized as a function of short-term removal of easily biodegradable organics and long-term transformations of recalcitrant organics. Changes in the aromaticity of bulk organics was apparent as the SUVA increased during short term SAT and decreased during long-term transformations. The changes in aromaticity did not affect the reactivity with chlorine and THMFP correlated with DOC. Trace anthropogenic compounds including APECs, naphthalene dicarboxylic acid, EDTA, adsorbable organic chlorine and adsorbable organic bromine are removed efficiently. EDTA, adsorbable organic iodine and fluorescence are persistent indicators of anthropogenic origin.

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