Irrigation with Reclaimed Water: Implications for Subsurface Recharge

Rebecca Singer

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Committee:
Sally Brown
Susan Kaufman-Una
Erica Cline

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Abstract

Irrigation with Reclaimed Water: Implications for Subsurface Recharge

Rebecca Singer

Chair of the Supervisory Committee:
Research Associate Professor Sally Brown
School of Environmental and Forest Resources

To determine the suitability of using reclaimed water for subsurface recharge, a soil column greenhouse study was performed to examine the leaching characteristics of two soil types irrigated with two types of class A reclaimed water: 1) membrane bioreactor (MBR) and 2) sand filter (SF) tertiary filtered wastewater, with tap water for a control. The two soils used in this study were Alderwood sandy loam and Earlmont-Snohomish silt loam. Each soil column was irrigated with one water type at one of three rates for 4 months. Irrigation rates were the standard agronomic rate of $250 m^3 ha^{-1}$, twice the agronomic rate (2X), and four times the agronomic rate (4X). At 2 months, grass was planted in each column to determine productivity under the varying irrigation rates and water types. Water characteristics examined before and after irrigation were pH, conductivity, total metals, ammonia, phosphate, nitrate and total EDC potency. Soil characteristics examined were pH, conductivity, total metals and total carbon and nitrogen. The pH was influenced by the source water but remained within the recommended EPA and WA State standards. Conductivity decreased with increased irrigation rate and soils remained non-saline throughout the study. EDC potency of MBR reclaimed source water and leachate did not differ from the control source water or leachate from either soil types. SF source water had high estrogenic potency that was significantly reduced via soil

filtration. Overall metal leachate concentrations were below standards for EPA drinking water and WA State Groundwater Quality (GWQ) with the exception of arsenic. All source waters including the tap water were above WA State GWQ standards as were the leachates, however, all metal concentrations met EPA recommended constituent limit for irrigation with reclaimed water. Orthophosphate and ammonia concentrations were low in both the source waters and leachates. Arsenic and nitrate leachate concentrations appear to be influenced by soil. Productivity was highest under the 4X irrigation rate for the control and SF water. The MBR 2X rate was only slightly higher than the 4X rate. This suggests that irrigation above the agronomic rate will not reduce productivity and has potential for recharge of groundwater based on the parameters measured in this study.

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Dedication

I would like to dedicate this thesis to my husband Jamie Singer and son Calvin. To Jamie, you have always been my biggest fan, providing me with endless encouragement and love. To Calvin, you're my inspiration for continuing my education.

Introduction

According to the US Geological Survey, irrigation and public supply are the highest consumptive uses of groundwater (USGS, 2005). Across the US, an estimated $128x10^3$ Mgal/day or 37% of all fresh water withdrawals were attributed to irrigation in 2005 with groundwater withdrawals accounting for $53x10^3$ Mgal/day nationwide (USGS, 2011). This rate of groundwater removal far exceeds what is replenished on an annual basis. Typically groundwater is replenished via infiltration of surface waters, however, the process of filling these aquifers can take several decades depending on subsurface material (Brady and Weil, 2002). For example, in the Pacific Northwest, subsurface parent material is either volcanic rock, with low permeability, or Basaltic rock, which has high permeability, overlaid with silt and clay. In the Puget Sound region of Washington the aquifer systems are unconsolidated basin-fill (USGS, 2009) (Figure 1.1). They are formed in depressions created by faulting and/or erosion and consist of silt and clay bound by the low permeable volcanic rock (USGS, 2009)(Figure 1.2). This can cause swift lateral movement of water rather than vertical movement, thereby contributing to the landslides to which this region is susceptible (Montgomery, Booth and Bolton, 2003). The Pacific Northwest Basin-fill aquifers, which encompass parts of Washington, Oregon and Idaho (Figure 1.3), recharge at about 200mm/yr in agricultural areas, well below the consumptive uses for those states (USGS, 2011).

Compounding the slow rate of recharge is the increase in impervious surfaces in urbanized areas. These surfaces not only impede infiltration but also create surges of runoff into storm drains and urban streams reducing surface infiltration of stormwater (Leopold 1968; Wissmar et al., 2004; Walsh et al., 2005). In the Puget Sound region of Washington State, local streams and rivers are associated with current and historic salmon runs. Within the Pacific Northwest, salmon are not only economically important but are also culturally important for many tribes (Montgomery, Booth and Bolton, 2003). Low salmon populations are threatening both the cultural and economic use of salmon, with many species now on the endangered or threatened species lists (NOAA, 2011). While many factors play into the decline of salmon populations, low flows in streams and rivers during the spawning season will likely result in a reduction or elimination of historic salmon runs. Due in part to the reduction in permeable surfaces, stream and river levels in this region are greatly reduced and often dry up in the summer. This is a result of decreased ground -water levels, which would normally percolate to the surface during these dry periods (Paul and Meyer, 2001).

To mitigate the reduction in subsurface recharge in urbanized areas and reduce the dependence on aquifers and surface waters in agricultural areas, many countries are using reclaimed water to recharge subsurface water flows through soil or surface irrigation with reclaimed water. Reclaimed water is municipal wastewater that has been treated so that it is suitable for reuse (Asano, 2001). In the United States, six states currently use reclaimed water for a variety of purposes, with California and Florida leading the way in the use of reclaimed water for agricultural irrigation (Lazarova and Bahri, 2005; NRC, 2012). In the Puget Sound there is an opportunity to take advantage of using reclaimed water as a source of irrigation. Millions of gallons of water are treated daily through the King County wastewater treatment facilities but only 2% of that is currently treated to meet reclaimed water standards for beneficial reuse (King County, 2012). The additional 98% of the treated effluent is discharged into the Puget Sound.

In King County WA, wastewater treatment facilities utilize one of two tertiary steps for the treatment of wastewater: sand filtration or MBR (membrane bio-reactive filtration). Both produce water that meets Washington States Department of Ecology (WA DOE) Class A standards for wastewater effluent discharge to surface waters (WA DOE, 2011). Table 1.1 outlines the water reuse requirements for irrigation with reclaimed water. Groundwater recharge through surface percolation must meet a minimum of Class A treatment and RCW 90.46 requirements in which groundwater must meet drinking water standards as measured in groundwater beneath or down gradient of recharge sites (WAC, 2012). Table 1.2 lists the most common contaminants of concern and their limits to meet groundwater standards as stated by the Washington State Department of Ecology (2011).

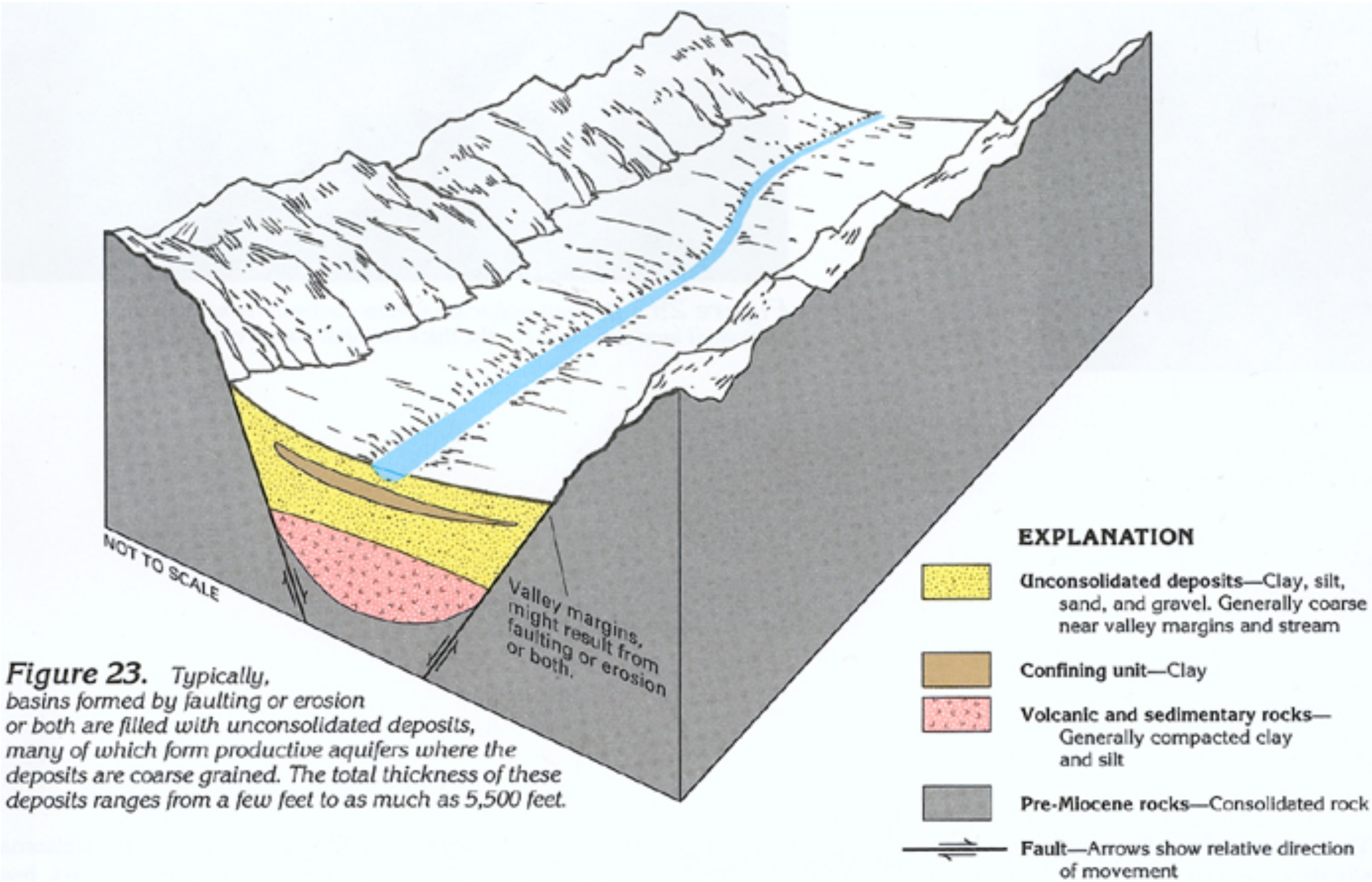


Figure 1.1 Unconsolidated basin fill where volcanic deposits are overlaid with unconsolidated clay, silt, sand and gravel confined by rock. Source: USGS http://pubs.usgs.gov/ha/ha730/ch_h/index.html.

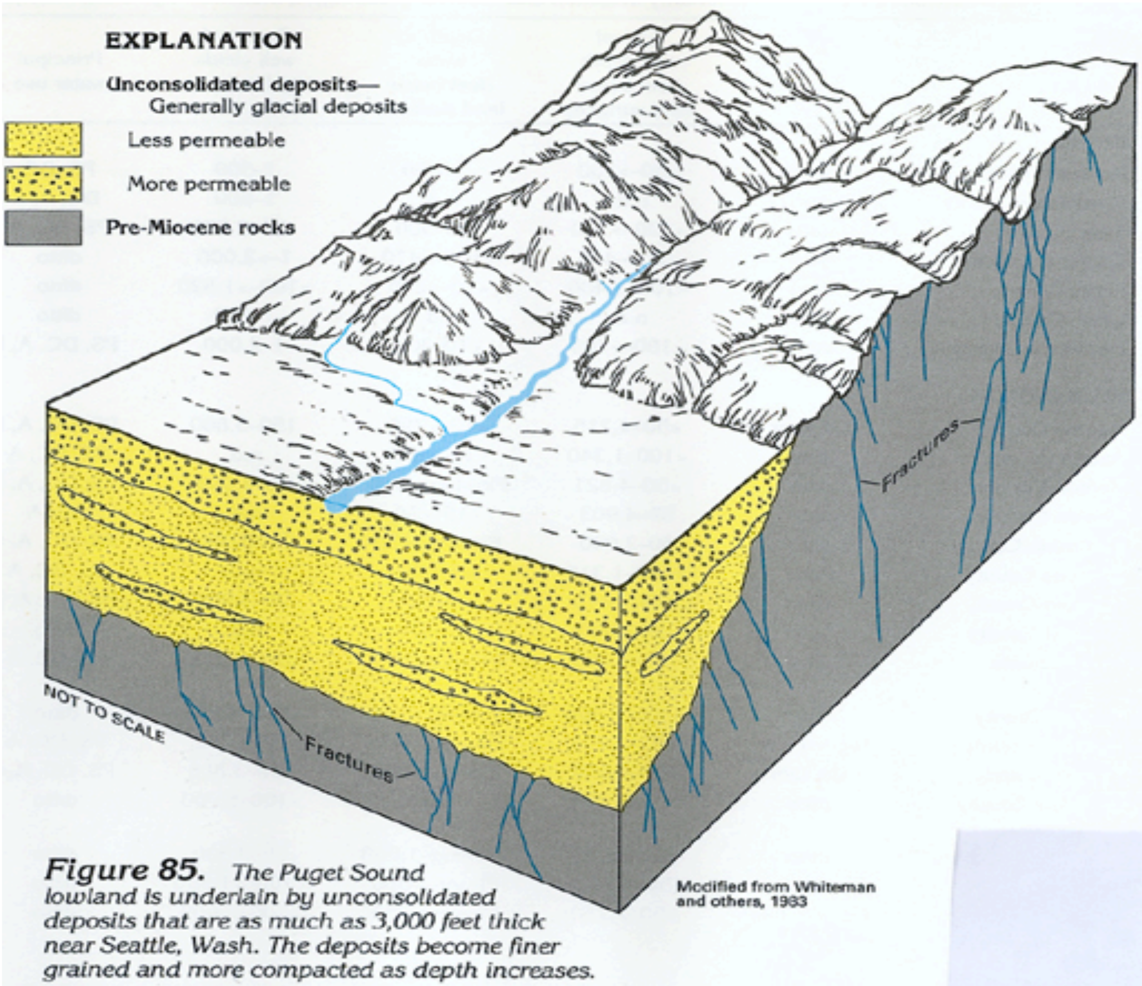


Figure 1.2. A closer examination of the unconsolidated deposit common in the Pacific Northwest as illustrated by the USGS. A mix of high and low permeable deposits overlay parent rock material. Source: USGS http://pubs.usgs.gov/ha/ha730/ch_h/index.html.

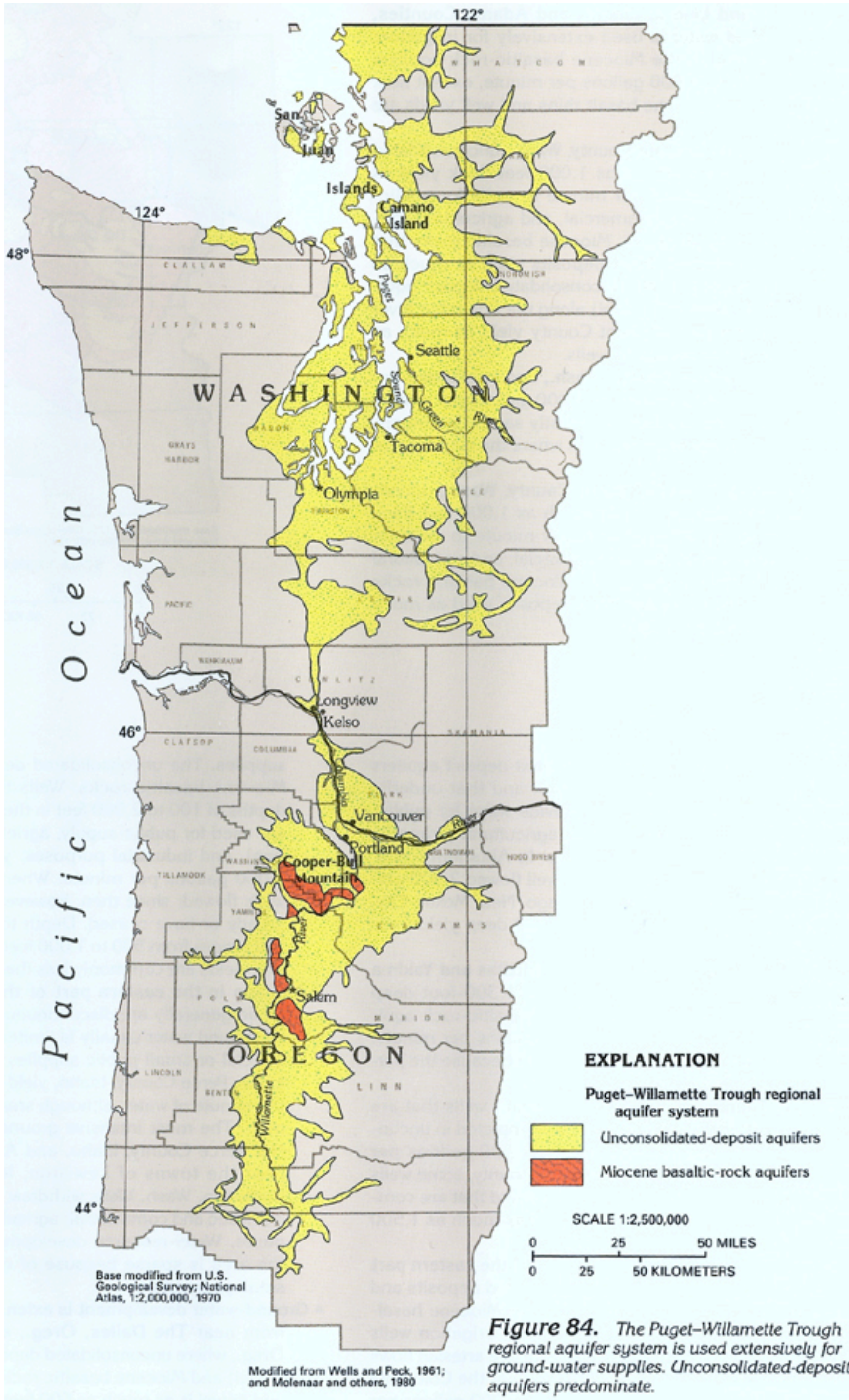


Figure 1.3. The Pacific Northwest Basin fill encompasses the Puget Sound aquifers in Washington State as well as the Willamette Valley of Oregon State. Areas of Idaho are also included in the Pacific Northwest Basin fill but are not shown on this map. Source: USGS http://pubs.usgs.gov/ha/ha730/ch_h/index.html.

While the use of reclaimed water is written into Washington State Legislation and the Revised Code of Washington, WA DOE requires that irrigation not exceed the agronomic rate to eliminate any impact to ground water (Sally Brown, personal communication, 2010). A consequence of this standard is that any application of reclaimed water to soils in excess of the transpiration requirements of the plants must meet Ground Water Quality Standards set forth by the WA DOE based upon EPA recommendations to ensure the lowest probability of contamination should irrigation result in leaching below the vadose zone (WA DOE 2005).

Table 1.1. Washington State Department of Ecology water reuse guidelines for irrigation based on EPA recommendations. Each classification is based on the level of disinfection after secondary treatment (Table 1.3). Source: Washington State Department of Health and WA DOE (1997).

Water Reuse	Class
Commercial Crops	
Trees/fiber/seed/sod ornamental/grazing	D
Pastures	C
Freeways/Landscapes	C
Recreational areas	A
Food Crops	
Spray Irrigation	A
No contact irrigation	B
Root crops	A
Orchars/vineyards-no contact with irrigation water	D
Physically or chemically altered food	D

Table 1.2. Washington State Groundwater Quality Standards. Common water constituents for contamination concern and the groundwater quality limits for recharge via soil filtration. Source: WA DOE 2011.

Water constituent	**Limit**
	ug L^{-1}
Arsenic	0.05
Cadmium	5
Chromium	50
Manganese	50
Nickel	0.1
Selenium	10
Silver	50
Zinc	5
	mg L^{-1}
Copper	1
Nitrate-N	10
Total N	10
pH	6.5-8.5

Concerns over the use of reclaimed water for subsurface recharge include the possibility of contaminating drinking water with metals, nutrients and endocrine disrupting compounds (EDC's). These concerns have limited the use of reclaimed water for recharge of subsurface waters in Washington State.

Current Washington State reclaimed water standards are based upon the *Water Reclamation and Reuse Standards* written in 1997. In 2006 the Departments of Ecology and Health were asked to develop reclaimed water standards for Washington State. The new reclaimed water guidelines will come into law (RCW 173-219) and become regulatory standards for surface application of reclaimed water for groundwater recharge.

The WA DOE groundwater recharge guidelines for reclaimed water are based on the assumption that the water will either be directly pumped to groundwater or will be unaltered by soil if the water is introduced to groundwater though soil filtration. However, filtration through soil may alter the water, potentially reducing concentrations of certain contaminants. Soils provide natural filtration for many pollutants (Wintgens et al.,2008) providing binding sites for ions to adhere to soil particle surfaces, especially in finer particles of clay and silt where surface area to volume ratio is high (Brady and Weil 2002). Microorganisms also act to break down compounds that enter the soil system. Bacteria work under both aerobic and anaerobic conditions using oxygen, sulfur and nitrogen as energy sources for metabolic processes (Maier, Pepper and Gerba, 2009). Plant roots and fungi contribute to filtration by absorbing macro- and micronutrients for their own growth and metabolic needs (Coleman, Crossley and Hendrix Jr., 2004). Because of this continual breakdown and growth that occurs within soils, the soil is often considered 'living' and its individual components and contribution to major nutrient cycling can be thought of as the planet's filtration system.

This paper will provide a review of past and current research on the use of reclaimed water as a source of subsurface recharge through soil filtration. As the pathway from RW effluent through soil and into groundwater takes place, concentrations and activity of endocrine disrupting compounds (EDCs), and water characteristics including nutrients, metals, pH and conductivity, may be altered. Many of these components will decrease and some will increase, but it is also important to understand how characteristics of irrigation waters and water from rainfall are altered as they percolate through soil in the Pacific Northwest region.

CHAPTER 1

Reclaimed Water

Public perception

The use of municipal waste for irrigation and fertilization of agricultural crops has been practiced for many years. Prior to the introduction of waste treatment facilities and indoor plumbing, human waste was encouraged as a soil amendment and utilized in many parts of the world as a means of disposal (NRC, 2012). The perception was that of a closed cycle, using human waste to fertilize the soils that would in turn provide food to many. Over time, humans have become separated from their own waste and educated about the health hazards associated with this waste, including disease causing pathogens, creating the "yuck" factor. According to the National Research Council (NRC) (2012), public opinions on the use of reclaimed water for personal use vary depending upon education, sex and age. However, public opinions about water reuse come from surveys that do not include interaction and discussions between community members and public works, which, Russell and Lux (2009) argue is key to changing perceptions. According to the NRC (2012), most people would rather drink untreated water from a river than drink reclaimed water, despite the fact that the reclaimed water may be cleaner. O'Conner (2007) reports the need for public awareness of the efficiency of contaminant removal as a key to public acceptance of reclaimed water.

Water Treatment

In the US, municipal wastewater must pass through tertiary treatment in order to be considered "reclaimed" and therefore used as an additional water source for crop and landscape irrigation (Table 1.3). However, at this same level of water quality, indirect groundwater recharge is recommended for potable aquifers, thus suggesting that the use of soil filtration through irrigation may also be beneficial.

In King County WA, wastewater treatment facilities use one of two tertiary treatments, either sand filtration (SF) or membrane bioreactor filtration (MBR). Both filtration methods have proven capable of removing wastewater contaminants to meet Class A requirements for reuse, reducing metals and nutrients. Wastewater treatment consists of three major steps, which are used worldwide. First, wastewater that is collected from household and industrial sewer lines and storm drains is filtered to remove all large particles, including non-biological waste such as trash. The screened wastewater is then put through a primary treatment in which all solids are removed through gravity settling or flotation; this includes oils and greases that solidify and collect on the top of the holding tank and solid waste that collects on the bottom. Following this, secondary treatment reduces pathogens and biological oxygen demand (BOD) through enhanced microbial activity by forced aeration and filtration processes. At this point the wastewater effluent is disinfected before either being released into open water or passing through an additional filtration system. These additional filtration systems are normally referred to as tertiary treatment. While there are many processes to get from primary to tertiary treatment, for the purposes of this paper we will focus on the tertiary treatment of wastewater effluent for reclamation.

Table 1.3. EPA water reuse guidelines based on level of wastewater treatment. EPA recommends groundwater recharge of potable aquifers only after tertiary treatment. This treatment level is currently used by Washington States King County for reclaimed water. Source: US EPA 2012.

	Water Treatment		
	Primary	**Secondary**	**Tertiary**
Disinfection Level	Sedimentation	Biological Oxidation, Disinfections	Chemical Coagulation, Filtration, Disinfection
Reuse Guide	No recommended use	Orchards and vineyards	Recreational Landscape
		Nonfood crops	Food Crop
		Freeway landscape	Toilet flushing, cleaning
		Groundwater recharge of nonpotable aquifer	Groundwater recharge of potable aquifer
		Wetlands, stream augementation	Water reservoir augmentation
		Industrial Cooling	

Tertiary Filtration

The process of filtering water through sand has been used for many years and is an effective form of wastewater treatment in the removal of suspended solids, pathogens, and metals (Hamoda, Al-Ghusain and Al-Mutairi 2004). There are two types of sand filtration, either pressure or gravity. Pressure filters are enclosed and water is pushed through sand using pressure while gravity filters are open and water is pumped on top of sand where gravity is allowed to pull it through (Huisman and Wood 1974). They are equally effective and are chosen based on community or city needs.

In membrane bioreactor filtration, secondary effluent is pushed through a porous filter ranging in pore size from 0.05 to 0.4μm and covered in bacteria (King County 2012). MBR technology is relatively new and has proven to be highly proficient at the removal of even the smallest bacterium. This technology however is more costly than SF and has not yet been used at multiple large-scale treatment facilities.

Both filtration systems are proficient at removing suspended particles and lowering biological oxygen demand (BOD) and chemical oxygen demand (COD). The BOD and COD of water is used to determine the presence of bacteria; the higher the BOD, the more bacteria are present and therefore the higher the requirement for oxygen to break down organic matter (Maier, Pepper and Gerba 2009). Actual removal efficiencies for each system will vary based on water characteristics, which in turn can fluctuate by season, population density, and surrounding industry. Concerns about beneficial use of reclaimed water for groundwater recharge center on the concentration of contaminants, including endocrine disrupting compounds (EDCs), nutrients, metals, and water salinity.

Beneficial Uses

The biggest benefit of using reclaimed water is the constant supply. Each day as much as 32 billion gallons of wastewater enters US treatment facilities (EPA 2011). As populations increase there is an increasing need for the use of recycled water in place of fresh surface or groundwater (NRC 2012) as these sources are quickly used up and slow to replenish. According to USGS (2005), Washington State used 5,600 million gallons of fresh water per day in 2005 (Figure 1.4) with irrigation being the largest use of fresh water for the State.

Surface water provided the largest supply of fresh water in the US in 2005 (Figure 1.5) with 270,000 MGD or 77.2% of the total fresh water use, this does not, however, include private wells.

Another benefit of using reclaimed water may be the additional nutrients that it can bring to crops or landscaping. Not unlike biosolids, which are currently used as a soil amendment, reclaimed water contains nutrients that may help to reduce fertilization needs. Current concerns over water reuse are the possibilities of eutrophication of fresh waters from excess nutrients in reclaimed water. While excess nitrogen and phosphorus pose environmental issues such as eutrophication of surface waters (NRC 2012), using reclaimed water (which is treated to a higher standard than wastewater effluent) for irrigation further reduces the amount of wastewater effluent currently being discharged into fresh waters and can also result in reduced use of synthetic fertilizers (Sala and Mujeriego, 2001; Carey and Migliaccio 2009).

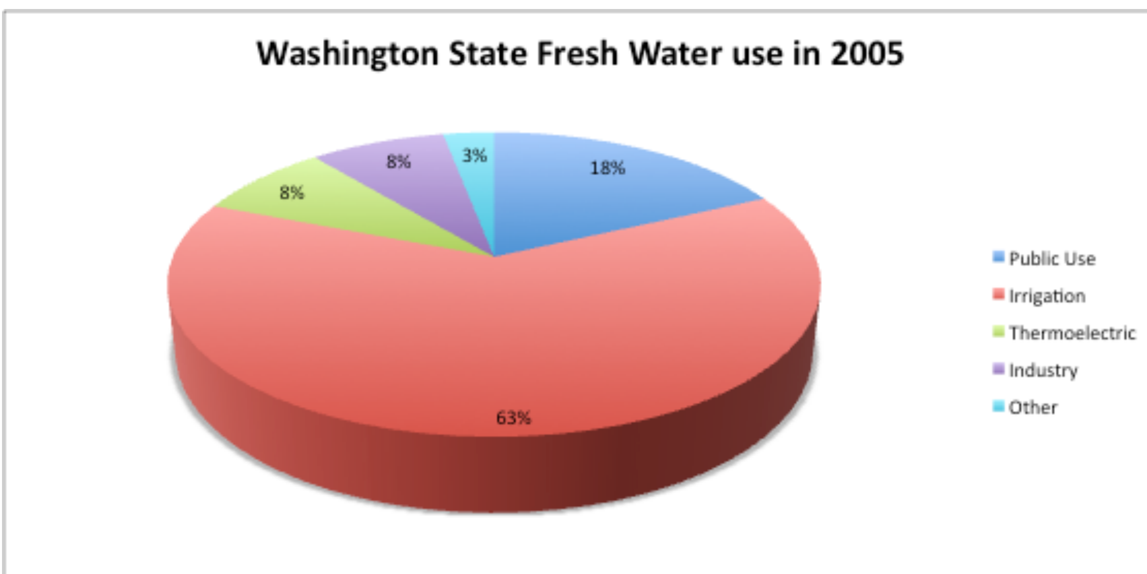
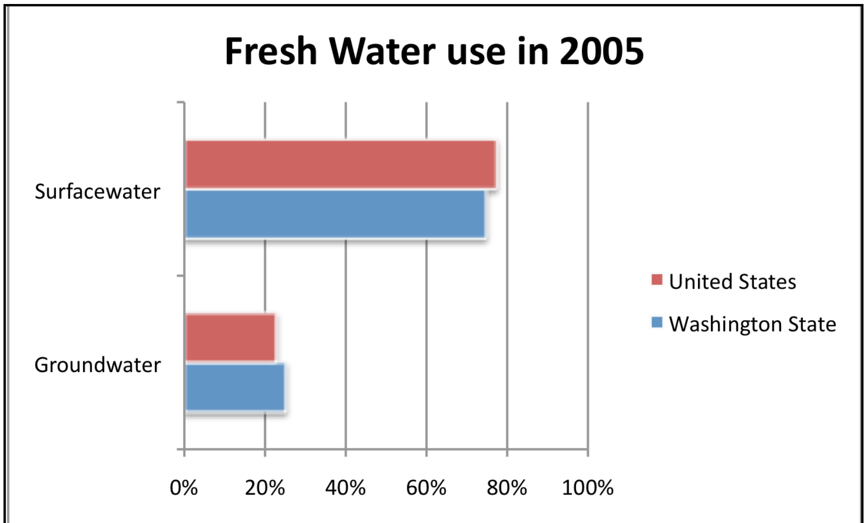


Figure 1.4. Washington States fresh water use for 2005. Irrigation was the largest consumer of fresh water at 63% of the total use of fresh water followed by public use which includes all domestic household use as well as non industry commercial uses. Source: USGS 2005.



	Total in millions of gallons per day	
	Washington State	United States
Groundwater	1410	79600
Surfacewater	4190	270000
Fresh water	5600	349000

Figure 1.5. A comparison of Washington States water use compared to the U.S. average. Washington used a higher percentage of groundwater than the National average in 2005. While surface water use is higher than groundwater use, the USGS (1998) reports that these sources need to be considered one and the same. Source: USGS 1998, 2005

Potential contaminants from reclaimed water

Endocrine Disrupting Compounds

The endocrine system is a network of glands responsible for growth, metabolism and sexual functions through the secretion of hormones. Endocrine disrupting compounds (EDC's) are compounds that can mimic or block hormonal responses and secretions in humans and wildlife (Colborn,Saal and Soto 1993; Toze 2004; DOE 2010). Naturally-occuring EDCs in the environment are those secreted by plants and released through human and animal waste (Table 1.4). On average, 5ug/L of estrogen is released per woman per day through urine, and 10ug/L testosterone per day per man, with the exception of pregnant women who may secrete as much as 1000 times this amount (Combalbert and Hernandez-Raquet, 2010). A range of common household and industrial chemicals also function as EDCs. Many of these compounds have lower potency as EDCs than actual

hormones; however, they are produced and often released to wastewater at significantly higher concentrations than natural hormones. Synthetic forms of EDCs come from industry, agriculture, medical and domestic uses of pesticides, detergents, plasticizers and synthetic hormones (Colborn,Saal and Soto, 1993; Falconer et al., 2006). Most commercial applications of herbicides and insecticides are used in measured doses; however, many chemicals such as triclosan and Bisphenol-A (BPA) enter the environment though daily use of plastics and detergents. Between 1999 and2000, Koplin et al. (2002), measured the concentration of 95 organic wastewater contaminants in 139 U.S. streams directly downstream from wastewater treatment plants or confined animal feeding operations.
Of the compounds that were identified, less than 1% of the total concentration was from reproductive hormones while 78% was attributed to plasticizers, other steroids and detergents. It must be noted, though that EDCs are ubiquitous in the environment, with these chemicals detected in a range of wildlife, far from WWTPs or CAFOs. In addition to being detected in treated wastewater, they have been detected in household dust, foodstuffs and drinking water, in concentrations ranging from nanograms to micrograms per liter (O'Connor, 2007; NRC 2012).

Table 1.4. Commonly found EDCs occurring naturally in the environment or through anthropogenic use of steroids, herbicides, insecticides and chemicals. Sources: Koplin et al., 2002; Falconer et al.,2006; Leet et al.,2011.

Hormones	**Synthetic Hormones**	**Herbicides**	**Insecticides**	**Chemicals**
17 β-estradiol Estrone Estriol Testosterone Dihydrotestosterone Androstendinone Androsterone	17α-Ethinylestradiol Diethylstilbestrol 17 β-trenbolone	Atrazine Simazine Methoxychlor 2,4-D	DDT Dieldrin Endosulfan Lindane Carbaryl cis-chlordane Chlorpyrifos Diazinon lindane methyl parathion	Phthalates Bisphenol A *p*-Nonylphenol PCBs Tributyltin 4-nonylphenol 4-nonylphenol monoethoxylate 4-nonylphenol diethoxylate 4-octylphenol monoethoxylate 4-octylphenol diethoxylate triclosan Diethylphthalate

Health Risks

Because of their ability to mimic or suppress hormone regulations and secretions, EDC's pose a threat to humans and wildlife from early life development through adulthood (Colborn, Saal and Soto, 1993; Crisp et al.,1998; Toze, 2004). The vast majority of health effects have been observed in aquatic environments. For example, male fish have shown signs of demasculinization (Vajda et al., 2011), spermatogenesis across generations (Anway et al., 2006), vitellogenin induction (Sanchez et al., 2011) and population collapse (Kidd et al., 2007) when exposed to EDC's in natural bodies of water. However, there is also concern for terrestrial fauna found near agricultural fields in which pesticides and herbicides are frequently used (Falconer et al., 2006). While laboratory trials are not performed on human subjects, documented cases of EDC exposure in the workplace and environment have been linked to breast cancer, testicular cancer, thyroid disorders, obesity, reproductive disorders, neurological and behavioral disorders (Yang et al.,2006; Diamanti-Kandarakis et al.,2009; Schug et al., 2011). Although these studies have raised concerns about the safety of these compounds, it is critical to note that the primary exposure pathways for humans are through direct contact and household dust. Concentrations of these compounds in reclaimed water have no clear pathway to human exposure.

EDC chemical properties

Understanding the physical properties of EDCs provides a basis for an understanding of their persistence, degradation or transport through soil and water. While their structures are diverse, most EDCs are aromatic with only slight polarity (Chang et al., 2009). Water solubility will vary based on the hydrophobicity of their structure (Combalbert and Hernandez-Raquet, 2010). The water solubility and log K_{ow} for eight of the EDCs from Table 4.1 are shown below (Table 1.5). Those with low water solubility and high log K_{ow} values, such as DDT, have a high affinity for soil organic matter and fats (O'Connor, 2007). Many of these compounds also have metabolites, new chemicals formed from the microbial decomposition of the parent compound. For example, DDT metabolizes to DDE and DDD (ATSDR 2002) and 17 β-estradiol (E2) is oxidized to Estrone (E1).

EDC Contamination Potential

Several studies have shown that many EDCs readily break down in (Ying and Kookana 2005; Xuan et al., 2008) and adsorb to (Sangsupan et al., 2006) soil; however, degradation rates and adsorption vary by soil type, aeration and microbial activity (Ying et al., 2003; Lorenzen et al., 2006; Ying et al., 2008; Stumpe and Marschner, 2009; Sun et al., 2010). Studies have also shown limited potential for plant uptake of these compounds (Roberts et al., 2006; Brown et al., 2008). These are important elements to consider when applying reclaimed water to land through irrigation for the purpose of groundwater recharge, due to the potential for runoff, leaching or soil accumulation. Soils provide essential binding sites for water and microbes while soil texture affects soil density and airspace. The movement, binding and breakdown of many EDCs may therefore be determined by soil factors that influence these characteristics.

Table 1.5. Water solubility and Log K_{ow} of eight Endocrine Disrupting Compounds. Source: http://www.ncbi.nim.nih.gov/

Compound	Water Sol. (mg/L)	Log K_{ow}
Atrazine	34.7	2.61
Estrone (E1)	30	3.13
Testosterone	23.4	3.32
Bisphenol A	120	3.32
17 α-ethynylestradiol (EE2)	11.3	3.67
17 β-estradiol (E2)	3.6	4.01
4-Nonylphenol	7	5.76
DDT	0.005	6.91

Table 1.6. Tula Valley, Mexico study on the potential leaching and soil accumulation of PPCPs and EDCs from untreated wastewater irrigation occurring between 10-90 years. Seven analytes listed below represent PPCPs and EDCs common to Mexico City wastewater. Source: Gibson et al., 2010.

Analytes in wastewater	Concentration range over 5 irrigations	Recovery from Leachate	Recovery from Soil
	ng L^{-1}	%	%
Ibuprofen	742-1406	6.0-37.2	.4-3.5
Naproxin	7267-13589	3.7-31.5	.3-7.1
Diclofenac	2052-4824	1.3-23.6	0.0-3.0
4-NP	1989-39326	3.1-18.5	0.0-24.9
Triclosan	84-1032	.1-2.2	2.9-22.1
BPA	148-3750	.3-8.0	.6-8.5
Carbamazepine	84-240	.08-16.1	55-104.9

Leaching Potential

Potential leaching of EDC's into groundwater systems can best be described by a "worst case" scenario, such as in the agricultural fields in the Tula Valley, Mexico. This valley has been irrigated with untreated wastewater that comes from Mexico City via above-ground canals for the past 10-90 years, depending upon the field site. Fields are flooded or irrigated via furrows once a month. Gibson et al. (2010) examined the soil profiles from the fields irrigated in this valley for the presence of PPCPs and EDCs common in the untreated wastewater for this region. Prior to soil filtration, irrigation water was analyzed. They found naproxen, 4-nonylphenol (4-NP), diclofenac and BPA had higher concentrations than ibuprofen, carbamazepine and triclosan (Table 1.6). Upon analysis of each soil horizon, naproxen, ibuprofen and carbmazepine were found in the A horizons of all soils, while 4-NP, triclosan and BPA were detected in some of the A-horizon samples, and diclofenac was <LOD in all samples. Troclosan, ibuprofen, 4-NP and carbamazepine were detected in the B-horizons. While movement of these compounds through soils was found, soil analysis found that the concentration of PPCPs and EDCs decreased with soil depth. No accumulation of 4-NP or BPA and low accumulation of triclosan were found in

the field after both 10 and 90 years of irrigation while carbamazepine was found to be more persistant (Gibson et al., 2010).

Biosolids have been used for decades as a soil amendment in agriculture and contain much higher concentrations of EDCs than reclaimed water. For this reason, examining land application of biosolids and the transport of EDCs under high loading rates will give some perspective to the effects of reclaimed water on EDC transport through soil. In 2010, Xia et al., published research examining the concentrations and accumulation of EDCs 4-NP, Triclocarbon (TCC), Triclosan (TCS) and Polybrominated diphenyl ethers (PBDE) at 0-120cm of soil after 33 years of biosolids applications. They found that even at the highest loading rate of 2218 billion gallons dry biosolids/ha all four EDC's decreased in concentration with soil depth with the highest concentration for all four found in the top 0-15cm which was comprised of mostly biosolids (Xia et al., 2010). Table 1.7 outlines the concentrations of EDCs by soil layer at the highest loading rate of 2218 billion gallons dry biosolids/ha, characterized as the worst-case scenario (typical rate is 16-20 million gallons dry biosolids/ha) (Xia et al., 2010). Xia et al. (2010) also noted that TCS was the only EDC that may leach and corn, grown in the biosolids amended soils, showed no signs of accumulation of EDCs within the plant tissue.

In a laboratory experiment by Weltin et al., (2002), soil columns were treated with biosolids and biosolids spiked with EDCs (100 fold greater concentration than biosolids alone) at an agricultural rate for German regulations of 5 tons dry mass/ha/3yrs, irrigated and tested for EDC movement using lysimeters. While the spiked biosolids columns exhibited greater concentrations of 4-Octylphenol (4-OP), 4-NP, EE2, E2 and BPA than in the unspiked biosolids columns, no significant leaching of any compound occurred for either treatment with no detection at all for BPA and E2 in the leachate. EE2 was found to be concentrated in the upper 20-30cm of soil and 4-OP and 4-NP in the upper 10cm of soils for both treatments while E2 only occurred in the upper 5 cm of the spiked biosolids and BPA showed only low detection in the unspiked biosolids and no detection below 10cm in the spiked biosolids (Table 1.8)(Weltin et al., 2002).

Field and lab trials show slow movement of EDCs in soils with low or no levels of leaching beyond 30cm. These low detections after high concentration applications indicate that EDCs may readily break down in soils. For example, 4-NP has been shown to quickly mineralize in many soil types (Topp and Starratt, 2000) and rapid degradation of 4-NP has been observed in aerobic aquifer material and water (Ying et al., 2003; Ying et al., 2008). While soil type may not inhibit the breakdown of EDCs, other soil properties might. One study found that the mineralization of E2 was higher in forest soils than agricultural soils and that when exposed to alanine or ammonium nitrate, mineralization of E2 stopped (Stumpe and Merschner, 2009). This study may indicate the mineralization process of E2 in different soil types is based on available nutrients. The forest soils from this research were from beech, spruce and oak forests, which are typically nitrogen limited, whereas agricultural soils are enriched with nitrogen inputs. Other studies have examined the effects of soil moisture and temperature on degradation of EDC's in various soil types. Colucci et al. (2001) tested the removal of E2 after 3 days incubation at 30°C and 13% moisture and found the %non-extractable E2 to be 90.7% in loam soil, 70.3% in sandy loam and 56.0% in silt loam and E1 to be 88.2%, 59.4% and 71.4% non-extractable, respectively. A subsequent study found that EE2 concentrations in a loam soil incubated at 30°C and 13% moisture for 44 days was below detection limits for estrogeneity based on a YES assay (Colucci et al., 2001).

Table 1.7. 33 years of biosolids applications at 2218 bg dry biosolids/ha. Detection of 4-NP, TCC, TCS and PBDE at increasing depths. Source: Xia et al., 2010.

	Biosolid amended Soils			
Soil Depth	TCC	TCS	PBDE	4-NP
cm	ug/kg dry soil			
0-15	1251	52	658	8834
15-30	371	25	105	1840
60-120	23	19	4.2	68

Table 1.8. A column study with Boisolids and EDC spiked biosolids soils. Concentrations of 4-OP, 4-NP and EE2 are give with increasing soil depths. Source: Weltin et al.., 2002.

Unspiked biosolid ammended soil columns					
Soil Depth	4-OP	4-NP	EE2	E2	BPA
cm	ug/kg soil				
0-5	313.5	222.3	29.8	0	0
5-10	13.8	13.3	93	0	2.8
10-20	44.3	53	72	0	2
20-30	125	134	60.3	0	0
30-50	0.5	8.5	13.5	0	1
50-90	4.8	9.3	9.3	0	2

Spiked biosoild ammended soil columns					
Soil Depth	4-OP	4-NP	EE2	E2	BPA
cm	ug/kg soil				
0-5	33,490	45,151	360.8	48	5.8
5-10	458.3	458.3	77.5	0	1
10-20	19	19	44.3	0	0
20-30	16	16	31.8	0	0
30-50	27.8	27.8	16	0	0
50-90	3.8	6.8	3.3	0	0

In the Pacific Northwest, many agricultural sites are located in valleys and become flooded in the winter months. Standing water and saturated soils can lead to anaerobic conditions that decrease the degradation rate of many EDCs (Ying et al., 2003; Ying et al., 2008; Sarmah et al., 2008). Table 1.9 outlines the half-lives of nine EDCs from the following studies. To test the degradation rate of EDCs under saturated conditions, Carr et al. (2011) examined the half-life of E1, E2, E3, EE2, triclosan and ibuprofen in soils that had previously been irrigated with treated wastewater effluent under saturated and field capacity conditions. They found that in soil previously exposed to treated wastewater effluent; the half-life of five of the six chemicals was longer in saturated soils than well-drained aerobic soils (Carr et al., 2011). The exception was E2 whose half-life was shorter in saturated soils than drained soil. E2 metabolizes to E1 even under anaerobic conditions (Ying et al., 2003; Ying et al., 2008), which may explain why E2 broke down more readily in saturated soils than the other compounds. Ying et al. (2003, 2008) tested E2, EE2, BPA, 4-NP and 4-OP degradation in aerobic and anaerobic aquifer material from Perth and Bolivar aquifers in Australia. They found that the EDCs in aerobic aquifer material exposed to aerobic conditions broke down more readily than in the anaerobic aquifer material also exposed to aerobic conditions and that degradation was significantly reduced under anaerobic condition for both aquifer materials. Ying et al. (2008) suggest that the difference in degradation rates between the two aquifer materials under aerobic conditions may be due to differences in the microbial communities between the two aquifers. It must also be noted that the aerobic aquifer material was enhanced with laboratory created effluent, providing more nutrients and possibly enhancing microbial activity.

Microbial activity appears to be a key factor in the breakdown of seven common EDC's; 4-NP, 4-OP, EE2, E2, E1, E3, and BPA (Ying and Kookana, 2005). In sandy loam agricultural soil, all seven of these compounds were found to completely degrade within 15 days under aerobic conditions and only E2 degraded under anaerobic conditions with a half-life of 24 days. No degradation of any of the compounds occurred after 70 days in sterile soils (Ying and Kookana, 2005). These findings are not unlike those of Xuan et al., (2008) who examined the degradation rate of E2 in a silt-loam soil of 0, 10, 20, 25, 33 and 100% sterility. They found a linear correlation between degradation rate and soil sterility, the less sterile the soil the higher the degradation rate. Stumpe and Marschner (2009), found EE2 mineralization to be nitrogen limited, with the addition of alanine or ammonium nitrate to test soil, EE2 degradation increased. However, this was not found to be the case for E2, in which additions of alanine or ammonium nitrate limited mineralization, suggesting different microbial degradation mechanisms. Testosterone has also been show to quickly degrade in temperate agricultural soil where degradation slowed when soils dried out or as soil temperatures fell below 23°C (Lorenzen et al., 2005). These results are not surprising as soil microbes require moisture that is typically above -15kPa (wilting point) and temperatures ranging from 10-40°C for optimum metabolic processes (Brady and Weil, 13th Ed, 2002; Coleman et al., 2nd Ed, 2004).

Table 1.9. Nine common EDC's found in the environment and their half-lives in days.

Endocrine Disrupting Compound	Half-Life (days)	Soil Type	Water Type	Moisture conditions	Reference
E1	2.7	20% non sterile silt loam	sterile water	aerobic	Xuan et al. 2008
	56.8	clay loam	reclaimed water	saturated	Carr et al. 2011
	33.4	clay loam	reclaimed water	field capacity	Carr et al. 2012
E2	3.0	sandy loam	river water	aerobic	Ying and Kookana, 2005
	0.2	aerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	8.4	aerobic aquifer material	groundwater	anoxic	Ying et al. 2008
	8.7	aerobic aquifer material	laboratory effluent	anoxic	Ying et al. 2008
	1.4	aerobic aquifer material	laboratory effluent	aerobic	Ying et al. 2008
	2.0	anaerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	107.0	anaerobic aquifer material	groundwater	anoxic	Ying et al. 2008
	0.9	20% non sterile silt loam	sterile water	aerobic	Xuan et al. 2008
	1.5	clay loam	reclaimed water	saturated	Carr et al. 2011
	4.0	clay loam	reclaimed water	field capacity	Carr et al. 2011
E3	1.5	20% strile silt loam	sterile water	aerobic	Xuan et al. 2008
	15.6	clay loam	reclaimed water	saturated	Carr et al. 2011
	8.7	clay loam	reclaimed water	field capacity	Carr et al. 2011
EE2	4.5	sandy loam	river water	aerobic	Ying and Kookana, 2005
	26.0	aerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	15.0	aerobic aquifer material	laboratry effluent	aerobic	Ying et al. 2008
	81.0	anaerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	1.9	20% sterile silt loam	sterile water	aerobic	Xuan et al. 2008
	207.0	clay loam	reclaimed water	staruated	Carr et al. 2011
	29.1	clay loam	reclaimed water	field capacity	Carr et al. 2011
BPA	7.0	sandy loam	river water	aerobic	Ying and Kookana, 2005
	0.6	aerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	1.6	aerobic aquifer material	laboratory effluent	aerobic	Ying et al. 2008
4-NP	4.6	sandy loam	river water	aerobic	Ying and Kookana, 2005
	1.8	aerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	1.6	aerobice aquifer material	laboratory effluent	aerobic	Ying et al. 2008
	7.0	anaerobic aquifer material	groundwaer	aerobic	Ying et al. 2008
4-OP	5.0	sandy loam	riverwater	aerobic	Ying and Kookana, 2005
	4.1	aerobic aquifer material	groundwater	aerobic	Ying et al. 2008
	3.3	aerobic aquifer material	laboratory effluent	aerobic	Ying et al. 2008
Triclosan	132.8	clay loam	reclaimed water	saturated	Carr et al. 2011
	88.0	clay loam	reclaimed water	field capacity	Carr et al. 2011
Ibuprofen	1706.0	clay loam	reclaimed water	saturated	Carr et al. 2011
	34.3	clay loam	reclaimed water	field capacity	Carr et al. 2011

EDCs have been shown to quickly degrade in many soil types under aerobic conditions and at various concentrations with minimal leaching potential. While EDC degradation has been examined using aquifer material and water to determine persistence in groundwater should leaching to the groundwater table occur, few studies have examined EDC occurrence in groundwater. In 2008, a National Reconnaissance of EDC contaminants in U.S. groundwater was conducted in the same manner as the National Reconnaissance for EDC's in U.S. streams by Koplin et al., (2002) to assess a baseline for EDC concentrations in groundwater systems (Barnes et al., 2008). While Barnes et al. (2008) report the detection of 35 of 65 organic wastewater contaminants, 25 of the 35 detected were reported at or below 1ug L^{-1} and 9 below 3ug L^{-1}. The highest detected contaminant was *N,N* Diethyltoluamide, an insect repellent, reported at 13.4 ug L^{-1} (Barnes et al., 2008). The reported EDC concentrations and frequency of detection for groundwater were lower than that of the streams examined, this study however, was conducted downstream of CAFO's, landfills and un-sewered residences where concentrations are expected to be high (Barnes et al., 2008).

Risk assessments for groundwater contamination of EDCs have been developed based on the adsorption potential, degradation rate, microbial activity and potential accumulation risks (Benotti and Snyder, 2009). Research has shown low EDC accumulation potential, even under high loading rates, with decreased concentrations with soil depth, high degradation rates under aerobic conditions and low detections in groundwater systems.

Nutrients

Soil nutrients vary depending upon soil type and fertilization history. This is due to the differences in parent materials found throughout the world. For example, in the Pacific Northwest, parent materials from glacier, volcanic and ocean deposits have occurred over millions of years and at different deposition rates, influencing the rate at which nutrients are released (Littke et al., 2001). Soil nutrients are also dependent upon vegetation type and land use (Brady and Weil, 2002). Forest systems recycle nutrients through the breakdown of organic matter while crops tend to lose soil nutrients through harvesting

(Brady and Weil, 2002). Within soil systems, nutrient cycling occurs through the weathering of mineral rocks and decomposition of organic matter where nutrient availability is variable depending upon type of vegetation and vegetation management, soil moisture, temperature and microbial activity. For example, nitrogen mineralization through decomposition depends upon the decomposition rate of leaf litter where deciduous leaves decompose faster than conifer needles and conifer needles decompose faster in moist versus dry soils (Johnson et al.,1982). Woods et al. (1982) found that the interaction of bacteria, amoebae and nematodes influences the rate of nitrogen mineralization, where N-mineralization increased in the presence of bacteria and amoebae interaction versus bacteria alone and bacteria and nematodes interactions. Nitrate and phosphate behave differently in soil and water due to their differences in cycling.

Phosphate tends to be a limiting nutrient with low mobility in soil. This is because the movement of phosphate ions in solution or fixation of phosphate ions to mineral particles is largely determined by soil pH, organic matter, vegetation and soil type (Brady and Weil, 2002). For example, optimum solubility of phosphate is at pH 6-7; at this pH level, iron, aluminum and calcium phosphates become soluble (Brady and Weil, 2002). Nitrate readily moves through soil when not taken up by plants. Nitrate ions are negatively charged and not attracted to the negatively charged soil colloids (Brady and Weil, 2002). The potential for nitrate leaching depends upon vegetation, water movement, and management practices. Due to the high mobility potential of nitrate and elevated levels that occur in reclaimed water, the use of reclaimed water for subsurface recharge has raised concerns over potential health risks should groundwater become contaminated.

Health and Environmental Risks

Due to its high mobility in soil, nitrate is the most common nutrient to contaminate groundwater, with as many as 20% of ground water systems in the U.S. exceeding the EPA MCL of 10mg L^{-1} (Townsend et al., 2003). Nitrate is not directly harmful to the human body; however, when pH levels in the gastrointestinal tract increase enough to support denitrifying bacteria, nitrites form (Bouchard et al., 1992; Ward et al., 2005). This is especially harmful in infants whose stomachs tend to be lower in acids (Bouchard et al.,1992). Of most concern is the development of Methaemoglobinemia in infants, most commonly known as "blue baby" syndrome. Nitrate is converted to nitrite when ingested, oxidizing hemoglobin to Methaemoglobine (metHb) and interfering with the bloods oxygen carrying capacity (van der Heijden, 1998; Ward et al., 2005). Normal levels of metHb are 1% for adults and 2% for children (Bouchard et al.,1992). When levels exceed 10% cyanosis occurs, at 20%, cerebral anoxia and at 50-60%, coma and death (Bouchard et al., 1992). Nitrate in drinking water, with levels as low as 2.5mg/L nitrate-N, has also been linked to cancer and reproductive disorders (Ward et al., 2005).

Phosphate is currently unregulated by the US EPA and typically poses little threat to drinking water due to its low mobility in soils. However, movement of phosphate into water systems poses environmental risks. Eutrophication occurs when excess nutrients such as nitrogen and phosphorus enter water and induce excessive algal growth (Brady and Weils, 2002). In saltwater systems the limiting nutrient is nitrogen and in fresh water it is phosphorus. In the United States, the Gulf of Mexico provides a prime example of eutrophication (US EPA, 2012). Nutrient rich freshwater from the Mississippi enters the Gulf, inducing algal blooms (Figure 1.6). When the algae die, oxygen is used in the decomposition process creating a hypoxic environment unable to support life (US EPA, 2012). Eutrophication also occurs in fresh water systems. In freshwater systems, algal blooms contaminate surface waters, producing toxins that cause detrimental health effects such as liver, neural and gastrointestinal damage (Maier et al., 2009).

There is concern about using reclaimed water for groundwater recharge because of the potential for nutrients in the reclaimed water to increase their concentration in groundwater. This is a concern for nitrate because groundwater can be a source of drinking water and, as discussed above, excess nitrate in groundwater has potential impact for human health. It is also a concern for both nitrate and phosphate because elevated concentrations of these nutrients can reach surface waters through movement in groundwater and result in eutrophication.

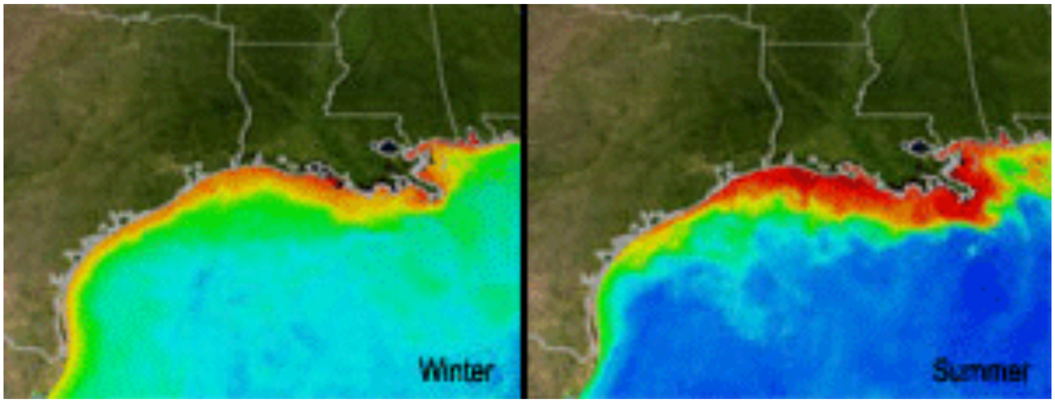


Figure 1.6. Eutrophication occurs along the Gulf of Mexico where the Mississippi river and Atchafalaya river flow, depositing excessive nutrients. In the summer months the "dead zone" are much larger than in the winter months due to excessive runoff from agriculture along the two rivers. Source: US EPA, 2012

Leaching potential

The use of reclaimed water for irrigation poses concern for nutrient movement into groundwater systems, particularly drinking water aquifers and fresh water systems such as streams and river through runoff. The USDA recently published a paper on the Water Quality in the Puget Sound Basin (2000) where multiple wells were tested (Figure 1.7). The wells were located across a range of land uses. Overall, nitrate levels were below drinking water standard (10mg NO_3- L^{-1}) for wells of varied land use and residential land use and above for agricultural land use (Ebbert et al., 2000). This trend was also seen in a nationwide examination of wells where agricultural wells had the highest incidences of nitrate, however, the nitrate concentrations were not always above EPA's MCL for groundwater nitrate (Burow et al., 2010). While nitrate concentrations in agricultural areas tend to be higher, Burow et al. (2010) noted that higher inputs do not always yield higher groundwater concentrations and that variations in nitrate concentrations varied based on well depth and age, with older deeper wells less likely to be contaminated. This is not unlike what Ebbert et al. (2000) documented in the Pacific Northwest, finding that shallow wells in residential areas had elevated nitrate concentrations but noted that they were below EPA's MCL. While many of the wells in the previous two studies indicate nitrate levels below MCL and a dependence upon well depth and age, the rate of nitrate leaching needs to be factored in. According to a recent study out of UC, Davis, nitrate can take years to centuries to reach groundwater depending upon the depth (Boyle et al., 2012). This simply means that shallower wells will be affected sooner than deep wells but that deep wells are not immune to contamination. In California 1 in 10 public wells currently exceeds the MCL of 45mg L^{-1} for NO_3 set by the California Department of Public Health, and 1/3 of all domestic supplies are above this level (Boyle et al., 2012). Similar to the Ebbert et al. study (2000), contamination levels in California are primarily due to agriculture use with 97% of nitrate loading in the UC, Davis study area attributed to croplands.

The potential for runoff of reclaimed water into freshwater systems is of concern due to the eutrophic effects of nitrogen and phosphorus. Runoff of excess nitrate and phosphorus into streams and rivers occurs in the agricultural areas of the Puget Sound basin (Ebbert et al.,., 2000). Nitrate use was correlated with concentrations in streams and rivers but phosphorus use was not (Ebbert et al., 2000). This may be due to phosphate's low mobility in soil, where phosphate binds to cations in soil solution for uptake and adsorbs to available binding sites in soil (McBride, 1994). Agricultural sources are not the only concern for excess nutrients in surface waters. According to the USGS, approximately 1.3 million tons of nitrogen is released from wastewater treatment facilities each year into surface waters (Mueller and Helsel, 2009). Phosphate levels in wastewater effluent have also increased as use of detergents has risen with population (Mueller and Helsel, 2009).

Movement of nutrients through soil to ground water occurs during both irrigation and rain events where irrigation water can be well water, surface water or reclaimed water (Sheikh et al.,1990; Sugita and Nakane, 2007). A recent study in Japan examined nitrate flow under various rainfall events through three different soil media; a homogenized Andosol, an Andosol over sand and sand with artificial macropores. Nitrate leached to groundwater depth in all soil types at the highest rainfall event (130mm over 120days) with preferential flow occurring in the macropore media (Sugita and Nakane, 2007). During the two lowest rainfall events (64mm over 384days and 108.8mm over 384days) no significant flow through occurred, as rainfall did not filter beyond the vadose zone (Sugita and Nakane, 2007).

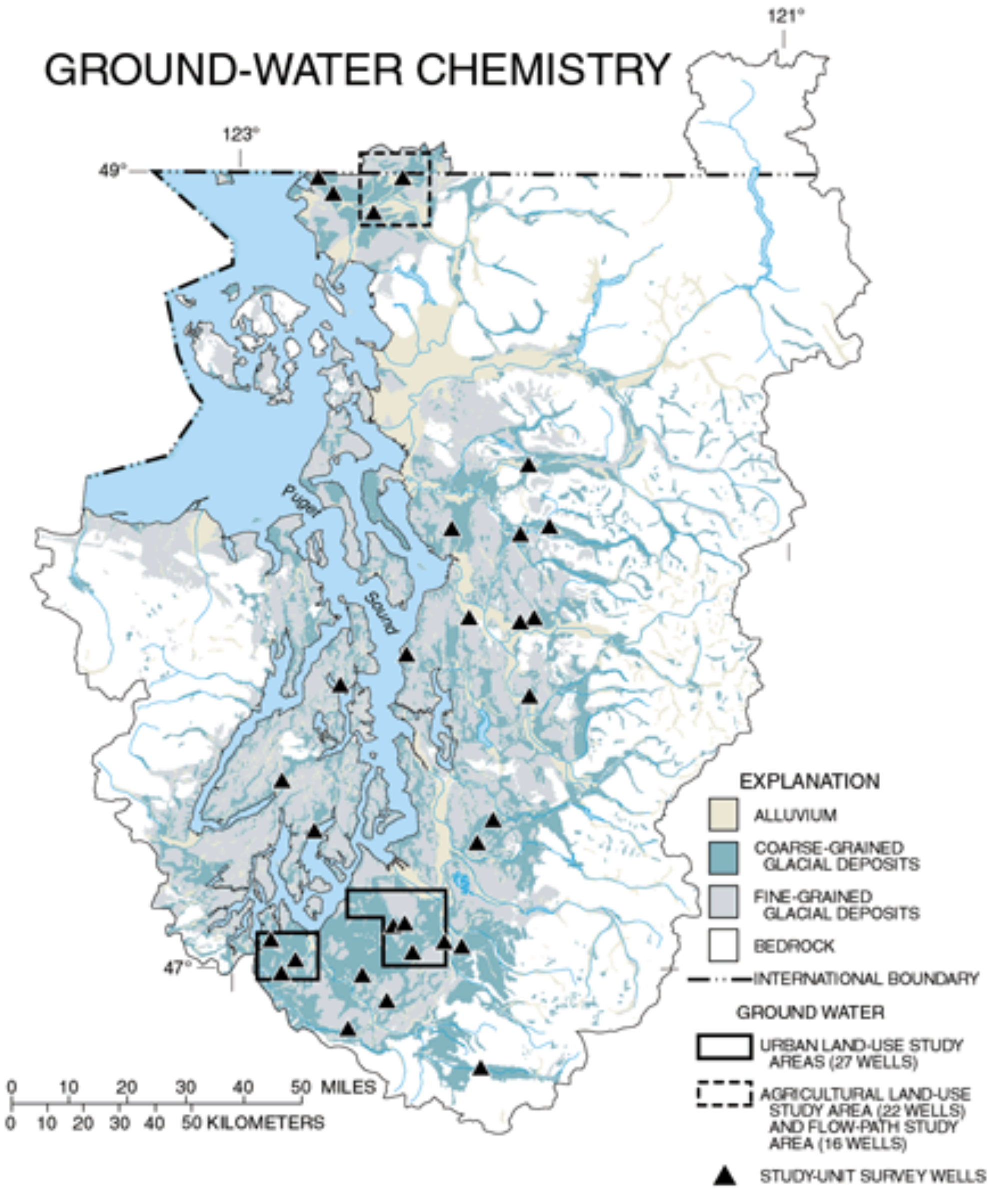


Figure 1.7. Groundwater survey area for the Puget Sound Basin. Each well tested is represented by a triangle. The agricultural test sites were in the northern part of the Puget Sound while urban land use was tested from the south. Source: Ebbert et al.,. 2000.

While the highest rainfall rate of 130mm over 120 days is less rain then the annual average for Seattle WA, it is representative of high rainfall over a short period of time and may indicate nitrate flow under irrigation events in which high amounts of irrigation occur in a short period of time. For example, in Prosser WA, apple orchards require 42in of water per year (WSU, 2012) over a growing season.

In 2009, Alemyehu et al. examined the use of reclaimed water compared to river water for groundwater recharge in Ethiopia. Using soil from the well field in which groundwater is currently mined; they constructed one-meter deep soil columns and irrigated the columns with either locally treated wastewater or river water from the river that currently recharges the well field. Water characteristics were measured before and after irrigation (Table 1.10). Ammonia and phosphate showed reductions of between 96-99% for each water type while nitrate showed an increase from both water types, with a 5% increase from the reclaimed water and a 78% increase from the river water after irrigation.

Table 1.10. Nutrients of reclaimed water (KTP) and river water (BAR) before and after filtration through 1 meter soil cores consisting of aquifer material from a well field currently mined for groundwater in India. Source: Alemyehu et al.., 2009.

	KTP		BAR	
mg L^{-1}	Influent	Effluent	Influent	Effluent
Phosphate PO_4^{-2}	4.09	0.18	3.96	0.12
Ammonia NH_3	35.18	0.47	12.26	0.37
Nitrate NO_3	10.19	10.75	4.37	7.8

The reclaimed water in this study is currently discharged into a tributary that is connected to the river feeding the well field. This research was aimed at providing an alternate means of discharge for the reclaimed water such as irrigation while, at the same time, providing groundwater recharge to the depleting groundwater supplies. Their data showed a significant decrease in both ammonia and phosphate via filtration but an increase in nitrate. The key here is that the decreases and increases occurred with both water types (river and reclaimed water). While treated wastewater typically has higher nitrate levels than river water, the increase in nitrate via filtration for the reclaimed water was much less than when irrigating with river water.

Another recharge study located in Australia examined changes in reclaimed water when filtered through the vadose zone prior to entering the groundwater. Bekel et al., (2011), tested both the reclaimed water and ambient groundwater prior to filtration and found that while water quality characteristics such as pH, temperature and conductivity were relatively the same between the two water types, nutrient concentrations of nitrate, ammonia and phosphate were higher in the reclaimed water. After filtration through the vadose zone (shortest filtration time of 3.7 days) phosphorus showed a reduction of 30%. This reduction hit a plateau at 271 days after filtration began; the authors suggest that maximum uptake of phosphorus had occurred at the plateau (Bekel et al., 2011). Total nitrogen concentrations did not decrease with filtration through the vadose zone, however, total Kjeldahl nitrogen showed a reduction of 49% in the recharged water and a 94% reduction in ammonia relative to the reclaimed water but an increase in nitrate of 77% (Bekel et al., 2011). The authors suggest that nitrification was occurring in the vadose zone.

Using reclaimed water for irrigation as a means of subsurface recharge has raised concerns over nutrient leaching to ground and surface waters as well as the potential to contaminate drinking water. As reported above, phosphate concentrations have been shown to decrease through the process of filtration but leaching may occur in conditions where phosphate is not a limiting nutrient or where soil conditions are not conducive to sorption (Domagalski and Johnson, 2011). The concentrations of leached nitrate, however, are dependent upon well depth (Blevins et al.,1996; Ebbert et al., 2000; Nolan et al., 2002; Kundu and Mandal, 2009; Burow et al., 2010), soil type (Blevins et al., 1996, Alemayehu et al., 2009) and crop root zones (Kundu and Mandal, 2009; Bekele et al., 2011). While nitrate tends to decrease with depth there is no doubt that leaching occurs. However, the movement of nutrients through soil due to irrigation or fertilization must be considered no matter the irrigation water type, which, as reported by Sugita and Nakane (2007) and Alemayehu et al. (2009), has limited effect on the leaching of nitrate. Whether under natural rain events or irrigation with river or well water, the potential for nitrate leaching exists, and seems to be influenced to a greater extent by land use and fertilization management (Ebbert et al., 2000;Burow et al., 2010; Boyle et al., 2012).

CHAPTER 2

Methods

A study was performed using intact soil columns to determine soil impacts on the use of reclaimed water for groundwater recharge through surface percolation. The study was conducted over eight months in two phases at the University of Washington's Center for Urban Horticulture greenhouse. A different soil type was used for each phase, a soil collected from a research forest (forest soil) in phase one and a soil collected from a working farm (agricultural soil) in phase two. In both phases two types of reclaimed water were used to irrigate each soil column. Leachate from each column was collected and tested for Endocrine Disrupting Compounds (EDCs), metals, nutrients, pH and electrical conductivity. Soil was collected at the end of each phase and analyzed for total metals, total carbon and nitrogen, pH and conductivity.

Experimental Design

Soil Descriptions

Forest soil was collected from Lee Memorial Research forest located in Snohomish County Washington (Figure 2.1). The forest is comprised of 67 hectares, dominated by Douglas-fir (*Pseudotsuga menziesii*), Big Leaf Maple (*Acer macrophylla*) and Red Alder (*Alnus rubra*) (UW, 2011). This is a secondary forest surrounded by residential communities. Human impact is high with trails heavily used by horses and pedestrians. Off-trail sites show signs of low or no impact as off-trail use is discouraged. Sword fern and native herbs dominate the understory vegetation. The soil of this site is an Alderwood sandy loam (Loamy-skeletal, isotic, mesic Vitrandic Dystoxerept) (NRCS, 2011) and will be referred to as forest soil throughout the remainder of this paper. The NRCS describes this soil as well to moderately drained with depth to water table being 69cm (2011). The soil is acidic, with a pH of 3.91.

The agricultural soil was collected from an organic farm located in the Sammamish Valley of Washington state (Figure 2.2). The Earlmont-Snohomish series is a silt-loam and is comprised of two soil taxonomies that can be found on this site. One is a fine-silty, mixed, superactive, nonacid, mesic Thapto-Histic Fluvaquents and the other is a fine-silty, siliceous, superactive, acid, mesic Fluvaquentic Endoaquepts (NRCS, 2011). Throughout the rest of this paper the combined soil taxonomies will be referred to as agricultural soil. This farm is conventionally tilled resulting in a plow pan at a depth of 7.5cm.

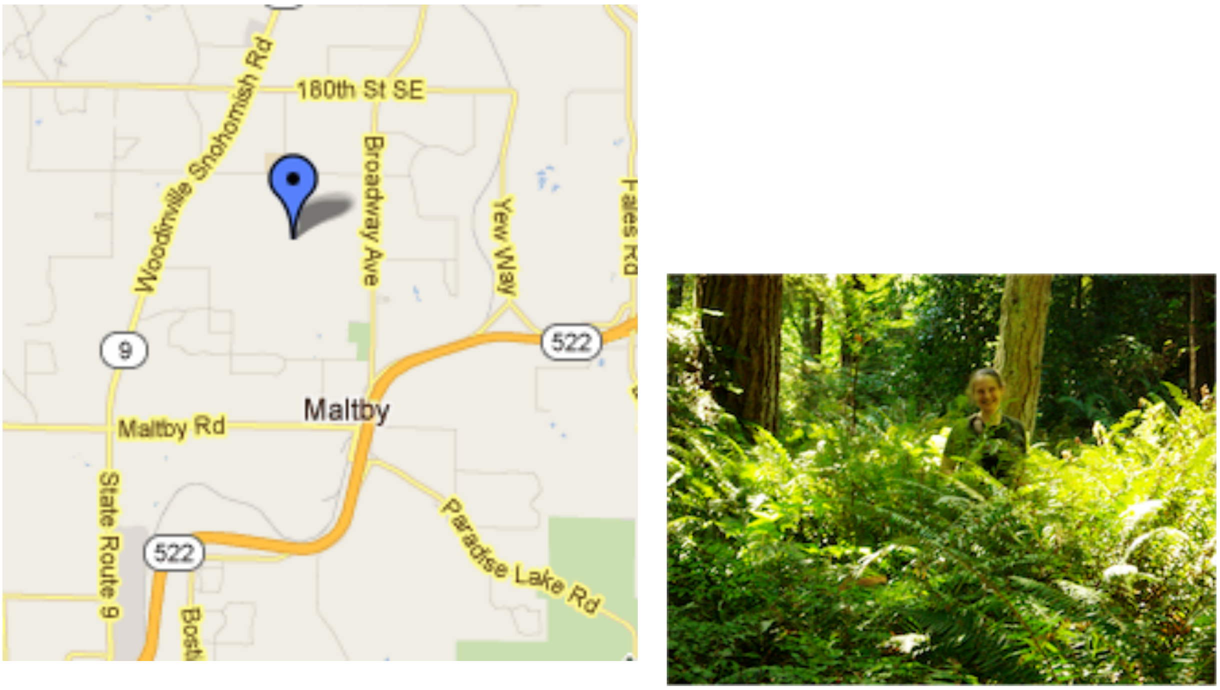


Figure 2.1. Lee Memorial Research Forest is located in Snohomish County in Maltby WA. This forest is located on 67 hectares surrounded by rural residential communities and is dominated by Red Alder and Douglas-fir.

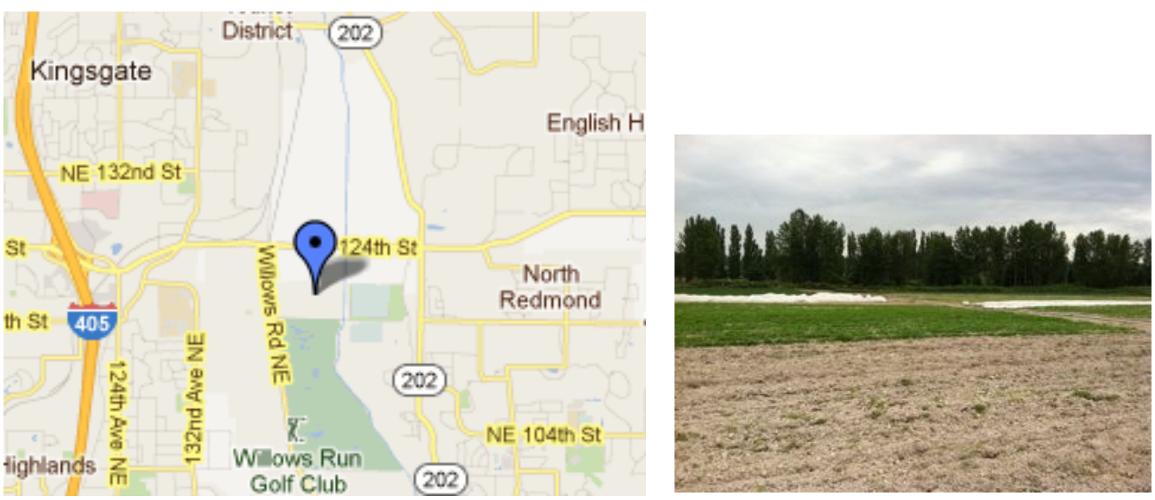


Figure 2.2. An organic farm located in the Sammamish Valley along the Sammamish River. Located between Redmond and Woodinville WA, the farm is surrounded by residential communities with a 60 acre park and golf course along the southern edge of the field.

The site is level and backed by the Sammamish River. The soil was collected about 200 meters from the river. This area had been forested until about 1900. At that time, the area was logged. The river was channelized and dredged to reduce flood risks and enhance drainage (King County, 2012). The NRCS describes these soils as poorly drained with a depth to the water table of 76cm (2011) and a pH of 5.46.Both sites are within the Puget Sound region of Washington State. Temperatures in this region are mild, averaging 72°F in summer months and 45°F in winter months with annual rainfall averaging 89cm (WRCC, 2011).

Intact soil cores

Soil cores were collected using 27 construction grade PVC pipes measuring 10cm in diameter and 30cm in length. Each core was hammered directly into the soil (Figures 2.3 and 2.4) and removed intact. After field collection, cores were transported to the Center for Urban Horticulture greenhouse at the University of Washington in Seattle. Cores were placed upright on wooden stands and held in place by metal drive clamps (Figure 2.5). Nine wooden stands were constructed using 2inx4in and 2inx2in lumber. The 2x4's were cut into 24in lengths and the 2x2's cut into 15in lengths. Each 2x4 served as a base with 3-2x2's attached at even intervals along the length of the 2x4. In phase one, due to the loose soil, it was necessary to pack one inch of acid washed sand in the bottom of each core and cap the ends with screen. Window screen was cut into squares big enough to cover the end of the core. The screening was doubled and taped around the end of the core with duct tape. The soil used in the second phase of the experiment did not require the use of sand but mesh screening was used to cap the ends as in phase one. 16-ounce plastic collection containers were placed under each clamped core (Figure 2.5). Soil cores were arranged in a Randomized Complete Block (RCB) design in which each block contained nine soil cores. Each soil core was then randomly assigned one of three water types and one of three irrigation rates.


Figures 2.3 and 2.4. Using PVC pipe measuring 10cm in diameter and 30cm in length, columns were hammered directly into the soil and removed intact. This photograph is at the agricultural site where a plow pan was reached at about 7.5cm in soils with a silt-loam texture.

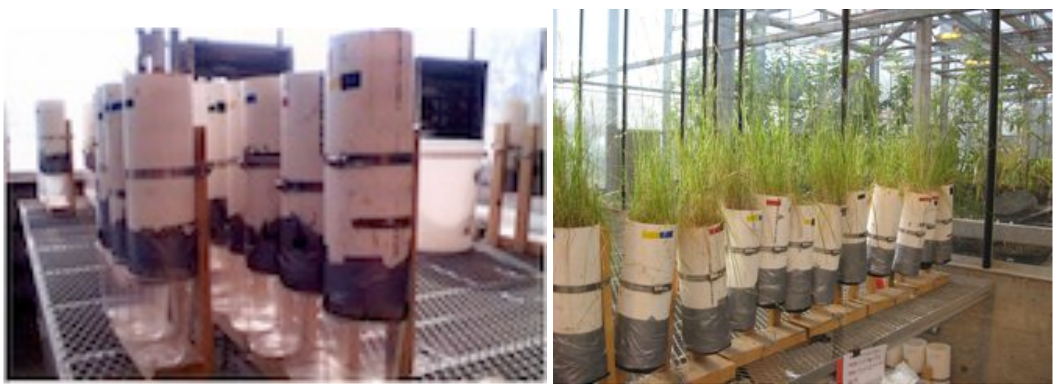


Figure 2.5. Soil columns were arranged on stands constructed with 2x4's and 2x2's. 16oz collection containers were placed at the base for leachate collection. Columns were held in place with metal drive clamps and stands were kept upright on a greenhouse bench using metal wire. The photographs below are the soil columns with and without grass.

Figure 2.6. Source water collection jars.

Reclaimed Water

Two types of Class A reclaimed water were used for soil core irrigation with tap water as a control. Membrane-bioreactor (MBR) filtered water was collected from the Carnation wastewater treatment facility in Carnation WA and the sand filtered (SF) water was collected from the South treatment plant located in Renton, WA. Both facilities are within King County. Source water metals (Table 2.1), nutrients (Table 2.2) and EDCs (Table 2.3) for MBR, SF and Control (tap) water were measured at the time of collection. Both types of reclaimed water are treated to meet WA DOE standards for Class A reclaimed water.

Watering Regime and Leachate Collection

Watering rates were set to the permitted reclaimed water irrigation rate. The rate is based on an estimated evapotranspiration potential for plants grown during the summer months in the Seattle region at a rate of 2.5cm per week or 250m^3 $hectare^{-1}$ to minimize the water's movement below the vadose zone. Within each complete randomized block, each soil core was randomly assigned one of three irrigation rates: 2.5cm(1X), 5cm(2X), or 10cm(4X) per week, to determine the effect of irrigation rate on water volume leaving each column and chemical characteristics of the leachate. Each soil core within each block was also randomly assigned one of three water types: MBR, SF, or Control. Source water was collected once every three weeks in six 5-gallon glass jars (Figure 2.6);, three jars per water treatment type or facility. Source water was stored at 4°C in the greenhouse. In phase one, the watering was divided into three intervals per week, for phase two it was divided into two intervals per week. The difference in watering intervals was due to the differences in drainage of the two soil types. Water was added using glass beakers, one beaker per water type to avoid cross- contamination, and collected in 16oz plastic food containers.

Phase 1:

Forest soil cores were watered three times per week. Leachate was collected within 24 hours of irrigation. Volume of leachate was measured and recorded. The collected leachate was then distributed into three collection containers for analysis. For pH, electrical conductivity (EC) and nutrient analysis between 5 and100ml of leachate was stored in 120ml plastic specimen containers. This volume was based on the total amount of leachate collected. Conductivity and pH were measured at the time of leachate collection. The pH was measured using a Denver Instrument Model 220 and conductivity measured using Orion Conductivity-Salinity Meter model 140. After pH and conductivity were measured, samples were preserved using 18M-concentrated sulfuric acid at 2ml/L acid to water sample (Standard Methods for Examination of Water and Wastewater, 18th ed) and frozen for nutrient analysis.

Table 2.1. Source water metal characteristics for each water types prior to irrigation; Membrane bioreactor (MBR), Sand filter (SF) and Tap (Control). Metals recorded are the average from source water collections over the course of the study.

Metals	**Water Source**		
	Control N=8	**MBR N=9**	**SF N=9**
		mg L-1	
Arsenic	0.0005±.00006	0.0008±.00012	0.0011±.00006
Cadmium	<MDL	0.00005±.000002	<MDL
Chromium	NA	NA	NA
Copper	0.066±.019	0.011±.003	0.011±.002
Lead	0.0009±.001	0.0002±.00003	0.0003±.00002
Selenium	NA	NA	NA
Silver	<MDL	<MDL	0.0001±.00004
Zinc	0.0018±.0014	0.061±.01	0.038±.004

Table 2.2. Source water nutrient characteristics for each water type prior to irrigation; membrane bioreactor (MBR), sand filtered (SF) and Tap (Control). Nutrients recorded are the average from source water collections over the course of the study.

Nutrient		**Source Water**	
	Control N=6	**MBR N=6**	**SF N=6**
		mg L^{-1}	
Nitrate	0.041±.03	3.22±.6	5.67±3.3
Ammonia	0.065±.07	0.22±.3	11.8±9.8
Orthophosphate	0.003±.01	1.93±.3	1.45±.4

Table 2.3. Source water EDC's for each water type prior to irrigation; membrane bioreactor (MBR), sand filtered (SF) and Tap (Control). EDC's are a measure of total estrogenic activity and recorded as the Relative Estrogenic Potency (REP_{50}).

Water Source	REP_{50}	Range
	ug L^{-1}	
Control	0.05	.03-.07
MBR	0.11	.06-.19
SF	307	149-578

Depending on volume, the remaining leachate was divided for total metals and EDC analyses. For metals analysis, leachate was collected in 500ml acid washed plastic bottles. For EDC analysis leachate was collected in 1L acid washed brown glass bottles. Leachate was stored at 4°C at the end of each collection day and collected over a one week period. For these analyses, blocks were homogenized by water type and rate in order to generate the required volumes for sample analysis. Every two weeks, containers containing leachate from the prior 6 waterings were taken to the King County Environmental Laboratory in Seattle Washington for analysis. Columns were watered over a four-month period. The columns were seeded with grass at 2.5 months and left to grow for the remaining 1.5 months.

Phase 2:

Agricultural soil was watered in the same manner as the forest soil, with the exception that two intervals per week were used rather than three. The agricultural soil leachate was also collected in the same manner as that of the forest leachate in phase 1; however, leachate samples for nutrient analysis were not treated with acid prior to freezing because samples were not held longer than 2 weeks prior to analysis (Standard Methods for Examination of Water and Wastewater, 18th ed). Due to low volumes of leachate generated, leachate was collected over a two-week period in order to attain sufficient volume of sample for EDC and metals analysis. The columns were seeded with grass at 2.5 months and left to grow for the remaining 1.5 months. For the agricultural soil, seeds were weighed out so that a precise number was added to each column, enabling yield measures at the end of the study.

Leachate Analysis

EDC Analysis

Endocrine Disrupting Compounds were measured using a Yeast Estrogen Screening (YES) provided by King County Environmental Laboratory in Seattle WA (King County, 2006). Leachate from each block for all watering rates within a water type was combined to generate sufficient volume for analysis. Generally, between 500 and 1000mL was collected each week for forest soil and every two weeks for agriculture soil and stored at 4°C until analyzed. The YES assay uses yeast that has been genetically modified with the human estrogen receptor (Figure 2.7). When this yeast is exposed to estrogenically active

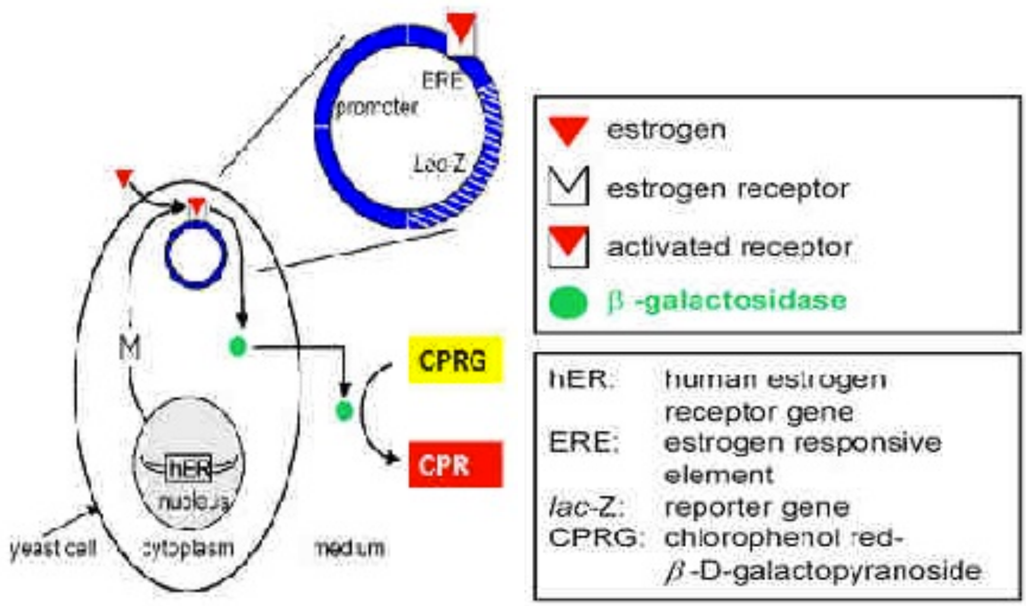


Figure 2.7. For the YES assay, yeast cells are modified with a human estrogen receptor (hER). Once estrogen binds to the receptor, this induces the release of an enzyme β-Galactosidase. The release of β-Galactosidase induces a color change in the yeast medium. Source: Routledge and Sumpter, 1996).

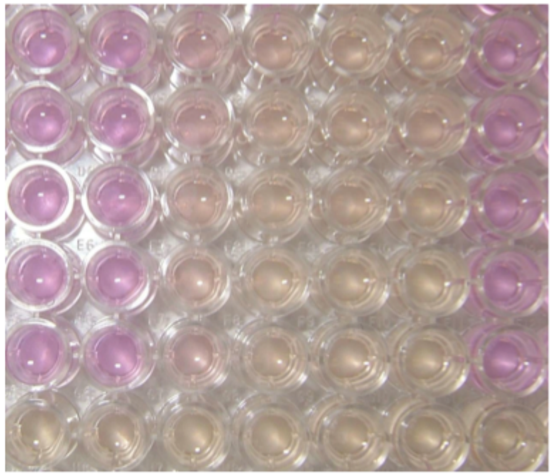


Figure2.8. Color response of β-Galactosidase excretion due to estrogenic binding to the estrogen receptor. When the medium turns red there is a positive response, blanks are light yellow and negative results vary in color from light yellow to pink.

compounds they bind to the estrogen receptor inducing a color change due to the release of β-Galactosidase (Routledge and Sumpter, 1996). The assay is based on measuring the light response of engineered yeast to EDCs in a sample. This light response is compared to the response from exposure to a known concentration of estradiol; a potent EDC. A positive result yields a deep red color, blanks are light yellow and negative results vary in color from light yellow to pink (King County, 2006) (Figure 2.8). This assay was developed to work for chemicals that induce a response to endocrine systems of a range of organisms. While it does not provide information on specific compounds and their concentrations in water samples, it can be used to predict the EDC potency of environmental samples (King County, 2006). Using Estradiol as a point of reference, the half maximal effective concentration (EC_{50}) was calculated. To determine the potency of the samples, the response of each sample was graphed against a slope of 1.0, the slope of the standard (estradiol) estrogenic response (Figure 2.9). A slope greater than 1.0 indicates a higher estrogenic response than the standard while a slope less than 1.0 indicates a lower response. The lower the EC_{50} of the sample, the steeper the curve and the higher the potency. The potency, relative to the standard, is recorded as the REP_{50} (relative estrogenic potency). The REP_{50} is calculated as a ratio of the EC_{50} standard to the EC_{50} sample and is calculated as: $REP_{50}=EC_{50}$ standard/EC_{50} sample.

Nutrient Analysis

Nutrient analysis was performed at the University of Washington Tacoma Chemistry Laboratory in Tacoma WA using a Westco SmartChem 200 nutrient analyzer (Figures 2.10 and 2.11). All samples were prepared and frozen until analyzed according to the Standard Methods for the Examination of Water and Wastewater (18th ed). Nutrients analyzed were nitrate (NO_3-N), ammonia (NH_3-N) and orthophosphate (PO_4^{-3}) and are reported as mg L^{-1}. Nitrate was measured using Westco Standard Operating Procedures (SOP) based on USEPA 353.2 revision 2.0 and Standard Methods, methods 4500 NO_3^-F section 6, 19th ed. (Westco, 2007). An application range of 0.02-2.0 mg L^{-1} nitrate-nitrite nitrogen was used for the calibration curve. For this procedure, samples are filtered through a cadmium column. For samples preserved with sulfuric acid, an Ammonium-Chloride EDTA buffer solution with

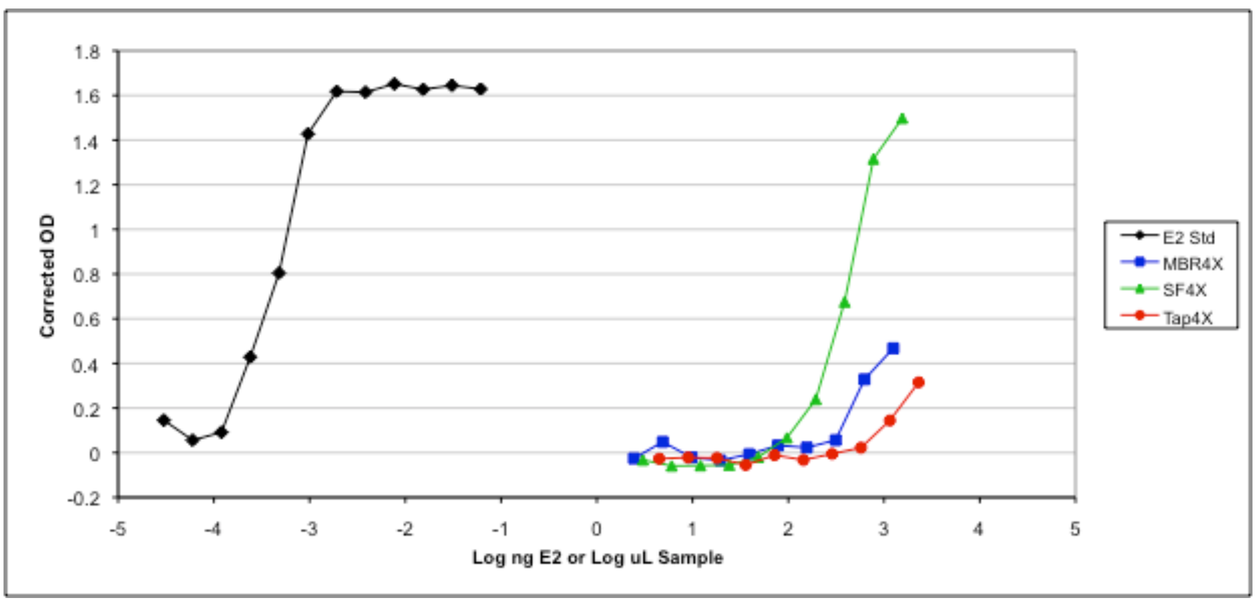


Figure 2.9. Estrogenic response curve where, membrane bioreactor leachate (MBR), at 4X irrigation, and Control leachate, at 4X irrigation, are below the E2 standard curve. The sand filter leachate, at 4X irrigation rate, was equal to the slope of the E2 standard. In this example, SF4X has an estrogenic response as potent as the E2 standard.



Figures 2.10 and 2.11. Westco SmartChem 200 nutrient analyzer. Computer image of machine layout

pH of 9.1 was used. Ammonia was measured using Westco SOP based on Standard Methods 4500-NH_3-N-G,(19th,20th,21st ed) and Standard Methods 4500-NH_3-H (18th ed)(Westco, 2007). An application range of 0.02-2.0 mg L^{-1} was used for the calibration curve. Orthophosphate was measured using Westco SOP based on Standard Methods (18th and 19th ed) 4500 P.B. 1,2 and 5 (Westco, 2007). An application range of 0.05-1.0 mg L^{-1} was used for the calibration curves. Quality controls consisting of standards, blanks and duplicate samples were run every 10-25 samples depending on the number of samples within each run.

Metals Analysis

Metals analysis was performed by King County Environmental Laboratory in Seattle WA. Leachate from 4X water rates was homogenized by water type. Generally, between 500 and 1000mL was collected each week for forest soil and every two weeks for agriculture soil and stored at 4°C until analyzed. The King County Environmental Laboratory used Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for total metals analysis following an acid digestion of the water sample (King County, 2009).

Soil Analysis

After each phase of the experiment, the soils were removed from the columns and homogenized (Figure 2.12). A subsample of each core was collected in 120ml specimen containers for metals analysis. The remaining soils were sieved to 2mm and ground for further analysis (Figure 2.13). Soil pH was measured with a soil to de-ionized water ratio of 1:1 for the forest soils and a 2:1 ratio for the agricultural soils. Soil conductivity was measured with a soil to de-ionized water ratio of 5:1 for both soil types. The pH was measured using a Denver Instrument Model 220 and the conductivity was measured using Orion Conductivity-Salinity Meter model 140.

Metals Analysis

Soil samples were taken to the King County Environmental Laboratory in Seattle WA within 24 hours of collection where samples were stored at -18°C until analyzed. Prior to analysis, samples were thawed at 4°C. Total metals were determined using an acid digestion. After removal of analytes from the soil into solution, samples were analyzed by ICP-MS (King County, 2007).

C/N Analysis

Total carbon and nitrogen (%) were measured with O_2 combustion and a He carrier using a Perkin Elmer CHN analyzer model2400. Sieved samples were weighed to between 30-40 micrograms. For each run, four blanks, five k-factors and two quality controls were run prior to samples;, thereafter, quality controls were run every 10 samples. Carbon and nitrogen are reported as percentages.

Statistical Analysis

Statistical analysis were run using SPSS version 19 statistical package. Main effects by water type and irrigation rate within each soil were examined. Level of significance examined at the $p<.05$. Interactions between the means were also examined using Duncan-Waller.

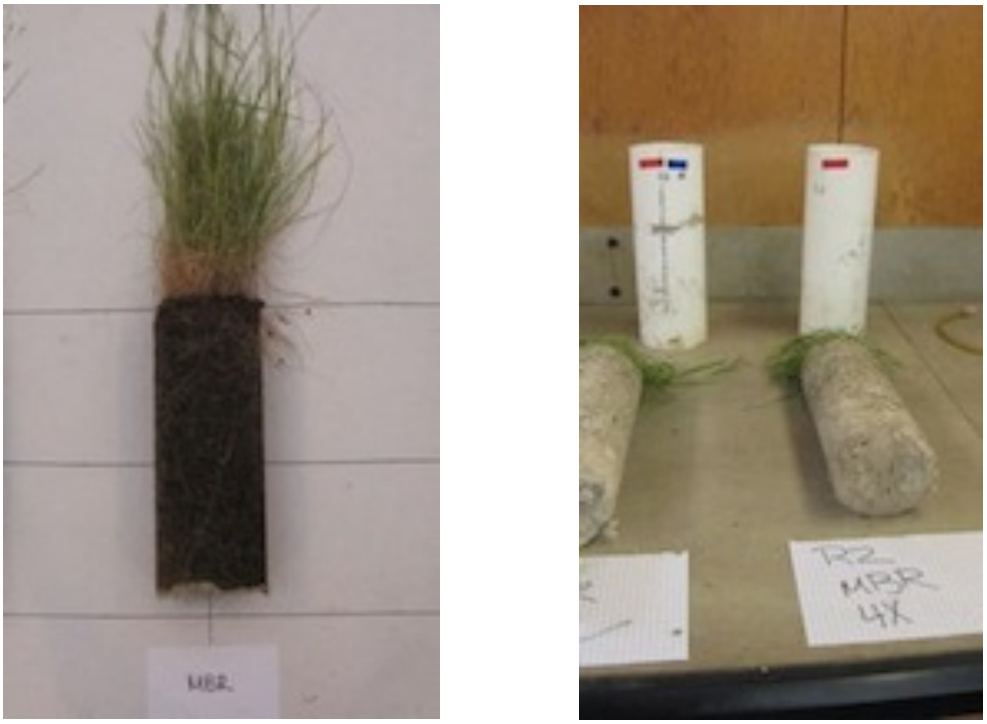


Figure 2.12. Intact soil cores removed after each phase and photographed prior to homogenization. The forest soil is on the left and agricultural soil on the right. These images clearly demonstrate the difference between the soil types.

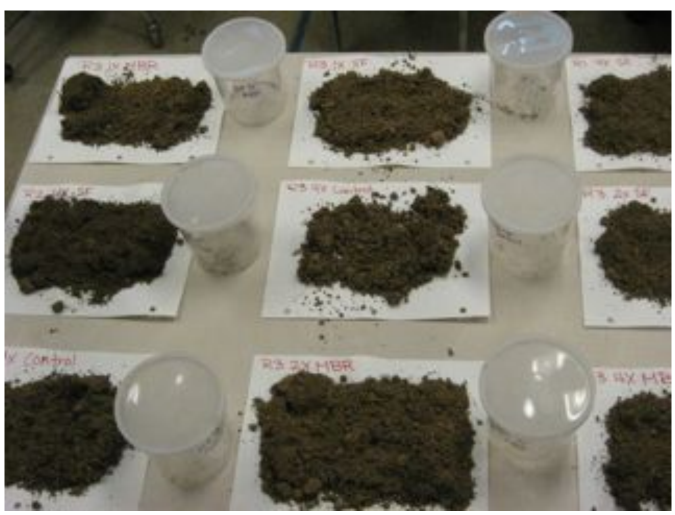


Figure 2.13. After homogenization, soils were air-dried for 48 hours and sieved to 2mm. Half of every soil sample was ground for pH, conductivity and CHN analysis. The remaining soil samples were archived for future analyses.

CHAPTER 3

Results and Discussion

Leachate

As expected, irrigation rate had the largest impact on leachate volume. In the agriculture soil, mean 1X leachate was 2.7mL. Leachate analyses were not performed on any leachate volumes under 3mL, therefore only 42 of 270 1X agriculture leachate samples were of sufficient volume to analyze. This volume of leaching also suggests that there would be little or no leaching beyond the root zone. Forest soil leachate was higher than the agriculture leachate at the 1X and 2X rates. Although mean agriculture soil leachate was higher than the forest soil leachate, the mean difference was only 32mL (Figure 3.1). At the 1X and 2X rate for both soil types, this resulted in low leachate volumes.

Overall leachates at the 1X and 2X rates were low with many of the volumes insufficient to perform analysis. Sufficient volume was obtained under the 4X rate for both soil types to perform all analyses. This rate also provided consistent leaching over the duration of each phase.

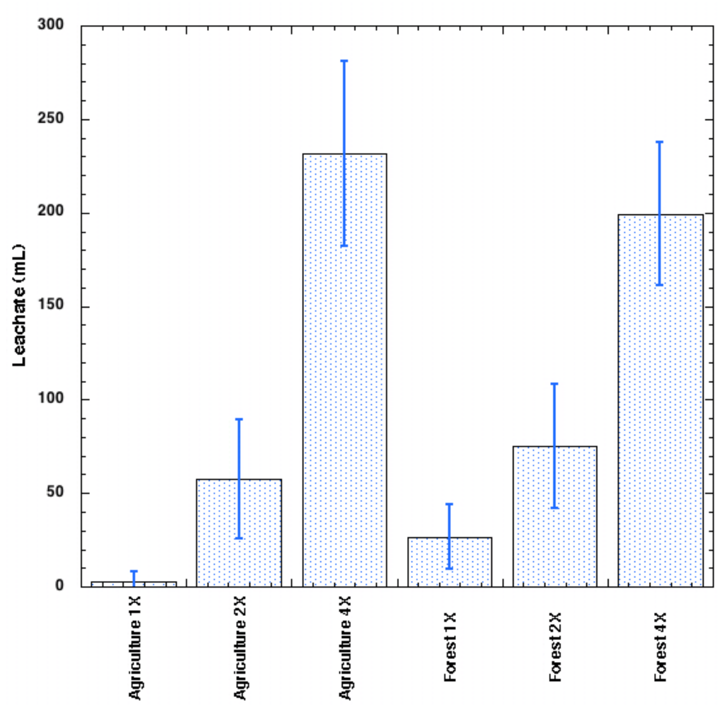


Figure 3.1. Leachate by irrigation rate and soil type.

pH

Source Water and Soil Leachate

Source water pH levels were all similar, ranging from 7.5-7.7 and within the EPA's MCL for drinking water and Washington State groundwater quality standards. The greatest influence on leachate pH was soil type. Both soils were acidic; agriculture soil pH was 5.46 and forest soil pH was 3.91, much lower than either of the source waters. Forest soil pH was significantly lower than the agriculture soil pH (Table 3.1). This was expected, as the forest soils in this study were a mixed Douglas-fir forest soil with documented pH values ranging from 4.1-5.2 in the Pacific Northwest region (Meigroet 1984; Giardina et al. 1995). Forest soil leachate pH was similar to that of the soil, remaining acidic throughout the duration of sampling, ranging from 3.53 for control 1X to 5.27 for SF 4X. The agriculture soil leachate pH, however, was more similar to that of the source waters, remaining neutral, ranging from 7.65 for control 1x to 8.22 for SF 1x. Although there were significant differences between water types in the agriculture soil leachate (Table 3.2), all the values were within the range of 7.7-8.2 and did not vary under different irrigation rates. Water type also altered leachate pH in the forest soil ($p < 0.000$, $F=17.6$) but the greatest influence on leachate in this soil was irrigation rate ($p <0.000$, $F=128$). All leachate pH values increased with irrigation rate but remained well below those of the source waters. The increase in pH for the forest leachate by irrigation rate is shown in Figure 2. Over time, there was a clear trend for increased pH in the forest soil leachate (Figure 3.3). The pH in the agriculture soil leachate varied over time with no clear trend (Figure 3.3). These results suggest that source water had a greater influence on leachate pH in the forest soil than the agriculture soil. This is expected as the forest soil was sandier than the agriculture soil and therefore would have a lower pH buffer capacity.

Soil

Soil pH was measured at the end of each trial to test if source water altered the pH of the soil. Irrigation rate and water type did not influence forest soil pH. The agriculture soil pH was only increased slightly by mean irrigation rate with pH increasing at the higher irrigation rates ($P<0.05$), however, there were no other influences (Table 3.3). Overall, soil pH was not affected by either water type or irrigation rate. These results are in contrast with several studies in which irrigation with reclaimed water markedly increased soil pH (Schipper et al. 1996; Qian and Mecham 2005; Sparling et al. 2006; Vogeler 2009). While the results of this study showed a slight increase in pH by mean irrigation rate in the agriculture soil, water source was not a factor. This is comparable to Schipper et al. (1996) who compared reclaimed water irrigation to stream water irrigation and found that loading rate was not a factor in pH variation; this suggests that nutrient cycling must be the driving factor in the pH increases found in their study.

Summary

Both the forest and agriculture soil were acidic, typical of this region. All source water pH values were within recommended standards. Agriculture soil leachate pH was similar to source water pH. Irrigation rate and water type did not influence leachate pH. In the forest soil, leachate pH values were not influenced by water type; however, irrigation rate had a short term influence. The forest soil pH was significantly more acidic than that of the source water. Forest soil leachate pH increased with irrigation rate, resembling that of the source water at the higher rate. Over time, however, all irrigation rates showed an increase in pH, suggesting that the source water pH may overcome the acidic soil pH.

Table 3..1. Soil pH and source waters measured at the beginning of the study.

Source Soil	pH
Agriculture	5.5
Forest	3.9
Source Water	
Control	7.6
MBR	7.7
SF	7.5

Table 3.2. Leachate pH values by water type, irrigation rate and soil type.

Water Type		Leachate pH			
		Agriculture		Forest	
	Rate	N	Mean	N	Mean
Control	1X	9	7.7±0.3	73	3.7±0.5
	2X	67	7.9±0.4	82	4.0±0.6
	4X	70	7.8±0.5	93	5.0±1.0
MBR	1X	10	8.0±0.5	66	4.0±1.0
	2X	67	7.9±0.5	88	4.1±0.7
	4X	69	8.1±0.4	102	5.5±1.3
SF	1X	18	8.2±0.3	65	4.0±0.6
	2X	67	8.0±0.5	91	4.4±0.9
	4X	68	8.0±0.4	93	5.3±1.1

Table 3.3. Soil pH at the end of study by water type, irrigation rate and soil type.

Water Type			Soil pH	
	Rate	N	Agriculture	Forest
Control	1X	3	5.9±0.2	4.1±0.2
	2X	3	6.2±0.3	4.3±0.3
	4X	3	6.3±0.07	4.0±0.3
MBR	1X	3	5.9±0.2	4.2±0.4
	2X	3	6.0±0.2	4.2±0.4
	4X	3	6.3±0.2	4.2±0.3
SF	1X	3	6.1±0.4	4.2±0.1
	2X	3	6.0±0.08	4.1±0.03
	4X	3	6.0±0.2	4.1±0.2

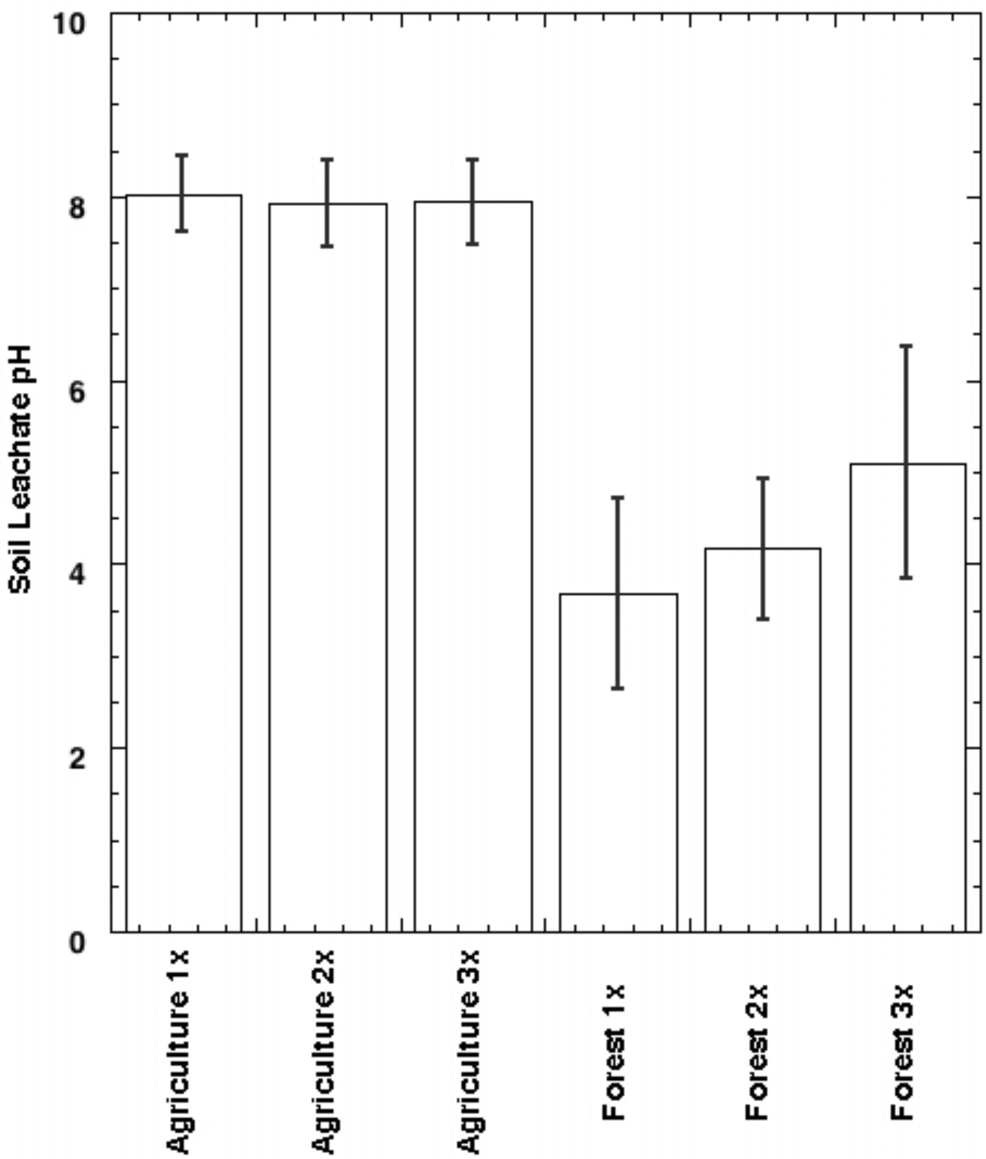
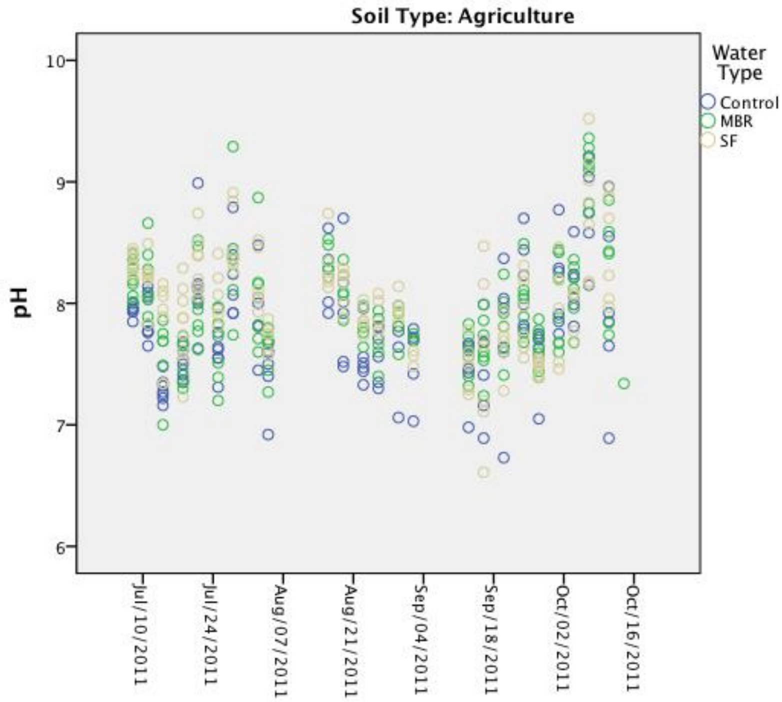


Figure 3.2. The effect of irrigation rate for the agriculture and forest soil leachate. Means are for each rate, averaged across all water types ± standard error. Within the forest soil, means with different letters are significantly different.



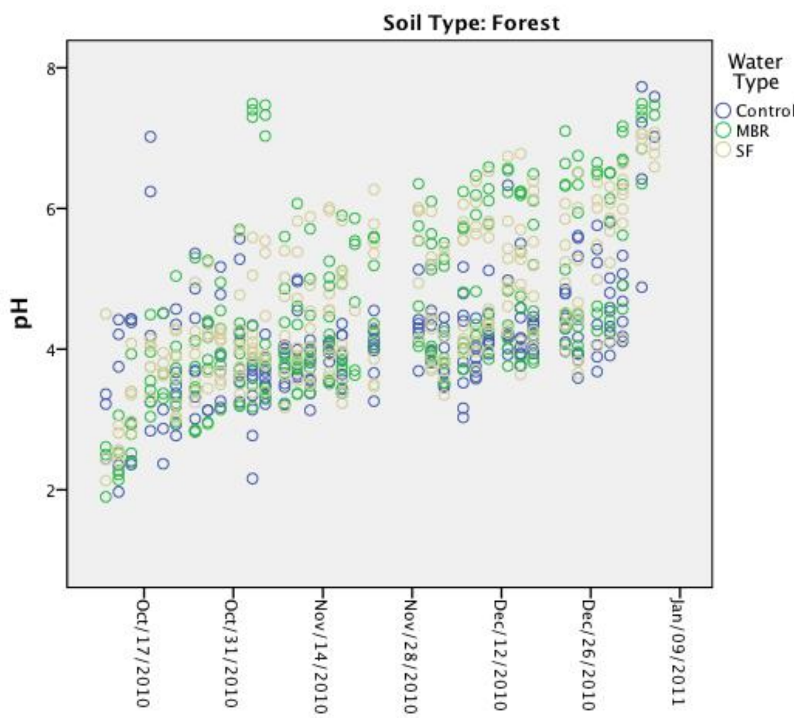


Figure 3.3. Agriculture and forest soil leachate pH over time.

Conductivity

Conductivity was reported for agriculture soil leachate only due to reading errors during phase 1 of the study for forest soils leachate. Soil electrical conductivity (EC) is reported for both soils.

Source Water

Control source water conductivity (67.1 uS cm^{-1}) was significantly lower than either MBR or SF source waters (452 and 572 uS cm^{-1}, respectively). The EC values for the source waters in this study meet the suitability of fresh water for irrigation guidelines, with no restriction required based on an EC value <700 uS cm^{-1} (Asano and Pettygrove, 1987; O'Connor et al. 2008). The groundwater quality standard for salinity in Washington State is based on total dissolved solids (TDS) of 500mg L^{-1} (WAC 173). Based on equation 1 (NRCS 2011), the approximate TDS for reclaimed source waters in this study are between 289-366mg L^{-1}, well below the groundwater quality standard set forth by the Washington State Legislature.

$$\text{TDS (mg L}^{-1}) = \text{EC (dS m}^{-1}) \times 640 \quad \text{where: dS m}^{-1} = \text{uS cm}^{-1} / 1000 \qquad (1)$$

Soil Leachate

The greatest influence on conductivity in the leachate collected from the agriculture soil was water type. Leachate EC differed by water type ($P<.000$, $F=257$), following the same differences observed in the source waters. Across all water types, leachate sample size from the 1X irrigation rate was minimal due to low leachate volume of water at this irrigation rate. While there was no significant difference in leachate EC between 2X and 4X irrigation rates, there was a tendency for EC to decrease with increased irrigation rate (Table 3.4).

At the end of the study, mean agriculture soil EC (145 uS cm^{1}) was significantly higher than the forest soil EC (55.4 uS cm^{1}); however, both soils are non-saline (EC 0<2 dS m^{-1}) based on the USDA (2011) salinity classification. Irrigation rate influenced soil EC differently between the two soils. In the agriculture soil, soil EC decreased as the irrigation rate increased while the forest soil showed an increase in soil EC with increasing irrigation rates (Figure 3.4). The increase in EC by irrigation rate in the forest soil was observed for all columns irrigated with reclaimed waters. This may suggest that source water influenced forest soil salinity; however, soil salinity remained low (maximum of 94uS/cm), never reaching a concentration that would be detrimental to plant growth (Table 3.5). The observed decrease in soil salinity in the agriculture soil may have resulted from the flushing of soluble salts. The trend of reduced salinity in the soil lead to the same trend for the leachate. All agriculture soil leachate had higher salinity concentrations than the source waters, suggesting that soil was the contributing factor to salinity levels. The agriculture soil in this study is enriched with composted manures. Soils amended with compost or fertilizers often have increased soil salinity that can be reduced under increased irrigation (NRCS 2011).

Summary

Overall, leachate EC in the agriculture soil showed a moderate decrease with increased irrigation rate. This was true for all water types. Again, as this soil has a history of composted manure amendments, salts from these amendments may have influenced soil salinity. Soil EC for both soils remained low, falling within non-saline soil standards. This is expected for this region as high precipitation flushes soluble salts from the soil system. These results are also similar to those found by Kim et al. (2010) who used SF reclaimed water from King County to irrigate crops. They found that soil salinity remained low under reclaimed water irrigation and that plant growth was not inhibited when compared to tap water irrigated plants.

Table 3.4. Agriculture soil leachate EC (μS/cm) for each water type by irrigation rate. The limited number of observations for the 1x irrigation treatment is the result of low leachate volume for this treatment. Values are means ± standard errors.

Water Type	Rate	N	Salinity EC (μS/cm)
Control	1X	5	254±290
	2X	64	387±205
	4X	70	252±133
MBR	1X	4	1109±440
	2X	61	612±162
	4X	69	533±77
SF	1X	1	1675
	2X	64	856±256
	4X	69	707±112

Table 3.5. Soil salinity at the end of the reclaimed water leaching trial for forest and agriculture soil. Means ± standard errors are shown. Means followed by an asterisk are significantly higher irrigation rates within the soil and water type ($p > 0.05$).

Water Type	Rate	N	Soil Type: Agriculture EC (μS/cm)	Soil Type: Forest EC (μS/cm)
Control	1X	3	188±8*	53±14
	2X	3	117±28	42±7
	4X	3	114±18	51±1
MBR	1X	3	168±48	45±6
	2X	3	123±18	68±23
	4X	3	151±23	82±11
SF	1X	3	164±27	41±1
	2X	3	150±3	52±3
	4X	3	129±14	65±9*

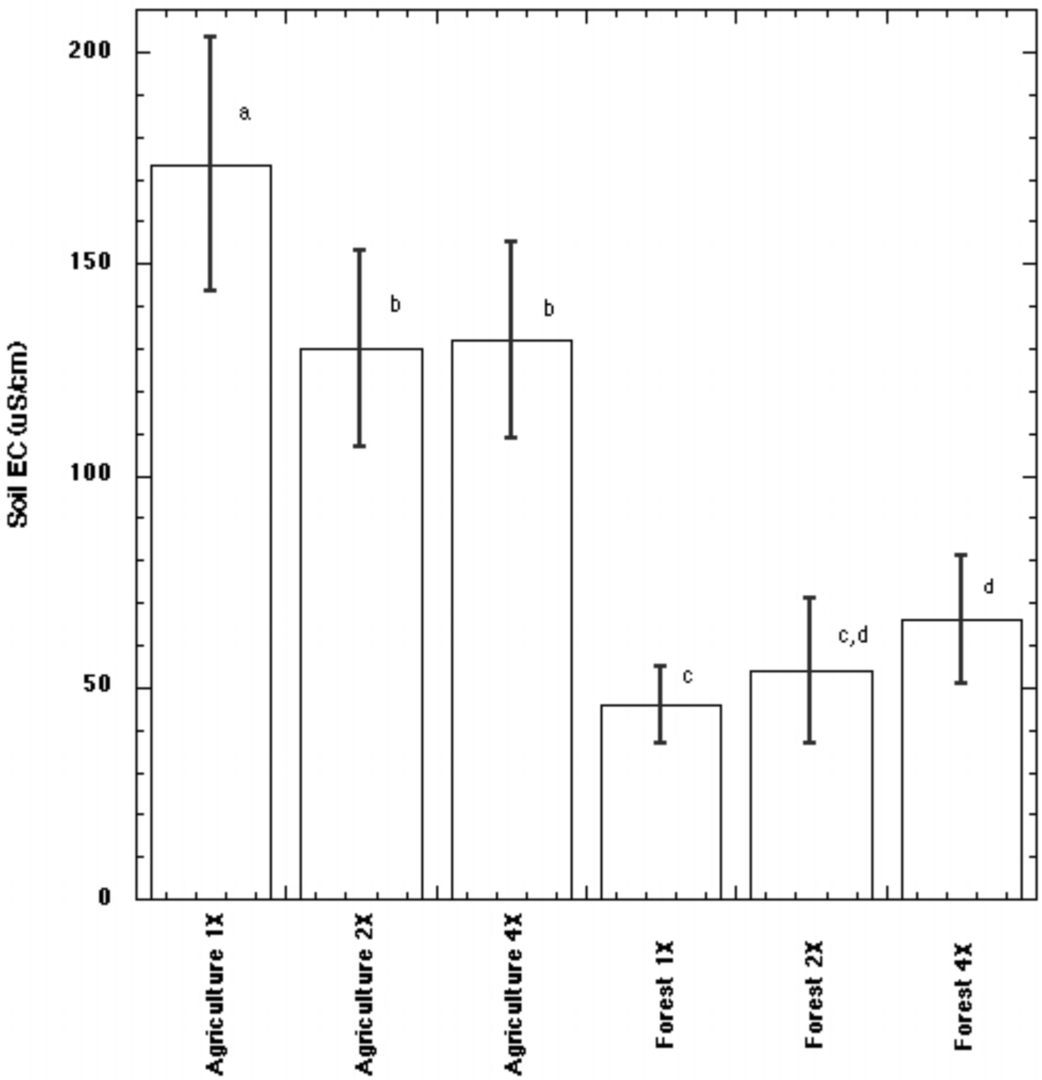


Figure 3.4. The effect of irrigation rate on agriculture and forest soil conductivity. Means for each rate, averaged across all water types ± standard error are shown. Within both soil types means with different letters are significantly different (P<.05).

EDC's

For this study, a yeast assay was used to measure the estrogenic potency of the different waters. This assay uses a color response to measure the estrogenic potency of the different samples. The color of the samples is compared with the color generated by the yeast after exposure to a known concentration of a particular estrogen. Responses are reported as a percent intensity or estrogenic potential of the known standard. Values less than 100 signify that the sample has less EDC potency than the estrogen standard. Values greater than 100 signify that the sample has greater potency than the standard. While this assay does not provide a quantitative value for each of the compounds that can impact estrogenic functions in organisms, it does give a measure of the estrogenic potency of the samples.

Source Water and Soil Leachate

For all source water samples analyzed, the estrogenic potency range of the SF source water (149-578%) was significantly higher than the control (<MDL-0.07%) and MBR (0.06-0.19%) source waters. The estrogenic potency of both the control and the MBR waters was close to the low end of the quantifiable limits. For all forest soil leachate samples collected, the estrogenic response in the MBR treatment was below detection limits (Table 3.6 and 3.7). Of the 4 samples analyzed, from this soil, only one sample from the control water treatment had sufficient estrogenic activity to quantify relative to the standard. Forest soil leachates for all water types are shown in Figure 5. In the agriculture soil, both MBR and control leachate had low but measurable estrogenic potency. The potency of the leachate from these treatments was slightly higher than the source waters, indicating that estrogenic activity was due to soil contribution and not source water (Figure 3.6). The slight increase in estrogenic activity seen in the agriculture soil leachate may be due to agriculture practices. The agriculture soils used in this study are amended using composted animal manure. Animal manures from cows, pigs and chickens are known to contain high levels of estrogens (Shore and Shemesh, 2003).

For both soil types, soil filtration had the greatest influence on SF source water. Of the three water types tested in this study, the estrogenic potency of the SF water was consistently high relative to both the other water types and the assay standard. For all samples tested, the estrogenic potency of the SF leachate was dramatically lower than the source water. SF source water estrogenic potency ranged between 149-578% relative to the E2 standard. The leachate estrogenic potency ranged from 0.7-99.7% for agriculture soils and <MDL-1.9% for forest soils. SF source water estrogenic potency was reduced by 86.2% in the agriculture soil and 99.6% in the forest soil (Figure 3.7). This study did not examine specific compounds or soil characteristics necessary to identify mechanisms responsible for the observed reduction. The YES assay measured total estrogenic activity and not the concentration of specific endocrine disrupting compounds. The large reduction in estrogenic potency of SF source water after filtration suggests that use of reclaimed water in excess of irrigation requirements for these two soils will not result in increased concentration of EDCs in subsurface waters. The observed reduction in estrogenicity may be the result of several factors including adsorption and transformation. In previous studies, EDC's have been shown to readily degrade in soil under aerobic conditions (Ying and Kookana 2005; Xuan et al. 2008).

Overall, leachate EDC activity for all types of water and both soil types was low with the greatest reduction from source water seen in the SF leachate. The reduction in estrogenic potential of the SF water leachate in the forest soil was greater than the agriculture soil. Many soil factors may contribute to estrogenic activity reductions seen in this study. These include soil texture, pH and microbial biomass. The retention time of the water in the soil (not measured) may also have affected the ability of the soils to reduce estrogenic potency of the source water. Soil leachate collected from the agriculture soil showed higher EDC activity than leachate collected from the forest soil. However, although EDCs were above detection limits for all water sources in this soil, the levels were low for both tap and MBR waters. Activity for the SF water passed through this soil was also significantly lower than source water activity. Forest soil leachate did not provide sufficient estrogenic activity to fully analyze the effects of filtration. There were only four forest soil leachate samples analyzed and only SF leachate provided more than one sample above the MDL.

EDC's were not measured in the soil therefore background levels were not determined. However, previous studies on EDC degradation and adsorption have been conducted on soils with similar textures to those used in this study (the agriculture soil is a silt-loam and the forest soil a sandy-loam). Both soil types have shown low extractability of E2 and no detection of EE2 at 3 and 44 days after addition of these compounds (Colucci et al., 2001). In another study, 4-NP, 4-OP, EE2, E2, E1, E3 and BPA were shown to completely degrade within 15 days in a sandy-loam soil (Ying and Kookana, 2005).

Summary

MBR and control water leachates were similar to one another and to their source waters. Both were also close to detection limits for EDCs. The SF source water had very high EDC activity; however, the leachate for both soils was significantly lower than the source with 86% reduction in agriculture soil and 97% reduction in the forest soil. Overall, filtration through the soil appeared to reduce EDC potency in the leachate.

Table 3.6. Source water estrogenic activity. Values are based on relative potency to the standard estradiol, calculated as $REP_{50}=EC_{50}$ standard/EC_{50} sample where EC_{50} is the half maximal effective concentration.

Source Water	n	Rep_{50} (ng/L) %potency
Control	9	.02 +/-.03
MBR	9	0.11 +/- .05
SF	9	307 +/- 147

Table 3.7. Estrogenic activity was lower in the leachate than in the source water across all water types in the forest soil.

Soil Type	n	Control	MBR	SF
		Rep_{50} (ng/L) %potency		
Forest	4	.09 +/-.17	<.0001	.88 +/-.79
Agriculture	10	.34 +/-.13	0.36 +/-.34	42 +/-37

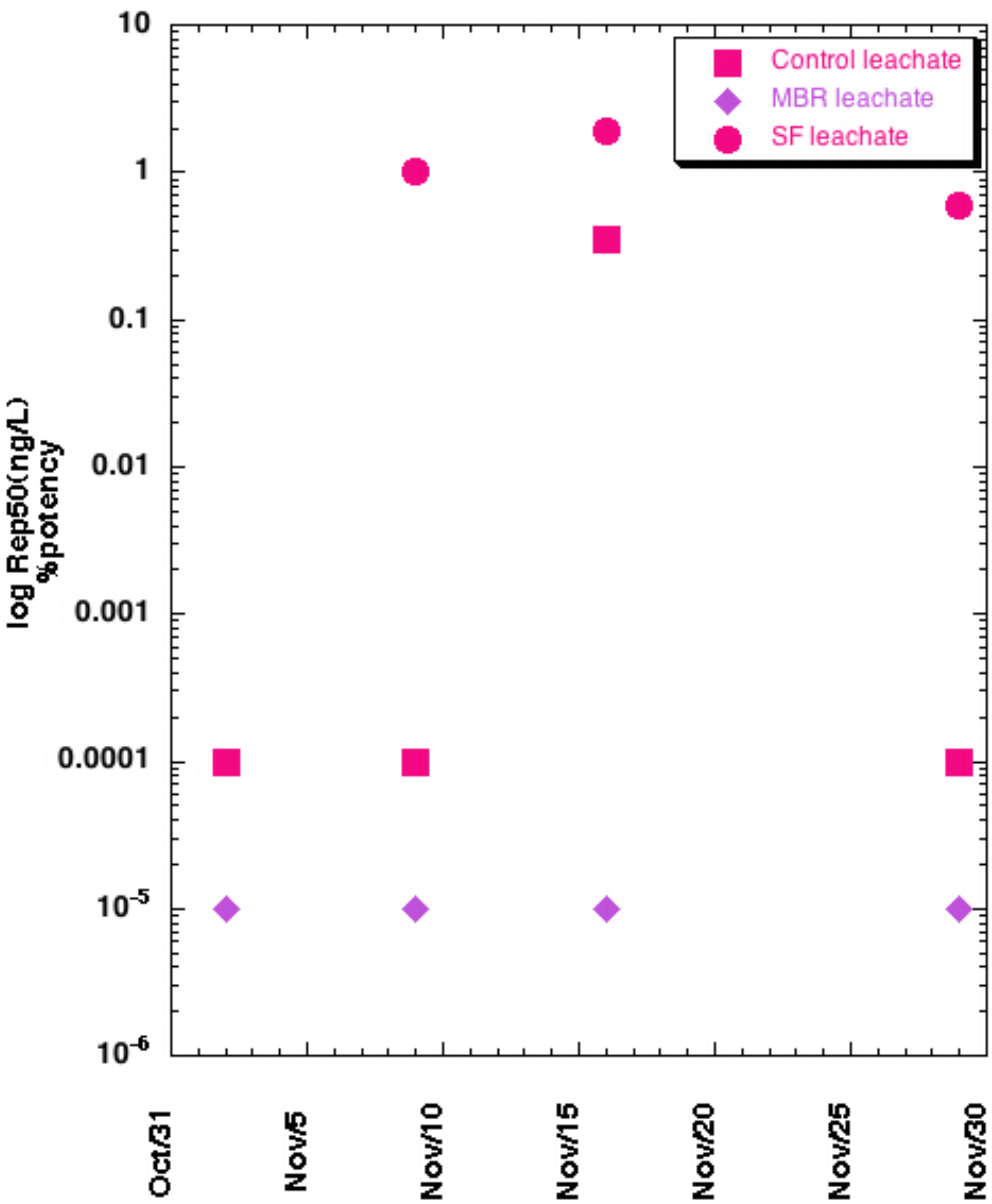


Figure 3.5. Forest soil leachate EDC potency of the control, MBR and SF waters.

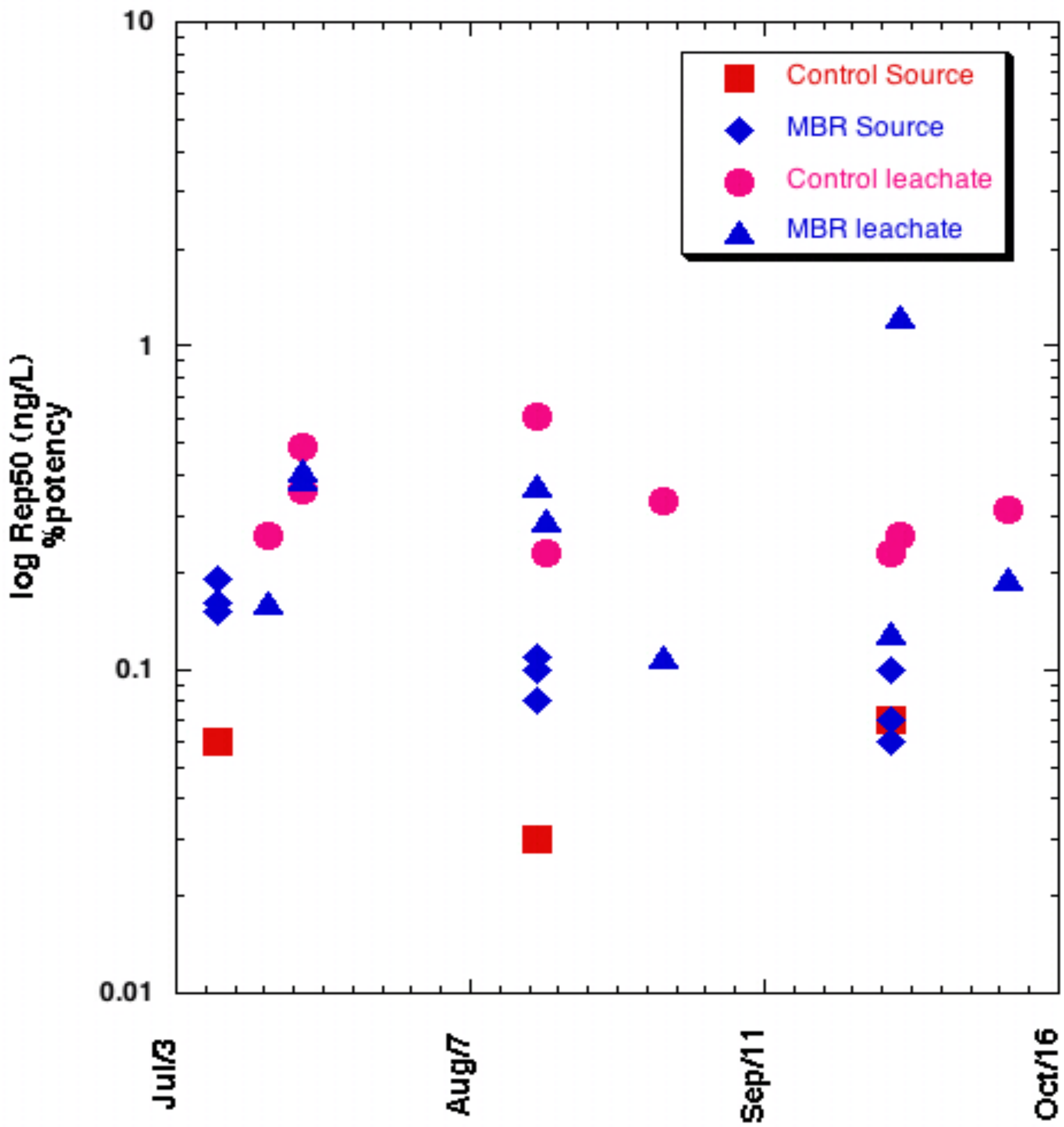


Figure 3.6. Agriculture soil MBR and control leachate and source waters.

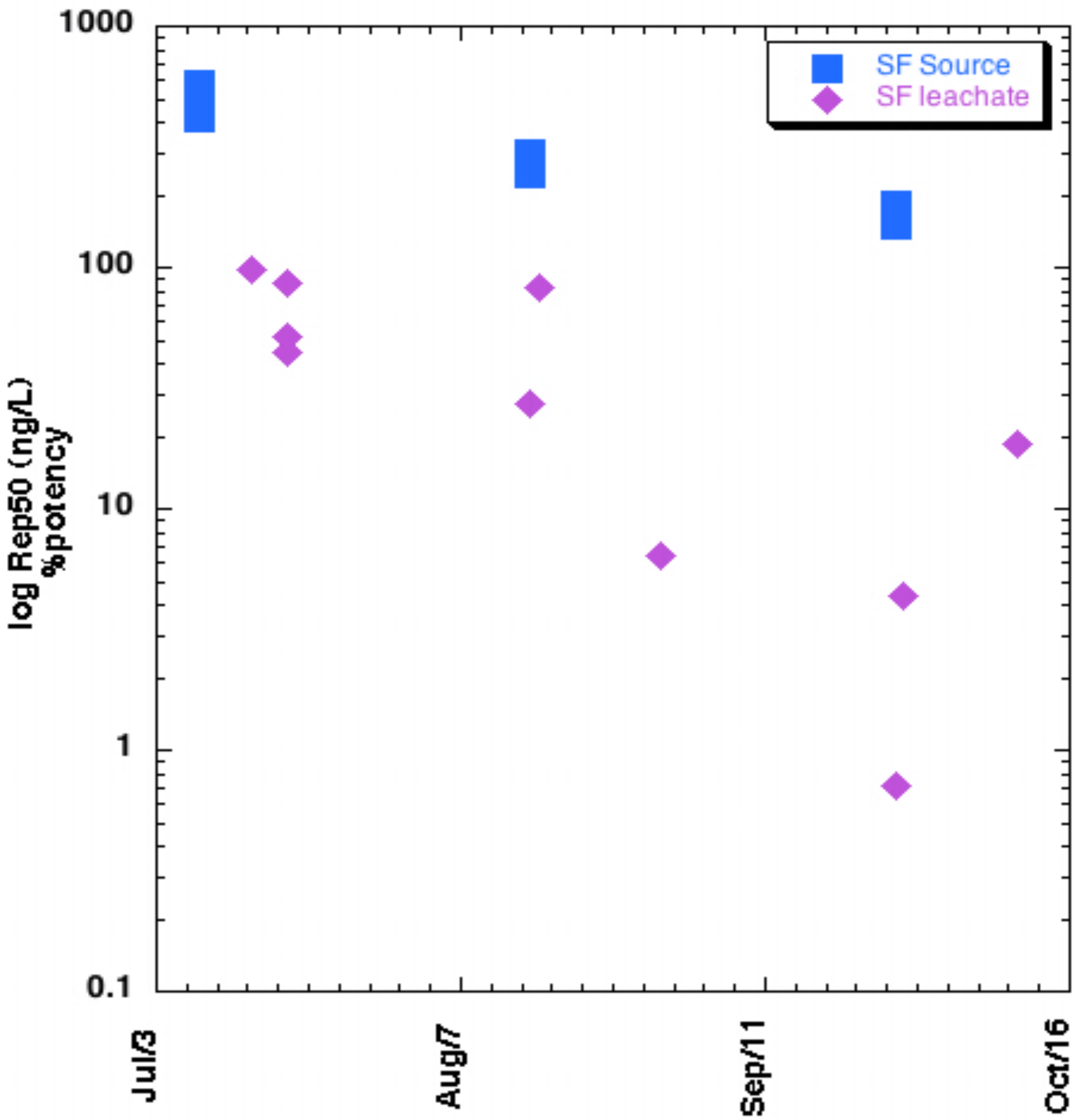


Figure 3.7. Agriculture soil SF leachate and source waters.

Metals

Source Water

Different regulatory agencies have different limits for metals in groundwater, irrigation water and drinking water. The source water metal concentrations for the three types of water tested in this study were generally below the EPA MCL for drinking water and Washington State groundwater quality limits with limited exceptions (Table 3.8). Arsenic concentrations exceeded Washington State groundwater quality standards for all water types, including tap water. Cadmium concentrations exceeded Washington State groundwater standards for the MBR source water. Manganese in the SF water exceeded EPA secondary drinking water regulation limits and Washington State groundwater quality. Finally, silver in the SF water exceeded Washington State groundwater quality limits. The EPA drinking water standards, Washington State groundwater quality criteria and source water metal concentrations are shown in Table 3.8. The control source water, water directly from the tap, had an average arsenic concentration of 0.46 ug L^{-1} (0.00046 mg L^{-1}), well above the Washington State groundwater limits, outlined in WAC 173-200-040, of .05ug L^{-1} . The drinking water MCL set by the EPA is 200 times higher than the Washington State groundwater quality criteria. The Washington State groundwater quality criteria for arsenic are based on human carcinogenic risk due to the cancer risks associated with long-term low-level exposure (WHO 2011).

Cadmium concentrations in MBR source water exceeded drinking water MCL by .048mg L^{-1} and groundwater quality criteria by .043mg L^{-1}. This may be due to leaching of cadmium from galvanized pipes in which water is transported or runoff from industrial sites (EPA 2012). Silver concentrations in the SF source water were at the recommended MCL for non-enforceable secondary drinking water regulations. Manganese in SF source water exceeded these recommendations. These standards are non-enforceable because they are thought to pose no health risks and are established for aesthetic purposes (EPA 2012). According to WHO (2011), manganese is associated with industry and automobile emissions. Manganese is also a necessary nutrient for both plants and animals. Levels of .05mg L^{-1} have been found acceptable for drinking water (WHO 2011, EPA 2012). SF source water silver concentration was .048mg L^{-1} above Washington States groundwater criteria.

According to WHO (1996), silver concentrations in natural waters are .2-.3ug L^{-1} (.0002-.0003mg L^{-1}) and are higher in water treated for drinking as silver is used for microbial disinfections (Heidarpour et al., 2011). Levels at 0.1mg L^{-1} in drinking water have been deemed safe for long-term exposure (WHO 1996, EPA 2012).

Leachate

Overall, no metal concentrations in the leachate of either soil type, any water type or irrigation rate exceeded the EPA's MCL for drinking water or Washington State groundwater quality criteria, with the exception of arsenic. Arsenic concentrations did not meet Washington States groundwater quality criteria for leachate of all water types, irrigation rates and both soil types. Arsenic concentrations ranged from .00049mg L^{-1} (Forest MBR 2X) to .0081mg L^{-1} (Agriculture MBR 4X). These concentrations are well below the EPA drinking water MCL of .01mg L^{-1}. Across all variables, the most important factor for arsenic concentrations in leachate was soil type. For all water types and irrigation rate, the leachate collected from the agriculture soil (mean= .006mg L^{-1}) had significantly higher arsenic ($P<.000$, $F=397$) concentrations than the forest soil (mean= .001mg $L^{-1)}$. Under the highest irrigation rate, arsenic concentrations for all water types were higher than the source water for both soils. While agriculture leachate volumes were not sufficient to run metal analysis at the 2X rate, the forest soil leachate volumes were sufficient to run metals analysis at the 2X rate. Arsenic concentrations in the forest soil leachate at the 2X rate were below source water levels for MBR and SF water types but above source water levels for the control (Figure 3.8). Tables 3.9 and 3.10 outline the agriculture and forest soil leachate metal concentrations. Although agriculture soil leachate arsenic concentrations were higher than forest soil leachate, they decreased with time at the 4X irrigation rate (Figure 3.9). Mean soil arsenic concentrations in the agriculture soil (5.89 mg/kg) did not change over time due to irrigation rate or water type. The higher concentrations of arsenic in leachate collected from the agriculture soil may be driven by high soil arsenic. Soil pH may be an additional factor. Some forms of arsenate, the oxidative state of arsenic in aerobic soils, adsorb better in low pH (McBride 1994), minimizing leaching.

Copper and lead were below EPA drinking water MCL and Washington State groundwater quality criteria for all soil and water types. In the agriculture soil, copper leachate concentrations were highest in the control leachate (.022mg L^{-1}) in comparison to the two reclaimed waters tested (MBR 0.016mg L^{-1} and SF 0.014mg L^{-1}). However, these concentrations are well below the US EPA and Washington State standard, with copper concentration in the control leachate 98% lower than the drinking water MCL and 97.8% lower than groundwater quality criteria. In general, leachate collected from the forest soil followed the same trend as the agriculture soil leachate, with concentrations for all water types at both 2X and 4X rates being below source water concentrations and below the US EPA MCL and Washington State standard. There was a single outlier in the data where the copper concentration in one sample collected from the 4X irrigation rate of the MBR leachate in the forest soil was higher than all other samples. While this outlier created a higher mean value for 4X MBR in forest soil, it was not above the MBR source water. Metals analyses were run on the agriculture soil only. Soil analysis indicated that mean copper concentrations (12.9kg/mg) did not change over time under any rate or water type. Leachate Cu concentrations were influenced by soil type, with mean 4X leachate Cu concentrations significantly higher in the agriculture soil (.017mg L^{-1}) than in the forest soil (.006mg L^{-1}). Results for Cu suggest that soil may be a more important factor in leachate water Cu concentrations than source water.

Lead concentrations in the control source water were higher than in MBR and SF source waters but were well below EPA drinking water MCL and Washington State groundwater quality criteria. In the agriculture leachate, lead concentrations for all water types were similar, ranging from .0028-.0036 mg L^{-1}. There was a lower but similar range in the forest soil 4X leachate (.0017-.003mg L^{-1}). The control leachate at the 2X rate was the only water/rate below the source water lead concentrations. Lead concentrations for the leachate collected from the Control were similar to that of the MBR leachate. Soil had the greatest influence on lead leachate concentrations. Mean agriculture soil lead concentration was 21.2mg/kg and did not change due to water type or rate. While soil lead concentrations did not change, the increase in leachate lead concentrations from the source waters may indicate a movement of lead through the soil system.

Overall, leachate metal concentrations were below current EPA drinking water MCL and Washington State groundwater quality standards. The only exception was that of arsenic, in which neither the source waters nor leachates met the Washington State groundwater quality. All source waters not only met EPA MCL for drinking water but also the EPA recommended constituent limit for irrigation with reclaimed water (US EPA 2004). It must also be noted that the control water leachate metal concentrations were similar to those produced under MBR and SF water types and also met the US EPA MCL for drinking water.

Summary

Water generally met criteria for all metals except arsenic where even the control was above groundwater quality criteria. Forest soil leachates exceeded the Washington State arsenic limit. The control leachate arsenic concentrations exceeded the control source water arsenic concentrations. As with the forest soil, agriculture soil leachate exceeded regulatory limits for arsenic. Agriculture soil was not influenced by irrigation rate and showed a potential tendency to decrease with time.

Table 3.8. EPA drinking water and Washington State groundwater quality standards for metals analyzed and source water metals concentrations. Chromium and selenium were not analyzed in the source water but were analyzed in the leachate waters.

Regulated Metals	Drinking water MCL (EPA 2012)	Groundwater Quality criteria (WAC 173-200)	Source Waters		
			Control	MBR	SF
	mg L^{-1}				
Arsenic	0.01	0.00005	0.00047	0.00084	0.00110
Cadmium	0.005	0.01	<MDL	0.05330	<MDL
Chromium	0.1	0.05			
Copper	1.3	1.0	0.06629	0.01134	0.01143
Lead	0.015	0.05	0.00085	0.00020	0.00003
Manganese	0.05*	0.05	0.00154	0.00535	0.06240
Selenium	0.05	0.01			
Silver	0.1*	0.05	<MDL	<MDL	0.09867
Zinc	5.0 *	5.0	0.00178	0.06073	0.03788

* Non-enforceable secondary drinking water regulations

Table 3.9. Metal analysis for Agriculture soil leachate at the 4X rate. One sample out of 8 from each water type was analyzed for chromium and selenium.

Total Metals	N	Control	MBR	SF
		mg L^{-1}		
Arsenic	8	0.0055±.0008	0.0081±.002	0.005±.0007
Cadmium	8	0.00008±.00002	0.00027±.00005	0.00016±.00002
Chromium	1	0.0069	0.00399	0.0074
Copper	8	0.022±.0027	0.016±.0012	0.014±.002
Lead	8	0.0037±.002	0.0033±.0011	0.0029±.0015
Manganese	8	0.041±1.05	0.033±.59	0.045±1.5
Selenium	1	0.00169	0.00134	0.00135
Silver	8	<MDL	<MDL	0.000089
Zinc	8	0.028±.01	0.042±.009	0.030±.006

Table 3.10. Metal analysis for Forest soil leachate at the 2X and 4X rate. One sample out of 7 SF water type at the 4X rate was analyzed for chromium.

Total Metals	Forest Soil 2X				Forest Soil 4X			
	N	Control	MBR	SF	N	Control	MBR	SF
			mg L^{-1}				mg L^{-1}	
Arsenic	**5**	0.00052±.00015	0.0005±.0001	0.00095±.0003	**7**	0.0011±.0005	0.0014±.0003	0.0015±.0003
Cadmium	**5**	0.00035±.00008	0.0004±.00007	0.00064±.00004	**7**	0.00021±.00003	0.00027±.000022	0.00043±.00008
Chromium	**0**	NA	NA	NA	**1**	NA	NA	0.001980
Copper	**5**	.0051±.002	.003±.0018	.0026±.0013	**7**	.0059±.0021	.0082±.002	.0039±.0026
Lead	**5**	.00069±.0002	.00067±.00032	.0018±.0007	**7**	.0018±.0013	.0029±.001	.003±.0007
Silver	**5**	<MDL	<MDL	<MDL	**7**	<MDL	<MDL	<MDL
Zinc	**5**	.086±.08	.096±.09	.067±.06	**7**	.027±.017	.028±.012	.052±.033

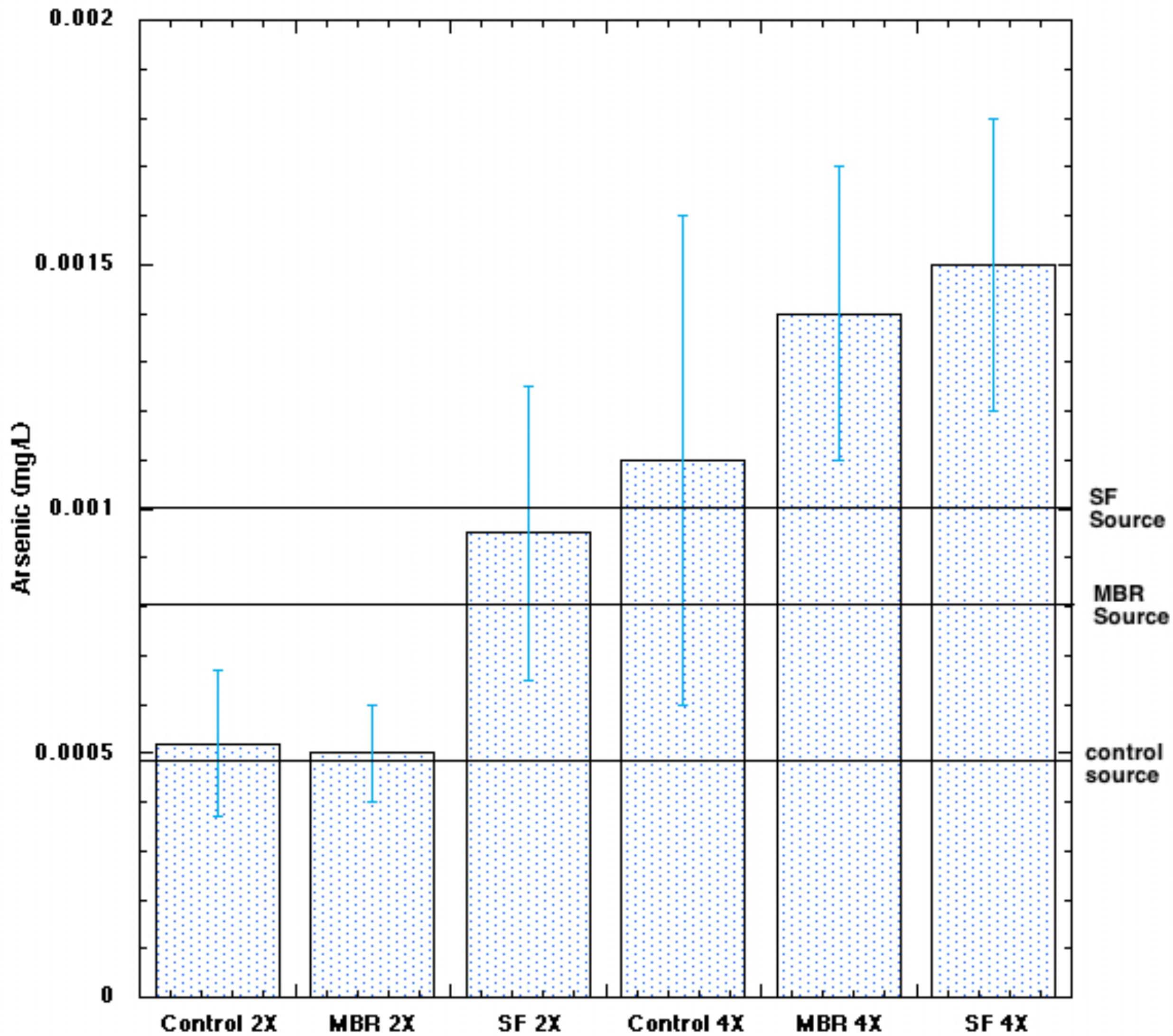


Figure 3.8. Mean Forest soil leachate arsenic concentrations (mg L^{-1}) for control, MBR and SF water types at 2X and 4X irrigation rates. Concentrations in source water are shown by a horizontal line.

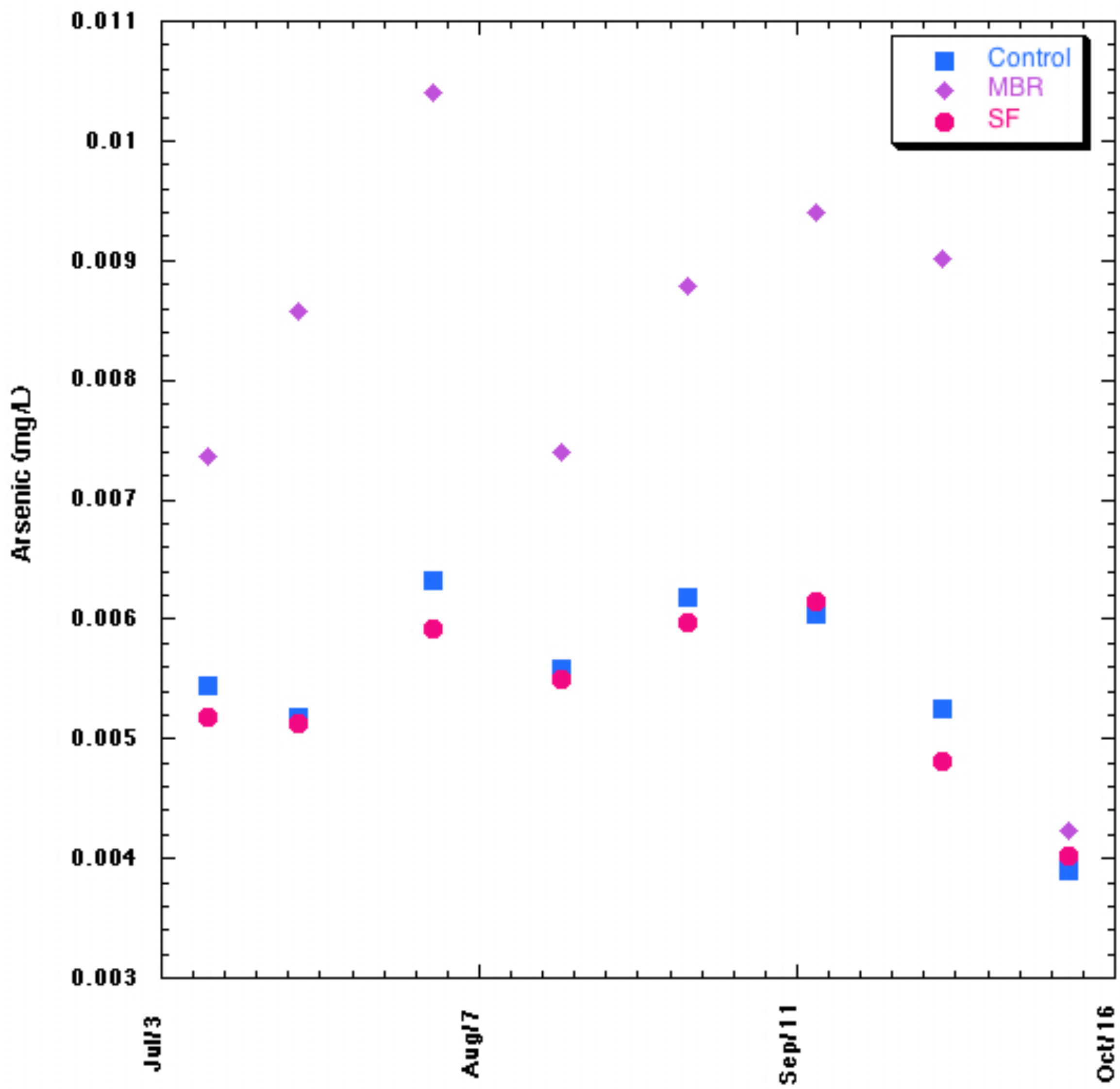


Figure 3.9. Agriculture soil 4X leachate for control, MBR and SF water types over time.

Nutrients

Source Water

Both the MBR and SF water had higher concentrations of ammonia, nitrate and orthophosphate than the control water. This was expected as reclaimed water typically has higher nutrient concentration than fresh water. Mean ammonia (NH_3-N in mg L^{-1}) concentrations were significantly higher in the SF source water (11.8 mg L^{-1}) than MBR (0.21 mg L^{-1}) and control (0.06 mg L^{-1}) source waters while mean nitrate (NO_3-N in mg L^{-1}) concentrations were significantly higher in both SF (5.7mg L^{-1}) and MBR (3.2mg L^{-1}) source waters than the control (0.04mg L^{-1}) (Table 3.11). While the EPA and Washington State do not directly regulate ammonia-nitrogen, WHO (2012) reports that NH_3 in drinking water is not a direct health risk and that typical concentration in surface and anaerobic groundwater are .2mg L^{-1} and 3mg L^{-1}, respectively. Due to high mobility and health risks, both the EPA and Washington State regulate nitrate for drinking water and groundwater quality with a limit of 10mg L^{-1} NO_3-N. All source waters met this standard.

Orthophosphate concentrations differed among the three source water types with the control as low as 0.003mg L^{-1} PO_4 and MBR as high as 1.93 mg L^{-1} PO_4 (Table 3.11). There are no current regulatory restrictions by the EPA on phosphate concentrations in drinking water or Washington State groundwater quality criteria, however, eutrophication is a concern and the US EPA has set a recommended limit of 0.05mg L^{-1} of total phosphate for streams that enter lakes (EPA 1986). This is not a recommended discharge concentration, however, but rather a whole stream concentration. According to the EPA Guidelines for Water Reuse (2004), nutrient levels of both nitrate and phosphate in reclaimed water are typically not high enough to pose either environmental or human/animal health risks and are not part of the long or short term irrigation limits for reclaimed water constituents. Although there are no strict limitations for phosphate in wastewater effluent, typical effluent phosphorus concentrations range between 0.5 – 1.5mg L^{-1} (Litke, 1999).

Leachate

Overall leachate orthophosphate concentrations were low with soil type having the greatest impact on concentrations. Mean PO_4 agriculture soil leachate (0.68mg L^{-1}) was significantly higher than the mean forest soil leachate (0.11mg L^{-1}). Source water PO_4 concentrations for both the MBR and SF were higher than mean leachate PO_4 concentrations for these waters. In contrast, the control source PO_4 concentrations were lower than mean control leachate PO_4 concentrations (Table 3.12). While statistical differences were observed across the different irrigation rates and water types for both soil types, leachate PO_4 concentrations did not follow any specific trend (Figures 3.10 and 3.11) nor did they change over time.

Like orthophosphate, the greatest influence on both ammonia and nitrate concentrations was soil type. In contrast with orthophosphate, mean ammonia and nitrate concentrations were higher in the forest soil leachate than the agriculture soil leachate. Mean ammonia and nitrate concentrations in the forest soil were 1.5 and 16mg L^{-1}, respectively and .74 and 10mg L^{-1} in the agriculture soil, respectively. In the forest soil, nitrate concentrations in the leachate from all types of water across all irrigation rates were above source water concentrations. Ammonia in the SF source water was significantly higher than in the control or the MBR source waters (11.8mg L^{-1} versus 0.07 and 0.22 mg L^{-1}, respectively). Ammonia concentration in the forest and agriculture soil SF leachates remained below SF source water concentrations (Table 3.12). For the other two waters (control and MBR), ammonia concentrations in the leachate were elevated in comparison to the source water across all irrigation rates. These results suggest that the forest soil was a source of at least a portion of the nitrate leached from each of the water treatments. It also suggests that the soil has some adsorption capacity for ammonia, as concentrations in the SF water influent were significantly reduced in the SF leachate. It is important to note that there was high variability for leachate ammonia and nitrate for all types of water at all irrigation rates. The variability may be related to retention time in the soil, soil microbial processes or other factors.

Mean leachate concentrations of ammonia in the agriculture soil were lower than in the forest soil across all water types and irrigation rates. For the MBR and SF leachate, ammonia concentrations in leachate were below or similar to source water concentrations across all irrigation rates. The highest leachate ammonia concentration in the agriculture soil was observed for the SF source water at the 4X rate (3.18mg L^{-1}). In general, ammonia concentrations in the SF leachate were higher than both the control and MBR leachate for all irrigation rates. However, the mean SF water 4X leachate ammonia concentration was lower than the source water concentration. This is a mean reduction of 8.6mg L^{-1} from the SF source water (11.8mg L^{-1}) with a mean leachate concentration of 3.18mg L^{-1} (+/- 3.85) at the 4X rate. There was also very high variability in the SF 4X treatment, indicating that the soil removed ammonia from some of the water more effectively than the rest. As with orthophosphates, leachate ammonia concentrations did not follow a specific trend (Figures 3.12 and 3.13) nor did they change over time.

Total soil nitrogen ranged between 0.33-0.45% for agriculture soils and 0.13-0.23% for forest soils with corresponding soil C:N ratios of 11:1 and 21:1, respectively. The higher total N and lower C:N ratio in the agriculture soil is likely related to a history of fertilization. The high carbon content of the forest soil is normal for an acidic forest soil with high soil organic matter (Brady and Weil 2002). More nitrate leaching was seen in the forest soil, with the highest leachate nitrate concentration observed for each water type at the 1X irrigation rate. Nitrate concentrations in leachate decreased with increased irrigation rate. The mean nitrate leachate concentrations were above EPA MCL for drinking water and Washington State groundwater quality of 10mg L^{-1} for all water types and rates with 2 exceptions. Control leachate in the forest soil at the 2X and 4X rates were below drinking and groundwater standards but were greater than half the limit (Figure 15). Source water nitrate concentrations were all below the EPA limits, suggesting that the soil was a source of nitrate for the leachates. forest soil leachate nitrate concentrations increased over time for all three water types (Figures 3.16-3.18). It is not clear why this occurred.

The agriculture soil leachate did not follow the same pattern of decreased nitrate leaching with increased irrigation rate as was observed in the forest soil leachate. In addition, although 5 of the mean leachate nitrate concentrations (Control 1X and 4X, MBR 4X, and SF 1X) were below the 10mg L^{-1} standard, the standard error for all treatments exceeded the EPA MCL and groundwater quality standard (Figure 3.14). As was observed in the forest soil, the leachate nitrate concentrations for all waters and all irrigation rates were higher than source water concentrations. This suggests that the soil was a significant source of nitrate for the leachate. There was a slight decrease over time in nitrate concentrations for the control and MBR leachate but no change in the SF leachate with time.

Nitrate Loading Rate

Total nitrate loading rates were calculated based on the nitrate concentration in the source water multiplied by the irrigation rate over 16 weeks. MBR 2X-4X and SF 1X-4X source water total nitrate levels were greater than the EPA MCL for total nitrate in drinking water of 10mg total NO_3-N (Table 3.13). Total nitrate loading from the SF source water was higher than both the control and MBR source waters. Over the 16-week period, total nitrate in the leachate of all water types was significantly lower than total nitrate inputs with one exception. The control leachate had higher total nitrate levels for all irrigation rates in the forest soil, ranging from .68-1.19mg versus the .135-.546mg input from the source water (Table 3.14). Total nitrate in leachate of all water types was higher in the forest soil than the agriculture soil, remaining consistent with the nutrient data for the forest soil in this study.

Summary

Soil type was the most important factor in determining leachate phosphate and ammonia concentrations. The agriculture soil had higher phosphate than the forest soil while the ammonia concentrations in the forest soil leachate were higher than the agriculture soil. Despite these soil effects, mean PO_4 and NH_3 concentrations in all leachates were low. Reclaimed water PO_4 and NH_3 concentrations were lowered via filtration while the control water leachate increased. These results suggest that the soil can be a source of these compounds for high purity water but can serve as a filter for reclaimed water with higher concentrations.

All leachate nitrate concentrations were significantly higher than the source waters and influenced by the soil. The highest concentrations occurred in the forest soil leachates with 7 of the 9 mean concentrations above the 10mg L^{-1} standard. In the agriculture soil, the lowest concentrations were in the control and MBR leachate at the 4X rate;6.62mg L^{-1} and 8.27mg L^{-1}, respectively. Overall, regardless of water type and rate, nitrate leaching will occur but will vary in concentration due to soil type. These results are similar to previous studies examining nitrate flow through soil with various water types in which rainwater, river water and reclaimed water all showed the potential for nitrate leaching (Sheikh et al., 1990; Sugita and Nakane, 2007; Alemyehu et al. 2009).

Table 3.11. Source water nutrient concentration ± standard error. All source water nitrate levels were below EPA MCL for drinking water and Washington State groundwater quality criteria of 10mg L^{-1}.

Nutrient	Source Water		
	Control	MBR	SF
		mg L^{-1}	
Nitrate	0.041±.03	3.22±.6	5.67±3.3
Ammonia	0.065±.07	0.22±.3	11.8±9.8
Orthophosphate	0.003±.01	1.93±.3	1.45±.4

Table 3.12. Leachate concentrations for agriculture and forest soil across all water types and rates ± standard error.

		Agriculture soil			Forest soil		
		Orthophosphate	Ammonia	Nitrate	Orthophosphate	Ammonia	Nitrate
			mg L^{-1}			mg L^{-1}	
Control	1X	0.18±.27	.06±.23	8.8±3.6	.09±.15	2.26±3.0	19.48±11.61
	2X	.37±.29	.27±1.2	10.58±4.3	.06±.11	1.45±2.44	9.63±4.50
	4X	.31±.22	.07±.18	6.62±4.8	.04±.08	.65±1.61	5.47±2.82
SF	1X	.84±.47	.83±1.11	9.64±4.42	.05±.07	1.70±1.81	24.60±14.14
	2X	.70±.34	.95±1.66	12.39±4.98	.07±.14	1.99±2.26	21.72±12.86
	4X	.89±.28	3.18±3.85	12,28±2.74	.10±.12	1.93±1.58	16.76±8.76
MBR	1X	1.16±.51	.07±.14	12.07±1.6	.16±.15	2.23±4.76	19.68±10.69
	2X	.73±.43	.10±.27	10.00±4.48	.07±.15	.83±1.05	15.27±8.86
	4X	1.01±.47	.07±.14	8.27±4.44	.37±.22	.74±.97	14.15±8.08

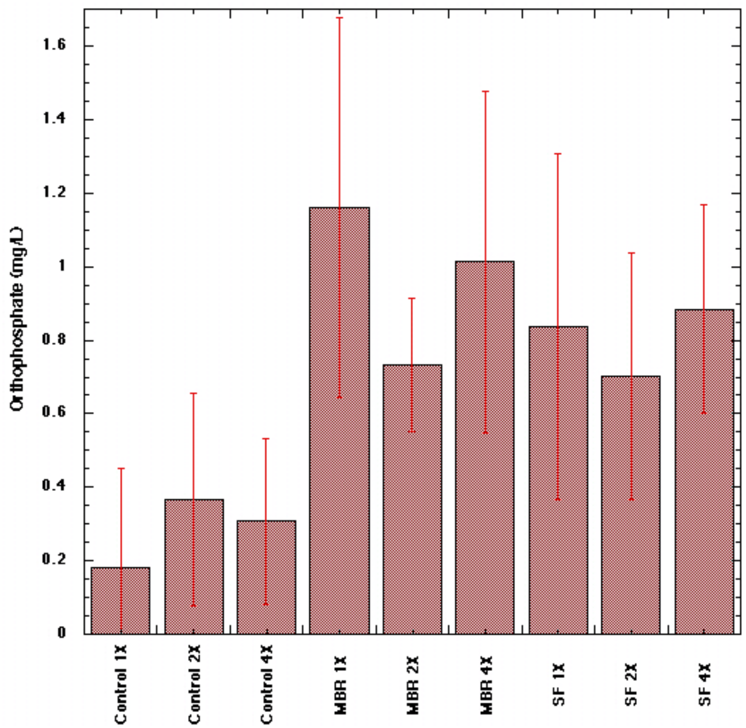


Figure 3.10. Mean Agriculture soil leachate orthophosphate concentrations for all water types at all rates ± standard error.

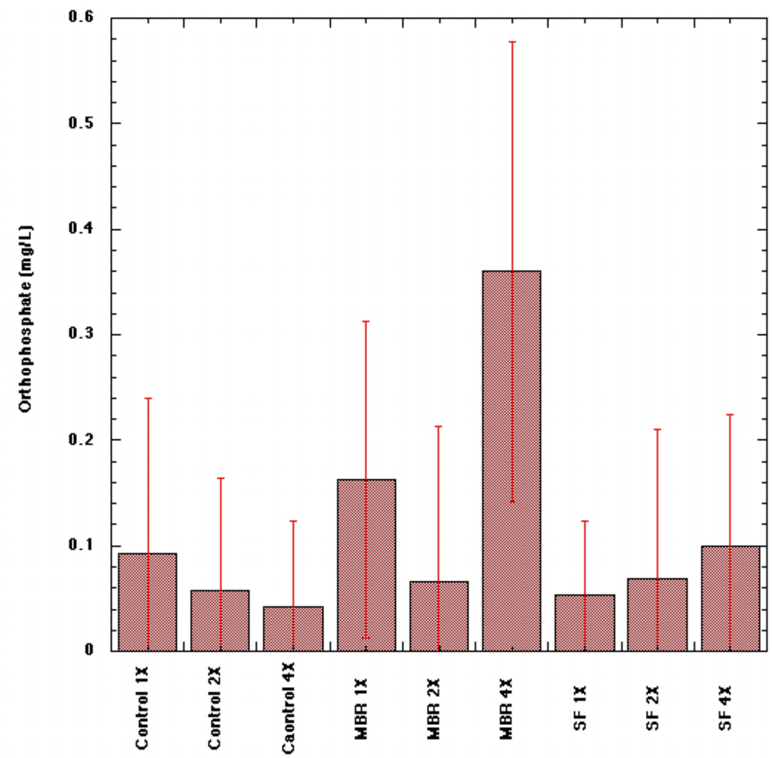


Figure 3.11. Mean Forest soil leachate orthophosphate concentrations for all water types at all rates ± standard error.

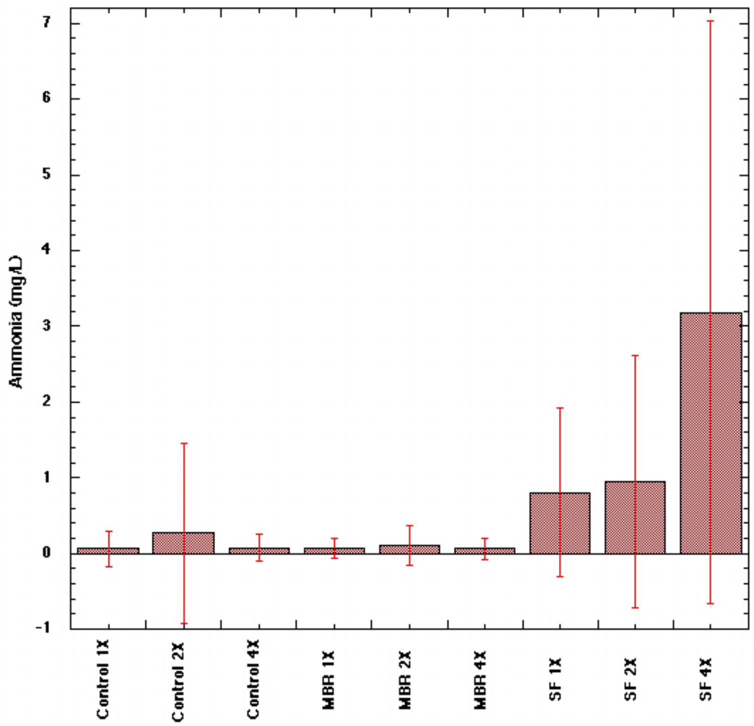


Figure 3.12. Mean Agriculture soil leachate ammonia concentrations for all water types at all rates ± standard error.

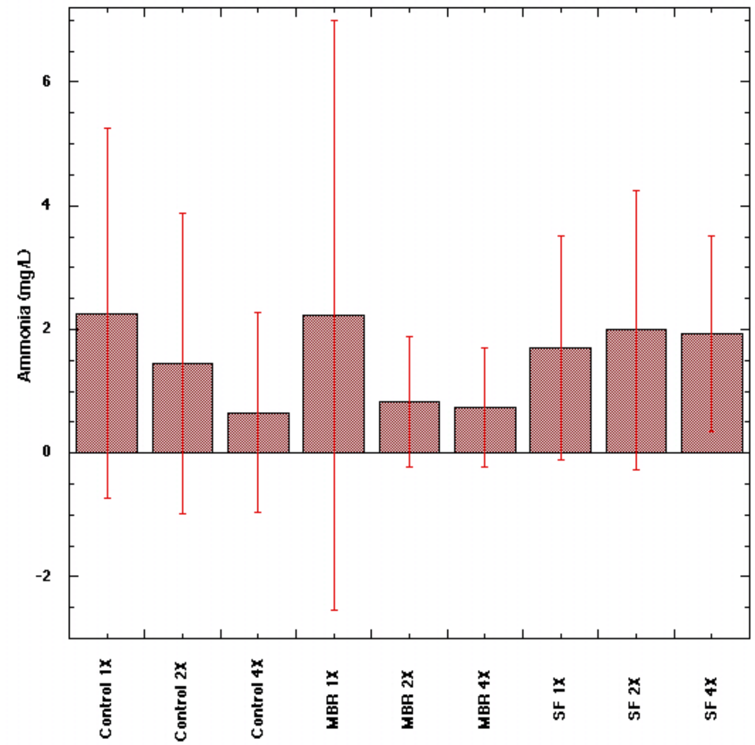


Figure 3.13. Mean Forest soil leachate ammonia concentrations for all water types at all rates ± standard error.

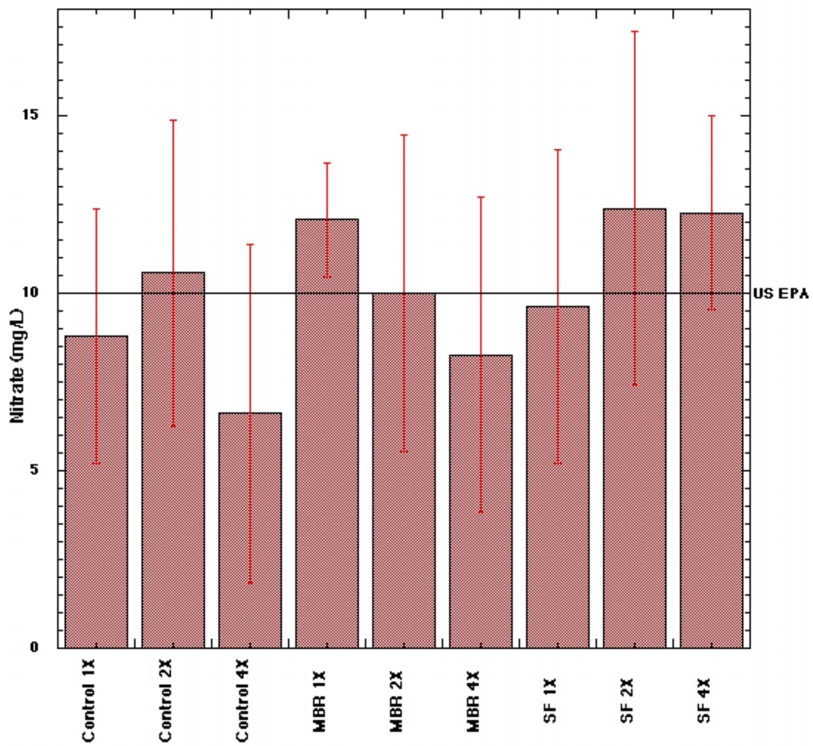


Figure 3.14. Mean Agriculture soil nitrate leachate for all water types at all rates ± standard error. The US EPA MCL for drinking water was used as a reference for contamination potentials.

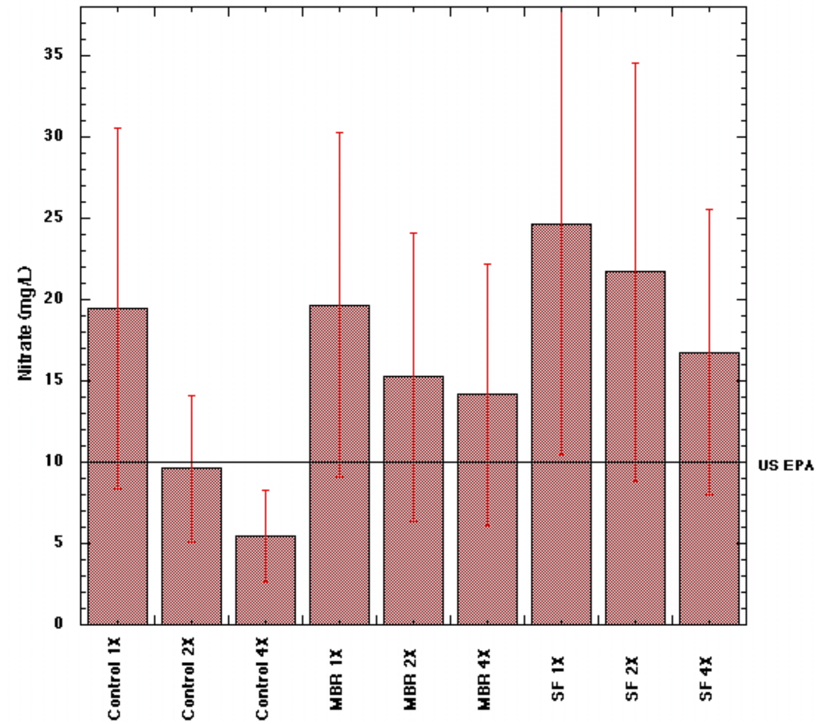


Figure 3.15. Mean Forest soil nitrate leachate for all water types at all rates ± standard error. The US EPA MCL for drinking water was used as a reference for contamination potentials

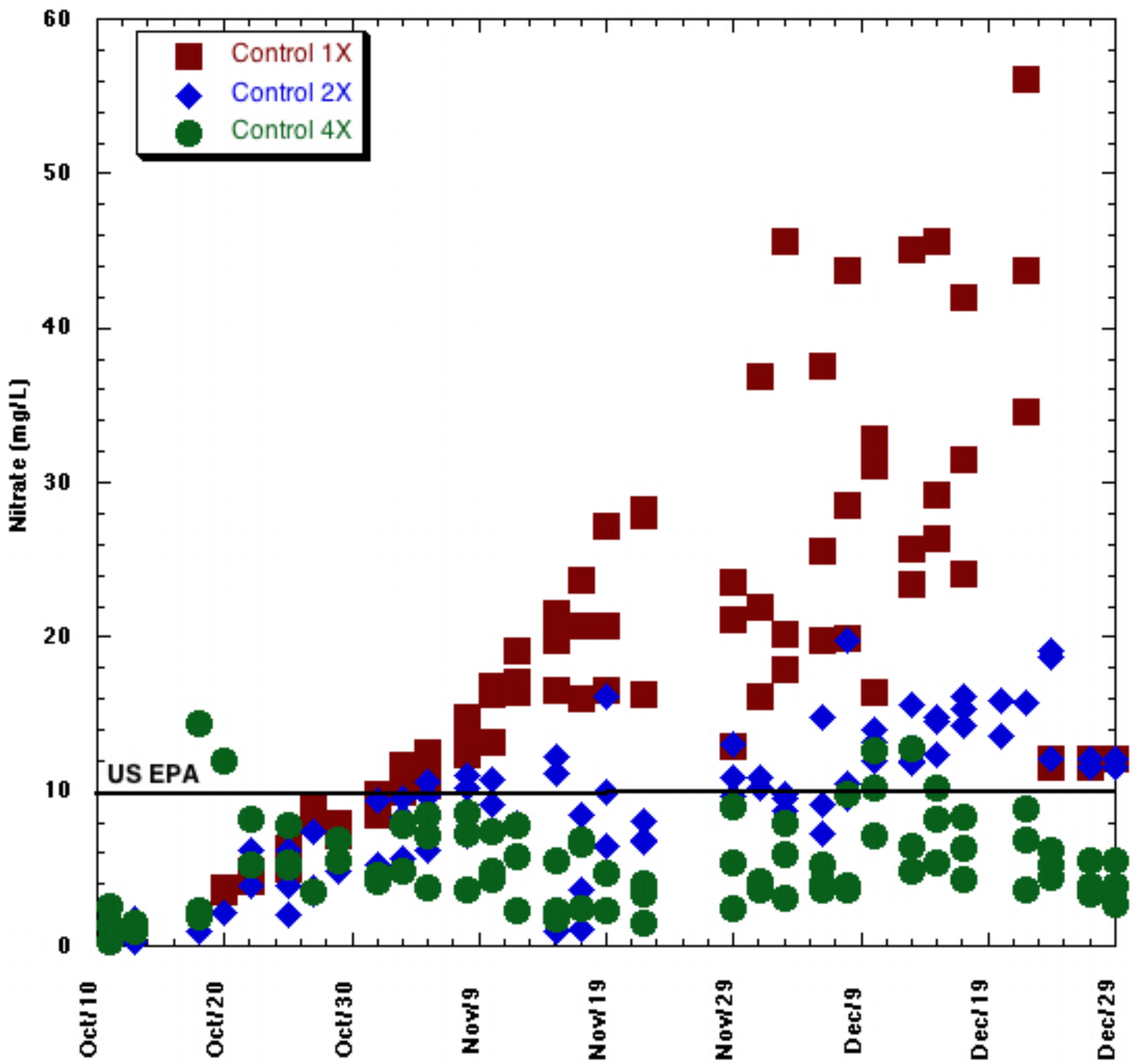


Figure 3.16. Forest soil control leachate nitrate concentrations over time. 1X leachate rate shows increase over time with concentrations well above the 10mg L^{-1} standard set by the EPA and Washington State.

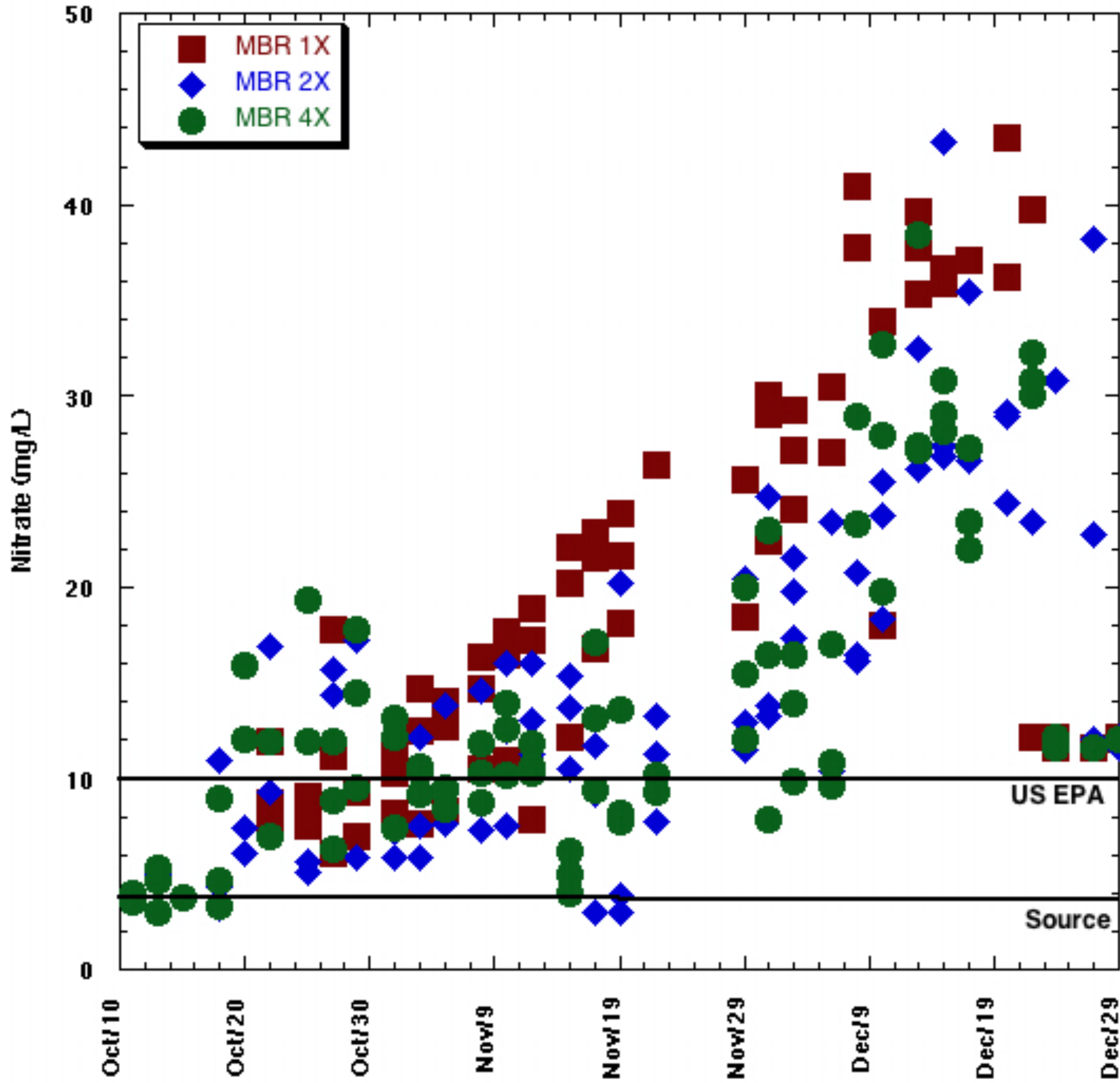


Figure 3.17. Forest soil MBR leachate nitrate concentrations over time. All rates shows increases over time with concentrations well above the 10mg L^{-1} standard set by the EPA and Washington State.

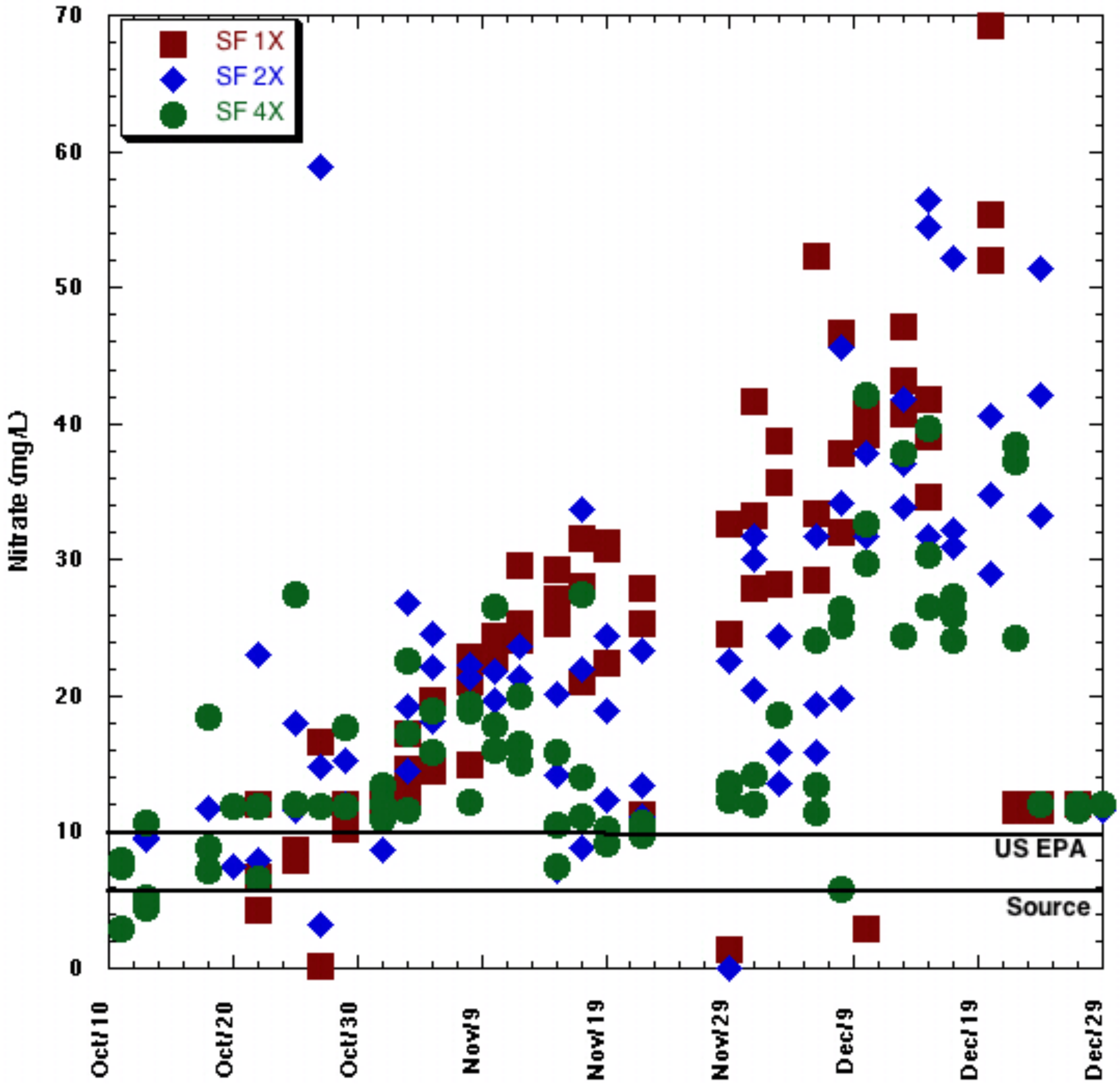


Figure 3.18. Forest soil SF leachate nitrate concentrations over time. All rates shows increases over time with concentrations well above the 10mg L^{-1} standard set by the EPA and Washington State.

Table 3.13. Total nitrate loading over a 16 week watering period.

	Source Water		
	Control	MBR	SF
Rate per week	NO_3-N(mg)		
1X (205.93ml)	0.135	1.061	18.316
2X (411.86ml)	0.270	21.219	37.357
4X (823.72ml)	0.546	42.438	74.715

Table 3.14. Total nitrate in leachate for each water type at each irrigation rate under both soil types.

	Total Nitrate in Leachate					
	Forest Soils			Agriculture Soils		
	1X	2X	4X	1X	2X	4X
	NO_3-N (mg)					
Control	0.68±0.5	0.85±.48	1.19±.66	0.12±.07	0.70±.45	1.57±1.2
MBR	0.68±0.5	1.33±1.0	3.0±1.9	0.16±0.1	0.57±.43	2.10±1.3
SF	0.92±.66	1.88±1.26	3.48±2.17	0.09±.07	0.80±.43	2.88±0.8

Grass Biomass

While grass was planted in the forest soil columns, biomass was not measured for this soil type. Overall biomass was significant by water type with SF water producing the higher biomass (4.9gms) than MBR and control; 3.4 and 3.2gms, respectively, in the agriculture soil. Table 15 provides mean biomass in grams by water type and irrigation rate. The higher biomass produced under the SF water type may be due to the higher nutrient concentrations in the source water. Grass biomass was significantly higher at the 4X than at the 1X rate under control water irrigation but there was no difference by rate under the MBR and SF water types (Figure 3.19).

Overall, grass productivity was not inhibited by increased irrigation rate or water type. Under the control water irrigation, biomass increased with rate. While biomass was not influenced by irrigation rate under the MBR and SF water types, the higher nutrient concentrations in the SF water significantly increased productivity.

Table 3.15. Grass aboveground productivity by water type and irrigation rate. Values are means ± standard error.

Water Type	Rate	N	Grass Biomass (grams)
Control	1X	9	2.6±0.3
	2X	9	3.1±0.5
	4X	9	3.9±0.5
MBR	1X	9	3.1±1.3
	2X	9	3.0±0.2
	4X	9	4.0±0.3
SF	1X	9	4.8±1.5
	2X	9	5.0±1.1
	4X	9	4.9±0.6

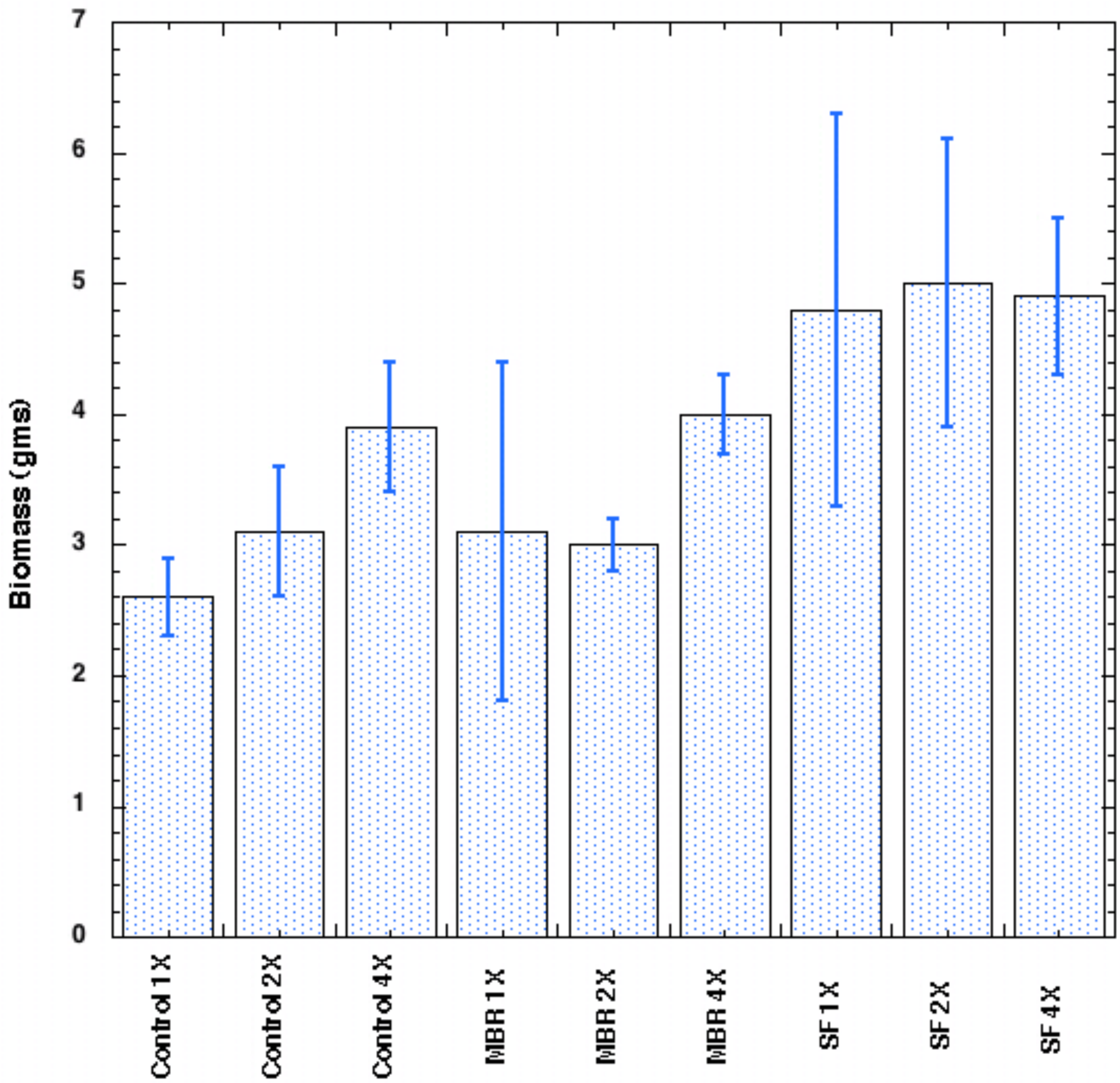


Figure 3.19. Grass biomass by irrigation rate for each water type; values are means ± standard error.

Conclusion

Overall, soil had a greater influence on leachate total metals, nutrients and EDCs than the source water. This research showed that each of the two soil types examined significantly reduced EDC potency. While ammonia and orthophosphate remained consistently low, nitrate was high in the leachate for all water types across all rates for both soils indicating the soils influence. The water was picking up nitrate as it filtered through the soil. All total metals were low and met groundwater quality standards except As. Like nitrate, the leachate concentrations were higher than the source suggesting that soil attributed As to the leachate.

Source water influenced pH and conductivity. Leachate pH resembled that of the sources water particularly in the agriculture soil and showed an increase over time in the Forest soil. Conductivity in the source water was high, as is expected in reclaimed water. The leachate reflected the source water at the lowest irrigation rate but decreased with increased rate.

Recommendations

In this study, I examined pH, conductivity, nutrients, metals and EDCS and found no evidence of any adverse effects that would argue against the use of reclaimed water at a rate to produce groundwater recharge. With the exception of arsenic and nitrate, all other water characteristics met EPA MCL for drinking water and Washington State GWQ. Arsenic and nitrate concentrations in the leachate were influenced by the soil. EDC potency was also influenced by the soil, decreasing with filtration. Plant productivity was not reduced under the higher irrigation rates needed for groundwater recharge. The 500m^3 ha^{-1} and 1000 m^3ha^{-1} rates provided sufficient leachate for both the sandy loam and silt loam soil types in western Washington. This rate will provide sufficient leachate needed for groundwater recharge.

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